第40回記念 フラーレン・ナノチューブ総合シンポジウム

The 40th Commemorative Fullerenes-Nanotubes General Symposium

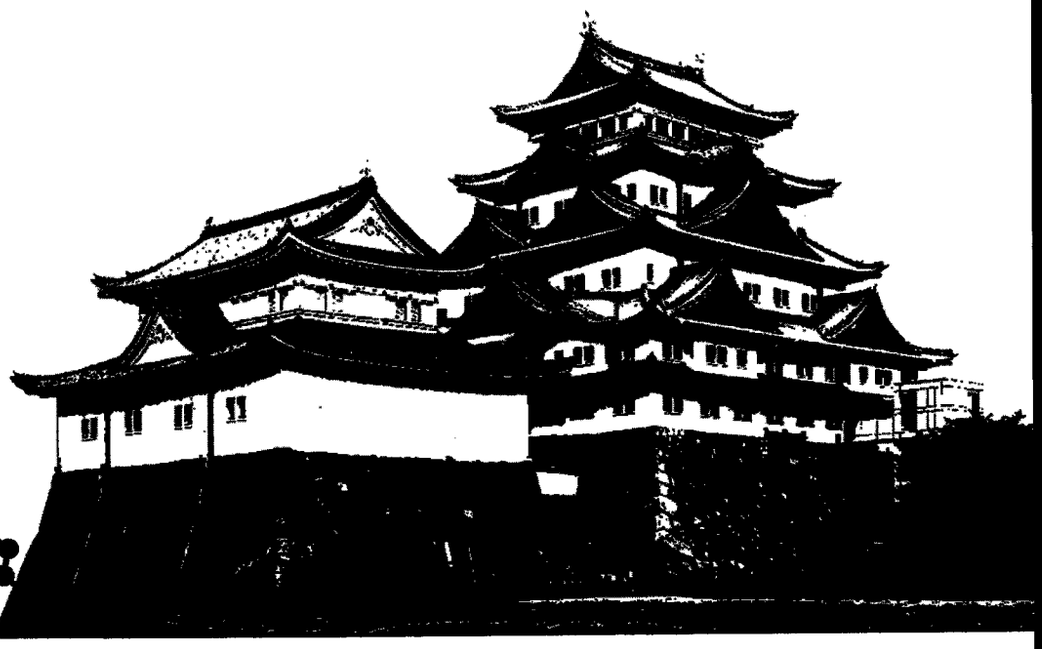
講演要旨集
Abstracts

2011年3月8日[火]-10日[木]

March . 8(Tue)-10(Thu), 2011

名城大学 天白キャンパス 共通講義棟北館

Meijo University Tenpaku Campus Lecture Hall (North), Nagoya, Aichi



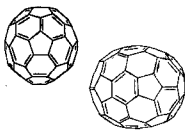
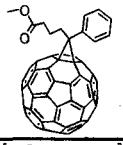
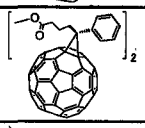
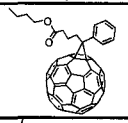
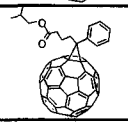
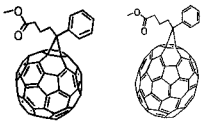
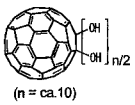
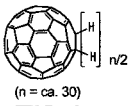
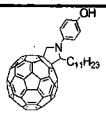
【共催】日本化学会
The Chemical Society of Japan

【協賛】日本物理学会 応用物理学会 高分子学会 電気化学会
The Physical Society of Japan, The Japan Society of Applied Physics,
The Society of Polymer Science Japan, The Electrochemical Society of Japan

【主催】フラーレン・ナノチューブ学会
The Fullerene and Nanotubes Research Society

F-NTRS®

nanom フロンティアカーボン(株)の フラーレンおよびフラーレン誘導体 製品一覧

銘　柄		分子構造	純度(HPLC面積%、代表値) 内容他	最低数量 (g)
nanom purple フラーレンC60	ST		99	10
	TL		99.5	2
	SU		99.5/昇華精製品	2
	SUH		99.9/昇華精製品	1
nanom orange フラーレンC70	ST		97	1
	SU		98/昇華精製品	0.5
nanom mix 混合フラーレン	ST		C60,C70,その他高次 フラーレンの混合物 ※微粒化品(ST-F)もあります	50
nanom spectra [60]PCBM (phenyl C61-butyric acid methyl ester)	E100		99	1
	E100H		99.5	1
	E102		99.9	0.5
nanom spectra E400 bis[60]PCBM (bis-phenyl C61-butyric acid methyl ester)			98/異性体トータル ※位置異性体の混合物	1
nanom spectra E200 [60]PCBNB (phenyl C61-butyric acid n-butyl ester)			99	1
nanom spectra E210 [60]PCBIB (phenyl C61-butyric acid i-butyl ester)			99	1
nanom spectra E123 [60,70]PCBM			[60]PCBM、[70]PCBMの混合物	1
nanom spectra [70]PCBM (phenyl C71-butyric acid methyl ester)	E110	 主成分	99/異性体トータル ※位置異性体の混合物	0.5
	E112		99.5/異性体トータル ※位置異性体の混合物	0.5
nanom spectra D100 水酸化フラーレン		 (n = ca.10)	$C_{60}OH_n$ n=10を主成分とする混合物	1
nanom spectra A100 水素化フラーレン		 (n = ca. 30)	$C_{60}H_n$ n=30を主成分とする混合物	1
nanom spectra G100			PRATO体。有機溶媒に可溶。	1

銘柄、取扱数量等は予告無く変更する場合がございます。予めご了承下さい。　　2011年2月1日現在

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＜本資料に関するお問い合わせ先＞
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Frontier Carbon Corporation

Abstract
The 40th Commemorative Fullerene-Nanotubes General Symposium

第 40 回記念フラーレン・ナノチューブ総合シンポジウム

講演要旨集

The Fullerenes and Nanotubes Research Society

The Chemical Society of Japan
The Japan Society of Applied Physics
The Physical Society of Japan
The Electrochemical Society of Japan
The Society of Polymer Science, Japan

主催：フラーレン・ナノチューブ学会

共催：日本化学会
協賛：日本物理学会・応用物理学会・電気化学会・高分子学会

Date : March 8nd(Tue)－10th(Thu), 2010
Place: Meijo University
1-501 Shiogamaguchi, Tempaku-ku, Nagoya 468-8502
TEL: 052-832-1151
Presentation: Special Lecture (25 min presentation, 5min discussion)
General Lecture (10 min presentation, 5min discussion)
Poster Preview (1 min presentation, no discussion)

日時：平成 23 年 3 月 8 日(火)～10 日(木)
場所：名城大学
〒468-8502 愛知県名古屋市天白区塩釜口 1-501
TEL：052-832-1151
発表時間：基調講演 (発表 40 分・質疑応答 5 分)
特別講演 (発表 25 分・質疑応答 5 分)
一般講演 (発表 10 分・質疑応答 5 分)
ポスタープレビュー (発表 1 分・質疑応答 なし)

展示団体御芳名(アイウエオ順、敬称略)

IOP英国物理学会出版局
アイクストロン(株)
(株)あすみ技研
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(株)ユニソク
理科研(株)

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9:45	一般講演3件 (ナノチューブの物性と応用) 9:45～10:30	一般講演4件 (ナノチューブの生成と精製) 9:30～10:30	一般講演3件 (ハイブリットカーボン) 9:45～10:30
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10:45	一般講演4件 (ナノチューブの物性と応用) 10:45～11:45	一般講演4件 (グラフェン) 10:45～11:45	一般講演4件 (グラフェン) 10:45～11:45
11:45	昼食　11:45～13:00		
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16:30			
17:00	ポスターセッション 17:00～18:20	ポスターセッション 17:10～18:30	
18:20			

3月8日(火)
チュートリアル　103講義室
15:00～16:30
講師　榎 敏明先生
東京工業大学大学院理工学研究科　教授

18:45～懇親会

基調講演 発表40分 質疑5分
特別講演 発表25分 質疑5分
一般講演 発表10分 質疑5分
ポスタープレビュー
発表1分 質疑なし

TIME TABLE

	Tue. Mar. 8	Wed. Mar. 9	Thu. Mar. 10
9:00	Plenary Lecture (S.Iijima) 9:00～9:45	Special Lecture (R.Yuge) 9:00～9:30	Plenary Lecture (Y.H.Lee) 9:00～9:45
9:45	General Lecture[3] (Properties and Applications of Nanotubes) 9:45～10:30	General Lecture[4] (Formation and Purification of Nanotubes) 9:30～10:30	General Lecture[3] (Hybrid Carbon) 9:45～10:30
10:30	Break 10:30～10:45		
10:45	General Lecture[4] (Properties and Applications of Nanotubes) 10:45～11:45	General Lecture[4] (Graphene) 10:45～11:45	General Lecture[4] (Graphene) 10:45～11:45
11:45	Lunch 11:45～13:00		
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13:30		Special Lecture (M.Hiramoto) 13:45～14:15	General Lecture[3] (Formation and Purification of Nanotubes) 13:30～14:15
14:15	Break 14:15～14:30		
14:30	Special Lecture (A.S.Barnard) 14:30～15:00	General Lecture[4] (Fullerenes) 14:15～15:15	Poster Preview 1min × [53] 14:15～15:10
15:10	General Lecture[4] (Hybrid Carbon) 15:00～16:00	Break 15:15～15:30	Poster Session 15:10～16:30
16:00	Poster Preview 1min × [54] 16:00～17:00	General Lecture[3] (Fullerenes) 15:30～16:15	
16:30		Poster Preview 1min × [54] 16:15～17:10	
17:00	Poster Session 17:00～18:20	Poster Session 17:10～18:30	
18:20			

18:45～ Banquet

Tue. Mar. 8
Tutorial Room103
15:00～16:30
Prof. Toshiaki Enoki

Plenary Lecture: 40min Presentation, 5min Discussion
Special Lectures: 25min Presentation, 5min Discussion
General Lectures: 10min Presentation, 5min Discussion
Poster Previews: 1min Presentation, No Discussion

座長一覧

3月8日（火）　（敬称略）

	時　間	座　長
基 調 講 演(飯島)	9:00 ～ 9:45	斎藤 晋
一 般 講 演	9:45 ～ 10:30	大野 雄高
一 般 講 演	10:45 ～ 11:45	片浦 弘道
一 般 講 演	13:00 ～ 14:15	菅井 俊樹
特 別 講 演(Barnard)	14:30 ～ 15:00	大澤 映二
一 般 講 演	15:00 ～ 16:00	小塩 明
ポスタープレビュー	16:00 ～ 17:00	沖本 治哉
ポスターセッション	17:00 ～ 18:20	宮田 耕充

3月9日（水）

	時　間	座　長
特 別 講 演(弓削)	9:00 ～ 9:30	宮本 良之
一 般 講 演	9:30 ～ 10:30	藤ヶ谷 剛彦
一 般 講 演	10:45 ～ 11:45	近藤 大雄
特 別 講 演(平本)	13:45 ～ 14:15	篠原 久典
一 般 講 演	14:15 ～ 15:15	加藤 立久
一 般 講 演	15:30 ～ 16:15	宮崎 隆文
ポスタープレビュー	16:15 ～ 17:10	北浦 良
ポスターセッション	17:10 ～ 18:30	田中 丈士

3月10日（木）

	時　間	座　長
基 調 講 演(Lee)	9:00 ～ 9:45	齋藤 理一郎
一 般 講 演	9:45 ～ 10:30	若林 知成
一 般 講 演	10:45 ～ 11:45	岡田 晋
特 別 講 演(長谷川)	13:00 ～ 13:30	吾郷 浩樹
一 般 講 演	13:30 ～ 14:15	齋藤 毅
ポスタープレビュー	14:15 ～ 15:10	千足 昇平
ポスターセッション	15:10 ～ 16:30	岸 直希

３月８日（火）

基調講演　発表40分・質疑応答5分
特別講演　発表25分・質疑応答5分
一般講演　発表10分・質疑応答5分
ポスタープレビュー　発表1分・質疑応答なし

基調講演（9：00-9：45）

一般講演（9：45-10：30）
ナノチューブの物性と応用

☆☆☆☆☆☆　休 憩　（10：30-10：45）☆☆☆☆☆☆

一般講演（10：45-11：45）
ナノチューブの物性と応用

☆☆☆☆☆☆　昼 食（11：45-13：00）☆☆☆☆☆☆

一般講演（13：00-14：15）
ナノチューブの応用

☆☆☆☆☆☆　休 憩　（14：15-14：30）☆☆☆☆☆☆

3月8日（火）

特別講演（14：30-15：00）

一般講演（15：00-16：00）
ハイブリッドカーボン

ポスタープレビュー（16：00-17：00）
ポスターセッション（17：00-18：20）

ナノチューブの生成と精製

3月8日（火）

ナノチューブの応用

ナノチューブの物性

３月８日（火）

グラフェン

ハイブリッドカーボン

若手奨励賞候補者

３月８日（火）

３月９日（水）

特別講演　発表25分・質疑応答5分
一般講演　発表10分・質疑応答5分
ポスタープレビュー　発表1分・質疑応答なし

特別講演（9：00-9：30）

一般講演（9：30-10：30）
ナノチューブの生成と精製

☆☆☆☆☆☆　休 憩　（10：30-10：45）☆☆☆☆☆☆

一般講演（10：45-11：45）
グラフェン

☆☆☆☆☆☆　昼食（11：45-13：00）☆☆☆☆☆☆

授賞式（13：00-13：45）

特別講演（13：45-14：15）

一般講演（14：15-15：15）
フラーレン

３月９日（水）

☆☆☆☆☆☆　休 憩　（15：15-15：30）☆☆☆☆☆☆

一般講演（15:30-16：15）
フラーレン

ポスタープレビュー（16：15-17：10）
ポスターセッション（17：00-18：30）

ナノチューブの応用

ナノチューブの生成と精製

３月９日（水）

ナノ炭素粒子

３月９日（水）

グラフェン

若手奨励賞候補者

3月9日（水）

３月10日（木）

基調講演　発表40分・質疑応答5分
特別講演　発表25分・質疑応答5分
一般講演　発表10分・質疑応答5分
ポスタープレビュー　発表1分・質疑応答なし

特別講演（9：00-9：45）

一般講演（9：45-10：30）
ハイブリッドカーボン

☆☆☆☆☆☆　休憩　（10：30-10：45）☆☆☆☆☆☆

一般講演（10：45-11：45）
グラフェン

☆☆☆☆☆☆　昼食（11：45-13：00）☆☆☆☆☆☆

特別講演（13：00-13：30）

一般講演（13：30-14：15）
ナノチューブの生成と精製

３月10日（木）

ポスタープレビュー（14：15-15：10）
ポスターセッション（15：10-16：30）

ナノチューブの物性

ナノチューブの生成と精製

フラーレン

3月10日（木）

内包ナノチューブ

3月10日（木）

ナノホーン

若手奨励賞候補者

Tuesday, March 8th

Plenary Lectures : 40 min (Presentation) + 5 min (Discussion)
Special Lectures : 25 min (Presentation) + 5 min (Discussion)
General Lectures : 10 min (Presentation) + 5 min (Discussion)
Poster Previews : 1 min (Presentation), No Discussion

Plenary Lecture (9 : 00-9 : 45)

General Lecture (9 : 45-10 : 30)
Properties and Applications of Nanotubes

☆☆☆☆☆☆ Coffee Break (10 : 30-10 : 45) ☆☆☆☆☆☆

General Lecture (10 : 45-11 : 45)
Properties and Applications of Nanotubes

☆☆☆☆☆☆ Lunch Time (11 : 45-13 : 00) ☆☆☆☆☆☆

General Lecture (13 : 00-14 : 15)
Properties and Applications of Nanotubes

Tuesday, March 8th

☆☆☆☆☆☆ Coffee Break (14:15-14:30) ☆☆☆☆☆☆

Special Lecture (14:30-15:00)

General Lecture (15:00-16:00)

Hybrid Carbon

Poster Preview (16:00-17:00)

Poster Session (17:00-18:20)

Formation and Purification of Nanotubes

Tuesday, March 8th

Applications of Nanotubes

Properties of Nanotubes

Graphene

Hybrid Carbon

Candidates for the Young Scientist Poster Award

Tuesday, March 8th

Wednesday, March 9th

Special Lectures : 25 min (Presentation) + 5 min (Discussion)
General Lectures : 10 min (Presentation) + 5 min (Discussion)
Poster Previews : 1 min (Presentation), No Discussion

Special Lecture (9:00-9:30)

General Lecture (9:30-10:30)
Formation and Purification of Nanotubes

☆☆☆☆☆☆ Coffee Break (10:30-10:45) ☆☆☆☆☆☆

General Lecture (10:45-11:45)
Graphene

☆☆☆☆☆☆ Lunch Time (11:45-13:00) ☆☆☆☆☆☆

Awards Ceremony (13:00-13:45)

Special Lecture (13:45-14:15)

General Lecture (14:15-15:15)
Fullerenes

☆☆☆☆☆☆ **Coffee Break (15:15-15:30)** ☆☆☆☆☆☆

General Lecture (15:30-16:15)

Fullerenes

Poster Preview (16:15-17:10)
Poster Session (17:10-18:30)

Applications of Nanotube

Wednesday, March 9th

Formation and Purification of Nanotubes

Carbon Nanoparticles

Graphene

Candidates for the Young Scientist Poster Award

Wednesday, March 9th

Thursday, March 10th

Plenary Lectures : 40 min (Presentation) + 5 min (Discussion)
Special Lectures : 25 min (Presentation) + 5 min (Discussion)
General Lectures : 10 min (Presentation) + 5 min (Discussion)
Poster Previews : 1 min (Presentation), No Discussion

Plenary Lecture (9 : 00-9 : 45)

General Lecture (9 : 45-10 : 30)
Hybrid Carbon

☆☆☆☆☆☆ Coffee Break (10 : 30-10 : 45) ☆☆☆☆☆☆

General Lecture (10:45-11:45)
Graphene

☆☆☆☆☆☆ Lunch Time (11 : 45-13 : 00) ☆☆☆☆☆☆

Special Lecture (13 : 00-13 : 30)

General Lecture (13:30-14:15)
Formation and Purification of Nanotubes

Poster Preview (14 : 15-15 : 10)
Poster Session (15 : 10-16 : 30)

Thursday, March 10th

Properties of Nanotubes

Formation and Purification of Nanotubes

Fullerenes

Thursday, March 10th

Endohedral Nanotubes

Thursday, March 10th

Nanohorns

Candidates for the Young Scientist Poster Award

基調講演
Plenary Lecture

特別講演
Special Lecture

1S – 1 ～ 1S – 2
2S – 3 ～ 2S – 4
3S – 5 ～ 3S – 6

1S-1

Science and Industrial Applications of Nano-carbon Materials

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The state of the art of synthesis of various nano-carbon materials that we have studied so far will be reviewed. One of challenge in the formation of SWCNT is to control its diameter and chirality, for which we have tried to grow SWCNTs by a conventional CVD method using metal catalyst of "uni-sized" metal clusters that are prepared by a mass-separator. Carbon nanohorn (CNH) aggregates are useful for nano-carbon materials where only large surface area and high dispersion are needed for medical applications, potable super-capacitor, polymer or metal composites etc. The usual size of CNH aggregates is about 80 nm in diameter but for some applications we need its smaller size, for example, less than 30nm for a bio-medical application. For this purpose we have developed a method to control a CNH aggregate size by optimizing vaporization conditions of CO_2 laser ablation of a carbon graphite rod. Some industrial applications will be introduced.

Formation of a large size graphene sheet by thermal CVD method using a copper substrate foil has been reported recently [1]. The method requires a high temperature CVD reactor (near 1000°C), so that it cannot be used in a conventional Si device process and therefore an alternative low temperature synthesis of graphene is needed. For this purpose we utilized a new surface-wave micro-wave CVD method which has been developed originally for the nano-diamond film growth at low temperature down to room temperature [2]. We shall demonstrate the growth of an A4-size graphene sheet grown at 300°C.

In the last half part of the presentation will be concerned with structural characterization of nano-carbon materials using atom-resolution electron microscopes as well as other characterization methods of Raman, photoluminescence and optical absorption spectroscopy, etc. The advantage of high resolution electron microscopy (HRTEM) over other techniques is to be able to characterize local atomic structures such as lattice defects and edge structures of nano materials which cannot be studied in conventional techniques. Another emphasis of HRTEM will be on dynamic observation of a reaction process which is not available for other high resolution probe microscope techniques such as STM. We thank for a recent progress of HRTEM technology such as aberration correction and EELS, which has made possible elemental analysis, distinction of valency and more on individual atom basis. Some latest examples of above mentioned observations will be demonstrated [3-12].

(1) S. Bae, et al. Nature Nanotech., (2010).
(2) M. Hasegawa et al., PRB, (2010).
(3) K. Suenaga, et al. Nature Nanotech. **2**, 358 (2007)
(4) Z. Liu, et al., Nature Nanotech., **2**, 422 (2007).
(5) Y. Sato, et al., Nano Lett, **7**, 3704 (2007).
(6) C. H. Jin, et al., Nature Nanotech. **3**, 17 (2008).
(7) C. H. Jin, et al., PRL, **101**, 176102(1)-(4) (2008).
(8) M. Koshino, et al., Nature Chemistry (2010).
(9) Z. Liu, et al., PRL, **102**, 015501 (1)-(4) (2009).
(10) C. H. Jin, et al., PRL, **102**, 195505 (1)-(4) (2009).
(11) C. H. Jin, et al., PRL, **102**, 205501 (1)-(4) (2009).
(12) K. Suenaga et al., Nature, **468**, 1088 (2010).

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1S-2

The Advantages and Applications of Nanocarbon Phase Transformations

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The family of carbon nanomaterials is a rich and exciting area of research, that spans materials science, engineering, physics and chemistry, [1]; and most recently, is having an impact in biology and medicine [2]. Although a wide range of applications are emerging, the basic science of nanocarbon is still receiving considerable attention, due to advanced methods allowing fabrication of carbon nanomaterials with different dimensionalities, and the existence (and co-existence) of more than one allotrope. The low dimensional sp^2-bonded structures have sp^3-bonded siblings, and like all siblings they share a complicated relationship. Just as fullerenes and nanotubes have unique properties (ideal for specific applications), diamond nanorods and diamond nanoparticles (nanodiamonds) are also unique, and have slowly carved out a complementary niché in the field of carbon-based nanotechnology. However, spontaneous, inefficient (reversible and irreversible) phase transformations prevail at small sizes, and most diamond nanomaterials are decorated with a full or partial fullerenic or nanotubular sheath [3]. For some applications this can be a hindrance, but one may argue that the most interesting and exciting properties are revealed when these materials are combined. As we will see in this presentation, we often find that the combination is greater than the sum of the two, and entirely new properties can emerge [4]. If we embrace the advantages of nanocarbon phase transformations, and learn to control this new structural degree of freedom, even more opportunities will undoubtedly materialize.

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[2] *Nanodiamonds: Applications in Biology and Nanoscale Medicine*, ed. D. Ho, Springer Science + Business Media, Inc., Norwell, MA, USA (2010).

[3] A.S. Barnard, *Diamond Relat. Mater.* **15**, 285 (2006).

[4] A. S. Barnard, *J. Mater. Chem.*, **18**, 4038 (2008).

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2S-3

Application of Flat-Panel Field Emission Lamp using Carbon Nanotube-Carbon nanohorn Cathodes

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Carbon nanotubes (CNTs) have been reported as one of the best cold cathode emitter for field emission display (FED) and field emission lamp (FEL) applications owing to their large aspect ratio, high mechanical strength, good electrical conductivity, and possibility of large-area application via thick film processing.[1-2] In the fabrication of the CNT cathodes for FEDs and FELs, CNTs are deposited on the substrate by direct growth,[3] electrophoresis,[4] or printing.[5]

For the FELs, a simple, scalable, and low-cost method of printing is especially appropriate. Here, we introduce recent progress in flat-panel FEL using CNTs and carbon nanohorns (CNHs). For the manufacture of highly efficient FE devices, we synthesized single-wall carbon nanotubes (SWNTs) on catalyst-supported single-wall carbon nanohorns (SWNHs) by chemical vapor deposition.[6] In the obtained SWNT-SWNH hybrids (NTNHs), the SWNTs diameters were 1–1.7 nm and the bundle diameters became almost uniform, *i.e.*, less than 10 nm, since the SWNTs were separated by SWNH aggregates. As a result, FELs using NTNH hybrids achieved highly bright and homogeneously bright emission as a result of having both the promising FE properties of SWNTs and the high-dispersion properties of SWNHs. We also confirmed that a stable long-term operating period for the lamp became possible by optimizing the CNT cathode preparation process.

Uniform lighting emission from a phosphor on the anode is essential for improving flat-panel FELs using CNTs. By developing triode-type CNT-FELs, our research groups have succeeded in decreasing the non-uniformity of lighting emission to half that of the diode-type CNT-FEL.

References:

[1] A. G. Rinzler et al. *Science*, **296**, 1550 (1995).

[2] J. M. Bonard et al. *Appl. Phys. Lett.*, **78**, 2775 (2001).

[3] T. Hirakoka et al. *J. Am. Chem. Soc.*, **128**, 13338 (2006).

[4] B. Gao et al. *Adv. Mater.*, **13**, 1770 (2001).

[5] J. Li et al. *Appl. Surf. Sci.*, **220**, 96 (2003).

[6] R. Yuge et al. *ACS Nano* in press.

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2S-4

Fundamentals and Recent Progress of Organic Thin-film Solar Cells

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Organic EL television was commercialized last year. Next target of organic electronics is organic solar cell. The present lecture includes fundamental science and history of organic solar cells, concept of organic p-i-n cells [1], nanostructure design of codeposited i-interlayer [2], ultra-high purification of organic semiconductors [3], and future prospects of organic solar cells.

High-purified organic semiconductors can be obtained by forming large single crystals (Fig. 1). p-i-n cells incorporating seven-nine (7N) C_{60} showed the world record conversion efficiency of 5.3% (Fig. 2). Essence of high efficiency is the utilization of entire visible light of solar spectrum without decreasing fill factor by the black-colored cell incorporating very thick (1 μm) C_{60}:H_2Pc *i*-interlayer.

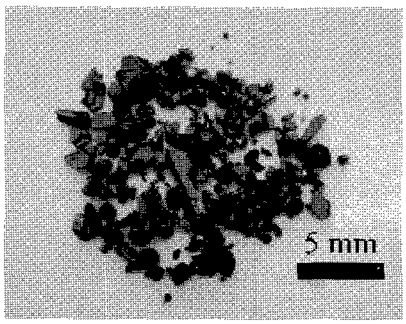

Fig. 1 Single crystals of seven-nine (99.99999, 7N) C_{60}.

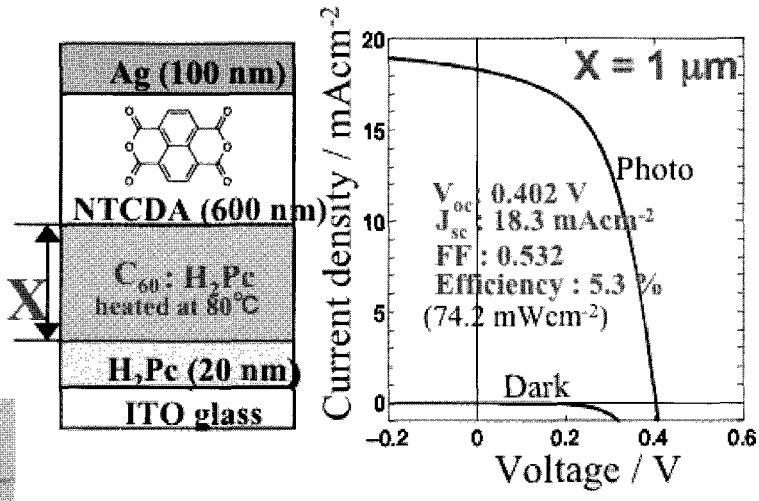

Fig. 2 p-i-n cell structure and current-voltage characteristics of p-i-n cell incorporating 7N-C_{60}.

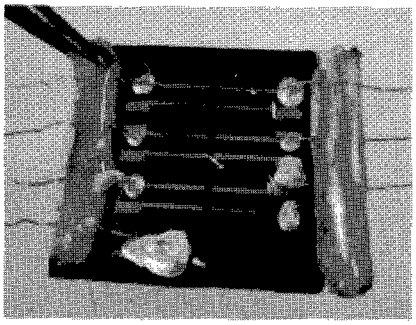

Fig. 3 p-i-n cell having 1 μm-thick C_{60}:H_2Pc codeposited i-inerlayer, which showed efficiency of 5.3%.

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3S-5

Carrier Control of Carbon Nanotube Transistor

Young Hee Lee

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Nanocarbons such as fullerenes, carbon nanotubes, carbon nanofibers, graphite oxides, and graphenes have been the key words in 21th century and has led nanoscience and nanotechnology. Due to the various allotropes of carbons, unexpected scientific new findings and their related applications have been extensively investigated. In this talk, I will focus key issues in CNT-based transistors: metal-CNT contact, chemical doping, doping-dependent conductivity, and trap charge doping, and ambipolarity. Pure carbon nanotubes have been known to exhibit ambipolarity. This is very different from the conventional semiconductors that are controlled by an intentional doping with extrinsic materials. The ambipolarity has been a serious drawback in adopting carbon nanotubes for CMOS technology. Carbon nanotubes show p-type behavior in ambient conditions. The difficulty arises from the absence of stable n-type dopants in ambient conditions. A series of chemical approaches have been done in our group to search for n-type dopants. NADH and viologen molecules have demonstrated successfully to show n-type behavior by donating electrons to nanotubes and furthermore show high stability in ambient conditions.[1-7] Trap-charge doping without chemical doping was also discussed.[8] In addition to these approaches, we will also demonstrate a way of utilizing ambipolarity of nanotubes without such intentional dopings that ambipolarity is in fact advantageous in fabricating CMOS inverter and logic circuits.[9] These doping ideas have been further used for CVD-grown graphene.[10-11]

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[11]. F. Gunes et al. ACS NANO 4, 4595 (2010).

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3S-6

Low-temperature graphene synthesis by using microwave plasma CVD

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Because of its high electrical conductivity as well as chemical and physical stability graphene-based films are expected to be utilized for transparent conductive films for next-generation electrical and optoelectronic devices and various other applications. Recently the synthesis methods of graphene by using thermal chemical vapor deposition (CVD) have been developed, in which large area graphene are synthesized on Ni[1] or Cu[2] substrates. In this thermal CVD, high temperature of 1000degC for the decomposition of CH4 and the duration of the order of hour are required. For the realization of graphene industries the fast synthesis methods at lower temperature are desirable.

In this study we have developed a low-temperature and rapid synthesis method of graphene on A4 size-Cu foils by using microwave (2.45GHz) plasma assisted CVD sustained by surface waves. The reaction gas is the mixture of CH_4, H_2 and Ar, the pressure is less than 10Pa, the substrate temperature during the deposition is about 400degC, and the duration of CVD is around 60seconds. After the deposition the Cu foil is etched away using FeCl3 aqueous solution, and the graphene films are transferred to glass plates. The typical sheet resistance is 1-2 kΩ/□, and the optical transmittance is about 80%at 550nm. Figure 1 shows the typical Raman spectrum (excitation wavelength 638nm) of the graphene. In addition we have fabricated a capacitive type touch panel. Figure 2 shows a picture of the demonstrated touch panel which works properly by the finger touch.

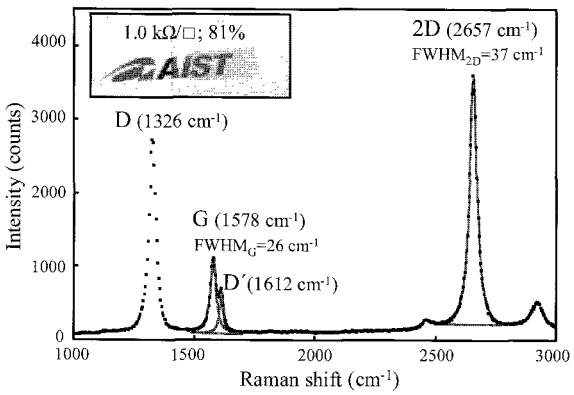

Fig.1 Typical Raman spectrum of graphene synthesized by microwave plasma CVD (Excitation wavelength 638nm).

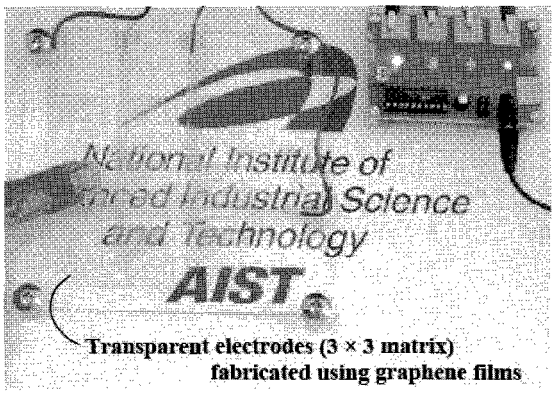

Fig.2 Fabricated capacitive type-touch panel using graphene.

(1) Q. Yu, J. Lian, S. Siriponglert, H. Li, Y. P. Chen, S.-S. Pei, Appl.Phys.Lett.93(2008)113103.

(2) X. Li, W. Cai, J. An, S. Kim, J. Nah, D. Yang, R. Piner, A. Velamakanni, I. Jung, E. Tutuc, S. K. Banerjee, L. Colombo, R. S. Ruoff, Science 324(2009)1312.

一般講演
General Lecture

1 – 1 ～ 1 – 16
2 – 1 ～ 2 – 15
3 – 1 ～ 3 – 10

1-1

Probing surfactant molecules on SWCNTs by Raman spectroscopy

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Raman spectroscopy of single-wall carbon nanotubes (SWCNTs) dispersed in water using five kinds of surfactant was investigated. It was revealed that G-band Raman spectral feature was strongly changed depending on the kind of surfactant, which means that Raman spectra of SWCNTs can be used for probing the surfactant molecules adsorbed on SWCNTs. By changing the relative concentrations of two surfactants in the solution, Raman spectral modulation detected a surfactant exchange process on the SWCNT surface. It was found that Raman spectral changes were not reversible, meaning that the surfactant exchange on the SWCNTs was irreversible reaction probably due to the different affinities. Interestingly, this irreversible surfactant exchange process was also confirmed by the different results on the metal semiconductor separation by density gradient ultracentrifugation for the different pretreatments. We claim that the only monolayer of surfactant molecules can be detected by the Raman measurement. This new probe of surfactant is very useful to analyze the mechanism of metal-semiconductor separation of SWCNTs where the surfactant plays very important roles.

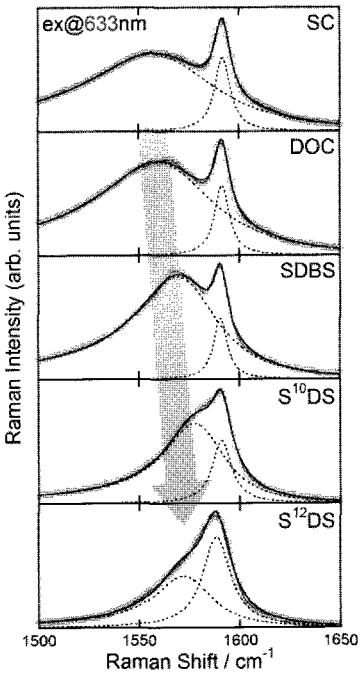

Figure 1. G-band Raman spectra of SWCNTs dispersed in 5 kinds of surfactant water solution.

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1-2

Evaluation of single-walled carbon nanotubes dispersed in surfactant solution by using Raman spectroscopy

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[3]*Nanotube Research Center, AIST, Tsukuba 305-8565, Japan*
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Abstract:

Raman spectroscopy is a powerful technique and has been extensively used for the evaluation of diameter/chirality distribution of single-walled carbon nanotubes (SWNTs). One of the characteristic features of Raman spectroscopy is that, it gives information about not only for semi-conductive nanotubes, but also for metallic ones [1]. On the other hand, recent progress in dispersion technique of SWNTs in DNA solution, indicates that, SWNTs can be well extracted from the soot prepared even in He atmosphere by making use of arc-burning technique [2]. Since the uniformity of SWNTs in solution is considered to be much better than that in as-grown soot or film, it is worth while investigating Raman spectroscopy of SWNTs dispersed in solution phase furthermore.

In this presentation, single-walled carbon nanotubes (SWNTs) were prepared by making use of arc-burning [2,3] and laser-oven technique, respectively, and those SWNTs were further dispersed by single-stranded DNA (ss-DNA) solution. Those dispersed SWNTs were then used as sample solution for Raman spectroscopy.

Fig.1 shows an example of Raman spectra of SWNTs (excitation wavelength: 532 nm) made with laser-oven (LV) technique in nitrogen atmosphere with different oven temperature. The figure clearly shows that the relative G-band intensity by semi-conductive SWNTs increases extensively, as the oven temperature increases. This behavior can be explained by considering about the diameter distribution of SWNTs prepared in each case.

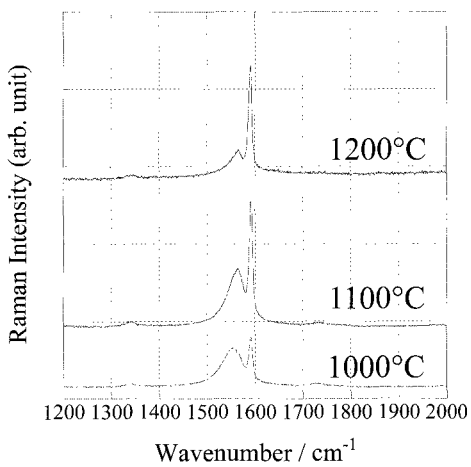

Fig.1

References:

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[3] S. Suzuki, K. Hara, T. Fujita, T. Mizusawa, T. Okazaki, and Y. Achiba, *J. Nanosci. Nanotech.*, **10**, 4060-4063(2010).

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1-3

Exciton-Exciton Interactions in Thin SWNTs Extracted from DWNTs

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Optical properties in single-walled carbon nanotubes (SWNTs) are governed by one-dimensional exciton effects, and studying exciton dynamics is of great importance to understand both transient and steady-state responses. In the high excitation density regime, a nonlinear relaxation process of excitons, i.e., bimolecular Auger recombination, takes place. Due to the exciton collision one exciton annihilates and the other exciton is excited into a higher state. Hence, a key parameter is the initial number density of excitons per tube generated by an optical pulse. In this work, we investigate exciton dynamics in the high excitation density regime in SWNTs with the (6,4) chirality by means of non-degenerate pump-probe spectroscopy, and reveal a pump-fluence dependence of the initial exciton number. We also estimate an exciton size by taking into account a phase-space filling effect on the change of absorption coefficient.

(6,4) SWNTs used in this work were prepared by an extraction method based on sonication and further density gradient ultracentrifugation of double-walled carbon nanotubes (DWNTs) [1]. The SWNTs were micelle-encapsulated by sodium cholate in water. Pump-probe measurements were carried out by using two optical parametric amplifiers (OPAs) pumped by a regenerative amplifier (1 kHz, 800nm, 120 fs), which was seeded by a Ti:sapphire laser (80 MHz, 800 nm, 80 fs). Pump and probe photon energies were 2.1 and 1.4 eV, respectively, which are resonant with the E_{22} and E_{11} band of (6,4) tube. Polarizations of the pump and probe pulses are parallel to each other.

Figure 1 shows the transmittance change ($\Delta T/T$) at E_{11} band in (6,4) SWNTs at the pump fluences of 0.024, 0.12, 0.95, and 4.8×10^{15} photons/cm^2. As the pump-fluence increases, the sharp rising at time origin and its steep decay till ~1 ps are pronounced. This behavior is explained by the bimolecular Auger recombination of excitons: As the number of excions generated by a pump pulse increases, the collision rate of them increases and the signal decay becomes fast. By fitting the experimental results to the analytical expression of the bimolecular Auger recombination model [2], the initial exciton number per tube is determined to be 2, 8, 19, and 38 for the corresponding pump fluence. Assuming the typical tube length of ~760 nm determined by AFM observations, the exciton size is estimated to be ~1.7(± 0.7) nm.

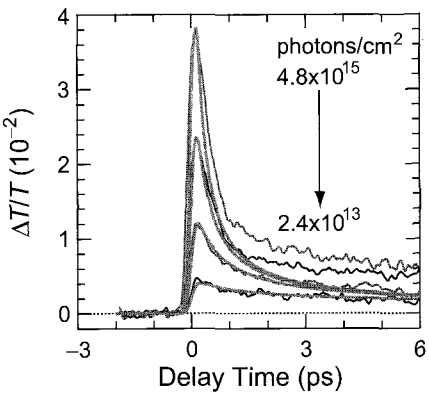

Fig. 1. Time evolution of differential transmittance ($\Delta T/T$) at E_{11} band in (6,4) SWNTs. Thin and thick lines represent the experimental and fitting results.

[1] Y. Miyata *et al.*, ACS Nano **4**, 5807 (2010).
[2] A. V. Barzykin and M. Tachiya, Phys. Rev. B **72**, 075425 (2005).

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1-4

Continuous Carrier Tuning in Metallic and Semiconducting SWNT Film

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Recent success in isolating SWNTs of narrow chirality distributions enabled making pure metallic (m-) and semiconducting (s-) SWNT films. Their unique feature is the existence of sharp peaks in the density of states at van Hove singularities (vHs's). Hence, it is expected that their conduction properties change dramatically when the Fermi level (E_F) is at a vHs. Chemical doping or field-effect transistor is unsuitable for the purpose because of the lack of precise and reversible E_F controllability, and the narrow controllable E_F range, respectively. The problems are solved by our electric double layer transistor (EDLT, Fig.1) technique, where the gate voltage (V_G) is applied through an electrolyte. We have realized superconducting transition in $SrTiO_3$ [1] and ZrNCl [2] with EDLT. Therefore, this work was done to investigate conduction properties of s- and m-SWNT films with EDLT.

The conductance, optical absorption spectra, and temperature dependence of the resistance of s- and m-SWNT films were measured at various V_G. The conductance of the s-SWNT film showed stepwise change against V_G (Fig.2). The absorbance spectra (Fig.3) indicate the steps correspond to reaching of the E_F to a vHs. The E_F shift across a vHs was also observed in the m-SWNT films. The conductance of the m-SWNT film sharply increased at the point and its temperature dependence changed from that of variable range hopping to a metallic behavior. These results demonstrate that the conduction properties strongly depend on the E_F, reflecting one dimensionality of SWNTs.

[1] K. Ueno *et al.*, *Nat. Mater.* **7**, 855 (2008).
[2] J. T. Ye *et al.*, *Nat. Mater.* **9**, 125 (2010).

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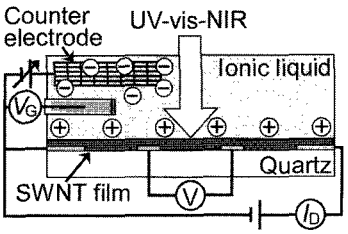

Fig.1. Illustration of electric double layer transistor. The gate voltage (V_G) was measured with a Ag/Ag^+ reference electrode. The conductance (I_D/V) was measured by 4-probe method. Ionic liquid: *N*, *N*-Diethyl-*N*-methyl-*N*-(2-methoxyethyl)ammonium.

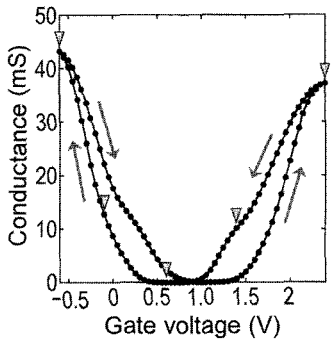

Fig.2. The conductance of a semiconducting SWNT film plotted against the gate voltage. Triangles indicate voltages, at which absorption spectra in Fig.3 were measured.

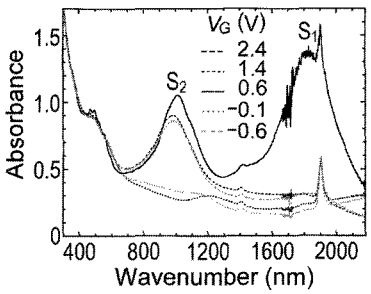

Fig.3. Absorption spectra of the semiconducting SWNT film at various gate voltages (V_G). S_1 and S_2 denote the transition between the first subbands and the second subbands, respectively.

1-5

Carrier mobility and on/off ratio of carbon nanotube thin-film transistors fabricated by gas-phase filtration and transfer process

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Carbon nanotube (CNT) thin-film transistors (TFTs) are expected to allow the fabrication of high-performance, flexible, and transparent devices with relatively simple techniques. Previously, we have presented a gas-phase filtration and transfer process to fabricate CNT TFTs, demonstrated high-performance CNT TFTs with a mobility of 35 $cm^2V^{-1}s^{-1}$ and an on/off ratio of 6×10^6, and flexible logic integrated circuits, including a 21-stage ring oscillator and master-slave delay flip flops, representing the first nanotube-based sequential logic [1]. Here, we present the detailed characterization of the high-performance CNT TFTs.

There are two models to estimate gate capacitance used for the carrier mobility evaluation: the parallel plate model and the rigorous model taking into account the realistic electrostatic coupling between sparse nanotubes and the gate electrode [2] (Figure 1). By the parallel plate model, the mobility of the TFT is evaluated to be 35 $cm^2V^{-1}s^{-1}$. On the other hand, the mobility is evaluated to be 634 $cm^2V^{-1}s^{-1}$ by the rigorous model. We will discuss which method is appropriate for the performance evaluation of CNT TFTs.

In the case of CNT TFTs, it is often reported that the on/off ratio degrades with increasing V_{DS} [2]. However, Figure 2 shows the transfer characteristics of a typical CNT TFT at various V_{DS} ranging from −0.5 to −5 V; the on/off ratio decreased slightly with increasing V_{DS}, but remains as high as 1×10^6 at $V_{DS}=-5$ V. In contrast, the on/off ratios decreased significantly for the TFTs with larger-diameter CNTs. The on/off degradation can be attributed to electrons tunneling through the narrow bandgap at the high drain field.

[1] D.-M. Sun *et al.*, *Nature Nanotech.* (2011) in press.
[2] Q. Cao *et al.*, *Appl. Phys. Lett.* **90**, 023516 (2007).

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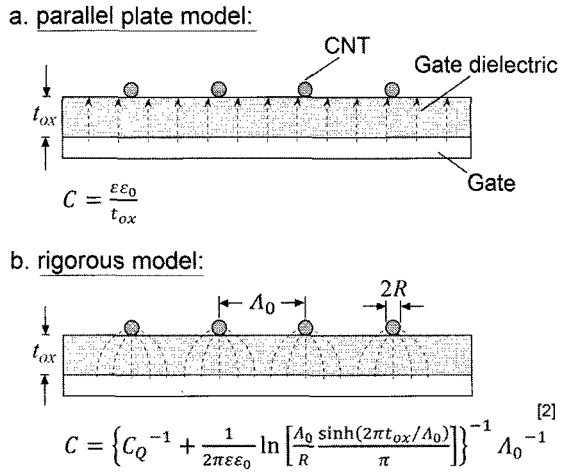

Fig. 1. Schematics of electric force lines in (a) parallel plate and (b) rigorous model.

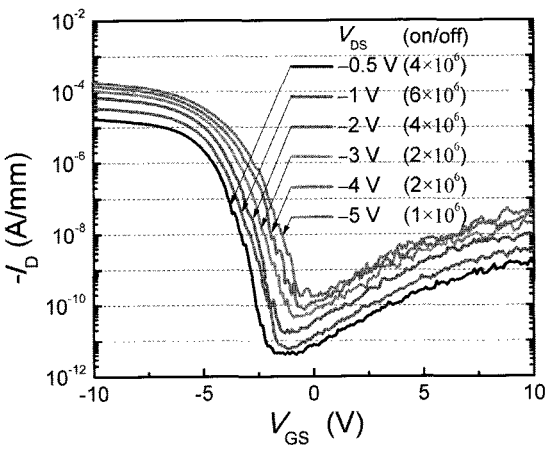

Fig. 2. I_D-V_{GS} characteristics at V_{DS} from −0.5 to −5 V.

1-6

High mobility thin-film transistors using length-sorted semiconducting single-wall carbon nanotubes

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Single-wall carbon nanotubes (SWCNTs) are a promising material for a channel of thin film transistors (TFTs) because of their high carrier mobility, flexibility, and solution processability. Recently, the performance of liquid-processed SWCNT-TFTs has been improved as the purification methods of semiconducting SWCNTs (s-SWCNTs) are developed. For instance, Rouhi *et al.* reported the TFTs using 99% s-SWCNTs (which were purified by density gradient ultracentrifugation) showed an on/off ratio of 10^4 and a mobility of 40 $cm^2V^{-1}s^{-1}$[1]. However, this mobility is still lower than that of TFTs fabricated by as-grown SWCNTs [2]. This suggests that it is essential to consider not only the purity but also the other factors such as nanotube length for further improvements of TFT performance.

In this study, we have fabricated TFTs using length-sorted, high-purity semiconducting SWCNTs. To obtain these samples, we have developed a separation/purification method based on gel filtration that have been reported by Moshammer *et al.*[3] and Tanaka *et al.*[4]. Our method includes a recycling filtration process of SWCNTs with an eluate containing competing mixtures of surfactants. This process allows us to extract micrometer-long and highly pure s-SWCNTs. We fabricated the TFTs using the aligned networks of separated SWCNTs. Figure 1 shows the I_D-V_{DS} characteristics of the TFT fabricated. The device has an on/off ratio ~10^6, a mobility of ~170 $cm^2V^{-1}s^{-1}$, and a normalized maximum transconductance of 0.78 Sm^{-1}. This corresponds to the highest performance compared with the SWCNT-TFTs that have been reported so far[2]. The present result represents an important milestone toward post silicon high-performance electronics.

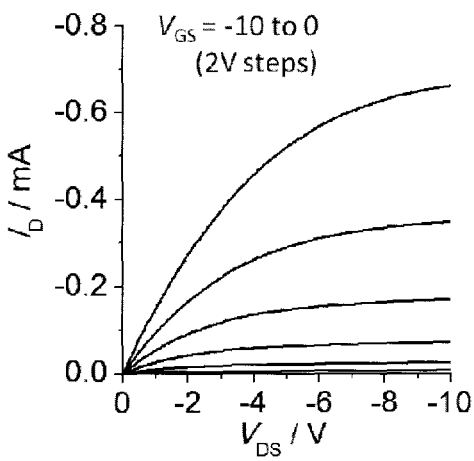

Figure 1 I_D-V_{DS} characteristics of TFT using high purity and micrometer-long s-SWCNT (channel width : 200 μm、channel length : 40 μm)

Reference
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[4] Tanaka et al., ***Appl. Phys. Express***, 2, 125002 (2009)

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1-7

Highly Flexible All-SWNT Field-Effect Transistors

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With the recent development of novel electronic devices there is a desire for flexible, transparent, high-performance field-effect transistors (FETs). A single-walled carbon nanotube (SWNT) is expected to be a strong candidate for realizing such next-generation devices due to their mechanical robustness and excellent electrical properties.

Based on our unique patterned-growth technique using a self-assembled monolayer (SAM) [1], we have reported that high-performance all-SWNT FETs can be easily fabricated [2]. Such all-SWNT devices can work on a flexible substrate without degrading their electrical properties [3], and may realize metal-free electronics. Here, flexible and transparent all-SWNT FETs were fabricated by a transfer printing method.

Figure 1 shows a schematic diagram of the flexible FET and SEM image of the all-SWNT FET before transfer. Poly(vinyl alcohol) (PVA) was spin coated onto the patterned SWNTs and then dried. An SWNT film attached to the plastic substrate acted as the global gate electrode. The transfer characteristics before transfer (on Si substrate) and after transfer (in PVA film) are shown in Figure 2. The resulting all-SWNT FET was highly flexible, and could be crumpled without degradation of the properties.

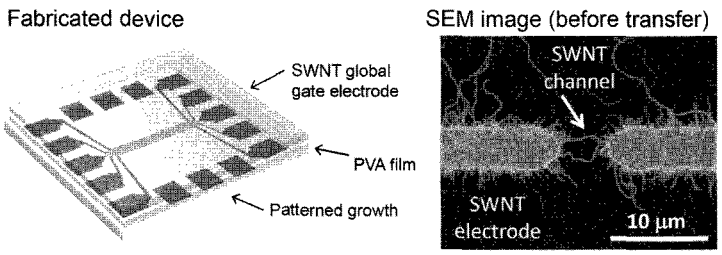

Fig. 1 Schematic diagram of the flexible all-SWNT device and SEM image of the channel region before transfer.

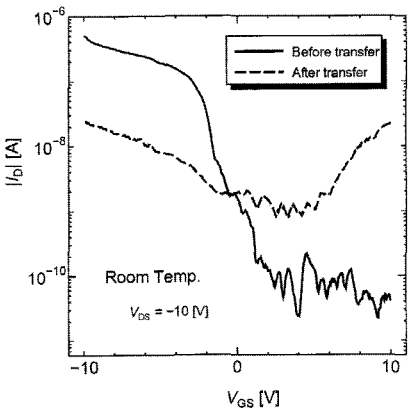

Fig. 2 Transfer characteristics before and after transfer.

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[2] S. Aikawa et al. *The 39th Fullerene Nanotubes General Symposium,* p.53 (2010).
[3] Q. Cao et al., *Appl. Phys. Lett.* **88,** 113511 (2006).

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1-8

Infrared Solar Cell Based on C_{60} Encapsulated Semiconducting Single-Walled Carbon Nanotubes

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Semiconducing single-walled carbon nanotubes (S-SWNTs) are quasi one-dimensional materials exhibiting interesting optical properties, which makes them promising candidates for fabrication of solar cells. More importantly, the near-infrared band gap transition of S-SWNTs makes them suitable to harvest the infrared solar spectrum.[1]

In this work, we have systematically investigated the possibility of making infrared solar cells, as schematically shown in Fig. 1(a), based on *n*-silicon and S-SWNTs including pristine S-SWNTs and C_{60} encapsulated semiconducting SWNTs (C_{60}@S-SWNTs) which serve as energy conversion material. Our results have demonstrated that S-SWNTs can be used to convert infrared light (800-1550 nm) into electrical energy under the configuration of solar cells, as shown in Fig. 1(b) where the *I-V* characteristic is measured under 1200 nm light illumination. Interestingly, the performance of solar cells based on S-SWNTs is much better than that observed in solar cells fabricated by SWNTs containing both metallic and semiconducting SWNTs, and the solar cells based on C_{60}@S-SWNTs are found to show a better power conversion efficiency than pristine S-SWNTs due to the charge transfer effect between SWNTs and C_{60} fullerene.[1] In addition, it is found that when the light energy is higher than two times of the first van Hove transition energy of S-SWNTs (E_{11}), the efficiency suddenly increases, suggesting the possibility for the occurrence of multiple exciton generation in the C_{60}@S-SWNTs based solar cell.

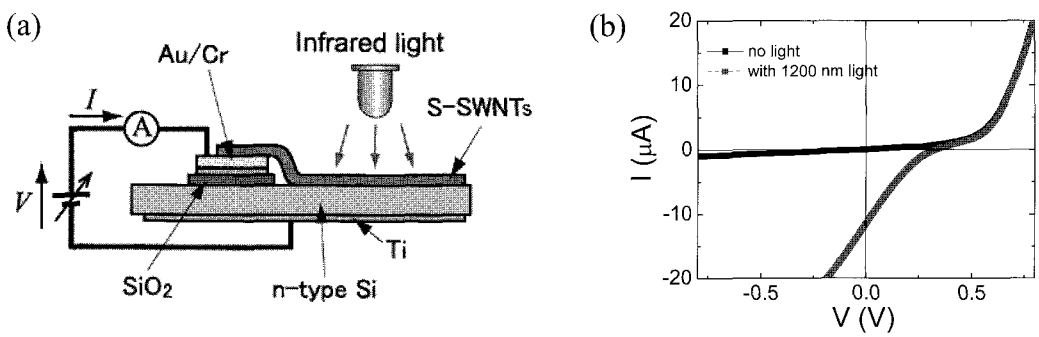

Fig.1: (a) Schematic illumination of solar cell based on S-SWNTs. (b) *I-V* characteristic of solar cell based on C_{60}@S-SWNTs measured under 1200 nm light illumination.

[1] R. Hatakeyama, Y.F. Li, T. Y. Kato, and T. Kaneko, *Appl. Phys. Lett.* **97**, 013104 (2010).

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1-9

Metal-free Fuel Cell Cathode Catalyst Prepared by Carbonization of Polybenzimidazole-wrapped Carbon Nanotubes

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Abstract: Polymer electrolyte fuel cell systems using non-precious metal as a catalyst are the strong request from industry side. One of the promising approaches for the non-precious metal cathode catalyst is the nitrogen-containing graphite structure proposed by Ozaki et al., which were prepared from the metal complex of the nitrogen-containing polymers[1]. We recently reported the pyridine-containing polybenzimidazole (PyPBI: **Fig. 1**) adsorbed to MWNTs through π–π interaction and formed PyPBI-wrapped MWNT (MWNT/PyPBI)[2]. Based on the finding, we fabricated the cobalt(II) or iron(II) complex of the MWNT/PyPBI (MWNT/PyPBI/Co and MWNT/PyPBI/Fe) and the composites were pyrolyzed at 600 °C for 1.5 h, followed by the washing with concentrated HCl in order to remove the cobalt species. Fig. 2 shows the linear sweep voltammograms of the composites (line: pyrolyzed MWNT/PyPBI/Co, dashed line: pyrolyzed MWNT/PyPBI/Fe), which were measured by rotating electrode voltammetry (1600 rpm) in 0.5 M H_2SO_4. We observed similar current on both catalysts for oxygen reaction (Fig. 2, lower). On the other hand, in Fig.2 (upper), lower current was observed for pyrolyzed MWNT/PyPBI/Fe, indicating pyrolyzed MWNT/PyPBI/Fe exhibited better catalytic activity for one step oxygen reduction than pyrolyzed MWNT/PyPBI/Co.

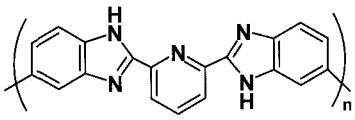

Fig. 1 Chemical structure of PyPBI

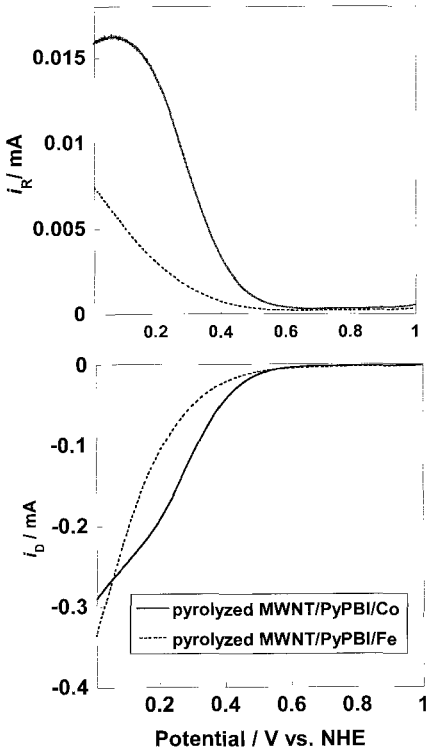

Fig. 2 Oxygen reduction voltammograms for the pyrolyzed composites. (Upper) ring current, (bottom) disk current

References:

1) J. Ozaki, S. Tanifuji, N. Kimura, A. Furuichi, A. Oya, *Carbon* **2006**, *44*, 1324.

2) T. Fujigaya, M. Okamoto, N. Nakashima, *Carbon* **2009**, *47*, 3227.

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1-10

Improved Dispersibility of Single-walled Carbon Nanotubes (SWNTs) Using Subtle Growth Ambient and Its Enhancement of Conductivity in SWNT/Polymer Composites

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Dispersing single-walled carbon nanotubes (SWNTs) in solvents is a key step for producing uniform SWNT composites, and extracting their intrinsic properties. Here we demonstrate that dispersibility of SWNTs is dramatically improved by subtle growth ambient, and the improved dispersibility affects conductivity in the SWNT/polymer composite.

SWNTs were synthesized using a "Super-growth" method which is based on chemical vapor deposition with small amount of molecular oxygen including water and acetone. SWNTs in dimethylform amide (DMF) were then subjected to a water-cooled sonication bath for five hours. DMF dispersion of acetone-grown SWNTs was homogenious and stable, although a part of SWNTs were readily aggregated and precipitated in dispersion of water-grown SWNTs (Figure 1). Quantitative laser diffraction data revealed that an averaged diameter and its homogeneity were improved by five times for acetone-grown SWNTs, compared to water-grown SWNTs.

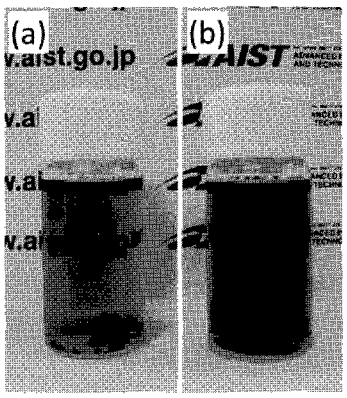

Figure 1. DMF dispersions of (a) water-grown and (b) acetone-grown SWNTs.

We then applied these dispersions to making conducting SWNT/polymer composites. In the composites, SWNTs would serve as conducting channels. For 0.2wt% SWNT, a composite made from acetone-grown SWNTs showed 0.36 S/cm of conductivity, roughly two times larger than that of a water-grown SWNT composite.

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1-11

Carbon Nanotubes with Temperature-Invariant Creep and Creep-Recovery from -150°C to 970°C

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Creep and creep recovery are important properties of viscoelastic materials. Creep is the time-dependent increase in deformation (strain) of a viscoelastic material subjected to a constant stress, and creep recovery is the time dependent elastic recovery from deformation. Creep and creep recovery (together referred to as creep recovery) are phenomena that can be found everywhere. For example, when we sit onto a cushion (applying a stress), the cushion gradually deforms to conform to our body (creep), and after we stand thereby releasing the stress, the cushion gradually recovers its shape (creep recovery). As exemplified, creep recovery is not an instantaneous process and occurs progressively over time. This aspect of creep recovery enables the gradual distribution of stress, and is thus very useful to prevent fracturing caused by stress concentration. Since conventional viscoelastic materials are composed of polymers, their operational temperature range of creep recovery is limited. Specifically, the operational range of the most temperature stable rubber, silicone rubber, is -55-300°C.

Here, we present the creep recovery from the nonaligned, entangled CNT material demonstrated at extreme temperatures (-150-970°C) where conventional viscoelastic materials fails (Fig.1). Quantitatively, the creep recovery properties such as deformability (how much the material can be deformed), percent recovery (the ability to return from deformation), and compliance (how easily a material deforms) were measured by shear-mode static loading-unloading. The CNT material showed the similar level of creep recovery properties (35% strain deformability, ~1.3E-6 Pa^{-1} compliance with ~70% percent recovery) with silicone rubber, yet kept stable behaviors from -150°C to 600°C. Furthermore, it showed the superior thermal resistance to both continuous exposure across low and high temperatures and long term exposure to stress at high temperatures. Based on our modeling, we interpret that the contacts between the long, traversing CNTs are the origin of the creep and creep recovery.

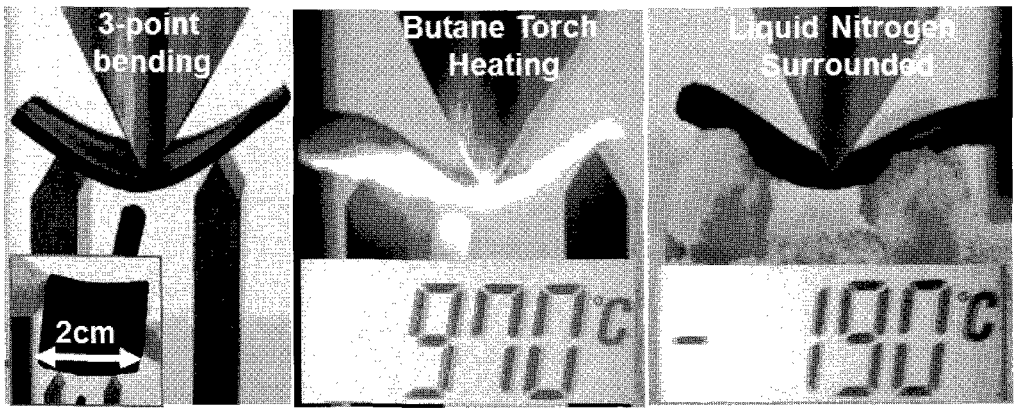

Fig. 1 The CNT materials show elasticity and compliance across -190-970°C by three-bending test.

[1] M. Xu, D. N. Futaba, T. Yamada, M. Yumura, K. Hata,. *Science* **330,** 1364 (2010).

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1-12

Applications of optical responsive carbon nanotubes cell cultured substrate

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Single-walled carbon nanotubes (SWNTs) are nanomaterials that possess remarkable electrical, mechanical, and thermal properties and have been explored for biological applications [1]. One of the applications of SWNTs in biology is the cell culture substrate, where the unique one-dimensional high aspect structure and hydrophobic nature of SWNTs gave better substrate to culture the cells [2]. In addition, SWNTs have unique near-IR (NIR) responsive properties such as strong photoabsorption, photothermal conversion and photoacoustic generation. In this report, we describe development and application of photo responsive SWNT substrate for the cell collection and the cell pattering. These tequniques is of interest especially for basic study of cells, stem cell research, organ culture, or tissue engineering.

SWNT-coated cell culture substrate was fabricated using the spray coating method. Near-IR laser pulse (1064 nm) was irradiated to the cells and, of interest, we found the quick desorption of the cells around irradiated area (Fig. 1), whereas the control dish without SWNT-coating does not lead any change in cells morphology. The results indicate the removal of the cells was obviously due to the effect of the SWNT-coating respond to the NIR laser irradiation. We assumed that the mechanism of the cell removal is the photoacoustic effect of SWNTs and the collapse of SWNTs substrate. By reducing the water layer above the cell, irradiated cells were successfully catapulted from the medium and captured at the top lid of the dish. We estimated the viability of the cells by means of fluorescent stain. The captured cells showed the red fluorescent, which clearly indicate the removed cells are dead. For the cell pattering, nonadhesive polymer functionalized with phospholipid was patterned the photo responsive SWNT substrate using polydimethylsiloxane stamp. We found the cells adhered on the non-pattering area. When the pattering area was irradiated by the NIR laser, the new cell adhesion area was formed in this irradiated area. It showed the nonadhesive polymer was detached from the SWNTs due to the heat generated by the photothermal effect of SWNTs.

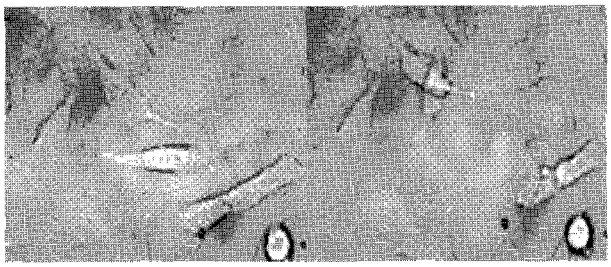

Fig.1 Microscopic images of SWNT-coated dish before NIR laser irradiation (left) and after irradiation (right).

[1] Z. Liu, S. Tabakman, K. Welsher, and H. Dai, *Nano Res.* **2009**, *2*, 85.
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1-13

Development of Multi-stage Ion Trap Mobility System

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Ion mobility measurements have been utilized to analyze structures of nanocarbon materials[1]. We have been developing an ion trap mobility system to enable long-term measurements and to enhance sensitivity[2]. However the trap system has low mobility resolution since the length of the particle movement is limited to several millimeters by the size of the trap. The system has also low sample injection and ejection efficiency so that it is difficult to connect other measurement systems such as mass spectrometers. Here we present the development of the multi-stage ion trap mobility system with the total trap length of 500 mm and an ion funnel[3] to enhance the mobility resolution and injection and ejection efficiency.

Figure 1 shows a schematic and an image of the system which consists of the ion funnel located at the top and the following stacked linear ion trap. The charged particles produced from NaCl water solution are converged by the ion funnel and are injected into the trap. RF electric fields with some DC gradients are applied to the linear trap electrodes to focus the particles and to analyze their mobility. The length of the trap is 500 mm which can realize much higher resolution than that of the previous system. The performance and the structural analyses will be discussed in the presentation.

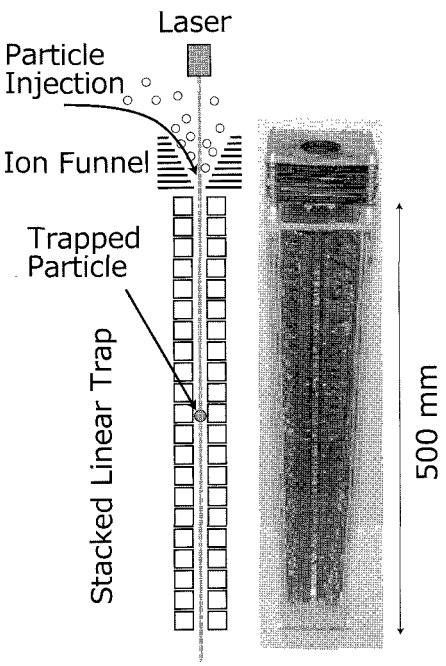

Fig. 1 Schematic and image of multi-stage ion trap mobility system.

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1-14

Electronic States of Linear Polyyne Molecules Embedded in Nano-Structured Molecular Assemblies

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The HOMO-LUMO transition of the electron in the polyyne molecule has a character of π–π. The single-electron excitation between the doubly degenerated orbitals gives rise to distinct three excited states of Σ^+, Σ^-, and Δ. The electric-dipole transition from the ground state is *fully allowed* for the former one, namely Σ^+, while not allowed (being *forbidden*) for the latter two. Under isotropic conditions such as in solutions, vibronic bands in the *forbidden* transition of the molecule are orders of magnitude weaker than those in the *allowed* transition. On the other hand, under anisotropic conditions in crystalline forms, the intrinsically *forbidden* transition of the molecule can be intensified due to symmetry lowering in the crystal field. We examined such systems as solid forms in which polyyne molecules were stabilized inside the cavity of α–cyclodextrin (α-CD), single wall carbon nanotubes (SWNTs), and the cluster of iodine molecules (I_6). Spectral changes for polyynes in the nano-structured molecular assemblies are presented and discussed along the symmetry considerations. The resonance excitation curve observed for the Raman signal of $C_{10}H_2$ in SWNT is discussed in comparison with the absorption spectra in the relevant excitation energies.

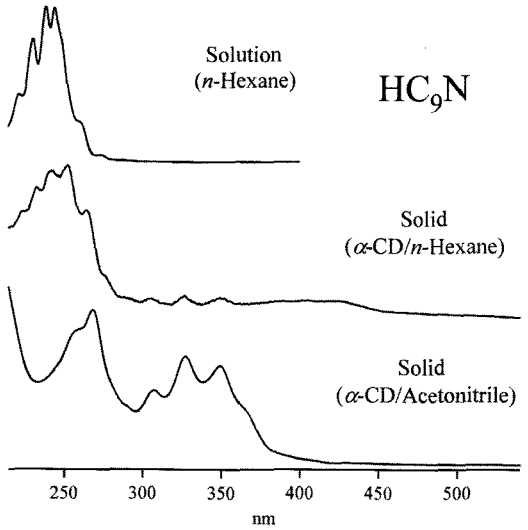

Fig. 1. UV/VIS absorption spectra for HC_9N in solution and crystalline solids of α-CD.

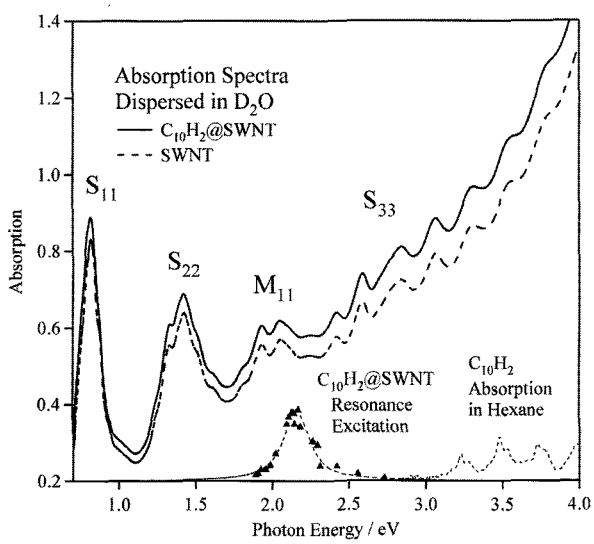

Fig. 2. Absorption spectra for SWNT with and without polyyne $C_{10}H_2$ measured for those dispersed with sodium cholate in D_2O.

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1-15

Size-Dependent Cellular Uptake of Carbon Nanoparticles

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Nanocarbons such as nanotubes, nanohorns and graphene ribbons have been considered as useful carriers for delivering drugs to cancer and other diseased sites. The nanocarbons have various sizes (lengths and diameters) and assemblies, which is believed to influence interactions of nanocarbons with cells and the drug delivery efficiency. Due to the lack of well-defined structures of nanocarbons with uniform sizes, it has been difficult to study the cellular uptake of nanocarbons depending on the nanocarbon sizes. We have recently succeeded in preparing small- and uniform-sized aggregates of single wall carbon nanohorns (CNHs) [1]. Using these small-sized CNH aggregates, we have evidenced for the first time that the cellular uptake of nanocarbons was size-dependent.

We used two-sized CNHs for this study: one was normal CNH aggregates (about 100 nm,) and the other was the small-sized CNH aggregates (30-50 nm, S-CNHs). S-CNHs were produced from 100-nm CNH aggregates by an oxidation exfoliation method. S-CNTs exhibited high hydrophilic properties, large pore volumes, and high potential for chemical or biological funtionalization. The normal-sized CNH aggregates (100 nm) were treated with light assisted oxidation [2] to make them hydrophilic as similar to S-CNHs.

Using the black color of nanocarbons (without fluorescent labels), the cellular uptake of S-CNHs and CNHs were easily observed with confocal microscopy and quantified by optical absorption measurements. The results showed that the uptake-quantities of S-CNHs by HeLa and macrophage (Raw 267.4) cells were much lower than those of large-sized CNHs. Furthermore, S-CNTs with noncovalent functionalization with DSPE-PEG completely avoided the phagocytosis by macrophage cells while the general sized CNHs did not.

The results suggest that S-CNHs are optimum for the drug delivery application as they are resistive to the macrophages phagocytosis due to the small sizes, which can be even more intensified by the PEG coating of S-CNHs.

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1-16

HRTEM observation of the platinum clusters interacting with carbon atoms at elevated temperatures

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Platinum is widely used as a catalyst in many fields of industrial chemistry, such as a catalytic-hydrogenation of organic molecules [1]. In addition, since platinum can form solid solution with carbon up to ~3 at.% at ~1,980 K [2], it has also be known as useful metal for catalytic-graphitization [3]. Actually, although the catalytic-activity of platinum for graphitization is considered to be less effective than the iron-group metals, platinum has been used as the catalyst of synthesis of carbon nanocapsules [4] and carbon nanotubes (CNTs) [4, 5]. Therefore, catalytic-activity of platinum has attracted significant research interests. Particularly, considerable efforts have been devoted to fabricate and characterize the platinum catalytic nanoparticles because of their unique and outstanding activity. However, the detailed size dependency of platinum cluster on catalytic-activity has not been clarified yet.

In this study, we have observed behaviors of platinum clusters on a surface of CNTs at several temperatures by a high-resolution transmission electron microscope (HRTEM) in order to estimate the "magic number" of platinum atoms for a most efficient catalytic behavior for graphitization. We try to figure out how the platinum clusters interact with carbon atoms by in-situ observation at elevated temperatures within column of HRTEM. In addition, we will discuss the cluster size dependency of the catalytic-graphitization based on the HRTEM observations.

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2-1

Cyclic purification of semiconducting and metallic carbon nanotubes using separation by Electric-field inducing Layer Formation

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Extraction of purely semiconducting (s-) single walled carbon nanotubes (SWCNTs) removing metallic (m-) ones is essential for the electronic application of SWCNTs such as carbon nanotube thin film transistors (CNT-TFTs). Separation methods of s- and m-SWCNTs providing highly pure and ion-free s-SWCNTs are required to improve the electronic device performance. Recently, we had proposed a separation method by "Electric-field inducing Layer Formation (ELF)" as an ion-free separation method with high purity of s-SWCNTs. Here, we report a cyclic ELF separation aiming at the improvement in the purity of separated SWCNTs.

SWCNTs were dispersed into D_2O with 1 wt% of polyoxyethylene stearyl ether (Brij 700, Aldrich) by sonication and ultracentrifugation. After the dispersing process, the concentrations of SWCNTs and Brij 700 in the solution were adjusted by adding Brij 700-D_2O solution. The adjusted solution was introduced into a vertical cell with a pair of electrodes, which was used for applying electric field to the solution by a DC power supply. For the separation, a constant voltage of 30 V was applied between the lower (anode) and upper (cathode) electrodes for more than 24 hours. Then, two colored layers were separately formed, and they were fractionated. After the fractionation, ELF method was repeatedly applied to the both of fractionated samples twice. Raman spectra by 633-nm laser excitation of pristine, 1-time and 3-times of separation sample are shown in fig. 1 and 2, for m- and s-SWCNTs, respectively. Purities of 1-time and 3-times separated s- (m-) SWCNTs are calculated as 92 (55) % and 97 (84) % from these spectra. These results suggest that cyclic ELF separations effectively improve the purity of separated SWCNTs.

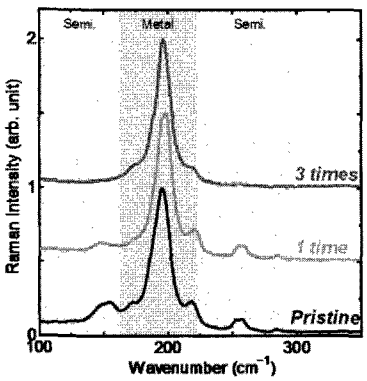

Fig. 1 Characterization of the effect of cyclic separations by Raman spectra in *m*-SWCNTs

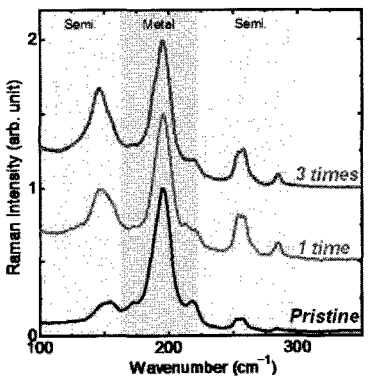

Fig. 2 Characterization of the effect of cyclic separations by Raman spectra in *s*-SWCNTs

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Diameter-Based Separation of Single-Walled Carbon Nanotubes through Selective Extraction with Dipyrene Nanotweezers

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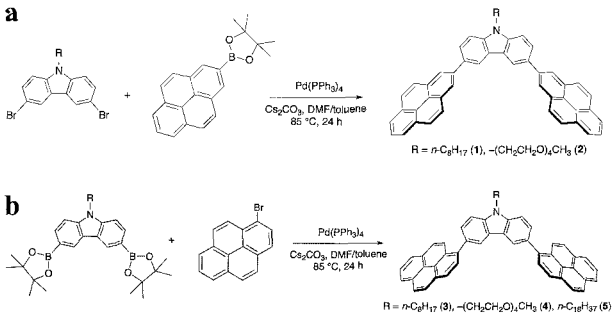
We have been developing host-guest methodology for separation of single-walled carbon nanotubes (SWNTs) according to the handedness and diameter with gable-type chiral diporphyrins, designated as porphyrin nanotweezers, consisting of two porphyrins and rigid spacer in between [1]. As an extension of our strategy, novel nanotweezers having two pyrenes instead of porphyrins have been designed, because pyrene is known to have high affinity toward SWNT surface [2]. The pyrene nanotweezers presented here consist of two 1- or 2-pyrenes and 3,6-carbazolylenes with various *N*-substituents. They were synthesized through Suzuki coupling reactions between 1- or 2-substituted pyrene with 3,6-disubstituted carbazoles as shown in Scheme 1. For the extraction of SWNTs, the 1- and 2-pyrene nanotweezers show the marked contrast; 1-pyrene nanotweezers **3** – **5** selectively extracted SWNTs with diameters ranging from 0.84 nm to 0.97 nm, while 2-pyrene nanotweezers **1** – **2** were not able to extract SWNTs at all. The marked difference in the extraction ability may be ascribed to the difference in the solubility and the stability of the complexes. As compared with the porphyrin nanotweezers previously reported by us [1], the pyrene nanotweezers have advantage in practical separation for diameter of SWNTs because of their facile synthesis.



Scheme 1. Synthesis of 2-pyrene nanotweezers **1** – **2** (a) and 1-pyrene nanotweezers **3** – **5** (b) via Suzuki-Miyaura coupling reactions.

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2-3

Effect of Sonication on the Length Distribution of Single Wall Carbon Nanotubes

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Single wall carbon nanotubes (SWCNTs) were frequently dispersed into suspension by sonication with the help of various dispersing reagents (detergents), not only for fundamental but also for applied research. Although it has been considered that the dispersing process using sonication might cut or shorten SWCNTs, to date its detailed cutting effect, such as dependences on detergents, sonication power, and so on, has not been fully clarified yet. In this work, we have investigated the differences in length distribution of SWCNTs between their sonication processes using various detergents.

Four detergents, sodium dodecyl sulfate (SDS), sodium dodecylbenzene sulfate (SDBS), sodium cholate (SC), and ethylene glycol (100) stearyl ether (Brij 700) have been intentionally selected to explore the effect of cutting SWCNTs during their dispersing. The length of SWCNTs in each sample, deposited on the aminopropyltriethoxysilane (APTES) functionalized silicon substrate, were statistically characterized by the analysis of topographic images taken by atomic force microscope (AFM). Diameter dependence on the length distribution after the dispersing process were also investigated.

As a result of dispersing SWCNTs by bath sonication at 70 W, although the length distributions of SWCNTs, especially in SDS dispersing, highly depended on the dispersing process, roughly SC and Brij 700 dispersing results show shorter length distributions compared with SDBS. In particular, the diameter dependence in length distribution showed clear contrast between SC and Brij 700 dispersing: Whereas the length distributions of SC dispersing showed relatively regular dependence on the SWCNTs diameter, less or almost no dependence on the diameter was observed in Brij 700 dispersing. Furthermore, when SWCNTs were dispersed by using Brij 700 with the horn-type sonication homogenizer at 300 W for 10 hours, all measured SWCNTs were even shorter and in the range less than 600 nm with the average length of 119 nm. These results suggest that Brij 700 possesses the considerably strong ability that effectively cuts SWCNTs at their dispersing process.

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QM/MD Simulation of SWNT Nucleation on Transition-Metal Carbide Nanoparticles

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[1]*Institute for Advanced Research and Department of Chemistry, Nagoya University, Nagoya 464-8602, Japan*
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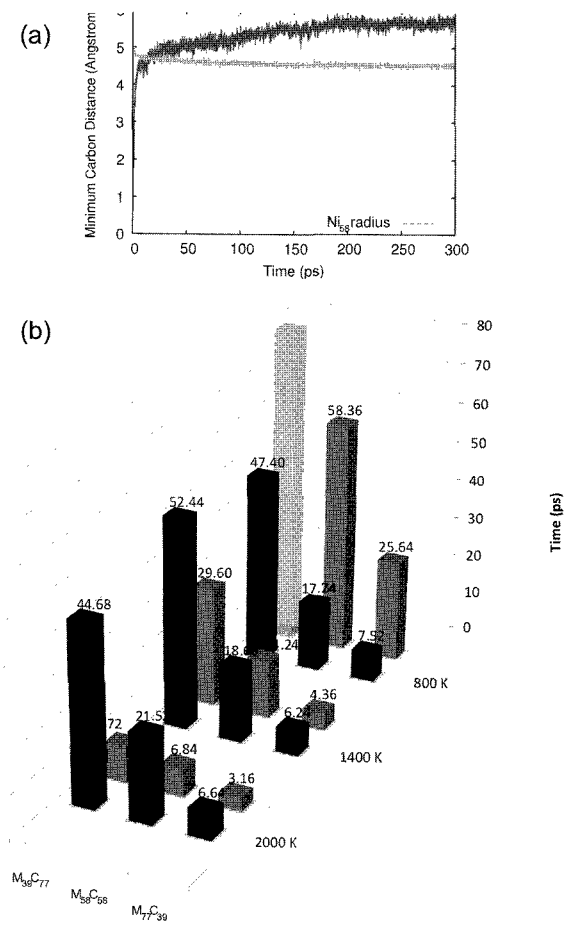

Figure 1. (a) Minimal distance (red) between all carbon atoms and Ni_{58} center of mass during SWNT nucleation from $Ni_{58}C_{58}$ nanoparticle. "Average carbon precipitation time" is defined as the first time at which this distance is greater than the Ni_{58} radius. (b) Average carbon precipitation times (ps) from Ni_xC_y and Fe_xC_y nanoparticles at 800, 1400 and 2000 K. Grey and brown columns represent data for Ni_xC_y and Fe_xC_y, respectively. Transparent columns indicate an average carbon precipitation time > 300 ps. All data averaged over 10 trajectories.

The mechanism and kinetics of single-walled carbon nanotube (SWNT) nucleation from Fe- and Ni-carbide nanoparticle precursors have been investigated using quantum chemical molecular dynamics (QM/MD) methods [1]. It was observed that SWNT nucleation occurred via three distinct stages, viz. the precipitation of the carbon from the metalcarbide, the formation of a "surface/subsurface" carbide intermediate species, and finally the formation of a nascent *sp*2-hybidrized carbon structure supported by the metal catalyst. The kinetics of SWNT nucleation exhibited distinct dependences on carbon concentration and temperature (see Fig. 1). In particular, SWNT nucleation from Ni_xC_y nanoparticles proceeded more favorably compared to nucleation from Fe*x*C*y* nanoparticles. The stability of the surface/subsurface carbide was also influenced by the phase of the nanoparticle itself. The observations agree well with experimentally available data for SWNT growth on iron and nickel catalyst particles.

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2-5

Stacking-order sensitive Raman modes of graphene

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Bilayer and multi-layer graphene are considered to be a candidate for semiconducting devices with an energy gap by applying the electric field. However, when we make a bilayer graphene, for example, the stacking order of the two layers does not always have so-called ABAB Bernal stacking order but some commensurate or incommensurate stacking orders which modify the electronic structure significantly. In nature, there is ABC rhombohedral stacking order of graphite, too. Thus characterization of the stacking order is now investigated by many methods. Here we propose that some combinational Raman spectra are useful for characterizing the stacking order such as overtone of oTO (M band), the combination mode of iTA+LO, whose frequency appear around 1700-1900cm^{-1} [1]. Especially, in the case of single layer graphene or folded bilayer graphene, overtone of oTO is completely suppressed because of the symmetry requirement. For the combinational modes, layer dependence of the frequencies as a function of laser excitation energy provides a much clearer explanation than the analysis by the conventional characterization of G' (2D) Raman bands. Combining with the calculated double resonance Raman spectra, we will discuss how we can understand the stacking order of graphene systems from the Raman spectra.

[1] C. Cong, Y. Ting, R. Saito, M. S. Dresselhaus, unpublished.

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2-6

Energetics and Electronic Structures of Graphene Adsorbed on HfO_2 Surfaces

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Graphene has the great potential to advance both the low-dimensional sciences and the nano-scale electronic engineering. Recently, the integration of the graphene with a scalable gate dielectric, such as high permittivity (high-*k*) materials, has been the subject of the research with the goal of the realization of graphene-based electronic devices. For the fabrication of the graphene on insulating substrates, an understanding of its interactions with the substrates is critical, since they could directly affect the intrinsic electronic properties of the graphene. However, its underlying characteristics of the interaction are still far from being explained. Thus, we here study the energetics, geometry, and electronic structure of graphene adsorbed on (111) surfaces of cubic hafnia (HfO_2) using first-principles calculations in the framework of density functional theory. To simulate a hybrid structure of graphene and HfO_2, we considered an oxygen-terminated (111) surface of a cubic phase of HfO_2 possessing a triangular lattice of O atoms at the topmost layer. The surfaces were simulated using a repeated-slab model that includes five HfO_2 layers, graphene, and a 7 Å -vacuum region.

We found that the graphene is bound to the HfO_2 surfaces via interactions with an interlayer spacing of 3.05 Å. The calculated binding energy is about 110 meV per C atom. The electronic structure of the HfO_2-adsorbed graphene originates primarily from that of the graphene near the Fermi level. However, a detailed analysis of the electronic structure shows that the linear bands at the Fermi level are slightly split, because of the interaction between the graphene and the HfO_2 substrate. The physical origin of this splitting is the hybridization between the π states of the graphene and the O $2p$ state with Hf d character.

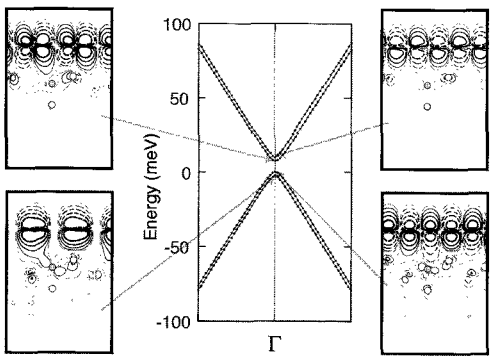

Fig.1. Contour maps of the electron states near the Fermi level at the Γ point in graphene adsorbed on HfO_2. Each contour denotes twice (or half) the values of the adjacent contour lines from ±0.128 $(e/Å^3)^{1/2}$. The solid and dotted lines show the positive and negative values, respectively. The two O atoms and one Hf atom that define a cross section are shown by white and gray circles, respectively.

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2-7

Large area CVD graphene from camphor for organic solar cells application

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We present synthesis of large area graphene sheets by control pyrolysis of solid botanical derivative camphor ($C_{10}H_{16}O$). At the very beginning of CVD based graphene, we demonstrated possible fabrication process of few layer graphene by thermal CVD from camphor. Few layer graphene sheets with minimum 3 layers or much higher number of layers were obtained by pyrolysing on Ni surface. Voltage aberration corrected high resolution TEM studies were done to observe the packing structure of the few layer graphene by directly imaging the atomic structure. Large area monolayer or bi-layer graphene were also synthesized from camphor on Cu foils. We have demonstrated graphene film synthesized from camphor can be transferred to arbitrary substrate for fabrication of transparent electrode.

Solution processed organic solar cells were fabricated on graphene based transparent electrode. A P3HT:PCBM solar cell fabricated on graphene shows very good dark current characteristic having minimum leakage current. Under illumination of light device performance is comparable with standard ITO based P3HT:PCBM solar cells. Details studies on organic solar cells fabrication in few layers graphene based transparent electrode will be discussed. The technique to fabricate few layer of graphene as transparent electrode from camphor is both viable and scalable for potential large area solar cells and other optoelectronic applications.

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2-8

Analysis of Magneto Resistance Fluctuations in Graphene Thin Films

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[B] Arizona state university.

[C] University of Buffalo.

In our recent years a chain of experimental studies on graphene electrical conductivity were carried out. Physical phenomena due to Weak localization states [1], universal conductance fluctuation [1,2] has provided us with clear expansion up to the observations under quantum interference basics understanding. As part of our research group background, Universal Fluctuation Conductance (UCF) for magneto- transport properties of graphene has been observed at low-temperature.

Hence by, our summery to the Japanese physics Society meeting two years ago[3] came to, the detailed observations of conductance fluctuations where external magnetic field was swept to observe the Fourier power spectrum analysis of Universal Fluctuation Conductance that clearly showed the periodicity (quasi-periodicity). The Universal conductivity had shown strong non-periodic behavior that varied with fluctuations hence the irrelevance to the presence Universal Fluctuation Conductance has been observed.

Experimental study research of electrical conduction in open semiconductor quantum dot research [4] has been reported. And in recent years, theoretical study[5] was accompanied alongside indicating such pseudo periodicity in graphene UFC observation is true. These experimental and theoretical facts shown in graphene materials strongly suggest the conductance fluctuation periodicity in electrical conduction mechanism.

Pursuing furthermore, the observed UCF at low temperature magneto-resistance of a relatively larger grapheme sample had gave us the lead. The analysis in bigger graphene samples area had implied that effect of impurities which also referred to as metallic-effect in graphene surface are even thought to be more susceptible than that of a small graphene samples area. As a result, the large graphene sample has not shown any quasi periodic fluctuation in our observations. Here by the final conclusion was generalized in the two graphene samples for the Universal Conductance Fluctuation observations.

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2-9

Fullerene Peapod– Poly(3-hexylthiophene) Hybrids

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Novel nanohybrids of single-walled carbon nanotubes (SWNTs) encapsulating C_{60} or C_{70} with poly(3-hexylthiophene) (P3HT) have been prepared and their photophysics and photoelectrochemical properties are studied in detail for the first time. Strong π-π interaction between the SWNT sidewalls and P3HT afforded successful dissolution of the so-called fullerene peapods into an organic solvent, as in the case of empty SWNTs. Fluorescence emission of P3HT in the SWNT–P3HT hybrids was completely quenched by the SWNTs regardless of the fullerenes insertion. Transient absorption and fluorescence lifetime measurements revealed the excited state dynamics of the nanohybrids, where exciplex formation from the short-lived P3HT singlet excited state (~ 0.2 ps) with the fullerene peapods and subsequent relaxation to the ground state within ~ 1 ps occurred dominantly. Significant difference in the photodynamics upon encapsulation of C_{60} or C_{70} was not detected, implying little participation of the fullerenes in the excited state event and thus the inability of the encapsulated fullerenes to generate the charge-separated state between the fullerene peapods and P3HT. Photoelectrochemical devices based on the peapod–P3HT nanohybrids showed almost the same incident photon-to-current efficiencies as those for the empty SWNT–P3HT-based device, which is in good agreement with the results of the time-resolved spectroscopies.

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2-10

Synthesis and Photophysical Properties of Metallofullerenes—Zinc Porphyrin Conjugates: Impact of Endohedral Clusters

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Novel covalent metallofullerenes (i.e., $Ce_2@I_h$-C_{80}, $La_2@I_h$-C_{80}, $Sc_3N@I_h$-C_{80}) —Zinc 5,10,15,20-tetraphenylporphyrin (ZnP) dyads (**1-3**) were prepared via [1+2] cycloaddition reactions of a diazo precursor. Their structures were characterized with the help of reference compounds (**4-6**). Combined studies of crystallography and NMR suggest a common (6,6)-open addition pattern for all the dyads and reference compounds. On the other hand, subtly different conformations, that is, a restricted and a comparatively more flexible one, emerge for **1**, **2** and **3**, respectively. In line with this difference are the electrochemical and spectral studies, which imply appreciably stronger I_h-C_{80} / ZnP interactions in **1** and **2** when compared to those in **3**. Density functional calculations reveal significant attractions between the two entities of these conjugates, as well as their separately localized HOMOs and LUMOs. The geometrical conformations and LUMO distributions of **2** and **3**, at our applied computational level, are slightly varied with their different endohedral clusters. The clusters also exert different impact on the excited state reactivity of the conjugates. For example, **1** and **2** undergo, upon photoexcitation, a fast charge separation process and yield a radical ion pair, whose nature, namely $(M_2@C_{80})^{\bullet-}$-$(ZnP)^{\bullet+}$) versus $(M_2@C_{80})^{\bullet+}$-$(ZnP)^{\bullet-}$) (M= Ce, La), varies with solvent polarity. **3**, on the other hand, affords the same $(Sc_3N@C_{80})^{\bullet-}$-$(ZnP)^{\bullet+}$) radical ion pair regardless of the solvent.

2-11

Electronic structure and entrapped cluster structure of C_{78} endohedral fullerenes

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Ultraviolet photoelectron spectroscopy has been revealing the valence band electronic structure of fullerenes and endohedral fullerenes, and now it has been verified to be a powerful tool to investigate the electronic structure of endohedral fullerenes as well as the geometry of entrapped clusters with an aid of theoretical calculation. We present the ultraviolet photoelectron spectra (UPS) of $Sc_3N@C_{78}$, $La_2@C_{78}$ and $Ti_2C_2@C_{78}$, all of them have D_{3h} (No. 5) symmetry, and the results of DFT calculation.

Figure 1 shows the upper valence band UPS of $Sc_3N@C_{78}$, $Ti_2C_2@C_{78}$ and $La_2@C_{78}$ obtained with $h\nu$ =30 eV incident photon energy. Their UPS are completely different from those of other endohedral fullerenes reported until now. In the UPS of other fullerenes, a large structure is observed at about 5.5 eV and a few structures appear at lower binding energy side. However, the corresponding peak of $Sc_3N@C_{78}$, $Ti_2C_2@C_{78}$ and $La_2@C_{78}$ shifted toward higher binding energy side by 0.3 eV and at lower binding energy side several complicated structures can be observed in the UPS of $La_2@C_{78}$ and $Ti_2C_2@C_{78}$.

The results of DTF calculation (B3LYP) and simulation spectra obtained by broadening of the Eigen-values with Gaussian functions are also shown in Figure 1. The abscissa of the simulation spectra is shifted so that the peak positions of each spectrum appear at the same region. The simulation spectra reproduced the UPS so well that the DFT calculation is good enough to elucidate the geometry of entrapped species. The geometries of entrapped clusters of these endohedral fullerenes are a Ti-C-C-Ti linear shape for $Ti_2C_2@C_{78}$ and a nitrogen atom centered planar triangle shape for $Sc_3N@C_{78}$.

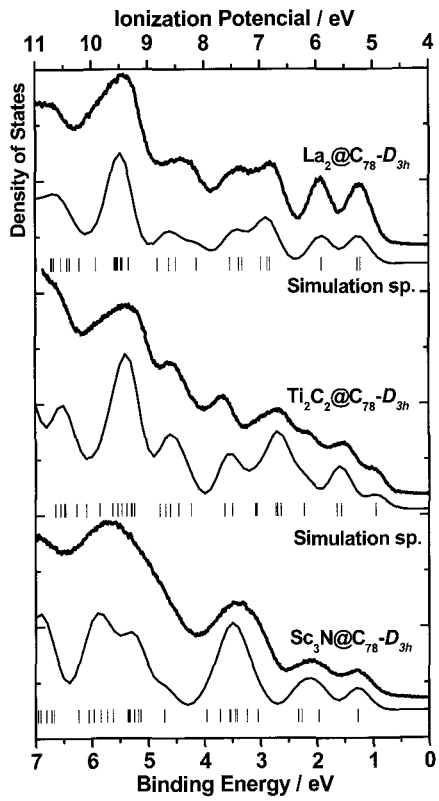

Fig. 1. The UPS of $Sc_3N@C_{78}$, $Ti_2C_2@C_{78}$ and $La_2@C_{78}$ and their simulation spectra.

It should be noted that their spectral onset energy is the same 0.7 eV although the amounts of transferred electrons from the entrapped clusters to the cage differ in these endohedral fullerenes. This suggests that the difference in the amounts of transferred electrons does not reflect the onset energy (corresponding band gap of the materials).

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2-12

Photo-Polymerization of C_{60} Thin Film using Optical Vortex Irradiation

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A state of the art photo-polymerization method of a C_{60} thin film has been studied using an optical vortex irradiation [1]. Since the beam has a herical wavefront and a rotation of angular momentum, a confinement force due to the photo pressure toward the center of the beam. Therefore, a highly-packed and uniform photo-polymerization can be expected in a C_{60} thin film compared with conventional laser beam. Moreover, a circular polymerization might be realized forming concentric-multiple-ring structures.

Photo-polymerization is one of the promising solutions for electrical device application of C_{60} molecules, where inter-molecular covalent bonds could protect an intercalation of oxygen atoms. Some kinds of beam irradiations have been performed so far. However, a shrink of inter-molecule distance causes a serious problem such an introduction of cracks into the thin film [2]. The film is divided into a lot of domains of a size of several μm^2. Consequently, a mobility of the film decreases a few orders of magnitude after the irradiation, although a good transport characteristic can be expected for within each domain.

In our trial of irradiation of a focused optical vortex (532 nm) on a C_{60} thin film, circular patterns have successfully resolved after the irradiations for a few minutes. The irradiated region does not have solubility into a toluene and the $A_g(2)$ peak of Raman spectrum shows polymerization of the C_{60} molecules. Moreover, no crack has been observed by SEM observation. These results suggest that a highly-packed and uniform photo-polymerization have been realized by optical vortex irradiation. The transport properties will also be discussed in the presentation.

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2-13

Synthesis of Polyhydroxylated Fullerene $C_{60}(OH)_6$ via Chlorofullerene $C_{60}Cl_6$ and its Characterization using ESI-MS Spectroscopy

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Polyhydroxylated fullerenes, known as fullerenols, have attracted much attention because they have useful properties and various potential applications. However, it is still an open question as to how many, and where, hydroxyl groups are added to the surface of fullerenes. Because the fullerenols reported so far have been a mixture of fullerenols with a different number of hydroxyl groups, along with their many isomers, only an average number of hydroxyl groups per fullerene cage has been determined using the elemental analysis. In this work, we synthesized a fullerenol consisting of a single isomer via chlorofullerene, and have characterized its structure by ESI-MS and ^{13}C NMR spectroscopy.

At the present stage of our work, we have synthesized fullerenol, $C_{60}(OH)_6$, and the number of hydroxyl groups has been determined from the negative ESI-MS spectrum. The reaction of $C_{60}Cl_6$ with water proceeded almost completely, and formed $C_{60}(OH)_6$ when Ag^+TPFPB^- was added to the system as a reagent. We supposed that the Ag^+ ions weakened C−Cl bond strength because of the strong interaction between Ag^+ ions and Cl atoms. Therefore, weak nucleophiles, such as water, can react with $C_{60}Cl_6$ to form fullerenol. We are identifying appropriate procedures to achieve complete substitution of the Cl moieties.

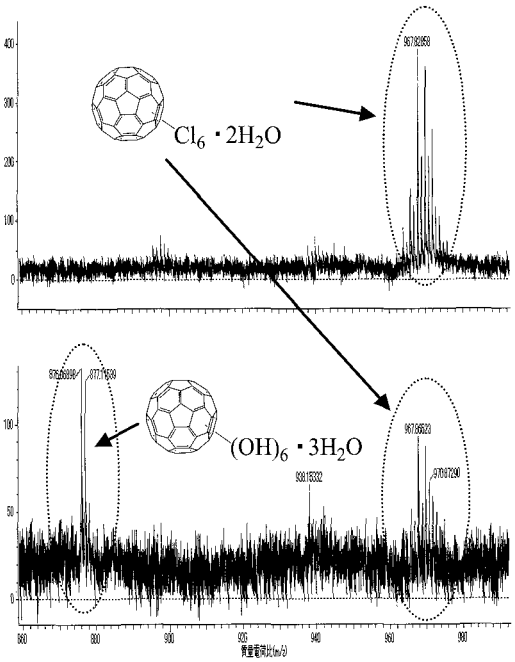

Fig 1. Negative ESI-MS spectra of $C_{60}Cl_6 \cdot 2H_2O$ (top) and $C_{60}(OH)_6 \cdot 3H_2O$ (bottom).

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2-14

Thermal and oxidative stabilities of multi-arylated [60]fullerene derivatives

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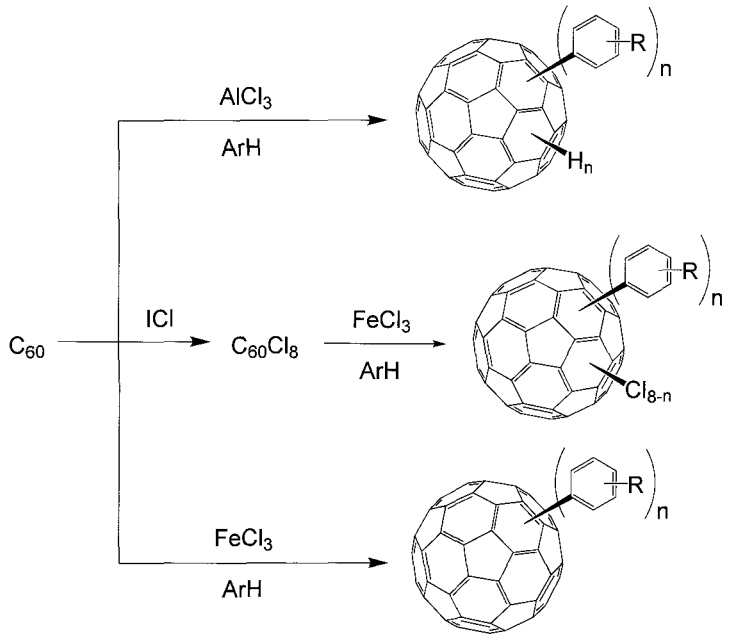
High thermal and oxidative stabilities, as well as high etching durability, are the crucial requirements for resist materials. A soluble carbon material, fullerene, has the high potential for dry etching durability and thus for higher resolution of semiconductor devices as compared to the current resist materials. However, pristine fullerene exhibits low solubility to the current common resist solvent in wet process, *e.g.*, propylene glycol methyl ether acetate (PGMEA). Thus, it is desired to synthesize the highly PGMEA-soluble fullerene derivatives without hetero atoms to retain the high carbon content by a facile synthetic method.

In this study, we synthesized multi-*hydro*arylated and multi-arylated [60]fullerene derivatives by three different methods, 1) hydroarylation of C_{60} mediated by $AlCl_3$, 2) arylation of polychlorinated fullerene $C_{60}Cl_8$ mediated by $FeCl_3$, and 3) direct multi-arylation of C_{60} mediated by $FeCl_3$ in various aromatic solvents. The products were found to exhibit the high PGMEA-solubility (>20 wt%) depending on the type and the number of aryl groups introduced. Moreover, the thermogravimetric analysis both under air and under N_2 revealed that the thermal and oxidative stabilities of one of them exceeded over 300 °C.



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2-15

Influence of UV Irradiation on Polymerization of LLIP-Prepared C_{60} Nanowhiskers

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Solid C_{60} has been known to be polymerized under irradiation of ultraviolet (UV) light and the molecules link together in a covalently bonded structure [1]. However, there has little study on the polymerization status of C_{60} nanowhiskers (C_{60}NWs) formed by the liquid-liquid interfacial precipitation method (LLIP method) [2]. In this presentation, we report the influence of UV irradiation on the polymerization of C_{60}NWs synthesized by the LLIP method. Raman scattering spectra of C_{60}NWs under specified UV region and irradiation time were measured according to the absorption spectra of C_{60} thin films prepared on LiF (100) and NaCl (100) substrates [3]. The spectrum shown in Figure 1 (b) exhibits that the LLIP-prepared C_{60}NWs are polymerized under a 263 nm UV irradiation with a power density of 8×10^{-3} mW/mm^2 for 12 h. We will interpret the detailed status of the polymerized condition in this research.

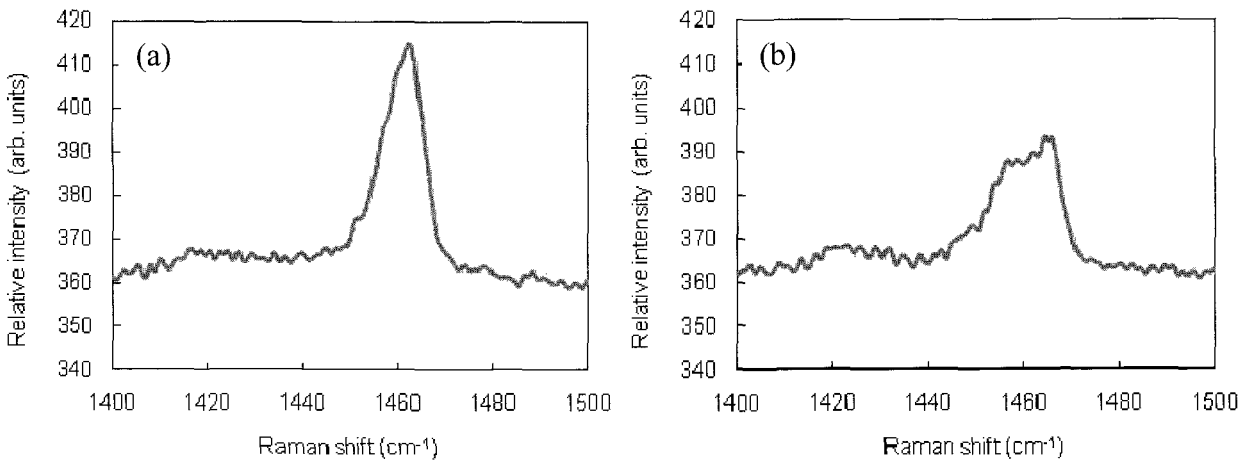

Fig. 1. The Raman spectra near the *Ag*(2) pentagonal pinch mode of the LLIP-prepared C_{60}NWs under a 263 nm UV irradiation with a power density of 8×10^{-3} mW/mm^2: (a) before irradiation and (b) after irradiation for 12 h.

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3-1

Coaxially Stacked Coronene Column inside Single-Walled Carbon Nanotube

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One of the most interesting features of molecular materials is the fact that their physical properties change with the molecular arrangement as well as the properties of the molecule itself. Self-organization is an efficient pathway through which organic molecules assemble to form well-ordered nanometre-scale objects that are hardly synthesized by conventional chemical reactions. In these systems, two or more molecules are held together and assembled by means of intermolecular (noncovalent) bonding such as ion-dipole or dipole-dipole interactions, hydrogen bonding, hydrophobic interactions, or π–π stacking.

Single-walled carbon nanotubes (SWCNTs) can offer a suitable interior space for accommodating molecules. The nanostructures produced by incorporating such molecules into SWCNTs are expected to exhibit several superior features. For example, because the diameter of SWCNTs can be adjusted to the size of the molecules, well-ordered molecular arrangements beyond a micro-metre long can be easily produced. The synthesized molecular arrangements are also expected to be strong and flexible against mechanical strain because the nanotube templates sustain the structure. Furthermore, the synthesized nanostructures are isolated from active molecules by the tube wall, which leads to the superior durability of the encapsulated molecules.

Here we demonstrate such an 1D SWCNT-templated nanostructure using planner π-conjugated molecules, coronenes. Encapsulated coronenes form nano-scale columns in a way that differs from 3D solid coronenes, resulting in electronic and optical properties peculiar to the 1D structure. The unique physical properties of the produced coronene columns and their biological application for molecular imaging probes will be discussed in detail.

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3-2

Growth of Carbon Nanotubes Filled with Metal Sulfide Nanowires

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The hybridization of metal/metal compound nanowires and carbon nanotubes (CNTs) has been tried as one of the ideas for improving the quality, such as stability and crystallinity, of metal/metal compound nanowires. Many researches on various metal/metal compound-filled CNTs have been reported to date. However, it is difficult to achieve long one-dimensional growth by one-step synthesis. We have succeeded in the one-step syntheses of copper sulfide-filled CNTs (CuS@CNTs) and nickel sulfide-filled CNTs (NiS@CNTs) by two types of vaporization methods using ethanol and carbon disulfide (CS_2), alcohol arc discharge and alcohol chemical vapor deposition (CVD), respectively. In this study, we investigated their effective formation conditions and structures.

CuS@CNTs were produced by conventional carbon arc discharge with ethanol vapor introduced into the arc plasma. Graphite rods were used for electrodes. A hole was drilled in the center of a graphite anode and filled with copper powder. The electrodes were set vertically in a vacuum chamber. The ethanol vapor was introduced into the chamber by bubbling argon through ethanol containing CS_2 of 10% heated at 50°C. NiS@CNTs were formed by alcohol CVD method. Ethanol solutions of $NiCl_2$ were sprayed on a Si plate maintained at 400°C followed by heating at 640°C for 30 min. in an Ar atmosphere. The CVD growth was carried out at 900-1000°C for 30 min. at a vapor pressure of ethanol containing a small amount of CS_2 in a vacuum.

The filling rate of CuS@CNTs was extremely high and few hollow CNTs were in the as-grown sample (Fig. 1(a)). The CuS@CNTs were classified into two types, thin (diameters of 20-50 nm) (Fig. 1(b)) and thick (diameters of 100-500 nm) (Fig. 1(c)), depending on the arc current. We assume that the additional carbon and hydrogen sources from the ethanol vapor lead to suitable density of carbon and hydrogen species in the arc plasma compared to that of the previous methods. The filling rate of NiS@CNTs was about 80%, and had diameters of about 100 nm and lengths of about 3 μm. Moreover, the NiS@CNTs grew vertically on the substrate. In this study we investigated growth conditions and mechanism of metal-compound filled nanotubes via the alcohol CVD process. We will present the detail of the structure of the two metal sulfide nanowire-filled CNTs in the presentation.

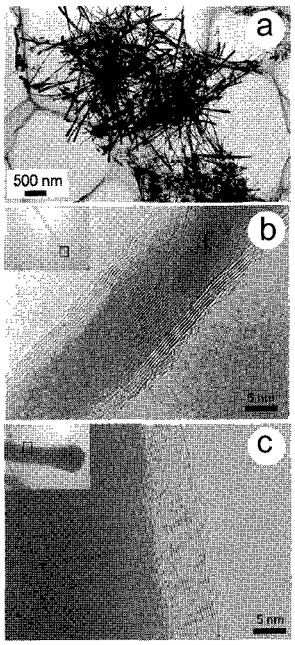

Fig. 1 (a) A typical TEM image of CuS@CNTs. High -magnification TEM images of (b) thin and (c) thick CuS@CNT.

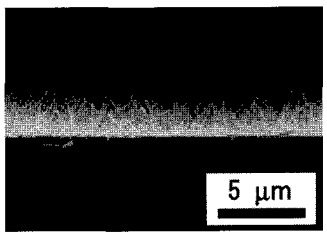

Fig. 2 A cross-sectional SEM image of NiS@CNTs grown on a substrate.

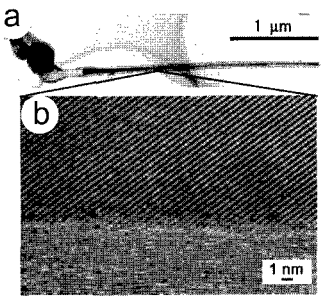

Fig. 3 (a) A TEM image of a NiS@CNT and (b) the high -magnification TEM image.

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3-3

First-principles study of K_XC_{60} encapsulated in boron-nitride nanotubes

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The important difference between boron-nitride nanotubes and carbon nanotubes is that boron-nitride nanotubes have large band gap independent of chirality and diameter whereas carbon nanotubes can be semiconducting or metallic. Thus, considering these nanoscale tubular materials as a host material to encapsulate atoms and/or molecules, boron-nitride nanotubes are more suitable nanotubes to investigate the encapsulated one-dimensional materials. Here, in order to examine the characteristics of one-dimensional alkali-doped fullerene compounds, we study the electronic structure of potassium-doped C_{60} encapsulated in the (10,10) boron-nitride nanotube shown in Fig. 1 using first-principles methods based on the density functional theory. We demonstrate that the material is one-dimensional metal where conducting electrons are only in the C_{60} chain. The Fermi-level density of states varies depending on the doping level and can be large in some cases, which indicates the possibility of various phase transitions including superconductivity as in the case of fcc K_3C_{60}. Interestingly, the Fermi-level density of states shows peculiar pressure dependence because of one-dimensional geometry. We also compute the electron-phonon couplings and discuss the difference from the three-dimensional fcc K_3C_{60}.

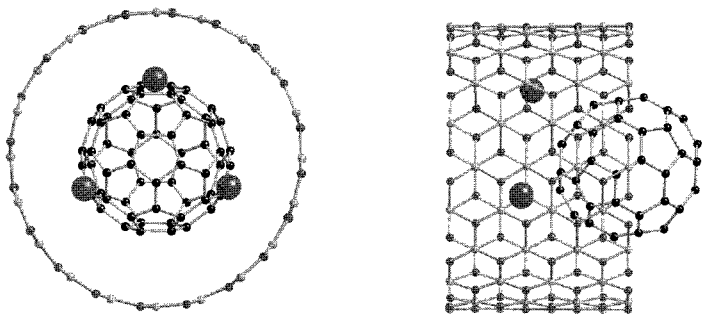

Fig. 1 Geometry of optimized K_3C_{60} encapsulated in the (10,10) boron-nitride nanotube.

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3-4

Epitaxial CVD growth of single-layer graphene over metal films crystallized on sapphire

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Graphene is emerging as a new building block of future nanoelectronics and microelectro-mechanical systems. Recently, catalytic CVD growth has attracted considerable interest as an effective means to produce large-area graphene films [1-3]. However, because most of the CVD growth has been done over polycrystalline metal films/foils, as-grown graphene has relatively small domain size and its orientation is not controlled. We studied the growth of graphene films over crystalline metal films deposited on single crystalline substrates and found the formation of square and triangular-shaped graphene sheets inside pits appeared on the crystalline metal film [4]. However, the graphene sheets were mainly few-layer and did not cover the whole area of the metal film.

Here, we performed atmospheric CVD over crystalline Co and Cu films deposited on c-plane sapphire substrates (Fig. 1) [5,6]. With the highly crystalline metal catalyst films, the preferential formation of uniform single-layer graphene is realized not only for Cu but also for Co. Moreover, as shown in Fig. 2, we observed the epitaxial relationship between single-layer graphene and Co (or Cu) lattices when synthesized at 1000 °C. The single-layer graphene showed the field-effect mobility of >1000 cm^2/Vs. We also demonstrate that other carbon sources, like amorphous carbon, can be converted to single-layer graphene by simply annealing over the crystalline metal films [7,8]. Our work expands a possibility of synthesizing single-layer graphene over various metal catalysts. Moreover, our CVD growth gives a graphene film with predefined orientation, and thus can be applied to graphene engineering, such as cutting along a specific crystallographic direction, for future electronics applications.

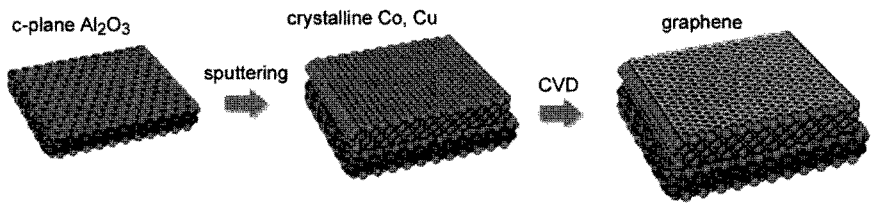

Figure 1. Schematics of the epitaxial CVD growth of graphene over crystalline metal films deposited on sapphire c-plane.

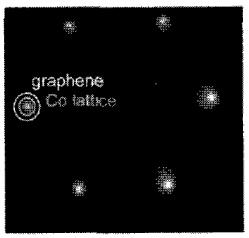

Figure 2. LEED pattern of graphene and Co lattices

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3-5

Low-temperature synthesis of few-layer and multi-layer graphene by chemical vapor deposition

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Graphene has been attracting much attention as a candidate for a novel material utilized in future electronics due to its excellent physical properties since a success in isolation from graphite [1]. For such applications, low-temperature synthesis of graphene on a desired substrate is important in order to prevent from thermal damages to devices during the synthesis process. However, there have not been many reports regarding low-temperature synthesis of graphene. In this study, we demonstrate synthesis of few-layer and multi-layer graphene at temperatures lower than 650°C by using thermal chemical vapor deposition (CVD), and fabricate graphene field-effect transistors (FETs) directly on a substrate without using graphene-transfer processes [2].

Graphene was synthesized by thermal CVD method with a mixture of acetylene and argon as the carbon source. As a catalyst, iron (Fe) films with thicknesses of 20-500 nm were sputtered on a SiO_2/Si substrate. The CVD was performed at 500-650°C. Analyzing the results, we have found that the thickness of multi-layer graphene depends on the catalyst thickness and the synthesis conditions including substrate temperature, partial pressure of acetylene and growth time. By optimizing the synthesis conditions, we have obtained few-layer graphene at temperatures between 590 and 650°C. Figure 1 shows a cross-sectional TEM image of few-layer graphene grown at 590°C. Furthermore, we have fabricated graphene FETs all over the substrate without transferring to another substrate. In the presentation, electrical properties dependent on the growth temperature will be also described.

This research is partly supported by the Japan Society for the Promotion of Science (JSPS) through its "Funding Program for World-Leading Innovative R&D on Science and Technology (FIRST Program).

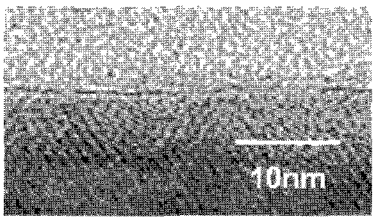

Figure 1 TEM image of few-layer graphene grown at a temperature of 590℃

[1] K.S. Novoselov *et al.*, Science 306 (2004) 666.

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3-6

Surface Synthesis of Graphene Materials using Polyaromatic Hydrocarbon Derivatives.

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Graphene ribbon is a promising material for Organic semiconductor with high mobility. Build-up surface synthesis of graphene ribbon is required for precise control of the structure and evaluation of electronic properties, because of its performance depends on its carbon structure.

Metal surface is an eligible template for self-assembled molecules due to its strong interactions between surface and molecules. We previously demonstrated a single-molecular processing technique using electrochemistry, termed 'electrochemical epitaxial polymerization'.[1,2] This technique is based on sequential electropolymerization of the monomer by applying voltage pulses to a monomer–electrolyte solution. Using this technique, we can control length, direction, and density of conjugated polymer wires, and produced single conjugated-polymer wires as long as 200 nm in uniaxial propagation on iodinemodified Au(111) electrode. Towards two-dimensional conjugated polymers,[3] we examined to produce conjugated graphene material on metal surface from small polyaromatic organic molecules by applying external stimuli. Thus obtained materials were evaluated by Raman spectra.

[1] H. Sakaguchi, H. Matsumura, H. Gong Nat. Mater. 3, 551 (2004).

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[3] D. G. Perepichka, F. Rosei Science 323, 216 (2009).

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3-7

Formation of Graphene on Insulator by Liquid Metal Flux Method

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Abstract: Much interest has been focused on graphene since the electric field effect in single-layer graphene was discovered in 2004 [1]. So far, graphene preparation has been achieved by three principal methods, exfoliation [1], CVD [2], and thermal decomposition of silicon carbide (SiC) [3]. Each of the methods has its distinctive drawbacks to hinder industrial use. Thus, we aspire to develop a new manufacturing process free of these challenges that will enable commercialization of graphene.

Here we report an unconventional approach to synthesize graphene, namely by liquid metal flux method. Our innovation was originally triggered by the report of Fujita *et al*, in which they show the graphitization at an interface between amorphous carbon and liquid gallium [4]. As is shown in Fig. 1, the method is based on a two-step process; the dissolution of carbon from a carbon source into a flux by heating up to ~1000 °C, and the segregation of carbon from the flux onto a substrate by cooling. Raman spectroscopy revealed that graphene can be formed directly on various substrates (Fig. 2). In the best case, the ratio of the intensity of the D-band to that of the G-band (D/G ratio) was less than 0.1, suggesting that the quality of graphene was acceptable for devices. We anticipate that the LPE method has the following merits. First, it will be scalable to produce large-area graphene. Second, it requires a heating temperature that is lower than that for thermal decomposition and nearly equal to that required for CVD growth of graphene. Third and most remarkably, graphene can be formed directly on a substrate, thus realizing "graphene on insulator" substrates.

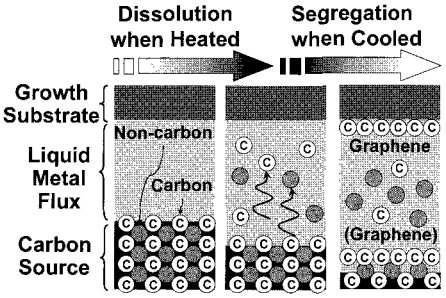

Fig.1. A principle of graphene formation by liquid metal flux method.

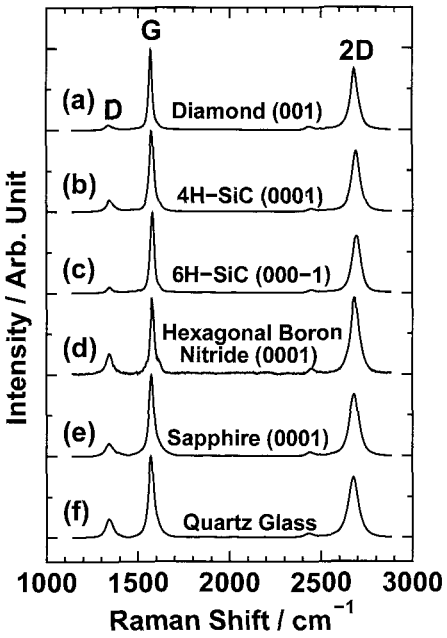

Fig.2. Raman spectra of graphene formed on various substrates by liquid metal flux method

Acknowledgment: The authors would like to thank Prof. Jun-ichi Fujita for valuable discussions. This work is partly supported by the Japan Science and Technology Agency.

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3-8

High rate growth of carbon nanotubes in tens of micrometer deep through silicon vias

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1. Introductio

Stacking chips in a three-dimensional (3D) manner is expected in downscaling of electronics. One key enabling technology for 3D chip stacking is the formation of through silicon vias (TSVs). The most popular method of making interconnects in TSVs is by plating of metals, such as copper. But, it takes a long time to fill the via by metal plating. We have developed mm-long single wall CNT (SWCNT) technology [1], where CNTs of tens of micrometer length grow faster than plating of metals. In this study, our CNT vias technology [2] is applied to tens of micrometer deep vias.

2. Experimental

40-65μm diameter, and 33μm depth vias are fabricated, and deposited catalyst layer by magnetron sputtering system, bottom Al 5nm, Fe 1.0nm, top Al 0.5nm. Then CNTs were synthesized by remote plasma CVD. CH_4 flow 5 sccm, and H_2 flow 45 sccm, growth temperature is 650℃, input microwave power was 120W corresponding to 30W/cm^3 in power density, growth pressure is 60 Torr.

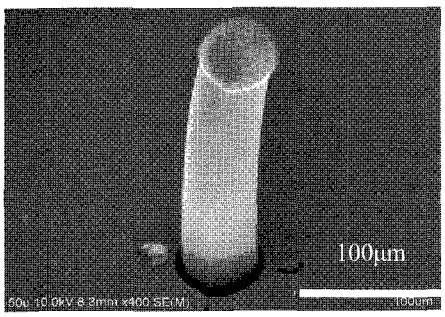

Fig.1 SEM image of CNTs grown from Si vias (Via diameter is 65um)

3. Result and Discussion

Figure 1 shows SEM image of CNTs grown from Si via (via height is 33μm, via diameter is 65μm). CNTs were grown up to via height in one minute. The relation between via diameter and growth rate is shown in Figure 2. Figure 2 said CNTs kept high growth rate (≈ 30μm / min) notwithstanding decrease of via diameter. Figure 3 shows Raman spectrum that CNTs grown on non pattern aria and CNTs grown from via. Laser wavelength is 633nm, and both CNTs grown on non pattern aria and CNTs grown from via are measured upper side. RBM peak is confirmed at 250cm^{-1}, this peak shows existence of single walled CNTs.

4. Conclusion

CNTs can be synthesized from the bottom of vias. Via diameter does not affect the CNT growth mode. The CNT growth rate is about 20 times higher than the rate of copper plating and applicable for TSV technology.

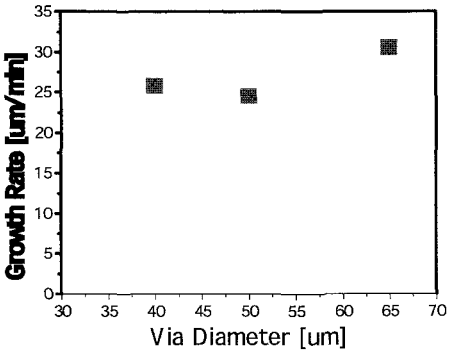

Fig.2 Growth rate of SWCNTs

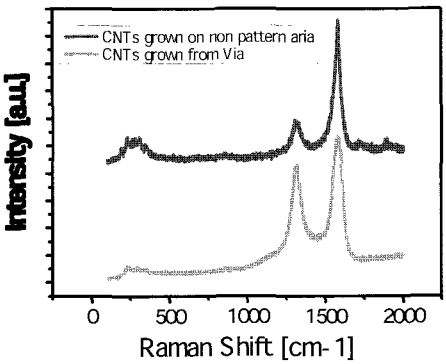

Fig.3 Raman spectrum (laser wavelength is 633nm)

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3-9

High-Density Growth of Horizontally Aligned Single Walled Carbon Nanotubes on Crystal Quartz Substrates

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Toward device applications of single walled carbon nanotubes (SWCNTs), the alignment control is of great importance. Horizontally aligned SWCNTs have been grown on crystal quartz substrates [1] and applied to fabrication of field-effect transistors (FETs) [2], but in order to increase the drive current and transconductance of FETs enhancement of the SWCNT density is desired. High-density growth has been studied [3], but optimum CVD conditions have not yet been determined.

On R-cut crystal quartz substrates [4], we performed a parametric study of CVD growth of horizontally aligned SWCNTs. Stripe patterns of Fe (~0.2nm) were deposited as catalyst by thermal evaporation, and synthesis was by the alcohol CVD method using ethanol as the carbon source. SEM images of horizontally aligned SWCNTs grown at 800 °C and various ethanol partial pressures are shown in Fig. 1. In the case of vertically aligned SWCNT growth, a higher decomposition rate and higher partial pressure of ethanol is known to be effective for rapid and high-yield growth [5,6]. On the contrary, high-density growth of horizontally aligned SWCNTs was achieved by lower decomposition rate and lower partial pressure of ethanol. Rapid growth of horizontally aligned SWCNTs is considered to result in bundling at the onset, preventing continuous and high-density SWCNT growth.

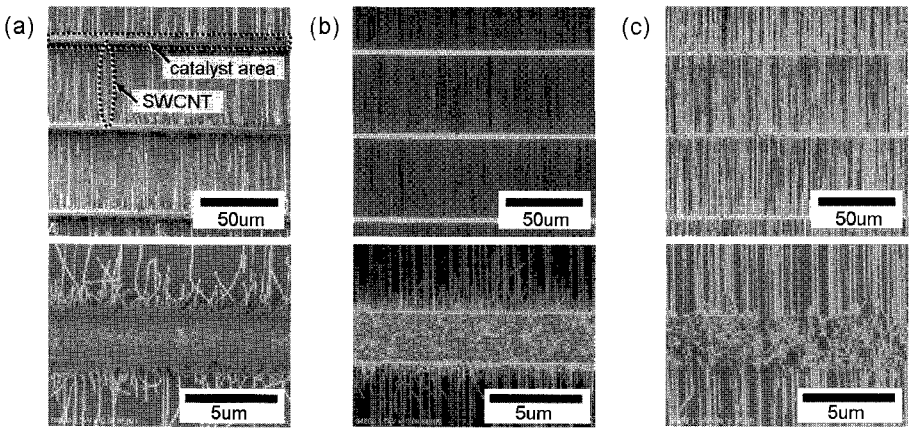

Fig. 1 SEM images of horizontally aligned SWCNTs grown at ethanol partial pressures of (a) 1300 Pa, (b) 300 Pa, and (c) 60 Pa. In the case of (c), ethanol was supplied by bubbling, with Ar/H_2 as the carrier gas.

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3-10

Highly selective growth of (6,5) carbon nanotube
- Why (6,5) nanotube is so special in the growth of carbon nanotubes-

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Controlling size and chirality distributions in the production of single wall carbon nanotubes (SWNTs) is undoubtedly one of the most important issues in the potential applications of the SWNTs to nano-material technology. So far, many experimental attempts have been carried out on the selective production of specific (n,m) tubes by various kinds of the SWNT production methods. Among these attemptions, so called "CoMoCAT" and "Co-MCM-41" are typical successful examples in which the (6,5) tube formation has been demonstrated to be of fairly prominence. In these experiments, the selection of the (6,5) tube seems to be realized by combination of CO disproportionation reaction and Co metal catalyst. The prominent growth of (6,5) nanotube in CVD experiments was also found in our recent alcohol CVD experiments for which carbon supply was taken place by simple decomposition of ethanol instead of CO disproportination reaction, contrary to the suggestion mentioned above.

On the other hand, the laser vaporization method combined with RhPd catalyst under some specific condition gives another good example for the highly selective SWNT growth of a single chirality, in which over 80% selective growth of (6,5) species has clearly been shown, suggesting the presence of some special reasons for the favorable growth of (6,5) tube. It should be interesting to note here that in the course of our laser vaporization experiments, there have been no evidence for the formation of the (5,5) nanotubes under similar condition optimized for the growth of the (6,5) carbon nanotube, although both (5,5) and (6,5) tubes possess similar chiral angle.

In the present paper, on the basis of both experimental and computational calculation evidences, we will discuss the growth process of a single wall carbon nanotube, placing a special emphasis on the properties of the reaction site of the growing-up carbon nanotubes.

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ポスター発表
Poster Preview

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2P－1 ～ 2P－54
3P－1 ～ 3P－53

1P-1

Carbon Nanotube Growth on ZnO(000-1) Substrates using Alcohol Gas Source Method

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Carbon nanotubes (CNTs) have been anticipated for application to various electronic devices. In order to achieve this goal, it is necessary to grow CNTs on semiconductor single crystal substrates. However, few have been reported on CNT growth on those surfaces, except for growth on insulating oxide surfaces such as SiO_2 and Al_2O_3. In this study, we attempted CNT growth on ZnO single crystal substrate using an alcohol gas source method [1]. ZnO is one of wide band gap semiconductors and has been expected for a variety of electronic applications. Therefore, CNT growth on ZnO is expected to be an important technique for fabrication of CNT devices.

ZnO(000-1) (O-face) substrates were used for CNT growth. After either Co or Pt catalyst was deposited on them, CNT growth was carried out using alcohol gas source method. Catalyst thickness was varied between 0.01 and 0.1 nm. The growth temperature and the ethanol pressure were varied between 400 and 700 °C, and 1×10^{-4} and 1×10^{-1}Pa, respectively. The grown CNTs were characterized by SEM, Raman spectroscopy and XPS.

Fig.1(a) shows an SEM image of CNTs grown at 700°C and 1×10^{-1} Pa using Co catalyst. Dense CNTs were grown, but a lot of grooves arouse on the ZnO surface after the growth. By decreasing both growth temperature and ethanol pressure, these grooves could be suppressed. Fig. 1(b) shows an SEM image of CNTs grown at 400°C and 1×10^{-4} Pa, indicating that CNTs grew on a flat ZnO(000-1) surface. For the purpose of increasing the CNT yield, we also carried out CNT growth using Pt catalyst. Fig. 1(c) shows an SEM image of CNTs grown at 500°C and 1×10^{-4} Pa using Pt catalyst. Compared with Co catalyst, the CNT density was drastically enhanced, keeping the ZnO surface flat.

A part of this study was supported by the Japan Society for the Promotion of Science (JSPS), a Grant-in-Aid for Scientific Research (C) 21510119. This work was partly performed in Nanotechnology Support Project in Central Japan (Institute for Molecular Science).

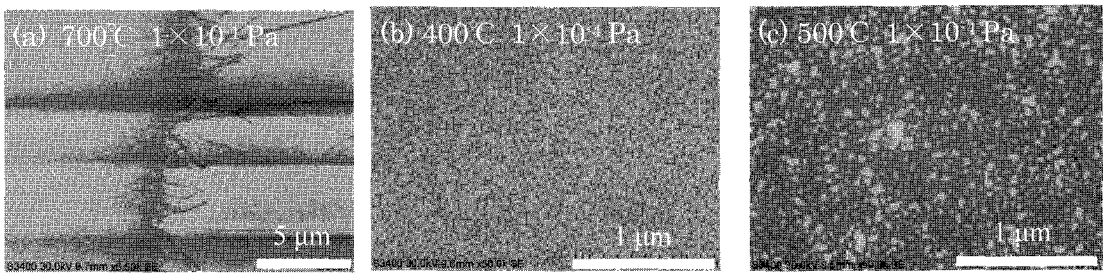

Fig.1 SEM images of CNTs grown on ZnO substrates

References

[1] T. Maruyama et al. J. Nanosci. Nanotechnol. 10 (2010) 4095.

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1P-2

QM/MD Simulations of Carbon Nanotube Cap Nucleation Using Acetylene Feedstock and an Fe_{38} Catalyst Nanoparticle

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The growth of carbon nanotubes by catalytic chemical vapor deposition (CVD) is of great interest for many applications, although the growth mechanism is still unclear. Since Fe substrate is known to be highly effective for the CNT growth in the CCVD process, and C_2H_2 is an excellent carbon source for high yield, we performed quantum chemical molecular dynamics (QM/MD) simulations to investigate the self-assembly process of carbon nanotubes from acetylene molecules on an Fe_{38} particle.

We found H of C_2H_2 transfers to the iron particle or other C_2H_2 units, followed by oligomerization of C_2H_x units to longer chains. Since oligomerization proceeds at a faster rate than hydrogen abstraction, the developing carbon structures C_xH_y remain hydrogenated with y<x. Compared to simulations with carbon-only source (C_2 or atomic carbon), the presence of hydrogen atoms prohibits ring-condensation and prevents fast sp^2 carbon network growth. Moreover, we find that hexagons are similarly likely to be formed compared to pentagons, which differs from the carbon-only simulations. In order to simulate the effect of the slower H removal processes, we shot C_2H_2 and at the same time removed H atoms randomly from the cluster on the metal particle. In our ~500 ps QM/MD simulations, we found that at a low H:C ratio, cap formation occurs as shown in Figure 1a, followed by base growth. If the H:C ratio is higher, 'standing wall' structures were formed, as shown in Figure 1b. We assume this kind of graphene-like sheet may coalesce to form the open tube, similar to the mechanism proposed by Eres *et al*, as shown in Figure 2. We demonstrate that, contrary to popular belief, SWCNT nucleation may occur in the absence of a pure carbon cap.

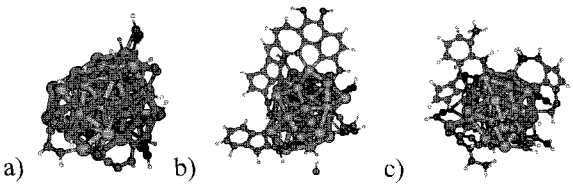

Figure 1. Last snapshots a) "standing wall" structures; b) "cap" structures,; c) "fragments"

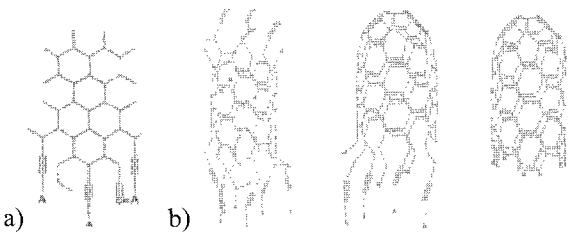

Figure 2. Proposed mechanism by Eres *et al.* (J. Phys. Chem. C 2009, 113, 15484): a) graphene fragment formation; b) coalescence and capped CNT formation.

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1P-3

PERIPUTOS: Purity Evaluation of SWCNTs Using Raman Spectroscopy, Effect of Surfactants

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It is really surprising that still we don't have a well-established way to evaluate the purity of single-wall carbon nanotubes (SWCNTs). From both the practical application and scientific research, reliable purity evaluation method is highly desired. Because the optical transition between one-dimensional van Hove singularities peaks is peculiar to SWCNTs, optical absorption can be a good probe for the purity evaluation. In this case, however, a background subtraction is needed and affects the obtained purity. On the other hand, we know Raman intensity is proportional to the optical absorption due to the strong resonance effect. In this case, we don't need to subtract the background because Raman intensity is automatically proportional to the net absorption of SWCNTs. Based on this idea, we recently proposed a new method, "purity evaluated by Raman intensity of pristine and ultracentrifuged topping of SWCNTs (PERIPUTOS)."[1] In this method, 100 % purity standard sample was prepared by sonication of SWCNT aqueous solution and following ultracentrifugation. Then the G-band Raman intensity was compared with that of the pristine sample.

In the previous report, we used sodium cholate (SC) as surfactant and did not try the other kinds of surfactants. In this work, we tested other surfactants for PERIPUTOS, such as deoxycholate (DOC), sodium dodecyl benzene sulfonate (SDBS), and sodium dodecyl sulfate (SDS). PERIPUTOS values obtained for commercially available SWCNTs (APJ, Meijo Nano Carbon) were 22.3 % for DOC, 23.4 % for SC, 23.7 % for SDBS, and 35.3 % for SDS. Because we used well mixed uniform sample, all the values should be the same. Higher value in SDS case indicates that the purification process to get 100 % standard sample was not sufficient probably due to less dispersion ability of SDS. Detailed analysis will be shown in the presentation.

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1P-4

SWNT growth under low pressure using Pt catalyst by Alcohol Gas Source Method in High Vacuum

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Carbon nanotubes (CNTs) have been anticipated for application in a lot of future nanodevices. To fabricate CNT devices in a conventional LSI process, it is desirable to grow CNTs under high vacuum. Recently, we reported single-walled carbon nanotube (SWNT) growth by alcohol gas source method in an ultra-high vacuum (UHV) chamber using Co catalyst [1, 2]. By this method, we could grow SWNTs under 1×10^{-1} Pa at 700°C. In this study, we attempted to grow SWNT under the lower pressure using Pt catalyst, which has high capability of decomposing ethanol.

Pt (thickness: 0.025 ~ 0.4 nm) was deposited on SiO_2/Si substrates by either an e-beam evaporator or a pulsed arc plasma gun. Then, they were heated up to the growth temperature (typically 700°C) in a UHV chamber, and ethanol gas (ambient pressure: 1.0×10^{-4} ~ 1.0×10^{-1} Pa) was supplied to grow SWNTs. For comparison, Co catalyst was also used for the SWNT growth. The grown SWNTs were characterized by scanning electron microscopy (SEM) and Raman spectroscopy.

Fig. 1 shows SEM images of SWNTs grown on Pt/SiO_2/Si ((a): EB, (b): plasma) and Co/SiO_2/Si substrates (c). Pt and Co thickness were both 0.1 nm, and the ethanol pressure were 1.0×10^{-4} Pa (Pt) and 1.0×10^{-1} Pa (Co), respectively, which were optimum conditions to obtain the maximum SWNT yields. In spite of the lower ethanol pressure, the SWNT yield grown with Pt catalyst was larger than that with Co. The enhancement mechanism of Pt will be discussed based on the decomposition of ethanol and diffusion of carbon atoms on catalyst surface.

This work was partially supported by the Japan Society for the Promotion of Science (JSPS), Grant-in-aid for Scientific Research (C) 21510119. We thank Prof Yakushi and Dr. Uruichi from Institute for Molecular Science for the Raman measurements.

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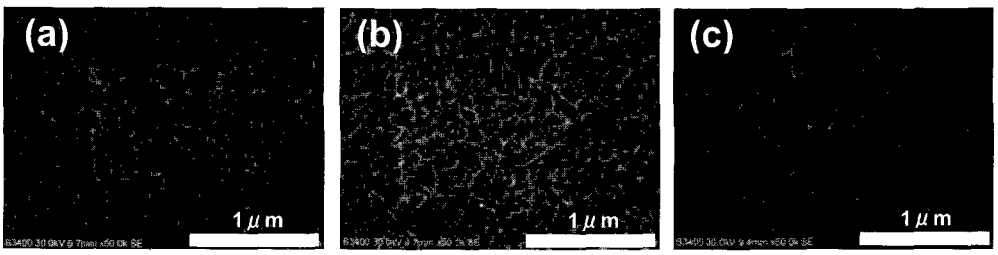

Fig.1

1P-5

Comparison of Carbon Nanotube Growth from 4H-SiC and 6H-SiC by Surface Decomposition using Raman Spectroscopy

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It has been reported that well-aligned zigzag-type carbon nanotubes (CNTs) could be produced by surface decomposition of SiC(000-1) [1]. However, most of studies in this field were investigated about CNTs from 6H-SiC and few have been reported about the effect of SiC polytypes on the CNT growth. In this study, we carried out CNT growth using 6H- and 4H-SiC and the difference was discussed based on results of Raman measurements.

After HF etching for 10 min, 6H- and 4H-SiC (000-1) C-face samples were annealed at 1700°C under high vacuum ($<10^{-4}$ Pa) for CNT growth. The annealing time was varied from 1 to 4 hours. The grown CNTs were characterized by Raman spectroscopy with an excitation wavelength of 532 nm.

Figure 1(a) shows Raman spectra of CNTs grown from 6H- and 4H-SiC after annealing for 1 hour. Although the G/D ratios were comparable between them, relative intensity of G band of CNTs grown on 4H-SiC was smaller than that on 6H-SiC. Raman spectra after annealing for 2 hours are shown in Fig. 1(b). The G/D ratio was slightly improved in both samples, but the thickness of CNT film on 4H-SiC surface was still smaller. On the contrary, the CNT growth drastically proceeded on 4H-SiC after annealing for 4 hours (Fig. 1(c)). The difference in the CNT growth rate will be discussed based on surface decomposition, taking into account formation of surface oxide layers during the heating.

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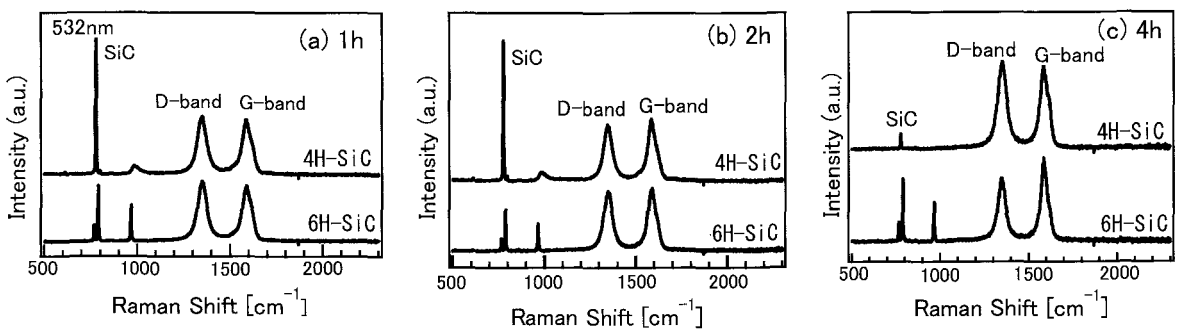

Fig.1

1P-6

Novel atomization and dispersion method of CNT using wet-type super atomizer "Nanovater"

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Abstract: Carbon nanotubes(CNTs) are usually in aggregated forms because of their higher intermolecular force caused by its rod-like structure. They are difficult to disperse into water or other solvents. Beads mill or ultrasonic are used to disperse CNTs, but these methods tend to cause defects in CNT's structure. And the method using media, such as bead mill, is liable to introduce contamination.

Authors are showing a new dispersion method of CNTs, wet type super atomizer by "Nonovater". It does not use any media, and is a very simple principle that uses collision of water. It can attain ultra-high pressure (max. 200MPa) in the solvents. Pressure and the number of pass-through are adjustable parameters. It means that we can change the collision energy to CNTs to control the atomization.

Fig.1(a) shows the transmittance of the SW-CNT solution before the treatment. After the 3,000 pass, the transmittance contrast increased, as shown in Fig.1(b). In other words, it can say that CNTs became well dispersed. So it is very important to atomize and disperse CNT to make their own properties such as absorption spectrum be prominent.

By this high-pressure treatment the length of the CNT became as short as 70nm in average, and D/G ratio increased a little, indicating the introduction of some damages to CNT. But it is much smaller than those by other methods such as beads-mill. Moreover, all liquid can pass the narrow (100um) nozzle, we can get highly uniform solution of CNTs.

CNT solution obtained by "Nonovater" can apply for various fields. We are studying for the application to optical device using CNTs.

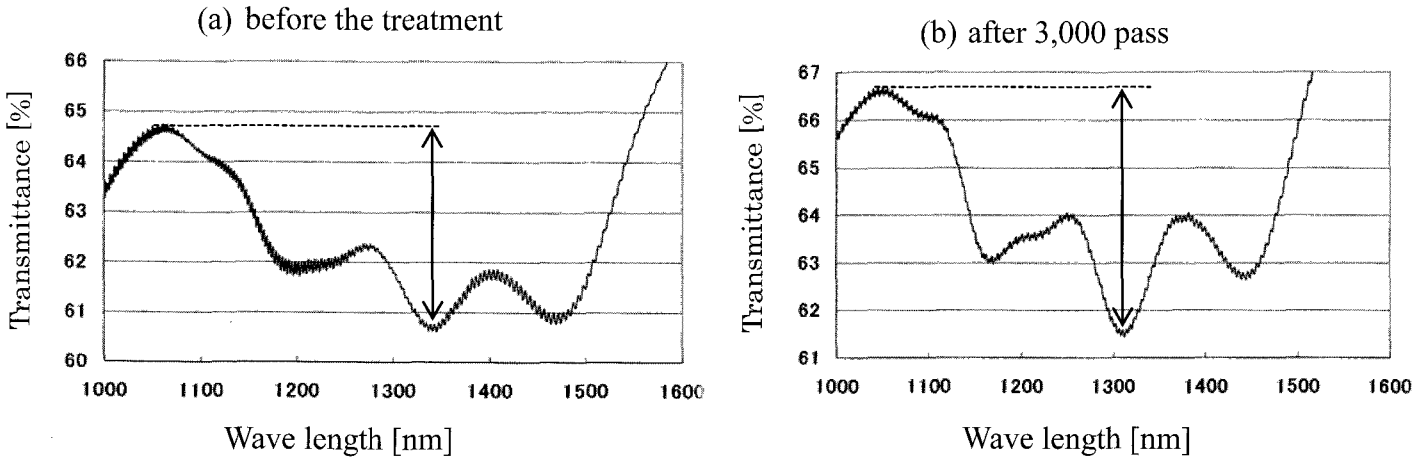

Fig.1 Transmittance of the solution of CNTs before(a) and after(b) the pressure treatment.

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1P-7

Molecular-assembled synthesis of single-wall carbon nanotubes

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The inner space of carbon nanotubes (CNTs) offers a fascinating platform to perform bottom-up synthesis of one-dimensional nanomaterials. One of the representative examples is the conversion of organic molecules such as fullerenes to single-wall CNTs (SWCNTs) through thermal annealing [1,2]. This reaction includes the fusion of individual molecules and can be regarded as a molecular-assembled fabrication of SWCNTs. It is very interesting to investigate the relation of precursor molecules to the chirality distribution of SWCNTs. However, the presence of outer CNTs precludes from obtaining signals of inner materials in optical evaluation such as optical absorption and photoluminescence spectra. Recently, we have developed an efficient method to separate inner materials from outer CNTs in solution phase [3]. This method allows us to investigate the detail chirality distribution and physical properties of SWCNTs constructed from molecular assembly.

In this study, we have investigated precursor-dependent growth of SWCNTs in CNTs. Various organic molecules as shown in Fig.1 were used as the precursors. These molecules were fused inside CNTs through thermal annealing to produce SWCNTs. The inner SWCNTs were extracted from outer CNTs by the method reported previously [3]. Optical absorption spectra reveal that the chirality of SWCNTs strongly depends on the precursor molecules even with the use of same outer CNTs. Our findings provide an important insight into the bottom-up synthesis of SWCNTs with desired structure and dopant.

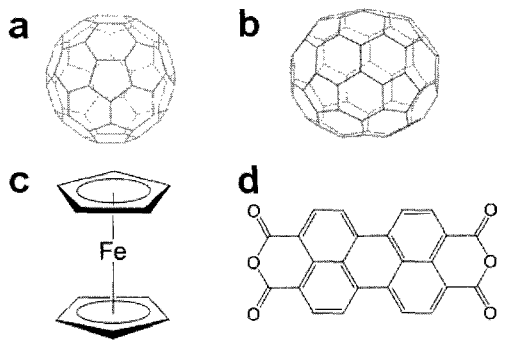

Figure 1. Molecular structures used in this study. (a) C60 fullerene, (b) C70 fullerene, (c) ferrocene, and (d) 3,4,9,10- perylene-tetracarboxylic dianhydride (PTCDA).

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1P-8

Effect of Sn catalyst concentration on purity synthesis of carbon nanocoil by substrate CVD with catalytic vapor supply

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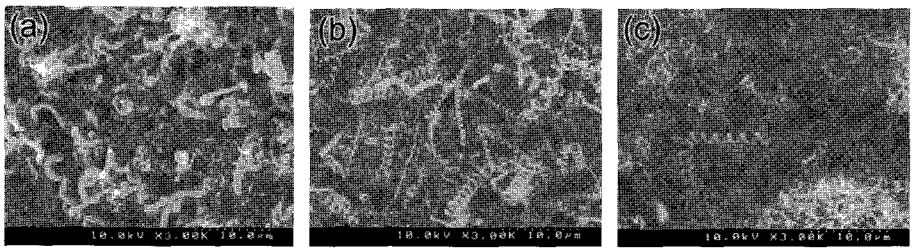
Carbon nanocoil (CNC) is a helical carbon nanofiber and is synthesized by chemical vapor deposition (CVD) with Sn/Fe catalyst. In our previous study, Sn catalyst was formed by dropping SnO_2 solution or vacuum evaporation on substrate [1]. On the other hand, we developed a continuous supply system of Sn in liquid into CVD reactor for improve the purity of CNC [2]. In this study, we report the effect of concentration of Sn catalyst solution. Si is used as a substrate and solution of Fe_2O_3 catalyst was dropped on Si substrate. Fe-coated substrate was heated in the air for 5 min at 400°C. The experimental conditions were as follows: N_2 gas flow rate, 1000 ml/min; C_2H_2 gas flow rate, 50 ml/min; solution of Sn catalyst flow rate, 0.144 ml/min; reaction temperature, 700°C; reaction time, 10 min. $Sn(CH_3)_4$ used as a Sn catalyst and was mixed with ethanol. At this time, the concentration of $Sn(CH_3)_4$ in ethanol was changed from 0.1 to 2%. Fig. 1 shows scanning electron microscopy (SEM) micrographs of carbon products at each concentration. The number of CNC was very few at concentration of 0.1%, and a lot of amorphous carbon impurity was synthesized at the same time. CNC was synthesized very much at concentration of 0.2%. At concentration of 2%, CNC was synthesized but purity was lower than concentration of 0.2%.

This work has been partly supported by the Outstanding Research Project of the Venture Business Laboratory from Toyohashi University of Technology (TUT); Global COE Program "Frontiers of Intelligent Sensing" from the Ministry of Education, Culture, Sports, Science and Technology (MEXT); Core University Programs (JSPS-CAS program in the field of "Plasma and Nuclear Fusion") from the Japan Society for the Promotion of Science (JSPS), Grant-in-Aid for Scientific Research from the MEXT, Toukai Foundation for Technology, Research Foundation for Materials Science, and Chubu Science and Technology Center.



(a) 0.1%. (b) 0.2%. (c) 2%.

Fig. 1 SEM micrographs of carbon products.

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1P-9

Length Sorting of Single-Wall Carbon Nanotubes using Size Exclusion Gel Chromatography

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Single-wall carbon nanotubes (SWCNTs) are promising material for various applications such as high-speed electronic devices. However, it is very difficult to control their electronic properties, precise diameter, and lengths in the growth process. SWCNTs have to be separated after the synthesis. So far we have developed effective separation methods of metallic and semiconducting SWCNTs using agarose gel[1,2]. Now we are focusing on the length sorting. The electronic devices comprised from long SWCNTs are expected to show higher performance[3]. In this presentation, we report a method for length sorting of SWCNTs by a size-exclusion chromatography and a simple length evaluation method.

Aqueous solution of SWCNTs was prepared by sonication and ultracentrifugation, and then the solution was concentrated by a long-time ultracentrifugation. Under the optimal conditions of the second ultracentrifugation, very short SWCNTs and impurities were successfully removed. The SWCNT solution was then applied to size exclusion chromatography using Sephacryl S-1000 gel (gel-filtration). Separated samples were roughly fractionated into three parts: above, within, and below the range of fractionation capability of the gel. The length distribution of SWCNTs of the each fraction was measured by atomic force microscope (AFM), and the length sorting was confirmed. Dynamic light scattering (DLS) was also measured for each fraction. Interestingly, clear peaks originating from length sorted SWCNTs were observed in DLS spectra although such peaks were hardly observed for the SWCNT solution before length sorting.

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1P-10

Control on the Electrochemical Process at Carbon Nanotube Synthesis at Room Temperature

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Development of well-defined Carbon nanotubes (CNTs) synthesis technique has been attractive challenge for future electrical, optical and catalytic materials.[1] In general, conventional synthesis techniques of CNTs such as arc discharge, laser ablation, chemical vapor deposition, etc., are based on the processes at high voltages, high laser power and high temperature. These high energy synthesis processes during CNT growth are expected to cause undesired defect formation due to high thermal fluctuation and less controllability of growth velocity and chemical reaction for well-defined structural control. Recently, we have employed an electrochemical technique, which is based on electrochemical reaction at room temperate in liquid phase and undergoes reaction at high speed, and succeeded in synthesizing single-walled carbon nanotube.[2] In this work, we investigated catalytic metal dependence for controlling carbon nanostructures by electrochemical process. The electrochemical system setup was a three electrode cell using an Au working electrode, a Pt counter electrode and an Ag/AgCl reference electrode (Fig. 1(a)). At first, Electrodeposition of Ni nanoparticles (NP's) as a catalyst on Au surface was carried out to prepare the surface for nanotube synthesis (Fig. 1(b)). From STM analysis of Ni NPs (Fig. 1(c)), we found that the Ni NP structure and size can be controlled by changing the deposition time. Fe and Co NPs formation was also confirmed by similar method and can be controlled the size by deposition time. Next, carbon deposition was performed using aqueous electrolyte solution containing 1 % acetic acid. Under the applied potential at -1.0 V, acetic acid molecules were reduced showing relatively large cathodic current. Raman spectra measurement showed the formation of graphitic carbon structure on each metal NPs on Au surface, however, we found that catalytic metal dependence was clearly observed for carbon structure. These results indicate the possibility of control of carbon structure by catalytic metal species.

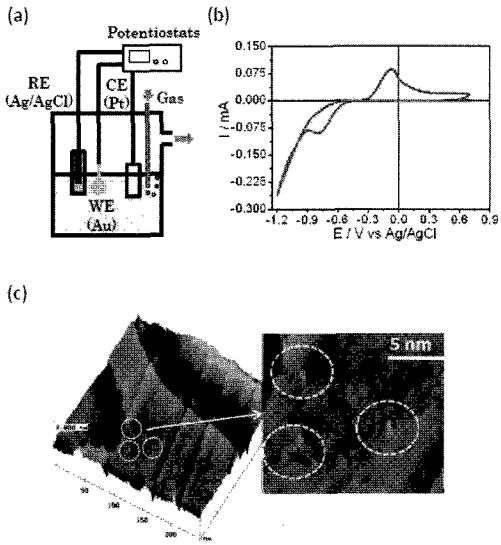

Fig. 1. (a) Schematics of electrochemical synthesis system with three electrode cell. (b) Cyclic voltammogram of Ni deposition on Au surface. (c) STM images of Ni nanoparticles formation on Au surface.

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1P-11

Selective synthesis of (6, 5) carbon nanotubes from C_{60} precursor

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Selective synthesis of single-wall carbon nanotubes (SWCNTs) with single chirality has highly promising applications since the electronic and optical properties strongly depend on their diameter and chiralities. Up to date, controllable synthesis [1] and post-synthesis separation[2] are two main strategies for obtaining chirality-pure SWCNTs. Selective synthesis of (6, 5) SWCNTs with purity of more than 60% were demonstrated in this work.

Briefly, C_{60} fullerenes were firstly encapsulated into SWCNTs (d≅1.5nm) and then annealed at 1200℃ for 24h under a vacuum of 10^{-6} Torr to produce double-wall carbon nanotubes (DWCNTs). The inner tubes were extracted from the DWCNTs using the ultrasonication and ultracentrifugation processes which we reported recently.[3] The extracted inner tubes were characterized by UV-Vis absorption, Raman scattering, photoluminescence (PL), and TEM observations. UV-Vis spectrum of the extracted tubes shows sharp absorption at 968nm and 568nm (Fig. 1a), corresponding to S_{11} and S_{22} bands of (6, 5) SWCNTs. Diameter of the extracted tubes was observed by TEM to be 0.76±0.05 nm. The PL map shows a further evidence for the selective synthesis of high pure (6, 5) SWCNTs (Fig. 1b).

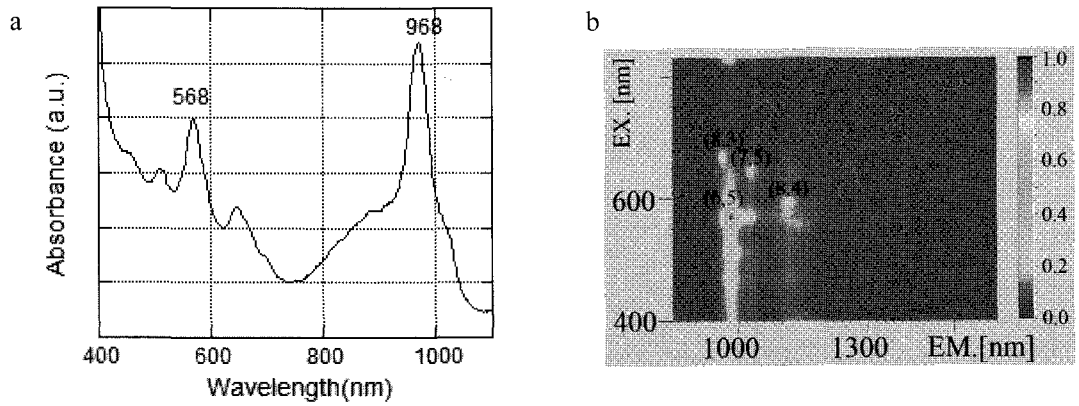

Fig. 1 (a) UV-Vis absorption spectrum and (b) 2D PL contour map of the extracted inner SWCNTs.

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2. M.S. Arnold, *et al.*, *Nature Nanotech.* **2006,** 1:60.
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1P-12

Synthesis of Multi-Walled Carbon Nanocoils over Sn/Fe/MgO Catalyst by Catalytic CVD

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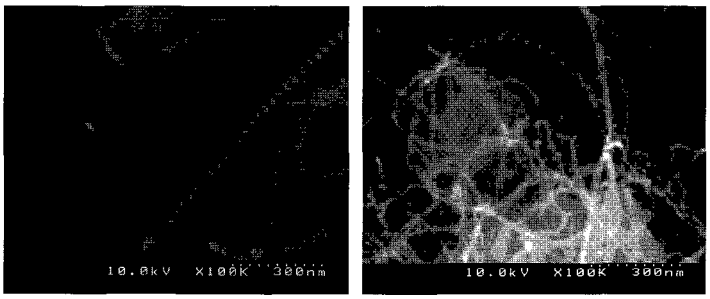
Multi-walled carbon nanocoils (MWCNCs) have been successfully grown using codeposited Sn/Fe catalysts supported on zeolite by chemical vapor deposition (CVD) [1]. MWCNCs with their unique helical structures have attracted considerable attention in applications such as field emission device, electromagnetic wave absorber and nanospring. Large scale production of MWCNCs is very important for the applications mentioned above. In this study, MgO was used as a catalyst support material instead of zeolite. First, NACEM-Fe (NIHON KAGAKU SANGYO CO., LTD, $Fe(C_5H_7O_2)_3$) and NACEM-Sn (NIHON KAGAKU SANGYO CO., LTD, $Sn(C_4H_9)_2(C_5H_7O_2)_2$) were mixed in deionized water. MgO was then added into the mixed solution and calcined at 100°C either with stirring for 21 h or without stirring for 20 h. MWCNCs were synthesized by catalytic CVD using acetylene. SEM micrographs of MWCNCs with Sn/Fe/MgO are shown in Fig. 1. MWCNCs could be synthesized in both the conditions and the tube diameter of MWCNCs grown was in a range of 20-30 nm.

This work has been partly supported by the Outstanding Research Project of the Venture Business Laboratory from Toyohashi University of Technology (TUT); Global COE Program "Frontiers of Intelligent Sensing" from the Ministry of Education, Culture, Sports, Science and Technology (MEXT); Core University Programs (JSPS-CAS program in the field of "Plasma and Nuclear Fusion") from the Japan Society for the Promotion of Science (JSPS), Grant-in-Aid for Scientific Research from the MEXT, Toukai Foundation for Technology, Research Foundation for Materials Science, and Chubu Science and Technology Center.



(a) With stirring (b) Without stirring

Fig. 1 SEM micrographs of MWCNCs synthesized with Sn/Fe supported on MgO

References: (1) M. Yokota, et al.: J. Nanosci. Nanotechnol, in press.

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1P-13

Carbon nanotube growth from C_{60}-fullerene nuclei with various source gases

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Chirality control of carbon nanotubes (CNTs) using chemical vapor deposition (CVD) remains a crucial issue for practical applications. It is well-known that the size and chirality of CNTs is decided by initial carbon cap structures during a nucleation stage as growth begins. Therefore, the cap formation process is a key to controlling the size and chirality of CNTs. Recently, it has been reported that fullerene-related molecules (fullerendione) can act as CNT growth nuclei in CVD process with ethanol, via forming hemispherical caps by thermal oxidation and initiating CNT growth at their open ends [1]. Although they found that the temperature for thermal oxidation strongly affects the cap structures and the diameter distribution of the as-grown CNTs, it has not been achieved a precise control of their size and chirality. In this study, in order to understand the growth mechanism, we investigate CNT growth from C_{60} fullerene nuclei under various conditions.

We used sublimed C_{60} fullerenes (MTR Ltd.) as CNT growth nuclei. C_{60} fullerenes dispersed in ethanol were spread on substrates such as Si, quartz, and silica-gels (not containing cobalt chloride). In the CNT synthesis using C_{60} fullerenes, it is important to prevent sublimation of the C_{60} fullerenes at the CVD temperature. For this purpose, we annealed the substrate in air ambience at 500-550 °C. This annealing process induced defects in the C_{60} fullerenes. A defective C_{60} fullerene molecule has a strong interaction with other C_{60} fullerenes and the substrate surface, resulting in prevention of the C_{60} sublimation. After the annealing in air, CNTs were synthesized in a furnace with two temperature zones, where the temperatures can be controlled independently for the separation of source gas (ethanol vapor and/or acetylene) cracking at 850 °C and CVD growth at 700-770 °C.

Figure 1 compares SEM images of the CNTs grown from C_{60} fullerenes and the conventional Co catalysis using CVD with (a)(d) ethanol, (b)(e) acetylene and (c)(f) mixture of ethanol and acetylene (volume ratio = 1:1). Observed growth yield of the CNTs significantly depends on growth nuclei as well as composition of the growth gases under the growth conditions optimized for the C_{60} fullerene nuclei. In the case of Co catalysts, the CNT yield is much higher for CVD with acetylene or mixture of acetylene+ethanol than that with pure ethanol. On the other hand, C_{60} fullerene nuclei give rise to higher yield for CVD with ethanol, contrary to Co catalysts. The reverse tendency between Co and C_{60} fullerenes for source gases should reflect nucleation and growth mechanism of the CNTs. The active growth species including OH group decompose disordered and unstable graphitic materials formed at the initial stage of CNT growth on Co catalysts. The C_{60} fullerenes with open ends, unlike Co catalysts provide the CNT cap structures in advance. The OH species have a function to remove disordered carbon materials and to prevent to terminate the growth process. Therefore, addition of a compound with OH group(s) such as H_2O in CVD process would be very effective to enhance the CNT growth from C_{60} fullerene nuclei, in agreement with the previous report [1].

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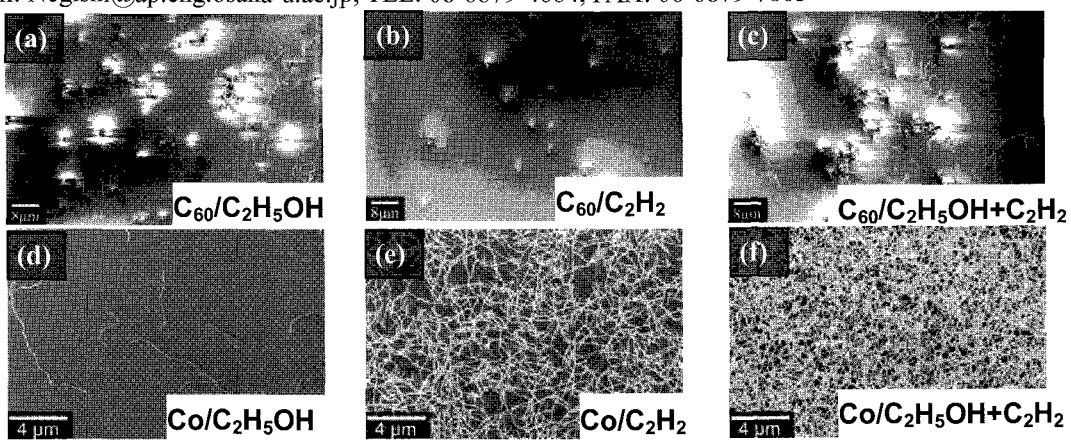

Fig. 1 SEM images of CNTs grown on SiO_2/Si from C_{60} fullerenes and Co particles by CVD with (a)(d) ethanol, (b)(e) acetylene and (c)(f) 1:1 mixture of ethanol + acetylene.

1P-14

Single-walled carbon nanotubes closing and opening: a density-functional tight-binding molecular dynamics study

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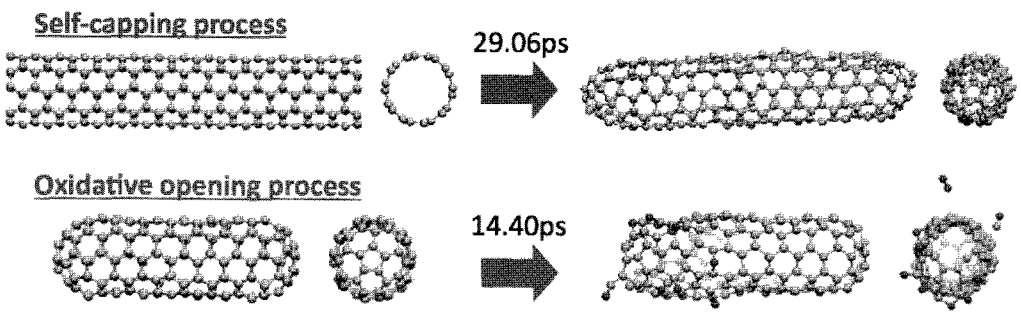
CNTs can be opened [1,2] and closed [2] experimentally, by heating under air or using aqueous chemical oxidation, and vacuum annealing, respectively. Here we report the simulations of SWCNT transformations, closing and opening process. Using canonical (constant temperature, NVT) molecular dynamics (MD) simulations based on the density-functional tight-binding (DFTB) quantum chemical method, we studied self-capping process of open-ended SWCNTs in vapor and oxidative opening process of capped SWCNTs, under high temperature respectively. For edge non-functionalized open-ended carbon only SWCNT model, with the exception of the (3,3) SWCNT the all-carbon ends of the open-ended (n,n) [n=3~10] armchair SWCNTs are able to self-cap during simulation times on the order of 100 ps. Edge-functionalized with oxygen containing group, more realistic open-ended ones can also close their ends after releasing their functionalities. There is dependency of self-capping time on SWCNTs diameter. Length dependency, however, has not been detected. Using "oxygen atom shooting", feeding atomic oxygen to capped SWCNTs, we reproduced oxidation process of SWCNTs. The oxidation process, making a hole on the surface of SWCNTs with releasing carbon oxides has been observed. We also found that caps are opened in shorter simulation times compared to sidewalls.



References

[1]C. Li *et al. Powder technology* (2004) **142** 175-179

[2]H.Z. Geng *et al. Chem. Phys. Lett.* (2004) **399** 109-113

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1P-15

Transition from [*n*]Cycloparaphenylenes to SWCNTs: SCC-DFTB Studies of Diels Alder Reactions and Raman Spectra

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[*n*]Cycloparaphenylenes (CPP) represent formally the shortest sidewall segment of armchair *(n,n)* single-walled carbon nanotubes (SWCNTs), therefore these beautiful macrocyclic ring strucures have been considered as synthetic building blocks for the organic bottom-up SWCNT synthesis [1,2]. As proposed by the group of Scott [2], a synthetic route might be realized in a step-wise Diels-Alder (DA) and hydrogen elimination reaction of CPP and subsequent reaction products with acetylene. We present self-consistent-charge density-functional tight-binding (SCC-DFTB) and density functional theory (DFT) calculations of [4+2] and [2+4] DA reactions on bay area and ring C-C bonds of [5]CPPs and longer (5,5) SWCNT belt structures with acetylene and s-cis [1.3]-butadiene, respectively. We show that the observed energetics of ever longer ring segments can be explained in terms of the Clar, semi-Clar, and Kekule structures characteristic for finite-length SWCNT fragments [3]. In addition, we compute Raman spectra based on SCC-DFTB for series of Clar, semi-Clar, and Kekule structures with increasing tube length and discuss the evolution of their features towards the Raman spectra of SWCNTs.

References

[1] H. Omachi, S. Matsuura, Y. Segawa, K. Itami, *Angew. Chem. Int. Ed.* **2011** in press

[2] E. H. Fort, L. T. Scott, *submitted, and private communication.*

[3] Y. Matsuo, K. Tahara, E. Nakamura, *Org. Lett.* **2003**, *5*, 3181.

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1P-16

Extraction of high purity and micrometer-long semiconducting single-wall carbon nanotubes

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Single-wall carbon nanotubes (SWCNTs) are a promising material for thin film electronics because of their high carrier mobility, flexibility, and solution processability. Realizing these fascinating properties of SWCNTs in realistic electronics requires a scalable chemical process to prepare pure semiconducting SWCNTs with high-crystallinity. However, the conventional processes always produce the low-quality (i.e., short length) nanotubes that degrade their intrinsic mobility. Furthermore there are still remaining impurity m-SWCNTs in separated semiconducting fractions.

In this study, we have developed a simple method to extract micrometer-long semiconducting SWCNTs with a purity of more than 99 %. Our method is based on the gel filtration [1,2]. We have found that a recycling process of the gel filtration effectively separates micrometer-long semiconducting SWCNTs from shorter ones. Figure 1 shows optical absorption spectra of before and after recycling gel filtration. The peaks of m-SWCNT (around 700 nm) were disappeared after recycling, indicating that the s- SWCNTs separated have a purity of more than 99%. In addition to the high-purity semiconductor separation, this method can be applied to length separation of semiconducting SWCNTs through the second recycling filtration. Figure 2 shows the length distribution of adsorbed and non-adsorbed s-SWCNTs. Micrometer-long s-SWCNTs are found to be included in non-adsorbed dispersion during the recycling gel filtration. The detail separation processes will be discussed in the presentation.

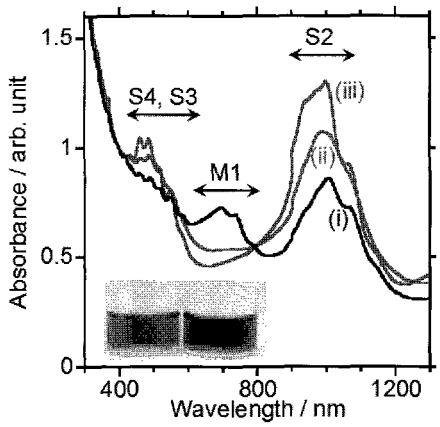

Figure 1 Optical absorption spectra of (i) the pristine sample and the separated sample by (ii) 1 time and (iii) 15 times recycling gel filtration.

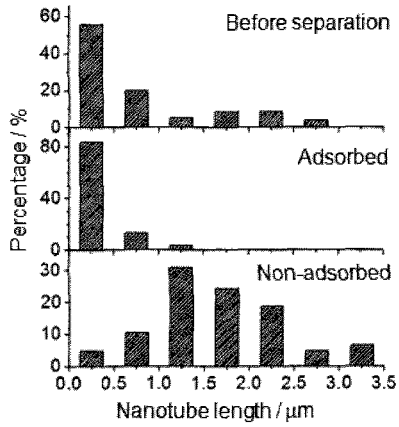

Figure 2 Length distributions of the purified semiconducting SWCNTs before the separation, in the adsorbed fraction, and in the non-adsorbed fraction.

Reference

[1] K. Moshammer et al., ***Nano Res.***, 2, 599 (2009)

[2] Tanaka et al., ***Appl. Phys. Express***, 2, 125002 (2009)

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1P-17

Electrode Properties of Nanocarbon-Polymer Composites

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Li ion secondary battery (LIB) has now come to be an indispensable energy device for portable electronic devices such as mobile phones and laptop computers. Recently, it is also expected to use LIB for larger electronic devices including electric vehicles. For such various demands for LIB, tremendous amount of investigation has been done to improve LIB. Various kinds of materials have been investigated as a new component which constitute the next generation LIB. For example, Si, Sn, CuO and $LiFePO_4$ have been proposed as new anode and cathode materials. We have to develop not only such electrode active materials but also another battery component such as current collectors, separators, electrolytes and so on. Here, we report the electrode properties of several kinds of nanocarbon-polymer composites. Polymer electrodes have the benefits of firm attachment of electrode active materials, flexibility, light weight.

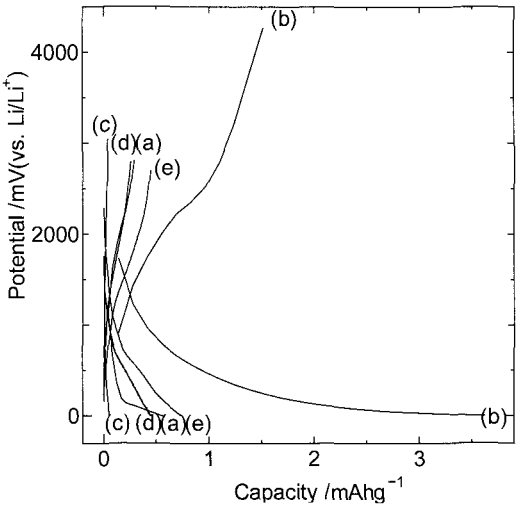

Fig.1 Charge-discharge curves of polymer electrodes including (a) Ni, (b) carbon black, (c) MWCNT, (d) nanohorn, (e) exfoliated graphite.

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1P-18

Electrical and Mechanical Properties of Carbon Nanotube/Polyisoprene Composites with Low Percolation Threshold and High Conductivity

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Polymer composite materials containing inorganic fine particles as fillers are widely used for various industrial fields as the structural and functional materials [1]. When the filler ratio is exceeded at a certain threshold value, various phase transitions occur, for example, from the viscous material to the elastic one or from the insulator to the conductor [2]. Various carbon materials have been used as fillers in a polymer for their functionalization and improvement in the electrical conductivity, mechanical strength and electromagnetic shielding property. In practical use for polymer- carbon composite materials, a high functionality and a low percolation threshold have been required from the viewpoints of physical properties, processing, and cost. In particular, carbon nanotubes (CNTs) among carbon materials have attracted a great deal of attention for extended nanotechnological applications because of their peculiar structure, multifunctionalities, high-specific surface area, and high aspect ratio.

The objective of this paper is to develop a practical conductive elastomer-material comprising of polyisoprene rubber (IR) with CNTs with the combinational techniques of ultrasonication (US) and rotation/revolution mixing without mechanical shear. For comparison, the composite materials were prepared by a conventional method with twin-screw (Banbury) mixer or extruder. Then, the relationships between the electrical properties of the composites and the structural characteristics of the CNTs (aspect ratio, disordered graphite degree, etc) were investigated as a function of the contents of the CNTs. Moreover, the performance of the composites such as tensile strength and stability was evaluated.

As a result, CNTs/IR composites exhibited a high conductivity and a low percolation threshold without decreasing their tensile strength, compared to the composites prepared with a Banbury mixer, which was inferred to give rise to the collapse of CNTs, followed by a high percolation threshold and a low conductivity. ESR measurements suggested that the addition of CNTs to IR inhibited degradation of the rubber because of CNT's radical scavenging capacity. The present results led us to the conclusion that the rotation/revolution mixing technique was expected to be a promising procedure for the preparation of various polymer composites containing CNTs.

[1] K. Kueseng, K. I. Jacob, *European Polym. J. 42 (2006) 220-227*

[2] A. Das, K. W. Stöckelhuber, R. Jurk, M. Saphiannikova, J. Fritzsche, H. Lorenz, M. Klüppel, G. Heinrich, *Polymer 49(2008) 5276-5283*

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1P-19

Cell aggregation to a carbon nanotube scaffold with dielectrophoresis

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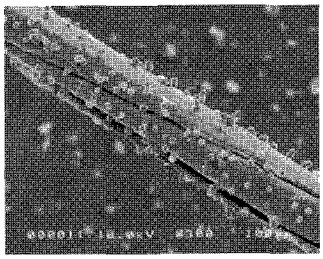
In regenerative medicine, it is important to grow a large number of cells on appropriate scaffolds. For that purpose, many types of cell scaffolds have been developed. Carbon nanotubes (CNTs) have attracted increasing attention owing to their mechanical, electrical, and structural properties. Because of these unique properties, increasing numbers of reports have focused on the use of CNTs as scaffolds in regenerative medicine. One of the most attractive properties of CNTs is their excellent conductivity, and they can thus provide electro-conductivity to a scaffold. Recently, many reports of cell positioning and patterning using electrical fields have been published. The dielectrophoretic approach is one of the most useful methods because of its ability to move cells in a non-uniform electric field. With this method, the scaffold with electro-conductivity would be able to attract cells efficiently. In this study, a threadlike CNT-scaffold was prepared and dielectrophoresis was performed to attract PC12 cells to the scaffold.

Single-walled CNTs (Meijo Nano Carbon Co., Ltd., Japan) were formed into a thread about 100μm in diameter. The CNT scaffold was connected to the electrode and soaked into PC12 cell dispersion. AC voltage was applied and PC12 cell were attracted to the scaffold within a few minutes. After 5 min, the ac voltage supply was stopped and cells were then incubated for 25 min at room temperature. The scaffold was fixed and cell numbers were counted using a scanning electron microscope (SEM). The cell number on the CNT scaffold incubated for 30 min without dielectrophoresis was also counted as control. The cell numbers with dielectrophoresis were approximately ten times higher than control. In order to evaluate the effect of dielectrophoresis to the cells, PC12 cell proliferation and differentiation after the dielectrophoresis was observed. Cells attracted to the scaffold were cultured for 8d and observed using a SEM. Cells showed good proliferation and covered the surface of the scaffold. PC12 cells attracted to the CNT scaffold were cultured with NGF for 8d and observed using a SEM and a fluorescence microscope. PC 12 cells were differentiated and neurite extension was observed.



This report shows that the PC12 cells were attracted to the thread-like CNT scaffold with dielectrophoresis and showed good proliferation and differentiation. These findings indicated that dielectrophoresis is the effective way to attract cells to the scaffold of the form that cells are hard to adhere.

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1P-20

Influence of Device Processing on Electrical Properties of Carbon Nanotube Field Effect Transistors

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Carbon nanotube field effect transistors (CNT-FETs) have attracted much attention because of their novel electrical properties based on quasi one dimensional structure. CNT growth using chemical vapor deposition (CVD) with patterned metal catalyst is one of the promising techniques to achieve position controlled fabrication of CNT-FETs[1]. In that fabrication process, CNT channels are contaminated by photoresist and solvents because photolithography and lift-off processes are performed to form pad electrodes after synthesis of the nanotube channels. Therefore development of fabrication process without contamination to the CNT channels is desired to bring out intrinsic properties of CNT-FETs. Clarification of influence of contamination on electrical properties of CNT-FETs is also required.

In this study we report the fabrication process of CNT-FETs having contamination-free nanotube channels. The influence of contamination by photoresist on the electrical properties of CNT-FETs was also investigated. We found that contamination by photoresist affects especially to on-current of CNT-FETs. The details will be discussed in our presentation.

[1] H.T.Soh et al., Appl. Phys. Lett., 75, 627 (1999).

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1P-21

Transparent Conductive Thin Films of Single-Wall Carbon Nanotubes Encapsulating Organic Molecules

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Single-wall carbon nanotube (SWCNT) thin films have attracted much attention in recent years as transparent conductive electrodes for plastic electronic devices. A lot of efforts have been dedicated on improvement of their resistivity. Chemical doping is one of the promising techniques to increase conductivity of SWCNT films. H.Z.Geng et al. reported that conductivity of transparent conductive films using SWCNTs can be improved by doping using dopants attached on the surface of nanotubes[1]. In addition to conductivity enhancement, improvement of stability is also required to employ doped SWCNT films as transparent conductive electrodes for commercial devices.

In this study we report properties of transparent conductive films using SWCNTs doped with organic molecules encapsulated inside nanotubes. Doping by molecular encapsulation provides stable conductivity enhancement because the dopant molecules are protected by nanotubes. The details will be discussed in our presentation.

[1] H.Z.Geng et al., J. Am. Chem. Soc., 129, 7758 (2007).

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1P-22

Thin-film transistors using aligned semiconducting single-wall carbon nanotubes separated by agarose gel chromatography

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Thin-film transistors (TFTs) using single-wall carbon nanotubes (SWCNTs) have attracted a great deal of attention for their possible use in transparent, flexible, high-speed, and high-current electronics. Recently, we found that TFT using a slightly aligned semiconductor enriched SWCNT (s-SWCNT) thin film shows drastically improved transfer characteristics [1]. To obtain higher on-currents and mobility, high density SWCNT thin film is required as well as high semiconductor purity. In this work, we fabricated TFTs using different densities of aligned s-SWCNT network.

In this study, s-SWCNTs separated by gel chromatography method [2] were used. The purity of semiconducting SWCNTs (in the s-SWCNTs) was ~90%. s-SWCNT solution was dropped onto a SiO_2/Si substrate covered with self-assembled monolayer of 3-aminopropyltriethoxysilane. The aligned thin film was prepared by N_2 blow in the drying process. The SWCNT density was controlled by changing waiting times before N_2 blow. Au/Ti electrodes were deposited as source and drain, resulting in back-gated TFTs with top-contact structure.

Figure 1 shows typical AFM images of low and high-density s-SWCNT films. It can be seen that s-SWCNTs were aligned in the vertical direction of the figure, although they are still forming random network. Typically, TFTs using low-density film showed a mobility of 5 cm^2/Vs and an on-off ratio of 10^4, while those using high-density film showed the mobility of 70 cm^2/Vs and the on-off ratio of 10^2. Detailed device characteristics of aligned s-SWCNT films will be discussed.

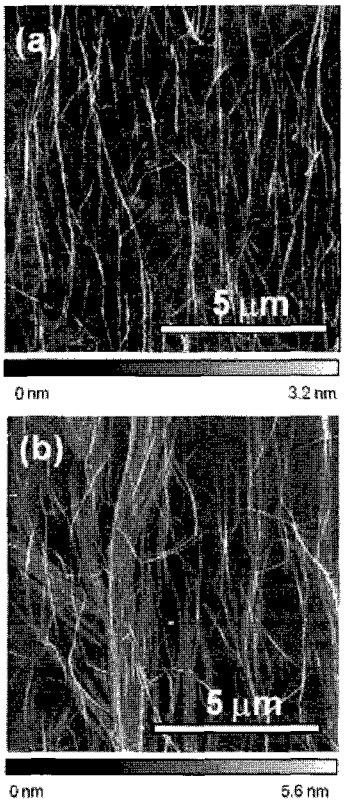

Fig.1 AFM images of (a) low and (b) high-density s-SWCNT thin films.

[1] S. Fujii et al., The 39th F-NT General symposium 2010, 2p-39
[2] T. Tanaka et al., Appl. Phys. Express **2** (2009) 125002

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1P-23

The simple method for analyzing the interaction between carbon nanotube and molecules

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Carbon nanotubes (CNTs) have unique π-rich, hydrophobic and curvature surfaces. In there, interfacial interactions of CNTs with molecules have been the focus of interests for the sake of solubilization of CNTs through physisorption [1] as well as many applications of CNTs. We have reported affinity chromatography technique using CNT-coated silica gel as a stationary phase to rank the interactions. However the analysis of the molecules having extremely strong interaction was quite difficult. Here we developed the simple method to evaluate the interaction for these molecules.

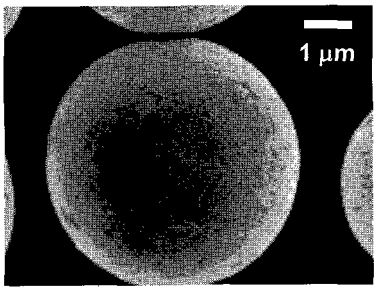

Fig. 1 SEM image of the SWNT -silica.

Figure 1 shows silica gel microparticles coated with single-walled carbon nanotubes (SWNTs) monolayer (denote as SWNT-silica) prepared by the simple mixing of pristine SWNTs dispersed in the 1-methyl-2-pyrrolidinone (NMP) with the amino-functionalized silica gel [2]. We prepared phthalocyanines (Ph-A ~ D) solutions in THF, and then shaked after the addition of SWNT-silica. These solutions were standed a few hours and the absorption spectra of the supernatants were measured (Figure 2). The absorbance of the solutions decreased by increasing the addition of the SWNT-silica. It was revealed that Ph-C interact strongly to SWNT compared to the other phthalocyanines. We attribute that large π-conjugation of Ph-C gives a strong affinity onto the SWNT surface.

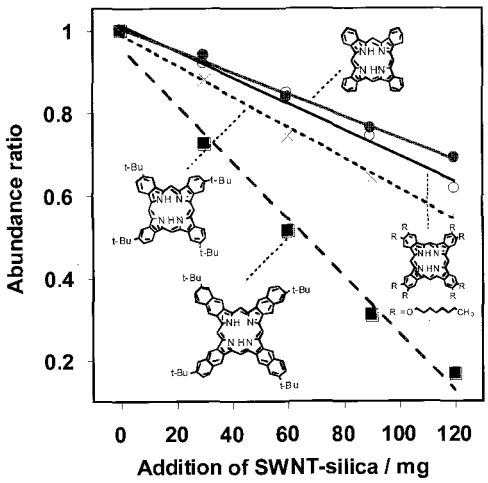

Fig. 2 Plots of abundance ratio of phthalocyanines to addition of SWNT-silica.

We believe that this simple method provides the promising opportunity for the systematic studies using wide range of molecules to achieve the understanding of the degree of interaction between CNTs and molecules.

[1] (a) N. Nakashima, T. Fujigaya, *Chem. Lett.*, **36**, 692. (2007).
(b) T. Fujigaya, N. Nakashima, *Polymer J.*, **40**, 577. (2008).
[2] T. Fujigaya, J. Yoo, N. Nakashima *Carbon*, **49**, 468. (2011).

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1P-24

Controllable Dispersity of Carbon Nanotubes

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In order to utilize carbon nanotubes (CNTs) effectively for many applications, dispersion of CNTs in various media is important. Although many different kinds of dispersants for CNTs have been reported, it is still important to develop novel unique CNT dispersant. Here we report a new CNT dispersant (**1**, Fig. 1) carrying a pyrene and long-chain-hemiacetal moieties. The synthesized dispersant gave a stable dispersion of the CNTs in an organic solvent. We found that the addition of an acid to the solution produced a precipitate (Fig. 2). This would be due to the elimination of the long-chain-hemiacetal moiety from the dispersant.

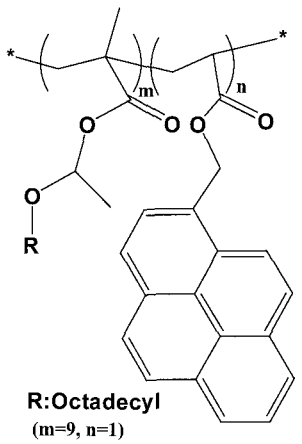

Fig. 1.Chemical structure of **1**.

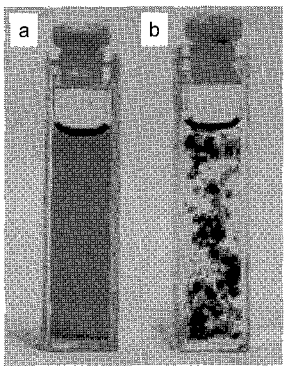

Fig. 2. A photo of CNTs dispersed by the aid of **1** in THF. before (a) and after (b) the adding an acid.

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1P-25

Highly Conductive Vein-Like SWNT Network

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Carbon nanotubes (CNT) have been studied as fillers in diverse multifunctional composites due to a wide range of the excellent properties. Dispersion technology of CNTs is challenging to realize commercial products such as coatings, heat sink, and structural members. Much efforts have been focused on dispersing CNTs individually into matrix, however, deterioration in CNT quality by damaging the surface and shortening was an inevitable problem [1].

Here we present the vein-like SWNT network comprised of long (hundreds of micron), flexible nanotubes which can reach the electrical, thermal conductivity and mechanical strength throughout matrices like polymers and metals. The SWNT network was made by dispersing an as-grown SWNT forest in solvent through a shear from wet-jet mill. Different shear was applied at 20-120 MPa of the jet pressure. First, the SWNT forest suspended in solvent showing the configuration like trunks of a tree. By the shear-induced dispersion, the trunks were transformed into fine meshes (Figure 1). The SWNT meshes were discretely laid on a flat substrate to observe the structure. An SEM observation of the SWNT meshes revealed that the nanotubes spread continuously across the whole system, which differs from a network through contacts of individually-dispersed nanotubes. The trunks from the starting SWNT forest were unraveled widely with an increase of the jet pressure, resulting in more meshes as well as a reduction in the mesh size. Bucky papers made from these SWNT meshes showed a high electrical conductivity.

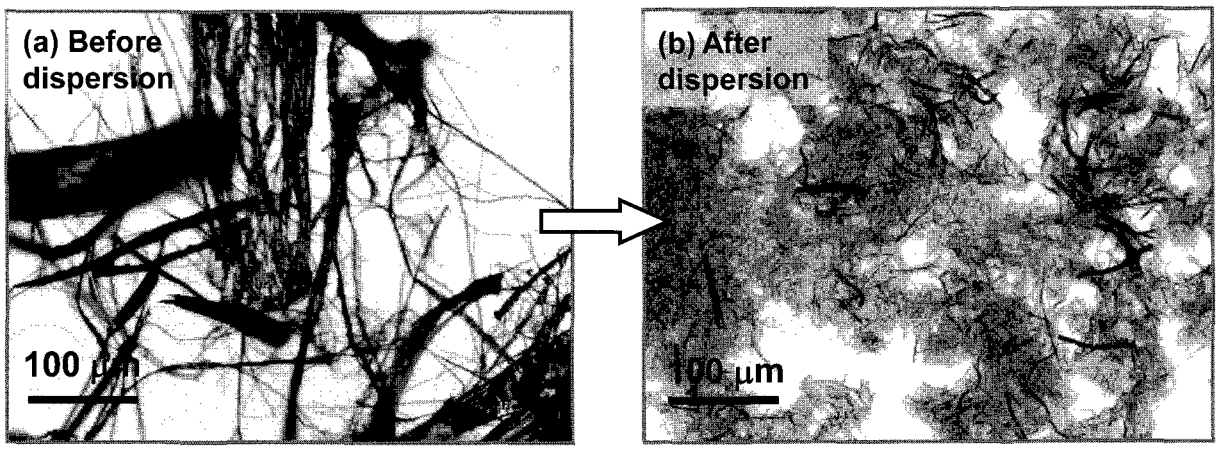

Figure 1 Optical microscope images of SWNTs (a) before and (b) after dispersion by wet-jet mill. These samples were spin-coated on flat substrates from SWNT/MIBK solution.

[1] P. M. Ajayan and J. M. Tour, *Nature*, **447**, 1066 (2007).

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1P-26

Ion-Gel Gating of Single-Walled Carbon Nanotube Films

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[2]*Department of Physics, Tohoku University, Sendai 980-8578, Japan*
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Recently, single-walled carbon nanotube (SWNT) is very attracting materials for flexible and printed electronics [1]. One of the difficult problems for SWNT film electronics is the transport control through density tuning. Generally, thick film shows metallic behavior, and semiconducting films are only obtained in very thin film. It is inevitable for SWNT transistors to fabricate moderate density films, and it makes the reproducibility of device fabrication drastically poor. Here, to break this limitation, we use one of the solid electrolytes, ion-gel, as the gate insulator for effective gating of thick SWNT film.

In this study, we selected thick SWCNT paper (> 200 μm), which is just metallic film for conventional transistor structure. We fabricated the electric double layer transistor using this SWCNT paper and one of the solid electrolytes, ion gal, which consists from poly(styrene-*block*-methyl methacrylate-*block*-styrene) (PS-PMMA-PS) triblock copolymer and *N*-Methyl-*N*-propylpyrrolidinium bis trifluoromethanesulfonyl imide) (P13-TFSI, Fig. 1) ionic liquid. We have laminated the SWCNT paper on SiO2/Si substrate and evaporated Au source/drain electrodes. Next, the PS-PMMA-PS/P12-TFSI solution in ethyl acetate was drop-casted onto the substrate. Finally, we put the Au plate on the substrate as gate electrode. All the measurement was done in the glove box with nitrogen atmosphere.

Fig.2 shows the transfer characteristic of ion-gel SWNT transistor. Importantly, 4 degits on/off ratio was obtained although the SWNT paper is very thick. It strongly suggests that the effective gating of whole SWNT film via ion-gel since it surrounds individual SWNTs and SWNT bundles completely. Moreover, operation voltage is quite low.

In summary, we successfully gated the SWNT thick film using ion-gel. This technique might improve the reproducibility of SWNT film transistor drastically.

This study was supported by Industrial Technology Research Grant Program from New Energy and Industrial Technology Development Organization (NEDO) of Japan.

Fig. 1 P13-TFSI

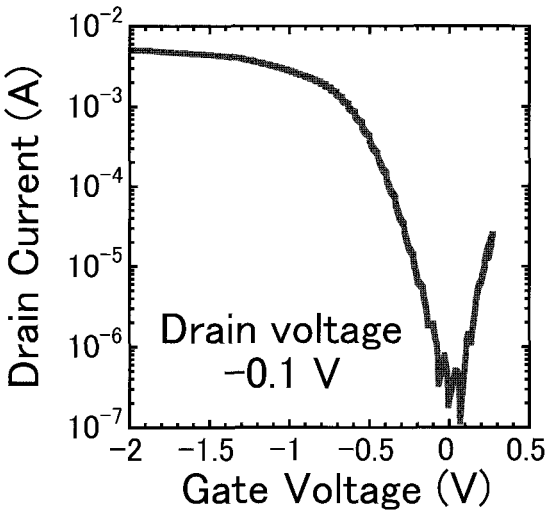

Fig. 2 Transfer characteristics

[1] H. Okimoto et al., *Adv. Mater.*, **22**, 3981 (2010).

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1P-27

Hybridization of DNA/carbon nanotube hybrid with biocompatible polycation.

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Single-walled carbon nanotubes (SWNTs) have the strong optical absorption and photoluminescence (PL) in near infrared region. Introducing of SWNTs to biological systems leads various applications such as imaging, photo thermal therapy, drug delivery system and so on. We reported that DNA solubilizes SWNTs in water [1] and the hybrids are highly stable even in the absence of unbound DNA [2][3]. DNA/SWNT hybrid has negative charge on the surface and allows interacting with cationic compounds. We studied a hybridization of DNA/SWNT with polycation by means of absorption spectra, dynamic lite scattering, atomic force microscopy and so on. Poly(L-lysine)-*graft*-polyethyleneglycol (PLL-*g*-PEG) having a high dispersibility, biocompability and strong interaction with DNA because of its cationic PLL main chain [4] was used as a polycation. From the titration, composition ration of the hybrid was determined as an approximately PLL-g-PEG : DNA/SWNT = 1 : 1. The ternary hybrid thus obtained (PLL-g-PEG/DNA/SWNT) possess remarkable stability in aqueous media, probably due to the grafted PEG chain. Cell uptaking efficiency was studied using HeLa cell, which was evaluated by Raman mapping of the cells after incubation with the both composites. Interestingly, we found that the dramatic improvement of the efficiency after the hybridization with PLL-g-PEG as shown in **Figure 1**.

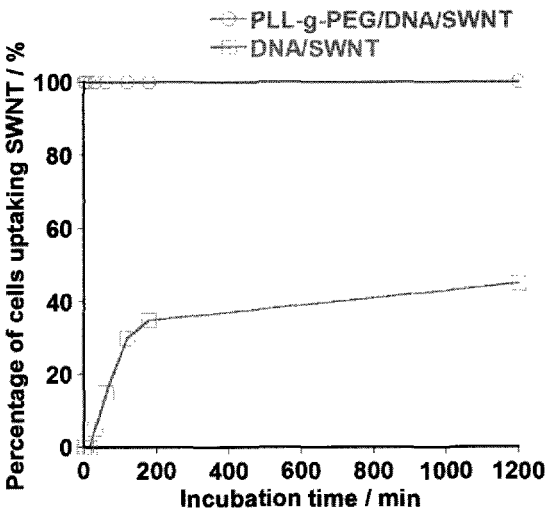

Figure 1. Polts of uptaking efficiency of DNA/SWNT hybrid with (circle) and without (square) biocompatible cationic polymer, PLL-*g*-PEG, by HeLa cells

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1P-28

Inkjet carrier doping to single-walled carbon nanotube film

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Single-walled carbon nanotubes (SWNTs) are promising materials for building electronic devices, in particular thin film transistors (TFTs). SWNT-TFTs fabrication using an ink-jet technique has attracted especially strong interest due to wide range applications such as flexible electronics and printing electronics. [1] However realistic circuits and devices require solutions to significant challenges associated with precisely controlling the electronic properties of the SWNT films. Here we report an ink-jet carrier doping to SWNTs thin film and fabrication of complementary circuits.

Figure 1 shows a schematic illustration of ink-jet carrier doping procedure. SWNTs thin film was printed sequentially using ink-jet technique on SiO_2/Si substrate. Furthermore, the PEI solution in methanol was printed position-selectively using ink-jet technique on SWNTs thin film since SWNTs can be functionalized by polyethylenimine (PEI) to switch their operation from p-type to n-type. This procedure converted the originally p-type SWNTs-TFT into the n-type one, and both p-type and n-type TFTs allows for design of complementary circuits. Indeed, we observed inverter characteristics (Fig. 2).

In summary, we have demonstrated ink-jet carrier doping to SWNTs-TFT and fabricated the logic circuit. In the future, these results promise to push the performance limit of SWNTs-based flexible and/or printed electronics.

This study was supported by Industrial Technology Research Grant Program from New Energy and Industrial Technology Development Organization (NEDO) of Japan.

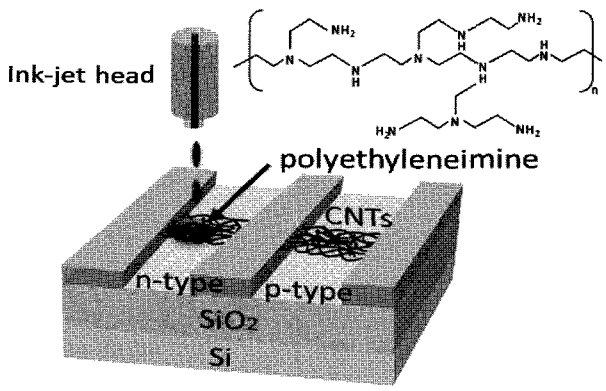

Fig.1 ink-jet carrier doping to SWNT thin film

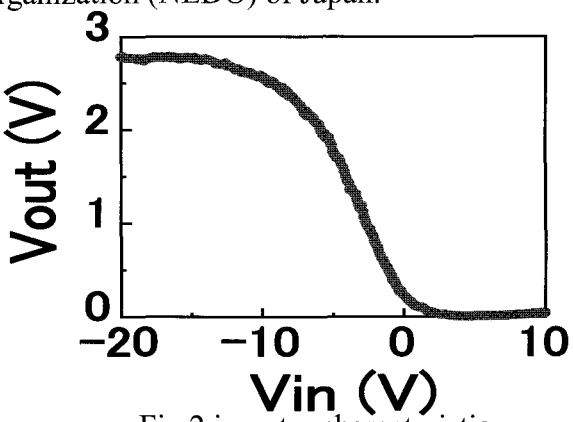

Fig.2 inverter characteristic

[1] H.Okimoto, T.Takenobu et al., Advanced Materials 2, 3981 (2010).

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1P-29

Chirality dependence of coherent phonon amplitudes in single wall carbon nanotubes

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In this presentation, we review coherent phonon (CP) spectroscopy of single wall carbon nanotubes (SWNTs). In a pump-probe experiment, when a very short laser pulse (~10 fs) is pumped to a SWNT sample, photo excited carriers as excitons appear at the same time in the excited states of SWNTs. Before recombination of the electron-hole pair, the lattice starts to vibrate coherently by exciton-phonon interaction in the same phase, which can be observed as an oscillation of transmittance in the probe pulse. After making Fourier transform of the transmittance with respect to time, we obtain the spectrum as a function of phonon frequencies. The phenomena observed in CP spectroscopy are similar to those in Raman spectroscopy in a sense that the exciton-phonon interaction is essential for making phonon. Theoretical characterizations of CP spectra is thus needed to explain the experimental results.

We calculate the dynamics of coherent phonons in SWNTs with different chiralities by following a microscopic theory developed by Sanders et al. and Stanton [1,2]. We improve the theory by including geometry optimization and curvature effects in the calculation [3], which is necessary for considering small diameter nanotubes. In particular, we examine coherent radial breathing mode amplitudes in semiconducting SWNTs by changing excitation energies within 0.5-4.0 eV. We find that the CP amplitudes are very sensitive to the change in excitation energies and that the phase of CP oscillations for each SWNT is strongly chirality dependent. From this simulation, we can also predict how the SWNT diameter changes in response to femtosecond laser excitation, especially to understand whether the diameter of a given SWNT will initially increase or decrease.

*This work is a collaboration between the authors with Gary Sanders and Prof. Stanton of the University of Florida, USA.

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1P-30

Density Functional Theory Calculations of the Cleavage of CC Bonds of Nanotubes by Diketone Formation

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Abstract: Kosynkin et al. reported longitudinal unzipping of carbon nanotubes by potassium permanganate ($KMnO_4$) to form graphene ribbons at 55–70 °C [1], and proposed that diketone formation is responsible for the cleavage of CC bonds of nanotubes. To our best knowledge there are a few theoretical reports on the diketone formation on nanotube surfaces up to now. The previous studies used too short (5,5) tube whose length of ~11 Å [2], and thus the results should be affected artificially by the edges terminated by H atoms as well as discrete energy levels of the short tube [3]. Accordingly, the structures of tubes whose CC bonds are cleaved by the diketone formation remained relatively unexplored. In the present study we employed density functional theory calculations to discuss the diketone formation on the (5,5) tube surface by using infinite-length model on the periodic boundary condition as well as the finite-length model whose length of ~27 Å.

Figure 1 shows optimized structures for (5,5) tubes whose CC bonds are cleaved by the formation of (a) two or (b) seven diketone. As shown in Figure 1, oxygen atoms are lined up along the tube axis, which cannot be seen in the previous studies. Then the cleavage of CC bonds in the seven-diketone-attached tube is more pronounced than that in the two-diketone-attached tube. As a result of the significant CC cleavage, the seven-diketone-attached tube has larger number of six-membered rings posing planarity rather than the two-diketone-attached tube case. Because of the attached oxygen atoms lined up along the axis as well as the CC bond cleavage, orbitals that mainly consist of *p* orbitals of oxygen atoms appears at frontier orbital regions.

(a) (b)

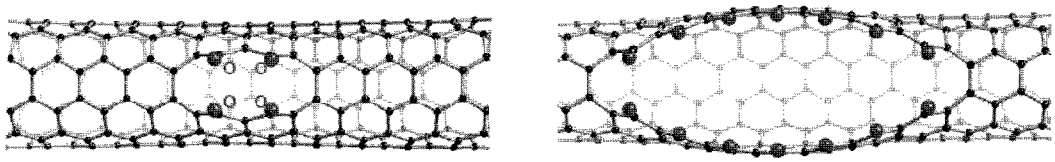

Figure 1 Optimized structures for (5,5) tubes whose CC bonds are cleaved by the formation of (a) two or (b) seven diketones.

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1P-31

G^+/G^- behavior of SWCNTs under the dispersion process

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It is well known that single wall carbon nanotubes (SWCNTs) show intense Raman peaks, "*G*-band", around 1593 cm^{-1}. The *G*-band consists of doublet, G^+ (higher frequency) and G^- (lower frequency). G^+ and G^- of semiconducting (s-) SWCNTs are assigned to longitudinal optical phonon mode (LO) and transverse optical phonon mode (TO), respectively, while those of metallic (m-) SWCNTs are assigned to TO and LO, respectively, due to the softening of LO in m-SWCNTs [1]. We measured G-band Raman spectra of the SWCNTs under the dispersion process in water using tip type ultrasonic homogenizer (Branson Sonifier) and G^+/G^- value was analyzed. Figure 1 shows G^+/G^- of SWCNTs produced by electric arc discharge method. Upper figure shows results of s-SWCNTs using 488 nm excitation and lower figure shows those of m-SWCNTs using 633 nm excitation. Interestingly, G^+/G^- of s-SWCNTs increased with the sonication, while that of m-SWCNTs decreased. This opposite behavior of G^+/G^- value is probably due to the opposite assignment of each peak and thus the intensity ratio LO/TO shows the similar behavior for both s- and m-SWCNTs. Present result suggests that LO/TO ratio can be used as an index of isolation status of SWCNTs in the solution. Detailed analysis will be shown.

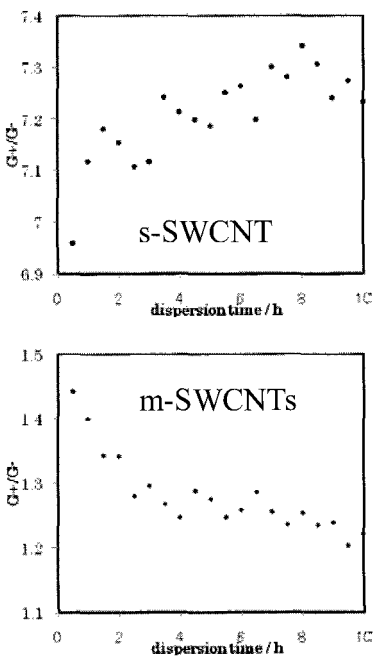

Figure 1. G^+/G^- of s-SWCNTs (upper) and m-SWCNTs (lower), against the dispersion time

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1P-32

Raman spectroscopy of SWNTs grown from boron- and nitrogen-containing feedstocks

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The thermal chemical vapor deposition (CVD) technique has great potential for highly controlled doped SWNT growth. However, there have been only a limited number of studies of the direct CVD growth of doped SWNTs. Another important issue for doped SWNTs is their characterization. Evaluating the carrier concentration has not often been clarified. In this study, we grew SWNTs by the thermal CVD method using B- and (or) N- containing feedstocks. Spectral shifts, which are indicative of carrier doping, were observed in the G band in Raman spectra.

Triisopropylborate and benzylamine were used as a B- and N-containing feedstock, respectively. Thermal CVD growth of relatively thin CNTs including SWNTs from either these two chemicals has been reported [1,2]. In this study, we also succeeded to grow SWNTs by supplying both two chemicals simultaneously, as shown in Fig. 1. The diameter of the SWNTs was evaluated to be 1-2 nm by Raman (RBM) and TEM measurements. In Raman spectra, hardenings of the G+ and G- bands were systematically observed for these SWNTs, regardless of the feedstock, as shown in Fig. 2. We think that the G band shifts are caused by electron-phonon interaction changes induced by the Fermi level shift. From the amount of the spectral shifts, the carrier concentration in these SWNTs was estimated to be ~0.4 %.

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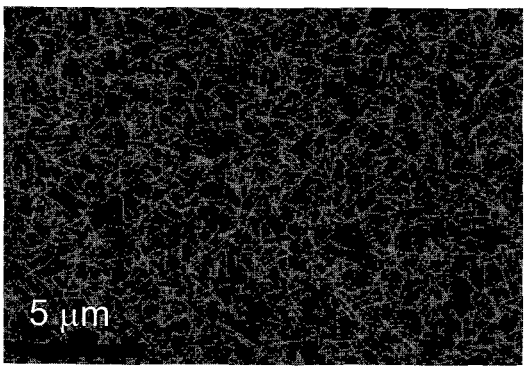

Fig. 1. SEM image of SWNTs grown from both triisopropylborate and benzylamine.

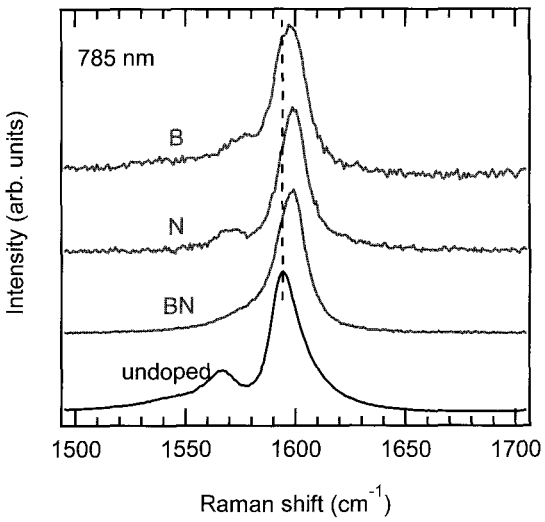

Fig. 2. Raman spectra of SWNTs grown from triisopropylborate (B), benzylamine (N), and both the two (BN). The undoped SWNTs were grown from ethanol.

1P-33

Dependence of Raman intensity and shift on different layer stacking of graphene

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Here we show that the calculated Raman intensity and shift of different layer stacking of graphene. It is known that the resonance condition for Raman scattering process and the properties of lattice vibration depend on the layer stacking of graphene. Thus the graphene sample can be characterized by using the Raman spectroscopy [1]. For example, the experiment and theory demonstrated that the Raman intensity and shift of the G' band, which is the overtone of the iTO phonon, are changed with increasing the number of graphene layers [2]. Moreover the Raman spectra from twisted bi-layer graphene have been reported [3]. To evaluate the origin and property of the Raman peaks of different stacking of graphene, we calculate the Raman intensity and shift of different stacking of graphene and the possible combination of phonon modes. Here the Raman spectra are calculated by using the extended tight binding (ETB) method and the force constant model [4]. The structure of the Raman spectra can be recognized by calculating the electron-phonon and -photon matrix elements, and the lattice vibration symmetry. From our calculated results we discuss the dependence of Raman intensity and shift on the structure of graphene [5]. The calculated results are compared with the experiment.

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1P-34

Polarization dependence of x-ray absorption spectra of Graphene

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Graphene, a single atomic layer of graphite has attracted much attention because of its unusual electronic properties. Recently, x-ray absorption spectroscopy (XAS) is used to determine the electronic properties of graphene [1]. It has also been shown in the experiment that the intensity of x-ray absorption spectra is strongly depends on the polarization direction of incident light [2]. We have also received some unpublished data by the courtesy of Professor Manabu Kiguchi of Tokyo Institute of Technology (TIT). Here, we calculated the x-ray absorption spectra for 1s- π^* and 1s-σ^* transition of graphene and compare with experimental result. Simple tight binding model is used to calculate the electronic band structure. X-ray absorption intensity is calculated within dipole approximation [3]. In case of x-ray absorption, the dipole vector for 1s- π^* transition is directed along the perpendicular direction of graphene plane. The dipole vector for 1s-σ^* transition lies along the graphene plane. So the intensity of 1s –π^* and 1s-σ^* transition change as a function of angle α, which is the angle between the pointing vector and the surface normal. It is found that intensity for 1s- π^* transition is proportional to $\sin^2\alpha$ and intensity of 1s-σ^* transition is proportional to $\cos^2\alpha$. Such an angular dependence can be used to select the final state symmetry. We also present a preliminary calculation of angle resolved photo emission spectra (ARPES) of graphene.

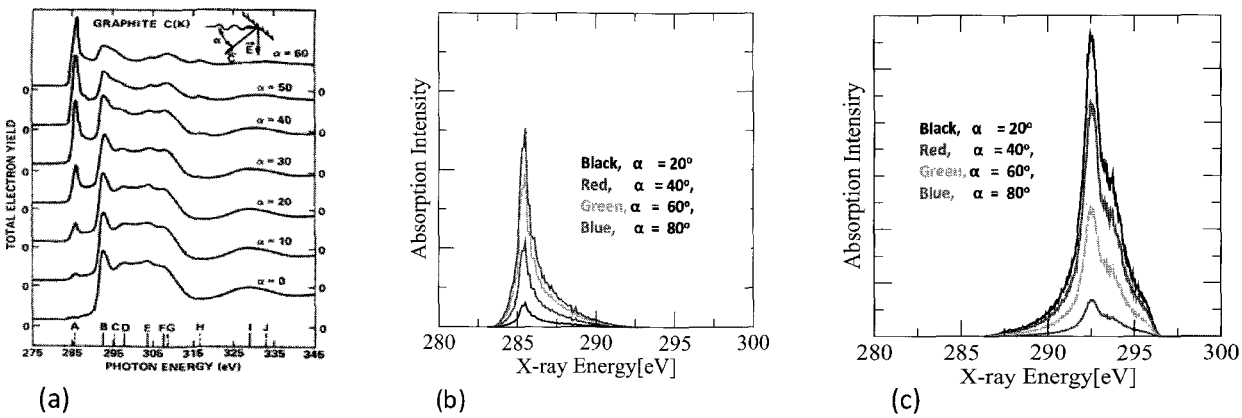

Figure: (a) Experiments: Carbon K edge photo absorption spectra of single crystal graphite at various angle of incidence α, between the crystal c axis and the electric field unit vector ε of the light (figure 1 of ref 2). (b) theoretical calculation of 1s- π^* transition and (c) 1s-σ^* transition at various angle of incidence α

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1P-35

Synthesis and Spectroscopical Characterization of Peripentacene

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Graphene has attracted a great deal of attention in recent years. It is known that high-purity and high-quality graphene, but in the limited size, can be obtained by mechanical exfoliation of graphite using a scotch tape. However, it is very difficult to obtain a large amount of graphenes enough for usual physical and chemical experiments. A chemical synthesis route by enlarging the number of benzene rings in polycyclic aromatic hydrocarbons (PAH) is one of the expected large scale synthesis methods.

To synthesize large-size PAH that will be treated as model graphene material, we tried to fuse pentacenes (**1**) at high temperatures under vacuum. By using this method, peripentacene (**2**) and trispentacene (**3**) can be synthesized through a dehydrogenation condensation reaction as shown in Fig. 1.

The obtained product was characterized by elemental analysis (C, H, and N), mass spectra, Raman spectra, Fourier transform infrared spectra (FT-IR), X-ray photoelectron spectra (XPS), and X-ray emission spectra (XES). In addition, we compared the observed electronic spectroscopic data and the partial electron density of states of peripentacene derived from the first principle calculations. The observed spectra were well reproduced by the calculations.

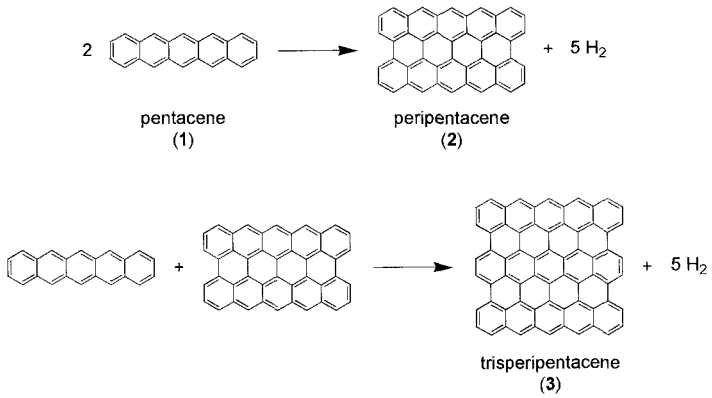

Fig.1 Dehydrogenation condensation reaction of pentacene.

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1P-36

Chemical and Electrical Characterization of Graphene Formed by Gallium Flux Liquid Phase Epitaxy

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Gradually nanocarbon materials are gaining momentum as prime candidates for enabling a technology jump to overcome the limits that are looming for traditional semiconductor devices. Since 2004, the high mobility of graphene places it in position to replace natural bandgap semiconductors if a scalable method of production can be developed. Some methods have been demonstrated for producing graphene and testing devices, notably exfoliation of graphite, [1] thermal decomposition of silicon carbide, [2] [3] and CVD growth on metal substrates. [4] [5] Each of these methods faces challenges to producing wafer size graphene of nanoelectronics quality.

The main difficulties are preparing films on insulating substrates, and also producing uniform and defect-free films. Exfoliation fragments the graphene, causes defects, and aids oxidation. CVD is able to provide large-area graphene films, but it has only been successful on conductive substrates like nickel. Transfer to other substrates is possible, but such a process suffers from similar problems to those encountered during exfoliation of graphite. Decomposition of silicon carbide, especially on the silicon face, is able to produce single layer graphene films, however it requires high temperatures of >1200°C.

Recently we introduced a new scalable process for forming graphene layers directly on an insulating substrate at temperatures of only 1000°C. This new process combines characteristics of other processes.[2][6] Gallium acts as a flux for carbon and catalyzes the formation of graphene. Graphene forms only where gallium contacts the substrate. In this paper, we present chemical and electrical characterization of uniform graphene films produced by this method.

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1P-37

Synthesis of Single-Layer Graphenes by Atmospheric Alcohol-Chemical Vapor Deposition

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Graphenes have attracted a great interest in recent years because of their novel electronic properties. Chemical vapor deposition (CVD) is expected as a simple and low-cost synthesis method of graphenes for industrial production. However, vacuum and explosive gases such as methane and hydrogen are generally required to synthesize single-layer graphenes in the CVD methods reported previously. Recently, Miyata et al. reported that CVD with flash cooling process can produce single-layer graphenes without using vacuum and explosive gases[1]. However, further study is required for development of simple CVD techniques toward large scale production of single-layer graphenes.

Here, we report a simple synthesis method of high quality single-layer graphenes from alcohol without using rapid cooling process. The graphenes were synthesized on Cu foils by thermal CVD under nitrogen atmosphere at ambient pressure. Fig.1 shows a Raman spectra of graphenes synthesize on Cu. 2D band with a narrow full width of half maximum of 35 cm^{-1} is observed as shown in fig. 1. The details will be discussed in our presentation.

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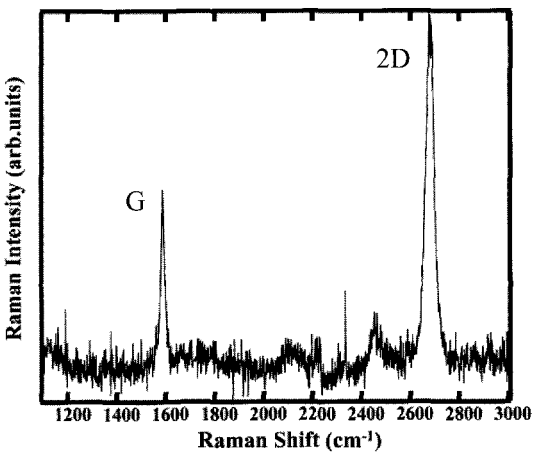

Fig.1 Typical Raman spectra of graphenes synthesized on Cu.

1P-38

Quantum capacitance of mono- bi- and tri-layer graphene with different stacking orders

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Graphene has been investigated as a semiconductor device due to its stability and high mobility at the room temperature [1]. It is expected that the graphene field effect transistor (GFET) will be a THz device. In order to get an energy gap of GFET, bi- or tri- layer graphene are widely investigated. However, it is known that the stacking order of graphene is not always AB Bernal stacking. Further, such devices generates heat by storing and emitting the electrostatic energy in a each switching process. Here we discuss the properties of the quantum capacitance (QC) of GFET for understanding electrostatic energy. In GFET, the capacitance is expressed by a serial connection of conventional geometrical capacitance and QC, as a function of gate voltage. QC is important because the electron effective mass of graphene is small and the effect of QC to the total capacitance is significant around K point of graphene [2].

In this paper we show that the calculated QC of mono-, bi-, and tri-layer grapheme with different stacking orders within the tight binding method [3]. We discuss the dependence of the QC on the gate voltage and density of carrier of different stacking for graphene. The calculated results are compared with the experiment [4].

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1P-39

Structural Changes of Carbon Nanowalls by Heat Treatment in Vacuum

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Carbon nanowall (CNW) is a two-dimensional carbon structure that stands perpendicular to the substrate like a wall. Since CNWs intrinsically consist of graphene sheets, they are expected to have high mobility. However, it has been revealed that amorphous carbon (a-C) layer exists in the surface of CNWs and/or at the interface between CNWs and substrates [1]. The removal of a-C is necessary for practical use of CNWs. In this study, we studied how the a-C was removed by heat treatment in vacuum.

Three specimens of CNWs were prepared by microwave plasma-enhanced chemical vapor deposition with different H_2/CH_4 flow rate ratios of 0/20, 20/20 and 40/20 sccm on SiO_2 (500 nm)/Si substrate [2]. The heat treatment was conducted by using an electrical furnace setup. Structural changes of CNWs were observed by scanning electron microscope (SEM) and Raman spectroscopy.

Fig. 1 shows SEM images of CNWs prepared with H_2/CH_4 of 0/20 after (a) growth and heat treatment at (b) 1100 °C. It was observed that the size of cone-like structures (shown by arrows) on CNWs was decreased through heat treatment at 1100 °C. In addition, the vertically aligned structure of CNWs was remained upon heat treatment even at 1200 °C in vacuum, although CNWs fell down on substrate through heat treatment at 640 °C in air [3]. This is because reaction rate of a-C with oxygen was suppressed by reduced oxygen in vacuum. Fig. 2 shows I_G/I_D dependence of CNWs on heat treatment temperature in vacuum. The I_G/I_D peak intensity ratios were obtained by peak fitting of each Raman spectrum. Increase in I_G/I_D, indicating the removal of amorphous carbon, was observed. On the other hand, full width at half maximum of D peak increased from ~ 40 to ~ 50 cm^{-1} after heat treatment at 1000 °C. This may be because defect was induced in the graphitic network of CNWs by heat treatment at high temperature.

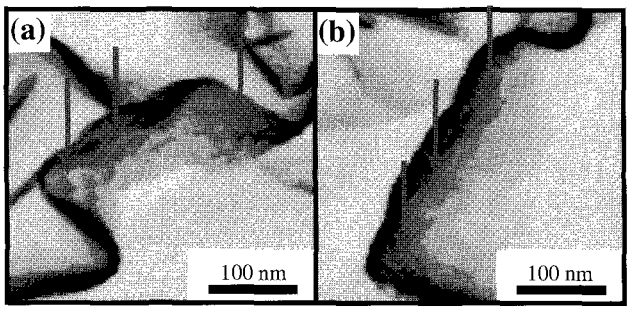

Fig. 1. SEM images of CNWs after (a) growth and (b) heat treatment at 1100 °C.

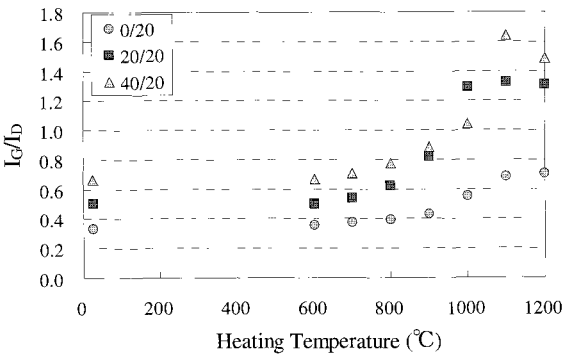

Fig. 2. I_G/I_D of CNWs prepared with H_2/CH_4 flow rate ratio of 0/20, 20/20 and 40/20 as a function of heat treatment temperature.

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1P-40

Electronic-structure control of thin film of graphite: Interlayer spacing and thickness dependency

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Magnetic properties of carbon materials are received much attention because of their potential for application in electronic devices. Recently, a rhombohedral (ABC-stacking) graphite thin film exhibits ferrimagnetic spin ordering on its (0001) surface. Calculated a mount of magnetic moment is found to be 0.036 μ_B/nm^2 [1]. The polarized electron spins on the top-most and bottom-most layers are coupled in antiparallel so that the net spin on the film vanished. Furthermore, by applying an electric field normal to the film, we demonstrated that surface magnetic state undergoes magnetic phase transition from ferromagnetic to ferromagnetic states [2]. These facts indicate that the magnetic properties of graphite thin films sensitively depend on the external conditions.

In this work, based on first-principles total-energy calculations, we systematically explore how the electronic and magnetic properties of graphite thin film depend on the interlayer spacing and number of layers. Our calculations show that there is a threshold interlayer spacing on the spin coupling between top-most and bottom-most layers. Under the interlayer spacing less that 0.3 nm (10% compress), the polarized spins on both surfaces are coupled in parallel instead of antiparallel in its equidistance. On the other hand, for the number of graphene layers less than seven, we cannot observe the spin polarization on both surfaces.

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1P-41

QM/MD Simulation of Graphene Hole Repair by C_2 molecules

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(a)

(b)

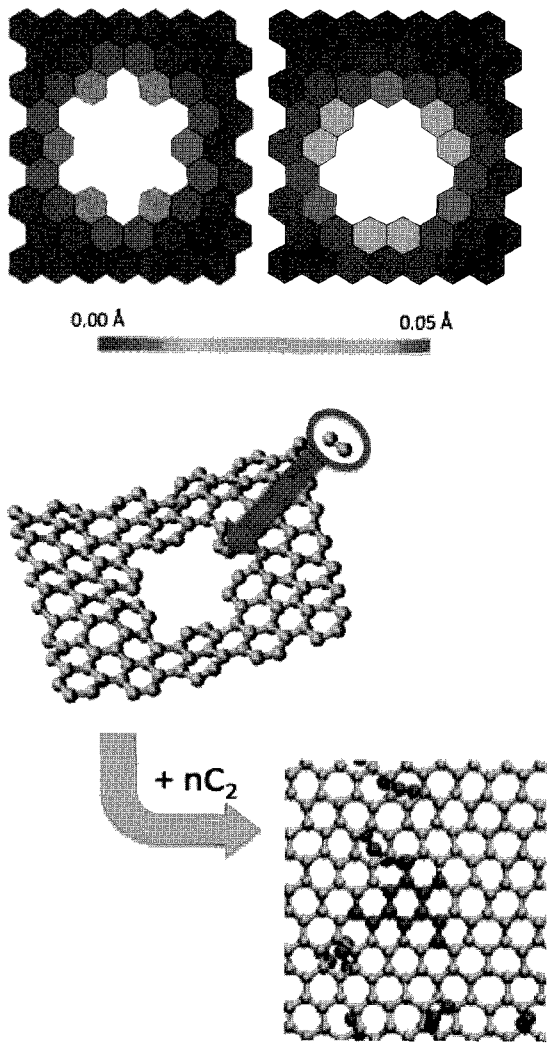

Figure 1. (a) Ring Bond Dispersion (RBD) plots of armchair (left side) and zigzag (right side) hole. RBD is defined according to ref. [1] Smaller RBD value indicates that the bond lengths in the hexagon have more uniform bond lengths (as in bulk). Edge hexagons are more distorted. (b) Armchair hole in graphene was gradually healed and repaired perfectly. Carbon atoms of vapor C_2 molecules are shown by red atoms. in bottom figure.

Hole repair in graphene due to exposure to C_2 molecules was investigated by using high-T QM/MD (quantum chemical molecular dynamics) simulations. We designed two holes with dominant armchair and zigzag edges, and performed ten trajectories respectively. Because hexagons at the edge of the holes were more distorted and reactive than hexagons in the bulk (see Figure 1 (a)), they were less stable and C-C bonds located on the edge of holes were easy to break. Some floating C_2 molecules, which approached carbon atoms on the edge, could combine with them, while others interacted with carbons far from rim part and left after some time. Due to the C2 molecules sticking at he hole edges, the holes gradually became smaller. Finally, pentagon- and heptagon-containing networks appeared in the holes, and in some trajectories, these defects were healed perfectly. In these situations, all carbons were bonded in a hexagonal lattice (see Figure 1 (b)), but in other trajectories, 5, 7 or 8-membered rings persisted during the simulation time. The simulations did not differ much between armchair and zigzag holes.

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1P-42

Field Emitter Using Upright Carbon Nanotwists with sputtered Pt coat

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In our previous study, carbon nanotwists (CNTw) on substrate were made to stand up by filament discharge (FD) treatment [1]. CNTw is one of fibrilliform carbon nanomaterials with a helical shape and has been shown as a good field emission material. The diameter of CNTw is larger than that of carbon nanotube (CNT). Therefore, CNTw is supposed to have less damage than CNT does by ion bombardment. In this study, CNTw emitter was coated with Pt by ion sputtering. Fabrication method of the CNTw emitter was the same as in Ref. 2. The thickness of Pt-coated film was 10 nm. Figure 1 shows SEM micrograph of Pt-coated CNTw emitter. Its upright condition was almost the same as non-coated emitter. Figure 2 shows *J-E* characteristics of the non- and Pt-coated CNTw emitters. Turn-on field of Pt-coated was a little higher than that of non-coated. Current density at 9 V/μm of Pt-coated was as low as one-third of that for non-coated. In the analysis of Fowler-Nordheim (F-N) plot of $\ln(I/V^2)$ against $(1/V)$, the slope of non-coated CNTw emitter was -10708.6 and that of Pt-coated was -3162.9, respectively, as shown in the inset of Fig. 2. The slope is thought to depend on the work function of CNTw emitter. The F-N plot shows that the work function was decreased by Pt-coating.

This work has been partly supported by the Outstanding Research Project of the Venture Business Laboratory from Toyohashi University of Technology (TUT); Global COE Program "Frontiers of Intelligent Sensing" from the Ministry of Education, Culture, Sports, Science and Technology (MEXT); Core University Programs (JSPS-CAS program in the field of "Plasma and Nuclear Fusion") from the Japan Society for the Promotion of Science (JSPS), Grant-in-Aid for Scientific Research from the MEXT, Toukai Foundation for Technology, Research Foundation for Materials Science, and Chubu Science and Technology Center.

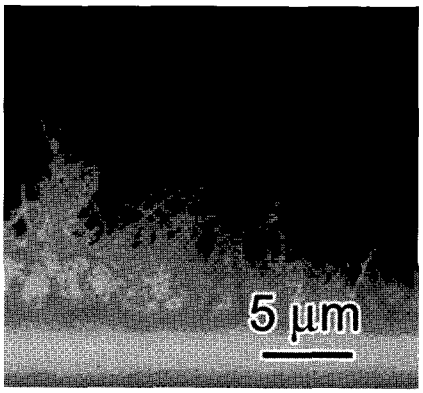

Fig. 1 SEM micrograph of Pt-coated CNTw emitter.

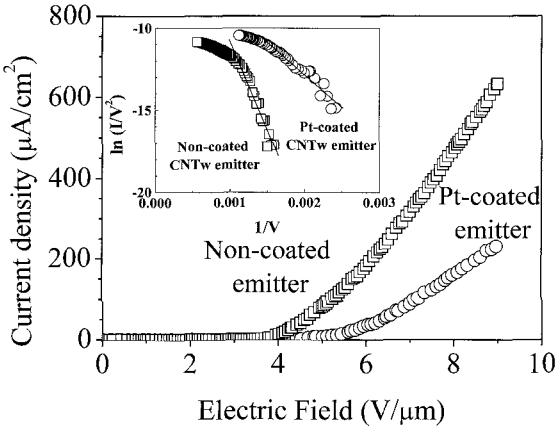

Fig. 2 *J-E* characteristics of CNTw emitters.

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1P-43

Evaluation of Dispersant Effectiveness of Lipid-PEG For Nano-Carbons Using Carbon Nanohorns

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Nanometer-sized graphene materials (NGMs) have presented versatile applications in various areas including nanobiology and medicine. Amphiphilic lipid-poly(ethylene glycol) (LPEG) materials are widely used as noncovalent functionalization agents for dispersing NGMs in aqueous solutions for biological studies. However, not much is known about the interaction between LPEG and NGMs, and how to select the optimum LPEGs is the critical issue. Taking advantage of the large available quantity of single-walled carbon nanohrons (SWNHs), a type of NGMs, we evaluated dispersant effectiveness of various LPEGs for NGMs by using SWNHs.

We compared the dispersion abilities of eight LPEGs: Two types (Ceramide-PEG and DSPE-PEG), which are frequently used for NGMs, were purchased, and the other six types were newly synthesized in this study. Each LPEG was composed of three domains: alkyl chains, PEG chains, and a liker group. LPEGs having the following structure achieve well dispersed SWNHs in water and PBS. The long alkyl and PEG chains were, indeed, favorable. The non-ionic linker group was more favorable than the ionic ones as we reported previously [1]. Interestingly, the single alkyl chains were as effective as double alkyl chains in terms of adsorption onto the SWNH surface. The surface coverage of excellent LPEG dispersants on SWNHs was high, and they were almost non-detached even when proteins were co-dispersed in PBS. Here, the quantities of attached or detached PEGs were determined by subtracting the PEG quantities in the filtrate from the starting PEG quantities. The PEG quantity in the filtrate was quantified by the Dragendorff method. Macrophage cellular uptakes of SWNHs coated with these excellent LPEG dispersants was extremely low, which is an advantage for drug delivery applications of SWNHs in order to avoid rapid capture by macrophages and to be excreted *in vivo*.

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1P-44

Long-term Structural Observation of Charged Particles by Ion Trap Mobility System

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Ion mobility measurements have been utilized to analyze structures of nanocarbon materials[1]. This measurements provide lots of advantages to clarify the new structures but have not been applied to observe "long-term changes". Here we present the observation of structural changes of charged particles for two hours by a new ion trap mobility system.

The charged particles were produced from NaCl water solution with concentration from 5 to 27 wt. % (saturated solution) by an atomizer where 10 kV was applied. The particles were trapped by an RF electric field (600 Vpp, 20 kHz) and were analyzed by mobility measurements with up-down movements induced by LF filed (9 Vpp, 2.5 Hz). The trapped particles were irradiated by a laser and were monitored by a digital camera.

Figure 1 shows traces of the charged particles produced from 27 % NaCl (saturated) solution moving in the trap. The amplitude gradually increased as the time elapsed from 0 to 12 min., and then decreased. The data show that the particle has the most compact structure at 12 min. since the amplitude is inversely proportional to the diameter. Figure 2 shows the dependence of the time profiles on the concentration, where each amplitude is normalized by the initial one. The overall trend in the lower concentration (5~15 %) is that the amplitudes decrease with time showing the size growth of particles by humidity absorption from air[2]. In the higher concentration conditions (20 and 27 %), on the other hand, the amplitudes increase in the early stage (0 to around 10 min.). The dependence on the concentration could be explained by crystallization of NaCl on the surface of the particle and melting. This long-term monitoring could be applied to the structural changes of nanomaterials.

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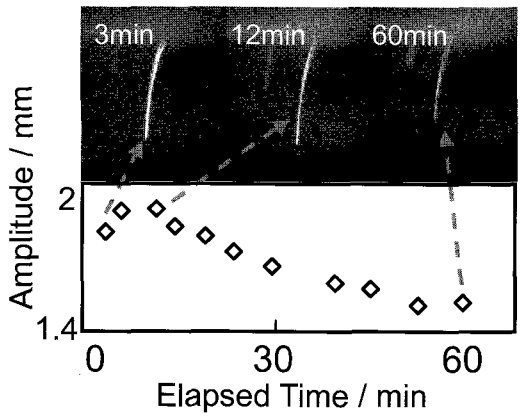

Fig.1 Traces of charged particles

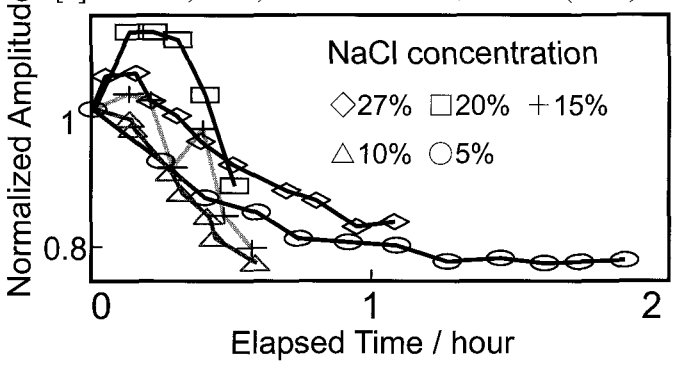

Fig.2 Concentration dependence of amplitudes

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1P-45

Preparation of supercapacitor using RuO_x-supported-Arc-Black and its specific capacitance

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We have studied the preparation of supercapacitor using ruthenium oxide (RuO_x) supported on Arc-Black (AcB) that is made by an arc discharge in N_2 gas [1]. In this presentation, we report the correlation between the RuO_x amount on AcB and its specific capacitance.

RuO_x were synthesized by dropping a NH_4HCO_3 aqueous solution into $RuCl_3$ aqueous solution and were supported on AcB with ultrasonication. After filtration and drying, RuO_x-supported-AcB (RuO_x/AcB) electrodes were prepared. The amounts of RuO_x were in the range of 20-47 wt.% by the measurement of Thermo Gravimetry Analyzer (TGA).

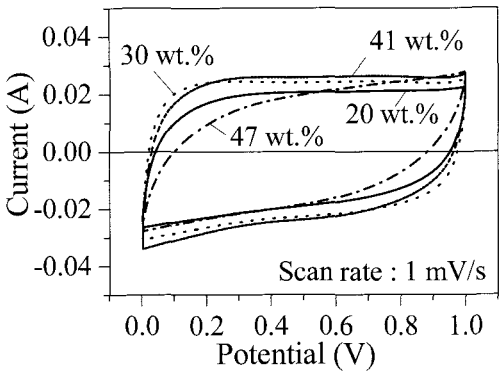

Fig.1. Cyclic voltammograms of RuO_x/AcB electrodes at different RuO_x amounts.

Fig. 1 shows cyclic voltammograms of the RuO_x/AcB supercapacitor electrodes. The specific capacitance increased with the RuO_x amount up to 41 wt.%. The maximum specific capacitance was obtained to be 224 F/g at the RuO_x amount of 41 wt.%. However, the electrode at the RuO_x amount of 47 wt.% showed a poor capacitance of 157 F/g.

This work has been partly supported by the Outstanding Research Project of the Venture Business Laboratory from Toyohashi University of Technology (TUT); Global COE Program "Frontiers of Intelligent Sensing" from the Ministry of Education, Culture, Sports, Science and Technology (MEXT); Core University Programs (JSPS-CAS program in the field of "Plasma and Nuclear Fusion") from the Japan Society for the Promotion of Science (JSPS), Grant-in-Aid for Scientific Research from the MEXT, Toukai Foundation for Technology, Research Foundation for Materials Science, and Chubu Science and Technology Center.

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1P-46

Electron-accepting properties of fullerenes at the liquid/liquid interface

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Electrochemical studies of fullerenes have much attention because of its specific behavior. There are several reports concerning on the calculation of molecular orbital and also the electrochemical detection of C_{60} and C_{70} by cyclic voltammetry method (CV). These researches demonstrated that C_{60} could be able to accept at least six electrons to form C_{60}^{6-}. Additionally, we reported that poly sulfide ion in aqueous solution was successfully collected by stirring treatment with fullerene/toluene solution. In this reaction, it was considered that C_{60} acted as electron accepter at the liquid/liquid interface [1]. In this study, the electron-accepting properties of fullerene at the interface were analyzed by Voltammetry for the Charge Transfer at the Interface of Two Immiscible Electrolyte Solution (VCTIES). This technique is powerful method to understanding the dynamic feature of the charge transfer, since it can measure simultaneously transfer potential and also the amount of transferred charges [2, 3].

At first, CV with K_2S and C_{60} were analyzed to calculate potential of electron transfer at water/o-dichlorobenzene (DCB) interface. After that, ion transfer was analyzed by VCTIES method. From CV analysis, it was showed that standard redox potential of S^{2-} ion was -0.45V vs. SSE and 1st redox potential of C_{60} was -1.01V vs. TPenAE. From these results, it can be considered that standard potential of electron transfer of S^{2-} ion and C_{60} was -0.86V vs. TPhE [4]. On the other hand, clearly peak shifts mean ion transfer were not observed in VCTIES. Then, it can be considered that electron transfer is more predominant than ion transfer in this reaction.

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1P-47

Facile and efficient synthesis of high-crystallinity double-wall carbon nanotubes

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Carbon nanotubes (CNTs) have attracted great interest in many industrial applications including electronics because of their unique and novel electronic properties. Realizing their full potential in actual electronic device applications requires the CNT samples with high crystallization and desired conducting properties. For this purpose, double-wall CNTs (DWCNTs) are attractive since they have metallic or semiconducting properties like single-wall CNTs as well as robust mechanical and chemical stability like multi-wall CNTs. Although there are many reports on the DWCNT synthesis[1-3], high-yield synthesis of high-quality DWCNTs is still an unsolved challenge for actual industrial applications.

In this study, we have investigated effects of catalysts and reaction conditions on the DWCNT synthesis by using alcohol chemical vapor deposition (CVD) with Fe/MgO catalysts. Ethanol was used as carbon source because of its safety and user-friendliness. In an improved condition, DWCNTs with a purity of 60% were synthesized as evaluated by transmission electron microscope (TEM) observations (Fig. 1a). For a purified sample, average outer and inner diameters were 1.4 and 0.7 nm, respectively (Fig. 1b), which is consistent with the optical absorption spectrum (Fig. 1c). Raman spectra of purified sample show high G/D ratio of around 130, suggesting the successful synthesis of high quality DWCNTs (Fig. 1d).

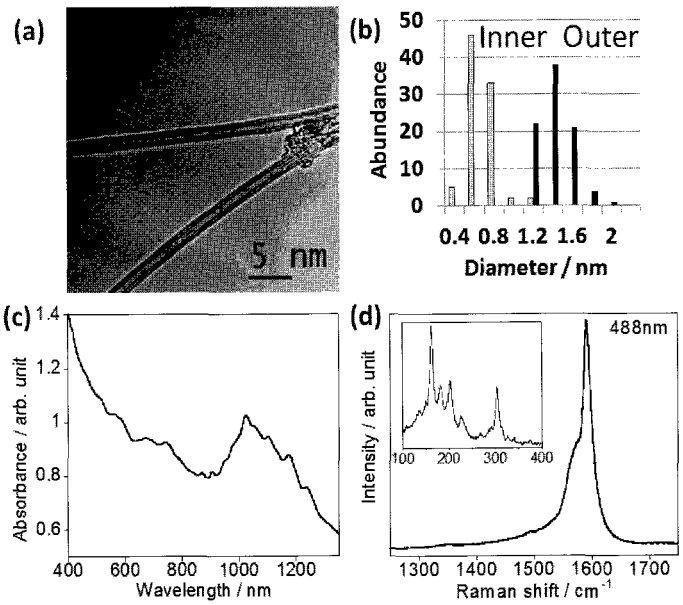

Fig. 1. (a) TEM image, (b) diameter distribution, (c) optical absorption and (d) Raman spectra of the purified sample.

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1P-48

Sorting of double-wall carbon nanotubes by electronic structure

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Double-wall carbon nanotubes (DWCNTs) have attracted much attention for thin film electronics because of their superior conducting properties, high thermal and chemical stabilities. To put them into practical use, it is necessary to separate DWCNTs with single electronic type. Although there has been a report on the sorting of DWCNTs by electronic structure so far [2], it is still unclear whether or not the separation has been mainly conducted for impurity single-wall carbon nanotubes (SWCNT) or DWCNTs. The presence of impurity SWCNTs is a critical issue because the dispersion process with ultrasonication induces the inner/outer shell separation that generates SWCNTs with wide-range diameters [3]. To solve this problem, the careful characterization of DWCNT purity and the precise separation by layer number are required.

In this study, we demonstrate the sorting of highly-pure DWCNTs by electronic type using multistep density-gradient ultracentrifugation (DGU). The DWCNT-rich samples supplied from Toray Industries Inc. were used as a starting material. This material was dispersed with sonication in water containing sodium deoxycholate (DOC). Firstly, isolated DWCNTs were enriched by using non-linear DGU as reported by Ghosh et al.[4] (Fig.1a). The isolated DWCNTs were then separated again by using DGU with mixed surfactants of sodium cholate (SC) and sodium dodecyl sulfate (SDS) as shown in Fig.1b.

High-resolution transmission electron microscope observations reveal that the fractions indicated by arrows in Fig.1a and b contain DWCNTs with a purity of more than 80%. Optical absorption spectra show that the M_{11} absorption intensity of metallic outer shells (600~800 nm) decreases after the second DGU process (Fig.1c). This result indicates that DWCNTs can be sorted by electronic type of the outer shells. In the presentation, the optical properties of separated DWCNTs will also be discussed.

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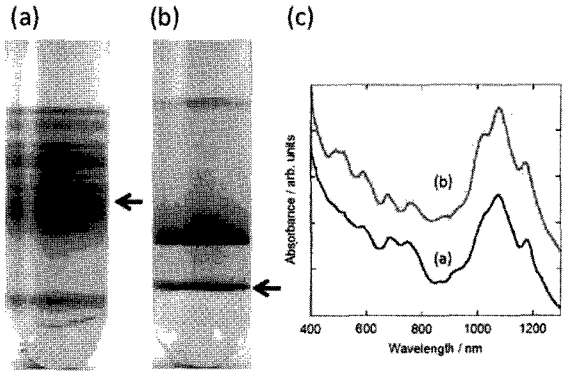

Fig.1 Photographs of centrifugal tubes after (a) the first and (b) the second DGU processes. (c) Optical absorption spectra of the fractions indicated by the arrows.

1P-49

Electronic Spectra of Polyyne-Iodine Complexes in Hexane

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Polyynes, $H(C{\equiv}C)_nH$ ($n{\geq}2$), are sp-hybridized carbon chain molecules with two hydrogen atoms at both ends. These molecules have cylindrically symmetric π-electron systems. These molecules exhibit absorption bands for the allowed transition in the UV and those for a forbidden transition in the near UV. The former is attributable to the electric-dipole-allowed transition from the ground state, $^1\Sigma_g^+$, to the excited state, $^1\Sigma_u^+$, while the latter is attributable to the symmetry-forbidden transition from the ground state, $^1\Sigma_g^+$, to the excited state, $^1\Delta_u$ [1]. We have reported that the allowed transition disappears and the forbidden transition increases in intensity upon addition of iodine molecules into the solution of polyyne molecules [2].

Figure 1 shows electronic spectra for polyyne-iodine complexes (solid line) and those for polyynes (dotted line) in hexane. The forbidden transitions intensified in the spectra for polyyne-iodine complexes shifts to longer wavelength as the carbon chain become longer. This observation suggests that the product formed from polyyne and iodine molecules retains the polyynic skeleton as intact. Figure 2 shows the intensity ratio of the band of the forbidden transition to a new band in the spectra of polyyne-iodine complexes. The figure shows that the ratio decreases as the number of carbon atoms increases.

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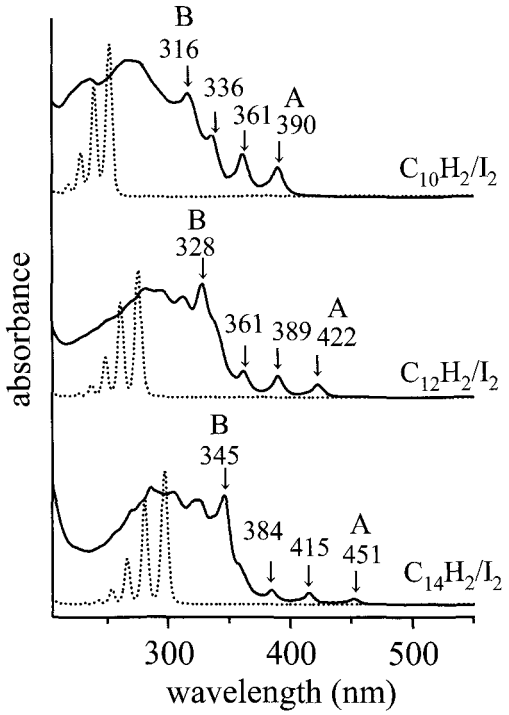

Figure 1. Electronic spectra of the polyyne-iodine complexes (solid line) and polyynes (dotted line).

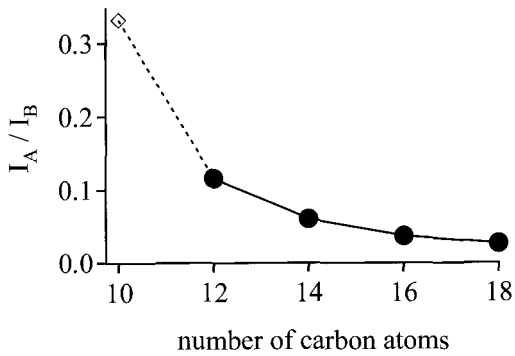

Figure 2. The intensity ratio of an intensified forbidden transition/new band.

1P-50

Significance of zigzag edges in electron transport properties of graphene sheets with periodic nanoholes

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For electronic applications of graphene, it is necessary to control its band gap because graphene itself is a semi-metal. A graphene nanomesh (GNM), which can be considered to be a highly interconnected network of graphene nanoribbons (GNRs), has recently been fabricated and shown to have a band gap [1, 2]. We have reported [3] the electronic structures of graphene having 2-dimensional (2D) periodic nanoholes with high-symmetry atomic configurations. In this article, we expand our research into 1-dimensional (1D) periodic nanoholes and irregularly shaped holes as more realistic models. We show their electron transport properties and discuss the significance of zigzag edges in determining the conduction gaps E_g.

Figure 1 shows the geometries and the current densities for graphene having 1D periodic nanoholes. We use the non-equilibrium Green's function method based on first principles. The semi-infinite graphene leads are speculated to result in a tiny E_g, removing the quantum confinement in the transport direction. Geometry (a) shows E_g of less than 0.1 eV as expected. Geometry (b), however, shows a quite wide E_g of about 0.5 eV and has two sequential zigzag edges. We have found even two sequential zigzags produce many edge states around the Fermi level E_F for the infinite geometry. These edge states do not contribute to the current, forming a wide E_g. Next, we show the correlation between E_g and the neck width w for graphene having irregularly shaped holes with large 2D periodicities in Fig. 2. The tight-binding approximation method is used to obtain the energy band structures. The E_g is defined as the energy gap between the bands with a certain dispersion based on the results for the 1D periodic nanoholes. The value of E_g is generally inversely proportional to w as well as experimentally [2]. The longer sequence of zigzag edges produces several flat bands around E_F. This results in a significantly wide conduction gap. On the other hand, the shorter sequence of zigzag edges gives dispersive bands near E_F, not completely localized to the edges. The consequent wide distribution of E_g may correspond to multiplateaus in the *I-V* curves observed experimentally [2]. We can conclude that zigzag edges play a critical role in determining the conduction gaps for graphene with both 1D and 2D periodic nanoholes. This suggests that control of the edge structures of the holes is significant for GNM device applications.

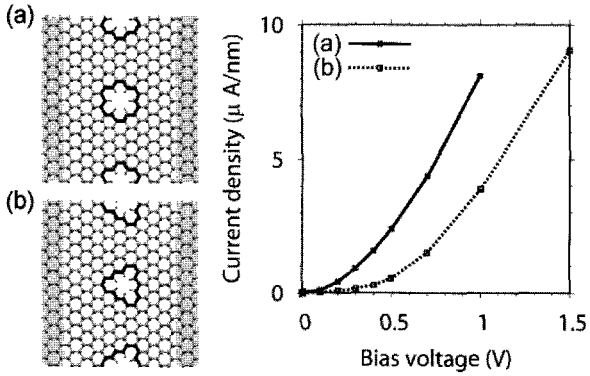

Fig. 1: Geometries and transport properties of graphene sheets with 1D periodic nanoholes (a) without and (b) with zigzag edges. The left and right sides of the models consist of semi-infinite graphene leads. All edge carbon atoms of the holes are terminated by hydrogen atoms.

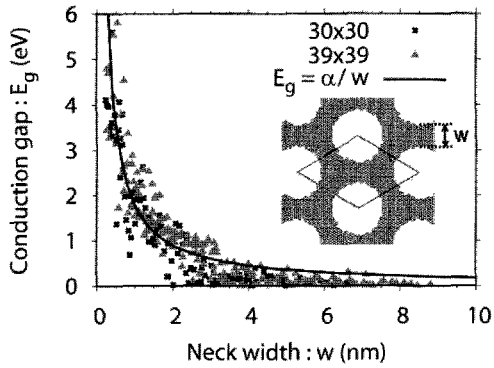

Fig. 2: Neck width (w) dependency of the conduction gap (E_g) for graphene with irregularly shaped holes. The solid curve is the fit of the data using $E_g = \alpha/w$ with α = 1.79 nm eV (cf. Experimental α = 0.95 nm eV [2]). The inset is an example geometry.

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1P-51

Spin-Related Novel Optical Phenomena in Single-Walled Carbon Nanotubes

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The interplay between conduction electrons and localized spins is one of fundamental and important problems in modern condensed matter physics giving us unexpected phenomena: It is well known that they induce resistivity minimum phenomena, known as the Kondo effect. Besides the conducting electrons, the fundamental question arises whether the interplay between photo-excited electrons and localized spins leads novel phenomena.

In this regard, semiconducting single-walled carbon nanotubes (CNTs) provide us an interesting research field of spin-related optical phenomena. Because of their quasi-one-dimensional structure, photo-excited electrons and holes in CNTs are strongly correlated and form a bound electron-hole pair, called an exciton, which has large binding energy, leading to remarkable stability up to room temperatures. Therefore, when there are localized spins in CNTs, optical phenomena are expected to exhibit wide variety.

In this paper, we demonstrate two interesting examples of novel optical properties of CNTs that are induced by localized spins based on the theoretical investigations:

(1) Recent experiments have shown the evidence in which the excitons correlate with localized spin induced by the defects in CNTs those are essential in the bipartite lattice of CNTs. However, unfortunately, the fundamental theory for this problem have not been addressed yet. We thus propose a theory that expresses the interaction between excitons and localized spins in CNT system[1]. Our theory solves one of the most important issue regarding the optically activated triplet dark excitons and first successfully provides a unified explanation for all the experimental conditions [2,3,4].

(2) It has bee pointed out that ultrathin magnetic nanowires encapsulated in carbon nanotubes are potential candidates for constituent elements in the next-generation spintronics and electronics devices with nanometer scale[5]. For the device application, the evaluation methods for detecting the magnetic state of the nano-wires are essential and important. For such methods, we theoretically propose a non-contacted optical probing method based on the optical response from such magnetic nanomaterials encapsulated in carbon nanotubes. Due to the exchange interaction between excitons and polarized spins in ferromagnets, triplet excitons acquire a finite oscillator strength and can thus be excited by light[6]. This mechanism certainly detects magnetic ordering of nano-materials encapsulated in carbon nanotubes.

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1P-52

Synthesis and characterization of AgI nanowires encapsulated in carbon nanotubes

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α-phase silver iodide(α-AgI) has been well-known as a solid state ionic conductor due to its superionic conductivity and is one of the promising candidates for solid-state electrolytes for various electrochemical devices. However, below 420 K, α-AgI undergoes a phase transition into the poorly conducting β- and γ-polymorphs, thereby limiting their applications. However, recently, we have found that AgI nanowires with a diameter of 10 nm can retain α-phase even at 313 K where size and morphology of AgI presumably plays a great role in this α-AgI stabilization. [1] To investigate the effect further, we have focused on low dimensional nanostructure of AgI, namely, AgI nanowire with a diameter of 5 - 10 nm. For this purpose, one-dimensional (1D) nanospace of carbon nanotubes (CNTs) has been employed. CNTs have unique 1D nanospace ranging in diameter from 0.4 to 50 nm, which can stabilize otherwise unstable nanomaterials. Here, we present a high yield synthesis and structural characterization of AgI nanowires that are formed in nanospace of thin-layer multi-wall carbon nanotubes (MWCNTs)

We have synthesized AgI@MWCNTs by the sublimation method already reported. [2] First, MWCNTs were oxidized in air at 823 K for 20 min to open end-caps. The cap-opened MWCNTs were then vacuum sealed together with AgI in a quartz tube under 10^{-4} Pa, which was followed by thermal heating at 823 K for 2 days.

Figure 1 shows high resolution transmission electron microscope (HR-TEM) images of AgI@MWCNTs. As clearly shown in Figure 1, dark contrasts can be seen in MWCNTs, and an estimated filling ratio of AgI is as high as ca.70 ~ 80 %.

In the presentation, we will discuss detailed characterization of structure and properties based on electron beam diffraction and HR-TEM.

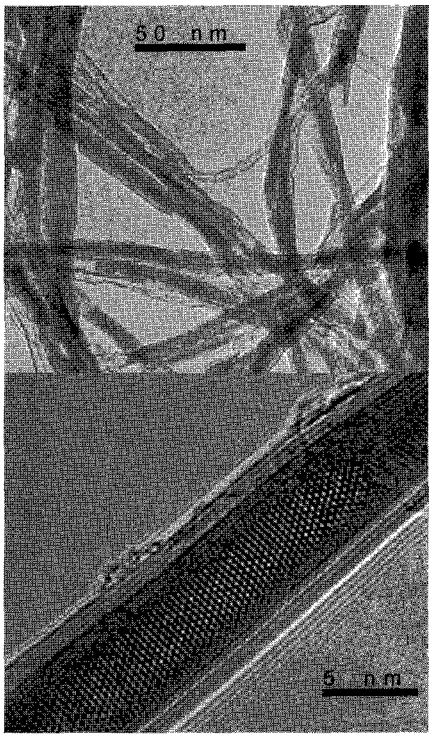

Figure 1. HR-TEM images of AgI@MWCNTs

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1P-53

Control of graphene etching by atomic structure of solid surfaces

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Graphene is one of the most notable materials in the recent progress of nanomaterial science and technology. In its device applications, control of the size, morphology, edge state, and shape is required because the electronic properties of graphene depend on those parameters. Crystallographic etching using catalytic metal nanoparticles can be applied to self-patterning of graphene, where carbon atoms of graphene are removed through a reaction between graphene and hydrogen catalyzed by metal nanoparticles during annealing in a hydrogen. Previously, we reported that etching of few layer graphene was guided by morphology of the sapphire substrates[1]. In this paper, we propose a new etching technique of single layer graphene that is controlled by atomic structures of well-defined solid surfaces.

Graphene flakes were deposited on sapphire (r-face) substrates by mechanical exfoliation of graphite[2]. A solution of $Fe(NO_3)_3 \cdot 9H_2O$ in isopropyl alcohol was spin-coated to form metal catalysts. The samples were then annealed at 900°C in a hydrogen - argon mixed gas for 10 min. Surface morphology was observed by AFM and layer number of the graphene flake was estimated by Raman spectroscopy.

Graphene attached on a sapphire r-surface was etched in a particular direction, resulting in the formation of graphene nanoribbons. We investigated the relationship between the atomic arrangement of sapphire surfaces and the graphene etching. We found that graphene was etched in a [1-10-1] direction, and morphology of the sapphire surface did not affect the graphene etching. This indicates that atomic structure of the sapphire surface can be used to control graphene etching. When sapphire c-surface is used for the substrate of graphene, the graphene etching proceeds in random directions. This is the first report on control of graphene etching using atomic structure of the substrate surface.

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1P-54

Structures and Electronic Properties of Scandium Carbide Endohedral Metallofullerenes

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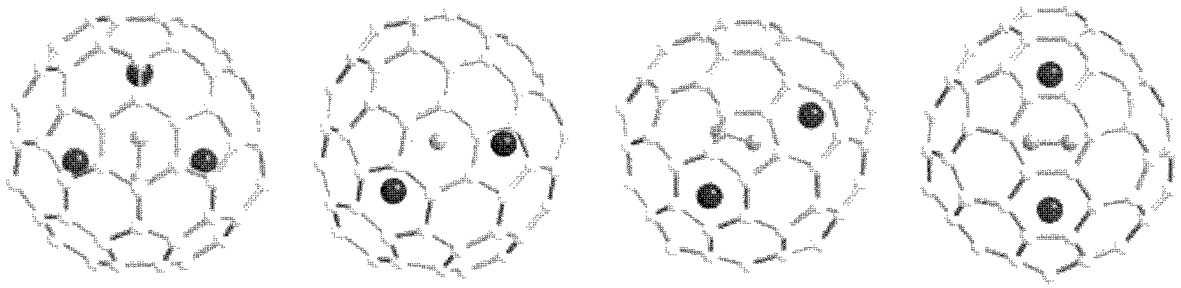
Endohedral metallofullerenes are known to have several unique properties. To apply these to new materials, it is important to clarify the endohedral structures and electronic properties. Scandium endohedral metallofullerenes have been extensively investigated both theoretically and experimentally. Among these, scandium carbide endohedral metallofullerenes are the most interesting because of the encapsulation of the C_2 unit together with several metal atoms, which is very important to the chemistry of scandium carbide endohedral metallofullerenes. However, so far there is no systematic theoretical investigation of scandium carbide endohedral metallofullerenes. We herein report density functional calculations of the endohedral structures, electronic properties, and bond information of C_2 unit of $Sc_3C_2@C_{80}$, $Sc_2C_2@C_{82}$, $Sc_2C_2@C_{80}$ and $Sc_2C_2@C_{84}$, respectively.



$Sc_3C_2@C_{80}$ $Sc_2C_2@C_{82}$ $Sc_2C_2@C_{80}$ $Sc_2C_2@C_{84}$

References

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2P-1

Synthesis and Applications of Cabon Nanotube Sponge Macrostructures

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Carbon nanotubes (CNTs) are novel nanostructures with excellent properties and promising applications in various fields. Preparation of macroscopic structures based on assembled CNTs represents an important step towards practical applications. The engineered porous structures based on CNTs will offer a combined feature of high porosity and high performance. Here, an original macroscopic structure based on three dimensional, highly porous CNT network (CNT sponge) was synthesized in a direct and controllable way. The properties of the CNT sponges were studied for paving the way to develop high performance materials and explore new applications, including adsorption of organic solvents and spilled oil, mechanical energy absorption, nanocomposites, etc.

CNT sponges are directly synthesized by chemical vapor deposition (CVD), using dichlorobenzene and ferrocene as carbon source and catalyst precursor, respectively. The CNT sponges consist of randomly overlapped multi-walled CNTs (MWNTs), which self-assembled into a porous, highly interconnected, three-dimensional framework. On the microscale, each CNT can be considered as a high aspect-ratio skeleton to construct the porous structure. Freestanding CNT sponges have uniform structure, high flexibility and stability, with apparent densities of 5-25 mg/cm^3, porosity of larger than 99 %. [1-3]

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2P-2

Cell proliferation on Carbon Nanotubes Coated Dishes in Different Cell Lines

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In recent investigation, carbon nanotubes (CNTs) have been utilized as scaffolds for cell cultures. Despite many researchers reported cell behavior on CNTs scaffolds, the effects of CNT scaffolds on cell proliferation are highly variety (diffuse or not clear). Therefore, systematic investigations using common conditions by one researcher are required for establishment of general trends in cell proliferation on CNTs. In the present study, we prepared culture dishes with homogeneous thin or thick films of non-modified CNTs and examined the effect of different cell lines on cell proliferation in these culture dishes.

We demonstrated that the ratio of cell proliferation was strongly affected by kind of cells and substrates. Interestingly, single-walled carbon nanotubes (SWCNT) thin films were found to be the most effective substrate for the proliferation of half of the cells used in this study (ex. Saos-2, HeLa, HEK293, NIH-3T3, and MDCK). Further, thin SWCNT films indicate high transparency and electro-conductivity. Therefore, thin SWCNT films may be used as a hybrid-biomaterial such as a biosensor or an electro-stimulator for cell controls.

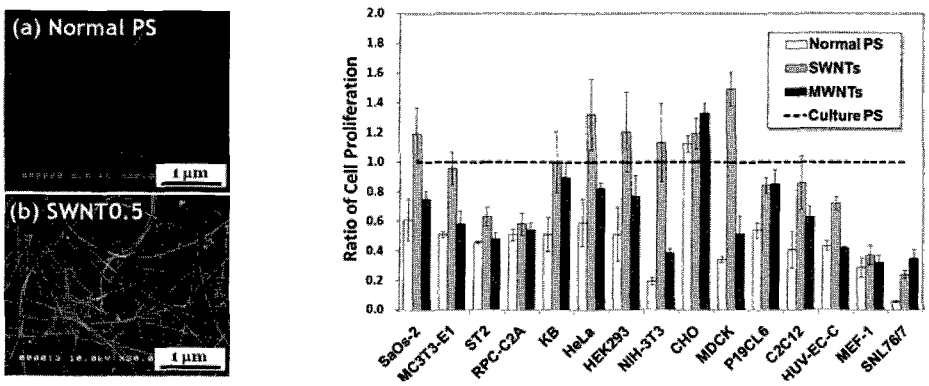

Fig. SEM images of CNT-coated dishes and cell proliferation of different cell lines on CNT-coated dishes.

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2P-3

Synthesis and characterization of highly conducting Carbon nanotube-Copper composite

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The ability of water-assisted CVD[1] to produce aligned close-packed single wall carbon nanotubes(CNT) with superior thermal and mechanical properties make them ideal materials for use in microelectronics[2]. However, their poor electrical conductivity has been a major obstacle in realizing this. To overcome this, we report the synthesis of conducting CNT-copper composite (conductivity $\sigma=10^5 Scm^{-1}$) through a novel organic phase electrodeposition. The composite has been thoroughly characterized using a number of spectroscopic and microscopic techniques. SEM-EDAX reveals a uniform distribution of copper in the CNT matrix. Powder X-ray diffraction and Micro-Raman analysis substantiate the observation that the high conductivity of the composite is due to a uniformly intertwined network of pure Copper and CNT. The development of this composite material augurs well for applications in microelectronics.

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2P-4

Formation of *trans*-polyacetylene from CoMoCAT carbon nanotubes by laser irradiation

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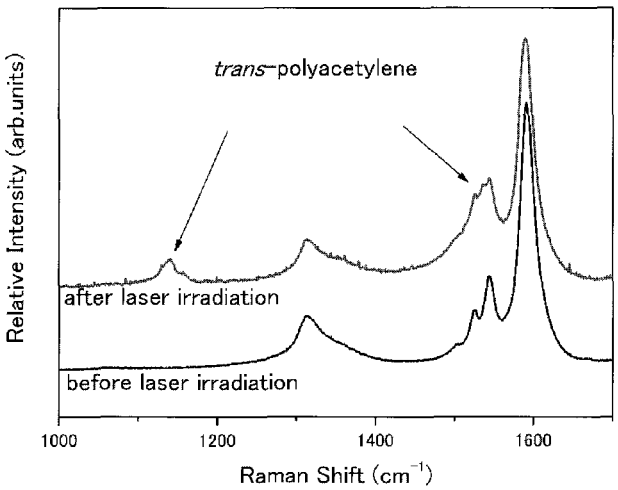
Laser irradiation has been extensively used for the synthesis of single walled carbon nanotubes (SWCNTs). It can be also used for the introduction of defects in SWCNTs [1]. Thus, the laser irradiation is interest for the tailoring of structures and properties of SWCNTs. In this paper, we report the formation of trans-polyacetylene from CoMoCAT SWCNTs by laser irradiation.

As-received CoMoCAT SWCNTs were used in this work. A suspension of nanotubes in ethanol was prepared by ultrasonication. The suspension was dropped on a clean quartz substrate and allowed to be air-dried at room temperature. The samples prepared in this procedure were used for laser irradiation experiments. The samples, which were exposed to air for less than one hour before laser irradiation, are called "short air-exposure" ones. Some of samples were kept in air at room temperature for more than six months before laser irradiation. They are called "long air-exposure" ones. The laser irradiation was carried out using a 532 nm from YAG laser. The power on the sample was 17.8 mW/μm^2.

Fig. 1 shows Raman spectra of "long-air-exposure" sample before and after laser irradiation. As seen in Fig.1, Raman spectrum of the irradiated "long air-exposure" sample exhibit the appearance of new peaks at 1138 cm^{-1} and 1514 cm^{-1}, compared with non-irradiated one [2]. These peaks are quite similar to main ones of trans-polyacetylene [3]. This means that the trans-polyacetylene can be formed in the irradiated sample.



On the other hands, no significant change in Raman spectrum of "short air-exposure" sample was observed even after irradiation.

In this presentation, the formation condition and mechanism of trans-polyacetylene from CoMoCAT SWCNTs are discussed in the light of the catalytic hydrogenation for the cutting of graphene and CNTs reported recently [4].

[1] D. Kang *et al.*, *Diamond Relat Mater.* **19**, 578-580 (2010)
[2] M. Hakamatsuka *et al.*, *Carbon.* (in press)
[3] H. Takeuchi *et al.*, *J. Mol. Struct.* **158**, 179-193 (1987)
[4] A. L. Elías *et al.*, *NanoLett.* **10**, 366-372 (2010)

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2P-5

Spinning multiwalled carbon nanotube fibers and sheets

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[2] *Department of Mechanical Engineering, Shizuoka University, Hamamatsu 432-8651, Japan*
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Because of high tensile strength of carbon nanotubes (CNTs) [1], the light weight and high strength composite materials using CNTs as fillers have been intensively studied.. Recently, we established growth method of ultra-long MWNT array using iron chloride [2]. Good things of the method are that millimeter scale long arrays are grown in short time and it has high drawability of MWNT web. The MWNT web is a two-dimensional MWNT network. Using the webs, we fabricated MWNT fibers and sheets. Since MWNTs are highly aligned in the drawn direction, the large scale MWNT structures fabricated from the webs are expected to show high mechanical and electrical properties in the aligned direction, and to show high anisotropic features. Such good material features would provide the advanced functions for many applications including the CNT composites.

MWNT arrays were synthesized using a conventional low pressure thermal chemical vapor deposition system. A smooth quartz substrate was placed in a horizontal quartz tube furnace with $FeCl_2$ powder, and MWNTs were grown at 830 °C. Densely grown MWNTs are vertically aligned on a quartz substrate. The height of the array reached 2.5 mm in 25 min with the growth rate over 100 μm/min. This growth rate is remarkably high. Our MWNT array samples have a high drawable feature. The MWNT webs are easily drawn using tweezers by pulling out the edge of the array, and can be drawn over 60 m just by drawing MWNTs with no twisting. During drawing, MWTs are drawn with taking neighbors one after another with the aid of van der Waals force. The spun MWNT fibers were fabricated by twisting the MWNT web. The unidirectionally aligned MWNT sheets were fabricated by stacking the MWNT webs and shrinking with ethanol. The tensile strength of a spun fiber, spun with 2 mm-long MWNTs, was 560 MPa. Electrical resistivity of the MWNT sheet with thickness of 0.8 μm was 2.5×10^{-3} Ω•cm in parallel direction, and anisotropy ratio was 7. Thermal conductivity in parallel direction was 70 W/m•K and anisotropy ratio was 8.

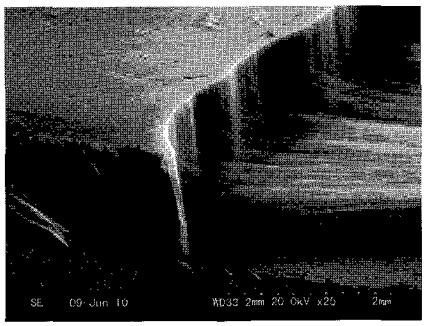

Fig. 1 Spinning MWNT web from a MWNT array

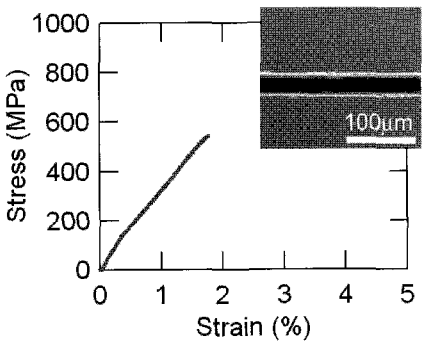

Fig. 2 Stress-strain curve of a spun MWNT fiber. Inset shows a typical spun fiber.

[1] B. G. Demczyk *et al. Mater. Sci. Eng.* A**334**, 173 (2002).
[2] Y. Inoue et al., *Appl. Phys Lett.* **92**, 213113 (2008)

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2P-6

Fabrication of Free-Standing Ultrathin Single-Walled Carbon Nanotube Films with Highly Conductivity and transparency

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It is well known that single-walled carbon nanotube (SWNT) thin films have shown great promise for foreseeable applications especially in thin film devices and solution-based deposition methods such as spray coating are the most reliable ways to fabricate thin SWNT films on different substrates. Solution-based deposition methods, including dip coating, spin coating, spray coating, solution casting, Languir-Blodgett deposition, and vacuum filtration, are the most reliable and cost-effective ways to fabricate large-area thin films of single-walled carbon nanotubes (SWNTs). However, the solution-based techniques depend on the wettability of the substrates, thus limits the substrates for such applications. Therefore, certain techniques, such as dry transfer, to relocate the films from the SWNT-deposited substrates to the target substrates of interest have been established, but the force involved in the transfer process easily destroys the original network structure of the nanotubes.

We now describe a simple approach for free-standing highly-conductive transparent SWNT films with 20-150 nm thickness by spray-coating from surfactant-dispersed aqueous solutions of improved floating-catalyst grown SWNTs.[1] After a HNO_3 treatment, dipping the SWNT films supported on glass substrates, resulted in a quick and nondestructive self-release to form free-standing ultrathin SWNT films on the water surface. The obtained films have a sufficiently high transmittance (i.e., 95 %), a very low sheet resistance (i.e., ~120 Ω/sq), and a small average surface roughness (i.e., ~3.5 nm for a displayed 10×10 μm area). Such floating SWNT films on the water surface were easily transferred to any substrates of interest, without any intense mechanical and chemical treatments, to preserve the original size and network structure of the SWNT films, which is a significant advantage over conventional indium-tin oxide (ITO) and therefore strongly promise to be "post ITO" for many applications.

References

1. Liu QF, et al. *J. Am. Chem. Soc.* **2010**, *132*, 16581.

2P-7

Development of Carbon Nanotube/Polybenzoxazole Composite Films

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Carbon nanotubes (CNTs) possess remarkable mechanical and thermal properties. The superior properties make CNTs excellent candidate to substitute for the conventional fillers in the fabrication of polymer nanocomposites **[1]**. On the other hand, polybenzoxazoles (PBO) are known to have excellent mechanical strength and thermal stability. CNT/PBO nanocomposites expect to have excellent properties applicable for practical applications such as super high mechanical strength nanofibers and high thermal conductive films. However, the poor solubility of PBO and CNTs hinders the fabrication of CNT/PBO nanocomposites.

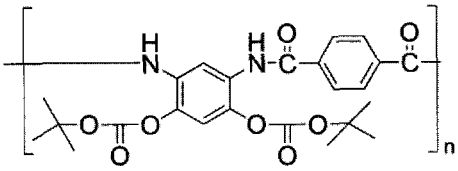

Figure 1. Chemical structure of **t-Boc prePBO**.

Recently, we successfully synthesized soluble PBO precursor (**t-Boc prePBO**: **Figure 1**) which acts as a solubilizer of single-walled carbon nanotubes (SWNTs) in dimethylacetamide (DMAc) **[2]**.

In this presentation, we report the fabrication of CNT/PBO films without using strong acid. CNT/**t-Boc prePBO** in DMAc was cast onto a glass substrate, and dried at 60 °C for 1 h, then at 80 °C for 1 h. The film was peeled off from the glass substrate by immersing the film in water and then dried at 80 °C for 4h in a vacuum. The obtained film was then heated in a stepwise fashion at 200, 250, 300 and 350 °C under vacuum for 1 h each. The FT-IR spectrum (**Figure 2 (bottom)**) of the obtained film shows the disappearance of the characteristic vibrations of the amide and t-Boc carbonyl groups at 1640 and 1740 cm^{-1}, respectively (**Figure 2 (top)**); while, the typical vibration mode for C=N in the oxazole ring appeared at 1620 cm^{-1}, manifesting the successful t-Boc decomposition and transformation to the PBO upon heating in the presence of CNTs.

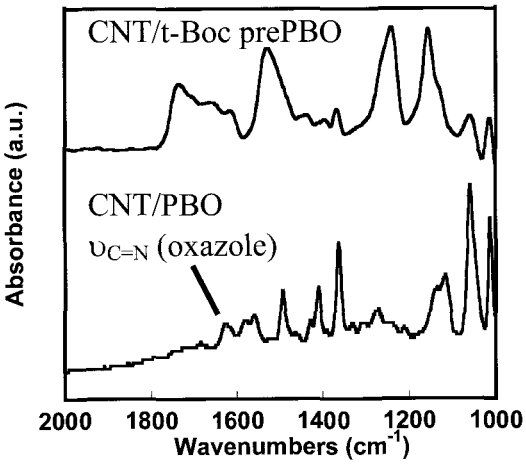

Figure 2. IR spectra of SWNT/**t-Boc prePBO** (upper) film and CNT/PBO (bottom) film.

[1] (a) T. Fujigaya, S. Haraguchi, T. Fukumaru, N. Nakashima, *Adv. Mater. 20*, 2151 (**2008**).
(b) T. Fujigaya, T. Fukumaru, N. Nakashima, *Synthetic Met. 159*, 827 (**2009**).
[2]T. Fukumaru, T. Fujigaya, N. Nakashima, *The 38th Fullerenes-Nanotubes General Symposium* 1P-35 (**2010**).

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2P-8

Preparation and evaluation of polymer gel capsules containing SWNTs

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Single-walled carbon nanotubes (SWNTs) are nanomaterials that possess unique π-rich and hydrophobic surface and effective photothermal property. We have reported these properties were quite useful to keep a drug molecules and release them upon photo irradiation [1]. For the development of a novel drug delivery system using the findings, in this report, we develop the preparation of poly (*N*-isopropylacrylamide) (PNIPAM) gel capsules containing SWNTs inside (SWNT/PNIPAM gel capsules).

SWNT/PNIPAM gel capsules were prepared by emulsion polymerization using sodium dodecyl sulfate (SDS) as surfactant. Fig. 1 shows the schematic illustration of the formation mechanism of SWNT/PNIPAM gel capsule. Fig. 2 is the merged image of the photograph and Raman mapping (mapped by G-band) of the SWNT/PNIPAM gel capsules on silicon substrate. It was revealed that all the capsules contain SWNT. The holding and releasing of the drug molecule in the capsule will be discussed.

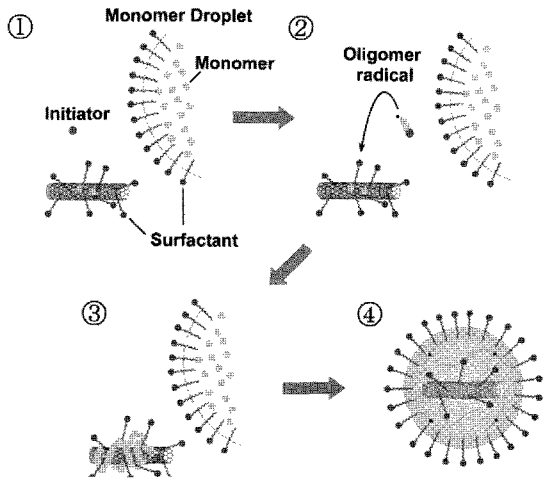

Fig.1 Schematic illustration of the formation mechanism of SWNT/PNIPAM gel capsule.

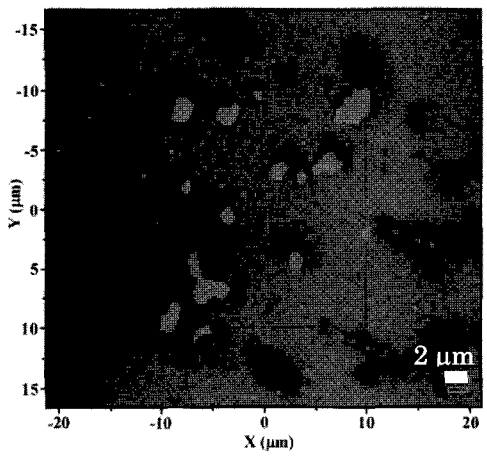

Fig.2 Merged image of the photograph and Raman mapping (mapped by G-band) of the SWNT/PNIPAM gel capsules.

[1]T. Morimoto, T. Fujigaya, and N. Nakashima, *Soft Matter*, in press.

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2P-9

Fine patterning of single-walled carbon nanotube thin-film by surface modification

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Recently, the flexible and printable electronics based on single-walled carbon nanotube (SWNT) thin-films is noteworthy. In particular, inkjet printing technology has the potential to reduce waste materials drastically, and it is expected to become the key technology for green manufacturing. We have already succeeded in the inkjet printing of high-performance SWNT thin-film transistor (TFT) [1], but further miniaturization is inevitable for application. Generally, the size limitation of inkjet microfabrication is restricted by the droplet diameter (several hundred μm). Here, we pattern the SWNT film, which is smaller than the droplet size, using the functionalization of the Si surface with self-assembled monolayers (SAMs).

Si substrate was modified with 1,1,1,3,3,3-hexamethyldisilazane (HMDS) SAMs to make a surface hydrophobic. We converted the specific area to hydrophilic surface using deep ultraviolet (wavelength of 184.9-253.7 nm) irradiation through a metal mask, which selectively removes the HMDS layer [2]. A size of patterned region was 200μm×1mm. We dropped SWNT dispersion in *N,N*-dimethylformamide (DMF) on the hydrophilic region by the inkjet technology, and dried them up at room temperature. The schematic diagram of fabrication procedures is illustrated in **Fig. 1**. The size of obtained thin-film was approximately identical to that of metal mask, indicating that the fine patterning less than droplet size is successfully achieved (**Fig. 2**). Importantly, the resulting 200μm is not the minimum size for this technology and, in principle, we can reduce the size to < 50 μm via metal mask and < 1 μm via optical lithography. This technique will also lead to an intentional liquid flow on the patterned substrate and, then, a novel method for SWNT alignment.

This study was supported by Industrial Technology Research Grant Program from New Energy and Industrial Technology Development Organization (NEDO) of Japan.

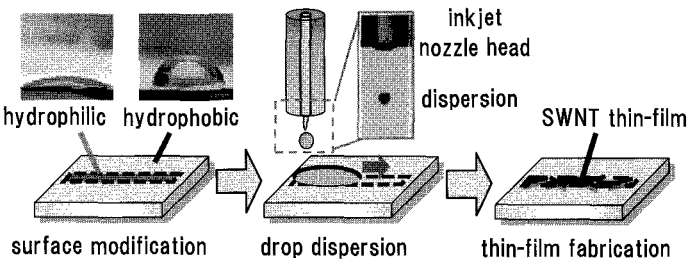

Fig.1 The schematic of fabrication process

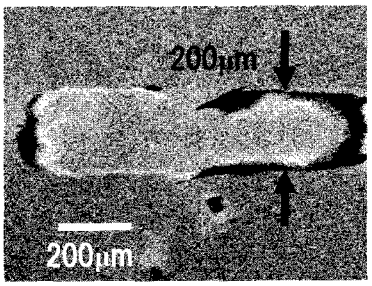

Fig.2 Scanning Electron Microscope (SEM) image of fabricated thin-film

[1] H. Okimoto et al., *Adv. Mater.*, **22**, 3981 (2010). [2] T. Minari, et al., *Appl. Phys. Lett.*, 92, 173301 (2008).

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2P-10

Further development of Aligned Carbon Nanotube Wafer based Strain Sensors

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SWNT thin films, or "CNT-wafers," have shown a new direction for multi-dimensional micro-electromechanical (MEMS) devices through their assembly and processing ability [1]. Interestingly, the ductile and brittle properties of the CNT-wafer open up opportunities beyond conventional MEMS devices.

We have developed a new class of wearable and "fully" stretchable devices (i.e. all device components are stretchable) that could deform as part of the human body as a form of ubiquitous motion monitoring. The sensing component of the gauge was a CNT-wafer, which, upon strain, did not break. Instead, the CNT-wafer fractured into numerous islands separated by gaps, and connected by suspended bundles bridging the gaps. This unique mechanism allowed for reversible strain measurement up to 280%, ~50 times more than conventional metal strain gauges, long cyclic lifetime (over 10,000 cycles), and millisecond-order response.

Here, we present detailed analysis of the signal response time and modeling of the sensor mechanism. Furthermore, we investigated the effects of environment and other directional motion on the sensor performance. As a demonstration of reducing environmental effects, we packaged the strain sensor. The packaged strain sensor exhibited strain property up to 150% with good linearity.

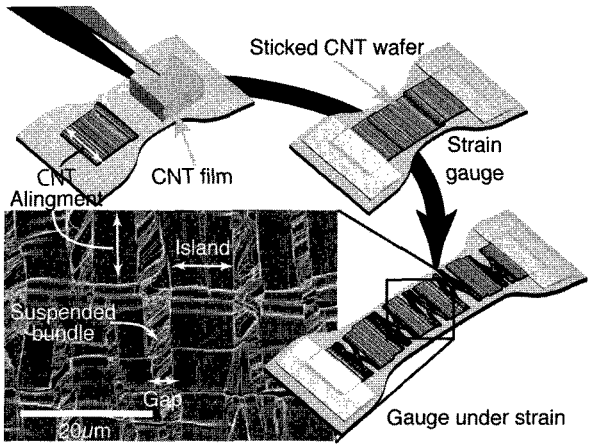

Fig. CNT strain gauge fabrication and surface structure of CNT wafer.

References:
[1] Y. Hayamizu, T. Yamada, K. Mizuno, R.B. Davis, D.N. Futaba, M. Yumura, and K. Hata, Nature Nanotech. **3**, 289 (2008)
[2] K. Hata, D.N. Futaba, K. Mizuno, T. Namai, M. Yumura, and S. Iijima, Science **306**, 1362 (2004).
[3] T. Yamada, Y. Yamamoto, Y Hayamizu, D.N. Futaaba, Y. Yomogida, A. Sekiguti, M. Yumura, and K. Hata, submitted.

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2P-11

A simulation of an atomic-scale metal/nanotube/metal junction

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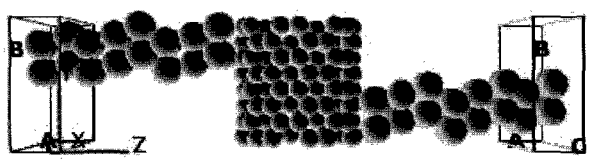
In study of nanotube electronic devices, electron transport through a nanotube-metal interface have been a central topic to be explored. At a metal contact on a wall of a tube, we have an in-commensurate interface. Local chemical reaction may happen, where the charge transfer may create or modify an effective potential barrier, which determines the electron transport properties through the junction. Usage of an accurate approximation method, like the generalized gradient approximation, allows us to evaluate these effects. However, a restriction from the boundary condition applied in some fast simulation schemes might prohibit us to perform simulations of a realistic model. We need to consider a tube without defects or edges to derive transport properties of a tube device as realization of a metal/one-dimensional electron gas (1DEG)/metal junction.

We consider an atomic scale configuration of a metal-tube-metal junction. (Fig. 1) An advantage of this configuration allows us to consider,

1) Metal/1DEG/Metal junction,
   1.1) A junction with a TL liquid with multi-components,
   1.2) A magnetic tunnel junction with CNT,
2) An analogue of double-tip STM measurement.

We tested this geometry using a simulation tool, atomistix tool kit (ATK). The electron-correlation effect may be considered after obtaining reliable material structures and single-particle description as a basis for the consideration. But, the transmission spectrum (Fig. 1: (b)) contains effects from scattering at electrode. Removal of this effect is also discussed.

(a)



(b)

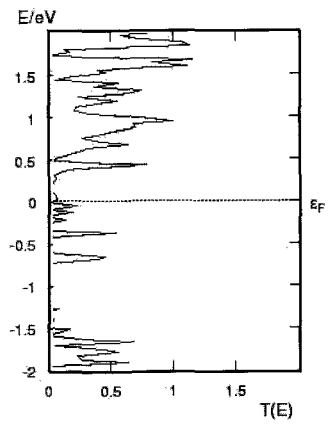


Fig. 1: (a) A Ni-wire/nanotube/Ni-wire junction. The periodic boundary condition is applied along the tube axis (Y-axis), so that the nanotube is treated as an infinite tube without edges. (b) An electron-transmission spectrum T(E) of the junction.

2P-12

Growth Termination of Millimeter-Tall Single-Walled Carbon Nanotubes

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Rapid growth of millimeter-tall single-walled carbon nanotubes (SWCNTs) in 10 min was realized by adding small amount of water to $C_2H_4/H_2/He$ during chemical vapor deposition (CVD) [1]. By using our real-time monitoring [2] coupled by combinatorial catalyst library [3], we found a window for millimeter-tall SWCNTs growing in several minutes using only C_2H_2/Ar without water addition [4]. This time, we investigated what is necessary for millimeter-tall SWCNT growth. Our method by simple gas components, combinatorial catalyst and real-time monitoring makes the discussion clearer.

A gradient thickness profile of Fe was prepared on Al-Si-O layer on a substrate and CVD was carried out on it. The sample was set in a tubular CVD reactor, heated to and kept at 700-850 °C for 5 min in 5 vol% H_2/ 50 ppmv H_2O/ Ar, and then CVD was carried out by switching the gas to 0.05-0.60 vol% C_2H_2/ 50 ppmv H_2O/ Ar under ambient pressure. Samples were monitored in real-time by a digital camera and CVD was continued until growth stopped.

Figure 1 shows photographs of SWCNTs grown at various temperatures and C_2H_2 pressures on combinatorial catalyst libraries. Optimum C_2H_2 pressure changed when the growth temperature was different. Maximum final height was 4.5 mm in 4.5 hours when CVD was carried out at 700 °C with 0.05 vol% C_2H_2. The effect of temperature and C_2H_2 pressure on growth rate and growth lifetime was investigated. Careful AFM analysis provided us an evidence for Ostwald ripening causing the size change of the catalysts. We propose the two mechanisms of growth termination: one is the growth termination by excess carbon feed and another is the size change of catalysts. The dominant mechanism changes with the catalyst and CVD conditions. Suppressing the two growth termination mechanisms and prolonging the rapid growth from small catalysts are the key for millimeter-tall growth of SWCNTs.

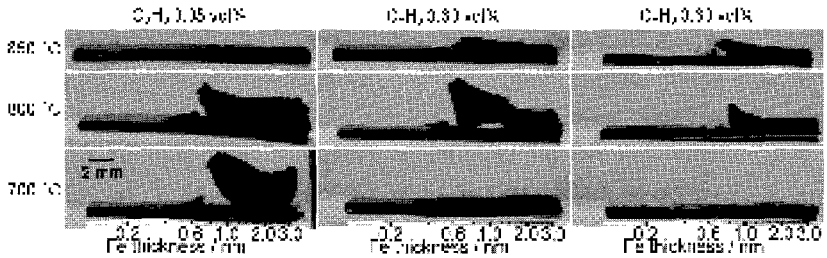

Fig. 1 Side-view photograph of SWCNTs grown on combinatorial catalysts at various CVD conditions.

[1] K. Hata, et al., *Science* **306**, 1362 (2004). [2] K. Hasegawa and S. Noda, *Jpn. J. Appl. Phys.* **49**, 085104 (2010) [3] S. Noda, et al., *Appl. Phys. Lett.* **86**, 173106 (2005). [4] K. Hasegawa and S. Noda, *ACS Nano, in press.*

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2P-13

Synthesis of Highly Aligned Carbon Nanotubes on Stainless Steel Substrates by a Thermal CVD Method with Camphor

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Highly aligned carbon nanotube arrays (HACNTA) have been expected to be employed in a wide range of applications, including electronic devices such as field emission display, supports of electrocatalysts for fuel cells, etc. The natural plant product, camphor $C_{10}H_{16}O$, were reported to be a suitable carbon source for thermal CVD process of high quality HACNTA with quartz substrates [1,2]. In this study, we used cut pieces of commercially available stainless steel (JISSUS304) plates as substrates and synthesized HACNTA with length of "submillimeter" on the substrates.

An Al buffer layer was deposited on the SUS304 substrates by direct current sputtering. A mixture of camphor and ferrocene (catalyst precursor) was inserted into the first furnace (300°C) and the vaporized mixture was sent with an Ar gas flow (100 ml/min) to the second furnace (850°C), where the SUS304 substrate was placed.

Fig. 1(a) shows SEM images of the carbonaceous products on the SUS304 substrate without the Al buffer layer. A small amount of non-aligned CNTs were grown. In contrast, on the substrate with the Al buffer layer, HACNTAs with thickness of 10-900 μm were grown, as typically shown in Fig. 1(b). We presumed that the Al buffer layer reduced the passivation oxide layer of the substrate surface and formed fine Al_2O_3 particles on the substrate. The finely concavo-convex substrate surface of the Al_2O_3 nanoparticles effectively inhibited aggregation of the catalyst nanoparticles and brought formation a large amount of catalyst nanoparticles with an optimum size for HACNT growths.

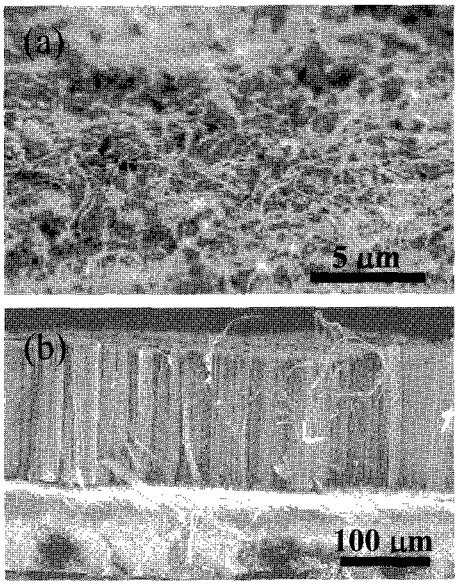

Fig. 1. SEM images of (a) CNTs grown on the SUS304 substrate and (b) HACNTs grown on the Al-sputtered SUS304 substrate.

[1] Kumar et al., *Chem. Phys. Lett.*, **374**, 521 (2003). [2] Yamada et al., *Key Eng. Mater.*, **320**, 163 (2006).

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2P-14

The enhancement of zigzag and near zigzag tubes in the production of single wall carbon nanotube by alcohol CVD

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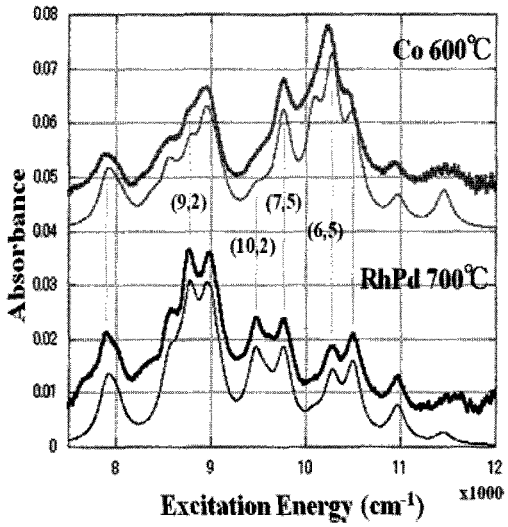
Controlling size and chirality distributions in the production of single wall carbon nanotubes (SWNTs) is undoubtedly one of the most important issues in the potential applications of the SWNTs to nano-material technology such as a nano-electronics, a nano-photonics as well as a nano-bioelectronics. So far, many experimental attempts have been carried out on the selective production or the enrichment of specific (n,m) tubes by various kinds of the SWNT production methods. Among these attemptions, so called "CoMoCAT" and "Co-MCM-41" are typical successful examples in which the (6,5) tube formation has been demonstrated to be of fairly prominence. In these experiments, the selection of the (6,5) tube seems to be realized by combination of CO disproportionation reaction and Co metal catalyst. Laser vaporization method combined with RhPd catalyst is another successful example in which the selective formation of near armchair tubes such as (6,5) and (7,6) species has clearly been shown. However, the experimental reports on the enrichment in a zigzag or a near zigzag tube production is very few, although the reason has not been clarified.

In the present paper, the effect of metal catalyst to the alcohol CVD on the synthesis of SWNTs by Rh and Rh/Pd mixed catalyst is characterized, and we demonstrate that the population of zigzag and near zigzag (n,m)species is extremely higher in comparison with those obtained by the Co-based system. Typical two absorption spectra in SDBS/H_2O solution are shown in the figure to compare how the (n,m) distributions change from Co- to RhPd-catalyst system.



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2P-15

Synthesis of CNTs by Antenna-edge Microwave Plasma CVD from Carbon dioxide and Methane Gas

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1. Introduction

Using carbon monoxide(CO) as reaction gas high quality carbon nanotubes(CNTs) are formed by arc discharge or laser ablation . Also in CVD, CO has a great advantage in CNT quality compared with other carbon containing gas [1]. Unfortunately, CO should be treated as toxic gas, which limit the popular usage like acethylene. The presence of oxygen has a vital role in forming CNT with high quality. The C:O= 1:1 might be a magic ratio as previously shown in diamond deposition [2]. To reproduce the same effect by keeping the same C:O ratio, the mixture of carbon dioxide(CO_2) and methane (CH_4) are proposed. The chemical reaction formula is $CO_2 + CH_4 \rightarrow 2C + 2H_2O$,which indictates that two major green house gases forms high quality Single-Walled Carbon nanotubes (SWNTs) and the byproduct is only water

2. Experiment

We have synthesized SWNTs by remote plasma CVD[3]. Si substrate coated with a sandwich-like structure Al_2O_3 / Fe / Al_2O_3 was used as catalyst for synthesis of CNTs. H_2 and the mixture gas of CO_2 and CH_4 (the ratio is fifty-fifty) were used as reactive gas in Remote Plasma CVD(RPCVD). And, microwave power and pressure in chamber are 60W and 20 Torr respectively. The CNTs is analyzed by Raman spectrometry(633nm).

3. Results & Conclusion

Figure 1 shows the relation between the concentration of G/D and the mixed gas of CO_2 and CH_4 when the concentration is changed. It is understood that G/D has improved with the concentration of the carbon source gas. Especially, G/D becomes the maximum at 80%. Figure 2 shows the high-quality vertical aligned CNTs obtained at 80%. High quality CNTs is synthesized when ratio of C and O is 1:1. In the case of CO_2 and CH_4, O in CO_2 and H in CH_4 interact with each other to moderate the effect of oxygen. Vertical aligned CNTs were synthesized from 80% carbon source gas as result. High quality CNTs synthesized from CO_2 and CH_4 expect might be an effective way to immobilize green house gases.

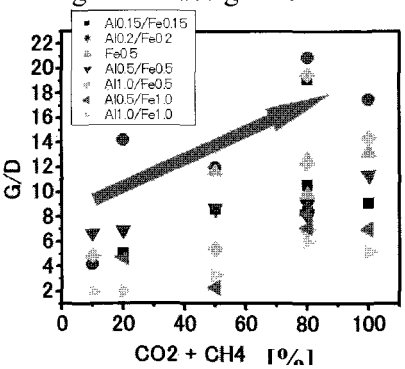

Figure 1. the relation between the concentration of the mixture gas from CH_4

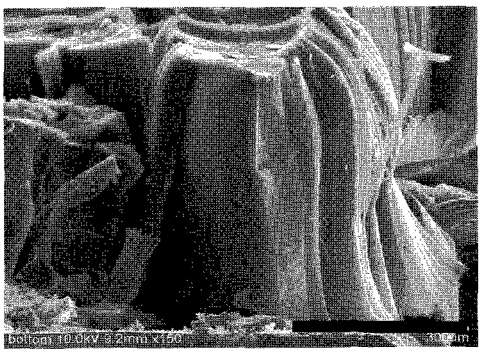

Figure 2. the SEM image of CNT when concentration of CH_4 and CO_2 is 80%

[1] T. Nishii et al. Proceedings of the 6th World Conference on Experimental Heat Transfer , Fluid Mechanics and Thermodynamics, 17(2008)

[2] P.K.Bachmann, et al. Diamond Relat. Mater. 12, 1(1991) [3] T. Iwasaki et al. Nano Lett. 8, 886 (2008)

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2P-16

Molecular Dynamics Simulations of Metal Nanowire Formation within a SWNT and the SWNT Growth Process by Catalytic CVD

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We reconstructed the Tersoff potential for use with metal-carbon structures, and applied it to cobalt, iron, nickel, and platinum systems. Potential parameters were acquired by fitting lattice constants and energies of various crystal structures. We confirmed this potential correctly reproduces many crystal structures.

In this study, we performed two simulations using our reconstructed potentials and the Brenner potential [1]. First, we simulated metal nanowire formation within a single-walled carbon nanotube (SWNT). Then, by adopting the simulation procedure of a previous report [2], we calculated the SWNT growth process by the catalytic CVD method. Classical molecular dynamics was used for both simulations.

Figures 1 and 2 show the cobalt and platinum nanowires formed inside a (5,5) SWNT. The morphology of the nanowire within the SWNT is dependent on the kind of metal. Other results for various SWNT chiralities and other metal species will be presented.

Figure 3 shows the growth process of a SWNT by the catalytic CVD method using cobalt catalyst. Carbon atoms are released from the cobalt cluster's surface, forming a tubular structure.

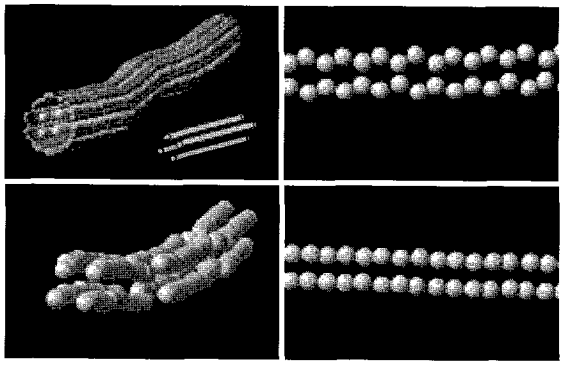

Fig. 1: Co nanowire inside a (5,5) SWNT

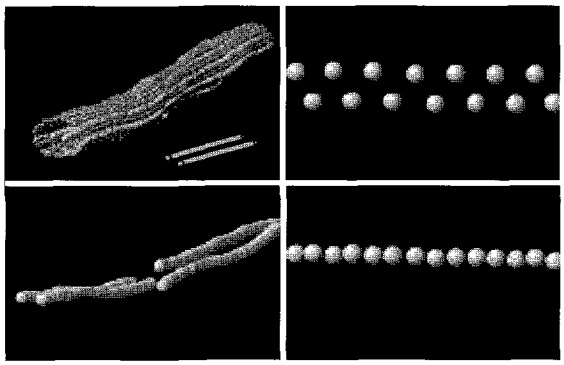

Fig. 2: Pt nanowire inside a (5,5) SWNT

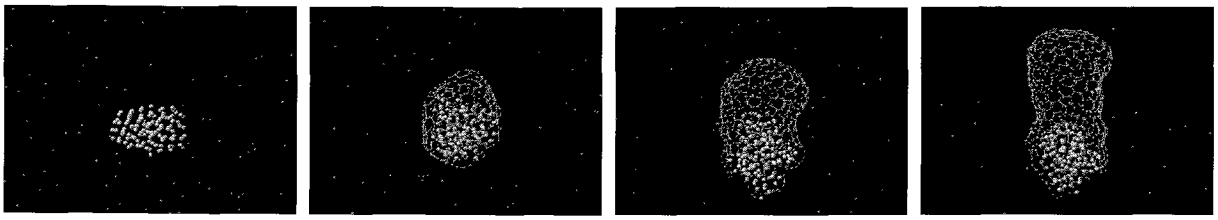

Fig. 3: Growth process of SWNT by Catalytic CVD method of cobalt catalyst (Left to right 0 ns, 10 ns, 20 ns, and 30 ns).

[1] D. W. Brenner, Phys. Rev. B, **42** (1990) 9458. [2] Y. Shibuta and S. Maruyama, Chem. Phys. Lett., **382** (2003) 381.

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2P-17

Selective growth of SWNTs on Ir catalyst combined with a laser vaporization method

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Controlling size and chirality of single-wall carbon nanotubes (SWNTs) is definitely of particular importance for the potential applications of SWNTs to the industrial field such as nano electronic devices, because the performance of SWNTs-based materials depends greatly on the diameter and chirality of the nanotubes. The ultimate goal in carbon nanotube production is to find a method and/or a catalytic system that would allow the growth of SWNTs of a single chirality. The laser vaporization method combined with RhPd catalyst has been shown to be one of the versatile methods in which the abundance of the SWNTs with a particular chiral index was found to be over 90% among other remaining SWNTs in the raw soot material.

In the present paper, we will demonstrate the experimental results on the chirality distributions of the SWNTs prepared by a laser vaporization method combined with Ir metal catalyst. Typical example of the SWNTs prepared by Ir catalyst is shown in Figs. 1and 2, in which the 2D fluorescence and absorption spectra of the sample by Ir in SDBS/H_2O solution are drawn to compare with those by RdPd under the same condition. Comparing these two spectra, it is clearly shown that the maximum of the size distribution for the SWNTs grown on the Ir catalyst shifts to the larger diameter size, resulting in the formation of (7,6) and (8,7) enriched SWNTs.

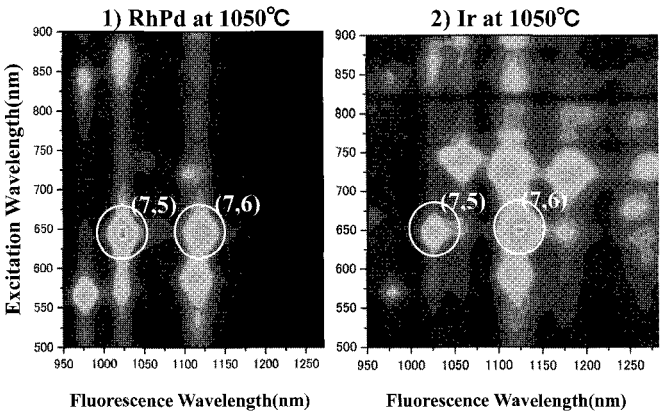

Fig.1: Fluorescence 2D mappings for the SWNTs prepared by laser vaporization with 1) RhPd and 2) Ir catalysts.

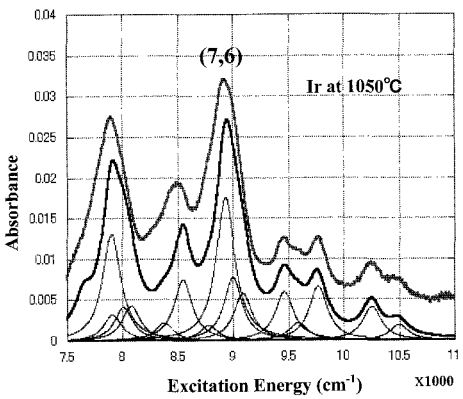

Fig. 2: Experimental and deconvoluted absorption spectra of SWNTs in SDBS/H2O solution. The deconvolution was carried out based on the fluorescence intensity for each (n,m) species.

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2P-18

Epitaxial growth of faceted Co nanoparticles and their application to carbon nanotube growth

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[c] *PRESTO-JST*

Metallic nanoparticles play an essential role in the catalytic growth of single-walled carbon nanotubes (SWNTs). It was reported that a graphene film epitaxially grows on single crystal fcc Ni(111) surface and that the orientation of the graphene matches with the underneath metal film [1]. This suggests that the crystallinity of the metal catalyst strongly infulences the graphitization. Therefore, it is interesting to apply highly crystalline metal nanoparticles to SWNT growth in terms of possiblity of controlling the SWNT structure including chirality. Here, we report preparation of crystalline Co nanoparticles on sapphire surfaces by high temperarute-sputtering and successive annealing processes.

The Co film with 10 nm thickness was sputtered onto a sapphire substrate at room temperature and 500 °C. Then, the substrate was the annealed at 900 °C in a H_2 flow, which converts the Co film to Co nanoparticles. We found that as-grown crystalline Co nanoparticles have unique faceted structure [2]. The structure of the Co nanoparticles was dependent on the sputtering temperature as well as the crystalline plane of sapphire. As seen in Fig. 1, the high temperature (500 °C) sputtering stimulated the epitaxial growth of faceted Co nanoparticles, while the room temperature-sputtered film gave a disordered film-like morphology together with irregular nanoparticles. The corresponding x-ray diffraction results indicates that the Co nanoparticles have a fcc structure. Thus, the as-grown nanoparticles are proposed to have half-octahedron with truncated {100} and {111} planes that can be explained by Wulff's theorem. The horizontally-aligned SWNT growth over these faceted Co nanoparticles is also presented.

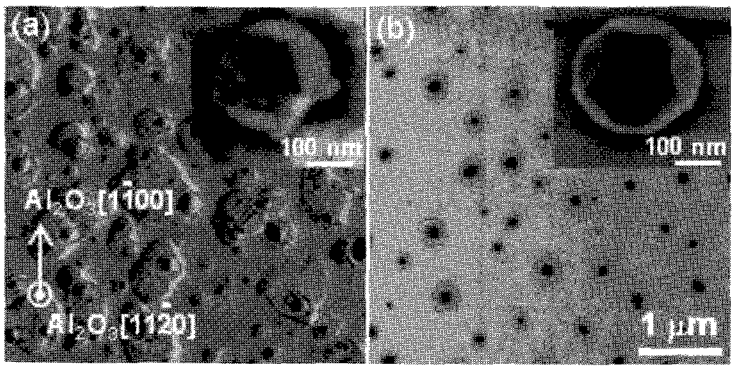

Figure 1. SEM images of Co/a-plane sapphire surface taken after H_2 annealing at 900 °C. The sputtering temperature is (a) RT and (b) 500 °C. Insets show the magnified images of typical Co nanoparticles.

References: [1] Y. Gomi *et al.*, *Surf. Sci.* **374** (1997) 61. [2] Y. Ogawa *et al.*, *Chem. Lett.* **39** (2010) 964.

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2P-19

New approach for chirality recognition of single-walled carbon nanotubes using fluorene-based copolymers

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Much attention has been paid to single-walled carbon nanotubes (SWNTs) because of their unique physical properties [1,2]. However, the coexistence of tubes with various chiralities SWNTs has interfered with fundamental research and fabrication of devices. Separation of the mixture of SWNTs into certain chirality components has attracted considerable attention, recently [3].

Here we report a method toward selective recognition and separation of specified SWNTs having selected chiralities. Our approach is to use a family of polyfluorene (PFO)-based copolymers, composed of fluorene and alkoxy benzene (OB and EHB) having normal or branched side chains (PFO-OB and PFO-EHB, Fig. 1). Fig. 2 shows the photoluminescence (PL) maps of the SWNTs dissolved in toluene solutions of copolymers, in which we observed a strong SWNT chirality dependence. In the case of PFO-OB, the strong PL intensity from (8,6)SWNTs appeared in the homopolymer (x:y = 100:0) became weak with increasing the contents of the OB unit (y) (Fig. 2, upper). Similar trend was observed also for PFO-EHB (Fig. 2, lower). Absorption spectra also supported the above selectivity tendency and we will discuss the detail of the selectivity of the SWNTs depending on polymer composition.

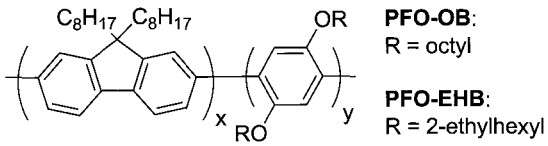

Fig. 1. Chemical structure of fluorene based copolymers.

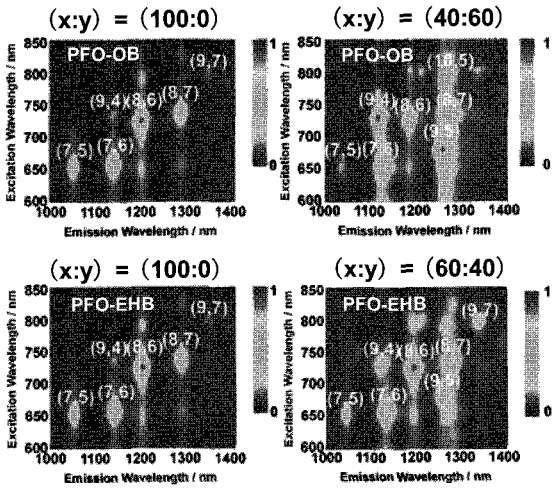

Fig. 2. PL maps of SWNTs with PFO-OB (upper left; x: y; 100: 0, upper right; 40:60) and PFO-EHB (upper left; x: y; 100:0, upper right; 60:40) .

References

[1] J. Bernholc, et al, *Annu. Rev. Mater. Res.* **32**, 347 (2002).
[2] H. J. Dai, et al, *Acc. Chem. Res.* **35**, 1035 (2002).
[3] C. H. Liu, et al, *Nanoscale* **2**, 1901 (2010).

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2P-20

Separation of Single-Wall Carbon Nanotubes using Four Kinds of Gel Column Chromatography

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[2] *CREST, JST, Kawaguchi, Saitama 330-0012, Japan*
[3]*Institute of Materials Science, University of Tsukuba, Ibaraki 305-8573, Japan*

The electronic and optical properties of single-wall carbon nanotubes (SWNTs) strongly correlate with their structures. Various growth methods such as CoMoCAT® process have been developed to control their chiralities and diameters, but the structure control of SWCNTs is still unsatisfied. Because co-existent of metallic (m-) and semiconducting (s-) SWCNTs in as-produced soot precludes their widespread electronic applications, additional post-synthetic separation is necessary.

Recently, agarose gel column chromatography (GCC) was developed for the metal/ semiconductor separation of SWCNTs [1,2]. In this method, selective adsorption of s-SWCNTs on the agarose gel beads leads to high-purity separation. Almost the same but slightly different effect is also reported for commercially available Sephacryl gel [3]. In this presentation, we report our effort on the M/S separation of SWCNTs by GCC using 4 kinds of commercially available gels: Sephacryl S-200, S-300, Sepharose 2B, and 4 Fast Flow. SWCNTs (SWeNT® SG76) were dispersed in sodium dodecyl sulfate (SDS) water solution by tip sonication and applied to the top of the gel columns after the ultracentrifugation. The m-SWCNTs were eluted with SDS solution, and the s-SWCNTs that remained in the gel columns were collected with sodium deoxycholate water solution. Analysis based on the optical measurements showed that S-200 gel showed the highest purity in M/S separation. To see the detailed separation process, a long column was applied. In the case of S-200, the semiconductor was separated into two fractions, while only one fraction was observed in the Sepharose. This additional separation process in S-200 could be attributed to the filtration of bundle size due to the size exclusion effect and leads to higher semiconductor purity. Detailed analysis will be discussed.

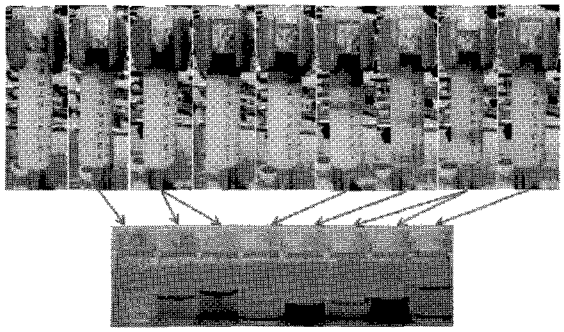

Figure1. Separation of SWeNT® SG76 SWCNTs by Sephacryl S-200.

References

[1] T. Tanaka et al., Nano Lett. **9**, 1497 (2009). [2] T. Tanaka et al., Appl. Phys. Express **2**, 125002 (2009).

[3] K. Moshammer, F. Hennrich, and M. M. Kappes, Nano Res. **2**, 599 (2009).

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2P-21

Effects of carbon source and growth temperature on diameter of horizontally-aligned single-walled carbon nanotubes on sapphire

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Single-walled carbon nanotube (SWNT) is a promising material for nanoelectoric devices. It has been demonstrated that single crystal substrates can assist horizontal SWNT growth [1,2], but mixed growth of metallic and semiconducting SWNTs remains a bottleneck for the future applications. This problem is caused by the fact that the as-grown SWNTs have some diameter distribution and, consequently, contain different chiralities. Thus, it is important to synthesize small-diameter SWNTs with a narrow diameter distribution while maintaining the horizontal alignment. Here, we study effects of carbon feedstock and growth temperature on the diameter of SWNTs grown on sapphire substrates.

Sapphire r-plane substrates were dipped into the Co-Mo salt solution to deposit the catalyst. SWNTs were grown by chemical vapor deposition (CVD) using either CH_4 or EtOH feedstock at 750 - 900 °C. As shown in Fig. 1, highly aligned SWNTs were obtained by CH_4 CVD as reported [2], but the nanotube density decreased significantly when the CVD temperature was lowered to 750 °C. On the other hand, the EtOH CVD gave high SWNT density even at 750 °C due to high reactivity of EtOH feedstock. However, the SWNT alignment was lost in the EtOH CVD. Raman spectra were measured at different points as shown in Fig. 2. While the diameter distributions in the methane CVD were almost independent on the reaction temperature, the ethanol CVD shifted to smaller diameter at lower reaction temperatures. We also present improvement of the SWNT alignment by addition of water vapor.

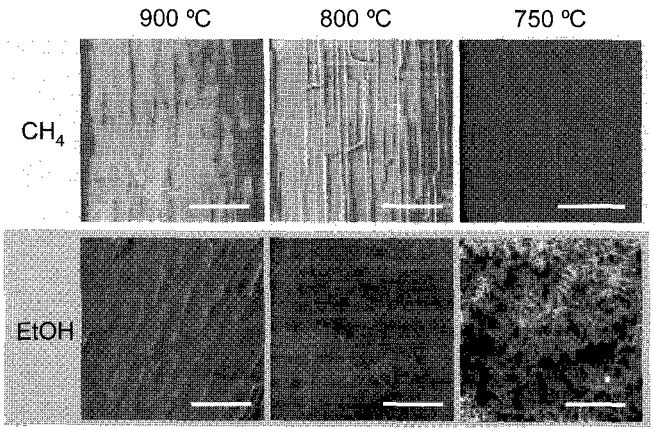

Fig. 1. SEM images of as-grown SWNTs from methane and ethanol at different CVD temperatures. Scale bars are 10 μm.

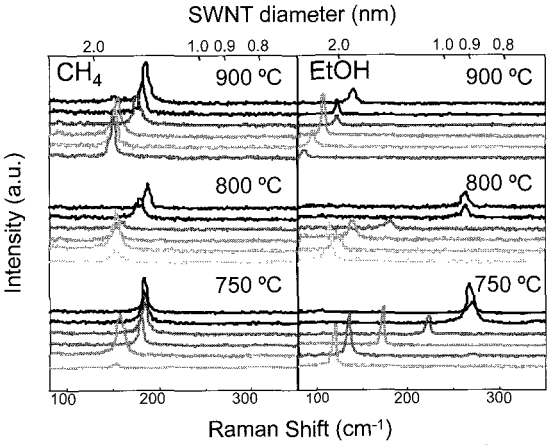

Fig. 2. Representative Raman spectra of the SWNTs grown from methane and ethanol measured with 514.5 nm excitation.

References: [1] H. Ago *et al., Chem. Phys. Lett.* **408** (2005) 433. [2] N. Ishigami *et al, J. Am. Chem. Soc.* **130** (2008) 30.

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2P-22

Chemical vapor deposition growth of carbon nanotubes using cluster templates

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[2] *Catalysis Research Center, Hokkaido University, Nishi 10, Kita 21, Sapporo 001-0021, Japan*
[3] *CREST, Japan Science and Technology Agency, Kawaguchi,* Saitama 332-0012, Japan

Carbon nanotubes (CNTs) are known to possess superior mechanical and electronic properties that initiated a broad research activity in multiple fields of nanoscience. The electronic structure of CNTs strongly depends on their geometrical structure such as the helicity.[1)] However, up to now, it is not possible to selectively grow CNTs with desired structure. Therefore, development of a precise control of the structure of CNTs is indispensable for the application of CNTs to nanoelectronics. To overcome this difficulty, we focused on clusters, which have uniform diameter and structure, as templates for chemical vapor deposition (CVD) growth of CNTs. Among various molecular and metal cluster templates, we have focused on gold clusters, fullerenes and Manganese clusters for CVD growth of CNTs. Especially, gold clusters are useful for CVD growth of CNTs due to the following reasons: (1) gold clusters have catalytic activity for CVD growth of CNTs [2)]and (2) a preparation technique of gold clusters with a uniform and desired diameter has been well-established recently.

In this study, we used gold clusters[3)] with average diameter of 1.3 nm (standard deviation was 0.3nm) as template for CCVD growth of CNT. The gold clusters were dispersed in ethanol (0.01 wt %) and spin-coated onto a quartz and silicon substrate. Prior to CVD growth, samples were heated in air at 500 degree for 30 min to remove poly (*N*-vinyl-2- pyrrolidone) wrapping the surface of Au clusters. After the heat treatment, CNTs were grown at 850 degree by CVD using ethanol as a carbon source.

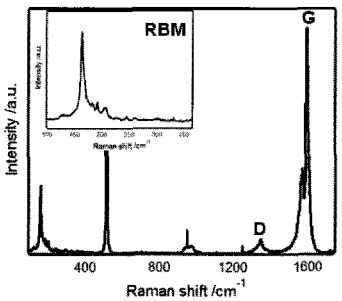

Figure 1, Raman spectra of grown CNTs from Au cluster

Figure 1 shows Raman spectrum of the products that shows characteristic Raman bands to CNTs. Diameter of CNTs estimated from position of RBM Raman bands ranges from 1.0 to 1.6 nm, which is compatible with the diameter of Au clusters used in CVD growth. Figure 2 shows distribution of diameter of CNTs estimated by TEM image. This result corresponds to the result of raman spectra and gold cluster size.

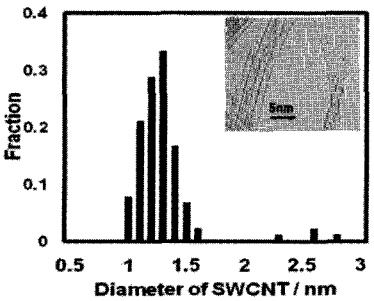

Figure 2, Distribution of the diameter of CNTs and TEM image

Reference 1) R. saito *et al.*, *Phys. Rev.* B., **46**, 1804 (1992)

2) D. Takagi *et al.*, *Nano. Let.*,**12**,2642(2006)
3) H. Tsunoyama *et al.*, *Langmuir.*,**20**,11293(2004).

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2P-23

Interaction-dependent Chirality Separation of Single-Wall Carbon Nanotubes by Multicolumn Gel Chromatography

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Small variations in diameter and chirality will bring striking changes in the electronic and optical properties of single-wall carbon nanotubes (SWCNTs). Therefore, mono-structured SWCNTs are essential for both the scientific research and practical applications such as electronic and optical devices. Recently, we developed simple methods for continuous separation of metallic (M)- and semiconducting (S)-SWCNTs using agarose gel [1-3]. Moreover, successively increasing sodium deoxycholate solution concentration during collection of S-SWCNTs permitted low-resolution diameter separation [2, 3], but further chirality separation is not possible.

In this presentation, we report a simple and effective method for large-scale chirality separation of SWCNTs using single-surfactant multicolumn gel chromatography (SS-MUGEC) that uses only one surfactant (sodium dodecyl sulfate) and a series of gel columns (commercial Sephacryl gel) [4]. We succeeded in isolating 13 kinds of single-chirality species from HiPco-SWCNTs (diameter, 1.0±0.3 nm) just by injecting an excess of nanotube dispersion into the gel column series. This simple method is based on the structure-dependent interaction of SWCNTs with the gel. The nanotubes with the highest interaction with the gel are preferentially adsorbed in the top column whereas the nanotubes with the lower interaction with the gel are adsorbed in the following gel columns. In this manner, chirality-separation of SWCNTs was achieved. Metallic SWCNTs were finally collected as unbound nanotubes because of their lowest interaction with the gel. Because this method is simple, quick, high-efficiency, continuous and inexpensive, separation in an industrial scale is expected. We believe that this brand-new powerful method for chirality-separation will open a new research field and accelerate the practical applications of SWCNTs.

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2P-24

Effects of Laser Wavelength and Power on the Selective Separation for Metal Single-walled Carbon Nanotubes with OPO Laser Irradiation

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As-synthesized single-walled carbon nanotubes (SWNTs) comprise of various chiral structures responsible for metallic (m) and semiconducting (s) SWNTs. Selective separations of m- and s-SWNTs have been requested for practical and advanced applications. Thereof, we have developed a new selective separation technique for m-SWNTs with nanosecond pulsed optical parametric oscillator (OPO) laser operated with wavelength tunability.[1] This paper is concerned with the effects of the laser wavelength and power on the selective separations of m-SWNTs from individually dispersed SWNTs with the dispersants such as carboxymethylcellulose (CMC) and dodecylbenzensulfonic acid sodium salt (NaDDBS) in aqueous solutions. Individually dispersed SWNTs exhibited the UV-vis-NIR absorption spectra with the characteristic peaks composed of three band regions (400-1600 nm) of M11, S11 and S22 corresponding to m-SWNTs first transitions, and s-SWNTs first and second transition bands, respectively. In the laser irradiation performance, the OPO laser was operated under the condition of 10 Hz with laser fluences in the range of 1.3 – 22.9 MW/cm^2 per one pulse at 2.16×10^5 pulse number. The characterization of SWNTs in the solutions before and after laser irradiation was carried out with UV-vis-NIR absorption/photoluminescence (PL) and resonance Raman spectral measurements, and dynamic light scattering (DLS). As a result, the OPO laser with a wavelength in the S11 or S22 region brought merely about the destruction of the dispersed s-SWNTs through photo-thermal conversion process, the m-SWNTs remaining unchanged. In the CMC dispersion system, the maximum collection efficiencies for m-SWNTs were achieved under the condition of a laser fluence of 6.4 MW/cm^2 at 778 nm (S_{22}) and 19.1 MW/cm^2 at 989 nm (S_{11}). Consequently, the OPO irradiation technique was suggested to be a promising method to efficiently gain m-SWNTs.

[1] Isamu Tajima et al. The 36th Fullerenes-Nanotubes General General Symposium Abstract 3P-5

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2P-25

Super-growth: Combining High Yield with High Crystallinity

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A number of obstacles face the carbon nanotube field, such as low cost, high yield, and high purity. Super-growth chemical vapor deposition (CVD) method, through the demonstration of high efficiency, vertically aligned single-walled carbon nanotube (SWNT) synthesis, has shown the potential to simultaneously overcome these three obstacles [1]. However, one aspect in the CNT field which remains a difficulty is the high yield, high purity synthesis with high crystallinity.

Here, we report the synthesis of high crystallinity, SWCNT forests based on super-growth CVD. Using an iron thin film catalyst and the sequential optimization of the temperature, the carbon level, and the water level, we succeeded in synthesizing SWNT forests with a 10-fold increase graphitic-to-disorder band ratio (G/D) from the typical ~7 to up to 70 while maintaining SWNT selectivity. Characterization of the forest structure through transmission electron microscopy and scanning electron microscopy showed exceptionally straight SWNTs. Furthermore, characterization of the forest properties, such as thermal diffusivity and dispersion, showed significant improvement compared to the standard super-growth SWNT forests.

References:

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2P-26

Purification and Characterization of Graphitic Polyhedra Grown by Laser Vaporization of Graphite Containing Silicon or Boron

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Graphitic carbon nanostructures are of great interest in fundamental research and application in various fields. We fabricated polyhedral graphite particles with diameters of 100–1000 nm by CO_2 laser vaporization of graphite at room temperature [1]. To form the particles with a 90% yield, a high-pressure (>0.8 MPa) Ar gas atmosphere was required to confine laser-vaporized carbon species and maintain their high temperatures. Transmission electron microscopy (TEM) images of the central parts of the particles showed closed shells (~5 nm in diameter) and concentric frameworks of graphene layers [2, 3]. The particles exhibited interesting behavior under high-pressure compression, probably due to a topological difference from bulk graphite [3]. However, for further investigation of other properties and applications of the particles, such as tribology [4] and battery electrodes, development of a larger-scale production and purification method is favorable. Here we report the coexistence of a small amount of silicon or boron promotes the growth of graphitic polyhedral (GP) particles and also report purification and characterization of the GP particles.

Laser vaporization of graphite containing Si or B (1 and 2 at.%) was carried out in the presence of Ar gas in the same way as reported in previous studies [1, 2]. A powder of Si or B_4C was mixed with a graphite powder and was pressed into pellets. The laser beam from a continuous wave Nd:YAG laser was focused on the pellet targets through a quartz window installed in a stainless-steel chamber filled with Ar gas (0.2 and 0.3 MPa) at room temperature. The laser size and the power density on the target were adjusted to 2 mm and about 18 kW/cm^2, respectively, and the laser irradiation time was set to 2 s. To purify the deposits containing GP particles, the deposits (10 mg), produced using 30–40 laser shots, were treated at 200–700 °C in a pure oxygen atmosphere for 1 h using an electric furnace.

The growth of GP particles was promoted even at low pressures of 0.1 and 0.2 MPa. After heat treatment in an oxygen atmosphere, the changes in the weights of deposits containing GP particles with incorporation of Si were measured and analyzed as a function of treatment temperature. The relative weights of the deposits gradually decreased up to 400 °C and rapidly decreased at 400–700 °C. TEM examination revealed that the removal of non-GP particles such as amorphous carbon and single-wall carbon nanohorn particles corresponded to the weight decrease. TEM examination also indicated the deposits became almost completely composed of GP particles at 550 °C. A similar behavior was also observed for GP particles containing B atoms. The removal of non-GP particles was confirmed by Raman spectra measurements. The XPS spectra of GP particles containing Si indicated the Si concentration is unusually high (Si/C= ~0.18).

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2P-27

The molecular structure and vibrational spectroscopy of hydroxylated nanodiamonds

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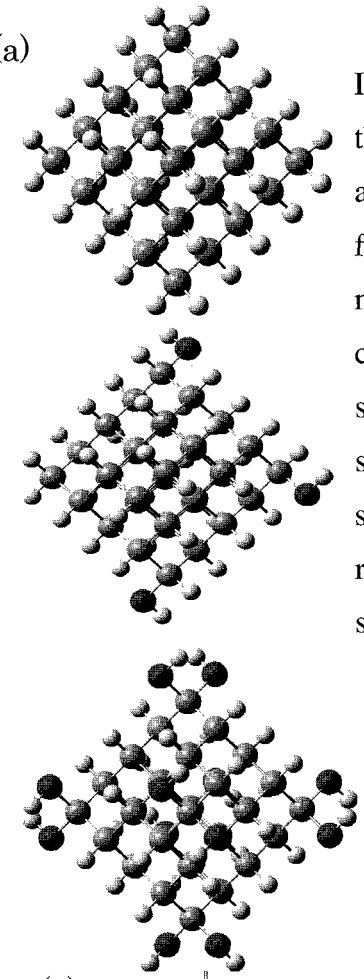
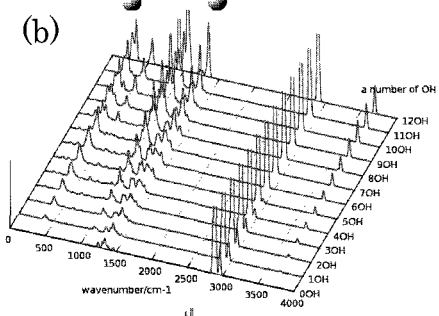
(a)



In expectation of nanodiamond's applications, to investigate the surface is important [1]. We express the theoretical study about nanodiamonds functionalized hydroxyl group, and focus on their stability and spectroscopic features. As a model, we prepared Octahedral one (Fig a). The calculations performed in two theories, self-consistent-charge density functional tight nanodiamond substituted vertex hydrogen atom to hydroxyl group is more stable, to avoid 1,3-diaxial interaction. In other words, repulsive effect between each atoms is dominant over stabilization by hydrogen bonds. From IR spectra, periodicity is observed (Fig b & c). The mass of hydrogen atoms which bind carbon made 10^5, and identify other hydrogen atoms which is contained hydroxyl group. By this change, we could see the spectra except CH bonds, and simplify them.

(b)



(c)

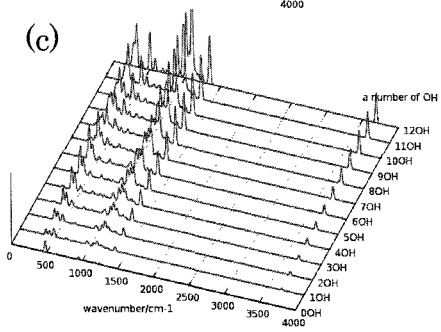


Figure 1

(a) Octahedral model. ($C_{35}H_{36}$,$C_{35}H_{36}O_3$,$C_{35}H_{36}O_{12}$)

(b) Spectra.

(c) Spectra using heavy hydrogen atom.

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2P-28

Observation of void in DMFC electrode composed with carbon nanocoil

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The void density in direct methanol fuel cell (DMFC) electrode has to be properly controlled for increase in performance. We have used arc-black (AcB), an amorphous carbon nanoparticle synthesized by arc discharge, as a catalyst support material in DMFC electrodes [1]. Recently, we showed that, when carbon nanocoil (CNC) was used in the DMFC cathode, the output became higher than that using AcB. Owing to its spiral shape, CNC can produce a lot of voids in the electrode. In this study, we made the DMFC cathodes using catalyst-supported AcB, CNC and crushed CNC and observed the voids in the electrodes by scanning electron microscopy (SEM). Fig. 1 shows SEM micrographs of the electrodes. (b) CNC electrode seems to have the biggest void and (a) AcB electrode the smallest.

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Fig.1. SEM micrographs of electrodes. (a) AcB, (b) CNC, (c) crushed CNC

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2P-29

Vibrational and NMR properties of Polyynes and Microscopic studies of Polyynes@SWNT

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Polyynes are finite-sized, one-dimensional linear molecules of carbon atoms with alternate single and triple C−C bonds and hydrogen termination at the both ends. They are commonly expressed by $C_{2n}H2$, where n is an integer. The bond-stretching phonon modes of such linear polyynes are calculated as a function of chain length within the density functional theory. There are two intense Raman bands so called α and β bands in the higher frequency region around 2000 − 2200 cm^{-1}. The frequency of α mode monotonically decreases with the increase of polyyne chain length while that of the β mode shows oscillating behavior, which are consistent with previous Raman measurements [1]. The nature of α phonon mode is such that it is the bond-stretching mode with fixed hydrogen atoms while the β mode is the bond-stretching mode with changing the length of the molecule. The relative Raman intensities of the two phonon modes are evaluated by optimized geometries for ground states and excited states. The vibration induced by the photo-excited carriers mainly consists of α mode, which explains the stronger relative Raman intensity for α mode than that for the β mode for all $C_{2n}H_2$ molecules. We also present a nuclear magnetic resonance (NMR) calculation for spin-spin coupling constants as a function of distance between ^1H and ^{13}C nuclei and, within ^{13}C nuclei, up to the polyyne center of symmetry. We compare the calculated results with recent NMR experiments [2]. In the case of spin-spin coupling among ^{13}C nuclei, since J_{CC} does not much depend on the atomic position but much on the relative distance between the two atoms, we expect a detailed analysis of fine structure of NMR shifts.

We recently obtained HRTEM image of polyynes@SWNT (polyyne inside single-wall carbon nanotube). We will report our microscopic study e.g. electron energy loss spectroscopy (EELS) for polyynes in the near future.

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2P-30

Chromatographic Separation of Highly Soluble Nanodiamond Prepared by Polyglycerol Grafting

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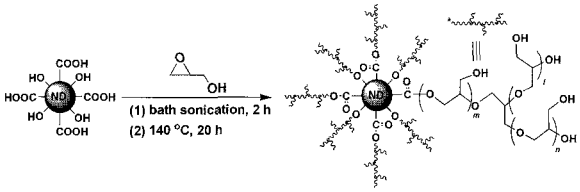
Biomedical applications of nanodiamond (ND) have been investigated extensively due to its low toxicity, non-bleaching fluorescence and high extensibility of the surface functionality through covalent organic functionalization. For the purpose, ND should first form a stable hydrosol under a physiological environment. In order to increase the solubility, we change the surface functionality of ND from conventional linear polyethers (PEG) [1] to hyperbranched polyglycerols (PG) (Scheme 1). We choose the PG functionality for the following reasons: high hydrophilic property, biocompatibility, hyperbranched structure and easy functionalization. As a result, the PG grafted ND (ND-PG) exhibited extremely high solubility (16 mg/mL) in phosphate buffer saline (PBS) [2].



Scheme1. Synthesis of ND functionalized by hyperbranched polyglycerol through ring-opening polymerization of glycidol

The solubilized ND-PG passed through silica-based columns in the size exclusion chromatography (SEC) under a flow of a pH 7.0 buffer as a mobile phase [2]. The scanning transmission electron microscopy (STEM) and dynamic light scattering (DLS) measurements of the fractions reveal that ND-PG is successfully separated according to their sizes (Figure 1). Size-sorting of ND-PG by SEC is believed to make a great progress in view of cancer imaging utilizing enhanced permeability and retention (EPR) effect in solid tumors.

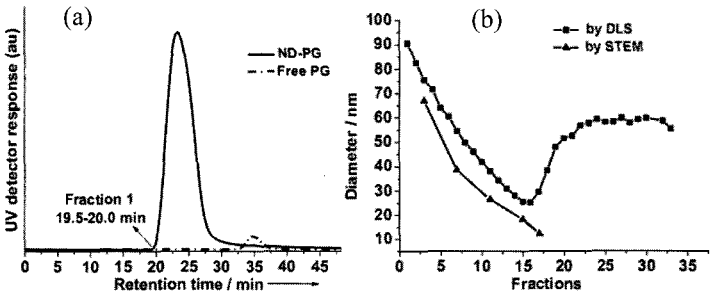


Figure 1. (a) Chromatograms in the elutions of ND-PG and free PG; (b) Median and average diameters (nm) of the eluted particles determined by DLS and STEM, respectively.

Reference: [1] T. Takimoto, N. Komatsu, et al., *Chem. Mater.*, **22**, 3462 (2010), [2] L. Zhao, T. Takimoto, N. Komatsu, et al., *Angew. Chem. Int. Ed.*, in press (10.1002/anie.201006310)

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2P-31

1 MeV electron irradiation-induced structural changes of nanometer-sized diamond particles

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Electron irradiation-induced structural changes of nanometer-sized diamond particles (NDPs) were *in situ* studied by transmission electron microscopy (TEM) and electron energy loss spectroscopy (EELS).

The NDPs with an average diameter of 4.8±0.5 nm were supplied by NanoCarbon Research Institute, which were produced by detonation techniques. The specimens for TEM observation were prepared by dispersing the NDPs into isopropyl alcohol and dropping the alcohol solution on a molybdenum microgrid coated with a lacy carbon film. The specimen was mounted on a specimen holder with a heating stage and irradiated at room temperature and 973 K in a high-voltage transmission electron microscope (JEM-1000K RS) equipped with a post-column imaging filter. The microscope was operated at an acceleration voltage of 1 MV. The structural changes of the NDPs during irradiation were observed by a CCD camera. The EELS measurements were carried out by using the imaging filter in the imaging mode.

During the electron irradiation at room temperature, the NDPs disintegrated into disordered carbon materials such as amorphous carbon. The disordered materials sublimated and finally disappeared. On the other hand, the irradiation at 973 K caused to the transformation of the NDPs into carbon onions. Figures 1(a) and 1(b) show TEM images of the NDPs at 973 K after a few minutes of irradiation and after 20 min, respectively. The graphitic layers began to be formed at the surface of the NDPs, and proceeded to the center of the NDPs. Figure 2 shows the core-loss spectra in the carbon K-edge region for the NDPs and the transformed carbon onions. A peak appearing at > 290 eV corresponds to the 1s → σ* transition. For the carbon onions, in addition to the σ* peak, a peak at 285 eV corresponding to the 1s → π* transition appears significantly. The spectra show that the changes in the chemical bonding in the NDPs, i.e., transition of sp^3 to sp^2 type bonding, occurred by the electron irradiation at 973 K. In this experiment, the transformation of the carbon onion to diamond during irradiation was not observed, though this reverse transformation has been reported for the onions with more than 10 nm in diameter at a temperature above 850 K[1].

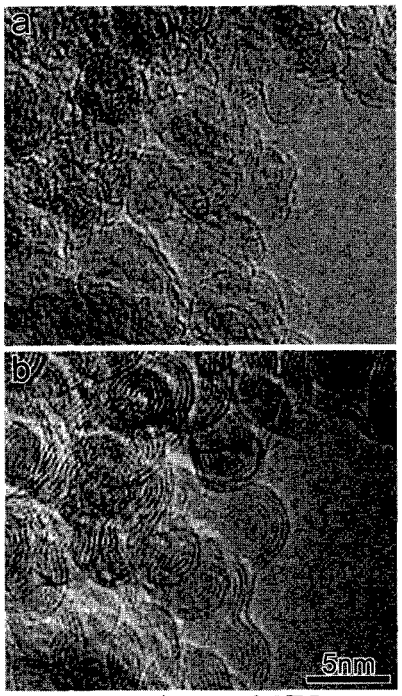

Fig. 1 TEM image of NDPs at a specimen temperature of 973 K after a few minutes of irradiation (a) and after 20 min (b).

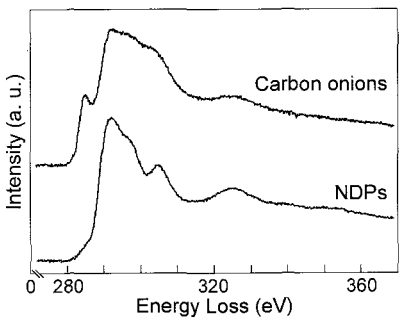

Fig. 2 EELS spectra of NDPs and carbon onions.

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2P-32

Superparamagnetic behavior of carbon nanofoam produced from iron free carbon powder

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Several previous studies [1,2] reported ferromagnetic behavior based on the localized zigzag edge states of graphene [3,4]. Such zigzag edge is generally unstable in air and subsequently reacts with some chemical spices. This kind of reaction normally quenches the ferromagnetism. On the other hand, mono-hydrogenated zigzag edges make the system somewhat stable and the ferromagnetic spin arrangement remains along the zigzag edge [3]. Mono-hydrogenated and di-hydrogenated zigzag edges are convenient for stabilizing the edge states without quenching the strong magnetism [5].

Although the carbon ferromagnetism includes quite interesting subjects for both the fundamental science and application technology, it is very difficult to exclude the magnetic impurity effect. In the previous study, about 100-300 ppm of iron was detected in both magnetic attractive (prod. in H_2) and in-attractive (prod. in Ar) carbon nanofoam (CNF). However, even detecting such quantities of iron, observed M_s (saturation magnetization) cannot be explained. In the present study, we carefully removed such ferromagnetic impurity from the starting materials by the following acid treatment and checked reproducibility of strong magnetism.

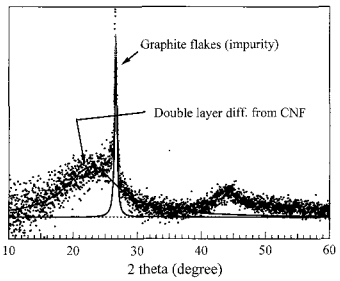

Fig. 1. XRD pattern of the product

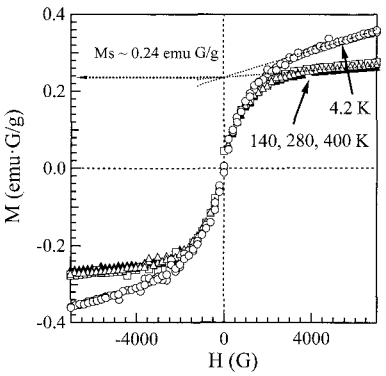

Fig. 2. MH curves at 4.2, 140, 280 and 400 K

500 mg of carbon powder (Kojyundo Kagaku 99.7 %, 5 μm) was treated in 20 ml of concentrated HCl for 1 day. After this treatment, liquid was slightly colorized in brownish yellow, indicating the existence of Fe^{3+} ion. Then the liquid was decanted. Carbon powder thus purified was rinsed twice by using ethanol. Then the powder was heated at 120 °C in vacuum and used for making the target for laser vaporization. CNF sample was produced by the laser vaporization in the flux (100 sccm) of 3 % H_2 containing Ar balance gas at 1000 °C. XRD profile of the product is in Fig. 1, which is the same as the previous CNF. MH curves at various temperatures are in Fig. 2, which clearly show easy saturatable feature at 400 K. Interesting fact is that no hysteresis was observed at 4.2 K, which indicates that the superparamagnetism is applicable down to 4.2 K.

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2P-33

Synthesis of Carbon Nanowalls by a Submarine-style Substrate Heating Method

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We have developed a new method for the synthesis of carbon nanotubes (CNTs) named submarine-style substrate heating method [1]. The method is based on the liquid-phase deposition method [2], in which a catalyst-coated silicon substrate is electrically heated to high temperatures around 1000 K in liquid hydrocarbon. The liquid-phase deposition method has realized a simple and rapid growth of CNTs. However, catalysts employed in the method need to be tough enough to bear the boiling in liquid hydrocarbon, which limits the catalysts applicable to the method. In the submarine-style substrate heating method, we applied a zeolite-supported metal nanoparticle catalyst, which used to be washed away during the synthesis in the liquid-phase deposition method, and succeeded in synthesizing single-walled CNTs and double-walled CNTs [1]. In this study, we have applied the method to synthesize carbon nanowalls (CNWs). CNWs are two dimensional carbon nanostructures consisting of plane graphene layers mounted vertically on a substrate, and are attracting attentions as materials for electron field emitters, nanoparticle supporters and so on. In the previous studies, CNWs were grown by microwave plasma enhanced chemical vapor deposition [3].

In the experiments, iron-cobalt composite catalyst supported on ultra-stable Y-type zeolite was employed. Catalyst-dispersed ethanol was dropped on a silicon substrate and dried to form a catalyst coating. The substrate was inserted into ethanol liquid (99.5% in purity) with the reaction space being filled with argon gas. The substrate was electrically heated to 1173 K for 10 min. Deposits on the substrate were analyzed with scanning electron microscopy and found to consist of wall-like structures with the unit of 10-100 nm in length, which is a typical feature of CNWs. The submarine-style substrate heating method will provide much simpler approach to the growth of CNWs.

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2P-34

Evolution of the DTA-TG curves as a function of sample mass containing LaC_2 nano-crystallites encaged in multi-shell carbon nanocapsules

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Abstract:

There has been great interest in the incorporation of metal elements into fullerenes, nanotubes, and fullerene-like multi-shell cage structures such as polyhedral multi-shell nanocapsules.

Polyhedral multi-shell nanocapsules containing La element were found for the first time in carbonaceous cathode deposits formed on the cathode surface in the conventional DC arc experiment for La fullerene formation [1, 2]. Electron diffraction (ED) revealed that the capsules were filled with LaC_2 single crystals, not La metals [2]. Transmission electron microscopy (TEM) characterization showed that the endohedral multi-shell nanocapsules were observed mostly in the cathode deposit, not in the fullerene soot on wall of the apparatus. Recently we reported that the endohedral multi-shell nanocapsules were obtained easily by vacuum heat treatment (1000 – 2200 °C) of La fullelene soot, which was prepared at special He pressure of 30-50 Torr [3].

It is well known that lanthanum carbide (LaC_2) is a water reactive and flammable solid. However, LaC_2 crystallites in carbon nanocapsules cannot react with water at room temperature, because water molecules cannot penetrate graphitic wall of nanocapsules. The presence of graphitic walls lowers reactivity of the encaged LaC_2 and shifts the combustion reaction of LaC_2 toward high temperatures [3]. Thus the combustion temperature of LaC_2 in carbon nanocapsules should be a good measure for estimating the toughness of the individual graphitic cages.

The toughness tests of carbon nanocapsules towards the combustion of LaC_2 are studied by simultaneous gravimetric and differential thermal analysis (TG-DTA) with a SEIKO TGDTA6300 apparatus. 0.4-1.6 mg of the sample is loaded in an alumina crucible and heated from room temperature to 930 °C (10 deg/min) in airflow (200 mL/min). We have revealed that the sample mass can significantly influence the results of TG-DTA data. The form of the signals in TG-DTA chart varies with the sample masses. For the sample masses above than 0.6 mg, one steep and sharp exothermic peak is observed on DTA curve, which is assigned as a runaway peak.

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2P-35

Chemical vapor deposition of BN-doped graphite thin films

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Graphene is one of the most promising materials as a constituent of future nanoelectronics because of the excellent electronic properties and chemical stability. Formation and tuning of a bandgap is crucial for electric applications of graphene. Doping of boron nitride, which has a large band gap, into graphene may be useful for the band gap tuning. CVD growth of BCN graphene films using a BN-containing feedstock has recently been reported [1]. Here, we report CVD growth of BN-doped graphene, using separated B- and N-containing feedstocks.

Doped graphene and graphite thin films were grown on a Ni film using the thermal CVD technique. Triisopropyl borate and benzylamine were the boron and nitrogen feedstocks, respectively. Both materials also served as a carbon feedstock, and we did not use any other carbon feedstock. In Raman spectra, the G, D, and G' bands were clearly observed, meaning that the films mainly consist of graphene. TEM observation also showed that graphene layers are formed on the Ni surface. Core-level x-ray photoelectron spectroscopy (XPS) measurements revealed that the film compositions are roughly expressed as $B_xC_yN_x$ ($0 \leq x \leq 0.15$). That is, B and N contents are close. The B, N, C 1s XP spectra of two films [samples 1 ($B_{0.12}C_{0.74}N_{0.14}$) and 2 ($B_{0.13}C_{0.72}N_{0.15}$)] are shown in Fig. 1. The results indicate that boron (nitrogen) atoms are predominantly bonded to nitrogen (boron). Despite the use of the separated B- and N-containing feedstocks, the films seem to mainly consist of graphene and boron nitride domains which are separated from each other.

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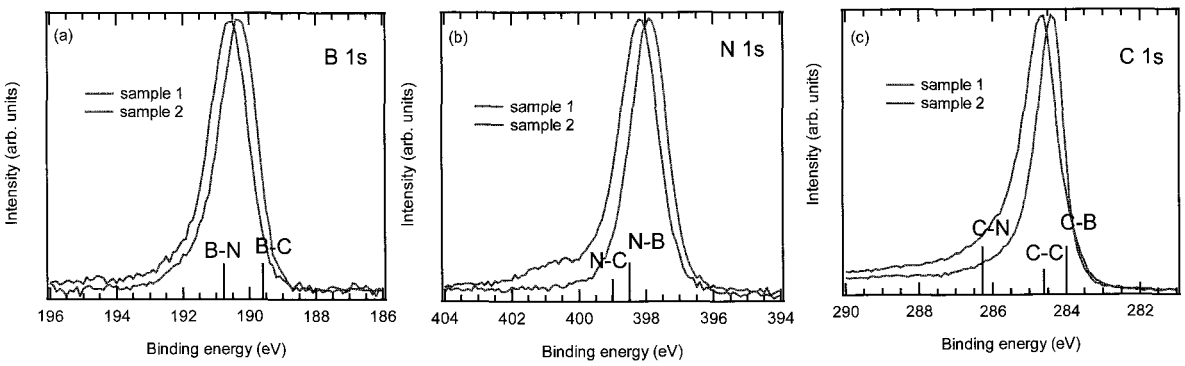

Fig. 1. (a) B, (b) N, and (c) C 1s XP spectra of two samples. Typical binding energy positions of are denoted in the figures.

2P-36

Theoretical Study of Aromaticity by Nucleus-Independent Chemical Shifts in Nanographenes

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The electronic structure of nanographene being fraction of a graphene sheet is of interest with respect to its aromaticity. In this work, a nanographene structure has theoretically been examined based on the DFT calculation (B3LYP/6-31G**). In particular, the NICS (nucleus-independent chemical shifts) values are employed for check of the aromaticity depending on the position of benzene-like ring.

A typical result is shown in Figs.1 and 2, where the markers are common in these figures. In Fig. 2 are shown the NICS values for the fictitious atom as the probe moving from the nanographene plane to 5 Å above in each position. Since the negative NICS value represents larger aromaticity, the center and the edge areas of this nanographene are more aromatic compared with others, signifying difference of the π-electron delocalization features.

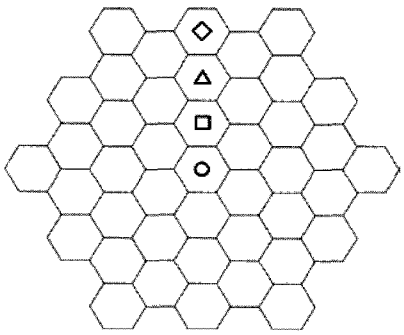

Figure 1. A nanographene structure with the armchair edge.

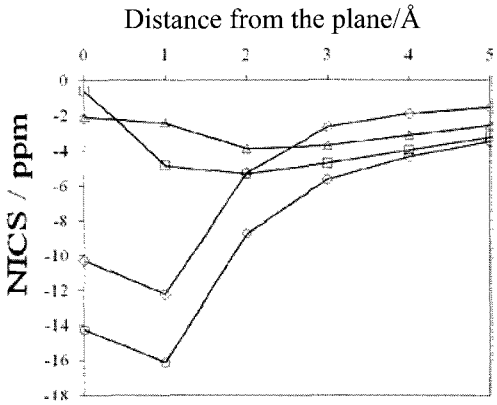

Figure 2. NICS results of the nanographene in Figure 1.

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2P-37

Comparison study on CVD synthesis of graphene using ethanol and dimethyl ether

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Graphene, a monolayer of carbon atoms arranged into a hexagonal lattice, has attracted great interest because of its unique structure and promising properties. [1] Chemical vapor deposition (CVD) is a powerful tool for large-scale and low-cost synthesis of nano-carbon materials. [2,3] However, comparable simple and controllable CVD growth of graphene remains a challenge. Herein, we demonstrate a facile and stable CVD method to synthesize graphene on a Ni film and compare the results obtained when using two different carbon sources: ethanol and dimethyl ether (DME).

Monolayer graphene was synthesized on Ni film by ethanol and DME without annealing gas or special cooling steps during CVD. To investigate the carbon source decomposition conditions in the CVD synthesis of graphene, gas-phase thermal decomposition of ethanol and dimethyl ether (DME) at low pressure and various temperatures was simulated using the chemical kinetic model. Temperature of CVD synthesis of monolayer graphene from DME is lower than that from ethanol, which is in agreement with predicted simulation results. Raman spectroscopy and scanning electron microscopy were used to characterize the synthesized and transferred monolayer graphene.

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2P-38

Direct Fabrication of Metal-Free Multilayer Graphene on Substrates

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Graphene attracts much attention for its significant electronic properties [1]. For its practical use, its fabrication is a crucial issue. Chemical vapor deposition (CVD) using metal films as catalysts is recently developed significantly [2,3]. When Ni [2] or Fe [3] are used as catalysts, carbon is dissolved in the catalyst by CVD at an elevated temperature and then graphene is precipitated from the catalyst by rapid cooling. However, CVD graphene has formed on much thicker metals and the control of its layer numbers is indirect. In CVD, the key process for graphene formation is the precipitation of graphene from carbon-metal solid solution. Based on this concept, we recently developed a novel method converting sputtered carbon into graphene by annealing and cooling of metal/carbon layers [4]. This method will realize more direct control over the layer numbers of graphene, but such graphene still has thick metals under it.

In this work, we developed a novel method yielding metal-free graphene directly on substrates. Graphene is precipitated from carbon-metal solid solution not by cooling [4] but by etching of metals at an elevated temperature. Briefly, C/Fe or Fe/C layers were sequentially deposited on SiO_2/ Si substrates by sputtering, set in a tubular quartz glass reactor, and reacted with 0.01 vol% Cl_2/ Ar at 5 Torr, 800 °C. Figure 1 shows typical scanning electron microscope (SEM) images with Raman spectra (inset) of the samples after annealing-cooling and after etching. Annealing-cooling process (a) converted sputtered carbon to graphene, in agreement with our previous report [4]. But annealing-etching process (b) yielded graphene with smaller D-band, which is possibly due to the graphene growth at a fixed temperature of 800 °C without decreasing temperature. Fe and C thicknesses were determined by XRF to be 0 and 19 nm, respectively, for the (b) annealing-etching sample which clearly shows metal free graphene. This method will provide a route for the direct formation of metal-free graphene patterns, simply by patterning the Fe/C layers.

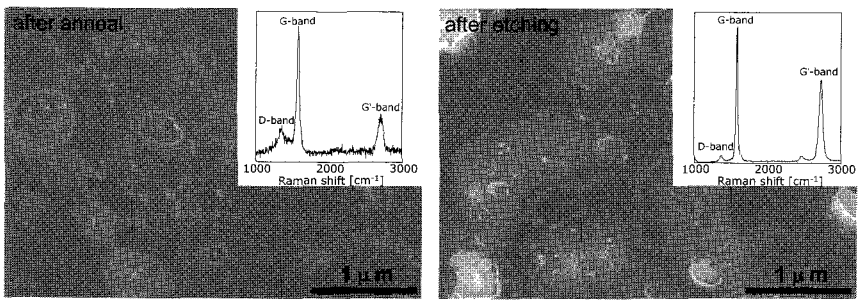

Fig. 1. SEM images of the surface at Fe/C = 2.07, inset is the representative Raman spectrum.

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2P-39

Energetics and Electronic Structure of Corrugated Graphene

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Graphene is now keeping in premier position in a constituent for the electronic devices in the post silicon era due to its perfectly planner structure and remarkable carrier mobility. Although, the technological advancing of graphene is rapidly, a little is known for the fundamental properties in its hybrid structures, such as structural undulation and interfaces with insulators/electrodes, those are essential in the device structures. Here, we investigate that the energetics and electronic structure of grapheme with structural corrugation with a period of about nano-meter scale based on the first-principles total-energy calculations within the framework of density functional theory (DFT). Our DFT calculation indicates that the energy cost for corrugation is found to be about a few tens meV per C atom indicating the possibility of structural undulation of graphene in ambient conditions. Under the corrugated structure, we find that the graphenes form tiny energy gap at the Fermi level. Furthermore, we also find that the conical structures of the conduction and valence bands are slightly distorted along parallel and normal to the corrugation.

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2P-40

Spatial Modulation of Electronic Structure of Graphene on Metal Surfaces

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Interaction between metal electrodes and graphene is one of fundamental factors to design the physical properties of graphene based nanoscale electronic devices. In particular, it is important to investigate how the metal electrode modulates the electronic structure of graphene as a function of a distance from an edge of the electrode. However, as far as our knowledge[1],fundamentals of electronic structure of graphene on metal electrodes are not addressed yet. Thus, we here investigate how the metal surfaces affect on electronic states of graphene by first principle total energy calculations. In particular, we investigate the spatial modulation on the electronic structure of graphene as a function of a distance from an edge of electrode (Au, Ag, Pd, and Pt). To give a theoretical insight, we consider a structural model shown in Figure. Above the metal electrode, local density of states (LDOS) for graphene is the same as that of graphene on metal surface.

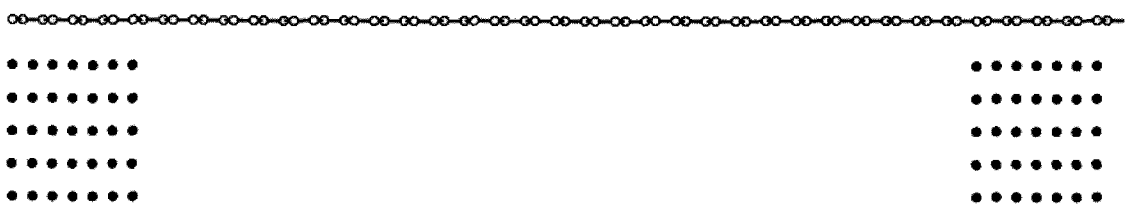

Fig. A structural model for graphene on metal surface. The gray circles and the black circles represent carbon atoms and metal atoms, respectively.

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2P-41

Raman Spectroscopic Study in a Bilayer Graphene Synthesized by Alcohol Chemical Vapor Deposition Method

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Graphenes have attracted wide interests from both fundamental physics and potential applications. The electronic band structure of a single-layer graphene has a characteristic linear and gapless dispersion at K point, which makes the electron to a massless Dirac fermion. The band structure of a bilayer graphene is strongly modified from a single-layer graphene because of the interaction between the layers depending on the stacking of the graphenes.

We investigated electronic band structure and interlayer interaction in graphenes synthesized by alcohol chemical vapor deposition (a-CVD) method [1] on the basis of microscopic Raman spectroscopy and comparison with a tight-binding (TB) theory. It was found that the number of layers in a-CVD graphenes was clearly identified by intensity ratio of G to 2D phonon peak and the linewidth of 2D phonon peak as well as exfoliated graphenes in the Raman spectra. The increasing of the intensity ratio with increasing number of layers indicates the interaction between each layer. We found that the strength of interlayer interaction of an a-CVD bilayer graphene is no more than one third the magnitudes of that of an exfoliated bilayer graphene from the detailed line shape analysis of 2D band of a bilayer a-CVD graphenes and TB theory.

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2P-42

All-carbon ferromagnetism derived from edge states in antidot-lattice graphenes

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Abstract: Ferromagnetism in carbon-based materials is controversial in contrast to traditional ferromagnets based on 3*d* or 4*f* electrons, because only *s* and *p* orbital electrons are present. The magnetic signals are also very small and the Curie temperature exceeds room temperature. In so many reports, appearance of ferromagnetism has been theoretically predicted in nano-graphite systems from viewpoints of edge-localized electrons and those spin polarization [1-3]. However, few independent observations have been reported to confirm the existence of ferromagnetic order in impurity-free carbon materials with high reproducibility, particularly in graphite [4, 5].

Here, we have studied electronic and magnetic behaviors of graphene nanoribbons (GNRs) in two material systems; (1) Low-defect GNRs fabricated by unzipping of CNTs with 3-stepped annealing [6] and (2) Antidot-lattice graphene (ADLG) with edges at hexagonal-shaped antidots [7]. In the poster, we present fabrication of monolayer ADLGs with hydrogen-terminated antidot edges by a non-lithographic method (i.e., using a nanoporous alumina template as etching masks). This allows exploration of the correlation of the edge electronic states with magnetism. We find appearance of room-temperature ferromagnetism derived from edge states of the antidots. The ferromagnetism changed to antimagnetic feature in ADLGs with oxygen terminated edges and disappears in bulk graphene without ADL. These prove presence of zigzag edge structure at the antidot edges and indicate importance of edge termination by foreign atoms. This finding must open a new door to all-carbon ferromagnetism and also (quantum) spin hall effect for novel spintronics devices.

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2P-43

Selective Edge Functionalization of Graphene by Room-Temperature Mild Plasma Treatment

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Graphene has recently received a great deal of attention because it possesses unique properties such as a linear energy dispersion relation and high carrier mobility. Graphene nano ribbons (GNRs), strips of graphene, are the counterparts of carbon nanotubes (CNTs) in terms of their all-semiconducting nature, and they could potentially solve the problem of the chirality dependence of the metal or semiconductor nature of CNTs in future nanoelectronics. The graphene edge structure is one of the most unique geometrical features of 2D graphene sheets; this is not seen in 1D CNTs. It has been theoretically predicted that, because of the narrow width of GNRs, their electronic state is strongly influenced by their edge structure. Thus, in order to obtain desirable properties for devices using GNRs, it is essential to be able to precisely control the edge structure and chemical terminations of GNRs.

In this study, we have developed a new type of functionalization and carrier doping method for graphene using a room-temperature NH_3 plasma gas phase reaction [1]. Evidence of the edge reaction and carrier doping was obtained by the detailed Raman mapping analysis and electrical measurement. The edge-functionalized graphene shows a pronounced D-peak only near the edge. The Dirac point position of the GNR device shifts to a negative gate-bias voltage direction after NH_3 plasma treatment. This is the first time that electrical data showing carrier doping and changes in edge Raman signatures have been observed in a correlate manner, suggesting that controlled room-temperature plasma reactions could be an important approach to doping without drastically perturbing the in-plane properties of graphene.

[1] Toshiaki Kato, Liying Jiao, Xinran Wang, Hailiang Wang, Xiaolin Li, Li Zhang, Rikizo Hatakeyama, and Hongjie Dai, Small, accepted.

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2P-44

Electronic structure and band gap control of graphene with holes

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Graphene is a good candidate material in future micro- and nanoelectronics because of the high electron mobility and its high stability. There are, however, some problems with using graphene widely to electronics. One of the fundamental problems is its lack of a band gap. In our previous studies [1,2], we have shown that periodic modification to graphene sheet introduces a band gap. Actually, some groups have demonstrated that a band gap is created in their graphene nanostructures with hexagonally packed holes (large atomic vacancies) [3,4]. With the development of fabrication technique, it would be possible to produce graphene with regularly spaced and size-controlled holes. In this work, we study the electronic structure as well as the total energy of graphene with regularly spaced holes (fig. 1) using the density-functional theory (DFT). Circular or hexagonal holes are periodically arranged in graphene sheet while the material keeps the symmetry of original graphene, D_{6h}. Carbon atoms at the edges of a hole are terminated by hydrogen atoms. Atomic configurations at the edges of a hole are found to be crucial to determine their energetics and substantial lattice relaxation takes place at armchair-edge regions. The material studied is predicted to be a direct-gap semiconductor. Band gap increases as a function of decreasing the neck width (edge-to-edge distance between two neighboring holes), which agrees qualitatively with the previous reports [4,5]. In this presentation, we will also discuss a scaling rule for the band gap values with a hole size itself and "hole density."

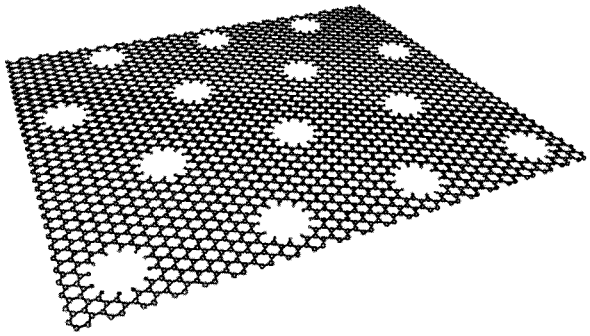

Figure 1: Overview of graphene with holes.

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2P-45

Density-Functional Tight-Binding Studies of Hexagonal Graphene Flakes

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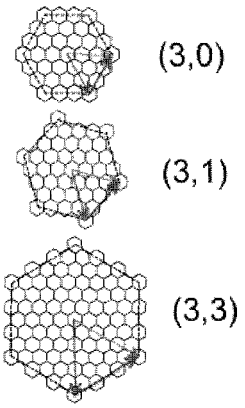

Figure 1. Definition of chiral vector in (n,m) HGFs.

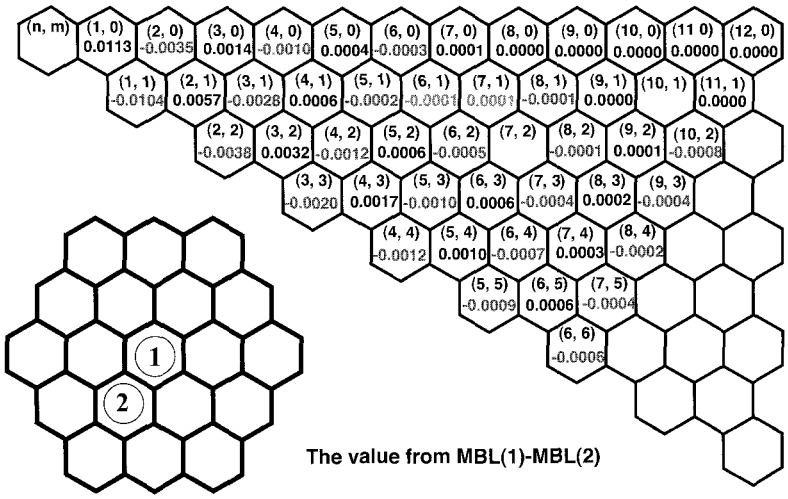

Figure 1: The MBL differences between the center ring and the second layer. (When the value is a positive number, the center pattern is Kekulé structure, when the value is a negative number, the center pattern is Clar structure.)

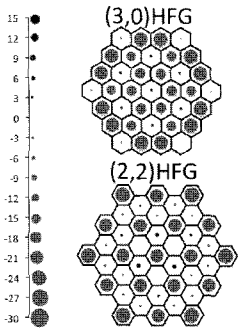

Figure 2: The NICS distribution of (3,0) and (2,2)

We theoretically studied bond length alternation (BLA) patterns in D_{6h}-hexagonal graphene flakes (HGFs), based on ring bond dispersion (RBD)[1] and mean bond lengths (MBL)[1]. We find structural Clar and Kekulé[1] patterns, breaking the bond equivalency of infinite graphene. MBL(1)-MBL(2) values predict that BLAs in zigzag-type (n,0) HGFs converge faster to graphite than armchair-type (n,n) HGFs (see Figure 1). Nucleus-Independent Chemical Shift (NICS) analysis confirms the existence of Clar or Kekulé patterns (see Figure 2). For the general (n,m) HGFs, we find the rule that when n+m is even, the Clar configuration dominates the electronic structures, and when n+m is odd, Kekulé dominates.

References:[1] F. J. Martín-Martínez et al, Org. Lett. 10 (2008) 1991

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2P-46

Morphology- and Position-Selective Growth of CNT Emitters on Glasses by Subsecond Heating Pulses

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To use carbon nanotubes (CNTs) in electronic devices such as field emitters, implementation of CNTs at specific position with controlled morphology is essential. Chemical vapor deposition (CVD) enables direct growth of such CNTs but has a main drawback in its high reaction temperature over a glass strain point ~ 500 °C. Extensive efforts have been made in lowering CVD temperature, however lower temperature results in exponentially smaller growth rate and longer growth time under Arrhenius' law. Here we propose an opposite approach: high temperature CVD in a short heating time tolerable for glasses. At the elevated temperatures ~ 800 °C, CNTs can grow to millimeter in height rapidly at several μm/s. This growth rate enables the implementation of CNT emitters in only 1 second or less. We previously demonstrated 1-second implementation of CNT emitters on glasses by a single current pulse [2].

This time, we improved the controllability of the emitter fabrication by using multiple current pulses and neck-patterned cathode lines. The cathode lines (Cr or Nb) with 0.1-0.3 μm thickness, 1-30 μm width and 10-200 μm pitch were formed on glass substrates by conventional electron beam lithography and sputtering processes. An Al_2O_3 buffer layer (20 nm) and a Fe catalytic layer (0.1-3.1 nm thickness) were subsequently sputtered on the cathode lines. The substrates were set in a tubular quartz glass reactor, and pulsed voltages (0.5-1.0 s) were applied to the lines under a gas atmosphere of 26 vol% H_2 / Ar for catalyst pre-annealing, and then under 0.5-1.0 vol% C_2H_2 / Ar at ambient pressure for CNT growth [1]. The combinatorial catalyst library [3] realized a variety of emitter morphologies and corresponding FE properties as shown in Fig. 1. A high current density (J) of 9 mA/cm^2 was recorded at an applied electric field (E) of 2.5 V/μm for the protruding VA-SWCNTs. The neck-patterned cathodes realized the position-selective heating and thus growth of CNT emitters owing to the higher resistivity of the neck than the other parts (Fig. 2).

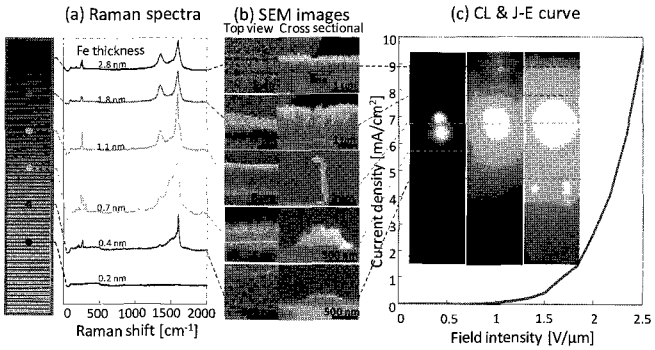

Fig. 1. A result of combinatorial FE measurement :(a) Raman spectra and (b) SEM micrographs recorded at specific positions, and (c) photographs of cathode luminescence and the obtained J-E curve.

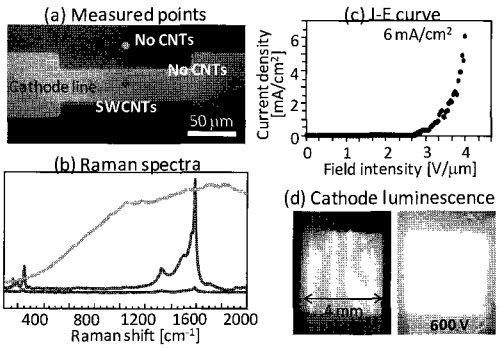

Fig. 2. (a) A SEM image of a necked cathode line, (b) Raman spectra recorded at three points indicated by different colors, (c) the J-E curve, and (d) images of cathode luminescence

[1] K. Hasegawa and S. Noda, *ACS Nano*, in press (2011). [2] K. Sekiguchi, et al,, 38th FNRS, 2P-39, Nagoya, Mar. 2010. [3] S. Noda et al., *Carbon* **44** (2006) 1414.

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2P-47

Highly-Efficient Synthesis of Nitrogen Atom Endohedral Fullerene by Controlling Fullerene and Plasma Ion Behaviors

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The nitrogen atom endohedral fullerene ($N@C_{60}$) is a spin active molecule with a long electronic spin coherence time, which makes it a promising candidate for a quantum computer [1]. Although $N@C_{60}$ has been studied over the last decade, its purity has been as low as 10^{-3} to 10^{-2} %. Therefore, the purpose of this research is to investigate the optimum condition for the high purity $N@C_{60}$ synthesis using a nitrogen radio-frequency (RF) discharge plasma under the external control of direct-current (DC) bias voltages applied to functional electrodes [2]. For this end, we examine the effects of substrate bias voltage (V_{sub}) and fullerene oven temperature (T_{ov}) on the $N@C_{60}$ synthesis, where V_{sub} can control the nitrogen ion (N_2^+) irradiation energy (E_i) to the fullerene.

Figure 1(a) shows dependences of the purity on V_{sub} with gas pressure (P_{N2}) as a parameter for RF power P_{RF}=500 W and T_{ov}= 850 °C. It is found that the purity has the maximum value at the optimum V_{sub} depending on P_{N2}. In addition, this optimum V_{sub} shifts to the negative direction with an increase in P_{N2}, which is considered to be caused by the collision of N_2^+ to neutral N_2 in order to keep the E_i of N_2^+ to C_{60} on the substrate. Based on these results, it is concluded that the suitable ion irradiation energy to C_{60} contributes to the highly-efficient synthesis of $N@C_{60}$. Furthermore, since the amount of the plasma ions irradiated to C_{60} increases with increasing P_{N2}, the reaction rate becomes high, and as a result, the purity increases.

Figure 1(b) presents dependences of the purity and C_{60} sublimation rate (R_{subli}) on T_{ov}. This result demonstrates the purity increases with an increase in T_{ov}, which implies that the nitrogen presumably does not enter into the C_{60} until 700 °C, although the evaporation of C_{60} and the ion irradiation energy are enough to synthesize $N@C_{60}$. This is because the C_{60} sublimates in an aggregation form and C_{60} thermal expansion is low. Therefore, high T_{ov} is an important factor for the synthesis of $N@C_{60}$ in high purity.

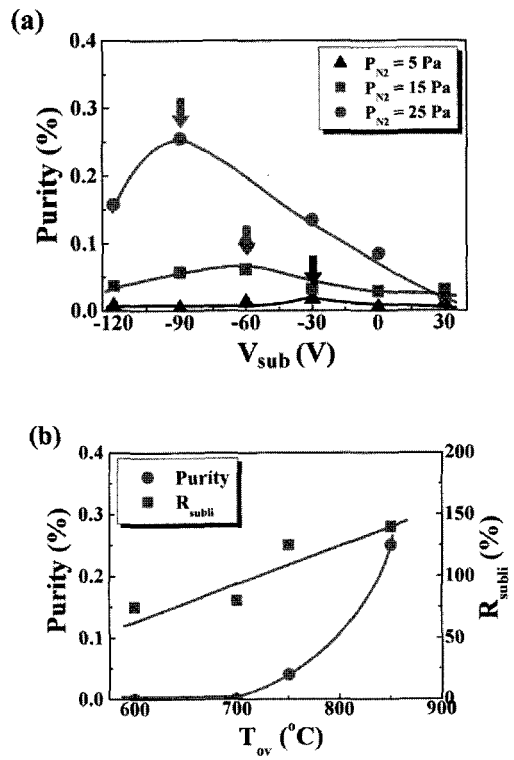

Fig. 1. (a) Purity as a function of V_{sub} and (b) purity and sublimation rate R_{subli} of C_{60} as a function of T_{ov} for V_{sub}= -90 V and P_{RF}= 500 W.

[1] W. Harneit: Phys. Rev. A **65** (2002) 032322.

[2] S. Miyanaga, T. Kaneko, H. Ishida, and R. Hatakeyama: Thin Solid Films **518** (2010) 3509.

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2P-48

Synthesis of Nickel Atom Endohedral Fullerene Using Plasma Ion Irradiation Method with Electron Beam Gun

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Although many kinds of endohedral fullerenes have been reported, a nickel atom endohedral fullerene (Ni@C_{60}) which is expected to make a single molecular magnetic device focusing on its magnetic moment [1] has never been synthesized until now. Using a plasma ion irradiation method, we have succeeded in synthesizing the Ni@C_{60}, where plasma ions generated by an electron cyclotron resonance discharge are irradiated to the fullerene which is previously formed [2]. This time, in order to efficiently synthesize the Ni@C_{60}, we adopt the plasma irradiation method with an electron beam gun.

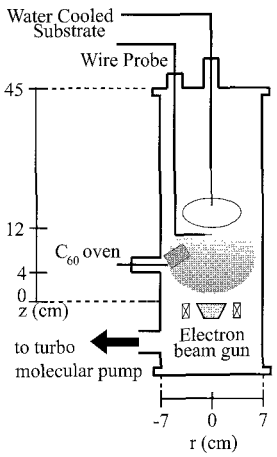

Fig 1 : Experimental apparatus.

An experimental apparatus is shown in Fig. 1. In this experiment, nickel atoms are evaporated and ionized using the electron beam gun. C_{60} molecules from an oven are sublimated to a substrate terminating the plasma, and the nickel ions are irradiated to the C_{60} molecules.

An ion current flowing into the substrate as a function of electron beam current (I_{EB}) is presented in Fig. 2, where a voltage of the substrate is constant (= –50 V). The ion current dramatically increases with increasing I_{EB}. Figure 3(a) shows a mass spectrum of the sample deposited on the substrate. A calculated isotope distribution of the Ni@C_{60} is presented in Fig. 3(b), and coincides with the distribution of the mass spectrum of the sample on the substrate. Therefore, we can conclude that the sample indicates the existence of the Ni@C_{60}.

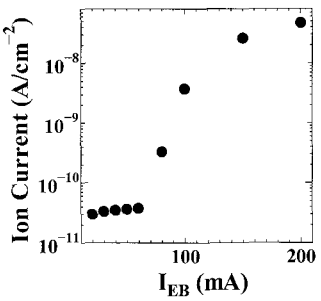

Fig 2 : An ion current into the substrate as a function of I_{EB}.

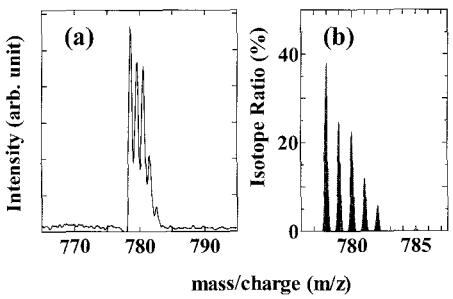

Fig 3 : (a)A mass spectrum of the sample deposited on the substrate. (b) An expected isotope distribution ratio of the Ni@C_{60}.

[1] J. L. Li *et al.*, Appl. Phys. Lett. **96**, 233103 (2010)
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2P-49

Transport Mechanisms in Single-Wall Carbon Nanotube Networks formed by Controlled Content-ratio of Metallic and Semiconducting Types

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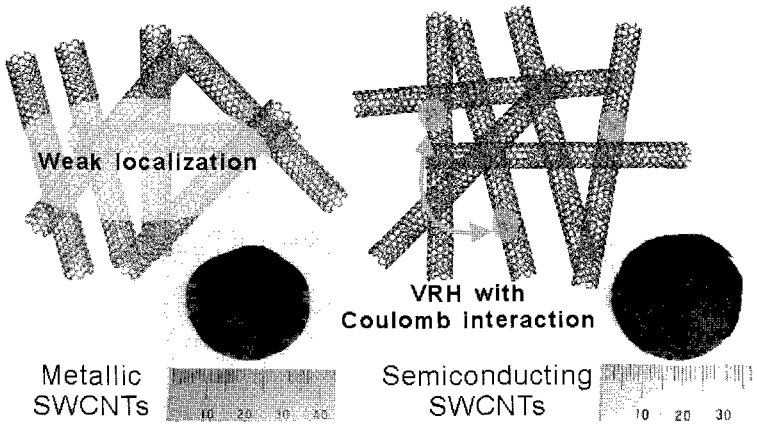
1. Tokyo Metropolitan University, 2. Riken, 3. Waseda University, 4. AIST, 5. JST-CREST

Abstract: A fundamental understanding of the conduction mechanisms in single-wall carbon nanotube (SWCNT) networks is crucial for their use in thin-film transistors and conducting films. However, the uncontrollable mixture state of metallic and semiconducting SWCNTs has always been an obstacle in this regard. We revealed that the conduction mechanisms in nanotube networks formed by high-purity metallic and semiconducting SWCNTs are completely different.[1] Quantum transport was observed in macroscopic networks of pure metallic SWCNTs. However, for semiconducting SWCNTs networks, Coulomb-gap-type conduction was observed, due to Coulomb interactions between localized electrons. Crossovers among a weakly localized state and strongly localized states with and without Coulomb interactions were observed for transport electrons by varying the relative content of metallic and semiconducting SWCNTs. Moreover, the dimensions of the hopping conduction become low as the content of metallic SWCNTs in the networks is decreased. We discuss here the detailed mechanisms of these conduction changes. It was found that hopping barriers, which always exist in normal SWCNT networks and are serious obstacles to achieving high conductivity, were not present in pure metallic SWCNTs networks.

This work was partially supported by a Grant-in-Aid for Scientific Research on Innovative Areas (No.21108523, "π-Space") from MEXT, and by Industrial Technology Research Grant Program in 2007 from NEDO.



References: [1] Yanagi, Udoguchi, *et al.*, ACS Nano **7** 4027-4032 (2010)

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2P-50

The shortest nano-peapods: Complexation of fullerenes with cycloparaphenylenes

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Host-guest chemistry for fullerenes has attracted much interest because of the great promising applications such as selective extraction and chemical functionalization. Recently, the group of Itami has reported the modular and size-selective synthesis of [*n*]cycloparaphenylene ([*n*]CPP) (**Figure 1**), the shortest single-wall carbon nanotubes with chiral index of (*n*,*n*).[1] The successful synthesis of these intriguing molecules has motivated us to produce a new complex of CPPs with fullerenes, which can be regarded as "the shortest nano-peapod".

Here we demonstrate the complexation of fullerenes with CPPs. The complexation was confirmed by using ^{1}H NMR (**Figure 2**). For example, the ^{1}H NMR spectrum of [12]CPP in $CDCl_3$ exhibits a sharp peak at 7.58 ppm for the aromatic protons. On the other hand, the spectrum of a solution of [12]CPP and fullerene mixtures shows a broad peak at 7.65 ppm. This peak shift suggests the formation of a host-guest complex of [12]CPP with fullerenes. Furthermore, the mass spectra imply the enrichment and partial separation of metallofullerenes after the complexation. We believe that the CPP-fullerene complexation should provide a method for selective extraction of metallofullerenes. In the presentation, we will discuss the fullerene-cage and encapsulated-metal dependent interactions between CPPs and fullerenes.

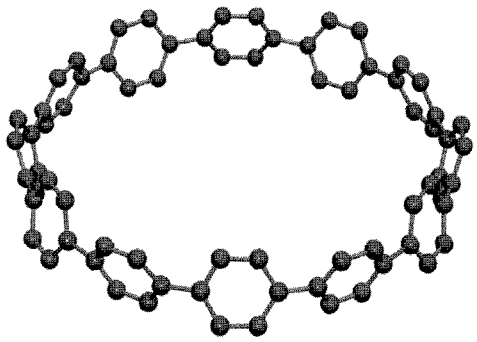

Figure1. Image of [12]CPP, the shortest (12,12) single-wall carbon nanotube.

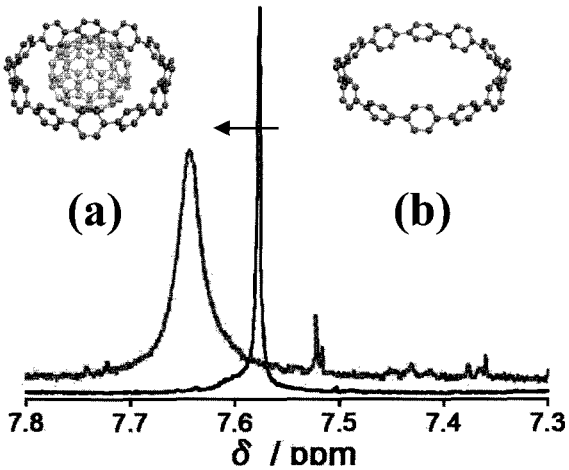

Figure2. ^{1}H NMR spectra of CPP (a) with and (b) without fullerene mixtures.

Reference: [1]. H. Takaba *et al.*, ***Angew. Chem. Int. Ed.*** 48, 6112 (2009). H. Omachi *et al.*, ***Angew. Chem. Int. Ed.*** 49, 10202 (2010). Y. Segawa *et al.*, ***Angew. Chem. Int. Ed.*** 50, in press (2011).

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2P-51

Femtosecond Coherent Phonon Spectroscopy of Single-walled Carbon Nanotubes in Different Environments

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The interactions between single walled carbon nanotubes (SWNTs) and proteins, charge transfer between them in particular, have not yet unveiled, although they are important physical process to realize medical applications, such as drag delivery [1] and biosensors [2]. In this study, a femtosecond pump-probe impulsive Raman measurement was employed to elucidate the charge transfer by observing ultrafast dynamics of radial breathing mode (RBM) of SWNTs. The samples were sodium dodecyl sulfate (SDS)-suspended SWNTs at pH = 3-7 and protein (lysozyme, hemoglobin, and pepsin)-suspended SWNTs in aqueous solutions.

The coherent RBM spectra for SDS-SWNTs at pH = 3-7 are shown in Figure 1. Mainly two peaks at 6.4 THz from (13, 2) tubes and at 7.2 THz from (12, 1) tubes are observed. As the value of pH increases, the ratio of the intensity of the lower mode to the higher mode increases. This enhancement is attributed to the change in electron-phonon interaction [3] as well as the modification of condition of Raman scattering, both of them are caused by charge transfer between SWNTs and protons [4]. Figure 2 shows the coherent RBM spectra for proteins-SWNTs conjugates, in which the dependence of the spectra on the proteins is clearly observed. We attributed the origin of this dependnece to not only charge transfer, but also difference in the conformation of proteins.

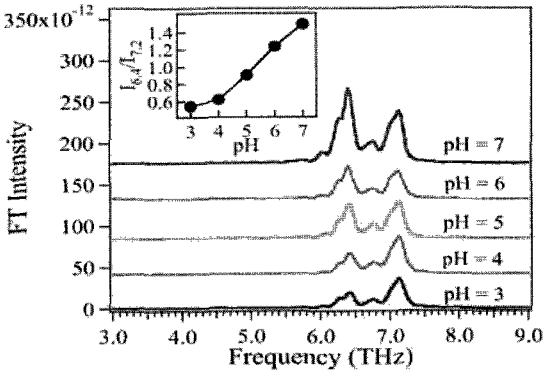

Fig. 1. The coherent RBM spectra of SDS-SWNTs at pH = 3-7. The inset shows the ratio of the intensities of main twe peaks.

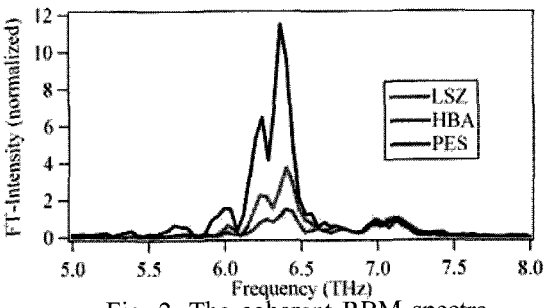

Fig. 2. The coherent RBM spectra of proteins–SWNTs conjugates.

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[2] A. Star, J. P. Gabriel, K. Bradley, and G. Gruıner. *Nano Lett.* **3**, 459 (2003)
[3] K. Makino, A. Hirano, K. Shiraki, Y. Maeda, and M. *Hase, Phys. Rev. B*, **80**, 245428 (2009)
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2P-52

Crystallographic features of graphene on SiC (0001)

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Graphene is a one-atom-thick carbon material, having a hexagonal honeycomb lattice. Graphene has an extremely high electronic mobility, in addition to anomalous electronic properties as a two-dimensional material, which raises hopes for its use in next-generation semiconducting devices. Although graphene is a promising material, some of the problems are left now. One of them is that the development of the mass production method of large-area and homogeneous graphene is required. The other is that graphene has no bandgap. In order to solve these problems, graphene produced by thermal decomposition of SiC attracts attention. By annealing SiC single-crystal in a vacuum or in an Ar atmosphere, Si atoms are removed from the surface, and then remaining C atoms form graphene spontaneously. In this study, we investigated the crystallographic features of graphene layers on SiC (0001) using high-resolution transmission electron microscopy (HRTEM).

Graphene-on-SiC samples were prepared by annealing on-axis and 4° off-axis SiC (0001) substrates at 1350~1450 °C. Thin specimens for observation were obtained by Ar-ion thinning method. Observations were carried out using JEM-2010-, JEM-2010F-, and EM-002B-type transmission electron microscopes (TEM) at an accelerating voltage of 200 kV.

First, we investigated the formation mechanism of graphene on SiC to find a clue toward the mass production method. Our TEM study suggests the following mechanism [1]. Initially, nucleation of graphene occurs at SiC steps, covering them with a few layers. These curved graphene layers subsequently grow over the terrace region. And the growth is occasionally pinned by lattice defects of the SiC substrate.

Next, an investigation using HRTEM showed that the stacking sequence of several layers of graphene exhibited an ABC-type stacking [2]. It did not depend on the stacking sequence of the SiC substrate. Although the stacking became disordered around the step of SiC, ABC-stacking was always observed on the terrace. Based on the previous theoretical reports, ABC-stacked graphene layers give rise to the electric-field-induced bandgap opening [3]. Thus, our present studies would be a key to overcome difficulties for graphene application.

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2P-53

Substituent Effects on the Reductive Functionalization of SWNTs

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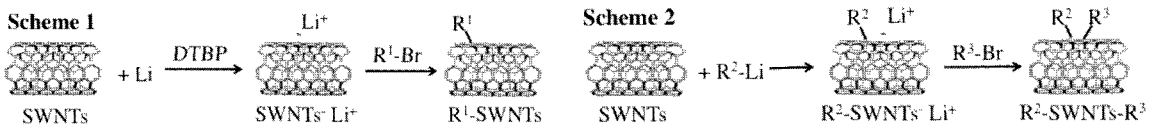
Single-walled carbon nanotubes (SWNTs) would have potential use in applications because of their excellent mechanical and electrical properties. The functionalization of SWNTs, strongly affects their solubility and electrochemical properties, is a current subject of intense researches. Billups *et al.* reported that reductive alkylation of SWNTs using lithium and alkyl halides occured in liquid ammonia to give alkylated SWNTs *via* an electron-transfer process. We reported two-step alkylation of SWNTs using alkyllithiums and alkyl halides. It is important to control the functionalization of SWNTs because the degree of the functionalization affects electric properties of SWNTs. Herein we present the substituent effects on reductive alkylation of SWNTs by which the degree of the alkylation can be controlled.

Reactions of SWNTs with lithium and alkyl halides (R^1Br) in the presence of 4,4'-di-*tert*-butylbiphenyl (DTBP) under argon gave alkylated SWNTs (R^1-SWNTs) (Scheme 1). Two-step alkylation (R^2-SWNTs-R^3) was conducted by addition of alkyllithium (R^2Li) and alkyl bromide (R^3Br) under argon (Scheme 2). The functionalized SWNTs obtained were characterized on the bais of their *vis*-NIR / Raman spectra and SEM and thermogravimetric analyses. The result showed the degree of functionalization of SWNTs was controlled by substituents. This might be explained by the steric repulsion between an initially introduced group on SWNTs and an alkyl group to be introduced secondary and reactivity of the corresponding radical species.



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2P-54

Generalized Preparation Method of the Catalyst for Single-Walled Carbon Nanotube Forest Growth from Various Iron Compounds

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Currently, catalyst for vertically-aligned SWNT forest growth was limited to only pure metal [1]. However, from application point of view, development of novel catalyst material might be a promising approach for the development of more economical or structure-controlled SWNT forest growth method. In this study, we surveyed the possibility of various iron-containing materials such as iron nitrate, iron chloride, and bucky ferrocene for the catalyst of SWNT forest growth.

Various iron-containing materials were deposited on sputtered Al_2O_3 layer by spin-coating or bar-coating, and introduced water-assisted CVD furnace. Vertically-aligned SWNT forests were successfully grown from every catalyst (Fig. 1). Unexpectedly, average diameters of all SWNT samples were in the narrow range of 2.8-3.1 nm. Suggestive evidences including XPS, AFM, and SEM-EELS observations indicated that Fe atoms contained in every deposited iron compound diffused into sputtered Al_2O_3 layer under annealing in H_2 ambient, resulting in the formation of Fe nanoparticle on sputtered Al_2O_3 layer with high density and, thus, the growth of SWNT forest with an average diameter around 3 nm in C_2H_4 ambient (Fig. 2). As a summary, present result showed the possibility that any iron-containing material can be used as the catalyst for SWNT forest growth.

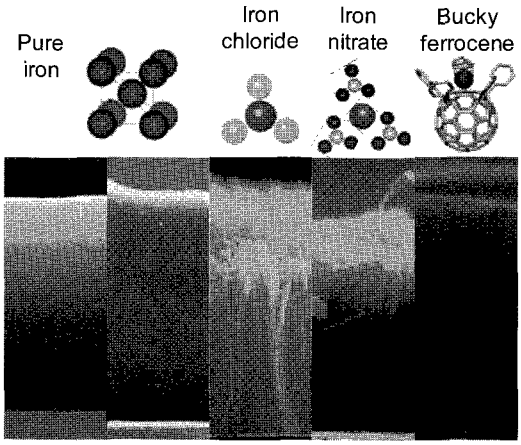

Fig. 1: SEM images of SWNT forest grown from various iron compound materials.

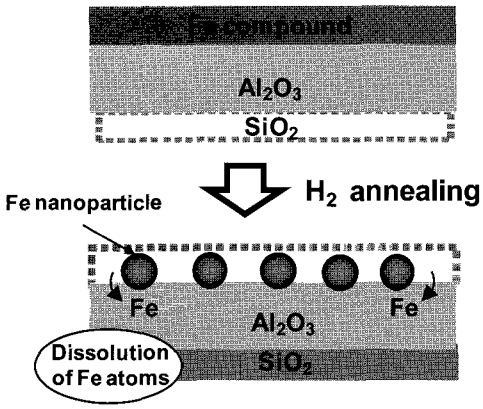

Fig. 2: Schematic representation of the Fe nanoparticle formation during annealing

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3P-1

Resonance Rayleigh scattering spectroscopy of CNTs grown on a tapered optical nanofiber

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Resonance Rayleigh scattering (RRS) spectroscopy is one of the effective methods to investigate the electronic transition of single wall carbon nanotubes (CNTs) [1] [2]. However, in the previous study, observed range is limited to higher order optical transitions because of experimental difficulties.

Then, we have developed a novel technique to study RRS of CNTs in the fundamental excitonic transitions range (~below 1.3eV) using CNTs grown on the tapered optical nanofiber [3], whose diameter is less than the wavelength of the light, and bright broadband super continuum light source (Super-luminescent diode). The advantage of this system is the reduction of background light. Only spontaneous emission of adjacent nanotubes can be channeled into the guided mode of a tapered optical nanofiber.

We observed the RRS spectrum whose linewidth (~1meV) is fairly narrower than the luminescence linewitdh (Figure 1). This difference may be related with the relaxation process after excitation. The intensity of RRS spectra strongly depended on the polarization of excitation light. They were also affected by the temperatures, molecular adsorption, and applied magnetic field.

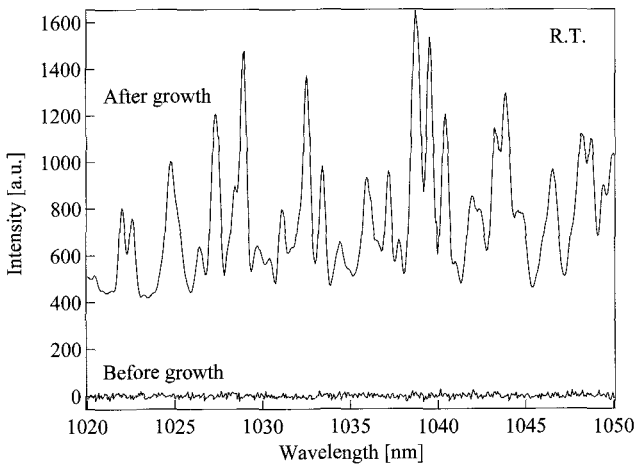

FIGURE 1. Resonant Rayleigh scattering spectrum of carbon nanotubes on a tapered fiber (Upper) and the reference spectrum (Lower).

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3P-2

Photoemission spectroscopy of double-walled carbon nanotubes based on host metallic SWCNTs

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Abstract: Double walled carbon nanotubes (DWCNTs) are an interacting material consisting of two sub systems of inner and outer single walled carbon nanotubes (SWCNTs). Particularly, the electronic structure of DWCNTs has been expected to substantially differ from the simple superposition of those of the inner and outer SWCNTs due to the intershell interaction [1]. Photoemission spectroscopy (PES) is a powerful tool to investigate the electronic structure of valence band in solid. Therefore, PES of DWCNT bundles have been reported previously [2]. However, the DWCNT bundles studied consisted of various sets of inner and outer tubes which can be semiconducting or metallic SWCNTs. Here, we report a PES study on DWCNTs in which high-purity metallic-SWCNTs (m-SWCNTs) were used as the outer SWCNTs. The m-SWCNT-enriched DWCNTs were synthesized from m-SWCNTs by heating SWCNTs after filled with C_{60}. In the following, this type of DWCNTs, having metallic outer tubes, is abbreviated to "m-DWCNTs". The starting buckypaper of m-SWCNTs were prepared by using density gradient ultracentrifugation technique. High-resolution PES experiments were performed at Hisor BL1. Figure 1 shows photoemission spectra of m-DWCNTs along with that of m-SWCNTs for comparison. Spectra are normalized by the number of C atoms. M1 peaks around 1 eV originate from the 1D Van Hove singularity of SWCNTs. The spectrum of m-DWCNTs is almost similar to that of m-SWCNTs, but we found that the M1 peaks slightly shifted. The result suggests the occurrence of charge transfer from the outer tubes to the inner tubes.

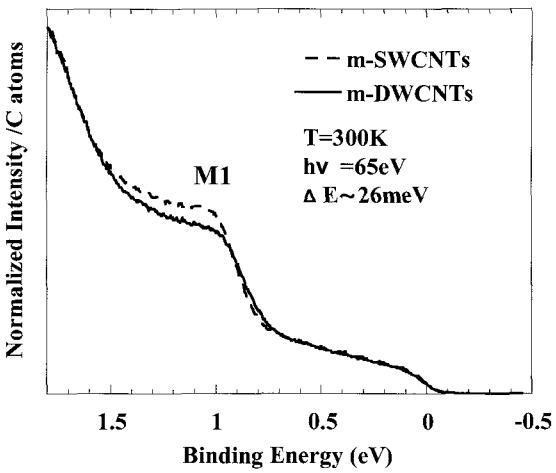

Figure.1

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3P-3

Computational Chemistry Study of the Interaction between Single-walled Carbon Nanotubes and Polysaccharides

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Abstract: In pristine single-walled carbon nanotubes (SWNTs), there exist SWNTs with multiple chirality structures. The optical properties of SWNTs, such as UV-vis-NIR absorption/ photoluminescence (PL) and resonance Raman, are strongly correlated with the chirality, as summarized in Chirality map[1]) and Kataura plot [2]) as a function of tube diameter or chiral angle. From our selective chirality separation study for the SWNTs individually dispersed in aqueous solution with density gradient ultracentrifugation (DGU) technique using polysaccharides as dispersants, the resulting optical properties revealed that the specific interactions existed between polysaccharides and the SWNTs with peculiar chiralities.[3-5]) Thereof, when chitosan was used in the DGU experiments, the (9, 4) and (7, 6) chiralities SWNTs were collected.Furthermore, when carboxymethylcellulose (CMC) was used in the DGU experiments, the (8, 5), (9, 6), (8, 6), and (9, 7) chiralities SWNTs were collected.

The objective of this paper is to gain an insight into the specific interactions between the polysaccharides and the SWNTs with peculiar chiralities on the basis of the molecular dynamics (MD) simulations in water, taking the tube diameter or chiral-angle as parameters. The MD calculation was carried out using a software of *Accelrys Discovery Studio 2.1* with a molecular force field potential of *CHRAMm* under the conditions of time interval of 1 fs and periodic boundary conditions. Firstly, molecular structures were optimized, then annealing 0 K → 1000 K → 300 K was performed in 17 ps (temperature gradient is ±0.1 K/fs.), and finally equilibration at 300 K in 1.5 ns was carried out at *NVT* ensemble.

As a result, it was found that although either chitosan or CMC intrinsically assumes an extended linear conformation in water, both the SWNTs complexes with the polysaccharides at stable energy states form the wrapping structures with the helical conformations of the polysaccharides. Essential intermolecular force between the polysaccharides and SWNTs was predicted to be originated from CH-π interaction. The chiralities of SWNTs involved in the specific interactions with each of the polysaccharides were able to be simulated.Consequently, it was inferred that chitosan specifically interacts with the semiconductor chiral-SWNTs with a similar diameter, whereas CMC strongly interacts with the metal and/or semiconductor chiral-SWNTs with a similar chiral-angle.

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3P-4

Macroscopic Wall Number Analysis of Single-walled, Double-walled, and few-walled Carbon Nanotubes by X-ray Diffraction

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For nanocarbon materials, as represented by carbon nanotubes (CNTs) and graphene, the number of layers (graphene shells or layers) is a fundamental structural parameter and many physical and chemical properties depend on the number of layers. This is particularly true for nanocarbon materials composed of few (~5) layers because this region is far from the 3-D bulk limit (i.e. nanofibers or bulk graphite). Wtihin this region the properties can greatly change as exemplified by the semiconducting behavior of single-walled carbon nanotubes and the metallic behavior of multiwalled carbon nanotubes. Therefore, identifying the wall number of CNTs is paramount in understanding their properties and applying them toward the appropriate applications. Currently, only transmission electron microscopy has been the standard method for wall number analysis for CNTs.

Here, we have focused on the (002) peak of the XRD pattern to develop a simple macroscopic method to determine the average wall number of CNTs in the range of SWNTs to few-walled MWCNTs. The key was the finding that the (002) peak could be decomposed into two basic components: the intertube structure (outerwall contacts) and the intratube structure (concentric shells). Wall number estimation became possible because the contribution of the intertube structure to the (002) peak increased linearly with wall number while the contribution of the intratube structure did not.

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3P-5

Dielectric Environment Effect on the Electronic States of (*n,m*) Single-Walled Carbon Nanotubes

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The redox properties (i.e. electronic densities, the Fermi levels, redox potentials) of single-walled carbon nanotubes (SWNTs) are related to the structures of SWNTs that have a specified diameter and chiral angle uniquely related to a pair of integers (*n,m*); the so-called chiral index. Electronic structure, one of the most fundamental features of SWNTs, also strongly depends on their diameter and chirality.

Here we report the finding that the electrochemical band gaps (E_g^{electr}) of (*n,m*)SWNTs are strongly affected by the change in dielectric environments around the isolated SWNTs. In situ photoluminescence (PL) spectroelectrochemistry[1] of the films containing isolated SWNTs cast on ITO electrodes was completed in several organic solvents and then the oxidation and reduction potentials, E_g^{electr} and Fermi levels of the individual (*n,m*)SWNTs in the solvents were determined. We discovered that the E_g^{electr} of the (*n,m*)SWNTs become greater as the solvent dielectric constants decreased, which is in sharp contrast to the optical band gaps that show virtually no solvent dependence.[2] Moreover, the states of the π-electrons in the SWNTs were evaluated from the dependence of the band gaps on the diameter of the SWNTs. The present study provides useful information for a deep understanding of the fundamental electronic properties of isolated (*n,m*)SWNTs in solvents.

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3P-6

Systematic First-Principles Study of Single-Walled Carbon Nanotubes with Helical-Symmetry Operation

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Many experimental and theoretical works of carbon nanotubes (CNTs) discussing the fundamental physics aspects and/or their possible applications have been reported so far. According to the study using the tight-binding approximation, their electronic structures depend on their diameter and chirality [1]. In addition, it has been pointed out from the first-principle electronic-structure calculations with structural relaxation that their electronic structures also depend sensitively on their geometrical parameters such as bond lengths and bond angles [2,3]. On the other hand, the synthesizing technique with the precise diameter and chirality control of CNT has not been established yet. Hence, the accurate measurements of not only the electronic properties but also the geometrical parameters of CNTs have been reported scarcely so far. Because it is very important to know the accurate electronic properties of CNTs for any possible electronic application, the first-principles calculations with the structural relaxation for CNTs should be of high importance. Recently, however, some interesting studies were reported and it has been reveled that near-armchair CNTs are relatively abundant in yield CNT samples [4,5]. In addition, the energetics of very thin nanotubes implies that the near-armchair nanotubes are energetically more favorable than armchair and zigzag nanotubes [3]. Therefore, the experimental measurement of the geometrical parameters and the electronic properties of near-armchair nanotubes may be achieved in the near future.

In the present work, we systematically study the geometries, electronic properties and energetics of isolated single-walled carbon nanotubes in the framework of the density functional theory (DFT). The diameters of the studied CNTs are in the range from 0.68 nm to 1.0 nm. The studied CNTs include (6,5) and (7,5) which are known to be the most abundant CNTs in some samples. Because of the huge number of atoms in the translational unit cell, the systematic first-principles studies have not been reported for these nanotubes. We adopt the real-space DFT computational code with helical-symmetry and the rotational symmetry. By using this method, we can handle all of the nanotubes in the same computational cost in principle. We discuss the influences of the structural relaxations on the geometrical parameters and the electronic properties. Moreover, we compare the total energy of the various optimized CNTs and examine the energetical favorability of the near-armchair nanotubes.

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3P-7

Structural Stability and Electronic Manipulation of Nitrogen-doped Carbon Nanotube

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Carbon nanotube (CNT) has been received much attention since it shows unique electronic properties such high carrier mobility, suggesting the possibility of realization of novel electron-device applications in carbon-based nano-electronics. For developments of CNT-based devices, a strict control of the electronic properties such as carrier type and carrier density is vital. Nitrogen doping is one of the most accessible means to tailor electronic properties of CNT. Nitrogen-doped CNTs have been synthesized experimentally and the existence of pyridine-type defects in N-doped CNTs has been reported [1]. Theoretical calculations has revealed that the electronic properties of pyridine-type defect in N-doped (10,0) CNT shows *p*-type semiconducting property [2]. Actually, the experimental electrical transport properties of N-doped CNT are reported to show the *p*-type behavior although N-doping is expected to induce *n*-type carrier [4]. For construct complex electronic devices with logic operations, it is essential to realize the functionalized CNTs that provide *p*-type and *n*-type conductions.

The impurity defect is generally expected to serve as a reactive site and the adsorption of several molecules would cause the change in the electronic structure. In this work, we investigate effects of the hydrogen adsorbed on the N-doped CNT using first-principles density-functional calculations. In the presentation, we will show that the electronic structures of N-doped CNT change dramatically depending on the number of hydrogen atoms adsorbed on N-doped CNT and also discuss the energetics of the hydrogen adsorption on the N-doped CNT.

This work was partly supported by grants-in-aid from MEXT Japan through Global Center of Excellence Program of Nanoscience and Quantum Physics of Tokyo Institute of Technology.

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3P-8

Kekulé Structures and HOMO-LUMO Gaps of Armchair Carbon Nanotubes with Finite Length

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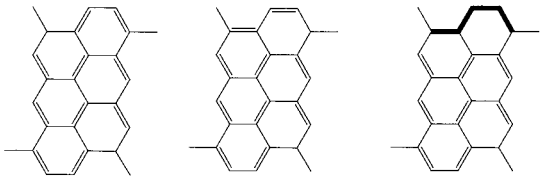
An interesting aspect of finite-length carbon nanotubes (CNTs) is the quantum finite-size effects of the energy gap between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO). It has been shown that the HOMO-LUMO gaps of zigzag CNTs oscillate with an odd or even number of hexagons in the circular plane of the nanotube [1]. It is known that for the armchair CNT, the HOMO-LUMO gaps show the oscillation depending on the number of carbon layers in the tubular length axis. The number of Kekulé structures (K) is an excellent index for the stability of benzenoid hydrocarbons. However, for conjugated polycyclic non-benzenoid structures, the algebraic structure count (ASC) should be used. The ASC for a conjugated molecule G is closely related to the constant term $a_N(G)$ in the characteristic polynomial for G:

absolute value of $a_N(G)$ = square of ASC(G)

If the algebraic structure count (ASC) is zero, then the molecule's pi-system has non-bonding molecular orbitals.

The size of the peripheral circuits in armchair $(n,n)_m$ CNT is 4n. So ASC should be used for the study of HOMO-LUMO gap in armchair $(n,n)_m$ CNT. Here m stands for the number of layers in CNT. For example, as shown in Fig. 1, the superposition of two Kekulé structures K_1 and K_2 for $(1,1)_3$ CNT produces one 4-membered circuit and so K_1 and K_2 possess opposite parities. We found that in the case of $(1,1)_m$ CNT, ASC=1 for m=1, ASC=1 for m=2, ASC=0 for m=3, and in the case of $(2,2)_m$ CNT, ASC=5 for m=1, ASC=13 for m=2, ASC=0 for m=3. Thus we showed that the HOMO-LUMO gaps in $(1,1)_m$ and $(2,2)_m$ CNT are zero if the number of layers m is 3.



K_1 K_2 K_1+K_2

Fig. 1 Superposition of two Kekulé structures K_1 and K_2 for $(1,1)_3$ CNT

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3P-9

Transport property of hydrogen adsorbed carbon nanotube : first-principles density functional study

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Carbon nanotubes (CNTs) are expected to be suitable for nano-device applications. For an example, FETs (Field effect transistors) made of CNTs are expected to have good performance for both speed and size compared with conventional FETs. Studies of defects and impurities in CNTs are necessary since they have crucial effects on electron transport properties of CNTs [1,2]. We study electronic structure and electrical transport property of hydrogen adsorbed CNTs using first-principles non-equilibrium Green's functional method implemented in OpenMX code [3].

We have investigated electron transmission of hydrogen adsorbed (6,0) CNT (Fig.1(a)) with pure (6,0) CNT leads. Our results indicate that electron transmission is significantly affected by hydrogen adsorption (Fig. 1(b)). We will discuss the hydrogen coverage dependence and current-voltage characteristics of hydrogen adsorbed CNTs.

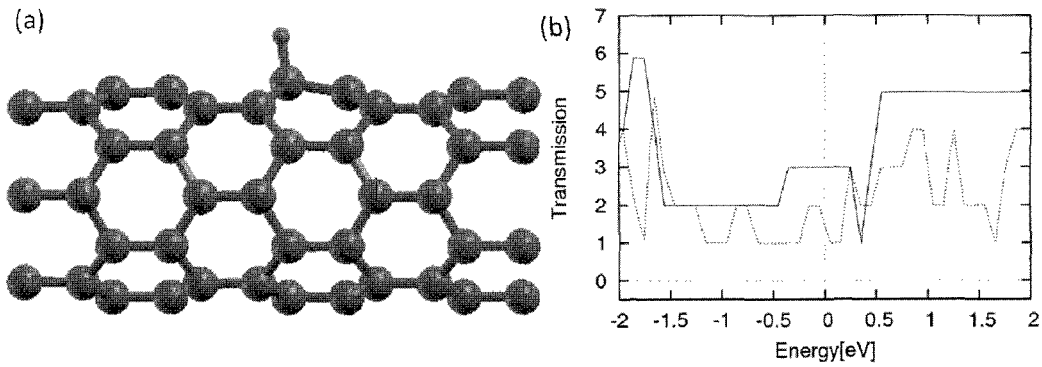

Fig 1. (a) Scattering region $C_{72}H$ of hydrogen adsorbed (6,0) CNT and (b) energy dependence of electron transmission for pure (6,0) CNT (solid line) and hydrogen adsorbed CNT (dotted line). Fermi energy is taken at the originof the energy.

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3P-10

Optical response of single-walled carbon nanotubes in far-infrared region

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A carbon nanotube (CNT) is one-dimensional and hollow cylindrical structure formed by wrapping a graphene sheet, and becomes either metallic or semiconducting depending on its geometry. Usually, single-walled carbon nanotubes (SWCNTs) have the order of a few nanometers in diameter and the order of several micrometers in length. Optical spectroscopy such as Raman scattering and photoluminescence is well-known to be effective technique to characterize their properties for electronic and optoelectronic applications. In addition, using infrared (IR) spectroscopy and terahertz time domain spectroscopy (THz-TDS), there has been reported the small band-gap and antenna effects of metallic SWCNTs [1-4]. The former has so far been reported theoretically and experimentally[1-3,5]. The small gaps in a few tens of meV at Fermi level were induced by the curvature effect and intertube interactions[5]. The latter, antenna effects by plasmon resonance have been predicted theoretically that frequency in far-IR spectroscopy and THz-TDS is proportional to the inverse tube length that has been one of the on-going themes in CNTs[4]. We here report optical response of SWCNTs by using FT-IR spectroscopy in mid- and far-IR range.

Several types of SWCNTs were used and prepared for thin films on silicon wafer and polyethylene IR card. For IR spectra obtained from arc discharge tubes, the signals exhibit a broad band around 100 cm^{-1} and a sharp peak near 5580 cm^{-1}. The latter is thought to be S1 interband transition of semiconducting SWCNTs. The former is considered to be a small gap and antenna effects-induced signal of metallic SWCNTs. To clarify the origin of this signal, we have investigated the doping dependence and F_4TCNQ was used as a dopant. Upon doping, the absorption intensity was enhanced in low-frequency region along with the strong reduction of the peak of S1 interband transitions. The possible mechanism for the experimental observations will be discussed.

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3P-11

Transport properties of individual boron-doped carbon nantoube under pressure

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Carbon nanotube (CNT), which has low resistivity, is expected to be applied to various devices, for example, transparent electrodes, nanowiring for LSIs, probes for scanning microscopes and so on. However, CNT shows semiconducting and metallic behavior depending on the chiral vector, and there have been no report on successful CNT growth with chirality control. In semiconductor, career doping reduce resistivity. This technique can be used for CNT and we reported boron-doped CNT has lower resistivity than it of pure CNT [1]. Another way to control resistivity is applying pressure. However, the transport properties of individual CNT under pressure have not been reported.

We investigated the effect of high pressure on the transport properties of individual boron-doped multi-walled carbon nanotube (MWNT). Boron-doped MWNT was synthesized by hot filament method [2]. Carbon nanotube was dispersed on substrate and four terminals were fabricated. Electrical resistance of individual MWNT was measured under high pressure up to 1.73 GPa. The resistance dramatically decreased with increasing pressure. I will present the detail of CNT growth, measurement method and results.

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3P-12

Redispersing Semiconducting Single Wall Carbon Nanotubes by DNA and Their Size Exclusion Chromatography

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Due to its absolutely isolated state in water and length sortability by using size exclusion chromatography (SEC), single wall carbon nanotubes wrapped by DNA (DNA-SWCNTs) have attracted much attention as a semiconducting material in the channel of printed thin film transistor (TFTs) [1,2]. Although various separation methods of metallic and semiconducting SWCNTs have been reported, the separation in structural properties such as their length would be also required for achieving high performance TFTs, because such structural properties should affect the dispersing characteristic and the way of forming SWCNT networks, which are expected to dominate their device performances. In this respect, the method of controlling both electronic and structural properties of SWCNTs is eagerly anticipated.

Here, for the purpose of length sorting of semiconducting SWCNTs (s-SWCNTs) and preparing uniform s-SWCNTs networks, we have tried to replace the dispersing agent (Brij 700) of s-SWCNTs obtained by Electric-field inducing Layer Formation (ELF) [3] with several kinds of DNA in order to sort obtained s-SWCNTs wrapped by DNA (DNA-s-SWCNTs) in length using SEC. Details of the redispersion and SEC results will be presented.

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3P-13

Growth control of carbon nanotubes on a metal tip apex

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Studies for application of carbon nanotubes (CNTs) to field emitters, SPM probes, and micro discharging electrodes have been actively carried out by many researchers. It has been considered that a method that enables growth of CNTs directly onto a metal tip apex by chemical vapor deposition (CVD) is a promising method for those applications. However, this method requires appropriate method to control the growth density and the growth direction of CNTs. In this study, we have examined the growth characteristics of CNTs on the metal tips for the purpose to improve the alignment of the growth direction of the CNT.

Tungsten (W) tips with apex curvature radii of approximately 1μm were fabricated by electrochemically etching a W-wire of 0.15 mm in diameter. Al underlayer (20 nm) and Ni catalyst layer (10 nm) were sequentially formed on the W-tip apex by a vacuum evaporation method. After that, CNTs were grown on the W-tip apex by a thermal CVD method. The CVD process was carried out for 10 min under the following conditions. The gas flow rates of Ar, H_2, and C_2H_2 were 50, 12.5, and 2.1 sccm, respectively. The pressure was 1 atm, and the temperature was 650°C. To apply a DC voltage during the CVD, a counter electrode plate to the W-tip was placed in the CVD reactor, and the voltage was applied between the W-tip and the counter electrode. The distance between the W-tip and the counter electrode plate was 1 mm. The applied voltage was varied between 0 and -350 V.

Fig. 1(a) and (b) show SEM images of CNTs grown on the W-tip without applying the voltage (0 V), and with applying the voltage to -350 V, respectively. Randomly oriented CNT growth is observed in Fig. 1(a). On the other hand, alignment of the CNT is observed in Fig. 1(b). The CNTs grow toward the outside of the tip. The growth direction is parallel to the electric field induced on the tip surface. It was confirmed that the alignment depended on the applying voltage and also on the other conditions such as catalyst species.

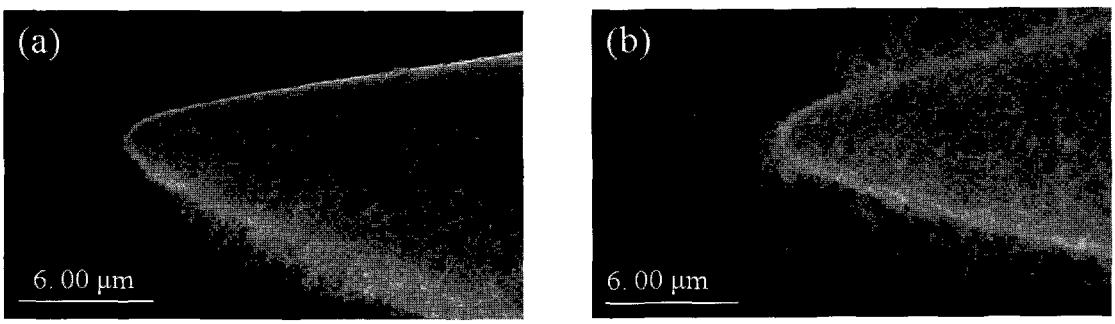

Fig. 1 SEM images of CNTs grown by CVD under application of DC voltages of (a) 0 V and (b) -350 V.

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3P-14

Effect of Al_2O_3 Film Thickness on Growth of MWCNT Forest with Graphite Roof

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In this study, the structure that is composed of multi-walled carbon nanotubes (MWCNTs) and graphite layer were synthesized from a bi-layer catalyst of iron (Fe) and aluminum oxide (Al_2O_3) by chemical vapor deposition (CVD). Firstly, Al_2O_3 film was deposited on silicon (Si) substrate with a silicon dioxide layer by vacuum evaporation. Then, Fe film was formed on the substrate by spin coating and calcination in the air at 780 °C. The CVD equipment used was developed in our laboratory. The acetylene (C_2H_2) and nitrogen (N_2) gases were used as source and dilution gases, respectively.

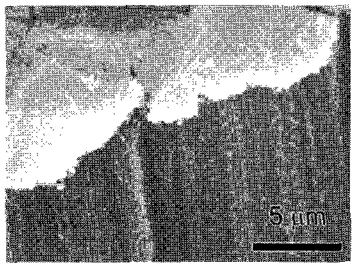

Fig. 1 SEM micrograph of the structure: aligned MWCNTs covered with graphite roof

Fig. 1 shows the scanning electron microscopy (SEM) of the structure. Aligned carbon nanotubes are covered with graphite roof [1]. Fig. 2 shows the effect of Al_2O_3 film thickness on the growth rate of the structure. As the Al_2O_3 film became thicker, the growth rate was decreased. The tallest structure with a height of approx. 60 μm was obtained, in which the thickness of graphite layers was approx. 0.5 μm.

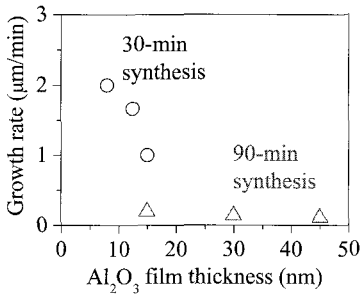

Fig. 2 Effect of Al_2O_3 film thickness on growth rate of MWCNT with graphite roof

This work has been partly supported by the Outstanding Research Project of the Venture Business Laboratory from Toyohashi University of Technology (TUT); Global COE Program "Frontiers of Intelligent Sensing" from the Ministry of Education, Culture, Sports, Science and Technology (MEXT); Core University Programs (JSPS-CAS program in the field of "Plasma and Nuclear Fusion") from the Japan Society for the Promotion of Science (JSPS), Grant-in-Aid for Scientific Research from the MEXT, Toukai Foundation for Technology, Research Foundation for Materials Science, and Chubu Science and Technology Center.

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3P-15

Effect of pH and NaCl Concentration on Metal/Semiconductor Separation of Carbon Nanotubes using Gel

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There are two electric types of single wall carbon nanotubes (SWCNTs), metallic (M) ones and semiconducting (S) ones. For their electrical application, it is required that these two types of SWCNTs are separated into the respective type. We have developed effective M/S separation methods using agarose gel[1-4]. In this presentation, we report the effects of pH and NaCl concentration on the M/S separation using gel.

M/S separation was conducted using batch separation method[4]. HiPco-SWCNT/sodium dodecyl sulfate (SDS) dispersion was prepared by sonication and ultracentrifugation. The dispersion and agarose gel beads (Sepharose 2B) were mixed, and then a solution (unbound) fraction containing M-enriched SWCNTs and a gel (bound) fraction containing S-enriched SWCNTs eluted from the gel were collected. When pH of the mixture was changed from 10.4 to 3.2, the amount of SWCNTs of bound fraction was decreased (Fig. 1A). Similarly by increasing NaCl concentration of the mixture (from 0 to 250 mM), the amount of gel-bound SWCNTs was decreased (Fig. 1B). In the case of 500 mM NaCl, all SWCNTs aggregated, and no M/S separation was detected. In both the cases (changes of pH and NaCl concentration), decrease of the amount of the bound or unbound SWCNTs accompanied with improvement of semiconducting or metallic SWCNT purity. Detailed methods and results will be discussed.

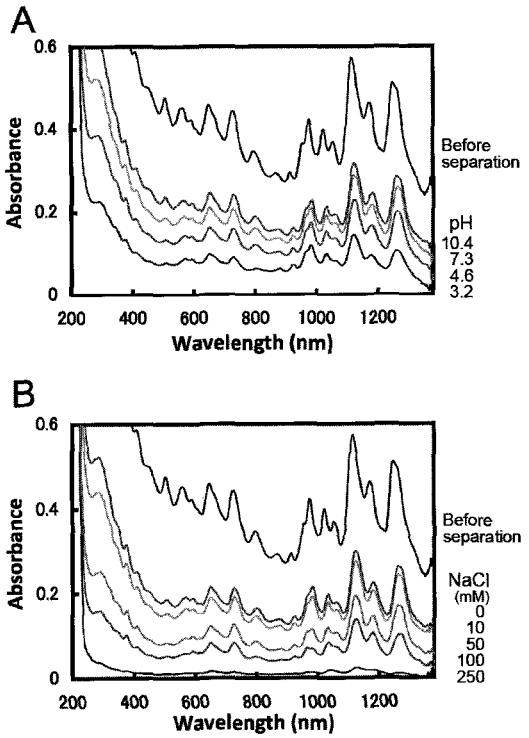

Fig. 1 Optical absorbance spectra of bound fractions after separation at different pHs (A) and NaCl concentrations (B).

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3P-16

Development of large scale vertically aligned high-temperature pulsed-arc discharge

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A high-temperature pulsed-arc discharge (HTPAD) is a production system of nanocarbon materials. The system utilizes width controlled pulsed arc discharge around ms for the vaporization of carbonaceous electrode in temperature controlled ambient rare gas around 1000 ℃ for the growth of the materials. With this width and temperature control, novel materials have been produced by the system such as high-quality double wall carbon nanotubes[1]. However, the production rate of the system is about 20 mg/hour because of low duty factor of the discharge (~3 %). Furthermore the horizontally aligned narrow tube reactor (ϕ26 mm) of the system prevents the vaporized carbonaceous materials from growth in free space and from being collected effectively in the trap since the vapor is transferred by the convection to be stacked on the surface of the tube and the electrodes. Here we present the development of a large scale vertically aligned HTPAD to improve these points.

Figure 1 shows the schematics of the system. The vertically aligned thick (ϕ100 mm) alumina tube reactor with independently controlled three heaters realizes free growth space without the wall perturbation. Ar gas flow from top to bottom also contributes to cancels the effect of the convection. Not only for the free growth, the large reactor tube enables us to install four parallel discharge electrodes pairs for the enhancement of the productivity.

With this system, the production rate is increased up to 1000 mg/hour, 50 times larger than the previous one. In addition to the productivity enhancement, the produced nanocarbon materials are also different: the large part of the products consist of SWNT with large diameters (2 to 3 nm) with little DWNTs even if the optimum condition for DWNTs is applied. The result show that the wall and flow have significant effect for the growth of nanocarbon materials. We are now optimizing conditions for novel materials.

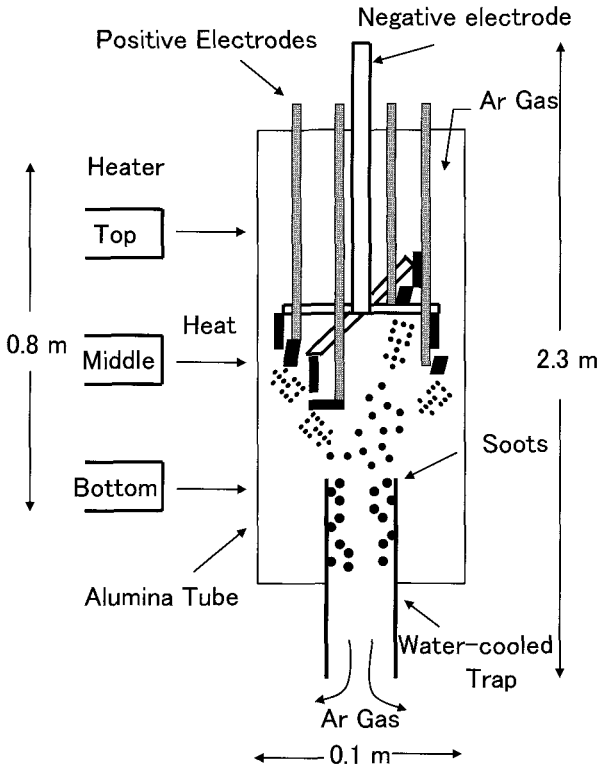

Fig.1 Schematic of large scale vertically aligned high-temperature pulsed arc discharge

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3P-17

Diameter Selection Techniques for Single-Wall Carbon Nanotubes With Around 1.4 nm Diameters

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Abstract: Single-wall carbon nanotubes (SWCNTs) with diameters around 1.4 nm, can encapsulate various kinds of organic molecules. The SWCNTs encapsulating molecules (peapods) can exhibit unique electronic and optical properties, and encapsulation of molecules is one of approaches to tune the properties of SWCNTs. Previously, we have prepared peapods with metallic or semiconducting types of SWCNTs,[1] but it is necessary to prepare samples with a single chirality in order to experimentally reveal the detailed interactions between encapsulated molecules and nanotubes. Thus, development of techniques to obtain a single chiral sample in this diameter region is important. Various techniques are reported to obtain a selected chirality for SWCNTs with diameters less than around 1.0 nm, but not for SWCNTs with diameters of around 1.4 nm. Metal-semiconductor (MS) separations can be easily achieved in 1.4 nm diameter SWCNTs. Therefore, it would be possible to prepare almost a single-chiral sample if we could apply MS-separations and diameter separations successively. Therefore, we investigated a diameter-sorting method which has high diameter selectivity on SWCNTs with around 1.4 nm diameters. First we examined density-gradient ultracentrifugation (DGU) methods. DGU using iodixanol, which is firstly developed by Arnold et al.,[2] causes both diameter and electronic selections.[2] However, the reported diameter selectivity by iodixanol-DGU is not so good for the nanotubes with 1.4 nm. Therefore, we investigate other gradient materials, such as sucrose[3] and cesium chloride, to check the selectivity with diameter of this region. As shown in Fig. 1, we found that relatively good diameter selection can be achieved by DGU using cesium chloride.

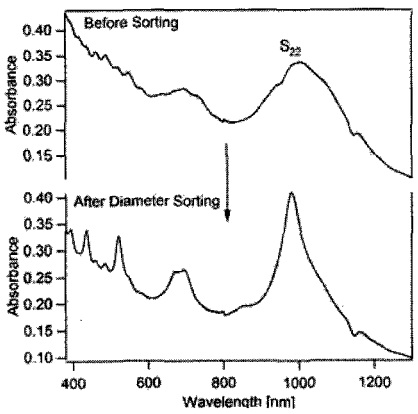

Fig. 1: Diameter sorting by using cesium chloride for gradient material on SWCNTs with diameters around 1.4 nm.

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3P-18

X-ray Structure of a Divalent Metallofullerene Yb@C_{80}

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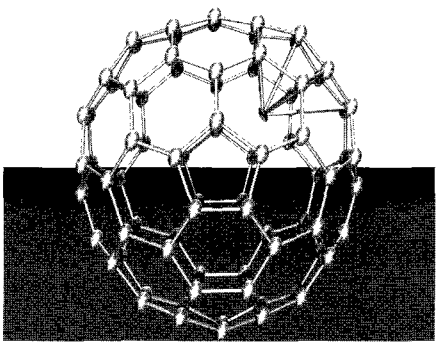
Structural elucidation of endohedral metallofullerenes (EMFs) has been of fundamental importance because successful results are valuable for understanding their properties and broadening their applications.[1] Recently, we have systematically determined the cage structures of Yb@C_{2n} (2n = 80, 82, 84) with ^{13}C NMR spectroscopy. The results revealed that the single Yb atom plays an important role in determining the cage structures of the resulting molecules. [2] However, as NMR technique is invalid to characterize the motional behaviors of the internal metal, single crystallography is always the final solution for EMF structures.

Here, we report the first X-ray results of pristine Yb@C_{2v}(3)-C_{80}, cocrystallized with Ni(OEP). It is disclosed that the Yb atom takes an off-center position apart from the C_2 axis, and it coordinates strongly with the adjacent cage carbons with Yb-C distances ranging from 2.45Å to 2.70Å (see picture). This is the first observation of the off-axis location of metal in mono-EMFs which is expected to be effective to induce unusual chemical behaviors of the cage carbons. Theoretical calculations disclose that this configuration is at least 6.19 kcal/mol more stable than any other possible conformer.



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3P-19

Electronic Properties of $M_2(C_2)@C_{82}$ (M=Sc, Ti, Fe) Endohedral Metallofullerenes

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The electronic structure of di-scandium, di-titanium and di-iron endohedral metallofullerenes (EMFs), $M_2C_2@C_{82}$ (M = Sc, Ti, Fe) (see Fig. 1), were investigated using density functional theory (DFT) and the self-consistent-charge density-functional tight-binding (SCC-DFTB, in the following abbreviated as "DFTB" [1]) method. The latter is computationally far more economical than first principles DFT, yet allows to capture the essential features of the electronic structure and to compute molecular structure and other properties with accuracy comparable to traditional DFT methods.

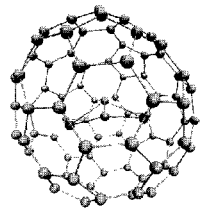

Figure 1. Optimized geometry of isomer 4 of $Sc_2C_2@C_{3v}$-C_{82} (8) at BP86/TZP

In order to validate the use of the DFTB method, we first computed orbital energies of empty cage isomers of C_{82}. We found that the DFTB method correctly reproduces the large (LUMO+2) – (LUMO+1) gap (more than 1 eV) of C_{3v}-C_{82} (IPR isomer #8), in good agreement with traditional DFT at the BP86/TZP level of theory [2].

For di-scandium and di-titanium (carbide) EMFs, we performed geometry optimizations using the DFTB and B3LYP/def-SVP methods starting from the six $M_2C_2@C_{3v}$-C_{82} isomers (different arrangement of metal atoms inside the cage) optimized at the BP86/TZP level of theory as reported by Valencia *et al.* [2]. We found that DFTB isomer energies well reproduce the trends obtained from the DFT methods. The agreement is not perfect, as DFTB sometimes fails to predict the most stable isomer by a few kcal/mol. We then analyzed the molecular orbital diagrams of isomer 4 and DFTB orbital occupation numbers correspond to the same formal charges predicted by DFT calculations.

Finally we investigated di-iron EMFs, which have not been synthesized yet. We considered all possible spin states, from singlet to undecet including symmetry-broken wavefunctions with anti-parallel spin alignments. In general, binding energies of iron inside the EMFs are much smaller compared to the more electropositive Sc and Ti metals, suggesting that synthesis of these species is unlikely because iron tends to form larger clusters before individual atoms can be encapsulated in fullerene cages.

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3P-20

Electronic property of Li@C_{60}

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Recently, Li@C_{60} can be produced in a macroscopic quantity so that the prospect for the investigation of its physical properties opens up. Isolation of Li@C_{60} is difficult because of its instability. Thus isolated Li@C_{60} is either in the state of a mixture with C_{60} or in the state of [Li@C_{60}] cation salts. In this presentation, we give ultraviolet photoelectron spectra (UPS) and X-ray photoelectron spectra (XPS) of Li@C_{60}.

Figure 1 shows the UPS of a [Li@C_{60}](PF_6) thin film prepared by vacuum sublimation. The UPS of C_{60} is also shown for comparison. Spectral onset energy of Li@C_{60} is 0.7eV below the Fermi level, which is much smaller than that of C_{60} (1.8 eV). In the spectra of [Li@C_{60}](PF_6), a peak S which is not present in C_{60} appears at binding energy of 1.5eV. This peak is considered due to be the result of electron transfer from Li atom to the LUMO of C_{60}. Except for the appearance of the peak S, the spectral shape of the UPS of Li@C_{60} and C_{60} is almost identical, but the peak positions of corresponding structures shift slightly; particularly shift of upper valence peaks located between 1 - 7 is drastic.

Figure 2 shows the UPS of the [Li@C_{60}](PF_6) deposited at various crucible temperature (550-800℃). The new peak S is observed at the film prepared at 550℃, but its intensity reduces gradually as the evaporation temperature becomes higher and finally it vanishes at the film prepared at 800℃; the spectra of [Li@C_{60}](PF_6) deposited at 800℃ becomes almost identical to that of C_{60}. It seems that encapsulated Li atom escapes from C_{60} cage when Li@C_{60} is heated at high temperature.

Figure 3 shows the result of curve fitting of the UPS with using Gaussian functions. The full width at half maximum (FWHM) of Li@C_{60} is wider than that of C_{60}. This could be due to dissolution of the orbital degeneracy of the HOMO and the HOMO-1 of C_{60} cage. It should be noted that the area of relative peak intensity is A : B : S = 18 : 9.6 : 1.5, which is an indication of one electron transfer from Li atom to the cage.

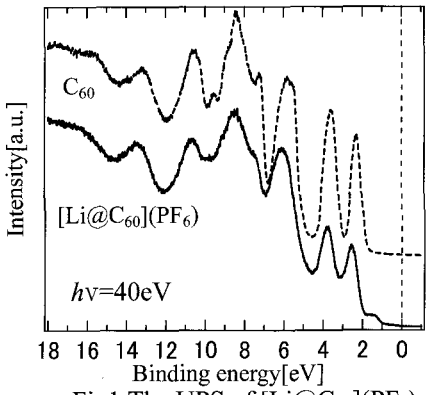

Fig1.The UPS of [Li@C_{60}](PF_6) and C_{60}

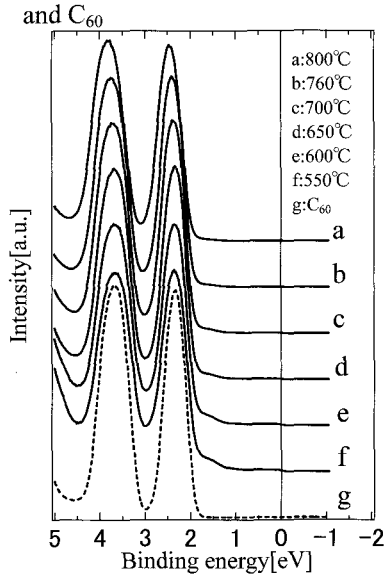

Fig2.UPS of [Li@C_{60}](PF_6) with changing evaporation temperature

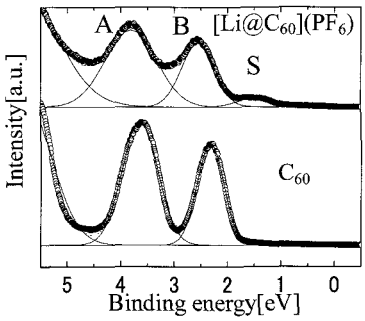

Fig3.UPS of [Li@C_{60}](PF_6) and C_{60} with their Gaussian fitting

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3P-21

Most stable structure and electronic structure of endohedral fullerenes $Sc_3C_2@C_{80}$ by density functional theory calculations

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Density functional theory calculations using Gaussian 03 program have been performed to elucidate the stable structure and the electronic structure of Sc_3C_2 entrapped in the C_{80} (I_h) fullerene cage. The structure of endohedral fullerene was optimized at the hybrid functional B3LYP level using the CEP-31G basis sets. The electronic structure was obtained by B3LYP level using 6-31G(d) basis sets for carbon, and TZVP basis sets for scandium.

Two geometries have been proposed for the entrapped Sc_3C_2 cluster ; trifoliate type and planar type.[1] (Fig.1)

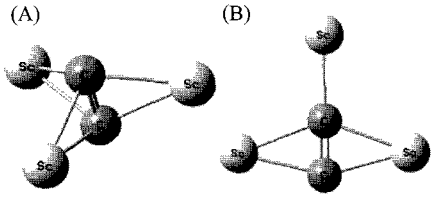

Fig.1 A : trifoliate type
B : planar type

Figure 2 shows the ultraviolet photoelectron spectra (UPS) of $Sc_3C_2@C_{80}$ and simulation spectra obtained from two geometries. The simulation spectrum obtained from the trifoliate Sc_3C_2 geometry reproduces UPS very well both in the relative intensity of corresponding peaks and their intervals, whereas that from the planar Sc_3C_2 geometry shows fair correspondence. Thus, the Sc_3C_2 cluster might take trifoliate geometry in I_h-C_{80} cage.

Figure 3 shows the trifoliate type $Sc_3C_2@C_{80}$ obtained from the geometry optimization.

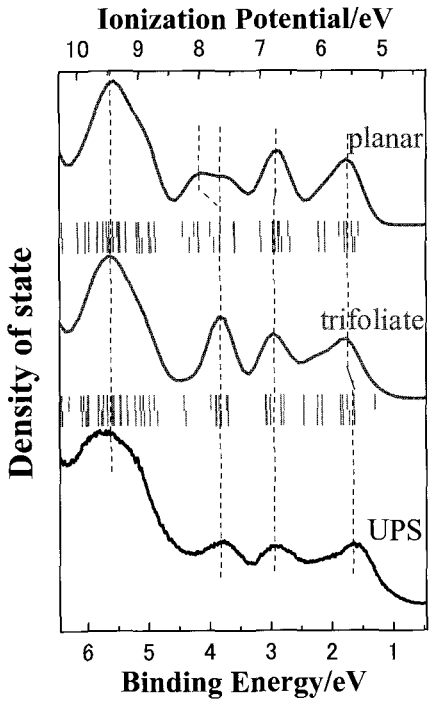

Fig.2 UPS and simulation spectra of $Sc_3C_2@C_{80}$

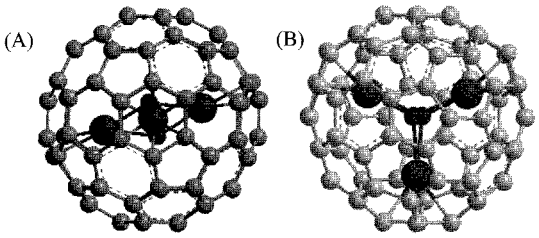

Fig.3 Trifoliate geometry of $Sc_3C_2@C_{80}$
A : side view
B : top view

[1] K.Tan et al., J Phys. Chem. A 2006, 110, 1171-1176

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3P-22

ESR measurement of N@C_{60} encapsulated by γ-cyclodextrin

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N@C_{60} can be a good magnetic probe which gives the information of position as well as of chemical environment. For the biological application the probe should be soluble in water. The encapsulation of N@C_{60} with γ-cyclodextrin was attained by a mechanochemical high-speed vibration technique [1)], and the aqueous solution of N@C_{60} was obtained. The ESR spectrum exhibited the broad triplet at 120K in frozen solution, as shown in Figure 1.

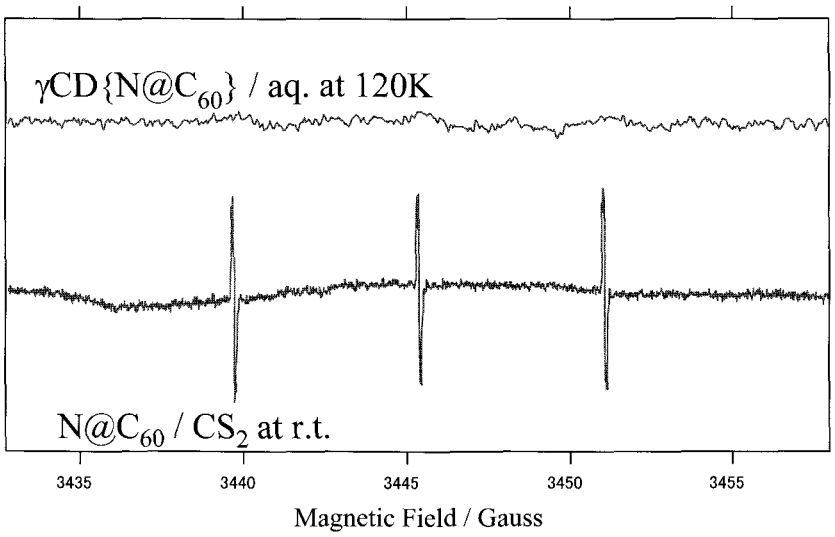

Figure 1. X-band ESR spectrum of N@C_{60} in γ-cyclodextrin at 120K.

References:
1. K.Komatsu, K. Fujiwara, Y. Murata, and T. Braun, *J. Chem. Soc., Perkin Trans 1,* 2962-2966(1999).

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3P-23

Implantation of Atoms into Fullerenes using High-Frequency Sputtering Apparatus

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Ion implantation is one of the methods for encapsulation of atomic species inside the fullerene cage. Unlike the popular method of arc discharge by which metallofullerenes are obtained for higher fullerenes as hosting cages, i.e., $M@C_n$, n=80, 82, and 84, there is in principle no limitation for the fullerene size as well as for the element to be implanted. The endofullerenes reported so far by ion implantation, or ion bombardment, are $Li@C_{60}$, $N@C_{60}$, $N@C_{70}$, $P@C_{60}$, $Ar@C_{60}$, and so on.

We have developed machinery for ion bombardment to produce $N@C_{60}$ at relatively high yield. There are several points to be improved for increasing the production efficiency. To increase the ion current reaching to the surface of the electrode where the fullerene molecules are bombarded with the ions is primarily of importance. The apparatus can provide a current of positive ions on the order of ~10 mA at 80 V. In addition, to keep the deposition rate being constant is also crucial, because the penetration depth of the ions into the sediment of fullerene molecules is not very large. For this, we have developed a PC-controlled programmable system of a crucible from which the fullerene molecules are sublimed to be deposited on the electrode. Combining the ESR detection and the HPLC separation, we can concentrate the target endofullerenes such as $N@C_{60}$ in solutions. Eventually, $N@C_{60}$ is detected by optical absorption in the chromatogram.

The apparatus was originally planed for sputtering solid materials of metals and semiconductors. A rod of solid elements can be set inside the plasma produced by high-frequency discharge of gases. When a positive high voltage is applied to the rod, electrons in the plasma are accelerated to sputter the surface of the rod. Then, atoms of the element of the rod are emanated into vacuum and ionized in the plasma. The ions are accelerated in the opposite direction to that of the electrons and collected onto the surface of an electrode to which fullerene molecules are deposited. In this way, the atomic species of a desired element of a solid form can be implanted into fullerene molecules. The detailed schemes and operation of the machinery will be presented.

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3P-24

Structures and Relative Stability of $Gd_2@C_{98}$

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Endohedral metallofullerene $Gd_2@C_{98}$ detected by chromatographic separation [1] was first reported by Balch *et al.* in 2008. However, the structural characterization of $Gd_2@C_{98}$ has not been achieved. The extensive DFT calculations [2] on the hex-anions of all C_{68}-C_{88} isomers (beyond IPR and non-IPR species) and IPR isomers of C_{90}-C_{98} for endohedral fullerenes where lanthanide atoms engaged in carbon cages were performed by Popov *et al.* Clearly, it is insufficient if C_{98} IPR isomers are considered only.

We herein report a systematical investigation on the endohedral metallofullerene $Gd_2@C_{98}$. According to the stability criterion, we propose that the non-IPR fullerene isomers with three or more fused pentagons cannot be efficiently stabilized by the encaged metal atoms and are still encountered with energetic penalty. Therefore, IPR isomers and the non-IPR species with one and two adjacent pentagon pairs were considered in our computations. Since the ionic model of $Gd_2@C_{98}$ were uncertain, so the total 17941 C_{98} isomers beyond IPR and non-IPR species (PA=0～2) are screened on the tetra-anion and hex-anion states by AM1 calculations. Furthermore, the best structures of C_{98}^{6-} and C_{98}^{4-} as well as their corresponding metallofullerenes $Gd_2@C_{98}$ were fully optimized at the B3LYP/6-31G(d) level of theory, respectively [3]. Vibration analyses on the best optimized geometries were carried out at the same DFT level of theory.

The results show that the lowest energy structure of $Gd_2@C_{98}$ is still an IPR isomer but three non-IPR structures are found to be also very stable. It is revealed that HOMO-LUMO gap of the lowest energy IPR structure labeled 230924:C_2 is 1.35eV. Energy ranking from 2 to 4 was structure which has one pairs of adjacent pentagons, the forth one labeled 168764:C_1 is energy different of 0.74kcal/mol to 230924:C_2 and has the biggest HOMO-LUMO gap (1.85eV).

To obtain further insight into the thermodynamic stability of $Gd_2@C_{98}$, we will investigate the entropy effects and evaluate the relative concentrations through the Gibbs free energy terms. The most thermodynamically stability of this system over a wide range of temperatures is reported and discussed.

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3P-25

A large-scale consecutive synthesis of metallofullerenes using the hybrid plasma method

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Endohedral metallofullerenes [1] can be synthesized typically in two ways similar to the synthesis of empty fullerenes, which involves the generation of a carbon-rich vapor or plasma in He or Ar gas atmosphere. The two methods have been routinely used to date for preparing macroscopic amounts of metallofullerenes: the high-temperature laser vaporization or 'laser-furnace' method [2] and the standard DC arc discharge method [3]. Both methods simultaneously generate a mixture of hollow fullerenes together with metallofullerenes.

The production of metallofullerenes can be followed by procedures to extract from soot and to separate/purify the metallofullerenes from the hollow fullerenes [1].
Metal-oxide/graphite composite rods, e.g. La_2O_3 to prepare $La@C_{82}$, are normally used as positive electrodes (anodes) after a high-temperature (above ca 1600 °C) heat treatment where the composite rods are cured and carbonized. At such high temperatures, various metal carbides in the phase of MC_2 are formed in the composite rods [1], which actually is crucial to an efficient production of endohedral metallofullerenes.

However, these synthesis methods are not suited for a gram and larger scaleproduction of pure metallofullerenes, where consecutive syntheses have not been possible because the supply of the graphite in the form of rods or discs is limited in scale. This precludes metallofullerenes from such large-scale synthesis during the past 20 years. Here, we have developed a high-yield consecutive synthesis of metallofullerenes using the so-called hybrid plasma method [4] together with specially manufactured composite metal-doped graphite power (see Fig.1). The overall production capability is 5-10 times as large as the conventional arc-discharge method. This opens a new era for the synthesis of endohedral metallofullerenes in large quantity.

Acknowledgment: The authors thank to Dr. Takashi Inoue and Mr.Yuji Takimoto (Toyo Tanso Co.Ltd.) for supplying a newly developed metal-doped graphite fine powder.

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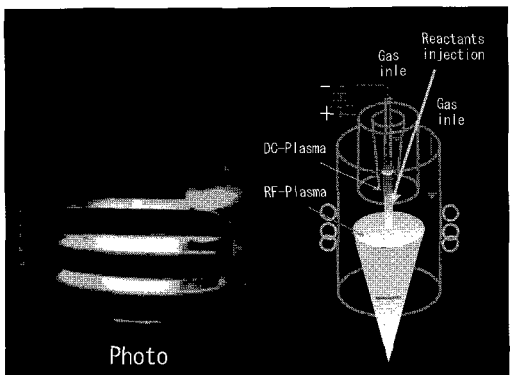

Fig.1 Schematic diagram of the present hybrid-plasma

3P-26

An Appearance of the New Electronic State in Fullerene Nano-Whisker due to UV Polymerization

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This study is aimed at clarifying the effect of UV polymerization into fullerene nano-whisker (FNW) without presence of oxygen.

Fullerenes electronics have been prevented by its instability and inability of performance in ambient atmosphere. It is important to archive air tolerability of the fullerene devices for applying broad applications such as solar cells, electron luminescence devices, field effect transistors, and gas sensors.

We have been making a study on polymerization of fullerene due to UV irradiation, especially on the FNW. FNW is a fine single crystal of C_{60} and prepared by liquid-liquid precipitation method [1]. Upon the system of *m*-xylene and isopropyl alcohol, FNW has several hundred nm of diameter and more than 10 μm of length. It is thought that the unique structure can be used to improve performances of the electronic devices. However, detail of the electronic structure is not elucidated about both FNW and UV polymerized FNW.

To elucidate more detail of electron behavior and polymerization effect, we applied the ESR measurement. The ESR magnetic susceptibility of FNW indicates that temperature independent behavior in vacuum which illustrate that electronic structure of FNW is almost metallic. The metallic behavior of pristine FNW is suddenly vanished when air is absorbed into FNW. New ESR spectrum is appeared when UV light is irradiated into FNW placed in ESR cavity. At the beginning, the new spectrum appeared and disappeared subserviently with UV irradiation, however stable signal is remained for 8 hour irradiation (Fig. 1). The saturation of intensity $\Delta y'_m$ is observed after irradiation for 12 h (Fig. 2). The remained spectrum has broad and weak temperature dependent peak width, and can be considered to be from electronic structure of polymeric phase. Furthermore, air exposure effect against UV polymerized FNW will be discussed to obtain air stable FNW as an *n*-type organic semiconductor.

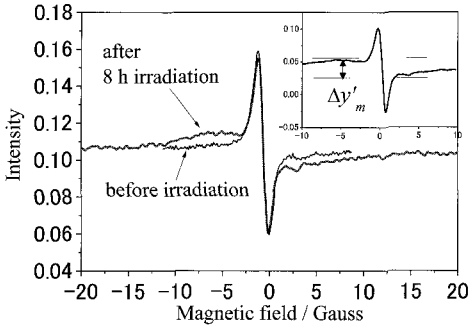

Fig. 1. ESR spectrum before irradiation (black line) and after irradiation (red line).

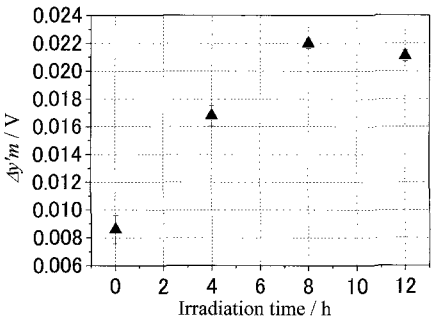

Fig. 2. Intensity of the new spectrum as a function of irradiation time.

[1] K. Miyazawa, *et al: J. Mater. Res.*, 20, 688 (2005).

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3P-27

Optical, Electric and Magnetic Properties of Thin Polymerized Fullerene C_{60} Films Deposited via Electron-Beam Dispersion

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[3]*Belarusian State University of Transport, Gomel 246653, Belarus*

Fullerenes C_{60} can be polymerized using high-pressure high-temperature treatment (HPHT), UV-Vis light irradiation in the absence of oxygen, electron irradiation, alkali metal doping, *etc.* We have used a novel method of electron-beam dispersion of pristine fullerite in vacuum with coating deposition onto the substrates in additional electrostatic field to form thin films of polymerized C_{60} [1]. The characteristic feature of the method is that the coating is deposited under the irradiation of electrons from the active gas phase containing excited fullerene molecules and positive fullerene ions. Under the potential of -300 V on the substrates and thus, under bombardment of accelerated fullerene ions, highly cross-linked 3D polymer of C_{60} has been obtained.

The estimation based on the optical spectra of the films, deposited onto the synthetic fused silica substrates, showed that the band gap of the polymerized fullerene films decreases with increase of the coating cross-linking approximately from 2.30 eV to 2.14 eV. *In-situ* measurement of the *I-V* curves of the layers deposited onto the quartz substrates with a system of 2 interdigital thin-film Ni electrodes showed that the highly cross-linked polymerized C_{60} film exhibits Schottky barrier to Ni electrodes. The estimated *in-situ* resistivity of the film is about 50 Ω·cm which is several orders of magnitude lower than that for the nonpolymerized C_{60} films. The films were also studied using magnetic force microscopy (MFM) and scanning spreading resistance microscopy (SSRM). Highly cross-linked C_{60} films exhibit stable magnetic contrast in MFM (Fig. 1). Magnetic domains correlate with the topography of the film. Similar magnetic domain maps were observed by Han *et al.* [2] at some areas of the bulk samples of C_{60} polymers synthesized using HPHT method. Electric and magnetic properties of the highly cross-linked C_{60} polymer films are discussed.

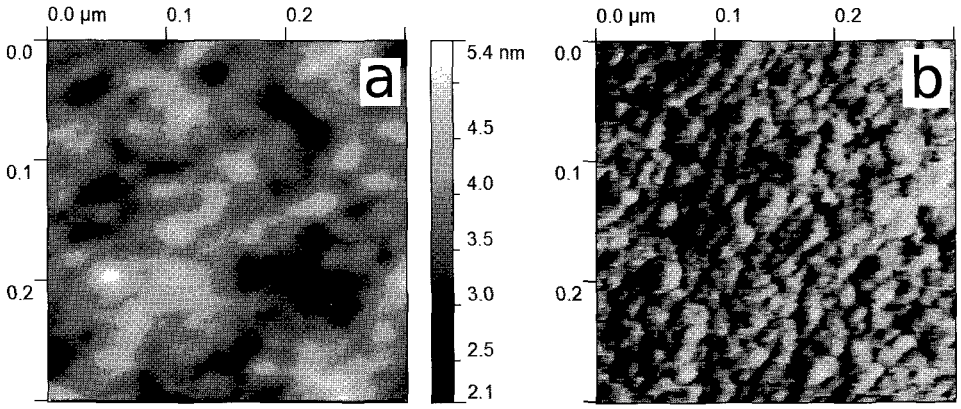

Fig.1. Topography (a) and magnetic contrast (b) AFM images of the highly cross-linked polymerized C_{60} film

[1] I. Razanau, T. Mieno, V. Kazachenko, *Thin Solid Films,* **519**, 1285 (2010).
[2] K.-H. Han, A. Talyzin, A. Dzwilewski, T. L. Makarova, R. Höhne, P. Esquinazi, D. Spemann and L. S. Dubrovinsky, *Phys. Rev. B*, **72**, 224424 (2005).
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3P-28

Fabrication and Characterization of $C_{60}(OH)_x$ Nanocrystals by a Reprecipitation Method

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Recently, various kinds of fullerene nanocrystals were reported to be easily grown by the precipitation methods[1-3]. Much interests are concentrated on these methods as the useful techniques for applications of fullerene materials. Polyhydroxylated fullerenes ($C_{60}(OH)x$:fullerenol) are promising materials for use in the field of life science and so on because of their water-solubility. In this study, we report the fabrication of $C_{60}(OH)_x$ nanocrystals by a reprecipitation method. The structural and morphological characterization of these crystals was performed by SEM and TEM.

Figure 1 shows the SEM image of $C_{60}(OH)_{20}$ (average composition) nanocrystals by using pyridine (good solvent) and *m*-xylene(poor solvent). In this presentation, the detailed relation between morphology of the crystals and solvating media will be presented.

Figure 1. SEM image of $C_{60}(OH)_{20}$ nanocrystals by the reprecipitation method using pyridine (good solvent) and *m*-xylene(poor solvent).

[1]H. Kasai, et al., *Jpn. J. Appl. Phys.* **31** (1992) L1132.

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3P-29

Structural characterization of fullerene-nanowhiskers by powder x-ray diffraction

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New types of needle-like fullerene crystals called fullerene nanowhiskers were reported to be easily grown by the liquid-liquid interfacial precipitation method[1] . Much interests are concentrated on fullerene nanowhiskers as one of the useful nanomaterials. Solvated structure of C_{60} nanowhiskers are reported by Minato et al[2]. However, the detailed structure of intrinsic C_{60} nanowhiskers and the difference form the bulk crystals are not fully understood yet. In this study, we report the structural characterization of C_{60}-nanowhiskers by powder x-ray diffraction at 120 K. The x-ray diffraction patterns of the crystals were measured with synchrotron radiation of λ=1.000 Å at BL-8B of KEK-PF.

Figure 1 shows the sample position dependence of the powder x-ray diffraction patterns of C_{60} nanowhiskers prepared by using *m*-xylene (good solvent) and 2-propanol(poor solvent) at 120 K. All diffraction patterns can be indexed with a hexagonal lattice. However, the ratio of peak intensity of each patterns is different according to tthe sample position. This suggests the existence of inhomogeneity by lattice defects in the crystal. In this presentation, the detailed crystal structure with lattice defects of C_{60}-nanowhiskers will be presented.

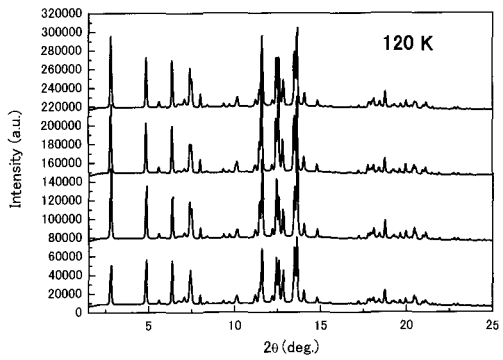

Figure 1. Sample position dependence of the powder x-ray diffraction patterns of C_{60} nanowhiskers at 120 K.

[1]K. Miyazawa, et al., *Journal of Materials Research,* **17**(2002) 83-88.

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3P-30

QM/MD Simulations of Dynamic Fullerene Self-Assembly in Carbon Vapor With Inert Carrier Gas

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[1]*Institue for Advanced Research, Nagoya University*
[2]*Fukui Institute for Fundamental Chemistry, Kyoto University*

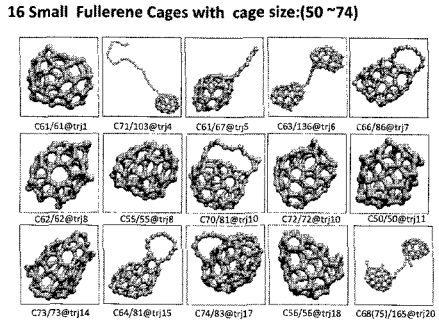

Figure 1. Small Fullerene cages with cage size very close to C_{60} and C_{70}

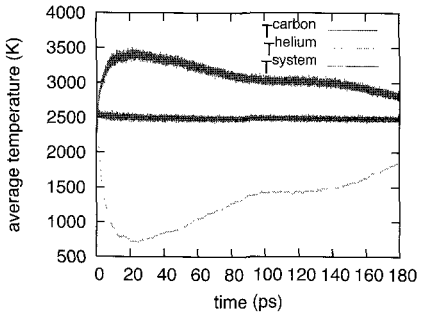

Figure 2. The temperatures defined by the nuclear kinetic energy of carbon clusters, He inert gases and the whole system averaged from 20 trajectories under the conditions where small cages were found.

Abstract: The dynamic fullerene self-assembly process in carbon vapor was studied using extensive quantum chemical molecular dynamics (QM/MD) simulations based on the density-functional tight-binding (DFTB) potential in conjunction with a finite electronic temperature. Model systems with different carbon densities and different number of helium atoms were employed in NVT simulations up to 200 ps. Similar to our previous NVT QM/MD simulations [1], only the formation of giant fullerene cages (> C_{80}) was found in pure carbon systems with relatively high carbon density. Interestingly, in the model systems closer to experimental carbon density, ~4.7×10^{20} cc^{-1}, and with an optimum C/He ratio in the system [2], smaller fullerene cages with cage size close to C_{60} and C_{70} were observed (see Figure 1). The addition of inert helium gas atoms was found to influence the temperature and diffusion of carbon species. In particular the local heating of carbon clusters plays an important role in the formation of small fullerene cages. This temperature evolution is closer to the experimental setup, where the hot carbon vapor is only slowly cooled down by the buffer gas [2]. In addition, it was found that the diffusion of carbon species was slowed down by thermal collisions between inert He gas and carbon species. Slower diffusion ensures longer growth/healing time for small polycyclic carbon clusters before they coalescence, eventually leading to the formation of smaller fullerene cages as opposed to NVT/high C density/no He simulations. We conclude that the initial cage size distribution of dynamically self-assembled fullerenes strongly depends on the carbon density, buffer gas pressure, and local temperature gradients. Our simulations demonstrate for the first time the abundant formation of small fullerene cages with cage size close to C_{60} and C_{70}.

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3P-31

Synthesis of non-IPR fullerenes from C_{70} in Liquid Phase by Irradiation of Intense Femtosecond Laser Pulses

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Ultrashort pulsed lasers have traditionally been used to probe the time-domain aspects of molecular dynamics, but quite recently, they have also started to be used for the study of a new type of chemical reaction that would be taken place only under extremely high intensity laser field [1]. Furthermore, under such extreme conditions, the most of the investigations so far have been carried out for the aims of reactions in gas phase, and a few of them in liquid phase [2]. In 2008, Hu et al. demonstrated that intense femtosecond laser irradiation to organic solvents directly initiates the synthesis of polyynes without additional introduction of any carbon particles [3], and we also confirmed the production of polyynes with various chain lengths from n-hexane by intense femtosecond laser radiation [4].

Fullerenes are usually synthesized by arc discharge, laser ablation, and combustion of hydrocarbon methods. In these methods, fullerenes are formed in gas phase. All of stable fullerenes extracted from the raw soot by organic solvents are known to satisfy so called "Isolated Pentagon Rule (IPR)".

In this study, we try to synthesize a new type of fullerenes from C_{70} in liquid phase using the intense femtosecond laser pulses, which would lead to successive C_2 losses from C_{70} and the resultant C_{68}, C_{66}, $\cdots$ would necessarily have non-IPR cage structures. The laser used for the experiment was a Ti: Sapphire (λ: 800 nm, pulse width: 100 fs, repetition rate:1 kHz) with a regenerative amplifier. C_{70} was isolated by high performance liquid chromatography and the mass spectrum of the purified C_{70} shows no peaks from other fullerenes than C_{70}.

When the femtosecond laser pulses were irradiated to the saturated C_{70} toluene solution, black powder-like materials were found to appear immediately and, after 2 hours irradiation, the red color due to C_{70} disappeared and the transparent light brown solution and the black powders were remained. Figure 1 shows the mass spectra of the black powders and the solution. The peak of C_{68} was distinct in both samples, but in black powders, the signal intensity of C_{68} as well as other smaller-size fragments is much larger than those in solution. All these results suggest the presence of successive C_2 losses and the resultant unstable species (C_{68}, C_{66}, C_{64}) would be easily aggregated.

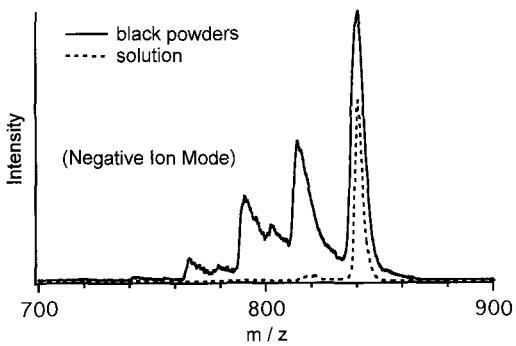

Figure 1. Mass spectra of the black powders and the solution.

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3P-32

Supramolecular Elementary Units in Porphyrin-Fullerene Composites Revealed by Solid-State NMR

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Characterization of the molecular-level donor-acceptor structure is crucial to design high-performance '*amorphous*' organic solar cells (OSCs). However, the details have been limited experimentally for such '*amorphous*' systems, due to the absence of periodic structure. Solid-state NMR is a powerful tool for elucidating the structure of amorphous systems.[1] Here, we report the first solid-state NMR experiments for a supramolecular OSC system composed of tetraphenylporphyrin derivatives (TPP) and C_{60} (Figure 1). This study focuses the existence of several different supramolecular elementary units possessing local stoichiometry between TPP and C_{60}. The TPP and C_{60}, dissolved in toluene, were rapidly injected into acetonitrile. This resulted in the formation of supramolecular composite clusters TPP/C_{60}. The gently centrifuged and dried clusters were employed for the solid-state ^{13}C NMR experiments. Fully-relaxed direct polarization / magic angle spinning ^{13}C NMR experiments without ^{1}H dipolar decoupling (DP/MAS/noDD), distinguished the C_{60}s in different states with quantitative molar ratios. In this experiment, C_{60} carbons can be selectively detected, because the resonance lines of TPP are effectively suppressed by not applying DD. In Figure 1, a ^{13}C NMR spectrum of TPP/C_{60} clusters in the amorphous states is presented (the resonance lines are denoted as A to F). Compared with the spectrum of pristine C_{60}, the TPP/C_{60} clusters display several upfield-shifted resonance lines, B – F, which indicate the occurrence of molecular-level complexation between TPP and C_{60}.

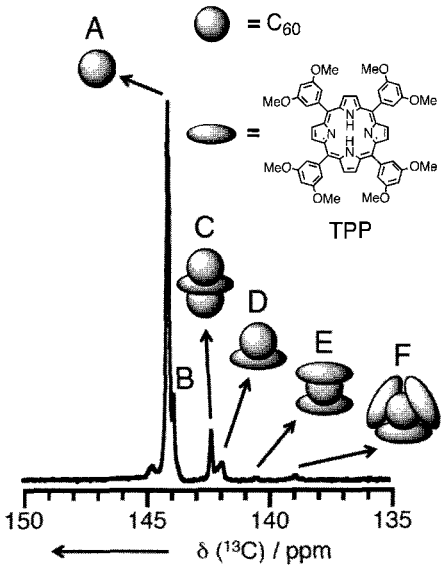

Figure 1. Fully-relaxed DP/MAS/noDD ^{13}C NMR spectra of TPP/C_{60} composites.

From various considerations, the peaks A, C, E, and F are assigned to free C_{60}, the C_{60} in C_{60}/TPP/C_{60} unit, the C_{60} in TPP/C_{60}/TPP unit, and C_{60} surrounded by three TPP molecules, respectively. The peak D appears between the peak C and D, suggesting the composition of C_{60}/TPP. The peak B is considered to be C_{60}s in defects, which are farther from the second neighbors of TPP. The origin of the upfield shifts is charge-transfer (CT) from TPP to C_{60}. Therefore, the peaks C to F result from four distinctly different degrees of CTs in this system, which would greatly affect the cell performance of the present solar cell.[2]

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3P-33

The thermal [2+2] cycloaddition of morpholinocycloalkenes with fullerene

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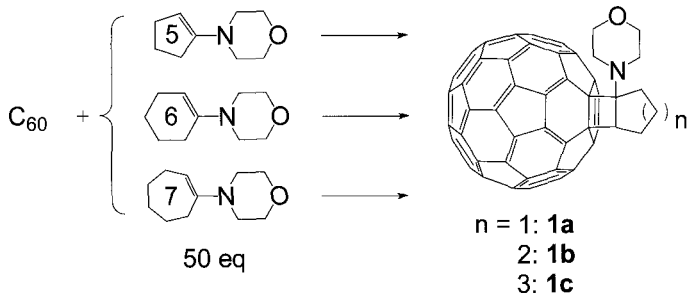
Chemical functionalization of fullerenes has attracted significant attention in view of the biological and electronic applications. Fullerene undergoes various nucleophilic additions, organometallic reactions and cycloadditions such as Bingel, Prato, Diels-Alder reaction, or addition of 1,3-dipoles. Although a variety of cycloaddition reactions have been developed, only a few [2+2] cycloadditions to fullerene have been reported. The reasons include the difficulty of the control of addition number and the absence of regioselectivity due to photoreaction. Here, we focused on thermal [2+2] cycloaddition [1] of the [60]fullerene with electron-rich double bond of enamines.

The reactions of excess morpholinocycloalkenes with C_{60}, run at reflux in dry toluene for 24 h, afforded the cyclobutane-fused fullerene derivatives **1a-c** (Scheme 1). And were conducted in dark under Ar atmosphere to avoid some photoinduced reactions, since there have already been a number of examples of photoinduced radical reactions of [60]fullerene with tertiary amines [2]. As noted in Table 1, the reactivity slightly decreases with extending carbocyclic ring. This result suggested that cycloheptene should undergo steric effect rather than cyclopentene.



Scheme 1. Synthesis of cyclobutane-fused fullerenes

Table 1. HPLC area ratio after 24h

1	solvent	C_{60} (%)	product (%)
1a	toluene	6	77 (70) [a]
1b	toluene	36	62 (54) [a]
1c	*o*-DCB	3	47

a: isolated yield

The Hydrolysis of cyclobutane-fused fullerene **1a** with an acid gave cyclopentanofullerene. The structure was determined by ^{1}H-NMR, ^{13}C-NMR, HSQC, HMBC, ^{1}H-^{1}H COSY. Unexpectedly, it was the same product as previously reported [3] β-substituted cyclopentanone adduct rather than α-substituted compound obtained from usual hydrolysis of enemines.

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[2] G.Schick, K.-D. Kampe, and A. Hirsch, *Chem. Commun.*, 2023 (1995).
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3P-34

Growth Control of C_{60} Fullerene Nanowhiskers

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C_{60} fullerene nanowhiskers (C_{60}NWs) can be synthesized by liquid-liquid interfacial precipitation method (LLIP method) [1], using good solvent solutions of C_{60} and poor solvents of C_{60}. It has been reported that the factors of light, temperature, growth periods, water and the kind and composition of solvents influence the growth of C_{60}NWs when the LLIP method was applied to the synthesis of C_{60}NWs [2, 3, 4]. These studies have been performed in various conditions to get thin and long C_{60}NWs. In addition, the growth control of C_{60}NWs is necessary to apply them to various fields. Although much attention has been paid to the growth mechanism of long C_{60}NWs (Fig. 1), there are little investigation about the synthesis of short C_{60}NWs. In this study, we have successfully synthesized the short C_{60}NWs as shown in Fig. 2 by LLIP method using various ratios of C_{60}-saturated solution and isopropyl alcohol (IPA).

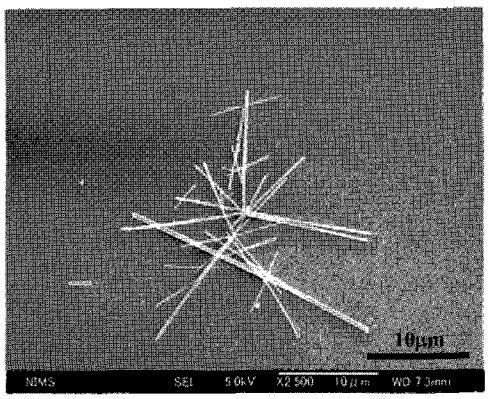

Fig. 1 SEM image of long C_{60}NWs prepared by LLIP method.

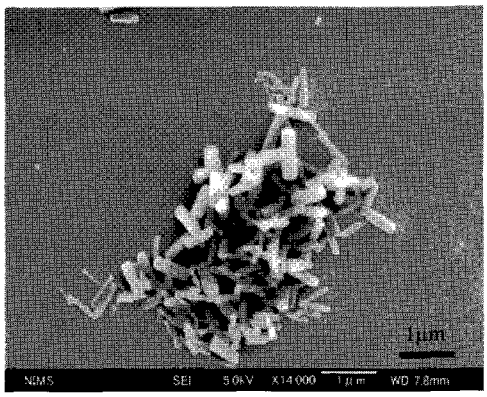

Fig. 2 SEM image of short C_{60}NWs prepared by LLIP method.

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3P-35

Effect of addition of Pt on Magnetic properties of iron-filled carbon nanotubes

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Carbon nanotubes (CNTs) filled with ferromagnetic metal show shape anisotropy originating from the high-aspect ratio of magnetic particles[1] and anticorrosivity due to having a graphite layer acting as a protective layer of the encapsulated metal, so that are expected to apply for magnetic recording media[2] and for biomedical applications[3]. It is desirable to be able to control the magnetic properties appropriately for these applications. It is important to clarify the influence of shape and the crystallographic structure of the metal filled in CNTs in the magnetic properties for those purposes. We have investigated magnetic properties of Fe filled CNTs synthesized by a thermal CVD (TCVD) method and an effect of Pt addition to the Fe was examined to enhance the coercivity.

Fe-filled CNTs were synthesized on SiO_x / Si substrates covered with 2 nm Fe on which 0.6~1.4 nm Pt layer was deposited. Ferrocene was used as a source gas and the TCVD was carried out under the conditions of 785℃ and 1 atm. The TCVD gives vertically oriented CNTs almost entirely filled with Fe [Fig. 1(a)]. It was confirmed that almost all of the encapsulated metal in the CNTs were the single crystal by selected area diffraction patterns (SAED). The SAED pattern that was identified as that of FePt was also obtained at the root of CNT grown on Pt(1.4 nm) / Fe(2.0 nm) / SiO_x / Si substrate [Fig.1(b)]. The coercivity of the CNTs perpendicular to the substrate was 1.1 kOe for Fe film. It increased up to 2.2 kOe by adding Pt layer on the Fe film [Fig.2]. On the other hand, the coercivity decreased by annealing of the CNTs in an Ar atmosphere that was carried out under an intention to enhances the coercivity. This indicates that the crystal structure of the FePt alloy was distracted by the annealing. Detailed investigation to enhance the coercivity is in progress.

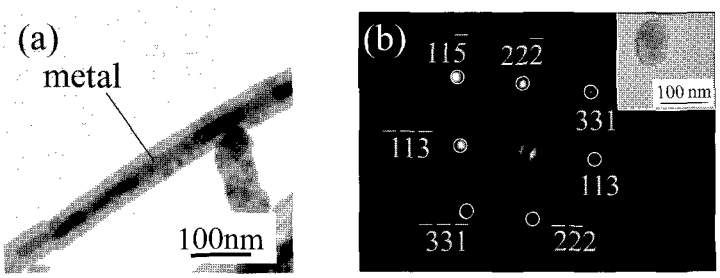

Fig.1 (a)TEM image and (b)SAED image of Fe-filled CNTs grown by TCVD method.

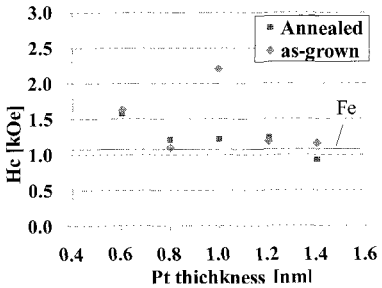

Fig.2 Dependence of Coercivity of Fe-filled CNTs on Pt thickness.

Acknowledgment: This study has been partly supported by JSPS KAKENHI and Mie University VBL.

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3P-36

Water Structure inside Finite Length Single-Walled Carbon Nanotubes : SWCNT-Edge Effect

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Water confined in nano space exhibits unusual behavior that cannot be observed in the bulk. In a previous work, we experimentally clarified that the phase behaviors of water confined in Single-Walled Carbon Nanotubes (SWCNTs) with diameters below and above ~1.5 nm are quite different from each other. That is, water confined in SWCNTs with diameters between 1.17 to 1.44 nm undergoes a liquid-to-solid like transition with decreasing temperature and forms ordered tubular ice structures, so-called ice nanotubes (ice-NTs), while water exhibits a wet-dry transition in a diameter range between 1.6 and 2.4 nm and is ejected from the inside of the SWCNTs at lower temperatures.

Around the intermediate diameter range, previous studies employing molecular dynamics (MD) calculations have predicted the existence of more complex nano-ice structures inside SWCNTs, such as multi-layer ice structures and ice-NTs containing one-dimensional water chain. These calculations were done on infinite length SWCNTs. In the present study, we focused on finite length SWCNTs with diameters ~1.4 nm to examine the effect of open ends of SWCNTs on water structure. It was found that the ice structure formed at low temperatures were strongly affected by pore diameters and the number of water molecules in the system. Corresponding powder X-ray diffraction (XRD) experiments on SWCNTs with a mean diameter of 1.46 nm strongly suggested the presence of such filled structure.

Besides, the effect of heat and hydrogen treatments for SWCNTs on the wet-dry transition is also examined for SWCNTs with mean diameters 1.68 and 2.40 nm by XRD experiments.

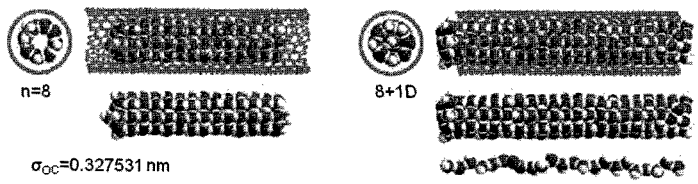

Figure Snapshot structures of water inside the SWCNTs. Water molecules are stuck on the inner wall of the SWCNT at first, and then fill the hollow space with increase in their number.

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3P-37

Dynamics of water confined in zeolite templated carbon

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Zeolite templated carbon (ZTC) is an ordered microporous carbon with interconnected nanometer scale cavities forming a three-dimensional diamond like structure. We report here on studies of water adsorption and its properties in ZTC framework by means of thermo gravimetric analysis (TGA), X-ray diffraction (XRD), differential scanning calorimetry (DSC), and NMR measurements. It was found that the amount of water adsorbed inside the ZTC reaches ~140 wt% at room temperature (RT) with a small lattice expansion. This corresponds to a mean water density of 0.61 g/cm^3 and the total density of water-ZTC system of 1.0 g/cm^3. Contrary to the bulk water, XRD measurements revealed that the water-containing ZTC exhibits a gradual lattice contraction by 3 % with lowering temperature from RT to 200 K. DSC measurements suggested that specific heat of the confined water decreases from 4.2 J g^{-1}K^{-1} at 310 K to 2.9 J g^{-1}K^{-1} at 206 K without any evidence for the first order phase transition in a temperature range between 160 K and 310 K. ^{2}H- and ^{1}H-NMR of heavy and light water adsorbed to ZTC clearly indicated that the water are highly mobile above ~200 K in ZTC: The rotational correlation time was estimated to be $\tau_{\mathrm{rot}} = \tau_{0,\mathrm{rot}} \exp(T_{0,\mathrm{rot}} / T)$ with $\tau_{0,\mathrm{rot}} = 1.0 \times 10^{-19}$ s and $T_{0,\mathrm{rot}} = 5021$ K, and the translational correlation time shorter than 1.0 μs above 200 K. The ZTC serves as a model system for fundamental studies of water with a three dimensional hydrogen network system in confined environments.

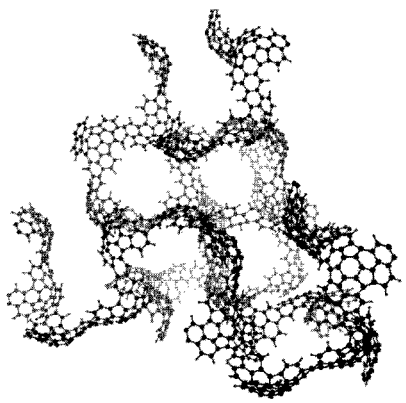

Fig. 1. Possible structural model proposed for ZTC solid.

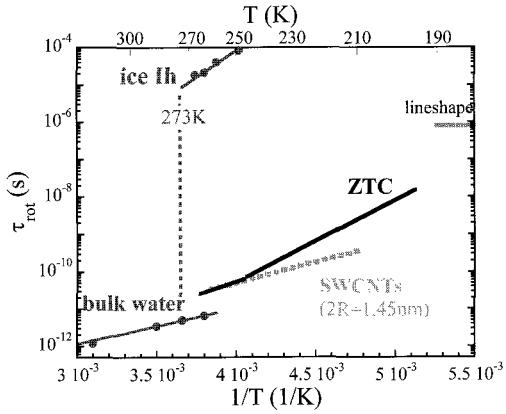

Fig. 2. Temperature dependence of rotational correlation time of water molecules in ZTC.

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3P-38

Growth of Inner Nanotubes from Confined Ionic Liquid inside a Tip-closed SWNT

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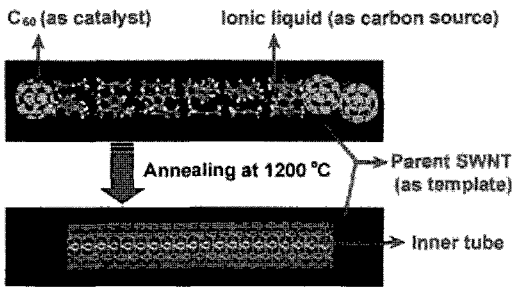
The interior space of the single-walled carbon nanotubes (SWNT) can be utilized for the encapsulation of molecules. It provides an ideal model for the study of the so-called confined nano-reaction.[1-2] Herein, we report the synthesis of carbon nanotubes from an ionic liquid encapsulated inside SWNT via a nanotemplate reaction (Scheme 1). Both single-walled and multi-walled carbon nanotubes can be generated in the channel of the parent SWNT using ionic liquid as the carbon source. In comparison to the reported catalytic and noncatalytic growths of the inner-tube from filled SWNT, a new types of growth mechanism, which involves C_{60} as the catalyst (or seed) in the first stage and finally fusing into the inner-tube network, is supposed and discussed. More importantly, we have developed a two-step filling process for the encapsulation of the ionic liquid in the tip-closed SWNT, where the fullerenes inserted at the end of the host SWNT act as a plug to prevent the leakage of the confined ionic liquid during heat treatment. This opens a new prospective path for the advancement of the tube chemistry of other liquids or low-thermal stability materials.



Scheme 1. Schematic diagram for the growth nanotube from confined ionic liquid in a SWNT template.

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3P-39

Growth of Carbon Nanotubes Filled with Metal Compounds and "Tee-like" Carbon Nanotubes by Alcohol CVD

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Many researches on various metal/metal compound-filled carbon nanotubes (CNTs) have been reported to date. However, it is difficult to achieve long one-dimensional growth via one-step synthesis. We have succeeded in the one-step syntheses of copper and copper sulfide-filled CNTs (Cu@CNTs and CuS@CNTs) by modified arc discharge methods. Moreover, we have succeeded in vertical growth of nickel sulfide-filled CNTs (NiS@CNTs) by alcohol chemical vapor deposition (CVD). In this study, we investigated effective formation conditions of nickel and copper compound-filled CNTs grown by alcohol CVD. In addition, we found CNTs having a "tee-like" structure during the investigation of copper-filled CNTs.

Metal (Ni or Cu) compound-filled CNTs were formed by alcohol CVD method. Ethanol solutions of $NiCl_2$ or $CuCl_2$ were sprayed on a Si plate maintained at 400°C followed by heating at 640°C for 30 min. in an Ar atmosphere. Furthermore, we used copper powder in the case of the CVD growth using copper. The CVD growth was carried out at 700-1100°C for 30 min. at a vapor pressure of ethanol containing CS_2 in a vacuum.

The filling rate of NiS@CNTs was about 80%, and had diameters of about 100 nm and lengths of about 3 μm. The NiS@CNTs grew vertically on the substrate. On the contrary, little copper-filled CNTs were formed by alcohol CVD using the sprayed substrate (Fig. 1(a)). Only very thick copper-filled CNTs having a diameter of about 500 nm grew at the highest growth temperature (1100°C) (Fig. 1(b)). In the case of the CVD using copper powder, CNTs shown in Fig. 2(a) were formed effectively at the growth temperature of 1000°C. Diameters of the CNTs gradually became thin at the root (Fig. 2(b)), and a polyhedral copper particle was deposited at the tip (Fig. 2(c)). The structure is just like a "tee" that you stick in the ground to support a golf ball before you hit it. The root was open-end structure shown in Fig. 2(d). We will present the detail of growth conditions, mechanism and structures of the NiS@CNTs and the "tee-like" CNTs in the presentation.

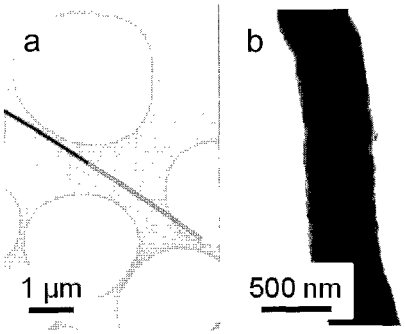

Fig. 1 TEM images of copper-filled CNTs formed by alcohol CVD using a $CuCl_2$· aq-sprayed substrate. (a) A typical thin copper-filled CNTs and (b) a thick copper-filled CNT grown at 1100°C.

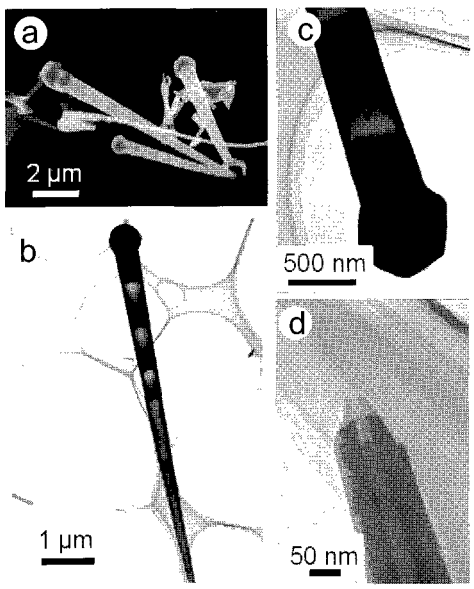

Fig. 2 "Tee-like" CNTs formed by alcohol CVD using copper powder. (a) SEM image, (b) a typical TEM image, (c) a polyhedral copper particle at the tip and (d) the open-end structure at the root.

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3P-40

Optical excited state induced by the interaction between rigid polymers and single-wall carbon nanotubes with large diameters

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Techniques to extract single-wall carbon nanotubes (SWCNTs) with specific structures (i.e., chiral induces) from the carbon compounds with various structures is important for the synthesis of functional nanocomposites as well as the investigation of fundamental properties. In the techniques of extraction, the polymer wrapping with polyfluorene is a powerful method which disperses selectively semiconducting SWCNTs with specific chiral indices[1]. However, the dispersed SWCNTs are restricted to small tube diameters (< 1.2 nm). In this work, we report that a fluorene-based copolymer is also effective in selecting the structures of SWCNTs with large tube diameters. Moreover, spectroscopic analysis suggests that the exciplex formation between SWCNTs and the polymers plays a key role in the effective extractions.

We find that poly(9,9-dioctylfluorene-alt-benzothiadiazole) (F8BT) can disperse selectively semiconducting SWCNTs with several large diameters (> 1.3 nm) in toluene. The excitation spectrum of F8BT in toluene is significantly different in spectral pattern from the absorption spectrum as shown in Fig. 1. In the excitation spectrum, two peaks are observed at the tail of the absorption band. The discrepancy between absorption and excitation spectra indicates excimer formation due to the rigidity of the polymer. On the other hand, as shown in Fig. 2, the SWCNTs wrapped by F8BT exhibit intense near-infrared emissions at an excitation wavelength of 515 nm. The excitation energy is a little lower than the absorption energy of F8BT excimer in Fig. 1. The result suggests that the emissions of the polymer-wrapped SWCNTs are not due to energy transfer[2] from the polymer to the SWCNTs, but are associated with exciplex formation between the SWCNTs with specific structures and the polymer.

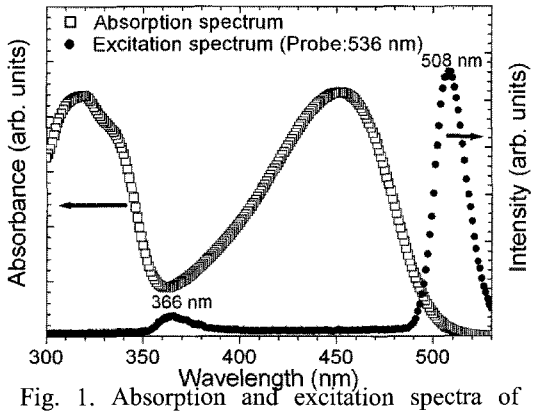

Fig. 1. Absorption and excitation spectra of F8BT in toluene (0.62 g/L).

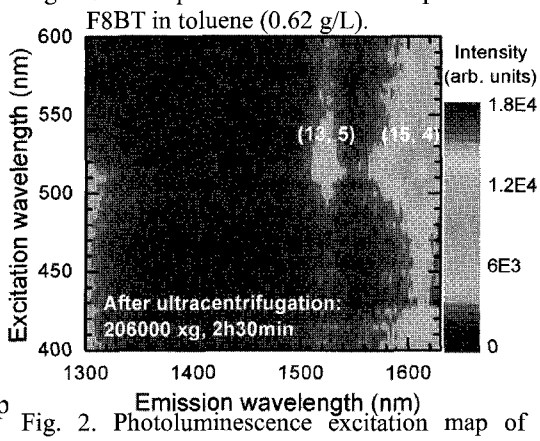

Fig. 2. Photoluminescence excitation map of SWCNTs wrapped by F8BT in toluene.

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3P-41

Polyynes and Cyanopolyynes Included in α-Cyclodextrin Crystals

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Inclusion compounds are known for their ability of trapping molecules to isolate desired molecular species into solutions or crystalline forms. Cyclodextrins (CDs) are cyclic oligomers of glucose having a cavity of nanometer scales inside the cup structure. They are α-, β-, and γ-CDs depending on the number of glucose units forming a ring structure, i.e., 6-mer, 7-mer, and 8-mer, respectively. Fullerene C_{60} can be trapped with two γ-CDs and the inclusion compound is soluble in water. Polyynes $C_{2n}H_2$ (n=4-8) and cyanopolyynes $HC_{2n+1}N$ (n=3-6) are the molecules of *sp*-hybridized carbon chains with alternating single- and triple-bonds. Solubility of these molecules is excellent for organic solvents but poor for water. Under the presence of CDs and water, polyyne molecules are trapped inside the cavity of CDs and solved into water. When the concentration of CDs in water is relatively high, CDs containing hydrophobic molecules eventually precipitate to form crystalline materials. We here present our recent progress on crystallization of α-CD containing size-selected polyynes or cyanopolyynes together with organic solvents such as hexane or acetonitrile.

The upper curve in Fig. 1 shows optical absorption spectrum of a solid film of α-CD containing a small amount of cyanopolyyne molecules of HC_7N. On a smooth back ground due to the scattering of light, two absorption bands are discernible in 220-270 nm and in 280-360 nm. The former is associated with the allowed transition of the HC_7N molecule, which appears in 190-240 nm in a solution of acetonitrile as in the lower curve in Fig. 1. The latter band in longer wavelengths is newly appeared or intensified by inclusion processes. We discuss on the mechanism for intensification of an intrinsically forbidden transition [1], which can become allowed by symmetry lowering in the crystal field.

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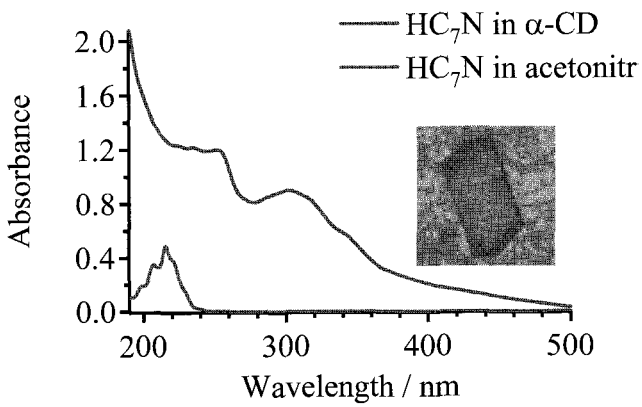

Fig. 1. Absorption spectra of crystalline α-CD with HC_7N and acetonitrule (upper trace).

3P-42

Optical Absorption Spectra of Single Wall Carbon Nanotubes Containing Hydrogen-End-Capped Polyynes Inside

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Single wall carbon nanotubes (SWNTs) can accommodate various molecules inside. Nishide et al. reported that hydrogen-end-capped polyyne, $C_{10}H_2$, can be trapped inside SWNTs and was stable well above 300°C as revealed by Raman spectroscopic studies [1]. Raman spectra of $C_{10}H_2$@SWNTs and $C_{12}H_2$@SWNTs with the excitation at 514.5 nm (2.41 eV) exhibited combination and overtone bands, indicating the resonance effect [2]. Malard et al. observed Raman excitation profile to find resonance at 2.1±0.15 eV for $C_{10}H_2$@SWNTs [3] and attributed it to the resonance absorption of the molecule [4]. However, the resonance energy ~2.1 eV is substantially lower, by >1.1 eV, than the energy for the absorption band of $C_{10}H_2$ in solutions [5]. Moreover, the resonance energy in SWNTs does not depend very much upon the size of polyynes, while the absorption band of polyynes in solutions systematically shifts to longer wavelength with increasing the molecular size.

For the study on the electronic states in $C_{2n}H_2$@SWNTs, we examined optical absorption spectra. The SWNTs formed by laser ablation were sintered in the solution of *n*-hexane containing size-selected polyynes, then sonicated and centrifuged with cholic acid in D_2O. The UV/VIS/NIR absorption spectra were recorded for $C_{10}H_2$@SWNTs and compared with those for SWNTs. The spectra do not differ very much between those for SWNTs with and without $C_{10}H_2$. The resonance curve for $C_{10}H_2$@SWNTs at ~2.1 eV may rather fit to one of the absorption bands of SWNTs.

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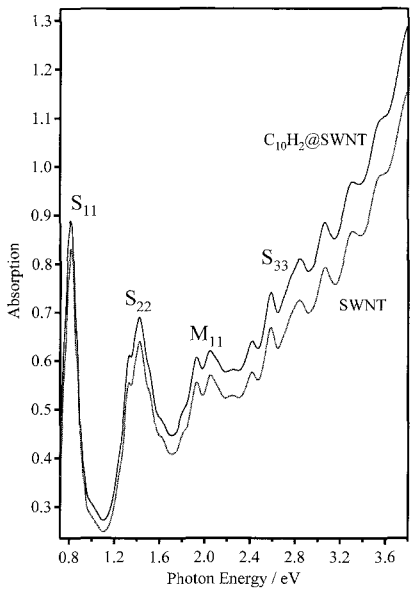

Fig. 1. Absorption Spectra for $C_{10}H_2$@SWNTs and SWNTs.

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3P-43

Synthesis of One-Dimensional Coordination Polymer of Size-Selected Polyynes and Silver Ions

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Coordination compounds are known for their variety of chemistry spanning from molecular structures to applications. Ions or clusters of noble metal elements are located at the center of some coordination bonds towards the molecules. The electrons are donated to or drown form the metallic center for stability. Polyyne molecules with π-electron systems can be also candidates for creating novel coordination compounds. Lucotti et al. reported surface-enhanced Raman scattering (SERS) of polyyne mixtures deposited on silver nanoparticles and observed indication for aggregation of those molecules [1]. Tabata et al. performed SERS experiments for size-selected polyynes $C_{2n}H_2$ (n=4-8) adsorbed on Ag island films to find systematic shifts in vibrational frequencies for the mode in 1800-2200 cm^{-1} according to the molecular size [2]. Compagnini et al. extended the SERS studies using other noble metal elements such as gold [3]. We here report on the synthesis of coordination polymer including size-selected polyynes stabilized with silver ions. Having a strand of coordination polymer of well defined structure, the interaction between the metal and the polyyne molecule is to be clarified through the detection of optical absorption and Raman scattering processes.

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3P-44

Weak Pre-Oxidation of Graphene-Based Nanomaterials for Enhanced Structure Distinction by Thermogravimetric Analysis

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Thermogravimetric analysis (TGA) is a powerful tool for analyzing graphenous nanomaterials. We previously reported that single-walled carbon nanohorns (SWNHs) and thin graphene sheets (TGS) having close combustion temperatures can be distinguished and even quantified by employing high resolution thermogravimetric analysis (HR-TGA) which can control the specimen temperature responding to the specimen weight-loss rate [1]. However, further discrimination of the graphenous structures in the SWNHs is not easy even by using HR-TGA. We show in this report that the structure analysis of the graphenous materials by HR-TGA can be empowered by weak pre-oxidation, the immersion in H_2O_2 solutions at room temperature.

As-grown product contained nanohorn aggregates composed of SWNHs (combustion temperature: 560°C) and TGSs (590°C), micrometer-sized graphitic balls (740°C), and small amount of non-graphitic materials (450°C) as estimated from the derivative curves of the weight-temperature curves of HR-TGA. As-grown products were immersed in H_2O_2 solution for 1 h, 1 day, or longer at room temperature. The combustion temperature of SWNH and TGS decreased rapidly by the H_2O_2 treatment for 1 h to 1 day, but not so much by the longer period immersions. At the same time, the number of oxygenated groups increased greatly as confirmed by TG-MS measurements. Apparently, the combustion temperature decreases were due to the number increase of oxygenated groups [2]. The combustion temperature decrease of TGS by the H_2O_2 treatment was larger than that of SWNHs, which is reasonable because TGSs have chemically weak at the edges.

Since the oxidation effect of H_2O_2 did not last for a long period, the second immersion in fresh H_2O_2 was performed. As a result, the combustion temperatures of SWNH and TGS further decreased, and even appeared a "new component" (500°C, 18%). To clarify the structure of the "new component", we stopped TGA at 500°C and took out the residue. TGA of the residue indicated that the "new component" was a part of SWNHs or has a structure similar to SWNHs. Although the exact structure assignment of the "new component" is difficult, it is certain that they are basically constructed of graphenes but had the defect sites which easily become full of oxygenated groups by the H_2O_2 treatment.

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3P-45

Interaction Between Carbon Nanohorns and Amino Acids

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Biomedical applications, including drug delivery and photo-hyperthermia agents for cancer therapy, of single wall carbon nanohorns (SWNHs) have been investigated [1-2]. SWNHs certainly interact with proteins, carbohydrates, fats, etc in a living body. Especially, the interaction with protein may strongly influence on the toxicicological assay of SWNHs or therapeutic efficacy of SWNH-based drug delivery. However, it is difficult to study how SWNHs interact with the proteins because the proteins have the complex structure and there are more than tens of millions of proteins exist in living body. Here, we clarify the interaction between SWNHs and amino acid, the elementary unit of protein, to get some information about the interaction of proteins and SWNHs.

We chose five types of amino acids (lysine, phenylalanine, histidine, tryptophan, and methionine). Each amino acid was dissolved in water (Concentrations: 0.05 to 0.5 g/L), in which as-grown SWNHs were added, mixed, and stirred for overnight. Then we filtered the aqueous dispersion of SWNHs and amino acids, and estimated the quantity of amino acid attached on SWNHs through measurement of the concentration of amino acid in filtrate by optical absorption spectroscopy. The results showed that all of these amino acids were adsorbed on SWNHs but the adsorbed quantities were different. Lysine with a C4 alkyl chain had a largest quantity adsorbed on SWNHs, followed by Tryptophan and Phenylalanine, each having a benzene ring. Quantities of histidine and methionine attached on SWNHs were smaller in quantities, probably because they did not have those hydrophobic groups. The detail about the adsorption state will be discussed in conference.

Acknowledgement: X.Z. and S.I. express their appreciation to the financial support from Balzan Foundation.

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3P-46

In-situ Raman Spectroelectrochemical Investigation of Potential Depended Electronic Structure of Single-Walled Carbon Nanotubes

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The electronic properties of single-walled carbon nanotubes (SWCNTs) strongly depend on their diameters and chiralities ((n,m): chiral indices). To develop the applications of SWCNTs such as double layered capacitors and electrochemical sensors, it is important to understand electronic structures of SWCNTs in a liquid. *In-situ* Raman spectroelectrochemistry is strong tool for investigating the properties of SWCNTs at potential applying condition [1, 2]. In this study, SWCNTs were synthesized onto an Au electrode (SWCNTs/Au) by CVD method. The relationship between the applied potential to SWCNTs and the electronic structure in an aqueous solution was investigated using *in-situ* Raman spectroelectrochemical measurements.

The intensity/potential profiles of the radial breathing mode (RBM) bands were plotted to evaluate the chirality dependence of the electronic structure (Fig. 1). In the case of semiconducting SWCNTs, plateau region of the peak intensity was observed. These results indicate that the potential range at the plateau region would correspond to the band gap of the semiconducting SWCNTs. The band gap energy increased with decreasing the diameter of semiconducting SWCNTs. This tendency was similar to the results expected by the theoretical simulation [3].

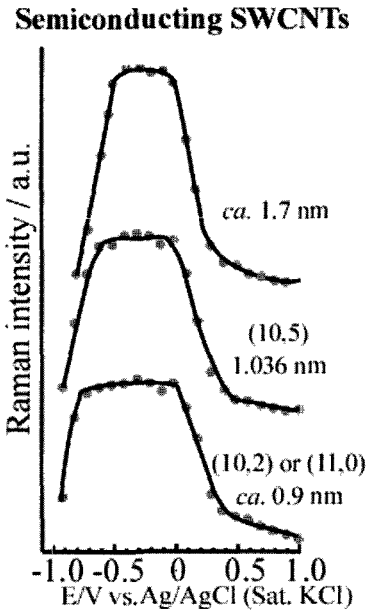

Fig. 1 The Raman peak intensity excited by 1.58 and 2.41 eV laser radiations at semiconducting SWCNTs as a function of electrode potential.

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3P-47

Synthesis of metal-nanowire@SWNTs and their physical properties

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Carbon nanotubes (CNTs) have attracted extensive interests for the application of nanoelectronic devices because of their unique structure and electrical properties. In any of such CNTs applications, control of electronic structure of CNTs is crucial, and chemical doping is one of the most important techniques to modulate the electronic structure of CNTs; encapsulating various atoms and molecules into CNTs inner-space is a stable chemical doping. In particular, recently reported metal-nanowire encapsulating CNTs[1] are expected to show a heavy electron doping due to a massive electron transfer from metal atoms to CNTs. In this study, in addition to electric properties, we have focused on investigation of doping-modulated electronic structure of the nanowire encapsulating CNTs using optical absorption spectroscopy. Single-walled carbon nanotubes (SWNTs) were synthesized by the arc-discharge method (SO-HT, Meijo Nano Carbon Inc.) and Europium metal were used to synthesize metal-nanowires inside inner-space of SWCNTs.

CNTs film, fabricated by vacuum filtration method [2], was used for characterizing optical and electrical properties of Eu-nanowire@SWNTs. In optical absorption spectra of SWNTs films, not only S_1 but also S_2 and M_1 peaks almost completely disappeared after Eu (donor) doping as shown in Fig 1. It indicates that CNTs have been heavily electron doped up to M_1 band by encapsulated Eu atoms. Raman and four prove resistance measurements of Eu-nanowire@SWCNTs films also show significant alternation that is caused by heavy electron doping. In this poster presentation, we will discuss doping effects of the Eu-nanowire @SWNTs in detail.

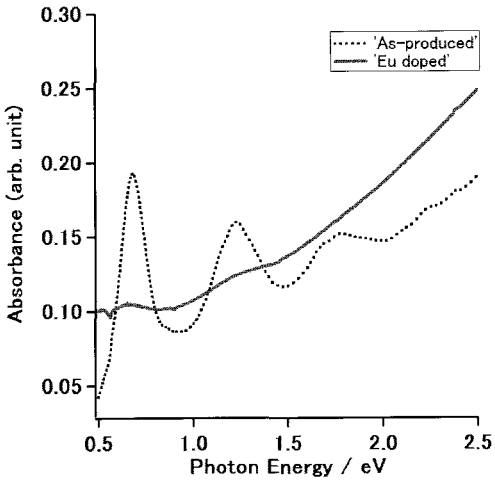

Fig1. Optical absorption spectra of SWNTs film before and after Europium doping

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3P-48

Fabrication and Electrical Transport Properties of Atom Encapsulated Single-Walled Carbon Nanotubes Thin Film Transistors

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Carbon nanotubes (CNTs) with nanometer-order diameter and millimeter-order length attract a great deal of attentions due to their novel applications such as next-generation nanoelectronic devices. Accommodation of various dopant atoms, molecules, and compounds makes it possible to modify the intrinsic electronic and optical properties of single-walled carbon nanotubes (SWNTs). According to our previous researches for the transport property of individual SWNT, alkali-metal-, alkali-earth metal- and halogen-encapsulated SWNTs are found to exhibit n-type and p-type semiconducting behaviors under the field-effect transistor (FETs) configuration, respectively. This indicates that alkali-metal, alkali-earth metal- and halogen atoms operate as an electron donor and an electron acceptor for SWNT, respectively [1, 2]. Based on this background, we utilize the atom-encapsulated SWNTs for the fabrication of high performance n-type thin film transistors (TFTs). In order to reveal the detailed effects of atom encapsulation on the transport property of SWNTs-TFTs, the direct comparison of electrical characteristics of SWNTs-TFTs are also carried out before and after the atom encapsulation with the same SWNTs-TFTs device.

Atom encapsulation is carried out by a plasma ion irradiation method. In this study, a Cs atom is used for the encapsulated atom. It is found that the transport properties of SWNTs-TFTs are clearly changed from p-type to n-type semiconducting characteristics by increasing the energy of ions during the encapsulation process. The highest encapsulation yield is realized under the 60 eV irradiation energy of Cs^+. Higher than this value, SWNTs are damaged by ion bombardment and transport properties are significantly lowered. The Cs encapsulated SWNTs-TFTs show very high stability under the various environments, such as air, water, and high temperature conditions. It should be noted that the n-type characteristics are observed even after the 400 °C annealing. This indicates that it is possible to fabricate very stable n-type TFTs by using the Cs encapsulated SWNTs thin films.

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3P-49

Separation of SWCNTs by gel chromatography using gradient of surfactant concentration

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Single walled carbon nanotubes (SWCNT) show metallic and semiconducting properties depending on their chiralities. Separations of metallic and semiconducting ones (MS separation) using gel chromatography have been reported.[1, 2] In this study, we investigate the diameter-selective MS separation of SWCNT by gel chromatography using the gradient of the surfactant concentration.

SWCNTs (HiPCO, diameter; 1.0 ± 0.3 nm) were dispersed into 2 wt% sodium dodecyl sulfate (SDS) for 12h by using an ultrasonication. The SWCNT dispersion was centrifuged at 23,470×g for 60 min to remove bundles and insoluble materials. A column (length: 20~30 cm) was filled with sephacryl gel (particle size: 25~75 μm) in 20% ethanol. The medium for the gel was then exchanged by 1 wt% SDS. The SWCNT suspension was applied to the top of the column, and 1 wt% SDS was applied to perform chromatography. The difference in the SDS concentration results in the gradient of the concentration at the interface between media. In this case, we observed the gradient-induced separation of SWCNTs depending on the SDS concentration in the column, where the lower and upper parts of the column were red and green, respectively. Figure 1 shows a series of absorption spectra which were measured from the SWCNTs sequentially collected in the eluants as indexed by "a" to "j" shown in Fig. 1. This indicates that SWCNTs with the larger diameter were eluted first, possibly due to the gradient of the SDS concentration. Thus, the gradient of the SDS concentration is effective for the diameter-selective MS separation of SWCNTs using gel chromatography.

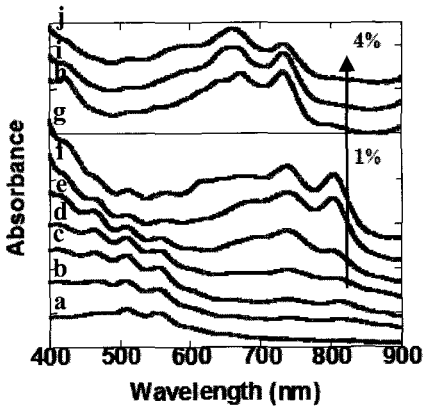

Fig. 1.A series of absorption spectra of collected SWCNTs.

Acknowledgement

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3P-50

Electrochromic Carbon Electrodes: Controllable Visible Color Changes in Metallic Single-Wall Carbon Nanotubes

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Electrochromism is the phenomenon of the optical reversible changes in a material during electrochemical redox processes. Various types of materials exhibit electrochromism, and there is sustained interest in this subject because of its fundamental and practical importance. Indium-tin-oxide (ITO) transparent conductive glasses are usually used for the electrodes to apply potentials on the electrochromic materials to change their colors, however, a system without using ITO is desirable due to increasing demands on rare metal resources. In addition, for practical purposes, the development of electrochromic materials that are electrochemically stable is of great importance for durable electrochromic devices. In this study, we solved these problems by using metallic single-wall carbon nanotubes (SWCNTs) as both electrodes and electrochromic components. We prepared metallic single-wall carbon nanotubes (SWCNTs) with diameters of 0.85nm, 1.0nm, and 1.4nm, exhibiting yellow, magenta, and blue-green colors, respectively, and controlled the colors electrochemically (Fig. 1).[1] It has been considered that SWCNTs would be un-stable at high-electro chemical potential, but we overcame this issue by preparing high-purity samples and using ionic liquids for electrolytes. Clear changes of the optical absorption spectra of the metallic SWCNTs with diameters of 1.4, 1.0, and 0.85 nm were observed. The changes are reversible and repetitive (more than 1000 times), and a relatively good coloration efficiency $(1.9 \pm 0.2) \times 10^2\ \mathrm{cm^2C^{-1}}$, which is sufficient for practical purposes, is achieved. Moreover, we present here a basic model of "All-Carbon Nanotube Electrochromic devices". The electrochromic color changes were achieved without using ITO layers or any electrochromic polymers; the metallic SWCNTs functioned as both the electrochromic components and electrodes, thus they can be termed "electrochromic carbon electrodes". Such electrochromic carbon electrodes are possible due to the following unique characteristics of metallic SWCNTs: (1) The stable color changes originate from electrochemically stable carbon characteristics; (2) the colors are caused by quantized conditions due to the nanotube structures; and (3) metallic nanotubes have a high conductivity. Metallic SWCNTs are thus unique and highly promising electrochromic carbon electrodes to develop durable electrochromic devices without rare metals.

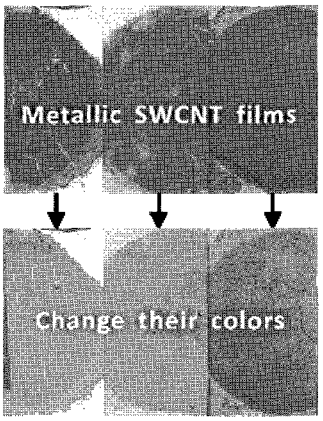

Fig. 1: Electrochromic color changes on thin films of metallic SWCNT with diameters of 1.4, 1.0, and 0.8 nm (from left to right).

This work was partially supported by a Grant-in-Aid for Scientific Research on Innovative Areas (No.21108523, "π-Space") from MEXT, and by Industrial Technology Research Grant Program in 2007 from NEDO.

Reference: [1] Yanagi, Moriya, et al., submitted in 2010.

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3P-51

Biocompatibility of Chitosan/Carbon Materials Composite Membranes for Tissue Engineering

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Carbon material such as single-walled carbon nanotube (SWNTs), multi-walled carbon nanotubes (MWNTs), and graphite have paid much attention as fillers of biomaterials for controlling biocompatibility. In our previous study, chitosan-based composite membranes containing SWNTs, MWNTs and graphite were found to exhibit an inhibitory effect on fibrinogen adsorption and platelets adhesion, compared to chitosan film. On the other hands, only chitosan/SWNTs composite membrane displayed the enhancement of cell attachment and proliferation. Thus, the carbon structures and morphologies were inferred to be strongly involved in biocompatibility control.

In this study, we have focused on a unique carbon material with micro-coiled filament-like structure, named carbon micro coil (CMC). CMC has been known to assume 3D helical/spiral structure, in which the diameters and lengths of CMC are in the range from 1 to 10 m, and from 100 m to 3 mm. The objective of this study is to investigate the effect of CMC on the biocompatibility of CS/CMC composite membranes, in comparison with the effects of the other carbon materials with different geometric structures from CMC.

CS/CMC composite membranes were prepared with various contents of CMC (3, 5, 10 wt%). Raman spectral measurements implied that CMC was mainly comprised of disordered graphite and amorphous carbons, whose abundance on the membrane surface was increased with the CMC content. CS/CMC membranes exhibited a strong inhibition effect against the adsorption of plasma FN at a CMC content of more than 5 wt%, in contrast to an intrinsic CS membrane without CMC. This result suggested that the surface characteristics involving the functions of specific carbon structure and bioactivity of CMC and the membrane morphology prevent blood platelets from adhering and acting on the membrane.

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3P-52

Evaluation of Thermal Conductivity of Single Carbon Nanotube Using Fluorescent Gel Temperature Sensor in Liquid

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[4]*Seoul National University, Seoul 151-742, Korea*

Carbon nanotube (CNT) has potential applications in various fields such as nanosensors. Although electrical and mechanical properties are investigated at single nanotube, measurement of thermal property of single CNT is difficult. Some groups measured the thermal properties of CNT by four-probe method in vacuumed condition. However, measurement by this method has problem of heat transfer from the CNT to the sensing electrodes being connected with the CNT.

Here, we propose a novel method how to measure the thermal conductivity of single CNT in liquid with polymer temperature sensor [1] as shown in Fig. 1. Single CNT was fixed to the silicon cantilever with nanomanipulation and EBID in SEM. The sensor is fixed to the end of the CNT by optical tweezers in liquid. Roles of the sensor are temperature sensing and heat input to the CNT. Here, IR laser was used to heat the sensor. Temperature sensitive quantum dots are impregnated in this sensor. Temperature is measured by detection of the color difference of the red (*Cr*) in the sensor signal. The error of *Cr* is less than ±3%. Sensitivity is -1%/K. Resolution and accuracy of the temperature are 0.019 K and 0.14 K, respectively. The error of the heat input is less than 4%. Thermal conductivity can be calculated based on the theoretical analysis of one dimensional heat conduction. The estimated error of the thermal conductivity is less than 10%.

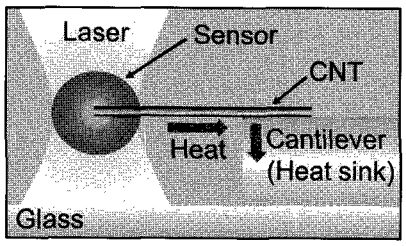

Fig. 1 Thermal conductivity measurement of CNT with temperature sensor in

Acknowledgements: This work was supported by KAKENHI (20246044) and CREST, JST.

[1] H. Maruyama, F. Arai, T. Fukuda, Lab on a Chip, 8-2, (2008), 346 - 351

Corresponding Author: Kyohei Tomita
Tel: +81-52-789-4493, Fax: +81-52-789-5213, E-mail: hisataka@mech.nagoya-u.ac.jp

3P-53

Structural dependence of Multi-Walled Carbon Nanotubes on fuel cell performance

○Shinya Kitamura, Takeshi Hashishin, Jun Tamaki, Kazuo Kojima

Department of Applied Chemistry, Ritsumeikan University, Shiga 525-8577, Japan

It is important that the control structure of multi-walled carbon nanotubes (MWNTs) was applied to electric devices such as field emission devices and batteries. In our previous study, alumina nanohole array was used as a template for the guide growth of MWNTs [1]. As one of fuel cell application, we tried to directly grown MWNTs on the surface of carbon paper (CP), which is composed of carbon fibers with 5 um in diameter, in order to reduce ohmic losses between an electric collector of CP and a catalytic layer of MWNTs. In our previous study, it was confirmed that the G/D ratio of as-grown MWNTs is increased with decreasing oxygen concentration by vacuum level during CVD process.

In this study, we investigated the changing amount of the G/D ratio under electrical power loading: 0.5 V for 6 h at 80 °C in air. As the results, it was tended that the performance of fuel cell for MWNTs/CP electrode, i.e., a maximum power density and open-circuit voltage (OCV), increased with increasing the G/D ratio, as shown in Fig. 1.

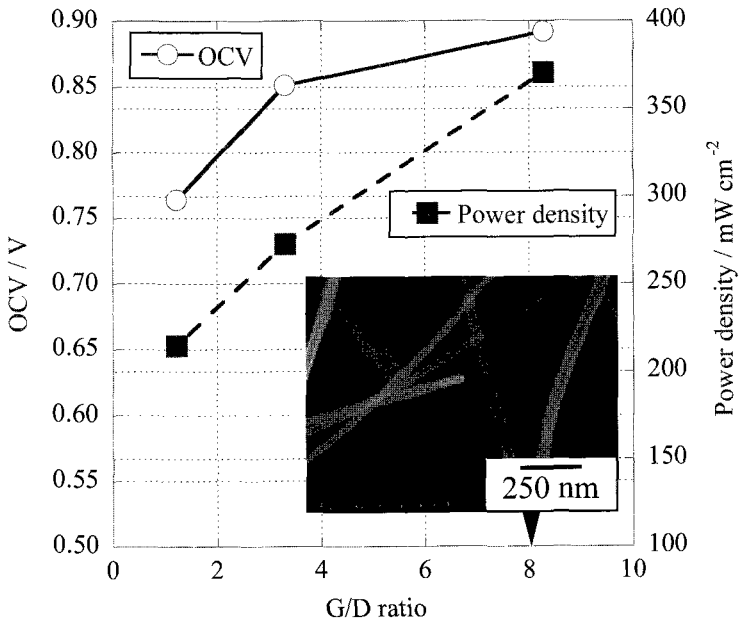

Fig. 1 Effect of G/D ratio on fuel cell performance.

[1] T. Hashishin, Y. Tono, and J. Tamaki, *Jpn. J. Appl. Phys*, **45**, 333-337 (2006).

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2011 年 3 月 8 日発行

第 40 回記念フラーレン・ナノチューブ総合シンポジウム
講演要旨集

＜フラーレン・ナノチューブ学会＞
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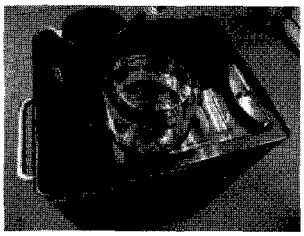
本装置はグラフェン・カーボンナノチューブや燃料電池用触媒を始めとする
各種ナノ粒子を分散させる事を目的に開発いたしました。

実施例：グラフェン・カーボンナノチューブの分散、燃料電池用触媒評価、
納入実績：各大学、自動車メーカー、光学機器メーカー、電子部品メーカー



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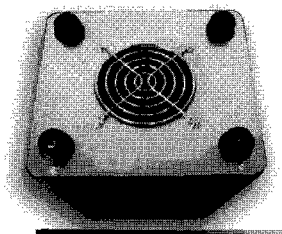
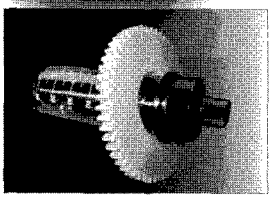


冷却ファン

冷却ファン及び専用回路の採用により長時間運転が可能。



・ギヤー板（品番：NG-350-50）
・50 mL 専用共振棒１本入りセット（品番：MM-50WS）

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NR-350仕様表（予告無く変更する場合があります）

品番	NR-350
品名	密閉式超音波分散装置　Nanoruptor
超音波周波数	20 kHZ
超音波出力	380,300,250,130 W（切替式）
電源	100 V、50/60 Hz、5.5 A
最低設置スペース概寸	400 (W) × 350 (D) × 680 (H) mm
発振ユニット概寸	400 (W) × 280 (D) × 160 (H) mm
処理ユニット概寸	250(W) × 200 (D) × 300 (H) mm
消音箱概寸	400 (W) × 350 (D) × 520 (H) mm
NR-350 全体重量	36 Kg
ランタイマー	599 サイクル
インターバルタイマー (ON)	0 ～ 59 秒、デジタル
インターバルタイマー (OFF)	0 ～ 59 秒、デジタル
処理本数	1 本 (50 mL チューブ) ～各種
付属品	消音箱、電源ケーブル、接続ケーブル、排水ポンプ、取り扱い説明書、ユーザー登録カード
備考	NR-350 は機器のみです。別途処理量に応じたアクセサリー（ギヤ・板＋チップ）をお買い求め下さい。

品名	品番	包装	希望販売価格
超音波密閉式分散装置 Nanoruptor®	NR-350	1 UNIT	￥1,950,000
*アクセサリユニットは含みません			
50 mL チューブ用チップ	MM-50WS	1 SET	￥54,000
使用可能チューブ：マルエム社製 50 mL ねじ口試験管			
ギヤー板	NG350-50	1 PC	￥9,000
冷水循環器	CP80-R	1 UNIT	￥264,000
冷水循環器接続チューブ	TU-100	1 PC	￥15,000

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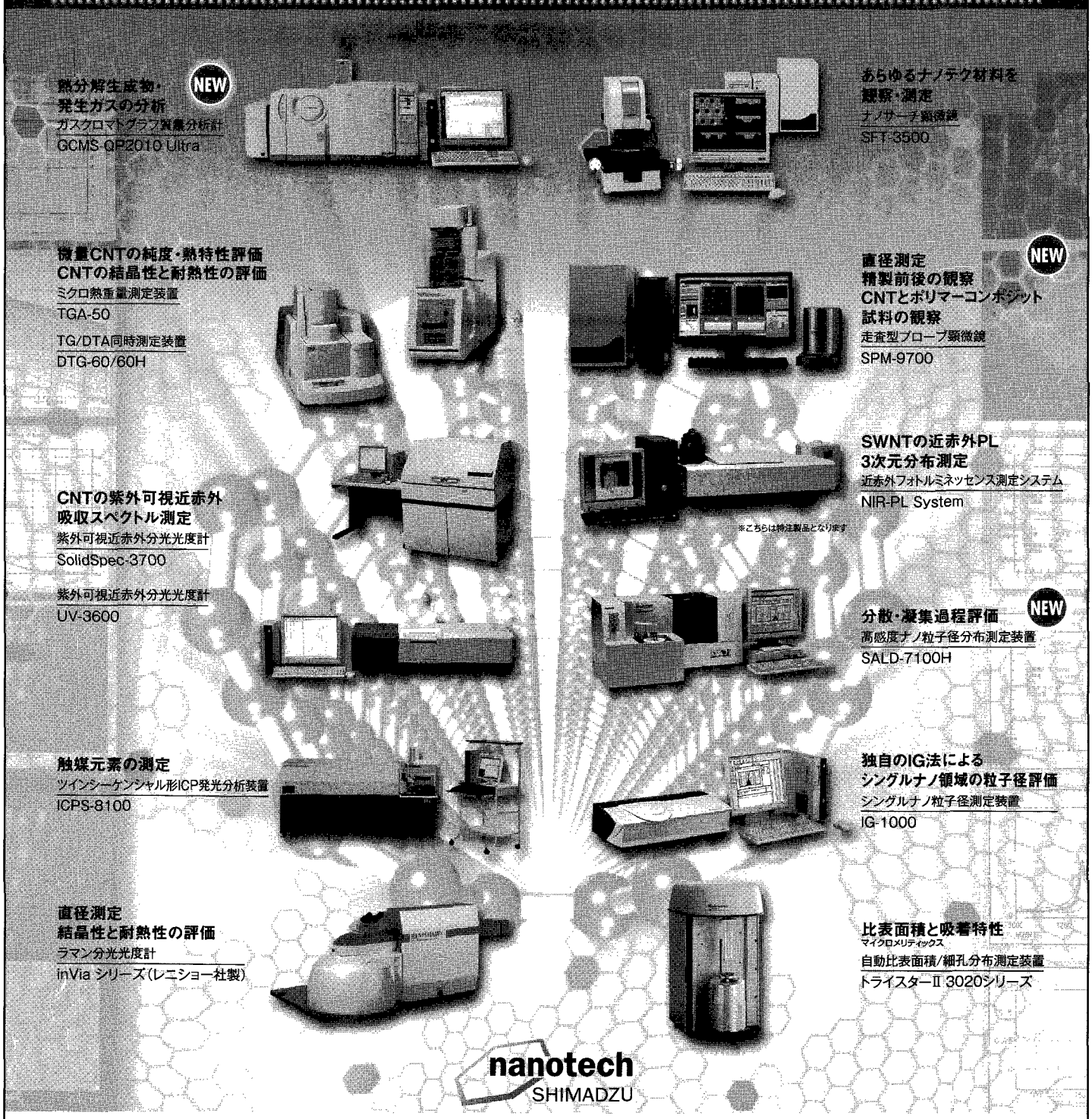

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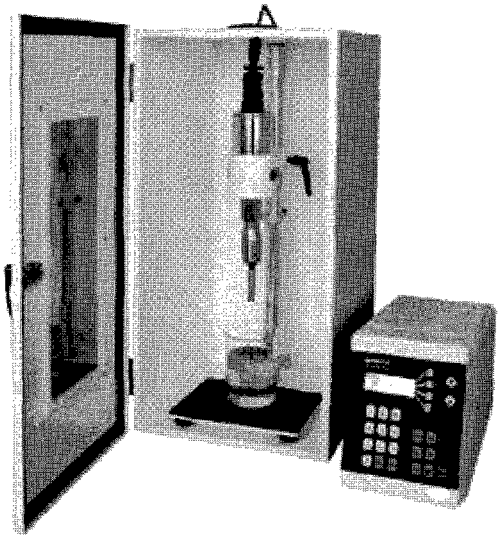
溶液中の粒子のナノレベル微細化・分散に

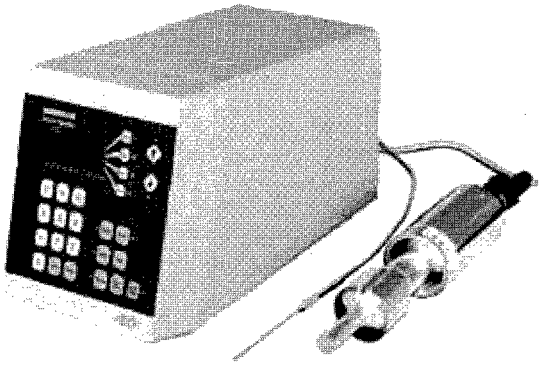
BRANSON 超音波ホモジナイザー

ホーン先端部の振幅の安定性を、より高めた Advance タイプ になりました。

近年のナノテクノロジーの発展及び粉体関連技術の向上により、より微細な粒子に対する乳化分散処理の要望が増えてまいりました。
超音波ホモジナイザーを使用し、均質な乳化分散処理を行い、安定させることにより製品の機能は向上します。
ブランソン社では 20kHz 機と、40kHz 機の 2 タイプを用意しております。
1 次粒子の凝集力にも拠りますが、20kHz 機では 100nm 程度までの分散力があります。40kHz 機は、さらに細かいレベルで分散ができる可能性があります。



20KHz 超音波ホモジナイザー
BRANSON　SONIFIER シリーズ



高周波 40KHz 超音波ホモジナイザー
BRANSON SLPe シリーズ

ブランソン社の製品は、ホーン先端部の振幅の安定性が高く、強力なキャビテーションが得られ、効率良く、再現性の高い分散処理が行えます。

主なアプリケーション

分散

カーボンナノチューブ　有機顔料　無機顔料　セラミック　セメント　感光体　記録材料
磁性粉　粉末冶金　酸化鉄　金属酸化物　シリカ　アルミナ　カーボンブラック
ポリマー　ラテックス　製紙　ファンデーション
研磨剤　電池　フィラー　光触媒　触媒　ワクチン　体外診断薬　歯磨き粉　シャンプー
半導体　電子基盤　液晶　貴金属　金属　宝石　タイヤ　発酵菌類　その他

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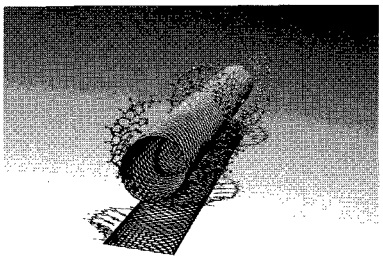
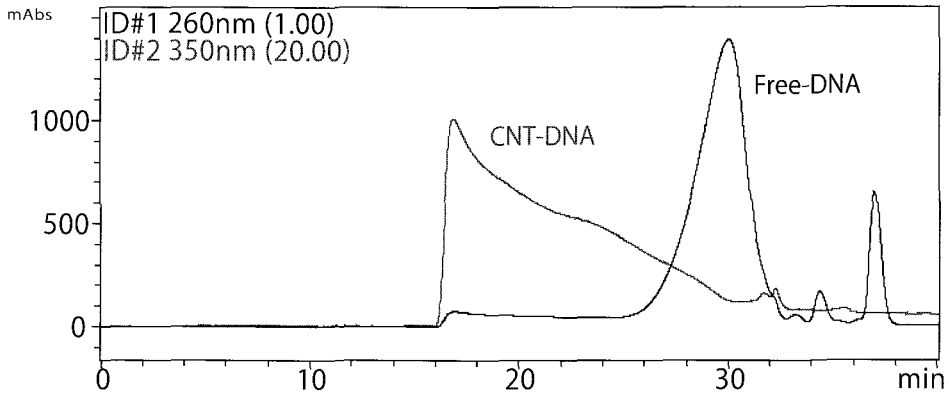


Image courtesy of Dr. Y. Ito, Univ. of Oxford

■分離例

カーボンナノチューブのサイズ分離

細孔径の異なる3種類のカラムを連結し、DNAでラッピングされたカーボンナノチューブを分離しました。



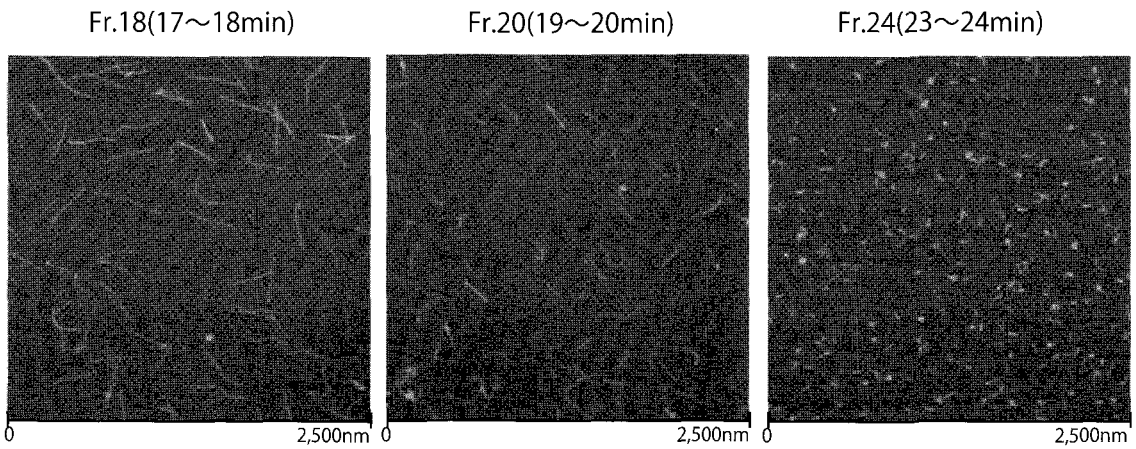
分析条件

カラム	COSMOSIL CNT-300 7.5mmI.D.×300mm	温　度	40 ℃
	COSMOSIL CNT-1000 7.5mmI.D.×300mm	検　出	UV260nm(×1), 350nm(×20)
	COSMOSIL CNT-2000 7.5mmI.D.×300mm	サンプル	DNA-wrapped CNT(CNT-DNA)
移動相	0.5mmol/l EDTA, 200mmol/l NaCl, 40mmol/l Tris-Tris HCl(pH7.0)	注入量	500μl
流　速	1.0ml/min	圧　力	8.1MPa

【サンプルのご提供 ： 名古屋大学大学院理学研究科物質理学専攻　篠原研究室】

AFM(原子間力顕微鏡)によるサイズ観察

上記分離時に分取した各フラクションをAFMにて観測し、CNTの長さを測定しました。



【撮影・データのご提供 ： 名古屋大学大学院理学研究科物質理学専攻　篠原 久典教授・浅田 有紀様】

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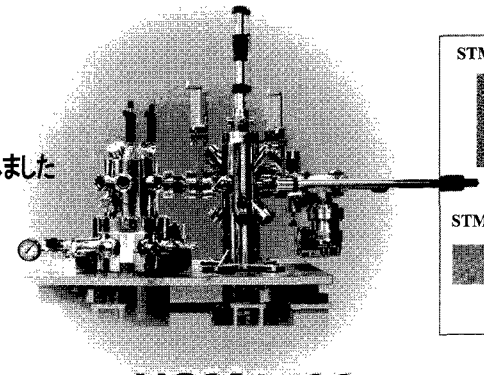
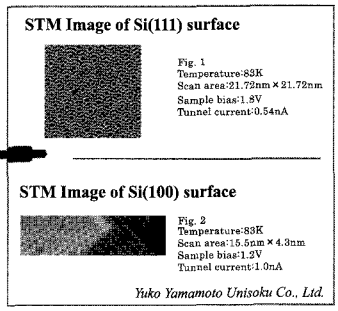
- ±0.5 テスラ磁場中測定に対応（オプション）
- レンズステージ組み込みによりトンネル発光観察、近接場励起による分光測定が可能。
- AFM、MFM、EFM, KFM測定対応可能（オプション）

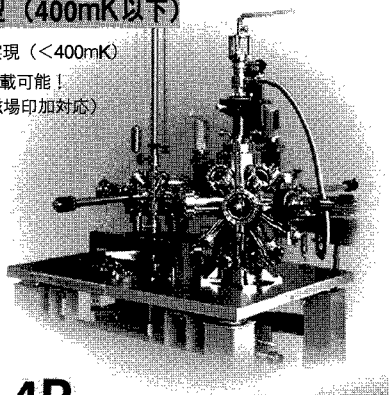




USM1300S 3He

超低温・強磁場対応型（400mK以下）

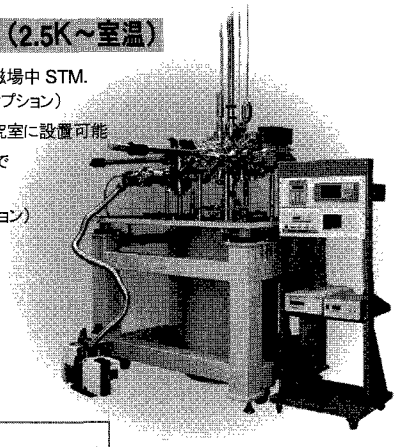
- 3He 使用で超低温測定を実現（<400mK）
- 1 テスラベクターマグネット搭載可能！（標準仕様は 7 テスラ垂直磁場印加対応）



USM1500

極低温・強磁場対応型（2.5K～室温）

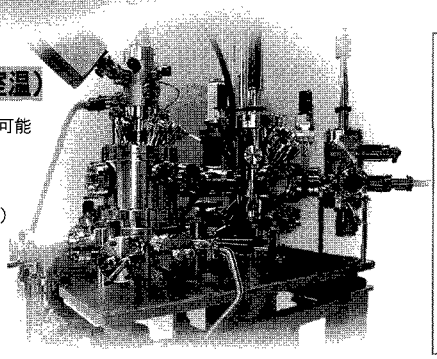
- コンパクトで低価格な極低温磁場中 STM.（8 テスラ超伝導マグネットはオプション）
- 全高 3m以内で標準的な研究室に設置可能
- 2.5K～室温まで幅広い範囲でSTM温度可変測定が可能
- AFM 測定対応可能（オプション）

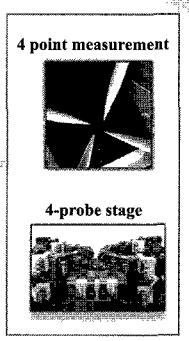


USM1400-4P

極低温・4プローブ多探針型（2.5K～室温）

- 2.5K～室温まで幅広い範囲でSTM温度可変測定が可能
- 各プローブ独立制御可能
- FE-SEM を標準装備
- AFM、MFM、EFM, KFM測定対応可能（オプション）





USM-1400 及び USM-1400-4P は
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共同で開発されました。

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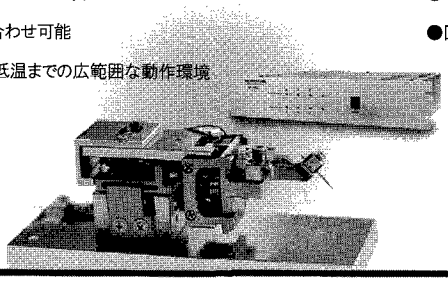
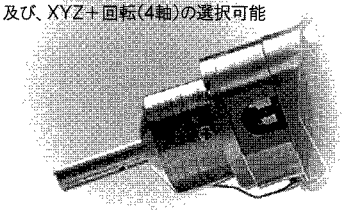
- 市販のSEM/FIB/光学顕微鏡に組み合わせ可能
- 大気中～超高真空まで、室温から極低温までの広範囲な動作環境
- マルチプロービングにも対応
- マニピュレーション、半導体ナノデバイスのIV測定、抵抗測定、EBIC測定等幅広い用途に対応



ナノ・マイクロ回転ステージ UP-200Rシリーズ

- 大気中、及び高真空中で微小回転動作と位置検出（オプション）のニーズに対応
- SEM,FIBへの組み込み可能
- 回転ステージのみ、及び、XYZ＋回転（4軸）の選択可能



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