第42回 フラーレン・ナノチューブ・グラフェン 総合シンポジウム

The 42nd Fullerenes-Nanotubes-Graphene General Symposium



講演要旨集 Abstracts

2012年3月6日(火)~8日(木) 東京大学 武田先端知ビル5F 武田ホール The University of Tokyo, Takeda Frontier Science Hall 5F

主催 フラーレン・ナノチューブ・グラフェン学会 The Fullerenes, Nanotubes and Graphene Research Society



日本化学会

The Chemical Society of Japan

協賛 日本物理学会 The Physical Society of Japan 応用物理学会 The Japan Society of Applied Physics 高分子学会 The Society of Polymer Science, Japan 電気化学会 The Electrochemical Society of Japan 東京大学GMSI The University of Tokyo Global COE Program "Global Center of Excellence for Mechanical Systems Innovation"

# … フロンティアカーボン(株)の **NONOM** 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	<mark>最低数量</mark> (g)
	ST		99	10
nanom nurnle	TL	AT A	99.5	2
	<u>su</u>		99.5/昇華精製品	2
///////////////////////////////////////	SUH		99.9/昇華精製品	1
·····	<u>sc</u>		99.9/昇華精製/単結晶品	1
nanom orange <u>ST</u>		(FB)	97	1
フラーレンC70	<u>su</u>		98/昇華精製品	0.5
<u>nanom mix</u> 混合フラーレン	<u>ST</u>		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	E100	-200	99	1
[60]PCBM	<u>E100H</u>		99.5	1
(prienyi Con-butyric acid methyl ester)	E102		99.9	0.5
nanom spectra bis[60]PCE (bis-phenyl C61-butyric acid	a E400 3M I 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 [60,70]PCE	a <u>E123</u> BM		[60]PCBM、[70]PCBMの混合物	1
nanom spectra	E110	- ary C	99/異性体トータル ※位置異性体の混合物	0.5
(phenyl C71-butyric acid methyl ester)	<u>E112</u>	主成分	99.5/異性体トータル ※位置異性体の混合物	0.5
<u>nanom spectra</u> [60]インデン付	a_Q100 加体		99	0.5
<u>nanom spectra</u> [60]インデン21	a Q400 寸加体	2	99/異性体トータル ※位置異性体の混合物	1
<u>nanom spectra</u> D100 水酸化フラーレン		(n = ca.10)	C <sub>60</sub> OH <sub>n</sub> n=10を主成分とする混合 物	1
<u>nanom spectra</u> 水素化フラー	a <u>A100</u> -レン	(n = ca. 30)	C <sub>60</sub> H <sub>n</sub> n=30を主成分とする混合物	1
銘柄 取扱数量等け予告無く変	すすろ提合がござい	ます ふんごてみてさい		

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<本資料に関するお問い合わせ先> フロンティアカーボン株式会社 営業販売センター【担当:梶原】 ※お問い合わせはHP http://www.f-carbon.comよりお願いいたします。 ※その他、下記メディアを通じて幅広い情報を発信中です。 Facebook: http://www.facebook.com/pages/フラーレン-普及委員会/229612930394983 Twitter: Fullerene\_nanom



**Frontier Carbon Corporation** 

# Abstract

# The 42<sup>nd</sup> Fullerenes-Nanotubes-Graphene General Symposium

第 42 回フラーレン・ナノチューブ・グラフェン総合シンポジウム 講演要旨集

The Fullerenes, Nanotubes and Graphene 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 The University of Tokyo Global COE Program Global center of Excellence for Mechanical Systems Innovation 主催:フラーレン・ナノチューブ・グラフェン学会 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 東京大学グローバル COE プログラム 機械システム・イノベーション国際拠点 March  $6^{\text{th}}(\text{Tue}) - 8^{\text{th}}(\text{Thu})$ , 2012 Date: Place: The University of Tokyo 7-3-1 Hongo, Bunkyo-ku, Tokyo 113-8656 TEL: 03-3830-4848 Presentation: Plenary Lecture (40 min presentation, 5min discussion) 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 24 年 3 月 6 日(火)~8 日(木) 場所:東京大学 武田先端知ビル5F 武田ホール 〒113-8656 東京都文京区本郷 7-3-1 TEL: 03-3830-4848

発表時間:基調講演
 特別講演
 一般講演
 ポスタープレビュー(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 (五+音順、敬称略)

アイクストロン(株) アルバックイーエス(株) (株)ATR エルゼビア・ジャパン(株) QuantumWise Japan(株) コスモ・バイオ(株) (株)コロナ社 サーモフィッシャーサイエンティフィック(株) (株)島津製作所 スペクトラ・フィジックス(株) (株)セントラル科学貿易 ナカライテスク(株) 日本電子(株) (株)ニューメタルスエンドケミカルスコーポレーション 日立工機(株) (株) 堀場製作所 (株)名城ナノカーボン 和光純薬工業(株)

# 広告掲載団体御芳名 (五+音順、敬称略)

アイクストロン(株) アルバックイーエス(株) QuantumWise Japan(株) コスモ・バイオ(株) サーモフィッシャーサイエンティフィック(株) (株)島津製作所 (株)セントラル科学貿易 東洋炭素(株) ナカライテスク(株) 日本電子(株) フロンティアカーボン(株) 和光純薬工業(株)

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プログラム早見表

	3月6日(小)		2月7日 (水)	3日8日(木)			
			<u>37/1(//)</u>		<u>улоц (</u> л)		
	受付開始 8:30~		受付開始 8∶30~		受付開始 8∶30~		
	講演開始 9∶30~		講演開始 9∶30~		講演開始 9∶30~		
9:30	基調講演(遠藤守信)	9:30		9:30	 一般講演 5件		
	9:30-10:15		(金属内包フラーレン・		(グラフェン)		
			フラーレンの化学)		9:30-10:45		
10:15			9:30-10:30				
	(ナノチューブの物性)						
	10:15-10:45	10:30	休憩 10:30-10:45				
10:45	休憩 10:45-11:00	10:45	特別講演(長崎幸夫)	10:45	休憩 10:45-11:00		
11:00	一般講演 4件		10:45-11:15	11:00	特別講演(佐藤信太郎)		
	(ナノチューブの物性)	11:15	一般講演 3件		11:00-11:30		
	11:00-12:00		(フラーレン固体・	11:30	一般講演 4件		
			フラーレンの応用)		(グラフェン)		
			11:15-12:00		11:30-12:30		
12:00	屋食	12:00	昼食				
	(幹事会)		12:00-13:15				
	12:00-13:15			12:30	昼食		
					12:30-13:45		
13:15	一般講演 3件	13:15	授賞式				
	(ナノチューブの生成と精製)		13:15-14:00	13:45	一般講演 2件		
	13:15-14:00				(ナノ炭素粒子)		
14:00	特別講演(宮本大輔)	14:00	特別講演(南信次)		13:45-14:15		
	14:00-14:30		14:00-14:30	14:15	特別講演(成田薫)		
14:30	休憩 14:30-14:45	14:30	休憩 14:30-14:45		14:15-14:45		
14:45	一般講演 4件	14:45	一般講演 4件	14:45	休憩 14:45-15:00		
	(ナノチューブの生成と精製・		(ナノチューブの応用・	15:00	一般講演 2件		
	ナノチューフの応用)		ナノチューブの物性)		(ナノホーン・その他)		
	14:45-15:45		14:45-15:45	15.00	15:00-15:30		
15.45		15.45		15:30	ポスタープレビュー		
15.45	ホスターフレビュー	10:40	ポスターブレビュー		(3P-1 ~ 3P-49)		
	(1P-1 ~ 1P-45)		(2P-1 ~ 2P-45)		15:30-16:30		
16.30		16.20		16.20	1°		
10.00	ホスターセッション	10.30	ホスターセッション	10.30	ホスターセッション		
	16:30-18:00		16:30-18:00		16:30-18:00		
18:00		L		L			
		10.00		10.00			

<u>3月6日(火)</u> 3月7日 (水) 16:00 基調講演 発表40分·質疑5分 18:30 チュートリアル 懇親会 (山上会館) 特別講演 発表25分 質疑5分 (講師:斎藤晋 18:30-20:30 一般講演 発表10分·質疑5分 東京工業大学 教授) 工学部 2号館 221号講義室 ポスタープレビュー 発表1分・質疑なし 16:00-17:30 17:30 20:30

# Time table

	March 6 (Tue.)		March 7 (Wed.)		March 8 (Thu.)
	Registration begins at 8:30		Registration begins at 8:30		Registration begins at 8:30
	Lectures begin at 9:30		Lectures begin at 9:30		Lectures begin at 9:30
9:30	Plenary Lecture (M. Endo) 9:30–10:15	9:30	General Lectures [4] (Endohedral Metallofullerenes • Chemistry of Fullerenes)	9:30	General Lectures [5] (Graphene) 9:30–10:45
10:15	General Lectures [2]		9:30-10:30		
	(Properties of Nanotubes)		an a		
10.45	10:15-10:45	10:30	Coffee Break 10:30–10:45	10.45	
10:45	Coffee Break 10:45-11:00	10:45	Special Lecture (Y. Nagasaki)	10:45	Coffee Break 10:45-11:00
11:00	General Lectures [4]	11.15	10:45-11:15	11:00	Special Lecture (S. Sato)
	(Properties of Nanotubes)	11:15	General Lectures [3]	11 20	11:00-11:30
	11:00-12:00		(Fullerene Solids •	11:30	General Lectures [4]
			Applications of Fullerenes)		(Graphene)
12.00		12.00	11:15-12:00		11:30-12:30
12:00	Lunch	12:00	Lunch		
	(Administrative meeting)		12:00-13:15	12.20	
	12:00-13:15			12.50	
13:15	General Lectures [3]	13:15	Award Ceremony		12:30=13:45
	(Formation and Purification		13:15–14:00	13:45	General Lectures [2]
	of Nanotubes) 13:15–14:00		10,10 11,00		(Carbon Nanoparticles)
14:00	Special Lecture (D. Mivamoto)	14:00	Special Lecture (N. Minami)		13:45-14:15
	14:00-14:30		14:00-14:30	14:15	Special Lecture (K. Narita)
14:30	Coffee Break 14:30-14:45	14:30	Coffee Break 14:30–14:45		14:15-14:45
14:45	General Lectures [4]	14:45	General Lectures [4]	14:45	Coffee Break 14:45-15:00
	(Formation and Purification		(Applications of Nanotubes $\cdot$	15:00	General Lectures [2]
	of Nanotubes •		Properties of Nanotubes)		(Nanohorns • Miscellaneous)
	Applications of Nanotubes)		14:45-15:45		15:00-15:30
	14:45-15:45			15:30	Poster Preview
15:45	Poster Preview	15:45	Poster Preview		( 3P–1 through 3P–49 )
	( 1P–1 through P–45 )		( 2P–1 through 2P–45 )		15:30-16:30
	15:45-16:30		15:45-16:30		
16:30	Poster Session	16:30	Poster Session	16:30	Poster Session
	16:30-18:00		16:30-18:00		16:30-18:00
10.00					
19:00		18:00		18:00	

	March 6 (Tue.)		March 7 (Wed.)	
16:00	Tutorial	18:30	Banquet (Sanjo Hall)	
	Lecturer: Prof. S. Saito		18:30-20:30	
	Tokyo Institute of Technology	20:30	Plenary Lecture: 40min	(Presentation) + 5min (Discussion)
	(Eng. Bldg. 2, Room #221)		Special Lecture: 25min	(Presentation) + 5min (Discussion)
	16:00-17:30		General Lecture: 10min	(Presentation) + 5min (Discussion)
17:30			Poster Preview: 1min (P	resentation)

# 座長一覧

3月 6日 (火)

(敬称略)

	時間	座長
基調講演(遠藤)	9:30 ~ 10:15	丸山 茂夫
一般講演	10:15 ~ 10:45	齋藤 理一郎
一般講演	11:00 ~ 12:00	加藤 立久
一般講演	13:15 ~ 14:00	野田 優
特別講演(宮本)	14:00 ~ 14:30	野田 優
一般講演	14:45 ~ 15:45	湯田坂 雅子
ポスタープレビュー	15:45 ~ 16:30	宮田 耕充
ポスターセッション	16:30 <b>~</b> 18:00	小鍋 哲

# 3月 7日 (水)

	時間	座長
一般講演	9:30 ~ 10:30	松尾 豊
特別講演(長崎)	10:45 ~ 11:15	篠原 久典
一般講演	11:15 ~ 12:00	北浦 良
特別講演(南)	14:00 ~ 14:30	阿知波 洋次
一般講演	14:45 ~ 15:45	大野 雄高
ポスタープレビュー	15:45 ~ 16:30	兒玉 健
ポスターセッション	16:30 <b>~</b> 18:00	沖本 治哉

# 3月 8日 (木)

	時間	座長
一般講演	9:30 ~ 10:45	山本 貴博
特別講演(佐藤)	11:00 ~ 11:30	大淵 真理
一般講演	11:30 ~ 12:30	長汐 晃輔
一般講演	13:45 ~ 14:15	齋藤 弥八
特別講演(成田)	14:15 ~ 14:45	日浦 英文
一般講演	15:00 ~ 15:30	岡崎 俊也
ポスタープレビュー	15:30 ~ 16:30	千足 昇平
ポスターセッション	16:30 <b>~</b> 18:00	佐藤 健太郎

#### 3月6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	
ポスタープレヒ		発表	1分	•	質疑応	答なし

1

#### 基調講演(9:30-10:15)

1S-1	二層カーボンナノチューブ
	遠藤守信
-船講?	宙 (10·15−10·45)

#### ー般講演(10:15-10:45) ナノチューブの物性

1-1	Temperature sensitive optical absorption of SDS-wrapped SWCNT aqueous solution: correlation with chirality sorting 〇劉華平、卜部泰子、田中丈士、片浦弘道	7
1-2	カーボンナノチューブに吸着したアミノ酸のエネルギー論と電子構造	8

# >>>>>> 休憩(10:45-11:00) < < < < < <

#### 一般講演(11:00-12:00)

○神谷克政、岡田晋

#### ナノチューブの物性

1-3	電気化学的手法による単層カーボンナノチュブにおける正、負トリオンの観測 〇朴珍成、松田一成、毛利真一郎、宮内雄平、中島直敏	9
1-4	キャリアドープした単層カーボンナノチューブの励起子ー電子弾性散乱 〇小鍋哲、松田一成、岡田晋	10
1-5	正孔ドープされた(6,5)単層カーボンナノチューブのトリオンの緩和ダイナミクス ○志水聖、小山剛史、宮田耕充、篠原久典、中村新男	11

1-6 金属単層カーボンナノチューブの励起子状態からの発光
 12 志水聖、○小山剛史、斎藤毅、宮田耕充、篠原久典、中村新男

#### >>>>>> 昼食(12:00-13:15) <<<<<<<

#### 一般講演(13:15-14:00)

#### ナノチューブの生成と精製

1-7	CNTフォレストの特性とCNTの形状の関係 〇フタバドン、桜井俊介、小橋和文、徐鳴、山田健郎、石康昭、湯村守雄、畠賢治	13
1-8	カーボンナノチューブの成長と制御 〇阿知波洋次、井上亮人、児玉拓也、金子愛実、橋本健朗、児玉健、岡崎俊也	14
1-9	Alignment Control of Carbon Nanotube Forests from Random to Nearly Perfectly Aligned by Utilizing Crowding Effect 〇徐鳴、二葉ドン、湯村守雄、畠賢治	15
特別講	演(14:00-14:30)	
1S-2	MWCNTの量産と用涂	2

**1S-2** MWCNTの量産と用途 宮本大輔

## >>>>>> 休憩 (14:30-14:45) <<<<<<<

# 一般講演(14:45-15:45)

ナノチューブの生成と精製	•	ナノチューブの応用

1–10	溶解度パラメーターに基づく汎用的方法による高導電性CNTゴム作成について 〇阿多誠介、水野貴章、小橋和文、湯村守雄、畠賢治	16
1-11	アセトニトリルを用いた小径・窒素ドープ単層CNTのCVD合成 〇E. エイナルソン、T. テゥーラキットセーリー、C. クランバーガー、趙沛、相川慎也、 S. ハリッシュ、千足昇平、丸山茂夫	17
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OKatsumasa Kamiya, Susumu Okada

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1S-2	Mass production and applications of MWCNT
	Daisuke Miyamoto

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# 基調講演 Plenary Lecture

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# 1**S-**1

#### **Double-walled carbon nanotubes**

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Double walled carbon nanotubes (DWNTs) are one of the ideal structural model for studying the interactions and coupling behavior between two different concentric tubules, and can be considered as the most simple multi-walled carbon nanotubes[1]. Moreover, their intrinsic coaxial structures make them mechanically, thermally and structurally more stable than single walled carbon nanotubes (SWNTs). Geometrically, the buffer-like function of the outer tubes in DWNTs [2] allows inner tubes to exhibit exciting transport and optical properties having a high level of structural perfection. This makes them promising in the fabrication of field-effect transistors, stable field emitters and lithium ion batteries, etc. In addition, the utilization of the outer tube chemistry makes DWNTs to be useful for anchoring semiconducting quantum dots as well as for use as effective multifunctional filler in producing tough, conductive transparent polymer films, while the inner tubes with diameter below 0.9 nm preserve their excitonic transitions. Namely, this is the peculiar DWCNT chemistry [3].

However, there is no systematic study on the effect of the intershell interaction as well as the configurations of the two concentric tubules. In the present paper on DWNTs, we report two different approaches of producing high-purity DWNTs (e.g., catalytically grown<sup>1</sup> and peapod-grown DWNTs [4]) and direct comparison on their respective optical and transport properties.

Fig.1 Optically and biologically active mussel rotein-coated double walled carbon nanotube [3]

#### References

M. Endo, H. Muramatsu, T. Hayashi, Y. A. Kim, M. Terrones, M. S. Dresselhaus, Buckypaper from coaxial structure, Nature 433, 476 (2005).
 T. Hayashi, D. Shimamoto, Y. A. Kim, H. Muramatsu, F. Okino, H. Touhara, T. Shimada, Y. Miyauchi, S. Maruyama, M. Terrones, M.S. Dresselhaus, M. Endo, Selective optical property modification of double walled carbon nanotubes by fluorination, ACS Nano 2, 485–488 (2008).



[3] Yong Chae Jung , Hiroyuki Muramatsu , Kazunori Fujisawa , Jin Hee Kim , Takuya Hayashi , Yoong Ahm Kim , \* Morinobu Endo , Mauricio Terrones ,and Mildred S. Dresselhaus., small 2011, 7, No. 23, 3292–3297.

[4] H. Muramatsu, T. Hayashi, Y. A. Kim, D. Shimamoto, M. Endo, V. Meunier, B. G. Sumpter, M. Terrones, M. S. Dresselhaus, Bright photoluminescence from the Inner tubes of peapod-derived double walled carbon nanotubes, Small 5, 2678–2682 (2009).

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#### Mass production and applications of MWCNT

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SHOWA DENKO K.K (SDK) produces three types of MWCNT (VGCFs<sup>®</sup>; VGCF<sup>®</sup>, VGCF<sup>®</sup>-H, VGCF<sup>®</sup>-X). Each characteristic of VGCFs<sup>®</sup> are listed in Table 1. The SEM images are shown in Fig. 1 . VGCFs<sup>®</sup> are manufactured by the catalytic chemical vapor deposition (CCVD) method which is a process suitable for mass production.

The advantage of CCVD method is ease of controlling the growth reaction of carbon nanotubes. In other words, the reaction condition of CCVD method is wider than the ark plasma method. In mass production, each reaction conditions are inevitably rough compared to a laboratory scale. Therefore, at the stage of research and development, it is important to seek the reaction conditions which obtain same result in the wide range.

Grade	Diameter	Length	Bulk Density	Thermal Conductivity	Electrical Conductivity	Production Capacity	Main Use
	nm	μm	g/cm <sup>3</sup>	W/(m/k)	Ω/cm	T/Y	- Mulli CSC
<b>VGCF®</b>	150	8	0.04	1200	10-4	200	Lithium Ion Battery Rubber Composite
VGCF®-H	150	6	0.08	1200	10-4		
VGCF®-X	15	3	0.08	-		400	Resin Composite

Table 1. Each characteristic of VGCF®s.

VGCF<sup>®</sup> and VGCF<sup>®</sup>-H are high purity and conductivity carbon nanotube. The features are mainly suitable as an additive of lithium ion battery, and it has become an essential material. Also in respect of the high thermal conductivity, it is expected as an interesting material.

VGCF<sup>®</sup>-X is high aspect ratio and conductivity carbon nanotube, and it is mainly used as an conductive additive to resin composite. It has been understood to obtain same conductive performance by the additive amount of 1/5 - 1/10 of carbon black and carbon fiber in using VGCF<sup>®</sup>-X. Therefore, VGCF<sup>®</sup>-X can reduce the degradation of the physical properties of the base polymer as compared to other carbon fillers.

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(A) (B)

Fig.1 SEM images of  $VGCF^{\otimes}$  (A) and  $VGCF^{\otimes}$ -X(B).

#### Neutron Capture Therapy by Gadolinium Fullerene

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Neutron capture therapy (NCT) is a suitable method for the treatment of intractable tumors such as brain tumors. NCT using 10 B (BNCT) has demonstrated efficacy in the treatment of tumors and is now established as a frontier radiotherapy. 10 B compounds based on boronophenylalanine (BPA) and sodium borocaptate (BSH) have undergone clinical trials to verify their efficacy in BNCT because they show low cytotoxicity without neutron irradiation. However, since selective accumulation in tumors is insufficient, improvements in targeting characteristics are desirable. We have recently developed boron-containing nanoparticles for passive targeting in tumors, which improves the BNCT efficiency<sup>1</sup>. Another important requirement for high-performance neutron therapy is the monitoring of the biodistribution of compounds, including neutron capture agents. Precise determinations of the capture compound concentration would facilitate minimization of the neutron source power and reduce damage to normal organs by neutron irradiation.

Gadolinium is a promising candidate for monitoring biodistribution by magnetic resonance imaging (MRI) because of the significant variations in the water relaxation time. In addition, Gadolinium has a high neutron capture cross section. Owing to these properties, gadolinium has anticipated as one of the candidates for NCT, possessing character of MRI contrast agent. However, gadolinium ion is too toxic to use in vivo. Even in Gd chelating compounds such as diethylenetriaminepentaacetic acid (DTPA), 1,4,7,10-tetraazacyclododecane-1,4,7,10-tetraacetic acid (DOTA) and hexane-2,4-dione are not applicable for NCT because of high dosage of these treatments.

We originally achieved the solubilization of intact fullerenes by synthetic block copolymers. For example, poly(ethylene glycol)-b-poly[N,N-(dimethylamino)ethyl methacrylate] (PEG-b-PAMA) solubilizes C60 to form extensively mono-dispersed nanoparticles with a diameter of 5 nm<sup>2</sup>. The solubility of C60 in PEG-b-PAMA aqueous solution reached 214 mg L<sup>-1</sup>. Analogously, we solubilized Gd@C82 in aqueous media using PEG-b -PAMA. Because PEG-b-PAMA is located on the surface of the fullerene cluster, the resulting complex is anticipated to have high biocompatibility. PEG-b-PAMA physically interacts with the fullerene to maintain the dispersion of Gd@C82, and this better preserves the properties of Gd@C82 as compared to chemical functionalization. In this paper, we demonstrate the solubilization of Gd@C82 using PEG-b-PAMA via physical entrapment and apply the Gd@C82 -PEG-b-PAMA-complexed nanoparticles (GdNPs) to GdNCT<sup>3</sup>.

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<sup>&</sup>lt;sup>3</sup> Y. Horiguchi, et al., *Sci. Technol. Adv. Mater.* 12, 044607 (2011).



<sup>&</sup>lt;sup>1</sup> S. Sumitani, et al, *Biomaterials*, in press

<sup>&</sup>lt;sup>2</sup> Y.Nagasaki, Sci. Technol. Adv. Mater. 11 054505(2010)

## Thin-film Formation and Spectroscopic Measurements of Carbon Nanotubes and their Applications

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Spectroscopic measurements are among the most important techniques to characterize single-wall carbon nanotubes (SWNTs). In particular, analysis of near infrared (NIR) optical spectra provides essential information for the understanding of their various properties, including purity, stability, structures as defined by chiral indices (n, m), localized and delocalized electronic states, aggregation behavior and isolation processes, electronic interactions between tubes and with dopants, etc. Furthermore, for a number of electronic and optoelectronic applications of SWNT, NIR spectroscopic measurements represent indispensable experimental techniques. We have been making efforts to expand the applicability of NIR spectroscopy to a wider range of SWNT samples.

Reliable and versatile optical measurements require thin-film samples. Also, thin-film formation is important for the realization of various optical, electronic and optoelectronic devices. For these reasons, we have been focusing on the preparation of high-quality SWNT thin films using various methods. We particularly pay attention to their structural control, because macroscopically measured properties of SWNTs strongly depend on their structures such as tube aggregation and tube orientation.

The results of our efforts are summarized as the following:

1) SWNTs solubilized by chemical functionalization were used to prepare Langmuir-Blodgett films; they can be deposited in a layer-by-layer fashion and tubes are found to be preferentially oriented in the dipping direction [1]. 2) High quality thin films were prepared by dispersing SWNTs in polymers such as gelatin and cellulose derivatives. The tubes are well-isolated and thus the films exhibit photoluminescence. Mechanical stretching of the film resulted in considerable orientation of tubes. Moreover, the NIR transparency of the matrix polymers expands the measurable wavelength range, enabling the NIR measurement of wider tubes [2,3]. 3) Extending a technique developed by other group for extracting highly pure semiconducting SWNTs using polyfluorene as a dispersant [4], we succeeded in preparing thin networked films consisting only of single chirality semiconducting SWNTs. 4) Using the above mentioned film, NIR photoconductivity spectra were measured for a single chirality SWNT, from which the dependence of the quantum efficiency on the excitation energy were derived, directly revealing exciton binding energies for specific chiralities. [5]. 5) Using FT-IR and a long-wavelength sensitive NIR detector, we realized IR-extended photoluminescence spectroscopy, revealing for the first time the chirality distribution of double-wall CNTs and arc discharge synthesized SWNTs [6,7]. 6) The thin-film techniques were utilized to develop highly sensitive gas sensors [8,9]. Also, optical gas sensing was developed, demonstrating that wider tubes possess higher gas detection sensitivity [10].

[1] JJAP, 42, 7629 (2003). [2] APL, 86, 073103 (2005). [3] APL, 88, 093123 (2006). [4] APL, 92, 243112 (2008). [5] To be submitted. [6] JPC(B), 110, 17420 (2006). [7] JPC(C), 112, 11194 (2008). [8] JJAP, 47, 7440 (2008). [9] Analyst, 134, 325 (2009). [10] J. Mater. Chem., (2012) DOI: 10.1039/c2jm15284c.

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# Application of graphene to transistors: CVD growth, nanoribbon formation, and electrical properties

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Graphene, a two-dimensional honeycomb carbon lattice, has excellent electronic, thermal, and mechanical properties. It is considered to be a promising material for future electronics devices. In fact, our goal is to use graphene as a transistor channel for future large scale integrated circuits (LSIs). In this talk, we explain our recent progress toward such an application. First, we demonstrate graphene growth all over a 200-mm wafer by chemical vapor deposition using Cu film as a catalyst (Fig. 1) [1, 2]. We explain how the grain size and orientation of graphene are affected by various growth parameters. Electrical properties depending on the grain structures are also addressed. We then describe self-organizing formation of Cu surface steps [3]. The formation mechanism of the ribbons is discuseed. Finally, we explain our recent results concerning devices using graphene nanoribbons (GNRs). Patterning of GNRs by Helium Ion Microscope (HIM) and the on-off operation of a GNR transistor thus fabricated are described [4]. Furthermore, we propose a novel dual-gate transistor with a GNR channel (Fig. 2) [5]. The operation of the new device is demonstrated.

This work was supported by JSPS through the FIRST Program, initiated by CSTP, Japan. This work was partly conducted at the Nano-Processing Facility supported by ICAN, AIST.



Fig. 1. (a) Graphene synthesized on a 200-mm  $Cu/SiO_2/Si$  wafer. (b) Cross sectional TEM image of graphene. (c) Bright field image of graphene on a TEM grid. (d) Selected area diffraction pattern obtained from a circular area of graphene partially shown in (c).

Fig. 2. (a) Schematic of a dual-gate GNR transistor. (b) Top-view of the actual device (HIM image).

- [1] S. Sato, et al. ECS Trans. 35(3), 219 (2011). [2] S. Sato, et al. ECS Trans. 37(1), 121 (2011).
- [3] K. Hayashi, et al. Extended Abstracts of 72th JSAP Fall Meeting 2011, Yamagata, 2a-ZF-9 (2011).
- [4] S. Nakaharai, et al., Extended Abstracts of the 2011 SSDM, Nagoya, 1300 (2011).
- [5] S. Nakaharai, et al. Appl. Phys. Express 5, 015101 (2012).

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# A Study of Plastic Bolometer based on Carbon Nanotubes for Ultra Low-Cost Infrared Image Sensors

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The demands for uncooled infrared image sensors have grown rapidly nowadays. Microbolometers are most popular high-performance uncooled far-infrared detectors and widely used for night-vision camera and thermography applications from military to commercial use. However, they are considerably expensive due to the cost of the fabrication processes and vacuum packaging. This is because, they use complicated MEMS structure and vacuum gap thermal isolation in the structure. In this paper, we propose a very low-cost potential infrared image sensor using carbon nanotube bolometers on a plastic substrate. Several papers were published about the bolometer using carbon nanotubes. Our structure is distinguished from them mainly on the following two points. The first is the thermal isolator made of a low thermal conductance polymer layer, and the second is a newly developed high-sensitivity (TCR > 2%) carbon nanotube thin film thermistor created on the thermal isolator.

In the experiment, 500µm-size single sensor cell was fabricated on a polyimide substrate. For the thermal isolation layer, parylene (p-Xylene polymer) was evaporated on the substrate. The single-walled carbon nanotube thin film thermistor was printed on the thermal isolation layer and an infrared absorb layer was formed on the thermistor (Fig.1). The IR irradiation test showed that the responsivity of our sensor is about 340 [V/W]. We also fabricated a 64-pixel (8-row, 8-column) bolometer array by the evaporation of metals and print processes without lithography(Fig.2(a)). Using the switching matrix and the measurement modules, we read out the resistance change of the each pixel while the part of sensor area was irradiated by the black body IR source (Fig.2(c)). Figure 2 (b) is the obtained image when the upper left part of the sensor was irradiated by the black body source of 300°C. This result shows that the basic operation of the IR image sensor was confirmed [1].

 Kaoru Narita, et al., "A Plastic Bolometer Array using Carbon Nanotubes for Low-Cost Infrared Imaging Devices", Proceedings of IRMMW-THz, Tu4C.3, 2011.







Fig.2: (a): Photo of 64(8x8)-pixel plastic bolometer array chip,(b): obtained image under the experiment described in figure c),(c): experimental setup using black body source and aperture.

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一般講演 General Lecture

$$1-1 \sim 1-13$$
  
 $2-1 \sim 2-11$   
 $3-1 \sim 3-13$ 

# 1-1

# Temperature sensitive optical absorption of SDS-wrapped SWCNT aqueous solution: correlation with chirality sorting

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Recently we developed simple and low-cost multicolumn gel chromatography method and realized industrial chirality separation of single-wall carbon nanotubes (SWCNTs) using an allyl-dextran-based gel as the medium [1]. This method is based on the chirality-dependent interaction strength of SWCNTs with the gel. Most recently, we found that an environmental temperature has a great influence on the interaction strength between SWCNTs and the gel [2]. Lowering/increasing an environmental temperature generally decreases/enhances the interaction of SWCNTs with the gel. The temperature effect strongly depends on the chirality of SWCNTs. On the basis of this finding, we proposed that an environmental temperature could modify the electronic structures of SWCNTs dispersed in sodium dodecyl sulfate aqueous (SDS) solution, which would be reflected in their optical performance.

In the present work, we systematically investigated the optical absorbance of SDS-wrapped (n, m) semiconducting SWCNT aqueous solution at various temperatures. The peak-shift and intensity change in S<sub>11</sub> optical absorption region of each (n, m) species as a function of temperatures are combined and normalized in Fig. 1. It is visible that both the peak shift and intensity change in optical absorbance of SWCNTs are chirality-dependent. As shown in Fig. 1a, the near arm-chair nanotubes such as (6, 5), (7, 6) and (8, 7) show more sensitive to temperatures in peak shift than the nanotubes with smaller chiral angels such as (7, 3), (10, 2) and (12, 1). Fig. 1b presents that the nanotubes with larger diameter or smaller chiral angles (i.e., (8, 7), (8, 4) and (10, 2)) show a rapid quenching in optical absorbance intensity with a decrease in temperatures while the nanotubes with smaller diameters such as (7, 3) and (6, 5) have a relatively stable optical absorbance intensity in a wide temperature range of 8-28 °C. This temperature-dependent optical performance of (n, m) species indicates that temperature

change could induce charge transfer between SDS surfactant coating and SWCNTs, resulting in the modification of electronic structures of SWCNTs. And this temperature control modification of electronic structures is strongly dependent on the chirality of SWCNTs.



Fig. 1. Peak shift (a) and intensity change (b) in  $S_{11}$  optical absorption region of SDS-wrapped (*n*, *m*) SWCNTs as a function of temperatures.

[1] H. Liu et al. Nat. Commun. 2, 309 (2011).

[2] H. Liu *et al.* The 41st Fullerenes-Nanotubes-Graphene General Symposium, p.27 (2011) Corresponding Author: H. Kataura TEL: +81-29-861-2551, E-mail: <u>h-kataura@aist.go.jp</u>

#### Energetics and Electronic Structures of Amino Acid Residues Adsorbed on Carbon Nanotubes

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Interactions of biomolecules with carbon nanotubes (CNTs), graphene, and carbon nanohorns have recently been the subject of a great deal of research with the goal of biomedical applications of the these nano-scale or low-dimensional carbon allotropes. In particular, the study of the interaction between CNT and protein is imperative in toxicology of the CNTs. Because protein is a polypeptide consisting of  $\alpha$ -amino acid residues, clarification of the interaction between amino acid residues and CNTs becomes a firm bridgehead toward systematic understanding of protein-CNT interactions. However, its fundamental characteristics are still far from being fully understood. We here study the energetics of adsorption of amino acid residues on single-walled CNTs (SWCNTs) and electronic structures of the resulting hybrid systems on the basis of the density functional theory (DFT). We consider four representative amino acid residues, lysine, histidine. isoleucine, and tryptophan, that take linear, all-*trans* conformations. They were adsorbed on (17, 0), (18,0), and (10, 10) SWCNTs in vacuum.

Our DFT calculations clarify that all of the four amino acid residues are bound to the SWCNTs. The binding energy is calculated to be in the range of 0.3–0.4 eV/molecule, and the calculated distances between the adsorbed molecules and CNT wall are in the range of 2.5–3.1 Å. Among the four kinds of amino acid residues, lysine has the largest binding energy, while tryptophan has the lowest one. All of the hybrid systems are semiconductors with a direct gap originating from the  $E_{11}$  gap of a semiconducting SWCNT and from the tiny gap of the metallic SWCNTs. Electronic states near the Fermi level originate primarily from those of SWCNTs. Detailed analysis of the electronic structure of the hybrid systems reveals that an amino acid residue interacts with a SWCNT at both of its side chain and terminal amino group through the hybridization between C and N 2*p* orbitals and the  $\pi$  states of the CNTs.



Fig. 1. Four amino acid residues studied in this work.

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# **Observation of Positive- and Negative-Charged Excitons in the Electrochemical-doped Single-walled Carbon Nanotubes**

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Since the semiconducting single-walled carbon nanotube (S-SWNT) has large exciton binding energy (400 meV) due to one dimensional property, it has been expected that the charged exciton (three-particle bound state) which consists of doped-charged particle (electron or hole) and exciton could exist in the doped carbon nanotubes system. This charged exciton is called to trion. Recently, the positive charged exciton (hole and exciton, positive trion) was observed in p-doped carbon nanotube at the room temperature by photoluminescence (PL) and absorption spectroscopy [1]. The positive trion optical spectra appear under the  $E_{11}$  optical transition energy, and the trion binding energy strongly depends on diameter and chiral angle. The three-particle bound state, trion, was also found on the individual SWNT over a large cw excitation intensity range, since exciton-exciton annihilation processes generate dissociated carriers to allow the trion creation upon a subsequent photon absorption event [2].

In order to understand in more detail the intrinsic properties of the trion in the SWNT, we should consider a negative charged exciton (electron and exciton, negative trion) in electron-doped carbon nanotube system. However since n-dopant is unstable in nature and it

is very hard to control the doping level, chemical doping is not available to observe a negative trion. Therefore the electrochemical doping is suggested to observe the negative trion in the SWNT by applying an electrochemical potential on the SWNT film of ITO electrode, and following the change of the Fermi level [3]. Finally, as shown in Fig. 1, we observed that the electrochemically measured negative trion has almost the same binding energy with the positive trion because the doped-hole and electron have almost the same effective masses in the carbon nanotube system and the trion spectra become strong when we increase an electrochemical doping level.

← ∆E → (75)Normalized PL intensity Positive trion (6,5) (7,6)+0.7V 0.0V Negative trion (8,3) 0.5V 1300 1000 1100 1200 Emission (nm)

Fig. 1. The trion spectra in the electrochemically doped-SWNTs

R. Matsunaga *et al.* Phys. Rev. Lett. **106**, 037404 (2011).
 S. M. Santos *et al.* Phys. Rev. Lett. **107**, 187401 (2011).
 Y. Tanaka *et al.* Angew. Chem. Int. Ed. **48**, 7655 (2009).
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# Suppression of Exciton-Electron Scattering in Doped Single-Walled Carbon Nanotubes

1-4

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Strong Coulomb interaction in single-walled carbon nanotubes (SWCNTs) leads not only to stable bound state of exciton and trion but also to interesting dynamical properties of the many-body exciton states and exciton-carrier state. Recently it was found that phase relaxation by the elastic scattering among the excitons dominantly contributes to the linewidth of optical spectra [2], much larger than the contribution of the Auger exciton recombination caused by the inelastic scattering among the excitons [3]. For doped SWCNTs, besides the elastic scattering between excitons, it is expected that the elastic scattering between excitons and charged carriers play a crucial role for determining the phase relaxation of the excitons.

In the present paper, we perform theoretical investigation on the dephasing process caused by the elastic scattering between excitons and electrons to unravel the dynamical processes of excited states in doped SWCNTs. Our calculation of the linewidth predicts that this scattering process shows strong suppression and nonlinearity associated with the doped electron density. This anomalous behavior is caused by a cusp-like structure in the dispersion relation of exciton that originates from the logarithmic singularity ascribed to the exchange self-energy [5].

#### References:

- R. Matsunaga et al. Phys. Rev. Lett. 14, 115 (2002).
   D. T. Nguyen *et al.* Phys. Rev. Lett. 92, 233105 (2008).
   F. Wang *et al.* Phys. Rev. B 73, 245425 (2006).
   L. Schultheis *et al.* Phys. Rev. Lett. 10, 2381 (2010).
- [5] S. Konabe, K. Matsuda, and S. Okada, Submitted.

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Fig.1 Calculated linewidth at 50K and 300K

#### Exciton Relaxation to A Trion State in Hole-Doped (6,5) SWNTs

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A composite particle of an exciton and an electron (or a hole) is known as a charged exction, called trion. The binding energy of trions in conventional semiconductors is usually very small (a few meV), and they are not stable at room temperature. In contrast, recent theoretical studies predicted the stability of trions at room temperature in SWNTs due to their large binding energies [1]. Recent experiments at room temperature showed positive trions in chemically hole-doped (*p*-doped) SWNTs [2] and all-optical trion generation in neutral SWNTs [3]. In this study, we investigate exciton and trion dynamics in *p*-doped (6,5) SWNTs at room temperature by time-resolved luminescence measurements.

The SWNTs used in this study were produced by the Co-Mo catalytic method

(CoMoCAT) process (SWeNT, SG-65). Enhancement of (6,5) SWNTs was carried out using the gel column chromatography. Hole-doping into SWNTs was done by adding HCl solution. Figure 1 shows absorption spectra of the undoped (dotted line) and *p*-doped (solid line) samples (estimated hole density, 0.97 nm<sup>-1</sup>). In the *p*-doped sample, the  $E_{11}$  exciton absorption at 1.27 eV is suppressed, and the trion absorption [2,3] appears at 1.08 eV.

Luminescence kinetics were measured using femtosecond time-resolved luminescence spectroscopy based on the frequency up-conversion technique [4]. Figure 2 shows luminescence kinetics of the  $E_{11}$  exciton (top) and the trion (bottom) in the *p*-doped sample. The  $E_{11}$  exciton luminescence shows a double-exponential decay with time constants of 60 and 540 fs (dashed line). In contrast, the trion luminescence cannot be fitted to a single-exponential function (dashed line) around the time origin, showing a rise behavior of luminescence. Using a single-exponential function with a rise term with a time constant of 60 fs (solid line), the decay curve is well reproduced. Since the rise time of the trion luminescence is in good agreement with the decay time of the  $E_{11}$ exciton luminescence, the observed results indicate the ultrafast exciton relaxation to the trion state.



Fig. 1. Absorption spectra of undoped and *p*-doped samples.



Fig. 2. Luminescence decay kinetics at 1.26 ( $E_{11}$  exciton) and 1.08 eV (trion) in the *p*-doped sample.

[1] T. F. Rønnow *et al.*, Phys. Rev. B **81**, 205446 (2010). [2] R. Matsunaga *et al.*, Phys. Rev. Lett. **106**, 037404 (2011). [3] S. M. Santos *et al.*, Phys. Rev. Lett. **107**, 187401 (2011). [4] T. Koyama *et al.*, Phys. Chem. Chem. Phys. **14**, 1070 (2012).

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#### Photoluminescence from Exciton State in Metallic SWNTs

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An exciton is a photo-created quasi-particle wherein an electron and a hole are in a hydrogen-like bound state due to the attractive Coulomb interaction. In metals, strong screening of the Coulomb interaction between an electron and a hole by free electrons largely prevents exciton formation. In one-dimensional systems, however, Coulomb interactions are enhanced to a remarkable extent thereby reducing the screening effect, and a stable exciton state is expected to be realized even in metallic one-dimensional systems. Here we experimentally demonstrate photoluminescence (PL) from the exciton state in metallic single-walled carbon nanotubes (M-SWNTs) [1].

The SWNTs used in this study were formed by the e-DIPS method. They had an average diameter ~1.78 nm with a full width at half-maximum of ~0.59 nm. Separation of M-SWNTs from the pristine material was carried out using the density gradient ultracentrifugation procedure. The inset of Figure 1 shows typical absorption spectra of the pristine and M-SWNT sample. In the pristine sample,  $E_{11}$  (~0.6 eV),  $E_{22}$  (~1.0 eV),  $M_{11}$  (~1.4 eV), and  $E_{33}$  (and  $E_{44}$ ) (~1.9 eV) transition bands are observed, while in the M-SWNT sample, the  $E_{11}$ ,  $E_{22}$ , and  $E_{33}$  bands are suppressed and the principal absorption band is the  $M_{11}$  band.

Figure 1 shows PL decay kinetics at 1.0 and 1.4 eV in the M-SWNTs sample. Ultrafast decay of the PL signal is observed at 1.4 eV, while no PL signal is detected at 1.0 eV (and below). If the residual semiconducting SWNTs existed in the sample, a strong PL from  $E_{11}$  state in semiconducting SWNTs should be observed. Consequently, the origin of the observed PL is not semiconducting SWNTs but M-SWNTs. To obtain the decay time constant,

we performed curve fitting with a single-exponential function convoluted with the instrument response function, and the fitted result is plotted as a solid curve in the figure. The time constant is obtained to be  $40 \pm 10$  fs.

Pump-probe measurements showed that bleaching of the  $M_{11}$  band absorption is recovered with a time constant of ~500 fs. This decay time is one order of magnitude longer than the PL decay time. Since the decay behavior of the absorption bleaching indicates the cooling dynamics of unbound electrons and holes, the ultrafast decay observed by the PL measurements is ascribed to the recombination process of excitons. Therefore, the exciton lifetime is found to be  $40 \pm 10$  fs, indicating a relatively stable exciton state in the presence of metallic electrons.

[1] T. Koyama et al., Phys. Rev. B 85, 045428 (2012).

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Fig. 1. PL decay kinetics at 1.0 and 1.4 eV. Inset shows absorption spectra of pristine and M-SWNT samples.

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Luminescence Intensity (counts) Absorbance oristine x 5 metallic \_1.4 eV 4 0.5 1.0 1.5 2.0 2.5 Photon Energy (eV  $10 \, \text{eV}$ 0 -0.3 0.3 0.6 0.9 0 Time (ps)

#### The World of CNT Forests

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Since the discovery of the carbon nanotube (CNT) 20 years ago, extensive effort has been made to harness, in applications, their exceptional intrinsic properties, such as the electrical and thermal conductivities, mechanical strength, etc. This obstacle has been further limited by the ability to process the CNTs, by either wet (dispersion) or dry (sheets, yarns, etc) methods, into functional forms while maintaining the intrinsic properties of the CNT.

Recently, the development of economical mass production technologies based on the Super-growth method has enabled large-scale production of SWCNT forests as exemplified by a pilot production plant. To promote the industrial use of SWCNTs, we are developing knowledge to guide end-users toward their specific application need. Specifically, we are undertaking the task to understand the relationship between the CNT forest structure, e.g. height, density, crystallinity, etc, and their properties both in the form of a forest and in the processed form. In this way, the form of the SWCNT for optimized function would be known. This is what we call the "World of CNT Forests." Therefore, this work encompasses two main endeavors: the ability to synthesize SWCNT forests of desired structural and standardized characterization processes. Here, I will present our progress on developing the technology for the synthetic control of SWCNTs, the development of standardized evaluation techniques, and understanding we have at the present.

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# Two-stage growth process of single-walled carbon nanotubes revealed by laser vaporization

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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 nanoelectronic devices, because the performance of SWNTs-based devices would much depend on the diameter, particularly on the chirality of carbon nanotubes. Therefore, the ultimate goal in carbon nanotube production is to develop a method which would allow the growth of SWNTs with a single chirality. Despite the promise, development of effective processes for chirality controlled production of high quality SWNT required for commercial applications demands a much better understanding and control of the microscopic mechanisms. Unfortunately, the complexity of the synthetic procedures has made experimental determination of the mechanism very difficult, and this complexity has also frustrated progress in realizing production of SWNT with a single chirality.

In the present work, we demonstrate a growth mechanism which has been strongly suggested by our experimental data of the laser vaporization accumulated during the last more than 10 years. The basic idea of the mechanism which is presented here has been reported previously in 2000 by Kataura et al.<sup>1</sup> in which the growth processes of SWNTs have been supposed to be essentially divided into two stages; cap-formation and tube-growth. The former process was supposed to be happened in the gas phase. Actually in the present work, the presence of the IPR satisfied cap structures have been strongly suggested to be formed in the gas phase prior to depositing on the metal catalyst in which the tube-growth takes place. In order to clarify the role of the cap formation in the gas phase, we have examined the SWNT formation with the use of 10 different metal catalysts possessing different physical properties. The resulting qualitative chirality distributions were found to slightly depend on the catalysts, reflecting the solidification timing during their cooling process.

However, from the view points of quantitative analysis for these 10 different metal catalysts, the production yields of SWNTs were found to significantly depend on the metal catalysts, most probably reflecting the ability of carbon diffusion on the metal surface. The carbon diffusion rate would partly determine the rate of the tube-growth process.

Finally, in the present work, the role of temperature on the growth of tube length will be discussed on the basis of wide-range temperature dependence of chirality distributions. It has been widely accepted that the chirality distribution is dependent on the preparation temperature. Generally, a near armchair structure is supposed to be more favorable at the lower temperature, suggesting the lower activation barrier in comparison with a near zigzag structure. The temperature dependence of specific chiral structure will be discussed in terms of both experimental trial of the SWNT production with a single chirality as well as theoretical approach of finding specific chiral structure in the tube-growth process.

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#### Alignment Control of Carbon Nanotube Forests from Random to Nearly Perfectly Aligned by Utilizing Crowding Effect

1-9

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As in the case for polymer chains, fibers, and proteins, alignment of the one-dimensional, high aspect ratio internal building blocks of a bulk material represents an important structure parameter. Due to the impact of alignment on properties, tailoring the degree of alignment of these components is of fundamental importance. An apt example is polyethylene (PE) used to make drink bottles where the hard cap is made from highly ordered PE while the flexible body is made from low order PE.

As being a one-dimensional material possessing the highest aspect ratio, carbon nanotubes (CNTs) follow a similar scheme. In this paper, we demonstrate a general approach to control the alignment of few-walled CNT forests from nearly random to nearly ideally aligned by

tailoring the density of active catalysts at the catalyst formation stage, which can be experimentally achieved by controlling the CNT forest mass density (Figure 1). We found that the catalyst density and the degree of alignment were inseparably linked because of a crowding effect from neighboring CNTs, i.e., the increasing confinement of CNTs with increased density. Therefore, the CNT density governed the degree of alignment, which increased monotonically with the density. This relationship, in turn, allowed the precise control of the alignment through control of the mass density. The wide variety of CNT forests with different alignments achieved in this work would be expected to open new opportunities for different CNT structures and forms or new post-processes.



Figure 1. Demonstration of precise alignment control nearly spanning the full range of random to nearly perfect alignment. (a) Photographs of the CNT forest with the heights of  $\sim$ 1mm at different degrees of alignment. (b) Scanning electron microscopy images showing the wide range of alignment with the HOFs ranged from 0.13 to 0.85.

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## A generalized approach to achieve highly conductive CNT/elastomers based on solubility parameters

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Electrically conductive elastomers or rubbers have been investigated to apply various fields like electro-magnetic shielding, vacuum seals and flexible electronic devices. In this work, we used mesh-like-dispersed SWNTs synthesized by water-assisted chemical vapor deposition, denoted as "supergrowth", to achieve long SWNTs (SG-SWNT). The SG-SWNT were qualified as the best available conductive fillers because they were very long and thus had an exceptionally high aspect ratio, yet were not heavily bundled, and easy to disperse.

First, we studied the effect of the matrix rubber on the conductivity by fabricating a series of SG-SWNTs rubber composites from an assortment of rubbers. Volume conductivities, measured on these conductive rubber sheets using the four-probe method, showed a strong dependence on the nature of the rubber matrix and ranged from a maximum of 13.8 S/cm for fluorinated rubber to a minimum of 1.1 S/cm for SEBS (poly[styrene-*b*-(ethylene-*co*-butylene)-*b*-styrene]) (Figure 1). We tried to thermodynamically explain the variation of volume conductivity. We propose the "solubility parameter" as an important parameter that determines the degree of CNTs dispersion in the rubber matrix, and thus the conductivity of the CNT-rubber composite.

This finding explains why fluorinated rubber has shown the highest conductivity among rubber matrices because the solubility parameter matched with that of the CNT. Based on this finding, we demonstrate addition of a small amount of fluorinated rubber into the rubber matrix as a unified and practical technology to improve the conductivity of the CNT-rubber composite for a wide class of rubber matrices.

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Figure 1. Volume conductivities of SG-SWNT composites with various rubber matrices.

# CVD synthesis of small-diameter nitrogen-doped single-walled carbon nanotubes using acetonitrile

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Synthesis of single-walled carbon nanotubes (SWNTs) with controlled chirality remains a major challenge in the nanotube community, yet is necessary in order to obtain pristine SWNTs with uniform electrical and/or optical properties. There are a number of reports in the literature showing success in reducing the average SWNT diameter and narrowing the diameter distribution, but most of these results were achieved by modifying the catalyst particles. Here we report a significant reduction in SWNT diameter and simultaneous nitrogen doping resulting from modifying the catalyst.

Conventional alcohol catalytic chemical vapor deposition (ACCVD) [1] was performed using ethanol feedstock containing varying concentrations of acetonitrile (CH<sub>3</sub>CN). Based on comprehensive spectroscopic characterization, the mean diameter of substrate-supported vertically aligned SWNTs was found to decrease from 2.1 nm down to 0.7 nm with the addition of less than 3% acetonitrile in the ethanol feedstock. Notably, the small-diameter SWNTs remained vertically aligned. A reduction in diameter was also found for SWNTs grown from zeolite-supported catalyst particles, indicating the effect is not critically dependent on catalyst preparation.

X-ray photoelectron spectroscopy was used to elucidate whether or not the nitrogen from the acetonitrile was incorporated into the SWNTs. Substitutional Ν doping was found to saturate at approximately 1 at.% (Fig 1), with the majority of the N being in an  $sp^2$  bonding environment. [2]

[1] S. Maruyama et al., Chem. Phys. Lett.360 (2002) 229.

[2] T. Thurakitseree et al. Carbon, *submitted*.

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**Fig. 1** Relationship between acetonitrile concentration and mean SWNT diameter (circles, left ordinate) as well as incorporated N concentration (squares, right ordinate). Inset shows region of low acetonitrile concentration.

# 1-12

# Catalyst control for the preferential growth of semiconducting single-walled carbon nanotubes

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One of the major problems on SWNTs for the widespread application in semiconductor electronics is the coexisting of metallic and semiconducting carbon nanotubes in the as-synthesized samples. Although several approaches including electrophoresis, gel-chromatography, and selective elimination of metallic SWNTs has been reported, the above postsynthesis separation processes often cause contamination or degradation of nanotubes. Recently, the preferential growth of metallic SWNTs achieved by varying the gas composition during pre-annealing process of the catalyst has been reported [1]. Here, we present our approach for the preferential growth of semiconducting SWNTs by controlling the pre-annealing process of the catalyst nanoparticle.

The combination of  $H_2O$  and  $H_2$  vapor has been chosen for the control of iron catalyst nanoparticle during the pre-annealing process. SWNT growths have been conducted on a clean quartz furnace system for the precise control of gas ambient. We have found that Raman spectra ( $\lambda$ = 532, 633, 780 nm) of SWNT thin films grown after the pre-annealing process with certain amount of  $H_2O$  and  $H_2$  suggested the preferential growth of semiconducting nanotubes with high reproduciblity. The performances of FET devices directly fabricated from the as-synthesized SWNT films are also presented.

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[1] A. R. Harutyunyan, G. Chen, T. M. Paronyan, E. M. Pigos, O. A. Kuznetsov, K. Hewaparakrama, S. M. Kim, D. Zakharov, G. U. Sumanasekera, E. A. Stach, *Scicence*, **326**, 116 (2009).

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# Future extraction analysis of conductive paths in the thin film of self-assembled single-wall carbon nanotubes

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Single wall carbon nanotubes (SWCNTs) have attracted much attention due to their excellent transport properties and chemical stability. [1] Such excellent properties promote printed electronics applications of SWCNTs, which include a thin film transistor (TFT), a transparent conductive film electrode (TCF), and so on. For these applications, SWCNTs are frequently applied as the thin film prepared by casting their suspension. [2] Prepared SWCNT thin films include locally aligned structures, ordered during the deposition, due to the strong self-organizing capability of SWCNTs. In terms of the local conductance of carriers along the orientation direction, such aligned SWCNTs should be superior to their random network.

In this work, we have prepared the locally and highly aligned SWCNT thin film according to the following procedure. At first, SWCNTs were dispersed with the help of polyoxyethylene (100) stearyl ether (Brij 700). From this dispersion, semiconducting SWCNTs enriched up to 97 % were extracted by the electric field induced layer formation (ELF) method. [3] The oxidized silicon wafer was functionalized with 3-aminopropyl triethoxysilane (APTES) and utilized as the substrate. SWCNT thin films were fabricated by dipping the substrate into the specially diluted dispersion of semiconducting SWCNTs. Repeating this procedure could increase the packing density of SWCNTs in the monolayer film up to ca. 35 SWCNTs/µm.

We have also fabricated TFT devices by using the above SWCNT thin film as the semiconducting channel. In the investigation into the transport property of TFT devices, high performances with significant uniformity have been demonstrated; 2.5 ( $\pm$  8 %) cm<sup>2</sup> / Vs in mobility and  $10^5$  (± 3 %) in On/Off ratio. In order to clarify the effect of locally ordered structure on the device performance, here we applied a novel analyzing method for specifying the morphology of SWCNT network based on the feature extraction framework. Images of the morphology observed by atomic force microscopy (AFM) were analyzed by this method and the result of the analysis revealed hidden morphological features in the prepared thin film of SWCNTs as follows: The pitch of the alignment is around 29 nm corresponding to the extremely high tube density of 35 SWCNTs/mm. Furthermore, the statistical interval of SWCNTs across the alignment is 150nm. Interestingly, the feature extraction analysis proved that 85 % of deposited SWCNTs forms one dominant conductive pathway in this case. However, because 15 % of such dominant path can be identified as dead-end branchs, it was concluded that approximately 25 % of SWCNTs is ineffective for the practical electric conduction. These results suggest the possibility for the further improvement of device performances by refining the self-assembled structure in SWCNT thin films. This work has been supported by NEDO.

[1] R. Saito, G. Dresselhaus, and M. S. Dresselhaus: Physical Properties of Carbon Nanotubes (Imperial College Press, London, 1998).

[2] M. Shiraishi, T. Takenobu, T. Iwai, Y. Iwasa, H. Kataura, M. Ata, Chem. Phys. Lett. 394, 110 (2004).

[3] K. Ihara, H. Endoh, T. Saito, F. Nihey, J. Phys. Chem. C 115, 22827 (2011)

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#### **Structures and Chemical Properties of Carbide Cluster Fullerenes**

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Encapsulation of metals inside fullerenes generates a new class of hybrid molecules, which are called endohedral metallofullerenes (EMFs). They show unique structures and novel properties distinctly different from empty fullerenes, and huge potential applications ranging from materials science to biomedicine.<sup>1</sup> Because of the complexity of the encapsulated metallic compounds, structural elucidation of EMFs has been an intractable issue. In particular, EMFs containing a metal carbide cluster is hard to be identified because two carbons are encapsulated inside the cage, instead of constructing the cage frame. As a result, many carbide cluster EMF species had been incorrectly assigned as conventional EMFs (Sc<sub>2</sub>@C<sub>2n</sub>).<sup>2</sup>

We present here the unambiguous structural identification of several new fullerene species containing a  $Sc_2C_2$  cluster, *namely*,  $Sc_2C_2@C_{2v}(5)$ - $C_{80}$ ,  $Sc_2C_2@C_s(6)$ - $C_{82}$ ,  $Sc_2C_2@C_{3v}(8)$ - $C_{82}$ ,  $Sc_2C_2@C_{2v}(9)$ - $C_{82}$ , and  $Sc_2C_2@D_{2d}(23)$ - $C_{84}$ , using both NMR spectroscopy and XRD crystallography.<sup>3</sup> Furthermore, chemical reactions of these new species with either a 1,3-dipolar reagent or a carbene reagent were systematically studied and the isolated derivatives were fully characterized using various techniques. It is observed that the cluster orientation and motion exert strong influence on the chemical properties of cage carbons.<sup>4</sup> When encapsulating multiple Sc atoms, cluster EMFs are always preferentially formed, which is obviously associated with the strong coordination ability of scandium, which favors the formation of various clusters, and the small ionic radius of Sc<sup>3+</sup>, which allows the encapsulation of the clusters inside normal fullerenes.<sup>5</sup>

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 <sup>(</sup>a) Chemistry of Nanocarbons, T. Akasaka, F. Wudl, S. Nagase, Eds.; Wiley-Blackwell: London, 2010. (b) X. Lu, T. Akasaka, S. Nagase, Chem. Commun. 2011, 47, 5942-5957.

 <sup>[2] (</sup>a) Takata, M.; Nishibori, E.; Sakata, M.; Inakuma, M.; Yamamoto, E.; Shinohara, H. *Phys. Rev. Lett.* 1999, *83*, 2214-2217. (b) Inakuma, M.; Yamamoto, E.; Kai, T.; Wang, C. R.; Tomiyama, T.; Shinohara, H.; Dennis, T. J. S.; Hulman, M.; Krause, M.; Kuzmany, H. *J. Phys. Chem. B* 2000, *104*, 5072-5077.

<sup>[3] (</sup>a) H. Kurihara, X. Lu, Y. Iiduka, N. Mizorogi, Z. Slanina, T. Tsuchiya, T. Akasaka, S. Nagase, J. Am. Chem. Soc. 2011, 133, 2382-2385. (b) H. Kurihara, X. Lu, Y. Iiduka, M. Hachiya, H. Nikawa, N. Mizorogi, Z. Slanina, T. Tsuchiya, S. Nagase, T. Akasaka, Inorg. Chem. 2012, 51, 746-750.

<sup>[4] (</sup>a) X. Lu, K. Nakajima, Y. Iiduka, H. Nikawa, N. Mizorogi, Z. Slanina, T. Tsuchiya, S. Nagase, T. Akasaka, J. Am. Chem. Soc. 2011, 133, 19553-19558. (b) H. Kurihara, X. Lu, Y. Iiduka, H. Nikawa, N. Mizorogi, Z. Slanina, T. Tsuchiya, S. Nagase, T. Akasaka, J. Am. Chem. Soc. 2012, in press. (c) X. Lu, K. Nakajima, Y. Iiduka, H. Nikawa, T. Tsuchiya, N. Mizorogi, Z. Slanina, S. Nagase, T. Akasaka, submitted.

<sup>[5]</sup> H. Kurihara, X. Lu, Y. Iiduka, H. Nikawa, N. Mizorogi, Z. Slanina, T. Tsuchiya, S. Nagase, T. Akasaka, Chem. Commun. 2012, 48, 1290-1292.

# Synthesis and Structure Determination of Tm@C<sub>82</sub>(I) – Ni(OEP) Co-crystals

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Metallofullerenes are one of the most attractive fullerene materials due to their unique structure having metal atoms within a hollow carbon cage <sup>[1]</sup>. The optical and magnetic properties might be affected by the position of the metal atoms. A controllability of the position of the metal atoms can be used as nanometer-scale switching as we have already reported <sup>[2]</sup>. The position of the metal atoms could also be changed by the interaction with ligands such as octaethylporphyrin nickel (Ni(OEP)) outsides the carbon cage. The effects of the interaction between metal atoms and ligands on the position of metal atoms are revealed in this study by the crystal structure analysis of two kinds of Tm@C<sub>82</sub>(I) – Ni(OEP) co-crystal with different Tm@C<sub>82</sub>(I) : Ni(OEP) compositions of 1:1 and 1:2.

The 1:1 crystal was obtained by means of layering a dusky red solution of saturated  $Tm@C_{82}(I)$  in 1 ml toluene over a red solution of 0.6 mg Ni(OEP) solution in 1 ml chloroform. These two layers were diffused slowly to form the corresponding single crystal. The 1:2 crystal was also obtained by means of drying the same solution described above for several weeks.

The X-ray diffraction measurement of the crystals was performed at BL02B1 beamline in SPring-8. The 1:1 crystal has a monoclinic lattice with space a space group of C2/m, a = 25.141(3) Å, b = 15.324(4) Å, c = 19.694(0) Å,  $\beta = 94.862(6)^{\circ}$ . In contrast, the 1:2 crystal has a monoclinic lattice with a space group of C2/m, a = 25.385(3) Å, b = 14.930(9) Å, c = 28.958(1) Å,  $\beta = 97.183(1)^{\circ}$ . The crystal structures were determined based on the charge density distributions obtained by the maximum entropy method (MEM) [M.Takata et al., Nature (1995)]. The MEM charge densities reveal the positional change of thulium atom within the carbon cage by changes of coordination structure of Ni(OEP).



Fig.1: Synthesis of 1 : 1 & 1 : 2  $\text{Tm}@C_{82}(I) - \text{Ni}(\text{OEP})$  co-crystals.

<sup>[1]</sup> Y. Yasutake, Z. Shi, T. Okazaki, H. Shinohara, and Y. Majima; *Nano Letters*, <u>5</u>, <u>6</u>, (2005), 1057
[2] H. Shinohara; *Rep. Prog. Phys* <u>63</u> (2000) 843
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#### UPS of Lu and Lu-carbide cluster encapsulated fullerenes

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We have presented ultraviolet photoelectron spectra (UPS) of endohedral fullerenes to elucidate their electronic structure. Here, we present the UPS of two Lu atoms, two Lu and carbon atoms encapsulated fullerenes and discuss them with an aid of the DFT calculation.

The UPS of Lu<sub>2</sub>@C<sub>80</sub>-C<sub>2ν</sub>, Lu<sub>2</sub>C<sub>2</sub>@C<sub>80</sub>-C<sub>2ν</sub>, Lu<sub>2</sub>@C<sub>82</sub>-C<sub>2ν</sub>, Lu<sub>2</sub>C<sub>2</sub>@C<sub>82</sub>-C<sub>2ν</sub>, Lu<sub>2</sub>@C<sub>84</sub>-C<sub>2ν</sub> and Lu<sub>2</sub>C<sub>2</sub>@C<sub>84</sub>-D<sub>2d</sub> were measured using a synchrotron radiation light source. The onset energies are much smaller than that of empty C<sub>82</sub> (1.2 eV) by around 0.2 ~ 0.6 eV. The UPS of Lu<sub>2</sub>@C<sub>80</sub>-C<sub>2ν</sub> and Lu<sub>2</sub>C<sub>2</sub>@C<sub>80</sub>-C<sub>2ν</sub>, and those of Lu<sub>2</sub>@C<sub>82</sub>-C<sub>2ν</sub> and Lu<sub>2</sub>C<sub>2</sub>@C<sub>82</sub>-C<sub>2ν</sub> resemble each other. These facts are another example to support an empirical rule that the electronic structure of the endohedral fullerenes is principally governed by the cage structure. These UPS of deeper valence band region (BE >5 eV) shows good correspondence with those of other endohedral fullerenes. However, two structures at about 9.5 eV and 11.0 eV are observed in the UPS of Lu atoms encapsulated fullerenes. These structures are attributed to Lu4f levels (Lu4f<sub>7/2</sub> and Lu4f<sub>5/2</sub>). The BE of these levels are summarized in Table 1. These

levels of Lu atoms encapsulated fullerenes are deeper than those of corresponding Lu and carbon atoms encapsulated ones by  $0.2 \sim 0.4$  eV. Further, they appear at explicitly larger BE than those of neutral Lu atoms. This shift relates to electron transfer; the entrapped Lu atoms donate electrons to the cage. Present findings suggest the entrapped C<sub>2</sub> atoms influence the electron transfer from the Lu atoms to the cage.

Table 1. The UPS onset energy of Lu atoms endoherdal fullerenes and their Lu4f levels in valence band region.

	Eonset	Lu4f <sub>7/2</sub>	Lu4f <sub>5/2</sub>
$Lu_2@C_{80}-C_{2v}$	0.62	9.6	10.9
$Lu_2C_2@C_{80}-C_{2v}$	0.73	9.5	10.6
Lu <sub>2</sub> @C <sub>82</sub> - $C_{2\nu}$	0.6	9.7	11.1
$Lu_2C_2@C_{82}-C_{2v}$	0.87	9.4	10.8
Lu <sub>2</sub> @C <sub>84</sub> - $C_{2\nu}$	0.68	9.6	11.1
$\mathrm{Lu}_{2}\mathrm{C}_{2}@\mathrm{C}_{84}\text{-}D_{2d}$	1.01	9.2	10.7
Lu metal	-	7.5	8.9

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# A reactivity index in cycloadditions of $C_{60}$

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In nucleophilic [4+2] cycloadditions to  $C_{60}$ , the reactive site is a double bond between the adjacent six-membered rings[1]. Since the LUMOs of  $C_{60}$  are three-fold degenerate, and are delocalized over the molecule, the frontier orbital theory encounters difficulty in explaining its reactivity.

In this study, we propose a reactivity index considering vibronic (electron-vibration) coupling, vibronic coupling density (VCD)  $\eta(\mathbf{r})$  [2] for a reactive mode, and apply it for the reaction. The VCD is defined by

$$\eta(\mathbf{r}) = \Delta \rho(\mathbf{r}) \times v(\mathbf{r}),$$

where  $\Delta \rho(\mathbf{r})$  is the electron density difference between a charge transfer state and a neutral state, and  $v(\mathbf{r})$  denotes the derivative with respect to a reactive mode of electron-nuclear potential  $u(\mathbf{r})$  acting on a single electron.

Figure 1(a) shows the VCD  $\eta(\mathbf{r})$  for the  $T_{1u}(z)$  electronic state of  $C_{60}^-$ . The VCD is distributed on the double bonds between the adjacent six-membered rings. Figure 1(b) shows the VCD for ethylene anion. From view of the VCD,  $C_{60}$  bears ethylene moieties. Since there are other electronic states,  $T_{1u}(x)$  and  $T_{1u}(y)$ ,  $C_{60}$  has six ethylene moieties in its cage. This is consistent with the experimental observation of a hexakis adduct with  $T_h$  symmetry[3].



[1] Y. Rubin et al., J. Am. Chem. Soc. 115, 344(1993).

[2] T. Sato et al., J. Phys. Chem. A 112, 758 (2008).

[3] B. Kräutler et al., Angew. Chem. Int. Ed. 34, 87 (1995).

**Figure 1:** Vibronic coupling density of the reactive mode. (a) C<sub>60</sub> and (b) ethylene.

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#### **Fabrication and Properties of Fullerenol Nanosheets**

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Polyhydroxylated fullerenes ( $C_{60}(OH)_x$ : fullerenol) have been thought to have potential applications in a variety of areas, including optoelectronics, medical therapeutics, biochemistry, polymer materials science, and electrochemistry, owing to their high solubility in a large variety of solvents (depending on the number of hydroxyl groups, *x*). The study of nanomaterials is one of the most active areas due to their interesting properties that differ from those of bulk substances, and their wide possibilities of applications. In this study, we report the fabrication of both  $C_{60}(OH)_x$  nanosheets and nanocrystals by the liquid phase reprecipitation method using two solvents of varying solubilizing ability. The morphology of the crystals was characterized by TEM and AFM.

Figure 1 shows the typical TEM (a) and AFM (b) images of  $C_{60}(OH)_{11}$ (average composition) nanosheets fabricated by using tetrahydropyran (good solvent) and deionized water (poor solvent). The thickness of the nanosheets was evaluated to be in the range of 10-200 nm. In this presentation, their detailed morphology, structure and properties will also be discussed.



Fig.1 TEM (a) and AFM (b) image of Fullerenol Thin Film by the liquid–liquid interfacial precipitation method using tetrahydropyran (good solvent) and deionized water (poor solvent).

[1] Akito M. *et al.*, Jpn. J. Appl. Phys. **48** 050206 (2009)
 [2] Chiang *et al.* J. Org. Chem., **59**, 3960 (1994)
 [3] H. Kasai *et al.*, Jpn. J. Appl. Phys. **31** L1132 (1992)
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#### Synthesis of the C<sub>60</sub> nanowhiskers that exhibited a good superconductivity

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A new form of single-crystal nanofiber of  $C_{60}$ , " $C_{60}$  nanowhisker", was discovered in a PZT sol containing a small amount of  $C_{60}$  in 2001 [1, 2]. The synthesis of fullerene nanowhiskers (FNWs) including  $C_{60}$  nanowhiskers ( $C_{60}$ NWs) can be performed by using a simple method named "liquid-liquid interfacial precipitation method (LLIP method)". In the LLIP method, a poor solvent of fullerene is layered on a good solvent solution of fullerene at a cool room temperature. The nucleation and growth of single-crystal fullerene nanowhiskers (FNWs) occurs through the precipitation of fullerene crystals at the liquid-liquid interface and the mutual diffusion of the two solvents.

Last year, the C<sub>60</sub> nanowhiskers doped with potassium (K) with a nominal composition of  $K_{3.3}C_{60}$  were found to exhibit an excellent superconductivity with a T<sub>c</sub> of 17 K [3] and a high J<sub>c</sub> greater than 10<sup>5</sup> A/cm<sup>2</sup>. The superconducting volume fraction of  $K_{3.3}C_{60}$  powder was less than 1 %, while that of  $K_{3}C_{60}$ NWs was greater than 80 % [4]. The C<sub>60</sub>NWs used in this discovery were the sample synthesized by the LLIP method using a C<sub>60</sub>-saturated toluene solution and isopropyl alcohol (IPA) at 10 °C, where the solution was ultrasonicated for 10 s after the formation of liquid-liquid interface and aged for 24 h. The sample was filtered and vacuum-dried for 2 h at 100 °C before the doping of K. The dried sample of C<sub>60</sub>NWs without K showed a Raman profile closely resembling to that of C<sub>60</sub> powder (99.5% pure, MTR Ltd.), indicating that the C<sub>60</sub>NWs have a crystal structure similar to the C<sub>60</sub> powder where the C<sub>60</sub>

It is shown that the  $C_{60}NWs$  synthesized by the LLIP method have a core-shell structure with a porous core containing a high-density of pores with radii from about 5 nm to 20 nm and a thin surface layer with a thickness less than 100 nm [5]. Hence, the high superconducting volume fraction of  $K_3C_{60}NWs$  must have been originated from the existence of nanopores that assist the rapid diffusion of K. The Raman profiles of K-doped  $C_{60}NWs$ were obtained under a N<sub>2</sub> atmosphere. The detailed Raman profiles of the K-doped  $C_{60}NWs$ will be presented at the symposium.

- [1] Fullerene Nanowhiskers, Ed. Kun'ichi Miyazawa (Pan Stanford Publishing, 2011)
- [2] K. Rauwerdink, J.-F. Liu, J. Kintigh and G.P. Miller, Microscopy Research and Technique 70(2007)513-521.
- [3] Success in Realizing Superconductivity in Fullerene Nanowhiskers, http://www.nims.go.jp/eng/news/press/2011/12/p201112270.html
- [4] Y. Takeya, R. Kato, K. Miyazawa, T. Yamaguchi and Y. Takano, Abstract of New Materials Science Using Regulated Nano Spaces, NIMS, Tsukuba, January 5th - 7th, 2012, pp. 33-33.
- [5] R. Kato and K. Miyazawa, Diamond and Related Materials, 20 (2011) 299–303.

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#### Superconducting properties of potassium-doped fullerene nanowhiskers

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Various types of fullerene-based supramolecular materials have been reported by Miyazawa et al. so far, such as nanowhiskers ( $C_{60}NWs$ ) [1-2], nanosheets, nanowires, and nanotubes. We have been interested in the physical properties of those materials composed of fullerene units. In this study, we tried to dope a potassium (K) into the  $C_{60}NW$  for the future application as superconducting light wires. First, superconductivity was observed at 17 K in the K-doped  $C_{60}NWs$ . The on-set superconducting transition temperature ( $T_c$ ), measured using a SQUID magnetometer, was independent of the K content (x) in the range between 1.6 and 6.0 in  $K_xC_{60}NW$ , while the superconducting volume fractions were changed with x as shown in Fig. 1. A peak of the shielding fraction was observed at x= 3-3.3 (as high as 80 %) in  $K_xC_{60}NW$ , as was the phenomenon in the K-doped fullerene compounds ( $K_xC_{60}$ ). However, there was considerable difference in the shielding volume fraction, for example, between  $K_{3.3}C_{60}NW$  and  $K_{3.3}C_{60}$ . The former showed more than 80 % and the latter showed less than 1 %. We believe the difference is caused from the structural defects, dislocations or nano-pores in  $C_{60}NWs$ , which assists K-migration in the materials.

We report the superconducting behaviors of our newly synthesized  $K_xC_{60}NWs$  in comparison to those of  $K_xC_{60}$  crystals. The upper critical field of  $K_{3.3}C_{60}NW$  was estimated as  $H_{c2}(0) = 159$  kOe using the Werthamer–Helfand–Hohenberg (WHH) formula as shown in Fig. 2. *M*-*H* curves and the critical current,  $J_c$ , by the Bean model will also be reported and discussed.



Fig. 1. K content dependence of shielding volume fractions.

Fig. 2. Upper critical field  $(H_{c2})$ 

[1] K. Miyazawa, Y. Kuwasaki, A. Obayashi, and M. Kuwabara, J. Mater. Res., 17, 83 (2002).
[2] K. Miyazawa, K. Hamamoto, S. Nagata, and T. Suga, J. Mater. Res., 18, 1096 (2003).
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# A Single-Walled Carbon Nanotube Twist Sensor by wrapping transfer method

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We previously reported the generalization of substrates for device applications by developing a method for the strong adhesion ("sticking") of aligned and densely-packed SWNT films (denoted CNT wafers) to arbitrary substrates. In this way, we could realize a fully- stretchable strain sensor capable of 280% strain with high durability, fast response, and low creep useable for human motion detection [1]

Here, we present a rational rod twist sensor that can measure a twist (400 rad/meter) more than four-times more than conventional optical fiber-based twist sensors by monitoring an increase in resistance due to fracturing of CNT wafers wrapped around a rod by using the adhesion and stretching properties of CNT wafers [2]. The key process in fabricating the twist sensor was to wrap the aligned SWNT thin film onto the surface of a rod with a predetermined and constant winding angle while preserving the internal network of the SWNT thin film. This difficulty is amplified because the delicate (thickness: ~400 nm) film must be assembled on the rod with centimeter length scale. To overcome these difficulties, we first assembled CNT wafers from aligned SWNT thin films on a Teflon flat substrate and then

rolled an elastomeric rod across the substrate. The weak adhesion force between the Teflon substrate and CNT wafer compared to the interaction among the SWNTs within the wafer and the adhesion force between the elastomeric rod and CNT wafer allowed simple and complete transfer of the entire CNT wafer onto the elastomeric rod with minimal structural distortion to the thin film. Therefore, we could wrap the CNT wafer on elastomeric rod and fabricate CNT twist sensor.



Fig. The steps in fabricating the twist sensor (left) and picture of the twist sensor (right).

[1] T. Yamada, Y. Hayamizu, Y. Yamamoto, Y. Yomogida, A. Izadi-NAjafabadi, D. N. Futaba, and K. Hata Nature Nanotech. 6, 296 (2011).

[2] T. Yamada, Y. Yamamoto, Y. Hayamizu, H. Tanaka, D. N. Futaba, and K. Hata Nano Lett. Submitted.

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## Microwave heating characteristics of nano-carbon fluids - toward new hot-water supply -

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Hot-water supply is one of the most basic utilities used in every household all over the world, for cooking, drinking, washing, bathing, and even for heating the house. In fact, nearly 30% of energy consumed by a household is used to heat water and  $CO_2$  emission in Japan amounts to 33 x 10<sup>6</sup> tons/year for hot water supplies alone. Currently, gas combustion and electric heaters are two major techniques to provide hot water in domestic use. These heating techniques, however, have been well developed and further improvements on efficiency are rather challenging. A new heating technique based on a totally different principle is needed for minimizing  $CO_2$  emission and saving energy.

It is known that solid carbon nanotubes are heated to over 1000 °C within a few tens of seconds by a house-use microwave oven. If this nearly explosive, rapid heating to high temperatures can be controlled, it may provide a highly efficient heating technique for hot-water supply. We propose that this can be achieved by forming nano-carbon fluids. For hot-water supply, water is heated through a heat exchange with the microwave-heated nano-carbon fluid. To understand microwave heating of nano-carbon fluids, various nano-carbons dispersed in a high-boiling point liquid are investigated.

The figure shows the irradiation time dependence for the nano-carbon fluids that contain various amounts of graphite particles. When the rate of temperature increase is relatively small, the temperature rise is well described by Newton's law of heating (cooling),

$$T = T_0 + T_{\max} [1 - \exp(-t/\tau)]$$

This equation is derived by assuming that (1) heating is uniform over the entire volume, and (2) the hot solids are at a constant  $T_{\rm max}$ . Since the carbon has been heated starting from the room temperature, these conditions imply that the temperature of each graphite particle has reached  $T_{\rm max}$  immediately after the microwave has turned on and has stayed constant, as seen with the present measurement time scale.

In the cases of rapid increase of temperature (for instance, under the conditions of higher carbon



concentrations, larger microwave powers, different kinds of nano-carbons), the temperature measurements become technically difficult and a different analytical method is required.

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# 2-10

# Fully Inkjet-Printed Transistors Based on Separated Single-Walled Carbon Nanotubes

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Single-walled carbon nanotubes (SWCNTs) are promising materials for building wide range application such as flexible and printed electronics. Recently, progress in purification techniques enables us to obtain samples of a specific electronic type (metallic (m-) or semiconducting (s-)) SWCNTs. However, the trade-off behavior between carrier mobility and on/off ratio was still a big open question. Very recently, we found clear answer for this longstanding puzzle, and realized very high-performance transistors with mobility of more than 30-50 cm<sup>2</sup>/Vs and on/off ratio of  $10^4$ - $10^5$  using one of the solid electrolytes, ion gel [1]. In this study, we applied this understanding to inkjet-printing of SWCNT transistors. Since one of the advantages in inkjet printing is density controllability, we investigated the relationship between s-SWCNT density and transport mechanism. Moreover, we have demonstrated the compatibility of inkjet printing for SWCNT using s-SWCNT as a channel and m-SWCNT as electrodes.

We fabricated fully inkjet-printed SWCNT transistors by m-SWCNT, s-SWCNT and ion gel (Fig. 1). Source and drain electrodes were inkjet-printed by m-SWCNTs. We

also inkjet-printed various density of s-SWCNT films on SiO<sub>2</sub>/Si substrate. The obtained performance of traditional back-gate type transistors was well explained by SWCNT density and high-density film shows miserably poor performance (Fig. 2, gray line, on/off ratio < 2). Finally, we additionally inkjet-printed one of the electrolytes, ion gel, on identical s-SWCNT films, and fabricated fully inkjet-printed transistors. In stark contrast to the back-gate type, printed ion-gel transistor of same s-SWCNT film reveals excellent on/off ratio (Fig. 2, black line, on/off ratio  $> 10^3$ ). These obtained results obviously indicate that the origin of metallization is not the percolation of of residual m-SWCNTs but the effect unintentional carrier doping by ambient condition. We believe that this is important first step for high-performance SWCNT printed electronics.

[1] Y. Yomogida et al., The 42nd FNTG General Sympo.

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Fig.2 Transfer characteristics

# Analysis of Operation Mechanism of Field Effect Transistor Composed of SWNT Network by Scanning Gate Microscopy

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Carbon nanotubes (CNTs) have been regarded as one of the most fascinating materials for scientific researches and industrial applications because of their potential for high-speed electronics due to the high electron velocity in CNTs and for flexible electronics due to their elasticity. Scanning gate microscopy (SGM) is one of such techniques for local study in semiconductor nano-structures. It has been applied for FETs consisting of a single-wall carbon nanotube (SWNT) [1] and the network [2].

In this paper, we have applied this technique for the study of SWNT thin-film FET to determine the mechanism of the FET operation. Two kinds of SWNTs, synthesized by CoMoCAT<sup>®</sup> process (sample A) and semiconductor enriched ones (sample B), were used in this study. Clear SGM responses were observed only at some points but not uniformly in a whole of the channel. We found that almost all of SGM responses are coming from inter-tube junctions in sample A. One of the possible mechanism is that a modulation of Schottky barrier between the metallic/semiconducting SWNT existing in the SWNT network. In contrast to the experiments, SGM images observed in sample B showed different responses; several concentric rings have been observed corresponding to somewhere of intra-tubes (Fig. 1). Back gate voltage dependence of ring diameters were also studied (Fig. 2). Such rings have been observed in SGM responses corresponding to Coulomb-blockade effect [3].



Fig.1 (a) AFM topographic image of sample B and (b) corresponding SGM image.



Fig.2 Back gate voltage dependence of line profiles across ring structure observed in sample B.

[1] A. Bachtold *et al*, Phys. Rev. Lett. **84**, 6082 (2000).
 [2] N. Aoki *et al*, AIP Conf. Proc. **1399**, 829 (2011).
 [3] M. T. Woodside and P. L. McEuen, Science. **296**, 1098 (2002).
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# 2-11

# Structural control of Multi-layered Graphenes and their applications for large capacity Lithium ion secondary battery electrodes

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Carbon materials are quite important elements in applications for various battery devices such as lithium ion secondary battery (LIB), capacitor, fuel cells and solar cells. Because of their superior properties of electrical conductivity, large surface area, thermal/chemical tolerance and structural flexibility, a lot of attentions have been paid for their practical integrations in the next generation energy devices. The monoatomic sheet structure of the graphene materials are suitable for the capacitor devices with high energy density electrical double layer energy storage and/or high density anodes for LIB devices. Owing to their structural variety of the mono/multi-layered graphene with tunable inter-layer distances and stacking numbers, improved lithium ion accommodation in these nano-carbon electrodes are expected, which exceeds a limit of 372 mAh/g of the graphite anodes. In this paper, the versatile fabrication process of mono/multi-layered graphene electrodes by Hummers methods and the structural characterizations for stacking number and inter-layer

spacing are reported. Also, the lithium storage properties of the graphene electrodes are investigated and, interestingly, large capacity of 540 mAh/g was obtained for the multilayered graphene electrodes. Moreover, the lithium storage capacity has been increased by expanding inter-layer spacing of multi-layered graphene, when mixed with carbon nanotube or fullerenes, to 784 mAh/g, which has been almost doubled capacity from the graphite crystals.



Fig. 1 Transmission electron microscope analysis of multi-layered graphene electrodes

Table 1				
Electrode Materials	Lithium storage capacity (mAh/g)			
Graphite	372			
Graphene	540			
Graphene + Fullerene ( $C_{60}$ )	784			
Graphene + Carbon nanotube (CNT)	730			

[1] Geim, A. K. & Novoselov, K. S. The rise of graphene. Nature Mater. 6, 183-191 (2007).

[2] Dinesh Rangappa et al., Chemistry - A European Journal (2010) 16, 6488

[3] EunJoo Yoo et al., Nano Letters (2008) 8, 2277

[4] Seung-Min Paek et al., Nano Letters (2009) 9, 72

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## Selective Formation of Graphene on Insulator by Liquid Phase Growth

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Graphene is one of the most intriguing nanocarbon materials since it has a lot of excellent physical and chemical properties. Of particular note is the highest field effect mobility among all the existing materials. The essential requisite on applying graphene to the practical use is to establish the formation technique of graphene on the surfaces of many kinds of materials, *e.g.*, graphene-on-insulator, which enable us to realize graphene-based electronics and green innovations. So far, graphene preparation has been achieved by three principal methods, exfoliation [1], CVD [2], and thermal decomposition of silicon carbide [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. Our novel formation method of graphene is based on the liquid phase growth (LPG) using a gallium flux as reported in the previous meetings [4, 5].

Here we report one of the applications of the LPG method to produce regular graphene structures using micro-scale templates. Figure 1(a) shows the procedure how to make the regular graphene structures; a sandwiched configuration composed of a glassy carbon plate, a

(a)

gallium flux, and a quartz glass substrate with square anti-dots ranging from 0.5 to 10 micrometer in size and 0.35micrometer in depth on the surface was annealed around 1000 °C for a few hours, and then cooled to room temperature. As shown in Fig 1(b) and (c), the LPG method enables us to form dish-shaped graphene structures selectively in the anti-dots. The D/G ratio of the graphene structures was determined to be less than 0.1, indicating they have rather good quality (Fig. 1(d)). The detailed atomic structures and formation mechanism will be discussed in the meeting.

# (b) (d) = (d) =

(c)

#### **References:**

- [1] K. S. Novoselov et al. Science 306, 666 (2004).
- [2] X. Li et al. Science 324, 1312 (2009).
- [3] C. Berger et al. Science 312, 1191 (2006).
- [4] H. Hiura et al. The 40th Commemorative Fullerene-Nanotubes General Symposium, 3-7 (2011).
- [5] M. V. Lee et al. The 41th Fullerene-Nanotubes General Symposium, 3-10 (2011).

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Fig.1 (a) procedure, (b) laser microscope image of regular graphene structures formed selectively in anti-dot structure on a quartz substrate, (c) magnified image of (b), and (d) Raman

spectrum and mapping images of regular graphene structures

# Laser Power dependence of G'Raman intensity in bilayer graphene

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The intensity of the four sub-peaks (P11, P12, P21 and P22) of the G'Raman band of AB stacked bilayer graphene are analyzed as a function of the laser power. We show that the intensity of the peaks depends on temperature and also depends on the laser excitation energy [1]. This special dependence is explained in terms of the electron-phonon (el-ph) coupling and the relaxation time of the photon-excited electron. Due to the small relaxation time of the photo-excited electron by emitting phonons, the relative intensities of the four sub-peaks are determined by some dominant relaxation process that give rise to some G' sub-peaks at the expense of others, thereby making the intensity of the peaks different from each other. Also, we report an anomalous behavior of the G' intensities for the 532nm laser energy, that shows a resonance regime in which a saturation of the P12 process occurs. This effect is a relevant phenomena that needs to be taken into account for certain applications of bilayer graphene in the field of nanotechnology.

[1] D. L. Mafra, P. T. Araujo, K. Sato, R. Saito, Jing Kong, M. S. Dresselhaus, unpuplished..

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## Quantum Dynamics Simulation of Laser-driven Electron Field Emission from Graphene Nano-ribbons

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Field emission from metallic tips with nanometer sharpness has been utilized to various devices because of highly bright and coherent electron source. Recent experiments on applying femtosecond laser pulses to such tips have realized a spatially and temporally localized source of ultrafast electron beam, predicting emerging applications such as an ultrafast electron microscopy [1]. So far little is known about the microscopic physics underlying femtosecond electron emission from nanotips. Although two phenomenological models, that is, photo-field emission and optical field emission depending on laser parameters have been proposed [2], theoretical analysis based on electron dynamics is lacking.

Our objectives in the present study are to investigate the femtosecond laser-driven electron emission from graphene nano-ribbons (GNR) and boron nitride nano-ribbons using the time-dependent density functional theory (TDDFT) calculations [3] and to elucidate the emission mechanism that depends on the applied laser parameters. We found in the present simulation that electron emission from GNR abruptly increases compared with that of laser-free case when the laser energy (frequency) approaches the value corresponding to the energy band gap at gamma point in the first Brillouin zone, indicating photoemission instead of photo-field emission and optical field emission. We discuss the effects of hydrogen termination, ribbon-edge structures and laser parameters on the emission mechanism.

[1] H. Yanagisawa et al. Phys. Rev. Lett. 103, 257603(2009); ibid. 107, 087601(2011).

[2] P. Hommelhoff et al. Phys. Rev. Lett. 96, 077401 (2006).

[3] J. A. Driscoll et al. Phys. Rev. B 83, 233405 (2011).

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# Intercalation behavior of organic molecules into pillared carbon consisting of silsesquioxane bridged graphene layers

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We have recently found that polar organic molecules were size-selectively intercalated into pillared carbon prepared from graphite oxide (hereafter GO) repeatedly silylated with methyltrichlorosilane in which graphene layers are connected with each other by silsesquioxane pillars. Considering the minimum molecular widths of the intercalated species, the width between two adjacent pillars for the entrance of them is well controlled between 0.36 and 0.4 nm and the pillars should incline from the normal against the graphene layers and they should be longer than 1.72 nm. In this study, the intercalation behaviors of various organic molecules into the pillared carbon were investigated in detail.

GO was silvlated with methyltrichlorosilane for 3 times and the resulting silvlated GO was heated at 500°C under vacuum. Various organic molecules such as *n*-alkymamines with various alkyl chain lengths, *n*-octanol and xylenes were intercalated by immersed the resulting pillared carbon in the solutions of them for 24 h.

Fig.1 shows the X-ray diffraction patterns of pillared carbon after immersion in the solutions of *n*-alkylamine molecules with various alkyl chain lengths. The diffraction peaks of pillared carbon shifted to lower angle after immersion in the solutions of alkylamines. This indicates that alkylamine molecules were intercalated into it. The shift of the diffraction peak became larger for alkylamines with longer alkyl chains and then became almost constant for alkylamines with 6 carbon atoms or more. Here, note that the plate like morphology of the

pillared carbon was almost unchanged even after immersion in *n*-butylamine. The interlayer spacing after intercalation of organic molecules increased with increasing in the length of them. It reached 2.24 nm and then became constant even when the molecular length further increased. This fact strongly suggests that the adjacent carbon layers are well connected with each other by silsesquioxane pillars, otherwise further increase of the interlayer spacing is expected.

[1] Y. Matsuo *et al.* Chem. Commun. **47**, 4009 (2011).

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Fig.1 X-ray diffraction patterns of pillared carbon prepared from  $(C_1Si)_{2,3}GO$  (A): before and after immersion in *n*-alkylamines with various alkyl chain lengths of (B): 3, (C): 4, (D): 6, (E): 8 and (F): 12. The peaks marked with "\*": residual *n*-alkylamines crystallized on the surface of pillared carbon.
#### Roll-to-roll deposition of graphene film by microwave plasma CVD

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Transparent conductive films are used in a lot of applications such as touch screens, solar cells and displays. Although ITO is the most commercial materials, a substitute material for ITO, due to limited supplying indium, is one of the key technologies to be solved.

Graphene based films are considered to be one of the appropriate transparent conductive films of which substitute of ITO since graphene consists of carbon atoms. Although the transparent conductive films based on graphene films were fabricated by thermal CVD [1] and reduction of graphene oxide [2], these reported techniques required higher process temperature and long time. For the transparent conductive film based on graphene films, it is necessary to develop continuous deposition of graphene film at low process temperature.

Roll-to-roll process is used in mass production for film depositions on flexible and plastic substrates. Therefore, a combination of roll-to-roll deposition and plasma CVD is expected to be solved the higher process temperature and long process time. However, it has not yet been established for industrial mass production up-to-now.

We report about continuous graphene film deposition on Cu foil with 297 mm in width by combination of roll-to-roll microwave plasma CVD deposition and fabrication of transparent conductive film based on graphene film by transferring method. A pair of winder and unwinder was built into linear antenna type microwave plasma CVD system [3]. Raman spectra indicate that a uniform graphene film is obtained in 297mm width is confirmed. Graphene based transparent conductive films are obtained by transferring graphene film from Cu foils to PET films. Uniform and high optical transparencies of transferred graphene/PET structures are obtained.

[1] S. Bae et al., Nature Nanotechnol. 5, 574 (2011).

[2] H. Yamaguchi et al., ASC Nano 4, 524 (2010).

[3] T. Yamada et al, submitted (2011).

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Graphene is a monolayer carbon sheet including high carrier mobility, flexibility, and high optical transmittance. These properties are advantageous if graphene is to be used as a component in electrical devices such as field effect transistors, solar cells, and various gas and chemical sensors. Chemical vapor deposition (CVD) is one of the most promising methods of growing graphene, which can produce large, relatively high-quality graphene sheets. However, the graphene growth by CVD is limited only to the metal catalyst surfaces such as Ni, Cu, or Co, which is one of the most serious problems for the practical application of graphene as electrical devices. Thus, the development of the method for the direct growth of graphene on the insulating substrate, especially on a SiO<sub>2</sub> substrate, is highly required. Furthermore, transport type control of graphene transistor [1] is also an important issue for the construction of logic circuits with graphene-based transistors.

We have realized a novel, simple, and scalable method for the direct growth of graphene on an insulating substrate by plasma CVD. It is revealed that by adjusting the growth parameters using plasma CVD, the graphene layer can be made to grow along the interface of the Ni layer and the SiO<sub>2</sub> substrate instead of on top of the Ni layer. After removing the top Ni layer, high-quality single- or few-layer graphene sheets are found to be directly grown on the entire substrate area in large scale ( $10 \times 10$  mm). The electrical transport property of directly fabricated graphene can also be controlled by introducing NH<sub>3</sub> gas during plasma CVD.

[1] Toshiaki Kato, Liying Jiao, Xinran Wang, Hailiang Wang, Xiaolin Li, Li Zhang, Rikizo Hatakeyama, and Hongjie Dai, Small 7 (2011) 574.

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# Electronic properties and relative stabilities of commensurate and incommensurate graphene/h-BN superlattices

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In recent years, heterostructures of graphene and hexagonal boron nitride (h-BN) have been studied intensively. The electron mobility of graphene on h-BN substrates is larger than that of graphene on silicon dioxide substrates [1]. It has been also demonstrated that graphene encapsulated in h-BN exhibits interesting properties such as metal-insulator transition [2]. In parallel with these experimental studies, we have investigated geometries and electronic properties of graphene/h-BN superlattices within the framework of the density functional theory [3-4]. Commensurate graphene/h-BN monolayer superlattices with lattice-matching have been found to be more stable than incommensurate superlattices without lattice-matching despite the intrinsic difference in lattice constants. It has been also found that graphene layers in graphene/h-BN monolayer superlattices could interact with each other through h-BN.

In this work, we report relative stabilities and electronic properties of commensurate and incommensurate graphene/h-BN superlattices based on density functional theory. Commensurate phases are found to be more stable than incommensurate phases not only in graphene/h-BN monolayer superlattices but also in graphene/h-BN bilayer superlattices [5]. In addition, pressure or thermal annealing should stabilize commensurate phases. To study electronic properties of incommensurate superlattices, we consider twisted superlattices where graphene and h-BN possess the same in-plane lattice constant but different orientation with each other (Fig. 1) in the twisted superlattices. Stacking geometries of these twisted superlattices are similar to those of incommensurate superlattices. In addition, the number of atoms in the supercell of a twisted superlattice should be small [6] compared with true incommensurate superlattices with a relatively small computational resource. It is found that graphene layers in twisted superlattices interact with each other weakly compared to commensurate superlattices.

[1] C. R. Dean, A. F. Young, I. Meric, C. Lee, L. Wang, S. Sorgenfrei, K. Watanabe, T. Taniguchi, P. Kim, K. L. Shepard, and J. Hone, Nature Nanotech. 5, 722 (2010)

[2] L. A. Ponomarenko, A. K. Geim, A. A. Zhukov, R. Jalil, S. V. Morozov,
K. S. Novoselov, I. V. Grigorieva, E. H. Hill, V. V. Cheianov, V. L. Fal'ko,
K. Watanabe, T. Taniguchi, and R. V. Gorbachev, Nature Phys. 7, 958 (2011)
[3] Y. Sakai, T. Koretsune, and S. Saito, Phys. Rev. B 83, 205434 (2011)
[4] M. Sakurai, Y. Sakai, and S. Saito, J. Phys. Conf. Ser. 302, 012001 (2011)
[5] Y. Sakai and S. Saito, Mater. Res. Soc. Symp. Proc. (Submitted)

[6] A. N. Kolmogorov and V. H. Crespi, Phys. Rev. B 71, 235415 (2005)

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**Fig. 1** Geometry of twisted superlattice.

## Impurity Adsorption on Nitrogen-Doped Graphene: A First-Principles Study of Energetics and Electronic Properties

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Graphene is known to exhibit unique and interesting properties such as high carrier mobility and massless Dirac fermion behavior, suggesting the possibility of realization of novel graphene-based electron-device applications in nanoelectronics. Substitutional nitrogen doping is one of the most accessible means to tune electronic properties of graphene-based devices. It has been reported that there are two major nitrogen-defect configurations in the N-doped graphene: substitutional nitrogen and pyridine-type defects [1]. The electronic properties of pyridine-type defect in N-doped graphene (Fig. 1) as well as N-doped (10,0) CNT are shown to have p-type property, whereas the substitutional nitrogen defect induces donor-type states [2-4]. Thus, doping with only the nitrogen is capable of producing both p-type and n-type conductivities. Therefore, for the development of practical graphene-based devices, it is essential to control strictly nitrogen-defect configurations and their electronic properties such as carrier type and carrier density.

Here, we study the impurity adsorption effects on the N-doped graphene using first-principles density-functional calculations. It is generally expected that the impurity defect serves as a reactive site, and it has been reported that the hydrogen adsorbed on the N-doped (10,0) CNT dramatically changes the electronic structure [4]. In the presentation, we discuss the energetics of the impurity adsorption, and reveal that the electronic properties of N-doped graphene dramatically change by impurity adsorption.

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Figure 1. Scanning tunneling microscopy (STM) image of pyridine-type defects in graphene [3].

[1] D. Wei, Y. Liu, Y. Wang, H. Zhang, L. Huang, and G. Yu, Nano Lett. 9, 1752 (2009).

- [2] Y. Fujimoto and S. Saito, Physica E 43, 677 (2011).
- [3] Y. Fujimoto and S. Saito, Physical Review B 84, 245446 (2011).
- [4] Y. Fujimoto and S. Saito, J. Phys.: Conf. Ser. 302, 012006 (2011).

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#### **Optimized De-agglomeration of Detonation Nanodiamond**

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Single-nano particles belong to a class of materials most difficult to disperse because of their large and active surface. Conversely, particle-sizes of once dispersed particles of this size range will be readily overestimated for the same reason. We encountered a good example of this pitfall in the case of the primary crystals in detonation nanodiamond (DN), for which a diameter of  $4.8\pm0.7$  nm has been considered as the final value for some time[1].

We have recently optimized the conditions of wet attrition milling, a method of choice for deagglomeration of crude DN product, long fixed by experience. Taguchi's engineering design method [2] was employed while fitting eight factors in two to three levels to  $L_{18}$ 

orthogonal array, and performing 18 experiments. Results were analyzed by solving for SN ratios of the measured values of particle sizes. The most critical operation parameter turned out to be the initial slurry concentration of agglomerated DN (Fig.1). With the other parameters optimized, an optimum set of attrition milling conditions led to well-reproducible production of high quality primary particles having a greatly reduced particle-size of  $3.7\pm0.6$  nm. We presume that we are close to the real size range, and suspect that the previous dispersed particles contained small amounts of incompletely dispersed fractions. Contamination from the zirconia crusher beads also dramatically decreased to 2-3 ppm from the previous level of 0.2% obtained under the un-optimized milling conditions. A number of other improved properties of dispersed DN particles will be presented.





**Fig.1** Dependence of the final particle sizes on the initial concentrations of agglomerated DN.



**Fig. 2** Aqueous colloidal solution of dispersed DN before (a) and after 50h of electrolysis (b). In the latter, two layers appeared: in the center of lower layer is a black mass, which is likely consisting of graphene, whereas the upper clear layer contains nanodiamond particles devoid of graphite layers.

found that DN colloidal solution is conductive upon applying direct voltage, that it stores electricity which is discharged spontaneously upon disconnection, that it produces electricity by inserting Cu/Zn electrodes (a quasi-Daniel cell), and that it can combine with metallic ions.

<sup>[1]</sup> Ōsawa, E., in Wudl, F. *et al.* (Eds.), '*Chemistry of Nanocarbons*,' Chapt. 17, pp. 413-432, John Wiley & Sons, Oxford, **2010**. [2] Taguchi, G. *et al.*, '*Taguchi's Quality Engineering Handbook*,' Wiley-Interscience, **2004**, 1696 pages. \*Corresponding Author: 81-(0)268-75-8381, OsawaEiji@aol.com.

# 3-11

### Surface Engineering of Nanodiamond for Targeted Cell Labeling

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Biomedical applications of nanodiamond (ND) have been investigated extensively due to its low toxicity, excellent biocompatibility and high extensibility of the surface functionality. Quite recently, we have grafted polyglycerol (PG) on the surface of ND and dissolved it under physiological environment [1]. Taking advantage of the extensibility of the PG layer, ND-PG is subjected to further surface modification to incorporate multifunctions such as fluorescence and targeting. As a result, some of the hydroxyl groups on PG were converted to azide and amino groups through stepwise organic





transformations. Then, near-infrared (NIR) dye (IRdye CW800) and  $\alpha_v\beta_3$ -integrin-targeting *cyclo*-RGD peptide were immobilized on ND-PG through amidation and Cu(I)-catalyzed "click" reaction, respectively (Figure 1).

To evaluate their targeting properties, various cancer cells including A549, U87MG, HeLa, and B16F10 were incubated in presence of NIR-dye conjugated ND with and without cvclo-RGD peptide (ND-PG-NIR-RGD and ND-PG-NIR. respectively). As



**Figure 2.** Fluorescence images (cy5 mode) of cancer cells treated with ND-PG-NIR with and without *cyclo*-RGD peptide.

shown in Figure 2, ND-PG-NIR was not uptaken by any kinds of the cancer cells. In contrast, ND-PG-NIR-RGD fluorescently labeled U87MG and A549, but did not do HeLa and B16F10. Because U87MG and A549 are known to express  $\alpha_v\beta_3$ -integrin, ND-PG-NIR-RGD was internalized into the cells through receptor-mediated endocytosis (RME) [2].

Reference: [1] L. Zhao, T. Takimoto, M. Ito, N. Kitagawa, T. Kimura, and N. Komatsu, *Angew. Chem. Int. Ed.*, 50, 1388 (2011), [2] P. Decuzzi and M. Ferrari, *Biomaterials*, 28, 2915 (2007) Corresponding Author: Li Zhao Tel: +81-77-548-2102, Fax: +81-77-548-2405, E-mail: <u>lzhao@belle.shiga-med.ac.jp</u>

### Structure Differentiation of Graphene-Based Materials by Oxidation with Hydrogen Peroxide

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We previously reported that single-walled carbon nanohorns (SWNHs) and thin graphene sheets (TGSs) in as-grown nanohorns had close combustion temperatures, but could be distinguished and even quantified by employing high resolution thermogravimetric analysis (HR-TGA) [1]. In addition, it was found that TGSs combustion occurred in a wide temperature range, suggesting that there were different types of TGSs. In this report, to clarify the types of TGSs, we pre-treated as-grown nanohorns by mild pre-oxidation with hydrogen peroxide at room temperature before performing HR-TGA, which two types of TGSs could be discriminated.

Analysis of derivative curves of weight-temperature curves in HR-TGA showed that as-grown nanohorns used in this study were composed of SWNHs (combustion temperature: 562 °C), TGSs (589 °C), and micrometer-sized graphitic balls (736 °C), and the weight ratio of SWNH and TGS was 55:45.

As-grown nanohorns were pre-oxidized with hydrogen peroxide for a certain period (from 1 h to 56 d) in room temperature. The combustion temperatures of both SWNH and TGS decreased by the pre-oxidation, which would be due to the increase of the number of oxygenated groups generated by the pre-oxidation. The weight ratio changes of SWNH and TGS during first one week were large, e.g. by 7 days pre-oxidation, the ratio of SWNH and TGS was 86:14 (31% increase in SWNH and 31% decrease in TGS). However, despite this marked change, the weight decrease of nanohorns before and after pre-oxidation was very small (about 10% decrease).

For the explanation of this large quantity imbalance, we assumed the existence of TGSs in two types. One type (TGS1) was oxidized with hydrogen peroxide, which made the combustion temperature to decrease to close to that of SWNHs, while the other type (TGS2) was less oxidative and no drastic change in combustion temperature resulted from the pre-oxidation. The theoretical calculation presented by Yoshizawa et al. [2], the layer number counting in TEM images, and XRD analysis suggested that TGS1 had the even layer numbers less than six, and TGS2 had the odd layer numbers or thicker than six.

<sup>[1]</sup> M. Irie, M. Nakamura, M. Zhang, R. Yuge, S. Iijima, M. Yudasaka. Chem. Phys. Lett. 500, 96 (2010).

<sup>[2]</sup> K. Yoshizawa, T. Yumura, T. Yamabe, S. Bandow, K. J. Am. Chem. Soc. 122, 11871 (2000).

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## 3-13

# Development of Multi-stage Ion Trap Mobility System with Laser Desorption/Ionization and Structural Observation of Polystyrene Particles

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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 and structural changes of salt solution particles were monitored for more than 2 hours[2]. However the trap system has low mobility resolution because of the small size of the trap. Furthermore the stability evaluation of the system is difficult since the structural change of the solution particles and the fluctuation of the system cannot be distinguished. Here we present the development of the multi-stage ion trap mobility system with laser desorption/ionization ion source, which enables us to enhance the resolution and to evaluate the stability with polystyrene particles.

Figure 1 shows a schematic diagram of the system which consists of the stacked ion trap and the observation and the desorption/ionization lasers. The charged particles produced solid were from polystyrene particles (FP-10056-2 Bay bioscience) with diameters of 10~14 µm by irradiating 3<sup>rd</sup> harmonic of YAG laser. The charged particles were then trapped in the electrodes and mobility measurement was performed for 3 hours. Figure 2 shows the amplitude profile of the polystyrene particles. The amplitude slightly increased from 0 to 10 min. but then became constant. This steady amplitude profile shows the high stability of the system and the structures of solid polystyrene particles. The enhance resolution and functions will be discussed.

[1] T. Sugai et al., J. Am. Chem. Soc. 123, 6427 (2001).

[2] M.Sawanishi and T.Sugai, The 38th symposium abstract p.37 (2010).





Fig. 1 Schematic diagram of apparatus

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ポスター発表 **Poster Preview** 

1 <b>P</b> – 1	$\sim$	1P - 45
2P – 1	$\sim$	2P - 45
<b>3P</b> -1	$\sim$	3P – 49

# Selective synthesis of aziridinofullerene through an acid-promoted denitrogenation of triazolinofullerene

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1,3-Dipolar cycloaddition reaction of azides with fullerene  $C_{60}$  at [6,6] conjunct double bond is a valuable method for chemical modification. The reaction gives triazolinofullerene intermediate, followed by thermal extrusion of nitrogen molecule affording the open [5,6]-azafulleroid and/or the closed [6,6]-aziridinofullerene on the nature of substituent of the azide. In the most cases, the open [5,6]-azafulleroids are more thermodynamically stable than the latter [1]. Therefore, it is difficult to synthesize the aziridinofullerenes by thermal denitrogenation.

In this study, we report the acid-promoted denitrogenation of various triazolinofullerenes exclusively afforded the corresponding aziridinofullerenes. The reaction seems to proceed through a  $S_N$ 1-like reaction involving a fullerene cation intermediate [2]. Furthermore, the reaction is markedly accelerated by trifluoromethane sulfonic acid.



[1] D. M. Guldi et al., J. Phys. Chem. A, 2000, 104. 8601.

[2] K. Itami et al., J. Am. Chem. Soc. 2011, 133, 2402.

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## Characterization of 56π-Fullerenes —Separation of Regioisomeric Mixtures—

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Because [60]fullerene is widely employed in the development of organic photovoltaic (OPV) devices, the control of its electronic state and morphology by addition of organic addends to the fullerene core has become a very important issue. For instance, an increasing number of addends can reduce the  $\pi$ -conjugation length, raise the LUMO level, and hence raise the open-circuit voltage ( $V_{OC}$ ) of the OPV device, which is beneficial for the device performance. Recently, 56 $\pi$ -electron fullerenes such as bis-PCBM [1], indene C60 bis-adduct (ICBA) [2-6], methanofullerene derivatives [7,8] have received much attention, because they have high LUMO levels and afford high  $V_{OC}$  values in photovoltaic applications. However, such 56 $\pi$ -electron fullerenes are inevitably regioisomeric mixtures, except for methanofullerene derivatives of 1,4-diadducts [7]. Herein we report separation of isomers of some 56 $\pi$ -fullerenes and characterization of structures and properties. These information would be useful for development of efficient OPV devices.

- [2] WO/2008/018931; US Patent Application 20090176994.
- [3] Y. He, H.-Y. Chen, J. Hou, Y. Li, J. Am. Chem. Soc. 132, 1377 (2010).
- [4] Y. He, G. Zhao, B. Peng, Y. Li, Adv. Funct. Mater. 20, 3383 (2010).
- [5] G. Zhao, Y. He, Y. Li, Adv. Mater. 22, 4355 (2010).

[6] Y.-J. Cheng, C.-H. Hsieh, Y. He, C.-S. Hsu, Y. Li, J. Am. Chem. Soc. 132, 17381 (2010).

[7] Y. Zhang, Y. Matsuo, C.-Z. Li, H. Tanaka, E. Nakamura, J. Am. Chem. Soc. 133, 8086 (2011).

[8] C.-Z. Li, S.-C. Chien, H.-L. Yip, C.-C. Chueh, F.-C. Chen, Y. Matsuo, E. Nakamura, A. K.-Y. Jen, Chem. Commun. 47, 10082 (2011).

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<sup>[1]</sup> M. Lenes, G.-J. A. H. Wetzelaer, F. B. Kooistra, S. C. Veenstra, J. C. Hummelen, P. W. M. Blom, *Adv. Mater.* **20**, 2116 (2008).

## Stable colloidal dispersion of indolino[60]fullerene in water and photocurrent characteristics of the film fabricated by electrospray deposition method

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Fullerenes have attracted great interest in many fields due to their unique chemical and physical properties. However, low solubility of the fullerenes in water or other polar solvents is a barrier for the potentially applicable use in practice. Recently, PCBM is often used as an electron acceptor material in organic photovoltaic cell (OPV) due to low reduction potential and good solubility in many organic solvents such as toluene and chloroform. From an industrial and environmental viewpoint, however, it is necessary to restrain the use of a large amount of organic solvents that harm to the environment and health, and to develop high performance and eco-friendly materials.

Indolino[60]fullerene is one of the candidate fullerene derivatives that have a lower reduction potential than PCBM and has been expected as a good acceptor material in OPV. [1] Our study is that stable colloidal dispersion of an indolino[60]fullerene in water was performed by a reprecipitation technique, mixing the indolino[60]fullerene in a good solvent with a poor polar organic solvent, and exposing to a vacuum to remove the excess good solvent (Fig. 1). Compared with PCBM, the colloidal behavior in dispersion stability in water

was totally different. Colloidal stability of the indolino[60]fullerene was quite higher than PCBM and kept stable in water for more than one month.

A novel electrospray deposition (ESD) method made it possible to form a thin film that colloidal particles of the indolino[60]fullerene were properly deposited on ITO substrate under controlled drying conditions. A preliminary photovoltaic sample (ITO/indolino[60]fullerene film/Al) showed short-circuit photocurrent as shown in Fig. 2. Since the colloidal solution has no stabilizing agent such as surfactants, the result would reflect the property of indolino[60]fullerene particles themselves. In addition, the ESD method can be carried out under normal atmospheric pressure at room temperature.[2] Therefore it can be easy and cost-effective approach to fabricate organic devices.

A combination of functional colloidal particles dispersed in water with the ESD method will play a key role in development of OPV in an environmentally-friendly way.

[1] Y. Numata *et al.*, *Chem. Lett.* **37**, 1018 (2008).
[2] T. Fukuda *et al.*, *Phys. Status Solidi. RRL*, **5**(7), 229 (2011).
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Fig. 1. Indolino[60]fullerene (left), and the colloidal solution in water (right).



Fig. 2. The photocurrent measured as a function of time while the light irradiation is on and off periodically, for the colloidal fullerene film.

# Electronic and Geometric Structures of C<sub>32</sub>: New Semiconducting Form of sp<sup>2</sup> and sp<sup>3</sup> Hybrid C Network

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Fullerenes are known to be an atom-like constituent unit for the various crystalline phases in which the fullerene molecules are weakly or tightly bound each other. For instance, under ambient condition,  $C_{60}$  are weakly bound to its adjacent molecules leading to a face-centered cubic (fcc) phase. Besides the fcc phase, polymeric phases of  $C_{60}$  have been synthesized by applying the high pressure and high temperature and irradiating right to the fcc  $C_{60}$ . In the polymeric phases, C atoms form one-, two-, and three-dimensional covalent networks those result in interesting structural and electronic properties. Here, we focus on the small fullerenes solid those are expected to intrinsically have a polymeric structure due to its remarkable reactivity. We study the geometric and electronic structures of novel sp<sup>2</sup> and sp<sup>3</sup> hybrid three-dimensional covalent network ( $C_{32}$ ) with tetrahedral symmetry based on the density functional theory (DFT). To express the exchange-correlation potential among the interacting electrons, we use the local density approximation (LDA). We adopt the ultrasoft pseudopotential for describing electron-ion interactions. The valence wave function is expanded in terms of plane wave basis set with cutoff energy of 25 Ry.

We find two stable tetrahedral structures of which lattice parameters are a=0.98 nm and a=0.96 nm. Figure 1 shows optimized structures of stable  $C_{32}$  solid. We find that the network comprises of both sp<sup>2</sup> and sp<sup>3</sup> C atoms. Although they possess three-dimensional covalent networks consisting mainly of sp<sup>3</sup> C atoms, the bulk modulus of these phases are 14.8 GPa and 15.9 GPa which are smaller than that of diamond. Thus the systems are not possible candidates for hard materials. Under the optimum geometries, we found that these phases are semiconductors with moderate indirect energy gap. The calculated energy gap is 1.7 eV and 1.1 eV for a=0.98 nm and a=0.96nm, respectively.

(b)

Fig. 1, Optimized structures of  $C_{32}$  solid with (a) a=0.98 nm and (b) a=0.96 nm.

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(a)

# Raman spectra analyses of fullerene nanowhiskers polymerized in various environments

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Rao et al. reported  $A_g(2)$  peak of the Raman spectrum of  $C_{60}$  film sifted from 1469 to 1460 cm<sup>-1</sup> by the photopolymerization of  $C_{60}$  molecules [1]. In the previous symposium, we reported the photopolymerization of  $C_{60}$  nanowhiskers in air by the Raman laser beam irradiation. In this study, to understand the structural change of photopolymerized  $C_{60}$  nanowhiskers in the various atmospheres, Raman spectra of the  $C_{60}$  nanowhiskers which were irradiated by Raman laser beam were investigated in air, solution, vacuum, and inactive gas.

 $C_{60}$  nanowhiskers were synthesized by the liquid-liquid interfacial precipitation method [2, 3] using a toluene solution saturated with  $C_{60}$  (MTR Ltd. 99.5%) and isopropyl alcohol (IPA). The Raman spectra of  $C_{60}$  nanowhiskers were obtained by use of a green laser with a wavelength of 532 nm (JASCO, NRS-3100).

Fig. 1 shows the Raman spectra and the results of Lorentz curve fitting analyses for  $C_{60}$  nanowhiskers irradiated in air and IPA, where we define the peak of Raman spectrum around 1460 cm<sup>-1</sup> as  $A_g(2)$ ' and that around 1469 cm<sup>-1</sup> as  $A_g(2)$ . The position of  $A_g(2)$ ' peak measured in air showed more widely scattered values as compared with those of  $C_{60}$  nanowhiskers irradiated in IPA.



Fig. 1 Raman spectra (heavy lines) of  $C_{60}$  nanowhiskers measured in air (a) and in IPA (b), respectively. The results of Lorentz curve fitting analyses (thin lines) are also shown.

- A.M. Rao, Ping Zhou, Kai-An Wang, G.T. Hager, J.M. Holden, Ying Wang, W.-T. Lee, Xiang-Xin Bi, P.C. Eklund, D.S. Cornett, M.A. Duncan, I.J. Amster, Science, 259, 955 (1993).
- [2] K. Miyazawa, Y. Kuwasaki, A. Obayashi and M. Kuwabara, J. Mater. Res., 17, 83 (2002)
- [3] Fullerene Nanowhiskers, K. Miyazawa (Ed.) (Pan Stanford Publishing, 2011).

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#### New Functionalization of Endohedral Metallofullerene with Silylene

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A large number of researchers have investigated the chemical reactivity of endohedral metallofullerenes which has proven to be greatly different from that of empty fullerenes [1, 2]. As the fruits of many years of studies, exohedral chemical functionalization is widely recognized as an essential method for tuning the physical and chemical properties of endohedral metallofullerenes, which have the possibility to open up a new field for nanometerials science.

We have reported the derivatization of endohedral metallofullerens by the addition of active silicon compounds [3]. Introduction of electropositive silicon atoms onto the surface of fullerene has induced remarkable changes of fullerene characteristics. For instance, the silylated fullerene derivatives have more electronegative charge on the cage than the parent fullerenes. Moreover, we have demonstrated that the number of the silicon atoms on the fullerene surfaces plays an important role in the electronic properties and the movement of the encapsulated metal atoms.

In this context, it is fruitful to continue to study about silvlation which is useful as adjuster of the electrochemical properties of fullerenes. Herein we report the preparation and characterization of the first mono-silvlated endohedral metallofullerene with silvlene generated from thermolysis of 9,9-bis(2,6-diethylphenyl)-9-silabicyclo[6.1.0]nonane.

#### References

[1] Endofullerenes: A New Family of Carbon Clusters; Akasaka, T., Nagase, S., Eds.; Kluwer: Dordrecht, 2002.

[2] Chemistry of Nanocarbons; Akasaka, T., Wudl, F., Nagase, S., Eds.; Wiley: London, 2010.

[3] Yamada, M., Akasaka, T., Nagase, S. Acc. Chem. Res. 2010, 43, 92.

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## ESR spectra of La2@C80-C3N3Ph2 and La2@C80 anion

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The intra-molecular dynamics of endo-metal ions has been of great interest for dimetallofullerenes. Two isomers of  $La_2@C_{80}-C_3N_3Ph_2$  were synthesized and purified by Tsukuba group of the author. The major isomer of  $La_2@C_{80}-C_3N_3Ph_2$  exhibited the ESR spectrum at room temperature as shown in the left-hand side of Fig. 1. The well resolved hyperfine coupling structure can be observed only at room temperature in solution. The intra-molecular rotation of two La ions within C<sub>80</sub> cage reflects the result that two La nuclear spins were observed identical.

 $La_2@C_{80}$  anion radical produced by electrochemistry exhibited the well resolved ESR spectrum similar to those of  $La_2@C_{80}$ - $C_3N_3Ph_2$ . The spectrum measured at 80K in a frozen solution is shown in the right-hand side of Fig. 1. In this case, however, the temperature change of the spectrum can be followed from 3K to 180K, which can be consistently ascribed to the process of the rotation at various temperatures.



Fig.1 ESR spectra of La2@C80-C3N3Ph2 (left) and La2@C80 anion (right). Uppers are observed, lowers are simulated.

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#### Synthesis and Characterization of Li@C<sub>60</sub>(OH)<sub>n</sub>: Notable Behaviors Induced by External Hydroxyl Group

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Chemical modification and metal encapsulation of fullerenes endow them with some unique characteristic properties. We are interested in the ionicity of Li@C<sub>60</sub> [1] and the hydrophilicity of fullerenols (C<sub>60</sub>(OH)<sub>n</sub>) because their combined properties seem to play a role in new materials chemistry. In this study, we synthesized Li@C<sub>60</sub>(OH)<sub>n</sub> by means of hydroxylation of Li@C<sub>60</sub> with fuming sulfuric acid or hydrogen peroxide and investigated the effects of encapsulated metal ion on their physicochemical properties in comparison with those of the corresponding empty C<sub>60</sub>(OH)<sub>n</sub>.



The kinds two of differntly hydroxylated fullerenols  $Li(a)C_{60}(OH)_n$  (n  $\approx$ 18 and 32) were prepared and characterized by IR spectroscopy, elemental analysis as well as thermogravimetric analysis. Although essential difference was no observed in IR spectra between  $Li@C_{60}(OH)_n / C_{60}(OH)_n$  (Fig. 1, (a)/(b) or (c)/(d)), the former metal encapsulated fullerenol forms the small-sized particle (1.5 nm) in mixed solvent of DMSO/water (3/7 v/v) as compared with the latter metal-free fullerenol (ca. 5 nm). Other interesting properties will also be described in the presentation.



Figure 1. IR spectra of (a)  $Li@C_{60}(OH)_{18}$ , (b)  $C_{60}(OH)_{16}$ , (c)  $Li@C_{60}(OH)_{32}$ , and (d)  $C_{60}(OH)_{36}$ .

[1] Sawa, H.; Tobita, H. *et al.*, *Nature Chem.* 2010, *2*, 678-683.
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# High-throughput metal/semiconductor separation of single-wall carbon nanotubes using gel column chromatography

1P-9

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Single-wall carbon nanotubes (SWCNTs) are promising material for various applications such as high-speed electronic devices. For the electrical application, metallic (M) and semiconducting (S) SWCNTs have to be separated after the synthesis because of the difficulty controlling their electronic properties in the growth process. In our project, we are constructing a large scale M/S separation system for verification of scalability of the gel column chromatography methods developed in AIST [1, 2]. We reported that cost reduction

and high-throughput separation were possible by using a new agarose-based gel at the last symposium. In this presentation, we show recent progress of our development.

SWCNT dispersion in sodium dodecyl sulfate solution was prepared by sonication and ultracentrifugation. Approximately 500 ml of column (XK50/30, GE Healthcare) filled with the agarose-based gel (Figure, center) connected with a liquid chromatography system (ÄKTA explorer 100, GE Healthcare) and used for the M/S separation. About 12 mg of SWCNTs were separated into M- and S-SWCNTs in 90 min using this system (about 8.0 mg/h). For improvement of the throughput, we tried two approaches; one was a use of a high pressure-resistant column (Figure, left; HiScale50/20), the other was a scale-up using a bigger pilot-scale column (Figure, right; BPG100/500). Detailed methods and results will be discussed.



Figure Three columns filled up with new agarose-based gel.

#### **References:**

[1] T. Tanaka et al., *Phys. Status Solidi RRL* 2011, **5**, 301
[2] T. Tanaka et al., *Appl. Phys. Express* 2009, **2**, 125002
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## Analysis of CVD Conditions for Tuning Graphitic Layers and Fiber Diameter of Multi-Walled Carbon Nanocoil

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Multi-walled carbon nanocoils (MWCNCs) have been successfully grown using Sn/Fe catalysts supported on zeolite and MCM-41 by chemical vapor deposition (CVD) [1, 2]. In the field of nanoelectrochemical system (NEMS), it is essential to synthesize MWCNCs with smaller fiber diameter that is implicated to have a high crystallinity and hence leading to a high electrical conductivity. In this study, CVD synthesis conditions were investigated to grow MWCNC with smaller fiber diameter (less than 20 nm). Fe catalyst was supported by

mixing Y-type zeolite (catalyst support material) and iron acetate in an ethanol solution. The mixture was then calcined at 100°C for 24 h in a furnace. Sn was deposited onto surface of Fe-supported zeolite by vacuum evaporation. Sn/Fe/zeolite was placed at the center of a quartz-made reaction tube for CVD synthesis. The reaction temperature, flow rate ratio of  $C_2H_2/N_2$  and reaction pressure were 650-850°C, 0.01-0.10 and 5-760 Torr, respectively. In this study, the optimal CVD conditions were found to be as follows: reaction temperature: 700°C, flow rate



Fig. 1 TEM micrograph of MWCNC

ratio of  $C_2H_2/N_2$ : 0.02 and reaction pressure: 5 Torr. Fig. 1 shows TEM micrograph of MWCNC grown under this CVD condition. Reduction of fiber diameter of MWCNC was successfully achieved. The fiber diameter is ca. 5 nm either at helical part or tip part of the MWCNC. It is very interestingly found that graphitic layers of helical part and tip part of the MWCNC are different, which are 5-8 and 4 layers, respectively.

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[References] [1] M. Yokota, *et al.*: J. Nanosci. Nanotechnol., **11** (3), 2344 (2011).
 [2] S. L. Lim, *et al.*: Trans. MRS-J, accepted.

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#### Flame Synthesis of Single-Walled Carbon Nanotubes

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Single-walled carbon nanotubes (SWCNTs) expectly have various applications. But their expensiveness limits their applications and therefore their low-cost mass-production is strongly demanded. Carbon vapor deposition (CVD), operated typically at rather low temperatures  $\sim 1000$  °C to prevent soot generation, is advantageous for productivity but disadvantageous for crystallinity of the SWCNTs. Flame synthesis has enabled the mass-production of carbon black and fullerene through non-catalytic reactions, but is less applied to CNTs requiring catalysts [1]. In this research, we target at efficient flame synthesis of highly crystalline SWCNTs by forming catalyst particles at a high density and in a short time.

We utilized premixed flame to decompose  $Fe(C_5H_5)_2$  in milliseconds, and then mixed the exhaust gas with  $C_2H_2$  feedstock to grow SWCNTs (Figure 1). Products were collected by a membrane filter and analyzed by scanning electron microscopy (SEM) and Raman spectroscopy.

The fuel to oxygen ratio in the premixed flame is important in controlling the chemical state of Fe. The temperature after gas mixing  $(T_{mix})$ , which was estimated by thermodynamic simulation, is important in terms of Fe particles nucleation and SWCNT growth. And, the nozzle geometry is important for mixing. These factors were systematically studied.

The Raman spectra and the SEM images (Figure 2) show the formation of SWCNTs. At low  $T_{\text{mix}}$ , SWCNTs were contaminated with many catalyst particles. At high  $T_{\text{mix}}$ , SWCNTs were formed at a high yield but with soot. At  $T_{\text{mix}} = 1400 \sim 1500$  K, SWCNTs were formed at high yield with less catalyst and soot contamination. We are now trying to improve the catalyst efficiency to enhance SWCNT yield and reduce catalyst/soot contamination by shortening the time for heating of carbon source and that for cooling the exhaust gases.



Figure 2. Raman spectra and SEM images.

[1] Wilson Merchan-Merchan et al., Prog. Energy Combust. Sci. 36, 696 (2010).

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## Wrapping of single-wall carbon nanotubes with large tube diameters by fluorene-pyridine copolymer

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Selective extraction of specific single-wall carbon nanotubes (SWCNTs) from mixtures of various structured tubes is a crucial technique for their application to photo-electronic devices and production of SWCNT-based low-dimensional materials with specific molecular arrangements<sup>[1]</sup>. In particular, the polymer-wrapping method with rigid polymers such as polyfluorene and polycarbazole is highly effective in extracting specific semiconducting SWCNTs<sup>[2-4]</sup> However, except polymer-wrapping with for  $(F8BT)^{[5]}$ , poly(9.9-dioctylfluorene-*alt*-benzothiadiazole) **SWCNTs** extracted via polymer-wrapping are restricted to small-diameter tubes less than 1.2 nm. Moreover, although F8BT can selectively extract specific large-diameter SWCNTs<sup>[5]</sup> as well as small-diameter ones<sup>[2,3]</sup>, diameter distribution of the F8BT-extracted SWCNTs is rather wide: the diameters are distributed over the range of 1.28-1.53 nm. Rigid polymers to be used for selective extraction are desired to have abilities not only to selectively extract specific chirality (n,m)species, but also to narrow the diameter distribution.

In this work, using poly(9,9-dioctylfluorene-alt-pyridine) (PFOPy) as a dispersing agent, we succeed in selective extraction of specific large-diameter semiconducting SWCNTs, the diameter distribution of which is remarkably narrow. The absorption spectrum of PFOPy-extracted SWCNTs clearly exhibits the absence of metallic SWCNT absorption, implying that semiconducting **SWCNTs** are preferentially extracted through ultracentrifugation. In addition, spectroscopic analysis of the photoluminescence excitation (PLE) maps discloses not only the preference of PFOPy to specific (n,m) SWCNTs, but also the strains on SWCNTs induced by PFOPy. Figure 1 shows the PLE map of PFOPy-extracted SWCNTs. The PFOPy-extracted SWCNTs show distinctly intense and sharp emissions of (13,5) (14,3), and (10,8) SWCNTs, indicating the preference of PFOPy to specific semiconducting SWCNTs with large diameters near 1.3 nm: the extracted SWCNTs are 1.24–1.38 nm in diameter. This diameter distribution is narrower than that of F8BT-extracted large-diameter SWCNTs (1.28–1.53 nm). Moreover, the emission wavelength of PFOPy-wrapped (15,4) SWCNTs is blue-shifted from 1616 to 1608 nm in comparison with

emissions of **SWCNTs** wrapped bv poly(9,9-di-n-dodecylfluorene) (PFD)<sup>[5]</sup>. This blue-shifted emission is interpreted to be due the strain on (15,4) SWCNTs to by PFOPy-wrapping. In contrast, the emission wavelengths of other (n,m) species are red-shifted because of a difference in dielectric constant between PFOPy and PFD.

- [1] M. A. Loi et al., Adv. Mater. 22 (2010) 1.
- [2] A. Nish *et al.*, Nat. Nanotechnol. **2** (2007) 640.
- [3] F. Chen et al., Nano Lett. 7 (2007) 3013.
- [4] F. A. Lemasson et al., J. Am. Chem. Soc. 133 (2011) 652.
- [5] M. Tange et al., J. Am. Chem. Soc. 133 (2011) 11908.
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Fig. 1. PLE map of PFOPy-wrapped SWCNT solution. Emission peaks of PFOPy- and PFD-wrapped SWCNTs are indicated by closed and open circles, respectively.

# Effect of the catalyst geometry on the mechanical bending of carbon nanotube micropillar arrays

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The grown structure of carbon nanotubes (CNTs) micropillar changes depending on the patterned catalyst geometry. Height of the micropillar was varied by the total catalyst area.[1] Hart et al. observed the partial growth enhancement of CNTs around a closely patterned region.[2] It is necessary to unveil the mechanism in order to apply such structure for via wiring for large scale integrated circuit and thermal bumps. In this study, the effect of the patterned catalyst geometry on the bending of CNTs micropillars has been investigated.

The substrates of different diameters having constant (Fig.1 (a)) or sinusoidal spacing (Fig.1 (b)) were patterned with keeping the constant total catalyst area. Iron (1 nm) and alumina (10 nm) was utilized as catalyst and supporting layer, respectively. Reduction of the catalyst by heating (775 °C) under an H<sub>2</sub> atmosphere for 10 min was followed by introduction of C<sub>2</sub>H<sub>4</sub> precursor gas (25, 100 sccm) to the chemical vapor deposition tube furnace at constant temperature (775 °C).

In Fig. 2 the deflection of CNT micropillar was decreased with increasing pillar diameter. This trend is explained by newly proposed two models, namely bimetallic-strip [3] and geometric models where the difference of growth rate in catalyst area causes bending. Theoretically calculated curves are in accordance with the experimental results. In this study, we found two local bending effects (repulsive (Fig. 3(a)) and attractive), where the existence of CNT-growth enhancing field around each catalyst area was considered. When the spacing between catalyst circles is short enough, the fields are overlapped each other, and the growth rates are enhanced more. In Fig. 3(b), approximately 7% longer CNTs pillar grown at dense catalyst area than sparse area indicates an enhancement of CNTs growth. Thus, the CNTs length on the near-side to other catalyst areas is increased, leading to repulsive deflection.



[1] G. H. Jeong et al., Carbon 47 (2009) 696, [2] A. J. Hart et al., J. Phys. Chem. B,110 (2006) 8250, [3] Y. Clyne, Key Engineering Materials, 116 (1996) 307.

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#### Carbon nanotube synthesis by coalescence of heterocyclic compounds

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The inner space of carbon nanotubes (CNTs) offers a fascinating platform for material synthesis. It has been reported that organic compounds such as fullerenes within CNTs can be converted into single-wall CNTs (SWCNTs) by thermal coalescence. Recently, we have found that the chirality of such molecular-derived CNTs depends on the molecular structure and its initial mutual orientation [1-3]. So far, the coalescence reactions have been mainly investigated for the aromatic compounds including graphene-like framework. In contrast, there has been no study reported on the coalescence of organic molecules composed of non-graphene framework. The systematic understanding of coalescence reaction for such molecules may, therefore, provide us a new insight into the correlation between precursor molecules and final products.

In this presentation, we report the synthesis and characterization of SWCNTs formed through the coalescence of a heterocyclic compound, sexithiophene (6T, Fig.1a). 6T molecules were encapsulated into SWCNTs (Meijo-SO) and were converted into inner tubes by thermal annealing. These processes were monitored by using HRTEM observations (Fig. 1b,c) and Raman spectroscopy. The inner tubes were finally extracted from outer tubes by ultrasonication to measure a photoluminescence (PL) map. The PL map reveals the preferential growth of SWCNTs with a chiral index of (6,5) (Fig. 2). The result indicates that near-armchair SWCNTs are the most stable structure even in the reconstruction process of sulfur and carbon atoms in the confined inner space.

[1] Y.Miyata, et al., ACS Nano 4, 5807
(2010). [2] J.Zhang, et al., Nanoscale,
3,4190 (2011). [3] Y. Miyata, et al. The
41st Fullerenes-Nanotubes-Graphene
General Symposium.
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Fig.1 (a) Molecular structure of sexithiophene (6T). HRTEM images of (b) 6T@SWCNT and (c) DWCNT.

Fig.2 Photoluminescence map of SWCNTs formed from molecular coalescence of 6T.

### Hydrogen Effects on Chirality Distribution of Single-Walled Carbon Nanotube Grown from Various Kinds of Catalysts

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One dimensional single-walled carbon nanotubes (SWNTs) are potential materials for future nanoelectronics. Since the electronic and optical properties of SWNTs strongly depend on their diameter and chiral angle, the selective synthesis of SWNTs with desired chiralities is one of the major challenges in nanotube science and applications. Recently, we have demonstrated a narrow-chirality distributed growth of SWNTs from an Au catalyst [1]. Based on the systematic investigation, an appropriate  $H_2$  concentration is found to be critical for the chirality distribution control of SWNTs grown from the Au catalyst.

In order to understand the detailed effects of hydrogen on the narrow chirality distribution growth of SWNTs, we have also investigated the hydrogen effects with various kinds of catalysts such as Pt, Ag, and Cu as nonmagnetic catalysts, and Fe and Co as magnetic ones. The SWNTs growth is carried out with diffusion plasma CVD. Figure (a) shows Raman scattering spectra of SWNTs grown with Co catalyst. Intensity of radial breathing mode (RBM) around 200 cm<sup>-1</sup> (I<sub>200</sub>) is suppressed by introduction of hydrogen (Fig. (b)). This indicates the growth of large diameter SWNTs is suppressed by adding an appropriate amount of hydrogen, which is consist with the previous result with Au catalyst.



Fig. (a) Raman scattering spectra of SWNTs grown under the different hydrogen flow rates.

(b) Averaged  $I_{200}$  as a function of hydrogen flow rate.

[1] Z. Ghorannevis, T. Kato, T. Kaneko, and R. Hatakeyama, Journal of the American Chemical Society 132, 9570 (2010).

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#### Efficient Production of Nanostructured Carbon by Nickel Oxide **Nanoparticles**

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The outstanding electronic, mechanical and thermal properties of carbon nanotubes (CNTs) and graphene have stimulated widespread interest for fundamental research and applications. In spite of the efforts devoted to establish universal synthetic processes, precise control over the products characteristics is still lacking and often strongly correlated to a metal catalyst.

This work demonstrates the growth of vertically arranged CNTs on Si substrate by alcohol catalytic chemical vapor deposition (ACCVD). The catalyst nanoparticles (NPs) were synthesized by precipitation (NiO) or sol-gel method (Ni/NiO), and distributed on Si by spin or dip coating. Carbon nanostructures were characterized morphologically by scanning electron microscope (SEM) and structurally by Raman spectroscopy and XRD (composition and crystallinity of NPs, data not shown).

High yield growth of CNTs using both Ni/NiO and NiO NPs is achieved, as shown in Fig.1. The diameter of multi-wall CNTs is about 10-20 nm, and single-wall CNTs are also confirmed (Raman spectroscopy in Fig. 1 (right)), where the calculated diameter is 1.08 nm. Low temperature synthesis of CNTs, down to 400°C, is also achieved which emphasizes the excellent catalytic capability of the NiO NPs.

The NiO NPs have been tested for the graphitization of solid amorphous C (a-C) precursor (Fig. 2). Combining the deposition of thickness-controlled (5-25nm) C features and NiO NPs on a SiO<sub>2</sub> substrate with vacuum thermal annealing treatment at 975°C, obtained from different nanoparticles. (Left) Ni/NiO by the a-C is transformed into crystalline, as deduced from Raman signal (not shown). Depending on the relation between NP size and as-deposited a-C thickness, CNTs or nanographene can be obtained.

[1] C. Chiu et al., J. Nanomaterials 906204 (2010).

[2] C. Chiu et al., Diamond & Related Materials 18 355 (2009).

[3] S. Iijima, Nature 354 56 (1991).

[4] M. S. Dresselhaus et al., J. Physics Reports (2004).

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Fig. 1. SEM and Raman spectroscopy of CNTs ACCVD. (Right) NiO by ACCVD.



Fig. 2. (Left) CNTs popping out from the thin nanographene/graphite pattern. (Right) Adjusting deposited a-C thickness only Ni nanoparticles as inclusions on nanographene/graphite sheet are present.

# Synthesis and optical characterization of N-doped single-walled carbon nanotubes

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Single-walled carbon nanotubes (SWCNT) have attracted much attention for a next generation semiconductor material because SWCNTs show superior electrical and optical properties to existing materials. For this purpose, it is necessary to control their electrical properties by adding foreign atoms like in the silicon industry. However, techniques like doping foreign atoms into SWCNTs and characterization of doping levels are not well established yet [1,2]. Here, we report the synthesis of nitrogen (N)-doped SWCNT by chemical vapor deposition (CVD).

The samples were grown by CVD at 850°C for 15 min using ethanol as the carbon source. To introduce N atoms, pyrazine ( $C_4H_4N_2$ ) is mixed into ethanol. Raman scattering measurements were carried out at room temperature excited by 532 nm laser. Photoluminescence (PL) maps were also employed for characterization.

Figure 1 shows Raman spectra of radial breathing mode (RBM) region. From bottom to top, pristine, 0.5 wt%, 1.25 wt%, and 2.0 wt% samples are displayed. Intensity of the RBM band at 270 cm-1 is enhanced with increasing the concentrations of pyrazine. Typical PL maps are shown in Fig. 2. Vertical and horizontal axes stand for excitation and emission energies, respectively. Several bright spots are clearly observed in the maps. Analyzing PL data at the fixed excitation energy (1.92 eV), the relative PL intensity of (7, 6) to (7, 5) nanotubes is linearly decreased with the increase in pyrazine concentration. We infer that the decrease in the relative intensity is due to the doping N to the (7, 6) nanotube preferentially.

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[1] Indhira O. M et al. Nat. Mater. 7, 878-883(2008).

[2] Jessica C.D et al. ACS Nano, 4, 1696-1702 (2010).

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# Coherent phonon spectroscopy of RBM and RBLM phonons in carbon nanotubes and graphene nanoribbons

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We develop a microscopic theory for the generation and detection of coherent phonons in single wall carbon nanotubes (SWNTs) and graphene nanoribbons (GNRs) within a numerical extended tight binding model and analytical effective mass theory [1-3]. In coherent phonon (CP) spectroscopy, ultrafast (sub-10 fs) laser pulses generate electrons and holes in the conduction and valence bands of a SWNT or GNR. If the pulse duration is less than the phonon oscillation period (20-100 fs), the photogenerated carriers couple to the phonons through the deformation potential electron-phonon interaction and the lattice undergoes macroscopic CP oscillations. The CP amplitudes satisfy a driven oscillator equation (derived from the Heisenberg equation) with a driving function that depends on the electron-phonon interaction matrix elements and the photoexcited carrier distribution functions. Coherent phonons are detected using a delayed probe pulse (up to 4 ps) to measure the time dependent oscillations in the differential transmission. Taking the Fourier transform of the differential transmission with respect to probe delay time, we obtain the CP spectrum as a function of phonon frequency with peaks in the spectrum corresponding to excited coherent phonon modes. Interesting CP modes in SWNTs and GNRs are the so-called radial breathing mode (RBM) [1,2] and radial breathing like mode (RBLM) [3], with the frequency of 5-7 THz, respectively, in which the tube diameter and the ribbon width can initially expand or contract depending on their types and excitation energies [2,3]. For SWNTs and armchair GNRs, such expansion and contraction simply originate from the k-dependent electron-phonon interaction with respect to the graphene Dirac point. In the case of zigzag GNRs, the so-called edge states play an important role in the generation of coherent phonons so that the CP amplitudes do not depend on the ribbon size [3]. Further, we discuss the extension of the electron-phonon and electron-photon interactions in SWNTs to the exciton-phonon and exciton-photon interactions because the excitonic effects in SWNTs cannot be neglected.

- [1] G. D. Sanders et al., Phys. Rev. B 79, 205434 (2009).
- [2] A. R. T. Nugraha, G. D. Sanders, et al., Phys. Rev. B 84, 174302 (2011).
- [3] G. D. Sanders, A. R. T. Nugraha, R. Saito, C. J. Stanton, submitted to Phys. Rev. B (2012).

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# Visible fluorescence from ultrathin single-wall carbon nanotubes of chiral index (4, 3)

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Ultrathin single-wall carbon nanotubes (SWCNTs) with a diameter of less than 0.5 nm have different unique properties from those for larger-diameter SWCNTs. For example, the ultrathin SWCNTs are expected to show light emission in visible region because of their large bandgap. <sup>1)</sup> However, efficient synthesis of such ultrathin SWCNTs has not been achieved yet probably due to their structural instability. The lack of available bulk samples, therefore, still makes it difficult to investigate their unique physical properties.

In this presentation, we report the observation of visible fluorescence of ultrathin SWCNTs. The ultrathin SWCNTs have been obtained by extracting inner shells from double-wall carbon nanotubes.<sup>2)</sup> The extracted sample shows photoluminescence peaks at 701 and 721 nm under light excitation at 412 and 539 nm, respectively (Fig. 1b). These peaks can be assigned, respectively, to (4, 3) and (5, 3) SWCNTs from the comparison with the experimental Kataura-plot.<sup>1)</sup> The presence of these ultrathin tubes was also supported by TEM observation (Fig.1c). Our finding provides an important insight for basic physical properties and opto-electronics applications of ultrathin SWCNTs.



**Fig. 1.** (a) Schematic illustration of a (4, 3) SWCNT. (b) Contour map and (c) a TEM image of the separated sample.

1) R. Weisman et al., Nano Lett. 3, 1235 (2003).

2) Y. Miyata et al. ACSnano. 4, 5807 (2010).

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### Acoustic wave measurement of single-wall carbon nanotube dispersion by the transient grating method

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Photoacoustic and photothermal property of carbon nanotubes (CNTs) is one of applicable properties for contrast agents of imaging or photothermal therapy [1]. For these applications, the preparation technique of CNT suspension and photothermal efficiency in dispersed CNTs in solution affects the performance of agents. In this study, photothermal property of dispersed single-wall carbon nanotubes (SWCNTs) samples in aqueous solution was investigated by using the heterodyne transient grating mothod.

Transient responses induced by photoexcitation of SWCNTs in aqueous solution were observed by the heterodyne transient grating method [2]. This method provides the information about the change of physicochemical property caused by pumped light, and the change is detected through the change of refractive index of probe light. The pump light was the third harmonic of an Nd: YAG laser with a wavelength of 355 nm, and the probe light was He-Ne laser with a wavelength of 633 nm. The pump and the probe beams are impinged on a transmission grating that is placed in front of a sample. The grating spacing of a transmission grating was 60 µm. We mainly focused on acoustic grating on dispersed solution of SWCNTs obtained by transient grating and compared with the structure of SWCNTs such as diameter distribution and the electronic structure. To clarify the effect of diameter distribution and electronic structure against acoustic grating response, several types of SWCNTs which have different diameter distribution and electronic structure were used for this research. Enriched metallic and semiconducting SWCNTs were obtained by size exclusion column chromatography method written in previous paper [3]. The intensity of transient responses was scaled with the area fraction of resonant band in visible region of absorption spectra and fairly compared with different dispersion.

The transient responses of nanosecond are shown in Fig.1. The result indicates that the thermal expansion of water strongly depends on the diameter distribution of SWCNTs. The type of electronic structure of SWCNTs affects the expansion related to their efficiency of

absorbance in UV region, but it causes little difference of the intensity of the acoustic grating response. The structure and the quality of carbon SWCNTs affect the acoustic grating response and their photothermal properties.

- [1] Z. Liu et al., Nano Res. 2, 85 (2009).
- [2] M. Okuda and K. Katayama, *Chem. Phys. Lett.*443, 158 (2007).

[3] K. Moshammer *et al., Nano Res.* **2**, 599 (2009). Corresponding Author: S. Kuwahara Tel: +81-3-3817-1899, Fax: +81-3-3817-1913,

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Fig.1 Acoustic grating response of SWCNTs dispersion with different diameter of samples.

#### **Electronic Properties of Carbon Nanotubes under the Electric Field**

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In recent years, carbon nanotubes are attracting much attention due to its possible application for semiconductor electronic devices in the next generation. Indeed, it has been demonstrated that the individual semiconducting carbon nanotubes can work as field-effect transistors (FETs) in which nanotubes form hybrid structures with other conventional materials, such as insulating substrates and metal electrodes. In FETs, since the electric field is essential for operating and functionalizing the electronic devices, it is the necessity to understand the behavior of carbon nanotubes under the electric field. Therefore, we aim to theoretically investigate the electronic properties of carbon nanotubes under the electric field.

All calculations are performed by using the density functional theory. To express the exchange correlation potential between interacting electrons, we apply the local density approximation. We use the pseudopotential method with the ultrasoft scheme to describe the interaction between valence electrons and ions. The effective screening medium (ESM) method is applied to investigate the behavior of carbon nanotubes under the electric field in the framework of the first-principles calculations.

We applied the electric field on the capped armchair and zigzag nanotubes with 7 angstrom diameter in parallel direction to their axes as shown in Figs. 1(a) and 1(b), respectively. Under the external electric field, we investigate the electrostatic potential on each C atomic site to uncover how the electric field affects on the electronic properties of the carbon nanotubes. We find that the potential modulation strongly depends on the atomic site. The fact indicates that the electric field inside the nanotube is nonuniformly screened by the valence electrons on C atoms on the nanotubes (Fig. 2). The structural analyses unravel that this unusual screening is ascribed to the bond alternation in the carbon nanotubes.

Fig.1 Structural models of capped (a) armchair and (b) zigzag nanotubes under electric field.



Fig.2 Electrostatic potential in armchair carbon nanotubes.

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## The strong effect of the dispersion process on the conductivity of a SWNT-rubber composite

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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. Although various applications of CNT composites have been developed, application of CNTs to high conductivity composite rubbers is still limited. High conductivity CNT-rubber composites are in large potential demand for applications such as flexible electrodes and electromagnetic shields for communication modules, medical devices and airplanes. For developing high conductivity CNT-rubber composites for such practical use, improvement of dispersion techniques is needed. As a step for improving dispersion techniques, we have prepared SWNT-rubber composites utilizing various dispersion methods and investigated the relation between dispersion methods, dispersed SWNT structures and electrical conductivity of the composites.

Here we present electrical conductivities of SWNT-rubber composites prepared using various dispersion techniques. We categorized dispersion methods into three groups, i.e., rotating shear, linear shear, and mechanical hammering, and we chose several typical dispersion techniques from each of the three groups. SWNT-rubber composite prepared using High-pressure jet-mill and Nanomizer showed higher conductivity (Figure 1). SWNT treated by these two processes showed smaller particle size about 50 µm by laser diffraction measurement, and SEM observation showed these particles are composed of well-developed mesh structure of finely debundled SWNT, which is considered to be in favor of electrical path formation. The results indicate that SWNT dispersion methods for high conductivity composite rubber can be improved by applying strong rotating shear under high pressure.



Figure 1. Electrical conductivity of SWNT-fluorinated rubber composites prepared using various dispersion methods. Each composite contains 10 wt% of CNT. High pressure jet mill and Nanomizer were performed utilizing high pressure as high as 100 MPa and 200 MPa, respectively



# Electrical properties of carbon nanotube networks decorated with cobalt oxide

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We investigated electrical properties of single-walled carbon nanotube (SWCNT) networks decorated with cobalt oxide particles. It is known that carbon nanotubes (CNTs) have different electrical properties such as metal and semiconductor depending on their chiralities. Semiconducting CNTs are attractive materials in a field of electrical devices because they can substitute a traditional semiconducting material. However, it is common that metallic and semiconducting CNTs co-exist after the synthesis and metallic CNTs should be removed to utilize semiconducting characteristics. In the mixture of metallic and semiconducting CNTs, doping is a good way to change the electrical property of CNTs into p-type [1] or n-type one [2, 3].

In this study, SWCNTs on Si substrate were decorated with cobalt oxide to enhance p-type electrical characteristics. First, SWCNT networks were prepared between Pt/Pd electrodes on Si substrate as shown in Fig. 1. Then, a solution containing cobalt precursor was prepared by dissolving  $Co(NO_3)_2 \cdot 6H_2O$  in ethanol and Si substrates with SWCNT networks were dipped for 1 hr, 2 hr, and 4 hr in the solution. And, the samples were heated at 300 °C under Ar atmosphere to deposit cobalt oxide on the wall of SWCNTs as shown in Fig. 2. SWCNT field-effect transistors (FETs) showed p-type electrical characteristics and on/off ratio increased in proportion to dipping time.



Fig.1 Structure of cobalt oxide-decorated SWCNT FETs

Fig.2 Atomic force microscope image of cobalt oxide-decorated SWCNT networks between electrodes

[1] D. Kang, N. Park, J.-H. Ko, E. Bae, and W. Park, Nanotechnology, 16, 1048–1052 (2005).
[2] B. H. Kim, T. H. Park, S. J. Baek, D. S. Lee, J. S. Park, J. S. Kim, and Y. W. Park, J. Appl. Phys., 103, 096103 (2008).
[3] V. Derycke, R. Martel, J. Appenzeller, and Ph. Avouris, Nano Lett., 1(9), 453–456 (2001).
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### High-Performance and Ultra-Flexible Single-Walled Carbon-Nanotube Film Transistors

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The recent technique for the separation of metallic and semiconducting SWCNTs opened a new route to high-performance SWCNT TFTs without the effect of metallic nanotubes. However, the trade-off behavior between carrier mobility and on/off ratio is still a big open question. Instead of present interpretation, in which the origin of this phenomenon is believed as forming pathways of residual m-SWCNT, we focused on the metallization of s-SWCNT by unintentional doping from ambient condition. If this is the case, we can recover semiconducting property through carrier de-doping. For this purpose, we applied electrochemical de-doping to s-SWCNT mat using electrochemical transistor (ECT). As the results, we observed direct evidences and found clear answer for the longstanding puzzle. Based on this understanding, we realized very high-performance transistors with mobility of more than 30-50 cm<sup>2</sup>/Vs and on/off ratio of  $10^4$ - $10^5$  using one of the solid electrolytes, ion gel. In addition, we fabricated ion-gel SWCNT ECT on flexible substrates and investigated the flexibility of these devices.

On SiO<sub>2</sub>/Si substrates, the traditional back-gate type transistor based on s-SWCNT mat reveals metallic behavior (gray line, Fig. 1). However, SWCNT ECT, prepared by the same s-SWCNT mat, shows excellent on/off ratio of  $10^4$ - $10^5$  (black line, Fig. 1), indicating that m-SWCNT is not the origin of metallic behavior. We measured capacitance of s-SWCNT mat and, finally, obtained extremely high mobility (~ 50  $\text{cm}^2/\text{Vs}$ ). In addition, we have tested bending durability of device on flexible substrates up to bending angle of 180 degree. As shown in Fig. 2, during the bending test, both on- and off-current of SWCNT ECT was almost constant, and transistor kept on/off ratio of  $10^3$ . Under the angle of 180 degree, the curvature radius of SWCNT film was 270 um. This curvature radius of 270 µm is smaller than that of recent minimum champion record in organic transistors μm). These results obviously (300 show the high-performance and ultra-high flexibility of SWCNT transistors and open the route to bendable electronics based on SWCNT thick film and ion gel.



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## Advantages of the Use of CNT as Fuel Cell Carbon Supporting Material Studied by Impedance Spectroscopy

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Fuel cell is key technology to convert hydrogen energy into electric power quite efficiently. Especially, polymer electrolyte fuel cell (PEFC) is promising candidate for the energy sorse of car, portable electronic device, and house. Improvement of the PEFC performance is the one of the main issue for the commercialization of the device. Carbon nanotubes (CNTs) is emerged as a alternative carbon supporting materials from carbon black (CB) due to their high electron conductivity, excellent electrochemical durability and fibrous structure. In this study, we investigate the effects of the CNTs for carbon suporting through the comparison of CB- and CNT-based PEFC. Up to date, systematic studies for this comparison have not been caried our yet since the preparation of the CNT-based electrocatalyst without maintaining the original structure was rather difficult.

We have reported the novel approach for the use of CNT as a electrocatalyst. CNT was initially wrapped by polybenzimidazole (PBI) and the platinum nanoparticle (Pt) was loaded on the PBI-wrapped CNT, where the PBI exfoliated the CNT bundle and as a glue for the Pt loading on CNT to fabricate the CNT/PBI/Pt composite [1-3]. PEFC fabricated using CNT/PBI/Pt was evaluated and showed excellent performance, in which the PBI in the electrocatalyst served as a electrolyte to convey proton in the cell [4]. Herein, we fabricated CB-based electrocatalyst in similar fashin and fabricated PEFC cell to compare the difference of the performance.

Fig. 1 showed the power density curves for CB-based (Fig. 1a) and CNT-based (Fig. 1b) PEFC measured at the three different temperatures. At each temperature, the CNT-based PEFC showed higher power density and the larger decreasing of the PEFC performance by decreasing of the operation temperature were observed. Impedance analysis for both cells were performed at the region of low current density. Large increasing of the due to the greater increasing of the resistivity for the proton conduction at CB-based PEFC was observed. Above results clealy indicates the proton pathway is smoothly connected in the case of CNT-based PEFC [5].



CB-based (top) and CNT-based (bottom) PEFC measured at 12 0 °C (bold solid), 100 °C (thin solid) and 80 °C (dotted line).

[1] Adv. Funct. Mater. 18, 1776-1782 (2008). [2] Small 5, 735-740 (2009). [3] Carbon 47, 3227-3232 (2009). [4] J. Mater. Chem. 21, 1187-1190 (2011). [5] Unpublished data

#### Toward graphene and single-walled carbon nanotube composite devices

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Single-walled carbon nanotubes (SWNTs) and graphene are remarkable new functional materials, leading the frontier nanoscience and nanotechnology in the next century. They are also ideal candidates for building blocks of future electronic nanodevices due to their unique electronic properties and exceptional flexibility. Tans *et al.* and Novolselov *et al.* have reported the preparation of SWNTs and graphene and observed the electric field effect in their sample [1, 2]. Here, we report the simultaneous synthesis of graphene connecting two SWNT regions, forming a transistor device morphology.

Figures 1(a) and (b) show the morphology as observed by scanning electron microscopy (SEM). The fabrication process is as follows. First, we used a standard optical photolithography process to generate patterns at desired locations on a Ni substrate (thickness ~25 um). Al (15 nm) and Co (0.2 nm) were deposited by sputtering. Next, SWNTs and graphene were synthesized simultaneously by alcohol chemical vapor deposition (ACCVD) at 850°C for 3 min [3]. The SWNTs will act as the source/drain, while the graphene acts as the channel. The graphene monolayer was identified by optical contrast in an optical microscope and subsequently confirmed by Raman spectroscopy. The SWNTs/graphene was transferred from the Ni substrate to poly(vinyl alcohol) (PVA). Figs 1(c) and (d) show Raman spectra ( $\lambda = 488$  nm) obtained from the corresponding electrode and channel locations indicated in Fig. 1(b). All measurements were performed at room temperature (293 K).



Fig.1 (a), (b) SEM image of the pattered SWNT/graphene regions; (c) typical Raman spectrum obtained from the SWNT region; (d) typical Raman spectrum obtained from the graphene region.

[1] S. J. Tans et al. Nature 393, 49 (1998).

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

[3] S. Maruyama *et al.* Chem. Phys. Lett. **360**, 229 (2002).

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### Design and preparation of a fuel cell electrocatalyst composed carbon nanotube-supported sulfonated polyimide and Pt

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Hybrid metal nanoparticles and CNTs are attractive materials especially as fuel cell electrocatalyst due to the large surface area, remarkable electric conductivity and excellent electrochemical durability of CNTs. In this study, we used sulfonate polv [(2,2-benzidinedisulfonicacid)-alt(1,4,5,8-naphthalenetetracarboxylicdianhydride)](SPI;Fig.1) as a polymeric anchors to load Pt nanoparticles on the surface of multi-walled carbon nanotubes(MWNTs). Sulfonated polyimides that function as proton conductive polyelectrolytes are considered to be as promising polyelectrolytes for polymer electrolyte fuel cell (PEFC). The use of polyelectrolyte as an anchoring unit is advantages in view of the practical application for the PEFC since the ion are required to move smoothly in the electrocatalyst layer and the electrolyte in necessary in the layer. The anchoring SPI effectively worked as a proton conductive path in the electocatalyst. Cyclic voltammetry measurements have revealed that the Pt nanoparticles deposited on the SPI-wrapped MWNTs have a high electrochemically active surface area. These results provide useful information for the design and fabrication of triple phase interface structures of fuel cell electrode catalysts with high efficient performance.



Fig.1 Illustration of a CNT/SPI/Pt.

- [1] Okamoto, Fujigaya, Nakashima, Adv. Funct. Mater. 18,1776 (2008).
- [2] Okamoto, Fujigaya, Nakashima, Small. 5, 735 (2009).
- [3] Fujigaya, Okamoto, Nakashima, Carbon 47, 3227-3232 (2009).

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## Structure Control of Hybrid Nanocarbon Materials based on Carbon Nanotubes and Carbon Nanowalls

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Carbon nanotubes (CNTs) have many superior properties and have attracted much attention, especially in the field of electronics such as field effect transistor (FETs). Carbon nanowalls (CNWs) are the nanocarbon materials consisting of nano scale graphene sheets. Vertically standing CNWs with high surface-to-volume ratio serve as an ideal catalyst support material for fuel cells and gas detectors. Noticeably, however, there are few works focusing on the hybrid of such nanocarbon materials, and a successful fabrication of hybrid materials with CNTs and CNWs has not been realized so far. A helicon discharge is known as a powerful method to generate high density plasmas under a low pressure condition [1]. Since neutral gas species are highly decomposed in the helicon plasma, it is possible to produce high quality nanocarbon materials by helicon plasma chemical vapor deposition (CVD). Based on this background, we attempt to fabricate a novel hybrid nanocarbon material with CNTs and CNWs (CNWs/CNTs) by helicon plasma CVD. Produced materials are characterized by scanning electron microscopy (SEM). It is revealed that there are no any CNWs on a SiO<sub>2</sub> surface after the helicon plasma CVD, whereas CNWs are grown on the surface of SWNTs. This indicates that CNTs enhance the nucleation of CNWs growth. Furthermore, it is found that the alignment of CNWs against to CNT can be controlled by adjusting ion energy  $(E_i)$ coming to the substrate during the CNWs growth. Thus, CNWs uniformly align with an increase in  $E_i$  (Fig. 1).



Figure 1: SEM images of CNWs/MWNTs. (a) $E_i = 60 \text{ eV}$ , (b) $E_i = 110 \text{ eV}$ , (c) $E_i = 130 \text{ eV}$ .

[1] G. Sato, W. Oohara, and R. Hatakeyama: Appl. Phys. Lett. 85 (2004) 18.
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#### Direct spinning and electrical resistivity of CNT yarns manufactured through eDIPS method

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Macroscopic structure-controlled assemblies of carbon nanotubes (CNTs) that utilize and expand their excellent yet microscopic properties including high mechanical strength and high electrical and thermal conductivity are desired for a wide range of applications. In particular, the CNT yarns would be useful as conductive wires for an applied technology including electronic devices which employ fine and flexible interconnections with the high conductivity. Considerable researches regarding the continuous spinning system to produce CNT yarns have been performed [1-4]. These researches have suggested that, besides a microscopic structure of CNTs (length, crystalinity, and so on), the orientation and interfacial controls of CNTs in their yarns significantly affect the electrical properties [5-7].

In this study, we have continuously synthesized CNTs with the diameter of 2-3 nm [8] by the enhanced direct injection pyrolytic synthesis (eDIPS) method [9] and directly spun them into yarns. The eDIPS method affords the production of high quality CNT of which highly controlled diameter. CNTs were synthesized by using toluene and methane as the primary and the secondary carbon sources, respectively. The CNT sock getting out of the reactor was introduced into a water bath with a reel consecutively in order to shrink and wind up the yarn. The CNT yarns were dried up and further compressed. The structural characterization of CNT yarns performed by SEM observation clearly showed that a set of process afforded uniformly-sized CNT yarns with rectangle cross-section with the width and height of ca. 170  $\times$  15 µm respectively. In addition, the partial orientation of CNTs in the yarn was also observed. The electrical resistivity evaluated by four-terminal method proved the electrical resistivity of CNT yarns in the order of 10<sup>-6</sup> Ωm along the long axis of yarns.

- [1] YL. Li et. al. Science, 304, 276 (2004)
- [2] XH. Zhong, Adv Mater. 22, 692 (2010)
- [3] B. Vigolo et. al. Science, 290, 1331 (2000)
- [4] M. Zhang et. al. Science, 306, 1358 (2004)
- [5] Q. Li et. al. Adv. Mater. 19, 3358 (2007)
- [6] K. Liu et. al. Nano Lett. 8, 700 (2008)
- [7] M. Miao Carbon, 49, 3755 (2011)
- [8] K. Kobayashi et. al. 2-11, The 41st Fullerenes-Nanotubes-Graphene General Symposium

[9] T. Saito et al., J. Nanosci. Nanotechnol., 8, 6153 (2008).

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#### Various mixtures of phospholipids for dispersing carbon nanotubes

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Phospholipids are bio-compatible compounds available with wide diversity in chemical

structures. Some of them self-organize to form vesicles in water. It has been known that, although common phospholipids such lecithin as (2C16-choline, see the right scheme for symbols) do not disperse single-walled carbon nanotubes (SWCNTs) in water, a phospholipid derivatized with polyethyleneglycol (2C18-PEG) disperses them well. Previously, we have reported that, by mixing a very small amount of 2C18-PEG to lecithin, the mixed phospholipid is able to disperse SWCNTs.





It is of great interest to find out if this mixing method applies to other kinds of phospholipids and to clarify any differences in their dispersing properties for understanding the dispersing mechanism. In this study, we report dispersing characteristics of SWCNTs by mixtures of 2C18-PEG with various kinds of phospholipids (changing n and X in 2Cn-X).

The cases of 2C18-PEG mixed with 2C16-choline and 2C18-choline are shown in the graphs. The critical dispersion concentration, the minimum concentration of 2C18-PEG at which SWCNT starts to disperse, are nearly independent of the alkyl chain length of choline lipids. In contrast, the maximum dispersed amount differs nearly 4 times. The results of systematic study in alkyl chain length and other head groups will be reported.



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## Electronic Structures of Carbon Nanotube Encapsulating Double-Decker Coronene Polymers

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Nano-meter scale space inside the carbon nanotube can accommodate foreign atoms or molecules those form unusual conformations. It is well known that the conformation for nanometer scale and low-dimensional materials plays crucial role to determine the electronic properties of resultant materials. For instance, the encapsulated  $C_{60}$  molecules form one-dimensional chain inside carbon nanotubes and they can easily transform into carbon nano-capsules via polymeric chains of  $C_{60}$ . As is shown in the previous works, electronic structures of such polymeric  $C_{60}$  chains and nano-capsules are totally different from that of the  $C_{60}$  solid with face-centered cubic structure. Recently, the encapsulation of coronene molecules into carbon nanotubes has been reported and, in some cases, the encapsulated coronene molecules coalesce with its adjacent forming coronene oligomers. Thus, in the work, we investigate the energetics and electronic structure of coronene polymers inside carbon nanotube by performing the first-principles total-energy calculations in the framework of the density functional theory (DFT).

Our DFT calculations show that the encapsulation reaction of double-decker coronene-polymers is exothermic for the nanotubes whose diameter is thicker than about 1.4 nm. The largest energy gain upon the encapsulation is about 1.5 eV per coronene molecule. We also found that the encapsulation energy strongly depends on the mutual arrangement between polymer chains. The electronic structure of the carbon nanotubes encapsulating double-decker coronene-polymer exhibits unusual properties. The hybrid systems are ranging from a metal to a semiconductor depending on the mutual stacking arrangement of encapsulated coronene polymers, although an isolated coronene polymer is a semiconductor with the energy gap of 0.7 eV. This unusual electronic structure is ascribed to the substantial interaction among the electron-states of each constituent.

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# <sup>13</sup>C NMR and x-ray diffraction studies of transformation process of C<sub>60</sub> fullerene peapods into double-walled carbon nanotubes

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Single-walled carbon nanotubes (SWCNTs) encapsulate many kinds of materials in their inner hollow cavities with a typical diameter of 1 nm. SWCNTs filled with fullerenes, so-called "peapods" have attracted considerable attention due to their peculiar structural and electronic properties. It is well known that fullerenes peapods are transformed into double-walled carbon nanotubes by high temperature annealing. However, the formation mechanism of peapod-derived DWCNTs is not yet understood. We have studied the growth process of inner CNTs from  $C_{60}$  fullerenes with using <sup>13</sup>C NMR and x-ray diffraction techniques. Fig. 1 shows the <sup>13</sup>C NMR spectral evolution as a function of annealing temperature and of the processing time. The observed spectra exhibit a narrow line (around 100 ppm) originating from encapsulated C<sub>60</sub> molecules superimposed on a broad powder pattern arising from inner and outer CNTs. The narrow line decreases gradually in intensity with increasing annealing time. The spectrum for the sample annealed for 14 hours at 1200°C shows only a broad powder pattern line shape typical for  $sp^2$  hybridized carbon. These results indicate encapsulated C<sub>60</sub> molecules coalesce into inner CNTs. The x-ray diffraction patterns in Fig. 2 also suggest the growth of inner CNTs by high temperature annealing. The growth process of inner CNTs from C<sub>60</sub> fullerenes will be discussed based on the NMR and x-ray diffraction results.





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#### SGM investigation of graphene nano structure

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Nano-structured graphene such as the graphene point contact is one of the most interesting systems in view of a study on the effect of potential barrier of the edge region of the sample and the carrier puddling at Dirac point on the transport properties of graphene. Scanning Gate Microscopy (SGM) is a powerful tool to investigate the effect of the local electronic structure on the transport properties [1]. In SGM, the effect of the local electrostatic modulation on the transport is obtained as the 2D conductance mapping as a function of the position of the scanning gate. In this study, the SGM instrument able to operate under UHV, at low temperature down to 2 K, in the magnetic field up to 8 T, is developed based on existing LT-STM system as schematically shown in Fig.1. Graphene point contact structure is characterized toward SGM investigation on graphene.

The point contact structure of few layer graphene was fabricated by annealing of SiC at  $1750 \,^{\circ}$ C and following photolithography and oxygen plasma etching processes, where the influence of the local potential by the scanning gate significantly affects on the electron scattering at a narrow bridging region between two electrodes. To compare the behavior of carriers in graphene with those in ordinary metals, we employed the Au point contact device on SiC as reference. SGM measurement was performed in lift-up manner, where tip went over 10 nm above the height mode scanned trajectory.

The point contact structure of graphene and Au having 700 nm channel width and 40 nm height was successfully fabricated as shown Fig. 2 a). SGM image of Au point contact showed no variation in the conductance, being consistent with the short mean free path and the higher Fermi energy of Au electron system.



Fig. 1 Schematic diagram for SGM measurement



Fig. 2 a) Optical microscope image of Au point contactb) STM height image of square region of a)

[1] M. A. Topinka, et al. SCIENCE 289, 2323 (2000)

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#### Covalent attachment of pyrene to graphene oxide

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Graphite oxide (hereafter GO) is easily exfoliated in polar solvents and thin film is easily obtained from the resulting dispersion. The reduction of GO thin film provides transparent and conducting electrode, however, the sheet resistance of the film with high transparency is still large because of the low conduction of electrons through the boundary between the reduced GO sheets [1]. In this study, in order to achieve higher affinity between GO sheets, they are covalently decorated with pyrene moiety.

GO was prepared by Hummers method from natural graphite powder with particle size of 57-74  $\mu$ m. It was reacted with 1-aminopyrene (abbreviated as Py; 1-50 mM) in dimethylformamide for 1-4 days. As a catalyst, 1-ethyl-3-(3-dimethylaminopropyl) carbodiimide hydrochloride (EDC) was added. N-hexadecylamine molecules were intercalated into the resulting samples and they were dispersed in chloroform. The Py content was determined from the absorption at 349 nm observed for the dispersion.

Fig.1 shows the X-ray diffraction patterns of GO reacted with Py under various reaction conditions. The diffraction peak at  $2\theta$ =11.8° due to GO shifted to lower angles with increasing in the reaction time or concentration of Py, and reached at  $2\theta$ =6.9°. The shift of diffraction peak was very small when only Py or EDC was added to the reaction system. The absorption peak ascribed to amide groups appeared in IR spectra of the Py attached samples and at the same time those of oxygen functional groups became weaker. These results indicate that Py moieties were covalently introduced not only to the edge of the GO sheets but also on

the layer surface of GO. Moreover, GO layer was considerably reduced, which was supported by the reduced intensity of the peak at 286 eV due to carbon atoms bonded to oxygen in XPS data for the samples reacted with Py. The interlayer spacing of the Py attached GO increased after intercalation of n-hexadecylamine and the resulting materials were well dispersed in chloroform. In UV spectra of the dispersions, the peaks at 244, 281 and 349 nm due to Py were observed and the content of Py reached 27 meq/100g of GO.

[1] Y. Matsuo, K. Iwasa, Y. Sugie, A. Mineshige and H. Usami, *Carbon*, **48**, 4011-4014 (2010)

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Fig.1 X-ray diffraction patterns of GO after reaction with Py under various reaction conditions.

#### Charging sites on graphene-FET synthesized from solid carbon source

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Kelvin force microcopies (KFM) are widely used to investigate electronic devices such as field effect transistors (FET). Electric potential distribution in graphene FETs are very crucial to understand the basic device properties. Especially, charge trapped in contaminations attached during device fabrication is strongly correlated to the field effect doping of charge carriers, electron and holes. Here, we investigate the electric potential distribution of graphene FETs using KFM technique.

Graphene FETs on SiO<sub>2</sub>/Si examined in this study were fabricated through a well established transfer technique of graphenes using a polymer film and a conventional photolithography technique, where the graphene was grown by solid phase CVD method using a Cu catalyst and polymethylmethacrylate as solid source of carbon. Grown tri-layer graphene was used as channel of FETs. Figure 1(a) shows the transfer characteristic FET. Figure 1(b) shows a topographic image of FET simultaneously obtained from KFM at the pressure of ~10<sup>-5</sup> Pa. The field effect mobility was estimated to be ~1000 cm<sup>2</sup>/Vs from the potential slope of the graphene channel measured from KFM. Thus, the graphene synthesized from solid source as well as that from gas source shows a good electronic property. Figure 1(c) shows the electric potential distribution related to a boxed region shown in Fig. 1(b) with

the presence of some contaminants, where the source-drain voltage and back gate voltage are fixed at 1 and -1 V, respectively. As shown in Fig. 1(c), contaminants are negatively charged, where the potential profile for A-B is plotted in Fig. 1(d). This implies that these negatively charged sites are one of origins of the positive shift of Dirac point shown in Fig. 1(a). Thus, we found that the negatively charged contaminants on graphene channel affect the hole doping in graphene-FETs even in the graphene synthesized from the solid source.

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Fig.1 (a) Transfer characteristic of graphene-FET,(b) AFM image, (c) KFM image, (d) Electric potential between A and B

### Synthesis of functionalized graphene nanoribbon by thermal polymerization of perylene bisimide derivatives

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Graphene nanoribbon (GNR) is predicted one of the most remarkable materials for the fabrication of nanoscale electronic devices. Thus, particular attention has been paid to prepare graphene into a GNR, where the opening of an energy gap in determining GNR optical properties was expected because of the confinement and edge effects.[1,2] Recently, preparation of atomically precise zigzag GNR was reported.[3] Acene type GNR has not been synthesized from small molecules.

We previously demonstrated a single-molecular processing technique using electrochemistry, termed 'electrochemical epitaxial polymerization'.[4,5] We synthesized 2D thiophene polymer by electrochemical epitaxial polymerization and thermal conversion.[6] This research, we examined build-up synthesis of functionalized GNR 2 by using the perylene bisimide derivative 1 as a monomer. We investigated synthesis of polymer on substrate surface. Thin film of 1 on substrate was prepared by vacuum deposition technique. Thus prepared film was thermally treated using an electric furnace. The materials prepared by thermal treatment were evaluated by Raman spectroscopy, UV-vis spectroscopy, etc.



Fig. 1. Polymerization of monomer 1.

- [1] V. Barone, O. Hod, G. E. Scuseria. Nano Lett. 6, 2748 (2006).
- [2] X. I. Li, X. Wang, L. Zhang, S. Lee, H. Dai. Science **319**, 1229 (2008).
- [3] T. Nakae, S. Mizobuchi, M. Yano, T. Ukai, H. Sato, T. Shinmei, T. Inoue, T. Irifune, H. Sakaguchi. Chem. Lett. in press.
- [4] H. Sakaguchi, H. Matsumura, H. Gong Nat. Mater. 3, 551 (2004).
- [5] H. Sakaguchi, H. Matsumura, H. Gong, A. M. Abouelwafa. Science 310, 1002 (2005).
- [6] Jining Cai, P Ruffieux, R. Jaafar, M. Bieri, T. Braun, S. Blankenburg, M. Muoth, A. Seitsone, M. Saleh, X. Feng, K. Müllen, R. Fasel. Nature 466, 470 (2010).
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## Reactions of Graphene and Metal Nanoparticles at High Temperature — Metal-Catalyzed Anisotropic Etching and Carbon Nanofiber Growth—

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Graphene, a two-dimensional sheet of carbon hexagons, can be grown on metal catalyst surface by chemical vapor deposition (CVD). On the other hand, annealing a graphene film supporting metal nanoparticles in  $H_2$  atmosphere induces the reverse etching reaction ( $C_{graphene} + 2H_2 \rightarrow CH_4 \uparrow$ ). It was reported that Fe and Ni nanoparticles can induce this

etching reaction for exfoliated graphene and it preferentially occurs along specific crystallographic orientations (mainly, zigzag direction) of graphene, as



**Fig. 1** Schematic of metal-catalyzed anisotropic etching of graphene.

shown in Fig. 1 [1-4]. This metal-catalyzed etching can be applied to the graphene engineering including the fabrication of graphene nanoribbons with defined edges.

Here, we report systematic study of the graphene-nanoparticle reactions at high temperature. We studied various metal nanoparticles, such as Ni, Mo, Pt, and Au, and found that all these metals show the anisotropic etching for few-layer exfoliated graphene. The etching yield increased with increasing the annealing temperature; high etchig density was observed at 1000 °C (see Fig. 2a), while a few etched lines were observed at 900 °C. Also, the width of etched lines became wider with increasing the annealing temperature, reflecting the increase of the metal nanoparticle size. Interestingly at high temperature, 1100 °C, growth of carbon nanofibers was observed instead of anisotropic etching (Fig. 2b,c).

In the presentation, we also show the result of the metal-catalyzed etching for our high-quality CVD-grown graphene with well-defined hexagon orientation [5-7]. Our recent attempt to fabricate graphene nanoribbons by anisotropic etching will also be demonstrated.



**Fig. 2** SEM images of exfoliated graphene after annealing at 1000 °C (a) and 1100 °C (b) in the presence of Ni nanoparticles. (c) TEM image of carbon nanofibers indicated in (b).

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**References:** [1] S. Datta, *Nano Lett.*, **8**, 1912 (2008). [2] L. C. Compos, *Nano Lett.*, **9**, 2600 (2009). [3] L. Ci, *Adv. Mater.*, **21**, 1 (2009). [4] T. Tsukamoto, *J. Phys. Chem. C*, **115**, 8580 (2011). [5] B. Hu, *Carbon*, **50**, 57 (2012). [6] Y. Ogawa, *J. Phys. Chem. Lett.*, **3**, 219 (2012). [7] C. M. Orofeo, *Carbon*, in press.

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#### Mechanism for Transition Metal-Catalytic Renovation of Defective Graphene

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Stone-Wales (SW) defect, composed of pentagon-heptagon pairs, is regarded as the most valuable reconstruction fragment because it can alter the electronic, mechanical, transport and magnetic properties of a graphene sheet.<sup>1-2</sup> However, the alternate properties caused by defects are sometimes unfavorable to applications of graphene in hyperfine nanodevices. Consequently, an important question is how to restore SW defects in graphene to obtain a pure periodic structure including only hexagons. In the present work, a novel metal-participating rearrangement mechanism of graphene is elucidated via density functional calculations. Results show that the barrier for the elimination of Stone-Wales defect can be decreased by the adsorbed transition metal atoms (Cu, Ni, Fe, Cr, Mo, and W). Especially, the tungsten atom can indeed lower the energy barrier markedly.

The reaction pathway for the W-catalyzed Stone-Wales transformation is exhibited in Scheme 1. It is found that the reconstruction with metal catalysis involves not only the migration of a  $C_2$  unit but also the movement of metal atom and carbon dimer perpendicular to the graphene plane. The activation barrier from the defective side is 2.86 eV, which is rather smaller than that of the Stone-Wales reaction without catalysis in graphene (more than 6 eV). Based on the transition state theory (TST), we consider that 1000 K is a proper temperature to yield the pure nanographene, at which the pre-existing defect might be restored rapidly and by which 5-7 pairs can hardly be regenerated. Such a conclusion might be of great importance for the fabrication of perfect nanographene in the laboratory by controlling the reaction temperature.



Scheme 1 Reaction pathway for the W-catalyzed Stone-Wales transformation in top and side views.

References:

- 1. Carlsson, J. M.; Scheffler, M. Phys. Rev. Lett. 2006, 96, 046806.
- 2. Boukhvalov, D. W.; Katsnelson, M. I. Nano Lett. 2008, 8, 4373.

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## Nitrogen-doped carbon nanosheets and their electrochemical applications

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Since the discovery of carbon nanotube and graphene, carbon-based nanomaterials are currently at the forefront of materials research because they can be used in many fields of electronics and biosensors due to their unique physical and chemical properties. Furthermore, theoretical and experimental investigations have shown that nitrogen doping in those carbon nanomaterials can tailor their electronic properties. Carbon Nan sheets (CNSs, also named as carbon nanowalls, graphene nanoflakes et al), one of carbon-base nanomaterials and consist of few layers of graphene, have also have attracted great attention because of their excellent properties and promising applications. Takeuchi *et al* reported that the electrical properties of CNSs can be adjusted by nitrogen addition in  $C_2F_6/H_2$  system using plasma-enhanced chemical vapor deposition [1], and also exhibited that the electrical structure and morphology of CNSs can be controlled by nitrogen addition during the synthesis of CNSs or by post-treatment of N<sub>2</sub> plasma. Both electrical structure and morphology of CNSs might also play very important role in the electrochemical properties of electrodes modified by CNSs. However, to the best of our knowledge, the electrochemical properties of the electrodes modified by nitrogen-doped CNSs have not been systematically investigated so far.

In this work, we investigated the effect of the  $N_2$  plasma treatment on the surface of the CNSs, which grew on the Cu substrate by microwave plasma-enhanced chemical vapor deposition at relatively low temperature. Figure 1 shows SEM images of CNSs before and after  $N_2$  plasma treatment. It can be seen that the morphological structure of CNSs has obviously been changed after  $N_2$  plasma treatment. The detailed results including the structures and electrochemical properties of nitrogen doped CNSs will be presented in the coming conference.



Figure 1 SEM images of CNSs before (a) and after (b) nitrogen plasma treatment.

W. Takeuchi et al., Appl. Phys. Lett. 92, (2008) 213103.
 W. Takeuchi et al., Appl. Phys. Lett. 98, (2011) 123107.

## Preparation of suspended graphene and graphene nanoribbons devices compatible with transmission electron microscopy

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Edge structure, width and defects of graphene and graphene nanoribbons (GNRs) significantly affect their physical properties. For example, the band gap of GNRs changes depending on the width of GNRs. The combination of TEM-based structural characterization and the physical property measurements is, therefore, essential to understand the intrinsic properties of graphene and GNRs. For this purpose, we have concentrated on

the preparation of the TEM-compatible device where graphene and GNRs are suspended between two electrodes for electronic properties measurement and the substrate underneath has been etched off to ensure penetration of electron beam through the sample (Fig. 1). Here, we report a preparation of suspended graphene and GNRs by a direct transfer of graphene grown by chemical vapor deposition (CVD) followed by plasma etching.

Graphene was grown by CVD at 1323 K using methane as a carbon source and copper as a substrate. After the CVD growth, copper substrate was etched off, and graphene was directly transferred onto the pre-fabricated substrate possessing electrodes and the penetrating hole. Figure 2 shows an electron diffraction pattern of the so-prepared suspended graphene. As clearly seen in the figures, the prepared suspended graphene is a clean monolayer graphene. Raman spectroscopy has also shown the successful preparation of suspended monolayer graphene device. After preparation of the suspended graphene, a plasma etching was performed to fabricate GNRs from graphene.







Fig. 2 An electron diffraction pattern of suspended graphene

In the presentation, details of the device preparation and characterization including TEM, Raman spectroscopy and transport properties will be discussed.

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# Anomalous Valley Magnetic Moment of Graphene

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# Abstract

There is an intrinsic valley magnetic moment (VMM) in graphene <sup>[?]</sup>, which can be used to design valley device. The accurate study of VMM is therefore very important, both from theoretical aspect and from practical aspect. However, since in graphene the effective coupling  $\frac{e^2}{\epsilon \hbar v} \sim 1$ , it is questionable that to what extent the perturbational calculation is valid.

To do this we first study carrier interactions. The study shows that, besides the well-known Coulomb repulsion between electrons, there are also four-fermion interactions associated with U-process. The four-fermion interactions are type dependent and one of them attracts carriers in different valleys. Correspondingly, the total relative contribution to VMM are

$$-\frac{e^2}{4\varepsilon\hbar v} - \frac{mV_s}{4\pi\hbar^2 v^2} = \alpha(-\frac{1}{4} + \frac{1.55\varepsilon\,m\,a}{4\pi\hbar v}),\tag{1}$$

where  $\alpha = e^2/(\varepsilon \hbar v) \approx 0.73$  when  $\varepsilon = 3$ . The first term is vertex correction and the second term four-fermion correction. If we choose m = 0.26 eV<sup>[?]</sup>, the relative modifications are about -18% and 3% respectively. Since the corrections are independent on the divergence of the loop calculations, VMM can be used to check the validity of the perturbational calculation.

[1] D. Xiao, W. Yao and Q. Niu, Phys.Rev.Lett. 99, 236809 (2007).
[2]S.Y. Zhou, et al, Nature Mater. 6,770 (2007).
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#### Geometries and Electronic Structures of Diamond Nanoparticles

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The investigation of the detailed structures and properties of the nanoscale diamond clusters has recently been the subject of research, with the purpose of developing applications in medical and biological fields such as new platforms for drug carriers and cell imaging. In addition, investigation of their geometric and electronic properties is highly desired in applications of nanotechnologies, since diamond nanoparticles act as effective seeds for the growth of carbon nanotubes and polycrystalline diamond films. However, despite the extensive experimental and theoretical outcomes, their fundamental characteristics are still far from being fully understood. In nanometer-scale clusters, reconstruction of surface atoms is important factor in determining their energetics, geometry and electronic structure due to the high surface-to-volume ratio, the multiple forms of the hybridizations, i.e., sp,  $sp^2$ ,  $sp^3$ , and bond flexibility in the small clusters. Thus, to specifically provide theoretical insight into the geometric and electronic structures of the diamond nanoclusters, we here studied the geometries and electronic structures of diamond nanoparticles on the basis of the density functional theory (DFT). As representative structural models for diamond nanoclusters, we consider nine diamond clusters with diameters ranging from 0.6 nm (35 C atoms) to 1.4 nm (253 C atoms).

Our DFT calculations clarify that the surface morphology strongly depends on the size of the diamond clusters. For clusters with diameters greater than 1 nm, the substantial surface reconstruction leads to a transformation of their outermost shell into a graphitic structure that wraps around the inner core. The surface reconstruction also results in both  $sp^3$  and  $sp^2$  bonding features in their electronic structures. Furthermore, a detailed analysis of the electronic structure of the diamond nanoclusters reveals that the electronic property depends sensitively on the size and surface morphology of the clusters. This finding implies that the surface reactivity of the diamond nanoclusters could be controllable by proper tuning of cluster size and its surface shape.



Fig. 1. Geometries for the (a) 147-, (b) 159-, and (c) 253-atom nanoclusters. Corresponding Author: Katsumasa Kamiya E-mail: kkamiya@comas.frsc.tsukuba.ac.jp Tel: +81-29-853-5922

#### Cytotoxicity of Carbon Nanohorns Depending on their Dispersion State

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Toxicity of nanometer-sized carbons depends on their size, shape, and functionalization. Long and rigid multi-walled carbon nanotubes show toxicity similar to that of asbestos, while short carbon nanotubes show less toxicity. Toxicity of carbon nanohorns (CNHs) are known to be small from *in vitro* and *in vivo* tests as long as the dosage is not in the abnormal level, which is reasonable as the CNH aggregate size is about 100 nm. The cytotoxicity of CNH appeared when the cellular uptake quantity of CNH was extremely large as studied by using macrophage RAW264.7, where the cell death mechanism was necrotic and apoptotic. The RAW264.7 cells generated ROS and caused lysosomal membrane destabilization by the high uptake of CNH, which could be the main reason of the cell death [1]. In that study, the cellular uptake quantity was increased by increasing the agglomerate size of CNH aggregates. In this study, we reduced the agglomerate size by increasing the dispersant agents of CNH, and studied the cytotoxicity of CNH.

The CNH dispersion was first prepared in PBS (10 mg/mL) using various amount of phospholipid PEG (DSPE-PEG: 1,2-distearoyl-*sn*-glycero-3-phosphoethanolamine-*N*-[amino-(polyethylene glycol) 2000] (ammonium salt)) as a dispersant agent (CNH: DSPE-PEG =  $1:0.25\sim1:3$ ). Then, the dispersion was diluted with culture medium (RPMI 1640, 0.125 mg/mL) and DLS analysis was performed. With the increase of DEPE-PEG, the agglomerate size decreased down to 100-150 nm, indicating that the CNH aggregates were dispersed almost individually in the culture medium.

CNH dispersed with DSPE-PEG in PBS was added to RAW264.7 cultured in culture medium of RPMI 1640. Final concentrations of CNH in the culture medium were 0.03, 0.1, and 0.3 mg/mL. The cell death was evaluated by Bradford assay and G6PD assay after 24 h incubation. The results showed that low concentration of CNH (0.03 mg/mL) had very low cytotoxicity irrespective of the DSPE-PEG quantity. Interestingly, the high concentration of CNH (0.1 and 0.3 mg/mL) induced the cell death that depended on the quantities of DSPE-PEG in a complex manner: With the increase of DSPE-PEG (1:0.25~1:0.5), the cytotoxicity increased, however, further increase of DSPE-PEG (1:0.5~1:3), the cytotoxicity increased. The reason for these unusual results will be discussed in the presentation.

[1] Y. Tahara, M. Nakamura, M. Yang, M. Zhang, S. Iijima, M. Yudasaka. Biomaterials. 2012 In press.

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## Influence of Graphitization Treatment of Carbon Nanocoils on Tensile Deformation Characteristics

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Carbon nanocoil (CNC) is a carbon nano fiber which has a helical shape. Its fiber diameter is 100-500 nm. We focus on the elongation of CNC for nanodevices application. Graphitized carbon nanofiber has been reported to have higher crystallinity than as-grown carbon nanofiber [1]. In study, we compared the tension this deformation characteristics between as-grown and graphitized CNCs. A CNC was fixed to a substrate by a focused ion beam (FIB). Then we observed the elongation and fracturing of CNCs by gradually changing the substrate height at a constant speed in the FIB chamber. We obtained experimental results of the tensile deformation of 8 as-grown and 8 graphitized CNCs. Fig. 1 shows a schematic representation of tension,  $N_F$ , shear,  $Q_F$ , bending moment,  $M_F$ , and torsion,  $T_F$ , at the cross section of a helical spring, which were caused by applying a uniaxial tensile, F [2, 3]. We focused on variation of the ratio of  $M_F$  to  $F(M_F/F)$  on the coil pitch, H.  $M_F/F$  can be expressed as follows [2]:

$$\frac{M_F}{F} = \cos\varphi \cdot R = \frac{RH}{\sqrt{R^2 + H^2}}$$

where  $H = h/2\pi$  [2]. We found that there is a strong correlation between  $M_F/F$  and H as shown in Fig. 2.

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[1] L. Ci, et al : Mater. Lett., 43 (2000) 291-294

[2] X. Chen, et al : Nano. Lett., 3 (2003) 1299-1304

[3] A.M. Wahl : MECHANICAL SPRINGS, Westinghouse Electric & Manufacturing: New York, 1944

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Fig. 1 (a) Schematic representation of the helical spring. (b) Resultant forces at the cross section of a helical spring [2, 3].



#### Hybrid Periodic Nano-ridges: Novel Structures and Properties

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Hybrid carbon materials at nano-scale have attracted much attention because of their novel physical and chemical properties. In the present work, we engineer a new hybrid carbon nanostructure, namely periodic nano-ridges (PNRs), which consist of graphene mono-layers and zigzag (8, 0) single-walled carbon nanotubes. As shown in Figure 1, two types of stable complexes are located at the PBE level of theory. In the first type (named as PNR-1), the zigzag nanotube is covalently bonded to the graphene layer and the distance between the bottom of nanotube and graphene is about 1.64 Å. As for another type (nominated as PNR-2), the complex is stabilized by a physical adsorption between two periodic structures and the corresponding distance is about 3.53 Å, which is similar to the interlayer distance in graphite. Thermodynamically, the binding energies are -14.95 and -0.82 eV for PNR-1 and PNR-2, respectively, which suggest that PNR-1, the chemical bonding compound, is more thermodynamically favorable. Moreover, the *ab initio* calculations are performed to explore the potential energy surfaces (PES) of the hybrid structures to study the intermolecular interaction (IMI) between graphene and nanotube. Kinetic simulations suggest that the nearest distance between nanotube and graphene is 2.00 Å at the transition state, as shown in Figure 1. The barrier from PNR-1 and PNR-2 are 3.45 and 0.87 eV, respectively.

In order to uncover the electronic properties of these two kinds of hybrid structures, the electronic band structures of PNRs have been investigated (Figure 2). It is known that graphene mono-layers are semi-metallic and (8, 0) zigzag nanotubes are semiconducting. Clearly, with nanotube bonded to or adsorbed on a graphene layer, band gaps arise. The band gaps of PNR-1 and PNR-2 are 0.059 and 0.117 eV, respectively, which means both the two structures are semiconducting. Furthermore, the band gap of each PNR appears between the highest point of the valence band and the lowest point of the conduction band at the same k-point. Consequently, a direct band gap is formed as one of desirable properties of photocatalysts. Additionally, in comparison with the pristine graphene or nanotube, the hybrid states above the Fermi level of the PNRs are increased remarkably, which provide a larger possibilities for chemical functionalization with other atoms or molecules.





**Figure 2** Electronic band structures of PNR-1 (a) and PNR-2 (b).

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### Observation of cluster growth by Fourier transform ion cyclotron resonance mass spectrometry

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Fourier transform ion cyclotron resonance mass spectrometry (FTICR) has been utilized to trace long-term cluster reactions with high mass resolution[1]. Clusters are trapped in an ICR cell under high magnetic field for more than 1 min. with cyclotron motion of  $\sim 100$  kHz. To enhance these properties, it is important to study the trap processes and the time profiles of the reactions. Here, we present the observation of fullerene growth with over 1 min. long periodic motion in the trap.

The experiments have been performed in The University of Tokyo.  $C_{60}^{+}$  ions were produced from solid fullerene with second harmonic YAG laser irradiation (532 nm, 10 Hz, and ~10 mJ) in a He supersonic jet from a pulsed valve (Jordan). Those ions were introduced to the ICR cell located in a high vacuum chamber (10<sup>-9</sup> Torr). After tens of these introduction cycles, the clusters were trapped in the ICR cell for a min. with very long cyclic motion of tens of Hz. The trapped clusters were then subjected to a high-frequency (10~130 kHz) electric field to excite FTICR motion and to measure mass spectra after several tens of seconds of the introduction. The S/N of FTICR signal was strongly dependent on this trap period. According to this long procedure  $C_{60}^{+}$  can grow to larger ones adsorbing C<sub>2</sub> molecules by-produced with the laser irradiation.

Fig.1 shows the laser power dependence of mass spectra. As the laser power increase, the growth of cluster from  $C_{60}^{++}$  up to  $C_{84}^{++}$  was observed. In particular,  $C_{74}^{++}$  emerged as the most salient peak at the laser power of 10 mJ. Almost no peak of  $C_{58}^+$  was detected throughout of the experiments, which is one of the dominant dissociation products from  $C_{60}$ with other mass spectrometry such as TOF or magnetic sector mass spectrometer [2].  $C_{70}^+$  is not so-called magic number showing that the growth products do not have stable fullerene structures. These results show that  $C_{60}^{+}$  adsorbs  $C_2$  molecules produced from  $C_{60}$  in the long trap processes of FTICR. The detection time of other mass spectrometry is around 1 ms which is much shorter than that of FTICR of 1 min. The product pattern do not depend on the number of the introduction cycles and the trap



Fig.1 Desorption laser dependence of  $C_{60}$  growth

period from 1 sec. to 1 min. suggesting the reaction time ranges from 1 ms to several sec.

<sup>[1]</sup> A. G. Marshall, et al. Mass Spectrom. Rev., 17 (1998)

<sup>[2]</sup> A.Pradeep and R. G. Cooks, J. Mass Spectrom., 135 (1994) 243-247

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#### Synthesis and Copolymerization of Fullerenol-Methacrylate Conjugate

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Modification of physicochemical properties of common polymers by introducing fullerene moiety is one of the attractive and promising strategies to create a wide variety of new organic materials. For example, it is reported that the addition of  $C_{60}$  improves the thermal stability of polymers based on its radical scavenging ability. However, the aggregation of  $C_{60}$  inevitably occurs in polar solvents/polymers, *e.g.* poly(methyl methacrylate) (PMMA), and causes the reduction in the mechanical strength. Therefore, polar fullerenol  $C_{60}(OH)_n$  which can be *dissolved* in polar solvents is preferable to be introduced to these polar polymers instead of the pristine  $C_{60}$ , especially by covalent bond.

In this study, fullerenol having methacrylate addend was synthesized by esterification of  $C_{60}(OH)_{10}$  with the corresponding acid chloride. The structure of product, as well as the number of addend introduced, was determined by IR and <sup>1</sup>H NMR spectroscopy along with thermogravimetric and elemental analyses. The obtained partially methacrylated fullerenol  $C_{60}(OCOC(CH_3)=CH_2)_n(OH)_{10-n}$  (n = 2) was then copolymerized with methyl methacrylate (MMA) to give a fullerenol-MMA copolymer. Molecular weight of the copolymer component was increased up to 869,000 (M<sub>w</sub>) probably due to the cross-linking by fullerenol, while that of PMMA synthesized in the absence of the fullerenol under the same condition was 34,000.



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## Electric properties of the methanol soaked fullerene nano-whisker field effect transistor

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Recently, it was reported that the crystallinity of fullerene nano-tube (FNT) was improved by soaking into methanol [1]. Generally, it is thought that good crystallinity of fullerene nano-whisker (FNW) shows high performance as a semiconductor. Therefore, in this study, we investigated the effect of methanol soaking on electrical conduction properties of FNW prepared by liquid liquid interfacial precipitation (LLIP) method [2].

As-grown FNWs were soaked into methanol. To clarify the soaking effect, three different soaking time lengths were used; the lengths were 30 minutes, 1 hour, and 2 hours, respectively. The FNW-field effect transistors (FNW-FETs) were fabricated using pristine FNW and the three types of soaked FNW. We measured the FET properties for pristine FNW-FET and three types of methanol-soaked FNW-FET.

After thermal annealing at 440 K in vacuum, the *I-V* characteristics of pristine FNW-FET (Fig. 1.) indicated that the drain current  $(I_{SD})$  increases with increasing gate voltage  $(V_G)$ . The behavior represents typical *n*-type FET operation. Figure 2 shows the *I-V* characteristics of the methanol soaked FNW-FET indicating almost non gate dependence. This result indicates that *n*-type property of FNWs was suppressed and the electrical properties became almost metallic by methanol soaking. This finding indicates the methanol soaking provides us one of the way to control electrical properties of FNWs. We will discuss the change of electrical conduction properties of FNW as well as observation using scanning electron microscope by methanol soaking.

[1]K. Naito and K. Matsui, *et al.* J. Phys.: Conf. Ser. **159**, 012020 (2009).
[2]K. Miyazawa, *et al.* J. Mater. Res. **20**, 688 (2005)

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**Figure 1.** *I-V* characteristics of pristine FNW-FET.



**Figure 2.** *I-V* characteristics of methanol soaked FNW-FET for 2 hours.

## Growth of star-shaped C<sub>60</sub> nanosheets

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Various shapes of  $C_{60}$  nanocrystals such as  $C_{60}$  nanowhiskers [1] and  $C_{60}$  nanosheets [2] have been grown by liquid-liquid interfacial precipitation (LLIP) method with the interface between  $C_{60}$ -saturated solution and poor solvent such as isopropyl alcohol (IPA). Their shape and structure depend on the growth conditions such as solvent. For example, in the growth of  $C_{60}$  nanowhiskers, toluene or m-xylene is used as good solvent. On the other hand, in the growth of hexagonal-shaped  $C_{60}$  nanosheets,  $CCl_4$  is used as good solvent. Therefore it is expected that further unique shapes and structures can be grown by the control of the growth condition. In this paper, we report the growth of star-shaped  $C_{60}$  nanosheets by the control of the volume ratio of solvents used.

 $C_{60}$ -saturated CCl<sub>4</sub> was made and introduced into the bottle. Then the IPA as poor solvent was gently added into the same bottle so that the liquid-liquid interface was formed. The bottle was shook so that the solutions were mixed. The mixture was kept at 5 °C. After a day, nanocrystals were precipitated. The hexagonal-shaped  $C_{60}$  nanosheets as shown in Fig. 1(a) were grown when the volume ratio of  $C_{60}$ -saturated CCl<sub>4</sub> to IPA is 1:2, as previous reports [2]. It should be noted that star-shaped  $C_{60}$  nanosheets as shown in Fig.1(b) were grown when the volume ratio of  $C_{60}$ -saturated CCl<sub>4</sub> to IPA is 1:1. The volume ratio can be related to the supersaturation for the growth. The reduction of IPA in this work means the decrease of the supersaturation which might lead to the growth of star-shaped nanosheet. The growth mechanism will be discussed with other results depending on volume ratio.



Fig. 1. Optical micrograph of (a) hexagonal-shaped and (b) star-shaped C<sub>60</sub> nanosheets.

[1] K. Miyazawa et al. J. Mater. Res. 17 (2002) 83
[2] M. Sathish et al. J. Am. Chem. Soc. 129 (2007) 13816
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#### Synthesis of C<sub>60</sub> fullerene nanowhiskers with controlled size

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The liquid-liquid interfacial precipitation simple method (LLIP method) has been used to synthesize various fullerene nanowhiskers. Since it is very important to study the size control of fullerene nanowhiskers for their practical application, we have been developing various methods by modifying the original LLIP method proposed in 2002 [1].

It is reported that the control of diameter of  $C_{60}NWs$  is possible by controlling the area of liquid-liquid interface[2]. So, we synthesized  $C_{60}NWs$  using several bottles of different inner diameters, and measured the length and diameter of  $C_{60}NWs$ .

In preparing  $C_{60}NWs$ , toluene was used as a good solvent and isopropyl alcohol (IPA) as a poor solvent of  $C_{60}$ .  $C_{60}$  powder (99.5% pure) was dissolved in toluene (2.8 mg/ml) and the  $C_{60}$ -toluene solution was ultrasonicated for 30 minutes to obtain a  $C_{60}$ -saturated toluene solution. The solution was filtered to remove undissolved  $C_{60}$  powder. IPA was gently added to the  $C_{60}$ -saturated toluene solution, and the solution of  $C_{60}$  and IPA was manually mixed 30 times. The synthesis temperature was 15°C.

Figs.1 and 2 show the mean length and diameter of  $C_{60}NWs$  synthesized by use of five glass bottles with different diameters. It is shown that the mean length and diameter of  $C_{60}NWs$  increase with increasing the diameter of glass bottle.



Fig.1 Relationship between the mean length of  $C_{60}$ NWs and the inner diameter of glass bottle.

Fig.2 Relationship between the mean diameter of  $C_{60}$ NWs and the inner diameter of glass bottle.

- [1] Fullerene Nanowhiskers, Kun'ichi Miyazawa (Ed.), (Pan Stanford Publishing, 2011).
- [2] T.Wakahara, K.Miyazawa, Y.Nemoto, O.Ito, Carbon49 (2011) 4644-4649

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## The Li<sup>+</sup>@C<sub>60</sub> functionalization —Synthesis of Li@PCBM cations

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Functionalization of fullerenes is widely investigated for the purpose of tuning their electronic properties, improving their solubility and/or morphology, and connecting them to other functional molecules. Undoubtedly, one of the most popular fullerene derivatives is [6,6]PCBM ([6,6]-phenyl-C<sub>61</sub>-butyric acid methyl ester) [1], which is now widely used as organic semiconductor devices, in particular, as an acceptor in organic photovoltaics [2].

Functionalization of endohedral metallofullerenes is also well established [3] and some of the products have been applied to organic photovoltaics [4]. However, as for the functionalization of endohedral metallo[ $\underline{60}$ ]fullerene (M@C<sub>60</sub>), only one example reported is multi-substituted Gd@C<sub>60</sub>s [5], for which the characterization is not satisfactory.

We recently succeeded in the synthesis and full characterization of endohedral metallo[60]fullerene  $[Li^+@C_{60}](SbCl_6^-)$  [6]. Herein, we report  $[Li^+@[5,6]PCBM](PF_6^-)$  (2) and its isomer  $[Li^+@[6,6]PCBM](PF_6^-)$  (3) as the first M@C\_{60}s functionalized by an organic group. Thus, the reaction of  $[Li^+@C_{60}](PF_6^-)$  with diazoalkane 1 gave 2, which then isomerized to 3 on heating to 90 °C (Scheme 1). Comparison of the reactivity toward these reactions between Li<sup>+</sup>@C<sub>60</sub> ion and empty C<sub>60</sub> will also be discussed.



Shceme 1. Synthesis of  $\text{Li}^+@[5,6]\text{PCBM}(2)$  and  $\text{Li}^+@[6,6]\text{PCBM}(3)$ .

[1] J. C. Hummelen, B. W. Knight, F. LePeq, and F. Wudl, J. Org. Chem. 1995, 60, 532.

[2] G. Yu, J. Gao, J. C. Hummelen, F. Wudl, and A. J. Heeger, Science 1995, 270, 1789.

[3] X. Lu, T. Akasaka, and S. Nagase, Chem. Commun. 2011, 47, 5942.

[4] R. B. Ross et al., Nature Materials 2009, 8, 208.

[5] a) R. D. Bolskar, A. F. Benedetto, L. O. Husebo, R. E. Price, E. F. Jackson, S. Wallace, L. J. Wilson, and J. M. Alford, *J. Am. Chem. Soc.* **2003**, *125*, 5471. b) É. Tóth, R. D. Bolskar, A. Borel, G. González, L. Helm, A. E. Merbach, B. Sitharaman, and L. J. Wilson, *J. Am. Chem. Soc.* **2005**, *127*, 799.

[6] S. Aoyagi et al., Nature Chemistry 2010, 2, 678.

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## The Shortest Metallofullerene-Peapod: Complexation of Metallofullerenes with [11]Cycloparaphenylene

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Endohedral metallofullerenes<sup>[1]</sup> have been known to form an interesting hybrid material with carbon nanotubes (CNTs), the so-called metallofullerene-peapods<sup>[2]</sup>. During the past decade, we have found that the metallofullerene-peapods exhibit such intriguing phenomena as local

band-gap modulation<sup>[3]</sup>, ambipolar characteristics for the field-effect-transistors [4] and a sudden transformation from peapods to metal nanowireencapsulating CNTs <sup>[5]</sup>. Virtually, all of these novel characteristics of the peapods are now known to be stemming from the charge-transfer between CNT and the metallofullerenes. However, the details of the charge-transfer interaction have not fully been understood yet. To shed much light on this, we have synthesized the world's metallofullerene-peapod, shortest (Gd@Cs2)@[11]cycloparaphenylene, trying to elucidate the structural and electronic properties of a building block of such metallofullerenepeapod.



Figure1 The world's shortest nano-peapod; the complex of Lu2@Cs2 with [11]cycloparaphenylene.

Here we show that a newly-synthesized cycloparaphenylene [6,7], [11]cycloparaphenylene in this case (hereafter referred to as [11]CPP), can effectively and selectively encapsulate a C2v-Gd@C82 metallofullerene molecule. The encapsulation has been confirmed by using optical absorption and photoluminescence spectroscopy. In the absorption maximum of Gd@C<sub>82</sub> at 631 nm, the red-shift of the peak was observed when [11]CPP was added to Gd@Cs2 solution, whereas such a spectral change has not been observed for [12]CPP, indicating that Gd@Cs2 is selectively entrapped within [11]CPP. Furthermore, the binding constant  $K_a$  of Gd@C<sub>82</sub> with [11]CPP in toluene solution was evaluated by fluorescence-quenching experiments. The obtained constant is 3.4 × 106 M<sup>-1</sup>, which is a higher affinity of Gd@Cs<sub>2</sub> to [11]CPP as compared with the corresponding empty  $C_{60}$  case. We will discuss the details of the charge transfer interaction between metallofullerenes and [11]CPP.

#### References

[1] H.Shinohara, Rep. Prog. Phys. 63, 843 (2000). [2] K.Hirahara et al., Phys. Rev. Lett. 85, 5384 (2000).

- [3] J.Lee et al., Nature 415, 1005 (2002).
- [5] R.Kitaura et al., Nano Lett. 8, 693 (2008).

[4] T.Shimada et al., Appl. Phys. Lett. 81, 4067 (2002).

- [7] H.Omachi et al., Angew. Chem. Int. Ed. 49, 10202 (2010).
- [6] H.Takaba et al., Angew. Chem. Int. Ed. 48, 6112 (2009).
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## ESR detection of $\gamma$ -Cyclodextrin-bicapped N@C<sub>60</sub> in water

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The encapsulation of  $C_{60}$  with  $\gamma$ -cyclodextrin ( $\gamma$ -CD) was attained by a mechanochemical high-speed vibration (HSV) technique. The 1:2 compositions of  $C_{60}$  and  $\gamma$ -CD was confirmed by NMR, X-ray crystal structure analysis and elementary analysis. The first X-ray crystal structure of  $\gamma$ -CD-bicapped N@C<sub>60</sub> is reported in Fig. 1a and 1b. The column of  $C_{60}$  and  $\gamma$ -CD stack mediated by hydrogen bonding was obtained.

The HSV technique was applied to the powder of  $\gamma$ -CD and C<sub>60</sub> containing N@C<sub>60</sub> at 5%. The obtained aqueous solution exhibited the peculiar electron spin resonance (ESR) spectrum of N@C<sub>60</sub>, as shown in Fig. 1c, which was due to the electron spin *S*=3/2 and the <sup>14</sup>N nuclear spin *I*=1. Furthermore the quintet ESR spectrum was obtained, which was attributed to the hyperfine structure of equivalent two nitrogen nuclei. The result suggests the formation of columnar dimer of  $\gamma$ -CD-bicapped N@C<sub>60</sub> in water.



Fig.1 X-ray structure of  $\gamma$ -CD-bicapped C<sub>60</sub> (a) Side view. (b) Top view along the C<sub>8</sub> axis. (c) ESR spectra of  $\gamma$ -CD-bicapped N@C<sub>60</sub> at 32 K.

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# Large-scale dispersion of multi-walled carbon nanotubes in protein solutions using a wet-type super atomizer

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The development of a large-scale dispersion method for carbon nanotubes (CNTs) is important for their industrial applications. In many cases, ultrasonication has been widely used for dispersing CNTs in both water and organic media. Although ultrasonication is a strong tool for disentangling the knotted CNTs, some destruction of CNTs occurs during the dispersion process. In addition, in the ultrasonication method, it seems to be difficult to provide a CNTs dispersion solution on a large-scale and control the reproducibility of the properties of the dispersed CNTs. Therefore, a large-scale and non-destructive method for dispersing CNTs according to the application is still required.

In this work, we have conducted the dispersion of MWNTs in aqueous solutions containing casein as a dispersant by using a wet-type atomizer "Nanovater" (Yoshida Kikai Co. Ltd.). Since the Nanovater uses collision of solution under ultra-high pressure (max. 200 MPa) to disperse CNTs, a reduction in the destruction of CNTs during the dispersion process can be expected. The prepared MWNTs dispersion solutions were subjected to the evaluation by UV-Vis-NIR absorption spectroscopy and thermo-gravimetry.

MWNTs (40 mg) produced by CVD method were mixed in casein aqueous solution (40 ml) and the resultant suspension was treated with the Nanovater under a pressure of 180 MPa. This treatment was repeated 20, 40, and 60 times to give the black dispersion solutions. The obtained dispersion solutions were centrifuged (20400 g, 30 min) to separate the supernatants from the residual materials. From the UV-Vis-NIR spectra for the supernatants, MWNTs were found to be dispersed well in the casein solution by the treatment with the Nanovater depending on the repeating treatment number. On the other hand, the residual materials obtained after centrifugation were treated with hydrochloric acid to hydrolyze and remove the proteinous components because the residual materials contained proteinous components other than MWNTs that originated from casein. From the amounts of the remaining components, the contents of MWNTs in the dispersion solutions were estimated. We will report and discuss the availabilities of the method by using the Nanovater and casein as a dispersant.

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## Effect of Buffer Gas on Growth of mm-Long Vertically Aligned Carbon Nanotubes by Chemical Vapor Deposition

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We report that mm-long vertically aligned carbon nanotubes (CNTs) was synthesized from a multilayer catalyst of iron (Fe<sub>2</sub>O<sub>3</sub>) and aluminum oxides (Al<sub>2</sub>O<sub>3</sub>) by chemical vapor deposition (CVD) using Ar/C<sub>2</sub>H<sub>2</sub> gas mixture. We have examined CVD conditions to grow long CNTs with a high number density and found that as the gas flow rate of C<sub>2</sub>H<sub>2</sub> feedstock is reduced, the CNT length became long. In this condition, the size of graphitic particles in the graphite layers attached on top of CNTs was also reduced [1]. In this study, we used Ar gas instead N<sub>2</sub> gas as a buffer In the experiment, sandwich structure of gas. Al<sub>2</sub>O<sub>3</sub>/Fe<sub>2</sub>O<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub> film was deposited on SiO<sub>2</sub>/Si substrate by vacuum evaporation. The CVD equipment used was developed in our laboratory [2]. The gas flow rate of C<sub>2</sub>H<sub>2</sub> was fixed at 50 ml/min; whereas that of





Ar was varied from 2000 to 4500 ml/min. The CVD was carried out at an atmospheric pressure and at a reaction temperature of 780°C. The reaction time was 60 min.

Fig. 1 shows the SEM micrograph of vertically aligned CNTs with a length of 1100  $\mu$ m. The Ar gas flow rate was 2500 ml/min. This is the longest CNTs grown by our CVD equipment. The sizes of the graphitic particles were also shown to be the smallest, ~150 nm indicating effective catalytic reaction for CNT growth.

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H. Atsumi, *et al.*: The 41<sup>th</sup> Fullerene-Nanotubes-Graphene General Symposium, 3P-17 (2011)
 Y. Hosokawa, et al.: Res. Lett. Mater. Sci., 2007, 59167 (2007)

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#### Global-characterization of DWCNTs in specimen by Raman spectroscopy

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Since the properties of carbon nanotubes (CNTs) depend on their structure, such as chirality, diameter, length, and layer numbers, the structural characterizationis fundamental and important as the initial approach for the application research of CNTs. Although transmission electron microscopy (TEM) is powerful method for the characterization in nanometer-scale, the TEM observation is unsuitable to characterize the statistical detail of the gross CNTs. Therefore, the establishment of the global-characterization method for CNT structures by the spectrographic analysis is eagerly anticipated.

Recently, we have reported that, in the enhanced direct injection pyrolytic synthesis (eDIPS) using methane as the secondary carbon source [1, 2], increasing the methane addition increases the proportion of DWCNTs in the product up to 50 % of the relative abundance based on the number of CNTs as shown in Figure 1a. In this presentation, we will report the characterization results by resonance Raman spectroscopy on the product mainly containing SW- and DWCNTs. Figure 1b showing the G-band peaks in the Raman spectra of products suggests that the G-band peak becomes rounded as increasing the proportion of DWCNTs. The result of curve fitting performed on these peaks by using the Voigt line profile showed the correlation between the tangential G-band feature and the relative abundance of DWCNTs in the product. The detail of the curve fitting analysis and the origin of the G-band of DWCNTs based on previous studies will be discussed at the presentation. This characterization method by using Raman might afford a useful index to evaluate DWCNTs in the specimen.

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Fig.1 Dependence of relative abundances of DWCNTs in the product on the methane flow rate (a). Raman spectra of tangential G-band (b) of typical samples.

<sup>[1]</sup> K. Kobayashi et al. 2-11, The 41st Fullerenes-Nanotubes-Graphene General Symposium.

<sup>[2]</sup> T. Saito, et al., J. Nanosci. Nanotech., 8, 6153 (2008).

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## Selective Metal/Semiconductor Separation for Double-Walled Carbon Nanotubes

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Double-walled carbon nanotubes (DWNTs) are potentially applicable to high sensitive field-effect transistors (FETs) because they possess mechanical strength and thermal stability greater than those of single-walled carbon nanotubes (SWNTs). However, DWNTs are generally obtained as a mixture of DWNTs with different chirality and length. According to the different combinations of the outer/inner tubes, DWNTs can be classified into four types: metallic (m)/semiconducting (s), s/m, m/m, and s/s. Hence, the separation of DWNTs is significantly important for their application to FETs. In the present study, we investigated the separation for DWNTs dispersed in water by column chromatography.

DWNTs were dispersed in water containing 2 wt.% sodium dodecyl sulfate (SDS) by ultrasonication (1h), and the DWNT dispersions were ultracentrifuged under the condition of 41,000 g for 3 h. The separation of DWNTs was carried out by the following two steps according to the previous report.<sup>1</sup> For the first step, chromatographic separation was conducted by passing the supernatant after the ultracentrifugation through a column (Sephacryl S-200HR, GE Healthcare Co.) with a eluent of 2 wt.% SDS solution. For the next step, DWNTs adsorbed on the column were collected by flowing 5 wt.% SDS solution through the column.

Consequently, UV-vis-NIR absorption, resonance Raman, and NIR-photoluminescence (PL) data revealed that the m/m and m/s types of DWNTs with high purity were collected in the eluted fraction for the first step, while the s/s and s/m types were enriched after the second-step elution. In this presentation, we will also present recent results regarding the transport characteristics (current vs. gate-voltage) for DWNTs sorted by this separation technique.

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

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#### MD Simulation of SWNT Growth Process by Catalytic CVD Method

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It is of great importance to understand the growth mechanism of single-walled carbon nanotubes (SWNTs) from catalytic chemical vapor deposition (CVD) method for the future control of chiralities and diameters. We performed classical molecular dynamics simulation of catalyst-nucleated SWNT growth process, adopting our reconstructed Tersoff-type potentials for metal-carbon systems [1] and the simulation procedure of a previous report [2]. By controlling temperature and carbon density (pressure), we successfully represent the growth process of SWNT (Figure 1).

Figure 2 shows the SWNT growth rates as a function of temperature. Growth rates show Arrhenius type dependence on temperature. By the slope of lines, activation energies of around 0.4 eV was estimated for iron catalyst, which well agrees to those of surface diffusion for solid catalyst [3]. This result indicates SWNT growth is governed by carbon atoms' diffusion on metal cluster's surface.



Fig.1 SWNT growth from iron.

Fig.2 Arrhenius plots of SWNT growth rate by iron.

#### **References:**

[1] T. Matsuo et al, to be submitted. [2] Y. Shibuta and S. Maruyama, Chem. Phys. Lett., 382 (2003) 381.

[3] R. T. K. Baker et al, J. Catal., **30**(1973)86.

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## Single Chirality Purification of Single Wall Carbon Nanotubes for Encapsulation of Organic Molecules

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Recent advancement of purification techniques for single-wall carbon nanotubes (SWCNTs) enables us to obtain high-purity metallic, semiconducting, and single-chiral state of SWCNT samples. Various techniques such as polymer, monomer, DNA rapping extraction, density-gradient sorting, and gel chromatography, have been proposed for single-chiral purification. As a result, it is now possible to obtain single chiral samples in high purity such as (6,5), (8,3), and so on. However, it is noteworthy that the diameters of the single chiral samples that have been obtained by now are less than or around 1.0 nm. As a result, it is difficult to put organic molecules into their inner hollow spaces. From the discovery of encapsulation of fullerenes inside the nanotubes, it is known that SWCNTs with diameter around 1.4 nm can encapsulate various kinds of organic molecules. SWCNTs encapsulating organic molecules (peapods) exhibit unique physical and chemical properties, but there has not been a technique to prepare single-chirality state of peapods, impeding detailed understanding of their physical/chemical properties and also device applications. Here we report the successful extraction of a single-chiral state of SWCNTs with (11,10) chirality (Fig. 1), which has 1.45 nm diameter, and their peapods. We achieved the single chiral extraction through the following purification approaches. First, we applied density-gradient ultracentrifugation by using cesium chloride as density medium (CsCl-sorting). CsCl-sorting can improve the sorting capability, and very useful for diameter sorting. Second, single-chiral

extraction is achieved by two steps purification; metal/semiconductor sorting and the CsCl-sorting. We succeeded to prepare nearly single chiral state of peapods by our purification procedures.

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Fig. 1 Photoluminescence mapping of a sample in a single-chiral state of (11,10) SWCNTs.

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# Preferential extraction of left- or right-handed SWNTs with narrow diameter range by use of chiral diporphyrin nanotweezers

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Chiral SWNTs have been separated according to the handedness through preferential extraction with tweezer-shape chiral host molecules in our group [1-4]. However, (n, m)-SWNTs optically enriched by the method have limited mainly to (6,5) and (7,6)-SWNTs [5]. Herein, we report on enantiomeric enrichment of (n, m)-SWNTs, such as (8,4), (9,1), and (9,4)-SWNTs, other than so far reported ones together with simultaneous diameter-based separation through preferential extraction of 76-CoMoCAT with 2,6-pyridylene-bridged chiral diporphyrin nanotweezers **1** (Fig. 1) [3, 6].

Separation of SWNTs according to the handedness is confirmed by circular dichroism (CD) of the SDBS/D<sub>2</sub>O solutions of the washed SWNTs after the extraction. The **SWNTs** extracted with chiral nanotweezers, (R)- and (S)-1, exhibit symmetrical CDs as shown in Fig. 2, indicating that the extracted SWNTs are optically active. The four prominent peaks observed in  $E^{S_{22}}$ region mean that the solutions include at least four kinds of optically active (n, m)-SWNTs. (8,4)-SWNTs exhibit the strongest CD intensity at 588 nm and (9,4) and (7,6)-SWNTs also give the relatively large CDs at 720 and 649 nm, respectively. Although no clear PL and only tiny absorption are detected for (9,1)-SWNTs, the CD at 691 nm has comparable intensity with those of (9,4), and (7,6)-SWNTs. This may imply that the nanotweezers 1 recognizes handedness and diameter independently discriminates and handedness more strictly than diameter in (9,1)-SWNTs.



Fig 1 Structures of chiral diporphyrin nanotweezers, (R)- and (S)-1.



**Fig. 2** CD spectra of SWNTs extracted with (*R*)- and (*S*)-1, and absorption spectra of SWNTs extracted with (*R*)-1.

[1] F. Wang, K. Matsuda, N. Komatsu, Nanoscale 2011, 3, 4117; [2] F. Wang, K. Matsuda, N. Komatsu, J. Am. Chem. Soc. 2010, 132, 10876; [3] X. Peng, N. Komatsu, J. Am. Chem. Soc. 2007, 129, 15947; [4] X. Peng, N. Komatsu, Nature Nanotechnology 2007, 2, 361; [5] G. Liu, N. Komatsu, in Handbook of carbon nano materials (Eds.: F. D'Souza, K. M. Kadish), World Scientific, 2012, in press; [6] G. Liu, T. Yasumitsu, L. Zhao, X. Peng, F. Wang, A. K. Bauri, S. Aonuma, T. Kimura, N. Komatsu, submitted.

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## Single-Walled Carbon Nanotube Synthesis at Low Temperature using Pt catalyst in Alcohol Gas Source Method

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Single-walled carbon nanotubes (SWNTs) have been anticipated for application in a lot of future nanodevices. So far, we have been reporting SWNT growth by alcohol gas source method in an ultra-high vacuum (UHV) chamber using Co catalyst [1]. Recently, using Pt catalyst, we succeeded in remarkable reduction of ethanol pressure during the SWNT growth at 700°C, while keeping the SWNT yield higher than those with Co catalysts [2]. In this study, we attempted to grow SWNTs at 500°C using Pt catalyst and investigated the structural property of grown SWNTs through Raman measurements.

Pt (thickness~0.2 nm) was deposited on SiO<sub>2</sub>/Si substrates by either an e-beam evaporator or a pulsed arc plasma gun. Then, they were heated up to the growth temperature (500-800°C) in a UHV chamber, and ethanol gas was supplied to grow SWNTs. The grown SWNTs were characterized by SEM, TEM and Raman spectroscopy.

SEM and Raman results showed that, irrespective of the growth temperature, the optimal ethanol pressures were between  $1 \times 10^{-4}$  and  $1 \times 10^{-3}$  Pa, confirming that Pt catalyst is suitable for SWNT growth in a high vacuum. In addition, as the growth temperature decreased, the optimal pressure was reduced and the average diameters of SWNTs became smaller. By optimizing the growth conditions, we could succeed in SWNT growth at 500°C using Pt catalyst. We will discuss the structural property of SWNTs grown with Pt catalysts.

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[1] K. Tanioku *et al.*, Diamond Relat. Mater., **17**, 589 (2008).
[2] T. Maruyama et al., Mater. Express, **1**, 267 (2011).
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## Sorting for Outer-layer Semiconducting DWNTs through Density-gradient Centrifugation

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Double-walled carbon nanotubes (DWNTs), consisting of two coaxial cylinders of graphene, have attracted much attention because they exhibit properties intermediate between single-walled carbon nanotubes (SWNTs) and multi-walled carbon nanotubes (MWNTs). Hence, DWNTs would be a promising candidate for new generational field-effect transistors (FETs) and biosensors. However, DWNTs exhibit different electronic behaviors depending on the combination of the outer/inner walls: metal (m)/semiconductor (s), s/m, m/m, and s/s. Because the polydispersibility of DWNTs hinder their industrial application to FET, the establishment of sorting technique for DWNTs is required for their industrial applications. Previously, we found out that density gradient ultracentrifugation (DGU) using mixture of carboxy methyl cellulose (CMC) and sodium dodecyl sulfate (SDS) as the dispersing agent was useful for sorting of SWNTs. In the present study, we investigated the DGU separation for DWNTs dispersed by mixed CMC and SDS.

DWNT dispersions were prepared using mixed dispersants of 1 wt.% CMC and 1wt.% SDS by ultrasonication (1.5 h) and by the following ultracentrifugation (41,000 g, 3 h). Density gradients in centrifuge tubes were performed by layering aqueous iodixanol solutions from 25% to 32.5%, in which only 30% iodixanol solution contained the DWNT dispersion. The centrifuge tubes were then centrifuged at 175,000 for 12 h.

A fraction band of enriched DWNTs was obtained from the upper layer after DGU. UV-vis-NIR absorption spectroscopy revealed that the absorption peaks corresponding to metallic CNTs ( $M_{11}$ , 400-600 nm) were lower than those corresponding to semiconducting CNTs ( $S_{11}$ , 800-1200 nm; S22, 600-800 nm) for the upper layer. This result suggests that the upper layer contained the s/s and s/m types of DWNTs with high purity. This fact was also confirmed by resonance Raman and NIR photoluminescence spectroscopies. The present DGU technique using the mixed dispersants of CMC and SDS would be a useful separation method for DWNTs. At present, further study with regard to the selective separation of the s/s and s/m DWNTs from outer-layer s-DWNTs is in progress under the DGU condition of lower density-gradient.

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# Effect of Charge of Solubilizer on the Electronic States of Single-Walled Carbon Nanotubes

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The redox properties 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.

We carried out in situ photoluminescence spectroelectrochemical measurements for films of cationic cellulose containing isolated SWNTs on ITO electrodes<sup>1,2</sup> to determine the redox potentials, Fermi levels, and band gaps of (n,m)SWNTs. In this study, the effect of charge of the cellulose matrix on the electronic properties of the SWNTs was examined, and the results were compared to those using the anionic cellulose matrix<sup>1,2</sup>.

#### **References**:

[1] Y. Tanaka, Y. Hirana, Y. Niidome, K. Kato, S. Saito, N. Nakashima, Angew. Chem. Int. Ed. 2009, 48, 7655.
[2] Y. Hirana, Y. Tanaka, Y. Niidome, N. Nakashima, J. Am. Chem. Soc. 2010, 132, 13072.
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#### **Evaluation of Thermal Conductivity of Single Carbon Nanotube in Liquid**

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Carbon nanotube (CNT) has potential applications in various fields such as nano-sensors. Although electrical and mechanical properties have been investigated at single nanotube, measurement of thermal property of single CNT was still difficult. Therefore, very little research on the thermal conductivity of single CNT in liquid was investigated.

Here, we propose a new method to measure the thermal conductivity of single CNT in liquid as shown in Fig.1. The thermal conductivity of the CNT is measured from the temperature difference between the ends of the CNT and heat flow in the CNT. Temperature at the edge of the CNT is measured by the temperature sensor. The sensor is made of polystyrene and contained Rhodamine B, which is used as fluorescent temperature indicator. Fluorescent intensity (FI) decreases according to temperature increase (-1.1 %/K) [1]. These sensors are fixed to the both ends of the CNT using optical tweezers in the electrolyte solution. Infrared laser (1064 nm) is irradiated to the sensor to generate temperature difference. The temperature difference is calculated by comparing the before and after FI from the sensors. Heat quantity Q is calculated by measuring the fluorescence distribution in the sensor. Thermal conductivity of single CNT  $\lambda_{CNT}$  is represented by equation (1).

$$\lambda_{CNT} = \frac{l}{\pi (d/2)^2} \cdot \frac{Q}{T_1 - T_2} \quad , Q = 4\pi\lambda_b \cdot \frac{T_2 - T_3}{1/r_1 - 1/r_2} \tag{1}$$

*l*: Length of CNT (5.5 µm), *d*: Diameter of CNT (140 nm),  $T_1, T_2, T_3$ : Temperature increase  $\lambda_b$ : Thermal conductivity of sensor (0.108 W/mK),  $r_1 = 0.5 \mu m$ ,  $r_2$ : Radius of sensor (2.5 µm)

Fig. 2 shows the experimental results. Fig. 2(a) shows the assembled CNT and sensors. Right sensor is used for compensation of the heat flow in water. Fig.2(b) shows time-course shift of relative FI of each sensor. Laser was irradiated to the center sensor at 10 s, and laser was turned off at 40 s. From this result, Temperature difference between the ends of CNT was 1.77 K, and Q was 7.06  $\mu$ W. As a result,  $\lambda_{CNT}$  is 1425 W/mK. This measuring method is expected to contribute significantly to nanotechnology and biotechnology.



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## **Energetics and Electronic Properties of Capped Carbon Nanotubes**

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Many experimental and theoretical works of carbon nanotubes (CNTs) discussing their fundamental properties and/or the 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 [1,2]. It has been also pointed out from the density functional theory (DFT) calculations with structural relaxation that their electronic structures also depend sensitively on their geometrical parameters [3,4]. 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. Given this situation, we have achieved the systematic DFT calculations by using the helical symmetry of CNTs and predicted the precise fundamental properties of CNTs [5]. Importantly, it is found that "near-armchair" CNTs including (6,5) and (7,5) CNTs are energetically more stable than other CNTs. This result corresponds well with the high abundance of near-armchair CNTs experimentally reported so far [6].

In the present work, in order to investigate further the additional reasons for the high abundance of near-armchair CNTs, we perform the first-principles calculations of several kinds of capped CNTs. The cap structures of CNTs are considered to play an important role in the nucleation and growth process of CNTs [7]. We discuss the energetical stability of cap structures of not only near-armchair CNTs but also zigzag and near-zigzag CNTs and address the importance of the arrangement of the pentagons in the cap structures. In addition, we also report the electronic properties of capped CNTs.



Figure: Most stable cap structure of (4,3) CNT. (a) and (b) represent top and side views respectively.

- [1] N. Hamada, S. Sawada and A. Oshiyama, Phys. Rev. Lett., 68, 1579 (1992).
- [2] R. Saito, M. Fujita, G. Dresselhaus and M. Dresselhaus, Appl. Phys. Lett., 60, 2205 (1992).
- [3] K. Kanamitsu and S. Saito, J. Phys. Soc. Jpn., 71, 483 (2002)
- [4] K. Kato and S. Saito, Physica E, 43, 669 (2011)
- [5] K. Kato, T. Koretsune and S.Saito, to be published.
- [6] S. M. Bachilo, L. Balxano, J. E. Herrera, F. Pompeo, D. E. Resasco and R. B. Weisman, J. Am. Chem. Soc. 125 11186 (2003)
- [7] H. Kataura, Y. Kumazawa, Y. Maniwa, Y. Ohtsuka, R. Sen, S. Suzuki, and Y. Achiba, Carbon 38, 1691 (2000)

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### **Effective Tip Structure of Carbon Nanotube Gecko Tape**

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The gecko tape is an adhesive tape mimicking the adhesion mechanism of gecko's foot. The adhesion is caused by van der Waals force and has an almost equal strength to that of generally used glue adhesives [1]. The adhesion can be obtained in case that a fine structure of a high aspect ratio is made on the surface. For this reason, recently, arrays of vertically aligned carbon nanotubes (CNTs) have been found to be the most probable material to mimic the actual gecko structure [2].

It has been revealed that the CNT shear adhesion increases with increasing CNT length and the length is an important factor enabling conformation to the surface roughness and enabling generation of a strong contact by side contact [3]. In this work, we have investigated an effective structure of the tip part of CNT gecko tape to increase the adhesion and its cyclic property.

Arc discharge-produced CNTs were aligned and protruded from the edge of a Si substrate to prepare a CNT cartridge. The tip part of single CNTs or bundled CNTs protruded from the cartridge was attached in normal direction to a Si cantilever for atomic force microscopy and then detached from it using a manipulator installed in a scanning electron microscope as shown in Fig. 1. The displacements of the Si cantilever for attaching and detaching gave the preload and the normal adhesion, respectively. For the bundled CNTs not only straight tips but also bent tips were examined.

Figure 2 shows the normal adhesion as a function of the preload for three samples. The bundled CNT can accept the preload higher than the single CNT and thus shows higher adhesion. The adhesion degrades with increasing the cyclic test number. On the other hand, the CNT with a bent tip shows the highest adhesion at any preload and the degradation of adhesion is small.

The structure of the CNT with a bent tip resembles gecko's seta which has a spatula. The bent tip works as the spatula. This result suggests that developing a process to produce vertically aligned CNTs embedded in a plastic tape in which the free end of CNTs is plastically bent brings CNT gecko tapes to a practical use.





[3] Y.Maeno et al. Appl. Phys. Express 3, 065102 (2010).

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Fig.2 Relationship between adhesion and preload

Preload [nN]

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## Property Control of Single-Walled Carbon Nanotubes Field Effect Transistor by Nitrogen and Fluorine Doping Using Plasma CVD

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Single-walled carbon nanotubes (SWNTs) are nano carbon materials consisting of a single graphene sheet. Since SWNTs have great and unique electrical properties, the development of high performance SWNTs field effect transistors (SWNTs-FETs) is expected to be a critical issue of next-generation nano electronics. For the purpose of realizing the high performance SWNTs-FETs, it is necessary to selectively utilize semiconducting SWNTs as a channel of FETs. In addition, it is also required to control the electrical properties of SWNTs-FETs for their practical applications. Based on these backgrounds, we investigate the effect of the reactive gases (nitrogen and fluorine) during the SWNTs growth on the electrical transport properties of thin film SWNTs-FETs.

The SWNTs growth is performed on a substrate layered with Co 0.2 nm, SiO<sub>2</sub> 300 nm, and Si by diffusion plasma CVD (Fig. 1) [1], where plasmas are possible to be generated under various pressures ranging from 50 Pa (low) to 10 kPa (high). On purpose to supply feedstock gases uniformly, mesh grids are used as electrodes. Since the growth process is carried out in a diffusion plasma region, the high quality SWNTs growth is realized. SWNTs-FETs are fabricated by forming source and drain electrodes (Au) on the top of SWNTs films using photo-lithography technique.

SWNTs are synthesized under the different nitrogen and fluorine flow conditions. The properties of SWNTs are studied by Raman spectroscopy and a vacuum probe station under the FET configurations. The G and 2D Raman peaks of synthesized SWNTs tend to upshift (G) and downshift (2D) with an increase in the nitrogen flow and growth time, resprectively. The electrical properties of SWNTs grown without the nitrogen flow show p-type semiconductor characteristics. On the other hand, n-type features are often observed for the SWNTs grown under the appropriate nitrogen flow (Fig. 2). In the case of adding fluorine flow, p-type features are enhanced. These results indicate that nitrogen and fluorine atoms can be doped to SWNTs bv introducing the appropriate amount of reactive gases flow during the SWNTs growth.

[1] T. Kato and R. Hatakeyama : Appl. Phys. Lett. 92 (2008) 031502.
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Fig.1 : Schematic of the experimental apparatus.



Fig.2 : Electrical properties of SWNTs grown with the additional nitrogen flow.

### Rheology of magnetic-field responsive carbon nanotube/ionic liquid gel

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Functional soft-materials that respond to physical stimuli have been extensively investigated for a past decade. Polymer gels containing magnetic materials are called magnetic polymer gels, and these gels respond to magnetic fields. Recently, a magnetic polymer gel was found to exhibit a reversible increase of the storage modulus by a factor of 500 upon application of magnetic field [1]. When mixed with ionic liquid, pristine carbon nanotubes (CNTs) form gels, called bucky gels. In bucky gel, CNTs constitute the framework of a 3D network stiffer than polymer. Therefore, we expect that the magnetic bucky gel, a bucky gel with magnetic particle, exhibits unique rheological behavior. In this study, we report the preparation and rheological property of magnetic bucky gels with several CNT concentrations.

Multi-walled carbon nanotube were suspended in a N, N-diethyl-N-methyl-N-(2-methoxyethyl) ammonium tetrafluoroborate, and the mixture was molded for 20 minutes, where the suspension gradually turned into a glossy, black paste. Then magnetic gel was prepared by mixing the ionic gel and  $Fe_3O_4$  particle (200-300 nm). The concentration of magnetic particle was 45 wt%. The dynamic shear modulus at 1.0 Hz was measured using a rheometer under a stepwise magnetic field. The field direction was perpendicular to the strain.

Figure 1 shows that the storage modulus (G') responses to the stepwise change of magnetic field between 0 and 500mT. It demonstrates that the change in G' is synchronous with the magnetic field. However, the variation of G' in the second step is smaller than that in the first step. In addition, G' behavior in the second step (red circles in Figure 2) changes with the concentration of CNTs in the gel. These behaviors have not been observed on magnetic polymer gels. Therefore, we consider that the specific behavior of



Figure 1. Schematic drawing of magnetic bucky gel.



Figure 2. Responses of storage modulus against magnetic field. CNT weights are (a) 10 mg and (b) 40 mg.

magnetic bucky gels is originated by the stiffer CNT network, which blocks the movement of the magnetic particles.

[1] T. Mitsumata et al. Chem. Lett., 38, 922(2009). Corresponding Author: Haruya Okimoto Tel/Fax: +81-238-26-3074 E-mail: haruya@yz.yamagata-u.ac.jp

# Carbon nanotube cantilever for measurement of interaction forces between antigens and antibodies

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Since carbon nanotubes (CNTs) have high aspect ratio, high mechanical strength and extremely light weight, CNT cantilevers enable ultrasensitive sensing applications such as mass and force sensors. The resonance of CNT cantilevers was used toward mass measurement of biological molecules in liquid [1]. In this study, we utilized the static displacement of chemically functionalized CNT cantilevers to measure interaction forces between antigens and antibodies.

We made defects on a CNT tip by irradiating the high power laser in air to induce carboxyl group to the tip. The CNT tip was then activated with a cross-linker to bind Immunoglobulin G (IgG) produced in rabbits. After washing with phosphate buffer, the CNT cantilever was immersed into IgG solution to form covalent bonds with IgG. On the other hand, we coated a tungsten tip with poly-l-lysine, which promotes the attachment of molecules that bind rabbit IgG. Goat antibodies against rabbit IgG was attached to the tungsten tip to measure interaction forces between the antibody-attached tungsten tip and antigen-bound CNT cantilever.

The measurement of interaction forces was performed under an optical microscope by measuring the static deflection of the IgG-attached CNT cantilever. The antigen-antibody bindings were observed while pulling and pushing the antibody-attached tungsten tip repeatedly (Fig. 1). From this result, the binding force between two molecules can be identified.

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[1] S. Sawano, T. Arie, and S. Akita, Nano Lett. 10, 3395 (2010).
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Fig. 1 Optical microscope images during interaction force measurement using a CNT cantilever.

# New synthesis of ultrafine nanoparticles from nanowires encapsulated in carbon nanotubes

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Ultrafine nanoparticles have known to possess properties that are distinctly different from that of bulk solids <sup>[1]</sup>. The development of solution phase synthesis of various ultrafine nanoparticles is, thus, of great importance to produce novel functional nanomaterials. In this study, we have developed a new solution phase synthesis of ultrafine nanoparticles based on a solution phase extraction of nanowires encapsulated in single-wall carbon nanotubes (SWCNTs). In this method, ultrathin nanowires are removed from interior space of SWCNTs to form ultrafine nanoparticles. We have focused on synthesis of AgI nanoparticles because AgI nanoparticles, whose diameter is

less than 10 nm, can retain superionic phase at room temperature <sup>[2]</sup>.

Figure 1(a) shows high resolution transmission electron microscope (HRTEM) image of AgI@SWCNTs synthesized by the sublimation method already reported <sup>[3]</sup>. As clearly seen, dark linear contrasts arising from AgI nanowires exist in SWCNTs. solution phase extraction of encapsulated The nanowires was then performed by a sonication of the sample with polyvinylpyrrolidone (PVP); PVP was used as a stabilizer for AgI nanoparticles by forming a micell with nanoparticles <sup>[4]</sup>. Finally, vacuum filtration was performed to separate AgI nanoparticles from SWCNTs. Figure 1 (b) shows HRTEM image of so-synthesized AgI nanoparticles, and their mean diameter was about 4 nm. To the best of our knowledge, they are one of the smallest AgI nanoparticles ever reported.

In the presentation, details of the synthesis method and further structural characterization of AgI nanoparticles will be discussed.

- [1]R. Ueda, Prog. Mater. Sci.35, 1 (2009).
- [2]R. Makiura, et al., Nature. Mater. 8, 476 (2009).

[3]R. Kitaura, et al., Angew.Chem.Int.Ed. <u>48</u>, (2009).

- [4]Y. Miyata, et al., ACSnano. 4, 5807 (2010).
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Fig.1. HRTEM images of(a) AgI@SWCNTs(b) Agl nanoparticles

## Fabrication of High Conducting NBR/SGCNT Composites Using a Wet-process

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Supergrowth carbon nanotubes (SGCNTs) with unique physical, chemical and electrical properties associated with an extremely high specific surface area have been realized as an ideal material for the fabrication of highly thermal and electrical conducting polymer composites. There are two well-known processes for the fabrication of the polymer/CNT composites. The first is based on a dry-process in, which the CNTs are directly dispersed in a melting polymer matrix. The second is based on a wet-process, in which both the polymer and CNTs are dispersed in aqueous or organic solutions before mixing to provide a composite material. Actually, each process has both merit and demerit.

The fabrication of the acrylonitrile-butadiene rubber (NBR)/CNT composites using a melt-mixed dry process were reported previously.<sup>1</sup> However, the electrical conductivity and the mechanical properties of the dry-processed NBR/CNT composites were found to be strongly affected by their mixing conditions, such as mixing time, rotor speed, and cooling rates. To overcome these problems, we use an aqueous solution wet-process for the fabrication of the NBR/CNT composites was carried out through the addition of a well-dispersed SGCNT/surfactant aqueous solution into a commercially available NBR latex solution. In order to remove the surfactant, the latex-based NBR/SGCNTs in the solution was precipitated in isopropanol and then dried in vacuum at 50°C for 12h. The electrical conductivity of the NBR/SGCNT composite films was measured using a four point

probe apparatus. As shown in Fig. 1, the electrical conductivity of the prepared NBR/SGCNT composites was increased proportionally with the increase in the SGCNT contents. In addition, the electrical conductivity of the NBR/SGCNT composite was also found to be much higher than that obtained by a dry-process. Mixing conditions for the synthesis of the NBR/SGCNT composites by the wet-process that influence on their electrical conductivity will also be discussed.

[1] B.M. Cho et al. J. Appl. Polym. Sci., 116, 555, 2010.
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Fig.1. Electrical conductivity of the wet processing NBR/SGCNT composite.

# Estimation of barrier height in CNT-FETs with graphitic carbon interlayer contacts

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It has been reported that the contact resistance of the CNT-FETs with p-channel behavior was decreased by inserting graphitic carbon (G-C) layer between contact metal and CNTs [1]. Although the reduction in the contact resistance has been attributed to the improved wetting at the contacts, the electrical characteristics of the G-C/CNT interface are not understood sufficiently. In this study, we have fabricated CNT-FETs with G-C interlayer contacts and studied the electrical properties of the contacts in detail. The barrier heights at the contact were measured based on the temperature dependence of the drain current.

Schematic cross section of the G-C interlayer between CNTs and Au electrodes of the CNT-FETs is shown Fig. 1. Graphitization by annealing (800°C, 15 min in vacuum) was confirmed by Raman spectroscopy and also by TEM observation. CNT-FETs showed p-type, and have larger transconductance than those with Au contacts, suggesting the reduction of the contact resistance in the devices with G-C interlayer. In order to eliminate the effect of the adsorbed oxygen on the electrical properties of the device, the devices were annealed at 200°C for 90 h in vacuum. Fig. 2 shows  $I_{\rm D}$ - $V_{\rm GS}$  characteristics of the CNT-FETs, which showed p-type conduction in air and ambipolar in vacuum after annealing. In order to study the origin of the conduction-type change, we measured the temperature dependence of the  $I_{\rm D}$ - $V_{\rm GS}$  characteristics in vacuum at a small bias voltage where the hysteresis was negligibly small. The barrier heights were 280~360 meV for electrons and 170~220 meV for holes as shown in Fig. 3. These values suggest that  $E_{\rm F}$  of G-C is located at slightly below the midgap of the CNTs in vacuum. This suggests that p-type conduction of the CNT-FETs with G-C interlayer in air is attributed to the adsorbed oxygen.



Fig.2.  $I_{\rm D}$ - $V_{\rm GS}$  characteristics of the CNT-FETs with G-C interlayer contacts.

Fig.3. Arrhenius plots at  $V_{GS} = -1.5$  and 1.5V.

[1] Y. Chai *et al.* IEEE Trans. ED. **59**, no. 1, pp. 12-19, (2012).
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# Enhanced Transparent Conducting Performance of CVD Nanotube Networks with Tailored Microstructure

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Flexible carbon nanotube transparent conducting films (CNT-TCFs) have gathered great interest owing to their high mechanical flexibility and compatibility to role-to-role fabrication under ambient, and many applications are expected such as flexible displays, touch screens, and transparent electrodes for liquid crystal displays. However, industrial applications of CNT-TCFs are still limited because of the insufficient transparent conducting performance even for those of SWCNTs (~ 500  $\Omega$ /sq at 85 % transmittance including base films) and of the high cost of SWCNTs (~1,000 USD/g). We recently realized high-yield production of sub-millimeter-long few welled CNTs (FWCNTs) and SWCNTs by semi-continuous [1] and batch [2] fluidized bed chemical vapor deposition (CVD) processes, respectively. The sub-millimeter-long CNTs are expected to provide fair electrical conductivity and mechanical flexibility by reducing the number of junctions among CNTs in their random networks.

In this work, we studied mild dispersion processes to suppress the shortening of CNTs and hierarchical control of the conduction paths for multilayer network films of (sub)millimeter-long SWCNTs and FWCNTs. Millimeter-long SWCNTs (1.5-4 nm diameter, 1.0 mm length, > 99 wt% purity) were synthesized in 10 min by on-substrate CVD from  $C_2H_4/H_2/Ar$  with water addition [3], and sub-millimeter-long FWCNTs (6–10 nm diameter, 0.4 mm length, 99 wt% purity, triple-walled on average) were synthesized by fluidized-bed CVD [1], both using Fe/Al-O catalysts. Their aqueous suspensions were prepared by mild sonication using sodium dodecyl benzene sulfate (SDBS) as surfactant. The CNT-TCFs were prepared by vacuum filtration methods. Fig. 1 shows the sheet resistances of SWCNT films with 80% optical transmittance (excluding base films). The monolayer film had a fair sheet

resistance although CVD-SWCNTs are used here (note that low resistive TCFs have been reported mostly for arc- or laser-SWCNTs). And the sheet resistance remarkably decreased for layer numbers of 2 or higher. The reduced number of junctions by mild dispersion and improved junctions by multiple-step filtration possibly yielded such improved performance. Transparent conducting performances of CNT-TCFs of other structures will also be reported and discussed in the presentation.

[1] D. Y. Kim, et al., Carbon 49 (6), 1972 (2011).

[2] D. Y. Kim, et al., Carbon 50 (4), 1538 (2012).

[3] S. Noda, et al. Jpn. J. Appl. Phys. 46 (17), L399 (2007).

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Fig. 1 Sheet resistance of multilayer SWCNT-TCFs of 80% optical transmittance.

## Inkjet printing of ultra-fine carbon-nanotube thin films

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Printability of single-walled carbon nanotube (SWCNT) is attractive properties for producing printed electronics on flexible substrates. We have already performed inkjet printing of SWCNT transistors at room temperature [1]. However, in inkjet technique, scaling down the size of thin film is about to reach the limitations imposed by the droplet size, because the size of thin film is determined by it. Recently, self-assembled monolayers (SAMs) being useful for tuning surface wettability due to its simplicity can, on one hand, build a wettability contrast, and, on the other hand, provide a method to reduce droplet size on substrates. We used this technique to overcome in the context of scaling down the device size, and successfully reduced the film width from 200  $\mu$ m to 100  $\mu$ m with ultraviolet (UV) irradiation through the metal mask [2]. This success strongly indicates that finer mask pattern leads to smaller device size. Here, we used the photo mask instead of metal mask to break down into finer width.

Figure 1 shows a schematic illustration of fabrication process. Si substrate was modified with 1,1,1,3,3,3-hexamethyldisilazane (HMDS) SAMs to make a surface hydrophobic. We irradiated UV through a photo mask (~ 5 $\mu$ m) to remove HMDS partially, and printed SWCNT inks. As shown in Fig. 2(a), the width of obtained thin film was drastically removed from 210  $\mu$ m to 20  $\mu$ m. In addition, we fabricated extremely narrow SWCNT films (< 1  $\mu$ m) using the strong coffee-stain effect at hydrophobic/hydrophilic interface (Fig. 2(b)). Such a SWCNT string produced by inkjet printing might open new route to ultra-fine SWCNT printed electronics.

In summary, we performed fabrication of fine SWCNT films (~ 20  $\mu$ m) using SAMs patterned by photo mask, which is necessary for inkjet-printed SWCNT electronics.





## Optical absorption and Raman scattering spectra of C<sub>10</sub>H<sub>2</sub> polyyne molecules inside single-wall carbon nanotubes

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Polyyne molecules,  $H(C=C)_nH$  (*n*=4-8), are trapped inside single-wall carbon nanotubes, forming  $C_{2n}H_2@SWNT$  [1,2]. In double-wall carbon nanotubes, even a growth of longer chains of sp-carbon structure from molecular  $C_{10}H_2$  is observed by HRTEM and Raman spectroscopy [3]. Concerning the electronic structure of the hybrid system of  $C_{2n}H_2@SWNT$ , the mechanism for the resonance enhancement of the Raman scattering signals for polyyne molecules around 2000 cm<sup>-1</sup> has been studied in detail [4,5]. The electronic structure of the hybrid system is a key for understanding of the mechanism for the optical properties. We have conducted large-scale synthesis of polyyne-encapsulating SWNTs, in order to observe optical absorption spectra of  $C_{10}H_2@SWNT$ .

Single-wall carbon nanotubes of relatively large diameter were produced by laser ablation of a graphite/Ni/Co composite pellet in an argon-gas flow. The SWNT-forming region was kept at 1250 °C for controlling of the diameter of SWNTs. After the treatment of as-grown SWNTs with hydrogen peroxide for purification, ~10 mg of the SWNT film was dipped in a solution of  $C_{10}H_2$  in hexane for 3 days under ambient temperature. The sample of  $C_{10}H_2@SWNT$  was dispersed in a solution of sodium cholate in D<sub>2</sub>O by sonication. Spectroscopic characterization was performed by Raman spectroscopy with the excitation at 532 nm and by optical absorption spectroscopy with a spectrophotometer.

Figure 1 shows Raman spectra of  $C_{10}H_2$ @SWNT. The peak at 173 nm for RBM frequency surmises that the majority of SWNTs are those of relatively large diameter, 1.35-1.40 nm. The peak at 2066 cm<sup>-1</sup> for a symmetric stretching  $\sigma_g$  mode of  $C_{10}H_2$ , namely "P" peak, is observed relatively strongly under the experimental condition [6]. According to the encapsulation of  $C_{10}H_2$ , other features are newly appearing, namely peaks for CH-stretching  $\sigma_g$  mode of  $C_{10}H_2$ at 3145 cm<sup>-1</sup>, for G+P combination at 3636 cm<sup>-1</sup>, and for 2P overtone at 4130 cm<sup>-1</sup>. The optical absorption spectra will be presented in the poster.

[1] D. Nishide et al. Chem. Phys. Lett. 428, 356 (2006).

[2] D. Nishide et al. J. Phys. Chem. C 111, 5178 (2007).

[3] C. Zhao et al. J. Phys. Chem. C 115, 13166 (2011).

[4] L. Malard et al. Phys. Rev. B 76, 233412 (2007).

[5] L. G. Moura et al. Phys. Rev. B 80, 161401 (2009).

[6] T. Wakabayashi et al. Eur. Phys. J. D 52, 79 (2009).

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Fig. 1. Raman spectrum of C<sub>10</sub>H<sub>2</sub>@SWNT.

## Semiconducting Bilayer Graphene Coated by Ionic Layers

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Semiconducting forms of graphene are indispensable to develop graphene based switching electronic devices taking advantage of their high carrier mobility. Various approaches to generate the semiconducting graphene have been proposed and implemented, such as a bilayer graphene under electric field normal to atomic layer, shredding of graphene and chemical modifications. In this work, we demonstrate the possibility of band gap engineering of bilayer graphene coated by ionic layers based on DFT-LDA calculation. Here we consider the structural model that the bilayer graphene is put between positive ions and negative ions forming molecular layers (Fig. 1(a)). The bilayer graphene inserted in ionic layers feel electronic field induced by the charge transfer between cation and anion molecular layers. This electronic field causes finite energy band gap of about 0.3 eV leading to the semiconductiong electronic properties on bilayer graphene. Figure 1(b) shows the electronic band structure of bilayer graphene inserted into the molecular layers comprising of 1-ethyl-3-methylimidazolium ion and tetrafluoroborate ion. We find finite energy band gap between  $\pi$  band and  $\pi^*$  band of bilayer graphene. The semiconducting bilayer graphene with intrinsic finite energy gap could be utilized into the normally-off semiconductor devices.



Fig.1 (a) Schematic picture of bilayer graphene inserted in an ionic liquid and (b) the electronic band structure of bilayer graphene coated by 1-ethyl-3-methylimidazolium ions and tetrafluoroborate ions. The Fermi level is set to 0 eV.

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## A novel reduction method for graphene oxide and expanded graphite by water freezing expansion

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Graphene has been regarded as prospective electrode material of lithium ion battery and ultra-capacitor since it has good electric conductivity and mechanical properties with extensive surface area. The optical transparency of graphene shows possibility as transparent electrode. However, it is hard to manufacture pure graphene single layer with extensive surface area required to commercialization. In the case of chemical exfoliation, it has the possibility of explosion during reactions between strong acid and strong base. Furthermore it produces unnecessary chemical combinations and byproducts cause decrease of electric conductivity of graphene.

In this study, graphene was manufactured by new manufacturing process combined physical and chemical method. The graphene manufacturing process was carried out safely compared with existed process. Expanded graphite was manufactured by physical expansion method with water freezing expansion for reduce exfoliation energy for graphene manufacturing. After that, it was oxidized by sulfuric acid solution diluted with THF. Finally, graphene oxide was reduced by borane-tetrahydrofuran. The characteristics of prepared expanded graphite and graphene were analyzed by field emission scanning electron microscope, thermo gravimetric analysis, differential scanning calorimetry, X-ray diffraction, raman spectroscopy.



Fig.1 FE-SEM images of graphite, graphite oxide and grapheme.

- [1] Geim, A. K. and Novoselov, K. S. (2007). "The rise of graphene". Nature Materials 6 (3): pp.183-191.(2007).
- [2] Y. Hernandez et al. "High-yield production of graphene by liquid-phase exfoliation of graphite", Nature nanotech. 3, p.563(2008).
- [3] C. Berger et al. "Electronic confinement and coherence in patterned epitaxial graphene", Science 312, p.1191(2006)
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#### Direct synthesis of hexagonal boron nitride on silicon wafers

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Hexagonal boron nitride (h-BN) is a fascinating substrate to maximize the potential applications of graphene-based electronics because it exhibits unique properties such as atomically-smooth surface and a large bandgap.[1] The use of h-BN on silicon wafers is highly desired because the h-BN/graphene hybrids could improve silicon-based devices such as high-speed electronics. For this purpose, large-area and thin-layer h-BN films have been synthesized on metal substrates by chemical vapor deposition.[2,3] Unfortunately, the ensuing transfer processes of h-BN cannot avoid impurity incorporation and film damages such as cracks and holes. Such issues should be solved if h-BN could be formed directly on silicon wafers.

In this presentation, we report the direct synthesis of h-BN on silicon wafers and quartz substrates using thermal CVD of ammonia borane (NH<sub>3</sub>BH<sub>3</sub>). The growth of h-BN was confirmed from optical absorption and Raman spectra. The samples show a distinct absorption peak at 6.1 eV and almost zero absorbance in the visible range (Fig.1a). It is found that the present sample is composed of double layer h-BN from the comparison with the spectra of monolayer h-BN.[3] The Raman peak at 1370cm<sup>-1</sup> is assigned to an in-plane vibration mode of the h-BN (Fig.1b). Furthermore, patterned growth of h-BN is also achieved by covering the substrates with gallium during the

CVD. The present findings provide a promising way to develop the potential applications of graphene, carbon nanotubes, and other electronic materials because of their compatibility to existing semiconductor processes.



Fig.1 (a) Optical absorption and (b) Raman spectra of thin h-BN films.

[1] C. R. Dean et al., Nat. Nanotechnol. 5, 5722 (2010). [2] Y. Shi et al., Nano.Lett. 10, 4134 (2010).

[3]. K. K. Kim et al., Nano Lett. in press.

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## Synthesis of Carbon Nanoribbons by the Submarine-style Substrate Heating Method

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Graphene is expected to be a material with very high mobility. However, when it is mounted on  $SiO_2/Si$  substrates, its mobility becomes degraded due to the carrier scattering by the  $SiO_2$  layer. Suspension of graphene sheets is one of the solutions to evade the scattering and to improve the mobility. Etching the  $SiO_2$  layer underneath a graphene sheet has been applied to achieve it [1]. It would be more straightforward if suspended graphene sheets are grown directly on the substrate. In this study, we have employed the submarine-style substrate heating method for the synthesis of nanocarbon materials and obtained ribbon-formed nanocarbon materials suspended between zeolite particles dispersed on Si substrates.

In the submarine-style substrate heating method, a substrate coated with catalysts is settled in a case with its bottom open. The case is immersed in alcohol (carbon source) while Ar gas is supplied to the case continuously, which keeps a gas space around the substrate. This method is not only as simple as the liquid phase synthesis [2], but also applicable to a wide variety of catalysts including organometalic compounds which dissolve in alcohol.

In this work, we used ethanol or 2-propanol as alcohol, and cobalt acetate and iron acetate supported on zeolites as catalysts.  $SiO_2/Si$  substrates were coated with the catalysts and heated with a carbon heater attached on the other side of the substrate. In the synthesis, the

temperature of the substrates were kept around 1173 K for 10 min. We analyzed products with FE-SEM and micro-Raman spectroscopy. In both cases using ethanol 2-propanol, ribbon-formed and nanomaterials were produced. They were found to be suspended between zeolite particles. Figure 1 shows one of the ribbon-formed materials obtained using ethanol. The 2D peak in the Raman spectrum was observed at 2697 cm<sup>-1</sup> with the FWHM of 73 cm<sup>-1</sup>. Judging from the peak profile, we think tentatively that the ribbon-formed nanomaterials could be few-layered graphene.



Fig.1 Ribbon-formed nanocarbon material (indicated with an arrow)produced with the submarine-style substrate heating method.

[1] K.I. Bolotin *et al.* Solid State Commun. 146, 351 (2008).
[2] M. Nishitani-Gamo et al., Jpn. J. Appl. Phys. 46, 6329 (2007).
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#### Effect of laser irradiation on the Raman spectra of graphene

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The study on irradiation effects on graphene is of very interest for tailoring its properties, understanding irradiated-damages, and producing new materials. The irradiation effects by ion and electron beams on graphene have been investigated by Raman spectroscopy so far [1,2]. It is expected that laser irradiation also gives rise to various effects on graphene, as carbon nanotubes [3]. In this paper, we report the effect of laser irradiation on the Raman spectra of graphene.

Graphene samples prepared by mechanical exfoliation and chemical vapor deposition were used for irradiation experiments. The samples were irradiated with a 532 nm from YAG laser. The irradiation power on the sample was  $\sim 200 \text{ kW/cm}^2$ .

Fig. 1 shows Raman spectra of monolayer graphene before and after laser irradiation. It is found that relative intensity of D band at ~ 1345 cm<sup>-1</sup> increases after irradiation. This means that some defects in monolayer graphene can be introduced by irradiation. In addition, the relative intensity of 2D band at ~ 2680 cm<sup>-1</sup>, especially higher-frequency component, decreases after irradiation. This might be understood from the origin of 2D band. Similar

behaviors were also observed for few-layer graphene. On the other hand, the same irradiation intensity led to no significant change in Raman spectra for multi-layer graphene. This shows that monolayer and few-layer grapphene samples easily suffer radiation damage, compared with multilayer graphene. Such laser irradiation effect on graphene will be discussed comparing with ion bombardment and electron beam irradiation.



Fig. 1 Raman spectra of monolayer graphene (a) before and (b) after laser irradiation.

- [1] L.G. Cancado et al., Nano Lett. 11, 3190 (2011).
- [2] D. Teweldebrhan, et al., Appl. Phys. Lett. 94, 013101 (2009)

[3] M. Hakamatsuka, et al., Carbon 49, 1869 (2011)

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# Electrical response of silsesquioxane bridged graphene layers to organic vapor

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We have recently reported that polar organic molecules were size-selectively intercalated into the pillared carbon prepared from graphite oxide (or graphene oxide; heareafter GO) repeatedly silylated with methyltrichlorosilane in which graphene layers are covalently connected with each other by silsesquioxane pillars [1]. In this study, this silsesquioxane bridged graphene films were prepared from various precursors and their electrical response to various organic vapors were examined.

Graphite oxide was silylated with octyltrichlorosilane and *n*-hexadecylamine was in tercalated into the resulting sample. The dispersion of *n*-hexadecylamine containing silylated GO was cast on quartz substrate and thin film was obtained. This was further silylated with methyltrichlorosilane ( $C_1S_1$ ) twice or 3-aminoprppylethoxysialne (APS) at various conditions. The product was heated at 500°C under vacuum and silsesquioxane bridged graphene films were obtained.

The resulting films possessed interlayer spacings of 1.3-1.8 nm. Various organic molecules including vinylene carbonate, diethoxyethane molecules were intercalated into the films and interlayer expansion was observed. This indicates that the obtained film samples possess similar soft pores to those of powder samples prepared previously [1].

Fig.1 shows the electrical response of silsesquioxane bridged graphene film prepared from

GO reacted with C<sub>1</sub>Si and then with APS for 6h to various organic vapors as a function of time. It increased quickly upon exposure to vinlylene carbonate vapor and the resistance increased by 10 % after 5h. On the other hand, exposure of the film to larger diethoxethane molecules resulted in the slower increase of the resistance and smaller increase of the electrical resistance. The slower diffusion and larger occupied volume in the interlayer gallery of diethoxyethane molecules would be responsible for the above electrical response.

Reference [1] Y. Matsuo *et al*. Chem. Commun. **47**, 4009 (2011).

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Fig.1 Electrical response of silsesquioxane bridged graphene film to vinlyene carbonate and diethoxyethane.

### Inner and outer double Raman scattering process of graphene

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In graphene, double resonance Raman (DRR) spectra are important not only for G' (2D) analysis but also weak Raman features (M band) which are sensitive to the stacking order of few layer graphene. From the analysis of experimental Raman spectra of graphene, it was considered that DRR intensity by intervalley scattering process was involved in the scattering of electronic states along the K $\Gamma$  line with phonons along the KM line (outer DRR scattering process) [1-3]. However, recently, experiment and calculation demonstrated that inner DRR scattering process, in which the scattering of electronic states along the KM line with phonons along the KM line with phonons along the KT line, also contributes to DRRI of graphene [4]. Moreover, the selection of the scattering process depends on phonon mode. To evaluate the scattering process of DRR peaks of graphene, we need to calculate electron-phonon matrix element for possible phonon combination modes of graphene. It is expected that such analysis will contribute to analysis of Raman spectra of strained graphene and of twisted bilayer graphene. In this paper, we show that electron-phonon interaction between particular initial and final electron states mainly contributes DRR intensity of graphene.

Here, we calculate electron-phonon matrix elements of graphene for possible phonon combination mode of DRR scattering process in order to find and evaluate main DRR scattering process for each Raman peaks graphene. Electron-phonon matrix elements are calculated by using the extended tight binding scheme, the deformation potential, and force constants model [5]. Our calculation results show that the DRR peak of the combination mode of iTO and LA phonons for intervalley scattering (2,450 cm<sup>-1</sup> Raman peak) comes from inner process. We will discuss other phonon combination modes of graphene and compare our calculation results with experiments.

[1] J. Kurti et al. Phys. Rev. B 65, 165433 (2002).

[2] A.C. Ferrari et al. Phys. Rev. Lett. 97, 187401 (2006).

[3] L.M. Malard et al. Phys. Rev. B 76, 201401 (2007).

[4] D.L. Mafra et al. Carbon 49, 1511 (2011).

[5] J. Jiang et al. Phys. Rev. B 72, 235408 (2005).

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## Electronic features of graphene nano-pore arrays

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**Abstract:** Graphene, an ultimate two-dimensional sheet with thickness as thin as one carbon atom, is attracting significant attention. In particular, edge states are of great interest with respect to high electronic density of states (EDOS), electron localization, and also polarized spin transport.<sup>1-3</sup> However, they had been reported only by theoretical works, because fabrication of edges by lithographic methods easily introduces defects and damages to edges and they tend to obstruct edge-related phenomena. In contrast, we for the first time experimentally reported edge-related phenomena in low-defect graphene nanoribbons (GNRs)<sup>4</sup> and graphene nano-pore arrays (GNPAs)<sup>5-7</sup> fabricated by non-lithographic methods (i.e., unzipping of carbon nanotubes and etching of graphenes using porous alumina templates as a mask). In hydrogen-terminated GNPAs with honeycomb like array of hexagonal nanopores, ferromagnetism and anomalous magnetoresistance oscillation arising from nano-pore edges were observed, because the nano-pore edges had possible zigzag-atomic structure by edge reconstruction after high-temperature annealing and the interpore regions can act as GNRs.<sup>5-7</sup>

Here, we report electronic features of the GNPAs. Even apart from magnetic behaviors, GNPAs can provide interesting and useful electronic features, because they act as a large ensemble of GNRs, which are fabricated at the interpore space as mentioned above. We observe semiconductive behaviors and single electron tunneling behaviors, which are sensitive to structures of the GNPAs and kinds of foreign atoms for termination of the nanopore edges. GNPAs will be promising for realization of integrated circuit consisting of GNRs, if the edge atomic structures can be controlled.

#### **References**:

- 1. Nakada, K., Fujita, M., Dresselhaus, G. & Dresselhaus, M. S., Phys. Rev. B 54, 17954 (1996).
- 2. L. Yang, C. H. Park, Y. W. Son, M. L. Cohen, S. G. Louie, Phys. Rev. Lett. 99, 186801 (2007).
- 3. K. Wakabayashi, Phys. Rev. B 64, 125428 (2001).
- 4. T.Shimizu, J.Haruyama, D. C.Marcano, D. V. Kosynkin, J.M.Tour, K.Hirose, K.Suenaga, *Nature Nanotechnology* 6, 45 (2011)
- 5. K. Tada, J. Haruyama, H. Yang, M. Chshiev, T. Matsui, H. Fukuyama, *Phys. Rev. Lett.* 107, 217203 (2011)
- 6. K. Tada, J. Haruyama, H. Yang, M. Chshiev, T. Matsui, H. Fukuyama, *Appl.Phys.Lett.* **99**, 183111 (2011)
- 7. T. Shimizu, J. Nakamura, K. Tada, Y. Yagi, J. Haruyama, Appl. Phys. Lett., 100, 023104 (2012)

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## Nanographene synthesized from platelet carbon nanofiber using supercritical fluid exfoliation

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Nanographene has attracted intense attention owing to the potential for manipulation of its characteristics, such as (semi-)conductivity and magnetism by the edge states [1]. As the application field of nanographene expands from electronics to magnetics, photoelectronics and electrochemical devices, techniques for the large-scale production of high-quality nanographene have become essential. In this study, supercritical fluid (SCF) exfoliation was applied to the scalable production of high-quality nanographene. Using this technique, undesirable introduction of functional groups/defects can be prevented during exfoliation [2].

Nanographene was synthesized from platelet carbon nanofiber (p-CNF), having a mean diameter of ca. 140 nm. The p-CNF consisted of a large number of nanographene platelets vertically stacked to the basal plane. Therefore, nanographene could be readily obtained by exfoliation. SCF exfoliation was performed in supercritical ethanol by placing ethanol and the p-CNF into a batch-type reactor. The reactor was placed into a furnace kept at 400 °C.

AFM measurement revealed that continuous heating of the reactor for 60 min generated sheet-like materials, a portion of which was less than 1 nm thick. It was concluded that such thin sheets were monolayer graphene and the exfoliation process was successful. Moreover, the lateral size of the thinner graphene sheets was distributed within the smaller size-range, which suggests that during the exfoliation process, cutting of the basal plane was progressed.

In order to enhance the yield of monolayer nanographene, the temperature profile was modified. A second heating protocol was used, in which the heating and cooling processes were intermittently repeated 6 times; the reactor was heated for intervals of 10 min. As a result, intermittent heating further enhanced the exfoliation and cutting processes.

Figure 1 shows representive Raman spectra obtained from products above-mentioned two heating protocols. It is well-known that 2D band shifts to the lower-wavenumber side as the laver of number graphene decreases. Moreover, if all of the defects can be assigned to the edge state, the intensity of D band is enhanced as the lateral size Fig.1 Representive Raman spectra obtained from products by decreases. Compared with the products by the initial continuous heating



continous and intermittent heating protocols (normalized by G band intensity).

protocol, Raman spectrum of products by intermittent heating shows the shift of 2D band to the lower wavenumber side and the enhancement of D-band intensity. This tendency is consistent with the results of AFM measurement. Moreover, we further discuss about the defects in the basal plane using the results of AFM and Raman spectroscopy. The details will be presented in 42<sup>nd</sup> FNG General Symposium.

[1] Y. W. Son et al. Nature 444, 347 (2006). [2] D. Rangappa et al. Chem. -Eur. J. 16, 6488 (2010). Corresponding Author: T. Tomai, Tel: +81-22-217-5816, Fax: +81-22-217-5828, E-mail: tomai@tagen.tohoku.ac.jp

## **Graphene Formation from Metal-Carbon Hybrid Films**

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Graphene has been attracting many researchers because of its unique properties. One of the great efforts has exerted to develop sophisticated methods for synthesis of large area graphene films. Recently, chemical vapor deposition on Cu foil has been demonstrated. [1,2] Those results opened the way to new industrial integration processes, however, the method needs complicated processes such as polymenthyl methacrylate coating and remove of Cu foil to transfer the graphene on a conventional substrate. Zheng et al. [3] proposed a new method in which the graphene was synthesized from a metal and amorphous carbon stacked film. They commented that their method might be extended to direct formation of graphene on a conventional substrate. In this presentation, we propose the use of metal-carbon hybrid film instead of the stacked film for direct formation of graphene.

Fe was employed as a metal and metal-carbon hybrid films were formed on oxidized Si substrates by sputtering of Fe target under  $CH_4$  and Ar mixed gas. The hybrid films were then thermally annealed in a vacuum at temperature range of 500 - 800 °C for 20

min. The thickness and composition of the films were measured by X-ray fluorescence analysis and X-ray photoelectron spectroscopy, respectively. The annealed samples were investigated by Raman spectroscopy, scanning electron microscope, and transmission electron microscope.

Fig.1 shows a surface morphology of annealed sample at 800 °C. Initial thickness of the sample was 20 nm and atomic ratio of carbon was 17 at%. Spherical shape particles and patches are observed. The particles are conformed as Fe. From the observation cross-section TEM, the patches consist of 4 - 9 layers graphene. Raman spectrum of the sample is shown in Fig.2. Although the size of obtained few-layer graphene is small, our results show the capability of the direct graphene formation on the substrate.

**Reference:** [1] X. Li et al., *Science* **324**, 1312 (2009) [2] S. Bae et al., *Nat. Nanotech.* **5**, 574 (2010) [3] M. Zheng et al., *APL* **96**, 063110 (2010)



**Fig.1** SEM image of an annealed sample at 800 °C.



**<u>Fig.2</u>** Raman spectrum of an annealed sample at 800  $^{\circ}$ C.

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### IR spectra of polyyne-iodine complexes in solutions

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Hydrogen-end-capped polyyne,  $H(C=C)_n H$  ( $n\geq 2$ ), is one of the simplest model compounds for the system of sp-hybridized carbon chain. The molecule has cylindrically symmetric  $\pi$ -electron systems, and exhibits absorption bands for the allowed transition in the UV and those for a forbidden transition in the near UV [1,2].

Recently, we reported that the allowed transition diminishes, while the forbidden emerges upon addition of iodine molecules into the solution of polyyne molecules under illumination with visible light [3]. This spectral change indicated the formation of a molecular complex by polyyne and iodine molecules [3]. The composition of the polyyne-iodine complex was determined to be 1:3 for polyyne : I<sub>2</sub> ratio from the concentration-dependence experiments [3]. The <sup>1</sup>H- and <sup>13</sup>C-NMR spectra showed that the polyyne-iodine complex has  $C_2$  symmetry [3].

In this work, we measured IR spectra for polyyne-iodine complexes in solutions for investigation of the molecular structure. Figure 1 shows IR spectra of  $C_{10}H_2$  (dotted line) and  $C_{10}H_2I_6$  (solid line). We assigned an absorption band at 625 cm<sup>-1</sup> to CH bending (Fig. 1a) and an absorption band at 3306 cm<sup>-1</sup> to CH stretching (Fig. 1b) modes of  $C_{10}H_2$ . In the spectra for  $C_{10}H_2I_6$ , absorption bands were observed at 610 (Fig. 1a) and 3085 cm<sup>-1</sup> (Fig. 1b). We consider that the spectral shifts from 625 to 610 cm<sup>-1</sup> and from 3306 to 3085 cm<sup>-1</sup> is due to the formation of the complex. These observations suggest that the molecular framework of  $C_{10}H_2$  is retained in the complex of  $C_{10}H_2I_6$ .

[1] E. Kloster-Jensen et al. Helv. Chem. Acta. 57, 1731(1974).

[2] T. Wakabayashi et al. Chem. Phys. Lett. 446, 65 (2007).

[3] Y. Wada et al. J. Phys. Chem. B. 115,8439(2011).



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## The Fate of PEG-Functionalized Single Wall Carbon Nanohorns after Intravenous Injection into Mice

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Carbon nanotubules such as single-wall carbon nanohorns (SWNHs) and nanotubes (SWNTs) have been extensively studied for application in drug delivery system and hyperthermia agents for cancer and other disease therapies. The pharmacokinetics of these nanocarbons after administration into living body certainly need to be clarified before practical application. Raman spectroscopy have been used to probe the long-term fate of SWNTs after administration into mice, but the Raman intensity of SWNTs might be influenced due to the existence of different components in different tissues leading a low accurate assessment. Our previous study [1] has shown that the *in vivo* biodistribution of SWNHs can be quantified by using  $Gd_2O_3$  labels embedded in SWNHs (Gd@SWNHs). In this study, we show that time course of the circulation, distribution and clearance of Gd@SWNHs functionalized with PEG in mice for a long-term, 4 months.

SWNH aggregates with two different sizes of about 70 nm and 100 nm were used, which were obtained by CO<sub>2</sub> laser ablation of graphite. SWNHs were labeled by Gd<sub>2</sub>O<sub>3</sub> particles as with previously non-covalently coated DSPE-PEG5k. The reported [1] and PEG-functionalized Gd@SWNHs (Gd@SWNHs-PEG) were dispersed in phosphate buffered saline and injected into mice through the tail veins (dose: 5 mg of SWNHs per 1 kg of body weight). Mice were sacrificed at time points of 1 h, 6 h, and 1-120 days after injection. The quantities of Gd@SWNHs-PEG in organs and in whole mice were estimated from the Gd quantities measured by ICP-AES.

The results showed that the Gd@SWNHs-PEG circulated in blood over 6 h and then mainly distributed in liver and spleen. The distributions of SWNH aggregates with two different sizes were similar. The quantities of SWNHs in liver changed with the post-injection time (PIT), while those in other organs did not change. The amount of SWNHs in liver increased and reached a maximum, about 70 % of the total injected quantity, at 24 h of PIT, and then decreased to about 30% at PIT 30 days. The total SWNHs in a whole mouse decreased for about 40% when PIT was longer than 30 days. About 10-15% SWNHs were detected in feces. It is presumed that disappeared SWNHs from liver excreted via biliary pathway.

[1] J. Miyawaki, S. Matumura, et al. ACS Nano 3, 1399 (2009).

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## Microbial growth in water containing nanoparticles of fullerene C<sub>60</sub>

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 $C_{60}$  is a carbon allotrope and is not soluble in water. However, nanoparticles made of  $C_{60}$  can be dispersed stably in water even without using any stabilizing agents. Such dispersions may have uses in biological or medical applications, which inevitably use water as a solvent. We have been working with preparation and physicochemical characterization of  $C_{60}$  nanoparticles dispersed in water.<sup>[1,2,3]</sup> During the course of the study, we encountered very frequent growth of microorganisms in dispersions stored in the laboratory. As  $C_{60}$  was a sole major carbon source in the dispersions, the finding suggests that these microorganisms utilize  $C_{60}$  for growth. Such microorganisms may play an important role in determining the ultimate fate of  $C_{60}$  released into the environment, but not much was known. This motivated us to initiate searches for fullerene degrading-microorganisms in natural environments.

Screening of microorganisms was carried out using minimal Davis (MD) medium containing nanoparticles of  $C_{60}$ . Nanoparticles were prepared by Mechano-Assisted Reduction of Size (MARS).<sup>[2,3]</sup> The medium was diluted 10 times to decrease the ionic strength of the medium and prevent coagulation of  $C_{60}$  nanoparticles. The standard formulation was also modified so that  $C_{60}$  was a sole major carbon source and only those that utilized  $C_{60}$  could grow in the medium.

From three environmental samples (soil, rain drops, cigarette butt), we have successfully isolated five microbial strains that exhibited robust growth only in the presence of  $C_{60}$  nanoparticles. Figure 1 shows cultures of an isolate, strain SL1-4, in MD medium with or without  $C_{60}$  nanoparticles. The organism grew and formed fibrous aggregates in the medium containing  $C_{60}$  after incubation at room temperature for 2 weeks, whereas growth was not observed in the  $C_{60}$ -free medium. Identification using 16S rRNA sequences revealed that two isolates showed high homology to microorganisms that degrade polyaromatic hydrocarbons (PAHs). Strain SL1-4 showed 96% homology to *Sphigopyxis* sp. TP340-8 that degrades

phenanthrene and fluoranthene, while strain SL1-2 showed 99% homology to *Variovorax paradoxus* that was found in enrichment culture using pyrene crystals as a sole carbon source. Considering the high chemical reactivity of  $C_{60}$ , our results suggest that these isolates are able to utilize  $C_{60}$  as a carbon source for growth.

- [1] S. Deguchi et al. Langmuir 17, 6013 (2001).
- [2] S. Deguchi et al. Adv. Mater. 18, 729 (2006).
- [3] S. Deguchi et al. J. Phys. Chem. C 114, 849 (2010).

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**Fig. 1.** Photograph showing the growth of strain SL1-4 in MD medium containing nanoparticles of  $C_{60}$  (right). Growth was not observed in the medium without  $C_{60}$  (left).

# Recent development in Electron Energy Loss spectroscopy and its applications to nanomaterial analysis

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Energy Electron Loss Spectroscopy has been proven many times to be the state of the art analysis method for material characterization. TEM and STEM performances have increased drastically with the development of Cs correctors as well as monochromators. Recent development is both CCD readout speed and electromagnetic optics allows us to develop a new spectrometer to take advantage of current TEM generation.

Spectrum-Imaging is a powerful approach in data acquisition for materials characterisation whereby a spectrum is recorded at each pixel position in an image to form a '3-D data-cube'. As a technique it is a powerful means for rapid materials characterisation at the nanometre level and is well established, especially in the field of materials science. With an atomic resolution, combined EELS and HAADF spectrum-imaging is a formidable approach for solving materials science problems. New spectrometers being able to be used with an acceleration voltage down to 60keV, contamination and sample damage can be greatly reduce. As shown in fig.1, single wall carbon nanotube's carbon atoms can be mapped without damaging the sample. A new technique called DualEELS<sup>TM</sup> allows to record two spectrum simultaneously which makes absolute quantification possible. In this presentation, we will show that counting atoms can now be achieve at the the sub-nanometer scale. Moreover, by using the new fast read out and scanning synchronisation, it is possible to obtain STEM-EEL spectra at a speed of 1000 spectra per second to insure that the local sample excitation caused by the beam doesn't last more than few milli-seconds.



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Fig.1. EELS mapping of Gd2O3@SWNH obtained at 80kV with a 1.9Å resolution. Sample courteisy of Dr. Yudasaka (AIST/NEC Japan)

## First-principles studies of interfacial charge transfer between graphene and

rutile (110) surface

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Charge transfer between two separate systems is of interest as it enables surface conductivity to arise in the semiconductor.<sup>[1]</sup> Recently, the interfacial charge transfer of graphene with different semiconductor has been investigated largely.<sup>[2]</sup> However, the intrinsic reason of charge transfer in graphene /semiconductor systems is not very understood to date. In this work, the interfacial charge transfer mechanism of graphene/rutile(110) is elucidated using density functional theory (DFT). Calculated results indicate that the interfacial charge transfer properties of graphene /rutile (110) are influenced by the surface morphology of rutile (110). The interfacial interaction of graphene with perfect rutile (110) surface is so weak that it scarcely affects geometrical structure and electronic structure of graphene (Figure 1a), and very few electrons (0.01-0.02e) are transferred from rutile to graphene. However, it is relatively easy to transfer electrons from oxygen-deficient rutile (110) to graphene, and cause a down-warping of graphene structure in those oxygen-deficient areas. (Figure 1b). It is revealed that graphene acts as a acceptor in graphene/rutile(110) system. And surface oxygen atoms of rutile (110) hinder the electrons transfer from titanium to graphene due to the big withdrawing electron ability of oxygen atoms. We also calculate density of states (DOS) of two systems. It is shown the oxygen vacancy induces negative shift in conduction bands edge of rutile, resulting into a narrow band gap (Figure 2). Decreasing the band gap of a metal oxide photocatalyst is one strategy towards increasing the adsorbed fraction of solar radiation, so it is predicted that the photocatalytic performance of  $TiO_2$  could be improved when  $TiO_2$ combines with graphene.



Figure1 optimized structures for graphene/rutile(110) , above, and graphene/rutile(110) with oxygen deficiency, bottom.



Figure2 Density of state for graphene/rutile(110), above, and graphene/rutile(110)) with oxygen deficiency, bottom.

#### **Reference:**

T. A. G. Eberlein, et al., Physical Review B. 78, 045403 (2008).
 Q. Liu, et al., Adv. Funct. Mater. 19, 894 (2009).

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### **Reactions of C<sub>60</sub> with Disilirane and Silirane** in the Presence of Transition Metal Complexes

3P-1

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Chemical derivatization of fullerenes with various reagents has been attracting much interest from mechanistic and synthetic viewpoints to provide functional materials. It has been demonstrated that the facile silvlation of fullerenes can be achieved with disiliranes [1], silvlenes [2], and silvl radicals [3] as reactive silicon species, which lower the oxidation potentials of fullerene derivatives due to the electron-donating property of organosilicon groups. Because these silulation procedures are conducted by irradiation, it should be noted that degradation of silvlated products might take place under photolyses. Therefore, it is valuable to develop alternative procedures for silvlation of fullerenes under mild conditions. Meanwhile, it is well known that organosilicon and organogermanium compounds are activated by transition metal complexes, which provide various catalyzed reactions of silvlation and germylation of unsaturated compounds. In our continuing research of silvlation of fullerenes, we investigate the validity of transition metal complexes as catalysts for silvlation of fullerenes, and recently reported that the silvlation of  $C_{60}$  using disilirane in the presence of palladium and nickel complexes afford the corresponding addition product. Herein, we report novel silvlation reactions of fullerenes catalyzed by transition metal complexes.

Reaction of C<sub>60</sub> and oxadisilirane 1 in the presence of tetrakis-(triphenylphosphine)palladium and triphenylphosphine in toluene produced compound 2. On the other hands, irradiation of C<sub>60</sub> and 1 in toluene afforded a 1,4-adduct of  $C_{60}$  and 1. When silirane 3 was employed as a substrate, compound 4 was obtained as the 1,2-adduct of 3 and  $C_{60}$ . The detail of these results and related reactions will be presented.



[1] Akasaka, T.; Ando, W.; Kobayashi, K.; Nagase, S. J. Am. Chem. Soc. 1993, 115, 10366.

[2] Wakahara, T.; Kako, M.; Maeda, Y.; Akasaka, T.; Kobayashi, K.; Nagase, S. Curr. Org. Chem. 2003, 7, 927.

Nakadaira, Y.; Fujitsuka, M.; Ito, O. J. Org. Chem. 1999, 64, 566.

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<sup>[3]</sup> Akasaka, T.; Suzuki, T.; Maeda, Y.; Ara, M.; Wakahara, T.; Kobayashi, K.; Nagase, S.; Kako, M.;

# Synthesis of [60]Fullerene-Based Rotaxanes Using Electron-Accepting Macrocycles

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We have so far synthesized a series of [60]fullerene-based [2]catenanes and [2]rotaxanes by using donor-acceptor interaction. Recently, [2]rotaxane 1 was successfully synthesized by combining a macrocycle containing electron-accepting naphthalenediimide moieties and a fullerene derivative bearing an electron-donating 1,5-dialkoxynaphthalene moiety as an axle compound. The synthesis of [2]rotaxane 2 carrying a more electron-donating TTF moiety instead of 1,5-dialkoxynaphthalene was also successful. The yields of 1 and 2, however, were extremely low. Thus, aiming at the increase of yields, we have designed and synthesized novel macrocycle 5, in which two naphthalenediimide moieties are bridged by rigid 2,7-naphthylene linkages, and applied 5 to the synthesis of [2]rotaxanes 3 and 4.

In the synthesis of [2]rotaxane 3, 6 and 5 were first mixed in  $CHCl_3$  at -30 °C to form pseudorotaxane. After 30 min, carboxylic acid 8, MNBA (2-methyl-6-nitrobenzoic anhydride), and DMAP were added to the mixture, which was stirred for further 10 h at the same temperature. [2]Rotaxane 3 was isolated by column chromatography and GPC in 5% yield, which is higher than that of 1. In a similar manner, [2]rotaxane 4 was also obtained in higher 18% yield. The increased yields of rotaxanes 3 and 4 relative to those of 1 and 2 are ascribed to the efficient formation of pseudorotaxane derived from more rigid macrocycle 5.



[1] Y. Nakamura, S. Minami, K. Iizuka, and J. Nishimura, *Angew. Chem., Int. Ed.*, 42, 3158–3162 (2003).
[2] Y. Kasai, C. Sakamoto, N. Muroya, S.-i. Kato, and Y. Nakamura, *Tetrahedron Lett.*, 52, 623–625 (2011).

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## High Purity Synthesis of N@C<sub>60</sub> Using RF-Plasma and Its Stability under UV-Irradiation

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Although the nitrogen atom endohedral fullerene (N@C<sub>60</sub>) has been studied over the last decade, its purity was as low as  $10^{-3}$  to  $10^{-2}$  %.<sup>1)</sup> Therefore, it is required to achieve the high yield synthesis of N@C<sub>60</sub>, where the control of C<sub>60</sub> behavior with changing oven temperature ( $T_{ov}$ ) is one of the effective methods. On the other hand, the properties of the synthesized N@C<sub>60</sub> have been measured by UV irradiation, however, there are few reports about stability of N@C<sub>60</sub> under UV irradiation. Therefore, the purpose of this study is to elucidate a synthesis mechanism of N@C<sub>60</sub> in order to improve the yield and to clarify the effects of UV irradiation on N@C<sub>60</sub>.

Figure 1(a) shows the purity and C<sub>60</sub> sublimation rate ( $R_{subli}$ ) as a function of  $T_{ov}$  under the conditions of an RF-power  $P_{RF} = 500$  W, grid voltage  $V_g = -90$  V, and substrate voltage  $V_{sub} = -90$  V.<sup>2)</sup> It is found that the purity increases with an increase in  $T_{ov}$  and the highest purity of 0.56% is realized although  $R_{subli}$  is almost constant from 800 to 1000 °C. The increase in the purity is considered to be caused by sublimation of C<sub>60</sub> with dispersed form as  $T_{ov}$  increases.

Figure 1(b) gives a dependence of electron spin resonance (ESR) spectra on UV-irradiation time  $(t_{uv})$ , where the UV wavelength is 365 nm. It is found that the ESR-peak intensity gradually decreases with an increase in  $t_{uv}$ . In addition, UV-visible absorption (UV-vis) spectra show that the peaks at 330 and 345 nm decrease with increasing  $t_{uv}$  [Fig. 1(c)]. Based on these results, the peaks at 330 and 345 nm in the UV-vis spectra are expected to correspond to N@C<sub>60</sub>, suggesting that the nitrogen atom N has escaped from the inside of  $C_{60}$  by enhanced vibrations of  $C_{60}$  or N under UV irradiation.



Fig. 1. (a) Dependence of purity and  $C_{60}$  sublimation rate on  $T_{ov}$ , (b) ESR spectra and (c) UV-visible spectra as a function of UV-irradiation time.

L. Franco, S. Ceola, C. Corvaja, S. Bolzonella, W. Harneit, and M. Maggini, *Chem. Phys. Lett.*, **422**, 100 (2006).
 S. C. Cho, T. Kaneko, H. Ishida, and R. Hatakeyama, *Appl. Phys. Exp.*, **5**, 026202 (2012).

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## Improvement of Open-Circuit Voltage in Inverted Organic Photovoltaic Devices by New Fullerene Acceptor

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#### Introduction

Organic photovoltaics (OPVs) have become increasingly important as renewable energy sources. Especially, inverted OPV cells have received special attention because of their stability. However, PCE of these devices had been lower than that of normal-structured OPV devices. Therefore, discovery of a novel semiconductor material that shows high performance

in inverted OPV devices is one of the important challenges. Herein, we introduce new fullerene acceptor SIMEF2 (Fig. 1) and report its photovoltaic performance in inverted solar cells.

#### **Results**

The configuration of the inverted OPV device follows: is as ITO/ZnO /P3HT:SIMEF2/ PEDOT:PSS/Au (Fig. 1). Through a comparison with device using most common acceptor PCBM, SIMEF2 was found to give higher  $V_{OC}$  without a decrease in  $J_{SC}$  (Fig.2, Table 1). The reason for the improvement of  $V_{\rm OC}$  is that the LUMO level of SIMEF2 (-3.72 eV) is higher than that of PCBM (-3.80 eV). The high  $J_{SC}$  value of the SIMEF2 devices is probably due to the steric bulkiness of the organic addends on SIMEF2 being similar to that of PCBM. This result indicates the usefulness of SIMEF2 and provides important insights toward overcoming the usual trade-off relationship between  $V_{\rm OC}$ and  $J_{\rm SC}$  in the development of highly efficient OPV devices.

[1] Y. Matsuo *et al.* Appl. Phys. Lett. **100**, (2012) in press.

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Fig.1 Device configuration and molecular structure of SIMEF2.



Fig.2 Photo *I-V* curves of device using SIMEF2 (black line) and PCBM (gray line) as an acceptor.

Table 1. Comparison of OPV device performance

acceptor	V <sub>OC</sub>	$J_{ m SC}$	FF	PCE
	[V]	[mA/cm <sup>2</sup> ]		[%]
SIMEF2	0.66	7.9	0.56	2.9
PCBM	0.56	7.8	0.55	2.4

## Ultraviolet Photoelectron spectra and the electronic structure of non-IPR Sc<sub>3</sub>N@C<sub>68</sub>

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Most fullerenes obey isolated pentagon rule (IPR) because of the stability of the cage, but some endohedral fullerenes that do not obey the rule (non-IPR fullerenes) have been isolated. It is believed that they are stabilized by the rearrangement of the electron energy levels induced by electron transfer to the cage. We present ultraviolet photoelectron spectra (UPS) and X-ray photoelectron spectra (XPS) of non-IPR endohedral fullerene  $Sc_3N@C_{68}$ and discuss them with the aid of DFT calculation.

The deeper valence band UPS (BE > 5 eV) of  $Sc_3N@C_{68}$  are analogous to those of other endohedral fullerenes. While the upper valence band UPS (BE < 5 eV) are significantly different from those of other endohedral fullerenes. A simulation spectrum generated from geometry optimized structure calculated by the DFT calculation reproduces the UPS very well. The structure of entrapped  $Sc_3N$  obtained from the geometry optimization is flat

as was reported by Olmstead et al [1]. The binding energy (BE) of Sc2p and N1s of  $Sc_3N$  cluster encapsulated fullerene is summarized in

Table 1. As the BE of Sc2p and N1s levels in Sc<sub>3</sub>N@C<sub>68</sub> is shifted to lower side than those of Sc<sub>3</sub>N@C<sub>82</sub> and Sc<sub>3</sub>N@C<sub>80</sub>, the electron density in the Sc<sub>3</sub>N cluster of Sc<sub>3</sub>N@C<sub>68</sub> is larger than that of other Sc<sub>3</sub>N encapsulated fullerenes.

#### Ref.

 M. M. Olmstead et al., Angew. Chem. Int. Ed., 42, 900 (2003).

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Figure 1. The optimized structure of  $Sc_3N@C_{68}$  by DFT calculation.

Table 1	.Sc2p	and	Nils	levels	of	$Sc_3N@C_{68}$
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	Sc 2p <sub>1/2</sub>	Sc 2p <sub>3/2</sub>	N 1s
$Sc_2O_3$	406.0	401.6	
Sc <sub>3</sub> N@C <sub>82</sub>	405.9	401.2	
Sc <sub>3</sub> N@C <sub>80</sub>	406.0	401.2	396.9
Sc <sub>3</sub> N@C <sub>78</sub>	405.7	400.9	396.5
Sc <sub>3</sub> N@C <sub>68</sub>	405.3	400.6	395.6
Sc	403.4	398.5	

## **Exploring ideal polymers for** water-solubilization of endohedral metallofullerenes

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Endohedral metallofullerenes (EMFs) are fullerene-based species that encage one or more metal atoms inside, which has yielded so far many potential bio-medical applications such as MRI contrast agents [1] and antitumors [2]. To accelerate these applications into practical use, it is essential to develop a sophisticated technique for water solubilization of EMFs. Recently, the wrapping of EMF clusters with a biocompatible polymer has been proposed [3]. Exploring effective polymers for the water solubilization is, therefore, highly required for a further control of cluster properties and biological functionalizations.

In this study, we have investigated the water solubilization of EMFs using a commercially-available biocompatible polymer, DSPE-mPEG (MW = 5000, Laysan Bio, Inc.). This polymer consists of both hydrophilic and hydrophobic segments (Fig.1). The Gd@C<sub>82</sub> metallofullerene was mixed with DSPE-mPEG in DMF, and then the solution was dialyzed in water as reported by Horiguchi et al [3]. In this aqueous solution containing DSPE-mPEG, EMF clusters have been stably dispersed for over a month. In contrast, we found that such stable dispersion could not be realized in water containing polyethylene glycol (PEG, MW = 400), which is composed of only hydrophilic segments. These results indicate that hydrophobic segments of

DSPE-mPEG strongly interact with  $Gd@C_{82}$ . The detail characterization of these water-soluble EMFs will be shown in the poster presentation.



Fig.1 The structure of DSPE-mPEG

[1] M. Mikawa et al., Bioconjug. Chem. <u>12</u>, 510 (2001).
 [2] X. Liang et al., PNAS <u>107</u>, 7449 (2010).
 [3] Y. Horiguchi et al., Sci. Technol. Adv. Mater. <u>12</u>, 44607 (2011).

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#### Synthesis and Characterization of Covalently Linked Porphyrin-La@C<sub>82</sub> Hybrids

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The study of covalent and non-covalent photoactive hybrids continues to be of interest for developing photosynthetic and optoelectronic applications. In this work, we report on three isomeric

covalently linked 5,10,15,20-tetraphenyl -porphyrin (H<sub>2</sub>P)-La@C<sub>82</sub> hybrids (i.e., M<sub>1-3</sub>P, as shown in the schematic figure), including their synthesis, electrochemistry, spectroscopic, and computational studies. X-ray structure of the corresponding reference compounds M<sub>3</sub> definitely demonstrated the addition site that involves a (6,6)-bond on the symmetry plan of the  $C_{2\nu}$ -C<sub>82</sub> cage and close to the endohedral La atom. By complementary spectroscopic



studies,  $M_1$  and  $M_2$  were proposed to have the same addition site as that of La@C<sub>82</sub>Ad-I (Ad=adamantylidene, major isomer).

The subsequent absorption spectral, electrochemical and computational studies on  $M_{1-3}P$  revealed evident electronic communication between the two redox-active units in the ground state. On the other hand, in the emission spectra of  $M_{1-3}P$ , nearly quantitative quenching of the  $H_2P$  fluorescence suggested efficient intramolecular energy/electron transfer events in the excited state. Thus, these covalent hybrids are expected to be useful in future design and creation of EMF-based materials for molecular electronic devices and photovoltaics.

## Protein-SWNTs complexes prepared by using a wet-type super atomizer

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Single-walled carbon nanotubes (SWNTs) have received much attention as promising materials due to their mechanical and electronic properties. For their industrial application, dispersion of SWNTs in water and organic media is important. Ultrasonication has been widely used for dispersing SWNTs. Since ultrasonication is too strong to disperse SWNTs without destruction and shortening of SWNTs, development of a method for dispersing SWNTs in water and organic media without ultrasonication treatment has been needed.

In this work, we examined whether SWNTs can be dispersed in water containing proteins, casein and bovine serum albumin (BSA), by using a wet-type atomizer "Nanovater" (Yoshida Kikai Co. Ltd.). Since the Nanovater uses collision of solution under ultra-high pressure (max. 200 MPa) to disperse CNTs, the destruction of CNTs during dispersion process can be reduced. The UV-Vis-NIR absorption spectra and Raman spectra for the prepared SWNTs dispersion solutions were measured to evaluate the structures and damages to the protein-SWNTs complexes.

HiPco SWNTs (20 mg) were mixed with 40 ml of casein solution (5 mg/ml) and the mixture was treated by the Nanovator under pressures around 180 MPa. Repeating this treatment enhanced the degree of dispersion of SWNTs. The resultant primary suspension was centrifuged and the supernatant was subjected to further evaluation as the dispersion solution. A comparison of the UV-Vis-NIR spectrum of the dispersion solution with that for the dispersion solution prepared by ultrasonication method showed that the Nanovator can be used for the preparation of SWNTs dispersion solutions. In addition, we will report the influence of the treatment with the Nanovator on the SWNTs by measuring the Raman spectra of the dispersion solutions.

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## Effect of Sn Catalytic Vapor Supply on the Initial Growth of Carbon Nanocoil

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Carbon nanocoil (CNC) is a helical carbon nanofiber and is synthesized by chemical vapor deposition (CVD) with Sn/Fe catalyst. We have synthesized CNC by continuous supply of Sn catalytic vapor to Sn/Fe catalyst layer formed on Si substrate [1]. The purity of CNC grown with Sn catalytic vapor supply was higher than that without the supply [1]. In this study, the initial growth process of CNC was observed for the examination of effect of Sn catalyst vapor. Si was used as a substrate and Sn film with a thickness of 40 nm was deposited on Si substrate by vacuum evaporation. Fe<sub>2</sub>O<sub>3</sub> catalyst was dropped on Sn/SiO<sub>2</sub>/Si substrate. The substrate was calcined in the air for 5 min at 400°C. The other conditions were the same as those in our previous study [2]. The concentration of Sn(CH<sub>3</sub>)<sub>4</sub> in ethanol was fixed at 0.2%. Synthesis times were 30 and 120 s. Fig. 1 shows scanning electron microscopy (SEM) micrographs of the substrate surfaces. As for the surface synthesized for 30 s, there seems no difference between the deposits with and without Sn(CH<sub>3</sub>)<sub>4</sub> supply was higher than that without supply. It is thought that by supplying Sn vapor, Sn was spread in the wide area on the Fe catalyst on substrate.

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(a1) With Sn(CH<sub>3</sub>)<sub>4</sub> (a2) Without Sn(CH<sub>3</sub>)<sub>4</sub> (b1) With Sn(CH<sub>3</sub>)<sub>4</sub> (b2) Without Sn(CH<sub>3</sub>)<sub>4</sub> Fig. 1 SEM micrographs of the substrates synthesized for (a) 30 s and (b) 120 s.

[1] Y. Ishii, *et al.*: The 41<sup>th</sup> Fullerene-Nanotubes-Graphene General Symposium, 3P-18 (2011)
[2] Y. Ishii, *et al.*: The 40<sup>th</sup> Fullerene-Nanotubes General Symposium, 1P-8 (2011)
Corresponding Author: Y. Suda, Tel: +81-532-44-6726, Fax: +81-532-44-6757, E-mail: suda@ee.tut.ac.jp
### One-Step Gel-Based Separation of High Purity Semiconducting Single-Wall Carbon Nanotubes

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Single-wall carbon nanotubes (SWCNTs) have promising applications in electronic devices especially for thin film transistors (TFTs). Unfortunately, the SWCNT-TFTs have been known to exhibit a trade-off problem between carrier mobility and on-off current ratios as as-grown samples were mixtures of metallic and semiconducting SWCNTs. To solve this trade-off problem, the TFTs must be created from high purity semiconducting SWCNTs which can be obtained through post-synthesis separation. A recent study shows successful separation of semiconducting SWCNTs with 99% purity using recycling gel separation method. This achieves the TFTs with high carrier mobilities and high on-off current ratios [1]. However, this method consumed a quite lot of time as it employed, what we call, a multistep separation process.

In this study, we have developed a method to obtain high purity semiconducting SWCNTs using singlestep gel filtration based on the previous work [1]. The method includes a fractionating process during the collection of semiconducting SWCNTs adsorbed on the gel. Figure 1 shows the optical absorption spectra of the fractionated semiconductor-enriched

samples. The peaks of metallic SWCNTs at 700 nm are not found in the first three fractions, indicating the high purity of semiconducting SWCNTs. Interestingly, the metallic peaks start to appear from the 5<sup>th</sup> fraction which means that the metallic SWCNTs have stronger affinity to the gel than semiconducting tubes. We have also found that the earlier fraction has slightly longer nanotubes than the later fraction. The detail separation processes will be given in the presentation.

#### Reference

[1] Y. Miyata et al., Nano Res., 4, 963 (2011)

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**Figure 1.** The normalized optical absorption spectra of the collected fractions of semiconducting SWCNTs. The numbers in the spectra represent their respective fraction.

# Purification of metallic single-wall carbon nanotubes using an agarose gel column

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Single-wall carbon nanotubes (SWCNTs) are expected to have potential applications due to their prominent properties. One of key challenges for the industrialization of SWCNTs is the commercial-scale production of high-purity SWCNTs separated into metallic and semiconducting species, because as-prepared SWCNTs contain both species and impurities such as amorphous carbon. Previously, we have developed metal/semiconductor separation of single-wall carbon nanotubes (SWCNTs) using gel columns.<sup>[1,2]</sup> However, in the method, the metallic SWCNTs are eluted together with amorphous carbon, which affects the purity. In addition, metallic SWCNTs obtained even by density gradient ultracentrifugation coexisted with some amorphous carbon.<sup>[3]</sup> Thus, a smart purification of the metallic SWCNTs is appeared to be necessary to develop applications of them.

In this study, using an agarose gel column, we tried the purification of the metallic SWCNTs obtained after metal/semiconductor separation. The results showed that the metallic SWCNTs dispersed at 0.25 %sodium deoxycholate (DOC) were adsorbed onto the agarose gel in the column. Subsequently, they were eluted by 2 % DOC solution. Absorbance spectra of the unpurified solution and the eluate were showed in Fig.1. The broad absorbance of the unpurified sample throughout the wavelength region was decreased by the purification.<sup>[4]</sup> indicating that the amorphous carbon was flowed out of the column, whereas the high-purity metallic SWCNTs were adsorbed and eluted by the DOC solutions. The method described here is useful for high-throughput purification of the metallic SWCNTs due to the simplicity of the gel column system using only one surfactant.

T. Tanaka *et al.* Appl. Phys. Express 2, 125002 (2009).
 A. Hirano *et al.* J. Phys. Chem. C 115, 21723–21729 (2011).
 E. H. Hároz *et al.* ACS Nano 4, 1955–1962 (2010).
 D. Nishide *et al.* Phys. Status Solidi B 246, 2728–2731 (2009).
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Fig. 1 Absorbance spectra of the metallic SWCNTs normalized at 300 nm before (dotted line) and after (solid line) the adsorption onto the agarose at 0.25% DOC and the subsequent elution at 2% DOC.

## Selective Separation of Semiconducting Single-Walled Carbon Nanotubes Using Polysaccharide/Surfactant Mixture as Dispersing Agents with Density Gradient Ultracentrifugation

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As-synthesized single-walled carbon nanotubes (SWNTs) are mixture of both metallic (m) and semiconducting (s) SWNTs with different diameters and chiralities. Thus, for versatile potential applications, it has been practically required to selectively separate as-synthesized SWNTs into pure fractions of a single chirality. Thereof, density gradient ultracentrifugation (DGU) techniques, based on a slight difference in the buoyant density of components, have been developed as an effective separation method, because of relatively low cost and facile processes. To solve the issues, we have scrutinized the dispersant conditions for SWNTs in the DGU treatment, based on a novel combination of polysaccharide and surfactant. Carboxymethylcellulose (CMC), an anionic polysaccharide, possessed a high dispersion activity for SWNTs, assuming an ordered polymer wrapping arrangement on SWNTs, in contrast to sodium dodecyl sulfate (SDS) with a random adsorption structure. Thus, the synergetic effect by combination of CMC and SDS possessing different adsorption mechanism as dispersant is expected to give rise to a slight difference in the amount of the dispersants on SWNTs with different electronic types, driving the DGU-based separation of SWNTs. The separation characteristics for SWNTs were measured by UV-vis-NIR absorption, resonance Raman, and NIR-photo-luminescence (PL) spectra. SWNTs dispersions were prepared with the mixed dispersants of CMC and SDS (1wt%:1wt%) under the conditions of ultrasonication times of 3 h and ultracentrifugation time of 1h at 163,000 g. Before DGU, density gradients in centrifuge tubes were performed by layering aqueous iodixanol solutions from 25% to 32.5%, in which only 30% dilution contained the SWNTs dispersed by CMC and SDS. Then, the centrifuge tubes were centrifuged at 175,000g for 12h. Therein, s-SWNTs with high purity (>97 %) and yield (about 1mg per dose SWNTs 10mg) were collected from upper layers in the tubes. Thus, the present DGU technique using the mixed dispersants of CMC and SDS would be an effective separation method for s-SWNTs.

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### Influence of temperature on a carbon nanotube resonator by molecular dynamics simulations

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The bending modes of carbon nanotube have been studied for ultralow mass and force sensing [1,2] and its tunable resonance frequency [3]. On the other hand, the nonlinear damping of flexural mode [3,4] has been shown to be vulnerable to temperature [1-4]. For this reason, we have studied the interaction between mechanical and thermal characteristics in a carbon nanotube cantilever resonator observing the phase space trajectories, strain-stress distributions, and lattice vibrational spectra.

The calculation was based on molecular dynamics simulations using the REBO potential, where a carbon nanotube was excited by sinusoidal mechanical force at a tube end with constant-temperature boundary condition. The result confirms that the localized strain distribution is in agreement with previous high-resolution transmission electron microscopy results [5]. But also it was found that the strain distribution using FFT with the strain signal at each atom has continuous configuration at excitation frequency. Particularly notable is the excitation near the 1st mode of resonance frequency which shows transient vibration mode. Non planar flexural movement is also observed as known by the experiment [6].

Based on the simulations, the dynamic Young's modulus and the damping coefficient will be extracted in the frequency domain for different nanotube length and chirality, and will be compared with the continuum theories. In addition, by carrying out the calculations for various temperatures, the interaction between the first resonance mode and the background phonons will be discussed based on the obtained dissipated thermal energy and the phonon energy spectra.

[1] B. Lassagne et al., Nano Letters, 8, 3735 (2008).

[2] A. Eichler et al., Nature Nanotechnology, 6, 339 (2011).

[3] V. Sazonova et al., Nature, **431**, 284 (2004).

[4] A. Eichler et al., Nano Letters, 11, 2699 (2011).

[5] J. H. Warner et al., Nature materials (2011) published online.

[6]S. Perisanu et al., PRB, 81, 165440 (2010)

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#### Soft x-ray irradiation effect of singe-walled carbon nanotubes

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Because of strong interplay between structure and electronic properties in single-walled carbon nantubes (SWNTs), structural modification causes to change in electronic properties. Thus, in order to establish the feasibility of SWNT-based nanoelectronics, developing effective method for modifying local structure of SWNT is required. Electron beam irradiation has been shown to lead to modify the nanostructure of carbon nanotubes.[1] However, the primary process and dynamics are difficult to understand because electron bombardment leads to complex effect involving knock-on, valence and inner-core excitation. In contrast to this, the excitation process of x-ray is dominated by inner-core excitation, which is much simpler than the electron irradiation. Thus, the structural change of SWNT induced by soft x-ray irradiation is presumably a prototype for studying the irradiation effect.

In the present paper, we report the results of Raman scattering study on the structural changes of SWNT induced by soft x-ray irradiation. SWNT films formed on CaF<sub>2</sub> substrates were irradiated by x-ray having a spectrum showing a peak at 277 eV with a FWHM of 210 Figure 1 shows Raman spectra of irradiated and unirradiated SWNT films. eV. These spectra were characterized by  $G^+$  band,  $G^-$  band, D band and Radial breathing mode (RBM). The irradiation gave rise to enhancement of the intensity ratio of D band to  $G^+$  band (D/G)from 0.025 to 0.097. The enhancement demonstrates that the x-ray irradiation generated defects in SWNTs. Furthermore, we found the x-ray irradiation led to remarkable high On the basis of the diameter-RBM frequency  $(d-\omega)$  dependence frequency-shift of RBM. described by the simple relation  $d=248/\omega$ [2], the irradiation induced shrinkage of SWNT from 1.53 nm to 1.46 nm. This result demonstrates the x-ray irradiation induced geometrical change of SWNT as well as defect formation.



Figure 1. Raman spectra of SWNTs measured before and after x-ray irradiation. The peak marked by \* is ascribed to CaF<sub>2</sub> substrate.

A. Hashimoto, et. al., Nature 430 (2004), 870.
 A. Jorio, et. al., Phys. Rex. Lett. 86 (2001) 1118
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### Sub-THz AC Transport in Defective Metallic Carbon Nanotubes: Nonequilibrium Green's Function Approach

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Metallic carbon nanotubes (CNTs) are expected to be able to respond to sub-THz signals, owing to their high carrier mobility. However, a dynamical response of metallic CNTs has hardly been clarified thus far, compared with their static response. Previous theoretical investigations have predicted that the AC response of pristine metallic CNTs behaves inductively [1] and the AC phase correlates with the DC conductance [2]. In contrast to the AC response of pristine metallic CNTs, however, our understanding of influence of defects on the AC response is not sufficient, in spite of its importance.

In this study, we have simulated the sub-THz AC response of metallic CNTs with a single atomic vacancy, using the Keldysh nonequilibrium Green's function method with the wide-band limit approximation and the nearest-neighbor  $\pi$ -orbital tight-binding model [3,4]. We found that a capacitive response is induced around the defect level (Fig. 1), which is attributed to electron scattering by that level, when the vacancy is at the center of CNT. In addition, this capacitive response appears remarkably in large-diameter CNTs (Fig. 1), because the defect states that scatter electrons are more localized in those CNTs. This is in contrast to the diameter-independent AC response of pristine metallic CNTs [1]. More interestingly, the AC phase depends on the position of vacancy as can be seen in Fig. 1 (note that admittance, Y, in sub-THz region can be expressed as  $Y(\omega) = G_{DC} + iE\hbar\omega$ ,  $G_{DC}$ : DC



Fig. 1. Emittance behaviors at the defect level as a function of the vacancy position, d, measured from the center of CNT in several armchair CNTs. Here,  $G_0$  is the conductance quantum.

conductance, E: emittance,  $\omega$ : AC frequency), while the DC conductance does not. Inductive response occurs even at the defect level when a distance between the vacancy and the center of CNT is larger than a certain threshold. This behavior of AC phase can be understood in terms of the parity symmetry [3]. In addition to details of the above, we will also discuss the AC response of metallic CNTs with multiple defects in the presentation.

- [1] T. Yamamoto et al., Phys. Rev. B 81, 115448 (2010).
- [2] T. Yamamoto et al., Phys. Rev. B 82, 205404 (2010).
- [3] D. Hirai et al., Appl. Phys. Exp. 4, 075103 (2011).
- [4] D. Hirai et al., Jpn, J. Appl. Phys. in press.

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## Femtosecond Coherent Phonon Spectroscopy of Lysozyme-SWCNT Conjugates in Aqueous Solution.

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The interactions between single-wall carbon nanotubes (SWCNTs) and proteins, in particular charge transfer between them, have not yet been unveiled, although they are important physical phenomena to realize medical applications, such as drug delivery carriers [1] and biosensors [2]. So far, we have investigated dynamics of coherent radial breathing mode (RBM) of SWCNTs in various conditions and found that environments around SWCNTs significantly affect their electrical and optical properties [3]. In this study, we investigated the ultrafast dynamics of coherent RBM of lysozyme-suspended SWCNTs (LSZ-SWCNT) in terms of secondary structure of lysozyme. Lysozyme is one of promising dispersants for SWCNT and the dispersibility can be controlled by adding alcohols [3]. Pump-probe transmittance measurement was employed by utilizing femtosecond optical pulses with 30 fs duration and 850 nm wavelength to excite and detect the coherent RBM. Samples investigated were LSZ-SWCNT aqueous solutions at neutral pH in the presence of three different alcohols (50 vol.%); ethanol (EtOH), 2,2,2-trifluoroethanol (TFE), and 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP), and LSZ-SWCNT aqueous solution without a additive.

Fig. 1 shows the coherent RBM spectra for LSZ-SWCNT conjugates, in which mainly two peaks at 6.4 THz from (13, 2) tubes and at 7.2 THz from (12, 1) tubes were observed. The intensity ratios of these two peaks vary among samples. We attributed this result to the deformation of lysozyme induced by added alcohols. Indeed, alcohols have a large effect on denaturation of lysozyme, depending on the type of alcohol, which has been confirmed by circular dichroism (CD) spectra [4]. Therefore, addition of the alcohols is likely to alter the structure of lysozyme including hydrophobic pocket which is expected to attach onto SWCNT,



Fig. 1. Coherent RBM spectra of LSZ-SWCNT aqueous solutions containing alcohols (TFE, EtOH, and HFIP) and no additive ( $H_2O$ ).

leading to the modification of phonon intensity associated with charge transfer.

[1] M. Zhang, T. Murakami, K. Ajima, K. Tsuchida, A. S. D. Sandanayaka, O. Ito, S. Iijima, M. Yudasaka, *Proc. Natl. Acad. Sci. U.S.A.* **105** 14773 (2008).

[2] A. Star, J. P. Gabriel, K. Bradley, and G. Gru1ner. Nano Lett. 3, 459 (2003).

[3] K. Makino, A. Hirano, K. Shiraki, Y. Maeda, and M. Hase, Phys. Rev. B 80, 245428 (2009).

[4] A. Hirano, Y. Maeda, T. Akasaka, K. Shiraki, Chem. Eur. J. 15, 9905 (2009).

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#### Production of Crystalline SWCNT aggregates

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Crystallization is a crucial step for ultimate-purification of the compounds and identification of their structure. Periodic potentials in solids reduce carrier scattering originated from disorders or dislocations, and then improve its conductive characteristics such as increase of carrier mobility, and also enable them to exhibit macroscopic quantum phenomena such as superconductivity. As regards to nano-carbon materials, their crystalline solid forms have demonstrated unique their remarkable phenomena, such as superconductivity in crystalline solid systems of fullerene and graphite by alkali metal doping. However, in the case of single-wall carbon nanotubes (SWCNTs), three dimensional crystalline systems of them have not been achieved yet. Recently, it becomes possible to obtain high-purity single-wall carbon nanotubes with a single chirality, however, how to crystallize them has been unsolved problem. Here we present an approach to make crystals of SWCNTs. We applied vapor diffusion methods on the crystallization of (6,5) chiral SWCNTs, and as a result, needle-like crystals are obtained. We clarified the characteristics of SWCNTs inside the crystals by

micro-Raman measurements and transmission electron microscope images. SWCNTs are aligned to the parallel to the crystal axis, and the purity was improved by the crystallization processes.

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Fig1. Raman spectra of samples before and after crystallization. (a) Radial breathing mode. (b) G-band. Results of polarized micro Raman measurements. (c) A picture of sample. (d) G-band intensity of needle-like crystal as a function of polarization angle. (e) Schematic

#### Contact resistivity estimation of CNT on SiC-metal contact using contact mode AFM current mapping

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#### 1. Estimation of CNT contact resistivity

To apply carbon nanotube (CNT) to electronic devices, it is important to estimate and reduce the contact resistivity. Previously, we have reported that vertically aligned CNT is synthesized using remote plasma CVD (RPCVD)<sup>[1]</sup>, and polished/open-ended using Chemical Mechanical Polishing. Open-ended CNT-metal contact resistivity is estimated to be  $1\sim 2 \times 10^{-8} \,\Omega \text{cm}^2$  at most using contact mode AFM current mapping. This value is more than 1 order of magnitude smaller than the contact resistivity of graphene<sup>[2]</sup>. Here we report the CNT on SiC<sup>[3,4]</sup>-metal contact resistivity and the comparison between RPCVD CNT and CNT on SiC.

#### 2. Electric resistance measurement of CNT on SiC

Length-controlled CNT is synthesized on the C-surface of n-type 4H-SiC substrate (specific resistance:  $10^{-2} \Omega \text{cm}$ ) with SiC surface decomposition method<sup>[3,4]</sup>. This CNT is double-layer dominant, the outer diameter is 2~3 nm, and densely aligned (surface density: >  $10^{13} \text{ cm}^{-2}$ ). SiC substrate is fixed on the bottom electrode (Au/Ti) using conductive paste (Ag), and current mapping is imaged using contact mode AFM (Fig. 2(a)). Fig. 1 shows the schematic illustration of AFM current mapping. While a few high electric current peaks exist in zero level region in case of RPCVD CNT (Fig. 2(b)), a few low current spots in high current region in case of CNT on SiC (Fig. 2(a)).

#### 3. Estimation of CNT on SiC-metal contact resistivity

Fig. 3 shows the relationship between resistance and length of both RPCVD CNT and CNT on SiC. If CNT outer diameter is 2.5 nm and the contacting diameter of CNT and AFM probe is ~10 nm, the number of contacting CNT is to 11. Normalizing the resistance of the intercept ( $35k \Omega$ ) in Fig.3 (Tarman method), the contact resistivity of CNT on SiC can be expected to be  $1 \sim 2 \times 10^{-8} \Omega \text{ cm}^2$  at most. This value is equivalent to RPCVD CNT contact resistivity,  $\hat{g}_{50}$ which means that the way of RPCVD CNT  $\hat{g}_{50}$ normalizing is reasonable.

1. T. Iwasaki, H. Kawarada et al., Nano Lett. 8, 3(2008)

2. K. Nagashio, A. Toriumi et al., Appl. Phys. Lett. 97, 143514 (2010)

3. M. Kusunoki et al., Appl. Phys. Lett.77, 531 (2000)

4. M. Kusunoki et al., Appl. Phys. Lett. 87, 103105 (2005)

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Fig. 1 Schematic image of AFM current mapping







### Enhancement and selection rules of near field optical transition in SWCNT

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The electromagnetic field localized near the surface of a metallic tip known as near field has provided new way to image single-wall carbon nanotube (SWCNT) in the Tip-Enhanced Raman Spectroscopy experiment or TERS [1,8]. The Raman signal of SWCNT by near field in TERS experiment has been found to be much stronger than the conventional resonance Raman signal[2]. These phenomena result from the enhancement of near field which is believed to be radiated by the collective oscillation of free electrons on the metallic surface known as surface plasmon coupling with laser light [3]. The numerical calculation of the scattered electric field from metallic tip also confirm the strong amplitude of near field [4]. However, the underlying physics of the interaction between near field and SWCNT is still unclear. Therefore, understanding near field enhancement and its interaction with SWCNT is important in order to understand experimental results.

In this paper, we have simply modeled the metallic tip as the metallic sphere whose diameter is the same as the diameter of the tip apex. The electromagnetic fields outside and inside the metallic sphere are then obtained analytically by solving vector Helmholtz equation in spherical coordinate [5]. The interested metals are Au and Ag whose dielectric constants as a function of wavelength are fitted with experiment data [6]. We calculate the maximum of electric field enhancement of Au and Ag spheres of He-Ne laser light as a function of radius and find that it is in the range of 3-5 for both of them. However, we show that the high electric field enhancement about 35 occurs at laser light 350 nm for Ag-sphere of radius 20 nm due to the effect of dipole resonance and skin depth of Ag-sphere. The enhancement as a function of radius of another wavelength will also be given. Further, we have studied near field-exciton interaction based on time-dependent perturbation theory and the concept of exciton in SWCNT [7]. We show the excitonic selection rules for the parallel component of near field. The calculation results will be compared to experiments [8].

- [2] N. Peica et al. Phys. Status Solidi B 247, 2818 (2010).
- [3] M. I. Stockman, Phys. Rev. Lett. 93, 137404 (2004).
- [4] Z. Yang et al. J. Raman. Spectrosc. 40, 1343 (2009).
- [5] G. Mie, Ann. Phys. 25, 377 (1908).
- [6] P. B. Johnson and R. W. Christy. Phys. Rev. B 6, 4370 (1972)
- [7] J. Jiang et al. Phys. Rev. B 75, 035407 (2007).
- [8] L. G. Cancado et al. Phys. Rev. Lett. 103, 186101 (2009).

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<sup>[1]</sup> A. Hartschuh et al. Phys. Rev. Lett. 90, 095503 (2003).

## Preparation and thermal properties of SiC/MWCNT nanocomposites

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The unique mechanical, electrical and thermal properties of both single- and multi-walled carbon nanotubes, have attracted extensive research attention in recent years. Numerous investigators have reported remarkable physical and mechanical properties for this new form of carbon. From unique electronic properties and a higher thermal conductivity than diamond to mechanical properties where the stiffness, strength and resilience exceeds any current material, CNTs offer tremendous opportunities for the development of fundamental new material systems [1-3]. Now, CNTs have been used to reinforce many kinds of materials including polymers, metals, and ceramics [4-6]. Considering the excellent thermal conduction of CNTs, which is twice as high as that of diamond, hence it is expected that this excellent property will be demonstrated by incorporating the carbon nanotubes into a ceramics material, so as to expand the use of CNTs further.

In this study, SiO<sub>2</sub>/MWCNT nanocomposite was obtained by precursor method. MWCNT was first functionalized by treatment with MCPBA(m-chloroperbenzoic acid). The coating route leads to adsorption of TEOS on the modified MWCNT surface. SiC/MWCNT nanocomposite was obtained by thermal treatment. The structures of the SiC/MWCNT nanocomposites were evaluated with transmission electron microscopy(TEM). As shown in Fig.1, the TEM image of the SiC/MWCNTs nanocomposite shows that the surface of the MWCNTs was covered by the SiC. It is expected that the thermal conductivity of SiC/MWCNT nanocomposites were identified by an X-ray diffraction(XRD). The thermal properties of SiC/MWCNT nanocomposite were performed using thermogravimetric analyzer (TGA) and laser flash apparatus(LFA).

[1] P. G. Collins *et al.* Science American 283, 62 (2000)
[2] M. Terrones, Annu. Rev. Mater. Res. 33, 419 (2003)
[3] A. Bachtold *et al.* Science 294, 1317 (2001)
[4] S. Curran *et al.* Synthetic Metals. 103, 2559 (1999)
[5] S. R. Dong *et al.* Mater. Sci. Eng. A 313, 83(2001)
[6] A. Peigney *et al.* Ceram. Intern. 26, 677(2000)
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Fig.1 TEM image of SiC/MWCNT nanocomposite

## Controlled Synthesis of Cyclic Olefin Polymer/Carbon Nanotube Composite Particles in Aqueous Solution

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Cyclic olefin polymer (COP) such as ZEONEX<sup>®</sup>, ZEONOR<sup>®</sup>, APEL<sup>®</sup>, ARTON<sup>®</sup> is a new class of optical polymer which possesses simultaneously high thermal stability and superior optical property over the traditional optical materials like PMMA and PC. However, due to its insulation resistance, these materials were not able to utilize for the electrical applications. To overcome this problem, we have synthesized a new type of the COP that exhibits a relatively high electrical conductivity in combination with its intrinsic superior thermal and optical properties through a homogeneous incorporation of a well dispersed supergrowth carbon nanotube (SGCNT) aqueous solution into a stabilized latex-based COP matrix at room temperatures. This work reports the synthetic procedure of the electrical conducting COP/SGCNT composite particles as well as its thermal and electrical characterizations.

The fabrication of the COP/SGCNT composites was carried out via two processes. The first is based on the addition of the SGCNT/surfactant aqueous solution into the pre-made COP latex. The second on the addition of the SGCNT/surfactant aqueous solution into the *in-situ* emulsion polymerization of the cyclic olefin monomer catalyzed by a Grubbs catalyst at elevated temperatures. The diameters of the polymer latex as well as its composite particles were precisely controlled by adjustment of the monomer/surfactant ratios as well as the emulsification conditions. The alternating interaction between the SGCNT and the polymer particle surface was controlled via the choice of the surfactants, *i.e.*, cationic, anionic, or nonionic. The molecular weights of the polymer particles were controlled using a chain transfer agent adding to the polymerization system.



The COP/SGCNT composite particles were collected by precipitation of the latex-based polymer solution in methanol, followed by vacuum drying at 50 °C for 12h. For further characterizations,

Fig.1: (a) SEM image of the COP/SGCNT composite particles; (b) Core-Shell the structure of the COP/SGCNT composite particles particles

the composite particles were

pressed at high temperatures under vacuum to yield uniformed thin films.

The electrical conductivity of the composite thin film was measured using a four point probe apparatus. The morphology of the COP and COP/SGCNT composite particles was observed by SEM (Fig.1a) and TEM. It was interesting to found that under a typical polymerization condition, we could produce a unique COP/SGCNT composite particle having a core-shell structure where core is SGCNT/COP and shell is COP (Fig. 1b).

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#### Nanotorosional actuator consisting of carbon nanotube

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A grand challenge confronting nanoscience today is the development of new functional devices that can function in a nanoworld. In this report, we present a nanoactuator, consisting of a carbon nanotube (CNT), with a new function. It can serve as a component actuator for future nanosized devices.

Using a transmission electron microscope (TEM) equipped with a manipulator, we recently demonstrated the transition between the flattened state and the tubular state in rather thick CNTs [1]. This unique transition behavior provides a new concept of a nanosized device: a nanotorsional actuator. The flattened CNT can be twisted. The transition from the flattened state to the tubular state reverses the twist and generates a torsional torque. Figure 1(a) portrays a proposed actuator in a flattened state. Two electrodes support a flattened and twisted CNT at both ends, which have a tubular shape. One end is fixed to the electrode. The other end, which is connected to the electrode with a CNT bearing structure [2], is free to rotate. Figure 1(b) portrays a TEM image of an initially flattened and twisted CNT corresponding to the state of Fig. 1(a). When a certain amount of current is applied to the CNT, the CNT changes its state to a tubular state with rotation at the free end, which turns back the initial twist, as shown in Figs. 1(c) and 1(d). The transition is reversible and controllable by the amount of current applied to the CNTs.

We have also discussed details of the phenomenon and possibility of the device, such as mechanism and response of the transition and output power of the actuator, with not only TEM observations but also molecular dynamics (MD) simulations. Both results clarified that the driving force of the transition is thermal energy. In addition, MD simulations indicate that a specific graphitic stacking order taken for the CNT inside determines the initial twist of a flattened CNT and thereby determines the rotational angle of the actuator.



Fig. 1 Schematics of the proposed nanotorsional actuator for (a) the flattened and (c) the tubular states. TEM images of a CNT corresponding to the states of proposed actuator: (b) the flattened and (d) the tubular states.

[1] R. Senga *et al.*, submitted to Appl. Phys. Lett. [2] J. Cumings and A. Zettl, Science 289 602 (2000)
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# Fabrication and properties of semiconducting single-walled carbon nanotubes/Si hetero junction diode

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Since the high carrier mobility, SWNTs are expected to the application to the various kinds of the electronic devices. Especially, semiconducting SWNTs (S-SWNTs) are direct band-gap materials and expected to be useful for photonic and optoelectronic applications [1]. The S-SWNTs are reported to show unipolar p-type behavior under ambient conditions and various chemical doping have been reported to convert from p-type to n-type.

In this study, we fabricated the various types of p-n diodes based on S-SWNTs/Si hetero junction with some deposition methods and characterized their electronic properties for clarify the fabrication condition of the diode with the near ideal characteristics and photovoltaic properties.

The SWNTs used in this study were purchased from Aldrich (CoMoCAT ( $0.8 \pm 0.1$  nm in diameter)). The ratio of the S-SWNTs in this material was about 90% or more. The SWNTs were dispersed in 1,2-dichlorobenzene at 0.5 mg/mL by ultrasonication, and SWNTs thin film was fabricated on the n-type Si wafer (100 orientation,  $\rho \ll 0.02 \Omega$  cm) in which layers of Cr and Au were deposited on the backside by using airbrush. Finally, Ag was deposited at 100 nm. The schematic of SWNTs/Si diode is showed in Fig. 1.

The thickness of the SWNTs thin film was estimated by both UV-vis absorption measurement and film thickness gauge. The current density-voltage (J-V) curve was measured both dark and AM1.5G condition (100 mW/cm<sup>2</sup>).

Fig. 2 shows one example of the *J-V* characteristics of p-SWNTs/n-Si device (transmittance of SWNT thin film at 550 nm is 46%). The photovoltaic parameters of this device is  $V_{oc} = 0.089 \text{ V}$ ,  $J_{sc} = -0.60 \text{ mA/cm}^2$ , FF = 0.258 and  $\eta = 0.014\%$ .

The relationship between the fabrication condition and the J-V characteristics for several kinds of SWNTs/Si devices will be presented.





[1] P.-L. Ong *et al.*, Nanotechnology **21** (2010) 105203.
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Fig.2 *J-V* characteristics of p-SWNTs/n-Si device in the dark and under AM1.5G condition.

## Polyvinylchloride as a New Dispersing Agent for Supergrowth Carbon Nanotube

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The pilot-scaled mass production of the supergrowth carbon nanotubes (SGCNTs) has attracted much interest from both industry and academic due to their superior physical, chemical and electrical properties over the existing CNTs. The application of the SGCNTs has become an important research topic in the related field in recent years. Our group has focused on the development of polymer/SGCNT composites that exhibit a high electrical conductivity in combination with the intrinsic superior mechanical properties of the polymer matrix.

There are two well-known processes for the fabrication of the polymer/CNT composites. The first one is based on the aqueous mixing of the polymer and CNT solutions with or without the assistance of a surfactant. The other is based on the organic solution process, in which both the polymer and CNTs are separately dispersed in an organic solvent before mixing to form the composites. Because of the fact that CNTs is a strongly hydrophobic material and extremely difficult to disperse in almost existing polymers and organic solvents, it is particularly important to develop an efficient dispersing agent for these polymer/CNT composite materials. This work reports an unprecedented result on the discovery of an efficient dispersing agent for the SGCNTs based on the polywinylchloride (PVC), which is a well-known as a low-cost and mass produced commodity polymer. The preliminary results on the mechanical and electrical conductivity of the PVC/SGCNT composites will also be discussed.

The dispersion of the SGCNTs in a PVC/dimethylacetamide (DMAc) 1 wt% solution was carried out using a bath-type sonication at room temperature for 1h. The resulting SGCNT/PVC solution was characterized by UV absorption spectroscopy. As shown in Fig.1, the absorbent intensities of the SGCNT/PVC solutions in the range of 400-1600 nm

wavelengths were very high and almost identical before and after the centrifugation. The result suggests the formation of an SGCNT/PVC solution without any aggregation. Similar experimental process was also applied for the fabrication of the HiPco/PVC/dimethylacetamide solution system. However, a well dispersing solution of this system was not achieved.

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Fig.1. The absorption spectra of the SGCNT/PVC/DMAc disperse solution.

# Migration of a Ni nanoparticle encapsulated in a carbon nanotube and joining of carbon nanotubes by electric current application

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Carbon nanotubes (CNTs) which have a hollow structure are promising nanoscale plumbing material for transport of atoms and nanoparticles. In this study, the behavior of a nickel (Ni) nanoparticle encapsulated in a CNT was observed during the passage of a current by *in-situ* transmission electron microscopy (TEM).

CNTs were attached to an edge of a gold (Au) plate of 50 µm thickness by dielectrophoresis, and then Ni was deposited on CNTs. A free end of a Ni-deposited CNT was brought into contact with a tip of an Au-coated tungsten needle inside a TEM. By applying an electric current to the CNT, Ni nanoparticles on the CNT were inserted into the CNT. The behavior of the Ni nanoparticle encapsulated in the CNT was observed by *in-situ* TEM with a television camera, and the current and voltage applied to the CNT were simultaneously measured.

Figure 1(a) shows the TEM image of a Ni nanoparticle encapsulated in a CNT. When the bias voltage was increased to 1.9 V, the current increased to 93  $\mu$ A. At the same time, the Ni nanoparticle moved in the direction of the electron flow (Fig. 1(b)) and the CNT was cut at the point of Ni nanoparticle (Fig. 1(c)). Figure 2 shows time-sequence series of TEM images of connection process of CNTs. The CNT2 tip was brought into contact with the Ni nanoparticle on the CNT1 tip. When the bias voltage was increased to 1.9 V, the current increased to 80  $\mu$ A and the Ni nanoparticle moved to the CNT2 tip (Fig. 2(a)). When the Ni nanoparticle was pressed on the CNT1 tip, the CNT1 cap opened and a CNT-Ni-CNT junction was formed (Fig. 2(b)). Finally, the Ni nanoparticle disappeared and two CNTs were reconnected (Fig. 2(c)).



Fig. 1 Time-sequence series of TEM images of migration of a Ni nanoparticle encapsulated in a carbon nanotube.



Fig. 2 Time-sequence series of TEM images of a connection process of carbon nanotubes.

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## Fabrication and Characterization of Thin Film Transistors Using As-Grown SWNTs

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Single-walled carbon nanotubes (SWNTs) are one of the most attractive materials for next-generation electronic devices. However, in a single-channel SWNT field-effect transistor (FET) it is difficult to obtain a large drain current and to fabricate integrated circuits because of variability of FET characteristics and limitations on current capability. In contrast, a SWNT thin-film transistor (TFT) can solve these problems [1, 2]. Here, we used an as-grown SWNT film as the FET channel because as-grown SWNTs demonstrate higher performance than solution-processed SWNTs.

Figure 1 shows the SEM image of a fabricated TFT on a Si substrate. The channel length

and width are 5 and 3  $\mu$ m, respectively. After fabrication of a photolithographically defined electrode array (Ti/Pt: 5 nm/15 nm), Fe particles acting as catalyst were deposited over the patterned photoresist using a pulsed arc-discharge plasma gun [3]. The residual resist was then removed and SWNTs were synthesized by standard alcohol CVD.

Typical transfer characteristics are shown in Fig. 2. A large on/off ratio of about  $10^6$  was obtained, however, the on-current remained at the few- $\mu$ A level. This is attributed to relatively poor contact between channel and electrode, but the drain current is expected to improve by process optimization.

References:

[1] E. S. Snow et al. Appl. Phys. Lett. 82, 2145 (2003).

[2] Q. Cao et al. Nature 454 495 (2008).

[3] D. Phokharatkul et al. Appl. Phys. Lett. 93, 053112 (2008).

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Fig. 1 SEM image of SWNT TFT.



## Resistance distribution measurement of CNT networks grown directly on Si substrate by conductive atomic force microscopy

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Carbon nanotubes (CNTs) are expected to be suitable for applications to thin film transistors (TFTs) because of their advantages of high mobility and flexibility. In order to implement high-performance CNT-TFTs, it is important to understand the electrical properties of the CNT networks. In the previous study on the measurement of the electrical properties of the CNT networks, the sample was prepared by the wet process [1, 2]. In such cases, there is a concern that the electrical properties of CNT networks are affected by the effect of chemical doping during the wet process. In this study, we measured resistance distribution of CNT networks grown directly on Si substrate with SiO<sub>2</sub> by thermal chemical vapor deposition using conductive atomic force microscopy (C-AFM). In the C-AFM, the conductive tip acts as a scanning local electrode and I-V characteristics between tip and Au electrode of the sample are measured.

Figure 1 shows the schematic view of C-AFM measurement and current distribution image obtained by C-AFM ( $V_{tip}=0.2$  V,  $V_{GS}=0$  V). There are two paths (path 1 and 2). Both paths cross each other where abrupt change in gray scale intensity was observed, suggesting the existence of a large inter CNT resistance. Figure 2 shows the resistance distribution along path 2 at  $V_{GS}=0$  V. The resistance shows step-like increase at the cross point (L=1250 nm). From the step of resistance value, the inter CNT junction resistance was estimated to be about 30 MΩ. The resistivity of CNT was estimated to be 18~320 MΩ/µm. These large values suggest that the CNTs are semiconducting and in off state at  $V_{GS}=0$  V.





Fig. 1 Current distribution image obtained by C-AFM

 $(V_{tip}=0.2 \text{ V}, V_{GS}=0 \text{ V})$ 

Fig. 2 Resistance distribution along path 2 ( $r_{GS}$  )

Inset is the schematic view of the C-AFM measurement.

[1] M. S. Fuhrer *et al.* Science **288**, 494 (2000). [2] P. N. Nirimalraj *et al.* Nano Lett. **9**, 3890 (2009). Corresponding Author: T. Mizutani

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### In situ transmission electron microscopy study on electric transport characteristic of a silicon nanoparticle held between carbon nanotubes

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Silicon nanoparticles (Si NPs) are expected to be applied to single electron transistors and electroluminescence devices [1]. Electric transport property of a single Si NP has not been studied in detail. In this study, we manipulated a Si NP using carbon nanotubes (CNTs) as a conductive probe in a transmission electron microscope, and studied the electric transport property of the single Si NP by *in situ* transmission electron microscopy (TEM) with simultaneous measurements of the bias voltage and current.

CNTs synthesized by arc discharge method were attached to the edge of a gold plate by dielectrophoresis, and Si was deposited on the surface of the CNTs at 873 K by electron beam evaporation. The gold plate was mounted on a stationary stage on a specimen holder of TEM. A gold-coated tungsten needle fixing a CNT was mounted on a piezoelectric translation stage on the specimen holder. The tip of the CNT protruding from the needle was brought into contact with a Si NP deposited on the CNTs in the microscope, and current-voltage (I-V) characteristic of the Si NP was investigated while observing the structure.

Figure 1 shows a TEM image of a Si NP used for I-V measurement. The Si NP of 25nm in diameter is held between two CNTs, as indicated by a downward arrow. The Si NP is crystalline and its surface is covered with natural oxide layers of 1-2 nm in thickness. Figure 2 shows I-V curves of the Si NP shown in Fig. 1. The current begins to increase exponentially at an applied voltage of 2.7 V. The I-V curves were analyzed using the Fowler-Nordheim (F-N) theory. The F-N plots, which are obtained from I-V curves shown in Fig. 2, followed approximately a straight line, suggesting that the current was caused by the F-N tunneling.



Fig. 1. TEM image of a Si NP held between two CNTs.



Fig. 2. *I-V* curves of a Si NP of 25 nm in diameter observed in Fig. 1.

[1] X. Zhou et al, J. Appl. Phys., 106, 044511 (2009).

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#### Continuous electron doping to SWCNT film with inkjet technique

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Carrier doping is extremely important technique and many researches about hole and electron doped SWCNTs have been already reported [1]. Particularly, p-type dopant is well studied and the continuous downshift of SWCNT Fermi level towards the valence band has been confirmed. In stark contrast to this, it is still difficult to investigate detail doping process in electron doped SWCNTs due to air instability of dopants. Recently, several air-stable electron donors have been reported through the transistor fabrication and opened a route for the detailed study of electron doping process. However, transistor measurement cannot distinguish the Fermi level shift of SWCNT from the lowering of Schottky barrier for electrons, and the direct observation of conduction band filling is strongly required. Here, we directly investigated charge transfer between SWCNTs and dopants by optical measurements, and clarified the detail electron doping process using continuous inkjet doping.

Figure 1 shows a schematic illustration of inkjet chemical doping process. SWCNT thin film was fabricated by inkjet technique on quartz substrate. On these SWCNT films, we printed the solutions of N-type dopants, such as Polyethyleneimine (PEI), 1-1'-Dibenzyl-4,4'-bipyridinium dichloride (Viologen) and NADH, and measured their absorption spectra. We repeated this cycle to investigate the printing times dependence of SWCNT Fermi level. Figure 2 represents the absorption spectra of both pristine and doped SWCNT film and the difference spectrum between them. The dopants for Figs. 2(a) and 2(b) are PEI and Viologen, respectively. These results obviously indicate the shift of Fermi level and we observed clear transition of SWCNT behavior from naturally-doped p-type to air-stable n-type by the printing times dependence.

In summary, we have combined continuous electron doping by inkjet printing with optical measurements, and successfully investigated the electron doping process of SWCNT. We will also quantitatively argue the relationship between the Fermi level shift and the amount of printed electron dopants, which suggests charge-transfer mechanism between them.



Fig.1Inkjet electron dopingFig.2 (Up) Absorption spectra of pristine and doped SWCNT film (Down) Difference spectrum[1]S. Matsuzaki et al. Appl. Phys. Express 4 (2011) 105101.Corresponding Author: Taishi Takenobu, TEL&FAX: +81-3-5286-2981 , E-mail: takenobu@waseda.jp

#### Fullerene encapsulation inside carbon nanotubes formed by surface decomposition of SiC

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It has been reported that well-aligned zigzag-type carbon nanotubes (CNTs) could be produced on SiC(000-1) by surface decomposition of SiC [1]. Electronic modification of these CNT films might lead to novel CNT devices because of their high CNT density and unique structure. In addition, encapsulating additional molecules into the inner-spaces of CNTs is one of promising methods to control the electronic property of CNTs [2]. In this study, we attempted to encapsulate fullerene into the insides of CNTs, while keeping the original CNT/SiC hetero-structures.

CNT films formed by surface decomposition of 6H-SiC(000-1) were used as samples. Opening of CNTs were carried out by annealing CNT films in nitric acid (60%) at 100°C for 4 hours. Then, for the purpose of encapsulation, the CNTs were exposed to the vapor of fullerene in a test tube at 800°C, which were evacuated to  $\sim 3 \times 10^{-3}$  Pa before heating. After these treatments, the CNT films were characterized by Raman spectroscopy and SEM observations. TEM observations were also carried out for CNTs after peeling off from the SiC substrates before and after the encapsulating treatments.

Fig. 1 shows a typical TEM image of a CNT after exposing to the vapor of fullerene. In the inner CNT, a lot of fullerenes were observed, which had not been seen before this treatment. Although a few fullerenes seem to adhere to the outside of CNTs, the density of fullerenes inside the CNT was much higher than the outside. indicating that fullerenes were well encapsulated into the inside of CNTs. We also investigated the effect of both opening and encapsulating treatments on the encapsulation yield into the CNT films.

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[1] M. Kusunoki et al., Chem. Phys. Lett. 366, 458 (2002). [2] T. Kato et al., Appl. Phys. Lett. 95 (2009) 083109.

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Fig. 1 TEM image of CNTs after the encapsulating treatment.

## Doping Properties of One-Dimensional π-Conjugated Molecules inside Single Wall Carbon Nanotubes

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According to the Gauss's law, there is no electric field inside the hollow spaces of charged cylindrical materials. So the charges on the surface of the cylinders do not influence the properties of materials inside the hollow space. Single-wall carbon nanotubes (SWCNTs) are cylindrical graphitic tube with diameter of about 1.0 nm. SWCNTs can encapsulate various kinds of organic molecules. It is well known that the SWCNTs can be charged by doping of electrons or holes, but how the encapsulated molecules can be doped has been under discussion. Clarification of the doping properties of encapsulated molecules is of great importance for correct understanding of electric phenomena inside nano-space. Here we clarify that encapsulated molecules can be doped by electro-chemical techniques, and their doping characteristics are quite different from those in a solution. We used  $\beta$ -Carotene (Car) as encapsulated molecules for the following three reasons: (1) Car is a model of one-dimensional  $\pi$ -conjugated molecules. (2) Raman signals from the encapsulated Car are strong and stable enough for detailed investigation. (3) Encapsulation of Car has been well confirmed by various techniques. We investigated the electro-chemical properties of Car inside semiconducting SWCNTs. We found that extraction of electrons of Car occurs clearly. The Raman intensity of C=C stretching modes of Car has decreased as the shift of the potential. When Car in a solution is doped by electrochemical technique, potential must be changed very quickly (more than 10 Vs<sup>-1</sup>) to recover the signal in order to avoid the diffusion and chemical reactions of doped Car. However, in the case of Car in SWCNTs, although the potential is very slowly changed (about  $1.0 \times 10^{-3}$  Vs<sup>-1</sup>), the signal can be recovered, suggesting the improvement of stability of Car as well as confinement effect of nano-space. Moreover, the dependence of Raman intensity on the potential is clearly different between Car in SWCNTs and in a solution, suggesting influence of surrounding semiconducting SWCNTs on Car. The extraction of electrons of Car occurred after that of the surrounding

semiconducting SWCNTs. Density-functional theory (DFT) calculations on Car inside semiconducting SWCNTs have shown that the highest occupied molecular orbital (HOMO) of located in Car is the middle of the semiconducting band gap. However, the energy of HOMO becomes lower as electrons are partially extracted. This lowering of HOMO energy is caused by the removal of on-cite Columbic repulsion in Car. Finally, the HOMO becomes lower than the valence band of semiconducting SWCNTs. These calculation results are well in agreement with experimental results.

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Fig1. DFT calculation of HOMO of encapsulated Car at 0 hole (left) and 0.5 hole (right)

### Preparation of nanographene sheets decorated by size-controlled Pt sub-nano/nanoclusters

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Recently, many studies regarding the functionalization of graphene by surface modification and/or metal nanocluster decoration have been conducted. Graphene and its composites have been shown to have advantageous properties as electrochemical catalysts in energy devices. Yoo et al. showed that 2-3 nm-Pt-nanocluster-decorated graphene contains sub-nano Pt clusters (<0.5 nm) and suggested that such sub-nanocluster has superior CO tolerance for an electrochemical catalyst of DMFC (direct methanol fuel cell) [1].

In this study, we focused on controlling the size of Pt nanocluster on graphene to clarify the dependence of Pt cluster size on the propertiy for electrochemical catalyst. In a previous study, carboxyl groups were shown to remain mainly at the edges of graphene oxide sheets, even after reduction. Futhermore, organic Pt ammine complexes attached at the edges of the

graphene sheets [2]. In this study nanographene oxide sheets were employed as graphene source because it was considered that nano-graphene sheet, which has a high edge-state density, was desirable as a support material for Pt nanoclusters prepared from Pt complexes. The TEM images of Pt nanoclusters on nano-graphene are shown in Fig. 1.

To prepare nano-graphene sheets decorated by Pt clusters with large surface area, the liquid phase reduction technique was



Fig.1 (a) STEM and (b) HAADF-STEM images of nanographene sheets decorated by Pt clusters

used on nanographene oxide sheets (< 100 nm), followed by vapor phase reduction of the Pt complex,  $(Pt(NO_2)_2(NH_3)_2)$ .

By varying the initial concentration of Pt complex, we precisely controlled the size of Pt nanoclusters with a narrow size distribution on the nanographene sheets with a relatively large surface area (270 m<sup>2</sup>/g). The mean diameters of Pt nanoclusters in 20, 5 and 2 wt% Pt nano-graphene were 2.4, 1.5 and 1.1 nm, respectively.

Moreover, we suggest that Pt-decorated nano-graphene sheets could offer excellent CO tolerance performance of Pt for the methanol oxidation reaction. Further details will be discussed in 42<sup>nd</sup> Fullerenes-Nanotubes-Graphene General Symposium.

[1] E. Yoo, T. Okata, T. Akita, M. Kohyama, J. Nakamura, I. Honma, Nano Lett. 9, 2255 (2009).

[2] R. Yuge, M. Zhang, M. Tomonari, T. Yoshitake, S. Iijima, M. Yudasaka, ACS Nano 2, 1865–1870 (2008). Corresponding Author: T. Tomai

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# Novel electric field effects on magnetic oscillations in graphene nanoribbons

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# Abstract

Graphene nanoribbons (GNRs) has drawn much attention in recent years in both theoretical and experimental fields because of its quasi-two-dimensional (2D) structure and its promising use as nanoscale transistors<sup>[1]</sup>. To date, many investigations have focused their attention on the electronic and magnetic properties of GNRS, revealing spectacular effects arising from the confinement of electron and hole gases<sup>[2]</sup>.

In our study, we investigate the de Haas-van Alphen effect of GNRs in the presence of an electric field and scattering from impurities. Using quantum electrodynamics theory, we calculate the energy eigenvalues and eigenstates. By employing quantum statistical approch, we derive the magnetization and magnetic susceptibility. We find that the magnetization and magnetic susceptibility are shown to be modulated through the dimensionless parameter  $(\beta = \frac{E}{v_F B})$ , suggesting that GNR should be a non-linear magnetic medium. Moreover, the amplitude of magnetic oscillations collapses due to impurity scattering and temperature in both zigzag and armchair nanoribbons.



A.K. Geim, and K.S. Novoselov, Nature Mater.6, 183(2007)
 Y. Zhang, Y.W. Tan, H.L. Stormer, P. Kim, Nature 438, 201(2005)
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# Influence of electrolytes for the preparation of graphene oxide via electrochemical method

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Chemically modified graphenes, including graphene oxides, reduced graphene oxides and their derivatives, have attracted a lots of attention due to its solution processability. Previously, we have reported a new electrochemical exfoliation method using a sodium salt as an electrolyte [1]. The advantage of this method is an environment-friendly process without using strong oxidants that are often employed in other popular oxidation procedures such as Hummers method. However, the effect of electrolytes for exfoliation of graphite is largely unknown. Herein, we have investigated the influence of electrolyte materials for graphene exfoliation.

Figure 1 shows an experimental setup, where an expanded graphite sheet is employed as both an electrode and a source of graphene for electrochemical exfoliation. A Pt plate and an Ag/AgCl electrode are used as the working and reference electrodes, respectively. Na<sub>2</sub>SO<sub>4</sub>, NaNO<sub>3</sub>, Na<sub>2</sub>CO<sub>3</sub>, CH<sub>3</sub>COONa, Na<sub>2</sub>HPO<sub>4</sub>, Na<sub>2</sub>SiO<sub>3</sub>, Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>-5H<sub>2</sub>O were used as electrolytes. Upon application of a dc voltage of 4-10 V, the graphite electrode was quickly broken into small pieces and spread into the solution. After the exfoliation, the graphite pieces were collected on a filter, washed with water and HCl, and dried in a vacuum oven.

Figure 2 shows the statistical thickness analysis for the graphene sheet from  $Na_2SO_4$  and  $Na_2HPO_4$ . The average thickness of their graphene is 2.41 nm from  $Na_2SO_4$  and 9.80 nm from NaHPO<sub>4</sub>, respectively. Graphite electrode was not exfoliated by  $Na_2CO_3$ , CH3COONa,  $Na_2S_2O_3$ -5H<sub>2</sub>O. This means that it is difficult to exfoliate graphite by the salts of weak acids.

In summary, this work shows that the size and thickness of exfoliated graphene via electrochemical method are related to the type of electrolyte.



Fig1 Schematic diagram showing the electrochemical apparatus.



Fig2 Statistical thickness analysis of graphene sheet from (a)Na<sub>2</sub>SO<sub>4</sub> and (b)Na<sub>2</sub>HPO<sub>4</sub>

[1] H. Okimoto et al., Abstract of the Fullerene-nanotubes-graphene symposium, 3p-7(2011).

[2] W.S. Hummers et al., J. Am. Chem. Soc., 80, 1339(1958).

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### Effect of hydrogen in cooling on graphene growth

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To apply graphene to device applications, high-quality, large-area graphene synthesis will be required. Chemical vapor deposition (CVD) has been used to synthesize graphene films on copper foils. In this study, we aim to clarify whether the flow of  $H_2$  during cooling affects the growth and quality of graphene films.

Graphene was synthesized on copper foils by thermal CVD method using  $CH_4$  with He as a carrier gas. Growth temperature and time were 1000°C and 15 min, respectively. During cooling process, we introduced 350 sccm He with a variety of flow rate of H<sub>2</sub> to consider whether H<sub>2</sub> affect the growth of graphene during cooling. Resultant graphene were evaluated by an optical microscopy and Raman spectroscopy after the transfer of graphene films to SiO<sub>2</sub>(300nm)/Si substrates.

Raman spectra from the graphene films grown with the H<sub>2</sub> flow rate of 50 sccm (Fig. 1) and 350 sccm (Fig. 2) show that G' peak increases with decreasing the H<sub>2</sub> flow rate, while D band peak increases with increasing the H<sub>2</sub> flow rate. Figure 3 summarizes G'/G and D/G ratios with respect to the H<sub>2</sub> flow rate. G'/G ratio tends to decrease with increasing the flow rate of H<sub>2</sub>, while D/G ratio increases with increasing the H<sub>2</sub> flow. These results indicate that graphene becomes thicker and more defective as the flow rate of H<sub>2</sub> increases, also proved by atomic force microscopy. This implies that H<sub>2</sub> may have an effect of inhibiting carbon atoms from constructing six-membered ring structure, or inducing etching damage to the graphene film.

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Fig. 1 Raman spectrum of the graphene grown with the  $H_2$  flow rate of 50 sccm.



Fig. 2 Raman spectrum of the graphene grown with the  $H_2$  flow rate of 350 sccm.



Fig.3 G'/G and D/G ratios of graphene with respect to the flow rate of  $H_2$ .

# Synthesis of a novel nanocarbon structure: multi-layer graphene formed at the both sides of catalyst metal film on a substrate

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Graphene has attracted great attention from many researchers due to its excellent physical properties such as extremely high electron mobility [1]. These attractive properties may lead to many applications, such as interconnects and channels of large scale integrated circuits. In this presentation, we demonstrate formation of a novel nanocarbon structure consisting of multi-layer graphene, where metal film is sandwiched by multi-layer graphene on a substrate. This unique structure is formed by a simple process: just depositing multi-layer catalyst film (Co/TiN/Co) on a substrate and supplying the substrate with acetylene at a temperature of 450°C.

Figure 1(a) shows the cross sectional TEM image of the sample, which appears to be composed of three layers. The first layer and third layer appeared to be a layered material such as multi-layer graphene. In fact, the distance between each layer was estimated to be approximately 0.37 nm, close to the distance between the graphene layers of graphite. Further, the first and third layers were assigned to be multi-layer graphene analyzed by electron energy loss spectroscopy and x-ray diffraction. The second layer was identified as the metal film originally deposited on the substrate. Namely, the metal layer was lifted up by graphene layers formed at the interface of the substrate and the metal film. At the same time, multi-layer graphene was also formed on the upper surface of the metal film. The structure is schematically illustrated in figure 1(b). The thicknesses of the upper and lower graphene

stacks were estimated to be approximately 30 and 15 nm. respectively. The composition of the metal remained unchanged, film although their thicknesses seemed to fluctuate to some extent. It has been found that, by controlling the thickness of the catalyst film and growth condition, the thickness of graphene is controllable. The details of the synthesis method will be described in this presentation.

catalyst substrate

This research is partly supported by the Japan Society for the Promotion of Figure 1 (a) TEM image and (b) schematic model of multi-layer graphene at the both ends of catalyst film on a substrate.

Science (JSPS) through its "Funding Program for World-Leading Innovative R&D on Science and Technology (FIRST Program).

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

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#### CVD synthesis of graphene / hexagonal boron nitride hybrid sheets

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Graphene has attracted much attention in recent years as important components for the next-generation electronic devices because of their excellent electronic transport properties. Hexagonal boron nitride (h-BN) is an insulating isomorphic of graphite with boron and nitrogen atoms. Because of their structural analogy, it is interesting to hybridize these two materials. Such a graphene/h-BN hybrid sheet can be regarded as a new two-dimensional atomically thin sheet with both metallic and insulating properties. Recently, chemical vapor deposition (CVD) has been demonstrated as an efficient method to synthesize single-layer graphene and h-BN films <sup>[1-2]</sup>. The growth of both of these has been shown to follow the so-called Frank van der Merwe model under controlled CVD conditions. This fact has motivated us to produce single-layer hybrid sheets of graphene and h-BN by using multistep CVD processes.

In this work, we report the CVD synthesis of graphene and h-BN hybrid sheets. For the synthesis of the hybrid sheets, the single-layer graphene with a grain size of around 10 µm was grown on Cu foils from methane at first. h-BN was, then, synthesized on the same Cu foils from ammonia borane. SEM observations reveal that such synthesized sheets are composed of micrometer-sized polygonal grains surrounded by narrow sheets with a width of around 1 µm (Fig.1a). Raman spectra of the sheets show that the polygonal grains and the surrounding narrow sheets correspond to graphene and h-BN, respectively (Fig.1b). The results indicate that h-BN can be synthesized through an in-plane epitaxial growth on the graphene edge. These results provide a promising way for novel hybrid materials such as two-dimensional super lattices of graphene and h-BN.



Fig1. (a) SEM image of graphene / h-BN hybrid sheets on a Cu foil synthesized by using CVD.

(b) Raman spectra of the sheet at different position.

[1] X. Li et al., science 324, 1312 (2009).

[2] K. Kim et al., Nano Lett. (2011) in press.

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### Growth of Nitrogen-doped Graphene by Chemical Vapor Deposition

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Graphene, a two-dimensional network of sp<sup>2</sup> carbon atoms, is attractive for electronic device applications because of its exceptional electronic and physical properties. From the perspective of practical graphene-based integrated devices, it is important to prepare high quality graphene sheets in large-area while controlling its electrical properties. The doping of the acceptor/donor to the graphene is a viable approach to tailor its physical and electronic properties. Theoretical predictions also show that the in-plane substitution of nitrogen atoms into the graphene can modulate its electronic properties to an n-type semiconductor <sup>[1]</sup>. However, it is difficult to prepare the nitrogen-doped graphenes in large area, and then various problems still remain for the growth.

We report here the growth of large-area nitrogen-doped graphene sheets by a chemical vapor deposition using ethanol as the carbon source. The samples were grown at  $975^{\circ}$ C on Cu/MgO(100) substrate. For nitrogen doping, pyrazine (C<sub>4</sub>H<sub>4</sub>N<sub>2</sub>) was added to ethanol, and doping level were controlled by varying the concentration of pyrazine. To characterize the nitrogen-doped graphene samples, we conducted Raman spectroscopic observation with 458 nm line of an Ar laser excitation.

Figure 1 shows Raman spectra of the samples doped with pyrazine of the several concentrations. For comparison, Raman spectra of undoped graphene and HOPG are also shown. As shown in Fig. 1, we observed the G- and 2Dpeak of graphene at the entire surfaces of the samples. And, the G/2D intensity ratio is roughly estimated about 0.5 for all samples. These results indicate the monolayer graphene was grown on all over the surface [2]. Figure 2 shows the plots of the G-peak frequencies and FWHMs. With increase in the pyrazine concentration, the G-peak gradually shifts to lower frequency side and becomes broadened. This suggests the systematic incorporation of nitrogen atoms in the  $sp^2$  of graphene<sup>[3]</sup>.

#### **References**:

[1] A. Lhebier *et al.*, Phys. Rev. Lett. **101**, 036808 (2008).
 [2] D. Graf *et al.*, Nano Lett. **7**, 238 (2007)

- [3] L.S. Panchakarla *et al.*, Adv. Mater. **21**, 4126 (2009). Corresponding Author: S. Kamoi
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Fig. 1 Raman spectra of the samples with several pyrazine concentrations.



Fig. 2 Plots of G-peak frequencies and the widths.

### Polarized Raman scattering study on graphene nanostructures on vicinal SiC substrate

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Graphene is a monolayer of carbon atoms arranged in a hexagonal honeycomb structure. Recently, graphene nanoribbons attract remarkable attention because it is predicted that graphene nanoribbons have a finite bandgap and show different magnetic and optical properties from bulk graphenes. The graphitization of silicon carbide (SiC) substrates is one of the promising approaches for fabricating epitaxial graphene. Especially, epitaxial graphene on vicinal SiC substrate grows anisotropically along the nano-steps on the surface <sup>[1]</sup>. Hence, formation of ribbon-like structure is expected on the epitaxial graphene along the steps.

The samples were prepared by the sublimation technique on Si-face of vicinal 6H-SiC (0001) substrate inclined to [1-100] direction. The number of graphene layers was evaluated by atomic force microscope. The polarized Raman spectra were observed at room temperature using 458 nm line of an Ar laser excitation.

Figure 1 shows polarized Raman spectra as a function of incident light polarization angles. The polarization angle is measured from [1-100] direction of SiC substrate. The inset shows the dependence of the G-peak intensity on the polarization angle. The data are fitted by following equation,

 $I(G)(\theta_{in}) = I(G)_{min} + [I(G)_{max} - I(G)_{min}]\cos^{2}(\theta_{in}),$ where  $\theta_{in}$  stands for the polarization angle <sup>[2]</sup>. The G-peak intensity strongly depends on the polarization angle and it gives maximum at  $\theta_{in}=0$ (polarization direction is parallel to [1-100]) and minimum at  $\theta_{in}=90$  (perpendicular to [1-100]). This result agrees with earlier theoretical and experimental reports <sup>[2, 3]</sup>, and suggests that the sample contains the graphene ribbon-like structure with the armchair edge.

#### **References**:

[1] S. Tanaka et al., Phys. Rev. B 81, 041406(R) (2010).

[2] K. Sasaki et al., J. Phys. Soc. Jpn. 79, 044603 (2010).

[3] C. Casiraghi et al., Nano Lett. 9, 1433 (2009).

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Fig.1 Polarized Raman spectra measured for different polarization angles of incident light. Inset shows the plot of G-peak intensity for various polarization angles.

#### Anisotropic Graphene Growth along Bunched Steps on Copper Surface

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Since the discovery of single-layer graphene uniformly formed on Cu foil surfaces by chemical vapor deposition (CVD) [1], initial stages of graphene growth have been investigated, focusing on the influences of CVD conditions and surface morphology to the growth kinetics. Previous studies reported that the nucleation occurred at defects such as impurities and surface steps, while the growth kinetics was rarely influenced by such defects [2, 3]. It is believed that surface adsorption of carbon species governs graphene growth on Cu, making the growth self-limiting. Therefore, the surface morphology is expected to play a quite important role not only in the nucleation but also in the subsequent growth of graphene.

In this study, we investigated the initial stages of CVD graphene growth on a Cu film to explore correlations between the surface morphology and graphene growth under low pressure condition. Actually, we tracked changes of the Cu surface morphology during the

graphene growth, revealing an interesting correlation. Surface steps on a Cu grain, which occurred during hydrogen annealing prior to the growth, were found to be the nucleation sites of graphene islands and to affect the subsequent growth substantially. We observed, for the first time, an anisotropic graphene growth on the Cu surface accompanied with morphological changes (Fig.1), resulting in graphene array formation (Fig.2). The resultant surface morphology is attributed to the step bunching during the growth. Detailed analyses suggest that the graphene arrays, which were preferentially formed along the steps, served as a partial shield of the Cu surface, preventing step-flow-like Cu atom diffusion and evaporation at the growth sites. As a result, the growth locations acted as a pinning site of the step motion, leading to the step bunching.

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X. Li *et al.*, Science **324**, 1312 (2009).
 J. M. Wofford *et al.*, Nano Lett. **10**, 4890 (2010).
 Q. Yu *et al.*, Nature Mater. **10**, 443 (2011).
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Fig.1 Laser microscope image of Cu film surface after graphene growth



Fig.2 SEM image of graphene array grown along steps on Cu surface

## Scanning Tunneling Microscopy Observation of Moiré Structure in the Transferred Graphene to HOPG

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Moiré structure originated from the lattice misorientation of two graphite layers has been reported on highly oriented pyrolytic graphite (HOPG) [1]. However, it is not easy to easily produce moiré structure in a large area. In this research, we succeed at producing moiré structure in large area and with good reproducibility by transferring monolayer graphene synthesized by chemical vapor deposition (CVD) method on HOPG [2].

Graphene used a commercial one synthesized on copper foil (Graphene Supermarket). Polymenthyl methacrylate (PMMA) was spin-coated on graphene as subordinate material and copper foil was dissolved by FeCl<sub>3</sub>. Then it was transferred on HOPG substrate and PMMA was dissolved by chloroform. Obtained sample was observed by scanning tunneling microscopy (STM).

Figure 1 shows STM images of transferred graphene on HOPG. In Fig. 1(a), moiré structure is extended to more than  $100 \times 100 \text{ nm}^2$  in area. Figure 1(b) shows other moiré structure with different periodicity. We observed various moiré structure with periods ranging from 1.5 nm to 10.5 nm (rotation angle is ranged from 1.3 ° to 9.4 °) on the same sample. This difference is originated from various domains of graphene as well as HOPG. These domains cause difference in direction of lattice orientation from place to place. Amplitudes of moiré structure are also differed and they are ranged from 0.03 nm to 0.36 nm. It is thought that this is reflected electron density stronger than height.



Fig. 1. STM image of moiré structure on the transferred graphene on HOPG. (a)Tunneling current: 0.8 nA, tip-sample voltage: 0.1 V, image size:  $150 \times 150$  nm<sup>2</sup>. (b) Tunneling current: 1.0 nA, tip-sample voltage: 0.1 V, image size:  $75 \times 75$  nm<sup>2</sup>.

[1] M. Kuwabara, D.R. Clarke, D.A. Smith, Appl. Phys. Lett. 56 (1990) 2396.
[2] William Regan et al., Appl. Phys. Lett. 96 (2010) 113102.
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#### Chemical doping of graphene thin films from organic conductor

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Transparent conductive films (TCFs) are critical components of a myriad of technologies including flat panel displays, light emitting diodes, and solar cells. Graphene-based TCFs have attracted a lot of attention because of their high electrical conductivity, transparency and low cost. Carrier doping of graphene would potentially improve the properties of graphene-based TCFs for practical industrial applications. However, controlling the carrier type and concentration of dopants in graphene films is challenging, especially for the synthesis of p-type TCFs.

Here, we describe a new method for doping graphene using the conjugated organic molecule, tetracyanoquinodimethane (TCNQ) as shown in Fig.1 [1]. Notably, TCNQ is well known as a powerful electron accepter and is expected to favor electron transfer from graphene into TCNO molecules, thereby leading to p-type doping of graphene films. Small amounts of TCNQ drastically improved the resistivity without degradation of optical transparency as shown in Fig.2. The sheet resistance increased by less than 10 % after 1 year at room temperature under ambient atmosphere. Such a stability is a quite critical issue of doping technique in any application fields. Moreover, doping mechanism of the chemical doping is investigated using the first-principles method based on density functional theory.



Fig.1 Schematic image of chemical doping



Fig.2 Optical and electrical properties of doped and non-doped graphene thin films

[1] R. Ishikawa et al. Nanoscale Research Letters 6, 111 (2011).

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## Non-equilibrium dynamics of dehydrogenation of *graphane* induced by the ultra-short laser pulse

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*Graphane* is hydrogen (H) terminated graphene on both sides of the sheet forming  $sp^3$ -like bond network. *Graphane* was theoretically proposed in 2007 [1], and the reality was experimentally suggested later[2,3]. Since C-H bonds on both side has the same binding energy, desorbing H atoms only from one side is thermodynamically inhibited.

In this presentation, we propose non-thermal way to desorb H atoms only from one-side of graphane with use of short-pulse laser shot. Figure 1 shows the first-principles simulation of the molecular dynamics based on time-dependent density the functional theory[4], representing H-desorption only from upper side of graphane with very short ( $\sim 2$ pulse laser causing asymmetric fs) time-variation of the electric field of laser shot. which causes large de-touching forces to H atoms only on one side.

We will present details of the numerical scheme [5,6] to perform this simulation and discuss application of the ultra-short laser pulse for structural change of materials as well as possible applications of the half-dehydrogenated structure.



Fig. 1 Molecular dynamics (MD) of graphane upon irradiation with pulse laser. Upper panel shows stable structure of graphane and the lower panel shows a snapshot of the MD representing one-side H desorption 40 fs after the laser shot.

[1] J. O. Sofo, A. S. Chaudhari, and G. D. Barber, Phys. Rev. B75, 153401 (2007).

[2] D. C. Elias, et al., Science, 323, 610 (2009).

[3] J. D. Jones, et al., CARBON 48, 2335 (2010).

[4] E. Runge and E. K. U. Gross, Phys. Rev. Lett. 52, 997 (1984).

[5] O. Sugino and Y. Miyamoto, Phys. Rev. B59, 2579 (1999); Phys. Rev. B66, 089901 (E) (2002).

[6] Y. Miyamoto and H. Zhang, Phys. Rev. B77, 165123 (2008).

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### Model Experiment of Production of Carbon Clusters by Impact of Asteroids

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It is expected that many types of carbon nanoclusters are produced by impact reactions of asteroids in space, when such reactions take place in a carbon-rich atmosphere. Particularly on Titan satellite, a large number of carbon clusters produced by impacts of asteroids are expected to be stored as there are much amount of cold methane in nitrogen atmosphere. [1] Here, impact production of carbon nanoclusters is examined in nitrogen gas using a two-stage light-gas gun to simulate the impact reactions in space. A small polycarbonate ball (or a stainless steel ball) is injected at about 6.5 km/s into a pressurized target chamber to collide with an aluminum target (or a hexane + aluminum target) in 1 atm of nitrogen gas. [2, 3] Reactions by changing the target material and the target temperature are carried out. After the impact, we carefully collect produced soot and analyze it by a TEM, a LD-TOF-MS, a Raman spectrometer etc. We confirm the production of many types of carbon nanoclusters such as metal-encapsulated carbon nanoparticles, carbon nanotubes, balloonlike nanocarbons, fullerenes, etc. Therefore, in space, many kinds of carbon clusters have been produced by impact phenomena, and they are stored on star's surfaces and in interstellar space. [1] Titan from Cassini-Huygens, ed. R. H. Brown, J. Lebreton, and J. H. Wait (Springer, Dordrecht,

2009) p. 75.

[2] T. Mieno and S. Hasegawa: Appl. Phys. Express 1 (2008) 067006.

[3] T. Mieno, S. Hasegawa and K. Mitsuishi: Jpn. J. Appl. Phys. 50 (2011) 125102.

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Fig. 2 TEM image of produced balloon-like carbons.

### Buffer gas optimization for structure control of carbon nanohorn aggregates prepared by CO<sub>2</sub> laser ablation

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Single-wall carbon nanohorns (SWNHs) are single-graphene tubules with nanometer-scale diameters, and about 2000 of them gather and form a spherical aggregate with diameters of 50-200 nm. Many fundamental and application studies have been done since its discovery in 1998 [1]. In spite of these vigorous studies, intentional morphology-control of the SWNH aggregates, *i.e.*, seed, bud, dahlia, and petal-dahlia types, has not been thoroughly investigated yet. In this study, we succeeded in morphology-selective preparation of SWNH aggregates by changing the buffer gas in  $CO_2$  laser ablation of graphite [2].

The CO<sub>2</sub> laser ablation was operated at 3.5 kW. During 30 seconds laser ablation, the target was rotated at rotation speed of 2 rpm. The buffer gases were He, Ne, N<sub>2</sub>, Ar, Kr, or Xe, and the gas flow rate was 10 L/min. The gas pressure in the chamber was controlled at 760 Torr.

Seed type for He, dahlia type for  $N_2$ , Ar and Ne, and petal dahlia type for Kr were prepared preferentially, respectively. In Xe, thin graphene sheets were the major product. The degree of graphitization increased with the mass number of the buffer gas. Although shapes of SWNH aggregates observed by a scanning transmission electron microscopy were quite similar for the samples prepared by buffer gas of  $N_2$  and Ar, thermogravimetric analysis and  $N_2$  gas adsorption results clearly indicated that SWNHs grown in  $N_2$  had considerably small surface area than those grown in Ar. We found that oxidation treatments made this discrepancy almost disappear, leading to possible costs reduction for production by substituting  $N_2$  for Ar buffer gas and progressing application to various promising fields. The details are shown in the presentation.

[1] S. Iijima et al. Chem. Phys. Lett. 309, 165 (1999).

[2] R. Yuge et al. Carbon, in press.

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### Structure and Phase Behavior of Water Confined in Zeolite Templated Carbon (ZTC)

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Zeolite Templated Carbon (ZTC) is a new porous carbon synthesized using the nanochannels of zeolite Y. (Fig.1) The novel characteristics of ZTC are its uniform nanopores with a diameter of ~1.2 nm, a long range periodicity derived from the parent zeolite Y, and high specific surface area of up to 4000 m<sup>2</sup>/g. A proposed model for ZTC is buckybowl-like nanographenes assembled into a three-dimensionally regular network<sup>[1]</sup>.

In this work, we carried out differential scanning calorimetry (DSC), NMR measurements, X-ray diffraction (XRD) experiments, and classical molecular dynamics (MD) calculations to clarify the structure and phase behavior of water confined in nanopores of ZTC. The phase behavior was investigated by DSC measurements and there was no evidence for liquid-solid transition as in the bulk down to150 K. The NMR measurements showed consistent results with the DSC measurements and also indicated that the confined water exhibits fast motion down to 200 K. As for the structure, it was indicated by the MD calculations that the confined

water cluster at low temperatures is not crystalline ice but a kind of an amorphous solid. The amorphous solid can be characterized by distorted hydrogen bond networks with very few dangling-bonds. XRD patterns were simulated by using the structure obtained by the MD calculations, and they were quite similar to those obtained by the experiments. (Fig. 2)



**Fig.1** Possible structural model proposed for ZTC solid.



(a) Observed 300K 26226K 245K 113K (b) Simulated 300 K 263 K 245 K 10 K 201/Å)

**Fig.2** Temperature dependence of (a) Observed and (b) simulated XRD patterns for wet ZTC. The broad peaks derive from water diffuse diffraction.

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### Influence of ZnO Powder Addition on Upright State of Carbon Nanotwists Treated by Dielectric Barrier Discharge

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Field emitter (FE) coated with dielectric material has good current-voltage characteristics. This is because the coated dielectric material reduces the work function of FE [1]. We have used carbon nanotwists (CNTws) as a base material of FE, and the printed CNTws on substrate were treated with dielectric barrier discharge (DBD) to make CNTws stand up on substrate [2]. CNTw is a kind of helical carbon nanofiber and is expected to be stronger against ion bombardment than carbon nanotube (CNT) because of its larger fiber diameter (100–200 nm). In our previous study, we coated Pt on FE surface and then treated the surface with DBD. However, Pt was rearranged from the surface of CNTw dot to substrate near the dot. In this study, we added ZnO powder (Kanto Chemical Co., Inc) to CNTw paste before printing. The CNTw paste was prepared by mixing ZnO powder into a mixture of an organic binder, silicone one and CNTw. The CNTw FE was fabricated by screen-printing the paste on a Si substrate and by calcining the paste at 400°C. We compared the upright state of CNTws between non-added- and ZnO-added-FEs. Figure 1 shows an SEM micrograph of surface of the CNTw dot with ZnO addition. Table 1 shows the average lengths of upright CNTws of non-added and ZnO-added. The average length of ZnO-added was shorter than non-added.

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Fig. 1 Upright CNTws with ZnO addition

[1] W. Yi, *et al.*: Adv. Master., 14, 1464 (2004).
[2] Y. Hosokawa, *et al.*: J. Phys. D: Appl. Phys., 41, 205418 (2008).
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Table	1. Average	length of	upright	CNTws.
	A			

	Average length (µm)
Non-added	2.5
ZnO-added	1.6

### 3P-48

### Laser ablation of graphite in solution with low density hydrogen-containing molecules

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In the 41<sup>st</sup> FNTG symposium, we reported preliminary results of laser vaporization of graphite in solvent of liquid Ar (hereafter LAr) by a nanosecond laser. The LAr (m.p.=-189.2 °C) was prepared in a bottle cooled by an LN<sub>2</sub>, in which a small amount of the hydrogen atoms was involved mainly because of the contamination of water (ice). Chemical species adsorbed onto the graphite surfaces were also a source of hydrogen. By the absorption spectrum of the hexane solution of irradiated sample, formation of polyynes, from  $C_8H_2$  to  $C_{12}H_2$ , were confirmed. The results indicate that a small amount of contaminants provides terminal hydrogen atoms.

In the present study, laser ablation experiments with higher purity of the LAr and graphite were performed to clarify the effect of these contaminants. The procedure of preparing the ablation target was modified as follows:

- 1. A vacuum line was connected to the cell, to prevent condensation of ambient water vapor. (Previously LAr was prepared in a  $LN_2$  cooled cell with flowing Ar gas, keeping the pressure to be slightly higher than 1 atm to prevent the cell from reverse flow of the air.)
- 2. The graphite target was preheated in an oven and then evacuated for several hours.
- 3. To prevent the LAr from freezing, commercial low-purity LAr was used for the coolant instead of LN<sub>2</sub>.

Other experimental procedure was the same with that in the previous study. That is, the laser used for the experiment was a Nd: YAG ( $\lambda$ =532 nm) with a duration of about 10 ns and 10 Hz repetition rate. The on-target power was about 150 mJ/pulse and a typical elapsed time of irradiation was 30 minutes.

The absorption spectra of the ablated samples were measured at LAr temperature without the solvent replacement (LAr to hexane). For all the irradiated samples examined so far, the typical peaks of polyynes were not observed. Absorption measurement of hexane solution at room temperature, where the LAr solvent was replaced by hexane, will be presented in the symposium.

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### 3P-49

#### Preparation and purification of iron oxide nanotubes

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Nanotube has potential ability due to its structural features of high aspect-ratio, large surface area which stems from inner and outer surfaces and inner space with molecular size. According to the recent study, nanotube structure can be formed by many materials, such as vanadium oxide,  $TiO_2$ ,  $ZrO_2$ ,  $Al_2O_3$  and  $Fe_2O_3$ , so on [1-5], as well as conventional carbon nanotubes. Preparation techniques of such metal-oxide nanotubes can be roughly classified into two methods: one is a template method using nanorod. Briefly, after covering the nanorod surface with metal oxide, nanorod as template was removed. The other is build-up method by peeling the bulk material into the sheet or the sheet-like structure and by rolling up such sheets to form the tube. In the present study, we traced the sample preparation technique reported in the patent [6], and evaluated the products with attention to surface contamination.

Production of iron oxide nanotubes was carried out by solving 1 g of block copolymer of polyethylene and polypropylene glycol (a Sigma-Aldrich, Phuronic F-127) into 10 g of 1-propanol without ethylene glycol. Next, 4 g of iron(III) nitrate nonahydrate (0.01 mol) was added to above solution, and stirred for 1 hour under sonication in order to make sol. The sol thus obtained was kept at 50 °C for 10 days without vibration. Then gelatinous product formed during this maturing process was taken out from the solution. Finally the gel was heated up to 120 °C with a ramp rate of 1°C/min and kept 4 hours under flowing dry air of 200 ml/min in order to roll up the sheet and to form tube structure. Remained surfactant was removed by rinsing the products in EtOH with sonication and separated centrifugally (10000 G, 30 min).



(a) and bottom (b) panels are taken, respectively, for the samples before and after heat treatment at 170 °C.





Figure 1a indicates a tip of the nanotube product, and we can recognize that the tube was covered by numerous contaminated materials, which maybe still remaining surfactant. Figure 2 is TG-DTA of as-produced sample. From this figure, it was found that roughly 40 % of surfactant still remained and such impurity species were started burn at 170 °C. Hence, in order to remove such contaminants, we heated as-produced sample up to 170 °C with a ramp rate of 1 °C/min and kept 4 hours under flowing dry air of 200 ml/min. TEM image of resulted product was shown in Fig.1b, which clearly indicates a removal of contaminated materials without damaging the tube structure.

#### References

M.E. Spahr et al., Angew. Chem. Int. Ed. 37, 1263 (1998). [2] G Armstrong et al., Chem. Commun. 2454 (2005).
 Min Chiao Tsai et al., J Nanopart Res, 10, 863 [4] J. Hwang et al, Advanced Materials, 16, 422-425 (2004)
 X. Qu, et al ACS Nano, 4, 1732-1738 [6] P2006-176368A

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- 分析に最適な条件を、全て自動で設定
- 豊富なライブラリによるラマンスペクトル検索



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# グラフェンの分布を5分でイメージング

■最高のイメージング性能 独自のコンフォーカル光学系採用により、理論限界に迫る 空間分解能 350nm を実現。強度分布の均一なライン照明 (特許取得済み)が試料上の400点でラマン散乱を同時に 励起するため、超高速イメージングが可能です。

|超高精度ピークシフト測定

焦点距離 500mm の分光器を搭載し、高波数分解能と光 学系の明るさを高いレベルで両立しました。高分解能グ レーティングと組み合わせることで、0.1cm<sup>-1</sup>を超える精 度でピークシフトを検出。応力測定に力を発揮します。

■オートメーションを追求

最大で4波長のレーザーを搭載でき、ソフトウェアから ワンクリックで切り替えて使用できます。わずらわしい光 学調整は一切不要です。グレーティングの切り替えやレー ザー強度の調整などもすべてワンクリックです。

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製造元



熱酸化したシリコン基板上に分布するグラフェン薄膜のラマン イメージ。炭素1原子のシートである単層グラフェンと、二層、 三層、四層の多層グラフェンが、それぞれどのように分布して いるかを、わずか数分の測定時間と350nmという高い空間分 解能でイメージングしています。

※このサンプルは物質・材料研究機構の津谷大樹様よりご提供頂きました。

#### ■RAMAN-11 標準仕様表

レーザー	532nm / 785nm / その他(電動切換)
イメージング方式	ライン照明 + ビーム走査、ほか各種モード
分光器	焦点距離 500mm 回折格子 3 枚(電動切換)
検出器	電子冷却 CCD 1,340×400 画素
光学顕微鏡	正立型 / 倒立型
空間分解能(x / y / z)	350nm / 500nm / 1000nm (@532nm)
分光分解能(FWHM)	1.6cm <sup>-1</sup> ( ピーク位置決め精度は 0.1cm <sup>-1</sup> )
ラマンシフト検出範囲	80cm <sup>-1</sup> ~ 5000cm <sup>-1</sup>

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本装置はカーボンナノチューブ・グラフェン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:カーボンナノチューブ・グラフェンの分散、燃料電池触媒評価 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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笹原

開発部

mkurihar@cosmobio.co.jp

ksasahar@cosmobio.co.jp

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



20KHz 超音波ホモジナイザー BRANSON SONIFIER シリーズ

あります。



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 歯磨き粉 シャンプー 研磨剤 電池 フィラー 光触媒 触媒 ワクチン 体外診断薬 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 乳化 エマルジョン製剤 農薬 トナー ラテックス 界面活性剤 クリーム 乳液 クリーム

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Column: Column size: Mobile phase:	4.6mmI.D250 Toluene	nm	х 2 - Ч 1 х				高	分離精製可	丁能!	
Flow rate: Temperature: Detection:	1.0 ml/min 30°C UV 325nm			•	Buckyprep		Bucky	prep-D		
Sample: Inj.Vol.	С <sub>60</sub> [Indene] <sub>n</sub> 1.0µl	(1.0mg/ml)								
						- •••••			NACAL	AI TESQUE, INC
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uckypi フラー 金属内 誘導体 <sup>導体化フ</sup>	repシリー レン分離 包フラー 化フラー <sub>ラーレン (Bi</sub>	ズの用 ・ レンの ・ レンの	金 マンダー の分離 の分離 -D)	-ドカ <del>-</del>	ラム     	金属内包ス	<ul> <li>▶ C</li> <li>▶ C</li> <li>▶ C</li> <li>▶ C</li> <li>▶ C</li> </ul>	OSMOS OSMOS OSMOS ⁄ (Buckypr	IL Buck IL Buck IL Buck	yprep yprep-N yprep-D
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Sample courtesy of Prof. H.Shinohara,

Department of chemistry, Nagoya University

### なければ、つくる。 どこにもない、ものづくり。

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