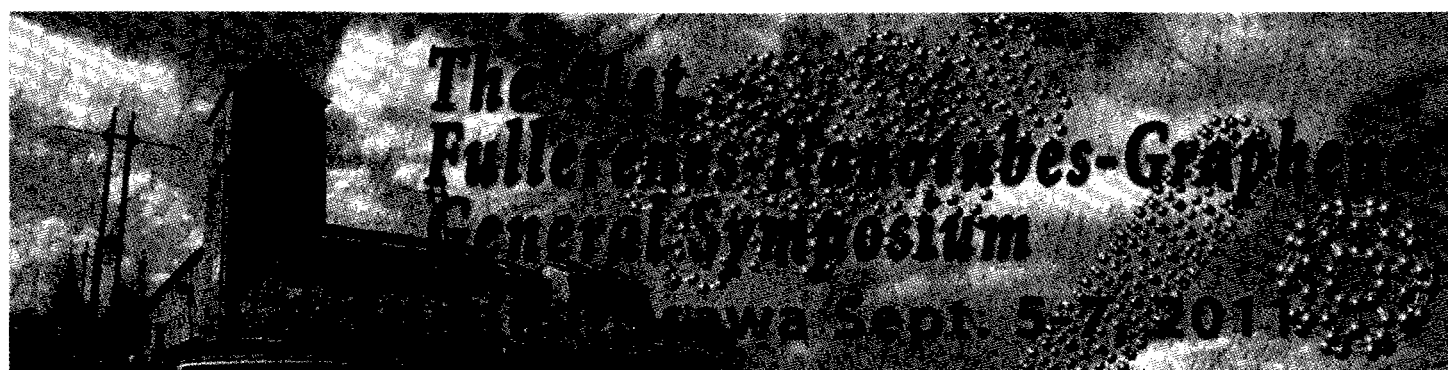


第41回

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 41st

Fullerenes-Nanotubes-Graphene
General Symposium



講演要旨集

Abstracts

2011年9月5日(月)～ 7日(水)

首都大学東京 南大沢キャンパス

Tokyo Metropolitan University, Minami-Osawa Campus

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

共催
日本化学会

The Chemical Society of Japan

協賛

日本物理学会
応用物理学会
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電気化学会

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

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Abstracts

The 41st Fullerenes-Nanotubes-Graphene General Symposium

第 41 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
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The Japan Society of Applied Physics
The Society of Polymer Science, Japan
The Electrochemical Society of Japan

主催：フラーレン・ナノチューブ・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・
高分子学会・電気化学会

Date: September 5th(Mon)–7th(Wed), 2011

Place: Tokyo Metropolitan University, Minami-Osawa Campus
1-1 Minami-Osawa, Hachioji, Tokyo 192-0397
TEL: 042-677-1111

Presentation: Plenary Lecture (40 min presentation, 5 min discussion)
Special Lecture (25 min presentation, 5 min discussion)
General Lecture (10 min presentation, 5 min discussion)
Poster Preview (1 min presentation, no discussion)

日時：平成 23 年 9 月 5 日（月）～ 7 日（水）

場所：首都大学東京 南大沢キャンパス 講堂 大ホール
〒192-0397 八王子市南大沢 1-1
TEL：042-677-1111

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

展示団体御芳名

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9:30	受付(9:00~)	9:25	受付(9:00~)	9:30	受付(9:00~)
	一般講演5件 (ナノチューブの生成と精製)		一般講演4件 飯島賞受賞対象者講演 大澤賞受賞対象者講演		一般講演5件 (グラフェン)
10:45	休憩	10:45	休憩	10:45	休憩
11:00	特別講演 (中西準子)	11:00	特別講演 (三澤透)	11:00	特別講演 (大橋良子)
11:30	一般講演2件 (ナノホーン)	11:30	一般講演2件 (ナノ炭素粒子・フラーレンの化学)	11:30	一般講演2件 (グラフェン)
12:00	昼食	12:00	昼食	12:00	昼食
13:15	一般講演5件 (ナノチューブの生成と精製)	13:15	若手奨励賞表彰式	13:15	一般講演5件 (グラフェン・ナノチューブの応用)
		13:30	総会		
14:30	休憩	14:00	一般講演2件 (金属内包フラーレン・その他)	14:30	休憩
		14:30	休憩		
14:45	一般講演6件 (ナノチューブの物性)	14:45	基調講演 (篠原久典)	14:45	特別講演 (Christian Kramberger)
16:15	ポスタープレビュー	15:30	一般講演3件 (ナノチューブの応用・内包ナノチューブ)	15:15	一般講演4件 (ナノチューブの応用)
		16:15	ポスタープレビュー	16:15	ポスタープレビュー
17:00	ポスターセッション	17:00	ポスターセッション	17:00	ポスターセッション
18:15		18:15	懇親会	18:15	

Time Table

September 5 (Mon)		September 6 (Tue)		September 7 (Wed)	
9:30	Registration (from 9:00)	9:25	Registration (from 9:00)	9:30	Registration (from 9:00)
	General Lectures [5] (Formation and Purification of Nanotubes)		General Lectures [4] Lectures by Candidates for the Iijima Award and the Osawa Award		General Lectures [5] (Graphene)
10:45	Break	10:45	Break	10:45	Break
11:00	Special Lecture (Junko Nakanishi)	11:00	Special Lecture (Toru Misawa)	11:00	Special Lecture (Yoshiko F. Ohashi)
11:30	General Lectures [2] (Nanohorns)	11:30	General Lectures [2] (Carbon Nanoparticles, Chemistry of Fullerenes)	11:30	General Lectures [2] (Graphene)
12:00	Lunch	12:00	Lunch	12:00	Lunch
13:15	General Lectures [5] (Formation and Purification of Nanotubes)	13:15	Poster Awards Ceremony	13:15	General Lectures [5] (Graphene, Applications of Nanotubes)
		13:30	General Meeting		
14:00		14:00	General Lectures [2] (Endohedral Metallofullerenes, Miscellaneous)		
14:30	Break	14:30	Break	14:30	Break
14:45	General Lectures [6] (Properties of Nanotubes)	14:45	Plenary Lecture (Hisanori Shinohara)	14:45	Special Lecture (Christian Kramberger)
		15:30	General Lectures [3] (Applications of Nanotubes, Endohedral Nanotubes)	15:15	General Lectures [4] (Applications of Nanotubes)
16:15	Poster Preview	16:15	Poster Preview	16:15	Poster Preview
17:00	Poster Session	17:00	Poster Session	17:00	Poster Session
18:15		18:15	Banquet	18:15	

座長一覧

(敬称略)

9月5日(月)

	時間	座長
一般講演	9:30～10:45	田中丈士
特別講演(中西)	11:00～11:30	片浦弘道
一般講演	11:30～12:00	秋山和彦
一般講演	13:15～14:30	柳和宏
一般講演	14:45～16:15	千足昇平
ポスタープレビュー	16:15～17:00	小塩明
ポスターセッション	17:00～18:15	宮田耕充

9月6日(火)

	時間	座長
飯島賞対象者講演 大澤賞対象者講演	9:25～10:45	岡崎俊也
特別講演(三澤)	11:00～11:30	兒玉健
一般講演	11:30～12:00	鈴木信三
一般講演	14:00～14:30	若林知成
基調講演(篠原)	14:45～15:30	丸山茂夫
一般講演	15:30～16:15	菅井俊樹
ポスタープレビュー	16:15～17:00	伊藤靖浩
ポスターセッション	17:00～18:15	沖本治哉

9月7日(水)

	時間	座長
一般講演	9:30～10:45	是常隆
特別講演(大橋)	11:00～11:30	日浦英文
一般講演	11:30～12:00	岡田晋
一般講演	13:15～14:30	吾郷浩樹
特別講演(Kramberger)	14:45～15:15	松田一成
一般講演	15:15～16:15	佐野正人
ポスタープレビュー	16:15～17:00	松田和之
ポスターセッション	17:00～18:15	宮内雄平

9月5日(月)

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

一般講演(9:30-10:45)

ナノチューブの生成と精製

- | | | |
|-----|---|----|
| 1-1 | レーザー法によるSWNTのカイラリティー制御 -Pd添加効果-
○児玉拓也、井上亮人、児玉健、橋本健朗、阿知波洋次、岡崎俊也 | 7 |
| 1-2 | 触媒CVD法による単層CNT成長の分子動力学シミュレーション
○野口拓哉、千足昇平、塩見淳一郎、丸山茂夫 | 8 |
| 1-3 | 高温NEXAFS法によるカーボンナノキャップ生成過程の観察
○丸山隆浩、榊原悟史、成塚重弥、雨宮健太 | 9 |
| 1-4 | リモートプラズマCVDにおけるCNTs成長位置での真空紫外光吸収
○落合拓海、大原一慶、稲葉優文、川原田洋 | 10 |
| 1-5 | スーパージョイント単層カーボンナノチューブフォレストの直径制御
○石 康昭、二葉ドン、湯村 守雄、島 賢治 | 11 |

☆☆☆☆☆☆ 休憩 (10:45-11:00) ☆☆☆☆☆☆

特別講演(11:00-11:30)

- | | | |
|------|-----------------------------------|---|
| 1S-1 | ナノ材料のリスク評価の枠組とCNTについての結果
中西 準子 | 1 |
|------|-----------------------------------|---|

一般講演(11:30-12:00)

ナノホーン

- | | | |
|-----|---|----|
| 1-6 | Searching Better Lipid-PEG for Nano-Carbons Dispersion in Biological Applications
○Mei Yang, Momoyo Wada, Minfang Zhang, Kostas Kostarelos, Sumio Iijima, Mitsutoshi Masuda, Masako Yudasaka | 12 |
| 1-7 | ¹ H NMR法を用いたカーボンホーンのPEG化合物による水分散機構の解明
○青柳将、湯田坂雅子、浅川真澄、清水敏美、飯島澄男 | 13 |

☆☆☆☆☆☆ 昼食 (12:00-13:15) ☆☆☆☆☆☆

一般講演(13:15-14:30)

ナノチューブの生成と精製

- | | | |
|------|--|----|
| 1-8 | 分子融合からの単層カーボンナノチューブのカイラリティー選択的形成
○宮田耕充、林宏恩、張錦英、藤原美帆、鈴木麻里恵、北浦良、片浦弘道、篠原久典 | 14 |
| 1-9 | 単層カーボンナノチューブのカイラリティーを認識する高分子デザイン
○赤崎浩二郎、小澤寛晃、藤ヶ谷剛彦、中嶋直敏 | 15 |
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○加藤雄一、井上彩花、新留康郎、中嶋直敏 | 16 |
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○松澤洋子、加藤晴久、大山晴美、西出大輔、片浦弘道、吉田勝 | 17 |
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○田中丈士、浅野敏、片浦弘道 | 18 |

☆☆☆☆☆☆ 休憩 (14:30-14:45) ☆☆☆☆☆☆

一般講演(14:45-16:15)

ナノチューブの物性

- | | | |
|------|--|----|
| 1-13 | コンタクトモードAFMによるCNTsの接触抵抗の評価
○稲葉優文、大原一慶、落合拓海、平岩篤、川原田洋 | 19 |
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○小鍋哲、岡田晋 | 24 |

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ポスターセッション(17:00-18:15) (罽)若手奨励賞候補

グラフェン

- | | | |
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9月6日(火)

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特別講演 発表25分・質疑応答5分
大澤賞飯島賞対象者講演 発表10分・質疑応答10分
一般講演 発表10分・質疑応答5分
ポスタープレビュー 発表 1分・質疑応答なし

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☆☆☆☆☆☆ 休憩 (10:45-11:00) ☆☆☆☆☆☆

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☆☆☆☆☆☆ 昼食 (12:00-13:15) ☆☆☆☆☆☆

若手奨励賞表彰式(13:15-13:30)

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☆☆☆☆☆☆ 休憩 (14:30-14:45) ☆☆☆☆☆☆

基調講演(14:45-15:30)

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9月7日(水)

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

一般講演(9:30-10:45)

グラフェン

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○藤本義隆、斎藤晋 | 38 |
| 3-4 | 周期ナノホールを持つグラフェンの安定構造と磁性に関する第一原理的研究
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| 3-5 | 2次元ポリマー化コロネン
岡田晋 | 40 |

☆☆☆☆☆☆ 休憩 (10:45-11:00) ☆☆☆☆☆☆

特別講演(11:00-11:30)

- | | | |
|------|---------------------|---|
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大橋 良子 | 4 |
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一般講演(11:30-12:00)

グラフェン

- | | | |
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| 3-7 | グラフェン/金属接合における見かけ上負の接触抵抗
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☆☆☆☆☆☆ 昼食 (12:00-13:15) ☆☆☆☆☆☆

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○相川 慎也、エリック エイナルソン、千足 昇平、西川 英一、丸山 茂夫 | 46 |
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☆☆☆☆☆☆ 休憩 (14:30-14:45) ☆☆☆☆☆☆

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- 3S-5 Plasmons in one and two dimensional nano-carbon 5
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ナノチューブの応用

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 ○藤ヶ谷剛彦, 佐田貴生, 中澤浩二, 中嶋直敏
- 3-16 単層カーボンナノチューブ内包高分子ゲルカプセルの作製と薬剤保持 51
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○竹腰健太郎、木津たきお、相川慎也、西川英一 | 154 |
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○伊藤靖浩、劉華平、藤井俊治郎、清水麻希、田中丈士、片浦弘道 | 155 |

September 5th, Mon.

- Special Lecture: 25 min (Presentation) + 5 min (Discussion)
- General Lecture: 10 min (Presentation) + 5 min (Discussion)
- Poster Preview: 1 min (Presentation)

General Lecture(9:30-10:45)

Formation and Purification of Nanotubes

- | | | |
|-----|---|----|
| 1-1 | Chirality control of SWNT by laser ablation method - Effect of Pd addition -
○Takuya Kodama, Akihito Inoue, Takeshi Kodama, Kenro Hashimoto, Yohji Achiba, Toshiya Okazaki | 7 |
| 1-2 | Molecular dynamics simulation of SWNT growth by catalytic CVD
○Takuya Noguchi, Shohei Chiashi, Junichiro Shiomi, Shigeo Maruyama | 8 |
| 1-3 | High temperature NEXAFS study of carbon nanocap formation by surface decomposition of SiC
○Takahiro Maruyama, Satoshi Sakakibara, Shigeya Naritsuka, Kenta Amemiya | 9 |
| 1-4 | VUV absorption of CNTs growth area separated from plasma with remote plasma CVD
○Takumi Ochiai, Kazuyoshi Oohara, Masafumi Inaba, Hiroshi Kawarada | 10 |
| 1-5 | Diameter control for Super-Growth SWCNT forests
○Yasuaki Seki, Don Futaba, Motoo Yumura, Kenji Hata | 11 |

☆☆☆☆☆☆ Coffee Break (10:45-11:00) ☆☆☆☆☆☆

Special Lecture(11:00-11:30)

- | | | |
|------|--|---|
| 1S-1 | Framework for evaluating risks associated with manufactured nanomaterials
Junko Nakanishi | 1 |
|------|--|---|

General Lecture(11:30-12:00)

Nanohorns

- | | | |
|-----|---|----|
| 1-6 | Searching better lipid-PEG for nano-carbons dispersion in biological applications
○Mei Yang, Momoyo Wada, Minfang Zhang, Kostas Kostarelos, Sumio Iijima, Mitsutoshi Masuda, Masako Yudasaka | 12 |
| 1-7 | Study on the mechanism of PEG-derivatives assisted dispersion of carbon nanohorn in water by ¹ H NMR measurement
○Masaru Aoyagi, Masako Yudasaka, Masumi Asakawa, Toshimi Shimizu, Sumio Iijima | 13 |

☆☆☆☆☆☆ Lunch Time (12:00-13:15) ☆☆☆☆☆☆

General Lecture(13:15-14:30)

Formation and Purification of Nanotubes

- | | | |
|------|---|----|
| 1-8 | Chirality-selective formation of single-wall carbon nanotubes from molecular coalescence
○Yasumitsu Miyata, Lim Hong En, Jinying Zhang, Miho Fujihara, Marie Suzuki, Ryo Kitaura, Hiromichi Kataura, Hisanori Shinohara | 14 |
| 1-9 | Recognition and extraction of right- and left-handed semiconducting single-walled carbon nanotube enantiomers using fluorene-binaphthol chiral copolymers
○Kojiro Akazaki, Hiroaki Ozawa, Tsuyohiko Fujigaya, Naotoshi Nakashima | 15 |
| 1-10 | Thermodynamics of the exchange of solubilizers on single-walled carbon nanotubes
○Yuichi Kato, Ayaka Inoue, Yasuro Niidome, Naotoshi Nakashima | 16 |
| 1-11 | Photochemical dispersibility tuning of carbon nanotubes by photocyclization of a water-soluble stilbene as an efficient dispersant
○Yoko Matsuzawa, Haruhisa Kato, Harumi Ohyama, Daisuke Nishide, Hiromichi Kataura, Masaru Yoshida | 17 |
| 1-12 | Low-cost metal/semiconductor separation of single-wall carbon nanotubes toward mass production
○Takeshi Tanaka, Satoshi Asano, Hiromichi Kataura | 18 |

September 5th, Mon.

☆☆☆☆☆☆ Coffee Break (14:30-14:45) ☆☆☆☆☆☆

General Lecture(14:45-16:15)

Properties of Nanotubes

- 1-13** Contact resistance estimation of open-end CNT by contact-mode AFM 19
○Masafumi Inaba, Kazuyoshi Oohara, Takumi Ochiai, Atsushi Hiraiwa, Hiroshi Kawarada
- 1-14** Electrical characterization of CNT forests along growth direction by micro-scale 4-probe method 20
○Shigeki Hano, Don N. Futaba, Motoo Yumura, Kenji Hata
- 1-15** Dumbbell shape cyclic voltammogram of SWCNT capacitor electrodes 21
○Shinji Kawasaki, Ayar Al-zubaidi, Tsuyoshi Inoue, Tomohiro Matsushita, Yosuke Ishii
- 1-16** Tailoring temperature invariant viscoelasticity of carbon nanotube material 22
○Ming Xu, Don N. Futaba, Motoo Yumura, Kenji Hata
- 1-17** Microscopic mechanisms of alignments of carbon nanotubes on sapphire surfaces 23
Sukmin Jeong, ○Atsushi Oshiyama
- 1-18** Multiple exciton generation by a single photon in single-walled carbon nanotubes 24
○Satoru Konabe, Susumu Okada

Poster Preview(16:15-17:00)

Poster Session(17:00-18:15) (✿)Candidates for the Young Scientist Poster Award

Graphene

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○Shota Kamikawa, Yuko Yagi, Junji Haruyama, D. V. Kosinkin, James Tour
- 1P-2** High-performance graphene flake anode for lithium-ion secondary batteries 54
○Rika Sorin, Hajime Chigusa, Kazuma Hanai, Akira Koshio, Masatou Ishihara, Yoshinori Koga, Masataka Hasegawa, Nobuyuki Imanishi, Yasuo Takeda, Fumio Kokai
- 1P-3** Thermal polymerization of pentacenes: Toward graphene-like molecules 55
✿ ○Yusuke Okai, Yosuke Ishii, Hidenori Kato, Masashige Takatori, Shinji Kawasaki
- 1P-4** Domain structure of CVD graphene grown on hetero-epitaxial Cu films 56
✿ ○Yui Ogawa, Hiroki Ago, Baoshan Hu, Masaharu Tsuji, Ken-ichi Ikeda, Seigi Mizuno, Hiroki Hibino
- 1P-5** Nitridation of graphene multi-layer using neutral beam irradiation 57
○Takeru Okada, Akira Wada, Seiji Samukawa
- 1P-6** Dynamics of O and H atoms on a graphene sheet induced by pulse laser: A TDDFT simulation 58
○Yoshiyuki Miyamoto, Hong Zhang

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- 1P-8** Diffusion of Li atom for graphite intercalation with edge oxidations: First-principles calculations 60
○Takazumi Kawai
- 1P-9** Upright position of Cu-coated carbon nanotwists treated by filament discharge 61
○Yuki Sugioka, Yoshiyuki Suda, Hideto Tanoue, Hirofumi Takikawa, Hitoshi Ue, Kazuki Shimizu, Yoshito Umeda
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○Yuki Sato, Takeshi Kodama, Haruo Shiromaru, Yohji Achiba

Applications of Nanotubes

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✿ | Towards the development of ultra high efficient coolants based on single-walled carbon nanotube suspensions
○ <i>Harish Sivasankaran, Kei Ishikawa, Erik Einarsson, Theerapol Thurakitserree, Pei Zhao, Makoto Watanabe, Shohei Chiashi, Junichiro Shiomi, Shigeo Maruyama</i> | 64 |
| 1P-13 | Diversifying applications from the “sticking” of aligned carbon nanotube wafers to arbitrary substrates
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Formation and Purification of Nanotubes

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| 1P-14 | Specific chirality separation of single-walled carbon nanotubes using fluorene-based copolymers with various backbones
○ <i>Fumiyuki Toshimitsu, Hiroaki Ozawa, Tsuyohiko Fujigaya, Naotoshi Nakashima</i> | 66 |
| 1P-15 | Making of the water dispersion of carbon nano-tube and fullerene using wet-type super atomizer “Nanovater”
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○ <i>Atsushi Hirano, Takeshi Tanaka, Hiromichi Kataura</i> | 69 |
| 1P-18
✿ | Isolation of ultrathin single-wall carbon nanotubes of (5,4) chirality
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○ <i>Kazushi Shimizu, Yuka Nagaya, Koji Tsuchiya, Tadahiro Ishii, Hirofumi Yajima</i> | 76 |
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| 1P-26 | Effects of OPO laser irradiation on the structural characteristics of single- and double-walled carbon nanotubes
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- 1P-28** Origin of the far-infrared absorption of single-walled carbon nanotubes 80
 ○Soon-Kil Joung, Toshiya Okazaki
- 1P-29** Post-process effects on the photoluminescence quantum yield of single-walled carbon nanotubes 81
 ○Shin-ichiro Mouri, Yuhei Miyauchi, Kazunari Matsuda
- 1P-30** First-principles calculation of electrical conduction in carbon nanotubes: The effect of hydrogen adsorption 82
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Nanohorns

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- 1P-33** Structural characterization of AgI nanowires encapsulated in carbon nanotubes using electron diffraction and Ag-NMR 85
 ○Shin-ichi Ito, Ryo Kitaura, Teppei Yamada, Hiroshi Kitagawa, Dong Young Kim, Suguru Noda, Hirofumi Yoshikawa, Kunio Awaga, Hisanori Shinohara
- 1P-34** Electrochemical properties of π -conjugated molecules encapsulated in single-wall carbon nanotubes 86
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September 6th, Tue.

- Plenary Lecture: 40 min (Presentation) + 5 min (Discussion)
- Special Lecture: 25 min (Presentation) + 5 min (Discussion)
- General Lecture by Candidates for Osawa and Iijima Award: 10 min (Presentation) + 10 min (Discussion)
- General Lecture: 10 min (Presentation) + 5 min (Discussion)
- Poster Preview: 1 min (Presentation)

General Lecture by Candidates for the Iijima Award (9:25-10:25)

- 2-1 Geometrical, electrical and energetical family patterns of single-walled carbon nanotubes: A helical-symmetry first-principles investigation 25
○Koichiro Kato, Takashi Koretsune, Susumu Saito
- 2-2 Gate modulation of the optical transitions in single-walled carbon nanotubes 26
○Yuhei Miyauchi, Zhengyi Zhang, Mitsuhide Takekoshi, Vikram Deshpande, Stéphane Berciaud, Chenguang Lu, Philip Kim, James Hone, Tony F. Heinz
- 2-3 Single-chirality separation of single-wall carbon nanotubes by one-step gel column chromatography 27
○Huaping Liu, Yasuko Urabe, Takeshi Tanaka, Hiromichi Kataura

General Lecture by Candidate for the Osawa Award (10:25-10:45)

- 2-4 Chemistry of fullerene multi-adducts: highly soluble fullerenes 28
○Ken Kokubo

☆☆☆☆☆☆ Coffee Break (10:45-11:00) ☆☆☆☆☆☆

Special Lecture (11:00-11:30)

- 2S-2 Search for fullerenes in the Orion nebula 2
Toru Misawa

General Lecture (11:30-12:00)

Carbon Nanoparticles

- 2-5 Electronic spectra of polyyne-iodine complexes in nonpolar solvents 29
○Yoriko Wada, Tomonari Wakabayashi, Tatsuhisa Kato

Chemistry of Fullerenes

- 2-6 Effect of Coulomb repulsions in the vibronic couplings of C_{60}^- 30
○Naoya Iwahara, Tohru Sato, Kazuyoshi Tanaka

☆☆☆☆☆☆ Lunch Time (12:00-13:15) ☆☆☆☆☆☆

The Young Scientist Poster Award Ceremony (13:15-13:30)

General Meeting (13:30-14:00)

General Lecture (14:00-14:30)

Endohedral Metalofullerenes

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○Takeshi Kodama, Koichi Kikuchi, Yohji Achiba

Miscellaneous

- 2-8 Characterization of charge and radius of particles by ion trap mobility with free fall in air 32
Yoshihiko Sawanishi, Masashi Shinozaki, ○Toshiki Sugai

☆☆☆☆☆☆ Coffee Break (14:30-14:45) ☆☆☆☆☆☆

Plenary Lecture(14:45-15:30)

- 2S-3 Synthesis and characterization of peapods, nanowires and graphenes 3
Hisanori Shinohara

General Lecture(15:30-16:15)

Applications of Nanotubes

- 2-9 Single-walled carbon nanotube as 1D array of reacting sites 33
Takafumi Nakashima, ○Masahito Sano

Endohedral Nanotubes

- 2-10 Low temperature melting and emptying of copper nanowire-filled carbon nanotubes 34
 ○Akira Koshio, Yoshiki Kimura, Shota Ueda, Fumio Kokai
- 2-11 Control of layer number in growth of carbon nanotubes by eDIPS method 35
 ○Keita Kobayashi, Masaharu Kiyomiya, Takayoshi Hirai, Takeshi Saito

Poster Preview(16:15-17:00)

Poster Session(17:00-18:15) (✿) Candidates for the Young Scientist Poster Award

Graphene

- 2P-1 Electrical transport properties of few layer graphene grown on graphene template by chemical vapor deposition 88
 ○Ryota Negishi, Yasuhide Ohno, Kenzo Maehashi, Kazuhiko Matsumoto, Yoshihiro Kobayashi
- 2P-2 Effect of transfer characteristics for PZT-graphene-FET by ionic liquid 89
 ○Junya Suzuki, Shogo Kataoka, Takayuki Arie, Seiji Akita
- 2P-3 Preferential growth of Ar-mediated epitaxial graphene on 6H-SiC 90
 ○Hailong Hu, Akkawat Ruammaitree, Daisuke Maeta, Hitoshi Nakahara, Koji Asaka, Yahachi Saito
- 2P-4 Observation of ferromagnetism and spin polarization at nanopore edges in low-defect graphene nanopore arrays 91
 ○T. Hara, S. Kamikawa, K. Tada, Y. Yagi, J. Haruyama, H. Yang, M. Chshiev
- 2P-5 Electronic structure of graphene with periodic array of holes 92
 ✿ ○Masahiro Sakurai, Susumu Saito
- 2P-6 A comparative study on alcohol and methane precursors in CVD synthesis of graphene films 93
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September 7th, Wed.

- Special Lecture: 25 min (Presentation) + 5 min (Discussion)
- General Lecture: 10 min (Presentation) + 5 min (Discussion)
- Poster Preview: 1 min (Presentation)

General Lecture (9:30-10:45)

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- 3-2 Band-gap engineering of graphite thin films by intercalation of hydrogen-potassium binary complex 37
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- 3-3 Formation, energetics, and electronic properties of nitrogen defects in graphene 38
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- 3-5 Two-dimensionally polymerized coronene: A metallic sheet of sp^2 C atoms 40
○Susumu Okada

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Special Lecture (11:00-11:30)

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September 7th, Wed.

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Christian Kramberger

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○*Seisuke Ata, Kazufumi Kobashi, Takeo Yamada, Don N. Futaba, Motoo Yumura, Kenji Hata*
- 3-15 Analysis of single cell collected from a carbon nanotube-coated substrate 50
○*Tsuyohiko Fujigaya, Takao Sada, Koji Nakazawa, Naotoshi Nakashima*
- 3-16 Preparation of polymer gel capsules containing single-walled carbon nanotubes and loading of drug molecules 51
○*Yusuke Tsutsumi, Tsuyohiko Fujigaya, Naotoshi Nakashima*

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- 3P-3 Control of stacking structure for multi-layer graphene 124
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 ○Kunihide Kaneki, Koji Ishii, Hiroshi Yamamoto, Nobuyuki Iwata, Hirofumi Yajima
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基調講演
Plenary Lecture

特別講演
Special Lecture

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2S – 2 ~ 2S – 3

3S – 4 ~ 3S – 5

Framework for evaluating risks associated with manufactured nanomaterials

Junko Nakanishi

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We were engaged in the new energy development organization (NEDO) Research Project "Risk Assessment of Manufactured Nanomaterials" which started in fiscal 2006 and completed last fiscal year. Here, I would like to briefly introduce framework of this project and some results obtained for five years.

The main aim of this project is to carry out risk assessment of representative manufactured nanomaterials (NMs) for managing their risks and to make a model framework for assessing risks from emerging technologies. Then, it became our substantial subject to carry out risk assessment of three NMs, nano titanium dioxide (TiO₂), fullerene (C₆₀) and carbon nanotube (CNT) chosen as representative NM and to publish their risk assessment documents.

Evaluating the toxicity due to NMs exposure, the pulmonary inflammation was chosen as an endpoint, which is thought to be the most sensitive adverse effect. Based on the results of rat inhalation exposure test, we decided the rat no-observed-adverse-effect-level (NOAEL). From this, the occupational exposure limit (OEL) for human was estimated. Considering that the NOAEL was derived on the basis of the sub-acute to sub-chronic inhalation exposure tests, we have proposed the OEL to be period-limited for about fifteen-year exposure, which should be reviewed in ten years or so, and to be noted as OEL(PL). The proposed OEL(PL) is 0.6 mg/m³ for TiO₂, 0.39 mg/m³ for fullerene and 0.03 mg/m³ for CNT.

In the case of CNTs, we discovered stimulating two things. First, the inflammation activity due to CNTs is strongly dependent on their BET specific surface area, that is to say, the more the BET specific surface area is, the stronger the inflammation activity exhibits. Second, the relation between the two is expressed by a common expression irrespective of CNT types. We can say that the inflammation activity is controlled by the size of nanotube diameter or number of walls of nanotube, because the BET specific surface area is determined by the number of walls. In other words, the distinction between multi-walled, double-walled and single-walled is not significant.

The risk assessment documents of three NMs and a leaflet regarding framework of risk assessment nanomaterials can be downloaded at the web site of <http://www.aist-riss.jp/main/>.

Search for fullerenes in the Orion nebula

○Toru Misawa¹, Poshak Gandhi², Akira Hida³, Toru Tamagawa⁴, and Tomohiro Yamaguchi³

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In the spectra of stars behind interstellar matter, a series of broad absorption features are recognized at $\lambda = 4000\text{\AA}$ to $1.3\mu\text{m}$. Since the first detection of these Diffuse Interstellar bands (hereafter DIB) [1], various molecules, including organic compounds (e.g., polycyclic organic hydrocarbons, fullerenes, carbon chains, and carbon nanotubes), have been proposed as the source of DIBs, because they are all stable even in space filled with high-energy particles. Nonetheless, their identity still remains elusive, which is one of the most long-standing unsolved mysteries in Astronomy.

Among ~ 300 DIBs, those at $\lambda \sim 9577\text{\AA}$ and $9632\text{\AA}$ are only ones that have specific candidates for their sources [2]. These DIBs have wavelengths that are very close to those of ionized C_{60} fullerene (C_{60}^+) measured in laboratory [3]. Indeed, fullerene is one of the most promising candidates because (i) two DIBs are identified simultaneously and (ii) C_{60}^+ is very stable even in space. Fullerene is also intriguing because it is one of the largest molecules in space, and much larger than polycyclic aromatic hydrocarbons (PAHs).

To strengthen this identity, we obtained spectra of three O/B stars (Figure 1) in or around the Orion nebula with the Subaru telescope. Two stars (HD 37022 and HD 37041) lie in the central region of the nebula, while the other star (HD 37150) is located at the edge of the nebula as a control target. As a result, we discovered additional 3 DIBs at $\lambda \sim 9017$, 9210 , and $9258\text{\AA}$ close to the laboratory measurements of other C_{60}^+ lines [4] (Figure 2).

Recently, emission lines from neutral C_{60} are also detected in a Mid-infrared spectrum of young planetary nebula, one of the most promising formation sites of fullerenes [5]. Now, an existence of cosmic fullerene is quite certain. We have embarked on a survey of DIBs around the Orion nebula to search for environmental dependence of the DIB sources.

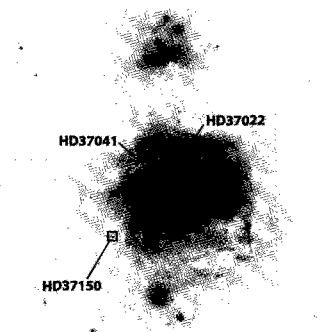


Fig.1 Infrared image of the Orion Nebula. The location of observed stars are marked with open squares.

- [1] M. L. Heger Lick Obs. Bull. **10**, 141 (1922)
- [2] B. H. Foing & P. Ehrenfreund Nature **369**, 296 (1994)
- [3] J. Fulara, M. Jakobi, & J. P. Maier Chem. Phys. Lett. **211**, 227 (1993)
- [4] T. Misawa *et al.* Astrophysical Journal **700**, 1988 (2009)
- [5] J. Cami *et al.* Science **329**, 1180 (2010)

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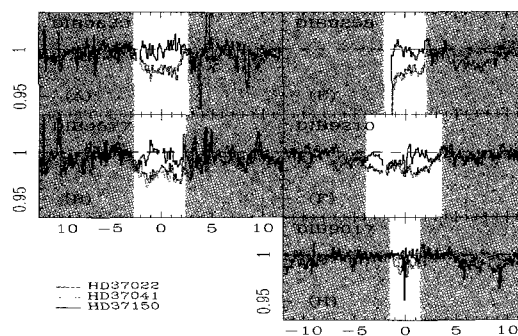


Fig.2 Five DIBs in the spectra of three target stars, as candidates of C_{60}^+ lines. These DIBs are detected toward HD 37022 and HD 37041, but not toward HD 37150.

Synthesis and Characterization of Peapods, Nanowires and Graphene

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First of all, I would like to congratulate Professor Shigeo Maruyama, the President of the Research Society, for the foundation of a new research society called “The Fullerenes, Nanotubes and Graphene Research Society” by incorporating graphene research into the former Fullerene and Nanotubes Research Society. This, surely, is a great advancement for the research society.

Peapods (or nano-peapods), nanowire-encapsulating carbon nanotubes (CNT) and graphene [graphene nanoribbons (GNR) to be exact] are mutually interrelating nanocarbons of recent interests. They exhibit unique structural and electronic/magnetic properties, and, furthermore, they can be applied to novel electronic devices such as transistor channels and transparent conducting films. Interestingly, they are also closely related to each other in actual syntheses.

Here, I will discuss each of these recent topics from our laboratory (one for each topics), which are (1) synthesis and properties of metal and metal-halides nanowire-encapsulating CNT (Fig.1) [1,2], (2) synthesis and solution-phase extraction of new peapod materials (Fig.2) [3,4] and (3) a simple CVD (chemical vapor deposition) synthesis of mono-layer graphene [5] and a novel preparation of high-quality GNR from CNT (Fig.3) [6].

The followings are the main important results illustrated by figures and transmission electron microscopy (TEM) images.

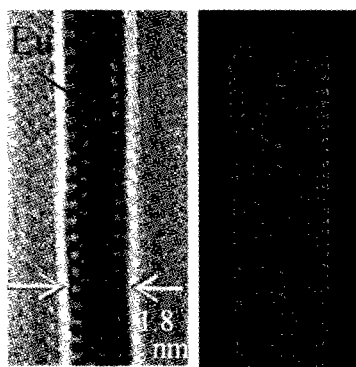


Fig.1 TEM image and the corresponding figure of Eu-encapsulated single-wall CNT.

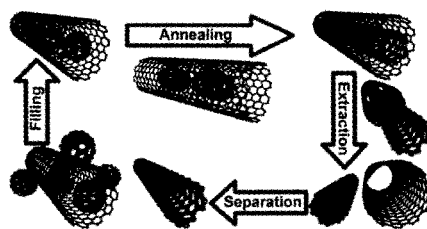


Fig.2 Schematic diagram of the solution-phase extraction of inner tube from fullerene-peapods.

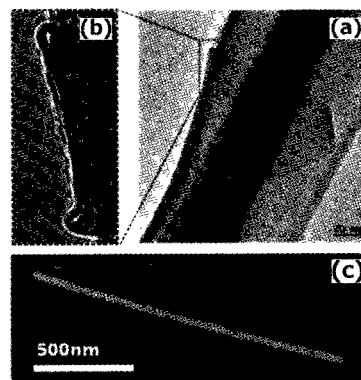


Fig.3 TEM images (a,b) and AFM image (c) of GNR from thin-layer multi-wall CNT.

- [1] R. Kitaura *et al.*, *Angew.Chem.Int.Ed.* 48, 8298 (2009).
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- [6] D. Choi *et al.*, manuscript in preparation.

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At the beginning of research on graphite thin films

Yoshiko F. Ohashi

More than 40 years ago, from 1967 to 1969, I was a postgraduate of Keio Univ. and investigating physical properties of arc-evaporated carbon films, when Professor Sanchi Mizushima noticed me peeling the arc-evaporated carbon film off the glass substrate with the cellophane adhesive tape and started making crystalline thin films of graphite. Arc-evaporated carbon films were expected to have physical properties different from those of crystalline graphite films, however, which no one still had studied in those days. Therefore, we had to examine them by ourselves, that is, Prof. Mizushima began to research physical properties of the graphite thin films experimentally for the first time. Graphite thin films were prepared as follows. The surface layers of a graphite crystal fixed on a glass substrate with thinly painted adhesive were peeled with cellophane adhesive tape, then the graphite crystal became thinner and translucent by repeating this work, and various thicknesses could be achieved. Consequently, each graphite film finally used as the specimen was stuck on the glass substrate. The first paper concerning this theme was published in 1971[1]. The thinnest film obtained in this study was around 10nm. The galvanomagnetic effect showed a remarkable change according to the decrease in film thickness. Afterwards, the electronic properties were measured in detail, a part of which was presented at the 10th Biennial Conference on Carbon in 1971 and published in 1973 [2]. In our research environment of those days, this research seemed to have roughly finished the first stage. Now, I learned indirectly a notable comment of Professor Mildred Dresselhaus in the conference mentioned above, that is, because of adhesive shrinkage at low temperature, the graphite film fixed on the glass substrate may distort to change its original characters. I felt that I should solve this problem however I had already discussed it with Prof. Mizushima. It had been concluded that the interaction between the graphite surface and the adhesive might be weak because the graphite was chemically inactive. Therefore, I hesitated to try to bring up this subject again. In 1978, Prof. Mizushima passed away and I changed the research object. About 20 years later, I decided to restart research on the graphite thin films, but to put them on the glass substrate without the adhesive. As for the bulk graphite crystal to make thin films, it is necessary for the crystalline to be of high quality. Otherwise, graphite films will crack during cleavage and become too small to be put electrodes up by the hand work. Fortunately, Professor Yoshihiro Hishiyama of Musashi Institute of Technology knew the condition mentioned above and kindly supplied kish graphite of very high quality. Then, I could challenge preparing graphite thin films again. A part of the results was published in 1997, where the process of making graphite thin films was described in detail for the first time, though obtained thinnest film was 18nm [3]. The pursuit of my making graphite thin films ended with retirement three years ago. Certainly, everyone will be more familiar to the remarkable development of this field by achieving graphene afterwards. I would like everyone to know Prof. Mizushima was the pioneer of research on the graphite thin film physics and his distinguished achievement. Finally, I would like to express my deep gratitude to Prof. Dresselhaus for her precious comment and to Prof. Hishiyama for his kind supply of graphite crystals of very high quality.

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Plasmons in one and two dimensional nano-carbon

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Plasma excitations in single walled carbon nanotubes and graphene comprise the same charge carrier and interband transitions but experience one- or two-dimensional confinement, respectively. Plasmons are collective longitudinal density waves in the electronic medium. They may be probed by inelastic scattering events, for instance with electrons [1] or x-rays [2]. The recoiled probe particles provide the energy as well as the momentum to create standing and running density waves in the one- and two-dimensional forms of nano-carbon. The dispersion relations of charge carrier as well as interband plasmons are found to differ fundamentally from their counterparts in bulk graphite. In the special case of freestanding vertically aligned single walled carbon nanotubes (VA-SWNT) a mode splitting occurs due to the distinction of one-dimensional on-axis propagation and circumferential containment of plasmons. Precisely these two modes are independently observed in VA-SWNT [3] as two distinct ultra violet absorption peaks. The comparison of the on-axis propagating π plasmon in VA-SWNT and in-plane propagating π plasmon in graphene reveals a quantitative match. In one and two dimensions the π interband plasmon becomes linear, with a slope of $4.85 \text{ eV\AA}$ or $7.4 \times 10^5 \text{ ms}^{-1}$ that is consistently measured in graphene and VA-SWNT.

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一般講演

General Lecture

1 – 1 ~ 1 – 18

2 – 1 ~ 2 – 11

3 – 1 ~ 3 – 16

Chirality control of SWNTs by laser ablation method -Effect of Pd addition-

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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 that would allow the growth of SWNTs with a single chirality. The laser ablation (vaporization) method combined with Rh/Pd catalyst has been shown to be one of the most probable candidates by which such an ultimate goal would be realized. Actually so far, the abundance of the SWNTs with a particular chiral index has been found to be over 90% among other remaining SWNTs in the raw soot material by our laser ablation-Rh/Pd catalyst system.

In the present paper, we will demonstrate the experimental results on the changes of the chirality distributions by changing mixing ratio of Rh/Pd catalyst in laser vaporization experiments. In Fig.1, absorption spectra of SWNTs prepared by the laser ablation at the same furnace temperature (1100°C), but with use of Rh/graphite rod containing *different Pd concentration* (the Pd concentrations are shown in the figure), are compared after dispersion and filtering of SWNTs in SDBS/H₂O solution. By comparing these absorption spectra, it is clearly shown that by increasing Pd concentration, the size distribution of SWNTs is systematically changed into the distribution peaking at the smaller diameter carbon nanotubes.

For example, the 0.5% Pd containing sample shows that the most abundant (n,m) species in SWNT distribution is (8,7), but by increasing Pd concentration up to 1.2%, it appears at (7,6). For the case of 1.2% Pd, furthermore, it should be noted that the abundance of the (7,6) particular species specifically increases comparing with other (n,m) species. On the basis of detailed analyses of absorption intensity as well as fluorescence intensity, it was found that the abundance of (7,6), (8,5 metallic) and (9,4) is over 80% in comparison with other (n,m) species for the sample prepared at the furnace temperature, 1100°C.

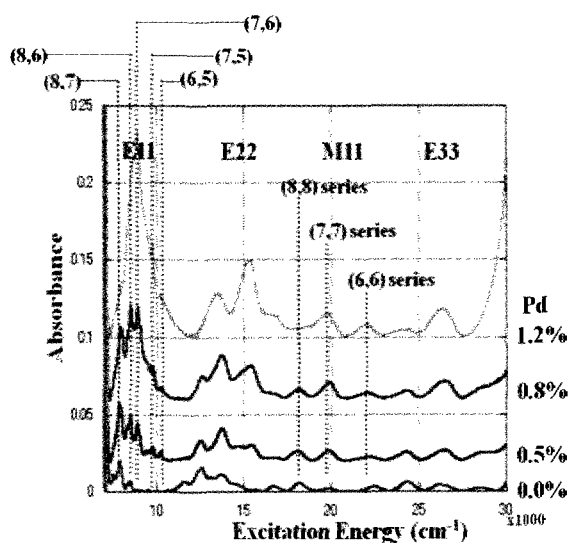


Fig.1 UV-Vis-nearIR absorption spectra of SWNTs prepared with different Pd concentrations.

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Molecular Dynamics Simulation of SWNT Growth by Catalytic CVD

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The growth mechanism of single-walled carbon nanotubes (SWNTs) by catalytic chemical vapor deposition (CVD) method has been widely discussed experimentally, but theoretical contributions were limited. Hence, we performed molecular dynamics simulation of the SWNT growth process in catalytic CVD method for different temperatures and different pressures of carbon sources. We used our reconstructed Tersoff-type potentials for metal-carbon systems [1] and the simulation procedure of a previous report [2].

Figures 1 and 2 show the SWNTs growth process by iron and cobalt at 1500 K. Iron-nucleated SWNTs have more defects and smaller diameters compared to cobalt-nucleated SWNTs. Figure 3 shows the temperature dependence of catalytic CVD. As for iron, if the temperature was higher than 1000 K, SWNTs were grown. In those cases, the higher the temperature was, the faster SWNTs grew. When the temperature was lower than 1000 K, the metal clusters were encapsulated by carbon cages. It was suggested temperature be a dominant factor for the SWNT growth.

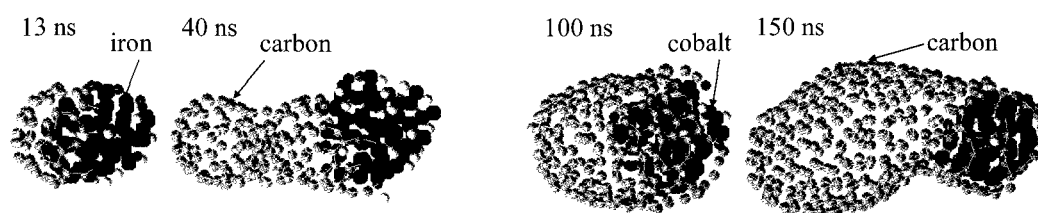


Fig. 1 Growth process of SWNTs by iron at 1500 K. Fig. 2 Growth process of SWNTs by cobalt at 1500 K.

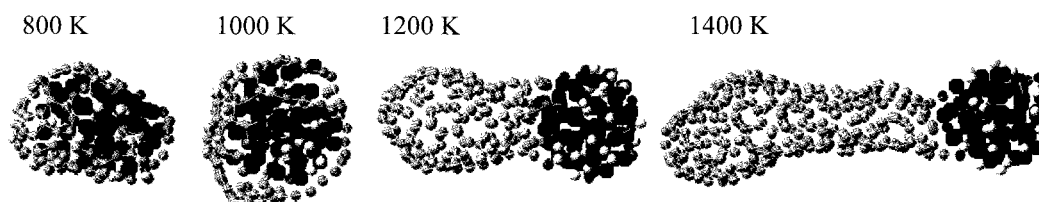


Fig. 3 Temperature dependence of catalytic CVD by iron at 60 ns.

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High Temperature NEXAFS Study of Carbon Nanocap Formation by Surface Decomposition of SiC

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Surface decomposition of SiC is a unique technique to grow carbon nanotubes (CNTs), because CNTs can be grown only by heating SiC crystals above 1200°C in a vacuum. By this method, aligned zigzag-type CNTs with fairly uniform diameters can be obtained without any catalysts [1]. It has been observed that nanosized cap structures, “carbon nanocaps”, are formed at the beginning of CNT formation and these carbon nanocaps determine the CNT structure. So far, several TEM and STM observations have been reported for carbon nanocap formation. However, those studies were performed at room temperature and it is essential to carry out *in situ* measurements to clarify the formation mechanism of carbon nanocaps. In this study, we carried out *in situ* near edge X-ray absorption fine structure (NEXAFS) measurements to observe carbon nanocap formation process directly.

6H-SiC(000-1) C-face substrates were gradually heated up to an intended temperature in a UHV chamber and C K edge NEXAFS spectra were measured, keeping the samples at the heating temperature. The NEXAFS measurements were carried out at the Photon Factory BL-7A of KEK and the spectra were obtained in Auger electron yield detection mode.

Fig. 1 shows C K edge NEXAFS spectra of SiC(000-1) at 1050 and 1250°C. At 1050°C, a sharp shoulder peak were observed at around 285 eV, corresponding to π^* resonance. This indicates that carbon layers were accumulated on the SiC surface. When the incident X-ray beam was perpendicular to the surface, the π^* resonance peak was suppressed, suggesting that C-C bonds were parallel to the surface. At 1250°C, the spectra were drastically changed and sharp π^* resonance peaks appeared accompanied with broad σ^* resonance in the region from 290 to 315 eV. This indicates that graphitization occurred, and carbon nanocaps were formed. Based on the NEXAFS results, a formation process of carbon nanocaps will be discussed.

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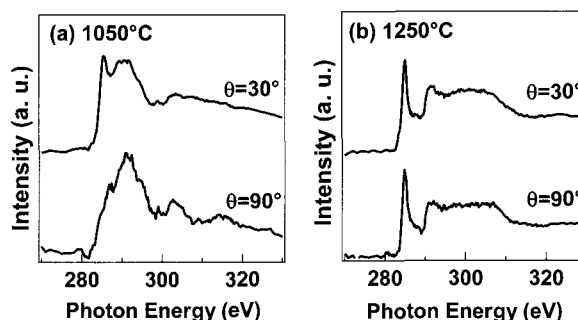


Fig.1 NEXAFS spectra of SiC(0001) heated at (a) 1050°C and (b) 1250°C. The incidence angle of X-ray is measured as an angle between the direction of X-ray and the sample surface.

VUV absorption of CNTs growth area separated from plasma with Remote Plasma CVD

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We have synthesized vertical aligned carbon nanotubes (CNTs) from methane (CH₄) and hydrogen (H₂) with remote plasma chemical vapor deposition (RP-CVD) [1]. In this apparatus, the position of decomposing CH₄ can be separated from one of the growth of CNTs, and then low temperature growth can be demonstrated. The carbon atoms in CH₄ that decomposed by a plasma fixed with the antenna edge reach the catalytic substrate and induce growth of CNTs. In this work, we measured the vacuum ultraviolet (VUV) absorption of the CNTs growth condition separated from plasma, for demonstrating the effect of RP-CVD.

Figure 1. show the VUV absorption system installed in RP-CVD. The VUV absorption spectra was measured by VUV monochromator and photomultiplier with the microdischarge hollow-cathode lamp (MHCL) as the VUV light source [2] at the CNT grown position, 40mm from the antenna edge. The light of 166nm from the discharge from the mixture of carbon dioxide and helium is absorbed by afterglow area of CH₄/H₂ plasma, and the absorbed fraction was calculated from the difference of absorption intensity when the plasma is present or absent in RP-CVD. It is measured where the plasma condition of CNTs growth was microwave power 60~120W, pressure 20~60Torr.

A lot of species of carbon and hydrocarbon such as carbon radical, ethylene, acetylene, etc, were generated from the CH₄/H₂ plasma [3]. If we assume the VUV absorption is mainly caused by carbon radical, the carbon radical concentration is calculated from the absorption fraction. For example, the absorption fraction 16% corresponding to carbon radical concentration of 10¹¹/cm³, has been obtained in the CNTs growth rate 250μm/h (normal condition) with microwave power 60W at 20Torr. In contrast, the fraction increases greatly to 65% corresponding to carbon radical concentration of 10¹³/cm³ at CNTs growth rate 2000μm/h; with microwave power 120W at 60torr. The products from CH₄/H₂ plasma including carbon radical can reach the substrate. The growth rate is enhanced by the increase of the VUV absorbing species, in which ethylene is well known as the carbon source for synthesis of vertical aligned CNTs [4]. The product containing carbon radical and/or ethylene contribute to the growth of CNTs.

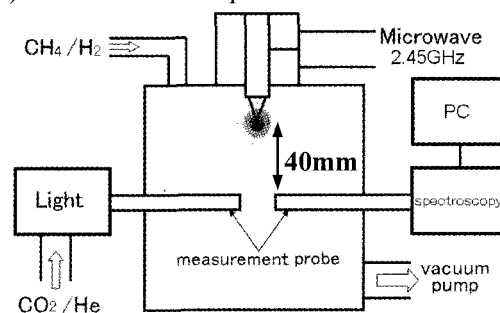


Figure 1. VUV absorption system

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Diameter Control for Super-Growth SWCNT forests

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Super-growth CVD has demonstrated the high-yield, high purity, synthesis of vertically-aligned single-walled carbon nanotube (SWCNT) forests on the millimeter-scale [1] through the introduction of a small and controlled level of growth enhancer into the growth ambient of chemical vapor deposition [1,2]. However, despite these achievements, the diameter range is limited to 2.8-3.0 nm. Thus, the achievement of SWCNT forests with small average diameter would expect to combine the strengths of Super-Growth CVD with the properties associated with smaller diameter SWCNTs, such as higher loading in composites to the spinning of high density yarns.

Here, we report the expansion of diameter control of SWCNT forests from 1.5 to 3 nm grown by the Super-Growth method. This was achieved through a combination of small catalysts produced by the arc plasma deposition (APD) technique and the optimization of the synthetic process to minimize catalyst aggregation. The characterization of the diameter were carried out by optical methods (Raman, Fourier transform infrared (FTIR), and UV-Vis spectroscopies) and transmission electron microscopy (TEM). These methods confirmed a diameter control range from 1.5-3.0 nm with 0.1 nm resolution. Further characterization of the forest structures as well as the physical properties will also be presented.

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Searching Better Lipid-PEG for Nano-Carbons Dispersion in Biological Applications

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Nano-graphene materials (NGMs) have presented versatile applications in various areas including nanobiology and medicine. Using Amphiphilic lipid-poly(ethylene glycol) (LPEG) materials to modify NGMs has been an established methodology for dispersing and biological applications [1, 2]. However, not much is known about the interaction between NGMs and LPEGs with the relation to the chemical structure, and how does the LPEG affect the biological interaction of NGMs with cells.

In this study, we reported the dispersant effectiveness of various LPEG for NGMs by using single-walled carbon nanohorns (SWNHs), and evaluate the biological effect of dispersed SWNHs with cells. It clarified that the long alkyl and PEG chains and non-ionic linker group [2] were favorable for the SWNHs dispersion in biological medium. It was also found that the LPEGs with single alkyl chains could attach strongly on SWNHs with high surface coverage ratio, and were not easily detached even when the proteins were co-dispersed in PBS. It is known that the cytotoxicity of PEG with ceramide group is high, therefore not suitable to use it for the NGM medical applications. In this context, we studied the cytotoxicity of the LPEGs that had high dispersant ability of SWNHs. In addition, we have checked the interaction of SWNHs coated with non-cytotoxic LPEGs with macrophages to find their usefulness as the carriers of therapeutic drugs or diagnostic imaging agents in body.

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Study on the Mechanism of PEG-Derivatives Assisted Dispersion of Carbon Nanohorn in Water by ^1H NMR Measurement

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Dispersing carbon nanotube (CNT) and carbon nanohorn (CNH) in water is crucial for their applications including bio-chemical use.^[1] Various surfactants were well used to assist dispersion of the CNT and the CNH in water. To improve dispersing ability of the surfactants, it is important to know interaction between the surfactants and the surface of the CNT and the CNH. Herein, we utilized high resolution magic angle spinning (HR-MAS) ^1H NMR measurement to study the mechanism of PEG-derivative surfactants (DSPE-PEG 2000 and 750) assisted dispersion of the CNH in water.

DSPE-PEGs which were not adsorbed on the CNH showed strong ^1H NMR signals, while the ones which were adsorbed on the CNH did not show the signals. These results suggested that movement of PEG units in the DSPE-PEGs were highly restricted like solid state, when the DSPE-PEGs were adsorbed on CNH in water. Molecular area of DSPE-PEGs adsorbed on the CNH were estimated from the ^1H NMR results (A_{obs}). For comparison, the theoretical molecular area of DSPE-PEGs were calculated from radius of gyration in solution reported before (A_{Rg}).^[2] The results were summarized in Table 1 and Figure 2. Interestingly, A_{obs} of DSPE-PEG2000 was smaller than A_{Rg} , while A_{obs} of DSPE-PEG750 was larger than A_{Rg} . These disagreements can be explained as followed. For longer PEG chain, the PEG chain to PEG chain repulsion was dominant. In contrast, interaction between the PEG chain and the surface of the CNT was dominant for shorter PEG chain.

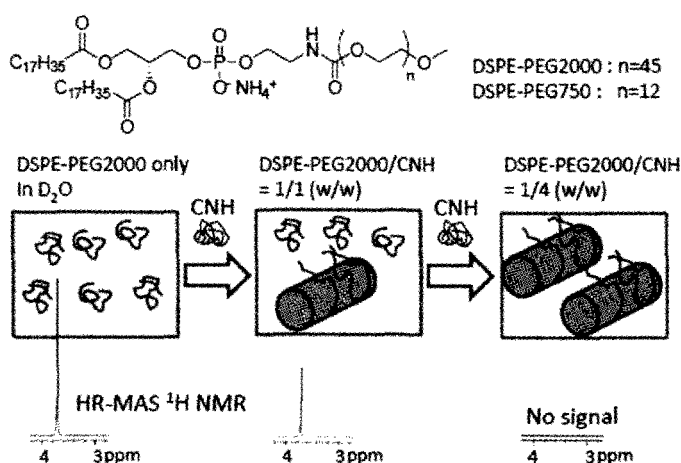


Figure 1. Schematic image of DSPE-PEG assisted dispersion of CNH.

	DSPE-PEG2000	DSPE-PEG750
$A_{\text{obs}}(\text{nm}^2)$	5.07	4.34
$A_{\text{Rg}}(\text{nm}^2)$	10.25	3.3

Table 1. Area of the PEG chain on the CNH and in solution.

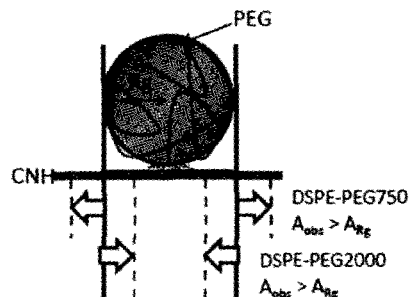


Figure 2. Size of the PEG chain in solution and on the CNH.

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Chirality-selective formation of single-wall carbon nanotubes from molecular coalescence

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The inner space of carbon nanotubes (CNTs) offers a fascinating platform to fabricate one-dimensional nanomaterials from molecular coalescence. One of the representative examples is the formation of inner single-wall CNTs (SWCNTs) from thermal coalescence of fullerene chains [1]. Recently, the extraction and separation of such inner tubes from outer ones has been accomplished with the present group [2]. This allows us to investigate the detail chirality distribution and physical properties of the inner tubes, which has been difficult due to the presence of outer ones.

In this presentation, we report that precursor-dependent formation of chirality-selected inner tubes and their formation processes. The inner tubes were formed from various organic molecules and isolated by using the method reported previously [2]. Photoluminescence maps show that their chirality distributions strongly depend on the precursor molecules even with the use of same outer tubes (Fig. 1). Interestingly, a PTCDA-derived sample contains the highest proportion of SWCNTs of (8,1) chirality, which has never been observed so far. These selective formations can be explained by energetic stability of intermediate state during the coalescence processes.

[1] S. Bandow et al. Chem. Phys. Lett. 337, 48 (2001). [2] Y. Miyata et al. ACS Nano 4, 5807 (2010).

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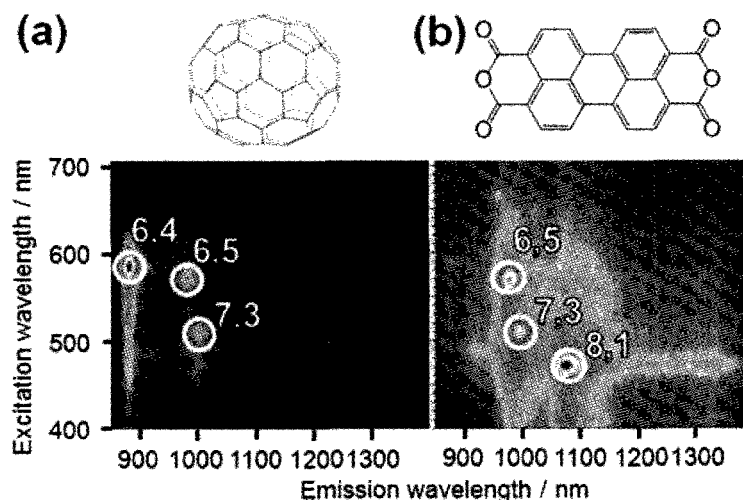


Figure 1. Molecular structure and photoluminescence maps of SWCNTs formed from molecular coalescence: (a) C70 fullerene and (b) 3,4,9,10- perylene-tetracarboxylic dianhydride (PTCDA).

Recognition and Extraction of Right- and Left-handed Semiconducting Single-Walled Carbon Nanotube Enantiomers Using Fluorene-Binaphthol Chiral Copolymers

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Single-walled carbon nanotubes (SWNTs) are nanomaterials with outstanding properties. Synthesized SWNTs are racemic mixtures of right- and left-handed SWNTs. Recently, several papers describing the separation of the racemic mixtures have been reported^{1,2}. However, for our knowledge, no report so far has been reported about the sorting of semiconducting SWNT enantiomers.

Here we describe a method to separate them. Our strategy is simple; i.e., as shown in Fig. 1, we designed and synthesized the copolymers of fluorene and (R or S) chiral binaphthyl compound (R6BIN and S6BIN, respectively) denoted (PFO)_x(R6BIN)_y or (PFO)_x(S6BIN)_y. Polyfluorenes (PFOs) and their derivatives are known to dissolve only semiconducting SWNTs and R6BIN and S6BIN are the so-called BINAP family that possessing powerful enantiomer sorting capability.

Fig. 2 (a) shows the typical CD spectra of the SWNTs solubilized by (PFO)_x(R6BIN)_y, in which evident CD peaks of the enantiomers of the semiconducting (6,5)SWNTs are observed. Similar behavior was observed when (PFO)_x(S6BIN)_y were used (Fig. 2 (b)).

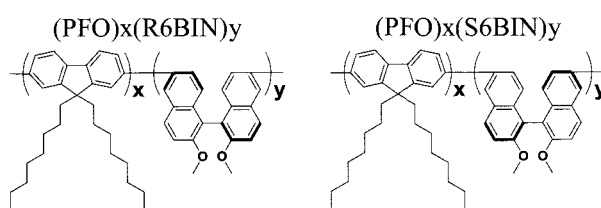


Fig. 1. Chemical structure of the copolymers of fluorene and chiral binaphthyl compound.

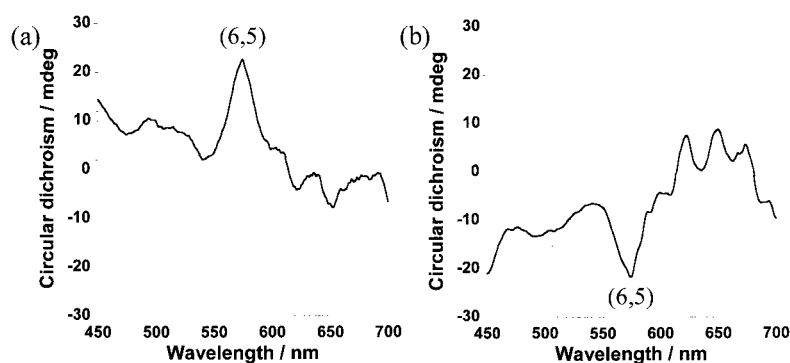


Fig. 2. CD spectra of SWNTs extracted with (PFO)₆₇(R6BIN)₃₃ (a) and (PFO)₇₂(S6BIN)₂₈ (b).

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Thermodynamics of the Exchange of Solubilizers on Single-Walled Carbon Nanotubes

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Exchange of Single-walled carbon nanotubes (SWNT) solubilizers has been used to prepare individually solubilized SWNTs and separate SWNTs with a different chirality. The benefit of this method is that it does not require sonication, so destruction or denaturation of the SWNTs is avoided. Furthermore, the exchange of the solubilizers adsorbed on the SWNTs is important to understanding the interaction between molecules and SWNTs.

In this report, we describe the thermodynamics of the exchange of solubilizers adsorbed on the SWNTs based on the analysis of the shifts in the near IR (NIR) absorption spectra of the SWNTs.^[1] HiPco-SWNTs (Unidym) were dissolved in aqueous micelle of sodium cholate (SC). Fig. 1 shows the absorption spectra of the solutions of SWNTs in the absence and presence of the oligo-DNA (20-mers of cytosine) at 30 °C. These spectral changes are accompanied by the isosbestic points as can be seen in the Fig. 1. This signifies that there are two species in the solution: the SC-solubilized SWNTs and the DNA-solubilized SWNTs. These species exist in equilibrium in the mixed solutions containing both SC and the DNA. Thus, we determined the equilibrium constants (K_a) of the exchange of solubilizers. Moreover, thermodynamic parameters, such as enthalpy (ΔH) and entropy (ΔS) of the solubilizer exchange of SC with DNA on the SWNTs were determined (Table 1). The dependence of tube diameter on K_a and changes in ΔH and ΔS will be also discussed.

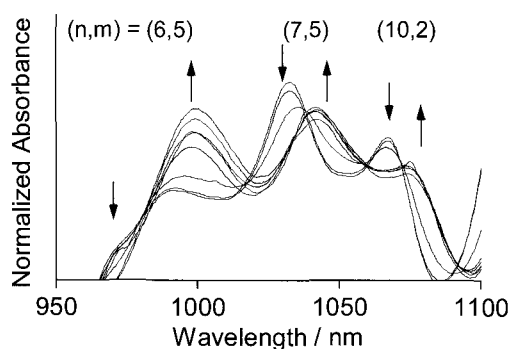


Fig.1 Absorption spectra of the SWNTs dissolved in solutions containing SC in the absence and presence of the DNA.

Table 1. Thermodynamic parameters of exchange of solubilizers.

Chiral index	ΔH [kJ/mol]	$T\Delta S$ [kJ/mol]
(n,m)		25 °C
(6,5)	26 ± 3	44 ± 4
(7,5)	13 ± 7	34 ± 7
(10,2)	25 ± 5	46 ± 5

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Photochemical dispersibility tuning of carbon nanotubes by photocyclization of a water-soluble stilbene as an efficient dispersant

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Although single-walled carbon nanotubes (SWCNTs) exhibit superior mechanical and electrical properties, the industrial applications of SWCNTs have been often limited by their insolubility in many conventional solvents. Bundled aggregation due to strong inter-tubular van der Waals interactions cause the poor solubility that acts as a barrier to both purifications and handling of the SWCNTs. In order to improve the solubility and to expand the potential application areas of the SWCNTs, various approaches including covalent and noncovalent modifications have been reported.[1] Especially, noncovalent methods using dispersants are of particular of interest, since molecularly-dispersed SWCNTs can be easily prepared without a significant decrease in the intrinsic electronic properties. Recently, a number of such dispersants with specific stimuli responsibility have been reported, because precise tuning of the dispersibility of the SWCNTs is necessary in many applications including switching devices, sensors, and drug delivery systems. As one of the representative stimuli, light is obviously promising due to being a noncontact process and has precise area selectivity.

Herein, we describe a novel water-soluble stilbene derivative that acts as an excellent and photochemically tunable dispersant for SWCNTs, based on photocyclization in an aqueous solution.[2] The nearly coplanar core of the stilbene dispersant (**1** in Figure 1) should be important to interact with surfaces of the SWCNTs via π - π interactions, resulting in a stable dispersion of the SWCNTs with individual rebundling confirmed by several spectroscopic techniques. Photoinduced cyclization for the dispersant (**2** in Figure 1) triggered re-precipitation of the SWCNTs due to detachment of the dispersant from SWCNTs surfaces (Figure 2).

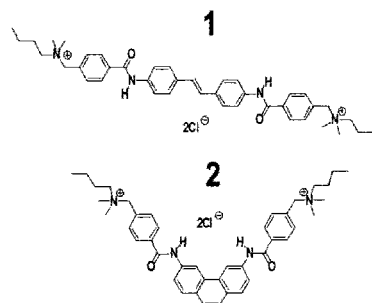


Figure 1. Chemical structure of a photofunctional dispersant **1** and a corresponding phenanthrene derivative **2**.

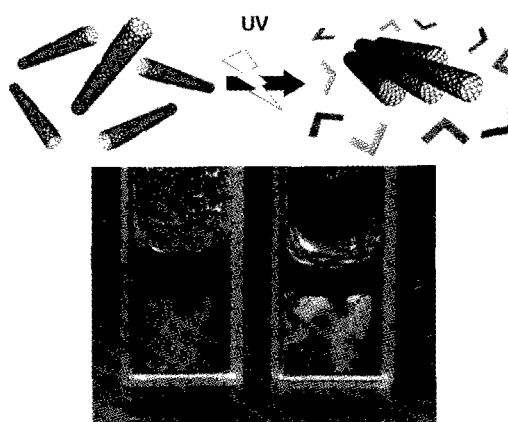


Figure 2. Schematic diagram of dispersibility change of SWCNTs by photoinduced structural change of the dispersant (upper). A photograph of the **1**/SWCNTs dispersion without and with photoirradiation (bottom).

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Low-cost metal/semiconductor separation of single-wall carbon nanotubes toward mass production

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There are two electric types of single wall carbon nanotubes (SWCNTs), metallic (M) ones and semiconducting (S) ones. For their electrical application, it is required that these two types of SWCNTs are separated into the respective type. We have developed various separation methods of M- and S-SWCNTs using agarose gel^{1,2}. In these methods, column separation is superior in terms of simplicity, rapidity, scalability, automation, etc². For the industrial mass-production of M- and S-SWCNTs, however, it is required to lower the cost of the separation further. In this presentation, we report the improvement of the M/S separation to obtain the separated SWCNTs at a low cost.

Among the chemicals used in the column separation, the cost of the gel (Sephacrose, GE healthcare) and elution solution containing a surfactant (sodium deoxycholate [DOC]) occupies the greater part of the total cost. We searched alternative gel and newly found an agarose-based gel which cost only about one-fiftieth of Sepharose gel. Figure 1 shows the optical absorbance of the separated SWCNTs by using the gel. For the elution of the bound SWCNTs, sodium dodecyl sulfate with NaCl solution can also be used instead of DOC solution³. These new separation condition enable us to save the separation cost drastically. Detailed methods and results will be presented.

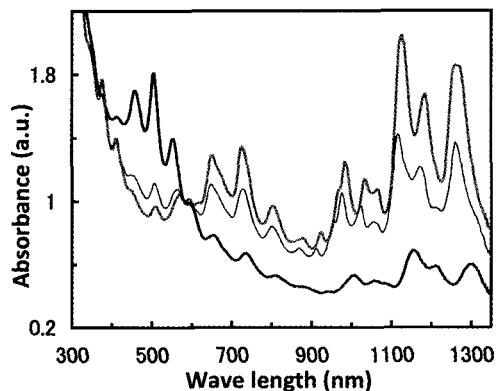


Fig. 1 Optical absorbance spectra of SWCNTs separated by the agarose-based gel. Black thick line, unbound fraction; gray thick line, bound fraction; black thin line, before separation.

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Contact resistance estimation of Open-end CNT by Contact-mode AFM

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1. Introduction To apply for electronics for device of carbon nanotubes, it is important to estimating contact resistance and also its reduction. Generally, contact resistance between CNT's open-end and metal is small. According to calculation result of electronic structure reported by Gao [1], contact resistance between the open-end of single wall CNT and Cu is $\sim 1.5 \times 10^{-11} \Omega \text{cm}^2$, and it is smaller than that of side wall of CNT.

We have made vertically aligned CNTs using remote plasma CVD (RPCVD), and estimated the contact resistance of CNTs by Kelvin method [2,3]. However, it was difficult to contact CNTs to electrode of upper side, and the result was distributed. In this time, we estimated the contact resistance of open-end CNT statistically by current mapping of contact mode Atomic Force Microscope (AFM).

2. Experiment First, we used sputtering machine to create lower side electrode (Ta/Ti) on Si wafer and deposit Al/Fe/Al as the catalyst layer. We used RPCVD to grow CNTs, and made them open-ended and adjust 1~3 μm at length using Chemical Mechanical Polishing (CMP). Finally, we used current mapping of contact mode AFM to estimate the feature of contact resistance.

3. Result & Discussion Fig.1 shows the model of open-ended CNT's contact resistance estimation. Fig.2 shows 2D current mapping and their current value is the same each other. Fig.3 shows the relation between the length of CNTs and resistance. The resistance is proportional to CNT length and the slice of this approximation line corresponds to the contact resistance. If the value is 13k Ω and the contact size of CNTs is estimated to 20nm², the normalized contact resistance can be estimated to $\sim 3 \times 10^{-9} \Omega \text{cm}^2$. This value is higher than the theoretical value by 2 powers of 10, yet very small for the contact resistance of LSI wiring.

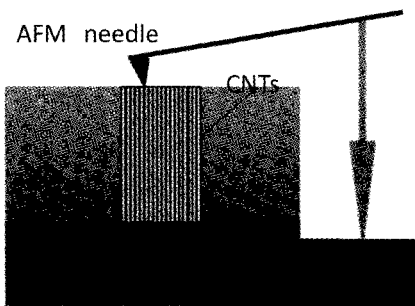


Fig.1 Model of open-ended CNT's contact resistance estimation



Fig.2 2D image of current mapping

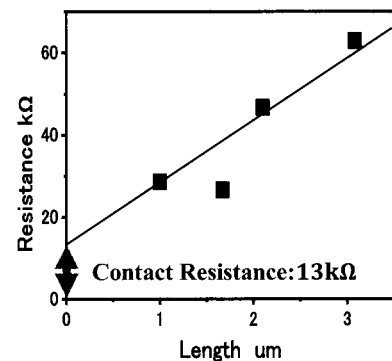


Fig.3 Relation between length of CNTs and resistance

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Electrical characterization of CNT forests along growth direction by micro-scale 4-probe method

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The properties of carbon nanotube (CNT) forests are highly dependent on the structure, such as wall number, density, crystallinity, etc. [1]. Because CNT forests are both sparse and anisotropic, some properties are difficult to accurately characterize. For instance, to characterize conductivity along nanotube axis without destroying the forest structure, two-probe method has been mainly used [2,3]. However, this includes contact resistance. Furthermore, in the case of CNTs which cannot independently stand, such as single-walled carbon nanotube (SWCNT) or few-walled CNTs, the forest consists of a random network section at the top (cap) and an aligned section (body). As these two sections are physically inseparable, measurement of the electrical properties often includes contributions from both.

Here, we report an electrical measurement technique to characterize the aligned “body” section of CNT forests. To eliminate the influence of the contact resistance, we employed the four-probe method. We fabricated a 100 μm-wide four-probe resistance set-up. This micro-scale four-probe was fabricated on the oxidized Si substrate by electron beam lithography technique and sputtered gold. By placing this probe in contact with CNT forests, the resistance along nanotube axis became measurable. We developed procedures for stable and reproducible measurement through examining the dependence of the resistance to applied contact strain. We found that the resistance was stable and reproducible in the region where the compression of forests was between 10-20%. We could calculate sheet resistance from the probe pitch and the contact length of the probe and forests. As the results of the measurement with this four-probe, the resistance of well-aligned section of SWCNT forests did not show a definite correlation with the forests height.

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Dumbbell shape cyclic voltammogram of SWCNT capacitor electrodes

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Electric double layer capacitors (EDLCs) are electrochemical systems that can be used as energy storage devices. Single-walled carbon nanotubes (SWCNTs) would be a good candidate for high energy density EDLC electrodes due to their exceptional properties of high electrical conductivity, high specific surface area, high charge transport capability, and tunable porosity. In fact, a lot of investigations have been done on SWCNT EDLC electrodes. However, the ion adsorption mechanism of SWCNT EDLC electrode has not yet been clearly understood, partly because most of the previous studies were performed with SWCNTs having relatively low crystallinity produced by CVD method.

In the present study, the electrochemical behavior of highly crystallized single-walled carbon nanotubes (SWCNTs), having a small diameter distribution, is investigated by cyclic voltammetry (CV), using triethylmethylammonium tetrafluoroborate in propylene carbonate as electrolyte. Unlike the CV curves previously observed by other researchers and referred to as the "butterfly" shape, the CV curve observed in the present study has big "humps" on both sides of the rest potential. The observed CV profile shape looks like dumbbell. It was found by the comparison between the electronic density of states (DOS) of SWCNTs and the dumbbell CV shape that the drastic increase of current in "dumbbell" can be explained by the van Hove singularity in the DOS of the semiconducting SWCNTs in the sample. In order to check the validity of the explanation, we have performed the separation of metallic and semiconducting SWCNTs by density gradient ultracentrifugation method, and measured CV curves of the separated two samples. As we expected, the two SWCNT samples show completely different CV profiles corresponding to each DOS shapes. Ion adsorption inside the nanotube is also discussed with attention to the change in CV curves with increasing sweep rate.

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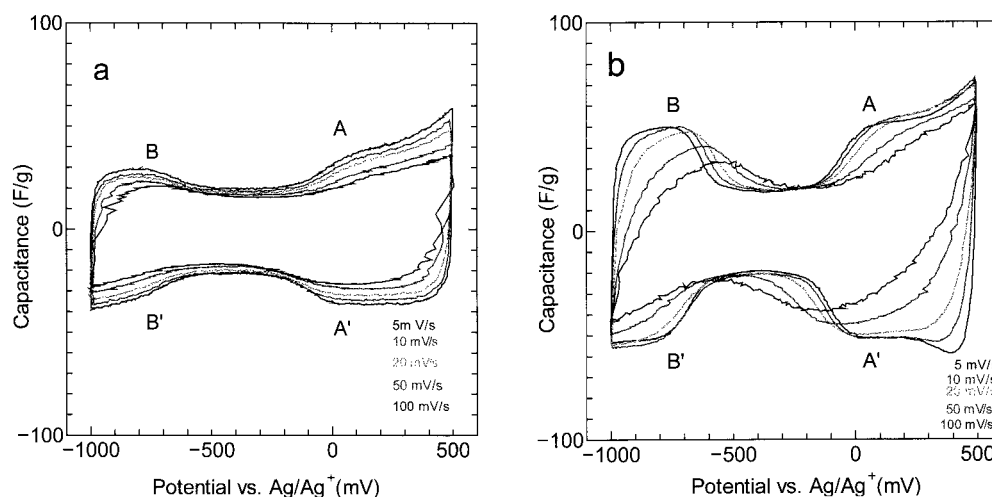


Fig. 1 Cyclic Voltammograms of (a) closed-end and (b) open-end SWCNTs under different scan rates.

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Tailoring Temperature Invariant Viscoelasticity of Carbon Nanotube Material

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Viscoelasticity describes the ability of a material to both dissipate energy (viscous) and reversibly deform (elastic) and permeates all levels of our lives from human tissue, shoe soles to vibration isolators. Tailoring viscoelasticity is of practical importance because the required mechanical properties can greatly differ with application. Over the long history of viscoelasticity development, thousands of materials have shown the disadvantage that the stiffness (storage modulus) and viscosity (damping ratio) are difficult to be simultaneously improved. It is this reason why a strong and highly viscous material is rare, which is yet highly required.

Using carbon nanotube (CNT) as building blocks, we fabricated a viscoelastic CNT material composed of long and entangled CNTs. The inherent thermal resistance of CNTs provided temperature invariant viscoelastic properties from -196-1000°C, far exceeding the operational range of conventional viscoelastic material [1]. Here, in contrast to existing conventional materials, the stiffness and viscosity of this material could be simultaneously improved. This allows for fabricating both highly elastic and highly viscous materials. We demonstrated that, over one order increase in density (3.3-36 mg/cm³), the storage modulus was increased one-order from 0.11 MPa to 1.05 MPa (similar to polymeric foams-like to soft rubbers), while the loss modulus was increased 30-fold from 0.0105 MPa to 0.322 MPa. It is in terms of 30-fold increase in the amount of dissipative energy. As a result, the damping ratio was increased from ~0.1 to 0.32 [2]. This unique phenomenon was explained by the zipping and unzipping of carbon nanotubes at contacts as the cause of the viscoelasticity. Both the contact density and contact length were observed to be increased with the material density. The storage and damping ratio were supposed to scale as the contact density and the contact length, respectively, which could be the reason for the increases in the elastic and viscous aspects in tandem. Furthermore, the thermal stability of CNTs and working mechanism created a new group of materials on the Ashby map which is compliant (soft) and yet operates at high and low temperatures. These results represent important and significant improvement in the well-established field of viscoelasticity, which is promising to unlock possibilities by overcoming the obstacles of conventional materials.

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Microscopic mechanisms of alignments of carbon nanotubes on sapphire surfaces

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Nanometer-scale devices using single-walled carbon nanotubes (CNTs) are expected to be boosters in post-scaling semiconductor technology that is challenged by physical limitation due to its cutting edge miniaturization. In order to utilize fascinating properties of CNTs for devices, however, it is imperative to align them on substrate surfaces in controlled ways. Chemical vapor deposition (CVD) on sapphire surfaces provides a promising stage: It is found that ultralong CNTs are produced along particular directions on the A (11-20) and R (1-102) crystallographic planes. Furthermore, it is reported that the chirality of the grown CNTs is almost controlled by choosing the surface orientation: i.e., zigzag-like CNTs are mainly observed on the A-plane while armchair-like CNTs on the R-plane.

Interaction between the CNT and the substrate plays an essential role in such selective growth of CNT on sapphire. However, nature of the interaction is still unclear. Strong chemical interaction or van der Waals (vdW) interaction is proposed to be responsible for the selective growth of CNTs based on speculative analyses or an empirical simulation [2]. Furthermore, the CNT-substrate interaction is expected to modify the electronic structures of the CNTs [3], thus being decisive in characteristics of the nano-devices. At this stage, reliable first-principle calculations that reveal the nature of the CNT-interface interaction, the mechanism of the selective growth and then the interplay between the atomic structures and the electron states are highly demanded.

In this presentation, we report on the total-energy electronic-structure calculations, using the density functional theory, that clarify stable and metastable atomic structures of CNTs on the A- and R-planes and resultant electron states of CNT-sapphire interfaces. On the stoichiometric surfaces, we find that the vdW interaction is dominant between the CNTs and the substrates and causes no directional preference. On the Al-rich surfaces which is also stable from our recent calculations, on the other hand, we find that strong chemical bonds are formed between C and Al atoms and the calculated interaction energy shows strong directional dependence, unequivocally clarifying the origin of the observed selective CNT growth in terms of energetics. The calculated energy bands in the most stable arrangements of the CNTs on sapphire show substantial modification of the corresponding energy bands of isolated CNTs, elucidating the importance of the CNT-substrate interaction.

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Multiple Exciton Generation by A Single Photon in Single-Walled Carbon Nanotubes

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Multiple electron-hole or exciton generation certainly advance the efficiency of photovoltaic devices, because the single photon create two or more electron-hole pairs or excitations. It has been demonstrated that such multiple generation has been realized in the system with low-dimension and nanometer scale, such as semiconductor nanocrystal and carbon nanotubes. During the process, the Coulomb interaction plays decisive role to induce energy transfer, which overcomes the dissipation process associating with phonons [1]. This process is called as the multiple exciton generation (MEG).

Single-walled carbon nanotube (SWNT) is possible prototype to examine the MEG due to its quasi-one-dimensional structure that leads to the substantial Coulomb interaction [2,3,4]. In the present paper, we aim to theoretically unravel the fundamentals process of the MEG in SWNTs. We show that the MEG by the direct photogeneration of multi excitons is likely to occur in SWNTs (Fig.1). On this process, we show that the substantial resonance between the excited states of the single exciton state and the multi-exciton states allow the multiple exciton states as a final state. In addition, we also demonstrated that the high efficiency of the MEG is attributed to the strong Coulomb interaction between excitons and to the singularity in the density of states of the multiple-exciton states. Our calculation gives the substantial increase of the conversion efficiency up to 170 % (Fig.2).

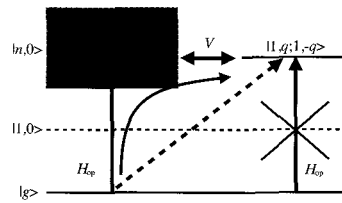


Fig.1 MEG process.

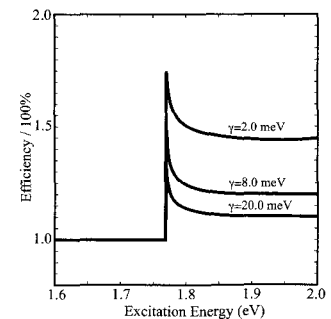


Fig.2 Conversion efficiency.

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Geometrical, Electrical and Energetical Family patterns of Single-Walled Carbon Nanotubes: A Helical-Symmetry First-Principles Investigation

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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]. In addition, it has been pointed out from the first-principles electronic-structure 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. Because it is very important to know the accurate electronic properties of CNTs for any possible application, the first-principles electronic structure study with the geometrical optimization for CNTs should be of high importance.

In the present work, by fully utilizing the helical symmetry of CNTs as well as their translational symmetry, we perform the systematic first-principles investigation of the geometries, the electronic properties and the energetics for chiral as well as armchair and zigzag CNTs. Consequently, the presence of the geometrical family pattern has been revealed for the first time. The bond lengths and the bond angles of CNTs show smooth variations from armchair to zigzag CNTs through chiral CNTs in each family. It is confirmed that the geometrical optimization plays a very important role in predicting electronic structures of chiral CNTs as well as achiral CNTs. The fundamental gap corrections associated with the geometrical optimizations should be sizable even in one nm diameter CNTs. According to a report of the shingle-chirality separation with high purity [5], the geometrical and electrical family patterns should be confirmed experimentally in the near future. Importantly, the presence of the energetical family pattern has been also revealed, and it is found that “near-armchair” CNTs including (6,5) and (7,5) CNTs are energetically more stable than other CNTs as in the case of small-diameter near-armchair CNTs [4]. This result corresponds well with the high abundance of near-armchair CNTs experimentally reported so far [6].

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Gate Modulation of the Optical Transitions in Single-Walled Carbon Nanotubes

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The carrier density and Fermi level in single-walled carbon nanotubes (SWNTs) can be widely tuned by means of electrostatic gating. This tunability offers an opportunity for investigation of many body effects in one-dimensional systems. Understanding of the effects of electron-electron interactions on excited states is both of fundamental interest and of importance for development of gate-tunable optoelectronics devices.

Here we demonstrate that the optical transitions of both metallic and semiconducting SWNTs are strongly modulated by electrostatic gating. We studied gate-induced changes in optical spectra of pristine, individual suspended SWNTs as a function of applied gate voltage using Rayleigh scattering spectroscopy [1]. We observed a significant broadening, red shift, and intensity decrease of exciton resonance peaks in Rayleigh scattering spectra. The broadening was nearly linear as a function of carrier density n . For metallic SWNTs, we observed the red shift of about 5 meV at $n=0.1\text{nm}^{-1}$, and the line width increased at a rate of about 100 meV·nm (with a line width of ~ 50 meV for pristine SWNTs reaching ~ 100 meV at $n=0.5\text{nm}^{-1}$). For semiconducting SWNTs, the red shift was about 5x larger and the broadening was 2x larger than for metallic SWNTs, indicating greater gate-induced changes of electron-electron interactions and dielectric screening effects in semiconducting SWNTs than in metallic species.

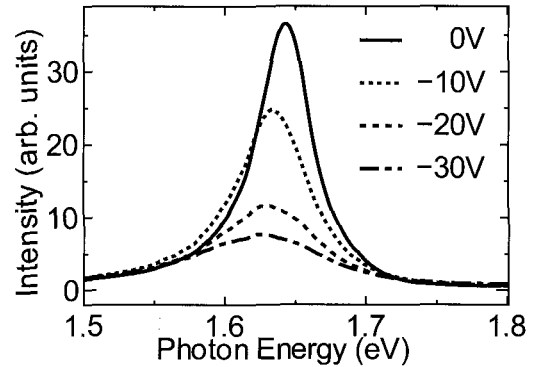


Fig. 1: Rayleigh scattering spectra of a (12, 12) metallic SWNT at various gate voltages from 0V to -30V. A gate voltage of -30V corresponds to $n\sim 0.5$ holes/nm.

[1] M. Y. Sfeir *et al.*, Science **306**, 1540 (2004).

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Single-Chirality Separation of Single-Wall Carbon Nanotubes by One-Step Gel Column Chromatography

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Mono-structured single-wall carbon nanotubes (SWCNTs) with the same electronic type and band gap are essential to pull out the original excellent-performance of SWCNTs as a building block of high-speed electronics. Recently, we achieved the chirality separation of semiconducting SWCNTs by a single-surfactant multicolumn gel chromatography using allyl-dextran-based size-exclusion gel (HR S-200, GE Healthcare) [1]. In this method, the high-purity single chirality SWCNTs can be obtained by two-step overloading the column series with SWCNTs dispersed in sodium dodecyl sulfate aqueous solution. This method is very powerful and can be applied to the mass production. However, multi-step separation decreases the total yield and increases the separation cost because of the complicated separation procedure.

In the present work, we report a simple one-step gel column chromatography method for single-chirality separation of SWCNTs. This method is based on the chirality selective interaction between SWCNTs and gels at a specific temperature. In this method, the separation temperature was carefully controlled from 10 to 30 °C with a step of 1-2 °C. At the lowest separation temperature, interaction between SWCNTs and the gel became weakest and then only some specific (n_1 , m_1) single species were bound in the gel because of their strongest interaction with the gel. After this process, all (n_1 , m_1) species were sorted out and we obtained the SWCNT solution containing no (n_1 , m_1) species. With an increase in the separation temperature, the interaction between SWCNTs and the gel increased and another (n_2 , m_2) species among the unbound nanotubes were bound in the gel. In this manner, we demonstrated that seven (n , m) single species could be successively separated from HiPco SWCNTs at a series of separation temperatures (Figure 1). This temperature-controlled gel chromatography allows single-chirality separation without repeating separation procedure, improving the separation yield and decreasing the separation cost. The effect of the temperature on the chirality separation will also contribute to clarify the chirality-separation mechanism of SWCNTs.

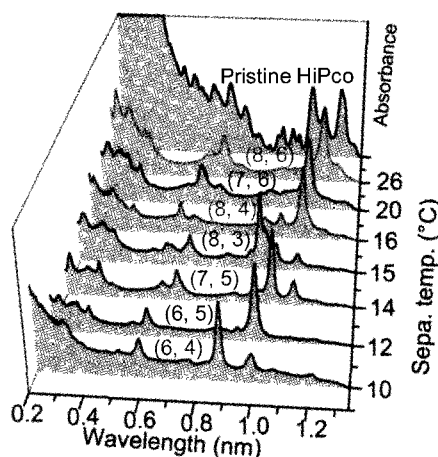


Figure 1. Optical absorption spectra of the (n , m)-enriched species separated at different temperatures.

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

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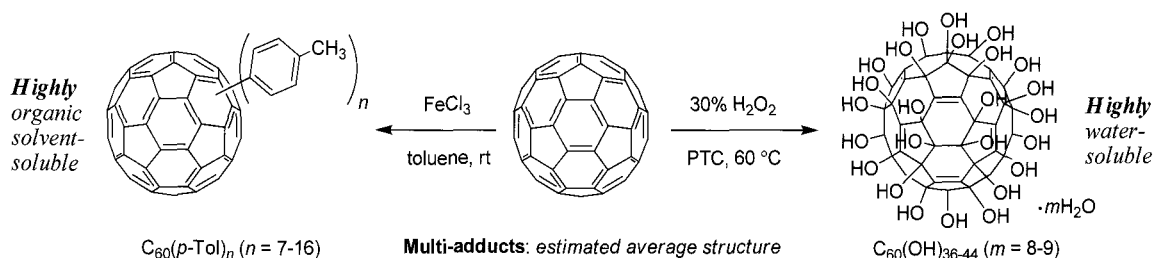
Chemistry of Fullerene Multi-Adducts: Highly Soluble Fullerenes

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Physical and chemical properties of fullerenes can be variously modified by designed introduction of substituents on the fullereryl π -conjugated surface. One of the most simple but important properties is solvent solubility. Due to the large non-polar spherical surface along with the strong π - π intermolecular interaction, even the introduction of a highly polar ionic group results in the considerable aggregation in polar solution. However, it is necessary to solubilize the fullerene derivatives into neutral water for the application to life science. Or it is desired to synthesize the highly organic solvent-soluble fullerene derivatives without hetero atoms to retain the high carbon content for the application to resist materials.

In this study, the multi-hydroxylated and the multi-arylated [60]fullerene derivatives were synthesized by facile methods, respectively.¹⁻³ The number of hydroxyl groups was found to be 36 to 44, depending on the reaction condition, and the obtained $C_{60}(OH)_{44}$ showed excellent water-solubility up to 65 mg/mL. The fullerenols also exhibited many interesting properties including the application to CMP slurry⁴⁻⁶ and to antioxidant.⁷⁻¹² On the other hand, the multi-tolylated fullerene showed high PGMEA-solubility (>25 wt%). These techniques were also utilized to the synthesis of some other multi-adducts.¹³⁻¹⁵



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Electronic Spectra of Polyynes-Iodine Complexes in Nonpolar solvents

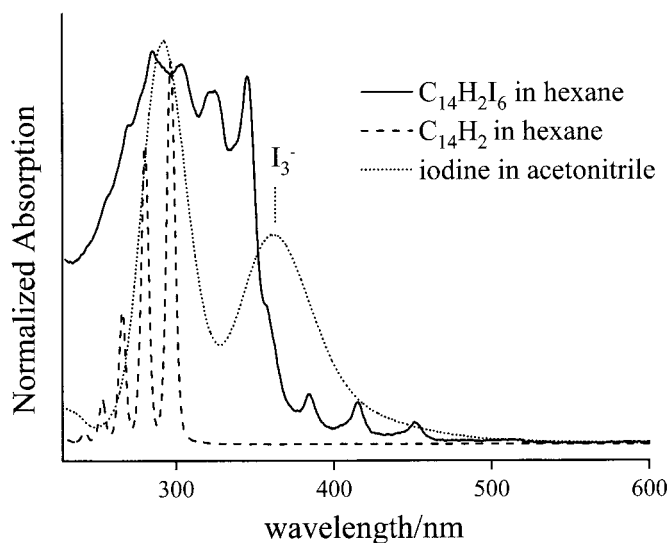
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Polyynes, $\text{H}(\text{C}\equiv\text{C})_n\text{H}$ ($n\geq 2$), are sp-hybridized carbon chain molecules with two hydrogen atoms at both ends. These molecules have cylindrically symmetric π -electron systems and exhibit absorption bands for the allowed transition in the UV and those for a forbidden transition in the near UV region [1,2]. We have reported that the allowed transition disappears, the forbidden transition increases, and new bands appear upon addition of iodine molecules into the solution of polyyne molecules under illumination with visible light [3]. The spectral change is related to the formation of a molecular complex of polyyne and iodine molecules by photoinduced reaction.

Figure 1 shows absorption spectra of polyyne-iodine complex, $\text{C}_{14}\text{H}_2\text{I}_6$, in hexane and iodine in acetonitrile. The spectrum for polyyne, C_{14}H_2 , in hexane is also merged for comparison. The spectrum of iodine in acetonitrile has two strong absorption bands which show maxima at 292 and 363 nm. These absorption bands correspond to triiodide, I_3^- [4]. The spectral region for I_3^- coincides well with that for the polyyne-iodine complex of $\text{C}_{14}\text{H}_2\text{I}_6$. The absorption maximum at 285 nm for $\text{C}_{14}\text{H}_2\text{I}_6$ fairly matches to the band maximum at 292 nm to I_3^- and the vibronic bands in 380–460 nm overlap well with the red tail of the band of 363 nm for I_3^- .



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Figure 1. Comparison of absorption spectra of polyyne-iodine complex, $\text{C}_{14}\text{H}_2\text{I}_6$, in hexane (solid line) and triiodide, I_3^- , in acetonitrile (dotted line). The spectrum of polyyne, C_{14}H_2 , in hexane is also merged for comparison (dashed line).

Effect of Coulomb repulsions in the vibronic couplings of C_{60}^-

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The vibronic couplings in C_{60}^- have been diligently investigated because of the importance in the mechanism of the electronic properties like the superconductivity of alkali-doped fullerenes. To determine vibronic coupling constants (VCCs) is important since they characterize the interactions. However the VCCs of C_{60}^- have not been definitely determined because of the disagreement between the experimental and theoretical constants. Moreover, though some authors tried to explain the order of the VCCs [1,2], they obtained different results from each other. Recently, we have succeeded in determining the constants accurately from the photoelectron spectrum of C_{60}^- and DFT calculation [3]. We found that the coupling to the bond-bending ($h_g(7)$) mode is strong while the coupling to the bond-bending ($h_g(2)$) mode is weak. In this work, to explain the order of the VCCs of C_{60}^- , we analyze the vibronic couplings using a concept of vibronic coupling density (VCD) [4]. The VCD η is defined by the product of the electron density difference between C_{60}^- and C_{60} and the potential derivative with respect to the normal mode. Since the integral of η over all space is equal to the VCC, the VCD gives a local picture of the vibronic couplings. The distributions of η for the $h_g(2)$ and $h_g(7)$ modes are almost antisymmetric and symmetric with respect to the cage surface of C_{60} at each C atom, respectively (See Figures 1(a) and (b)). Therefore the integral of η for the $h_g(2)$ mode cancels around each atom and the VCC is weak from the symmetry reason. On the other hand, η for the $h_g(7)$ mode does not cancel and the coupling is large due to the symmetry. Moreover, the VCC for the $h_g(7)$ mode is large because of the delocalization of η on the C-C bond encircled by the dotted ring in Figure 1(b). This delocalization comes from the σ density on the C-C bond. We found that the σ density appears due to the Coulomb repulsion between the electron in SOMO and the other occupied electrons.

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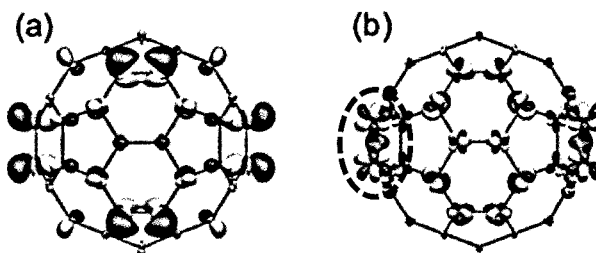


Figure 1: η for the (a) $h_g(2)$ and (b) $h_g(7)$ modes. White and gray areas indicate positive and negative densities, respectively.

Production and characterization of $Y_2@C_{80}$

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So far, two types of di-metallofullerenes have been reported: the first one is that two metal atoms are encapsulated mainly in C_{78} and C_{80} cages, and the second is that also two metal atoms are encapsulated, but in different cages such as C_{82} and C_{84} . Y-metallofullerenes have been known as a species belonging to the latter type and actually, $Y_2@C_{82}$, $Y_2C_2@C_{82}$, and $Y_2C_2@C_{84}$ have been isolated and characterized.

In 2008, Zuo et al. reported the isolation of a new type of metallofullerene; $Y_2@C_{79}N$, in which $C_{79}N$ has the structure such that one carbon atom sitting on the $I_h C_{80}$ cage is replaced by a nitrogen atom [1]. From the theoretical calculation, it was suggested that one additional electron originated from the substituted nitrogen atom resides in a bonding orbital localized between the two yttrium atoms. Moreover, it was also showed that $Y_2@C_{79}N$ has a rather large HOMO-LUMO gap in contrast with a very narrow band gap of $Y_2@C_{80}$, and the difference in HOMO-LUMO gap between these two species has been strongly suggested as reason why $Y_2@C_{79}N$ was successfully extracted as a stable species in solution. Such a situation, in turn, strongly suggests that $Y_2@C_{80}$ anion would be stable in solution.

In 2005, we reported that metallofullerenes are extracted selectively and directly from the raw soot with mixed solvent of triethylamine (TEA) and acetone (mixing ratio was 1:3) [2]. In this method, metallofullerenes are reduced by TEA and the resultant anions are solvated and stabilized by acetone. So, in this study, we intended to try to extract $Y_2@C_{80}$ anion from the raw soot directly by the mixed solvent and to characterize $Y_2@C_{80}$.

Soot containing Y-metallofullerenes was produced by direct-current (60 A) arc discharge of Y/C composite rods (Y:C=2:98) under a 400 Torr He atmosphere. The obtained raw soot was divided into two parts and each part was extracted with CS_2 or with mixed solvents of TEA and acetone, respectively. Fig. 1 shows the typical LD-TOF-MS spectra of the CS_2 extract and the mixed solvents extract. In the CS_2 extract, the signals due to empty fullerenes are rich, but in the mixed solvents extract, Y-metallofullerenes are mainly extracted and empty fullerenes are almost disappeared.

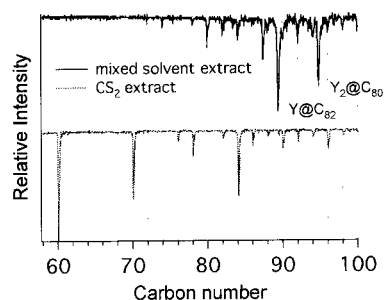


Fig. 1 LD-TOF-MS spectra of extracts.

[1] T. Zuo, et al. *J. Am. Chem. Soc.* **130**, 12992-12997 (2008).

[2] T. Kodama, et al. *Chem. Lett.* **34**, 464-465 (2005).

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Characterization of Charge and Radius of Particles by Ion Trap Mobility with Free Fall in Air

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Ion mobility measurements have been utilized to analyze structures of nanocarbon materials[1]. We have been developing an ion trap mobility system to enable long-term measurements of charged particles with enhanced sensitivity[2]. The ion mobility of the particle is dominated by the ratio q/r , where q and r are the charge and the radius of the particle, respectively. So far the system cannot determine the two parameters independently because the mobility measurement clarifies only the ratio q/r . For the structural studies of nano materials it is crucial to clarify the two parameters. Here we present the independent radius and the charge determination by the ion mobility with free fall movement in air.

Figure 1 shows the experimental setup which consists of stacked ring electrodes with radio-frequency (RF) voltage for ion trap and low-frequency (LF) voltage for ion mobility. Charged particles were produced by an atomizer with high-voltage (10 kV) and were trapped where their movement was monitored by a camera with laser irradiation. At first the ion mobility was observed with RF and LF voltages for the determination of q/r and then the free fall was observed without any voltage for the determination of r . The terminal velocity of the free fall is dominated by the ratio m/r where m and r are the mass and radius of the particle, respectively. This ratio m/r is actually proportional to r^2 and we can tell the radius directly because m is proportional to r^3 . Figure 2 shows the charge as a function of the radius. The results show that the charge increases with the radius with some distribution. The charge is much smaller than that expected from the high-voltage (10 kV) applied to the atomizer.

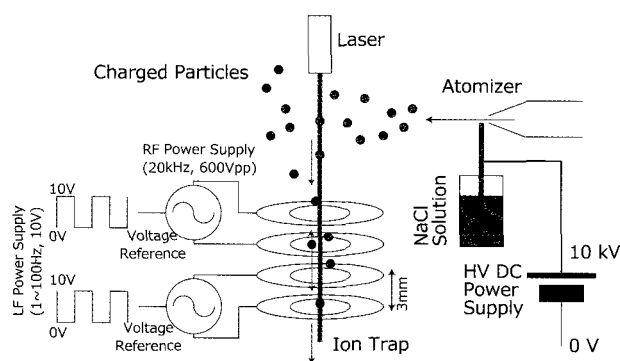


Fig.1 Ion trap mobility system

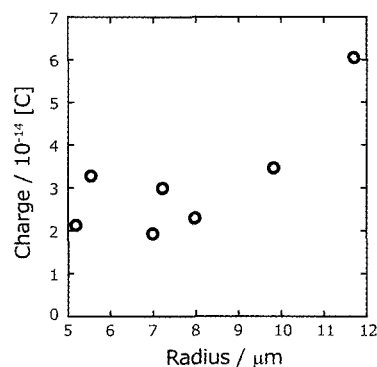


Fig.2 Particle charge dependence on radius.

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Single-Walled Carbon Nanotube as 1D Array of Reacting Sites

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For large molecules reacting with a single-walled carbon nanotube (SWCNT) in solution, the length segment occupied by a reacting molecule is considerably larger than the tube diameter. A SWCNT looks like a very thin wire which allows only one molecule to react at a given length segment, but has many reacting segments along its axis. In other words, a SWCNT may be considered as a 1D array of reacting sites. In this study, we are interested in characterizing how 1D nature of reacting sites is reflected in the reaction kinetics.

One of the problems in kinetic studies is that SWCNTs do not disperse in common solvents unless surfactants or polymers are added. Whereas small molecules can penetrate through the additive layers adsorbed around SWCNTs, large molecules are severely blocked to approach. We have conducted a series of experiments to find a condition to disperse SWCNTs stably in buffer solution without any additives. It was found to be in tris buffer at low temperatures with the concentrations less than 5 ng/mL.

Cytochrome c (Cyt-c) is a heme protein with diameter of ca. 3.5 nm, considerably larger than the diameter of HiPco (0.7-1.2 nm). The heme group undergoes a redox reaction, which can be followed easily by absorption spectroscopy. We have found that simply mixing Cyt-c with dispersed SWCNTs in tris buffer reduces Cyt-c. Atomic force microscopy shows that most SWCNTs are dispersed individually. Raman and UV-Vis absorption spectroscopy reveal that SWCNTs in tris buffer are heavily n-doped, which explains the reducing ability.

The amount of reduced Cyt-c was followed as a function of time for various initial oxidized Cyt-c concentrations at a fixed SWCNT concentration. It increases almost linearly at first, then levels off to a limited value after 20 hr. The very slow kinetics indicates that adsorption of Cyt-c on SWCNT is a rate determining step. The early stage is described well by Langmuir kinetic equation and the limited amount follows Langmuir isotherm. This implies equivalence and independence of each reacting site of 1D array. Then, the kinetics changes to logarithmic after several hr (Figure 1), meaning that the velocity decreases exponentially with the product concentration. In many reactions on 2D surfaces, the velocity decreases linearly and the kinetics becomes parabolic. The exponential dependence demonstrates a high sensitivity of 1D system to adsorption. Finally, 40 hr later, the adsorbed Cyt-c covers SWCNTs completely and quenches the reaction, creating a situation similar to a poisoning effect in catalysis.

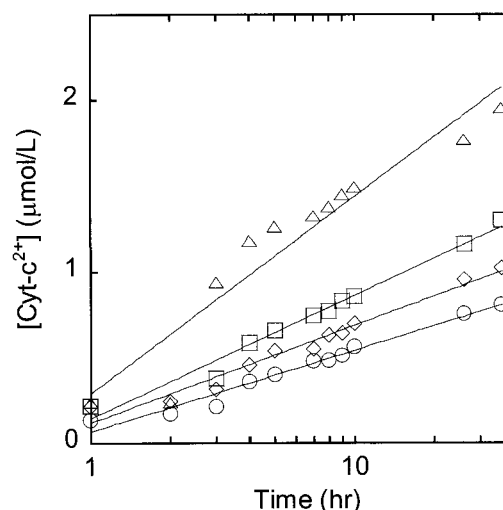
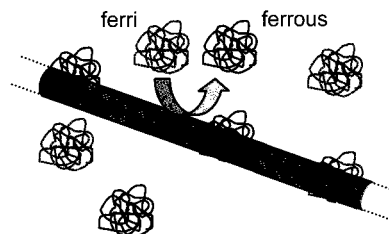


Figure 1. Logarithmic plot of the kinetics for various initial Cyt-c concentrations.

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Low temperature melting and emptying of copper nanowire-filled carbon nanotubes

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Hybridization of metal/metal compound nanowires and carbon nanotubes (CNTs) has been tried as one of the ideas for novel one-dimensional nanostructures suitable for nanoelectronic and sensor applications. Long one-dimensional hollow structures in CNTs give unusual nanospace for formation and crystallization of nanowires. We have reported on effective formation of copper nanowire-filled CNTs (Cu@CNTs) and copper sulfide nanowire-filled CNTs (CuS@CNTs) via modified arc discharge method. In addition, we have found that copper nanowires in Cu@CNTs had unusual instability compared with copper sulfide nanowires in CuS@CNTs. In this study, we investigated that copper nanowires in Cu@CNTs melted at temperatures lower than its bulk melting point and we could empty Cu@CNTs by melting out the CNTs.

Cu@CNTs and CuS@CNTs were produced by conventional carbon arc discharge with hydrogen gas and ethanol vapor introduced into the arc plasma, respectively. Graphite rods were used for electrodes. A hole was drilled in the center of a graphite anode and filled with copper powder. The electrodes were set vertically in a vacuum chamber. In the case of CuS@CNT formation, the ethanol vapor was introduced into the chamber by bubbling argon through ethanol containing carbon disulfide of 10% heated at 50°C. As-grown samples were heated at 200-1100°C in vacuum.

In the case of Cu@CNTs formed by hydrogen arc discharge, we have also found that copper melted and came out from the tip of CNT by heat treatment at the temperature of more than about 400°C in vacuum (Fig. 1). Hollow CNTs, which have thin 4-5 layers and large diameters of about 50 nm, remained after removal of copper. The inner diameter distribution was very narrow. This result is similar to structural changes of CNTs formed by RF plasma method [1]. On the contrary, CuS@CNTs were thermally stable and kept the filling structure at about 1000°C. This result indicates that the filled copper and copper sulfide nanowire would be very different from each other in interaction at the interface between the nanowires and inner wall of CNT and cannot be explained by size effects such as reduced melting points. We must investigate another cause.

[1] A. Koshio *et al.*, J. Phys. Chem. C, **111**, 10 (2007).

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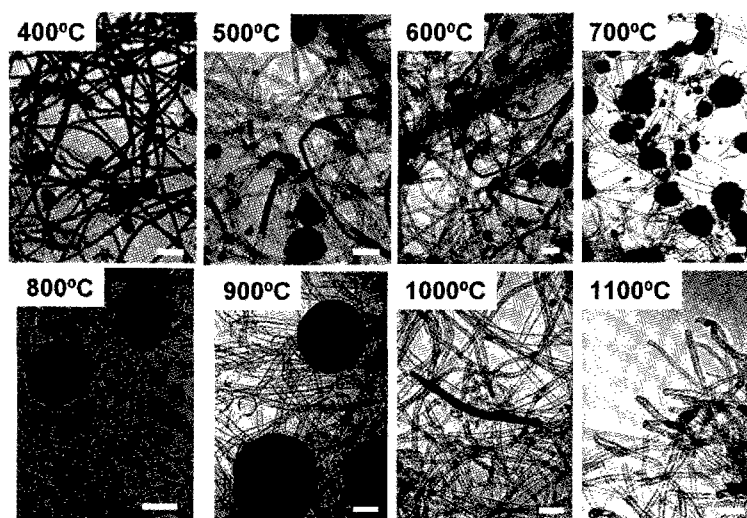


Fig.1 TEM images of Cu@CNTs heated in vacuum. Scale bars are 100 nm.

Control of layer number in growth of carbon nanotubes by eDIPS method

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Considerable research efforts have been devoted to synthesize double-wall carbon nanotubes (DWCNTs) because of their superiority in structural and electronic properties promising for the expected technological applications, especially for a tip of atomic force microscope [1], a transparent conductive film [2], a field emitter [3], and so on. Diverse applications increase the necessity of the mass-production of high-quality DWCNTs at low-cost. Various chemical vapor deposition (CVD) methods have been investigated to realize such mass-production of CNTs. In particular, enhanced direct injection pyrolytic synthesis (eDIPS) method [4] is promising due to the continuous process for CNT production. In addition, CNTs obtained by eDIPS method are well graphitized, comparable to that by an arc discharge and a laser vaporization. To date we have investigated eDIPS method mainly for the diameter control in the production of single-wall CNTs [4].

In this work, we have investigated the effect of carbonaceous gas as an additional carbon source on eDIPS production. Additionally the concentration of promoter (thiophene) in the feedstock has also been optimized for the production of DWCNTs. It was found that the flow rate of the carbonaceous gas considerably changes the productivity and relative abundance of DWCNTs. Figure 1 shows the typical TEM image of DWCNTs selectively produced by this work. We will also discuss the growth mechanism of DWCNTs based on these results.

The study is supported by NEDO. We thank Mr. Y. Hashimoto, Mr. H. Katayama, Mr. K. Hoshi, Ms. A. Kobayashi and Ms. T. Owada for the experimental help.

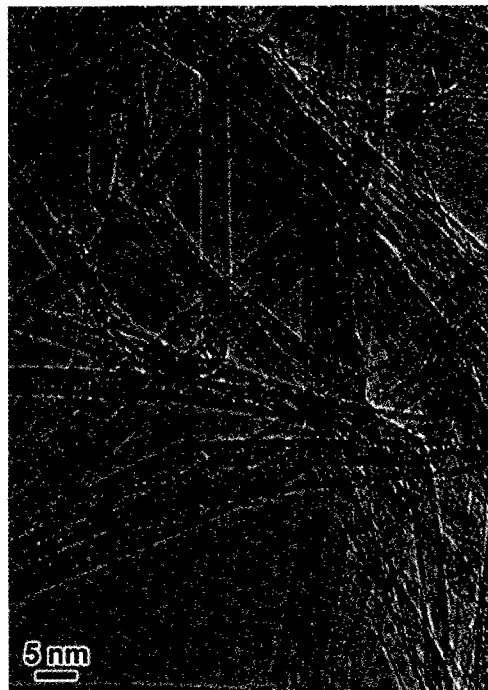


Figure 1 Typical TEM image of DWCNTs selectively produced by this work

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- [2] M. Maeda and Y. Ozeki, Japan patent 2006-269311 (2006).
- [3] S. Uemura *et al.*, *J. Soc. Info. Display*, **11**, 143 (2003).
- [4] T. Saito, *et al.*, *J. Nanosci. Nanotech.*, **8**, 6153 (2008).

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First principles calculations of lithium intercalation into graphene layers

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Lithium-ion batteries currently are power sources for portable electronics and electric vehicles, using the electrochemistry of lithium transition metal oxide cathode and graphite anode. Recently, Wang *et al.* reported that graphene nanosheet anode demonstrated a good cyclic performance and reversibility under long-term cycling over 100 cycles [1]. However, its specific capacity still remains unsatisfactory compared with the theoretical capacity of graphene anode. In addition, the mechanism of lithium (Li) intercalation into graphene nanosheets is not clear. At the start of study on the Li intercalation reaction of graphene anodes, it is important to elucidate the diffusion process of Li atom on the step edge of graphene layers.

In this study, density functional theory (DFT) calculations are performed to obtain the potential energy surface (PES) of Li atom on the step edge of graphene sheets using the projector-augmented wave (PAW) method in the framework of local density approximation (LDA) [2]. The supercell used in the slab model consists of two graphene layers, which are shifted relative to each other: *AB* stacking structure. The bottom layer is composed of a graphene extended infinitely over the two-dimensional plane, and is assumed to have no defects. The top layer with edge structure is prepared by removing a few tens carbon atoms from an infinite graphene. It is assumed that carbon atoms at the edges are hydrogen terminated.

The PES indicates no intercalation barrier of Li atom. The deintercalation barrier of Li atom is ca. 1 eV. Thus, Li atom can be easily intercalated between hydrogen-terminated graphene layers. Figure 1 shows the schematic drawing of Li migrations. The Li atom on a graphene sits preferentially on the center of the carbon atom hexagon (hollow site). The stable position for Li atom in between two graphene layers is the hollow site of one graphene and the top site of another graphene. Thus, Li *2s* electrons are expected to interact with π^* orbital of graphene. The optimal migration path of Li atom on a graphene layer is via the center of the carbon-carbon bond (bridge site). The calculated potential barrier on a graphene layer is ca. 320 meV. This value is in good agreement with the previous theoretical result [3]. For Li atom intercalated into two graphene layers, the potential barrier for the migration path is less than 100 meV, and is much lower than the half of potential barrier from a hollow site to a top site on a graphene. The Li atom in between two graphene layers exhibits less charge transfer than one on a graphene.

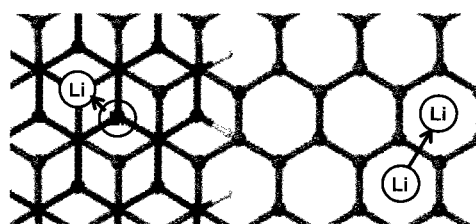


Fig.1 Schematic drawing of Li migration paths. The blue and gray spheres represent carbon atoms in top and bottom layers, respectively. The white spheres are hydrogen atoms.

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Band-Gap Engineering of Graphite Thin Films by Intercalation of Hydrogen-Potassium Binary Complex

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Graphite is known to be a starting material for various compounds in which the nanometer-scale or low-dimensional carbon network play decisive role for determining their physical and chemical properties. Among them, graphite intercalation compounds (GICs) are the one of representative and legendary materials possessing interesting physical properties. The geometric structure of the GIC is characterized by the layered structure in which the graphene and intercalant are alternatively stacked normal to the plane.

In this work, we demonstrate the possibility of band gap engineering of graphite thin films in terms of the intercalation of a hydrogen-potassium complex based on DFT-LDA calculation. The complex is known to be a ternary GIC compound, KH-GIC, and has been synthesized in the previous experiment [1]. Here we consider the KH-GIC thin film with stage-2 structure comprising a pair of bilayer graphene and the KHK layer as shown in Figure. In the structure, due to the intrinsic dipole moment of sandwiched KHK layer, bilayer graphene possesses finite energy gap between π -band and π^* -band at the K point. The result indicates the possibility of band gap engineering in thin films of graphite by considering the legendary compound of graphite. Although the system is a metal due to the charge transfer from K to C, hole injection into the compound results in the semiconducting graphite with finite energy gap which could be applicable as the constituent for the semiconductor switching devices.

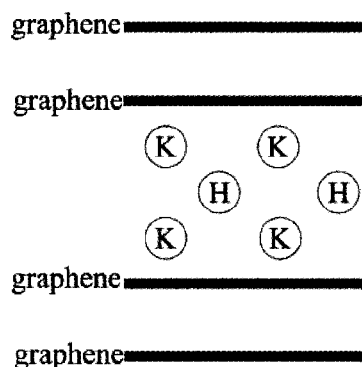


Fig. Schematic picture of slab model of hydrogen-potassium-graphite ternary intercalation compounds. In the model, potassium atoms and hydrogen atoms are put between bilayer graphenes.

Reference

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Formation, Energetics, and Electronic Properties of Nitrogen Defects in Graphene

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Owing to the experimental realization of a graphene sheet, graphene research is now rapidly growing as an active research field, and the unique electronic properties such as massless Dirac fermion behavior and high carrier mobility make graphene-based materials the promising candidates for next-generation nanoelectronics device materials. One of the important ways to control electronic properties such as carrier type and carrier density is doping with an impurity. Nitrogen is a good dopant for carbon-related materials. Doping with the nitrogen into graphene has been performed experimentally, and the observation of the N-doped graphene by X-ray photoelectron spectroscopy revealed the existence of several nitrogen-defect configurations in graphene [1]. However, our knowledge as to detailed atomic geometries and electronic properties of nitrogen-doping defects in graphene is still limited.

In this work, we perform the first-principles electronic-structure study within the density-functional theory that clarifies the atomic structures, energetical stabilities, and electronic structures of the nitrogen defects in graphene. Formation energies obtained for three kinds of defects (Fig. 1) suggest that forming the substitutionally N-doped defects in graphene becomes the most favorable (Fig. 1(a)). We also discuss the energetics corresponding to the “formation processes” of these N defects. It is revealed that the nitrogen-vacancy complex defects can be formed if there are some vacancy defects (Figs. 1(b) and (c)). We demonstrate the scanning tunneling microscopy images of several N-doping defects in graphene for their future experimental identifications. In addition, we address similarities and differences between the graphene and the carbon nanotubes [2] regarding the energetics and the electronic properties of the nitrogen defects.

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

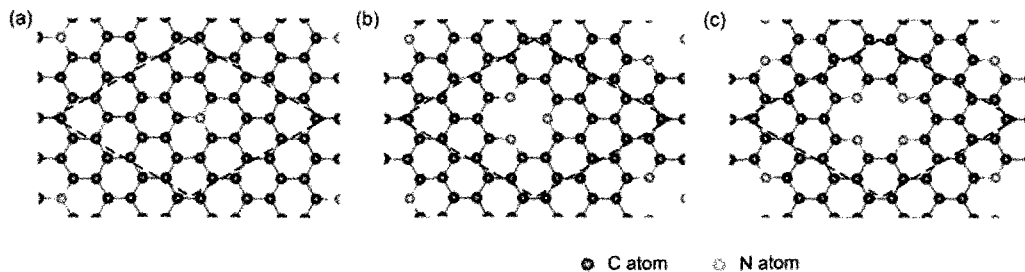


Fig. 1 Atomic geometries of nitrogen-doping defects: (a) substitutional nitrogen, (b) trimerized pyridine-type, and (c) tetramerized pyridine-type defects.

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First-principles study on stable geometry and magnetism of graphene with periodic nanoholes

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Graphene sheets with two-dimensional (2D) periodic nanoholes have recently been fabricated and shown to have a band gap [1, 2]. We also have theoretically investigated [3] the fundamental electronic transport properties of graphene having 2D periodic nanoholes, with planar high-symmetry atomic geometry and nonmagnetic spin configuration. In this article, we study the most stable geometry and magnetism by considering nonplanar geometries and magnetic spin configurations to know how they affect the electronic transport properties.

We examine graphene with three sizes of holes modeled by removing 6, 1, and 4 atoms (6-, 1-, and 4-atom holes). We have performed spin-polarized density functional calculations. The most stable geometries and the corresponding energy band structures are shown in Fig. 1. We have found that the geometries where all carbon atoms are terminated by a hydrogen atom are favored. For 6-atom holes, the nonmagnetic planar configuration as shown in Fig. 1(a) is the most stable. On the other hand, for 1- and 4-atom holes, the nonplanar geometries and ferromagnetic configurations are the most stable. These are more stable by 1.9 eV and 2.1 eV than the nonmagnetic high-symmetry configurations, which we investigated in the previous work [3]. The energy gain from the spin configuration is only 0.1 eV; most of it is attributed to the geometry relaxation.

It is interesting to compare the formation energies among 6-, 1-, and 4-atom holes. They are obtained to be 0.6 eV, 2.2 eV, and 2.4 eV, respectively. The formation energy for 6-atom holes is by far the smallest. The strain caused by steric hindrance among the hydrogen atoms is considered to be one of the reasons of the high formation energies for 1- and 4-atom holes.

The spin splitting is notable around the Fermi level. We have found, however, considering the nonplanar geometry and the magnetism makes little difference in the transport properties.

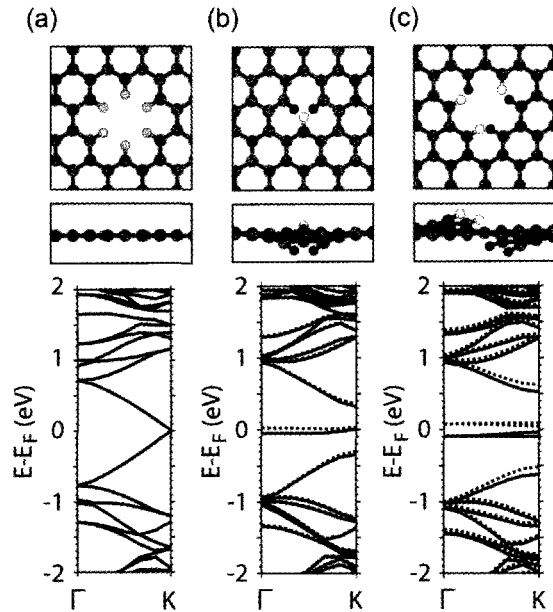


Fig.1 Most stable geometries (top and side views) and corresponding energy band structures for (a) 6-, (b) 1-, and (c) 4-atom holes with (8×8) periodicity. The dark gray, light gray, white, and black spheres represent the carbon atoms, the hydrogen atoms in, above, and below the graphene sheet, respectively. The solid and dotted curves in the band structures represent majority and minority spin, respectively.

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Two-dimensionally polymerized coronene: A metallic sheet of sp^2 C atoms**Susumu Okada**

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Using a first-principles total-energy procedure within the framework of density functional theory, we study the geometric and electronic structures of polymerized coronene in which additional C_2 units adjoin the coronene molecule forming a fused pentagon. We found that the polymer is energetically stable. Moreover, the energy per C atom is higher than that of an isolated graphene sheet by 0.2 eV. Our calculations also show that the polymer is a metal with a substantial density of states at the Fermi level. A detailed investigation of the wave functions at the Fermi level shows that the electronic properties of the material is similar to that of an isolated coronene molecule. Our first-principles molecular dynamics simulation also showed that the polymer can spontaneously form from dense defects in the graphene at any temperature.

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Facile fabrication of fully flattened carbon nanotubes: thin-layer graphene analog

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The graphene nanoribbon(GNR) is one of the most promising candidates for the fabrication of nano- electronic devices such as thin-film transistors of very high-mobility [1]. Lithographic and chemical methods have been used to produce GNRs from few layers graphene and from unzipping of carbon nanotubes(CNTs). However, only few amounts of GNRs have so far been produce by using previous methods which entail structure defects on GNRs. Here, we report a novel high-yield fabrication method of another type of GNRs: fully flattened CNTs [1,2] using solution-phase extraction of inner tubes from large-diameter multi-wall CNTs (MWNTs).

Our previous study [3] shows that inner CNTs can be efficiently extracted from double-wall CNTs by vigorous sonication with water containing surfactants. Here, we have applied this method to extract 1-3 layers CNTs of large diameter from arc-grown MWNTs for the fabrication of fully flattened CNTs (hereafter called GNRs) due to its high purity and crystallinity. Solution-phase process were carried out according to the previously reported procedures [3]. The obtained solution contains many GNRs, and we found that approximately 80% of MWCNTs provide GNRs of high quality and purity.

Figure 1 (a) shows a typical low -magnification TEM image of fully flattened CNTs extracted, which clearly show GNR structure with a ribbon width of typically 30nm. The magnified image Fig1 (b) shows a cross sectional view of a triple layer barbell-like structure, indicating that CNTs are flattened to form GNRs. To the best of our knowledge, this obviously is the first TEM image that clearly shows cross-section of flattened CNTs (GNR). Figure 1 (c) is an AFM image of GNR (length 1.2μm, width 40nm and height 2.64nm) corresponding to 4 layer GNRs.

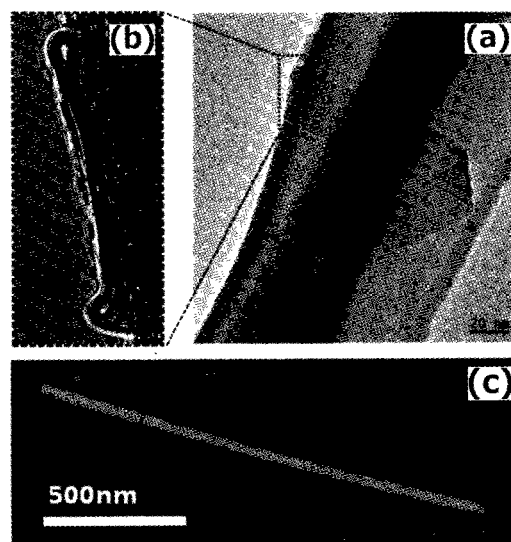


Figure1. (a)TEM image of a flattened CNT (b) magnified image of its cross-section (c)AFM image of flattened CNT

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Negative Contact Resistances Apparently-Appeared at Graphene/Metal Contacts

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Charge carriers in graphene show intrinsically ultrahigh mobility, and thus graphene is now recognized as a promising material for future electronic devices. The carrier transport properties should be measured using metallic electrodes. However, metal-graphene contacts introduce an additional resistance, known as contact resistance, R_C . This resistance is a limiting factor for the performance of electronic devices. The relative contribution of R_C to the total device resistance becomes larger in devices with shorter inter-electrode spacings, *i.e.*, in shorter channel devices. Therefore, R_C becomes a predominant factor to consider when attempting to achieve miniaturization and integration of graphene devices. We have studied the effect of metal contacts to transfer characteristics (the gate voltage V_G dependence of the drain current I_D) of graphene field-effect transistors (FETs) [1-4]. The metal contacts have been reported to affect the electronic property through charge transfer (CT) from the metals to graphene [5]. In this presentation, we show that the CT is accountable for apparently-appeared “negative” R_C .

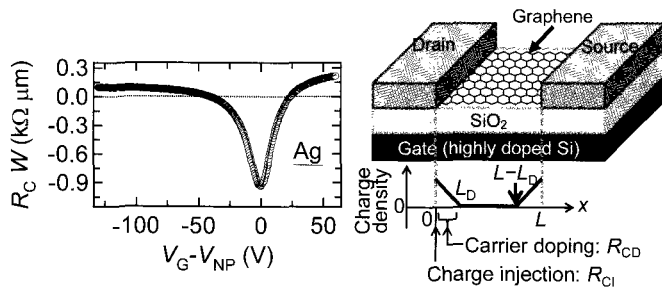


Fig.1 (Left) R_C - V_G characteristics of Ag contacts. Open circle: Experimentally-obtained values by the TLM analysis. Thin solid line: the result of a least-squares fit to a model calculation. (Right) Structure of a graphene FET and two R_C components detected by the TLM analysis.

The left panel of Fig. 1 shows the V_G dependence of R_C , which is normalized by the contact width W , of graphene FETs with Ag contacts, where R_C was extracted by the commonly-used transfer length method (TLM). Surprisingly, the extracted R_C becomes negative near the charge neutrality point, V_{NP} (V_G corresponding to the minimum I_D in transfer characteristics). R_C extracted by the TLM or four-terminal measurement should include a contribution from an additional resistance due to metal-contact doping R_{CD} , in addition to the actual tunnel resistance precisely at the metal-graphene contacts, R_{CI} (the right panel of Fig. 1). In this study, a diffusive-transport model [2,4], which includes charge carrier doping from metal electrodes to graphene channels and charge-density pinning at the metal contacts, was employed to examine the R_{CD} - V_G characteristics. The model was found to reproduce the experimentally observed dip structure well using the TLM (the thin solid line in the right panel of Fig. 1). The apparently negative R_C is considered to be a characteristic feature of Dirac-cone systems.

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Study of carbon nanowalls formation by plasma-enhanced chemical vapor deposition on copper supports

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Graphene is the basic structural element of other graphitic materials including graphite, fullerenes, and carbon nanotubes. Vertically aligned few layers graphene is commonly known as carbon nanowall (CNW), a nanostructured material that shows promise for its use as field emission and storage/sensing elements due to the sharp edges and high surface area. CNWs are often synthesized by microwave plasma-enhanced chemical vapor deposition (MPECVD). [1]

We are currently studying the effect of substrate characteristics, such as material or sample size, together with microwave or electric field or plasma distribution for the structuring of C to form nanosized entities by means of MPECVD. In this communication, we present the results and analysis of CNWs growth on Cu foils. The use of Cu serves as a convenient material to the present investigation, thanks to its low C solubility, temperature and reactivity properties and conductivity, while it is profusely used in a bunch of real applications. Its as-purchased foil state represents a simple route for commercial purposes.

In Figure 1, the areal distribution of CNWs on the Cu substrate under the same processing conditions is evidenced to depend on sample size and shape. Dark zone corresponds to CNWs, as shown in Figure 2, whereas bright area is covered by a-C, as determined by SEM and Raman spectroscopy. We have determined, as well, the necessity to isolate the Cu foil from the Mo sample stage in order to make possible the CNW growth. These phenomena are attributed both to the electric field discontinuity and plasma distribution around the sample. Placing Cu foil directly on the sample stage prevents the formation of vertically aligned graphene, and only horizontally distributed turbostratic graphite is obtained when using our standard MPECVD processing conditions.

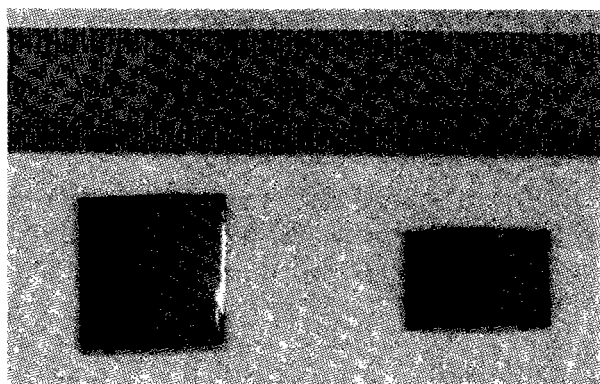


Figure 1. CNW distribution as a function of sample size.

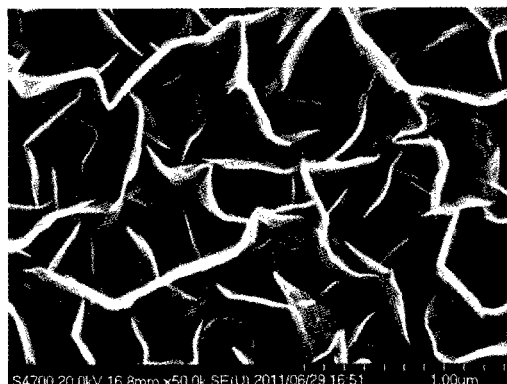


Figure 2. Morphology and density of CNWs.

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Effects of Room Temperature Plasma Treatment on the Selective Edge Functionalization of Graphene Nano Ribbon

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The graphene edge structure is one of the most unique geometrical features of 2D graphene sheets; this is not seen in 1D carbon nanotubes (CNTs). It has been theoretically predicted that, because of the narrow width of graphene nano ribbons (GNRs), their electronic state is strongly influenced by their edge structure. Thus, in order to obtain desirable properties for devices using GNRs, it is essential to be able to precisely control the edge structure and chemical terminations of GNRs.

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

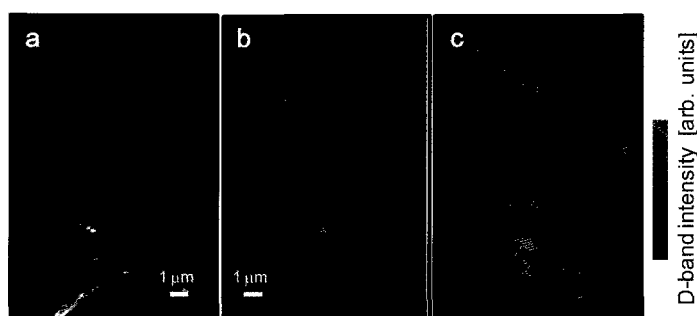


Fig. 1: (a) Atomic force microscopy image of graphene before the plasma treatment. (b, c) D-band intensity Raman mapping images of before (b) and after (c) the plasma treatment.

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Improvement of Gallium Melt-Assisted Interfacial Graphene Growth

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Metals catalysts have been used by a number of researchers to catalyze graphene growth. The most prominent is chemical vapor deposition (CVD) growth of graphene on copper or nickel.[1-2] The metal is typically heated to near the melting point of the metal in the presence of a hydrocarbon gas. Whether the metal film or a surface region of the metal actually melts is still open to debate, but other groups have intentionally melted metal substrates and formed graphene.[3] A related method is the catalyzed transformation of the surface of amorphous carbon into graphene by heated gallium.[4] These methods require a transfer step to produce graphene on a non-conductive surface. In our version of melt-assisted interfacial graphene (MAIG) growth, we used gallium to assist in silicon carbide (SiC) decomposition and epitaxial growth. This lowers the temperature required for SiC decomposition and also catalyzes graphene structure formation.[5-6]

In the current presentation we show improved graphene growth by gallium-MAIG, including uniform films, composite structures, and self-organized patterns in the graphene.

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Characterization of Polymer-Laminated All Carbon Nanotube Flexible Transistors

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We have fabricated all single-walled carbon nanotube field-effect transistors (FETs) on Si substrates [1]. Such all-nanotube devices can easily realize not only fabrication of a flexible device by transfer onto a plastic substrate, but also conversion to ambipolar transport [2].

Figure 1 shows a schematic diagram of the polymer-laminated all carbon FET. Both the active layer (SWNT channel and SWNT source/drain electrodes) and the gate electrode were attached to a thin poly-vinyl alcohol (PVA) film (thickness: a few μm) acting as the gate dielectric layer. PVA is generally a good gas barrier, thus it is expected that this polymer-laminated structure may suppress the device degradation caused by air exposure [3].

Figure 2 shows the transfer characteristics of the as-fabricated device measured after fabrication (solid line) and again one month later (dotted line). There is scarcely any change of the properties. A slight increase in I_D may be due to a small amount of oxygen molecules penetrating the PVA layer.

Here, both the characteristics of the polymer-laminated all carbon flexible transistors with ambipolar behavior, and their transport mechanism will be discussed.

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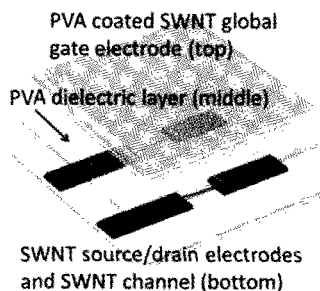


Fig. 1 Schematic diagram of the polymer-laminated all carbon nanotube flexible FET.

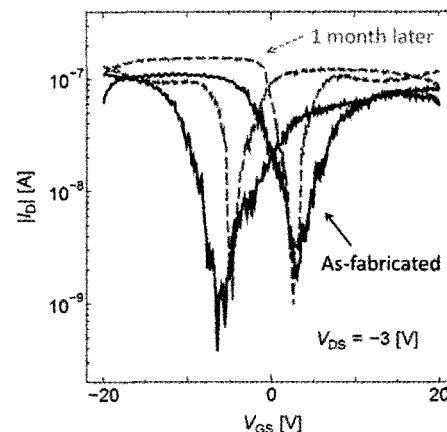


Fig. 2 Transfer characteristics of the as-fabricated device (solid line) and the same device after one month (dotted line).

Fabrication and Characterization of a Carbon Nanotube Field Emission Electron Source for Scanning Electron Microscope

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A carbon nanotube (CNT) is expected as the next generation field emission material. Our previous study on emission properties of CNTs [1] revealed that even a thick ($\phi \sim 20\text{nm}$) multi-walled nanotube (MWNT) have a small emission area which results in brightness enhancement by 1-2 orders of magnitude higher than that of a conventional tungsten field emission electron source.

In this study, aiming at actual application to electron microscopes, a single MWNT emitter is mounted on a field emission scanning electron microscope which is commercially available (HITACHI S-800).

A MWNT is fixed onto a tungsten needle, as shown in Fig.1, by using nano-manipulators in an environmental SEM. In order to fix a MWNT tightly, we carried out electron beam induced deposition (EBID) by supplying $\text{W}(\text{CO})_6$ from a gas nozzle. We investigated performance, e.g. beam alignment, beam stability, life time, image quality etc. As a result, it is shown that a CNT emitter has better beam stability ($< 1\%$) than a tungsten emitter (Fig.2). We also succeeded in observing SEM images with the resolution of $\sim 20\text{nm}$, which is comparable to that obtained from a single crystalline tungsten emitter (Fig.3).

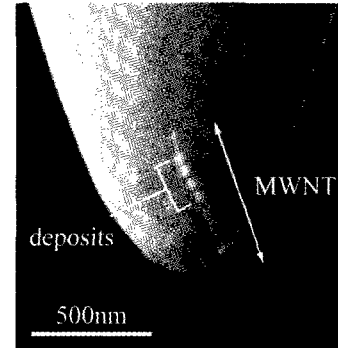


Fig.1 SEM image of a MWNT emitter after an operation as a FE-SEM electron source.

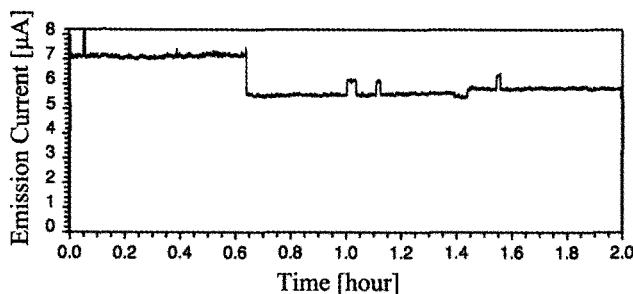


Fig.2 Emission current stability of a CNT emitter under a constant extraction voltage operation at 0.9kV.

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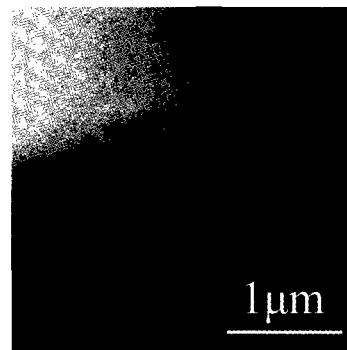


Fig.3 FE-SEM image taken by the CNT emitter. The specimen was a bundle of MWNTs.

Multi-dimensional, multi-layer, micro-scale, circuit-like patterning of conducting CNT-Cu composite

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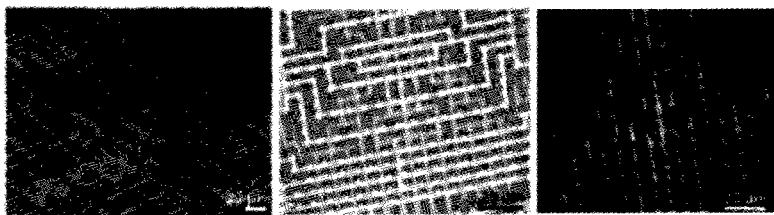
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Supergrowth carbon nanotubes (CNT) possess a plethora of interesting properties like high thermal conductivity, high electron mobility, low mass density and ability to transport and withstand high current densities. In spite of these properties, there are several obstacles in the path towards successful integration of CNT into microelectronic circuits and devices. Primary among these obstacles is their poor electrical conductivity and inability to manipulate and process them into desired electronic components at the micro-scale. In this report, we overcome these two major hindrances by developing a conducting CNT-Copper (CNT-Cu) composite with a conductivity of 10^5 Scm^{-1} . This presents a conductivity improvement of three orders of magnitude compared to pure CNT. Further, the composite lends itself to intricate, multi-dimensional patterning through standard lithographic procedures.

Linear 3-dimensional arrays fabricated with CNT-Cu composite showed a high degree of surface uniformity. As the next step, micro-scale circuits similar to back-end LSI circuits have been engineered with CNT-Cu composite. The conductivity of such structures was found to be independent of its dimensionality. Taking a step further, the mechanical stability of aligned CNT beams was combined with the electrical properties of Cu leading to achievement of spatially suspended CNT-Cu circuits. Extending this, we have also achieved multi-layer, circuits comprising of fully suspended CNT-Cu lines. Such spatially overlapping CNT-Cu lines exhibit complete electrical isolation from each other as confirmed from elemental mapping by SEM-EDX. The adjacent CNT-Cu lines in a given layer and across multiple layers are engineered without any dielectric medium bridging them. The absence of a dielectric material between the CNT-Cu lines in these circuits renders them as 'air-gap' circuits. Such circuits are thought to be devoid of parasitic capacitance between adjacent conducting lines, thereby improving their performance and efficiency. This novel route for realization dielectric-less, air-gap circuits with CNT-Cu composite is believed to be significant for developing CNT-based microelectronic applications at the industrial scale.

Figure : A. Large scale, 2-D circuit pattern with CNT-Cu composite. Spatially overlapped multi-tier, air-gap CNT-Cu circuits(B) and their electrical isolation (C) are also shown.



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Conductive yet mechanically durable CNT rubber composite through a vein-like SGT network

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Electrically conductive elastomers or rubbers have been widely used in various fields like electro-magnetic shielding, vacuum seals and flexible electronic devices. Conventional fillers such as carbon black, carbon filler and metallic filler are required in relatively large volume fraction (>20%) in composites to achieve the desired conductivity for such applications. This huge volume fraction requirement of the fillers inevitably leads to reduction of the elasticity, deformability, durability and processability of the composite. Therefore, there exists a clear antinomy between the conductivity and mechanical properties of elastomer composites which need to be overcome.

Super-growth CNT (SGT) offer several unique properties such as high aspect ratio, high purity and good dispersibility. When subjected to jet-milling, SGT forms a vein-like network, imparting unique properties to CNT based conductive elastomers. It is observed that the SGT vein-like network traverses the entire dimension of the composite uniformly, as opposed to HiPCO CNT which is found to form isolated, globular islands. This difference in the percolation and distribution of SGT in the elastomer is reflected in its largely invariant conductivity under strain, in contrast to HiPCO based elastomer which shows a steady degradation of the conductivity under similar strain. Thus, a composite made by combining jet milled SGT with fluorinated rubber exhibits minimal change in conductivity with repeated stretching. (Figure1). The intrinsic ability of vein-like SGT network to withstand strain without losing the entanglement is critical for the observed invariance in conductivity of the SGT- fluorinated rubber composite.

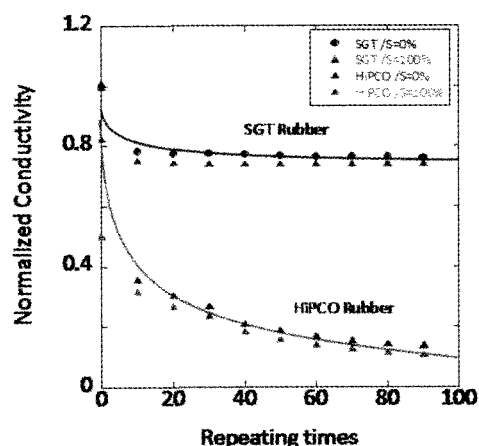


Fig. 1 Conductivity change of jet milled SGT and HiPCO with fluorinated rubber under 10% repeatedly stretching.

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Analysis of Single Cell Collected from A Carbon Nanotube-Coated Substrate

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

We have developed SWNT-coated cell culture substrate, which enables a single cell collection by irradiating a near-IR laser pulse (1064 nm) to the cell of interest. The mechanism of the cell collection is the shock wave generation triggered by the photoacoustic effect of the irradiated SWNTs. The captured cells showed the red fluorescent, which clearly indicate the cell membrane of the removed cells was disturbed.

As a functional analysis for the catapulted single cell, we carried out an RNA analysis using the real-time reverse transcription polymerase chain reaction (RT-PCR) technique. We observed an increase in the fluorescent intensity corresponding to the gene amplification which is extracted from the collected single cell (Fig. 1, solid line). Based on the control experiment carried out in the absence of the catapulted cell that shows a very weak fluorescent (Fig. 1, dotted line), it is obvious that the signal originated from the genetic information of the catapulted single cell and the catapulted cell retains the genetic information. It is worth emphasizing that a functional analysis using the captured single cell is possible.[2]

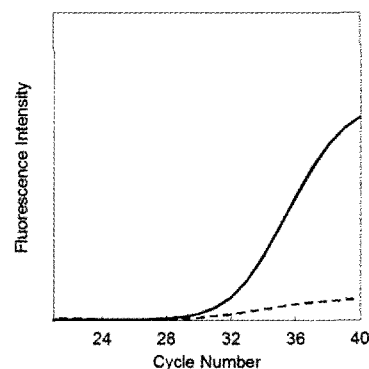


Fig. 1 Monitoring the fluorescence on the PCR cycles in the presence (solid line) and absence (black line) of the catapulted cell.

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Preparation of polymer gel capsules containing single-walled carbon nanotubes and loading of drug molecules

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Single-walled carbon nanotubes (SWNTs) have unique π -rich and hydrophobic surface and remarkable photothermal property. We have reported these properties were quite useful to keep drug molecules and release them upon photo irradiation [1]. For the development of a novel drug delivery system using these functions, in this report, we prepared the poly(*N*-isopropylacrylamide-co-poly(ethylene glycol methacrylate)) gel capsules containing SWNTs (SWNT/PNIPAM/PEG gel capsules).

SWNT/PNIPAM/PEG gel capsules were prepared by the emulsion polymerization using sodium dodecyl sulfate (SDS) as a surfactant. The size of the gel capsules was confirmed with dynamic light scattering (DLS). The average diameter of the gel particles was found to be 128 nm with DLS measurement. Indeed, in transmission electron microscope (TEM), the particles having a 100 – 200 nm in diameter were observed (Fig. 1).

After simple mixing of the gel capsules solution with anticancer drug, doxorubicin (DOX) (Fig. 2), for 24 hours, this solution was centrifuged and the absorption spectrum of the supernatant was measured. The absorbance of DOX at 500 nm was decreased after mixing with the gel capsules followed by centrifugation (Fig. 3). The result indicated that DOX molecules were loaded into the gel capsules. The releasing of DOX molecules from the gel capsules will be discussed.

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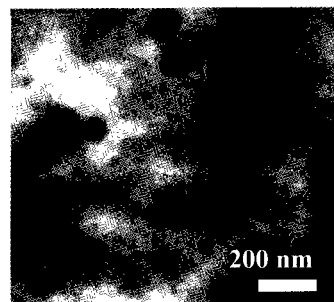


Fig. 1 TEM image of SWNT/PNIPAM/PEG gel capsules.

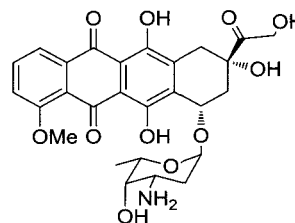


Fig. 2 Chemical structure of DOX.

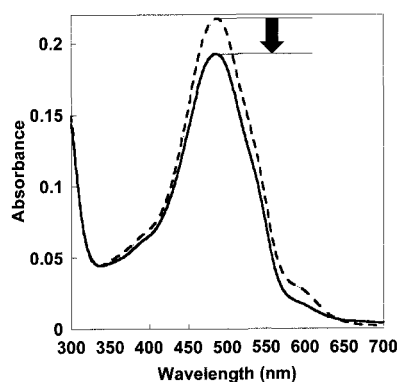


Fig. 3 Absorption spectra of DOX solution (dotted line) and the supernatant after mixing with DOX (solid line).

ポスター発表
Poster Preview

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2P – 1 ～ 2P – 34

3P – 1 ～ 3P – 34

Electrical features of narrow graphene nanoribbons derived from chemical unzipping of carbon nanotubes

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Graphene, an ultimate two-dimensional carbon sheet, is attracting considerable attention.^{1,2} In particular, it is especially important to introduce an energy band gap into graphene to enable its use in conventional semiconductor device operations, because pristine graphene is a zero-band-gap material. Previously, we reported formation of graphene nanoribbons (GNRs) by chemical unzipping of carbon nanotubes (CNTs) combined with three-step annealing [1]. We showed that the GNRs have very low defects and also show energy band gaps as large as 55 meV even in large-width GNRs such as 70nm-width GNR.

Here, in this work, we have formed narrower GNRs with width < 50 nm according to similar unzipping and three-stepped annealing methods. In contradiction to the large-width GNRs, we find that conductivity of the narrow GNRs is still low even after three-step annealing and, hence, the forth annealing is indispensable and important.

Moreover, we find that the observed energy band gaps do not follow the relationship for the large-width GNRs, which is inversely proportional to the GNR width, and they are smaller than those expected from the relationship. These results are much different from Stanford group's reports [2, 3]. The reasons are discussed.

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High-Performance Graphene Flake Anode for Lithium-Ion Secondary Batteries

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Increasing charge-discharge capacities of anodes is considered to an attractive way to improve the performance of lithium-ion secondary batteries (LISBs). In graphite commonly used as an anode material in commercialized LISBs, Li can form an intercalation compound with a stoichiometry of LiC_6 , giving a maximum theoretical capacity of 372 mAh/g. As alternatives to graphite, disordered graphene materials, prepared via reduction of prefabricated graphene oxide, were recently studied and found to show high reversible capacities of more than 500 mAh/g. However, the disordered graphene anodes have not provided a plateau region in charge-discharge profiles, which favors practical applications. In this study, graphene flakes (GFs) were ultrasonically fabricated and applied as an anode.

GFs were prepared by sonicating 20-mg exfoliated graphite nanoplatelets (XG Sciences, xGnP-5, 5 μm in an average size and 5–10 nm thick) in 20-mL N-methyl-2-pyrrolidone, using a Sonics Vibra Cell. Sonication time was varied from 10 min to 10 h at a power of 20 W. Transmission electron microscopy investigation indicated that the sizes and thicknesses of GFs prepared by sonication for 1 h were 1–4 μm and 2–7 nm, respectively. Figure 1 shows a Raman spectrum of the GFs. The feature consisting of a weak D (1343 cm^{-1}) and a strong G (1575 cm^{-1}) bands was similar to that of exfoliated graphite nanoplatelets. The 2D band at 2718 cm^{-1} indicated that the GFs were composed of several layers. Charge-discharge profiles were

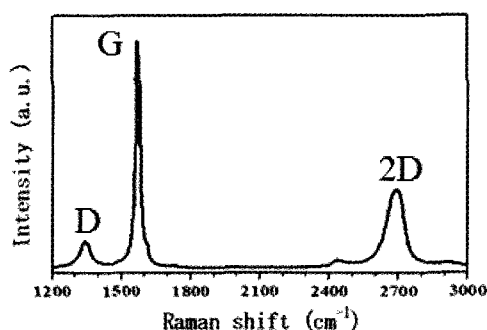


Figure 1. Raman spectrum of GFs

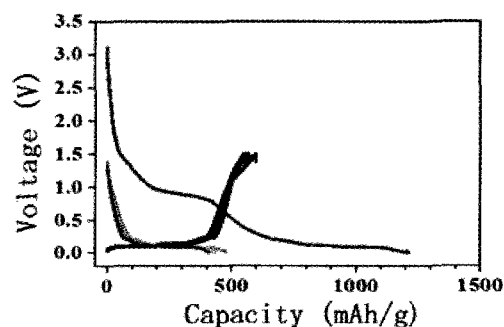


Figure 2. Charge-discharge curve

collected for GFs prepared by 1 h sonication and assembled in a CR 2016-type coin cell configuration. A Li metal foil served as a counter electrode and electrolyte consisted of 1:1 w/w mixture of ethylene carbonate and diethyl carbonate containing LiClO_4 (1 M). The discharge capacities of first, second, and 10th cycles were 1200, 470, and 400 mAh/g, respectively (Fig. 2), exceeding the theoretical capacity of graphite. In addition, plateau regions were observed at voltages of $\sim 0.2\text{ V}$ favorable for practical applications.

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Thermal polymerization of pentacenes: Toward graphene-like molecules

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

To synthesize large-size PAH that will be treated as model graphene material, we have studied thermal fusing reaction of pentacene [1]. In the last symposium, we reported that peripentacene (pentacene dimer) and trispentacene (pentacene trimer) can be easily synthesized through a dehydrogenation condensation reaction [2]. However, the obtained materials synthesized by the previous procedure contain numerous by-products, and we could not obtain the molecules larger than trisperipentacene. In order to obtain larger size molecules, we optimized the experimental conditions such as reaction temperature, and pressure. As a result, we have successfully obtained large molecules up to pentacene octamer (Figure 1). We will discuss the effective synthetic parameters and fusing mechanism in the symposium.

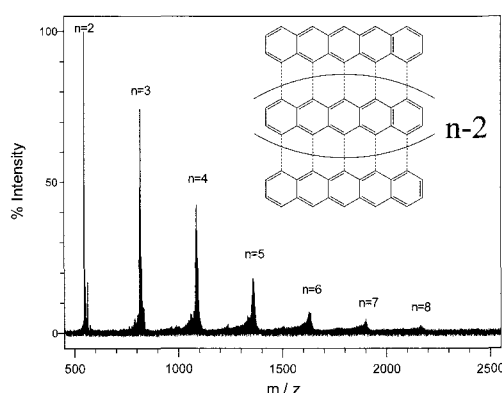


Fig.1 Laser desorption/ionization time of flight mass spectra of the obtained material.

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Domain structure of CVD graphene grown on hetero-epitaxial Cu films

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Graphene is attracting a great interest for electronics application due to its extraordinary high carrier mobility, optical transparency, and mechanical flexibility [1]. Recently, chemical vapor deposition (CVD) over Cu foil becomes a promising method to grow large-area single-layer graphene [2]. One main drawback of the CVD-grown graphene is that the graphene film consists of a number of small domains with random orientations, reflecting polycrystalline nature of the Cu foil. We previously demonstrated the orientation-controlled single-layer graphene growth over hetero-epitaxial Co and Cu films deposited on single-crystal substrates [3,4]. However, there still lacks information on domain structure of the graphene film which strongly influences the physical properties of graphene. Here, we studied the domain structure of CVD graphene in terms of crystal plane of Cu film.

Graphene was grown by CVD with CH₄ and characterized by low energy electron microscope (LEEM) and Raman spectroscopy. Both the Cu(111) and Cu(100) film gave uniform single-layer graphene, but different domain structures were clearly observed. The dark-field LEEM and Raman mapping image of D-band indicated that the graphene film grown on Cu(111) has only one orientation for areas over 1 mm² without clear domain boundaries (Fig. 1(a-c)). On the other hand, the graphene film grown on Cu(100) showed multi-domain structure with two preferential orientations (Fig. 1(d,e)). Weak D-band was also seen along the domain boundaries (Fig. 1(f,g)). These results suggest that the boundary of the neighboring graphene domains having the same orientation can be seamlessly connected during growth. Our work offers a promising approach to realize a “single crystalline” graphene free from domain boundaries.

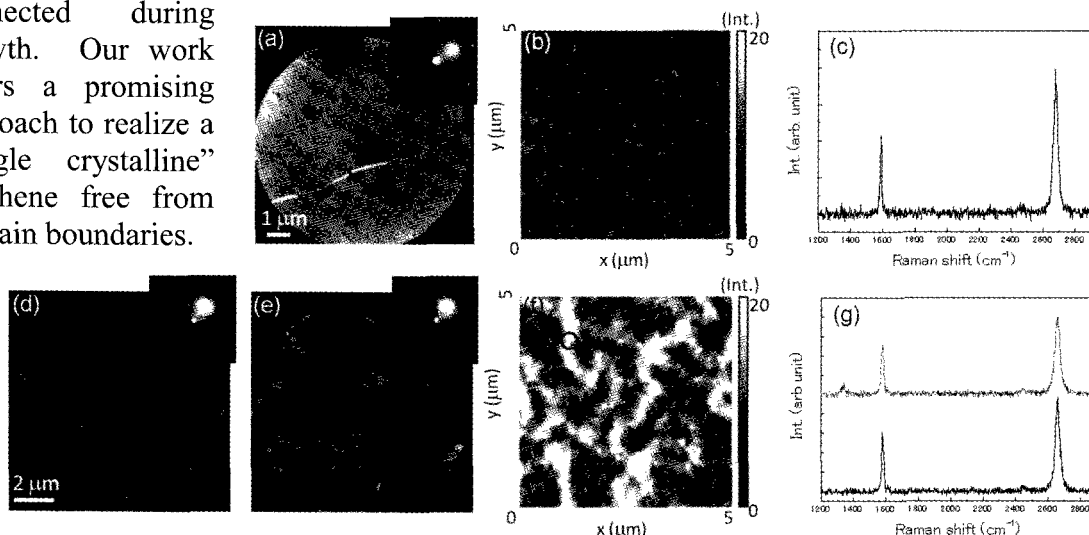


Figure 1 (a) LEEM image and LEED (inset) pattern of single-layer graphene grown on Cu(111)/MgO(111). (b,c) Raman mapping image of D-band and typical spectrum of the graphene film transferred from Cu(111). (d-g) Data of graphene film grown on Cu(100)/MgO(100). Spatial distribution of the D-band (f, g, bright line) can be related to the domain boundary.

References: [1] A. K. Geim and K. S. Novoselov, *Nat. Mater.* 6, 183 (2007). [2] X. Li *et al.*, *Science* 324, 1312 (2009). [3] H. Ago *et al.*, *ACS Nano*, 4, 7407 (2010). [4] B. Hu *et al.*, submitted.

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Nitridation of Graphene Multi-layer Using Neutral Beam Irradiation

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Since its experimental realization in 2004, graphene, a single layer of hexagonal carbon atoms, has shown exciting specific properties. Graphene is a narrow gap semiconductor with holes as the major carrier. In order to construct electronic devices with logic operation, both p- and n-type conductions and the control of the carrier density in an active channel are required. Doping with foreign atoms, such as N and B, has proven to be an effective way to modify the electronic properties of carbon nanotubes and extend their applications. In particular, nitrogen doping brings a carrier which could turn carbon nanotube into n-type semiconductors. It is also feasible to modify the electronic properties of graphene. Although several doping methods have reported so far, process damages (defect generation) cause degradation of electronic properties.

Here we introduce ultra-low damage neutral beam system [1] which consists of a plasma and process chambers that are separated by a carbon aperture. Charged species and ultra-violet photon from the plasma can be effectively eliminated by the aperture. As a result, only the neutral beam arrives the surface of the sample at the substrate in the process chamber. In fact, this method has provided enough evidence of effectiveness for carbon nanotube modification [2]. In this study, we selected nitrogen gas for plasma generation and adopted multi-layer graphene to investigate nitridation mechanism. Graphene multi-layer was irradiated by nitrogen neutral beam with controlled energy of approximately 10 eV for 300 s at room temperature. The surface modification was analyzed by x-ray photoelectron spectroscopy (XPS). Figure 1 shows XPS spectra of graphene in the region of N1s. Peak around 402 eV was appeared after nitrogen neutral beam irradiation, indicating that the carbon atoms were substituted to nitrogen atom. Additionally, n1 and n2 peaks mean sp² and sp³ hybridization, respectively, hence several C-N bonding state are existing. Therefore neutral beam irradiation shows the usefulness of nitridation at low temperature. Further information, such as defect formation and beam penetration depth, will be discussed at conference.

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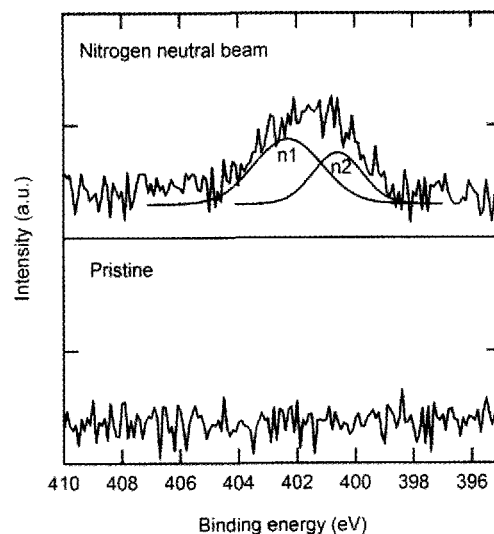


Fig. 1: XPS spectra of graphene multi-layer. Pristine (bottom) and neutral beam irradiated (top), respectively.

Dynamics of O and H Atoms on a Graphene Sheet Induced by Pulse Laser: A TDDFT simulation

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Cleaning graphene from its adsorbents is one of important technology for application of graphene to electronic devices. Chemisorbed atoms on graphene make strong bonding with carbon atoms and thus desorbing these atoms need thermal energy as well as additional chemical species. Alternative to the thermal process is the use of femtosecond laser shot that excites electrons and cause ultrafast dynamics. We have performed the time-dependent density functional simulation to describe electron-ion dynamics on a graphene sheet being adsorbed with either O or H atoms triggered by laser shot. The pulse width of the laser was set very narrow (~ 5 fs) and the time-averaged polarity of electric field (E-field) of laser is asymmetric.

We numerically solved the time-dependent Kohn-Sham equation with existence of time-varying external potential that mimic the femtosecond laser shot as

$$i\hbar \frac{d\psi_n(r,t)}{dt} = [H_{KS}(r,t) + V_{ext}(r,t)]\psi_n(r,t).$$

Where $\psi_n(r,t)$ represent the Kohn-Sham orbital of electron and $H_{KS}(r,t)$ is the Kohn-Sham Hamiltonian, and $V_{ext}(r,t)$ is the scalar potential which mimic the optical E-field.

The time evolution of Kohn-Sham wave function and subsequent molecular dynamics was computed by the code FPSEID[1] and energy conservation rule, which keeps the potential energy plus the kinetic energy of ions minus the work done by external potential (optical E-field) as constant[2], was satisfied throughout the simulation using plane-wave basis set and norm-conserving pseudopotentials.

I this presentation, I will discuss and demonstrate dynamics of epoxy and hydroxyl group on a graphene sheet[3] and dynamics of hydrogen atom of graphane (H-terminated graphene on both sides) depending on pulse shape (phase shift) and maximum intensity of the E-field of the pulse.

All calculations were made by using T2K supercomputer system at Tsukuba University and the work was partly supported by MEX HPC Strategic Program and by the International Joint Work Program of Daeduck Innopolis under the Ministry of Knowledge Economic (MKE) of the Korean Government

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[3] Y. Miyamoto and H. Zhang, *submitted*.

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Observation of radiative cooling of chain-form carbon cluster and polyynes ions by ion storage experiments

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For carbon clusters smaller than C_{10} , chain form species are believed to be dominant whereas the energy differences of chain- and ring-form clusters are rather small for even-numbered clusters. That is, the even-numbered chain-form clusters are less stable compare to the odd-numbered clusters. Understanding of the chain growth mechanism is needed to find a reason of exclusive production of the chains. On the other hand, termination of the both ends of the even-numbered carbon chain yields stable polyynes. Recently, polyynane anions C_nH^- ($n=4,6,8$) were found in interstellar media [1], and the abundance ratio of anions to neutrals has been discussed based on the rate for neutral/electron two-body collision [2]. Both in the formation of carbon clusters and polyynane anions, cooling processes play a critical role since the cluster growth and electron attachment are exothermic reactions.

In the present study, carbon cluster anions (C_n^- : $n=4,5,6$) and polyynane anions C_nH^- ($n=4,6,8$) extracted from a cesium sputter ion source or laser ablation source were stored in an ion storage ring at energies of 15 - 20keV. Neutral species produced during the storage were detected as a function of the storage time.

Photo-detachment excitation spectra of C_6^- are shown in Fig.1, where broad bands characteristic of hot ions can be seen. The spectral shape changes depending on the storage time, due to depletion cooling and radiative cooling. A change in the energy distribution of radiating anions was observed for C_5^- .

The decay plots of the C_nH^- ($n=4,6,8$) are shown in Fig. 2. Slow single-exponential decays are most likely due to collision-induced electron detachment by residual gases in the ring. Faster decays appearing shorter than 20 ms storage would be due to electron detachment of metastable anions. Although each the decay curve cannot be fitted by a single exponential function, it is clear that the overall decay of longer polyynes is faster than that of the shorter ones. We will discuss the decay rates comparing the ones from the theoretical model.

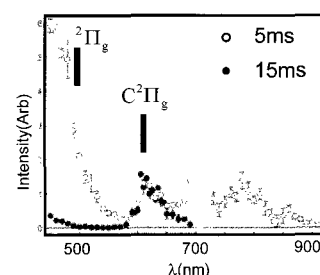


Fig.1 Action spectra of C_6^- at different storage times. The bars indicate known band origins.

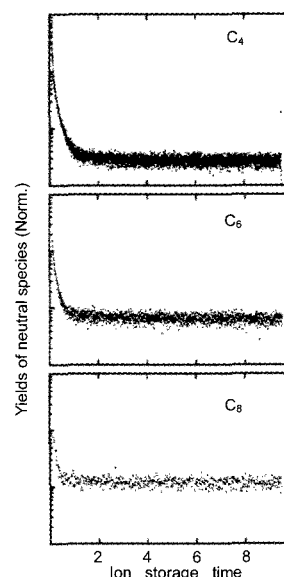


Fig. 2 Decay profiles of metastable C_4H^- , C_6H^- , C_8H^- stored in the ring.

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Diffusion of Li atom for Graphite Intercalation with Edge Oxidations: First-Principles Calculations

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Recently, lithium ion rechargeable batteries (LIBs) attract much attention for one of the most efficient storages of energy [1]. The LIBs have been used for rather small size electronic devices such as cellular phones, notebook PCs. Now, people begin to use LIBs for larger scale applications as electric-powered vehicles, and smart grid network. The merits of LIBs compared to other batteries are huge storage per volume and rechargeable properties for more than thousands of times. For the applications of large scale applications, we need further large capacity and long life time. For further developments of these properties, it is necessary to clarify the degradation mechanisms in atomic scale. Recent research shows that the main degradation is occurred at anode graphite surface.

In this presentation, I will present diffusion barriers for a lithium atom into graphite from the step edge of graphite. The process is one of the important rate-determining processes. I used first-principles calculations with nudged elastic band method to determine the diffusion barriers. The diffusion barrier is around 0.5 eV, which is comparable to the desolvation energy of lithium ion from electrolyte. Thus, the diffusion barrier is rather low for lithium insertion and the lithium will rather easily diffuse into graphite at room temperature condition. When the hydrogen termination of graphite step edge is replaced by the oxidized one [2], the diffusion barrier is dramatically changed. For example, the carbonylic termination attracts lithium atom at the step edge and then, the lithium atom would be trapped at around the step edge of graphite. This trapped lithium atom will disturb the diffusion of other lithium atoms. I will show the diffusion path and potential energy variation for several oxidized edge structures.

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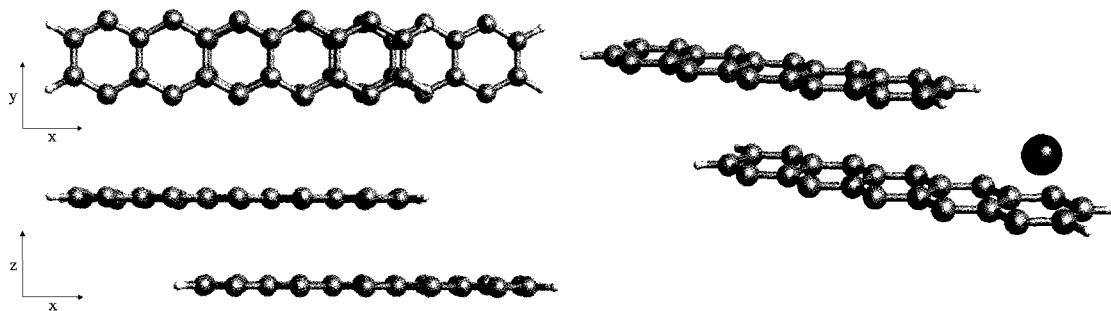


Fig.1 The schematic views of unitcell for graphite step with hydrogen termination. Large sphere indicate a lithium atom and small gray sphere indicate carbon atoms.

Upright Position of Cu-Coated Carbon Nanotwists Treated by Filament Discharge

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Field emitter (FE) with metal coating on its surface has good current-voltage characteristics. This is because coated metal reduces the work function of FE [1]. We used carbon nanotwists (CNTws) as a base material of FE, and CNTws were treated with filament discharge (FD) to make CNTws stand up on substrate [2]. CNTw is a kind of helical carbon nanofiber and CNTw is expected to be stronger against ion bombardment than carbon nanotube (CNT) because of large diameter (100–200 nm). In this study, we coated Cu on the surface of FE and then treated the FE with FD. Experimental parameters were the thickness of Cu film. The CNTw paste was prepared by mixing CNTw into a mixture of an organic binder and silicone one. The CNTw FE was fabricated by screen-printing the paste on a Si substrate and by calcining the substrate at 400°C. The surface of the FE was coated with Cu film by an ion coater and then treated by FD in nitrogen gas. Figure 1 shows SEM micrographs of CNTw field emitters with 30-nm-Cu film. Table 1 lists upright position CNTws as a function of film thickness. The number of CNTws with 30-nm-Cu film on substrate was less than that with 10-nm-Cu film. By contrast, the number of CNTw with 30-nm-Cu on the printed dots was larger than that with 10-nm-Cu film.

This work has been partly supported by the Research Project of the Venture Business Laboratory from Toyohashi University of Technology (TUT); Global COE Program "Frontier of Intelligent Sensing" from the Ministry of Education, Culture, Sport, Science and Technology (MEXT); Core University Programs (JSPS-CAS program in the field of "Plasma and Nuclear Fusion") from the Japan Society for the Promotion of Science (JSPS); and Grand-in-Aid for Scientific Research from the MEXT, The Hori Sciences and Arts Foundation, Tokai Foundation for Technology, and Research Foundation for Materials.

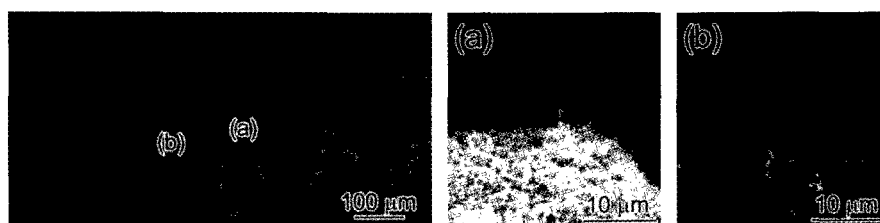


Fig. 1 SEM micrographs of CNTw field emitters with 30-nm-Cu film. (a) On dot surface, and (b) on substrate near the dot.

Table 1 Upright position of CNTws as a function of film thickness.

Thickness of Cu film (nm)		10	20	30
Number of upright CNTws	On dot surface	—————→ increase		
	On substrate near the dot	—————→ decrease		

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Laser ablation of graphite in liquid Ar

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Laser ablation of graphite in an organic solvent is an efficient method of synthesizing polyynes [1], yielding a longest-chain polyyne ($C_{28}H_2$) with using graphite pellets and decalin solvent [2]. Although the mechanism of polyyne formation is not fully understood, an intuitive idea is that a chain-form carbon cluster is initially formed and the ends of the chain are terminated by H atoms by some unknown processes. The source of terminal hydrogen must be the solvent. If the termination prevents the chain from elongation, reduction of the hydrogen source would lead to a change in the clustering processes, pushing the size distribution of polyynes toward longer ones and/or yielding isomers.

In the present study, graphite pellets or a suspended graphite powder in solvent of liquid Ar (hereafter LAr) was irradiated by nanosecond laser. The LAr (m.p. = $-189.2\text{ }^{\circ}\text{C}$) was prepared in a bottle cooled by an LN_2 . The hydrogen atoms would not be involved in the target materials except in water (ice) in the LAr and in chemical species adsorbed onto the graphite surfaces. The laser used for the experiment was a Nd: YAG ($\lambda = 532\text{ nm}$) 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. During irradiation, Ar gas was slowly flowed in cell to push out the air.

To transfer the products from the LAr to a hexane solvent, a two step procedure was employed since hexane freezes at the LAr temperature. We prepared a liquid propane (LP) in an LN_2 cooled bottle. First, the LP near m.p. ($-187.6\text{ }^{\circ}\text{C}$) was added to the laser-irradiated LAr solution and mixed. To remove the LAr, then, the temperature of the mixed solution was raised to the dry-ice/methanol temperature ($-78\text{ }^{\circ}\text{C}$), which is fairly higher than the b.p. of the LAr ($-185.8\text{ }^{\circ}\text{C}$) and lower than the b.p. of the LP ($-42\text{ }^{\circ}\text{C}$). At the dry-ice/methanol temperature, the n-hexane (m.p. = $-95\text{ }^{\circ}\text{C}$) was added to the LP solution and mixed. Finally the temperature of the mixed solution was raised to the room temperature where the LP was evaporated.

The absorption spectrum of the hexane solution of irradiated sample was measured after filtering out the graphite powder. A typical result is shown in fig. 1. The peaks of polyynes from C_8H_2 to $C_{12}H_2$ are clearly identified, indicating rather small amount of contaminants provides terminal hydrogen atoms. To clarify the effect of these contaminants, further experiments are now underway.

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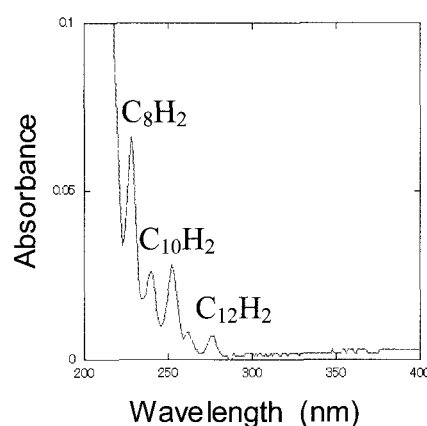


Fig. 1 Absorption spectrum of product resulting from laser irradiation of graphite pellet in liquid Ar.

Characterization and Field Emission Properties of Multi-Walled Carbon Nanotubes Prepared by Irradiating a CO₂ Laser onto Boron-Containing Graphite

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Carbon nanotubes (CNTs) have been reported as excellent candidate of cold cathode emitter for field emission display (FED) and field emission lamp (FEL) application due to their large aspect ratio, high mechanical strength, good electrical conductivity, and possible large-area application by thick film processing [1-2]. For practical development of FEL, the improvement of the lifetime is one of most important subjects, which needs the progress of crystallinity of individual CNT [3]. In this study, we tried to synthesize CNTs with the fine crystallinity and investigate their FEL properties.

CNTs were synthesized by irradiating of a CO₂ laser with high power in continuous wave mode onto a boron-containing graphite target (10wt/% for boron) at room temperature. The pressure of Ar atmosphere was controlled in 50, 150, 400, or 760 Torr. TEM and SEM observation showed that multi-walled carbon nanotubes (MWNTs) were formed preferentially. The diameter of obtained MWNTs was in the range of 5 to 40 nm. The quantity and degree of graphitization of synthesized MWNTs increased with the Ar gas pressure. We also found that a large area field emission device with MWNT cathodes made by screen printing indicated good β value of $3.6 \times 10^4 \text{ cm}^{-1}$, and sufficient reliability for long term operations over 150h, suggesting promising application to field emission devices. The details are shown in the presentation.

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Towards the development of ultra high efficient coolants based on single-walled carbon nanotube suspensions

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Abstract

In the present work, we report measurements of the effective thermal conductivity of dispersions of single-walled carbon nanotube suspensions in ethylene glycol. Single-walled carbon nanotubes (SWNTs) were synthesized using the alcohol catalysed chemical vapour deposition method [1]. Resonant Raman spectroscopy was employed to determine the diameter of SWNTs by measuring the frequency of the vibration of its radial breathing mode (RBM). The nanofluid was prepared by dispersing the SWNTs using sodium deoxy cholate (SDC) as the surfactant. Nanotube loading of up to 0.3 wt% was used. Thermal conductivity measurements were performed by the transient hot-wire technique. Good agreement, within an uncertainty of 2%, was found in published thermal conductivities of the pure fluids. The enhancement of thermal conductivity increases linearly with respect to nanotube loading. The maximum enhancement in thermal conductivity was found to be 15% at 0.3 wt% loading. The experimental results were compared with the Hamilton-Crosser model [2], the Nan et al. model [3] and the Hashin-Strikman model [4]. It was found that the enhancement estimated by the Hashin-Strikman model was in close agreement with the experimental results, while the rest of the analytical models consistently underestimated the enhancement.

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Diversifying Applications from the “Sticking” of Aligned Carbon Nanotube Wafers to Arbitrary Substrates

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We previously reported the development of aligned and densely-packed SWNT films called “CNT wafers” through which the fabrication of multi-dimensional micro-electromechanical (MEMS) devices was demonstrated [1]. However, this limited the device to the rigid and flat growth substrate thereby reducing the processing options for single-layer (i.e. single alignment) device fabrication.

Here, we present the generalization of the device substrate by developing a method for the strong adhesion (“sticking”) of CNT wafers to arbitrary substrates. Though similar to pressure-sensitive tape, the need for pressure is eliminated, thus extending the possibility to multi-layer and multi-oriented CNT wafers. By understanding the mechanism of “sticking,” our device substrates were generalized from flat silicon wafers to curvilinear flexible and stretchable substrates with good adhesion ($>10\text{N/cm}^2$). In so doing, we could open up diverse opportunities in device design. By using a stretchable substrate, we fabricated a fully-stretchable strain sensor capable of 280% strain with high durability, fast response, and low creep useable for human motion detection [3]. Further, by using a stretchable, non-flat, and twistable substrate, we fabricated a torsion sensor. In addition, this “sticking” method allowed for the layer-by-layer assembly processing of CNT wafers to fabricate a functional low power nonvolatile resistive random access memory (RRAM) from multi-layered arrays of suspended, yet intersecting, aligned CNT lines with perpendicular relative alignment.

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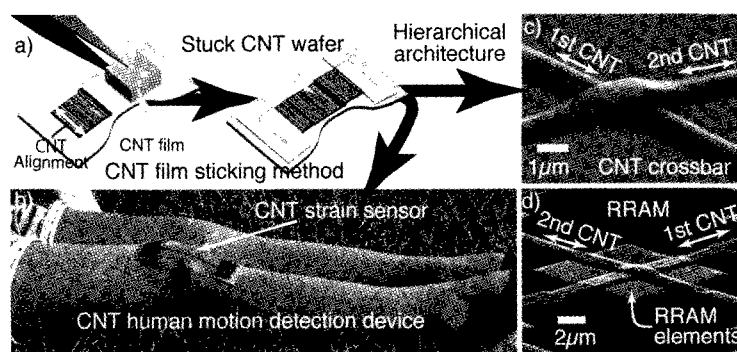


Figure: a) image of sticking method,
b) Human motion detection device from CNT strain sensor,
c) Hierarchical CNT crossbar, d) RRAM device into CNT crossbar

Specific chirality separation of single-walled carbon nanotubes Using fluorene-based copolymers with various backbones

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Selective separation of single-walled carbon nanotubes (SWNTs) from their various chirality is crucial issue for fundamental studies and applications toward next-generation nanotechnology. SWNTs' unique physical, optical and electrical properties [1,2] will be exhibited more efficiently only when they are separated into certain chirality components. It is desirable to develop strategic purification methods to separate SWNTs with a specific chirality.

Here we report our approach toward selective recognition and extraction of (n,m)SWNTs with a specific chirality using polyfluorene (PFO)-based copolymers (Figure 1) [3,4,5] that exhibiting such performance. For example, by using copolymer **2**, one-pot extraction of 97%-enriched (6,5)SWNTs was possible.

In order to clarify the origin of such chiral specific recognition, molecular mechanics simulation were performed for the SWNTs wrapped with each copolymer. The cooperative interactions between the copolymers and SWNT-walls well explained experimentally obtained results.

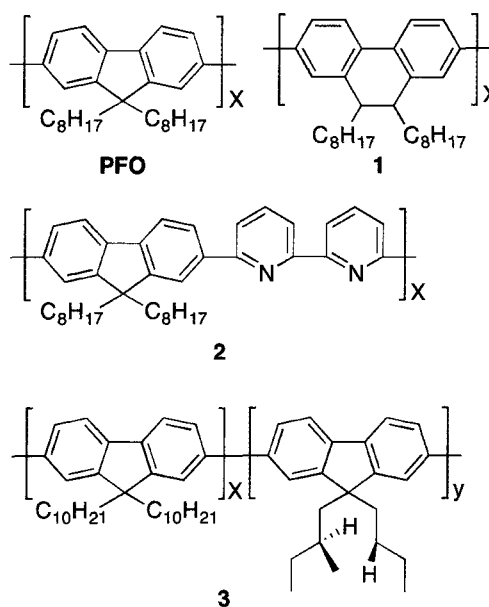


Figure 1. Chemical structures of PFO-based copolymers (**1**, **2** and **3**). copolymers.

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Making of the water dispersion of Carbon nano-tube and fullerene using wet-type super atomizer “Nanovater”.

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Graphene compounds such as carbon nano-tube(CNT) and Fullerene are useful for various field such as electronics, cosmetics and pharmaceuticals. So these compounds are needed to disperse into the solution. But they are usually in aggregated forms because of their higher intermolecular force. They are difficult to disperse into water.

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

Fig.1(a) shows the medium particle diameter of MW-CNT. After the high-pressure treatment, it becomes smaller with the number of pass-through. And diameter depends on pressure. The effect of dispersion caused from turbulent flow inside the nozzle. The velocity of water reaches about 290m/s at the pressure of 200MPa.

We proved this instrument is available for dispersing fullerene also. Fig1(b) shows the relationship between medium diameter and the number of pass. Diameter becomes smaller with the number like as CNT. Without any surfactant, diameter did not become smaller than 2 μ m. It is much larger than the size of Fullerene molecule. So it causes aggregation in the water. We can get sub-micron particle of Fullerene by “Nanovater” with some surfactant.

“Nonovater” can apply for dispersion of CNT and Fullerene into the water.

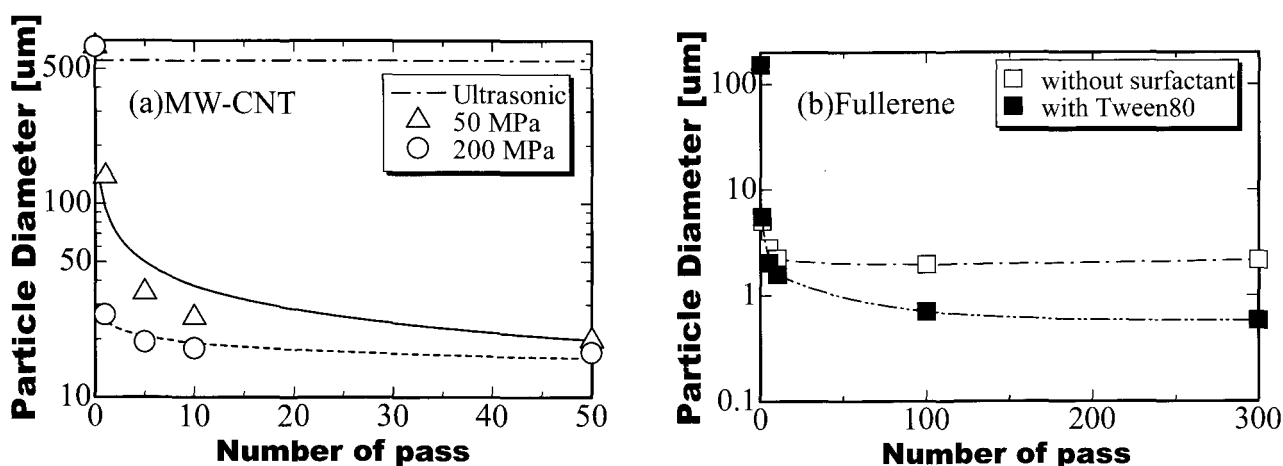


Fig.1 Relationship between particle diameter and number of pass-through..

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Evaluation of length for dispersed single-walled carbon nanotubes by using atomic force microscopy (AFM) technique

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Abstract:

Recently, it was found that single-walled carbon nanotubes made by using arc-burning (ARC) technique in helium or nitrogen atmosphere, and those by using laser vaporization (LV) technique, were successfully dispersed in surfactant or DNA solution [1, 2]. Also, Raman spectroscopy of these solutions with different excitation wavelength revealed that the diameter and chirality distribution of SWNTs depended on the ambient temperature in the case of LV technique [3]. In this presentation, in order to evaluate the length of these SWNTs dispersed in DNA solution, atomic-force microscopy (AFM) was applied for them.

Figure 1 shows a preliminary result of AFM image of SWNTs dispersed in DNA solution. The dispersed SWNTs were deposited on a mica film and washed by water, and used as a sample after air-drying. The image was taken with the AFM apparatus (SHIMADZU SPM-9700). It was demonstrated that the average length of SWNTs is rather short, less than 1 μm , but longer than 100 nm. This observation is consistent with the finding that Raman spectra of those solutions did not show the spectral feature in the mid-frequency (IFM) region, which could be recognized when the average length of SWNTs is less than the excitation wavelength [4].

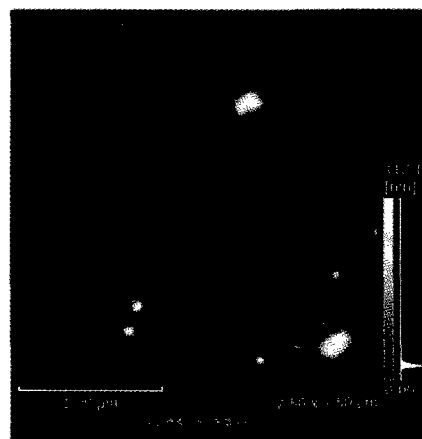


Fig. 1

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Mechanistic insight into metal/semiconductor separation of single-wall carbon nanotubes using agarose gel column

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We have developed metal/semiconductor separation of single-wall carbon nanotubes (SWCNTs) using agarose gel columns.^[1] When SWCNTs dispersed in sodium dodecyl sulfate aqueous solution were loaded into the agarose columns, their semiconducting species were adsorbed onto the agarose gel while their metallic ones were not, leading to the metal/semiconductor separation. Despite the success of this approach, less is known about the mechanism of the separation.^[2]

In this study, we examined the agarose concentration dependence of the separation using the column. An amount of the semiconducting species obtained from the elution decreased with increasing concentration of agarose, indicating that a smaller amount of the semiconducting species was adsorbed on the agarose at higher concentrations. To clarify the relation between the adsorbability of SWCNTs and the agarose concentration, various concentrations of SWCNTs were adsorbed onto 2, 4, 6% agarose gels in the equilibrium state. Results showed that concentration of the unadsorbed SWCNTs increased with increasing concentration of agarose (Fig. 1). Finally, an effect of the adsorbability on the separation using the agarose gels columns was considered. The amount of adsorbed SWCNTs to the top of the column increased as the adsorbability of SWCNTs onto agarose increased. Thus, the agarose concentration dependence of the separation is attributable to the adsorbability of SWCNTs onto the agarose gels.

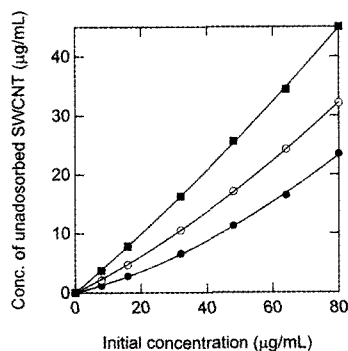


Fig. 1 Concentrations of unadsorbed SWCNTs onto the agarose gels at various initial concentrations of SWCNTs. Closed circles, 2%; open circles, 4%; closed squares, 6%.

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Isolation of ultrathin single-wall carbon nanotubes of (5,4) chirality

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Semiconducting single-wall carbon nanotubes (SWCNTs) with widely-tunable bandgaps have attracted great interest in their applications including opto-electronics. It is known that presently-available SWCNTs with diameters of 0.7~3 nm show near-infrared light emission. In contrast, ultrathin nanotubes with a diameter of less than 0.7 nm have wider bandgap that can create light emission close to visible region because the bandgap is inversely proportional to the nanotube diameter. The bulk fabrication of such ultrathin nanotubes, therefore, allows us to use nanotube-based devices over a wide range of wavelengths.

Recently, we demonstrated a novel method to extract ultrathin inner shells from double-wall carbon nanotubes (DWCNTs).¹⁾ Here, we report the first isolation of ultrathin SWCNTs with a chiral index of (5,4) from thin DWCNTs. The DWCNTs were synthesized by using ethanol chemical vapor deposition with Fe/MgO catalysts as reported previously.²⁾ Their inner tubes can be extracted through ultrasonication and then isolated by using density gradient ultracentrifugation (Fig. 1a). The optical absorption spectrum and contour map of photoluminescence (PL) of the separated sample show a highly enhanced E_{11} absorption and emission due to (5,4) SWCNTs, respectively (Fig. 1b,c). This result indicates that the synthesis of thin DWCNTs can provide an effective route to prepare ultrathin SWCNTs.

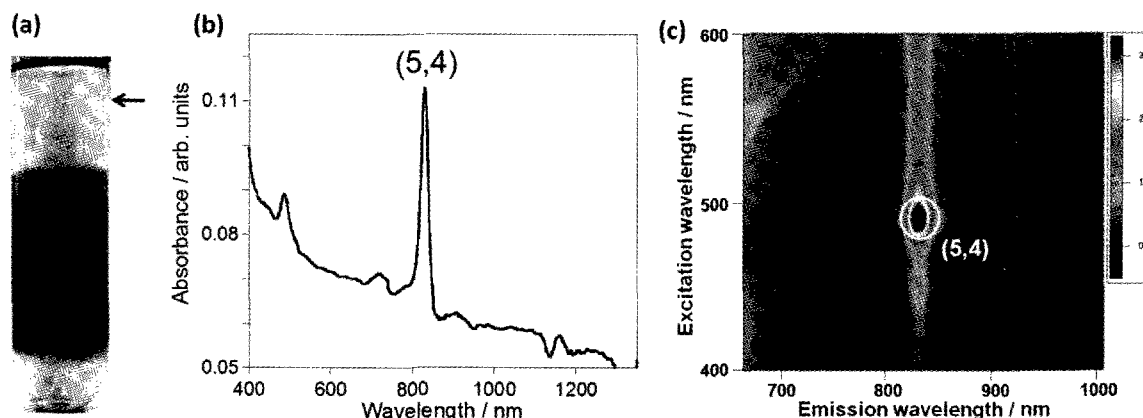


Fig. 1. (a) Photograph of a centrifugal tube after the density gradient ultracentrifugation process, (b) optical absorption spectrum and (c) contour map of photoluminescence of the separated fraction indicated by an arrow in (a).

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Effects of KOH Addition on Morphology of Highly Aligned Carbon Nanotubes Prepared by Liquid-phase Synthesis

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Highly aligned carbon nanotubes (HACNTs) have been synthesized on Si substrates by “liquid-phase synthesis” [1]. Our group has also developed “one-step liquid-phase synthesis” of HACNTs on commercially available stainless steel substrates in an alcoholic solution of a catalyst precursor such as ferrocene $\text{Fe}(\text{C}_5\text{H}_5)_2$ [2]. Furthermore, we have recently found that addition of KOH has a remarkable promotion effect of HACNT growth in the one-step synthesis [3]. In this study, effects of KOH addition were examined on the morphology of the deposits in a wider range of KOH concentration (C_{KOH}) in detail.

A cut piece of commercially available stainless steel plate (JIS SUS304 $5 \times 25 \times 0.1$ mm) was used as a substrate, which was resistance-heated at 800°C for 15 min by applying an alternate current in 0.01 M ferrocene methanol solution containing KOH.

Fig. 1 show HACNTs prepared (a) without addition of KOH and (b), (c) with addition of KOH. Fig. 2 summarizes variations of the heights and morphologies of HACNT with C_{KOH} . With addition of up to ca. 5 mM KOH, the good quality HACNTs formed, and the height increased with increasing C_{KOH} due to the promotion effect and had a maximum of 120 μm . Beyond 5 mM, the height decreased, and interestingly double layered CNTs with an outer amorphous carbon layer were frequently observed in the specimens for TEM observation as shown Fig. 1 (d). The addition of $>$ ca. 7.5 mM led to formation of much by-products like particulate matters and soot. The addition of KOH was found to give two effects, a promotion for the HACNT growth and formation of the double layered CNTs.

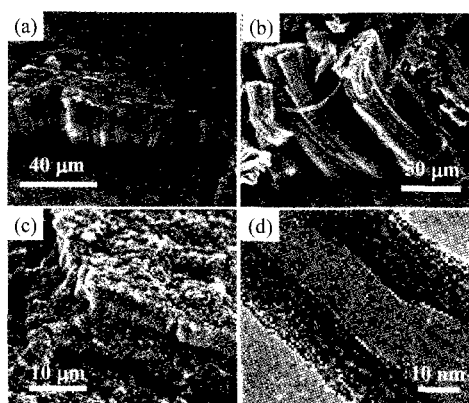


Fig. 1. SEM images of HACNTs prepared (a) without addition of KOH, (b) with addition of 5 mM and (c) 10 mM KOH. (d) TEM image of CNTs prepared with addition of 5 mM KOH.

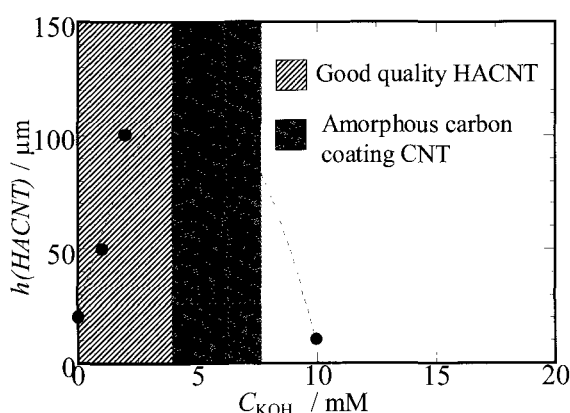


Fig. 2. Variations of the heights of HACNT and morphologies with concentration of KOH.

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Single-walled carbon nanotubes sorted by a gel-filtration chromatography using bovine α -casein

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Sorting single-walled carbon nanotubes (SWNTs) according to the structural features (length, diameter, and chirality) and electronic type is an important issue for their industrial applications. We found that HiPco SWNTs could be well-dispersed in aqueous solutions using bovine α -casein as the dispersant. The α -casein-SWNT dispersion was separated into two fractions (F1 and F2) on a gel-filtration column with Sephacryl S-500 and the AFM observation of these fractions showed that F2 fraction mainly contained short length SWNTs ranging 100-400 nm long (Fig. 1).

In the present study, we characterized the separated short length SWNTs by means of UV-Vis-NIR absorption spectroscopy, Raman spectroscopy, and photoluminescence spectroscopy. To replace α -casein adsorbed on the SWNTs by SDBS, the F2 fraction was lyophilized and dispersed again into 1% SDBS-D₂O solution. After ultracentrifugation the obtained supernatant was used for characterization.

From the UV-Vis-NIR absorption spectrum of the F2-SDBS dispersion, it was found that the SWNTs were well-debundled. The PL spectrum showed that the contents of (8, 4), (6, 5), (8, 3)-SWNTs were decreased and consequently (7, 6)-SWNTs might be enriched in the supernatant comparing to those of the pristine HiPco SWNTs. We will discuss the effectiveness of the combination of dispersion with α -casein and gel-filtration chromatographic technique on sorting SWNTs according to length and chirality.

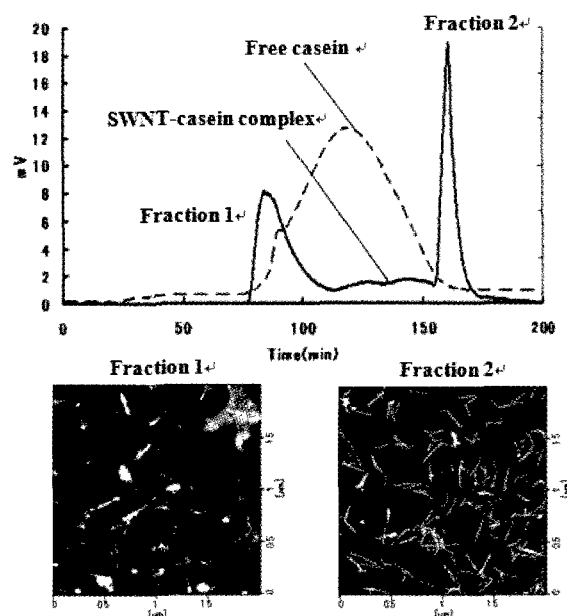


Fig. 1: Separation of the α -casein-SWNT dispersion on a gel-filtration column and the AFM images of the separated F1 and F2.

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Production of single wall carbon nanotubes by laser ablation

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For producing single wall carbon nanotubes (SWNT) of high crystallinity, we have developed an apparatus of laser ablation equipped with a furnace to realize vaporization and condensation of carbon species under the condition of elevated temperatures. We have investigated the temperature dependence and flow-rate dependence in the diameter distribution of SWNTs. Since the SWNTs of larger diameters are formed at relatively high temperatures [1], a new furnace was introduced to reach as high as $\sim 1400^{\circ}\text{C}$. A nanosecond pulsed-laser system of Nd:YAG was operated at 532 nm (0.3 J/pulse at 10 Hz) for vaporization of a rotating composite pellet of C/Ni/Co of 98.8/0.6/0.6 atomic percent. The laser-ablated condensing carbon vapor was carried by an argon-gas flow at atmospheric pressure and deposited on the surface of a copper-made water-cooled conical trap placed at about 18 cm downstream of the target inside an alumina tube. After cooled down to ambient temperatures, soot-like materials were collected and examined by Raman spectroscopy.

Recently, using laser ablated SWNTs, hydrogen-end-capped linear carbon molecules, namely polyynes $\text{H}(\text{C}\equiv\text{C})_n\text{H}$ ($n=5,6,7$), were successfully encapsulated inside the SWNTs [2], which was then extended up to $n=8,9$ [3]. These molecules stabilized inside the SWNTs are detected by a Raman signal characteristic for the symmetric stretching mode in $1900\text{--}2100\text{ cm}^{-1}$. For the mechanism of the Raman signal, we studied absorption spectra for polyyne-containing SWNTs (Fig. 1). The laser-ablated SWNTs of relatively large diameter will be of great help to have better yield in encapsulation thus high-density molecular assembly of polyyne molecules inside the SWNTs.

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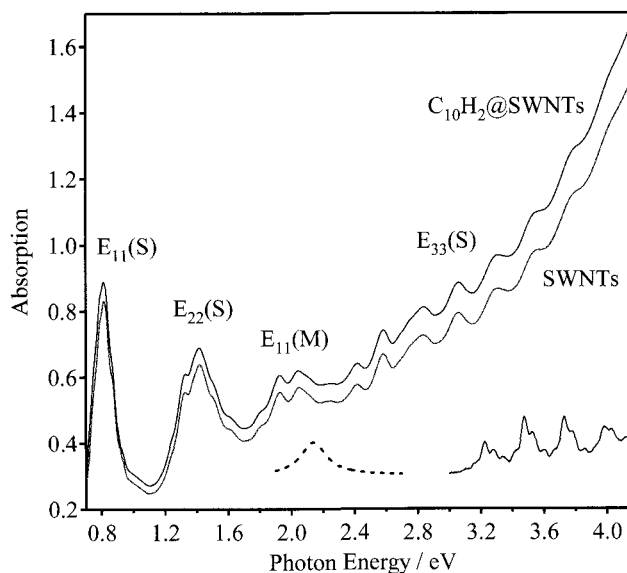


Fig. 1. Absorption spectra for $\text{C}_{10}\text{H}_2@\text{SWNTs}$ v.s. SWNTs dispersed by using cholic acid in D_2O .

Effects of Catalysts Types on the Narrow-Chirality Distributed Single-Walled Carbon Nanotube Growth by Plasma CVD

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Recently, we have demonstrated a narrow-chirality distributed growth of single-walled carbon nanotubes (SWNTs) from an Au catalyst [1]. Based on the systematic investigation using the different combinations of catalyst types (magnetic or nonmagnetic) and chemical vapor deposition (CVD) methods (thermal CVD (TCVD) or plasma CVD (PCVD)), PCVD with the Au catalyst under an appropriate H₂ concentration was found to be critical for the chirality distribution control of SWNTs.

We have also investigated the effects of other nonmagnetic catalysts such as Pt, Ag, and Cu. The chirality and diameter distribution was analyzed by photoluminescence excitation/emission (PLE) spectroscopy, UV-vis-NIR absorption spectroscopy, and Raman scattering spectroscopy with multi-lasers excitation. We found there is a similar tendency for the structure selectivity of SWNTs with those catalysts. By adjusting H₂ concentration, the narrow-chirality distributed growth of SWNTs can be realized from various nonmagnetic catalysts. These narrow-chirality distributed SWNTs grown from the nonmagnetic catalyst could be attractive to both fundamental studies of intrinsic magnetic properties of SWNTs and industrial applications to nanoelectronics.

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Diameter and Metal-Semiconductor Sorting on Single Wall Carbon Nanotubes with Diameters around 1.4 nm

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Single-wall carbon nanotubes (SWCNTs) with diameters around 1.4 nm, can encapsulate various kinds of organic molecules. The SWCNTs encapsulating molecules (peapods) can exhibit unique electronic and optical properties, and encapsulation of molecules is one of approaches to tune the properties of SWCNTs. Previously, we have prepared peapods with metallic or semiconducting types of SWCNTs,¹ but it is crucial to prepare samples with a single chirality in order to experimentally reveal the detailed interactions between encapsulated molecules and nanotubes. Thus, development of techniques to obtain a single chiral sample in this diameter region is important. Various techniques are reported to obtain a selected single chirality for SWCNTs with diameters less than around 1.0 nm, but not for SWCNTs with diameters of around 1.4 nm. Metal-semiconductor (MS) separations can be easily achieved for 1.4 nm diameter SWCNTs. Therefore, almost a single-chiral sample will be obtained if we could apply MS-separations and diameter separations successively. Here, we investigated a diameter-sorting method which has high diameter selectivity on SWCNTs with around 1.4 nm diameters. Previously we reported that diameter sorting by CsCl is possible.² In this study, we clarified that diameter sorting after metal-semiconductor separations is possible as shown in Figure 1, suggesting one of promising routes to obtain single-chiral nanotubes with more than 1.0 nm diameters.

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

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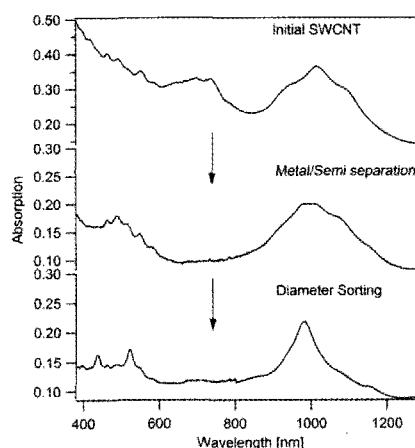


Fig 1: Diameter and metal-semiconductor sorting on SWCNTs with diameters around 1.4 nm

Selective Separation of Semiconducting Single-walled Carbon Nanotube 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, DGU techniques, based on subtle differences in the buoyant density of mixture 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 power for SWNTs, assuming an order 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 subtle differences 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 probed by means of UV-vis-NIR absorption, resonance Raman, and NIR-photo- luminescence (PL) spectra. The SWNTs dispersed solutions were prepared with the mixed dispersants of CMC and SDS (1wt%:1wt%) under the conditions of ultrasonication times of 1-5 hrs and ultracentrifugation time of 1hr at 163,00 g. Before DGU, density gradients in centrifuge tubes were formed by manually layering aqueous dilutions of iodixanol from 25% to 32.5%, in which only 30% dilution contained the SWNTs dispersed by CMC and SDS. CMC and SDS were not added into the iodixanol dilutions except 30%. Then, the centrifuge tubes were centrifuged at 175,000g for 12h. As a result, the purity and yield of s-SWNTs by the DGU separation was dependent on not only the initial amount and relative ratios of CMC and SDS as dispersant agents of SWNTs but also the ultrasonication time. Therein, s-SWNTs with high purity (97 %) and yield (1mg per dose SWNTs 10mg) were collected from upper layers in the tubes under the condition of ultrasonication time of 3h. At the present, further studies are in progress with regard to the selective separation of DWNTs with the same DGU techniques.

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Facile growth of suspended carbon nanotubes by chemical vapor deposition using electroplated iron catalyst

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The physical properties of CNTs strongly depend on chirality, defects, the number of walls and encapsulated chemical species. To combine two different measurements of physical properties and TEM-based structural characterization is, therefore, essential to understand the basic properties of CNTs. For this purpose, we have focused on a preparation of suspended single-wall CNTs between electrodes. Here, we report a facile preparation method of suspended single-wall CNTs between electrodes using the chemical vapor deposition (CVD) with electroplated Fe nanoparticles on the edge of Pt electrodes.

Fe catalyst nanoparticles were electroplated on Pt electrodes by applying AC current (30 nA) for 10 second by immersing the electrode in Fe electroplating solution (FCO-200E Kojundo Chemical Lab.). After the deposition of Fe nanoparticles, suspended CNTs were grown by the alcohol catalytic chemical vapor deposition (ACCVD) method. In the ACCVD, the reaction temperature was lowered down to 750 °C to achieve singly-bridged CNT. Figure 1 shows the number of successfully suspended CNTs. The success ratio of formation of suspended CNTs was typically 40 %, whereas that of a suspended singly-bridged CNT was 7 %. Figure 2 shows a TEM image of such a suspended single CNT. Figure 3 shows the corresponding I-V characteristics of the suspended CNT. Using this technique, we can obtain information on structural and electric properties of exactly the same CNTs at one time.

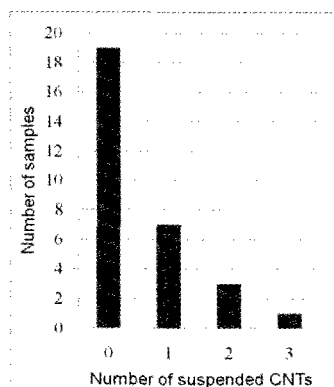


Fig. 1 The number of suspended CNTs.

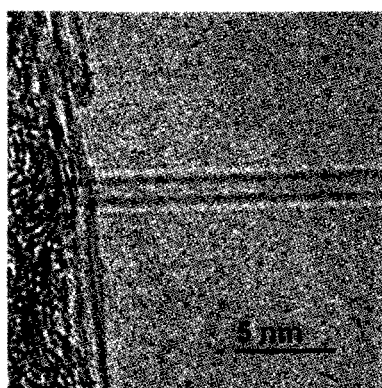


Fig. 2 TEM image of a suspended CNT.

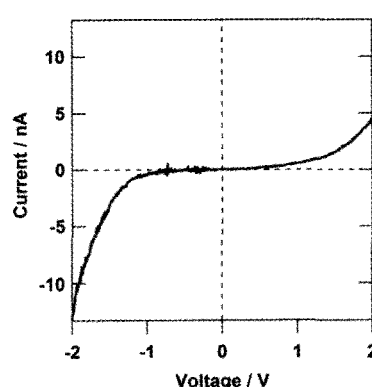


Fig. 3 I-V characteristics of a single suspended CNT.

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Effects of OPO Laser Irradiation on the Structural Characteristics of Single- and Double-walled Carbon Nanotubes

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As-synthesized single-walled carbon nanotubes (SWNTs) comprise of various chiral structures responsible for metallic (m) and semiconducting (s) SWNTs. Selective separations of m- and s-SWNTs have been requested for practical and advanced applications. Thereof, we have developed a new and promising selective separation technique for m-SWNTs with nanosecond pulsed optical parametric oscillator (OPO) laser operated with wavelength tunability.¹⁾ In a previous Conference, we have presented the effects of the laser wavelength and power on the selective separations of m-SWNTs from individually dispersed SWNTs with the dispersants such as carboxymethylcellulose (CMC) and dodecylbenzensulfonic acid sodium salt (NaDDBS) in aqueous solutions.²⁾ Individually dispersed SWNTs exhibited the UV-vis-NIR absorption spectra with the characteristic peaks composed of three band regions (400-1600 nm) of M_{11} , S_{11} and S_{22} corresponding to m-SWNTs first transitions, and s-SWNTs first and second transition bands, respectively. It was found that the OPO laser with a peak wavelength in the S_{11} or S_{22} region brought merely about the destruction of the dispersed s-SWNTs through photo-thermal conversion process, whereas the m-SWNTs remaining unchanged owing to their high thermal conductivity functions. In the CMC dispersion system, the maximum collection efficiencies for m-SWNTs were achieved under the condition of a laser fluence of 6.4 MW/cm^2 at 778 nm (S_{22}) and 19.1 MW/cm^2 at 989 nm (S_{11}).²⁾ This paper was concerned with the effects of the laser irradiation with the wavelengths at side bands around the peaks on the structural characteristics of individually dispersed SWNTs. The yield of m-SWNTs collected by the laser irradiation with the side-wavelength was larger than that with the peak-wavelength. At present, in order to gain more insight into the effectivity of OPO laser irradiation for selective chirality separation of SWNTs and DWNTs, further studies are in progress with regard to the resonance transition effect of the laser irradiation on the liquid- and/or solid-state SWNTs and DWNTs.

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In-situ Raman measurements of SWCNT EDLC electrodes during ion adsorption and desorption

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Owing to their high specific surface area and high electric conductivity, single-walled carbon nanotubes (SWCNTs) are expected as new electrode materials for electric double layer capacitor which is a high power electric energy storage device. However, it is not clarified how the atomic and electronic structures of SWCNTs change by ion adsorption/desorption. In the present study, we performed in situ Raman measurements of SWCNT EDLC electrode under the applied potentials using alkali halides (NaCl, NaI, NaBr) aq. electrolytes.

SWCNTs (Meijo Nanocarbon Co. Ltd., SO type) were used in the present study. Fig. 1 shows the change in the Raman spectrum of the SWCNT electrode with increasing potential in NaBr electrolyte. As shown in Fig. 1, a new shoulder peak appears at around -0.6 V in the lower wavenumber side of G-band. The intensity of the shoulder peak decreases with increasing potential from -0.6 V to -0.3 V. However, the intensity again increases at around -0.1 V. The two potential values: -0.6 and -0.1 V at which the shoulder peak become to be intense correspond to the points where the capacitance of the electrode drastically changes (Fig. 2). It is indicated that the shoulder peak directly relates to the ion adsorption of the electrode.

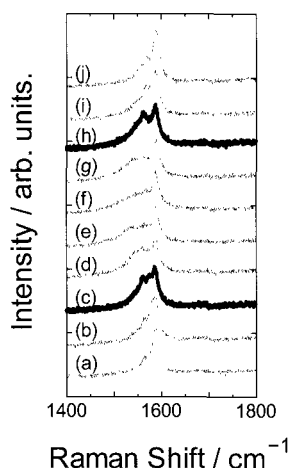


Fig. 1 Change in Raman spectrum of SWCNT EDLC electrode with increasing electrode potential: (a)-0.8 (b)-0.7 (c)-0.6 (d)-0.5 (e)-0.4 (f)-0.3 (g)-0.2 (h)-0.1 (i)0.0 (j) 0.1 V using NaBr electrolyte.

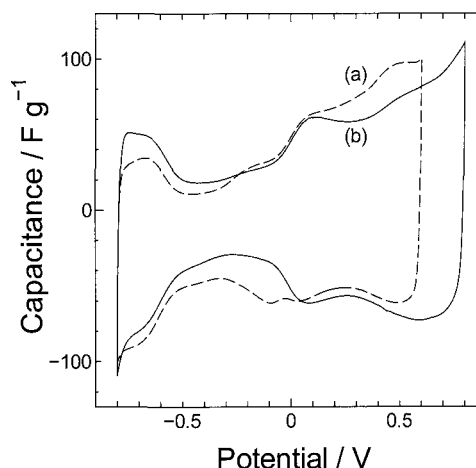


Fig. 2 Cyclic Voltammograms of SWCNT EDLC electrodes using (a) NaBr (b) NaCl aq. solution electrolytes.

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Origin of the far-infrared absorption of single-walled carbon nanotubes

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A single-walled carbon nanotube (SWCNT) has one-dimensional and hollow cylindrical structure formed by wrapping a two-dimensional (2D) graphene sheet. Their diameter and chirality determine whether SWCNT is semiconducting or metallic. The electronic energy gap of semiconducting SWCNTs with a diameter of 1 nm is approximately ~ 1 eV for E_{11}^S . This energy gap arises from the quantization of the electron wave vector along the circumference of SWCNT [1]. In addition to the interband transition (M_{11}) of large energy-gap, metallic SWCNTs could produce small energy-gap of a few tens of meV around Fermi level, which corresponds to far-infrared (IR) ranges, due to the finite curvature and intertube interactions [2]. On the other hand, theory predicted that antenna effects by plasmon resonance may also induce optical absorption in the far-IR ranges [3]. The peak frequency is expected to be proportional to the inverse tube length, which has been one of the on-going themes in CNTs [3].

We here report origin of far-infrared absorption of SWCNTs with different tube length and chemical doping. The thin films of several types of SWCNTs on silicon wafer were used for the measurement. For arc discharge tubes (Meijo-Arc), the obtained IR signal exhibited a broad band around 100 cm^{-1} and a sharp peak near 5580 cm^{-1} . The latter corresponds to be S1 interband transition of semiconducting SWCNTs. The former is considered to be a small gap or antenna effects-induced signal of metallic SWCNTs. To clarify the origin of this signal, we have investigated the chemical doping effect on the spectrum. Upon hole-doping with $F_4\text{TCNQ}$, the absorption intensity was enhanced or not decreased depending on substrate in low-frequency region along with the strong reduction of the peak of S1 interband transitions. Further, we also carried out the tube length dependence by means of sonication which was used to disperse SWCNTs bundles into suspension. Depending on the tube length observed with atomic force microscopy (AFM), the peak positions of the IR signals in low-frequency were shifted, whereas those of the S1 interband transitions were not shifted. These behaviors can be explained by the antenna-effect-induced IR absorption [3]. The detailed mechanism for the experimental observations will be discussed.

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Post-process effects on the photoluminescence quantum yield of single-walled carbon nanotubes

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Single-walled carbon nanotubes (SWNTs) are attractive materials for future optoelectronic devices. Photoluminescence (PL) quantum yield is one of the important parameters for the application of light-emitting devices. Since the recent progresses of sample preparation techniques, the yields reached to 10^{-2} - 10^{-1} [1-3]. Further improvements are required to realize highly efficient optical devices. It has been reported that the quantum yields of solution dispersed SWNTs are about one order smaller than that of the air suspended SWNTs [2]. One of the key factors to restrict the quantum yield could be the post-growth processes such as sonication, centrifugation, and stir. We studied the post-process effects on the quantum yield of SWNTs.

PFO was used as a dispersing agent in this study, because of high structural selectivity and isolation abilities of SWNTs [3,4]. The very clear absorption peaks were observed and the absorption background was remarkably suppressed in the PFO-dispersed SWNTs. We found that the PL quantum yields estimated from the absorption and PLE (PL excitation) measurements are independent of their synthesized procedure (HiPCO, CoMoCAT, and ACCVD) under the same post-process condition. It means that the difference of the growth process is not important for improving the quantum yield of the solution dispersed SWNTs. Figure 1 shows the normalized absorbance (open squares) of the (7, 6) peak and the PL quantum yield (closed circles) as a function of the sonication time by a tip-type sonicator. The absorbance, which is proportional to the amount of isolated SWNTs, increases with an increase of the sonication time. On the other hand, the PL quantum yield decreases with the passage of the sonication. This result indicates that the sonication process causes the introduction of nonradiative centers in the SWNTs. Recent studies suggested that the nonradiative exciton recombination at the quenching sites, such as structural defects or the ends of the nanotube, affects the PL quantum yield [5]. The effective exciton diffusion length limited by the nanotube length or defects becomes shorter by the sonication process. The physical mechanism of the limitation of the PL quantum yield will be discussed.

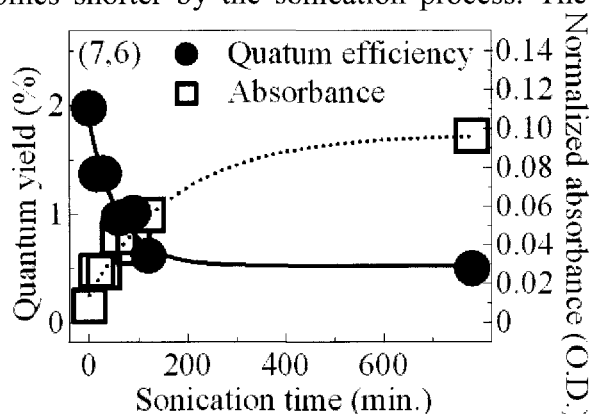


Fig. 1 PL quantum yield (left) and normalized absorbance (right) plotted as a function of the sonication time.

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First-Principles calculation of electrical conduction in carbon nanotubes : the effect of hydrogen adsorption

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FETs (Field effect transistors) made of CNTs are expected to have good performance for both speed and size compared with conventional FETs. Studies of hydrogen impurities in CNTs are necessary since they have crucial effects on electronic structure and electrical transport properties of CNTs [1,2]

Using first-principles density functional calculations and non-equilibrium Green's functional method implemented in OpenMX code [3], we have studied electronic structure and electrical transport properties of low-coverage hydrogens adsorbed CNTs as shown in Fig. 1(a) and (b). We have investigated the effect of hydrogen adsorption on the atomic structures and electronic structures of CNTs. We will discuss the effect of spin polarization and hydrogen-hydrogen interaction on current-voltage characteristics of CNTs.

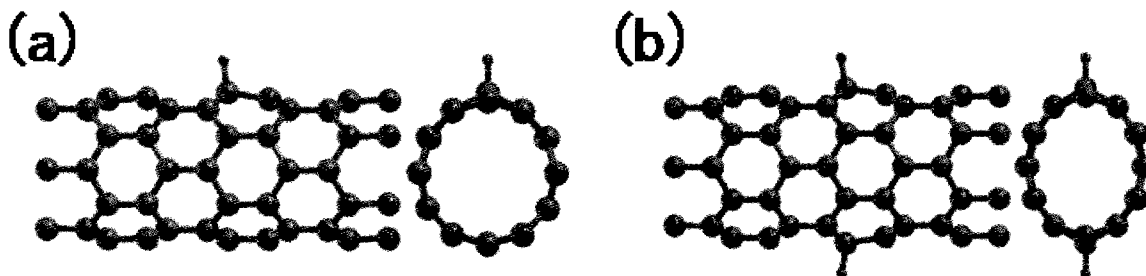


Fig.1 (a) one hydrogen atom adsorbed (6,0) CNT and (b) two hydrogen atoms adsorbed (6,0)CNT.

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Increase of Quantities of Materials Encapsulated inside Nanohorns by Controlling Thermal Hole Closing Rate

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Single-walled carbon nanohorns (SWNHs) are potentially useful in biomedical fields, and their applications to drug delivery, MRI imaging, tissue engineering, etc. have been studied. In these studies, biodistribution measurements of SWNHs are an essential issue. For the biodistribution measurements of SWNHs, Gd₂O₃ nanoparticles embedded inside SWNHs are useful as a label as previously reported [1, 2]. The measurements of the Gd quantity in organs by ICP enable the quantitative evaluation of the SWNH biodistribution in mice. The ultrastructural localization of Gd₂O₃-embedded SWNHs in the liver tissues is easy because the Gd element has high contrast in TEM observation. To extend the lower detection limit of SWNHs in the organs, the quantity of Gd₂O₃ nanoparticles embedded in SWNHs should be increased. In this report, we show that such increase is possible by controlling the chemical groups at the edge of holes of SWNHs.

The Gd₂O₃ nanoparticles incorporation process includes four steps: 1) The hole opening of SWNHs by oxidation, 2) incorporation of Gd acetate, 3) hole closing by heat treatment, and 4) washing with HCl to remove Gd₂O₃ nanoparticles located outside of SWNHs. In this process, the first oxidation greatly influences to the incorporated Gd₂O₃ quantities. The largest Gd₂O₃ quantity, 7-8%, was achieved when the holes were opened by slow combustion (1 °C/min, dry air) up to 500°C. We found that this quantity increased to 15% when the holes were opened by H₂O₂ oxidation.

One advantage of the H₂O₂ oxidation over the air oxidation is that the former creates abundant oxygenated groups at the hole edges. We previously evidenced that the oxygenated groups at the hole edges increased the hole closing rate by the heat treatment. We tentatively consider that the increase of the Gd₂O₃ quantities encapsulated inside SWNHs is due to the increase of hole-closing rate caused by the abundant oxygenate groups located at the hole edges.

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1P-32

Synthesis and Characterization of Some PCBM Analogs for Organic Solar Cell

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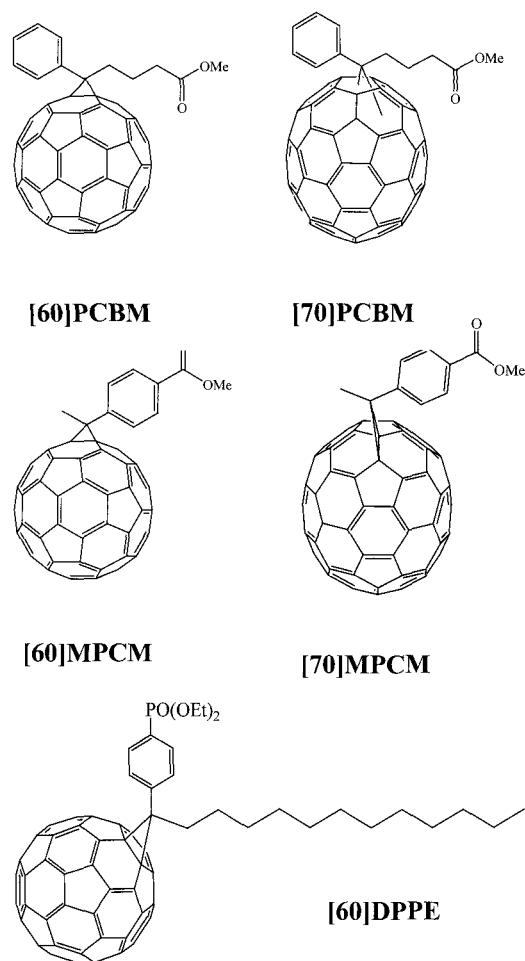
Organic photovoltaic cells have received much attention in the field of organic electronic devices. To improve the performance of these devices, modification of the active layer has been recognized as a crucial strategy. Fullerene derivatives may play the most important role in organic photovoltaic devices because they are the key electron acceptor components of the active layer. In the present study, we have synthesized and characterized some new fullerene derivatives based on the synthetic route for making PCBM [1].

The main purpose of the present study is to overcome two major problems: difficulty in forming a homogeneous film due to the limited solubility of C₆₀/C₇₀ derivatives, and lower electronic mobility due to the tendency of amorphous film formation with C₆₀ and C₇₀ amorphous structure.

To improve the solubility of the C₆₀ and C₇₀ derivatives in organic solvents, the alkyl chain group is introduced on one side of the carbene moiety with the *p*-substituted phenyl group. These derivatives were characterized by UV-Vis, IR, CV, and DSC, as well as ¹H and ¹³C NMR spectroscopy. The purity of the products has been identified as the most important issue for the fabrication of photovoltaic cells.

We have been trying to increase the purity of the products by HPLC and therefore the performance of the organic photovoltaic cell devices. In addition, the effect of the newly obtained C₆₀ and C₇₀ derivatives will be investigated in comparison with the effects of [60]PCBM and [70]PCBM.

The OPV efficiency [2] by using these compounds with P3HT, compared with PCBM system, will be also discussed.



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[2] We thank Prof. Jin Jang and Ms. Misun Ryu (Kyung Hee University) for measurements of OPV efficiency.

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Structural characterization of AgI nanowires encapsulated in carbon nanotubes using electron diffraction and Ag-NMR

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α -phase silver iodide (α -AgI) is one of the most promising candidates for solid-state electrolytes for various electrochemical devices due to its superionic conductivity. Unfortunately, α -AgI can not exist below 420 K, thereby limiting their applications. Recently, However, we have found that AgI nanoparticles with a diameter of 10 nm can retain α -phase even at 313 K where size and morphology of AgI presumably plays an important role in this α -AgI stabilization.^[1]

To synthesize α -AgI nanostructures, we have focused on one-dimensional (1D) nanospace of carbon nanotubes (CNTs). CNTs have unique 1D nanospace ranging in diameter from 0.4 to 50 nm, which can stabilize otherwise unstable phases of nanomaterials. Here, we present a high yield synthesis and structural characterization of AgI nanowires that are formed in nanospace of thin-layer multi-wall carbon nanotubes (MWCNTs).

We have synthesized AgI@MWCNTs by the sublimation method reported previously^[2] Figure (a) shows high resolution transmission electron microscope (HR-TEM) images of AgI@MWCNTs. As clearly shown in Figure (a), regulated dark contrasts can be seen in MWCNTs, and an estimated filling ratio of AgI is as high as 70 ~ 80 %. Electron diffraction images from isolated single AgI@MWCNTs show clear and distinct diffraction spots that are indexed as α -AgI phase. (Figure (b)).

In the presentation, we will discuss further detailed structural characterization based on electron diffraction, X-ray diffraction and Ag-NMR

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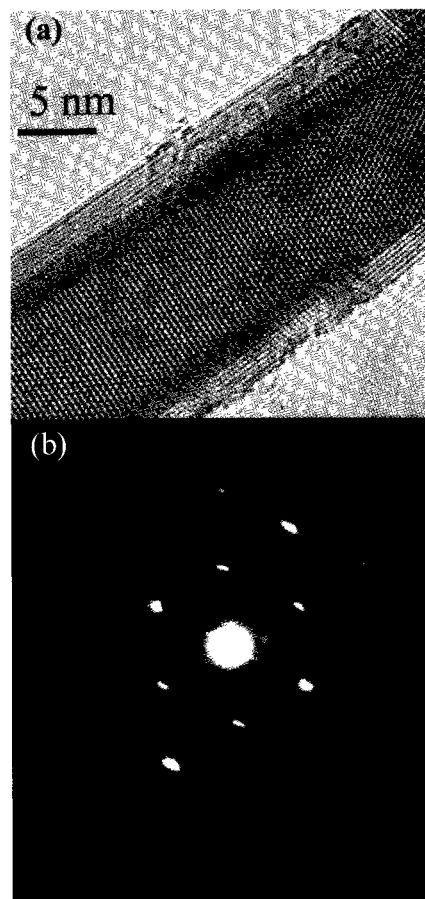


Figure (a). HR-TEM images
(b).Electron beam diffraction images

Electrochemical Properties of π -conjugated Molecules Encapsulated in Single-Wall Carbon Nanotubes

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Encapsulation of organic molecules is one of approaches to tune the properties of single-wall carbon nanotubes (SWCNTs). SWCNTs encapsulating dye molecules show unique optical properties, and have been investigated for their opt-electronic applications. For example, excited energy transfer from encapsulated dye molecules to the surrounding nanotubes is observed,¹ and also photoemissions from the dyes are detected.² Those different excited-energy-relaxation processes seem to depend on the electronic structures of SWCNT-dye complexes, however, details have not been revealed yet. One of the bottle-necks impeding the detailed understanding is optical absorption by surrounding SWCNTs, which veils the optical properties of encapsulated dyes. Recently, it is reported that electrochemical doping can remove the optical absorption of SWCNTs in visible region,³ indicating the possibility of selective excitation of dyes inside the nanotubes. Thus, in this study, the optical properties of encapsulated dye molecules are investigated by using electrochemical-Raman measurements, and the influence of graphitic environment on the dyes is evaluated. We prepared β -Carotene (Car), which is model for π -conjugated molecules, encapsulated semiconducting SWCNTs (Semi), and opt-electrochemical measurements are performed on the samples. Figure 1 shows the changes of Raman spectra as a function of applied potential. The Raman signal of G-band decreases as the shift of potential, but no significant changes on the signals of C=C stretching mode from Car are not observed. Figure 2 shows the difference between the changes of normalized Raman signals of Car in solution and in Semi as a function of applied potential. There is clear difference between the two, indicating the strong influence of surrounding graphitic nanotube-walls on the electronic structure of encapsulated Car.

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

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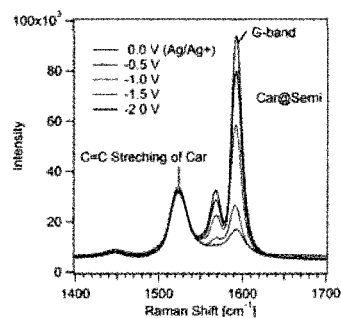


Fig. 1: Raman spectra of Car@Semi as a function of applied potential.

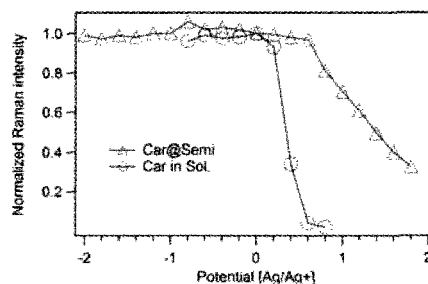


Fig 2: Normalized Raman intensities of Car in solution and in Semi as a function of applied potential.

^{13}C NMR study of transformation process of C_{60} 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 (e.g., C_{60}), so-called “peapods” in which fullerene molecules form a quasi-one-dimensional 1D array, 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 (DWCNTs) 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 ^{13}C NMR techniques. The C_{60} peapod samples were prepared by a vapor reaction method using highly purified SWCNTs with an average diameter of 1.38 nm. The starting raw materials were fabricated by a pulsed laser ablation method with a Ni/Co-catalyzed carbon rod containing naturally abundant 1.1 % ^{13}C isotope. The pristine C_{60} materials were nominally 30% ^{13}C enriched in order to increase the ^{13}C NMR signal from the encapsulated C_{60} . Fig.1 shows the NMR spectra of the samples before and after annealing. Motional narrowing of the NMR line due to rapid isotropic reorientations of C_{60} molecules is quite apparent for the sample before annealing, whereas broad powder pattern line shape typical for sp^2 hybridized carbon is observed for the high temperature annealed sample. These results indicate encapsulated C_{60} molecules coalesce into inner CNTs. Detailed will be discussed in the poster session together with x-ray diffraction results.

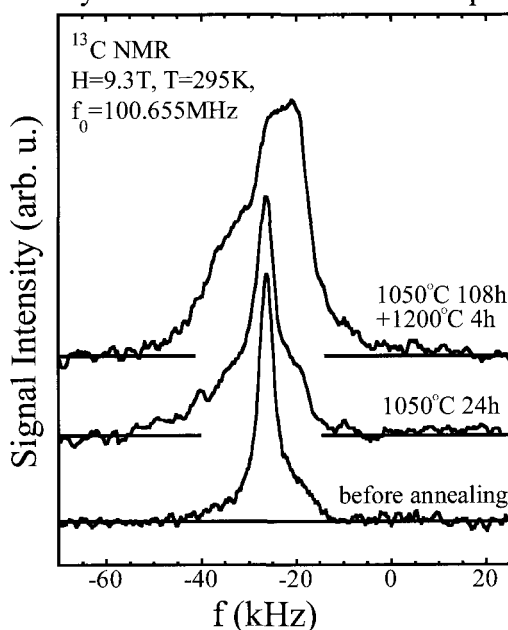


Fig. 1. ^{13}C NMR spectra for C_{60} peapod samples before and after annealing.

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Electrical transport properties of few layer graphene grown on graphene template by chemical vapor deposition

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The precise control of the stacking structure and the layer numbers in graphene remain a critical issue for practical applications to such graphene-based devices as field effect transistors. In previous work [1,2], we demonstrate a synthesis of graphene layers on graphene template prepared by the mechanical foliation of graphite crystal using the sloped-temperature chemical vapor deposition (CVD) apparatus with ethanol. The structural analysis using Raman spectroscopy and atomic force microscopy (AFM) indicates that the graphene layer is formed via layer-by-layer growth mode and the graphene layers grown on graphene template have a disordered stacking like a turbostratic structure. In this work, we report the electrical transport properties of few layer graphene grown on a single-layer graphene as growth template using the CVD.

The single-layer graphene as growth template was obtained from natural graphite crystal by mechanical exfoliation. The single-layer graphene was confirmed by Raman spectroscopy. After then, the graphene was grown by the sloped-temperature CVD using a furnace with three temperature zones, in which temperatures for carbon feedstock decomposition and graphene growth can be controlled individually. The temperatures used in the experiments were 900 °C and 720-744 °C for thermal decomposition and graphene growth, respectively. After the growth, the film thickness of the grown graphene was evaluated by AFM. The field effect transistors using the grown graphene (GG-FET) and mechanical exfoliated graphene (G-FET) as a channel were fabricated by the conventional lithographic techniques.

Figure 1 shows the temperature dependence of a sheet resistivity (ρ) as a function of the gate voltage for the GG-FET with 8 layer graphene grown by CVD before the fabrication of the GG-FET. The observed feature resembles the ambipolar field effect and attributes to the density of states (DOS) for the graphene. It should be noted that the value of ρ at the Dirac point decreases as the temperature increases. The tendency is similar to the few layer graphene prepared by mechanical exfoliation than the single-layer graphene [3]. This result means that the electrical properties associated with the DOS of graphene changes from single-layer to few layer graphene by CVD process. Figure 2 shows the mobilities for the GG-FET(○) and G-FET(◆) with different layer numbers. The mobility for G-FET with single-layer graphene is $\sim 1,000 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$. The mobility is a minimum value in bilayer-graphene, and the mobility increases with the layer number because the influence in the remote Coulomb scattering caused by the charged impurity at the interface between the graphene and the SiO_2 substrate decreases with increasing layer number [3]. On the other hand, the mobilities for the GG-FET show 300-400 $\text{cm}^2\text{V}^{-1}\text{s}^{-1}$, and are almost constant values for the layer number (dash line). This result suggests that the defects and the disordered stacking structure like a turbostratic in the graphene layers grown by CVD have a strong influence on the electrical transport properties and improvement in the CVD growth conditions is necessary for the GG-FET with high mobility.

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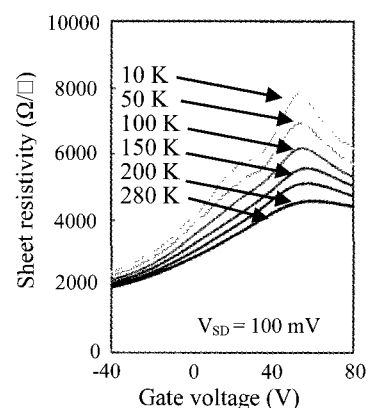


Fig. 1 Temperature dependence of the sheet resistivity for the GG-FET with 8 layer graphene grown by CVD.

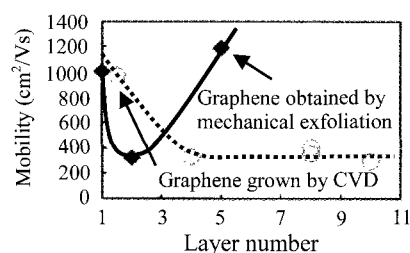


Fig. 2 The mobilities for the GG-FET (○) and the G-FET (◆) with different layer numbers at room temperature. The trends are indicated by the solid and the dash lines, respectively.

Effect of transfer characteristics for PZT-graphene-FET by ionic liquid

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The expected transfer characteristics corresponding to the ferroelectric manner for graphene channel field effect transistors with the ferroelectric gate insulator were hardly observed on the inorganic ferroelectric material, even on the epitaxially grown ferroelectric crystal [1]. In this study, we examine the effect of ionic liquid as a dielectric medium on the gate channel for graphene with a polycrystalline $\text{PbZr}_{0.52}\text{Ti}_{0.48}\text{O}_3$ (PZT) as a ferroelectric film.

Figure 1(a) shows a transfer (I_d - V_g) characteristic for a PZT-graphene-FET before applying the ionic liquid. As-prepared PZT-graphene FET exhibits no ferroelectric gate characteristics in the transfer characteristics. To improve the capacitive coupling between the gate and the graphene channel, we covered the graphene channel with the ionic liquid. Figure 1(b) shows the transfer characteristic just after the application of ionic liquid. The transconductance is improved from 0.47 to 0.77 μS . The hysteresis is almost vanished. Thus, the application of the ionic liquid is effective to improve the gate coupling and to screen the stray charge on the PZT. However, the hysteresis still showed the anticlockwise manner, so that the ferroelectric response of the PZT gate insulator was not appeared. This implies that the surface of the graphene channel is sufficiently couples to the gate voltage, although the interface between the PZT and the graphene channel still affects the transfer characteristic. This may be due to the high viscosity of the ionic liquid. Furthermore, the Dirac point for increasing the gate voltage indicated by blue line shifts toward the higher voltage. Thus, the trapped charge is still present (not compensated) on the PZT surface. Figure 1(c) shows the transfer characteristics after a few days. Although the transconductance of the device degraded to 0.17 μS , the hysteresis loop shows clockwise manner which is expected from the polarization inversion of the PZT ferroelectric gate insulator. The development of the hysteresis loop corresponding to the ferroelectric properties of the PZT implies that some part of the graphene-PZT interface was filled with the ionic liquid. Thus, we have realized the efficient coupling of the gate potential to the graphene channel by covering the graphene with the ionic liquid.

Acknowledgements This work was partially supported by Grants-in-Aid for Scientific Research of Japan Society for the Promotion of Science.

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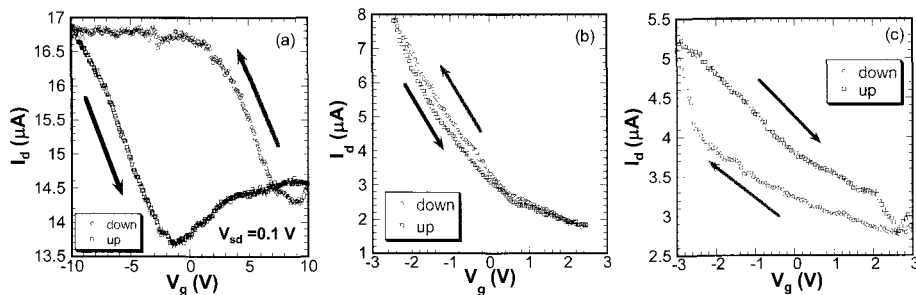


Fig.1 (a) Transfer characteristic of PZT-graphene-FET. Arrows indicate the sweep directions of V_g , (b) I_d - V_g property after dropping ionic liquid and (c) I_d - V_g property after a few days.

Preferential growth of Ar-mediated epitaxial graphene on 6H-SiC

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Graphene exhibits extraordinary physical properties, including exceedingly high charge carrier mobility, current-carrying capacity, mechanical strength and thermal conductivity. It is a viable candidate for all-carbon post-Moore's law electronics. Epitaxial growth of graphene on hexagonal SiC, a highly resistive material, is currently considered as the most likely avenues to graphene-base electronics [1]. Up to now, however, graphitization of SiC is not yet well understood. In the present work, the growth mechanism of Ar-mediated epitaxial graphene is studied.

Epitaxial graphene was prepared on 6H-SiC(0001) in 10 mbar Ar ambience. To investigate the initial stage of graphitization, the sample was annealed at 1600 °C for 30 seconds. As shown in AFM topographic image (Fig. 1(a)), many pits, most in triangular shape, appear in the middle of terraces after heating. In addition, the depressions were observed at the step edges. The AFM phase image (Fig. 1(b)) shows clearly the contrast, suggesting the two different materials of graphene (dark brown) and SiC (light brown). It is also identified by low-voltage SEM (see Fig. 2) that nucleation of graphene starts both at step edges and terrace pits, which is different from the UHV-annealing [2]. Furthermore, the edge of graphene region, especially for triangles, is preferentially along the SiC[11-20] azimuths, implying the graphene has zigzag edges. With increasing heating time, the graphene coverage increases via the lateral growth (expansion on the terraces). Meanwhile, the edge orientations are maintained.

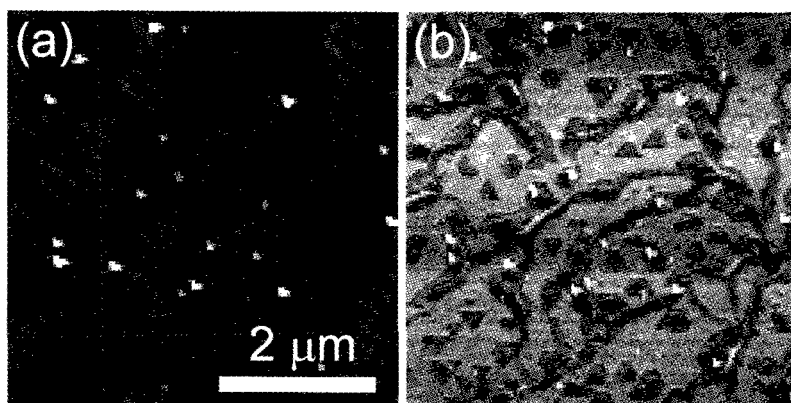


Fig. 1. (a) AFM topographic and (b) corresponding phase images of a 6H-SiC(0001) substrate annealed for 30 seconds at 1600 °C.

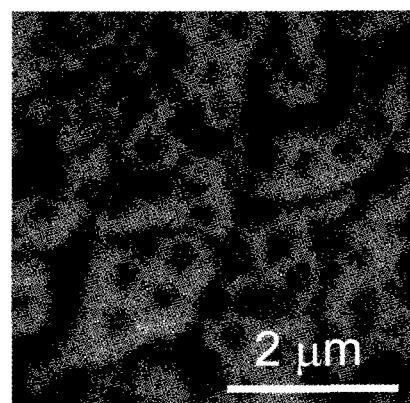


Fig. 2. SEM image of the sample at initial graphitization stage taken with an accelerating voltage of 2 kV).

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Observation of ferromagnetism and spin polarization at nanopore edges in low-defect graphene nanopore arrays

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Ferromagnetism in carbon-based materials is unique compared with conventional ferromagnetism that arises from $3d$ or $4f$ electrons, because only s and p orbital electrons cause it. Many theories have predicted the appearance of ferromagnetism in carbon-based systems from the viewpoints of edge-localized electrons. In particular, edge atomic structures of graphene have been of great interest. Theoretically, the so-called zigzag edge has localized electrons due to the presence of flat energy bands near the Fermi level. The localized electron spins are strongly polarized, resulting in ferromagnetism [1]-[3]. However, in most experimental studies, ferromagnetism has been observed in uncontrollable and complicated carbon-based systems.

Here, in the present study, we measure magnetization of graphenes with honeycomb-like arrays of hexagonal nanopores, which have a large ensemble of hydrogen-terminated and low-defect pore edges that are prepared by a nonlithographic method using nanoporous alumina templates [4]. We observe large-magnitude room-temperature ferromagnetism derived from localized electron spins existing at the nanopore edges. As the origin for the observed ferromagnetism, we show correlation of zigzag pore edges with Raman spectrum showing low ratios of D/G peaks after high-temperature annealing, which indicates possible alignment of pore edges to zigzag structures [5][6]. Magnetic force microscopy image also proves presence of a large density of polarized spins in the interpore region, which correspond to graphene nanoribbons (GNRs). We also show result of the first principle calculation based on quasi-GNR model with very small disorder at zigzag pore edges. All the results suggest that the observed ferromagnetism is attributed to polarized spins localizing at the pore edges. This promises to be a realization of rare-element free, controllable, and mobile magnets and spintronic devices.

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Electronic structure of graphene with periodic array of holes

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Since the pioneering experiments by K. Novoselov *et al.*, graphene, a single-layer sheet of graphite, has become one of the most active research materials in physics, chemistry, and engineering due to its unique electronic properties. Although the pristine graphene shows excellent transport properties, it is metallic and therefore may not be suitable for applications to modern semiconducting devices. The band gap formation in graphene is of high importance from the viewpoint of the nanoelectronics applications. In the previous studies, we have shown that not only periodic array of nanotubes but also periodic array of holes would be a promising solution to open up a band gap in graphene [1,2].

In this work, we study the electronic structure of graphene with a triangular array of holes using the density-functional theory (DFT) with emphasis on the relation between the band gap and the geometries. Hydrogen atoms are used to passivate the edge dangling bonds. We find that the lattice geometry plays an important role in determining its electronic structure. When holes are along the “armchair” direction, the material is always semiconducting [3]. On the other hand, depending on the hole periodicity along the “zigzag” direction, graphene with periodic holes can be metallic or semiconducting. It is consistent with the previous report [4]. In general configuration, we find that the band gap is either open or close. For example, the material shown in the fig. 1(a) is predicted to be a semiconductor with a direct band gap. In the presentation, we discuss the lattice-geometry dependence on the band-gap opening, which can be associated with the Brillouin zone folding (fig. 1(b)).

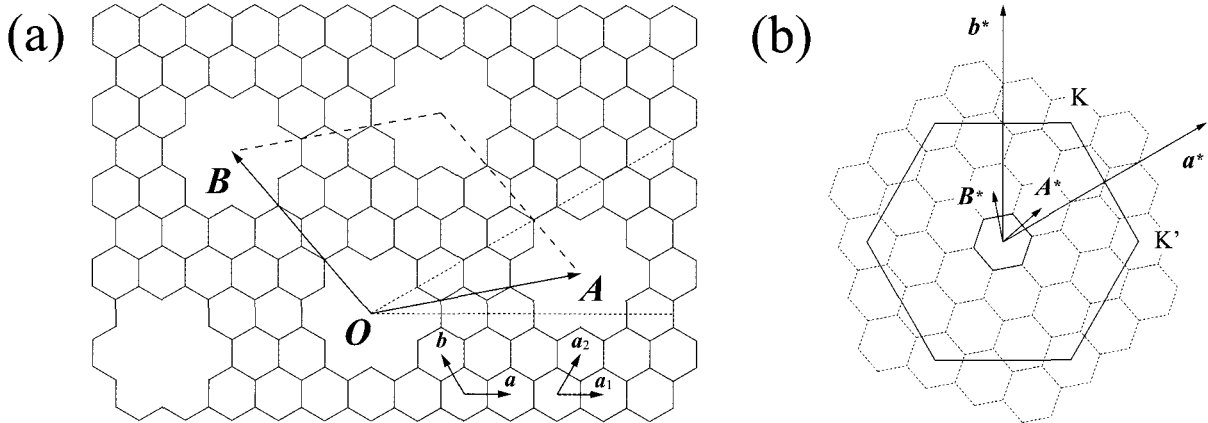


Fig. 1: (a) Schematic illustration of graphene lattice with periodic holes of 6-atomic-site vacancies. In this case, $\mathbf{A} = 4\mathbf{a}_1 + 1\mathbf{a}_2$ and $\mathbf{B} = -5\mathbf{a}_1 + 4\mathbf{a}_2$. (b) The first Brillouin zone (small solid hexagon) is given by the reciprocal lattice vectors $\mathbf{A}^*$ and $\mathbf{B}^*$. The large hexagon corresponds to the first Brillouin zone of the original graphene, given by the reciprocal lattice vectors $\mathbf{a}^*$ and $\mathbf{b}^*$.

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A comparative study on alcohol and methane precursors in CVD synthesis of graphene films

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Industrial applications of graphene-based electronics highly require a facile synthesis method of large-area graphene films with uniform thickness and high quality. Chemical vapor deposition (CVD) has been demonstrated as an efficient method to synthesize large-area graphene films. In particular, uniform and high quality graphene films have been synthesized on copper (Cu) foils from various precursors including methane.^[1] Alcohol has also been reported as a safety solution precursor for graphene growth on nickel foils by the present group^[2] and on Cu foils by Guermoune *et al.*^[3] The systematic understanding of the quality and growth conditions for these precursors is necessary for the future industrial-scale production of high-quality graphene films.

In this work, we have conducted a comparative study of graphene synthesis on Cu foils from methanol and methane. Centimeter-scale graphene films were grown by using CVD at various reaction temperature and precursor pressure to characterize the distributions of grain size and layer number. In the both precursors, uniform single-layer graphene films with similar quality were produced on the Cu foils prepared in the same manner as determined by optical transmittance and Raman scattering (Fig.1). One of the major differences of each growth condition is the reaction temperature employed. Methanol can be converted to graphenes at much lower temperature than methane by 150 degree. The results suggest a promising usage of alcohol for facile low-temperature synthesis of uniform and high quality graphene films.

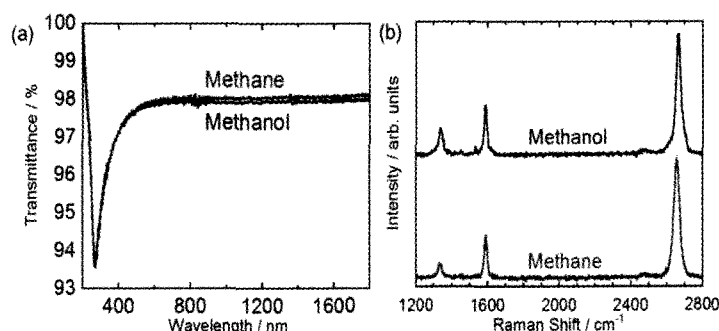


Fig.1 (a) Optical transmittance and (b) Raman spectra of graphene films synthesized from methane and methanol.

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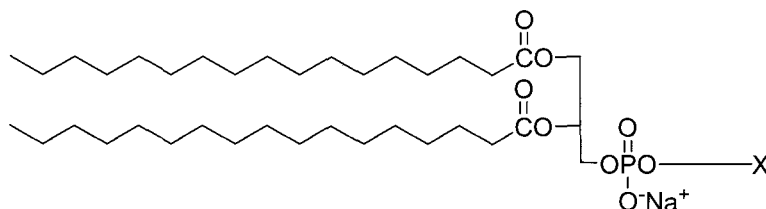
Phospholipids for Dispersing Carbon Nanotubes

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The most commonly used surfactant to disperse single-walled carbon nanotubes (SWCNTs) in water is sodium dodecyl sulfate (SDS). The majority of academic works characterizing SWCNTs have been done in SDS solutions, yet the dispersing mechanism is not well understood. Because of toxicity, SDS cannot be used in biological studies and applications involving human contacts. It is, therefore, desirable to develop a readily available, non-toxic surfactant system that helps us to understand the dispersing mechanism.

SDS disperses SWCNTs below the critical micelle concentration, as long as it is above the critical aggregation concentration. This fact indicates that encapsulating SWCNTs in micelles is not necessary and adsorption of SDS on SWCNT is a key step. Furthermore, entropy of mixing requires considerable dynamics of adsorbed SDS molecules. We postulate that adsorption is driven by not only hydrophobic interaction (which is due to water molecules), but also van der Waals interaction between ethylene hydrogen of the alkyl chain and carbon hexagons of the graphitic surface. Based on this idea, we consider double alkyl chains compounds for stronger adsorption. Among them, phospholipids (PL) stand as a good candidate, for its non-toxicity, availability, and chemical diversity.



We have investigated various PL derivatives with different head groups (X in the above scheme) in water. Although all of them showed excellent wetting on SWCNTs, X = polyethyleneglycol (PEG-PL) was the only good dispersant as reported previously by Dai's group [1]. DPPC (X = choline), the most common PL that forms vesicles, alone could not disperse at all. Here, we report dispersing characteristics by a mixture of PEG-PL with DPPC. Large vesicles have been removed by centrifugation. Without DPPC, about 30 $\mu\text{mol/L}$ of PEG-PL is required. An addition of 3 mmol/L of DPPC reduces the necessary amount to 3.0 $\mu\text{mol/L}$. Moreover, the concentration dependence of PEG-PL is unusually sharp; all-or-nothing within 0.1 $\mu\text{mol/L}$. The "critical dispersion concentration" will be discussed in more detail.

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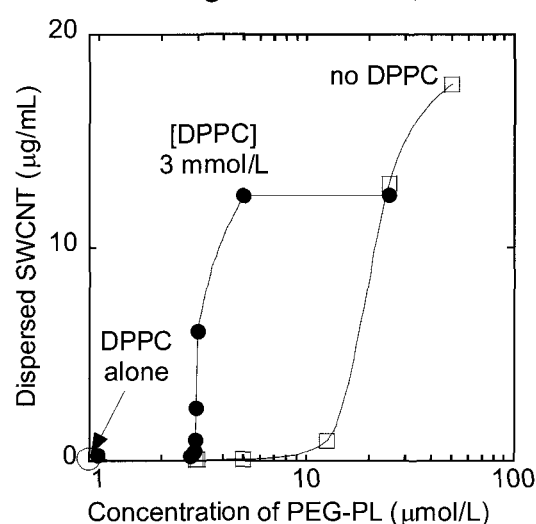


Figure 1. PEG-PL concentration dependence of the dispersed amount.

High Performance of CNT-Containing Rubber Materials Prepared with a Rotation/Revolution Mixer

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Carbon nanotubes (CNTs) have been expected to be effective as fillers in polymer matrices for their functionalization due to their outstanding electrical and mechanical properties and their peculiar structure. However, because of the highly entangled agglomerates owing to strong *van der Waals* interaction and graphite-like surface, it is difficult to individually disperse CNTs in polymer matrices. To mix CNTs with a polymer matrix, a Banbury mixer is usually used. A high mechanical shear generated by the mixer however causes a serious collapse of CNTs during the mixing process. In our previous study, we demonstrated a novel mixing technique, the combination of ultrasonication and a rotation/revolution mixing without mechanical shear, to produce electrically conductive composite materials consisting of styrene-butadiene rubber (SBR) and CNTs. The results indicated that the percolation threshold of the composites by our novel mixing method was significantly low (< 1 phr, phr : parts per hundred rubber), which was 1/10 compared with that of the composites prepared with a conventional Banbury mixer [1].

In the present study, we will report the electrical and mechanical properties of the composite materials comprised of natural rubber (NR) and multi-walled carbon nanotubes (MWNTs) fabricated using the rotation/revolution mixer. In comparison with the composite of isoprene rubber (IR), the main component of NR, and MWNTs, the MWNT/NR composite had a higher percolation threshold (1–2 phr). This is probably because the formation of percolation networks in the NR composites was prevented by a small amount of impurities such as proteins forming a gel-like structure around MWNTs. The antioxidation effect of MWNTs incorporated into NR was also examined. FT-IR spectra revealed that the intensity of the peak corresponding to carbonyl group ($-C=O$) for the MWNT/NR composite remained unchanged even after heat treatment, which suggested that the degradation of NR was suppressed by the addition of MWNTs. This antioxidation ability of CNTs was strongly dependent on the difference in structural characteristics of CNTs, in which some CNT species had no antioxidation ability. The disordered structure of CNTs was suggested to give rise to the antioxidation, since there exist considerably high charge density around the defects such as pentagons, heptagons and holes involved in a high affinity to radicals (polymer radicals or peroxy radicals) generated by the heat treatment.

At present, further studies are in progress with regard to the mechanical properties of the MWNT/NR and MWNT/IR composites, and the results will be presented in the *Conference*.

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Graphitization of amorphous carbon on a carbon nanotube surface by Joule heating

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The behavior of the noncatalytic formation of graphite layers from amorphous carbon was studied by *in situ* transmission electron microscopy (TEM) with simultaneous measurements of the bias voltage and electric current. The amorphous carbon coating the surfaces of multiwall carbon nanotubes (MWNTs) suspended between gold electrodes was transformed into graphite layers via the formation of glass-like carbon by Joule heating. The structural transformation of amorphous carbon into graphite without catalytic metal can be utilized for the purification of carbon nanotubes, the improvement of the electronic properties of nanotube-based devices, and the development of bottom-up engineering for the fabrication of graphitic structures.

Figure 1 shows a time sequential series of high-resolution images of the structural changes in amorphous carbon coating the MWNT surface. The dark region on the right-hand side of Fig. 1 is the gold surface, and the bright region is the vacuum. The MWNT consists of three walls of graphite layers and its tip is closed, as shown in Fig. 1(a). The MWNT surface is covered with amorphous carbon, which is about 1.5 nm thick. When bias voltages of up to 1.6 V were applied to the MWNT and maintained, the current increased abruptly to 61.0 μA . At the same time, amorphous carbon was transformed into glass-like carbon (Fig. 1(b)). After the decrease to 0 V, the bias voltage was again applied up to 1.8 V, which resulted in a current of 71.8 μA , and the glass-like carbon was transformed into three layers of graphite along the outer wall of the MWNT (Fig. 1(c)). Although several out-curved regions remained in a part of the surface after the transformation, the MWNT sustained a high current with a density of up to $3.1 \times 10^8 \text{ A/cm}^2$.

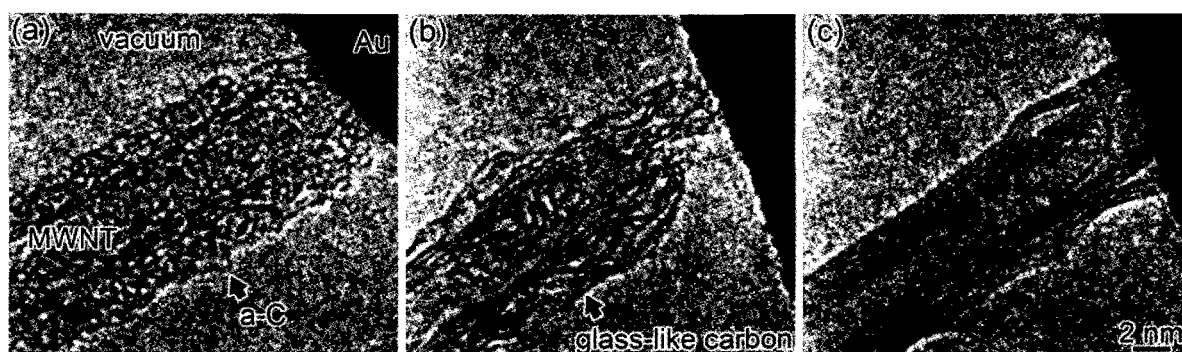


Fig. 1. A time sequential series of high-resolution images of the structural change in amorphous carbon (a-C) on the surface of a multiwall carbon nanotube (MWNT) suspended between gold (Au) electrodes.

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Effect of Temperature Increase Rate on Carbon Nanotube Growth by Surface Decomposition of SiC

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SiC surface attracted much attention because it is a starting substance to grow nanocarbon materials, graphene [1] and carbon nanotubes (CNTs) [2]. In general, graphene layers are grown on the SiC surface by rapid heating up to $\sim 1400^{\circ}\text{C}$. On the other hand, CNTs have been grown by heating SiC carbon-face by heating slowly above 1300°C . However, effect of heating condition on the formation of nanocarbon materials has never been clarified enough. In this study, we focused on CNT growth by surface decomposition of SiC, and investigated the effect of rate of temperature increase on CNT formation by Raman measurements.

We used SiC(000-1) carbon-face as samples. After HF heating for 10 min, they were introduced into a high vacuum chamber ($< 5.0 \times 10^{-7}$ Pa). Then, they were annealed under O_2 atmosphere (1.0×10^{-3} Pa) at 1700°C for 1 hour. The rate of temperature increase was varied between 5 and $30^{\circ}\text{C}/\text{min}$.

Fig. 1 shows Raman spectra of the samples heated with various increase rates. Relative intensities of peaks derived from SiC substrates became weaker as the rate of temperature increase became low. This is because the total heating period became longer as the increase rate was lower. It should be noted that G/D ratio became larger as the temperature increase rate decreased. When the rate was $30^{\circ}\text{C}/\text{min}$, the D band intensity was larger than that of G band and the G/D ratio was 0.74. In contrast, the G band intensity became larger than that of the D band at $5^{\circ}\text{C}/\text{min}$. In addition, the FWHM of G band became narrower as the increase rate decreased. These results indicate that lower rate of temperature increase is effective to improve the crystallinity of CNTs in the surface decomposition of SiC. The effect of rate of temperature increase on CNT growth will be discussed.

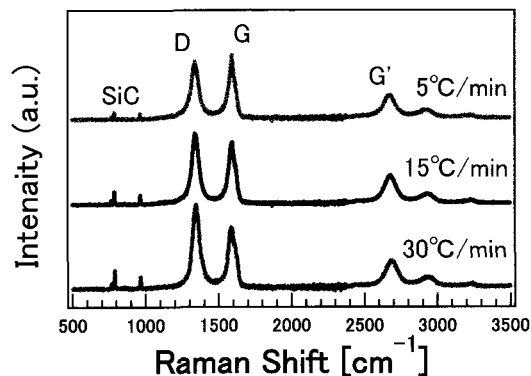


Fig.1 Raman spectra of CNTs grown by surface decomposition of SiC under various rate of temperature increase.

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CVD Growth of Single-Walled Carbon Nanotubes from C₆₀

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Single-walled carbon nanotubes (SWNTs) are of great interest due to their unique and useful characteristics such as chemical and physical properties. The properties of SWNTs depend on their chiralities strongly, so chirality control of SWNTs is a crucial issue for practical applications. In general, metal catalysts including Fe, Co and Ni are used for SWNT growth. However, it is difficult to control the particle size of metal catalyst at CVD growth temperature. Recently, it has been reported that fullerendione can act as SWNT growth nuclei[1]. Since the melting point of C₆₀ is about 1200 °C, so C₆₀ structure is stable at CVD growth temperature. In this study, in order to investigate the SWNT growth from C₆₀, we used C₆₀ molecule as the catalyst of SWNT growth.

C₆₀-saturated toluene solution (3mM) was spread on silicon substrates. CVD was performed with two different temperature furnaces. The upper stream furnace (850 °C) heated ethanol gas (450 sccm, 1.2kPa) and the down stream one heated the silicon substrates.

Figure 1(a) shows SEM image of solvated C₆₀ crystals before the CVD. As shown in Fig. 1(b), SWNTs are synthesized from solvated C₆₀ crystals. Raman scattering spectra from SWNTs and solvated C₆₀ crystals are shown in Fig. 2. Raman scattering reveal that SWNTs were grown from solvated C₆₀ crystals and the structure of C₆₀ molecules was left even after CVD process.

It is important to suppress sublimation of C₆₀ at the CVD temperature in order to grow by using C₆₀. In solvated C₆₀ crystals, the solvent molecules strongly connect C₆₀ molecules, resulting in suppression of C₆₀ sublimation. The present result suggested that C₆₀ could act as a catalyst of SWNT growth.

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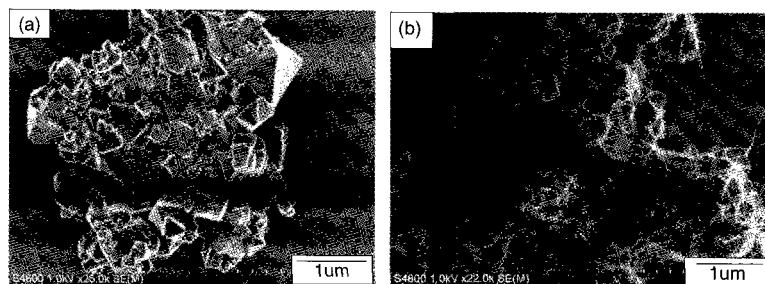


Fig. 1 SEM image of solvated C₆₀ crystals (a) before and (b) after CVD.

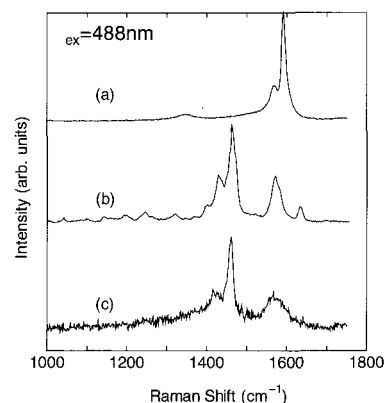


Fig. 2 Raman scattering spectra from (a)SWNTs, solvated C₆₀ crystals (b) before and (c) after CVD.

Surfactant concentration dependence in selective separation of SWCNT by sephacryl gel chromatography

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The large-scale chirality separation of single walled carbon nanotubes (SWCNTs) using a single-surfactant multicolumn gel chromatography method has been reported [1]. In this method SWCNTs are bound in the different columns by difference of interaction strength between SWCNTs and gel. As a result of high concentration surfactant application into each column, chirality separation of SWCNTs was achieved. However, the role of surfactant for the interaction between SWCNTs and gel surface is still open subject. In this study, we investigate the effect of surfactant concentration on the chirality separation of SWCNTs preparing the concentration gradient of the surfactant along the flow axis.

SWCNTs (HiPCO) were dispersed into sodium dodecyl sulfate (2wt% SDS) for 9h by using an ultrasonication. The SWCNTs dispersion was centrifuged at $23,470\times g$ for 60 min. A column with a length ~ 15 cm was filled with sephacryl gel in 20% ethanol. The medium for the gel was then exchanged by 1wt% SDS. Following the application of SWCNTs suspension to the top of the column, 2wt% SDS was applied to perform chromatography with a rate of 0.12 cc/min. As a result, the SDS concentration gradient was formed along the flow direction by the diffusion of SDS. The SDS concentration decreases from top to lower parts in the column. In this case, SWCNTs with thicker diameter were firstly collected followed by the thinner SWCNTs. This indicates that the thicker SWNTs are collected under the condition of lower concentration of SDS. Thus, the continuous chirality separation was realized by the SDS concentration gradient. It is noted that the lengths of each separated SWCNT are almost identical measured from AFM unlike reported in Ref. 2. Thus, we revealed that chirality separation by sephacryl gel chromatography strongly depends on surfactant concentration.

Acknowledgement

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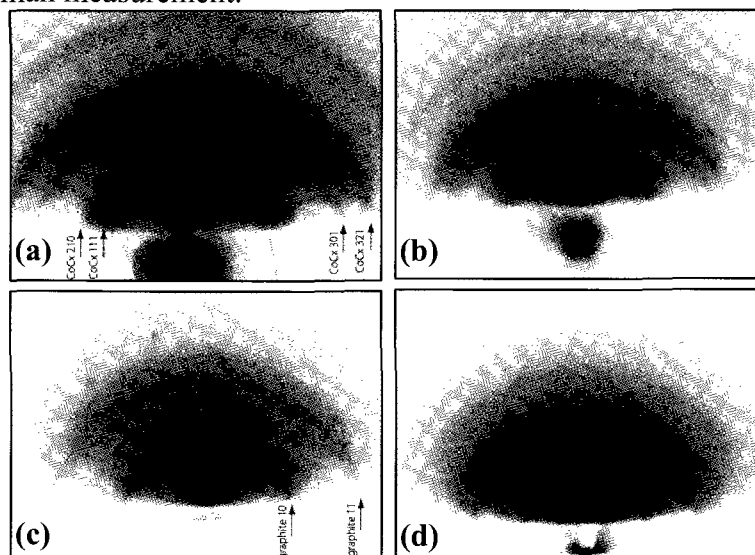
***In-situ* RHEED Study on Growth Process of Carbon Nanotubes by Chemical Vapor Deposition**

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Carbon nanotubes (CNT) were synthesized by chemical vapor deposition (CVD) using an ethanol gas in ultrahigh vacuum chamber, and the growth process of CNT was *in-situ* investigated by reflection high-energy electron diffraction (RHEED). Cobalt (Co) and nickel (Ni) films of about 0.3nm thickness were used as catalyst for the growth of CNT. The films were prepared on silicon substrates coated with silica films by high-vacuum electron beam deposition. A base pressure of 5×10^{-6} Pa was kept before CVD in order to minimize the effect of the residual gas on the CNT growth. The substrate was heated around 600°C, and pressure was kept less than 10Pa of ethanol for several hours during CVD in order to observe *in-situ* electron diffraction (ED) pattern. The growth of CNT was investigated by scanning electron microscopy (SEM) and Raman measurement.

Figure 1 show a sequence of changing ED pattern from Co/SiO₂/Si substrate during CVD. The ED pattern before CVD (Fig 1(a)) exhibits reflections from cobalt carbide because of pre-thermal treatment in ethanol gas of 0.01Pa. Figure 1(b) shows an ED pattern on the eve of CNT growth. ED patterns in Figs. 1(c) and 1(d) were taken just after the CNT growth and after the CVD process, respectively. The change in the ED patterns between Figs.



1(a) and 1(d) is clear, suggesting the growth of single wall CNT (SWNT).

Figure 2 shows Raman spectra corresponding to Figs. 1(a) – 1(d), in a frequency range of RBM, 80 – 400 cm⁻¹. The Raman spectra shows that the growth of SWNT has begun at the stage of Fig 1(b), though RHEED did not detect it at the stage of Fig. 1(b).

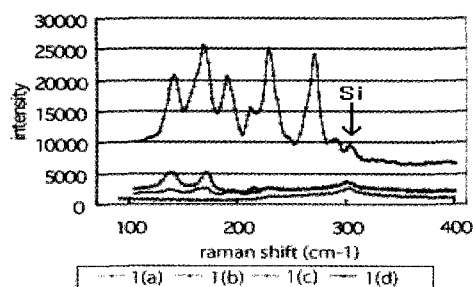


Figure 2. Raman spectra corresponding to Figure 1.

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Large-scale separation of metallic and semiconducting single-wall carbon nanotubes using gel column chromatography

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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 separation system for verification of scalability of the gel column chromatography methods developed in AIST [1, 2]. In this presentation, we will show recent progress of our development.

Approximately 500 ml of column filled with dextran-based gel beads (Sephacryl S200, GE Healthcare) was prepared and connected with a chromatography system (ÄKTA explorer 100, GE Healthcare) (Fig. 1). SWCNTs dispersion in sodium dodecyl sulfate (SDS) solution was prepared by sonication and ultracentrifugation, and the solution was injected to the column using the chromatography system. Un-bound fractions flowed SDS solution and bound fractions eluted by sodium deoxycholate solution contained M- and S-SWCNTs, respectively. We obtained 10 mg and 20 mg of M- and S-SWCNTs, respectively, in a separation in about 4 hours. Large-scale M/S separation using agarose-based gel will also be presented.

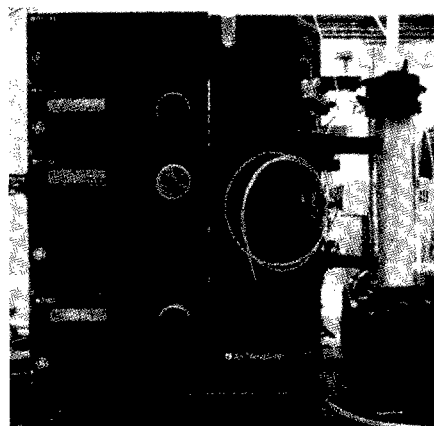


Fig. 1 Chromatography system equipped with a 500 ml column

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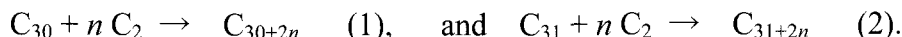
Formation mechanism of (5,5) and (6,5) chiral carbon nanotubes

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Theoretical study of the formation mechanism of (5,5)- and (6,5)-chiral carbon nanotubes (CNTs) has been carried employing the B3LYP/ 6-31G method. It is known that the (6,5) CNTs are much more abundant than the (5,5), when formed by the laser ablation, while fullerenes are rich among the carbon aggregates with the (5,5) chirality rather than the CNTs.

The stepwise additions of C_2 molecules to C_{30} and C_{31} have been focused,



The C_{30} and C_{31} are the seeds of the (5,5) and (6,5) CNTs, respectively, whose structures are illustrated in Fig.1. The C_{30} has five “bays (arm chairs)” and five “bridges” locating alternatively on the edge. The C_2 molecules tend to be bound at the bays forming the six- or five-membered rings in the reactions (1). The addition of a single C_2 is exothermic by ~ 8 -10 eV. The products can be designated by the labels of the form $[p,q]$ with the values of p and q being the numbers of the six- and five-membered rings, respectively. Eg.[1,0] or [0,1] for C_{32} .

It is found that one of the $[n,0]$ isomers, in which n six-membered rings are situated in the neighboring bays are the most stable for each n up to 3, namely, C_{36} , while the $[0,4]$ structure becomes the global minimum for C_{38} , which can be regarded as the precursor of the C_{40} fullerene. The barriers of the successive isomerization reactions from the high-energy isomers to the most stable fullerene precursor are low enough to be overcome by the excess energy gained by the C_2 addition to C_{36} : the reaction channels of the fullerene-formation become accessible during the sequential C_2 additions. Thus, it is natural to expect that the major part of the growing (5,5) CNTs undergoes the isomerization reactions to the fullerenes at the certain sizes such as $n = 38, 48$, and 58 , and the surviving CNTs yield the longer tubes, in harmony with the experimental observations.

On the other hand, one of the bridges consists of three carbon atoms in C_{31} as seen in Fig.1. The C_{31+2n} where the bays A through E are filled with the six-membered rings in this order are the most stable for each n up to five. Thus, the C_{41} has the form with a near-arm chair (zigzag) part at **a** in the figure. It is worth noticing that the HOMO has large amplitude at this position, giving rise to the reactive carbon for the further C_2 additions. It is also notable that the reactive carbon transfers to the neighboring bay by the adding a C_2 molecule, indicative of the “Near Arm Chair Travel Mechanism” for the growing (6,5) CNTs. Indeed, it is found that the structure with the near arm chair moiety is more stable than other isomers whose bays are bound by the C_2 in the different manners for each n up to 97, except for a few sizes, by the extensive and elaborated calculations. Those results strongly suggest the “Near Arm Chair Travel Mechanism” for the appreciable growth of the (6,5) CNTs observed by the experiment.

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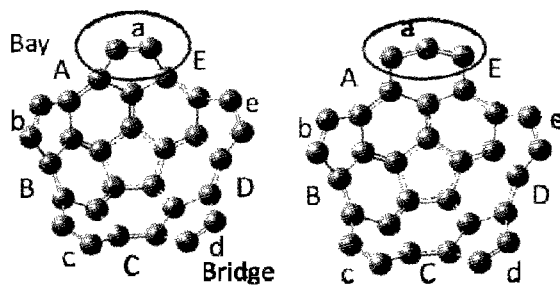


Fig.1. Structures of (5,5) C_{30} and (6,5) C_{31} .

Bays are labeled by A-E, bridges by a-e.

Temperature-dependent separation of single-wall carbon nanotubes using gel

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There are two electric types of single wall carbon nanotubes (SWCNTs), metallic (M) ones and semiconducting (S) ones. For their electrical application, these two types of SWCNTs are required to be separated into the respective type. We have developed effective M/S separation methods using agarose gel^{1,2}. In the last meeting, we reported the effects of pH and NaCl concentration on the M/S separation using gel. In this presentation, we report the effect of temperature at the separation.

M/S separation was conducted using column method². HiPco-SWCNT/sodium dodecyl sulfate (SDS) dispersion was prepared by sonication and ultracentrifugation. The dispersion was applied to a column filled with gel beads (Sephacryl S200). In the separation, S-SWCNTs were selectively adsorbed to the gel. When the adsorption was conducted at different temperatures (22°C and 40°C), the amount of adsorbed SWCNTs at 40°C were higher comparison with that of 22°C (Fig. 1). Then, stepwise elution by decreasing temperature was conducted from 40°C to 10°C at 1% SDS (Fig. 2). After the elution by temperature, concentration of SDS was increased stepwise to fractionate the remaining S-SWCNTs. S-SWCNTs with different diameters could be separated by this method. Detailed methods and results will be discussed.

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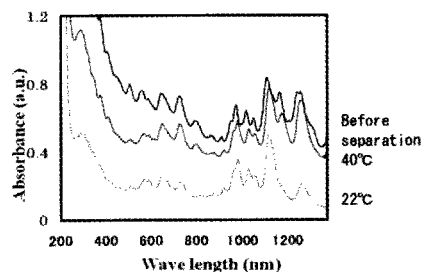


Fig. 1 Optical absorbance spectra of adsorbed fractions at different column temperature. (Sephacryl S200)

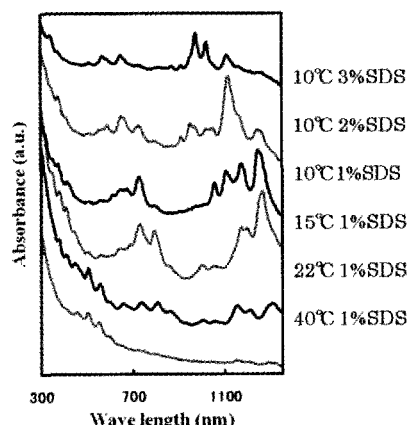


Fig. 2 Stepwise elution by different column temperature. (Sephacryl S200)

Crystallinity Improvement of SWCNT forests through the Synthesis Optimization using the Super-Growth Method and their Properties

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To address the issue of the low crystallinity of single-walled carbon nanotube (SWNT) as synthesized by the Super-growth method [1], we applied an optimization scheme to realize a 10-fold increase in crystallinity based on the graphitic-to-disorder band ratio (G/D) measured by Raman spectroscopy. Transmission electron microscopy (TEM) characterization of the CNTs showed no loss in SWNT selectivity and an increase in straightness. This scheme sequentially optimized the humidity content (ppm), growth temperature, and carbon input level. Despite this 10-fold increase, SWNT forests, that is, vertically aligned SWNTs could be synthesized.

Here, we present an outline of our approach for crystallinity improvement and characterization of their properties. Examination of the synthetic conditions for yield and crystallinity showed opposite trends indicating that simultaneous optimization of both yield and crystallinity appears inherently impossible. Evaluation of the physical and chemical properties, such as electrical and thermal conductivities, dispersion, etc. showed improvement compared to the standard crystallinity Super-growth CNTs. For example, thermal diffusivity showed a significant increase though the laser flash method and was similar to the level of isotropic graphite.

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Influence of molecule adsorption on the conductance of a suspended single-walled Carbon nanotube

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The molecule adsorption effect on the electron transport in a single-walled nanotube (SWNT) was studied by using a single SWNT or the SWNT films on the substrate [1, 2], although the properties of electron transport are highly sensitive to both the surface state of the SWNT and the substrate. To avoid the disturbance from the substrate, we have measured the electron transport in a SWNT with the suspended geometry, and investigated the influence of adsorbed molecules on the conductance.

The SWNTs were grown by means of alcohol chemical vapor deposition on a SiO₂ (280 nm)/Si (n⁺) substrate which was used as a backgate electrode. We fabricated the ohmic contacts by electron beam lithography, and the SiO₂ layer was chemical etched (~100 nm) to make suspended SWNT-FET device (Fig.1). The sample was annealed in the vacuum to clean the surface, and was subsequently exposed to the ethanol vapor with the He carrier gas at room temperature. We have measured the characteristics of electron transport at the temperatures of 300K~4.2K.

The gate voltage dependence of the source-drain (S/D) current in the ethanol adsorbed SWNT is plotted solid curve in Fig.1. We observed the remarkable unipolar (p-type) feature in the ethanol adsorbed SWNT instead of the coulomb blockade which is measured in a clean SWNT. After partial annealing by joule heating of the S/D current, the polarity of the SWNT drastically changes to the n-type channel, as show broken curve in Fig.1. Moreover, the ethanol adsorbed SWNT shows hysteresis in S/D current versus gate voltage (Fig.2), which may be attributed to the charge trap in the adsorbed molecules on the SWNT. The experimental results of electron transport in ethanol adsorbed SWNT measured at 4.2 K will be discussed in detail.

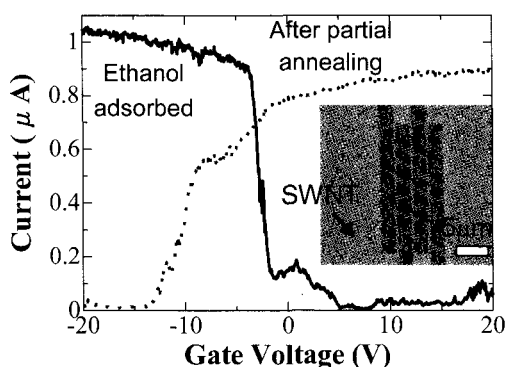


Fig.1 Backgate voltage dependence of the S/D current in the ethanol adsorbed SWNT measured with S/D voltage of 0.5 V at 4.2 K. Inset: SEM image of the sample. The length of SWNT between electrodes is 0.5 μm

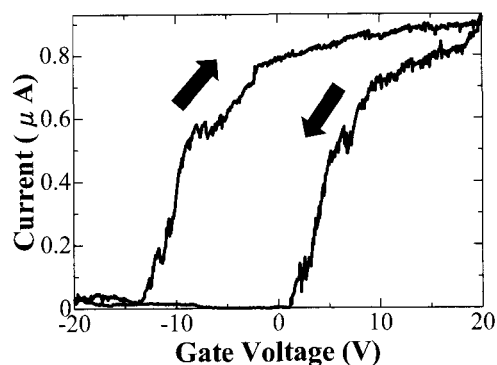


Fig.2 Hysteresis feature observed in the gate S/D current profile. ($V_{sd}=0.5$ V, $T=4.2$ K)

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Temperature dependence of the band gap of carbon nanotubes

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Carbon related materials have large phonon energies and strong electron-phonon couplings. Thus it has been known that there are sizable effects of lattice vibrations on the electronic structures. For example, in diamond, the significant temperature dependence of the band gap was observed experimentally, indicating that the indirect band gap is reduced by approximately 0.4 eV due to the electron-phonon coupling even at the zero temperature[1]. Furthermore, recent sophisticated density-functional-theory (DFT) study revealed that first-principles study can quantitatively reproduce the temperature dependence of the electronic structure that comes from the electron-phonon coupling[2].

In the carbon nanotubes, there are several experimental results suggesting the temperature dependence of the band gap. Since the temperature dependence also indicates the chirality-dependent band-gap renormalization even at the zero temperature, theoretical prediction of the effect of electron-phonon coupling is of great importance for understanding optical excitation measurements. Although theoretical study using tight-binding model predicts the temperature dependence of the band gap in the same order[3], more reliable theoretical study is desired to analyze the experiments more quantitatively. To this end, we compute the phonon modes and the electron-phonon couplings of the carbon nanotubes using first-principles calculations based on the DFT and the density-functional perturbation theory. In the calculation, both self-energy term and Debye-Waller term are included as shown in Fig. 1, which should be crucial for quantitative prediction. We discuss the diameter and chirality dependence in the renormalization of the band gap. The possibility of metal-insulator transition will be also discussed.

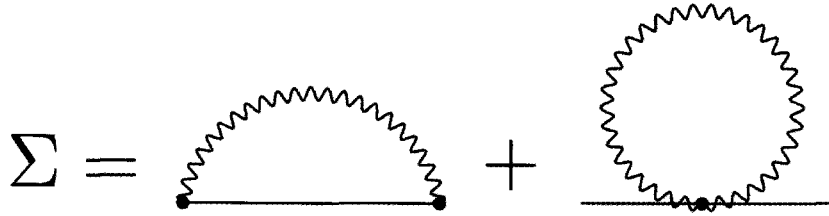


Fig. 1 Diagrams for self energy. First term is called self energy term or Fan term and second one is called Debye-Waller term.

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Detection of individually-dispersed SWCNT using Raman spectroscopy

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Dispersion of single wall carbon nanotubes (SWCNTs) into aqueous solution is one of the most important issues to their practical use to the conducting films and electronic devices because of a lack of good solvent. A serious problem is that there is no good way to know the dispersion status of SWCNTs quickly.

The G-band of SWCNT consists of doublet, G^+ (higher frequency) and G^- (lower frequency). G^+ and G^- of semiconducting SWCNTs are assigned to longitudinal optical phonon mode (LO) and transverse optical phonon mode (TO), respectively, while those of metallic SWCNTs are assigned to TO and LO, respectively, due to the softening of LO in metallic SWCNTs [1,2]. We found that the intensity ratio LO/TO increases drastically under the dispersion process and proposed a simple and useful way to see the dispersion status of SWCNTs using Raman spectroscopy without ultracentrifugation [3]. In this presentation, we will show detailed experimental analysis, which reveals what is going on in the dispersion process.

In this work, we used SWCNT produced by electric arc method (APJ, Meijo NanoCarbon) with 1.4 nm in diameter. SWCNTs were sonicated in the presence of 2% sodium cholate (SC). Figure 1(a) indicates the amount of individually dispersed SWCNTs under the dispersion process which is determined with absorbance after ultracentrifugation. Figure 1(b) shows Raman intensity ratio LO/TO of metallic SWCNTs for 633 nm excitation without ultracentrifugation. The change in LO/TO value agrees well with the change in the absorbance of supernatant after the ultracentrifugation. It implies that LO/TO could be a good index for individual dispersion *in situ* detectable without ultracentrifugation procedure. Detailed analysis will be shown.

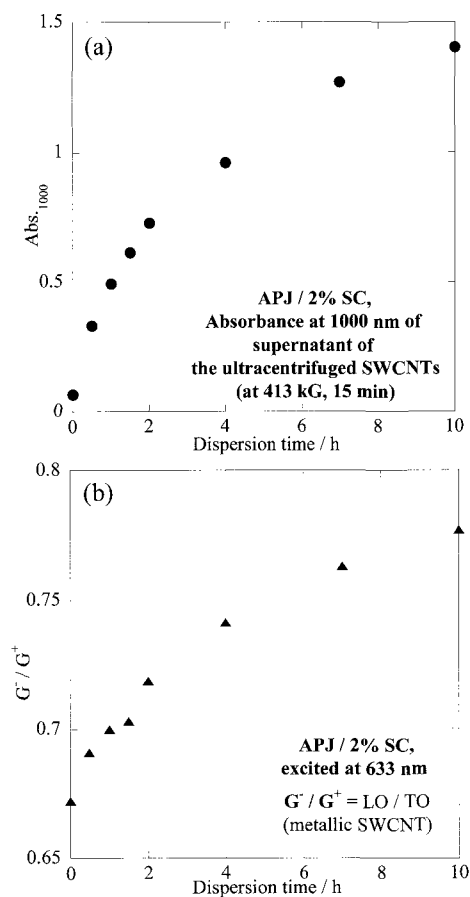


Fig. 1. (a) Absorbance at 1000 nm of supernatant of the ultracentrifuged SWCNTs. (b) LO/TO ratio of SWCNTs without ultracentrifugation.

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Selective Synthesis of (6,5) Single-Walled Carbon Nanotubes from Acetonitrile

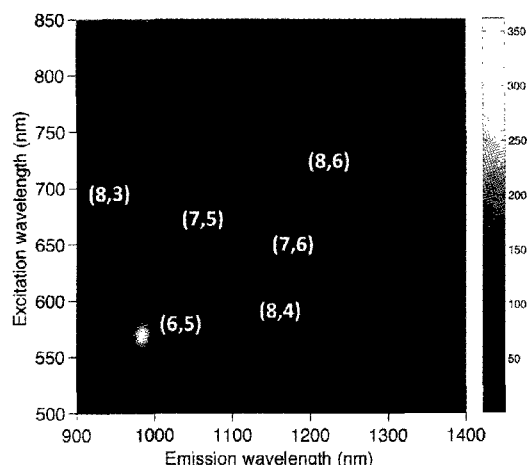
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Modifying electrical and optical properties of single-walled carbon nanotubes (SWNTs) can be obtained by morphology control^{1,2} or chemical doping^{3,4}. The direct synthesis of SWNTs with controlled structure, however, is still a major challenge. In this study, we investigated the optical properties and structure of SWNTs synthesized from acetonitrile. Co/Mo binary catalyst was deposited on amorphous quartz substrate by a liquid dip-coating process⁵ with a precursor of 0.01 %wt of each metal. SWNTs were synthesized by the no-flow chemical vapor deposition (CVD) using acetonitrile as the carbon source. The dip-coated catalysts were purged by Ar containing 3 % of H₂ (Ar/H₂) while heating up to growth temperature. After the temperature reached 800 °C, the CVD chamber was evacuated and sealed before introducing acetonitrile. The SWNTs were thoroughly characterized by resonance Raman spectroscopy using three excitation wavelengths (488, 514, 633 nm), optical absorption spectroscopy, as well as photoluminescence excitation spectroscopy (Figure).

Resonance Raman and optical absorbance spectra suggest the SWNT diameters are very small, and the diameter distribution is much more narrow than SWNTs synthesized from ethanol. Additionally, nitrogen may be incorporated into the nanotube structure, as suggested by a high G to D ratio, redshift of the 2D peak position, and blue shift of G-band⁶. Surprisingly, selective synthesis of (6,5) SWNTs can be also achieved using this method.



Photoluminescence excitation map of dispersed SWNTs synthesized from acetonitrile. Only small-diameter peaks are detected, and the (6,5) peak is clearly dominant.

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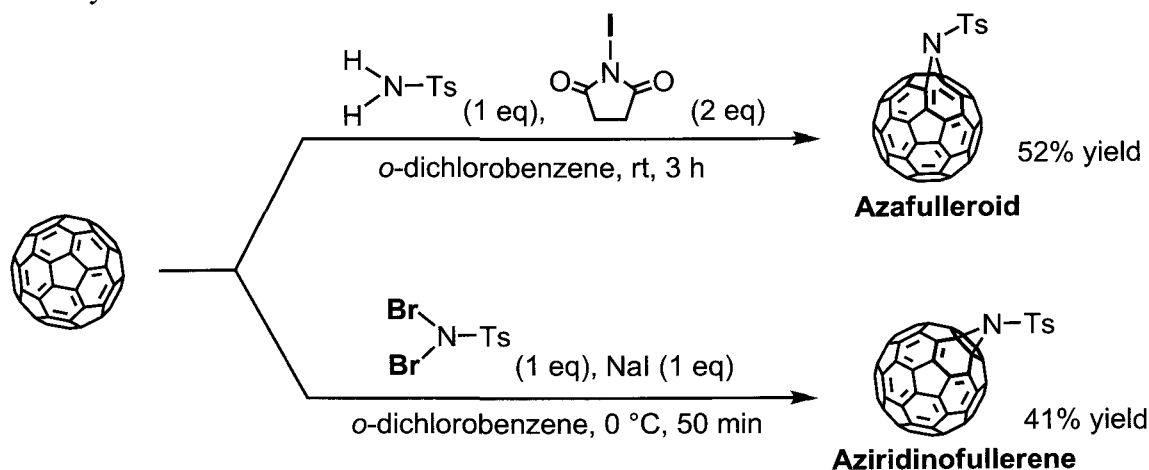
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Highly Selective and Efficient Synthesis of Aziridinofullerenes and Azafulleroids Utilizing *N,N*-dihaloamide reagents

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In view that heterocycle-fused fullerene derivatives have emerged as promising candidates for optoelectronic materials in the past few decades, development of synthetic methodologies for heterocycle-fused fullerenes is of significant importance. In this regard, we have developed a selective synthetic method for aziridinofullerenes from C_{60} using *N*-chloro arenesulfonamides as an N_1 unit, and we also showed that the products are efficiently converted to the corresponding azafulleroids through a rearrangement catalyzed by a chloramine salt [1]. Given conventional synthetic methods for these compounds require the use of azide reagents, which are explosive and toxic, as well as high reaction temperatures, and additionally they inevitably accompany the production of the mixture of aziridinofullerenes and azafulleroids [2], our method is advantageous in terms of the safe procedure and the high product selectivity. Nevertheless, the method still remained to be further improved to satisfy wider substrate scope and milder conditions. Herein we report a highly selective and efficient synthetic reaction of aziridinofullerenes and azafulleroids, in which *N,N*-dihaloamide intermediates would play the key role in determining the product selectivity.



When C_{60} was treated with an equimolar amount of *p*-toluenesulfonamide and *N*-iodosuccinimide (2 equiv) in *o*-dichlorobenzene at room temperature for 3 h, aziridination reaction proceeded smoothly to exclusively give the corresponding azafulleroid in as high as 52% isolated yield without any formation of the aziridinofullerene. In contrast, the reaction of C_{60} with an equimolar of *N,N*-dibromo-*p*-toluenesulfonamide in the presence of NaI (1 equiv) at 0 °C selectively gave aziridinofullerene in 41% yield. The present reactions were found applicable to wide range of amides and *N,N*-dibromoamides, giving rise to azafulleroids and aziridinofullerene in good isolated yields with high selectivity.

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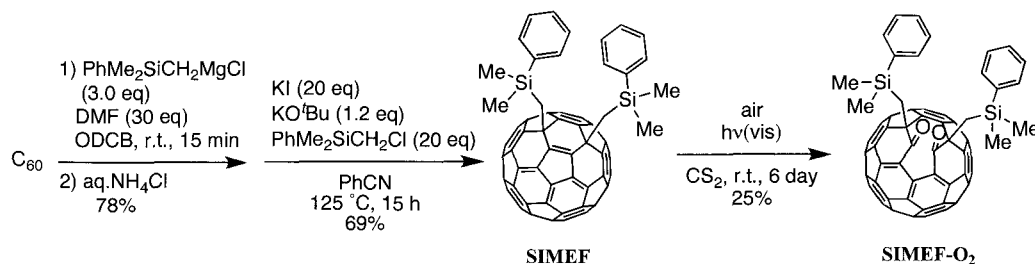
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Synthesis, Structures, and Properties of an Oxidized Product of the 1,4-Bis(silylmethyl)[60]fullerene (SIMEF)

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The chemical modification of fullerene can improve its electrochemical and photophysical properties, and can change the structure of the fullerene cage. Open-cage fullerenes has been paid special attention from the structural point of view. In this work, we found that an open-cage fullerene can be prepared by the oxidation of a 1,4-Bis(silylmethyl)[60]fullerene, SIMEF ($= \text{C}_{60}(\text{CH}_2\text{SiMe}_2\text{Ph})_2$), which has been known to be an n-type organic semiconductor.^{[1], [2]} The effect of opening the fullerene cage on the change of electronic properties and the structure were investigated in this study.



SIMEF was oxidized in the CS_2 solution with molecular oxygen under light irradiation to afford $\text{C}_{60}(\text{CH}_2\text{SiMe}_2\text{Ph})_2\text{O}_2$, SIMEF- O_2 as the main product. The structure of SIMEF- O_2 was determined as an open-cage fullerene with a diketone moiety located at the 5,6-double bond by spectroscopic methods and X-ray crystallographic analysis (Figure 1). SIMEF- O_2 showed improved solubility compared to its precursor SIMEF. SIMEF- O_2 was found to have a lower LUMO-level because of electron-withdrawing nature of the ketone groups. This caused the decrease of open-circuit voltage, V_{OC} (0.56 V) in organic photovoltaic devices. As a result, power conversion efficiency of SIMEF- O_2 device was half of that of SIMEF device (Table 1).



Fig.1 Structure of SIMEF- O_2

Table 1. LUMO level and OPV properties of SIMEF- O_2

Acceptor	LUMO (eV)	V_{OC} (V)	J_{SC} (mA/cm^2)	FF	PCE (%)
SIMEF	-3.74	0.75	10.0	0.67	5.1
SIMEF- O_2	-3.84	0.56	8.3	0.54	2.5

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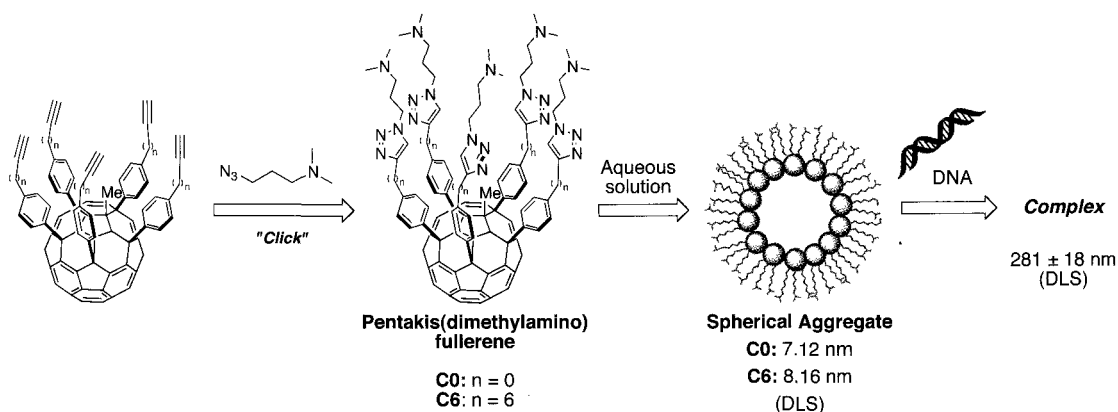
Self-Assembly and DNA Binding of Cationic Pentasubstituted [60]Fullerene Amphiphiles

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Pentasubstituted [60]fullerene derivatives ($R_5C_{60}X$, R = aryl, X = H, alkyl, or metal) have highly symmetric and rigid structure derived from the nature of fullerene, which gives $R_5C_{60}X$ a potential to form well-defined self-assembled structures in a solution state. It has been known that $R_5C_{60}K$, a potassium salt of the pentasubstituted fullerenes, forms bilayer vesicles in water.^[1] On the other hand, introduction of a variety of hydrophilic groups to the substituents (R) on $R_5C_{60}X$ would afford self-assembled structures in water with diverse characteristics corresponding to the introduced functionalities. As a motif similar to the amphiphilic $R_5C_{60}X$, our group has developed tetrapiperazino[60]fullerene epoxide (TPFE), a fullerene derivative with four cationic moieties, which binds DNA through electrostatic interaction and efficiently transports it into cells.^[2] Investigation of this compound revealed that TPFE aggregated in aqueous media before complexation with DNA, but the structure of the aggregate was ill-defined, which made it difficult to study structure-activity relationship in DNA delivery.

In this study, a series of cationic fullerene derivatives were designed by introduction of amine functionalities to $R_5C_{60}Me$ through ‘click’ reaction.^[3] Pentakis(dimethylamino) fullerene derivatives, **C0** and **C6**, were dissolved in aqueous conditions, and formation of spherical supramolecular structures in acidic solutions was confirmed by atomic force microscopy (AFM) and dynamic light scattering (DLS) measurements. The size of the aggregate was determined to be 7–8 nm, suggesting micelle-like structure. Furthermore, **C6** was able to bind DNA to give a complex with the size of several hundred nm.



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Spherical Aromaticity of Fullerene Dianions Studied with Endohedral Dihydrogen as NMR Probe

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The magnetic properties of fullerenes caused by the spherical π -conjugated systems have attracted enormous interests since their discovery. The NMR chemical shifts of encapsulated atoms such as helium-3 [1] or dihydrogen [2] inside the cages are very sensitive to the π -electron ring currents and thus can be used as the useful criteria of the aromaticity. We recently disclosed that the overall aromaticity of C_{60} decreases drastically upon two-electron reduction based on unusual downfield shift of the NMR signal of the endohedral dihydrogen ($\Delta\delta = 26.4$ ppm) [3].

In this work, we performed two-electron reduction of C_{70} encapsulating dihydrogen [4] using $NaSCH_3$ as a reducing agent in acetonitrile- d_3 . The resulting red-brown solution showed a sharp NMR signal for the encapsulated dihydrogen of $H_2@C_{70}^{2-}$ at $\delta = -13.80$ ppm, corresponding to a downfield shift by $\Delta\delta = 10.2$ ppm relative to that of $H_2@C_{70}$ (Fig. 1). This result apparently demonstrated that the overall aromaticity of C_{70} also considerably decreases upon two-electron reduction, while the extent is less than half of the corresponding shift observed in $H_2@C_{60}$.

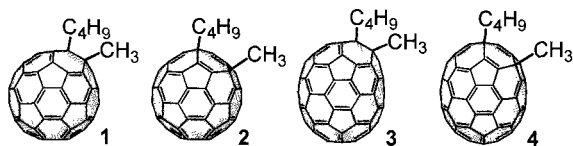


Table 1 Electrochemical Reduction Potentials^a

compound	E_{red}^1	E_{red}^2	E_{red}^3	LUMO ^b
1	-1.20	-1.60	-2.14	-3.07
2	-1.17	-1.60	-2.09	-3.08
3	-1.21	-1.59	-1.98	-3.00
4	-0.99	-1.45	-1.97	-3.27

^a Values in V vs. Fc/Fc^+ ; with 0.1 M Bu_4NBF_4 as supporting electrolyte; Pt wire as counter electrode; scan rate of 20 $mV s^{-1}$.

^b Values in eV calculated at the B3LYP/6-31G* level.

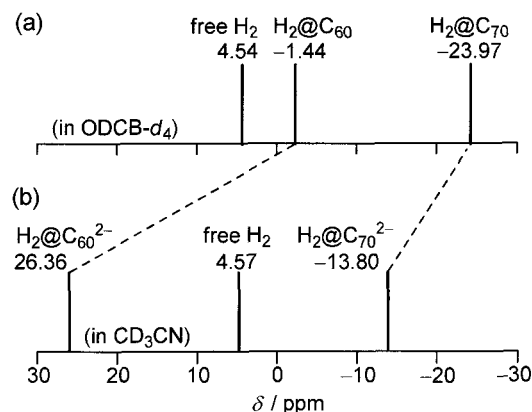


Fig. 1 1H NMR chemical shifts of $H_2@C_{60}$ and $H_2@C_{70}$ in (a) neutral and (b) dianionic states.

To further extend this study, C_{60} and C_{70} derivatives **1-4** bearing two alkyl groups at 1,2- or 1,4-position were prepared and their redox properties were first examined by cyclic voltammetry in *o*-dichlorobenzene (ODCB) (Table 1). Among them, only 1,4-dialkyl C_{70} derivative **4** was found to exhibit excellent reducibility which is even slightly higher than that of pristine C_{60} and C_{70} ($E_{red}^1 = -1.09$ V and -1.05 V, respectively). The aromaticity of dianions of C_{60} , C_{70} and **4** were interpreted based on the results of the theoretical calculations, which will be presented in detail.

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Photo-polymerization of C₆₀ Nanosheets

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Various new types of C₆₀ nanocrystals called C₆₀ nanowhiskers [1] and C₆₀ nanosheets [2] have been grown by liquid-liquid interfacial precipitation (LLIP) method with the interface between C₆₀-saturated solution and isopropyl alcohol. Their unique shapes are attracting much interest for various applications such as nano-scale devices. It is known that C₆₀ crystals are very sensitive to the light [3]. The understanding of the effect of light on C₆₀ nanocrystals is important for not only fundamental studies but also practical applications. In this paper, we report the polymerization of C₆₀ nanosheets by laser irradiation.

Two kinds of C₆₀ nanosheets were grown by LLIP methods. One was grown with C₆₀-saturated toluene solution with ferrocene and was called FFN [4]. The other was with C₆₀-saturated CCl₄ solution and called FCN [2]. They were irradiated with a 532 nm from YAG laser.

Fig. 1 shows optical microscopic images of FFNs. They exhibit hexagonal shapes with ~250 nm in thickness and several tens of micrometers in diameter. The shape and size of FFN are similar to those of FCN. Fig. 2 shows Raman spectrum of FFNs which is also similar to that of FCNs. It should be noted that the response of FFNs for irradiation is quite different from that of FCNs. The detailed changes will be clarified by means of Raman spectroscopy.

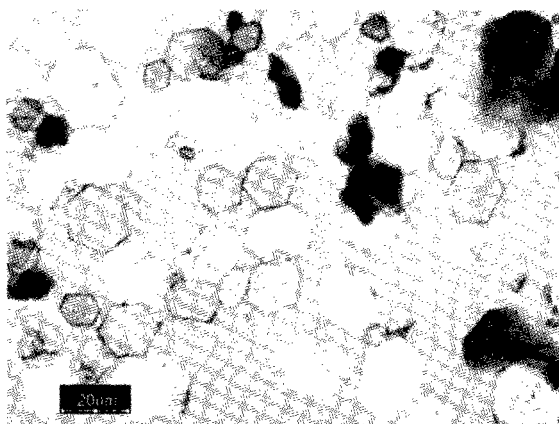


Fig. 1. Optical micrograph of FFNs.

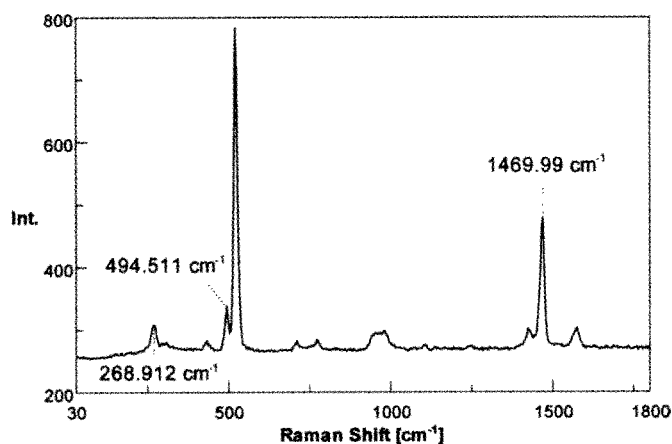


Fig. 2. Raman spectrum of FFNs.

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Raman spectra analyses of the heat-treated photopolymerized fullerene nanowhiskers

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In 1993, Rao et al. reported the photopolymerization of C₆₀ films [1]. Tachibana et al. showed the photopolymerization of C₆₀ nanowhiskers by the Raman laser beam irradiation [2]. In the present study, the influence of heat-treatment on the structure of the photopolymerized C₆₀ nanowhiskers is investigated.

C₆₀ nanowhiskers were synthesized by the liquid-liquid interfacial precipitation method [3] using a toluene solution saturated with C₆₀ (MTR Ltd. 99.5%) and isopropyl alcohol (IPA). Then, the C₆₀ nanowhiskers dispersed in IPA were polymerized by the irradiation of Xe lamp light with a wavelength of 263 nm for 24 hour.

To understand the structural change of the photopolymerized C₆₀ nanowhiskers by heat treatment, Raman spectra of the photopolymerized C₆₀ nanowhiskers were investigated before and after the heat treatment in air or in vacuum at temperatures of 50, 100, 200 and 300 °C. The Raman spectra of C₆₀ nanowhiskers were obtained by use of a green laser with a wavelength of 532 nm (JASCO, NRS-3100).

The photopolymerized C₆₀ nanowhiskers heated at temperatures lower than 200 °C in air, or 300 °C in vacuum maintained their initial shape.

The A_g(2) photopolymer peak intensity around 1460 cm⁻¹ of both the samples heat-treated in air or vacuum decreased compared with that of the samples without the heat treatment.

Hence, it is suggested that the photopolymerized C₆₀ molecules return to the monomer state of C₆₀ owing to the temperature increase.

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Framework transformation of endohedral metallofullerene

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Shigeru Nagase ², Takeshi Akasaka ¹

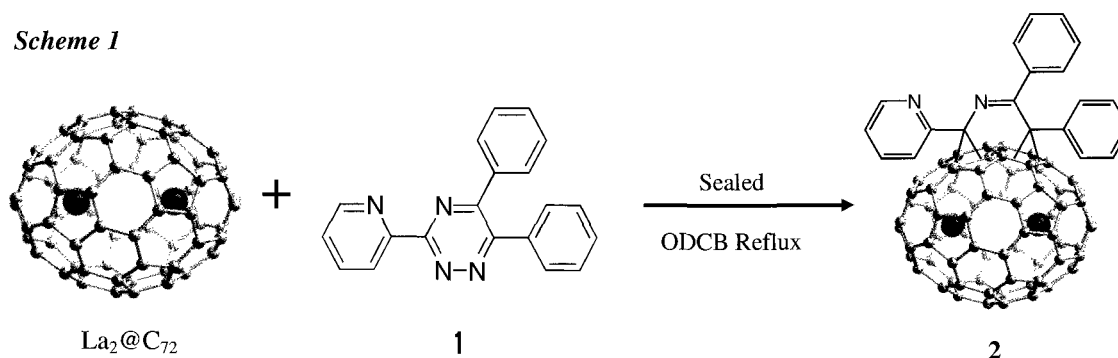
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Endohedral metallofullerenes (EMFs) have attracted special interest for their electronic properties, which clearly differ from those of empty fullerenes due to electron transfer from the encaged metal atoms to the fullerene cage.^{1,2} Recently, various derivatives of EMFs have been synthesized by different reactions, and some of them have been isolated and structurally characterized. Most reports have focused on derivatization of the cage, while only a few papers deal with transformation of the framework of fullerenes.³

Here we report on the reaction of endohedral metallofullerene La₂@C₇₂ with 5,6-diphenyl-3-(2-pyridyl)-1,2,4-triazine (**Scheme 1**) and characterization of **2** by means of spectroscopic analysis and theoretic calculation.

Scheme 1



References:

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Synthesis and characterization of electron donor-acceptor conjugates based on $\text{La}_2@\text{C}_{80}$ and tetracyanoanthraquinodimethane

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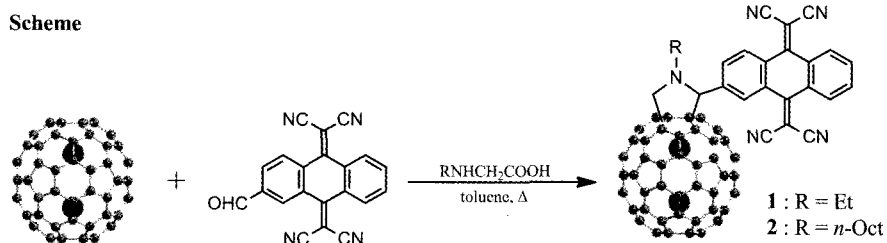
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Since the first report on extraction and isolation of endohedral metallofullerene $\text{La}@\text{C}_{82}$ in 1991, many kinds of endohedral metallofullerenes have been investigated^[1]. It is well known that endohedral metallofullerenes have relatively high reduction potential and low oxidation potential compared with hollow fullerenes, as the result of electron transfer from the encapsulated metal atom to the carbon cage.

Recently we have reported an electron donor-acceptor conjugate involving $\text{Ce}_2@\text{C}_{80}$ and zinc porphyrin (ZnP)^[2]. It was found that $\text{Ce}_2@\text{C}_{80}$ -ZnP leads a reductive charge transfer (i.e., formation of $(\text{Ce}_2@\text{C}_{80})^{\bullet-}(\text{ZnP})^{\bullet+}$) in non-polar media, while an oxidative charge transfer (i.e., formation of $(\text{Ce}_2@\text{C}_{80})^{\bullet+}(\text{ZnP})^{\bullet-}$) in polar-media. To the best of our knowledge, it is an only example of the intramolecular electron transfer from fullerene to the substituent to date.

Here, we report the synthesis of new type of electron donor-acceptor conjugates consisting of $\text{La}_2@\text{C}_{80}$ as an electron donor and 11,11,12,12-tetracyanoanthraquinodimethane (TCAQ) as an electron acceptor. The target molecules (**1**, **2**) were prepared by 1,3-dipolar cycloaddition of azomethine ylides generated in situ to $\text{La}_2@\text{C}_{80}$ (Prato reaction) and isolated by two-steps HPLC separation. **1** and **2** were characterized using spectroscopic methods and electrochemical analyses by cyclic and differential pulse voltammetries.



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Multi-functionalization of Paramagnetic Endohedral Metallofullerene

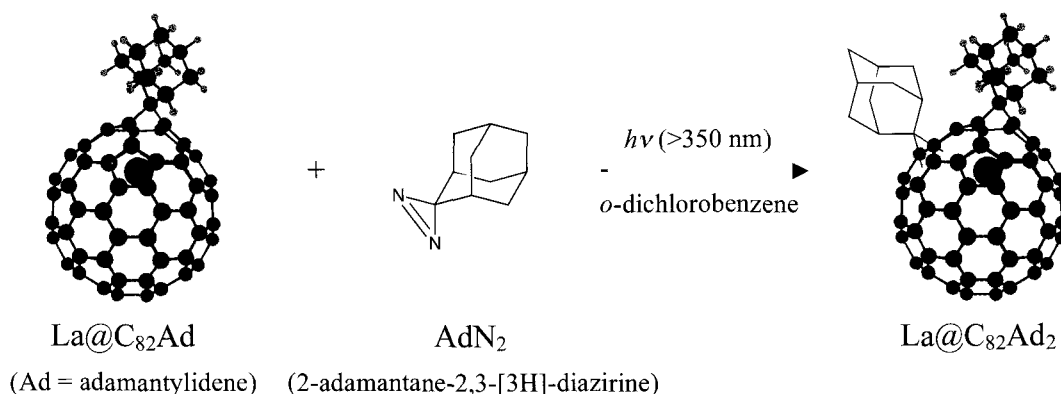
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Since the first success in the extraction of endohedral metallofullerenes in 1991, paramagnetic endohedral metallofullerene La@C₈₂ has been most widely investigated as a prototype [1]. For instance, our group has already reported that the reaction of La@C₈₂ with 2-adamantane-2,3-[3H]-diazirine (AdN₂) resulted in the formation of La@C₈₂Ad in a regioselective manner and the single crystal of La@C₈₂Ad had remarkable charge-transport properties [2, 3]. On the other hand, multi-functionalization of endohedral metallofullerenes is of particular interest because it may let us know about the chemical reactivity of the endohedral metallofullerene derivative and novel properties.

Herein, we successfully synthesized the bis-adducts of La@C₈₂Ad₂. Their characterization was carried out by HPLC, Vis-NIR, ESR and MALDI-TOF Mass spectroscopic analyses and theoretical calculations.



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Formation and separation of nitrogen-doped fullerenes

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Endohedral fullerenes comprise a versatile group of compounds with remarkable properties especially in magnetic resonance [1]. Various types of metallofullerenes mostly with atoms of the rare-earth elements inside have been isolated and characterized so far [2]. Recently, ion implantation has been applied to incorporate atoms in a fullerene cage to identify atomic nitrogen in C_{60} [3]. We have continued to study on the formation process as well as the method for separation and concentration of $N@C_{60}$.

The apparatus for producing $N@C_{60}$ has been improved for yielding higher efficiency. First, a 500-W high-frequency power supply was employed to discharge nitrogen gas at ~ 3 Pa to achieve ion current of ~ 10 mA at the electrode where the C_{60} film was bombarded with the cations. The increase in the number of nitrogen cation, namely the ion current, is crucial for increasing the production efficiency. The relation between the yield of $N@C_{60}$ and the ion current was investigated thoroughly. Second, sublimation of C_{60} was controlled by a programmable crucible system to achieve a constant deposition rate of C_{60} . This is also important, since the penetration depth of the cations of a moderate acceleration voltage, ~ 80 eV, is not very large, perhaps one or at most a few molecular layers in the C_{60} sediment.

Separation of endohedral $N@C_{60}$ molecules from the mixture with empty C_{60} molecules is also an important task, because as-prepared crude materials after ion bombardment contain more than $>10^4$ empty- C_{60} molecules for one target-molecule of $N@C_{60}$. By using a multiple-step recycling-HPLC system, we performed separation and concentration to obtain a solution of purified $N@C_{60}$, $>90\%$ (Fig. 1), confirming its UV/vis absorption spectra.

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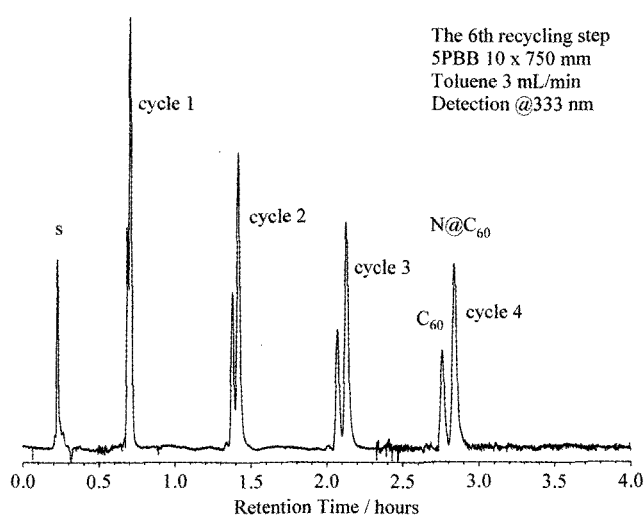


Fig. 1. The final step in recycling HPLC for separation of $N@C_{60}$ from C_{60} as detected by UV absorption at 333 nm.

Radiochemical Approach for Synthesis of Carboxy Metallofullerenes

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Water-soluble endohedral metallofullerene (EMF) is expected to be applicable for the drug deliver system (DDS). Actually, $\text{Gd}_3\text{N}@\text{C}_{80}[\text{DiPEG5000}(\text{OH})_x]$ ^[1] will be used as high sensitive magnetic resonance imaging (MRI) contrast reagent in near future. In these water-soluble EMF, carboxy EMFs^[2] are one of the promising candidate for the DDS, because these are conjugated with desired peptide of morbidity parts by amide bond.

We had reported some properties of EMFs encapsulating radioisotope of ^{225}Ac ^[3]. Actinium-225 is considered to be a promising nuclide for radioimmunotherapy because ^{225}Ac decays with successive cascade and an alpha particle emitted from ^{225}Ac and its daughter is high linear energy transfer (LET) radiation. However, it is difficult to make clear their properties directly due to the trace amount of production for the EMFs encapsulating radioisotopes. In this study, we report synthesis and properties of carboxy EMFs encapsulating La which is homologous element with Ac by radiochemical approach.

La EMF was prepared by arc discharge method. Crude fullerene extracts containing La EMFs were irradiated by thermal neutron at JRR-4 reactor of Japan Atomic Energy Agency (JAEA). Activated EMF was separated from irradiated fullerene by AlCl_3 and dissolved to o-dichlorobenzene (DCB). For the addition of ethylenecarboxyl group, succinic acid peroxide (SAP)^[4] was added to DCB solution. This solution was stirred and heated at 80 °C for 48 hours in Ar gas flow. Produced carboxy adducts were extracted by 0.2 M NaOH solution and injected into Sephadex G-25 size exclusion gel column with deionized water as eluent. Eluate from the column was collected every 2 minute. UV/vis absorption spectra, gamma-ray spectra and pH was measured for each fraction.

Production yield of carboxy EMF was estimated from the radio activity in pristine DCB solution and in extracted aqueous solution, and found to be 66.6 %. Fig.1 shows the elution curve monitored by gamma-ray and pH of eluate. Almost all of radio activity from ^{140}La was observed in 12-18 min. The color of these radioactive fractions were dark yellow. The UV/vis spectra of these fractions found no characteristic absorption peak. These results indicate the presence of carboxy EMFs in these fractions.

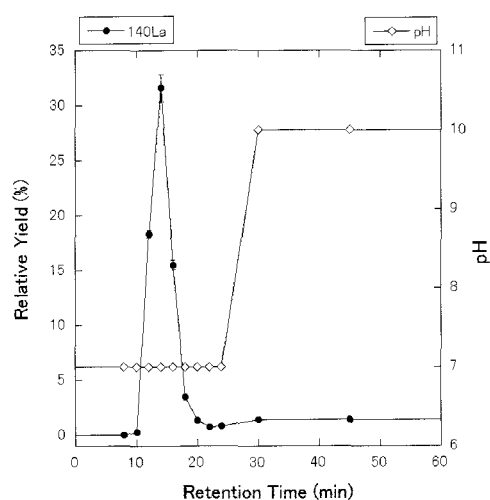


Fig.1 Elution curve by Sephadex column

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Improvement of Metallofullerene separation using Lewis acid.

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Various methods for the separation of metallofullerenes have been reported. One of more efficient way to separate the metallofullerenes is electrochemical separation making use of the difference of the redox potential between metallofullerenes and hollow species. Stevenson *et al.* succeeded to separate metallic nitride endohedral fullerenes and oxometallic fullerenes from hollow species by using AlCl_3 as Lewis acid in carbon disulfide (CS_2) solution [1]. Aim of this work is to confirm this separation method being applicable for the separation of ordinary metallofullerene species such as $\text{La}@\text{C}_{82}$ and to improve the separation efficiency of metallofullerenes from hollow species. In this study, we quantitatively discuss about the separation yield for the metallofullerenes encapsulating lanthanoid elements from hollow fullerenes.

Endohedral metallofullerenes (EMFs) of lanthanoid was prepared by arc discharge method. Crude fullerene extracts containing EMFs were extracted from generated soots and were irradiated by thermal neutron at JRR-4 reactor of Japan Atomic Energy Agency (JAEA). Activated EMFs by neutron irradiation were solved in some solvent and proper quantity of Lewis acid was added. These solutions were stirred for 10 min and 24 h. After that, added Lewis acid was filtered and washed by water followed by acetone. Finally, CS_2 was passed into the filter to recover the EMFs and then γ -ray emitted from each solution was measured by Ge semiconductor detector.

Figure 1 shows the contents percentage (contents%) of La for each treated step of EMFs separation by various solution and Lewis acids estimated from the radioactivity ratio. In this figure, a bar colored black, gray and white shows the contents% of finally recovered La in CS_2 (recovered), unreacted La which passed through the filter (unreacted), and insoluble La component on the filter (insoluble), respectively. From these results, the maximum separation yield of La EMFs is found to be 60 % in case using AlCl_3 as a Lewis acid. In other hand, beyond the half contents% of “insoluble” is observed for the case using FeCl_3 for Lewis acid. It can be said that AlCl_3 was better Lewis acid than FeCl_3 for the separation of La EMFs. About the detail of these results will be shown in the poster session.

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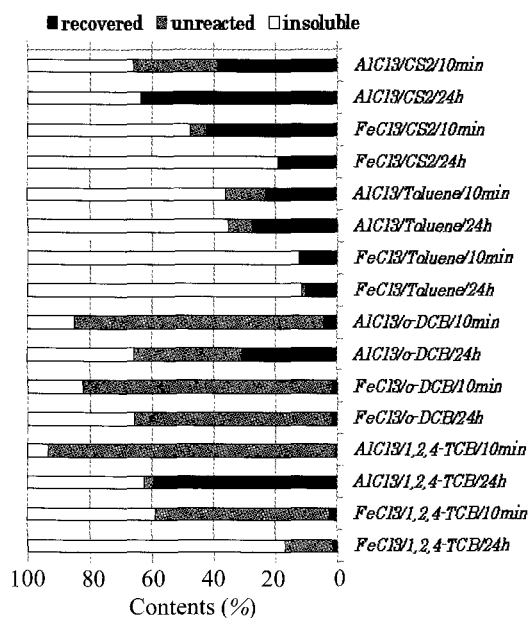


Fig.1 Contents% of La observed in each treated step of EMFs separation: labels on the ordinate axis indicate Lewis acid/solvent/ reaction time.

Positional ordering of a Li cation inside C₆₀ at low temperature

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C₆₀-based metallofullerenes have a potential to accelerate the practical use of fullerene materials because C₆₀ is the most abundant fullerene and metal encapsulation is a promising way to control the physical properties. Recently, bulk synthesis, complete isolation and structure determination of [Li@C₆₀](SbCl₆) have been successfully carried out [1]. The endohedral structure of Li@C₆₀ is different from the gas endohedral C₆₀. A Li cation occupies in the off-centered two sites in the C₆₀ cage at 370 K. The displacement of the Li cation from the cage center is 1.3 Å which is close to the theoretically predicted values. The two sites for the Li cation are close to Cl atoms of SbCl₆ anions outside the C₆₀ cage. These results suggest the existence of electrostatic attractive interaction between the Li cation and SbCl₆ anions through the C₆₀ cage and the thermal hopping of the Li cation between the two sites. To understand the thermal motion of the Li cation inside the C₆₀ cage, temperature dependence of the endohedral structure of Li@C₆₀ at low temperature is studied by x-ray structure analysis using synchrotron radiation (SR).

The SR x-ray diffraction experiment was carried out using [Li@C₆₀](PF₆) single crystal at SPring-8 BL02B1. The endohedral structure of Li@C₆₀ and molecular arrangement of the PF₆ salt are different from that of the SbCl₆ salt. The anion replacement effect supports the existence of electrostatic interaction between the Li cation inside and the anions outside the C₆₀ cage. The charge density distribution of the PF₆ salt obtained by the maximum entropy method demonstrates that a Li cation is highly disordered over positions ~1.5 Å from the cage center at 300 K. The gradual localization of the disordered Li cation is observed on cooling below 100 K.

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Field emission microscope study on electron emission from exfoliated multilayered graphene

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Graphene is a two-dimensional material consisting of carbon atoms and nowadays is attracting considerable attention because of unique physical and chemical properties. Moreover, edges of graphene possess special electronic properties that may have interesting effect on field electron emission. In the present study, field emission (FE) characteristics of multilayered graphene are investigated by field emission microscopy (FEM).

Multilayered graphene sheets were prepared by rubbing bulk graphite onto a tip of tungsten (W) needle with micromanipulators inside a scanning electron microscope. Structures of graphene emitters were observed by transmission electron microscopy (TEM). FE patterns of graphene emitters were observed by FEM, and current-voltage characteristics were simultaneously measured.

Figure 1 shows TEM images of the graphene emitter in (a) low and (b) high magnification, respectively. Figure 1 (b) indicates the graphene emitter is few-layer graphene. Figure 2 shows typical FEM images of this graphene emitter. The FE pattern of Fig. 2 (a) shows a stripe pattern which is usually consisting of paired bright spot. As FE was continued, the stripe pattern changed to unclear pattern, as shown in Fig. 2 (b). Figure 3 shows current-voltage characteristics of (a) the stripe pattern and (b) the unclear pattern corresponding to Figs. 2 (a) and 2 (b), respectively. As shown in Fig. 3, FE current from the emitter showing the stripe pattern tend to be high compared with that showing the unclear pattern. From Fowler-Nordheim plot, the emission area for the stripe pattern is derived to be $\sim 3\text{nm}^2$, indicating that the stripe pattern originates FE from a very narrow area of graphene edge.

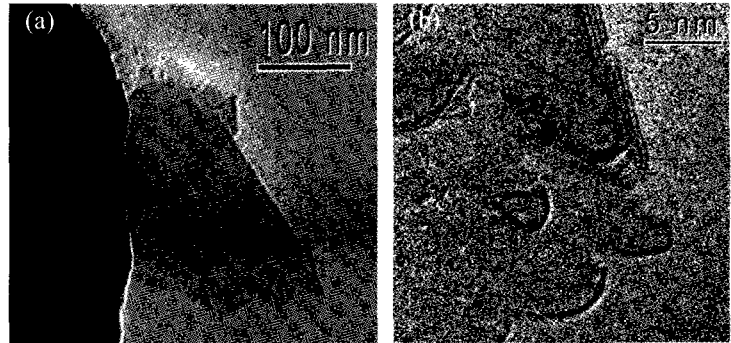


Fig. 1. TEM images of multilayered graphene emitter in (a) low and (b) high magnification.

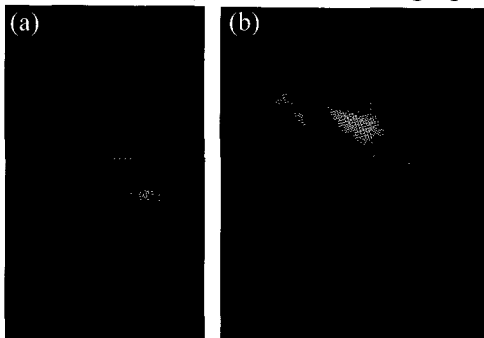


Fig. 2. FEM images of a multilayered graphene emitter. The initial pattern (a) changed to (b) after several minutes at $\sim 3\mu\text{A}$.

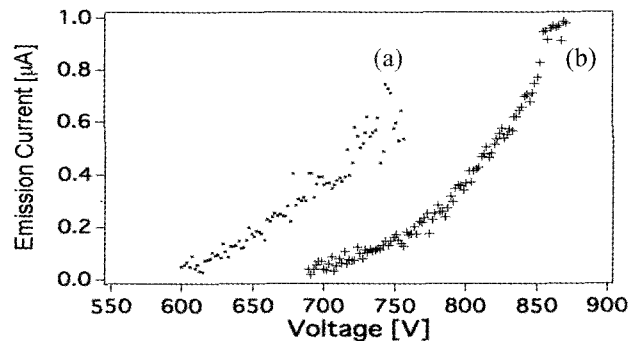


Fig. 3. Current-voltage characteristics for (a) the stripe pattern and (b) the unclear pattern corresponding to figs. 2 (a) and 2 (b), respectively.

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Electronic properties of graphene/hexagonal boron nitride superlattices

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Monolayer and few-layer graphene have intensively studied in recent years. In addition, monolayer and few layers of hexagonal boron nitride (*h*-BN) have also attracted much interest. Heterostructures composed of graphene and *h*-BN have been studied recently. It is found that graphene on *h*-BN substrate exhibits improved electron mobility compared with the electron mobility of graphene on silicon dioxide substrate [1]. The chemical vapor deposition growth of *h*-BN on graphene has been also reported [2]. Theoretically, on the other hand, we design alternately layered superlattices composed of graphene and *h*-BN monolayer based on the density functional theory [3]. We compare the total energies of superlattices with several stacking sequences and identify the most stable stacking sequence (Fig. 1). It is found that the interlayer interaction between a boron atom and a carbon atom is more favored than the interaction between a nitrogen atom and a carbon atom. In fact, the distance between a boron atom and the nearest carbon atom in the superlattice with the most stable stacking sequence is shortest among possible stacking sequences. Interestingly, the most stable superlattice is found to exhibit metallic electronic properties. It is also revealed that the electronic structure of the superlattices depends on the stacking sequences [4]. Moreover, we study superlattices composed of graphene and *h*-BN bilayer. We find that the graphene/*h*-BN bilayer superlattices possess interesting electronic properties depending on the stacking sequences. The superlattice with the shortest stacking period is found to possess semiconducting electronic properties. On the other hand, the superlattices with longer stacking periods are found to possess linear dispersion relations in the vicinity of the K and H points in the first Brillouin zone.

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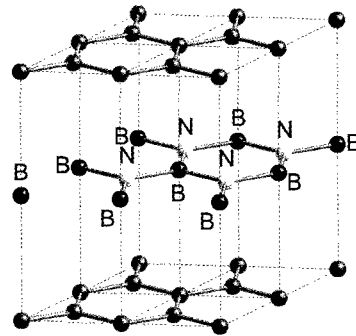


Fig. 1 The crystal structure of a superlattice

Control of stacking structure for multi-layer graphene

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Graphene is one-atom-thick two-dimensional sheet with hexagonal carbon structure and stacks to form graphite with 0.34 nm inter-layer spacing. Well-known HOPG and Kish graphite which have used to get mechanically exfoliated single or bilayer graphene show the traditional Bernal stacking geometry so-called AB stacking. Theoretically, the bilayer graphene with AB stacking geometry has a split energy band structure due to strong inter-layer interaction [1] and can make energy band gap open up to 0.25 eV with perpendicularly applying electric field [2]. Raman spectroscopy has given important information to evaluate a number of graphene layers for mechanically exfoliated graphene sheets on SiO₂ substrate. Especially, the 2D (G') band which appears around 2600 cm⁻¹ has different peak shape, position, intensity dependent on a number of these layers because of double resonance Raman scattering process [1]. However, for the Chemical vapor deposition (CVD) grown bilayer graphene, the 2D band does not show a change of peak shape, intensity, and position comparison to single layer graphene, since the CVD grown bilayer graphene forms of a variety of Moiré patterns due to typical defects such as wrinkles and ripples around multi-step boundaries of catalyst (Ni, Cu, etc) [3], and then has a similar energy band structure to single layer graphene due to very weak inter-layer interaction.

We heat-treated a graphite oxide with incremental annealing temperature, in which the inter-layer spacing is approximately two times larger (0.7 nm) than the graphite. As increasing the temperature up to 2900 °C, the inter-layer spacing becomes completely reduced to the graphitic inter-layer spacing 0.34 nm. In Raman spectroscopy analysis, we took each different Raman spectra for different annealing temperature, 1400, 1800, 2200, 2500, 2900 °C, and then observed a change of D and 2D band peaks. As the result, we understood that since the sample annealed at the 2200 °C shows much reduced D band and very sharp 2D band with large peak intensity, it behaves like single layer graphene. Furthermore, as annealing the temperature to the 2500 °C, the 2D band becomes same with that of the graphite. This means that we can change the stacking geometry from Moiré patterns (no AB stacking) to AB stacking at the specific high temperature. We expect that this study will give lots of fundamental information for bilayer graphene applications.

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CVD synthesis of graphene by Joule heating a metal catalyst enabling rapid heating and cooling

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Chemical vapor deposition (CVD) has been widely used to produce graphene on the surface of various metal substrates [1,2]. Such CVD-synthesized graphene typically demonstrates low defects, and the method is considered to be a potential candidate for a large-scale and low cost technique to obtain high quality graphene. However, a drawback of utilizing CVD is the high temperature process which normally requires heating a metal catalyst up to 1000 °C in a quartz furnace, thereby limiting the process throughput due to high heat capacity of the system. In addition, the cooling rate of a metal substrate during the CVD synthesis was found to play an important role to obtain high quality and controlled number of graphene layers [2]. We here demonstrate a facile, versatile, and high-throughput way which utilizes direct Joule heating of a metal foil to synthesize large-scale graphene.

Figure 1 shows a schematic diagram of our CVD system. In contrast to a recent report by Lee *et. al* [3] in which thermally evaporated Ni thin film on a SiO₂/Si substrate was heated by applying electrical current, a suspended Cu foil was Joule-heated. In this experiment, a constant current of 48.50 A was fed through Cu foil (15 mm width, 210 mm length, and 25 μm thickness) with a H₂ flow rate of 50 sccm during pre-annealing and 50 sccm H₂ and 20 sccm CH₄ under 1 Torr during the synthesis. The maximum heating and cooling rates were 45°C/s and -98°C/s, respectively as shown in Figure 2, which is approximately ten times faster than conventional thermal CVD [1] and comparable to flash cooling method [2]. It should be noted that the temperature of the Cu foil was estimated by using thermocouple and measuring the resistivity of Cu foil, and actual heating and cooling rates may be faster than aforementioned values. Additionally, these rates can be further enhanced by decreasing the thickness of the metal foil. The obtained graphene was coated with poly[methylmethacrylate] (PMMA) followed by Cu-etching and finally transferred onto a SiO₂/Si substrate for electrical measurements. The Hall mobility of the graphene after PMMA removal was 1000 cm²/Vs at sheet carrier concentration of 9.9×10^{12} cm⁻², yielding sheet resistance of 630 Ω/sq.

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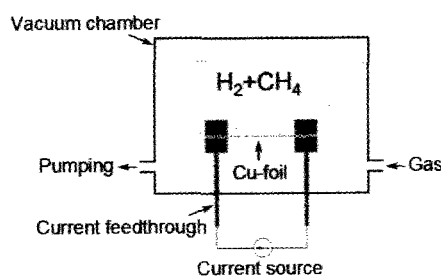


Figure 1. A schematic diagram illustrating CVD system utilizing direct Joule heating.

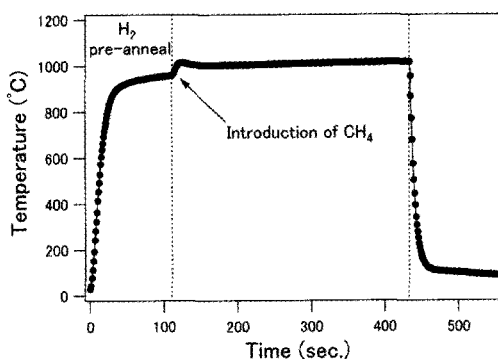


Figure 2. A typical temperature profile of Cu-foil showing rapid heating and cooling.

First-principles calculations of di-hydrogen on graphene

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Carbon nanomaterials have attracted much attention since they are candidates for post-silicon devices materials. Since hydrogen is a common impurity in graphene [1-3], it is important to clarify how the hydrogen impurity affects the electronic structure of graphene. By using first principles electronic-structure calculations, we study the di-hydrogen on graphene. We use 128-site supercell with the rectangle shape of the $17.04 \times 19.68 \text{ \AA}^2$ size. In geometry (a) [Fig.1 (a)], the nearest neighbor two hydrogen atoms are located on the same side and in geometry (b) [Fig. 1 (b)] the two hydrogen atoms are located on the opposite side. We find that two the hydrogen atoms located on the opposite side Fig 1 (b) has 0.60 eV lower energy than those of geometry (a) [Fig . 1(a)]. The stability of geometry (b) is due to the fact that the bond angle of H1-C1-C2 in Fig. 1. (b) is 107.78° and this bond angle is close to that of the sp^3 bond angle (109.5°). Both geometries are found to be nonmagnetic. In geometry (c), the second nearest neighbor two hydrogen atoms are located on the same side and in geometry (d) two hydrogen atoms are located on the opposite side. We find that geometry (d) has 0.10 eV lower energy than geometry (c). Both geometries are found to be spin-polarized.

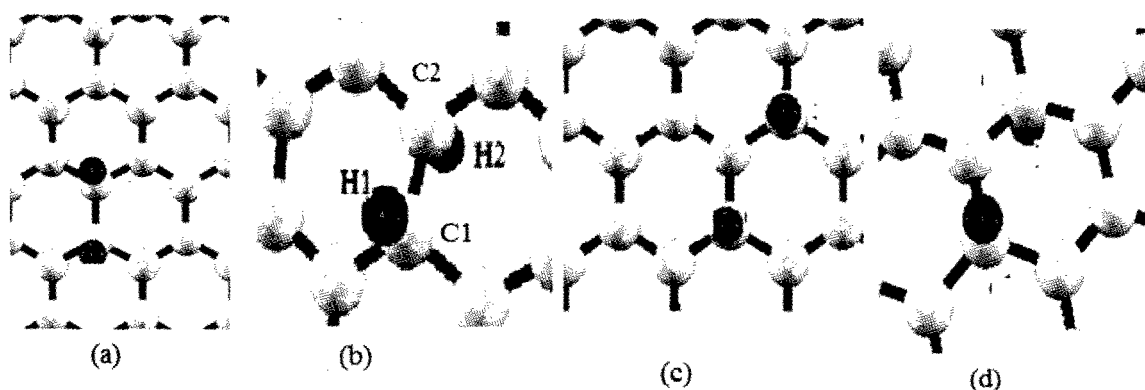


Fig. 1. Geometries of two hydrogen atoms on graphene.

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FT-IR study of electrical properties of graphene oxide and photoreduced graphene oxide

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Graphene oxide (GO) nanosheets are expected to be raw materials for the mass production of graphene nanosheets [1]. Several reduction techniques have been developed to remove oxygen-containing functional groups from GO nanosheets [2]. Matsumoto *et al.* reported that the electrical conductivity was improved by 10^5 - 10^7 times after mild photoreduction of GO nanosheets [3]. In their measurements, two-electrode systems were employed, in which the contact resistance could affect the observed resistivity greatly. In this work, we have investigated the electrical resistivity of GO and photoreduced GO (rGO) through photoreflexion measurements in the infrared region. The samples were deposited from water suspensions on filter papers using the vacuum filtration. Micro FT-IR reflection spectra were measured at several positions of the deposited films at room temperature. One of the spectra with the highest intensities in the GO sample or the rGO sample is shown in Fig. 1. Increase of reflectivity in the lower energy region was observed for both spectra, and is attributed to the free carrier absorption. As the onset energy of the increase is higher in rGO than in GO, it is expected that the conductivity of rGO is better than that of GO. We have applied the Drude model to analyze these spectra, and obtained the resistivity of 0.022 Ωm and 0.0072 Ωm for GO and rGO, respectively. This improvement in the resistivity was not as drastic as that observed in the transport measurements [3]. There is a possibility that the specific resistivity of these materials has been obtained in this work, evading the influence of the contact resistance.

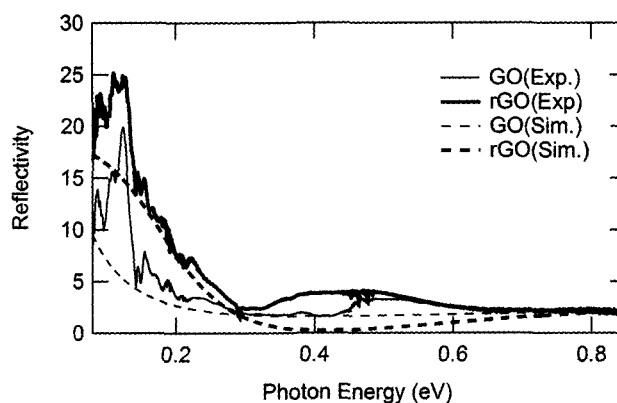


Fig. 1 Reflection spectra of GO and rGO films with respect to the photon energy. The Drude model was applied to simulate the reflection spectra.

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Synthesis of graphene oxide via electrochemical method

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Chemically modified graphene including graphene oxides, reduced graphene oxides (GO) and their derivatives have attracted lots of attention due to its solution processability. Several techniques have been developed for preparing graphene sheets. Especially, the production of GO was well documented by Hummers et al., where the graphite powders were oxidized in aqueous media [1]. Another way is a direct exfoliation method from expandable graphite[2]. These method is required strong oxidant or surfactant for preparation of graphene solution. Herein, we demonstrate highly efficient synthesis of graphene by exfoliation from expanded graphite, which can be easily scaled up for large-scale production.

Figure 1 shows an experimental setup, where grafoil (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. Acid(H_2SO_4 , HNO_3 , HCl) and their salts(Na_2SO_4 , NaNO_3 , NaCl , Na_2CO_3) was used as electrolytes. With a dc voltage of 4-10 V, the graphite electrode was quickly broken into small pieces and spread in the solution. After the exfoliation, the graphite pieces were directly filtered, washed with water and HCl , and then dried in a vacuum oven to obtain bulk powders of graphene oxide.

The morphologies of the bulk GO powders were analyzed by SEM (Figure 2). Not only large-sized but also small-sized graphene flakes are clearly visible. This means that the intercalation agent in the expanded graphite assisted to exfoliate graphene from the electrode during electrolysis.

In summary, GO sheets can be easily prepared by electrolytic exfoliation of expanded graphite sheet. This work provides an efficient approach to obtain a cost-effective and scalable production of graphene ink, which may pave a way toward future applications in flexible/printable electronics.

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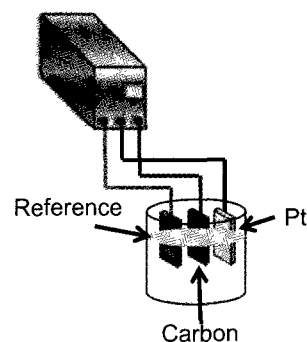


Fig1 diagram of the apparatus for synthesis of graphene oxide.

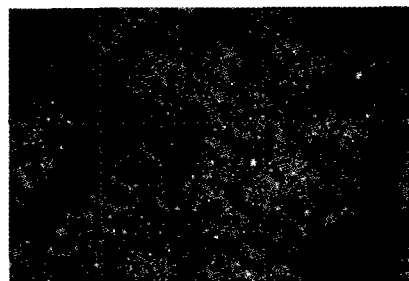


Fig2 SEM image of graphene oxide

Morphology and Electrochemical Properties of Carbon Nanosheets by Microwave Plasma Enhanced Chemical Vapor Deposition

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Plasma enhanced chemical vapor deposition (PECVD) is a popular technique in the synthesis of carbon-based nanomaterials, such as nanotubes of nanofiber [1], nanodiamond films [2], and graphene films [3], with high mass production at low temperature. Carbon nanosheets (CNSs, also named as carbon nanowalls etc.), which consists of two or a few layers of graphene nanosheets, have attracted great attention because of their excellent properties and promising applications. Previously, we demonstrated that the CNSs can be obtained by MPECVD technique at 450-500 °C using CH₄ and Ar as reaction gases [4]. The CNSs placed directly on the surface of glassy carbon electrode demonstrate faster electron transfer kinetics and simultaneously detect dopamine, ascorbic acid and uric acid with high selectivity and sensitivity. We also found that the flake size of CNSs depend on the CH₄ supplies [5]. In this study, we investigated relationship between the local morphology and electrochemical properties of CNS. The detailed results will be presented in the coming conference.

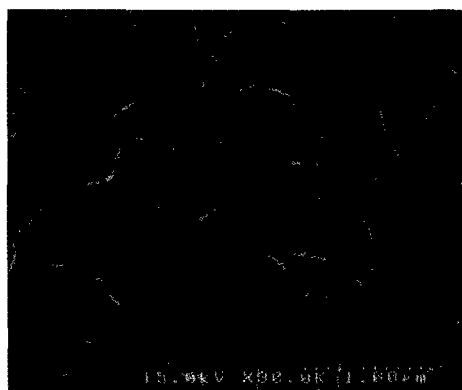


Fig. 1 A typical SEM image of CNSs grown by MPECVD with Ar (20 sccm) and CH₄ (5sccm) on the Cu substrate.

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Water Adsorption in Zeolite Templated Carbon

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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 $4000 \text{ m}^2/\text{g}$. A proposed model for ZTC is buckybowl-like nanographenes assembled into a three-dimensionally regular network^[1] Although this model is an ideal ordered structure, actual ZTC has been considered to have disordered or randomly oriented structures.

In this work, we carried out X-ray diffraction (XRD) experiments to clarify the structure of ZTC encapsulating water. For dry ZTC, two sharp Bragg peaks were found and they are indexed to (111) and (220) for a cubic lattice, as reported previously. (Fig.2(a)) When the ZTC was exposed to water vapor at room temperature, the (111) peak intensity was lowered drastically. We performed simulation of XRD patterns employing the structures obtained by molecular dynamics simulations in water-ZTC systems. The results showed that the (111) peak intensity varies depending on the amount of adsorbed water and also adsorbed sites of water. With detailed analyses, it was found that the observed decrease in (111) peak intensity corresponds to the adsorption of 140 wt% of water inside nanopores of ZTC.

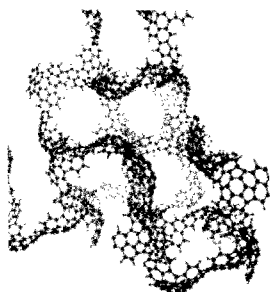


Fig.1 Possible structural model proposed for ZTC solid.^[1]

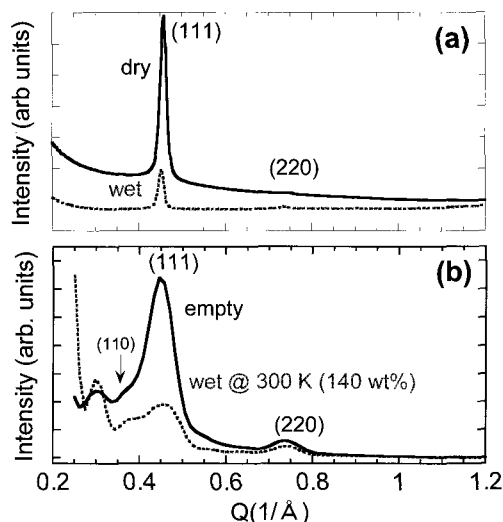


Fig.2 (a) Observed and (b) simulated XRD patterns at 300K. Black solid lines are for dry (empty) ZTC, while grey dashed lines for wet ZTC.

Reference: [1] H. Nishihara *et al.* Carbon **47**, 1220 (2009).

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Synthesis of TiO₂ nanotubes and C₆₀ doping

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Anatase type titanium dioxide, TiO₂, is well known as photocatalysts, and used widely for germicide, hydrophilic coating, solar energy conversion and dye sensitized electrode. TiO₂ nanotubes (TiO₂-NTs) can be prepared by refluxing anatase type TiO₂ powder in NaOH aqueous solution [1,2]. In the present study, we prepared TiO₂-NTs by using this hydrothermal reaction.

TiO₂-NTs were synthesized by adding 1.5 g of anatase type TiO₂ powder (Sigma-Aldrich ≥ 99 %, 325 mesh) to 100 ml of a 10 M aqueous solution of NaOH. This mixture was refluxed at 190°C for 12h. After cooling down to room temperature, the solution was neutralized by adding 2M of HCl and the products was settled down. Sucked up sediments was rinsed several times by distilled water and dried. The products in this stage include TiO₂-NTs and unreacted TiO₂ powder. In order to separate the nanotubes, 500 mg of the products was dispersed in 60 ml of ethanol by using ultrasonic horn agitation for 1h. Then the solution was centrifuged at 2000 G for 30 min and the supernatant was collected for the present study.

C₆₀ doing was carried out by two kinds of methods. One is the liquid phase and the other is vapor phase doping. In the former doping, TiO₂-NTs were dispersed in a toluene solution of C₆₀ and the mixture was directly spray coated onto the quartz plate. Prior to the vapor phase doping, TiO₂-NTs were heated at 400 °C in vacuum for 48 h and such heat treated TiO₂-NTs (HT-TiO₂-NTs) was spray coated on to the quartz plate. This spray coated HT-TiO₂-NTs were exposed to C₆₀ vapor at 400 °C for 48 h in a vacuum sealed glass ampoule. In Fig. 1, we show UV-vis-NIR spectra taken for liquid phase doped sample together with the spray coated films of undoped TiO₂-NTs and C₆₀. From this figure, it is obvious that no interaction between TiO₂-NT and C₆₀ was recognized, i.e., absorbance of TiO₂-NT/C₆₀ is just a superposition of each absorbance of TiO₂-NT and of C₆₀. While C₆₀ hot vapor exposed HT-TiO₂-NTs sample (Fig. 2) indicates enhanced absorbance in the region of ~500–1000 nm. This means that the charge transfer between HT-TiO₂-NT and C₆₀ modifies the band structure.

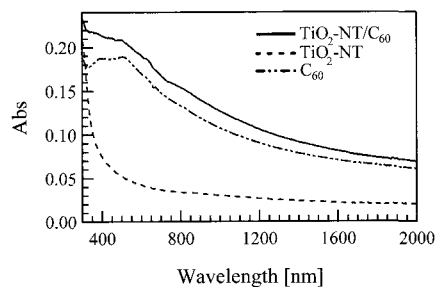


Fig. 1. UV-vis-NIR spectra of spray coated films using the solutions of TiO₂-NT/C₆₀, C₆₀ and TiO₂-NT.

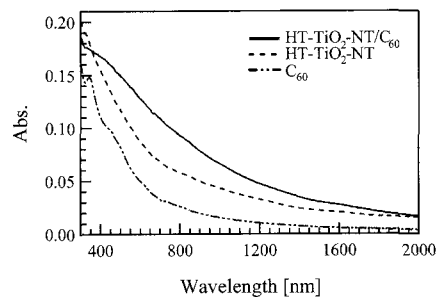


Fig. 2. UV-vis-NIR spectra of hot vapor doped HT-TiO₂-NT/C₆₀, HT-TiO₂-NT and vacuum deposited C₆₀.

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Hybrid Nanomaterials of Carbon Nanowalls and Single-Walled Carbon Nanotubes Fabricated by Helicon Plasma CVD

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Single-walled carbon nanotubes (SWNTs) have superior electrical properties and have attracted much attention, especially in the field of electronics such as field effect transistor (FETs). Carbon nanowalls (CNWs) are the nano carbon 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 nano carbon materials, and a successful fabrication of hybrid materials with SWNTs 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 nano carbon materials by helicon plasma chemical vapor deposition (CVD). Based on this background, we attempt to fabricate a novel hybrid nanocarbon material with SWNTs and CNWs (CNWs/ SWNTs) by helicon plasma CVD. Produced materials are characterized by scanning electron microscopy (SEM) and a vacuum probe station under the FET configuration. It is revealed that there is no any CNWs on the SiO₂ surface after the helicon plasma CVD, whereas CNWs are grown on the surface of SWNTs. This indicates that SWNTs enhance the nucleation of CNWs growth. We carry out an electrical transport measurement for the same SWNTs-FETs device before and after the growth of CNWs. SWNTs-FETs are fabricated by forming source and drain electrodes (Au) on the top of SWNTs films using photo-lithography. Figure 1 shows typical source-drain current (I_{DS}) vs. gate bias voltage (V_G) characteristics of before (a) and after (b) the CNWs growth. Coulomb oscillation like features appear after the CNWs growth (b), which indicates CNWs might play a role as a Coulomb dot in this system.

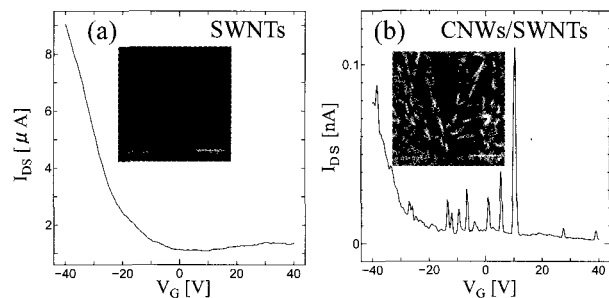


Figure 1: Electric characteristics (Room temperature) of SWNTs-FET before (a) and after (b) the CNWs growth.

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Influence of Surfactants on the formation of Semiconducting SWCNT Thin films towards FET applications

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Thin film transistors (TFT) using single wall carbon nanotubes (SWCNTs) have attracted a remarkable attention because of their excellent transport properties. Recent advances in the metal/semiconductor separation realized high-purity semiconducting SWCNTs in large quantity [1]. Now we can easily prepare SWCNT-TFTs using solution processes without any additional process such as electrical breakdown. However, SWCNT thin-film preparation process has not been well established yet. Although there are many candidates of surfactants for aqueous dispersion [2,3], we don't know how each surfactant molecules affect the transport properties of SWCNT-TFTs.

In this work, we are first focusing on four kinds of surfactants, such as sodium dodecyl sulfate (SDS), sodium cholate (SC), sodium deoxycholate (DOC), and sodium dodecylbenzene sulfonate (SDBS) for the thin film formation of solution processed SWCNT-TFTs. Semiconducting SWCNTs separated by gel chromatography method were used. S-SWCNTs Thin films were prepared by dropping a semiconducting SWCNT solution on the surface of SiO₂/Si substrate functionalized by self assembled monolayer of aminopropyltriethoxysilane (APTES). Following nitrogen gas blow and rinsing formed a thin film on the substrate. Although the optimum preparation parameter should depend on the surfactant, we adopted the same procedure for all the surfactants to see the difference in the resultant morphology in thin films.

Figure 1 shows atomic force microscopy (AFM) images for (a) SDS, (b) SC, (c) DOC, and (d) SDBS. Different network topology was clearly observed for each AFM image. SDS formed thick bundled network, while SC formed random network of thin bundles or isolated SWCNTs. In the case of DOC and SDBS, the formation of thin film was unstable. In the presentation, detailed transport properties will be discussed.

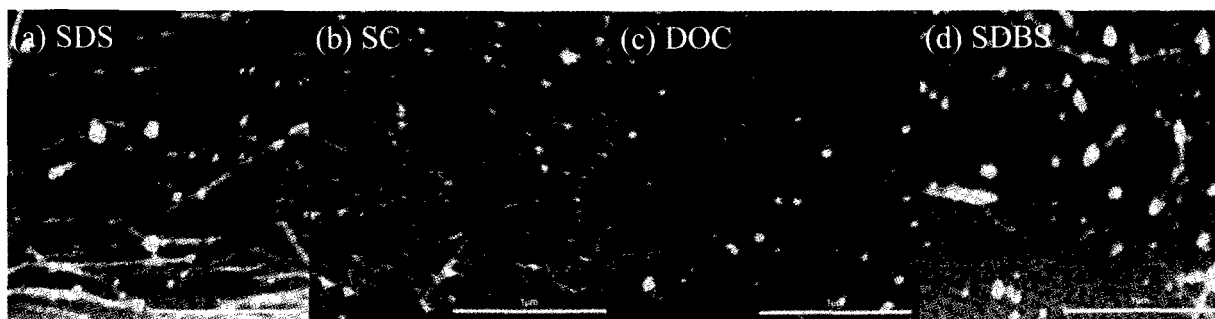


Fig.1 AFM images of the thin films. (a) SDS (b)SC (c)DOC (d) SDBS (Scale bar, 1 μ m.).

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Effect of Chemical Oxidation on the Physicochemical Properties of Double-walled Carbon Nanotubes

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Recently, double-walled carbon nanotubes (DWNTs) have attracted a great deal of attention in their specific optical properties and possible technological applications in various fields of science because of the possession of advantageous features of both single-walled carbon nanotubes (SWNTs) and multi-walled carbon nanotubes (MWNTs), such as electric and thermal stabilities. We have attempted to fabricate a novel field effect transistor (FET) type biosensor with a high sensitivity using DWNTs obtained from Toray Industries, Inc., whose outer wall were modified by chemical oxidation. We succeeded to develop an ultrasensitive biosensor for 250aM bovine serum albumin (BSA) solution, in spite of the unspecific substrate. In order to gain an insight into the fabrication of an ultrasensitive biosensor for specific substrate, we investigated the effect of the chemical oxidation on the physicochemical properties of DWNTs with various spectroscopic techniques and DLS. DWNTs were modified with mixed acid (sulfuric acid : nitric acid=3:1). Then, the mixture was heated and refluxed at 40-80°C for 3-12 hours. The characterization of chemical oxidized DWNTs was made with resonance Raman spectral measurements and UV-vis-NIR absorption/photoluminescence (PL). The functional groups of the surface were characterized by Fourier transform infrared spectroscopy (FTIR), and the amount of carboxyl groups were determined by neutralization titration. As a result, the amount of carboxyl groups of surface was dependent on treatment temperature and time. The detailed results including the structural characteristics of DWNTs will be presented and discussed in the Symposium. At a present, further studies are in progress with regard to a modification of ligand molecule with a high affinity for specific substrate.

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Synthesis of Multi-Walled Carbon Nanocoils by CVD with Catalyst of Fe-Supported Zeolite Thin Film on Cu Foil

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Multi-walled carbon nanocoils (MWCNCs) have been successfully grown using co-deposited Sn/Fe catalysts supported on zeolite and MCM-41 by chemical vapor deposition (CVD) [1]. For applications, synthesis for high yield of MWCNCs still remains unresolvable. It was reported that Zn/Cu catalyst was efficient for synthesis of CNC [2]. In this study, Fe-supported zeolite was deposited on Cu foil instead of Sn/Fe catalyst to produce Fe/Cu alloy during CVD synthesis of MWCNCs. Acetylene was used as a source gas with 20 ml/min of flow rate for 10 min. SEM micrographs of MWCNCs with Fe-supported zeolite/Cu and Fe-supported zeolite/Sn/SiO₂/Si (for comparison) were shown in Fig. 1. MWCNCs were successfully synthesized using Fe/Cu catalyst and the yield of MWCNCs seems almost the same as the Fe-supported zeolite/Sn/SiO₂/Si substrate.

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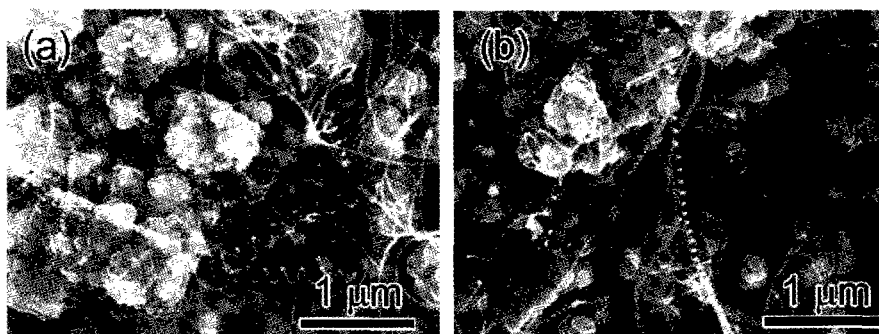


Fig. 1 SEM micrographs of MWCNCs synthesized by
(a) Fe zeolite/Cu and (b) Fe zeolite/Sn/SiO₂/Si

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High density growth of horizontally-aligned SWNTs and methane concentration dependence

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The increase of the density of horizontally-aligned single-walled carbon nanotubes (SWNTs) is an important task for electronic applications, because the high nanotube density is useful for high-current device operation. Horizontal alignment has been demonstrated on quartz (SiO_2) and sapphire ($\alpha\text{-Al}_2\text{O}_3$), which is explained by anisotropic SWNT-substrate interaction. The density of aligned SWNTs reaches up to 40 tubes/ μm on quartz [1], while that on sapphire is still ~ 10 tubes/ μm [2]. For further improvement of nanotube density, understanding the growth mechanism and behavior of the catalyst metal is important.

We found that scratching the sapphire surface with metal wires gave aligned SWNTs very easily. The SWNT yield was strongly dependent on the metal wire: Co and Fe wires gave high-dense aligned SWNTs, while Ni, Au, and Mo showed a low catalytic activity. In the previous literature of the needle scratching method, it was proposed that the scratched substrate itself acts as a catalyst for the SWNT growth [3]. Our study suggests that the metal nanoparticles scattered from the metal wire act as the catalyst. From the systematic study of growth conditions, high density (~ 20 tubes/ μm) was realized by Co wire, when pure CH_4 (100%- CH_4) was introduced into the CVD chamber. Figure 1 shows the effect of the CH_4/H_2 ratio. Contrary to our previous study [2], high-dense nanotubes were grown without adding H_2 . We will discuss the formation of metal nanoparticles and the observed CH_4 concentration dependence.

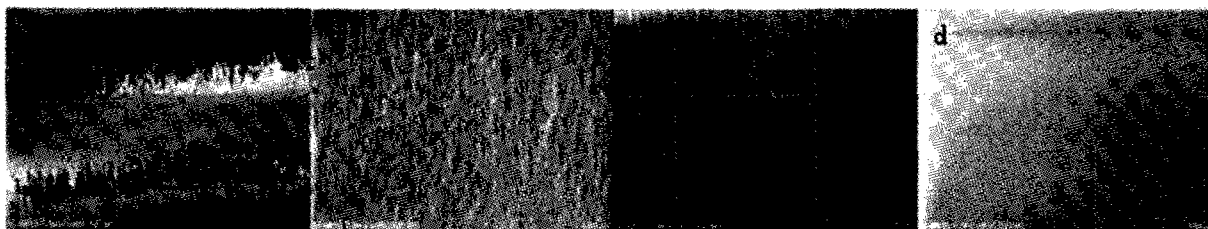


Figure 1 SEM images of SWNTs grown on sapphire r-plane scratched with a Co wire. The CH_4 concentration is (a) 100%, (b) 74%, (c) 50% and (d) 37%. Total $\text{CH}_4\text{-H}_2$ flow rate was fixed to 380 sccm.

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Synthesis of Single-Walled Carbon Nanotubes by Double-beam Laser Ablation Method

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We developed the novel equipment for synthesis of single-walled carbon nanotubes (SWNTs), called double laser ablation (DLA) method. The two targets were ablated at the same time by the incident double YAG lasers, as shown in figure 1. The YAG laser was split to two lasers and the targets, set with the angle of 30 degrees between targets, were ablated. A carrier gas was flowed from the back of the targets. The generated plumes were merged and ablated carbons and/or catalysts traveled to the way to the heated space. In this system, there are two noticeable . One of those is that an ablated materials are not able to re-deposit on the target, the other is that the carbon and catalysts targets are selected identically.

Table 1 shows synthesis condition. The laser was irradiated and synthesized for 20 minutes on this condition.

Figure 2 show the Raman spectra with excitation laser of 532nm. The figures show G-band in 1582 cm^{-1} and D-band in 1350 cm^{-1} . In addition, there is a peak thought to be RBM around 273 cm^{-1} .

It is thought that the synthesis of CNT is possible by the equipment made this time.

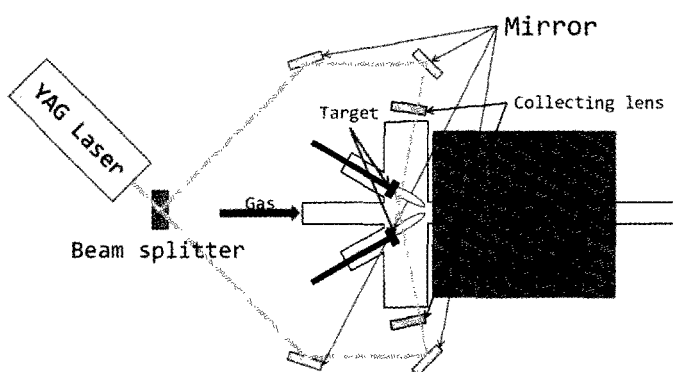


Fig 1. The new equipment figure

Table 1. Synthesis condition

Heater temperature (°C)	1000
Pressure (kPa)	66.6
Carrier gas	Ar
Flow quantity (ccm)	100
Laser	YAG
Laser wavelength (nm)	532
Fluence (J/cm^2)	2
Pulse repetition rate (Hz)	10
Target	Graphite
Catalyst	Ni,Co 2wt%

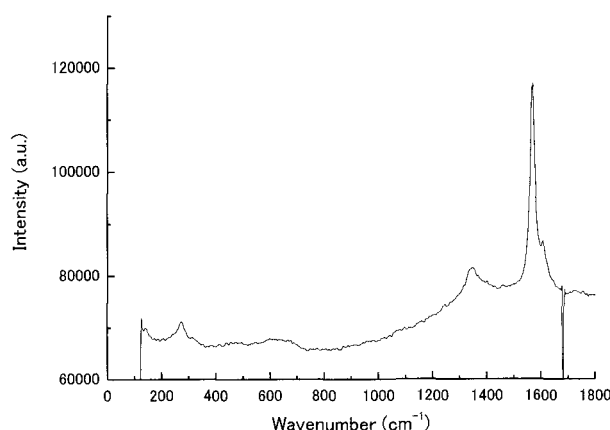


Fig 2. Raman excitation wavelength of 532nm.

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Effect of Thickness of Top Al_2O_3 Layer in Multilayer Catalyst on Growth of Aligned Carbon Nanotubes Combined with Graphite Roof

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In this study, carbon composite structure was synthesized from a multilayer catalyst of iron (Fe) and aluminum oxide (Al_2O_3) by chemical vapor deposition (CVD). The purpose of this study is to synthesize a long and aligned carbon nanotubes (CNTs) enough for various applications. The structure of multilayer catalyst was similar to Ref. 1. Firstly, Al_2O_3 film was deposited on silicon (Si) substrate with a silicon dioxide layer by vacuum evaporation with $\phi 0.2$ mm-Al-wire. Thickness of Al_2O_3 film was assumed to be proportional to the volume of the Al-wire. Next, Fe film was formed on the substrate by spin coating of 3% Fe_2O_3 solution and calcined in the air at 400°C . The CVD equipment used was developed in our laboratory [2]. Acetylene (C_2H_2) and nitrogen (N_2) gases were used as source gas and dilution gas, respectively. The structure was synthesized at 780°C .

Fig. 1 shows the aligned carbon nanotubes with graphite roof [3]. Fig. 2 shows the effect of top Al_2O_3 film thickness on the growth rate of the CNTs. Slope of the growth rate on synthesis time as shown in Fig. 2 became to be gentle, as the top Al_2O_3 film became thicker. The tallest structure with a height of approximately $900\text{ }\mu\text{m}$ was obtained. Thickness of the graphite roof was approximately $0.5\text{ }\mu\text{m}$.

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

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Fig. 1 Aligned carbon nanotubes with graphite roof.

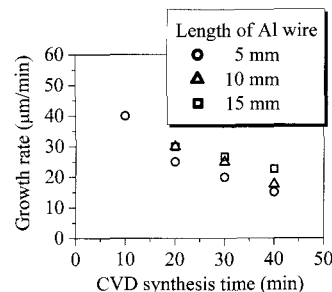


Fig. 2 Effect of top Al_2O_3 film thickness on growth rate of CNTs.

Effect of Sn Film Thickness on the Purity of Carbon Nanocoil Grown by CVD

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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. $\text{Sn}(\text{CH}_3)_4$ was used as a Sn catalyst and was mixed with ethanol. Though CNC was synthesized at $\text{Sn}(\text{CH}_3)_4$ concentration of 0.2% [1], purity of CNC was about 10%. In this study, in addition to $\text{Sn}(\text{CH}_3)_4$, Sn-deposited substrate was used for CNC synthesis. Si was used as a substrate and Sn film was deposited on Si substrate with an oxide layer by vacuum evaporation. Fe_2O_3 catalyst was dropped on Sn/SiO₂/Si substrate. This substrate was calcined in the air for 5 min at 400°C. The other conditions were the same as that in our previous study [1]. The concentration of $\text{Sn}(\text{CH}_3)_4$ in ethanol was fixed at 0.2%. Sn film thickness was changed from 0 to 60 nm. Purity of CNC was determined by the ratio of CNC and carbon nanofiber (CNF). Fig. 1 shows the purity of CNC on surface at different Sn film thicknesses. As the Sn film became thicker, the purity was improved. The purity became lower when Sn film was too thick. Fig. 2 shows scanning electron microscopy (SEM) micrographs of cross-section of the carbon deposition on 40-nm-Sn film. The purity of CNC with $\text{Sn}(\text{CH}_3)_4$ supply was higher than that without the supply.

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

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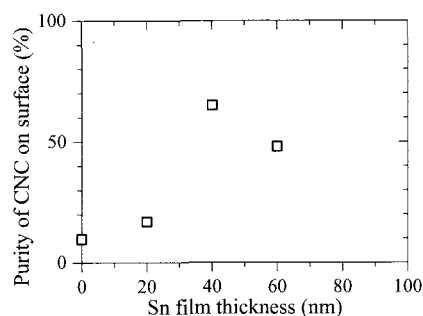
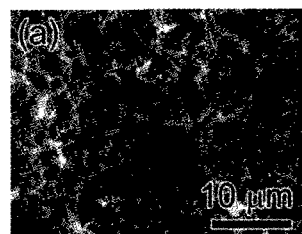
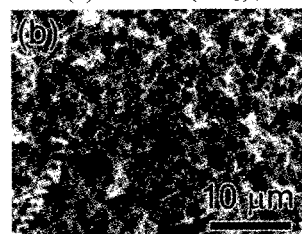


Fig. 1 Purity of CNC on surface at different Sn film thicknesses.



(a) With $\text{Sn}(\text{CH}_3)_4$



(b) Without $\text{Sn}(\text{CH}_3)_4$

Fig. 2 SEM micrographs of cross-section of carbon deposition on 40-nm-Sn.

Toward the production of SWNT with a single chirality -Effect of foreign gas pressure-

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Controlling chiral distribution of single walled carbon nanotubes must be one of the most important issues to be pursued for the potential applications of SWNTs to nano-electronic, nano-optoelectronic as well as bio-electronic nano-devices, because the characteristics 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 definitely to develop a method that would allow the growth of SWNTs with a single chirality. In the earlier study by our research group, we have demonstrated that very narrow diameter distribution was realized by the laser vaporization of graphite with Rh/Pd catalyst in He atmosphere, in which He was believed to work efficiently on the growth of carbon nanotubes, particularly, from view point of “*selective production of specific chiralities*”. The presence of foreign gas is thought to be necessary not only for cooling very hot laser ablated carbon vapor materials (might be related to initial cap formation) but also for feeding hot atmosphere to keep continually the growth of nanotubes (related to the growth of the tube length direction).

In the present work, we will demonstrate some experimental results on how the foreign gas plays a role on realizing very narrow size distribution and why He gas atmosphere work on the growth of specific carbon nanotube with a single chirality. We have systematically changed gas pressure under different furnace temperature and the resulting soot materials were examined by optical absorption spectra after initially dispersed in SDBS/H₂O solution and filtered by 15000g centrifugation. Typical example is shown in Fig.1, where the absorption spectra prepared at different pressure condition are compared.

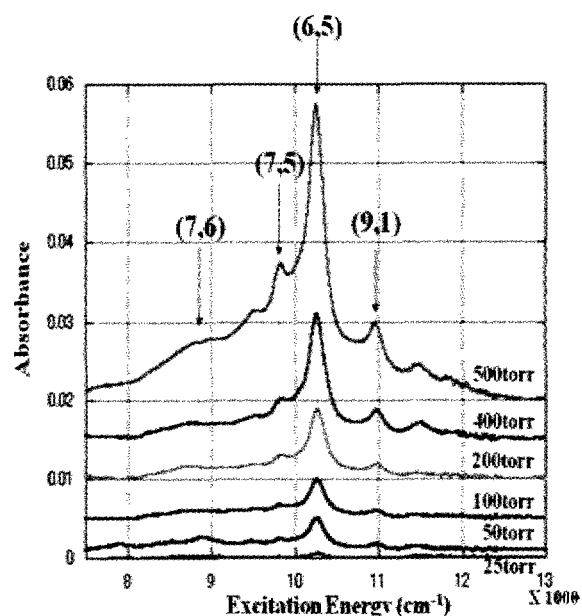


Fig.1 Absorption spectra in the E₁₁ energy region of semiconducting SWNTs by changing He pressure from 2500 torr to 500 torr .

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Sequential Formation of Catalyst Particles and Single-Walled Carbon Nanotubes in Floating Catalyst System

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Chemical vapor deposition (CVD) method is now widely used in producing single-walled carbon nanotubes (SWCNTs). SWCNTs can be synthesized either on substrates by supported catalysts or in the gas-phase by floating catalysts. The latter method is advantageous in continuous operation, which can be easily realized by feeding both sources for SWCNTs and catalysts simultaneously [1,2]. However, this simultaneous feeding causes inherent contamination of catalysts in SWCNTs, and therefore it is important to enhance the catalytic performance and reduce the amount of the floating catalyst particles based on their better understanding.

In this study, floating catalyst Fe particles were formed by thermal decomposition of ferrocene ($\text{FeC}_{10}\text{H}_{10}$) vapor and SWCNTs were grown from C_2H_2 . Two types of experiments, i.e. simultaneous feeding and sequential feeding of $\text{FeC}_{10}\text{H}_{10}$ and C_2H_2 were performed. In the former experiments, $\text{FeC}_{10}\text{H}_{10}$ and C_2H_2 were fed simultaneously from the inlet of the reactor just like ordinary gas-phase synthesis of SWCNTs. In the latter experiments, on the other hand, only $\text{FeC}_{10}\text{H}_{10}$ was fed from the inlet and C_2H_2 was fed at 0, 5, 7, 9, 11 cm from the inlet of the furnace using a narrow inner tube. The aim of sequential feeding is separate control of catalyst and SWCNT formation. Morphology and diameter of the product were analyzed mainly by scanning and transmitting electron microscopes (SEM and TEM) and Raman spectroscopy (Figs. 1 and 2). Computational fluid dynamics was also conducted to simulate the heating and mixing of gases and decomposition of $\text{FeC}_{10}\text{H}_{10}$. We found that addition of C_2H_2 just after $\text{FeC}_{10}\text{H}_{10}$ decomposition maximizes the catalyst performance to yield SWCNTs. Detailed mechanism of catalyst particle formation and SWCNT formation will be discussed.

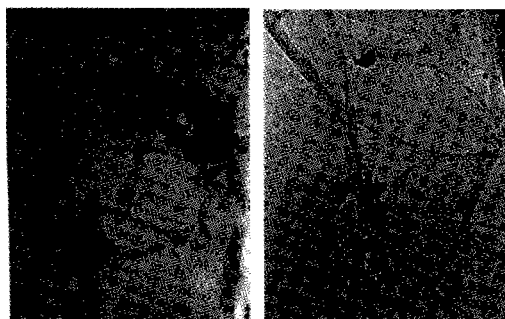


Fig. 1. TEM images of SWCNTs synthesized by simultaneous (left) & sequential (right) feeding.

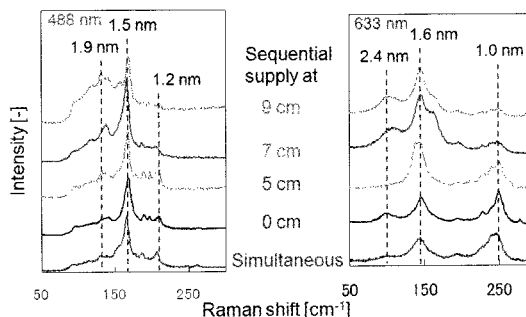


Fig. 2. Raman spectra of SWCNTs synthesized by feeding C_2H_2 at different positions.

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Synthesized carbon nanotube by liquid phase pulsed arc using metal electrode: Optical emission spectrometry on arc plasma in liquid

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Carbon nanotubes (CNTs) are distinctive in their mechanical, chemical, and physical properties; hence, they are considered a promising next-generation carbon material, for example, nanowires, polymer composite materials, secondary cell electrode materials, field emission devices and biosensor elements.

CNTs are synthesized by vacuum arc discharge, laser ablation, and chemical vapor deposition (CVD). However, these methods are generally very expensive and complex equipment. In contrast, electrical arc discharge in water is particularly simple and cost-effective because it does not require vacuum devices. In almost all of the researches employing arc discharge in liquid phase, CNTs produced are composed of carbon atoms supplied from the graphite electrodes. Then we have previously demonstrated novel producing the shorter and high-crystallinity CNTs with liquid xylene as a carbon supplier. However, the sample contains a high proportion of carbon impurities and metal particles. Moreover, The CNT growth mechanism is uncertain in this method.

Here we report that the CNT growth on the electrode surface depend on the arc duration time, repeat count of pulsed arc discharge and liquid description. In addition, we investigate liquid phase plasma with optical emission spectrometry analysis. Schematic diagram of experimental apparatus and Typical emission spectrum shown in Figure 1 and Figure 2.

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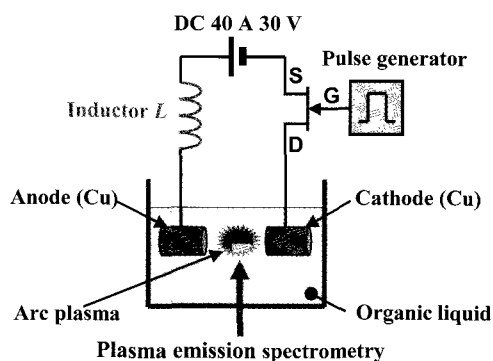


Fig. 1 Schematic diagram of the experimental set up used for pulsed arc discharge in Organic liquid using copper electrodes.

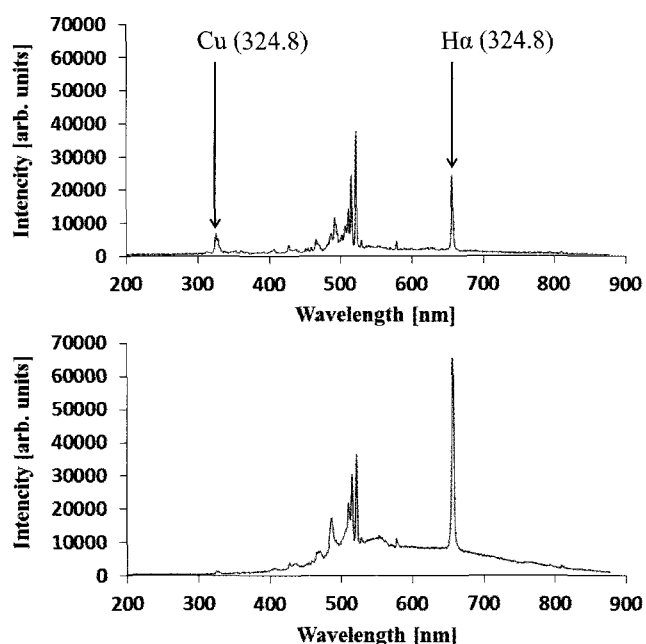


Fig. 2 Typical emission spectrum of liquid phase pulsed plasma (a) arc in ethanol, (b) arc in o-xylene.

**Fabrication of micro-electrodes on carbon nanotubes
using a shadow mask method**

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Single-walled carbon nanotubes (SWCNTs) show metallic or semiconducting properties depending on chirality, and various applications using SWCNTs are expected, such as nanowiring, probes for scanning probe microscopes, single molecule field effect transistors, and so on. In order to develop electrical devices using CNTs, it is necessary to investigate the electrical transport properties of an individual CNT. Usually, when we investigate the electrical transport properties of CNTs, we need to dissolve CNTs to solvent before the fabrication of electrodes. And EB lithography technique is used to fabricate electrodes. Some chemicals used during these processes can contaminate CNTs. Since CNTs are very sensitive to surrounding environment, this contamination may change the properties of CNTs [2]. In this study, we have developed the technique to fabricate electrodes without contamination.

CNTs were synthesized by a thermal chemical vapor deposition method on SiO₂ substrate. In order to fabricate electrodes on CNT, we use the shadow mask technique referring to Uchihashi's report [1]. The Ti film with the thickness of 2 μm was used as a shadow mask. Small patterns were etched on the Ti mask, using focused ion beam (FIB). This Ti mask was placed on a SiO₂ substrate and Pd was evaporated. After removing the mask, patterned electrodes were formed on the SiO₂ substrate. In the presentation, I will discuss the detail of this technique.

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Transient thermal response of an individual multiwall carbon nanotube

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Transient properties are important for practical application of multiwall carbon nanotubes (MWNTs). In this study, we propose the measurement method of transient thermal response of an individual MWNT under the Joule heating.

An individual MWNT was suspended between Pt electrodes with a $2\sim 3\ \mu\text{m}$ gap fabricated on the quartz substrate, where the quartz layer below MWNT was etched to fabricate the suspended structure. To improve the contact resistance, we evaporated Pt on the contact of MWNT. In order to investigate the transient thermal response, the voltage pulse with the width of $100\ \text{ns} \sim 10\ \text{ms}$ was applied to the suspended MWNT in the vacuum. The optical emission spectra of the suspended individual MWNT under the pulsed current flow were measured by an optical-microscopic spectroscopy system. Corresponding temperature was determined from the fitting of the measured spectrum to the Planck's black body radiation law. According to the Stefan-Boltzmann law, the emission intensity is directly proportional to the T^4 , where T is the temperature of the MWNT. As a result, the observed emission spectrum corresponds to not the average temperature but the highest temperature during the transient state. In the steady state, the temperature is almost proportional to the input power as shown in Fig. 1. A thermal conductivity of the MWNT is estimated to be $124\ \text{W/m-K}$ from the slope, the length ($\sim 2.5\ \mu\text{m}$) and the cross section of the MWNT. Using this thermal conductivity, the finite element method (FEM) calculation with the ideal boundary condition revealed that the suspended MWNT shows the response time of $\sim 40\ \text{ns}$ for the temperature response. Figure 2 shows the pulse width dependence of the measured temperature, where the duty ratio of all of the pulse width was 20% and the applied voltage was $2.48\ \text{V}$. The temperature increases with increasing the pulse width and is almost saturated at the pulse width of $1\ \mu\text{s}$ around $1200\ \text{K}$. This implies that the temperature of the suspended MWNT follows well to the electrical pulse within the time constant of $\sim 100\ \text{ns}$. This time constants are comparable to the time constants calculated from the FEM calculation. The transient response of the temperature less than $100\ \text{ns}$ was successfully measured by the proposed pulse voltage method.

Acknowledgements This work was partially supported by Grants-in-Aid for Scientific Research of Japan Society for the Promotion of Science.

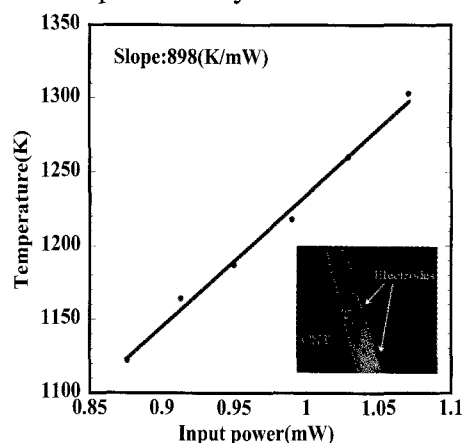


Fig.1 Input power dependence of the steady state temperature
For the MWNT and the OM image of the light emission

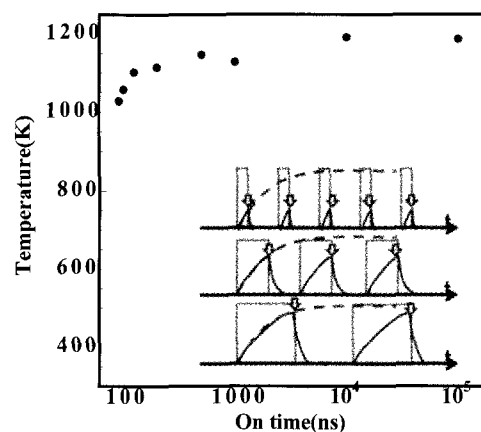


Fig.2 Pulse width dependence of the temperature
and timing chart for transient response.

First-principles calculation of adatom-vacancy pair on carbon nanotubes

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It is found that in single-walled carbon nanotubes (CNTs), probing with a tip of scanning tunneling microscopy induces a defect at 95K. [1] Meanwhile, a hydrogen thermal desorption spectroscopy shows that defects which are considered to be adatom-vacancy pairs are healed at around 44~70K. [2] We study the healing barriers of adatom-vacancy pair by using first-principle calculations which are based on the spin-polarized generalized gradient approximation (GGA) implemented in the code PHASE [3]. We use the 128-site supercell for graphene and the 160-site supercell for (5, 5) armchair edge CNT.

We carry out calculations of graphenes (Fig.1(a)) and CNTs (Fig.1 (b) and (c)). In graphene, the formation energy for the adatom-vacancy pair is 9.83 eV. In the CNTs, we study the two geometries (Fig.1 (b) and (c)) and find that the geometry in Fig1 (b) is the most stable. The bond length of five-member ring (the C₁-C₂ bond length in Fig.1(a)) in graphene is 1.85 Å whereas the length in Fig. 1(b) is small (1.61 Å). The healing barrier in graphene (Fig.1 (a)) is 0.06 eV, which is much smaller than that in the CNT (Fig.1 (b)) (0.49 eV). We find that this difference between the healing barriers in the graphene and CNT is related to the bond length of the five-member ring.

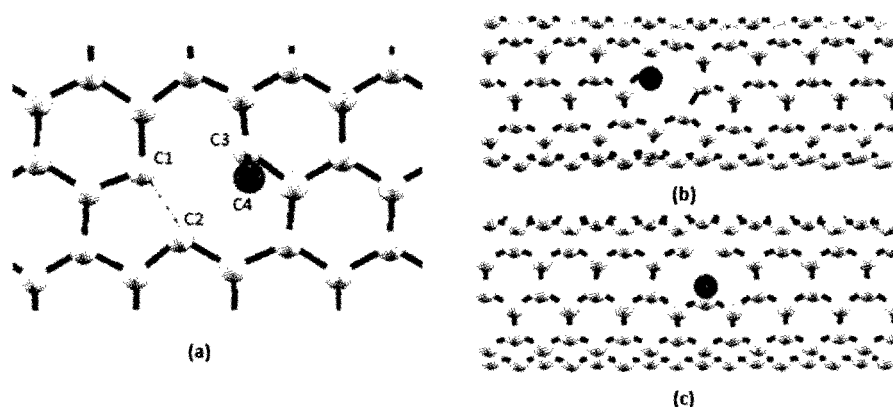


Fig.1 Geometries of graphene and CNTs with adatom-vacancy pair defect

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Comparison of Elongation Characteristics between As-Grown and Graphitized Carbon Nanocoils

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Carbon nanocoil (CNC) is predicted to have a high mechanical strength, and we focus on the elongation of CNC. In this study, we compared the extension between as-grown and graphitized CNCs. Graphitized Carbon nanofiber has been reported to have a high crystallinity [1]. A CNC was picked up by the focused ion beam (FIB) probe and its bottom was attached to a Si substrate by the Pt ion beam (Acceleration voltage: 30 kV, beam current: 30 pA). Then, we observed the elongation and fracturing of CNCs by gradually changing the height of Si substrate in the FIB chamber. Fig. 1 shows scanning ion microscopy (SIM) micrographs of as-grown CNCs for (a) free length and (b) stretched. Table 1 shows experimental results of the extension of 6 as-grown CNCs and 6 graphitized CNCs. In Table 1, the stretch ratio per unit turn of as-grown CNCs was on an average of around 125%, a little bit higher than that of graphitized CNCs of around 120%. From these results, we found that as-grown CNCs were stretched more than graphitized CNCs.

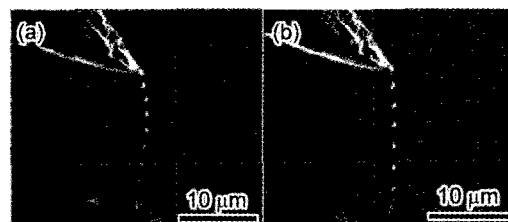


Fig. 1 SIM micrographs of as-grown CNCs for (a) free length and (b) stretched.

This work has been partly supported by the Research Project of the Venture Business Laboratory from Toyohashi University of Technology (TUT); Global COE Program "Frontier of Intelligent Sensing" from the Ministry of Education, Culture, Sport, Science and Technology (MEXT); Core University Programs (JSPS-CAS program in the field of "Plasma and Nuclear Fusion") from the Japan Society for the Promotion of Science (JSPS); and Grand-in-Aid for Scientific Research from the MEXT, The Hori Sciences and Arts Foundation, Tokai Foundation for Technology, and Research Foundation for Materials.

Table 1. Comparison of extension ratio between as-grown and graphitized CNCs.

		Coil free length (μm)	Fiber diameter (μm)	Number of effective turns	Stretch ratio (%)	Stretch ratio per unit turn (%)
As-grown	Average	12.2	0.5	6	120	125
CNC	Standard deviation	4.8	0.1	2	10	10
Graphitization	Average	10.8	0.4	7	110	120
treated-CNC	Standard deviation	3.6	0.1	3	10	15

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Chirality-dependent coherent phonon amplitudes in carbon nanotubes: a closer look to the electron-phonon interaction

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Ultrashort laser pulse pumped to a single wall carbon nanotube (SWNT) sample can induce photo-excited carriers which appear at the same time in the excited states of the SWNT. Before recombination of the electron-hole pairs, the lattice starts vibrating coherently by an electron-phonon interaction in the same phase through a process known as coherent phonon spectroscopy. Coherent phonons in SWNTs were first observed experimentally by Gambetta *et al.* [1]. Following this work, Lim and Kono *et al.* performed some experiments to understand the mechanism behind the coherent phonon generation [2,3]. Recently they could also observe that depending on (n, m) chiral indices and resonant excitation energies some SWNTs start coherent vibrations of their radial breathing mode (RBM) by increasing their tube diameters (expansion), while some others start vibrating by decreasing their diameters (shrinkage).

In a previous study, Sanders *et al.* (PRB 79, 205434, 2009) simulated the coherent phonon dynamics in SWNTs and phenomenologically reproduced the experimental SWNT coherent phonon vibrations. However, the reasons for the SWNT diameter expansion or shrinkage were not clearly discussed. In the present work [4], using an effective mass theory for the electron-phonon interaction, we find that such phenomena simply originate from the 1D Brillouin zone properties of each SWNT type or family, i.e., the position of the cutting line with respect to the K-point of the 2D Brillouin zone of graphene. Furthermore, we calculate the coherent RBM phonon amplitudes for many SWNTs with diameters in the range of 0.7-1.1 nm, which are mapped as a function of (n, m) for optical transition energies E_{11} or E_{22} found within the range of 1.5-3.0 eV. Based on this map, we then discuss the chirality dependence of the coherent phonon amplitudes. The map should also be useful as a guide for experimentalists to predict the SWNT lattice behaviors in response to the ultrafast excitation.

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Diameter dependent structure and properties of Eu Atomic wires inside Carbon Nanotubes

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Atomic wires, which are ultrathin nanowires with a diameter corresponding to one to several atoms, have attracted wide research attentions because of their unique electronic structures and properties arising from their unique one-dimensional nano-structures[1]. However, the experimental characterization of electronic structure of such atomic wires has not well-established yet because they are quite unstable due to their high surface energy originating from large superficial area. To overcome this problem, we fabricated atomic wires inside carbon nanotubes (CNTs) which protect the atomic wires from oxidation and disintegration. Here, we synthesized Eu atomic wires with a diameter-selective way, and compared each of those structure, electronic states and magnetic properties.

We synthesized Eu atomic wires inside CNTs by the procedures reported previously [2]: vacuum sealing of cap-opened CNTs and Eu in a Pyrex glass under 10^{-4} Pa followed by heating at 823 K for 2 days. The diameter of such Eu atomic wires strongly depends on the diameter of CNTs. When we used single-wall CNT ($\phi \sim 1.8$ nm), 9 channel atomic wire was formed (Fig.1, left), whereas double-wall CNT prefers to encapsulate a single-channel nanowire of 0.8 nm across (Fig.1, right). As clearly seen in the TEM images, the structure of Eu atomic wires are significantly different from that of bulk Eu crystals. Furthermore, from electron energy-loss spectroscopy (EELS) measurement, we confirm that the spectrum of Eu atoms inside double-wall CNTs (Fig.2, blue) differs considerably from that of reference Eu^{3+} of Eu_2O_3 (Fig.2, red), suggesting that reactive Eu nanowires can survive without oxidation due to total encapsulation by CNTs.

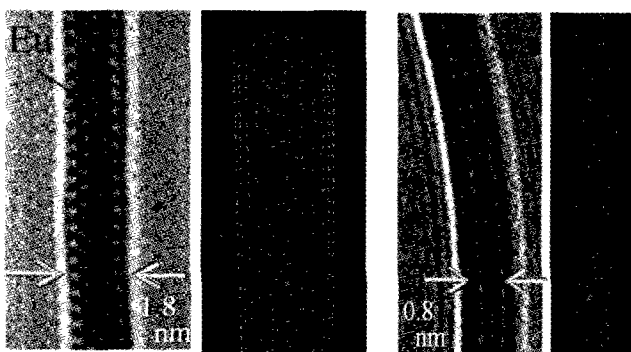


Fig. 1 TEM images and structure models of atomic wire inside single-walled CNT (left) and double-walled CNT (right).

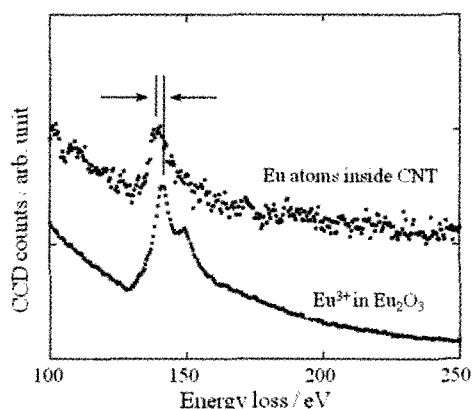


Fig. 2 EELS spectra of Eu atomic wire inside CNT (blue) and Eu^{3+} in reference Eu_2O_3 (red).

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Visible light emissions from nanocarbon fragments

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Depletion of fossil fuels and desirability of low CO₂ emissions have heightened the need for efficient lighting device with low energy consumption. Light emitting diodes (LEDs) have attracted much attention from the above-mentioned point of view. In order to propagate the LED light, a class of stable, efficient, inexpensive, high color rendering performance, and less toxic phosphor materials is strongly required. Nanocarbon fragments, especially nanocarbon fragments attached by some chemical groups, have significantly large band gap which may correspond to a visible light energy. Therefore, it is expected to develop new fluorescent materials based on the nanocarbon fragments. Recently, we found accidentally that mesoporous carbon-silica composites (MCSs) oxidized in air can emit very bright white light under low energy ultra-violet light [1]. The emission is so strong that we can clearly see the white light excited even under very weak UV of a portable pen type LED (370 nm) lighting device in daytime (not in the dark room) by our naked eyes. The room temperature PL spectra from the air-oxidized MCSs excited at 370 nm are shown in Fig. 1. As can be seen in the figure, the spectra cover almost the entire visible light wavelength region. Therefore, MCSs have good potential to replace the widely-used fluorescent lighting devices. Another interesting photoluminescence material is the fragments of carbon nanotubes. We will discuss its photoluminescence property in the symposium.

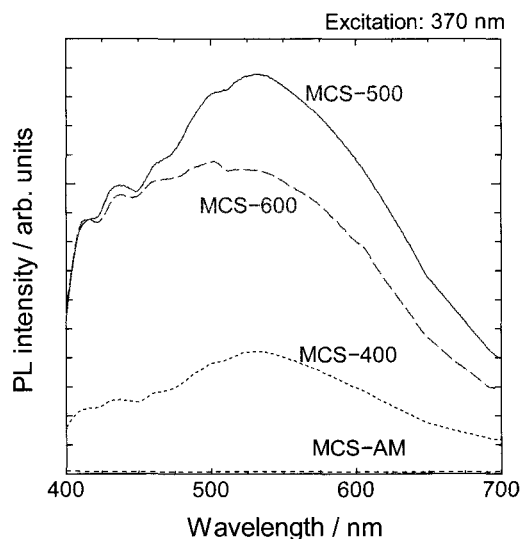


Fig. 1. Room temperature PL emission spectra of (a) MCS-400, (b) MCS-500, and (c) MCS-600 excited at 370 nm.

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Magnetic behavior of carbon nanoparticles prepared from iron controlled carbon powder by laser ablation

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Carbon magnet is of great interest in the view point of whether or not the zigzag edge of graphene indicates the ferro- or ferrimagnetism [1,2]. Theoretical argument of carbon magnetism predicts the ferromagnetic spin order along the mono-hydrogenated and di-hydrogenated zigzag edges of graphene [3]. On the experimental aspects, there are several interesting observations reporting ferromagnetic behavior [4-6]. However, it is usual to be doubted whether the magnetism is originated in the spurious origin associated with a trace amount of magnetic elements of Fe, Co and Ni. In the present study, we carefully controlled the Fe content in the starting carbon powder for the laser ablation.

Starting carbon powder (Kojyundo Kagaku 99.7 %, 5 μm) includes Fe with the concentration of ~ 400 ppm which is determined by atomic absorption spectroscopy (AAS). To remove, we first soaked the carbon powder in the concentrated HCl (36 %) for 1 day. Next, slightly colorized liquid in brownish yellow was decanted, and remaining solution in the precipitated carbon powder was completely removed by rinsing in ethanol several times. After drying liquid, we checked the Fe level of purified carbon powder by AAS and confirmed the level is in a few ppm maximum. Next the Fe controlled solution was added to the purified C-powder dispersed in ethanol, and the mixed solution was well sonicated. Then the solution was completely evaporated and used for the laser ablation. Fe contents of prepared carbon powder are 0 (purified C-powder), 200, 400 and 500 ppm, etc. Temperature dependences of the magnetic susceptibility χ_g for the carbon nanoparticles prepared by ablating the Fe controlled carbon powder in the high T (1000 $^{\circ}\text{C}$) Ar flux containing 3 % H_2 are in Fig. 1. A small hump at around 100 K in 0 ppm sample is associated with adsorbed O_2 [7]. Temperature behavior of 0 ppm sample is similar to that of nanohorns [8], and from this figure we can say that the graphitization is enhanced for 200 ppm sample [9]. While much increase of Fe content up to 400 ppm induces defect formation in the carbon network [10]. Then the sudden increase of χ_g was observed for 500 ppm sample, and this magnetism is possibly originated in the Fe nanoparticles. However, we cannot understand why the sudden increase on χ_g was observed in between 400 and 500 ppm. Figures 2a and b represent the magnetization curves taken at 280 and 4.2 K, respectively. These results also support sudden increase in M between the Fe contents of 400 and 500 ppm. In the present study, strong carbon magnetism was not confirmed.

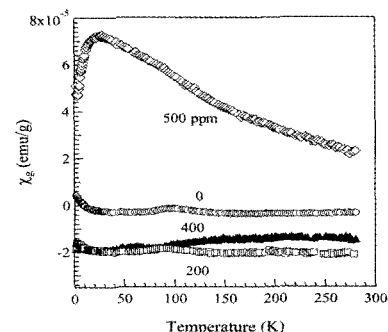


Fig. 1. Temperature dependence of χ_g

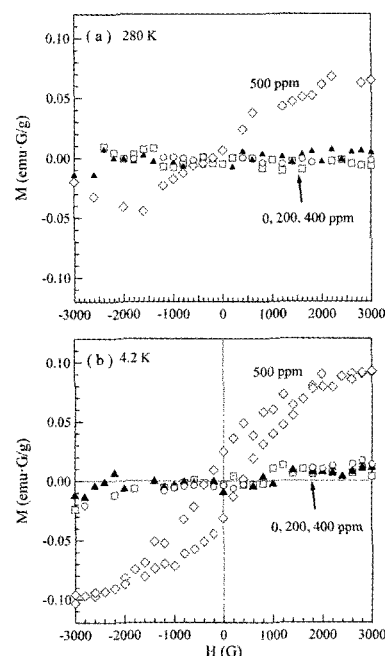


Fig. 2. MH curves at (a) 280 and (b) 4.2 K

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Heat treatment of multi-phase AC arc-discharge soot and formation of carbon encapsulated metal-carbide nanoparticles

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Nearly 20 years after their discovery [1, 2], no real large-scale industrial application of carbon encapsulated metal nanoparticles (CEMNs) has yet started. Although graphitic CEMNs are very important compounds due to their potential application for the disposal of radioactive waste metals such as rare earth and actinide metals [3], they are still laboratory materials, and their very low conversion efficiency from starting metal/carbon materials to the CEMNs, resulting from the conventional synthetic technology, is certainly one of the main explanations of present status. Conventionally, the well-known process of being applied in the CEMNs production was so called cathode deposit method in the arc plasma process, in that CEMNs were synthesized in the carbonaceous deposit on cathode electrode [1, 2], the yields of CEMNs were usually very low.

Today, one of the other promising techniques producing CEMNs is heat treatment (1000 – 2200 °C) of DC arc metal/carbon soot [4]. Average diameter of metal nanoparticles increased with temperature. Average number of graphene sheets covering metal-carbide nanoparticles in soot also increased with temperature, which leads to the more shielding of oxygen diffusion, resulting in the increase of the ignition temperature of metal-carbide of CEMNs in air.

Table 1 summarized ignition temperature of LaC₂ encapsulated in CEMNs in air. Sample A corresponds to as grown soot synthesized in twelve-phase AC arc discharge in 85 Torr He. Samples B, C, D, E, and F correspond to heat-treated samples of soot at 1300, 1520, 1700, 1860, and 2000 °C in vacuum. As shown in Table 1, the ignition temperature increased with the temperature of heat treatment (HT) of the AC arc soot, which is much higher than ignition temperature of the corresponding heat-treated DC arc soot.

Table 1. Temperature of HT and ignition temperature of carbon encapsulated LaC₂ nanoparticles (°C).

Samples	A	B	C	D	E	F
Temperature of HT	-	1300	1520	1700	1860	2000
Ignition Temp.	450	450	461	472	498	508

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Synthesis of coronene oligomers in carbon nanotubes

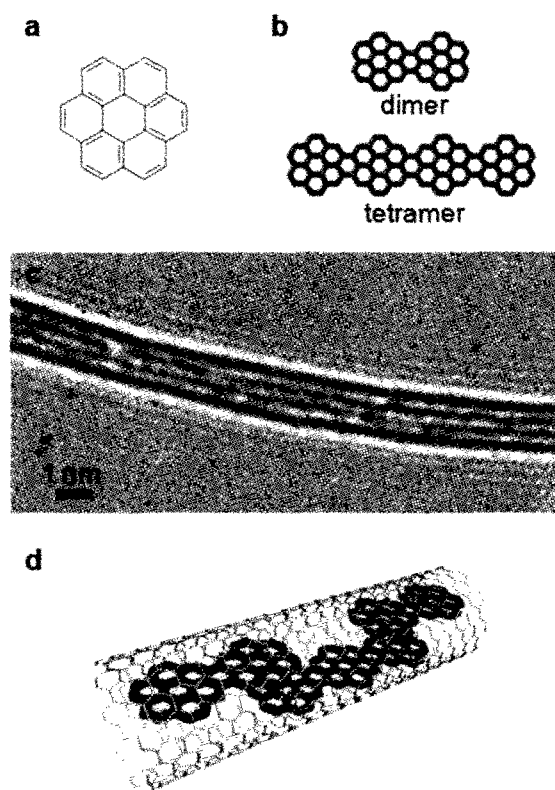
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Carbon nanotubes (CNTs) have chemically and thermally stable one-dimensional (1D) nano-space that is regarded as an ideal molecular reactor. In this reactor, a wide variety of organic molecules can be encapsulated and transformed into other nano-materials. For example, thermal fusion of fullerenes and polyynes result in the fabrication of single-wall CNTs and carbon-chains, respectively [1,2]. Recently, we have developed an efficient method to separate inner materials from outer CNTs in solution phase [3]. These processes allow us to fabricate novel nanomaterials and also to investigate their fascinating properties.

Here, we report the fabrication and extraction of oligomers of coronenes, which is one of the representative polycyclic aromatic hydrocarbons (Fig.1a,b). Coronenes were encapsulated in single-wall CNTs with an average diameter of 1.4 nm by vapor-phase reaction. The sample was characterized by using high-resolution transmission electron microscope (HRTEM) and optical spectroscopy.

HRTEM observations revealed that more than 90% of CNTs contain linear-shaped materials with a typical length of 3~10 nm as shown in Fig.1c. Raman spectra of the sample show characteristic vibrational peaks similar to those of coronene dimmers (the so-called 'dicoronylene'). Interestingly, the materials extracted from CNTs have displayed photoluminescence whose wavelengths differ from that of coronenes. These results indicate that coronene monomers have been converted into coronene oligomers in CNTs (Fig.1d) during the vapor-phase reaction.



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Fig.1. (a) molecular structure of coronene.
(b) schematic models of coronene oligomers.
(c) HRTEM image of coronene oligomers@CNT.
(d) schematic model of coronene oligomers@CNT.

Growth of carbon nanotube from one-dimensional coalescence of aromatic compounds

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Apart from the commonly known unique electronic and optical properties, carbon nanotubes (CNTs) with a chemically stable interior space can provide an ideal template for the studies of various nano-confined reactions [1, 2]. Among which is the transformation of filled precursors, such as fullerenes, into an inner tube. The growth of an inner tube within a parent tube is highly desired, as they represent a means of controlled growth of CNTs that has been difficult to achieve using the conventional metal catalysed growth. From a previous work of the present group [3], bulk extraction of the inner tubes grown has been achieved. In this way, possible synthesis and extraction of the chirality specific and small-diameter tubes can perhaps be realised, shedding much light on the fundamental science as well as the future opto-electronics applications of materials produced from the nano-confined reactions.

Herein, we have investigated the growth and properties of CNTs fabricated from coalescence of a wide variety of aromatic compounds such as pentacene and perylene derivatives. It has been observed that linear-shape compounds like pentacene form one-dimensional arrays inside CNTs as shown in Fig. 1. These arrays tend to be converted into the inner tubes as confirmed from Raman spectra (Fig. 2). Detailed optical measurements with photoluminescence and absorption spectroscopy of the materials will be shown in the presentation.

[1] R. Kitaura, *et al.*, *Angew. Chem. Int. Ed.* **2009**, 48, 8298., [2] C. Zhao, *et al.*, *J. Phys. Chem. C* **2011**, DOI: 10.1021/jp201647m., [3] Y. Miyata, *et al.*, *ACS Nano* **2010**, 4, 5807.

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Fig. 1. HRTEM images of the pentacene arrays filled CNTs.

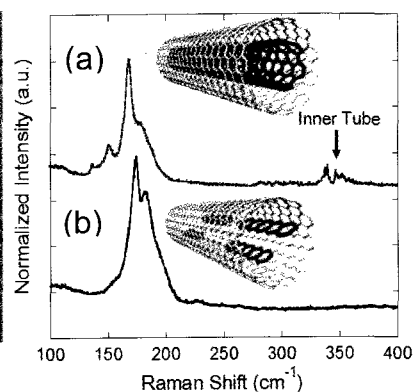


Fig. 2. Raman spectra of the inner tube generated (a) from the pentacene filled CNTs (b).

One-step Synthesis of Metal-Encapsulated Carbon Nanotubes by Pulsed Arc Discharge in Water

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One-step synthesis of metal-encapsulated carbon nanotubes (CNT) is interesting because it can synthesize an as-grown sample with high quality owing to post process-free. We have synthesized metal-encapsulated CNT in one-step process based on the arc discharge method in water [1,2]. Here, we investigated that which kinds of metal are easy to encapsulate, and that the filling rate depends on the cathode materials.

Figure 1 shows the schematic of experimental setup. The beaker was filled with pure water, the electrodes were sunk and the pulse arc electrical discharge in water was performed. A graphite rod was used as the anode, in contrast, metal rods, W, Mo, Zr, Cu, Ni, Al, Zn, and Fe, were used as the cathode in this experiment. We found that W, Mo, and Zr particles were encapsulated when the pulse arc discharge was used. On the other hand, in the case of DC arc discharge (20 A, 30 V) in water, no metals inside CNT were observed. Furthermore, when Ni or Cu was used as the cathode, polyhedral metal-filled nano-capsules were synthesized.

[1] N. Sano, H. Wang, M. Chhowalla, I. Alexandrou, and G. A. J. Amaratunga, *Nature* 414, (2001) 506.

[2] Y. L. Hsin, K. C. Hwang, F.-R. Chen, and J.-J. Kai, *Adv. Mater.* 13, (2001) 830.

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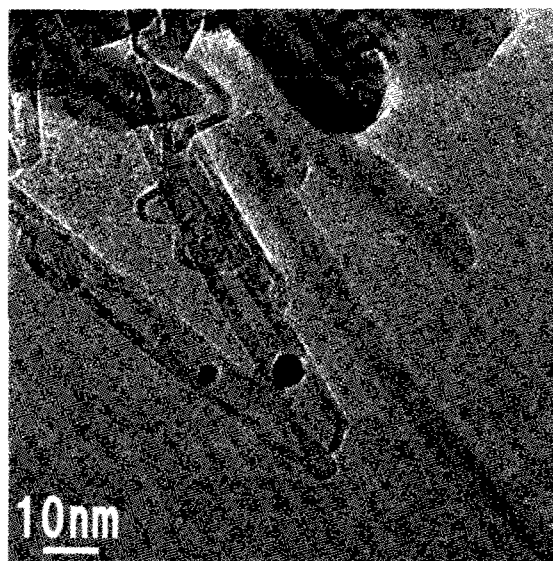
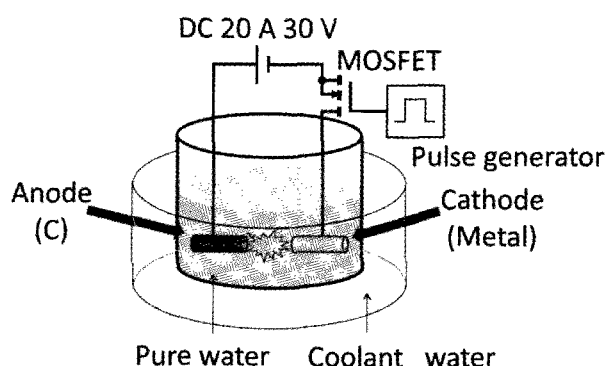


Fig.1 Schematic diagram of experimental setup for arc discharge in water.

Fig.2 TEM image of as-synthesized W-encapsulated CNT prepared by the pulsed arc discharge in water.

Carrier Control of Semiconducting Single-Wall Carbon Nanotubes by Encapsulating Organic Molecules

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Recently, high performance thin-film transistors (TFTs) have been realized using semiconducting single-wall carbon nanotubes (s-SWCNTs) separated from a mixture [1, 2]. Normally, s-SWCNT-TFTs show p-type behavior in the air because adsorbed oxygen molecule acts as hole dopant. To fabricate an inverter as a building block of logic circuits, not only p-type TFTs but also n-type TFTs are necessary. One of the best ways of carrier control of s-SWCNTs is molecular encapsulation inside s-SWCNTs (so-called peapods) because encapsulated molecules are protected by SWCNT wall and thus stable.

Before fabricating peapod-TFTs, it is needed to identify which s-SWCNTs can encapsulate molecules because empty s-SWCNTs behave as p-type and deteriorate the n-type transport characteristics. As the first step, we synthesized ferrocene (FeCp_2) peapods using unsorted HiPco SWCNTs, and then measured optical properties. Figure 1 shows the photoluminescence-excitation (PLE) map of FeCp_2 peapods dispersed in 2 % sodium deoxycholate (DOC) aq. Excitation and emission wavelength of (8, 6)-, (8, 7)-, (9, 5)-, (10, 5)-, (11, 3)- and (12, 1)-SWCNTs were both red-shifted, which indicates that these s-SWCNTs are encapsulating FeCp_2 . An electron transfer from FeCp_2 to s-SWCNT is suggested from a tiny but clear red shift of G-band in the Raman spectrum of peapods (Fig. 2). These results suggest that diameter sorted s-SWCNTs [3] can be used for FeCp_2 -peapods, and namely for n-type TFTs.

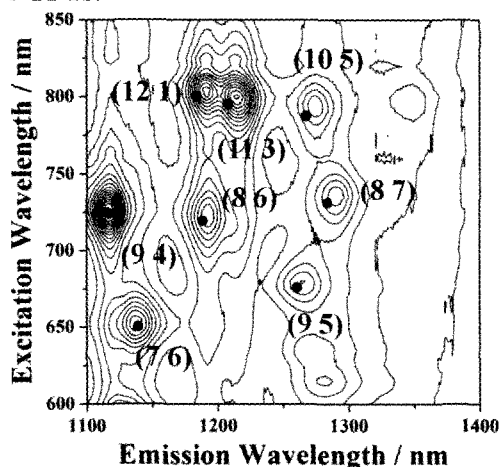


Fig. 1 PLE map of FeCp_2 peapods dispersed in 2% DOC aq. Black dots indicate the peak position of pristine HiPco SWCNTs.

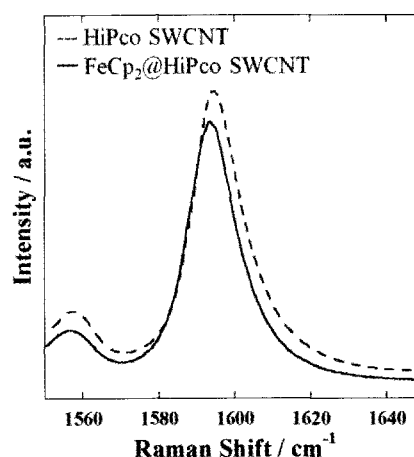


Fig. 2 Raman Spectra of HiPco SWCNTs and FeCp_2 peapods Bucky papers. Excitation wavelength is 633 nm.

[1] C. Wang *et al.*, *Nano Lett.*, **9**, 4285 (2009). [2] Y. Asada *et al.*, *Adv. Mater.*, **22**, 2698 (2010).

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

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2011 年 9 月 5 日発行

第 41 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

<フラーレン・ナノチューブ・グラフェン学会>

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丸山研究室内

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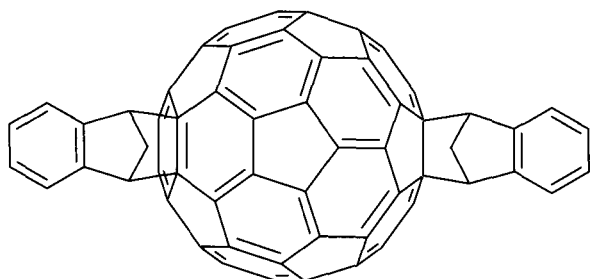
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印刷 / 製本 大学生協プリントオンデマンドセンター (U-POC)

新規フラレンインデンス付加体 ICBA

Luminescence Technology 社(Lumtec 社)では新しいフラレン誘導体である Indene-C₆₀ Bisadduct (ICBA)を取り扱っています。高い LUMO 準位(-3.74 eV)が報告されており、太陽電池における新しい電子アクセプターとして注目を集めています。



LT-S9030 ICBA

組成式: C₇₈H₁₆

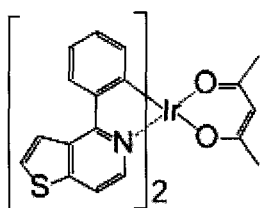
M.W. : 953.4

CAS No. : 1207461-57-1

吸収波長: 318 nm (in CH₂Cl₂)

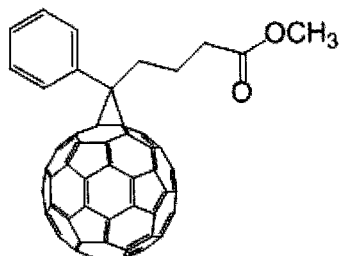
純度: >99%

有機 EL 材料



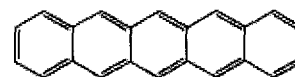
PO-01

有機太陽電池材料



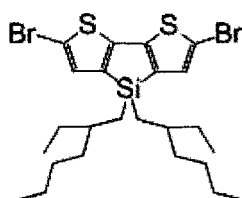
PC₆₁BM

有機薄膜トランジスタ材料



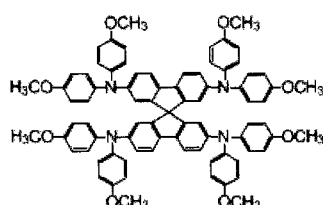
Pentacene

有機太陽電池中間体



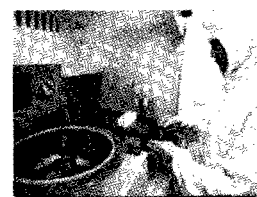
2,6-dibromo-(4,4-di-2-ethylhexyl)-dithieno[3,2-b:2',3'-d]silole

色素増感太陽電池材料



Spiro-MeO-TAD

ITO コードガラス およびパーティニング 受託サービス



和光純薬工業株式会社

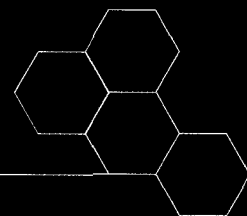
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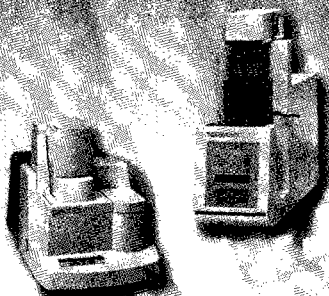
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SEI-3500

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CNTの結晶性と耐熱性の評価
マイクロ熱重量測定装置
TGA-50
TG/DTA同時測定装置
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直径測定
精製前後の観察
CNTとポリマーコンポジット
試料の観察
走査型プローブ顕微鏡
SPM-9700

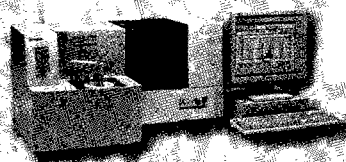
NEW

CNTの紫外可視近赤外
吸収スペクトル測定
紫外可視近赤外分光光度計
SolidSpec-3700



SWNTの近赤外PL
3次元分布測定
近赤外フォトルミネッセンス測定システム
NIR-PL System

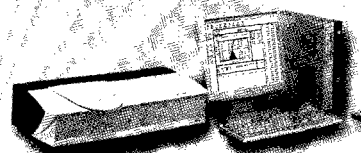
紫外可視近赤外分光光度計
UV-3600



分散・凝集過程評価
高感度ナノ粒子径分布測定装置
SALD-7100H

NEW

触媒元素の測定
ゾインナーケンヤル形ICP発光分析装置
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独自のIG法による
シングルナノ領域の粒子径評価
シングルナノ粒子径測定装置
IG-1000

直径測定
結晶性と耐熱性の評価
ラマン分光光度計
inVia シリーズ (レニショー社製)



比表面積と吸着特性
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自動比表面積/細孔分布測定装置
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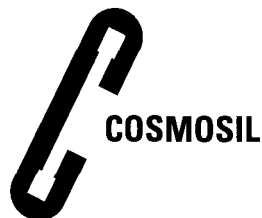
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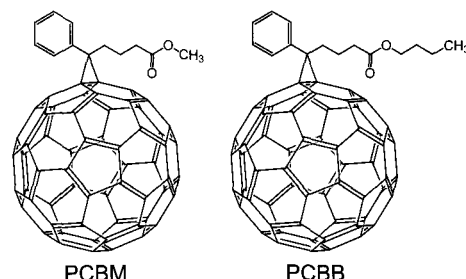
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TEL075-823-1468 FAX075-841-9325 <http://www.an.shimadzu.co.jp>

誘導体化フラーレンの分析例



PCBM は、[6,6]-Phenyl-C₆₁-Butyric Acid Methyl Ester（フェニルC₆₁酪酸メチルエステル）の略で、誘導体化フラーレンの1種です。PCBMは、p型共役ポリマーと混合して有機太陽電池を作製するのに用いられるn型半導体材料であり、これは、フラーレン専用カラムであるコスモシル Buckyprepを用いることにより分析・精製を効率的に行うことが可能となります。今回は、PCBMとその類似体であるPCBBおよびBis-PCBMの分析例についてご紹介します。



■分析例

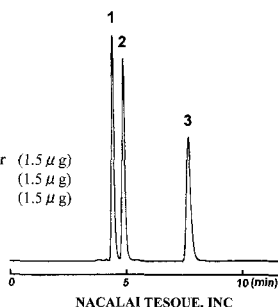
コスモシル Buckyprepによる分析例

COSMOSIL Application Data

Column: Buckyprep
Column size: 4.6mm I.D.-250mm
Mobile phase: Toluene
Flow rate: 1.0 ml/min
Temperature: 30°C
Detection: UV325nm

Sample:

1; [6,6]-Phenyl-C₆₁ Butyric Acid Methyl Ester (1.5 μg)
2; [6,6]-Phenyl-C₆₁ Butyric Acid Butyl Ester (1.5 μg)
3; C₆₀ (1.5 μg)



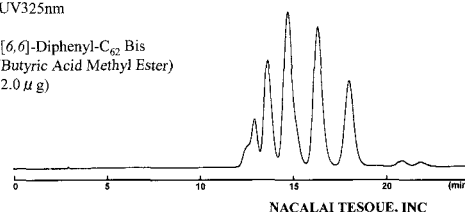
AP-1066

COSMOSIL Application Data

Column: Buckyprep
Column size: 4.6mm I.D.-250mm
Mobile phase: Toluene/ Methanol = 50/50
Flow rate: 1.0 ml/min
Temperature: 30°C
Detection: UV325nm

Sample:

[6,6]-Diphenyl-C₆₀ Bis
(Butyric Acid Methyl Ester)
(2.0 μg)



AP-1154

■フラーレン関連充填剤の固定相と物性一覧表

充填剤名称	Buckyprep	Buckyprep-M	PBB	PYE	NPE
シリカゲル	全多孔性球状高純度シリカゲル				
平均粒子径	5 μm				
平均細孔径	約120 Å				
比表面積	約300m ² /g				
固定相構造					
化学結合基	ピレニルプロピル基	フェノチアジル基	ペンタブロモベンジル基	ピレニルエチル基	ニトロフェニルエチル基
特長	フラーレン分離のスタンダード	金属内包フラーレン分離に効果的	C ₆₀ 、C ₇₀ 等の大量分取に最適	フラーレンの分離や構造異性体の分離に	誘導体化フラーレンの分離に効果的

詳しい情報はWeb siteをご覧ください。

ナカライテスク株式会社

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波長可変チタンサファイアレーザー 3900S

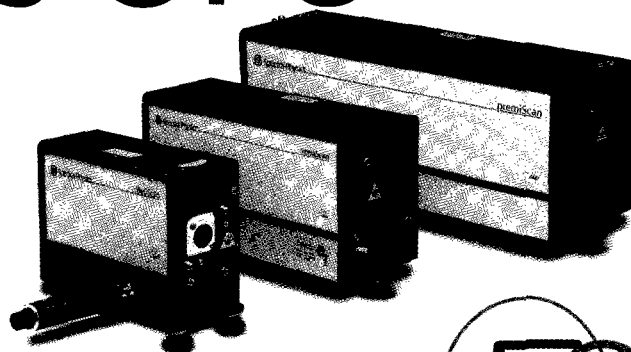
- 優れた操作性、メンテナンス性と高い変換効率
- 高い安定性を実現し、675~1100nmの超広帯域発振が可能
- フラール・ナノチューブの分光用およびフォトルミネセンス光源として最適

【主な仕様】

平均入力：5Wおよび10W
 発振波長域：700-1000nm (5W励起)
 発振波長域：675-1100nm (10W励起)
 線幅：40GHz以下 (1GHz以下のオプション有り)
 ノイズ：1%以下
 安定性：3%以下
 空間モード：TEM₀₀

ナノ秒チューナブルOPO Scan Series OPO

- 410nmから2.63μmの広帯域波長可変OPO
- ブロードバンド (10-500cm⁻¹)、ミッドバンド (3-7.5cm⁻¹) を選択可能
- UVオプションにより206nm-420nmの紫外波長領域をカバー
- ScanMaster™ソフトウェアによるグラフィックインターフェイスで簡便な操作性
- 独自のキャビティデザイン、特殊なコーティング技術により長い結晶寿命を実現
- Quanta-Ray®のNd:YAGレーザー (INDI、LAB、PROシリーズ)との組み合わせで幅広い励起出力に対応



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溶液中の粒子のナノレベル微細化・分散に

BRANSON 超音波ホモジナイザー

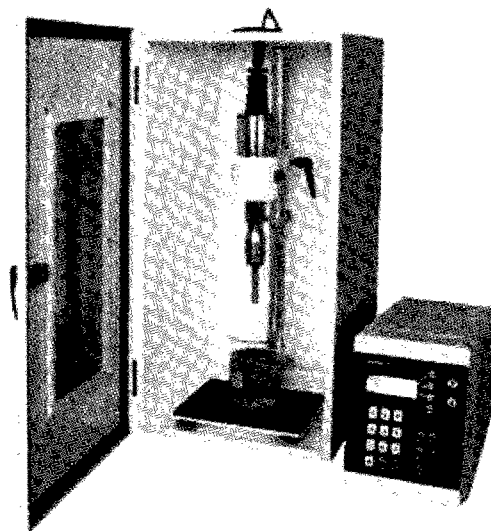
ホーン先端部の振幅の安定性を、より高めた Advance タイプ になりました。

近年のナノテクノロジーの発展及び粉体関連技術の向上により、より微細な粒子に対する乳化分散処理の要望が増えてまいりました。

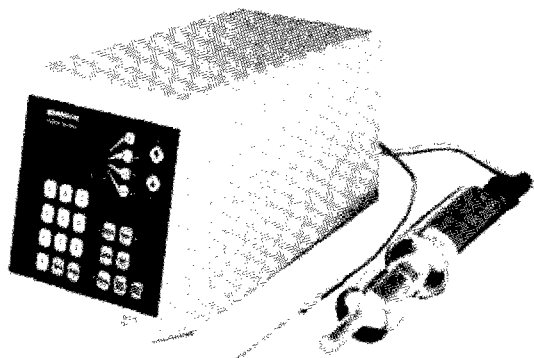
超音波ホモジナイザーを使用し、均質な乳化分散処理を行い、安定させることにより製品の機能は向上します。

ブランソン社では 20kHz 機と、40kHz 機の 2 タイプを用意しております。

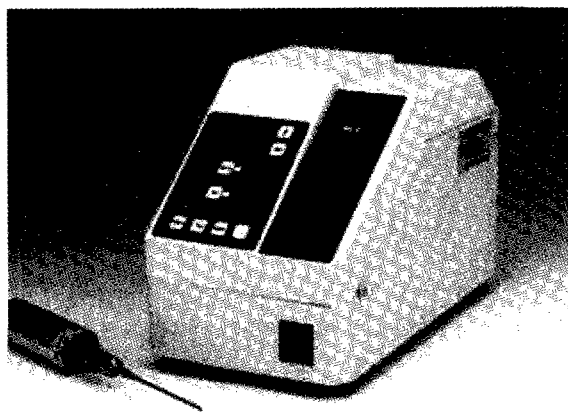
1 次粒子の凝集力にも拠りますが、20kHz 機では 100nm 程度までの分散力があります。40kHz 機は、さらに細かいレベルで分散ができる可能性があります。



20KHz 超音波ホモジナイザー
BRANSON SONIFIER シリーズ



高周波 40KHz 超音波ホモジナイザー
BRANSON SLPe シリーズ



ブランソン社の製品は、ホーン先端部の振幅の安定性が高く、強力なキャビテーションが得られ、効率良く、再現性の高い分散処理が行えます。

主なアプリケーション

分散

カーボンナノチューブ 有機顔料 無機顔料 セラミック セメント 感光体 記録材料
磁性粉 粉末冶金 酸化鉄 金属酸化物 シリカ アルミナ カーボンブラック
ポリマー ラテックス 製紙 ファンデーション
研磨剤 電池 フィラー 光触媒 触媒 ワクチン 体外診断薬 歯磨き粉 シャンプー
半導体 電子基盤 液晶 貴金属 金属 宝石 タイヤ 発酵菌類 その他

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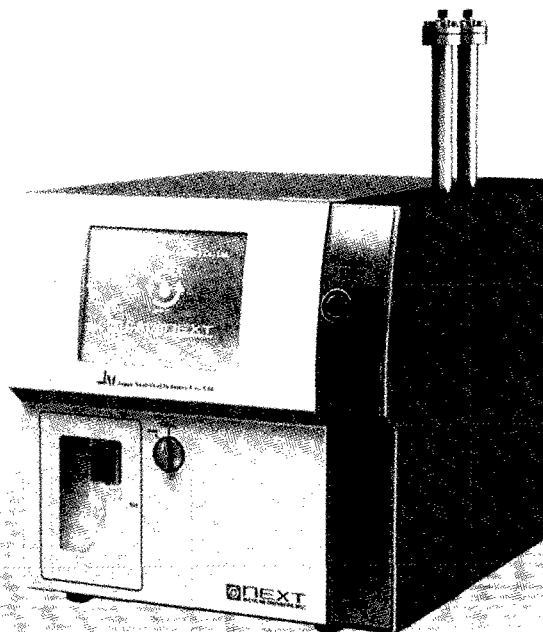
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おかげさまで2,500台を超える装置が国内外で活躍しています。

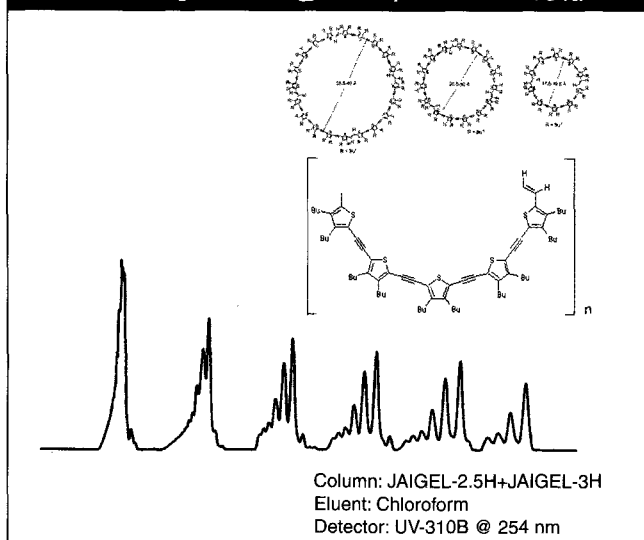
装いを新たにnEXTシリーズを発売!!

“高性能”・“使いやすさ”・“メンテナンス性能”を追求した究極の装置。

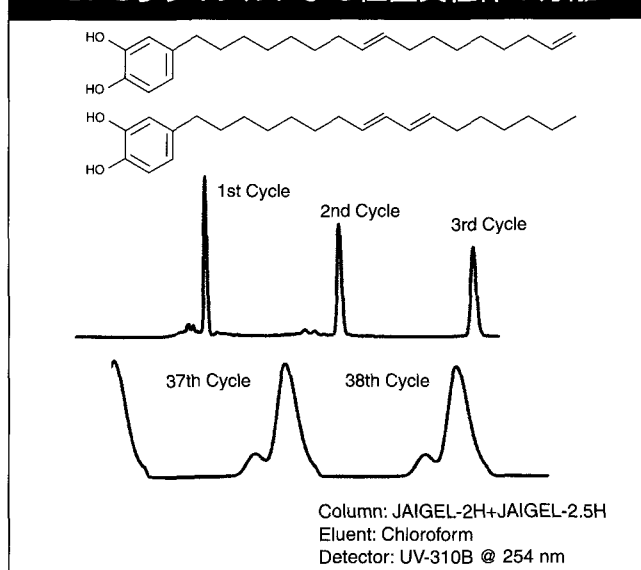
1/3ボディーサイズ(従来機比較)。nEXTを皆様のラボで是非ご採用ください。



GPCリサイクルによる Macrocyclic Oligothiophenesの分離



GPCリサイクルによる位置異性体の分離



JAI 日本分析工業株式会社

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NanoAmando[®] 水性コロイド



NanoCarbon Research Institute Ltd.

株式会社ナノ炭素研究所

<http://nano-carbon.com>

一桁ナノダイヤモンド分散粒子

特 徴

ナノアmando水性コロイドは、爆轟法ナノダイヤモンドの凝膠体をビーズミリング等の特殊プロセスを経て解砕し、一桁ナノの一次粒子として完全分散させた製品です。粒子表面には強く配向吸着した不凍水和層が存在するために、粒子同志が結合することなく、極めて安定なコロイドです。細胞毒性は皆無で、用途としては水性及び油性潤滑剤、複合メッキ強化添加剤、CVD結晶成長核、蛍光発光素子、表面誘導体、有機太陽電池(光吸収率向上)、触媒担体、等、幅広い応用展開が期待されています。

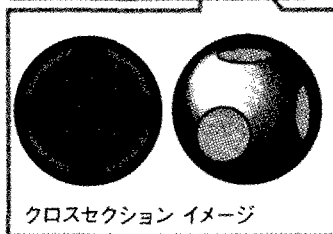
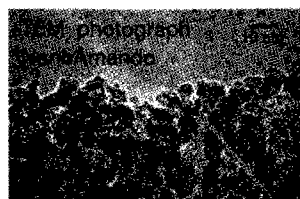
仕 様

添加物：なし

粒 度：4.7±0.6nm (100vol%)

濃 度：5% (標準在庫品)、2% (特注品)、水 (脱イオン水) で任意の濃度に希釈可能

その他エチレングリコールコロイド (最大2%)、DMSOコロイド (標準5%)、水性ハードゲル、水性ソフトゲル (特注品) があります。



クロスセクション イメージ



金属ナノチューブと 半導体ナノチューブを選別可能!

Nan[⊙]Integris

密度勾配超遠心分離法 (Density gradient ultra-centrifugation) により、金属SWNT (単層カーボンナノチューブ) と半導体SWNTの作り分けが可能になりました。

◎ 製品および規格 ◎

ISONANOTUBES[™]：均一な電気的特性を持つSWNT

IsoNanotubes-S：半導体SWNT

純度：90%、95%、98%、99%

SWNT径：1.2~1.6nm

納入形態：水溶液

SWNT含有量：1mg、10mg

IsoNanotubes-M：金属SWNT

純度：70%、95%、98%

SWNT径：1.2~1.6nm

納入形態：水溶液

SWNT含有量：1mg、10mg



販売代理店

株式会社 ニューメタルス エンド ケミカルス コーポレーション

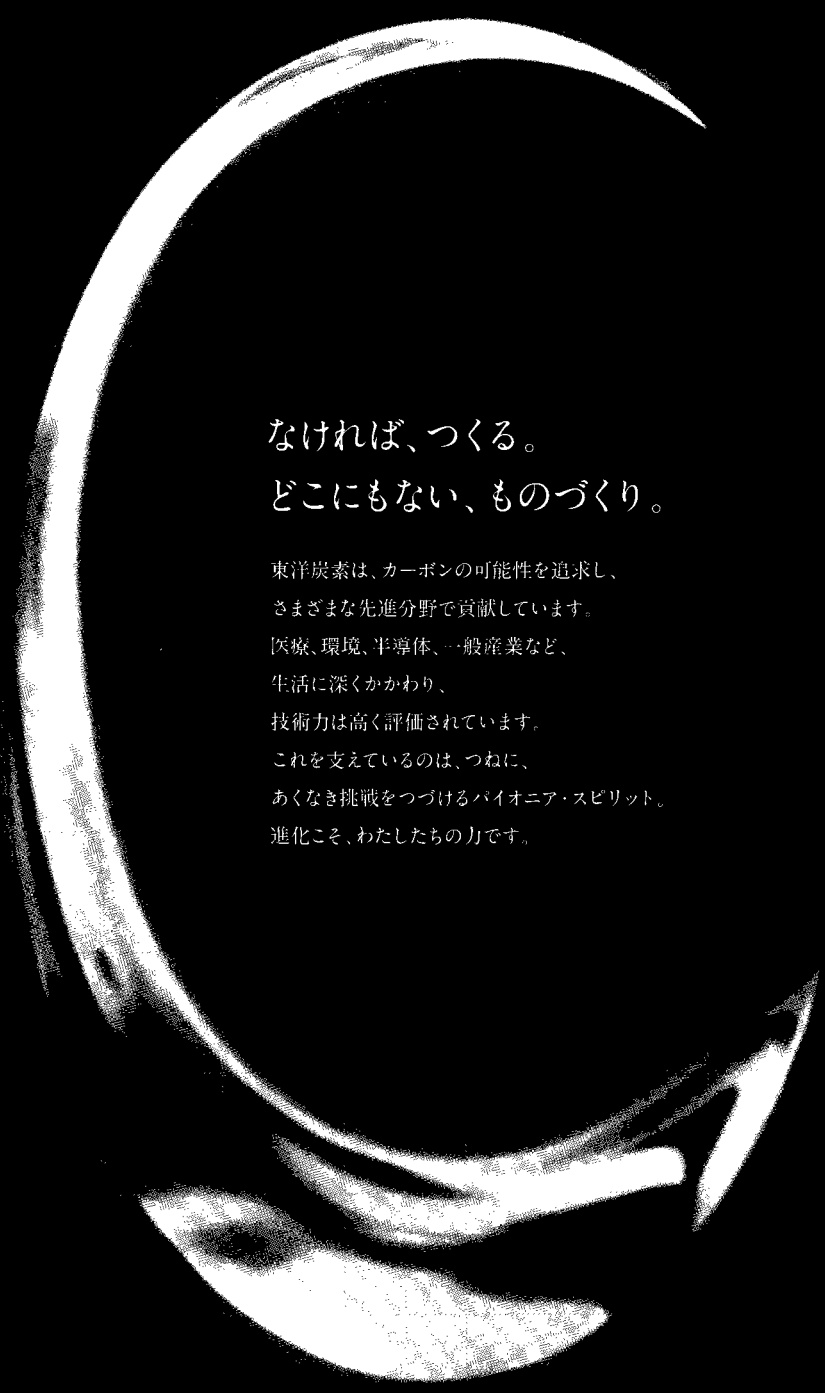
URL：<http://www.newmetals.co.jp>

本社 東京都中央区京橋1-2-5 京橋TDビル Tel.03-5202-5624 Fax.03-3271-5860

担当：電子材料営業部 伊藤 E-mail：ito@newmetals.co.jp

大阪支店 大阪市中央区北浜2-5-23 小寺プラザビル Tel.06-6202-5108 Fax.06-6223-0987

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生活に深くかわり、
技術力は高く評価されています。
これを支えているのは、つねに、
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進化こそ、わたしたちの力です。



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東洋炭素株式会社

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XE

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インテル® Xeon® プロセッサ向けに再コンパイルした場合の アプリケーション・パフォーマンスの向上

SPECfp*_base2006 (C/C++) 浮動小数点演算ベンチマークの推定値

インテル® C++ コンパイラー 12.0

1.69X

Windows® 版

インテル® C++ コンパイラー 11.1

1.32X

Windows® 版

比較対象コンパイラー

Microsoft® Visual Studio® 2010/PGI® C++ コンパイラー 10.6 (いずれか速い方)

69%
の
高速化

機能に関するテストと評価は、特定のコンピューター・システム、コンポーネント、またはそれらを組み合わせて行ったものであり、このテストによるインテル製品の性能の標準値を表しているものではありません。システム・ハードウェア、ソフトウェアの設計、構成などの違いにより、実際の性能は掲載された性能テストや評価とは異なる場合があります。システムやコンポーネントの購入を検討される場合は、ほかの情報も参考にして、パフォーマンスを総合的に評価することをお勧めします。インテル製品の性能評価について詳しい情報をお知りになりたい場合は、http://www.intel.co.jp/performance/resources/benchmark_limitations.htm を参照してください。構成情報については、次の Web サイトをご覧ください：<http://software.intel.com/en-us/articles/benchmark-info/#ICC> (英語)。

① インテル® Composer XE

高速化のための C++/Fortran コンパイラー

最新プロセッサ上で高速に動作できるようにバイナリーを自動生成します。優れた互換性により、Visual Studio® や GCC® 上での開発が可能です。

② インテル® Inspector XE

スレッド / メモリーエラー検出ツール

メモリーリーク、メモリー破壊、データ競合やデッドロックなどの並列プログラミングにおける問題を素早く検出できます。

③ インテル® Parallel Advisor 2011

並列化対応、パフォーマンス分析ツール
数回のクラシメントのみでパフォーマンスの問題となる原因を特定でき、ソースコードと連携させて表示することのできる高度なプロファイラーです。

④ インテル® Parallel Advisor 2011

画期的な並列化のアドバイザー

並列化すべき候補や並列化後のパフォーマンス予測を、簡単な操作で表示させることができます。
(Windows® 版のみ提供)

無料評価版はこちら : <http://www.xlsoft.com/intel>

製品の詳細に関するお問い合わせ先 :

XLISOFT

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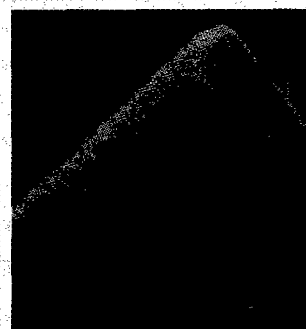
Tel: 03-5440-7875 Fax: 03-5440-7876 E-mail: intel@xlsoft.com

インテル® ソフトウェア製品のパフォーマンス / 最適化に関する詳細は、<http://software.intel.com/en-us/articles/optimization-notice> (英語) を参照してください。
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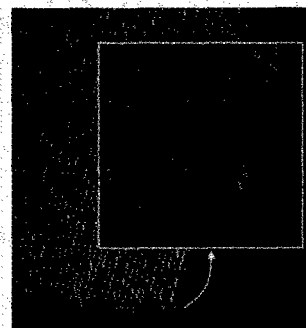
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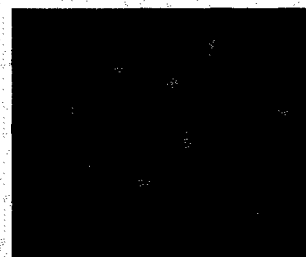
カーボンナノチューブ&グラフェン成長用CVD装置 **Black Magic**



Dense CNT



Horizontal SWCNT



Graphene

- 装置導入後、すぐに希望のCNTやグラフェンを成長可能
- オリジナルのレシピ付き「Thermal CVDとPlasma CVDの2モードに対応」
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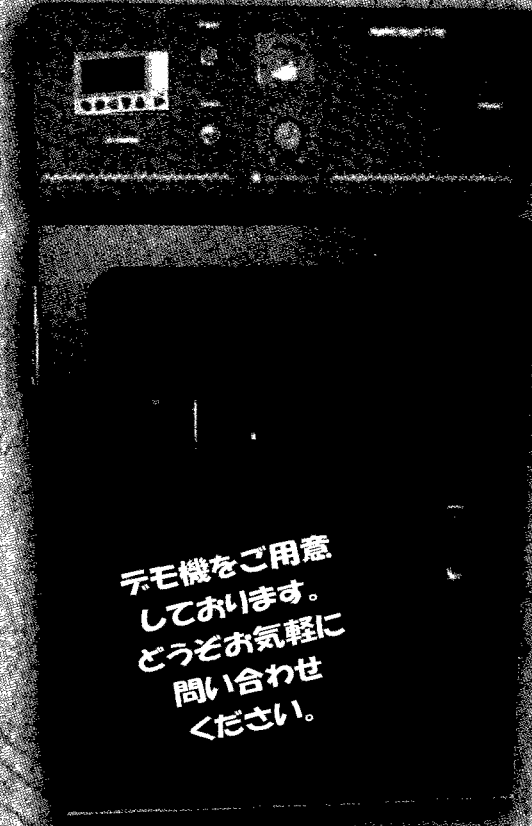
ALWAYS ONE STEP AHEAD

ナノラプター NANORUPTOR® サンプル密閉式超音波分散装置

バイオの技術をナノテクへ

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。

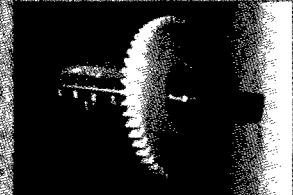
実施例：カーボンナノチューブ・グラフェンの分散、燃料電池触媒評価
納入実績：各大学、自動車メーカー、光学機器メーカー、電子部品メーカー



デモ機をご用意
しております。
どうぞお気軽に
問い合わせ
ください。



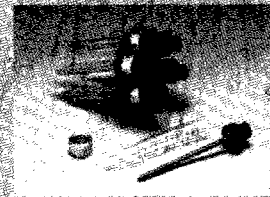
回転機構付破碎槽



標準50mlチューブ



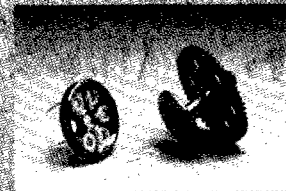
高効率新型破碎槽



15mlチューブ



1対4 - 収束装置付破碎槽



1.5mlチューブ

対象試料 / 特長

- カーボンナノチューブ、グラフェン、グラフェン導電性ナノ粒子
- 密閉処理（ナノリスク低減）、消磁の蒸発、複数試料の同時処理（100μl～20ml）、試料チューブの選択により、複数試料を同時に処理できます。
- 再現性良好：回転機構の採用により均一な超音波照射が可能です。
- 低騒音：高性能防音箱の採用により、超音波特有の騒音を防止。
- 温度制御が容易：バスタブ式なので低温から40℃まで任意に設定可能（オプション）。

NR-350仕様（予告無く変更する場合があります）

品番	NR-350
品名	密閉式超音波分散装置 Nanoruptor
超音波周波数	20 KHz
超音波出力	380/300/250/130 W（切替式）
電源	100 V、50/60 Hz、5.5 A
最低設置スペース幅寸	400 (W) × 350 (D) × 680 (H) mm
発振ユニット寸	400 (W) × 280 (D) × 160 (H) mm
処理ユニット寸	250 (W) × 200 (D) × 300 (H) mm
消費箱寸	400 (W) × 350 (D) × 520 (H) mm
NR-350 全体重量	36 kg
ランタイム	599 サイクル
インターバルタイマー (ON)	0～59 秒、デジタル
インターバルタイマー (OFF)	0～59 秒、デジタル
処理本数	1 本 (50 mL チューブ) ～ 各種
付属品	高性能消音箱、電源ケーブル、接続ケーブル、排水ポンプ、取り扱い説明書、ユーザー登録カード

備考

NR-350 は機器のみです。別途処理量に応じたアクセサリ（キヤ・板 + チューブ）をお買い求め下さい。

品名	品番	包装	希望販売価格
超音波密閉式分散装置	NR-350	1 UNIT	¥1,950,000
50 mL チューブ用チューブ	MM-50WS	1 SET	¥54,000
使用可能チューブ：マルエー社製 50 mL ねじ蓋試験管			
キヤ・板	NG-350-50	1 PC	¥9,000
冷水循環器	CP80-R	1 UNIT	¥264,000
冷水循環器接続ケーブル	TU-100	1 PC	¥15,000

販売

人と科学のステキな未来へ



コスモ・バイオ株式会社

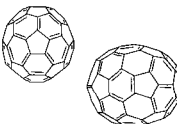
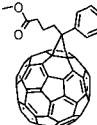
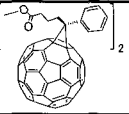
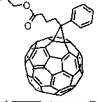
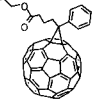
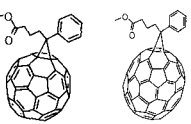
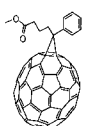
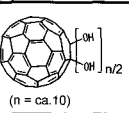
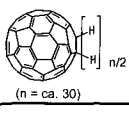
〒135-0016 東京都江東区東陽2-2-20 東陽駅前ビル
URL: <http://www.cosmobio.co.jp>
TEL (03) 5632-9610 FAX (03) 5632-9619
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製造



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TEL (045) 261-8388 FAX (045) 252-8935
技術部長 伊藤
e-mail: k-ito@bioruptor.jp

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

銘柄、取扱数量等は予告無く変更する場合がございます。予めご了承下さい。

2011年2月1日現在

当社製品は、下記2社から購入いただけます。詳細は直接お問い合わせください。

・関東化学株式会社 試薬事業本部

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<http://www.kanto.co.jp> E-mail:reag-info@gms.kanto.co.jp

・第一実業株式会社 新事業推進室【担当: 鎰広(カギヒロ)】E-mail:masaru.kagihiro@djk.co.jp

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<本資料に関するお問い合わせ先>

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〒806-0004 福岡県北九州市八幡西区黒崎城石1-1

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