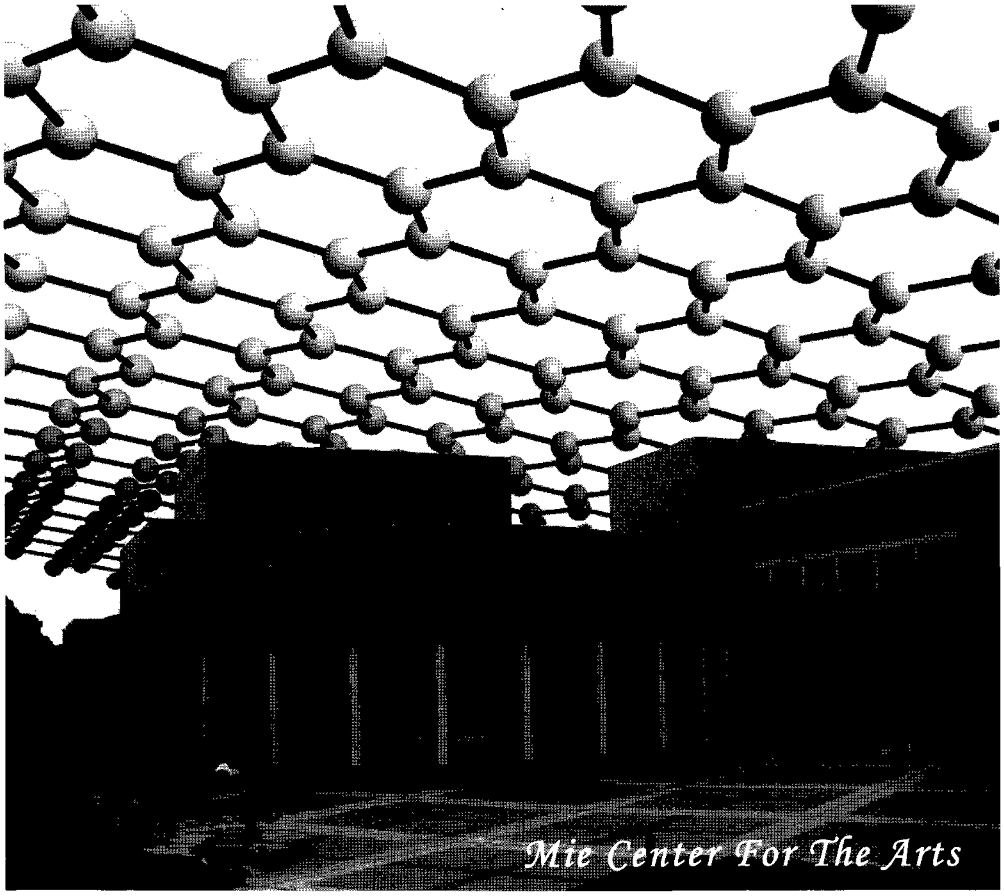
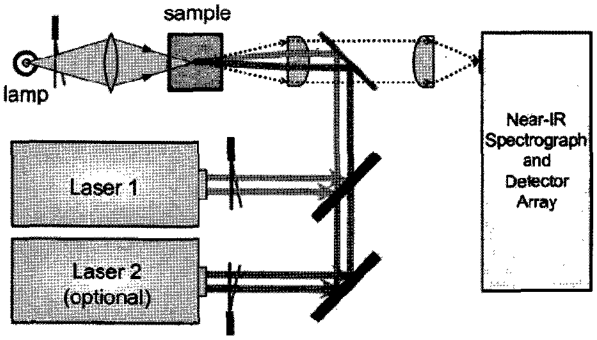
Abstracts
The 31st Fullerene-Nanotubes General Symposium
第 31 回フラーレン・ナノチューブ総合シンポジウム

講演要旨集



July 12–14, 2006, Tsu, Mie
平成 18 年 7 月 12 日–14 日
三重県総合文化センター

The Fullerenes and Nanotubes Research Society
フラーレン・ナノチューブ学会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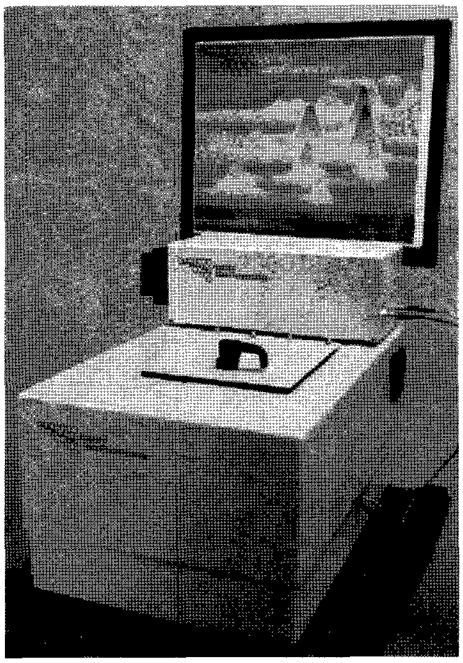

Abstracts
The 31st Fullerene-Nanotubes General Symposium

第31回フラーレン・ナノチューブ総合シンポジウム

講演要旨集

The Fullerenes and Nanotubes Research Society

The Chemical Society of Japan
Japan Society of Applied Physics

主催：フラーレン・ナノチューブ学会

共催：日本化学会
協賛：応用物理学会

Date: July 12th(Wed)–14th(Fri), 2006
Place: Mie center for the arts
1234 Ishinden Kozubeta, Tsu, Mie 514-0061
TEL: 059-233-1114

Presentation: 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18年7月12日（水）～14日（金）
場所：三重県総合文化センター
〒514-0061 三重県津市一身田上津部田1234
TEL：059-233-1114

発表時間：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（五十音順、敬称略）

アプリオリ（株）
エムエス機器（株）
大塚電子（株）
コスモ・バイオ（株）
（株）サイエンスラボラトリーズ
サイバネットシステム（株）
（株）島津製作所
住友商事（株）
（株）セントラル科学貿易
ナカライテスク（株）
日本分光（株）
フロンティアカーボン（株）
（株）堀場製作所

広告掲載団体御芳名（五十音順、敬称略）

（株）アイリン真空
アプリオリ（株）
大塚電子（株）
オザワ科学（株）
コスモ・バイオ（株）
（株）サイエンスラボラトリーズ
サイバネットシステム（株）
（株）栄屋理化
産業タイムズ社
（株）島津製作所
スペクトラ・フィジックス（株）
住友商事（株）
（株）東京プログレスシステム
ナカライテスク（株）
フロンティアカーボン（株）
（株）堀場製作所
（株）マツボー

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9:30	一般講演　4件 （ナノチューブの物性） 9:30〜10:30	9:30	一般講演　4件 （ナノホーン　2件） （炭素ナノ粒子　2件） 9:30〜10:30	9:30	一般講演　4件 （金属内包フラーレン　2件） （フラーレンの化学　2件） 9:30〜10:30
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特別講演　発表25分　質疑5分
一般講演　発表10分　質疑5分
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13:00	Special Lecture 2 (Saito) 13:00-13:30
13:30	General Lecture [4] (Formation and Purification of Nanotubes) 13:30-14:30
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13:00	Meeting 13:00-13:15
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16:30	

Special Lecture: 25 min (Presentation) + 5 min (Discussion)
General Lecture: 10 min (Presentation) + 5 min (Discussion)
Poster Preview: 1 min (Presentation), No discussion

座長一覧

7月12日（水）　　　　　　　　　　　　（敬称略）

	時　間	座　長
特別講演（葛巻）	9:00 ～ 9:30	小海　文夫
一般講演	9:30 ～ 10:30	岡田　晋
一般講演	10:45 ～ 12:00	丸山　茂夫
特別講演（齋藤）	13:00 ～ 13:30	阿知波　洋次
一般講演	13:30 ～ 14:30	小塩　明
一般講演	14:45 ～ 16:00	佐野　正人
ポスタープレビュー	16:00 ～ 17:10	若林　知成 若原　孝次
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7月13日（木）

	時　間	座　長
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一般講演	10:45 ～ 12:00	片浦　弘道
特別講演（阿多）	13:15 ～ 13:45	白石　誠司
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7月14日（金）

	時　間	座　長
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7月12日(水)

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

特別講演(9:00-9:30)

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☆☆☆☆☆☆　休憩　(10:30-10:45)　☆☆☆☆☆☆

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ナノチューブの物性

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☆☆☆☆☆☆　昼食　(12:00-13:00)　☆☆☆☆☆☆

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☆☆☆☆☆☆　休憩　(14:30-14:45)　☆☆☆☆☆☆

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ナノチューブ:生成と精製

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7月12日（水）

ポスタープレビュー（16:00-17:10）
ポスターセッション（17:10-18:40）

フラーレンの化学

金属内包フラーレン

フラーレン固体

ナノチューブ：生成と精製

7月12日(水)

ナノホーン

ナノチューブの物性

ナノチューブの応用

7月12日（水）

その他

7月13日（木）

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

特別講演（9:00-9:30）

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☆☆☆☆☆☆　休憩　(10:30-10:45)　☆☆☆☆☆☆

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☆☆☆☆☆☆　昼食　(12:00-13:00)　☆☆☆☆☆☆

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☆☆☆☆☆☆　休憩　(15:00-15:15)　☆☆☆☆☆☆

ポスタープレビュー（15:15-16:30）

7月13日(木)

ポスターセッション(16:30-18:00)

フラーレン生成

フラーレンの化学

金属内包フラーレン

フラーレン固体

炭素ナノ粒子

ナノチューブ:生成と精製

7月13日(木)

内包ナノチューブ

ナノホーン

ナノチューブの物性

ナノチューブの応用

その他

7月14日（金）

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

特別講演（9:00-9:30）

一般講演（9:30-10:30）
金属内包フラーレン

フラーレンの化学

☆☆☆☆☆☆　休憩　(10:30-10:45)　☆☆☆☆☆☆

一般講演（10:45-11:45）
フラーレンの化学

☆☆☆☆☆☆　昼食　(11:45-13:00)　☆☆☆☆☆☆

特別講演（13:00-13:30）

一般講演（13:30-14:30）
ナノチューブの物性

☆☆☆☆☆☆　休憩　(14:30-14:45)　☆☆☆☆☆☆

一般講演（14:45-15:45）
ナノチューブの物性

ナノチューブの応用

一般講演(15:45-16:30)

ナノチューブの応用

July 12th, Wed.

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

Special Lecture (9:00-9:30)

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

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

General Lecture (10:45-12:00)
Properties of Nanotubes

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

Special Lecture (13:00-13:30)

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

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

July 12th, Wed.

General Lecture (14:45-16:00)

Formation and Purification of Nanotubes

Poster Preview (16:00-17:10)

Poster Session (17:10-18:40)

Chemistry of Fullerenes

Metallofullerenes

July 12th, Wed.

Fullerene Solids

Formation and Purification of Nanotubes

Nanohorns

July 12th, Wed.

Properties of Nanotubes

Application of Nanotubes

Miscellaneous

July 13th, Thur.

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

Special Lecture (9:00-9:30)

General Lecture (9:30-10:30)

Nanohorns

Carbon Nanoparticles

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

General Lecture (10:45-12:00)

Endohedral Nanotubes

Application of Nanotubes

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

General Meeting (13:00-13:15)

Special Lecture (13:15-13:45)

General Lecture (13:45-15:00)

Fullerene Solids

July 13th, Thur.

☆☆☆☆☆☆ Coffee Break (15:00-15:15) ☆☆☆☆☆☆

Poster Preview (15:15-16:30)
Poster Session (16:30-18:00)

Fullerene Formation

Chemistry of Fullerenes

Metallofullerenes

Fullerene Solids

Carbon Nanoparticles

Formation and Purification of Nanotubes

Endohedral Nanotubes

Nanohorns

July 13th, Thur.

Properties of Nanotubes

Application of Nanotubes

Miscellaneous

July 14th, Fri.

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

Special Lecture (9:00-9:30)

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General Lecture (9:30-10:30)
Metallofullerenes

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Chemistry of Fullerenes

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○Makoto Yanagisawa, Kentaro Tashiro, Takuzo Aida

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

General Lecture (10:45-11:45)
Chemistry of Fullerenes

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

Special Lecture (13:00-13:30)

3S-2 Chemical Modification and Photofunctionalization of Nanocarbon Materials 6
Hiroshi Imahori

General Lecture (13:30-14:30)
Properties of Nanotubes

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

July 14th, Fri.

General Lecture (14:45-15:45)
Properties of Nanotubes

Application of Nanotubes

General Lecture (15:45-16:30)
Application of Nanotubes

特別講演
Special Lecture

1S – 1 ～ 1S – 2
2S – 1 ～ 2S – 2
3S – 1 ～ 3S – 2

特別講演1

1S-1

Characterization of Carbon Nanotubes by Nanoprobe Manipulation in Transmission Electron Microscope

○Toru Kuzumaki

Institute of Industrial Science, The University of Tokyo, 4-6-1 Komaba, Meguro-ku, Tokyo 153-8505, Japan

A carbon nanotube (CNT) is a very promising candidate for applications in various fields. For increasing its engineering use, it is essential to develop a mass production process for high-quality CNTs. Although chemical vapor deposition methods are useful in the large-scale synthesis of CNTs, they have various atomic structures and morphologies that depend on the synthesis process or catalysts. The characteristics of even commercially available CNTs, including those synthesized by arc discharge, are not always identical. It is not certain whether nanoscale fibers that are commercially referred to as CNTs exhibit characteristics similar to those expected. However, there has been slow progress in the characterization of individual CNTs, while various applications and synthesis techniques have been proposed. It is important to clarify the characteristics of individual CNTs and standardize them for engineering applications. In the present study, characterization of various types of CNT by nanoprobe manipulation in a transmission electron microscope (TEM) is described.

Figures 1(a) and 1(b) show an MWCNT (a) before and (b) after deformation, and Fig. 1(c) shows force–displacement (F-D) diagram of the MWCNT. The points indicated by arrows in Fig. 1(c) correspond to the TEM images in Figs. 1(a) and 1(b), respectively. The applied force was released by the formation of a buckling like structure on the inner wall of the bent MWCNT (indicated by arrows in Fig. 1(b)). Young's modulus of the MWCNT estimated from Euler's buckling force is 0.92 TPa[1]. The nanoprobe manipulation technique in the TEM enabled the measurement of the force acting on various types of the MWCNTs while observing a clear deformation process. A series of experimental results suggest that the mechanical characteristic of MWCNTs is in positive interrelation with its crystallinity.

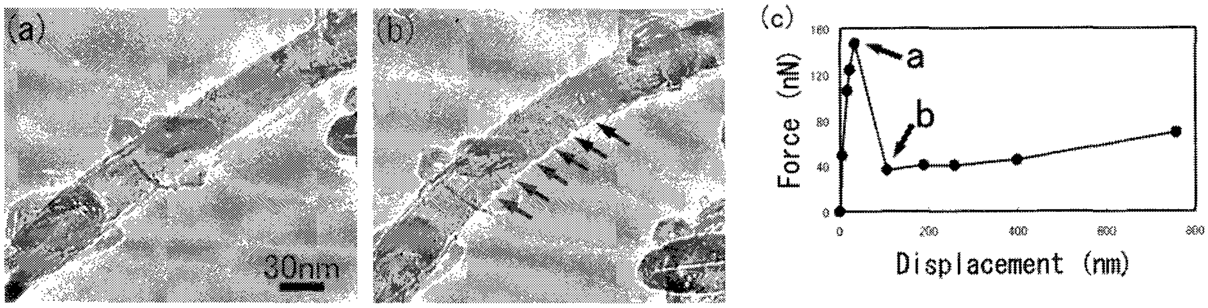

Figure 1 TEM images of MWCNT (a) before deformation and (b) after deformation, and its force-displacement diagram (c).

References: [1] T. Kuzumaki and Y. Mitsuda, Jpn. J. Appl. Phys., **45**, 364 (2006)

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特別講演2

1S-2

In situ TEM Studies on Carbon Nanotube Field Emitters and Nano-conveyors

○Yahachi Saito, Yasunobu Suzuki, Kensuke Okumura and Kazuyuki Seko
Department of Quantum Engineering, Nagoya University, Nagoya 464-8607, Japan

Application of carbon nanotubes (CNTs) to electron emitters in field emission displays (FEDs) is now attracting considerable attention. Electron emitters in FEDs are required to provide low threshold voltages for electron emission, emission stability and uniformity. In order to seek for CNTs that satisfy the above requirements, we studied the field emission (FE) from individual CNTs by in situ transmission electron microscopy (in situ TEM) [1]. The development of reliable experimental techniques for controlled manipulation and delivery of nanoscale materials is of extreme importance for realizing many nanotechnological applications. We also applied the in situ TEM to study a mass transport phenomenon on CNTs which was induced by electric current. Recent experiments by Regan et al. [2] demonstrated controllable, reversible atomic scale mass transport between indium nanoparticles deposited on CNTs. In our experiments, a free end of a multi-wall nanotube (MWNT) fixed on a tungsten needle was inserted into a reservoir of indium, instead of depositing In on the CNT, and the similar reversible transport of indium was observed by the application of electric voltages between the reservoir and the tungsten needle.

1. Dynamic behaviour of CNT field emitters

In the electric field a bundle of CNTs branched off at their tips and showed sublimation starting from their tips. For open MWNTs, peeling of outer graphite layers and subsequent sublimation of the layers were observed. The closed MWNTs did not show severe peeling of layers when the emission current was moderate, though sublimation of a few layers was observed at higher current.

2. Mass transport on CNT surfaces

When the voltage of the W needle was biased -1.1V (the corresponding current was ~90 μA) against the In reservoir, the metal began to melt. With the further increase of the voltage up to -1.7V (~200 μA), In droplets appeared on the surface of MWNTs. Under the constant voltage, growth and shrinkage of indium droplets on the MWNT surface were observed, as shown in Fig.1. Direction of In transport was reversed by applying the opposite potential to the W needle; i.e., In was always transported to a cathode.

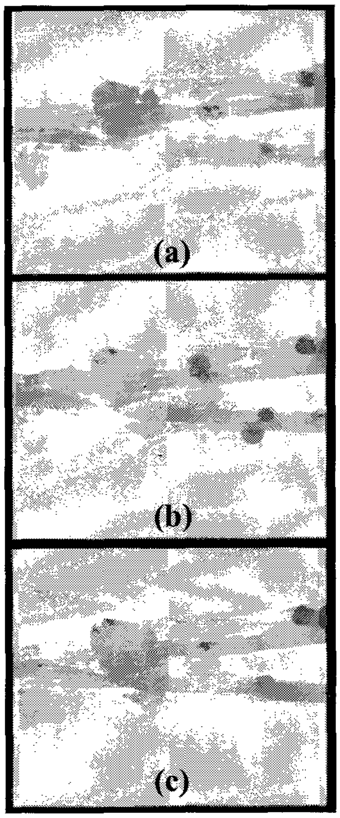

Fig.1

[1] Y. Saito et al., Diamond & Related Materials **14**, 1843 (2005)
[2] B. C. Regan et al., Nature, **428**, 924 (2004)

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特別講演3

2S-1

Nanopore Control and Physical Adsorption Properties of Single Wall Carbon Nanohorn Assemblies

○ K,Kaneko, T. Utsumi, C.－M. Yang, T. Ohba, K. Urita, R. Abdraim, Y. Hattori, H. Tanaka, H. Noguchi, H. Kanoh, M. Yudasaka*, and S. Iijima*

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Single wall carbon nanohorn (SWNH) consists of tube and corn parts and the internal tube spaces are closed. SWNH particles form a colloid assembly which has interstitial nanopores. As SWNH has a single carbon wall structure, SWNH can have a superhigh surface area for surrounding media. Therefore, opening of SWNH particles and control of interstitial nanopores have been requested in order to extend their application potential.

This paper shows the fundamental physical properties and nanopores structures as an introduction. Then the nanoporosity control with addition of nanowindows and reconstruction of the assembly structure will be shown. The nanoporosity control was done with four kinds of the treatment: Oxidation treatment with O_2, acid treatment, steam activation with $Ca(NO_3)_2$ deposition, and fluorination. The relationship between the nanopores and the physical adsorption properties for CH_4 will be shown.

The O_2 oxidation of SWNH at 823 K can add nanoscale windows on SWNH, increasing the surface area up to 1420 m^2/g from 380 m^2/g. The nanowindow-donated SWNH can adsorb more supercritical H_2 and CH_4 than closed SWNH. The HNO_3 treatment of SWNH increased interstitial nanoporosity, giving a larger adsorption capacity for CH_4. The steam activation can also add nanowindows to increase nanoporosity, which is less efficient than oxidation method with O_2. The fluorination can decrease the nanoporosity.

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2S-2

Policy Recommendations from "Research Project on Facilitation of Public Acceptance of Nanotechnology"

○Masafumi Ata, Yumi Negami, Ken-ichi Ishibashi, Mizuki Sekiya

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Four Japanese public research institutes[1] played a core role in implementing the research project entitled "Facilitation of Public Acceptance of Nanotechnology" under the financial support of the "Special Coordination Funds for Promoting Science and Technology" of Ministry of Education, Culture, Sports, Science and Technology (MEXT). The project was carried out with broad level of cooperation from many parties, including but not limited to universities, the private sector, journalists and non-governmental organizations. This project involved comprehensive research regarding the public acceptance of nanotechnologies, and the project promoted research through five working groups[2]. The findings from the research project were summarized and reported to the MEXT in March 2006.

We present a variety of recommendations in the talk that will help nanotechnologies become accepted in Japanese society, foster an atmosphere of public trust for these technologies, and ensure that future societies benefit from them. The recommendations include actions that we as public research institutes should take now, that corporations should keep in mind as they move forward, and that the Government should promote in its policies[3]. To make the point of story more objective one, research trend of societal issues of nanocarbon materials is highlighted, standardization of carbon nanotubes, as well.

[1] National Institute of Advanced Industrial Science and Technology (AIST, www.aist.go.jp), National Institute for Environmental Studies (NIES, www.nies.go.jp), National Institute of Health Sciences (NIHS, www.nihs.go.jp), National Institute for Materials Science (NIMS, www.nims.go.jp)

[2] WG 1 "Risk Assessment of Nanomaterials" by AIST (Research Center for Chemical Risk Management)
WG 2 "Health Impacts of Nanomaterials" by NIHS (Biological Safety Research Center)
WG 3 "Environmental Impacts of Nanomaterials" by NIES (Environmental Health Sciences Division, Environmental Chemistry Division, Research Center for Environmental Risk), University of Occupational and Environmental Health
WG 4 "Ethical and Societal Impacts " by NIMS (Ecomaterials Center), Nagoya University, Yokohama National University
WG 5 "Technology Assessment and Research on Economic Effects to Promote Public Acceptance of Nanotechnologies" by AIST (Technology Information Department, Metrology Institute of Japan, and Nanotechnology Research Institute), Nanotechnology Business Creation Initiative (NBCI), private corporations, universities, journalists, NGOs, etc.

[3] As the conclusion of this project, on February 1, 2006 we organized an international symposium entitled "Exploring the Small World: Role of Public Research Institutes" at the U Thant Hall of the United Nations University in Tokyo. Report on the International Symposium is now in press.

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3S-1

Nano-patterning by single-molecule manipulation of fullerenes

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Nano-Patterning has been performed by single-molecule manipulation of fullerene molecules with scanning tunneling microscope (STM). Close-packed C_{60} layer was prepared on a Si(111)-(7 x 7) surface by thermal deposition under ultrahigh vacuum of 10^{-10} Torr. The STM tip was placed on a target molecule in the C_{60} close-packed layer at sample bias voltage V_S and tunneling current I_t set points of 2.0 V and 1.5 nA, and the V_S was applied from –2.0 to 0.0 V by 2.0 mV steps for 3 – 15 ms. The C_{60} molecules were removed, and the voids were formed corresponding to sizes from one to three molecules. This phenomenon may be based on a field-evaporation, which is realized as evaporation of S atoms in MoS_2 surface [1]. These molecular-size voids could be easily transferred by an application of V_S from the STM tip to the molecules adjacent to the voids. The removal of C_{60} molecules and movement of voids could be achieved at both negative and positive V_S. Consequently, the STM tip enabled a fine patterning with molecular-size voids on the C_{60} close-packed surface to be made at the precision of single molecules [2].

The STM tip was placed on the C_{60} close-packed layer at V_s and I_t set points of 2.0 V and 0.2 nA; the tip-molecule distance is longer than that for formation of molecular voids. The V_s of –3.0 or –3.3 V was applied from the STM tip to the close-packed layer for 30 s. This provided a beautiful polymer ring of C_{60}. The outer and inner diameters of polymer rings increased with an increase in V_s. The formation of polymer ring shows that both polymerization of C_{60} molecules and depolymerization are induced at the same time by the application of V_s. Here we proposed a model that the holes injected from the STM tip propagate radially and consume the energy in the close-packed layer, and the holes with high energy near the center induce depolymerization and the holes with low energy can induce only the polymerization. In fact, the energy required for the polymerization is expected to be lower than that for depolymerization. Thus, our model well explains the formation of polymer ring.

Furthermore the electrons injected from the STM tip were also found to produce the polymer ring. The outer and inner diameters were larger than those of the ring formed by hole-injection. This result may be explained by the difference in electron-phonon coupling in LUMO/LUMO+1 and HOMO/HOMO-1. Furthermore, I will show interesting STM images produced by interaction of holes and electrons with various types of scatterers in the close-packed C_{60} layer [3]. Consequently, it can be concluded that fullerene molecules are promising materials for nanometer-scale science and technology.

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[3] R. Nouchi, K. Masunari, T. Ohta, Y. Kubozono, Y. Iwasa, submitted.

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特別講演6

3S-2

Chemical Modification and Photofunctionalization of Nanocarbon Materials

Hiroshi Imahori

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Recently, many studies have been focused on nanocarbon materials including fullerenes and nanotubes. In particular, chemical modification and photofunctionalization of such nanocarbon materials have attracted much attention toward the development of solar energy conversion systems. We have prepared a variety of nanocarbon material-based nanostructures for molecular photovoltaics. In this talk, we will present the following three topics: i) bottom-up fabrication of porphyrin-fullerene composites, ii) hydrogen-bonded porphyrin-fullerene arrays, and iii) chemical modification of carbon nanotubes. First, we have developed novel photoelectrochemical systems based on supramolecular complexes of porphyrin and fullerene on nanostructured SnO_2 electrodes. The bottom-up self-assembled film of the composite clusters exhibited an incident photon-to-photocurrent efficiency (IPCE) of up to 59%. Secondly, hydrogen bonding effects on surface structure and photoelectrochemical properties have been examined in a mixed film of porphyrin and fullerene composites with and without hydrogen bonding on ITO and nanostructured SnO_2 electrodes. Both the ITO and nanostructured SnO_2 electrodes modified with mixed films of porphyrin and fullerene composites with hydrogen bonding revealed efficient photocurrent generation compared to the reference systems without hydrogen bonding. These results show that hydrogen bonding is a highly promising strategy for the fabrication of donor and acceptor composites on nanostructured semiconductor electrodes, which exhibit efficient photocurrent generation. Finally, Bingel reaction has been successfully applied to sidewall functionalization of single-walled carbon nanotube (SWNT). The basic physical properties of functionalized SWNT by Bingel reaction have been examined in detail for the first time. More importantly, the electronic properties of SWNT are largely retained after sidewall modification by Bingel reaction without apparent selective reactivity for metallic and semiconducting SWNTs. Thus, the present covalent functionalization is a potential methodology for constructing molecular devices in which SWNTs modified with photoactive and/or electrochemically active chromophores can be employed without losing their intrinsic electronic properties of SWNTs.

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一般講演
General Lecture

1 – 1 ～ 1 – 18
2 – 1 ～ 2 – 14
3 – 1 ～ 3 – 19

1-1

Mechanical and Electrical properties of Carbon Nanotubes

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Mechanical and electrical properties of carbon nanotube (CNT) are affected by its defects or crystallization. We have investigated a relation between the mechanical strength and the maximum allowable current as an electric property for multi-walled CNTs.

Carbon nanotubes used in this study were synthesized by chemical vapor deposition (CVD) and annealed at a temperature over 2000 °C. The mechanical strength of the CNTs was measured from the resonant frequencies of CNT cantilever vibrations in a scanning electron microscope (SEM). After the mechanical strength was measured, the free end of the CNTs was contacted with a Pt-coated silicon cantilever by a SEM manipulator. Then an excess current was applied to the CNT to induce electrical breakdown. The maximum allowable current density I_{max} was obtained from the excess current and length and diameter of the CNT.

Figure 1 shows a relation between Young's modulus and I_{max}. The Young's modulus of the CNTs were widely spread in a range of 0.1~1.9 TPa. The CNTs with a higher I_{max} show a higher Young's modulus. The value of I_{max} saturates to 3μA/nm when the Young's module is higher than 1TPa. Whereas highly graphitized CNTs which are synthesized by arc discharge show similar Young's modulus, the value of I_{max} is around 7μA/nm. This indicates that the defects affecting the mechanical strength are different from those affecting the electrical conduction. It is noted that the Young's modulus was measured in a small deflection limit. The molecular dynamics simulation in this region predicted that pinhole defects in CNTs do not affect the resonant frequency [1]. Therefore, the defects in the examined CNTs might be mainly the pinhole defects.

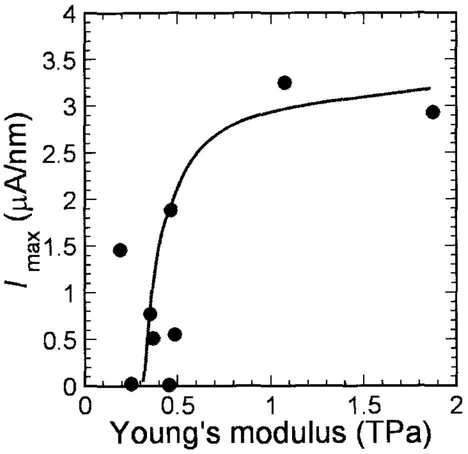

Fig.1 Relation between Young's module and maximum allowable current

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Acknowledgment: The authors acknowledge Nikkiso Co.,LTD. for providing CNTs.

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1-2

Diameter effect for plastic bending of carbon nanotube

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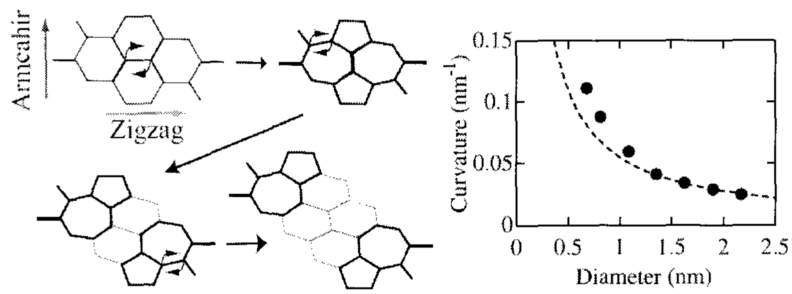
Getting control over plastic deformation of carbon nanotubes (CNTs) is vital to prepare functional elements for miniaturized electronic and mechanical devices. Recently, Nakayama *et al.* succeeded in plastically deforming single-wall carbon nanotube (SWNT) *in-situ* in transmission electron microscope (TEM)[1]. The Stone-Wales (SW) defect nucleation and splitting of two 5-7 defects cause plastic deformation. Plastic bending of single-wall carbon nanotubes (SWNTs) is analyzed using minimum energy path calculation with a bond-order potential. The calculation demonstrates that plastic deformation is thermodynamically favorable above a threshold “yield curvature” ρ_{yield}. This threshold behavior is the consequence of an interesting plastic confinement effect at the nanoscale. The exact derivation is rather cumbersome, but an approximate scaling can be found straightforwardly. Roughly speaking, the 5-7 defects will migrate from the point of the highest stress to the neutral plane where the stress is zero. Therefore, migration length of 5-7 defects is proportional to tube diameter D. From elastostatics and dislocation theory, ρ_{yield} should be roughly proportional to D^{-1}.We see that the approximate scaling agrees quite well with the actual numerical results.



(a) (b)

Fig.1 (a) The process of plastic deformation for bond rotation, (b) the yield curvature ρ_{yield} versus the tube diameter D.

References: [1] Y. Nakayama *et al.*, Jpn J. Appl. Phys. 44 L720.(2005)

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1-3

Thermal conductivity of an SWNT with micrometer length

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With expectations for SWNTs to possess high thermal conductivity, there has been a number of theoretical, numerical and experimental works reported to identify the thermal conductivity of SWNTs and their dependence on the geometrical parameters. With recent advances in synthesis and measurement techniques, a few experimental studies were recently reported on thermal conductivity of suspended SWNTs with lengths of a few micrometers [1, 2]. Now, the demand for reliable numerical simulation results is greater than ever not only for validations of the experimental results but also for probing the detail characteristics heat conduction that are not accessible with experiments. Here, we intend to provide a dataset on thermal conductivity using non-equilibrium molecular dynamics simulations (MD) for a wide range of nanotube length up to 3.2 μm, which covers the lengths investigated in the experiments.

An important feature of the SWNT thermal conductivity lies in the length dependence. The thermal conductivity depends on the length because the phonon ballistic limit is longer than the typical length of SWNT in practical situations. The results of the measurements (Fig. 1) indicate that there are two length regimes; the shorter length regime where the contribution of diffusive-ballistic phonon transports from a wide range of phonon branches including optical phonons [3], and the longer regime where the phonon transport is dominated by the key phonons with ballistic length longer than the tube length. In the latter regime, the thermal conductivity diverges with power-law dependence with respect to the nanotube length, which indicates that the limit of ballistic phonon transport exceeds 3.2 μm. Furthermore, the diameter dependence of the thermal conductivity reveals the dimension of heat conduction.

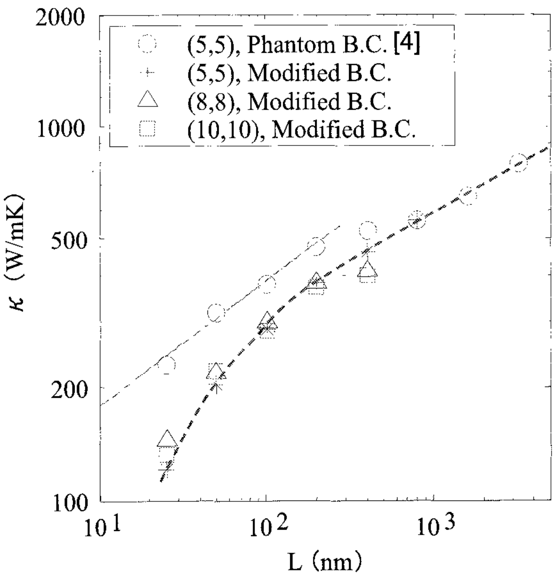

Fig. 1. Length dependence of thermal conductivity of SWNTs for different temperature control techniques and nanotube diameters.

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1-4

Field-Effect Modulation of Contact Resistance between Carbon Nanotubes

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Thin-film field-effect transistor (TFT) of carbon nanotubes (CNTs) has attracted great attention for applications [1]; the advantages of CNT-TFTs are their high current capacity, stability and simple fabrication-process. Although great progress in performance of CNT-TFTs has been reported, detailed mechanism of device operation has not been clarified. Local transport can be measured by using of conducting AFM with nano-meter resolution [2] and the technique was applied to the evaluation of field-effect transistor of CNTs [3]. In this study, we have investigated local transport measurement of CNT-TFT by conducting AFM and observed modulation of contact resistance between CNTs by field-effect.

Figure 1 shows a schematic of conducting AFM measurements on CNT-TFT. CNT-TFTs were fabricated by solution process [4]. Local current images of a CNT-TFT for three different gate voltages are shown in Fig. 2. Clear gate voltage dependence of current was observed. Especially, large modulation of resistance was observed at contact resistance between CNTs. It is concluded that the contact resistance between CNTs can be controlled by gate voltage in CNT-TFTs.

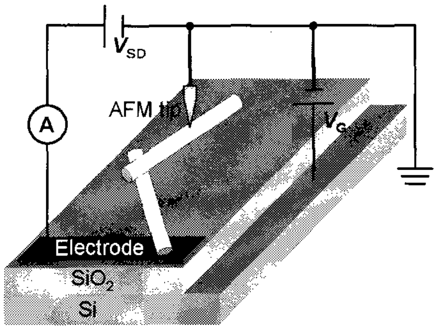

Figure 1. A schematic of conducting AFM measurements on CNT-TFT.

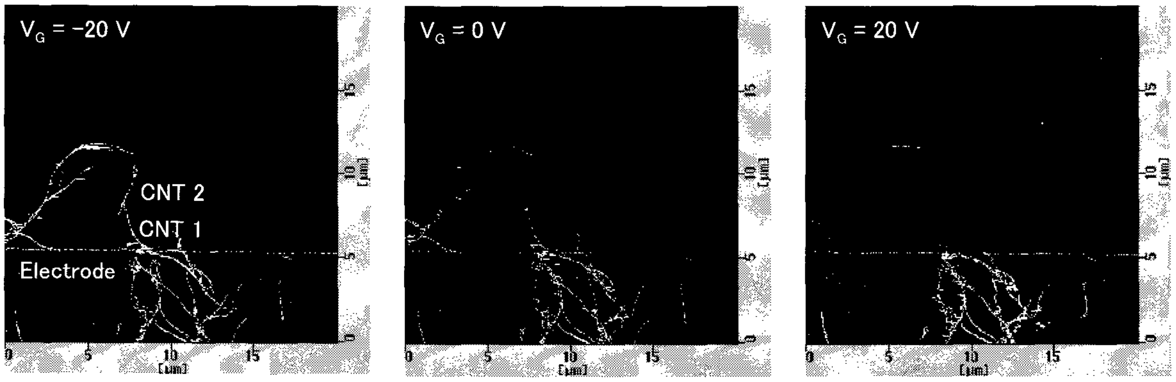

Figure 2. Local current images of a CNT-TFT for V_G = -20, 0, 20 V.

References: [1] E.S. Snow et al. Appl. Phys. Lett. **82**, 2145 (2003). [2] A. Fujiwara et al., Appl. Phys. Lett. **80**, 1993 (2002). [3] Y. Yaish et al. Phys. Rev. Lett. **92**, 046401 (2004). [4] M. Shiraishi et al. Chem. Phys. Lett. **394**, 110 (2004).

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1-5

FEM Observations of Behavior of Single Gas Molecule on Pentagon at Multi-walled Carbon Nanotube Tip

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By field emission microscopy (FEM) using multiwall carbon nanotube (MWNT) with clean surface, we have reported that six pentagons located at a tip of MWNT and behavior of a single gas molecule on the pentagons can be observed [1], contrary to established theory that conventional resolution of FEM is about 2nm due to uncertainty of electrons. When a surface of MWNT tip is clean, a six pentagonal rings image corresponding to six pentagons can be observed. Adsorption of a gas molecule onto a pentagon often brings about a change from a pentagonal ring image to a bright circular spot image with stepwise increase of emission current, and vice versa. This time, different types of bright spot images were observed, and we report them.

MWNTs were produced by arc discharge in helium gas. Clean surfaces of MWNTs were obtained by resistive heating for about a minute in an ultra-high vacuum with 6×10^{-8} Pa. Figure 1(a) shows an FEM image from a single MWNT after an adsorption of a molecule on a pentagon. The molecule was obtained as a gourd-shaped bright spot indicated by an arrow. The bright spot image indicated flip-flop motions between adsorption states shown in Figs. 1(a) and 1(b), and then changed a brighter circular spot as shown in Fig. 1(c). The gourd-shape of the bright spot suggests that the adsorbate was a diatomic molecule such as H_2, N_2, or CO, and its molecular axis was parallel to the substrate pentagon. The change of FEM image into Fig. 1(c) can be explained as following; the molecular axis was stood perpendicular to the substrate pentagon by the electrical field, so the emission current was enhanced due to increase of the dipole moment of the molecule.

This work has been supported by the Japanese Ministry of Education, Culture, Sports, Science and Technology for the Cooperation of Innovative Technology and Advanced Research in Evolution Area project, and for the foundation of Grant-in aid for Scientific Research (B), No. 18360023.

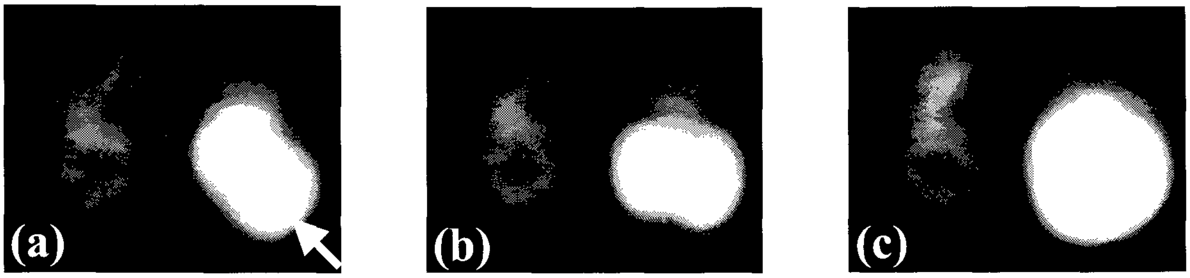

Fig. 1. FEM images from a MWNT adsorbed a single gas molecule onto a pentagon

[1] K. Hata *et al* : Ultramicroscopy, **95** (2003) 107.

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1-6

Electronic structure calculation of gate-biased carbon nanotube: Possible Stark effect

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Abstract:

The nanotube field-effect-transistor (FET) structures are fabricated in many groups and their characteristics are attracting much interest in many aspects. Applied gate-bias may rather drastically modify the electronic structure of nanotube. Understanding of the precise electronic structure in FET is expected to provide key knowledge to design new functional nanotube device.

We have performed first-principles calculations of gate-biased carbon nanotube, which represents a section of the nanotube in an FET structure. Gate bias introduces charge carrier into the nanotube, which is assumed to connect with electron reservoir. Continual chemical potential shift is actually made possible in the recently developed calculation technique, i.e. the ESM method.[1] The calculated charge density shows that bias-induced charge accumulation occurs in both metallic and insulating nanotube, when the bias is strong enough depending on the electronic band structure. The band structure around the conduction-band bottom (CBB) or the valence-band top (VBT) is almost identical even when the chemical potential is shifted and the extra charge is introduced. Thus the rigid band picture holds rather well. But, the induced charge density is accumulated on a side of the wall close to the gate electrode. The electron wave function which is in CBB and the hole wave function which is in VBT are modified spatially, but in an opposite direction with each other. Thus the Stark effect is clearly seen in the gate-biased nanotube. Since the nanotube is an ideal quantum wire, the quantum confined Stark effect is expected.[2] Our data supports this picture. Estimation of the attraction between an electron and a hole is possible in an appropriate picture of the Frenkel exciton. If we construct the model of a gate-biased nanotube, electrons move in the circumference direction on the tube, feeling a cosine potential due to the gate-bias. If the motion is in a spiral as shown for a chiral BC_2N nanotube,[3] the one-dimensional electron motion is suffered by a cosine potential due to the gate bias and the specific exciton formation is expected in the nanotube.

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1-7

Self-repairing of Atomic Vacancies on Densely Defective Nanontubes

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Atomic imperfections in the nanotubes are known to play crucial role to determine the electronic properties of them. The atomic defects (e.g. vacancies and interstitials) result in particular electron states of which wave functions are localized near the defects with dangling bond character. These localized states usually induce the reconstruction of the atoms around the defects, which reduces dangling bond energies albeit increase in stress energies. Such competition between electronic and elastic energies produces rich variety of atomic reconstructions of the nanotubes. In the present study, we perform the first-principle total-energy calculations on the densely defective carbon nanotubes. Our density functional calculation shows that the divacancy array on the armchair nanotube spontaneously transforms into the topological line defect consisting of octagons and fused pentagons [Fig.1(a)]. In another divacancy arrangement [Fig. 1(b)], we find that the Stone-Walles type bond rotation takes place with the energy barrier of about 1 eV repairing the atomistic defect. The results indicate that the tattered nanotubes with dense atomic vacancies are easily transformed into perfect cylindrical nanotubes under thermal annealing.

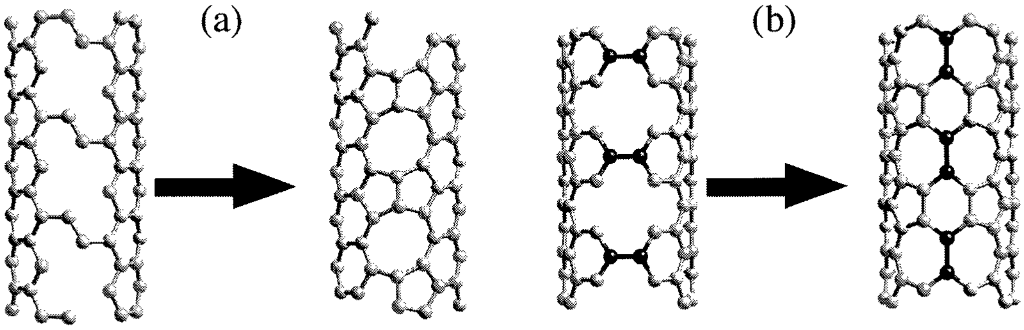

Fig. 1: Reconstruction pathways for (a) the divacancy array with tilted arrangement and (b) the divacancy array with parallel arrangement. In (b), dark atoms denote the atoms concerning with the bond rotation.

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1-8

Theoretical Calculations for Mono-Vacancy Diffusion on Carbon Nanotubes

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For the development of carbon nanotube devices with high performance and high stability we have to take into account of defects on nanotubes, since defects such as vacancies and adatoms easily alter the properties of nanotube devices.

In this paper, we will investigate the diffusion of mono-vacancy (MV) on nanotubes since MV may change not only mechanical properties but also electronic properties of nanotube. Recently, atomic scale TEM measurements[1] successfully observe the mono-vacancies on nanotubes, although the diffusion of MVs are not observed, yet. We consider the several diffusion paths which include two or three diffusion barriers along each path. Using the tight-binding potentials with nudged elastic band method, we find that the diffusion of vacancies on carbon nantoubes is anisotropic and depend on the diameter and chirality of nanotubes (see Fig.1). We will also discuss the effect of curvature on carbon nanotubes by comparing with the diffusion on a flat graphene sheet.

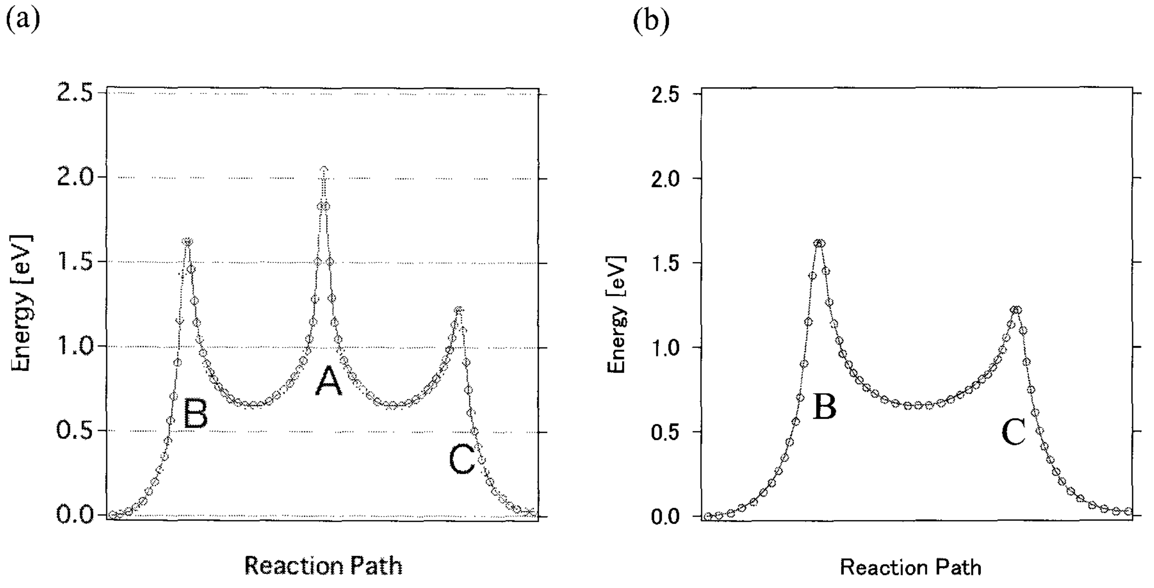

Fig.1 Energy variation for mono-vacancy diffusion on (17,0) nanotube along (a) the tube axis direction and along (b) the circumference direction. The labels 'A','B','C' indicate the different reaction along the diffusion path. The detail would be explained in the presentation.

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1-9

Pressure-Induced Phase Transition of Carbon Nanotubes and Tetragonal New Crystalline Solid Carbon Phase: A Molecular Dynamics Study

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Solid C60 is known to show pressure-induced phase transition from van der Waals solid to covalent-bond solids, i.e. the so-called polymerized C60 with several distinct crystalline phases including one-dimensional and two-dimensional polymerized networks. The same kind of phase transitions under pressure would be an interesting issue to be addressed in the future. In the case of C60, the purified crystalline sample of solid C60 became available soon after the macroscopic production of C60. On the other hand, in the case of carbon nanotubes, the macroscopic production of single-wall nanotubes has been achieved but the production of uniform-topology sample is still to be achieved in the future. Therefore, the pressure induced phase transitions of carbon nanotube solids is now only be studied using the predictive theoretical method.

In this talk, I will review various pressure induced phase transitions of nanostructured carbon materials studied by using the constant-pressure molecular dynamics methods. Especially the nanotube solids under the external pressure of about 20 GPa is found to show rich variety of phase transitions. Among them, the phase transition from single-wall carbon nanotubes into new tetragonal crystalline phase of carbon is of high importance and interest due to its complete four-fold coordination like diamond. We will report the energetics and the electronic properties of this new tetragonal phase studied using the density functional theory.

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1-10

Optically Active SWCNTs

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d) Graduate School of Science, Kyoto university, Kyoto 606-8502

We have reported that specific range of diameters of CNTs are extracted through selective complexation with diporphyrin nanotweezers to give much narrower diameter distribution.[1] The separation of CNTs based on molecular recognition was applied to optical resolution using chiral diporphyrin nanotweezers (Fig. 1), resulting in obtaining optically active SWCNTs. SWCNTs (CoMoCAT) were extracted under sonication in the presence of (*R*)- or (*S*)-**1**. After removal of the nanotweezers, SWCNTs extracted with (*R*)- and (*S*)-**1** showed the symmetrical CDs in the range of 300-1100 nm (Fig. 2). These results indicate that the extracted SWCNTs are optically active and, therefore, their chirality is recognized by the chiral nanotweezers.

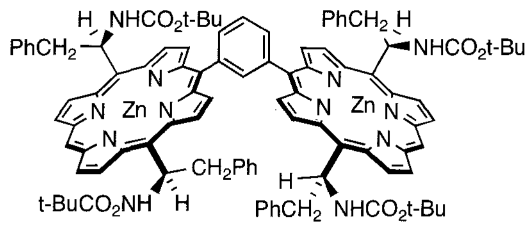

Fig. 1 Diporphyrin nanotweezers, (*R*)-**1**

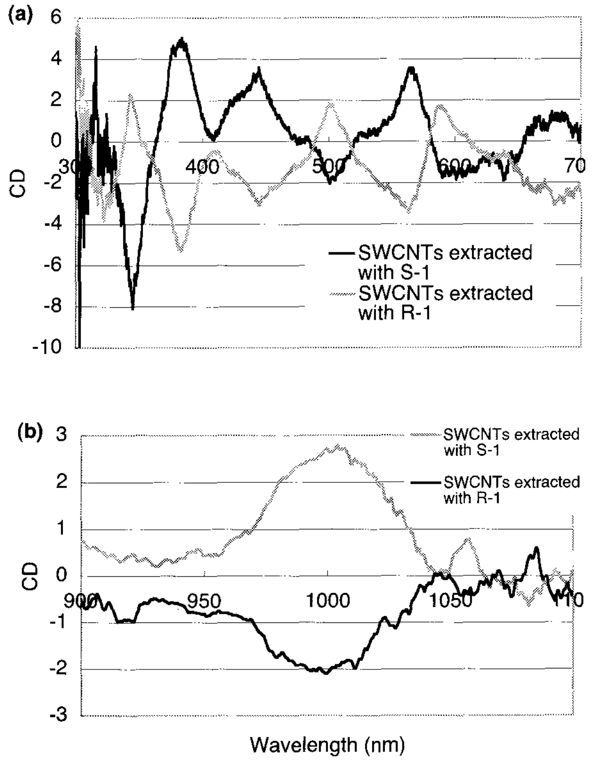

Fig. 2 CD spectra of extracted SWCNTs with (*R*)- and (*S*)-**1** in the range of 300-700 nm (a) and 900-1100 nm (b).

We thank Prof. Yasushi Kawai (Nagahama Institute of Bio-science and Technology) for CD analysis at 900-1100 nm and International Innovation Organization, Kyoto University for financial support.

[1] N. Komatsu, M. D. Milton, A. Osuka, *et al.*, The 29th Fullerene-Nanotubes General Symposium, Kyoto.

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1-11

Spectroscopic study on the purified single-walled carbon nanotubes

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As-prepared single-walled carbon nanotubes (SWNTs) were dispersed in organic solvents via a wet chemistry procedure, and were fractionated by a dispersion-centrifugation cycle. Optical absorption and resonant Raman spectra confirmed that heavily functionalized amorphous carbon was fractionated into the early centrifuged solutions, whereas lightly functionalized graphite fragments as well as polyhedral carbon and metal catalysts particles were fractionated into the late centrifuged solutions and residue, and then highly pure and well dispersed SWNTs were collected from the middle centrifuged solutions. In sharp contrast to the starting materials, the purified and well-separated SWNTs demonstrate many fine features, highly elevated intensity of the semiconducting absorptions in their UV-vis-NIR spectra. By referring to an "impurity-free" sample, the relative purity of the soluble sample reaches a value as high as 160% with monodispersity of 5%. A determination of the extinction coefficients shows that the concentration dependence of the absorbance follows the Lambert–Beer's law very well, and higher values in absorptivity than those reported previously are achieved.

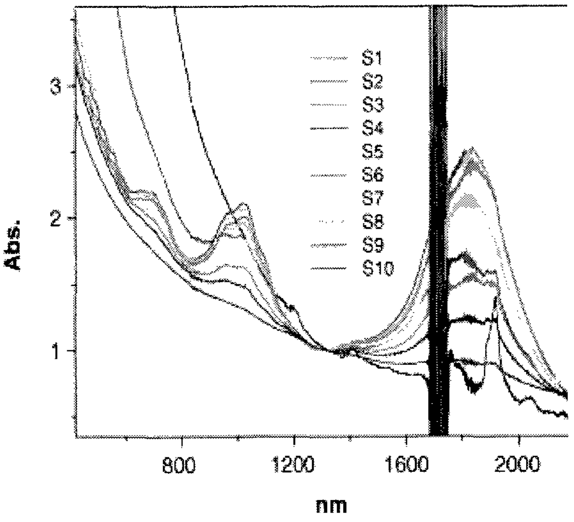

Fig. 1. The vis–NIR spectra of fractionated solutions S1 to S10 normalized at 1316 nm.

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1-12

Cationic surfactant dispersion of Single-Walled Carbon nanotubes: hydrophilic chain length effects

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The dispersion of Single-Walled Carbon nanotubes (SWNTs) in aqueous solutions was achieved in the presence of cationic surfactants from the trimethylammonium bromide family. The surfactants differ from each other by only two carbon atoms in the hydrophilic chain and have similar chemical properties. However, the critical micelle concentration (CMC) and solubility are quite different from each other. At 5 mg/ml all surfactants have a good solubility but the shorter member in the family, namely decyltrimethylammonium bromide, is not exceeding CMC. This kind of behavior prompted us to perform additional dispersions for this single surfactant at higher concentrations.

The HiPco nanotubes were dispersed at a 0.25 mg/ml initial concentration in a 5 mg/ml surfactant aqueous solution. The dispersion procedure employed ultrasonication with a 3 mm diameter titanium microtip at 2 W/ml power densities for 1 hour in an ice bath. Immediately, the solutions were ultracentrifugated at about 200,000 g for 1 hour. The upper ~70 % of dispersion have been collected carefully and was used for further analysis by absorption, emission and Raman spectroscopies.

Surprisingly, the low hydrophilic chain surfactants are not able to disperse the nanotubes, while for the average length chains the dispersions are not stable in time.

At the same concentrations, the short hydrophilic chain surfactants could not overcome the strong van der Waals attractions between nanotubes and therefore they could not assure a stable dispersion.

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1-13

Dispersion of carbon nanotubes in water by designed amphiphilic oligopeptides

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Dispersion of CNTs in organic and aqueous solutions is one of the important factors for applications of carbon nanotubes to industries,. For this purpose, some physical adsorption techniques using sodium dodecyl sulfate [1], cholic acid derivatives [2], DNA [3,4], polymers [5], and polypeptides [6,7] have been reported. In many cases, an amphiphilic property is commonly required for their effective dispersion of CNTs in aqueous media.

We have developed amphiphilic linear oligopeptides to disperse CNTs in water. In the present design, Gly and Phe residues were adopted as the hydrophilic and hydrophobic regions in these peptides, respectively (Fig 1). The dispersion of CNTs was estimated by means of UV-Vis absorption spectroscopy and TEM. All peptides were synthesized by solution method using Boc-chemistry and determined by ^{1}H-NMR and elemental analysis. For dispersion of CNTs, each peptide was dissolved in water (about 0.5%) and CNT (1 mg) was added the peptide solution. After sonication, the obtained suspensions were centrifuged, and then the supernatants were used for all experimental analyses.

The UV-Vis spectra of the supernatants showed that the designed peptides can disperse CNTs in water and almost of CNTs form bundled structures. The formation of the CNT-bundle was also confirmed by TEM images. These results demonstrated that amphiphilic oligopeptides can disperse CNTs in aqueous solutions.

Fig. 1. Schematic representation of amphiphilic linear oligopeptides.

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1-14

Fullerene cap growth and formation of carbon nano materials
-N(naphthalene) and P(phenalenyl)-center Growth Model-

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In the present paper, we will propose a new growth model for the formation of "fullerene nano cap structure", in connection with understanding general formation mechanism of so called "carbon nano materials" such as fullerenes, metallofullerenes, carbon nanotubes and carbon nanohorn, etc. The presence of the fullenere cap structure has commonly been shown as a key carbon network structure by which the structures of fullerenes, metallofullerenes and carbon nanotubes are well characterized. However, so far, there has still been a limited numbers of knowledge directly related with understanding the growth process of these materials. However, understanding the growth mechanism and controlling network generation of carbon nano materials must be essentially important for the potential application of them to nano size devices or wires. Of particular importance is to directly control both diameter and chirality of single wall carbon nanotubes as grown process.

In the present model, first, we assume that for all carbon nano materials, the formation of fullerene cap structure is commonly taken place. Furthermore, we also assume that at very early stage of the growth of these materials, the fullerene cap structures or almost cap-like structure commonly plays an essential role on determining the isomers of fullerenes as well as the diameter and/or even chirality of carbon nanotubes. We propose here that only two types of carbon π system works as a center(like a seed of crystal growth) of growing carbon 5/6 network, i.e., naphthalene(N-center) and phenalenyl(P-center) skeleton. Characteristic features of these two types networks are the followings. "N-center" has ten π electrons, thus it is stabilized by itself without adding or removing electrons. On the other hand, "P-center" has thirteen, odd number π electrons, and adding one more electron results in stabilization of the skeleton. Therefore, the P-center is a good system in connection with metal atoms and plays a role on the formation of metallofulerenes, but the N-center is good for formation of empty fullerenes and carbon nanotubes. In the present work, we will demonstrate the result how some experimental evidences such as selection of isomers in empty and metallofullerene formation are rationalized by the present model. We will also present the reason why diameter distributions of carbon nanotubes are so narrow and why some of chiral induces are so favorable.

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1-15

The Effect of Water in Super-Growth Chemical Vapor Deposition

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The introduction of a small and controlled amount of water into the growth ambient of standard chemical vapor deposition (CVD) (hereafter denoted as super-growth) was reported to increase the synthesis efficiency of SWNTs to unprecedented heights [1]. From this water-stimulated catalytic activity [2], dense, impurity-free, and vertically-aligned SWNT forests with millimeter-scale heights could be grown and be patterned into scaled-up macroscopic organized structures with defined shape. These remarkable features make the super-growth CVD quite unique from existing SWNT synthesis methods, such as arc discharge, laser ablation, and other methods of CVD.

Characteristics of super-growth CVD, such as high efficiency, catalyst free tubes, and carbon nanotube forests are well established [1-3], but the origin of what makes the super-growth possible has not yet been identified. To understand the cause of super-growth CVD and the principle of water effects, microscopic observation of the effects is necessary.

Recently, we developed a new approach to direct analyze microscopic phenomenon associated with the catalysts by transmission electron microscopy (hereafter denoted as Ball CVD) [4] and combined it with super-growth CVD to direct analyze the water effects microscopically. Here, we report the first microscopic and spectroscopic confirmation of the role of water in super-growth CVD by the Ball CVD procedure. Electron energy loss spectroscopy (EELS) mappings revealed the removal of the carbon coating of the catalyst particles, and the strong dependence on the growth of carbon nanotubes on the water level.

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1-16

Exhaustive mapping of Co-Mo catalytic activity against their compositions in growing SWNTs from ethanol

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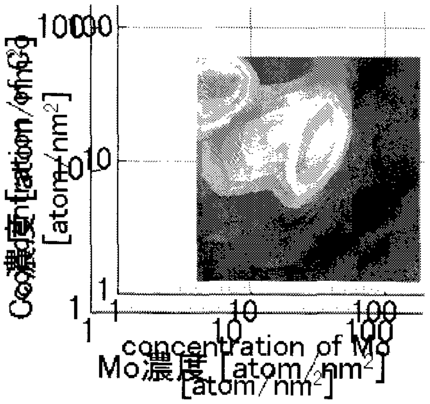
In the direct growth of SWNTs on substrates by CVD methods, preparation of the catalyst nanoparticles is a crucial issue. Co-Mo binary catalysts effectively grow SWNTs either from CO [1] and from alcohol [2]. However, different values are reported as the optimum Co/Mo atomic ratio; 1/3 for the former [1] and 1/1 for the latter [2]. The structure of catalyst nanoparticles should be determined not only by the composition but also by the load of catalyst metals, and optimum conditions should depend on the CVD conditions.

In this study, by using a combinatorial method [3], the SWNT growth by alcohol catalytic CVD with Co-Mo catalyst was systematically investigated. From the mapping of catalytic activity against the concentration of these metals, it was found that both of these two regions were catalytically active. Furthermore, at high pressure and longer time, the third region with a larger catalytic activity appeared at a large Co/Mo ratio (Fig.1). The mechanism for this incubation is unknown but this catalyst may be practically important in growing SWNTs at least from ethanol. Nanoparticle structure of each region after annealing under H_2 atmosphere and after SWNT growth by CVD was analyzed by SEM. Nanoparticles grew larger after CVD; indicating the agglomeration of Co nanoparticles were accelerated by forming the solid solution with carbon (Fig.2).



FigFig.1 Map of catalytic activity against **the**the concentration of metals

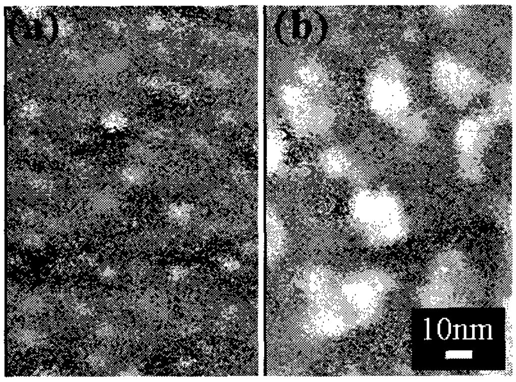


Fig.2 SEM images of Co nanoparticles
(a) after annealing under H_2 atmosphere
(b) after CVD reaction (SWNTs were removed)

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1-17

Low resistance contact formation mechanism for carbon nanotube via determined by hard x-ray photoemission spectroscopy

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Carbon nanotubes (CNTs) have been expected for use as wiring materials to solve several problems in future ULSI interconnects. Recently, we have succeeded in forming CNT vias whose resistance is in the same order as that of W plugs [1, 2]. To improve the via resistance, we have investigated the electronic structures at the interface between CNTs and metal electrodes using by hard x-ray photoemission spectroscopy (PES). The PES measurements were performed at the BL47XU in the SPring-8 with the approval of the Japan Synchrotron Radiation Research Institute (JASRI) (Proposal No. 2005B0912).

We measured Ti 2*p* core-level spectra of substrates after CNT growth for the following three catalyst/under-layer structures: (a) Co 1-nm/Ti 2-nm film, (b) Co 2.5-nm/Ti 6-nm film and (c) 4.5-nm Co particles/TiN 5-nm film on silicon substrates. The growth temperature was 450-510 ℃. As the carbon source, a mixture of acetylene and argon gases was used. The resistance values of a 2 μm-diameter-via were about 1 MΩ, 0.7 Ω [1] and 0.59 Ω [2] for (a), (b) and (c), respectively. In the spectra (b) and (c), we have found features originated from the titanium carbide (TiC) and titanium nitride (TiN), respectively. On the other hand, only a titanium oxide layer was observed in the sample (a), which can be a reason for the high resistance. These results indicate that the existence of the TiC or TiN contact layer should be very important to realize low-resistance CNT vias.

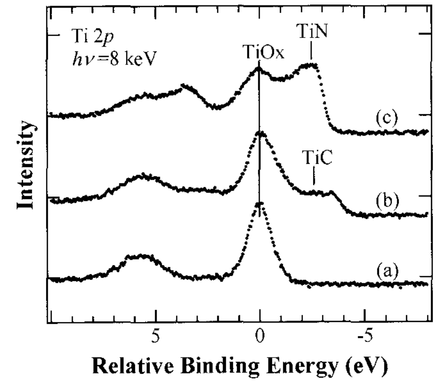

Figure 1 Ti 2*p* core-level spectra after the CNT growth.

Acknowledgement: The authors thank Dr. N. Yokoyama of Fujitsu Laboratories Ltd. for their support and useful suggestions. This work was supported by the Advanced Nanocarbon Application Project, which was consigned to JFCC by New Energy and Industrial Technology Development Organization (NEDO) of Japan.

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1-18

Formation of Vertically Aligned Carbon Nanofibers Having an Array of Conical Cavities

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Catalytic chemical vapor deposition (CVD) has been extensively investigated as a promising method for growing of carbon nanofibers (CNFs). It is well known that various structures of CNFs are formed by controlling growth conditions, such as metal catalysts and reactant gases. We have previously reported that CNFs having an array of conical cavities with lengths of 300–800 nm were formed by alcohol CVD using indium tin oxide (ITO) and Fe as metal catalysts. We named these CNFs "conical-cavity CNFs (CC-CNFs)" because they have a unique structure containing conical cavities in a one-dimensional array at uniform intervals. Recently, we have reported that the CC-CNFs were easily snapped at their nodes that correspond to the bases of the conical cavities. Moreover, we succeeded in growing the CC-CNFs vertically on a substrate by controlling the amounts of the metal catalysts we used. These results suggest that vertically aligned arrays of conical cavities formed in CNFs make new carbon architectures possible.

A substrate was prepared for CVD by spraying it with ethanol solutions of $InCl_3$, $SnCl_2$, and $FeCl_3$ on a Si plate maintained at 400°C followed by heating it at 600°C for 30 min. in an Ar atmosphere. The CVD growth of the CNFs was carried out for 30 min. at a vapor pressure of ethanol containing a small amount of CS_2.

Figure 1 shows a typical SEM image of tangled CC-CNFs obtained in our previous work. Observation by TEM revealed that the inner structure consisted of an array of periodic conical cavities with lengths of 300–800 nm (Fig. 2). Nodes of the CC-CNFs, which correspond to the bases of the conical cavities, are weak due to their very thin structure. The CNFs can easily be cut in a 1–10 pitch at the nodes by snapping the branches with mechanical force, such as ultrasonic irradiation. Figure 3 shows vertically aligned CC-CNFs obtained when small amounts of metal catalysts were deposited on a Si substrate. We explored the most effective growth conditions of the vertically aligned CC-CNFs and studied a possible formation mechanism of the one-dimensional array of conical cavities.

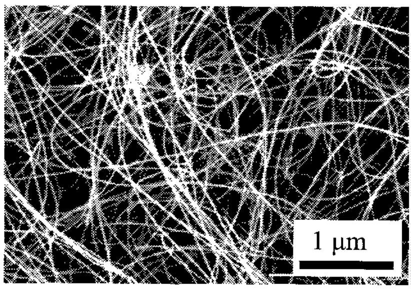

Fig. 1 As-grown tangled CC-CNFs.

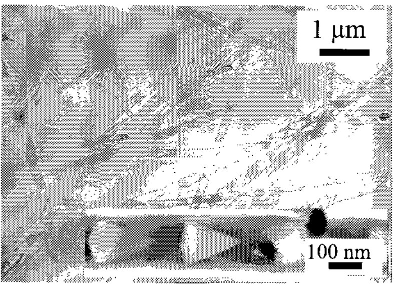

Fig. 2 TEM image of CC-CNFs having array of conical cavities.

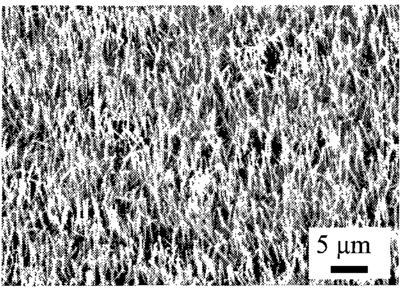

Fig. 3 Vertically aligned CC-CNFs on Si substrate.

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2-1

Single-Wall Carbon Nanohorns Carrying a Photosensitizer of Zinc Phthalocyanine for Photodynamic Therapy

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The single-wall carbon nanohorn (SWNH) [1] is a new type of nanocarbon material. Its large surface areas and plentiful inner nanospaces suggest several potential applications. The unique physicochemical properties and the size of a single aggregate of SWNHs, along with freedom from potential toxicity, suggest possible applications in the medical field, such as in drug delivery systems (DDS). Recently, the possibility of using SWNHs as an anticancer drug carrier was demonstrated [2]. In this study, we have used SWNHs to entrap a photosensitizer of zinc phthalocyanine (ZnPc) for photodynamic therapy

The technique for incorporation of ZnPc to SWNHs used here was similar to our previous study. The results of TEM and EDX showed that a large amount (40-50 wt.%) of ZnPc was incorporated into the SWNHs. A measurement of the local mass thickness with STEM demonstrated that ZnPc in SWNHs had a quite uniform distribution. Fluorescence spectra confirmed that ZnPc within SWNHs (ZnPc@NHs) rapidly induced the fluorescence quenching of 9, 10 dimethylanthracene. This indicated that the ZnPc in SWNHs retained its photophysical property of singlet oxygen generation, which is critical for photodynamic therapy. We also examined the interaction of ZnPc@NHs with a plasma protein, bovine serum albumin, using the fluorescence technique. Results showed that ZnPc@NHs interacted with the albumin in an aqueous solution. This will be helpful with regard to drug transfer and the selectivity of tumor targeting.

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2-2

Modification of the surfaces of single-walled carbon nanohorns using a conjugate between polyethylene glycol and a peptide aptamer, NHBP-1

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Single-walled carbon nanohorns (SWNHs) have come under the spotlight as a novel nanocarrier in drug delivery. It has been already shown that SWNHs can be loaded with small drugs such as dexamethasone and cisplatin, and that the loaded drugs are slowly released from the complex.[1,2] To develop the SWNHs as a drug carrier, however, the hydrophobic surfaces of SWNHs, which lead to the formation of large agglomerates, should be modified to acquire biocompatibility. To endow SWNHs with biocompatibility, polyethylene glycol (PEG) is one of promising materials. The immunogenicity of PEG is known to be very low and it has been widely used in biomedical applications to reduce undesirable interactions. Murakami et al. have found that the conjugates of PEG and a hydrophobic anticancer drug, doxorubicin, adsorbed onto the surfaces of SWNHs and solubilized them in aqueous media.[3] To expand the compatibility of SWNHs as a drug carrier, the development of new dispersants that don't use drugs as binders will be of important. In this talk, we report the development of a new dispersant for SWNHs in which PEG is linked to a peptide aptamer (=a binder) against SWNHs.

The peptide aptamer, NHBP-1, which specifically binds to the surfaces of SWNHs, has been previously isolated from a phage display library.[4] The N-terminus of NHBP-1 was conjugated with PEG *via* an amide linkage. To make dispersed solutions of SWNHs, the PEG-NHBP conjugates were mixed with SWNHs in water for several hours. The PEG-NHBP non-covalently bound to SWNHs, and the SWNHs/PEG-NHBP complexes were homogeneously dispersed in aqueous media. The loading of a drug onto the SWNHs/PEG-NHBP complexes will also be reported.

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2-3

Colloidal properties of nanodiamond dispersion

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Nanodiamond (ND) produced by detonation has been expected as a novel nanocarbon material with exclusive sp^3 configuration. However the promotion of the science and the industry of the ND prevented by the extremely tight agglutination among the primary particles. Therefore the properties of the primary particle have never been investigated well. Recently, we succeeded in isolating the primary particles of ND by the microbeads milling technique[1], and become available in gram-quantities under the commercial name, NanoAmando®. The primary particles of ND can be dispersed as a stable colloid in water and also in a few polar organic solvents. The colloidal properties of dispersion are essential to reveal the property of a ND particle, and promote the science and technology of ND. We investigated the size distribution, pH resistibility, viscosity, ζ potential and color of ND colloidal solution.

The disintegrated ND suspension contains >90wt% of primary particles. The colloidal stability of ND against pH variation shows that the surface of the ND particle is hydrophilic and has few acidic functional groups. The viscosity of the ND colloid reveals that the effective volume of the primary particle of ND is about ten times larger than the original volume of particle. This means that the thick electric double layer on ND particles makes the apparent diameter 2.2 times larger. The high ζ potential (~50mV) and low ion concentration in ND suspension (less than ~100 ppm determined by the elemental analysis) support the thick electric double layer. Above 4%(w/v) concentration of ND, the colloid exhibits time evolution of the viscosity (the thixotropic phenomenon) to form stable gel structure, as the result of the development of the hydrogen-bond network surrounding ND particles. Strong absorbance of light by ND particles and the turbidity of the aggregates by Rayleigh scattering explain both absorption spectra of colloidal solution and rigid gel film of ND. The color (absorption in the visible region) of ND suspension may be attributed to the Plasmon of the particle surface, the lattice defects in the particle or surface modification from-sp3-to-sp2 of carbon.

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2-4

Protective Nature of the Outer Graphitic Cages against Oxidation of the Inner LaC_2 Crystallites in Nanocapsules

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Abstract:

There has been great interest in the incorporation of foreign materials into fullerene-like carbon structures (C_{60}, nanotubes, nanocapsules). Nanocapsules filled with LaC_2 crystallites were discovered in carbonaceous cathode deposits grown by arc discharge under an inert gas atmosphere [1, 2]. Although rare-earth carbides are hygroscopic and readily hydrolyze in moist air, the carbides in the capsules did not degrade even after a decade of exposure. Moreover, empty nanocapsules and nanotubes are more resistant to oxidation than other forms of carbon (such as diamond, soot, graphite, and C_{60})[3, 4]. Therefore higher oxidation resistance is also expected for the filled nanocapsules. In this study protective nature of the outer graphitic cages of stuffed nanocapsules was demonstrated.

Nanocapsules stuffed with LaC_2 were heated in thermogravimetric analyser in the range of 20 – 950 °C at a heating rate of 10 °C/min in excess air. Below 460 °C essentially no weight loss was observed, suggesting no oxidation of LaC_2 in the nanocapsule. One of heating runs was stopped at 460 °C and the sample was examined by transmission electron microscopy (TEM) and energy dispersive X-ray spectroscopy (EDS). The observation showed that all carbon nanocapsules including filled and empty nanocapsules seen in the sample were completely unchanged, suggesting no degradation of nanocapsules up to 460 °C. On the other hand no undamaged nanocapsules were observed in the heating run stopped at 580 °C. Figure 1 shows a typical TEM image of damaged nanocapsules.

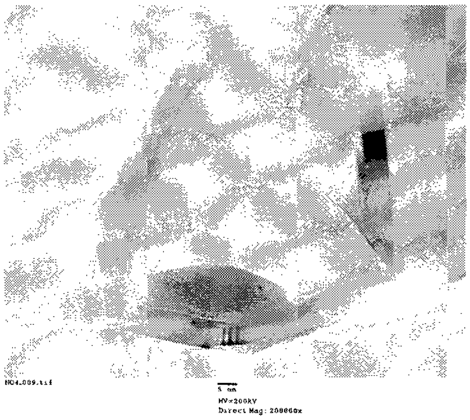

Figure 1. TEM image of degraded nanocapsules.

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2-5

Encapsulation of polyyne molecules into single-wall carbon nanotubes

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Polyyne molecules ($C_{2n}H_2$, $n \geqq 2$), linearly bonded *sp*-carbon materials, are a model for ideal one-dimensional chemical structure. Although polyyne molecules are well known as one of the interstellar molecules, they are easily decomposed by attacks of air or humidity. Thus to date, investigations on the polyynes have been done in vacuum environments, dilute solution, or in space field, and almost the studies are done by using mixture (not isolated) polyynes. In this work, we report a novel hybrid material: the polyyne-peapods. Well-purified polyyne solution ($C_{10}H_2$ in *n*-hexane) and single-wall carbon nanotubes were treated in liquid phase, and SWNTs encapsulating $C_{10}H_2$ inside were synthesized. Characterizations of obtained materials were performed by using Raman and X-ray diffraction spectroscopy.

Figure 1 shows Raman spectra of polyyne-peapods excited at 514 nm. Thick solid line is the spectrum of $C_{10}H_2$-doped SWNTs and thin dotted line is of pristine SWNTs. In addition to usual Raman band of SWNTs (RBM, G, and G' etc.), a salient signal at 2066 cm^{-1} was clearly observed only in polyyne-doped sample, which can be attributed to a stretching vibration of $C_{10}H_2$ molecules. The Raman spectra obtained in the present work is the first detection of polyyne molecules in the "laboratory room" (= under ambient, at room temperature, and on solid), suggesting a labile polyyne molecules were successfully encapsulated and stabilized in SWNTs.

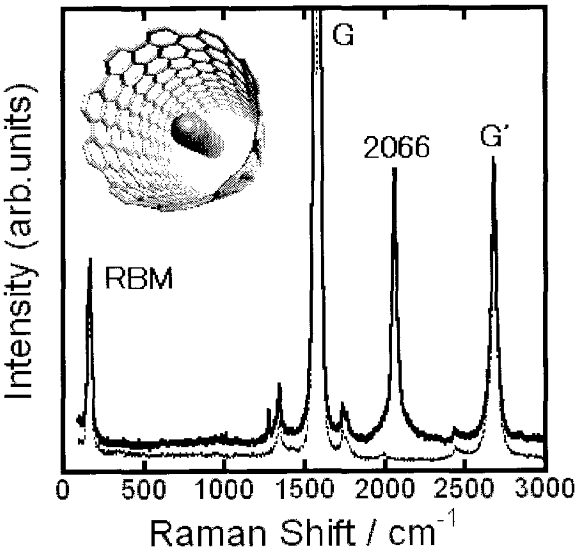

Fig. 1: Raman spectra of $C_{10}H_2$-doped (solid) and pristine (dotted) SWNTs

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2-6

A High-Yield Synthesis and Characterization of C60@DWNT Nanopeapods

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Here we report a high-yield synthesis of C60@DWNT nanopeapods by the vapor reaction method[1]. DWNTs of large diameters (1.5-5 nm) were prepared by CH4 cracking over Fe/MgO catalysts at 900 □. At the Fe to MgO ratio of 0.03 the best selectivity to DWNTs was obtained. A short reaction time (10 min) was found to be able to reduce amorphous carbons in the DWNTs. An air flow of 50 ml/min was introduced to the reactor when cooled to 450 □ for 10 min in order to remove the amorphous carbon. A simple purification operation, including liquid nitrogen treatment and diluted acid washing, was adopted to obtain a purity of 96 wt% (by TGA). After the purification the DWNTs were heated in open air at 450 □, which is a very important process for opening nanotubes. DWNTs with excessive C60 were sealed in a glass ample under $5\text{x}10^{-5}$ Torr and heated at 500 □ for 2 days. The as-prepared nanopeapods were characterized by TEM observation (Figure 1) and Raman spectroscopy.

The inner diameter distribution ranging from 1.5 nm to 5 nm of the present DWNTs is considered as a significant factor to achieve a high yield synthesis of nanopeapods. As a comparison, DWNTs purchased from CNI company, which has a inner diameter distribution around 1 nm, are also used to synthesis nanopeapods, and we found that the yield of peapods is very limited due to smaller diameters of the DWNTs. The arrangements of C60 in DWNTs are observed to be different with diameters of nanotubes. The stability of the nanopeapods under electron beam is also discussed.

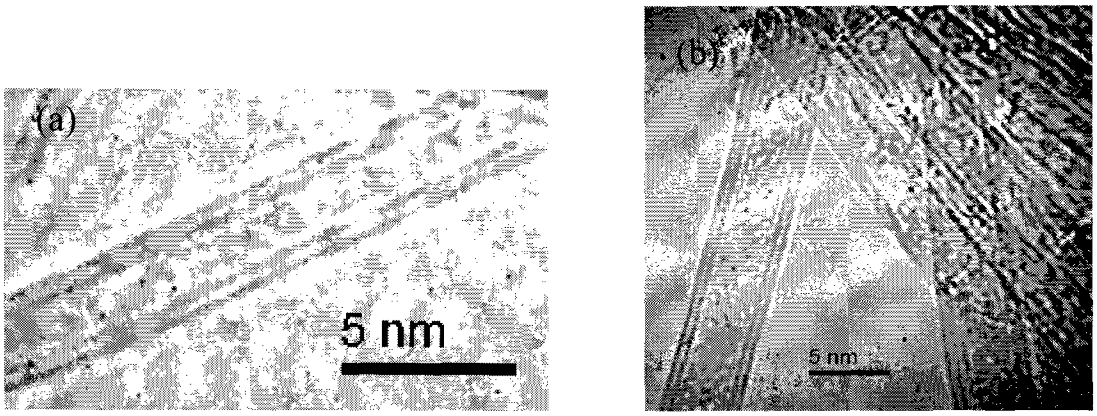

Figure 1. HRTEM images of the C60@DWNT peapods. (a) the single chain phase peapods; (b) a bundle of DWNTs peapods, indicating a high yield of peapods.

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2-7

Field-emission properties of titanium carbide-coated carbon nanotubes

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The investigation of field emission from carbon nanotubes (CNTs) has been focused on how to increase the stability and uniformity and to decrease the turn-on voltage as field-emission devices. In this work, the effect of titanium carbide (TiC) coated on the surfaces of CNTs has been studied for the improvement of the field-emission properties.

Carbon nanotubes were prepared by low temperature thermal CVD with the combination of preheating acetylene gas and using binary catalysts of patterned Co/Ti film [1]. The grown CNTs were then coated with 1 nm-thick Ti layer by electron beam evaporation. The carbonization of the Ti layer was performed by the same CVD process mentioned above. The field emission properties from the sample before and after TiC coating were measured at a pressure of 10^{-6} torr.

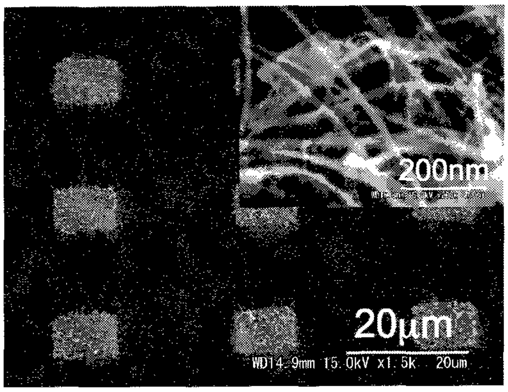

Fig. 1 SEM image of grown CNT patterns. The inset is an enlarged image.

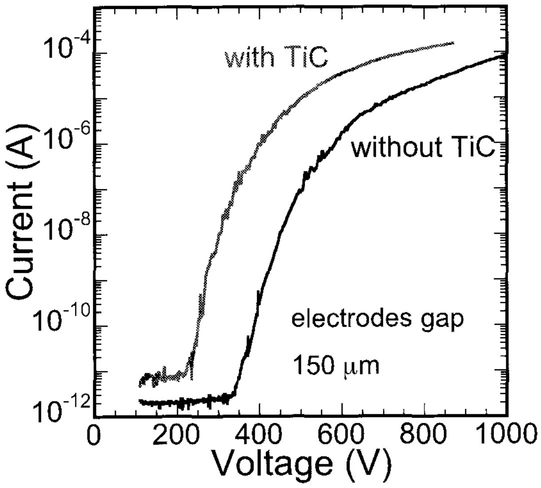

Fig. 2 Field emission current plotted as a function of applied voltage for the samples before and after TiC coating on CNTs.

Figure 1 shows the SEM image of low-temperature grown CNTs. The diameters of the CNTs are ranged form 10 to 20 nm and their length is less than 5 μm. Figure 2 shows the voltage-current curve of the sample before and after TiC coating. It is found that the turn-on voltage is largely decreased from 340 V to 220 V after the TiC coating. This result is explained by lowering the effective work function of the emitter by coating the TiC layer with the low work function of 2.35 eV. This consideration is also been confirmed by the decrease the slope of the F-N plot for the TiC coated CNTs. Furthermore, the improvements of uniformity and stability of field emission from the TiC coated CNTs have also been observed.

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2-8

Formation of Honeycomb-Patterned Single-Walled Carbon Nanotubes

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Microporous thin films have received increasing interest in recent years because of their potential application in the fields of electronics, biotechnology and photonics. There are a number of techniques that have been studied for the production of well-controlled microporous films, such as colloids particles and block copolymer as templates, for instance. François et al. first have reported that honeycomb-patterned porous polymer films are able to be prepared by simple casting from a carbon disulfide solution of polystyrene-polyparaphenylene block copolymer under high humidity[1]. Hexagonally packed water microdroplets acted as the template around which the polymer in the solution, then honeycomb structure is creating.

This study aims to fabricate carbon nanotube-based honeycomb structures. In this study, we prepared a polyion complex of single-walled carbon nanotubes (SWNTs) and trialkylmethylammonium chloride (**1**, Figure 1), and have succeeded to fabricate SWNTs-based honeycomb structure by casting from a chloroform solution of a SWNTs-**1** composite nanomaterial on a glass substrate (Figure 2). Details will be reported at the meeting.

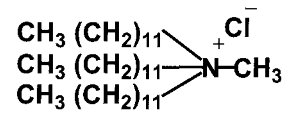

Figure 1. Chemical structure of **1**.

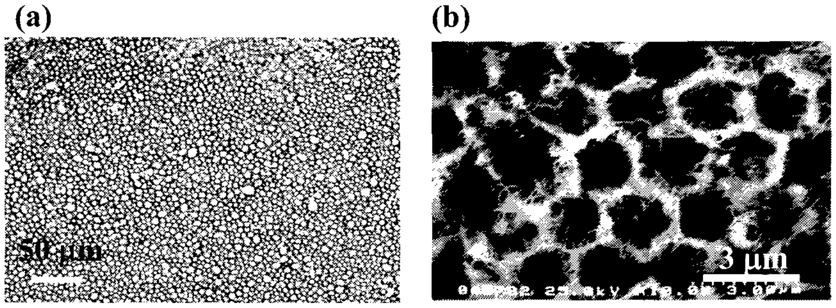

Figure 2. Microscope images for a cast film of SWNTs-**1**.

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2-9

Carbon nanotubes as lubricant additives

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In the future, a new research area in tribology is finding less polluting new additives as well efficient as those used today, in terms of friction reducing and antiwear properties. Traditional additives are mainly organic compounds containing sulphur and phosphorous. Their antiwear mechanism is based on a tribochemical reaction leading to the generation of harmful liquid and gaseous products. The purpose of this study is to investigate the tribological properties of some carbon nanotubes (NTs) when used as additives in a lubricant base oil. Because of their unique morphology, these "nanobjects" are thought to have interesting tribological properties. Because they contain only carbon and metal catalysts, they are expected to be less harmful for the environment. Moreover, their structure, without dangling bonds, confers them chemical inertness. Finally, their nanometric size could allow them to enter more easily into the contact gap and to become tribologically active directly in the contact area. NT additives could be used in smaller quantities than organic compounds in order to obtain good tribological properties. Tribological performances of Ni/Y-based single wall carbon nanotubes (SWNTs) additives have already been reported in a previous work [1]. SWNTs are able to reduce significantly both friction and wear in boundary lubrication. However, the mechanism of action is very complex and not known. Particularly, the role of the metal needs to be clarified. In this work, we compare the tribological performances of Ni/Y-based SWNTs, metal-free SWNTs, Fe-based multi-wall carbon nanotubes (MWNTs) and metal-free MWNTs.

Carbon nanotubes can present very interesting tribological properties in terms of friction reduction and anti-wear efficiency. These properties can be explained by the formation of a metal-doped DLC-like tribofilm during friction tests. Better tribological properties are observed in the case of single wall carbon nanotubes containing Ni/Y catalyst particles. This suggests that catalyst particles are necessary to obtain good tribological properties with NT additives

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2-10

Molecular spin-electronics: spin-dependent transport in C_{60} fullerenes

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In addition to charge, spin is another important degree of freedom in electrons. The discovery of the giant magnetoresistance (GMR) effect [1] induced a practical use of the spin-polarized carriers in materials, for instance recording and memory. Recently, much effort has been devoted in extending the spin-dependent transport phenomena to molecular electronics, because weak spin-orbit interaction in molecules let us expect long spin lifetime. The first experimental result of 'molecular spin-electronics' was reported by Tsukagoshi *et al.* [2] in 1999. They observed spin-dependent transport in multi-walled carbon-nanotubes. But there are some technical issues in this research field, and not so many results, which are reliable, were reported so far [3].

In the present work, we have chosen to use the C_{60} fullerene as the materials for molecular spin-electronics. We think fullerene is one of the most suitable molecules for spin-electronics because of its comparatively high mobility and expectation of weak spin orbit interaction arising from its element, carbon. We fabricated a C_{60}-Co nano-composites device (Fig. 1) to observe spin-dependent transport in C_{60}s. In preparation of samples, we fabricated gold electrodes, of which gap was 10 μm (length) × 3.5 mm (width), onto glass substrates by photolithography and then C_{60}-Co nano-composites were deposited in high vacuum. Here Co nano-particles are embedded in C_{60} molecules. The ratio of C_{60} to Co was estimated to be C_{60}-Co_{11} (11 Co atoms per one C_{60} molecule). Finally we covered the nano-composite by capping layers for preventing the Co clusters from oxidization.

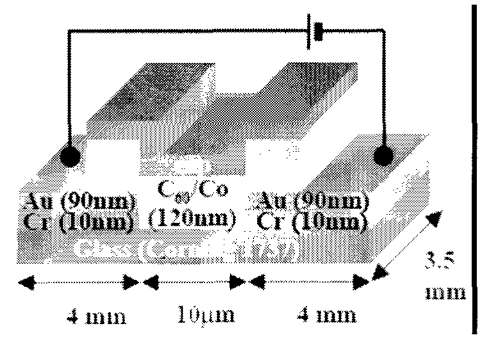

Fig. 1 Schematic of the device structure.

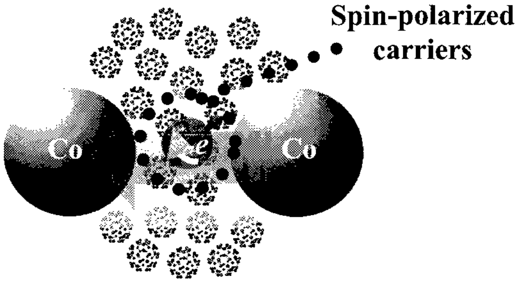

Fig. 2 Schematic image in the C_{60}-Co

Magnetoresistance (MR) measurements were carried out using cryostat with superconducting solenoids, and we observed a MR effect to be about 8% at 4.2 K, where the observed MR was ascribed to magnetization of the Co nano-particles. Although the MR effect decreases as the temperature increases, we succeeded in observing the MR effect even at room temperature. This result shows that spin-dependent transport in C_{60} was conducted (Fig. 2) and this work can be of help to develop the research field of molecular spin-electronics.

This study was supported by New Energy and Industrial Technology Development Organization (NEDO).

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2-11

Electronic States and Phonons in C_{60} Superconductors

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Since the finding in high T_c in C_{60} fullerides in 1991, a series of C_{60} superconductors have been reported to date. However, some of them were not realistic if one can accept the sophisticated recent theories for explaining the mechanism of C_{60} superconductivity. We have continued to clarify whether some questionable fullerides are indeed superconducting or not, because this is scientifically very important. Another important issue in C_{60} superconductors has been the determination of phonons mediating superconductivity. We have made experiments for settling down these two issues. Recent careful studies of rare-earth C_{60} fullerides have successfully shown that the previous assignment of the superconducting phase in $RE_{2.75}C_{60}$ (RE=Yb and Sm) is not correct [1] and the real superconducting phase resides in the t_{1g}-associated band [2]. Furthermore, the superconductivity appearing from C_{60} doped with La comes from the La carbides [3]. We have now been approaching to survey the phonons mediating Cooper electron pairs using H_2-endohedral C_{60} [4].

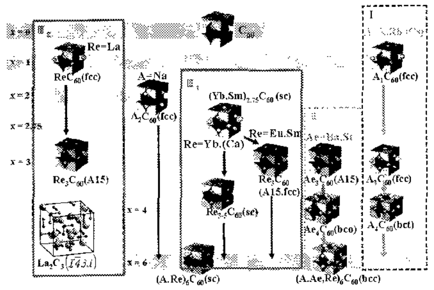

Fig.1 Structural sequence in C_{60} superconductors.

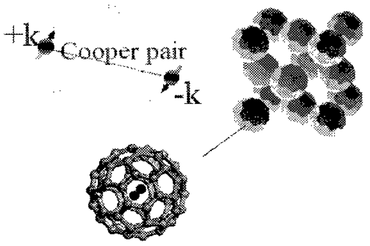

Fig.2 Survey of phonons by applying H_2-endohedral C_{60}.

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2-12

Morphology of C_{60} Crystals Synthesized in a Microfluidic Device

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Since their initial discovery in 1985 [1], Fullerene C_{60} has attracted significant attention for their unique physical and chemical properties [2]. In terms of technological issues, fabricating C_{60} crystals with complex shapes for practical uses is a very important challenge. Recently, the liquid/liquid interfacial precipitation method for the synthesis of needle-like C_{60} nanowhisker crystals was reported [3,4]. However, the bulk structures of these C_{60} crystals were all uniform and were single-dimensional.

Here, we report unusual structures of C_{60} crystals including tubes, trees, branches, hollow-ended columns, multiple pods, short prisms, and needles synthesized in a microfluidic device using a simple liquid/liquid interfacial precipitation method. The C_{60} crystal morphology is categorized mainly by temperature, and is similar to the morphology of snow crystals [5]. This simple method yields complex geometries of C_{60} crystals quickly, and could be applied to all materials synthesis techniques that use liquid/liquid interfacial precipitation.

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2-13

Synthesis of polymerized fullerene nanowhiskers by *in-situ* UV light irradiation

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It is well known that high molecular weight polyfullerene is prepared from photochemical reaction in fullerene solutions [1]. Recently, photochemical polymerization by laser irradiation after the crystallization in fullerene nanowhiskers is reported [2]. In the present study, we report the synthesis of polymerized C_{60} -nanowhiskers (C_{60}-NWs) by irradiating ultara-violet (UV) light *in-situ*.

The saturated *m*-xylene solution of C_{60} was prepared and pored into a bottle. Then isopropyl alcohol was added into the bottle to form a liquid-liquid interface [3]. The bottle was capped and kept under UV light (400W mercury lamp) at room temperature. The fibrous crystals were precipitated from the liquid-liquid interface.

Fig.1 shows the FT-IR spectra for (a) pristine C_{60}, (b) C_{60}-NWs grown under fluorescent lamp [4] and (c) C_{60}-NWs grown under UV light. Similar spectra is observed for pristine C_{60} and C_{60}-NWs (fluorescent lamp). However, new absorption peaks at 1106, 1200, 1385, 1470, 1630 and 1730cm^{-1} are appeared for C_{60}-NWs (UV). These absorption peaks are similar to those of one-dimensional C_{60} polymers prepared under high pressure and temperature [5].

Detailed results and the other properties of polymerized fullerene nanowhiskers will be discussed at the meeting.

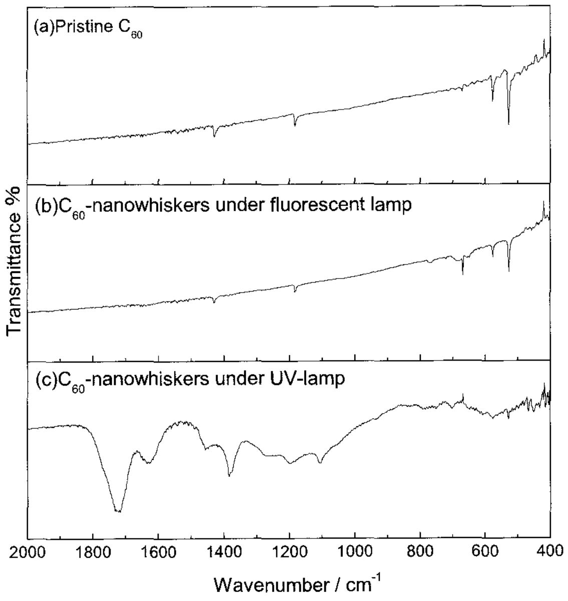

Fig.1 FT-IR spectra for (a) pristine C_{60}, (b) C_{60}-NWs grown under fluorescent lamp, (c) C_{60}- NWs under UV-lamp.

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2-14

Synthesis and Properties of fullerene derivative nanowhiskers

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Recently, a new type of fibrous fullerene crystals called fullerene nanowhisker has been reported by a liquid-liquid interfacial precipitation method. Considerable interests have been generated in the structure and properties of fullerene or fullerene-derivative nanowhiskers. In this study, we present the results of the synthesis and structural investigation of $C_{61}H_2$ –nanowhiskers ($C_{61}H_2$-NWs). The saturated *m*-xylene solution of $C_{61}H_2$ was prepared in a bottle. Isopropyl alcohol was added into the bottle to form a liquid-liquid interface. The fibrous crystals were precipitated from the liquid-liquid interface. Fig.1 shows the x-ray diffraction patterns of both $C_{61}H_2$-NWs at room temperature. The profile can be assigned to hexagonal structure with a=23.994 Å,c=10.203Å. Fig.1 shows the wide line ^{13}C-NMR spectrum for $C_{61}H_2$-NWs at room temperature. Peaks at 143.4 and 137.2 ppm which are attributed to the $C_{61}H_2$ and 126.4 and 21.2 ppm attributed to the *m*-xylene are observed.

Detailed results for NMR and the other properties will be discussed at the meeting.

Figure 1. X-rey diffraction profile for $C_{61}H_2$-NWs at room temperature.

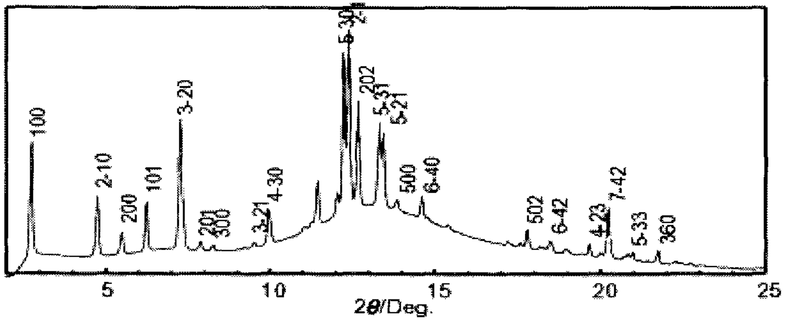
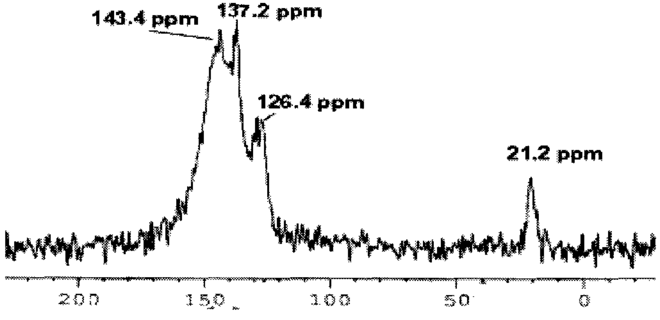


Figure 2. Wide-line ^{13}C-NMR spectrum for $C_{61}H_2$-NWs



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[2]M.Tachibana et al., *Chem.PhysLett.*, **374**, 279 (2003)
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3-1

Observation of Endohedral Metallofullerenes Diffusion Tendency on Self-Assembled Monolayers

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Single-molecular switching devices composed of a single functional molecule have been extensively studied as a basic component in molecular nanoelectronics. With regard to single functional molecules for creating single-molecular switching devices, endohedral metallofullerenes are one of the candidate materials owing to their electric dipole moment resulting from the exchange of electrons between an encapsulated metal atom and a fullerene cage. In the case of the strong interaction in endohedral metallofullerenes such as endohedral metallofullerenes deposited onto Si(111) substrate directly, it is difficult to switch the molecular orientation since molecular motion tends to be restricted[1]. On the contrary, in the case of weak interaction in endohedral metallofullerenes such as the top of the multilayer islands of endohedral metallofullerene, it is difficult to observe the molecular orientation switching since metallofullerenes rotate freely due to thermal fluctuation[2]. Thus, in order to realize molecular orientation switching, adequate interaction is required. Self-assembled monolayer (SAM) is expected to be a suitable interlayer to control the interaction between endohedral metallofullerene and metal substrate[3,4].

Here, we demonstrate the interaction control between a endohedral metallofullerenes ($Tb@C_{82}(I)$[5]and $Lu@C_{82}(I)$) and an Au(111) substrate by using several kinds of SAMs. We use several kinds of SAMs as the interlayer. We compare the STM images of endohedral metallofullerenes on SAMs. From high-resolution STM images of $Tb@C_{82}$ and Lu@C82 molecules on SAMs, we observe that the diffusion tendency of endohedral metallofullerenes show the SAMs dependence. We discuss the differences of diffusion tendency of endohedral metallofullerenes on SAMs by taking account of the electrical interaction due to the molecular length of SAMs.

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3-2

Ultraviolet Photoelectron Spectroscopy of Erbium Encapsulated C_{82}

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Ultraviolet photoelectron spectra (UPS) of erbium atom(s) encapsulated C_{82}, C_{2v}-Er@C_{82}, C_{3v}-Er_2C_2@C_{82} and C_{3v}-Er_2@C_{82} will be presented. The UPS were measured at BL8B2 of UVSOR in IMS. The spectra of C_{2v}-Er@C_{82} are almost identical to those of La@C_{82} or Tb@C_{82}. This finding is another evidence that the electronic structure of mono-metal atom encapsulated fullerenes is mainly dominated by the cage structure and a principal role of the entrapped atom is to donate electrons to the cage.

The UPS of C_{3v}-Er_2C_2@C_{82} and C_{3v}-Er_2@C_{82} (Figs1 and 2) resemble those of Y_2C_2@C_{82} (III) or Y_2@C_{82} both of them have the same C_{3v} symmetry. Slight difference among these UPS is in the second band located between 1.9 and 2.9 eV. The second band of Er_2C_2@C_{82} (III) or Er_2@C_{82} seems to consist of at least two components, while that of Y_2C_2@C_{82} (III) or Y_2@C_{82} seems to consist of a single envelope. This could be due to the overlap of Er 4f electrons.

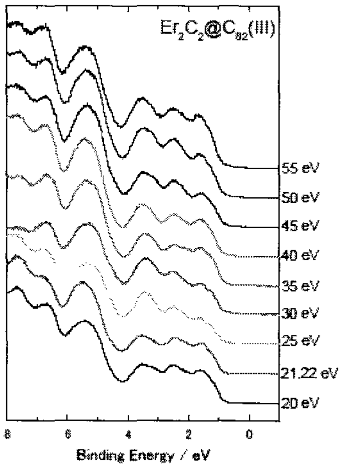

Figure 1 UPS of C_{3v}-Er_2C_2@C_{82}

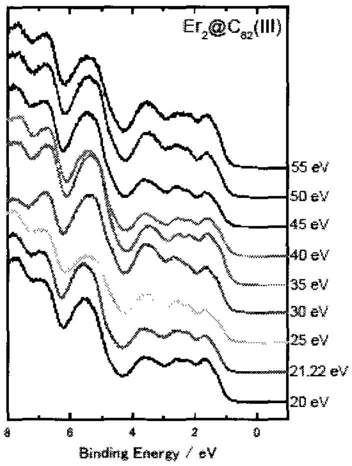

Figure 2 UPS of C_{3v}-Er_2@C_{82}

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3-3

IR/Raman Properties Calculations of Isotopically-Designed Icosahedral Clusters ~In case of Fullerene or Borane anion~

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We have examined hartree-fock or density functional calculations to fullerene or $(B_{12}H_{12})^{2-}$ icosahedral clusters with different isotopic ratios. The results of the simulations are summarized as follows. Using the IR/Raman-active mode [1]-[4] under C (C-12 and C-13) or B (B-10 and B-11) isotope control, we analyzed the wave numbers shift in the vibrational frequency by reduced mass depending on the composition of the B or C isotope. In particular, the A_g mode of B-10 enriched $(B_{12}H_{12})^{2-}$ anion showed degeneracy with the H_g mode [5]. In the calculation of the $B_{12}T_{12}$ anion, wherein H was substituted with T, the spectral number varied not only with the isotopic composition of 12 boron atoms but also with the isotopic configuration. On the other hand, the IR-active F_u mode in isotope-modified fullerenes was found to split into several spectra. Regarding engineering applications in nano electronic devices, it seems to become important to study how an isotope affects the interaction between the cluster vibration and carriers (e.g., not only BCS theory in superconductivity).

A part this work was carried out under the Visiting Researcher's Program of Advanced Research Center of Metallic Glasses, Institute for Materials Research, Tohoku University.

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3-4

Cyclic Dimers of Group 9 Metalloporphyrins: How High The Affinity of Host Molecules toward Fullerenes Can Be?

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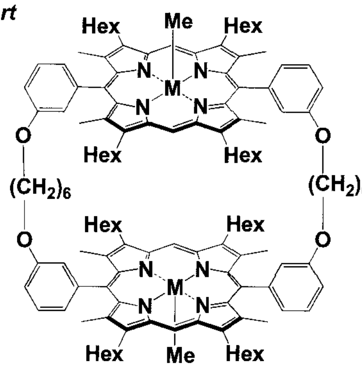
Design of host molecules having extremely high affinity toward fullerenes is interesting in that the strong host-guest interaction would be useful for the construction of carbon-rich supramolecular assemblies and modifications of chemical/physical properties of carbon cages as well as substances inside the cages. Here we report the results of our pursuit of fullerene hosts with higher affinity, by focusing on the interactions between fullerenes and group 9 metalloporphyrins [1].

We have reported that cyclic dimers of metalloporphyrins, especially having group 9 metal ions such as Co(II) and Rh(III), show high affinity toward fullerenes. The association constant K_{assoc} between C_{60} and a cyclic dimer methylrhodium porphyrin (**1**; **Chart**) in benzene at 25 °C was exceeded 10^7 M^{-1}, which was the largest value for the host-fullerene complexation events in aromatic solvents so far. These observations prompted us to investigate interactions between an iridium porphyrin analogue of **1** (**2**; **Chart**) and fullerenes. Since the K_{assoc} value for the formation of the inclusion complex **2**□C_{60} in benzene was too large for the accurate evaluation by the spectroscopic titrations, we used 1,2-dichlorobenzene, a better solvent for fullerenes, for the quantitative comparison of the K_{assoc} values of **1**□C_{60} and **2**□C_{60}, where the latter value is 400 times larger than the former. In agreement with this observation, upon addition of equimolar amount of **2** into a benzene-d_6 solution of **1**□C_{60}, **2** trapped almost all C_{60} included by **1**.

Chart



1: M = Rh
2 M = Ir

[1] *Angew. Chem. Int.Ed.*, **2001**, *40*, 1857; *J. Am. Chem. Soc.*, **2002**, *124*, 12086; *Angew. Chem. Int.Ed.*, **2006**, *45*, 3542.

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3-5

Synthesis of Organofullerenes Highly Soluble in Polar Solvents

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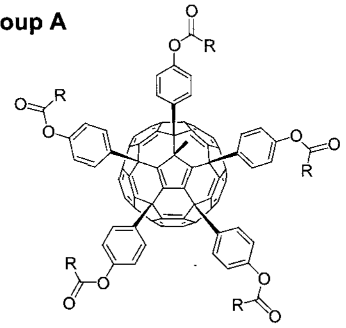
Recently, a wide range of fullerene derivatives have been reported. However, it is generally difficult to give fullerenes high solubility by derivatization. We modified side chains of pentaorganofullerene derivative, developed by Nakamura et al.[1], based on two different concepts and evaluated the solubility of the products in polar solvents.

Fullerene derivatives of Group A were prepared in excellent yield by esterification of $C_{60}(4\text{-}C_6H_4OH)_5Me$ under basic condition with a small excess of acid chlorides (RCOCl). Derivatives with branched R group exhibited higher solubility in PGMEA (propylene glycol monomethy ether acetate), a polar solvent generally used in industrial processes. Further, we found that derivatives which possess bulky and rotatable part on the ester moiety exhibited excellent solubility. In this context, $C_{60}(4\text{-}C_6H_4OCH_2CO_2tC_4H_9)_5Me$ also exhibited remarkable solubility in PGMEA (> 100mg/mL).

On the other hand, fullerene derivatives of Group B were synthesized by deprotection of methyl ethers with tribromoborane or iodotrimethylsilane. These compounds exhibited excellent solubility not only in esters but also in alcohols such as methanol and ethanol.

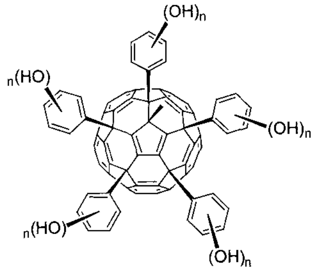
Further, we will discuss thermal and air -stability of these derivatives.

Group A



R = *i*-C_3H_7, *t*-C_4H_9, CH_2-*i*-C_3H_7, CH_2-*t*-C_4H_9

Group B



n = 2, 3

References:

[1]M. Sawamura, H. Iikura, and E.Nakamura, *J. Am.Chem.Soc.*, **1996**, *118*, 12850,

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3-6

Preparation of Metal Particles Dispersed Carbon Materials by Pyrolysis of Buckymetallocenes.

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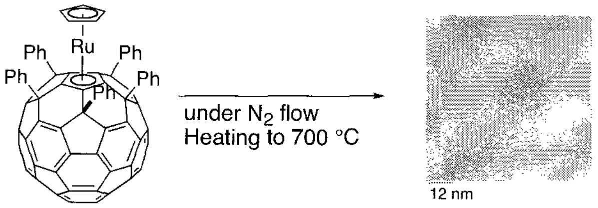
The hybrids of fullerene and transition metal complex molecules, such as buckymetallocenes; $M(\eta^5\text{-}C_{60}R_5)(\eta^5\text{-}C_5H_5)$ (M = Fe[1], Ru[2]) were synthesized in our group. The buckymetallocenes were the most stable molecules among the known fullerene-metal complexes even if under the oxidation and reduction conditions, due to the strong coordination of η^5-pentaorgano[60]fullerenyl ligands to transition metals. During a part of our continuous studies, we found thermal treatments of buckymetallocenes under an inert atmosphere gave carbonaceous materials which contain metal particles. Metal particles were highly dispersed on carbon substrate. In a buckyruthenocene case, obtained ruthenium particles were observed ~ 2 nm by XRD and TEM analysis, and showed catalytic activities towards hydrogenation reactions.



Ru in Carbon
Ru particle ~ 2 nm

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[2] Y. Matsuo, Y. Kuninobu, S. Ito, and E. Nakamura, *Chem. Lett.*, **33**, 68 (2004).

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3-7

Electrochemical Properties of an Open Cage Fullerene Embedded in a Lipid Cast Film on an Elctrode

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Koichi Komatsu[2], and Naotoshi Nakashima[1]

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Abstract: "Molecular surgery" of C_{60} is one recent topic in fullerene chemistry. Rubin *et al.* developed a synthetic methods to open a cage on C_{60} [1], and Komatsu *et al.* described a "molecular suture" of open cage fullerene (OCF, Figure 1) [2]. The goal of this study is to understand an electron transfer between an electrode and the OCF on electrode. We have described that C_{60} embedded in a cast film of ammonium lipids on an electrode undergoes three-consecutive reversible one-electron transfer reaction in an aqueous system [3]. Here, electrochemical behavior of OCF embedded in cast film of tetra-*n*-octylammonium bromide (TOAB) on electrode in aqueous solution was studied by means of cyclic voltammetry (CV). Two-consecutive one-electron reduction waves from OCF were clearly observed in CV for a OCF/TOAB film on a basal-plane pyrolytic graphite (BPG) electrode (Figure 2, curve a). On the contrary, no such behavior was observed for an OCF solely-modified electrode (Figure 2, curve b). Stronger binding of electrogenerated OCF-anions with TOAB is considered to be important for the electrochemistry of OCF on the electrode.

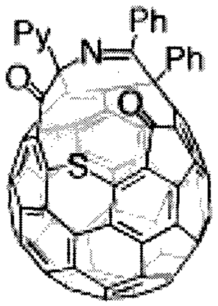

Figure 1. Chemical structure of OCF

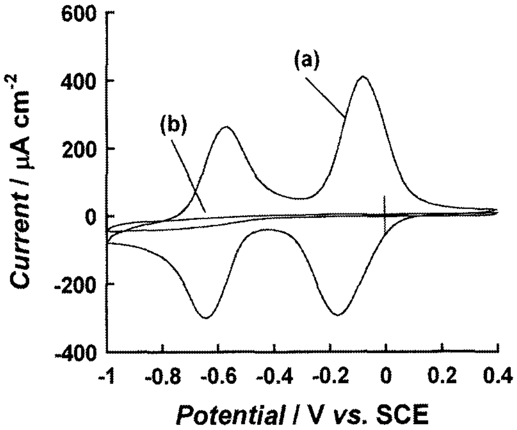

Figure 2. CV responses for (a) an OCF/TOAB (molar ratio ; 1/19) film-modified electrode and (b) an OCF film-modified electrode. Scan rate : 100 mV/s.

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3-8

Alkali Metal Switching of Photoinduced Electron Transfer in Supramolecular Fullerenes

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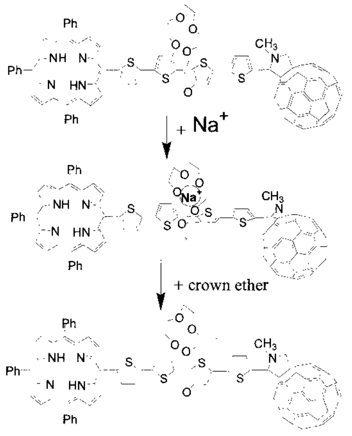
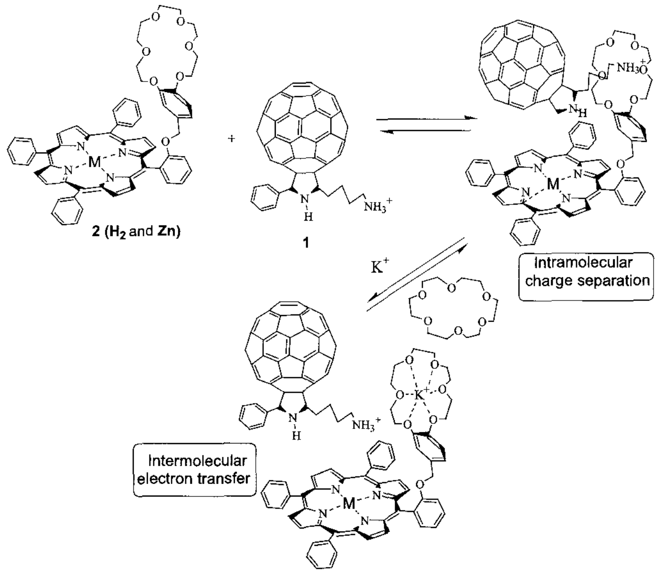
To control the electron transfer process by external process is quite important. In our previous study, we succeeded in switching intra-molecular electron transfer of the crown-ether connected oligothiophene by adding Na^+ and external crown-ether.[1]

Reversible intra- to intermolecular electron transfer was accomplished by adding K^+ to porphyrin-fullerene rotaxane formed using porphyrins with crown ether and C_{60} functionalized with an alkyl ammonium cation. In the absence of K^+, the charge-separation takes place within the rotaxane via the excited singlet states as shown in the fluorescence lifetime measurements, generating the radical ion pairs with the lifetime of 20 – 60 ns. On addition of K^+, the rotaxanes are dissociated, retarding the intramolecular charge separation, rather intermolecular electron transfer occurs via the excited triplet states. Further addition of crown ether extracts K^+ complexed with external crown-ether appending to porphyrin, recovering the rotaxane being capable of charge separation within the rotaxanes.





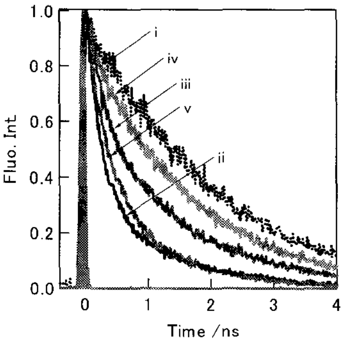


Fig. 1. Fluorescence decays for (i) ZnP, (ii) ZnP + C_{60}, (iii)(iv) ZnP + C_{60} + K^+, and (v) ZnP + C_{60}+K^+ + 18-crown-6-ether in benzonitrile

[1] Oike, T.; Kurata, T. Takimiya, K.; Otsubo, T.; Aso, Y.; Zhang, H.; Araki, Y.; Ito, O.*J. Am. Chem. Soc.* (2005), 127, 15372. Corresponding Author: Osamu Ito TEL FAX: +81-22-217-5608 , E-mail: ito@tagen.tohoku.ac.jp

3-9

IR-extended Photoluminescence Mapping of Carbon Nanotubes in the 1000-2300nm Range

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The measurement of photoluminescence (PL) from carbon nanotubes (CNTs) as a function of excitation and emission wavelengths is an indispensable technique to characterize this new form of carbon. Despite its practical usefulness and necessity, however, the detectable emission wavelength is usually limited to <1600nm because of several experimental restrictions. Here we address this issue both by building a new experimental setup for PL mapping and by devising a sample preparation technique.

Our PL measurement system consists of a CW Ti-sapphire laser (695-1055nm) as an excitation source and a FTIR spectrophotometer equipped with an IR-extended InGaAs photodiode for light detection up to 2300nm. The laser provides the maximum monochromatic power ~1W for almost the entire tuning range and the FTIR spectrophotometer enables quick and broad-band PL detection with a better S/N ratio than conventional grating-type monochromators due to its inherent brightness and the suppression of detector's dark current.

Another factor limiting the emission wavelength range is the strong IR absorption by D_2O (>1800nm) used for the surfactant-aided preparation of individually dispersed CNTs. Thus we prepared thin film samples by casting and drying a hot CNT/SDBS/gelatin dispersion (40°C) on silica substrates, eliminating absorption by D_2O. The point here is that, as we reported before [1], gelatin's gelation upon cooling successfully prevents the re-bundling of CNTs that would take place during drying, thus realizing CNT thin films that luminesce in a broad wavelength range.

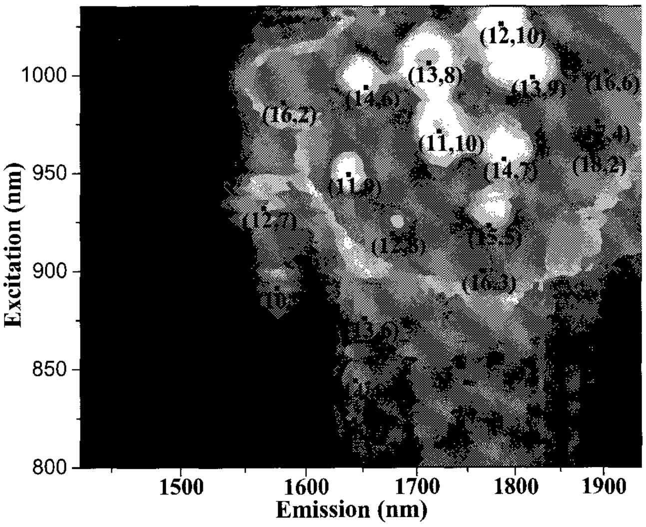

Fig. 1 PL mapping for Carbolex/SDBS/Gelatin film.

Figure 1 shows PL mapping results for Carbolex AP-grade CNT, revealing the chirality distribution of arc discharge CNT for the first time. We stress that the present efforts have made possible the PL characterization of both single- and double-wall CNTs whose diameters are larger than 1.3 nm, an important milestone for the experimental research of CNT.

[1] Y. Kim, N. Minami, and S. Kazaoui, Appl. Phys. Lett. **86**, 73103 (2005).

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3-10

Photoluminescence Quenching in Peapod-Derived Double-Walled Carbon Nanotubes

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An important breakthrough in the carbon nanotube spectroscopy came in 2002 when photoluminescence (PL) signals have been recorded from isolated single-walled carbon nanotubes (SWNTs) that were wrapped with sodium dodecyl sulfate (SDS) [1]. Since then, two-dimensional PL excitation/emission mapping has been widely recognized as a powerful tool for the characterization of the unique electronic properties of the SWNTs associated with their low dimensionality, and for the analysis of the detailed tubule distribution of the bulk samples [2]. Although PL properties of SWNTs are well established, it is yet unclear whether PL can be obtained from multi-walled carbon nanotubes (MWNTs). In particular, one might expect that the inner core tube is protected from the environment and its intrinsic optical properties are preserved. Double-walled carbon nanotubes (DWNTs) may answer to the above question because they have the simplest structure among MWNTs, which make it easier to interpret the experimental observations.

Here we report a detailed study of PL from the peapod-derived DWNTs, together with optical absorption and resonant Raman spectroscopy. The peapod-derived DWNTs are more suitable for studying PL from the inner tubes because the diameters of the residual SWNTs in the samples are similar to those of the outer DWNT shells. The results reveal that the PL signals originated form DWNTs are severely suppressed even though the optical absorption and the resonant Raman spectra show the characteristic features of DWNTs. This suppression is a consequence of an interlayer interaction between the inner and the outer tubes that efficiently quenches the PL signals of the DWNTs.

[1] (a) M. J. O'Connell *et al., Science* **297**, 593 (2002). (b) S. M. Bachilo *et al., Science* **298,** 2361 (2002).
[2] (a) T. Okazaki *et al., Nano Lett.* **5**, 2618 (2005). (b) T. Okazaki *et al., Chem. Phys. Lett.* **420**, 286 (2006).

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3-11

Cross-polarized optical absorption of single-walled carbon nanotubes probed by polarized PLE spectroscopy

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We have identified the excitonic phonon side-band in photoluminescence excitation (PLE) spectra by using ^{13}C single-walled carbon nanotubes (SWNTs) [1]. At the same time, we found certain small peaks in PLE spectra were 'pure' electronic without the isotope shift. In order to prove these unassigned peaks, we performed polarized photoluminescence excitation (PLE) spectroscopy for micelle-suspended SWNTs. Using a simple theory for PL anisotropy [2], the observed PLE spectra are decomposed into 'pure' components of the photoexcitation for incident light polarized parallel and perpendicular to the SWNT axis. Fig. 1 shows decomposed PL map for (6,5) and (7,5) nanotubes. Fig. 1 (a) and (c) correspond to collinear ($I_{//}$) and perpendicular ($I_{\perp}$) dipoles, respectively. Dotted lines indicate the emission energies of respective SWNTs. Solid lines indicate the position of Raman lines for G and G' bands. Peaks for $I_{\perp}$ spectra are indicated by circles. Decomposed PLE spectra of (6, 5) and (7, 5) SWNTs for collinear ($I_{//}$) and perpendicular ($I_{\perp}$) dipoles are drawn in (b) and (d). The PLE spectra for (6, 5) SWNTs are magnified (×2) and offset for comparison in (b) and (d). Similarly, distinct peaks corresponding to perpendicular excitation were observed for several (n, m) SWNTs. The measured transition energies for perpendicular excitations were blue-shifted compared to the qualitative values predicted within a single-particle theory. The results indicate a smaller exciton binding energy for perpendicular excitations than for parallel excitations [3].

References

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[3] Y. Miyauchi, M. Oba, S. Maruyama, submitted to Phys. Rev. Lett.

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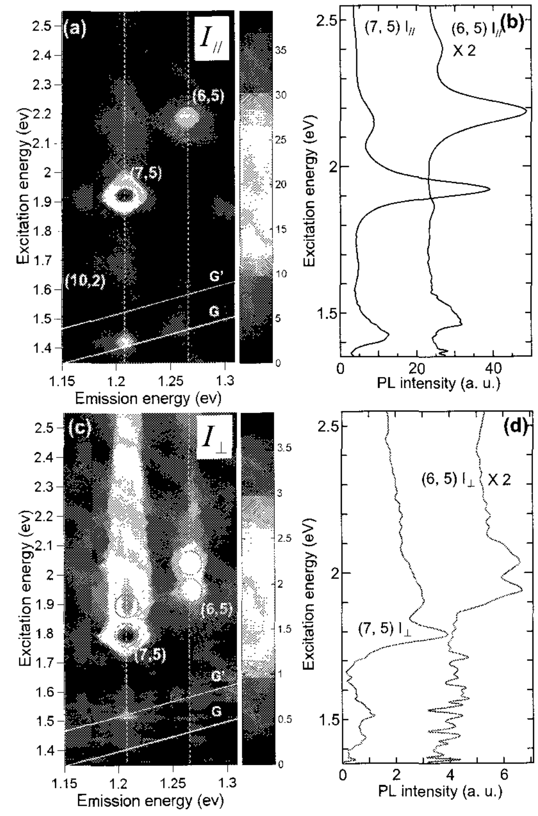

Fig. 1. Decomposed PL maps.

3-12

Exploring the structure and properties of vertically aligned SWNT films

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Our group recently developed a method [1] by which vertically aligned single-walled carbon nanotube (VA-SWNT) films [2,3], shown in Fig. 1a, can be detached from the substrate on which they are grown simply by submersion into hot water. The detached films can then be reattached on an arbitrary surface. We have employed this hot water detachment/reattachment technique to further investigate the structure and properties of VA-SWNT films independent from their substrates. Analysis of a VA-SWNT film transferred onto a TEM grid (Fig. 1b) shows the films consist mostly of individual SWNTs and small SWNT bundles. As a result, the overall properties of the VA-SWNT films (e.g. electrical and optical properties) are determined by the properties of individual SWNTs, rather than resembling a bulk material.

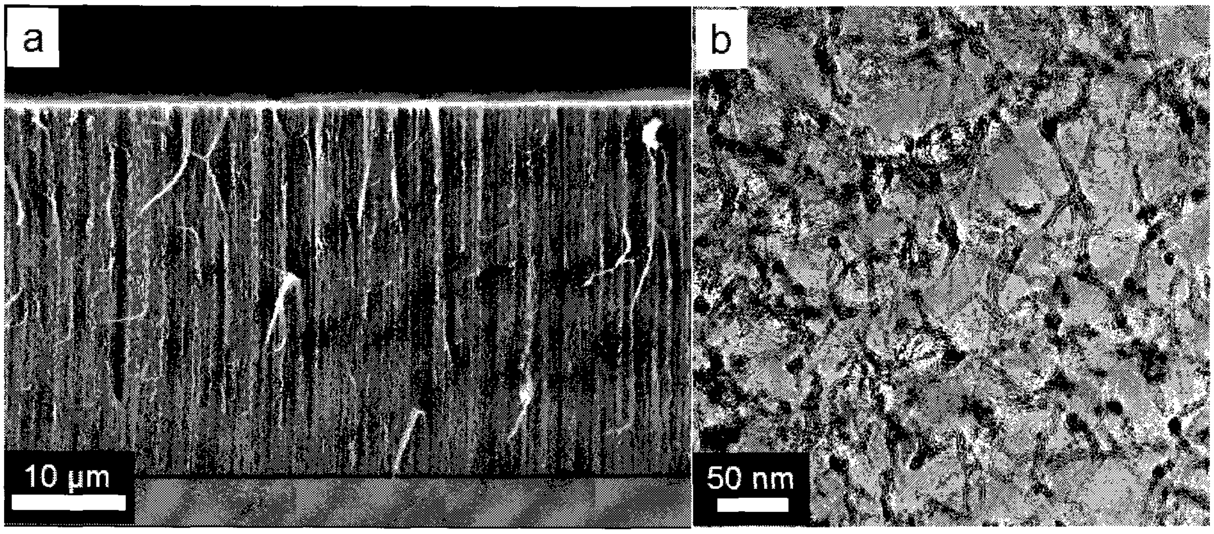

Fig. 1. (a) SEM image of a VA-SWNT film grown from alcohol, and (b) a TEM plan view showing the VA-SWNT film consists of mostly small bundles and individual SWNTs.

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3-13

Photoinduced Electron Transfer of Chemically Modified Carbon Nanomaterials

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Carbon nanomaterials have been extensively studied, because of their unique materials properties. In particular, photophysical properties dispersed in solutions have attracted a great deal of attention, because of wide applications such as solar cells. Here, photophysical and photochemical properties of carbon nanomaterial, which were dissolved in solution after chemically modifications, have been studied by the steady-state and transient spectroscopic methods.[1] By the steady-state photo-illumination in the presence of electron mediators (methylviologen dication, MV^{2+}), the accumulation of the $MV^{\bullet+}$ was confirmed at 600 nm band in the absence and presence of BNAH as shown in Fig. 1. This indicates that electron-rich species was generated by the photo-excitation of the carbon-electroactive compounds, from which MV^{2+} accepts electron. On the other hand, hole may be trapped by the defects of carbon materials or by added hole-trap (BNAH etc).

Fluorescence time profiles and transient absorption spectra support that photosensitized electron-transfer/electron-mediating processes including carbon nanomaterials are established.

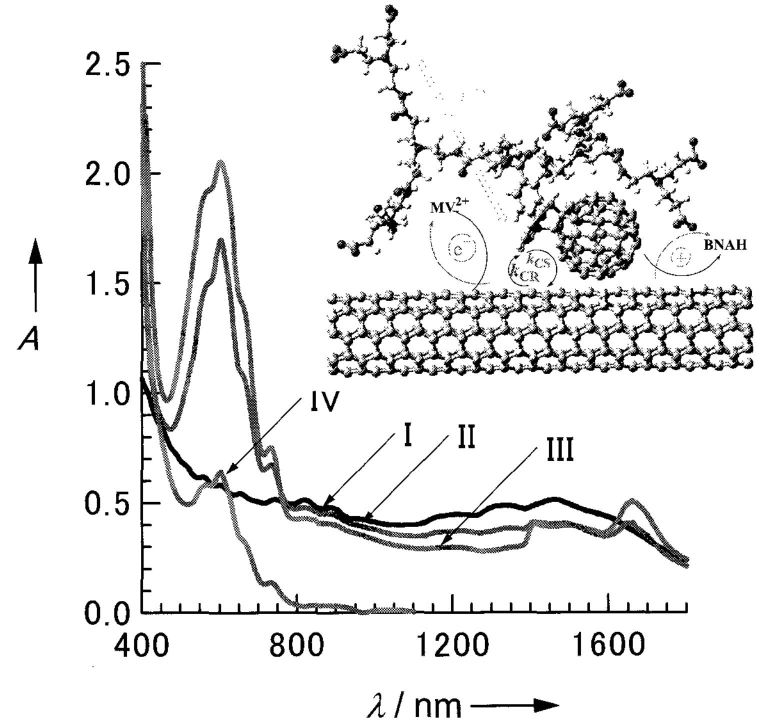

Figure 1. Absorption spectra showing accumulation of $MV^{\bullet+}$ at 600 nm observed by photo-irradiation of SWCNT-C_{60} dendrimer.

[1] (a) Y. Takaguchi, M. Tamura, Y. Sako, Y. Yanagimoto, S. Tsuboi, T. Uchida, K. Shimamura, S. Kimura, T. Wakahara, Y. Maeda, and T. Akasaka, *Chem. Lett.* **2005**, *34*, 1608. (b) S. D. A. Sandanayaka, H. Zhang, Y. Takaguchi, M. Tamura, Y. Araki, O. Ito, *Chem. Commun.* 2005, 5160.

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3-14

Modification of Single-Walled Carbon Nanotubes with Photoactive Chromophores and Their Photophysical Properties

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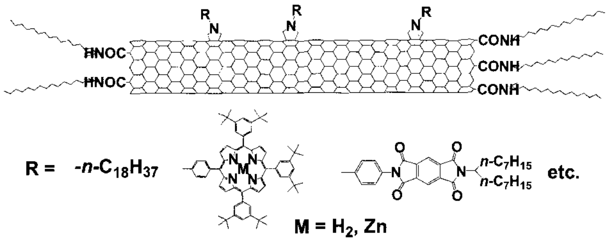
In recent years, there has been much interest in solubilization and functionalization of single-walled carbon nanotubes by covalent bond toward the applications of photonic molecular devices. Solubilized carbon nanotubes, however, still have diversity in length, diameter, and chirality (semiconducting or metallic), which results in obscurity of various properties. We report herein syntheses, structures, and photophysical properties of doubly functionalized, shortened single-walled carbon nanotubes which exhibit only semiconducting properties.

First, long alkyl chains were introduced to the tips of acid-treated, shortened carbon nanotubes (~300 nm) through condensation reaction of the terminal carboxylic group with long alkyl amine to provide the sufficient dispersibility. Subsequent cycloaddition reaction with azomethine ylide (Prato reaction) was carried out for the sidewall to tether photoactive chromophores including porphyrin and pyromellitic diimide (Chart 1). The doubly functionalized carbon nanotubes exhibited high solubility in common organic solvents. Structural characterization was performed by using transmission electron microscopy, resonance Raman spectroscopy, UV-vis-NIR absorption spectroscopy, and thermogravimetric analysis. In particular, Raman spectra with excitation wavelength of 785 and 514 nm revealed that only semiconducting carbon nanotubes were obtained after sidewall functionalization (Figure 1). Relaxation of the excited state in chromophore-modified carbon nanotubes is significantly different from that in functionalized carbon nanotubes without the chromophores, suggesting the charge-transfer interaction between the carbon nanotubes and the chromophores in the excited state.

Chart 1



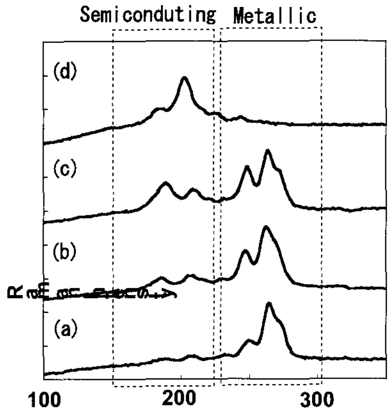


Figure 1. Raman spectra (514 nm excitation) of (a) pristine HiPco, (b) after acid treatment, (c) after functionalization at tips, and (d) after Prato reaction (R = n-$C_{18}H_{37}$).

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Noncovalent porphycene-functionalized single-walled carbon nanotubes in water

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Porphyrins are functional dyes with a variety of unique physical (photophysical), chemical and biological properties. We have already reported that porphyrin molecules dissolve single-walled carbon nanotubes (SWNTs) in organic solutions [1]. Considerable interest has been focused on the structures and properities of several porphyrin-SWNTs composites [2]-[3].

In this paper, solubilization behavious of water-soluble porphycenes (**1**), which were constitutional isomers of porphyrins, toward SWNTs were examined. By means of UV-vis-NIR absorption spectral measurements, it was revealed that compound **1** could disperse SWNTs in water as bundled structures. Figure 2 showed an AFM image on mica from the solution. The top heights of the images were found to range 2-6 nm, indicating the coexistence of bundled and individually dissolved SWNTs.

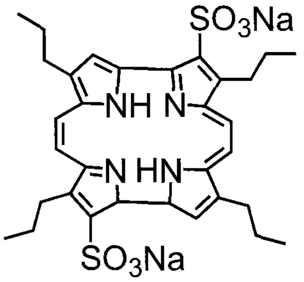

Fig.1. Chemical structure of **1**

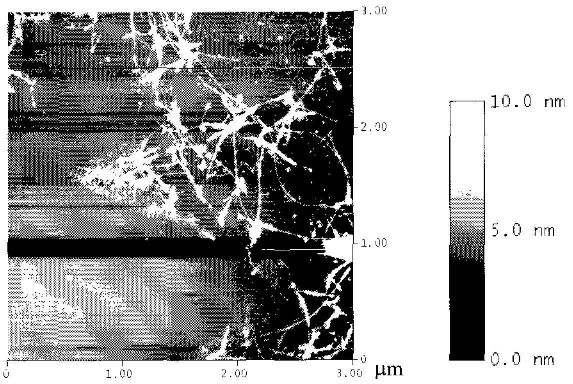

Fig.2. An AFM image of SWNTs solubilized with compound **1**

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3-16

Chirality Discrimination of Single-Walled Carbon Nanotubes using π-aromatic Amphiphilic Compounds.

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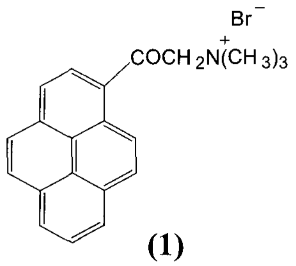
Carbon nanotubes (CNTs) have been in the forefront of nanoscience and nanotechnology because of their many unique properties. Our current interest is the design of CNT solubilizers as well as the applications of soluble CNTs[1-6].

The separation of metallic and semiconducting single-walled carbon nanotubes (SWNTs) is important since their electrical properties are different, and hence there is a strong demand in the separation of them in IT and related areas. A considerable attention has focused on the separation of metallic and semiconducting SWNTs by means of the combination of individual dissolution of SWNTs, followed by a selective reaction (or adsorption) toward metallic or semiconducting SWNTs. The ultimate goal in this area is to discriminate SWNTs with single chiral interger, (n,m). However, for our knowledge, no strategy has been given for this ultimate separation. We present here one step toward the discrimination of SWNT chirality. We recently reported that by means of near-IR photoluminescence study, SWNTs dissolved by pyrene-carrying ammonium compound **1** showed a narrower distribution of SWNT chirality compared to those of conventional micellar-solubilized SWNTs [7]. We here synthesized several pyrene (or anthracene)-carrying compounds and measured the near-IR photoluminescence spectra of SWNTs dissolved with these compounds to compare SWNT chirality discrimination ability to that of compound **1**, and the results will be reported at the meeting.



(1)

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3-17

Effect of Chemical Modification for SWNTs-FET Properties

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Single wall carbon nanotubes (SWNTs) having semiconducting properties are promising as electronic materials for nano-scale devices in the future, and the electrical properties of SWNTs are of significantly fundamental and practical interests. It is well known that the field effect transistors (FETs) fabricated using semiconducting SWNTs show high performance in terms of the mobility. However, carriers in pristine SWNTs are mostly holes, therefore, SWNTs -FETs usually show p-type properties. We reported the FET properties of individual SWNTs exohedrally modified by Si-containing organic moieties in the previous meeting [1], and demonstrated that p-type nanotubes can be converted to n-type ones. However, because of ununiformity of the surface-chemical modification of SWNTs, the evaluation of the true effect of the exohedral modification on FET properties is extremely difficult. In this meeting, we will present comparison of the FET properties of exohedrally silylated SWNTs between separated individual and spread-sheet samples. From the experimental results, it will be demonstrated that an n-type property can be enhanced by exohedral modification also in the case of the spread-sheet samples in a similar manner to the individual ones (Fig.1). We will discuss the effect of surface silylation on the electronic states of these SWNTs in more detail.

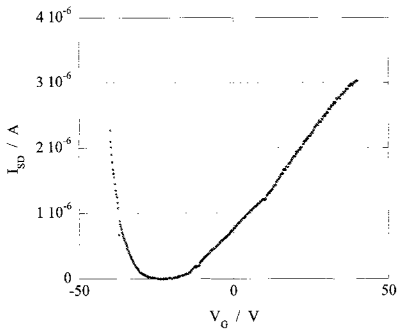

Figure 1. I_{SD}-V_G curve of exohedrally silylated SWNTs (film)-FET.

[1] R. Kumashiro et al., The 29th Fullerene-Nanotubes General Symposium, 3-2 (2005).

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3-18

Ferroelectric gate carbon nanotube field effect transistor using PZT as gate insulators

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Nanoscale electronic devices using carbon-nanotubes are expected to be future sensing or computing applications. In particular, single-wall carbon-nanotube field-effect transistors (CNT-FETs) are one of the key devices for nanoelectronics and their functions have recently been demonstrated. In this study, we describe the fabrication and electrical characteristics of CNT-FETs with ferroelectric thin films as gate insulators. The ferroelectric-gate CNT-FETs were fabricated using single-wall CNTs synthesized from alcohol by catalytic chemical vapor deposition and sol-gel derived $PbZr_{0.5}Ti_{0.5}O_3$ thin films. The ferroelectric-gate CNT-FETs show the modulation of the drain current with the gate voltage and the threshold voltage shift (memory window) on the drain current-gate voltage characteristics. This result indicates that carriers in CNTs are controlled by spontaneous polarization of the ferroelectric films. The ferroelectric-gate CNT-FETs offer a promise as potentially useful nanoelectronics devices, such as nonvolatile memory elements and high-sensitivity sensors. This is because ferroelectrics exhibit complex couplings between their electrical, structural, mechanical, thermal, and optical properties, and because CNTs have unique mechanical and electrical properties,

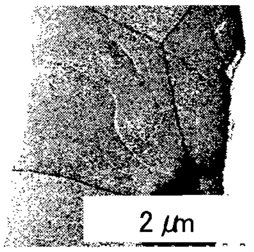

Fig.1. SEM image of the ferroelectric-gate CNTFET.

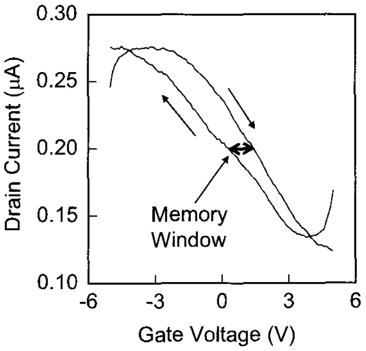

Fig.2. I_d-V_g chrematistics of the ferroelectric-gate CNT-FET.

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3-19

Room temperature resonance tunneling transport through C_{60}-filled double-walled carbon nanotubes

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Fullerene C_{60} and carbon nanotubes have attracted great attention as promising candidates for nanoscale electronic devices. Up to now, various nanodevices with novel transport properties, such as single C_{60} transistor, carbon nanotube-field effect transistors (FETs) and single-electron transistors (SETs), have been realized experimentally[1-3]. However, experimental work on making resonant tunneling diodes (RTDs) and resonant tunneling transistors (RTTs) based on carbon nanotubes is only beginning to emerge.

In this study, we report novel electric transport properties of resonance tunneling field-effect transistors fabricated using C_{60}-filled metallic double-walled carbon nanotubes (DWNTs). The samples of C_{60}-filled DWNTs are prepared by both plasma irradiation and chemical methods. The devices exhibit strong resonance tunneling characteristics and distinct negative differential resistance with high peak-to-valley ratio about 1300 is observed at room temperature, as shown in Fig.1. The applied gate voltages show a great influence on the transport behavior due to resonant tunneling through the discrete energy levels of C_{60} molecules. In particular, at high bias voltages, the tunneling current can be completely dominated by the Coulomb oscillation peaks with uniform conductance, exhibiting a strong single-electron tunneling effect.

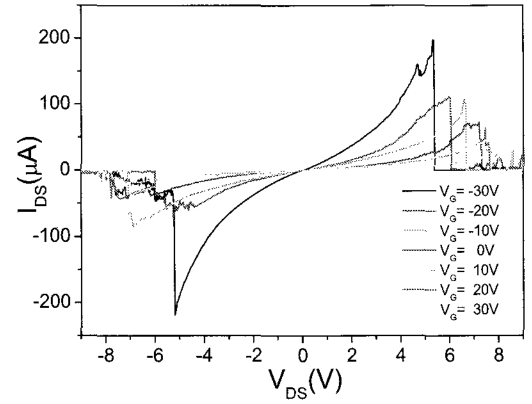

Fig.1 Characteristics of I_{DS}-V_{DS} curves measured with different V_G ranging from -30 to 30 V

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ポスター発表
Poster Preview

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1P-1

Extraordinary Binding Constants of Flat Azulene with Fullerenes

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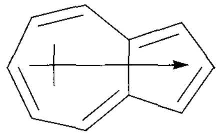
Azulene is a nonalternant aromatic hydrocarbon featuring quite unique characteristics of blue color and a permanent dipole moment of 1D. Azulene has both electron-donating and -withdrawing ability with its low ionization potential and low aromatic resonance energy. Despite such unique properties of azulene, no complexation study between azulene and fullerenes has been reported yet. Here we report the complexation study of azulene with fullerenes for the first time.



Azulene

The binding constants have been determined in toluene by fluorescence spectroscopic method. The emission band of azulene near 750 nm has got significant quenching effect with the gradual addition of [60]- and [70]fullerenes, indicating effective complexation between azulene and fullerenes. The binding constants of azulene with [60]- and [70]fullerenes have been estimated to be 9.4×10^4 and 9.8×10^4 dm^3/mol, respectively. Although azulene is a very flat and simple hydrocarbon which does not possess any cavity, its affinity towards [60]- and [70]fullerenes are remarkable in sense that the presently determined binding constants are found to be largest among the macrocyclic molecules such as calixarenes [1] and porphyrines [2] and even comparable with other designed host molecules like bridged dicalixarenes [3] except for cyclic diporphyrins [4]. One notable feature of the present investigation is that azulene does not show any sort of selectivity towards [60]- and [70]fullerenes unlike other macrocyclic receptor molecules [5].

This study was supported by Industrial Technology Research Grant Program in 2005 from New Energy and Industrial Technology Development Organization (NEDO) of Japan.

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1P-2

Antioxidant Activity of Water-soluble Fullerenes on *β*-Carotene

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Fullerene characterized as an antioxidant is believed to reduce various reactive chemical species, such as free radicals, and their characteristic features have been disclosed to furnish many useful medical technologies. We have recently reported that a number of water-soluble fullerenes behave as effective reactive oxygen species (ROS)-scavengers in cell cultures and can protect human skin keratinocytes from UV irradiation and oxidative damage by *tert*-butyl hydroperoxide [1,2].

Despite numerous studies on the radical scavenging activity of water-soluble fullerenes, little is known about their kinetic analysis on *β*-carotene, which has frequently served as a criterion for determining antioxidant activity. We evaluated the antioxidant activity of unfunctionalized water-soluble fullerenes, namely polyvinylpyrrolidone (PVP)-entrapped C_{60} and *γ*-cyclodextrin (CD)-bicapped C_{60}, based on the coupled autoxidation of linoleic acid and *β*-carotene. In addition, we originally performed the *β*-carotene bleaching assay using hydrogen peroxide and irradiation as alternative promoters besides linoleic acid. Antioxidant activity in the *β*-carotene–peroxide and –irradiation system was calculated as percent of inhibition relative to control (% AOA, % Inh) using k_{obs} and absorbance values, respectively.

Antioxidant activity of water-soluble fullerenes

β-carotene–linoleic acid system (% AOA)		*β*-carotene–hydrogen peroxide system (% AOA)		*β*-carotene–irradiation system (% Inh)	
PVP/C_{60}	88.5%	Radical Sponge®	89.8%	*γ*-CD/C_{60}	79.8%
Radical Sponge®	85.7%	PVP/C_{60}	56.2%	PVP/C_{60}	79.2%
γ-CD/C_{60}	65.9%	*γ*-CD/C_{60}	42.5%	Radical Sponge®	79.1%

Radical Sponge® of cosmetic ingredient mainly consists of PVP/C_{60} and 1,3-butylene glycol.
% AOA = $100(k_{\mathrm{control}}-k_{\mathrm{sample}})/k_{\mathrm{control}}$, % Inh = $100(\Delta\mathrm{Abs}_{\mathrm{control}}-\Delta\mathrm{Abs}_{\mathrm{sample}})/\Delta\mathrm{Abs}_{\mathrm{control}}$.

The fact that water-soluble fullerenes inhibited the degradation of *β*-carotene under UV-vis irradiation revealed no significant photosensitivity of fullerenes. We have confirmed that PVP/C_{60}, *γ*-CD/C_{60} and commercial cosmetic ingredient, Radical Sponge® can utilize as effective and safe antioxidant.

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1P-3

Photophysical Properties of 1,4-Bisadduct of C_{60}: A Laser Flash Photolysis Study

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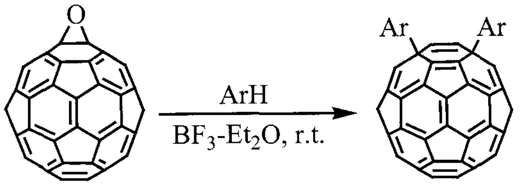
Recently, we synthesized 1,4-bis(*p*-phenyl)-1,4-dihydro[60]fullerenes by the reaction of fullerene mono-epoxide **1** and the nucleophilic aromatic compounds in the presence of boron trifluoride etherate as a Lewis acid catalyst (Scheme 1.)[1].

We report photophysical properties of the singlet and triplet excited states of 1,4-bisadducts **2** and **3** in toluene studied by laser flash photolysis. T-T absorption spectra of **2** and **3** are weak and broad in comparison with that of C_{60}. The lifetimes of the triplet state are shorter than that of C_{60} in N_2-degassed toluene. The phosphorescence from the singlet oxygen is observed for aerated toluene solutions of C_{60}, **2**, and **3** after laser pulsing (Fig. 1). From the phosphorescence quantum yields, the triplet yields of **2** and **3** are obtained as ca. 0.5. This value is half that of C_{60} at room temperature. Fluorescence quantum yields of **2** and **3** are found to be very small (ca. 10^{-4}). On the basis of these results, we consider that the nonradiative transitions, $T_1 \rightarrow S_0$ and $S_1 \rightarrow S_0$, of **2** and **3** take place more efficiently than those of C_{60}.



1

2 Ar=$C_6H_5CH_3$
3 Ar=$C_6H_5OCH_3$

Scheme 1. Synthesis of 1,4-bisadduct of C_{60}.

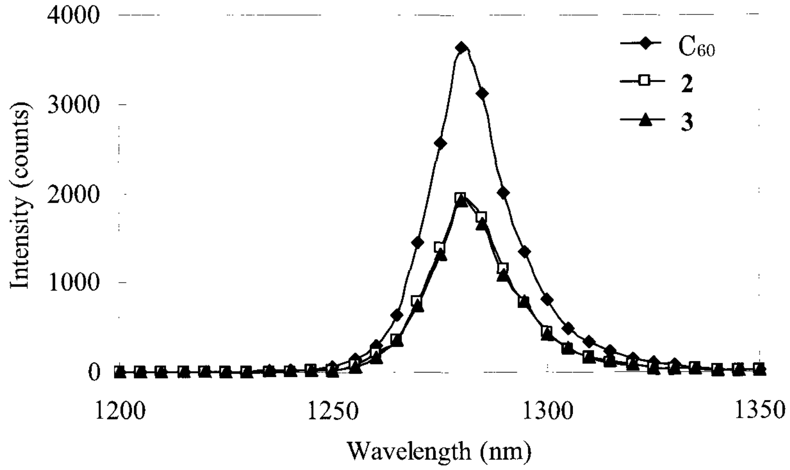


Fig.1 Emission spectrum from singlet oxygen generated by laser irradiation (532 nm) of C_{60}, **2** and **3**.

[1] T. Hara, Y. Tajima, T. Terada, T. Sasaki, K. Takeuchi, The 29th Fullerene-Nanotubes General Symposium, **2005**, 67.

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1P-4

Regiochemistry of Multiple Hydroarylation of C_{60} with Aromatic Compounds Catalyzed by $AlCl_3$

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Regioselective chemical modification of fullerene has been one of the most significant subjects in both academic interest and practical use in the fullerene chemistry since the multiple addition of functional groups to fullerene is usually non-regioselective. Such a multiple hydroarylation of [60]fullerene catalyzed by $AlCl_3$ was found by Olah in 1991 [1] and was proved to have a great potential for the practical application [2]. However, no information concerning with the regiochemistry has been reported. In this study, we first isolated the mono- and bis-adducts of the $AlCl_3$-catalyzed Friedel–Crafts [60]fullerenation of toluene and anisole and elucidated their regiochemistry by spectroscopic method.

The reaction of C_{60} was carried out in the presence of 30–100 equiv of $AlCl_3$ and 30 equiv of aromatic compounds in *o*-dichlorobenzene at room temperature under argon atmosphere. In order to obtain the maximum yield of each mono- and bis-adduct, the reaction was monitored by HPLC (Figure 1). The each adduct was isolated by using preparative HPLC equipped with a Buckyprep column. The structures were determined by FABMS, ^1H and ^{13}C NMR as well as 2D NMR.

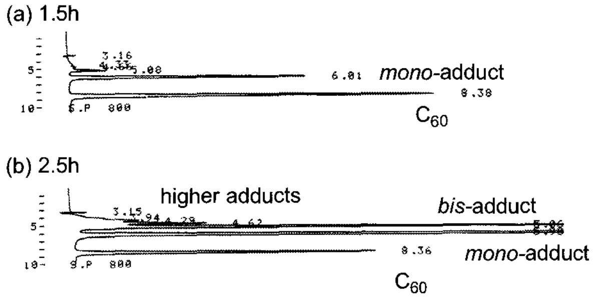
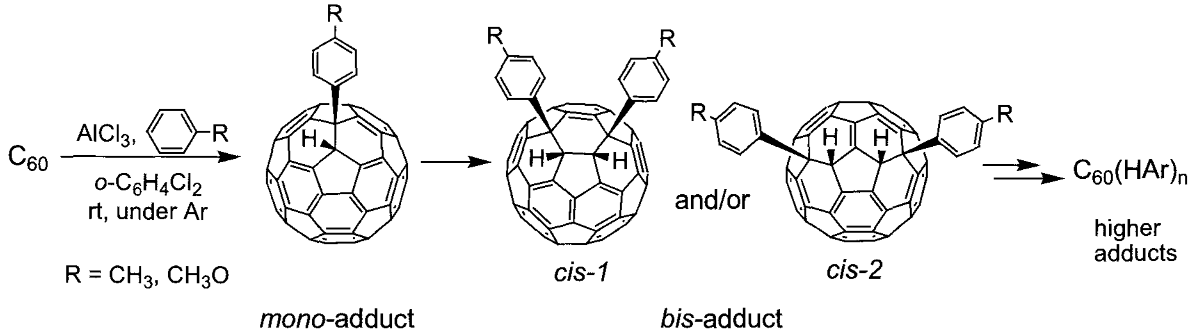


Figure 1. HPLC chart of the reaction of C_{60} with toluene catalyzed by $AlCl_3$ for (a) 1.5h (b) 2.5h. Buckyprep column; toluene 1 ml/min; UV = 310 nm.



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1P-5

Regulation of the self-organized structure of the fullerene/porphyrin molecular system packed in a water-soluble amino acid dendrimer

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Fullerene/porphyrin system is expected as the potential photoactive devices such as solar cells. The self-organization of the amphiphilic molecules is a versatile method to obtain large-scale constructs. Thus, we have synthesized an L-lysine dendrimer (**1**) with links to porphyrins and a fullerene, in which the molecular surface was modified with carboxylate groups (Fig. 1).[1] This dendrimer underwent the self-aggregation in the aqueous system to form a variety of structures including the helical fibers and the spherical particles.

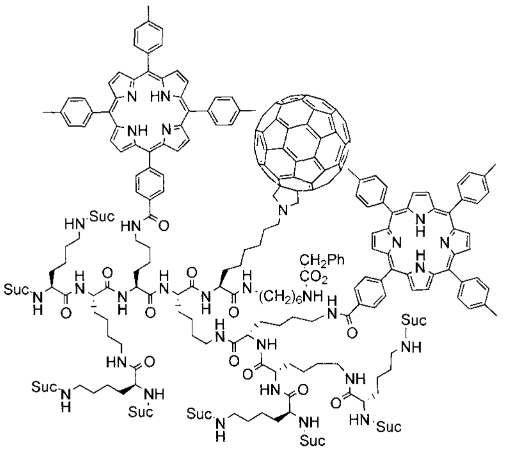
Fig. 1. Water-soluble dendrimer **1**. -Suc = -CO(CH$_2$)$_2$COO$^-$.

Helical fibers of $\sim$20 μm diameters were observed in the SEM analysis upon casting the aqueous solution (3.0 μM, pH 8.0) of **1** (Fig. 2a). Two strings of $\sim$10 nm diameter twist with each other in the right-hand way with the helical pitch of $\sim$40 nm. In the same SEM sample, a plane wire-like structure without helix was also observed. It should be noted that the change of pH or the sample concentration was ineffective; merely small plate-like structures were observed and the fiber or the wire was not formed.

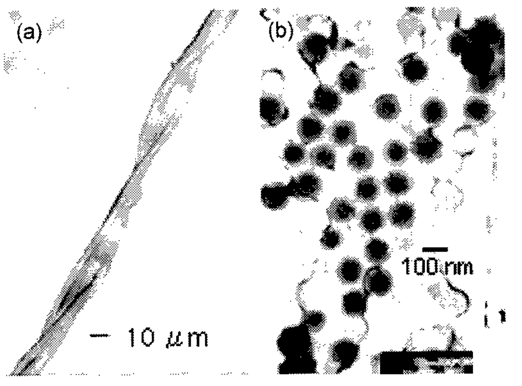

Fig. 2. Self-assembled structures of **1**.
(a) SEM image (prepared from the aqueous solution).
(b) TEM image (prepared from 10% cyclodextrin in H$_2$O).

Dynamic light scattering measurements of the aqueous solution of **1** indicated the existence of several sizes of aggregates from 60 to 400 nm. In fact, the TEM analysis (collodion film) showed spherical particles of 90-170 diameters with some size distribution, when the sample was prepared from the aqueous solution (12 μM) of **1**. It is yet unclear why the SEM showed fiber/wire structures and the TEM showed the particles, but difference in the sample preparation may account for. It is interesting that the dendron **1** formed the $\sim$ 100 nm particles with the narrow size distribution when 2-hydroxypropyl-β-cyclodextrin was added as the surfactant (Fig. 2b).

The self-assembling of the fullerene/porphyrin system was further examined by (1) preparing the dendrons with the different chemical structure, (2) spectroscopic examination in the aqueous solution, which will be presented at the poster.

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1P-6

Effects of milling intensity on the rate of C_{60} oxidation by ambient molecular oxygen

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We recently demonstrated a solid-state oxidation of C_{60} under mechanical stressing by mere ambient gaseous oxygen [1]. Obtained products were mixture of CS_2 soluble $C_{60}O$ (epoxide, ≒5%) and CS_2 insoluble $C_{60}O_n$ (contains both epoxy and carbonyl types of oxygen, average number of n=5.3,≒36%). We found some evidence to suspect formation of singlet oxygen ($^1O_2$) through energy transfer from mechanically excited fullerene. In this paper we examine effects of mechanical stressing, on the rate of oxidation, in order to examine whether and to what extent mechanochemical effects in narrow definition is operating. As we used a vibrating ball mill, where one ball of 5cm in diameter is vibrating on the bottom of a mortar, we varied i) amplitude of ball vibration frequency between 0.5mm and 2.0 mm, ii) material of the milling ball made of either agate (170g) or stainless steel (507g), and iii) reaction time between 1h and 5h, respectively. Reaction yields determined by HPLC gained with increasing amplitude, by using stainless apparatus, or by increasing reaction time. Reaction using stainless steel apparatus with 2mm amplitude gave 26% yield after 1h and 98% after 3h milling time. IR analyses of all the products reveal that they contain both C-O-C epoxide and C=O carbonyl types of oxygen. Furthermore, $^1O_2$ scavenger, 4-oxo-TEMP, inhibited oxidation. The inhibition was irrespective of the materials of the ball and mortar, as we demonstrated in our previous study. From these results, we conclude that, reaction mechanisms of oxidation in every case are identical and activated species is also $^1O_2$.

Reference: [1] Hiroto Watanabe, Eitaro Matsui, Mamoru Senna, Abstract of the 30th Commemorative Fullerene-Nanotubes General Symposium, 2006, p. 152.

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1P-7

Inhibition of the mechanochemical oxidation of C_{60} by gaseous oxygen by the coexistence of aromatic compounds

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As we recently demonstrated oxidation of fullerene via a mechanical stressing under oxygen atmosphere, we observed a mixture of CS_2 soluble $C_{60}O$ (epoxide) and CS_2 insoluble $C_{60}O_n$ (contains both epoxy and carbonyl types of oxygen, average number of n=5.3) [1]. We also found that oxidation was completely inhibited by adding singlet oxygen ($^1O_2$) scavenger (4-oxo-TEMP). From these findings, we considered that $^1O_2$ plays a decisive role as an activated species and is generated through energy transfer from mechanically excited fullerene. Since direct observation of the excited state of fullerene during milling is impossible with our reaction system, we try in this study to examine effects of adding various aromatic compounds to the reaction system to elucidate more detailed reaction mechanisms. We therefore added equimolar amount of 9,9'-bifluorenylidene (BF), i.e. dimer of fluorene. BF is known to be a quencher of excited fullerene. C=C double bond in BF is capable of reacting with $^1O_2$. All the resulted powder mixtures with BF after milling were solved into toluene. HPLC analysis in a toluene solution of the reaction mixture revealed that the oxidation of fullerene was completely inhibited i.e. unreacted fullerene was fully recovered. Oxidative products of BF were not detected either. BF has obviously quenched excited states of the fullerene, as expected. We subsequently tried to add an equimolar amount of Rose Bengal (RB), whose HOMO-LUMO band gap energy is close to that of fullerene. RB is known to be excellent $^1O_2$ generator from its excited states. We observed that RB completely inhibited $C_{60}O$ (epoxide) formation, and suppressed formation of the CS_2 insoluble fullerene oxide either. From those observations, we further discuss about reaction and excitation mechanisms of present mechanochemical oxidation of C_{60}.

Reference: [1] Hiroto Watanabe, Eitaro Matsui, Mamoru Senna, Abstract of the 30th Commemorative Fullerene-Nanotubes General Symposium, 2006, p. 152.

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1P-8

Generation and Properties of Arylated C_{60} Cations

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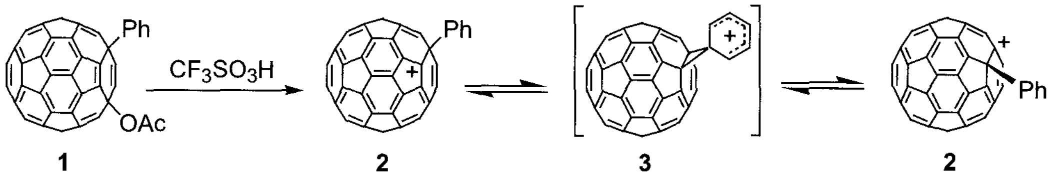
Carbocations possessing a positive charge on a spherical π-conjugated system of a fullerene cage are uncommon, owing to the electronegative nature of the fullerene cage. We have reported the generation and observation of C_{60} and C_{70} cations having an attached chloroalkyl group.[1] Here we report the generation of phenylated C_{60} cation (PhC_{60}^+) by the ionization of $PhC_{60}OAc$ (**1**) in a superacid. The structure and property of this cation was investigated by spectrometry, trapping experiments, and DFT calculations.

Acetate **1**, prepared by a reported method[2], was dissolved in CF_3SO_3H, giving a reddish purple solution. Vis-NIR analysis showed absorption maxima at 472, 750, and 1104 nm, which are similar to those observed for chloroalkylated C_{60} cations[1], indicating that the cation generated from **1** has the structure **2**. However, the ^{13}C NMR spectrum of this solution indicated only 17 sp^2 carbon signals at δ 127–150, while the structure **2** has 34 nonequivalent sp^2 carbons. Some of the sp^2 signals were broadened, and the cationic center and the sp^3 carbon bearing the phenyl group were not observed at the expected positions (δ ~170 and ~70, respectively). These observations suggest the rapid interconversion between two equivalent structures by the 1,2-shift of the phenyl group (eq 1), and that the observed NMR spectrum corresponds to the time-average of the two structures. The signals were further broadened at –40 °C and sharpened at 100 °C, as expected from the change in the rate of the exchange. This interconversion is expected to proceed through an arenium ion **3**. DFT calculations (B3LYP/3-21G) showed that **3** is 14.5 kcal/mol higher in energy than **2** and is a transition state. Quenching a CF_3SO_3H solution of **2** with CF_3CH_2OH gave a mixture of two regioisomers of ether $PhC_{60}OCH_2CF_3$ (51%) in approximately 1:1 ratio.

The effect of the substituent on the phenyl ring upon the structure and stability of cations ArC_{60}^+ will be also discussed.



1 **2** **3** **2** (1)

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1P-9

Mechanistic Studies on the Encapsulation of a Water Molecule by an Open-Cage Fullerene Derivative

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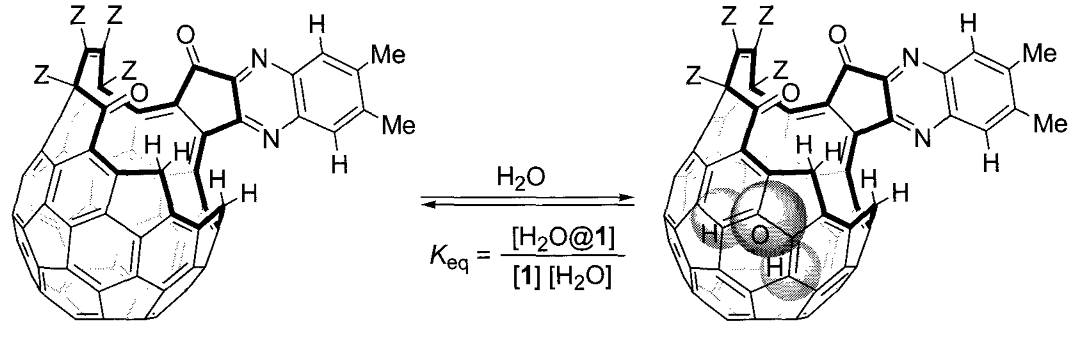
A carbon–carbon bond of the fullerene cage can be cleaved by an organic reaction. The product, a so-called open-cage fullerene, has an opening large enough to insert an atom or a small molecule into the cavity of the fullerene. Unlike the formal endohedral fullerenes, these derivatives can hold and release substrates in a reversible manner. This property offers molecular sensing and storage as potential applications.

The narrow orifices of previous open-cage derivatives had restricted the insertion to helium and hydrogen (H_2).[1] Recently, we have constructed a wide opening on C_{60} by successive cage scissions. The orifice in the product **1** is the largest one at present, and it spontaneously encapsulates one water molecule to form H_2O@**1**.[2] In this presentation, we would like to report NMR studies on the formation of H_2O@**1**. In the ^1H NMR spectrum, a water molecule trapped in **1** appeared as a sharp singlet at δ -11.4 ppm in $CDCl_3$. The fraction of H_2O@**1** reached up to 75% and was dependent on the water content of the solvent. The equilibrium constant of the formation of H_2O@**1** was estimated to be in the range of 30–80 l/mol.



1 ($Z=CO_2Me$) H_2O@**1**

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[2] S.-i. Iwamatsu, T. Uozaki, K. Kobayashi, S. Re, S. Nagase and S. Murata, *J. Am. Chem. Soc.*, **126**, 2668–2669 (2004).

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1P-10

Encapsulation of a D_2 Molecule inside an Open-Cage C_{60} and Synthesis of $D_2@C_{60}$

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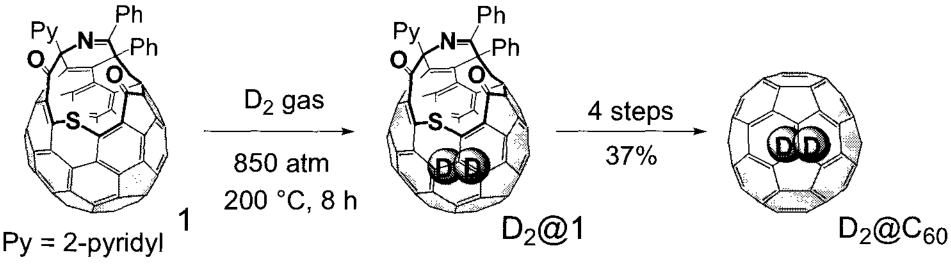
The molecular surgery approach is useful to synthesize yet-unknown endohedral fullerenes and their derivatives. We have already synthesized endohedral C_{60} encapsulating a hydrogen molecule in its cage via synthesis of open-cage C_{60} derivative, insertion of a H_2 molecule inside it, and restoration of the opening.[1,2] We report herein the synthesis and properties of $D_2@C_{60}$.

By applying high pressure D_2 gas (850 atm) to the open-cage C_{60} derivative **1** having a 13-membered-ring orifice[3] at 200 °C for 8 hour, encapsulation of D_2 was achieved quantitatively in the same way as encapsulation of H_2.[4] The closure of the orifice was attained by four-step organic reactions to give $D_2@C_{60}$ as a brown powder in 37% yield based on **1**. In the ^{13}C NMR spectrum, a peak corresponding to the cage of $D_2@C_{60}$ appeared at 142.841 ppm, which is slightly up-field shifted compared with the chemical shift of $H_2@C_{60}$ (142.844 ppm), suggesting smaller van der Waals interaction of D_2 with C_{60} than that of H_2. The ^2H NMR spectrum of $D_2@C_{60}$ showed a sharp singlet at -1.45 ppm corresponding to a D_2 molecule inside the cage, which is almost the same as the chemical shift of H_2 in $H_2@C_{60}$ (-1.44 ppm). A difference in energy barrier was also observed for the escape from **1** between H_2 and D_2 molecules.



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1P-11

The Bingel Monoadducts of La@C$_{82}$; Synthesis and Characterization

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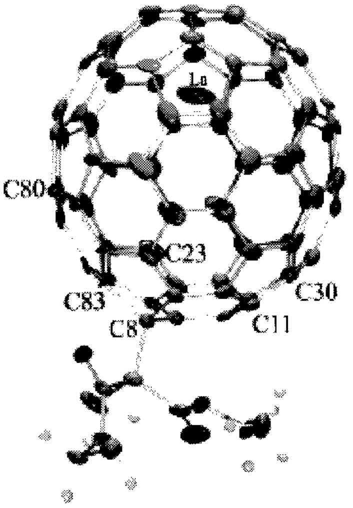
Endohedral metallofullerenes (EMFs) have attracted special attention because they engender new spherical molecules with unique electronic properties and structures. The Bingel reaction is one of the most widely applied reaction in fullerene chemistry. $\mathrm{Gd@C_{60}[C(COOC_2H_5)_2]_n}$ (n=1-10) was obtained as the Bingel adduct of EMFs.[1] Recently, the Bingel adduct of EMFs ($\mathrm{Y_3N@C_{80}}$) was also reported, in which a malonate group has been attached to a specific [6,6] double bond of a C$_{80}$ cage.[2] In this work, we performed the Bingel reaction on La@C$_{82}$ and its products distribution was found to be very different from those of empty fullerenes as well as previously reported EMFs.

We carried out the reaction of La@C$_{82}$ with diethyl bromomalonate in the presence of DBU (1,8-diazabicyclo[5,4,0]undec-7-ene) in dry toluene to afford five monoadducts of La@C$_{82}$ (mono-A,-B,-C,-D, and –E), which were isolated by the multistage high-performance liquid chromatography (HPLC).[3] Among them, mono-A,-B,-C, and –D were revealed to be regioisomers of a singly bonded monoadduct being ESR-inactive. Mono-E was ESR-active and suggested to be a cycloadduct as a conventional Bingel adduct. The structure of mono-A was unambiguously determinated by X-ray single-crystal analysis. The structures of others were investigated by NMR spectral analysis and theoretical calculations.



ORTEP drawing of mono-A

References:

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1P-12

Addition of adamantylidene to $La_2@C_{78}$: structural determination of monoadduct $La_2@C_{78}(Ad)$

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It is well known that the chemical and electronic properties of an empty fullerene could be modified upon incorporation of metallic guest species, awarding plentiful, various materials with novel properties and potential application perspectives associated with the incarcerated metal.[1] The endo-metal-containing fullerene could be further functionalized exohedrally, affording some new derivatives that bear special functional groups and present intriguing properties. A communication between the dynamic motion of the two cerium atoms within $Ce_2@C_{80}$ and exohedral groups, for example, is fulfilled either by disylilation of this molecule with 1,1,2,2-tetrakis-(2,4,6-trimethylphenyl)-1,2-disilirane or through [2+3] cyclo-addition of an N-trityloxazolidinone to it.[2] So far, however, functionalization of metallofullerenes is focused on the most abundant species, $La@C_{82}$, $La_2@C_{80}$, and $M_3N@C_{80}$; rare attention has been given to those with smaller cages because of their scarcity. Recently, we have isolated a new metallofullerene, $La_2@C_{78}$, with enough quantity for reaction.[3] Here we report functionalization of $La_2@C_{78}$ with 2-admantane-2,3-[3H]-diazirine. Four isomers of monoadduct $La_2@C_{78}(Ad)$ synthesized photochemically have been isolated by HPLC and characterized by mass, UV absorption, CV, DPV, and NMR spectroscopic analyses.

1. *Endofullerenes: A New Family of Carbon Clusters*; T. Akasaka & S. Nagase Eds., Kluwer Academic: Dordrecht, **2002**.
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1P-13

Chemical Reactivity and Redox Property of Sc_2C_{84}

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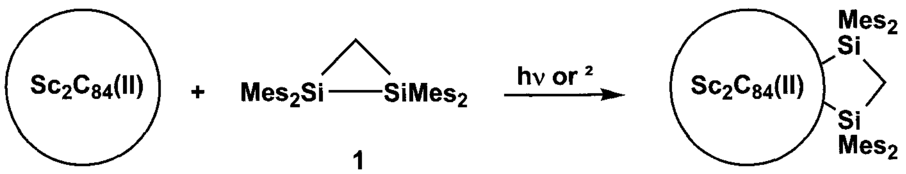
Endohedral metallofullerenes have attracted special attention as new spherical molecules with unique properties unexpected from empty fullerenes.[1] Much work has been carried out on metallofullerenes with Sc, Y and La atoms encapsulated inside C_{82} and C_{84} cages. Among them, scandium metallofullerenes are of special interest because of their high variety in fullerene size as well as their relatively high yields. In this context, it is very important to disclose the chemical reactivity of typical scandium metallofullerenes. For Sc_2C_{84}, three isomers (I, II and III) have been isolated. Sc_2C_{84} has been known as one of most abundant scandium fullerenes. We have already found that Sc_2C_{84}(III) reacts with disilirane **(1)** photochemically to afford a 1:1 adduct, but not thermally .[2]

Here we report the chemical reactivity of Sc_2C_{84}(II), which shows higher reactivity toward **1** than Sc_2C_{84}(III). The redox property of Sc_2C_{84}(II) is also investigated by CV measurement.



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1P-14

Chemical Functionalization of Scandium Metallofullerenes

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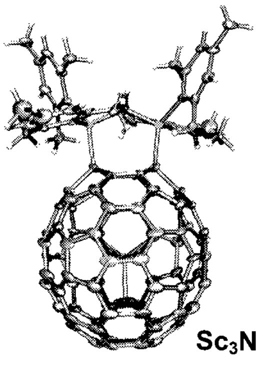
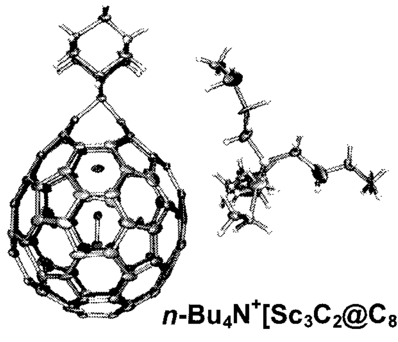
Endohedral metallofullerenes have attracted special interest, because of the unique properties unexpected for empty fullerenes. In particular, exohedrally derivatized scandium metallofullerenes are very interesting for their potential usefulness as novel materials.

Characterization of Bis-silylated $Sc_3N@C_{80}$. One of the most important developments in fullerene chemistry in recent years is the design of $Sc_3N@C_{80}$ derivatives since $Sc_3N@C_{80}$ can be isolated in a remarkably high yield.[1] Very recently, we revealed the chemical reactivity of $Sc_3N@C_{80}$ with disilirane in viewpoint of redox potentials and HOMO-LUMO.[2] Here we report the full characterization of the bis-silylated $Sc_3N@C_{80}$ by means of NMR, vis-near-IR absorption and CV spectroscopy, and X-ray single-crystal structure analysis.

Characterization of Carbene Derivative of $Sc_3C_2@C_{80}$. Sc_3C_{82} is the first endohedral metallofullerene encapsulated three metal atoms.[3] The EPR spectrum of Sc_3C_{82} suggests geometrical equivalency of three scandium atoms. Surprisingly, we disclosed the molecular structure of $Sc_3C_2@C_{80}$ (not $Sc_3@C_{82}$) by ^{13}C NMR spectroscopy and X-ray single-crystal structure analysis.[4] $Sc_3C_2@C_{80}$ has the largest endohedral cluster (Sc_3C_2) encapsulated in an I_h-symmetric C_{80} cage appears to be the most interesting. We will discuss the structure and electronic property of the adamantylidene derivative of $Sc_3C_2@C_{80}$ in detail.



$Sc_3N@C_{80}(Mes_2Si)_2CH_2$



n-$Bu_4N^+[Sc_3C_2@C_{80}(Ad)]^-$

References: (1) Stevenson, S. et al., *Nature* **1999**, *401*, 55. (2) Iiduka, Y. et al., *J. Am. Chem. Soc.* **2005**, *127*, 9956. (3) Shinohara, H. et al., *Nature* **1992**, *357*, 52. (4) Iiduka, Y. et al., *J. Am. Chem. Soc.* **2005**, *127*, 12500.

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1P-15

Fermi Level Effects on Electrical Conductivity of C_{70} Films

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Electrical conductivities of the crystalline C_{70} films on both silicon and quartz substrates were measured by a non-contacting technique utilizing surface acoustic wave (SAW) device as a function of temperature. Different temperature-dependent conductivities were obtained from the C_{70} films on both silicon and quartz substrates. In the case of the C_{70} film on silicon substrate, the conductivity depends on both film structure and gas adsorption at temperatures below about 200K. A sharp decrease in electrical conductivity, which depends on film structure, was observed around 200K. Also, a strong peak in conductivity, which depends on gas adsorption, was observed at about 340K. On the other hand, in the case of the C_{70} film on quartz substrate, a thermally activated conductivity was observed in the temperature range from 16K to 400K. We believe that there is a charge transfer process between the film and the substrates when the C_{70} film was grown. In the C_{70} film/silicon substrate structure, electrons are injected into the C_{70} semiconductor film, and so the conductivity, which Fermi level is near conduction band, is observed. On the other hand, in the C_{70} film/quartz substrate structure, holes are injected into the film, and the conductivity, which Fermi level is near valence band, is measured.

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1P-16

Air-Stable Solution-Processed Organic Thin-Film Transistor Based on Perfluoroalkyl Substituted C_{60} Derivative

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We have reported high performance solution-processed n-type organic thin-film transistors (TFTs) based on long-chain alkyl-substituted C_{60} derivatives [1-2]. However, C_{60} and its derivatives don't exhibit TFT performance in air, because O_2 and H_2O gases act as trap spices of electron transport. In this study, for realizing an air-stable n-type organic TFT, we newly synthesize a perfluoroalkyl substituted C_{60} derivative, C60-fused *N*-methylpyrrolidine-*para*-perfluorooctyl phenyl [C60PC8F17, see Fig.1(a)]. Since perfluoroalkyl chains are well-known materials for having high gas barrier, a C60PC8F17-TFT is expected to exhibit *n*-channel characteristics in air.

A film of C60PC8F17 was fabricated on highly doped silicon wafers covered with SiO_2 by spin coating from chloroform solution under ambient condition. Source and drain gold electrodes were deposited on the film. The TFT characteristics were measured in a vacuum and air at room temperature.

Fig. 1(b) shows drain current-drain voltage (I_D-V_D) characteristics of C60PC8F17-TFT after exposure to air for 24 hours. The device showed good *n*-channel characteristics in air, whereas the TFTs employing alkyl-substituted C_{60} derivatives were not operated under the same condition. The field-effect electron mobility in saturation regime is calculated to 0.002 cm^2/Vs. This result indicates that perfluoroalkyl chains play an important role for the air stability of the TFT performance.

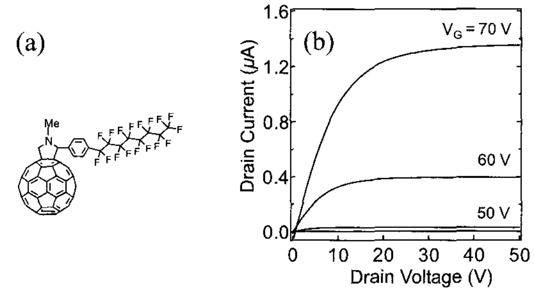

Fig. 1 Molecular structure of C60PC8F17 (a) and I_D-V_D characteristics of C60PC8F17-TFT in air (b).

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[1] M. Chikamatsu et al., Appl. Phys. Lett. **87**, 203504 (2005).

[2] M. Chikamatsu et al., The 30th Fullerene-Nanotubes General Symposium, 1P-16 (2006).

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1P-17

In situ Electric Transport of CsC_{60} Thin-Films

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When C_{60} is doped with alkali metals, several phases can be made starting from one to six of the alkali metal composition per C_{60}. Among these phases, one of the most curious phases for metal-insulating transition is A_1C_{60}, which is categorized as an one-dimensional Mott insulator. The electronic properties of A_1C_{60} have been only magnetically studied so far. This is because high quality A_1C_{60} can be made in a powder form. In order to have fundamental understanding, the transport measurements are essentially important.

We have tried to measure in situ conductivity as a function of temperature for the high quality CsC_{60} in a high vacuum chamber. CsC_{60} was chosen among AC_{60}, (A=K, Rb and Cs) since the other metallic phase can be excluded in the phase sequence of Cs_xC_{60} and a ideal experiments is considered to be made. For achieving uniform doping with the exact stoichiometry of 1 : 1, the C_{60} thin film grown in high vacuum deposition was heated at 423 K during the Cs doping using Saes getter.

As shown in Fig..2, the doping was first fixed when the lowest value of conductivity was observed, and then the conductivity was measured with changing temperature. It can be apparent that the doping is controlled in a good accuracy since no hysteresis in the measurement curve was detected. We are now planning to employ this high quality CsC_{60} thin film to Field Effect Transistor physical technique to attein continuoes carrier control.

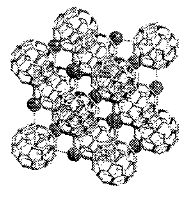

FIG.1:crystal structure of AC_{60}

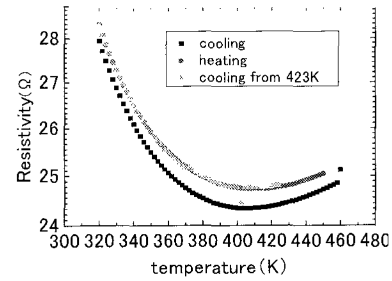

FIG.2: temperature dependence of resistivity.

[1] Akinobu Isurugi et al., The Physical Society of Japan, 61th Annual Meeting , 27pRC-5, 3/27 (2006).

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1P-18

Growth of carbon nanotubes with acutely tapered tip shape by RF-plasma enhanced chemical vapor deposition

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A radio frequency plasma enhanced chemical vapor deposition (RF-PECVD) method is expected as a method to grow carbon nanotubes (CNTs) at low temperature, which is inevitable for establishment of fabrication process of field emission displays (FEDs). We have recently found that the CNTs growth at low temperature less than 600 ℃ is possible by the RF-PECVD method. Here we report CNTs with unusually sharp tip shape grown at the low growth temperature.

CNTs were grown in an RF-PECVD apparatus with conventional planar type capacitively-coupled plasma source. A discharge frequency was 13.56MHz. Silicon (100) single crystal (10x10 mm^2) with 3 nm of catalyst iron (Fe) film was used as a substrate for CNTs growth. The process of CNTs growth was carried out with the following procedure. The substrate was annealed as a pretreatment at 650 ℃ in a vacuum of about 4.0×10^{-3} Pa. After the pretreatment, the substrate temperature was dropped to 550 ℃ and plasma was generated in an atmosphere of CH_4 and H_2. Gases flow rates were 80 sccm for CH_4 and 20 sccm for H_2. Pressure during the CNTs growth was 67Pa. The CNTs grown on the substrates were observed by a scanning electron microscope (SEM) and a transmission electron microscope (TEM).

Figure 1 is an SEM image of CNTs grown on the substrate. Vertically aligned CNTs are densely grown on the substrate. TEM observation of the CNTs showed that the CNTs have acute-angled cone shape or pencil-shape at the tip part as shown in Fig.2. Average diameter of the CNTs was around 10 nm. This structure is clearly different from that of the CNTs grown under conditions. No such the tip shape was found in the CNTs grown at higher growth temperature in this study. This acute tip shape is probably originated in a behavior of the catalyst particle at the early stage of the CNTs growth.

This work is in part supported by Cooperation of Innovative Technology and Advanced Research in Evolution Area (City Area) project of Ministry of Education, Culture, Sports, Science and Technology and by Mie University Satellite Venture Business Laboratory (SVBL).

Fig.1 SEM micrograph of vertically aligned CNTs grown on the substrate.

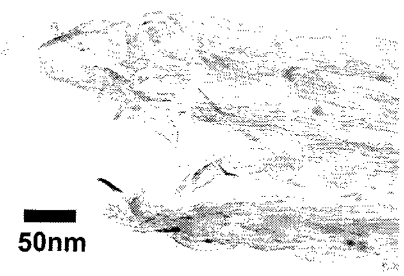

Fig.2 TEM micrograph of tip part of the CNTs.

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1P-19

Control of the innermost tube diameters in MWNTs by evaporating the boron doped carbon rod by RF plasma

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Control on the diameter of innermost parts of multiwall carbon nanotubes (MWNTs) is very important subject in the development of the materials for nano-capsule. By using the radio frequency (RF) plasma, closely filled MWNTs, that have the innermost tube diameters of 0.4 nm, can be easily obtained with high purity [1]. Recently, we found that the diameters of innermost tubes can be changed between the samples produced by evaporating the composite carbon rods with various boron concentrations by the RF plasma.

The composite carbon rod was prepared by filling the B mixed carbon powder into a 1.2 mm diameter cylinder-hole drilled at the center of a 5 mm diameter carbon rod. This carbon rod was shaped like a needle on a lathe. We changed the concentration of B in the carbon powder between 0 and 30 % by weight, and vaporized the composite rod by RF plasma generated in the mixture gas flow of Ar/H_2 (14 % of H_2). MWNTs thus prepared were characterized by using transmission electron microscopy (TEM), Raman scattering and thermogravimetric analysis (TGA). Figure 1 indicates the diameter distributions of the innermost tubes (solid bars) and corresponding outer tubes (hatched bars), and typical high-resolution TEM images. Increase of the inner tube diameter can be clearly recognized for the MWNTs prepared by using the 10 % of B-doped carbon rods, and the inner tube diameters reached to ~3-5 nm with the outer tube diameter of ~9 nm when using the 30 % of B-doped carbon rod. Raman spectra recorded in the R-mode region also indicated consistent results with those of TEM. TGA showed the decrease of combustion temperature, which is lower than that of closely filled MWNTs by ~40°C.

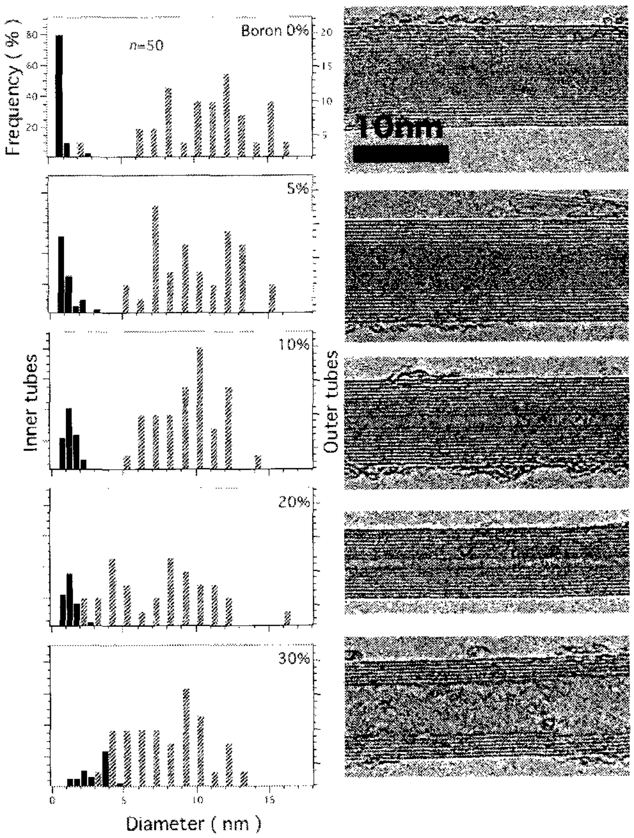

Fig. 1. Size distributions of innermost tubes of MWNTs and corresponding outer tubes, and TEM images. Solid and hatched bars mean, respectively, the inner and outer tubes of MWNTs. High-resolution TEM images are in the right column.

[1] A. Koshio, M. Yudasaka, S. Iijima, Chem. Phys. Lett. **356**, 595 (2002).

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1P-20

Formation of Boron-Catalysted Straight and Long Multiwall Carbon Nanotubes by Laser Vaporization

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It is well known that multiwall carbon nanotubes (MWNTs) are grown effectively by chemical vapor deposition (CVD). However, few studies are reported on MWNT generation using laser vaporization. Here, we report that the “straight” and “long” MWNTs are efficiently formed by room temperature laser vaporization of a mixture of graphite and boron in an Ar atmosphere.

Target pellets (diameter: 13 mm, thickness: 5 mm) containing boron (1 to 60 at.%) were prepared by mixing powders of boron carbide and graphite. The target pellet was placed into a stainless-steel chamber. After evacuated the chamber, Ar gas (0.1-0.9 MPa) was introduced to the chamber. The target pellet was irradiated by using a CW-Nd:YAG laser (laser power density: 13.3 kW/cm^2, spot size: 2 mm^2) for 2 seconds. The products obtained under different experimental conditions were characterized by transmission electron microscopy (TEM) and scanning electron microscopy (SEM).

Figure 1 shows a TEM image of a typical product obtained using a target containing 20 at. % boron. Ar gas pressure used was 0.1 MPa. Straight MWNTs were found to efficiently grow under this condition. The MWNTs showed outer diameters in the range from 12 to 40 nm, inner diameters in the range from 2 to 10 nm, and lengths more than 25 μm. Figure 2 shows a typical high-resolution TEM image of a MWNT, indicating that the MWNT has high crystallinity. The diameters of the MWNTs were increased as Ar gas pressure increased. When Ar gas pressure was 0.9 MPa, thick MWNTs with outer diameters of 100-300 nm were prepared. We believe that of MWNTs by laser vaporization occur in a short reaction time (for seconds) compared to that in a CVD method (for more than minutes). For the growth of straight and long MWNTs, we consider that a specific catalytic activity of boron plays an important role.

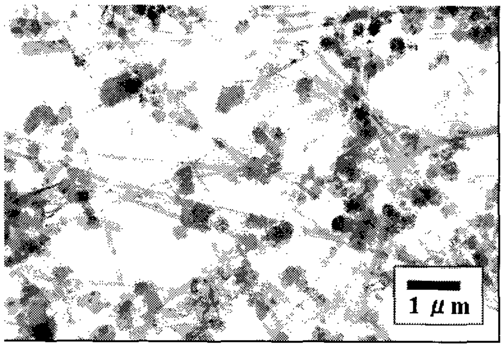

Fig. 1 TEM image of MWNTs.

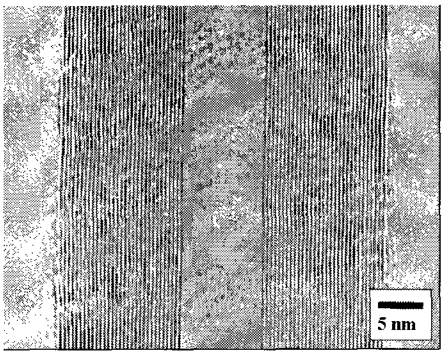

Fig. 2 High-resolution TEM image of a MWNT.

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1P-21

Production and purification of camphor-grown carbon nanotubes

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Our group is known for growing single-wall nanotubes (SWNTs) and multiwall nanotubes (MWNTs) from an unconventional carbon precursor, camphor, by catalytic chemical vapor deposition method [1]. Using zeolite powder as a catalyst support, we have optimized the relative concentrations of camphor and catalyst to achieve an exceptionally high growth rate of MWNTs at atmospheric pressure. Simple pyrolysis of 1g camphor over 0.1g Fe-Co-impregnated zeolite at 650°C for 15 minutes inflates the zeolite about 40–50 times by volume and yields approximately 0.5g MWNTs. Transmission electron microscopy of as-grown material reveals MWNTs in a narrow diameter range of 5–15 nm with negligible amorphous carbon. Thermogravimetric analysis (TGA) also confirms the absence of amorphous carbon and graphite particles in our samples. In this presentation we focus on the purification parameters of camphor-grown MWNTs. Against the available report of dissolving zeolite support in 6M NaOH solution, we prefer to use 3M NaOH solution for zeolite removal. Our optimized purification process ensures zeolite removal over 95%. For instance, a typical TGA of zeolite-purified MWNT sample is shown in Fig. 1. Remaining 4.5% is nothing but the metal which can easily be removed by HCl treatment.

[1] M. Kumar, Y. Ando, *Carbon* 43 (2005) 533-540.

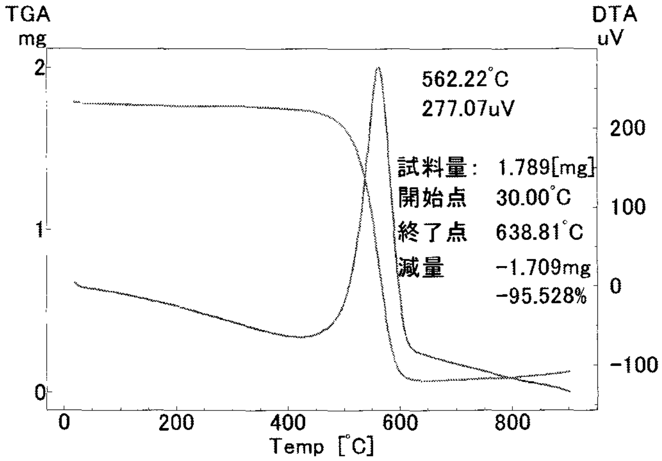

Fig. 1 TGA of camphor-grown MWNT sample after 3M NaOH treatment.

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1P-22

Aligned SWNT growth using size-controlled catalysts on sapphire

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Aligned growth of single-walled carbon nanotubes (SWNTs) on sapphire substrates and their characterization were reported by Ago et al. [1]. But the detail of the growth, especially the mechanism of the alignment has not been fully understood. In this paper, we report the growth of aligned SWNTs from size-controlled catalysts and discuss the mechanism of the aligned growth.

Co-ferritin [2] and Fe-Dps were used as catalysts in addition to ferritin [3]. SWNTs were grown by thermal CVD on A-face and R-face surfaces of sapphire substrates and were characterized by SEM, AFM, and Raman spectroscopy.

Figure 1 shows the diameter distribution of SWNTs analyzed from AFM images. Growth of SWNTs aligned to [1,-1,0,0] direction on A-face was confirmed [1]. Observed diameter distribution (0.7 ± 0.2nm) was significantly narrower than the previous result (1.3 ± 0.3nm) [3]. A similar tendency was observed for the growth by Co-ferritin and Fe-Dps.

Figure 2 show a SEM image from a sapphire substrate with fabricated protrusions. The SWNTs begin to grow around a protrusion without any preference of growth direction and tend to align to a specific direction as the growth proceeds. This phenomenon suggests that the alignment is based on the tip-growth mechanism.

References: [1] H. Ago et al., *CPL* **408** (2005) 433, **421** (2006) 399. [2] G. H. Jeong et al., *JACS* **127** (2005) 8238. [3] C. Zhou et al., *JACS.* **127** (2005) 5294.

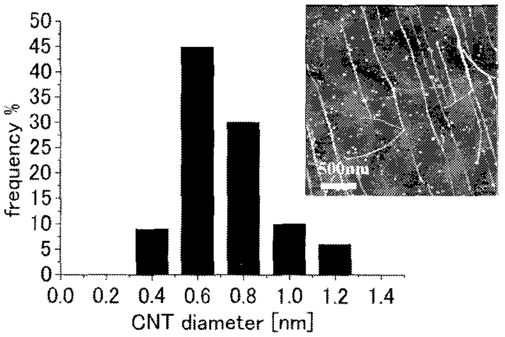

Fig.1 AFM image of aligned SWNTs grown by ferritin catalyst and their diameter distribution

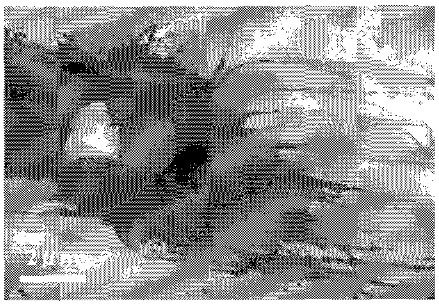

Fig. 2 SEM image of SWNTs grown around a protrusion fabricated on sapphire substrate

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1P-23

A new growth mechanism of single-walled carbon nanotubes synthesized by catalytic decomposition of alcohol

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The growth mechanism of SWNTs is a basic and important question, and two competitive approaches have been used for the description of CNTs growth, namely tip growth and base growth [1, 2]. In this work, we suggests a new growth mechanism which combine both tip and base growth model of SWNTs. Discrete Co catalytic nanoparticles are obtained on SiO_2 substrates by pulsed arc plasma deposition (ULVAC Inc.) (shot number is 5 pulses) and used for growth of isolated single-walled carbon nanotubes (SWNTs) with chemical vapor deposition (CVD) approach. Ethanol vapor was adopted as a carbon source with a flow rate of 50 sccm at 750 °C for 60 min., and the vacuum pressure was controlled at 5 Torr. Fig. 1 is a typical AFM image of isolated SWNTs. At the both ends of the nanotube named OO' are found metal particles, in contrast to another nanotube named OO'', for which a metal particle can be found only at the end of the position O. It is suggested that for the SWNT OO' the particle located at O is not only used to fix the nanotube but also as a catalyst, which can supply the carbon feedstock for CVD growth, besides the catalyst particle at position of O', as shown in Fig. 2. Having this idea in mind, it is not difficult to understand the fact that the same diameter nanotubes OO' and OO'' have different length under the same CVD growth parameters. For the nanotube OO'', carbon feedstock can only be supplied from the catalyst particle located at O (base-growth model), while for the nanotube OO', carbon feedstock can be supplied from catalyst particles from both ends (base growth plus tip growth). Our new finding suggests that the base and tip growth mechanism can coexist in one SWNT growth.

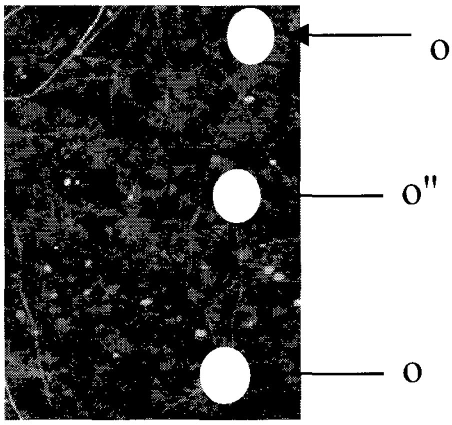

Fig. 1 AFM image of SWNTs grown substrates. Image size: 1.5 μm×2.0 μm

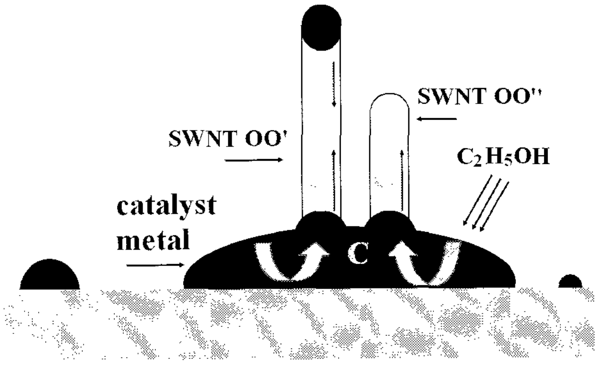

Fig. 2. Mechanism of SWNTs formation on a large metal catalyst

[1] C. Bower et al., Appl. Phys. Lett. 77 (2000) 2767. [2] M. Chhowalla et. al., J. Appl. Phys. 90 (2001) 5308

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1P-24

Synthesis-Condition Dependence of Carbon Nanotubes Growth by Alcohol CCVD Method

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Morphology and properties of carbon nanotubes (CNTs) must be controlled for any applications. For the use of mechanical properties, for example, macroscopic length of CNTs is preferable. On the other hand, a selective growth or separation of metallic and semiconducting CNTs has to be performed, when CNTs are used in electronic devices. Carbon nanotubes are synthesized by arc discharge, laser ablation and, in recent years, chemical vapor deposition(CVD) method for these applications. Especially, alcohol catalytic CVD(ACCVD) method has advantage to apply to electronic devices because CNTs can be easily synthesized directly on a substrate in this method. Growth conditions of this method and their effects have been experimentally studied so far [1]. In this study, we report dependence of CNTs growth on ethanol gas flow rate and thickness of catalyst film by ACCVD method.

Figure 1 shows Raman spectra of carbon nanotubes synthesized from Cobalt thin films deposited on SiO_2-coated Si substrate. Higher peaks of G-band and RBM are observed by higher flow rate of ethanol gas with 10Å Co film in Fig. 1(a), and by thinner Co film with ethanol gas flow of 6.0 l/min. in Fig. 1(b).

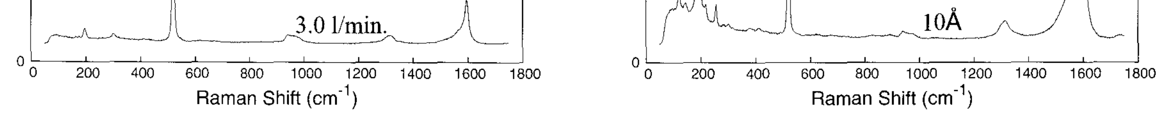

Figure 1. Raman spectra of carbon nanotubes synthesized (a) from Co film of 10Å thickness with different ethanol gas flow, (b) from Co films of different thickness with ethanol gas flow of 6.0 l/min. The spectra were obtained by 632.8 nm laser excitation. The spectrum and respective baseline are shifted for clarity.

[1] S. Maruyama, R. Kojima, Y. Miyauchi, S. Chiashi, M. Kohno, *Chem. Phys. Lett.* **360**, 229 (2002).

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1P-25

Direct Synthesis of Single-Walled Carbon Nanotube Forests on Ni-Based Alloys

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Among the known methods to synthesis single-walled carbon nanotubes (SWNTs), chemical vapor deposition (CVD) provides direct growth of carbon nanotubes (CNTs) on substrates, and thus is the preferred growth method of SWNTs for nano-electronic applications. Generally, SWNTs synthesis is limited to insulating substrates such as Si wafers or quartz, and could not carry out on conducting substrates. Only the synthesis of multi-walled carbon nanotubes (MWNTs) grown directly on Ni substrate was reported[1], due to large thickness of catalyst films or poisoning of catalytic activity on the surface of conducting substrates.

Here we report a highly efficient growth of SWNTs and double-walled carbon nanotubes (DWNTs) on conducting metal substrates. Catalytic thin films of Al_2O_3 (35 nm) / Fe (1 nm) were sequentially sputtered onto metal substrates, which were commercially used Ni-Fe-Cr alloys. Highly efficient CNTs synthesis was carried out using water-assisted CVD at 750°C with an ethylene carbon source (100 sccm) and water (200 to 300 ppm) as a catalyst activity enhancer and preserver [2,3]. As a result, we found that substrates made of Ni-based alloys with Cr or Fe were excellent for SWNT synthesis. Fig.1 shows successful syntheses of CNT forests were achieved on various alloys spanning many standard metals, such as Fe, Ni, Inconel® 601, YEF 426, NiCr®, YEF 50, SUS 430, SUS 304, SUS 310S. From detailed TEM analysis revealed that CNTs grown on Ni, Fe, and two Fe-Cr alloys (SUS 430, SUS 304), consisted not only of SWNTs but also a significant proportion of MWNTs. Our approach opens up an economical route for the mass production of SWNTs (DWNTs) forests and also enables straightforward assemble of CNTs into nano-electronic devices, such as field emission displays.

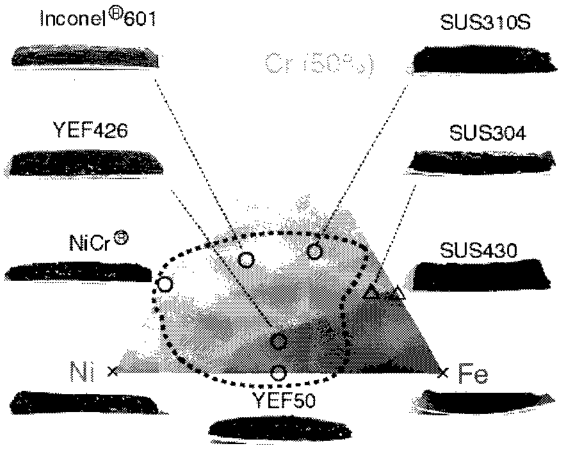

Fig 1. Correlation between components of Ni-Fe-Cr alloys and their photograph.

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[1] Y. Hua, K. Huoa, H. Chena, Y. Lub, L. Xua, Z. Hua, Y. Chena, *Mater. Chem. Phys.*, in press.
[2] K. Hata, D. N. Futaba, K. Mizuno, T. Namai, M. Yumura. S. Iijima, *Science.*, **40**, 397 (2004).
[3] D. N. Futaba, K. Hata, T. Namai, T. Yamada, K. Mizuno, Y. Hayamizu, M. Yumura. S. Iijima, *J. Phys. Chem. B.*, **110**, 8035 (2006).

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1P-26

Highly Efficient, Catalyst Free, and Density Controllable SWNT Forests Synthesized From Wet Fe-Mo Nanoparticle Catalysts by Super-Growth

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The chemical vapor deposition (CVD) method has been recognized as an effective means to synthesize single-walled nanotubes (SWNTs) on substrate. However, The CVD method has suffered severely low catalyst activity. We already reported a significant breakthrough addressing low efficiency of catalytic activity of SWNTs synthesis can be achieved by the addition of small and controlled amount water into a CVD growth (Super-Growth CVD) [1]. In this super-growth CVD process, catalytic thin films of Al_2O_3 (10 nm) / Fe (1.2 nm) were sequentially sputtered onto silicon wafer and a SWNT forest mass density was constant at 0.037 g/cm^3 [2]. However, the density of forests can not control by changing thickness of Fe film.

Here we report highly efficient growth of SWNTs from wet iron-molybdenium (Fe-Mo) nanoparticles catalysts by super-growth. The high activity of the nanoparticle catalysts, and the ability to deposit them densely on substrates without aggregation enabled to synthesize SWNT forests with the assistance of water. Key characteristics of the SWNT forests such as height, and quality were similar or even superior to those of forests grown from dry-sputtered catalytic metal films. Our approach can be extended to provide further controllability in SWNT synthesis demonstrated by the density control between *ca.* 0.01 g/cm^3 to 0.05 g/cm^3 (Fig. 1) achieved by the changing the amount of Fe-Mo nanoparticles deposited on the substrate. These results open up an economical and scalable approach towards mass-production of SWNTs by the super-growth.

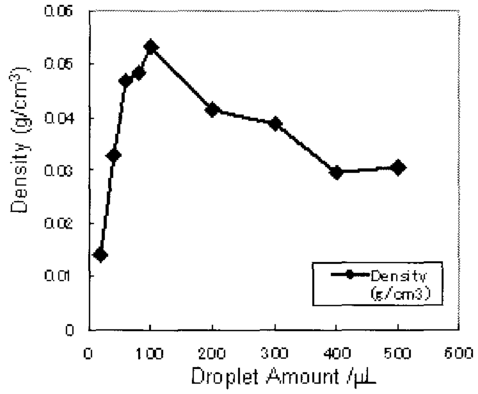

Figure 1. Density control of SWNTs forest

References:

[1] K. Hata, D. N. Futaba, K. Mizuno, T. Namai, M. Yumura, S. Iijima, *Science,* 2004, **306,** 1362.

[2] D. N. Futaba, K. Hata, T. Namai, T. Yamada, K. Mizuno, Y. Hayamizu, M. Yumura and S. Iijima, *J. Phys Chem. B,* 2006, **110,** 8035.

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1P-27

Gas-flow control of SWNT diameter using Super-growth CVD

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Catalytic chemical vapor deposition (CVD) represents one of the promising candidates for the mass production of carbon nanotubes (CNTs). The “Super-growth” technique, which has demonstrated the highly-efficient and highly pure synthesis of single-walled carbon nanotubes (SWNTs) by adding a small and controlled level of water into the CVD growth environment, has achieved millimeter-long SWNTs in a 10 minute growth time [1]. This breakthrough technique opened the door for the scientific and industrial application of SWNTs, such as electrical devices, storage materials, nano-reactors, etc. However, the current SWNT mean diameter for the Super-growth technique is typically 3 nm [2], which precludes the use of super-growth SWNTs for semi-conducting uses. Unfortunately, precise diameter control of SWNTs remains a severe obstacle in the CNT field. Therefore, in order to open all roads to develop potential SWNT applications, the realization of mass production of diameter-controlled SWNTs is necessary.

From this viewpoint, we investigated rational and scalable methods to tune the mean diameter of the super-growth SWNT forests. Here, we report a straightforward approach to control the diameter by simply adjusting the total gas flow rate without the need to change the catalyst amount. Preliminary results have shown our ability to vary the mean SWNT diameter from 2.2 to 3.3 nm.

References:

[1] K. Hata, D. N. Futaba, K. Mizuno, T. Namai, M. Yumura, and S. Iijima, *Scinece* 2004, **306**, 1362.

[2] D. N. Futaba, K. Hata, T. Namai, T. Yamada, K. Mizuno, Y. Hayamizu, M. Yumura, and S. Iijima *J. Phys. Chem. B*, 2006, **110**, 8035.

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1P-28

Spinning of High Strength Fiber Using SWNTs synthesized by the Enhanced Direct-Injection-Pyrolytic-Synthesis (e-DIPS) Method

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We have developed a novel large-scale synthesis method for single-walled carbon nanotubes (SWNTs) with high purity to be the core material for nanotechnologies. This method modified from the DIPS (direct injection pyrolytic synthesis) method has dramatically improved an accurate control of the reaction conditions to achieve high purity and a high degree of graphitization. The purity of the SWNTs synthesized by the enhanced DIPS method was increased from the previous level of ca. 50% to 97.5%, and the structural defects in the SWNTs was reduced to one tenth of the previous level. Furthermore, the catalytic efficiency has also been increased to 3900%, which represents one hundred times the previous productivity.

As shown in Figure 1, there is no need for purification processes, surface treatments or use of binder in order to spin high strength threads (SWNT wire, see Figure 1E) and to make thin films (SWNT sheets, see Figure 1D), probably due to their high quality. These SWNT wire and sheets would be applicable for ultra-tough airplane materials, transparent electrode, and mesh materials for cell culture.

We have measured the properties of the SWNT sheet and SWNT wire, such as tensile strength and sheet resistance, as well as the basic properties of the as-grown high-quality SWNTs. Details will be presented at the meeting.

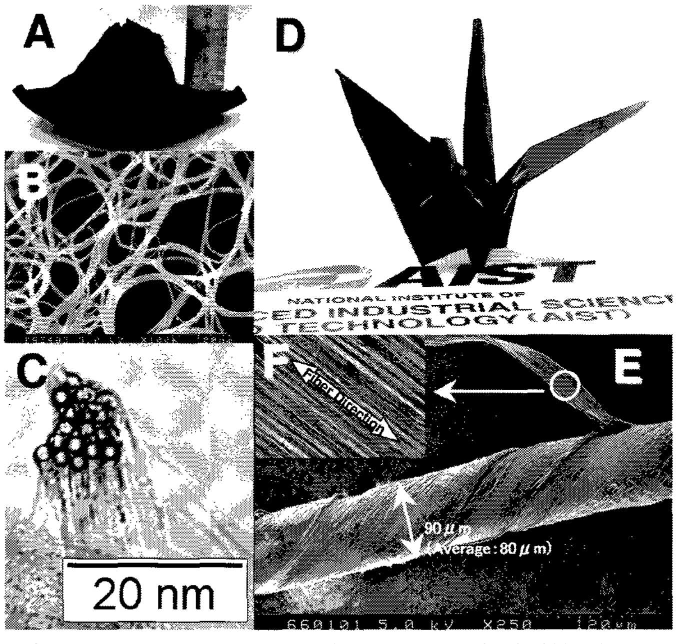

Figure 1. SWNTs grown with e-DIPS method. (A) Picture of as-grown sample. (B) SEM and (C) TEM images. (D) An *origami* crane made from a non-purified high quality SWNT sheet (sheet thickness: approximately 9 micrometers). (E) SEM image of high strength SWNT wire produced without surface treatment and binder. (F) Enlargement of the part in (E) suggested by the white circle.

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1P-29

Synthesis of SWNTs by the zeolite-CCVD method with IR-furnace

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and Hisanori Shinohara[1,2,3]

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The CCVD (catalytic chemical vapor deposition) method is of great importance not only from fundamental point of view but from industrial bulk synthesis of carbon nanotubes (CNTs), since it enables us to scale up simply with reasonable cost. We have reported the high yield synthesis of SWNTs and DWNTs by the zeolite-CCVD method [1]. So far, the CCVD synthesis has been employed convective heat transfer for growth energy. Here, we report entirely new system for CNTs growth by radiative heat transfer with an IR-furnace.(cf. Fig.1)

The conventional conductive heat transfer CVD provides heating energy through reactants and buffer gas. IR heating, in contrast, provides radiative heat transfer directly to reactants. We have employed TMP (Turbo Molecular Pump) to achieve high vacuum (10^{-6} Torr) with less impurities. A mass flow controller (HORIBA-STEC, SEC-8400S) regulate flow rates of reactant EtOH as carbon source. The IR heating realizes much faster response of descent and ascent of temperature as compared with that of conductive heating. One can obtain information on an accurate carbon amount of supply necessary for studying growth mechanism of CNTs. Indeed, we have obtained high yield of SWNTs with a shorter reaction times. Figure 2 shows a typical TEM image for as-produced samples. The SWNTs synthesized show a somewhat wide diameter distribution (d = 0.7 ~2.5 nm). In the IR-furnace, the floating EtOH decomposes promptly close to metal catalysts due to radiative heating which is contrasted to gradual decomposition by conductive heating with electric furnace.

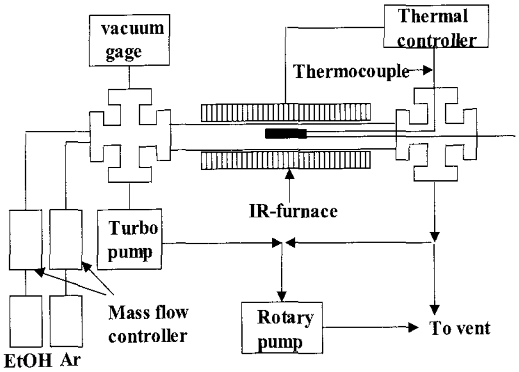

Fig.1 Schematic of synthesis system with IR-furnace

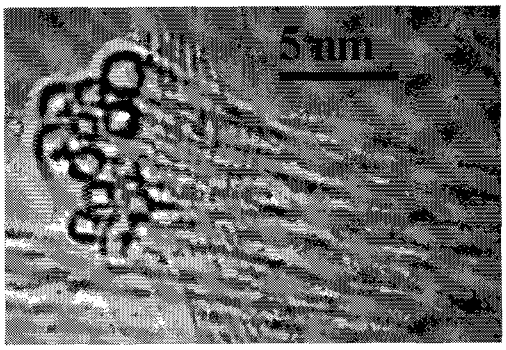

Fig.2 TEM image of SWNTs obtained from zeolite-CCVD with IR-furnace

References:
[1] T.Hiraoka et al. Chem. Phys. Lett. **382** 679 (2003)

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1P-30

The effect of a platinum catalyst on the formation of SWNTs with narrow diameter distribution by alcohol-CCVD method

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It is well known that single-wall carbon nanotubes (SWNTs) are synthesized by alcohol-CCVD method, and their chirality and diameter distributions depend on catalytic metal. Therefore, the study on the effect of catalyst is important to elucidate not only the generation mechanism, but also production of SWNTs with a single chiral distribution.

In this work, SWNTs were synthesized by Alchol-CCVD method using ethanol as carbon source, and platinum and cobalt were used as a catalyst deposited on porous glass(PG)[1]. Samples were analyzed by TEM, Raman spectroscopy, and fluorescence spectroscopy. Obtained Raman and fluorescence spectra are shown in Figs.1 and 2. When cobalt was used as a catalyst, the Raman spectra showed wide diameter distribution at each temperature. On the other hand, when platinum was used instead of cobalt, the diameter distribution was found to change narrow. Especially at 900℃, the difference was significant. Raman spectra obtained by platinum catalyst consist of only two peaks at 245cm^{-1} and 260cm^{-1}, showing sharp contrast to those by cobalt catalyst, consisting of a lot of peaks(145cm^{-1}-260cm^{-1}), particularly in the larger diameter region. In conclusion, the present results suggest the potential ability of Pt as a catalyst for generation of SWNTs with small and very narrow diameter distributions even at high temperature.

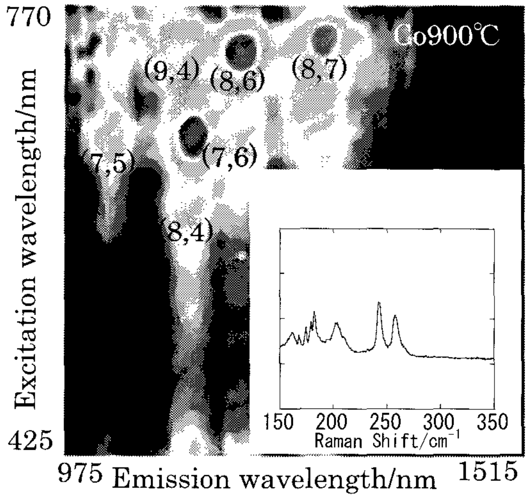

Fig.1

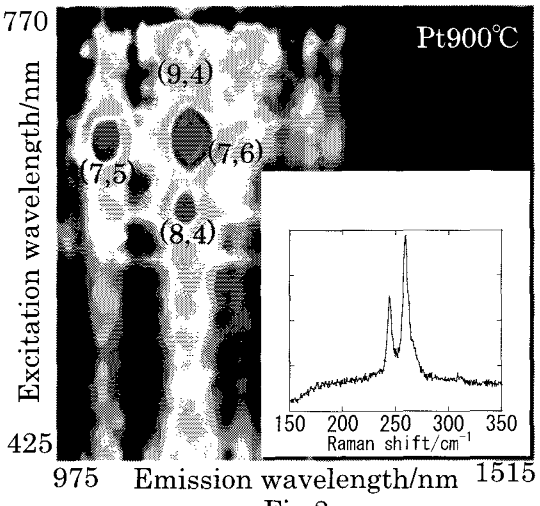

Fig.2

Reference: [1] Y.Aoki et al., Chem. Lett., 562, 34(2005)

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1P-31

Efficient Growth of Single-Walled Carbon Nanotubes using Fe-Co Bimetallic Catalysts

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We are now paying our greatest attention to metallic catalysts for the goal of efficient and chirality-controlled growth of single-walled carbon nanotube (SWNT). In a Fe-Co bimetallic catalyst system, we have previously presented a model to explain the efficient growth mechanism of SWNTs on Si/SiO_2 by chemical vapor deposition (CVD) [1, 2]: Preferential diffusion of Fe to the SiO_2 top substrate layer prevented Co from diffusion to the SiO_2 layer or aggregation to large particles, thus efficient generation of nm-sized Co particles resulted in high yield of SWNT.

Here, we determined the catalyst composition to maximize the yield of SWNT as follows: The Fe-Co bimetallic catalyst was loaded on a Si/SiO_2 substrate by spin coating, dropping ethanol solutions of Fe- and Co acetate. We varied the Fe concentration in the solution in 0-0.01wt% keeping the Co concentration at 0.01wt%. Figure 1 shows relative intensity of the G band in Raman spectra of SWNT plotted against the Fe concentration. The G-band intensity is peaked at around 0.005 wt% of Fe, thus most efficient growth of SWNTs. We consider that diffusion of Fe atoms into the SiO_2 top layer is saturated at this concentration, and generation of nm-sized particles of Co is promoted most efficiently.

As the latest finding, we also introduce a 2-stage CVD process that leads to a more efficient growth of SWNT than single-stage processes as above: Here, a catalyst of Fe is first loaded on a substrate and annealed. Then, a Co catalyst is loaded on the substrates to start the growth of SWNT. More details will be presented in the symposium.

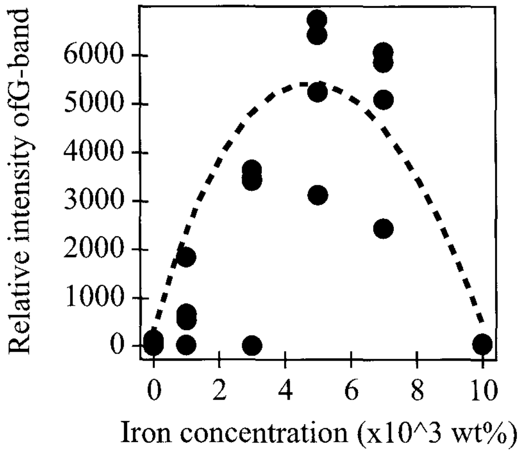

Fig.1
Relative intensity of G-band in Raman spectra of SWNT for different Fe concentrations in ethanol solution. Co concentration was kept constant at 0.01 wt%.

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[2] T. Murakami, *et. al.*, J. Appl. Phys. (submitted)
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1P-32

Ultradispersion of Catalytic Metal Particles on Structured Arc-Soot for DMFC Electrode

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Carbon nano-horn (CNH), which is a kind of the nanocarbon, attracts the attention as an electrode material of Direct Methanol Fuel Cell (DMFC) (1). It was showed that it has been able to be synthesized as an arc-soot nano-carbon (ASNC) by the arc discharge method under specific condition (2). In addition, it was indicated that the non-dahlia-like ASNC, prepared at 80 kPa, supported the finer Pt-Ru particles with highly dispersion(3). But, the dahlia-like ASNC has a low electrical conductivity and this degenerates a cell paformance. Hence, we used the device that can continuously synthesize ASNC to synthesize a structured ASNC.

In this study, at first we synthesized the structured ASNC, 80 kPa under N_2 atmosphere, as shown in Fig.1. And Pt and Ru were dispersed on the structured ASNC through a batch reaction based on colloid formation and reduction in ethylene glycol solution. The activity of the synthesized catalyst was evaluated, and the influence of the ASNC structure was evaluated. Additionally, The DMFC electrode was made with the synthesized ASNC and the cell was tested. As a result, the structured ASNC showed good cell paformance.

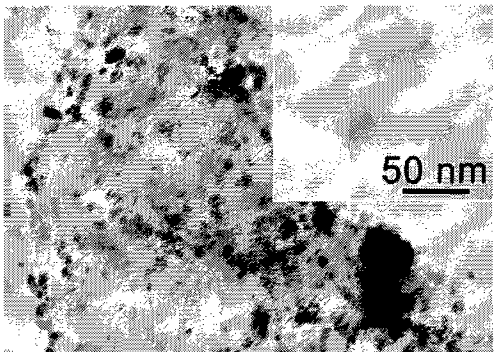

Fig.1. TEM micrograph of Pt-Ru particles dispersed on structured arc-soot nanocarbon.

This work has been partly supported by the Excellent Research Project of the Research Center for Future Technology from Toyohashi University of Technology, the 21st Century COE Program "Intelligent Human Sensing" from the Ministry of Education, Culture, Sports, Science and Technology, and JSPS Core University Program.

[1] T. Yoshitake, *et al., Physica B.*, **323**, 1627 (2002)
[2] M. Ikeda, *et al.*: *Jpn. J. Appl. Phys.*, **41**, L852 (2002)
[3] K. Higashi, *et al.*: *Appl. Plasma Sci.*, **13**, 99 (2005)

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1P-33

Synthesis of Arc-Soot Nano-Carbon by Newly Developed Contentious Production Apparatus

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Arc discharge method is one of the methods to prepare various carbon nanomaterials such as multi-walled carbon nanotube (MWCNT), single-walled carbon nonatube (SWCNT), and carbon nanohorn (CNH). On the other hand, we have developed a torch arc method using a welding arc torch for syntheses of MWCNT and CNH in open air[(1)].

The contentious production apparatus of nanocarbon was newly developed, which had two arc torches located with a certain angle. Both electrodes of arc torches were endlessly supplied, in order to operate for a long time. In the apparatus, the constant amount of gas flows in from the torches and evacuated by the pump. Pressure in chamber was constantly controlled by a conductance valve, balancing the gas supply and exhaust.

Arc soot including cocoon-like CNH was synthesized under nitrogen gas flow. The arc soot was characterized by measuring compressive resistivity and bulk density. The results are shown in Fig.1 and 2. When the arc soot was compressed, it has high electric resistance and low bulk density. The result indicates this arc soot is lower specific gravity than conventional arc discharge method. This work has been partly supported by the Excellent Research Project of the Research Center for Future Technology from Toyohashi University of Technology, the 21st Century COE Program "Intelligent Human Sensing" from the Ministry of Education, Culture, Sports, Science and Technology, and JSPS Core University Program.

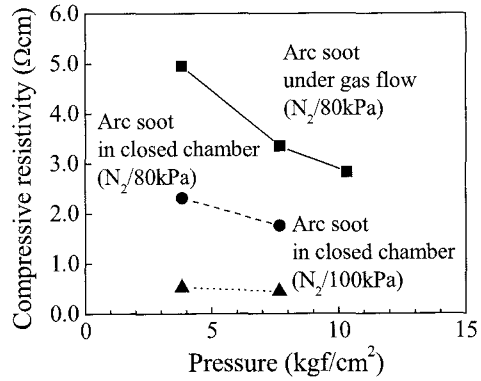

Fig.1 Compressive resistivity of arc soot

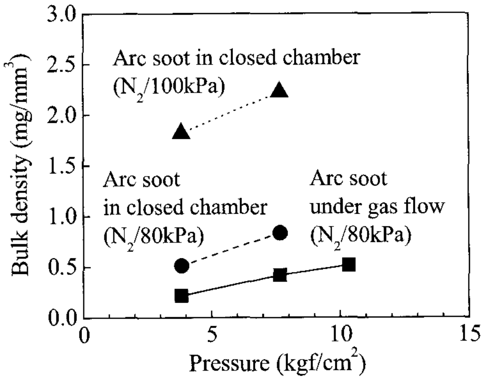

Fig.2 Bulk density of arc soot

Reference: (1) H. Takikawa, *et al*: *Physica B*, **323** (2002)

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1P-34

Ruthenium Dispersion on Arc-Soot Nanocarbon and Oxidization

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S. Itoh[2], T. Yamaura[2], K. Miura[3], K. Yoshikawa[3]

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Electrochemical capacitors have a greater response speed and longer lifetime than secondary batteries. Electrochemical capacitors can be classified into two groups: an electric double layer capacitor (EDLC) and a pseudo-capacitor. The former charges electrons on the double layer formed in the interface of electrode and electrolyte. The latter charges electrons on the surface of electrode by the faradic reactions [1].

The pseudo-capacitor electrode consisted of RuO_2 has proposed. It has been investigated that the RuO_2 was dispersed on carbon electrode in order to reduce the amount of expensive Ru [2]. In this study, RuO_2 dispersed nano-carbon was prepared as the following procedure. The arc-soot as nano-carbon was prepared by the arc discharge method. Metallic Ru was supported on the arc-soot through a batch reaction based on colloid formation and reduction in ethylene glycol solution. Then the dispersed Ru was heated and oxidized in air (573 K, 1 h).

XRD patterns of arc-soot, Ru-dispersed arc-soot, RuO_2-dispersed arc-soot are shown in Fig.1 as well as graphite. The result indicates that the Ru was amorphous as-dispersion and crystallized RuO_2 was formed after oxidization.

This work has been partly supported by the Excellent Research Project of the Research Center for Future Technology from Toyohashi University of Technology, the 21st Century COE Program "Intelligent Human Sensing" from the Ministry of Education, Culture, Sports, Science and Technology, and JSPS Core University Program.

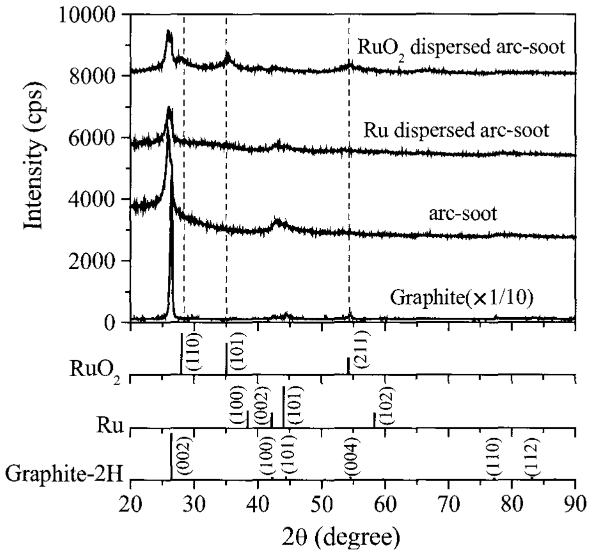

Fig.1. XRD pattern of materials

[1] T. Nanaumi, *et al.*, *Electrochemistry*, **70**, 681-685 (2002)
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1P-35

Organic-Vapor Stimulated Reversible Incorporation and Exit of C_{60} in/from Single-Wall Carbon Nanohorns

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Various molecules are incorporated inside single-wall carbon nanohorns (SWNHs) [1] through holes at room temperature in liquid phase [2-6]. Larger diameter (2-5 nm) of the internal nanospaces of SWNHs gives motional freedom and moderate confinement to the incorporated molecules, and thus allows them to be easily released to outside SWNHs by immersion in solvents [4-6]. Here, we report that the incorporated molecules exit outside and the exited molecules re-enter inside SWNHs even in dry conditions at room temperature by exposure to appropriate organic vapors.

We used C_{60} as the first example to demonstrate reversible entrance and exit in/from hole-introduced SWNHs (NHox). C_{60}-incoporated NHox (C_{60}@NHox) was obtained by drying NHox-C_{60}-toluene mixture [6]. An X-ray diffraction (XRD) pattern of C_{60}@NHox showed a broad diffraction peak around $2\theta = 20^\circ$, suggesting small crystalline size and disordered arrangement of the incorporated C_{60}. After exposure to ethanol vapor at room temperature, new sharp peaks corresponding to (111), (220), and (311) diffraction peaks of C_{60} crystal with an estimated size of about 70 nm appeared. Such large C_{60} crystals deposited outside NHox were indeed observed by transmission electron microscopy. Interestingly, the exited C_{60} again entered inside NHox by exposure to toluene vapor, which was confirmed from a disappearance of the diffraction peaks of the C_{60} crystal. We also found that the movements of C_{60} from inside to outside NHox and vice versa were repeatable.

The phenomena were considered by assuming C_{60}-toluene pseudo-solvate formation inside NHox and its stability. Thermo-gravimetric analyses of C_{60}@NHox indicated that small amount of toluene was co-incorporated with C_{60} having molar ratio of C_{60}:toluene $\approx$ 1:2. This ratio agrees with the reported value for C_{60}-toluene solvate [7]. When the C_{60}@NHox was exposed to ethanol vapor, overall stabilization energies of ethanol clusters would overcome those of the incorporated C_{60}-toluene pseudo-solvates, giving rise to ejection of the pseudo-solvates to outside NHox. Because the pseudo-solvates would be unstable on outer surface of NHox having negative curvature, they decompose into the C_{60} nano-crystals. Upon exposure to toluene vapor, on the other hand, the C_{60}-toluene solvate would be re-formed, move-around, and enter inside NHox through the holes.

Selection of vapors should depend on the materials to be incorporated. Thus, the presented demonstration would not only offer new easy method of internalization and externalization of various materials for nano-porous materials, but new idea about hybrid systems accompanied by environmentally-responsible material transportation in/from nanospaces.

Acknowledgement: We thank Dr. T. Azami and Dr. D. Kasuya for preparing SWNHs.

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1P-36

Solubilization of Single-Wall Carbon Nanohorns with an Anticancer Drug-Polymer Conjugate

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Single-wall carbon nanohorns (SWNHs) are newly discovered carbon nanoparticles with an average diameter of 80-100 nm, and composed of single-wall carbon nanotubes with corn-shaped caps.[1] By oxidation, SWNHs are transformed into a porous structure (oxSWNHs) with "nanowindows ($<\phi$ 2 nm)" on the tubes, and then oxSWNH has about four-times larger surface area than as-grown SWNH. We have recently reported that oxSWNHs adsorb dexamethasone[2] or cisplatin[3] and these drug-oxSWNH complexes perform sustained drug release. On the contrary to these promising properties as a drug carrier, oxSWNHs are poorly dispersed in an aqueous environment. Here, we describe a simple procedure for dispersing oxSWNHs in aqueous solution using a polyethylene glycol-doxorubicin (PEG-DXR) conjugate, in which DXR is a clinically used anticancer drug.[4]

In this method, oxSWNHs are first dispersed in organic solvent and added by PEG-DXR. Next, the mixture of oxSWNHs and PEG-DXR are diluted with water to obtain the PEG-DXR-treated oxSWNHs. The modified oxSWNHs were well dispersed in water, which permitted them to pass through a gel filtration column. This dispersibility was inhibited by the co-addition of DXR, which implies that PEG-DXR interacts with oxSWNHs via its DXR moiety. The average diameter was estimated to be about 160 nm by dynamic light scattering measurements. PEG-DXR-oxSWNHs induced DXR-dependent apoptosis in human lung cancer cells. Histopathological analyses indicated that PEG-DXR-oxSWNHs intravenously administered into normal mice mainly accumulated in macrophages in the liver and spleen.

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1P-37

Release-control of C_{60} by polyamine-plugs on nanohorn holes

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Single-wall carbon nanohorns (NHs) have inherent hollow spaces, and the holes of the sheath walls can be opened easily by the heat treatment in oxygen (NHox). Various kinds of materials, such as C_{60} [1] and Pt-compound [2], can be incorporated and released in/from the nanospace of NHox. We have reported previously that Gd-acetate clusters had the cap effects, which suppressed the C_{60}-release from the C_{60}-incoporated NHox [3]. However, the Gd acetate cannot be used for the living systems, therefore we used various polyamines to plug the holes of NHox in this study.

The C_{60} was incorporated inside NHox (C_{60}@NHox) by the nano-precipitation [4], and the holes of NHox were plugged by several types of amines with different molecular sizes. The smallest molecule was 1,4-diaminobutane (Bu) and the largest one was spermine. By immersing C_{60}@NHox in toluene, about 90% of C_{60} was released, while Bu-plugged C_{60}@NHox, only 10%. The released C_{60}-quantities increased as the molecular sizes became larger, and the spermine-plugged C_{60}@NHox released 60% of C_{60}. This means that the polyamines and carbonyl groups at the edges of holes were covalently bonded, and the small-sized amines plugged the holes more effectively than the large ones. This tendency was explained as follows. When the molecular size was small, the number of polyamines attached to the holes edges increased, and the net hole sizes decreased. When the large polyamines were attached to the holes, the number was limited due to the small hole size (1~2 nm) or its own steric hindering effect. Our results indicate that the chemical modification of the hole edges with polyamines will exhibit various performances for the release of materials from inside NHox to outside.

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1P-38

Magnetization drops in superconductive multi-walled nanotubes

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Superconductivity (SC) in carbon nanotubes (CNTs) is attracting a significant attention from viewpoints of both SC in one-dimensional conductors and SC in carbon-related materials. From the former viewpoint, only three groups have reported SC in CNTs including our report [1]-[3]. From the latter one, it has been found that highly *B*-doped diamond [4] and CaC_6 [5] could exhibit SC, interestingly with the similar $T_c = 11\sim12K$.

Here, we report measurement results of magnetization in superconductive multi-walled CNTs (MWNTs). We measured magnetization in arrays of MWNTs that exhibited a sign of SC, in which resistance gradually drops from T_c with decreasing temperatures but does not saturate even at T=1.5K. We found that most of such samples exhibited gradual and unsaturated drops in magnetization as temperature decreases. We will discuss correlation of this magnetization drop with Meissner effect. Moreover, we found that magnetic anisotropy is only about 30 % in the amplitude of magnetization drop. If the drop is attributed to Meissner diamagnetism, this weak anisotropy implies that graphite structure of the MWNTs is a dominant factor for the origin of SC rather than influence of curvature [6].

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1P-39

Controlling bandwidth of edge states and superconductivity in carbon nanotubes

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The energy spectrum of the π-electrons near the Fermi level consists of not only delocalized bulk states but also localized edge states [1]. Theoretically, edge states are zero energy eigenstates at the Fermi energy (flat-band). Experimentally, a direct measurement by scanning tunneling microscopy and spectroscopy of graphite edge has been observed a sharp peak of local density of states near the Fermi energy [2], which can be identified as the edge states. An interesting point is that the peak is located not just at the Fermi energy but below it by about 20 meV. We propose a mechanism, which reduces the energy of the edge states. The mechanism consists of next nearest-neighbor (NNN) hopping process in addition to the original nearest-neighbor tight-binding one. The NNN gives a finite bandwidth to the edge states and explains the measurements [3].

The edge states play a decisive role at the interface between nanotube and an electronic contact because they enhance the local density of states. The contact is also important for emergence of superconductivity observed in multi-walled carbon nanotubes [4]. Thus, it is valuable to examine the effect of the edge states on the superconductivity. Interestingly, the bandwidth can be controlled by on-site energy at edge sites since the NNN can be represented as the on-site energy. The bandwidth is a parameter governing correlation effects such as magnetic ordering and superconductivity. By controlling the on-site energy by means of an electrode, it is possible to control the correlation effect. We argue the possibility of edge state's superconductivity in nanotubes.

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1P-40

Electrical Conductance of Bulk Single-, Double- and Multi-wall Carbon Nanotubes

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During the past 10 years many studies have been reported on the electrical conductance of individual carbon nanotubes (CNTs), whereas the bulk electrical conductivity measurements have been limited. Yoshida *et al.* [1] reported that the conductance mechanism of bulk CNTs (MWNTs) can be interpreted as the so-called variable range hopping conductance. Here, we report a systematic study on the electrical conductance of various type of bulk CNTs and consider conductance mechanisms of bulk CNTs.

We have measured the electrical conductance of HiPco-SWNT (designated as 1.SWNT), double-wall CNTs (DWNT) made by TORAY Co. Ltd. (2.DWNT), CCVD-multi-wall CNTs (3.MWNT) and high-temperature (2000 ℃) treated MWNTs (4.MWNT2000). We found that MWNT2000 has much smaller defect than CCVD-MWNTs. Temperature dependences of resistance for these four types of CNTs were measured by the four probe method.

Figure 1 shows temperature dependence of bulk conductance of these CNTs samples. The observed resistances normalized at 295 K are in proportion to $T^{-1/4}$. [2] Therefore, the conductance mechanism of the bulk CNTs can be interpreted within the framework of 3D hopping conductance. [1] One can calculate hopping lengths by slopes of the individual plot. The obtained hopping lengths become shorter according to MWNT, DWNT, SWNT, and MWNT2000. Although the hopping length of MWNT2000 is shorter than any other samples, electrical resistance is large. This suggests that electrical resistance is reflected by mechanical flexibility of CNTs. Since MWNT has solid and stiff structure, the number of mutual contact points of MWNTs in a bulk sample is much smaller those of other flexible CNTs. Consequently, the number of hopping pathways of conducting electrons is small and thus the electrical resistance becomes higher.

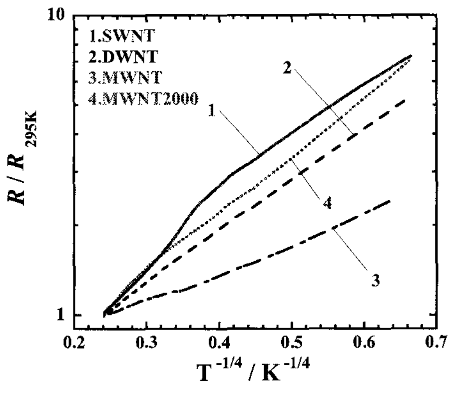

Figure 1. Temperature dependence of normalized resistance of various CNTs.

Acknowledgements:
I thank Toray Chemical Research Laboratories for supplying DWNTs.

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1P-41

Current-induced improvement of contact resistance between carbon nanotube and Pt electrode

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The formation of a low-resistance contact between carbon nanotubes (CNT) and metal electrodes is an important factor for establishing CNT electronic devices. In this study, we have investigated the current-induced improvement of contact resistance.

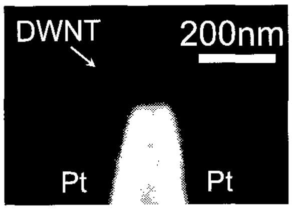

Fig.1. (a) SEM image of a DWNT suspended between a pair of Pt electrodes

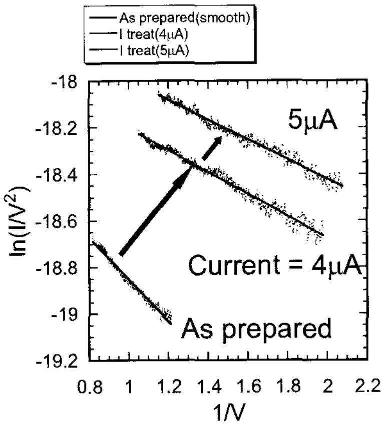

Fig.2. Fowler-Nordeheim plot of the I-V characteristics at low temperature

An individual double walled carbon nanotube (DWNT) was suspended between a pair of Pt electrodes as shown in Fig.1. Current-voltage (I-V) characteristics were measured at temperatures from 4K to 295K with a limitation of the maximum applying current. At a low current limitation less than 4 μA, the two terminal resistance is almost constant around 4 MΩ at room temperature. This resistance mainly comes from the contact resistance consisting of Schottky barrier and Ohmic resistance at the interfaces. At a low temperature, the Fowler-Nordeheim plot of the I-V characteristics well falls on a straight line in a high-electric field region as shown in Fig.2. This implies that the carriers mainly tunnel through the barrier with the height of 0.26 eV. However, the barrier height is lowered to 0.17 eV at the current limitation of 4 μA. When the current limitation increases to 5 μA, the contact resistance is improved to 2.7MΩ at room temperature with the tunnel barrier of 0.16 eV. These results indicate that the moderate Joule heating at the interface lowers the barrier height, and further heating reduces the Ohmic resistance. The origin of this change seems to be the de-hydration and the crystallization of a-C at the interface by the Joule heating.

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1P-42

Synthesis and Structural Characterization of Lithium Intercalated Single-walled Carbon Nanotubes

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Single-walled carbon nanotubes (SWCNTs) have attracted much interest as an anode material of Li ion secondary battery due to their high reversible capacity [1]. However, since the Li ion insertion mechanism into SWCNTs is still not well understood, it is hard to design the optimized SWCNT anode. In order to elucidate the insertion mechanism, we have performed syntheses and structural analyses of Li-SWCNT compounds. The Li-SWCNT compounds were synthesized by solid phase reactions of mixtures of lithium azide and open-end or closed-end SWCNTs in an evacuated silica glass tube. Figs. 1 and 2 show the changes in XRD and Raman spectra as a function of x in LiC_x (SWCNT), respectively. As shown in Fig. 1, the G-band of LiC_x (open-end SWCNT) showed firstly an upshift with increasing Li content up to LiC_6 and then showed a downshift from LiC_6 to LiC_3, while that of closed-end SWCNTs shifts monotonously toward higher wavenumber side with increasing Li content. The bundle structure of closed-end SWCNTs was degraded by doping a small content of Li, in contrast, the Li intercalated open-end-SWCNTs maintain the bundle structure (Fig. 2). These experimental results indicate that the structure of lithium intercalated SWCNTs greatly depends on the tube-end structure.

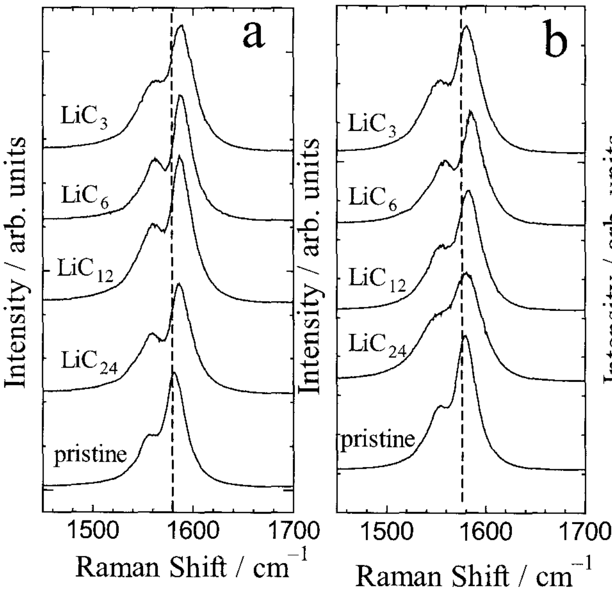

Fig. 1 Observed Raman spectra of LiC_x((a) close-end and (b) open-end SWCNTs).

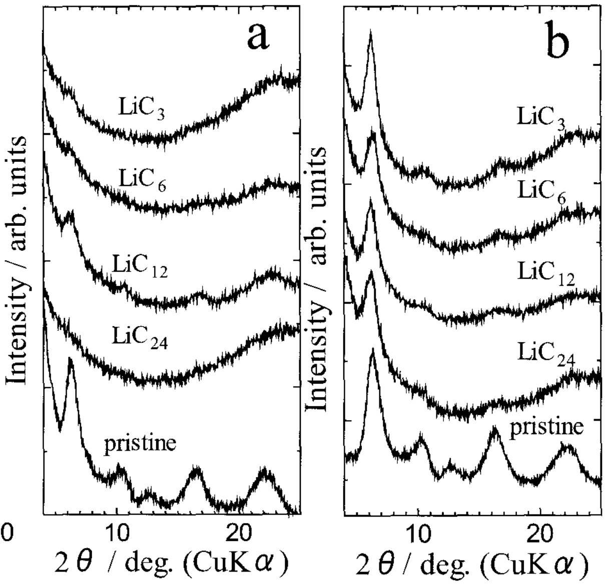

Fig. 2 Observed XRD patterns of LiC_x((a) close-end and (b) open-end SWCNTs).

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1P-43

Field emission microscopy of MWNTs deposited with aluminum

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Field emission of electrons from a multiwall carbon nanotube (MWNT) with a closed end occurs preferentially from pentagons at the cap when the nanotube surface is clean [1]. It has also been shown that the electron emission is enhanced from the adsorbed molecules when residual gas molecules adsorbed on the surface [2]. In this work, effects of aluminum deposited on the surface of MWNTs were studied by field emission microscopy (FEM).

MWNTs produced by arc discharge were attached to a tungsten hairpin by graphite-bond. The distance between a CNT emitter and a screen was ~30 mm. Aluminum was deposited onto an apex region of a CNT emitter by using a tungsten filament in the FEM chamber. The amount of aluminum deposited on the CNT cap was changed from ~1 nm to ~10 nm in terms of mean film thickness. The base pressure of the FEM chamber was ~5 × 10^{-10} Pa.

Figures 1 shows FEM patterns from MWNTs before and after the aluminum deposition, respectively. Both patterns were taken at the same applied voltage of 2.6 kV. Figure 2 shows stability of emission current corresponding to the FEM patterns shown in Fig. 1. Flickering of spots in the FEM patterns decreased by the aluminum deposition (Fig. 1). And, fluctuations of the emission current reduced after the aluminum deposition, as shown in Fig. 2. The cause may be the stabilization of MWNTs-to-MWNTs electrical contact.


before deposition after deposition

Fig. 1. FEM patterns at 2.6 kV

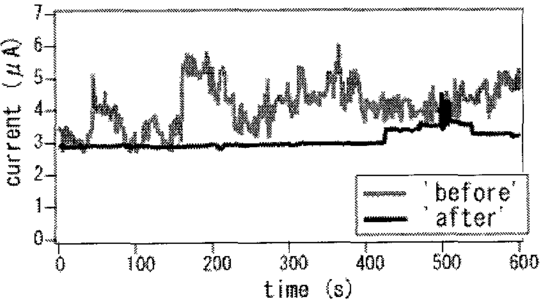

Fig. 2. Stability of emission current

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1P-44

Irradiation Damage Specific to Rolled-Up Graphene Sheet

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Our previous studies have shown that low-energy (<<threshold energy of knock-on damage) electron irradiation inevitably damages single-walled carbon nanotubes (SWNTs) [1]. The damage is also caused by VUV photon irradiation in ultra high vacuum. Here, we show that the curvature-induced strain energy plays a crucial role in the damage and that the damage is prominent in a rolled up graphene sheet, but not in a planar one.

Figure 1 shows the radial breathing mode (RBM) region of the Raman spectra of SWNTs before and after white synchrotron radiation light (hν<<1 keV) irradiation at room temperature. Remarkably, after the irradiation, only the intensity of the lowest wavenumber peak at 195 cm^{-1} remains high, although all of the other peaks almost completely disappeared. This indicates that among the observed SWNTs, the largest diameter SWNTs have the highest tolerance against the irradiation damage. The irradiated SWNTs can recover from the damage simply by annealing in Ar, indicating that, in contrast to knock-on damage and gas-radical-assisted damage, the number of carbon atoms is preserved. Figure 2 shows photoluminescence (PL) spectra of SWNTs irradiated by 20-keV electrons at 523 and 295 K. The diameter dependence of the damage is clearly observed again. Moreover, the result indicates that the formation and healing of the defects are in competition at least at 523 K. Further experiments showed that the defects in SWNTs (d~1 nm) are healed even at room temperature or below. The strong diameter dependence of the damage is predominantly ascribed to the diameter dependence of the activation energy of healing. Our results show that the strain energy in sidewalls plays an essential role in stabilizing the defects and that the damage is characteristic in thin nanotubes, but not in graphite.

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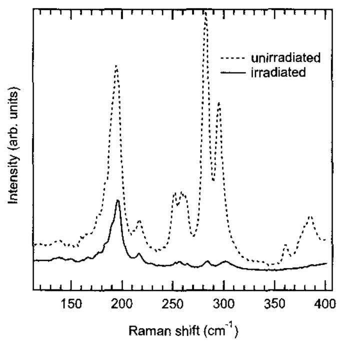

Fig. 1. Raman spectra of SWNTs before and after the irradiation (λ_{ex}=633 nm).

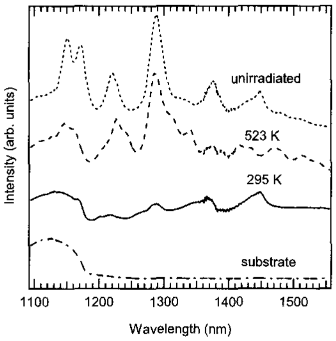

Fig. 2. PL spectra of SWNTs irradiated at 523 and 295 K (λ_{ex}=785 nm).

1P-45

First-Principle Study of Current Voltage Characteristics of Carbon Nanotube Wire Functionalized with Hydrogen Atoms

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Carbon nanotubes (CNTs) have been attracting much attention for making molecular devices, since CNTs are expected to give a high-speed transistor due to ballistic conduction. Recently, it has been suggested that individual metallic single-walled CNT (SWCNT) with tunneling barriers resulting from division into short sections can be used for the single-electron transistor (SET) [1] and that SWCNT functionalized with hydrogen atoms on the side wall can be expected to be used for a quantum dot [2].

On this background, in the present study, we examined the CNT(6,6) wire functionalized with hydrogen atoms (H-CNT) shown in Fig. 1 which modeles a nano-device with a quantum dot inside . We calculated current-voltage (*I-V*) characteristics of H-CNT model using TranSIESTA-C program package [3]. Fig. 2 shows the I-V characteristics of H-CNT model. In the presentation, we will report the peaks in Fig. 2 indicated a resonant tunneling effect and related results. We conclude that H-CNT model is of interest for such a nano-device.

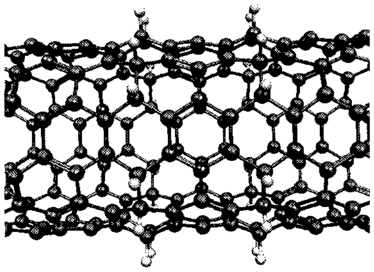

Fig. 1 CNT(6,6) wire functionalized with hydrogen atoms (H-CNT).

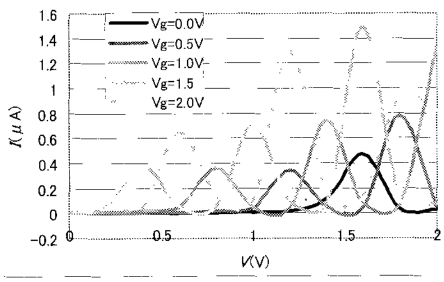

Fig. 2 *I-V* Characteristics of H-CNT model.

References:

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1P-46

Covalent Attachment of a Protein Molecule to the Tip of Carbon Nanotube

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We have investigated trapping of protein molecules on the tip of open-ended multiwall carbon nanotubes (MWNTs) in aqueous buffer solutions. The open-ended MWNTs were prepared by the oxidation of arc produced MWNTs in air at 700°C on a SiO_2 wafer(Fig.1(a)). Chemical reaction using carbodiimide (EDC) forms a chemical bond between an open-end tip of MWNT and a protein molecule, GroEL. After the chemical reaction(Fig.1(b)), the products on the substrate were rinsed by pure water. The remained materials were characterized by atomic force microscopy. Since the size of the protein is lager than the tip diameter of open ended nanotubes, only one protein is expected to attach the open-ended tip. The AFM observation revealed that only one protein attached to the open-ended tip of nanotube (Fig.1(c) arrow). It is noted that proteins attached to the un-oxidized nanotubes were hardly detected. This indicates that the proteins made a covalent bond to the open-ended tip of nanotubes and the binding energy between the protein and the nanotube tip is larger than that of the van der Waals interactions between the protein and the side wall of the nanotubes.

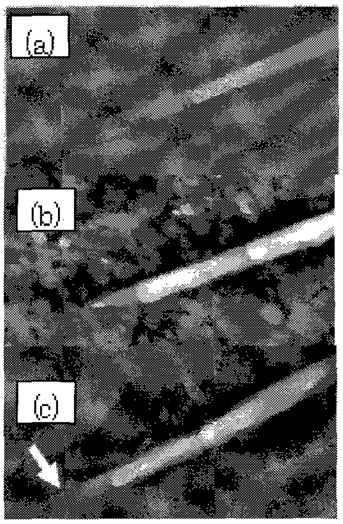

Fig.1 AFM images of trapping a protein molecule on the tip of MWNT

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1P-47

Response of Osteoblastic Cells Grown on a Carbon Nanotube Scaffold

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We have investigated carbon nanotubes (CNTs) for biomedical applications and found several unique properties. One of them is the applications of multi-walled (MW) and single-walled (SW) CNTs as scaffolds for cell culture [1,2]. In this study, alkaline phosphatese activity (ALP) of osteoblastic cells was measured to evaluate osteogenic property in addition to the morphology, proliferation.

Both number and size of cells on the CNT scaffold were larger than scaffolds without CNTs. Activity of ALP was higher on CNTs than scaffolds without CNTs. Specially, the number of cells on SW was larger than on MW. The activity on SW was similar to that on MW at 3 days, while the activity on SW was higher than that on MW at 7 days (Fig. 1). The results suggested that SWCNTs could be suitable for scaffolds for osteoblast.

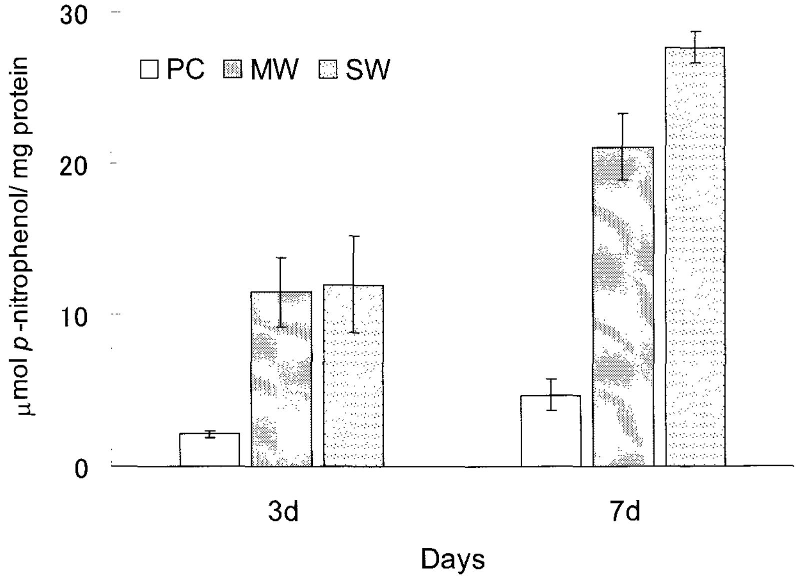

Figure1 Alkaline phosphatese activity of cells on scaffolds

[1] N. Aoki, A. Yokoyama, Y. Nodasaka, T. Akasaka, M. Uo, Y. Sato, K. Tohji and F. Watari, *J. Biomed. Nanotechnol.* **1**, 402 (2005).

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1P-48

人工複合糖質高分子による *Streptococcus mutans* の発育阻害

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北大院歯

Inhibition of *Streptococcus mutans* growth by artificial glycol-polymer

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世界中で最も蔓延している疾患であるう蝕は、歯面上に形成されるバイオフィルム中のミュータンスレンサ球菌（mutans streptococci）により人体中で最も硬い組織である歯質が不可逆的に侵される特異な細菌感染症である。代表的原因菌である *S. mutans* は、スクロースや N-Acetyl-Galactosamine などの糖質を発酵し、。

歯面への初期付着に関しては、ペリクルを形成している糖タンパク質糖鎖への *S. mutans* 由来レクチンとの相互作用や静電的、疎水的相互作用が付着機構として考えられている。そこで本研究では、効率的な口腔内細菌付着阻害剤の開発を目的として、ナノ材料として注目されているカーボンナノチューブとの相互作用を検討することとした。

はじめに口腔内細菌として Streptococcus mutans JC2 を用いて、菌溶液に添加したカーボンナノチューブによる沈降効果を検討した。カーボンナノチューブとしては多層カーボンナノチューブ（直径約 30 nm MWNT(nano)および約 200 nm MWNT(MTR)）と単層カーボンナノチューブ(SWNT)を任意量添加し、２時間インキュベート後、上澄み液の光学密度（OD700）を測定することにより遊離細菌数を算出した。その結果、MWNT(Nano)および SWNT は、コントロールに比較し大きな沈降効果を示した。これは、カーボンナノチューブが凝集し沈降するとともに細菌を吸着する効果があるものと考えられる。また MWNT(MTR)は凝集力が比較的弱いため遠心後も上澄み中へ一部が残存してしまい、正確な値を求めることができなかった。

次に、菌の吸着状態を走査型電子顕微鏡(SEM)にて観察した結果、SWNT 凝集体内部への取込みや表面への細菌の吸着が観察され、一部では菌表面での SWNT の彎曲も観察された。同様な形態は、直径約 60 nm 以下の MWNT(Nano)においても観察された。

以上の結果より、カーボンナノチューブは S. mutans を吸着し、一定の直径以下では柔軟性を示しながら相互作用することが判明した。

1P-49

Development of a Gas Sensor by Using a Carbon Nanotube/Polymer Composite Material

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Both single-walled and multi-walled carbon nanotubes (SWNTs and MWNTs) are interesting molecular wires that have unique electronic properties which have great potential to be used in future developments in solid-state nanoelectronics. From the viewpoint of applications to new nano-devices, we have been conducting research into the development of a nano gas sensor based on new functional carbon nanotubes. Here, we report on the basic characteristics of a gas sensor based on carbon nanotubes (mainly SWNTs) and polymer composite material.

The gas sensor based on composite material composed of polyethylene glycol (PEG)-grafted SWNTs (PEG-SWNTs) and the conductive polymer polyaniline ($C_{12}H_{14}N_4$, M~5000) is spin-coated on a glass plate (26 mm x 46 mm) having four comb-like electrodes (dimensions: 11 mm x 18 mm, gap: 1 mm) shown in Fig.1. The electrodes of Au thin film is formed by the vacuum evaporation method using the comb-like mask pattern. PEG-SWNTs are synthesized by heat-treatment at 70°C for 24 hr with stirring of a toluene solution that included Azo-PEG (macro azo initiators, Wako Pure Chemical Ind. Ltd.). The gas sensor is installed in a vacuum chamber and its impedance is measured using an impedance analyzer (HP: 4192A) and a digital multimeter (Advantest, TR6847).

Figure 2 show the impedance-versus-time characteristics for the cases of acetone, ethanol, and chloroform vapors. Under a vacuum, an increase in the impedance due to the desorption of gas molecules is observed. Therefore, the gas was introduced after a fixed time (30~60 min) had passed. It was found that the changes in the impedances as a function of time for acetone and ethanol were clearly different. In the case of chloroform the impedance is decreased with time. This is due to the presence of chlorine and indicates a reaction which is obviously different from those of the other two gases. Thus, we have demonstrated that this sensor is capable of detecting specific gases.

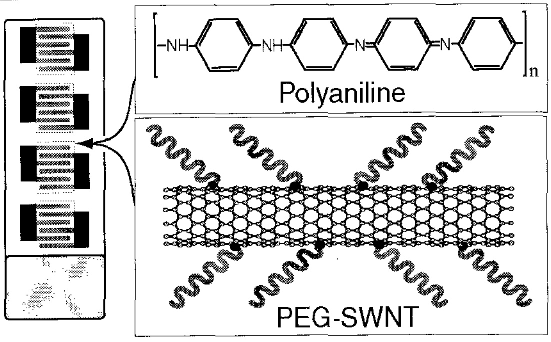

Fig.1

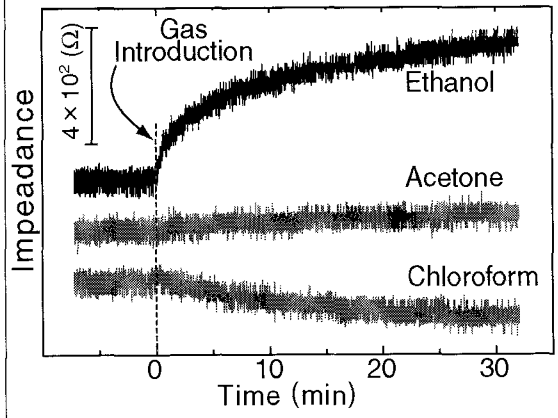

Fig.2

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1P-50

Development of Bio-Nano Sensor by Using Carbon Nanotube Compound Materials

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We are accomplishing the research on the development of bio-nanosensors using nanocarbon materials such as fullerene or carbon nanotubes, with the aim of investigating application of these new devices in the field of biomedical engineering. Characteristic evaluation of bio-nanosensors based on single-walled carbon nanotubes (SWNTs) is demonstrated by using biotin (vitamin B_7) which binds in the peculiarity with avidin, a glycoprotein. The avidin-biotin system has become a universal tool in many biotechnological applications such as the marker of a protein and a nuclear acid.

The fabricated FET-chip uses back-gate type FET with an Al-Si electrode as shown in Fig. 1(a). A SiO_2 insulating layer (thickness: 290 nm) formed on top of the n-type Si wafer by thermal oxidation. The source-drain electrode patterns fabricated by photolithography are made of Ti/Al-Si (50/200 nm), and are composed of pad-type (gap: 1, 5, 10, and 50 μm, respectively) and one stripe-type (gap: 10 μm). The SWNTs network, which is dropped onto the between source-drain electrodes in the FET-chip, are composed of the mixture of avidin modified SWNTs and polyethylene glycol (PEG)-grafted SWNTs (PEG-SWNTs). In order to immobilization of avidin, purified SWNTs gave oxidation processing to form carboxyl radical groups at the ends and sidewalls. Concretely, The carboxyl radical modified SWNTs (COOH-SWNTs) are synthesized by oxidization treatment at 150 C° for 5 hr by sulfuric acid with potassium permanganate. On the other hand, PEG-SWNTs are synthesized by heat-treatment of toluene solution including Azo-PEG (macro Azo initiators) at 70 C° for 24 hr with stirring. The immobilization of avidin and COOH-SWNTs is used 1-Ethyl-3-(3-dimethylaminopropyl)carbodiimide, hydrochloride and N-Hydroxysuccinimide.

Figure 1(b) and (c) are the impedance-versus-time characteristic in case of the electrode-gap at 1μm when biotin and other vitamins (B_1, B_6, and C, respectively) are injected. Black arrows are initial injection time, and black arrows with the circle are time to have injected the sample again. An increase in impedance, resulting from a change of state of the SWNT network surface due to avidin-biotin binding, is observed when biotin is injected [Fig.1(b)]. On the contrary, injection of other vitamins results in decrease in impedance of the solution [Fig.1(c)]. On the other hand, when only PEG-SWNTs is fixed on the electrodes, impedance decreases after injection of all vitamins. It is thought that the vitamins do not bind directly with PEG-SWNTs because impedance recovers almost to its initial value when the electrode is washed with distilled water.

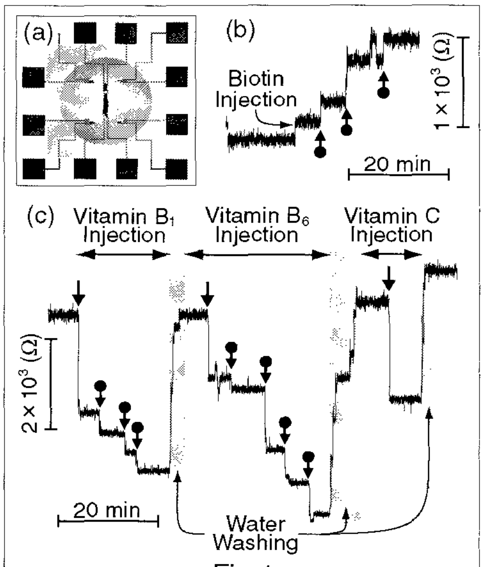

Fig.1

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1P-51

A Biosensor Using a Top-Gate Single-Wall Carbon Nanotube Field-Effect Transistor for Real-Time Sensing of Proteins

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and Kazuhiko Matsumoto[2,3,5,6]

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To establish home medical-care facilities in places distant from hospitals, wearable biosensors—which are compact and simple and can perform measurements in real-time—must be developed. This system that provides home medical-care facilities in places distant from hospitals is termed "Personal Quality of Life (PQOL)." Protein sensing is the key technology required for the construction of the PQOL system. A single-wall carbon nanotube field-effect transistor (NT-FET) has potential for use as the above mentioned biosensor.

NT-FET protein sensors detect species on the basis of an antigen-antibody reaction. Although this type protein sensors have been studied more than other type of sensors, antigens were immobilized directly on a carbon-nanotube channel, and antigens were sensed was by measuring the change of electron mobility in conventional studies. For this type of NT-FET protein sensor, impurities (such as oxygen, water or damage caused by adsorbed photo resist on the carbon nanotubes) degrade the electromobility or charge capacitance of the NT-FET. We investigated a top-gate NT-FET device in which the carbon nanotubes were covered by silicon nitride to avoid these contaminations. This NT-FET with top-gate structure achieved real-time and high-sensitivity sensing of proteins, that is, pig serum albumin (PSA). The sensitivity limit of this NT-FET protein sensor is at least 20 nmol/l of PSA solution. Depositing silicon nitrides to form the top-gate structure provides an n-type characteristic and highly stable CNT-FET, since the CNTs are isolated by oxygen, water, and other contaminations in air.

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1P-52

The Raman Spectroscopic Study on the UV Irradiation of Polyyne Molecules in Solution

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Abstract: We developed a method for the size separation of polyyne molecules ($C_{2n}H_2$, n=4-8) by using high-performance liquid chromatography (HPLC). Having a milligram quantity of the size-separated sample, we performed non-resonant Raman, resonant Raman, surface-enhanced Raman spectroscopy (SERS) [1], and ^1H and ^{13}C NMR spectroscopy [2]. Recently, for the purpose of concentration and stabilization, the molecules of a specific size, i.e., $C_{10}H_2$, were treated with SWNTs and detected by the Raman spectroscopy. The molecules trapped in the SWNTs show remarkable stability against the heat well above 300 °C under the dry air condition [3]. In this report, we focus on the basic research on the spectroscopic characterization of the purified polyyne molecules in solution.

The molecule, namely $C_{10}H_2$, is known to absorb UV light below the wavelength of its electronic absorption band peaking at 252 nm (the dipole-allowed Σ-Σ transition among the π-π*s). The laser excitation near the absorption edge strongly enhances the Raman scattering cross section by the resonance effect. Even for a dilute solution of the order of 10^{-4} mol/l, we observed Raman scattering signals. Figure 1 shows a typical Raman spectrum of $C_{10}H_2$ in *n*-hexane at room temperature. The sample solution was irradiated by the UV laser pulses at 262 nm (the frequency-doubled output of a nanosecond dye laser system). The scattered light was then collected in the direction normal to the incident laser beam. The peaks corresponding to the Raman shifts in 2000 - 2200 cm^{-1} are attributable to the normal mode frequencies of the collective C-C stretching motions. In addition to the prominent peak at 2123 cm^{-1}, some weaker peaks are discernible. We compared the observed frequencies and relative intensities with the results of the DFT calculations.

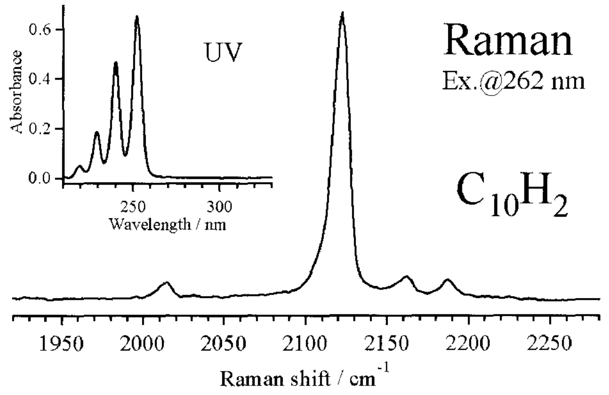

Figure 1. Raman and UV absorption spectra of $C_{10}H_2$ in *n*-hexane.

References:

[1] H. Tabata et al. Carbon submitted. [2] T. Doi et al. CPL submitted. [3] D. Nishide et al. CPL submitted.

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1P-53

Functionalization of Single-Walled Carbon Nanotubes by Bingel Reaction and Their Structural and Photophysical Properties

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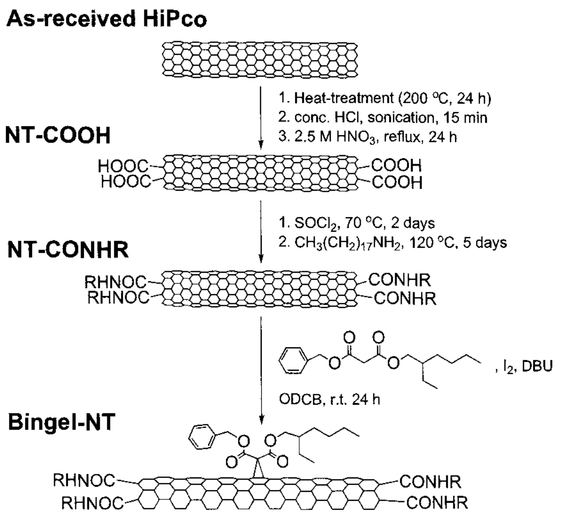
The unique one-dimension structure and extraordinary optical, electrical, thermal, and mechanical properties of single-walled carbon nanotubes (SWNTs) have resulted in an outburst of scientific investigation aiming the applications in various molecular devices. In this context, preparation of SWNT composites and polymers requires debundling and solubilization of SWNTs, which in their pristine form are insoluble in organic solvents. Covalent functionalization of SWNTs is one of promising approach to overcome this problem. However, covalent functionalization leads to severe damage on the nanotubes and loss of their electronic properties. We report herein a SWNT doubly functionalized at both tips and on sidewall with multiple alkyl and phenyl substituents to give sufficient solubility of the nanotube derivative in organic solvents (Scheme 1). Regarding the sidewall functionalization, we applied Bingel reaction which is one of the most frequently employed methodology for the functionalization of fullerenes. Structure and physical properties of the SWNTs in each step were examined by using AFM, TEM, and TGA measurements, and UV-vis-NIR absorption and resonant Raman spectroscopies. Notably, electronic properties of **Bingel-NT** are largely retained after the sidewall modification of **NT-CONHR** without apparent selective reactivity for metallic and semiconducting SWNTs (Figure 1). Thus, our approach is highly promising for constructing molecular devices in which SWNTs modified with chromophores can be used without losing their intrinsic electronic properties of SWNTs.

Scheme 1.



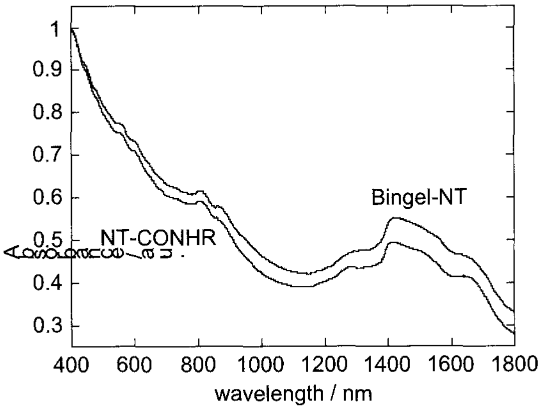


Figure 1. UV-vis-NIR absorption spectra of SDS-coated Bingel-NT and NT-CONHR in D_2O (SWNT : SDS = 1 : 9 by weight). Both spectra are normalized at 400 nm for comparison.

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1P-54

Cell proliferation of osteoblasts on multi-walled carbon nanotubes with different diameter

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The developments of carbon nanotubes (CNTs) for tissue engineering[1] and regenerative medicine[2] have attracted a great deal of attention. We have been investigated cell proliferation of osteoblasts (the bone-forming cells) cultured on multi-walled carbon nanotubes (MWCNTs) with different diameter *in vitro* study. Our recent studies employing *in vitro* and *in vivo* experiments showed their fine properties as scaffolds for cell culture.[3-5] MWCNT scaffolds showed that the osteoblast grew well.[3] Here, MWCNT scaffolds were formed on polycarbonate membranes by filtration. Cell proliferation and morphology were investigated by using a scanning electron microscopy and a enzyme-linked immunosorbent assay (ELISA) kit for detecting the transforming growth factor-beta 1 (TGF-β1). The effect of diameter on cell proliferation of MWCNT scaffolds will be reported in detail.

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1P-55

Synthesis of carbon nanocoils using organic metals as a catalyst

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Carbon nanocoils have attracted much attention in the field of nanotechnology, such as a nano-spring, reinforced composite materials and an electromagnetic wave absorber, etc, due to their specula morphologies.

The catalyst film of ITO/Fe [1] or Fe-In-Sn-O has been successfully used for the synthesis of carbon nanocoils, so far. In this study, the effectiveness of carboxylic acid metals as a precursor of the catalyst for nanocoils' growth has been investigated.

Carboxylic acid metals with the mole ratio of Fe/In/Sn =3/1/0.1 was dissolved into organic solvent. The Fe-In-Sn catalyst was formed by spin coating the solution on Si substrates and sintering at 450 °C. Carbon nanocoils are synthesized by the thermal CVD using acetylene as a reaction gas and He as a carrier gas at 700 °C.

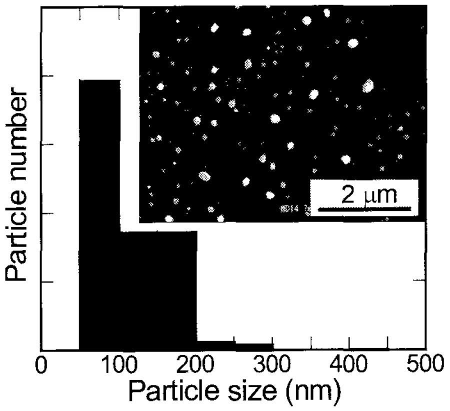

Fig.1 Distribution of catalyst-particle size on the substrate. Inset shows a SEM image of the particles.

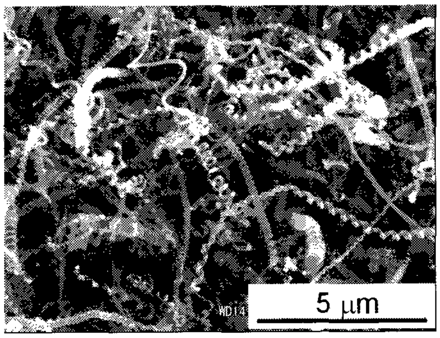

Fig.2 SEM image of the grown carbon nanocoils.

It is observed that catalyst particles are made on the substrate after heating at 700 °C, as shown in the inset of Fig.1. When the mole concentration of Fe is 0.15 mol/l, catalyst particles are dispersed on the substrate with the size of 50 ~ 100 nm, as shown in Fig.1. Figure 2 shows a SEM image of the grown carbon nanocoils using the catalyst shown in Fig. 1. It is found that carbon nanocoils are synthesized uniformly all over the substrate. The line diameter of the grown nanocoils is ranged from 50 nm to 150 nm but the nanocoils with the line diameter of 50 ~ 100 nm are distributed most, which is consistent with the catalyst-particle size. The diameters of coils are several hundreds of nanometer. The average line diameter of the nanocoils can be controlled by adjusting the mole concentration of Fe/In/Sn in the solution. The yield of the nanocoils is as high as those synthesized by using ITO/Fe. It is revealed that carboxylic acid metals are efficient as a precursor of the catalyst for nanocoil's growth.

[1] M. Zhang, Y. Nakayama and L. Pan, Jpn. J. Appl. Phys. 39 (2000) L1242.

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1P-56

Creation and analysis of Aluminum and Carbon Nanotube Composites Using High Pressure Torsion Process

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In the past studies of making aluminum and carbon nanotube (CNT) composites for structural materials, CNT reacted with aluminum to produce an aluminum carbide because thi sintering process requires heating [1-3]. The aluminum carbide is fragile and thus, when tensile test is carried out, cracks are initiated in aluminum carbides and the composite is prone to be fracture [4].

In this study, aluminum and CNT composites are fabricated using a process of high pressure torsion (HPT) which does not require heating. Aluminum powders in 99.99% purity with an average powder size of 75 μm were mixed with 5 vol% of single wall CNTs (SWCNTs) in ethanol while the solution in ultrasonic vibration. The solution was dried in air at room temperature. The dried mixture was then subjected to a process of HPT with an applied pressure of 2.5 GPa, where the mixture was inserted between the upper and lower anvils with depressions of 10 mm in diameter and 0.25 mm in depth on each anvil. While applying the pressure, the lower anvil was rotated for up to 30 turns with respect to the upper anvil with a rotation speed of 1 rpm. Microstructure observations were undertaken using scanning electron microscopy and transmission electron microscopy (TEM). Vickers microhardness was measured across the diameter of the sample. It is shown that the hardness of the sample containing SWCNTs is twice as high as the sample without SWCNTs. TEM observation revealed that the SWCNTs are uniformly dispersed in the aluminum matrix and the grain size is smaller for the sample with SWCNTs than the sample without SWCNTs.

This work was supported by Carbon Nanotube support project of Sumitomo Corporation and The 21st Century Center Of Excellence Program.

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1P-57

Automatic Consecutive-Substrate CVD System for Mass Production of Carbon Nanocoils

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[c]*Shonan Plastic MFG Co., Ltd.*
[d]*Product Development Center, Futaba Corporation.*

Carbon nanocoil, which is helical carbon fiber with sub micron diameter, can be synthesized by catalytic CVD with substrate. In conventional CVD system, productivity was very low, due to long heating and cooling procedure every time. Thus the new substrate-CVD system was developed in order to obtain higher productivity. In the new system, 8 substrates with catalyst were automatically handled one after another from substrate cassette, reaction chamber, to collection pot by using robot arms, controlled by a sequencer according to the process condition inputting from touch panel, under keeping the furnace temperature. The result showed the new system could produce CNC more than 10 g in 180 minute.

This work has been partly supported by the Excellent Research Project of the Research Center for Future Technology from Toyohashi University of Technology, the 21st Century COE Program "Intelligent Human Sensing" from the Ministry of Education, Culture, Sports, Science and Technology, and JSPS Core University Program.

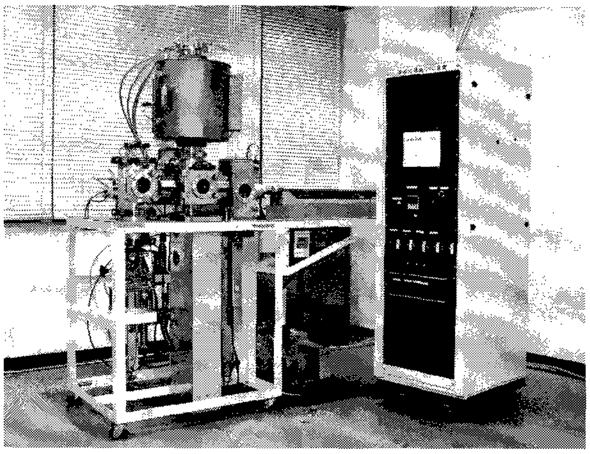

Fig. 1 The appearance of a device

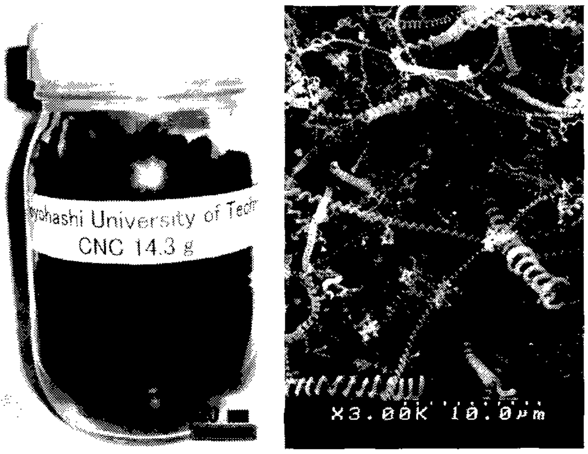

Fig. 2 Photogragh of CNC by one cycle

References: B. Chen, Y. Fujimura, H.Takikawa, Y. Hibi, T.Sakakibara, S.Itoh: *Trans. Mater. Res. Soc. Jpn.*, **29**, 559 (2004)

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2P-1

Production of Onion-like Fullerenes and Carbon Nano-Capsules by Means of Explosion Reaction of a Rail Gun

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It is informed that much amount of C_{60}^+ ions, [1] onion-like carbon clusters, [2] and many kinds of carbon compounds exit in our solar system. These clusters are produced by the special reaction of carbon particles ejected from carbon stars. And, carbon compounds tend to be ejected from asteroids for long years. The explosion, collision, optical reaction would take place and stable carbons survive.

In order to simulate the production of carbon clusters in space, the rail-gun experiment has been carried out. [3] A carbon bullet is accelerated in vacuum by the rail gun and it collides the solid target, by which the carbon atoms are explored, heated and cause molecular reaction. After diffusion and cooling process, the produced carbon sample deposits on an inner-wall of the reaction chamber. Previously, from this experiment, C_{60}, higher fullerenes and metallo-fullerenes are successfully produced from a poly-carbonate bullet. [3] Here, in order to modify the reaction condition, the collision-sublimation experiment in atmospheric helium gas is carried out. The target camber is shown in Fig. 1.

When a poly-carbonate bullet with carbon powder hits a metal target, onion-like fullerenes (with diameter of about 20 nm) have been produced for the first time, which is confirmed by a TEM observation as shown in Fig 2. When a poly-carbonate bullet with carbon powder hits liquid-propanol in a cupper bottle set in front of the metal target, carbon capsules (with diameter of about 40 nm) have been produced. This sample shows Raman peaks of same new carbon-compounds.

[1] B. H. Foing *et al.*, nature **369** (1994) 296.
[2] S. Wada *et al.*, Astron. Astrophys. **345** (1999) 259.
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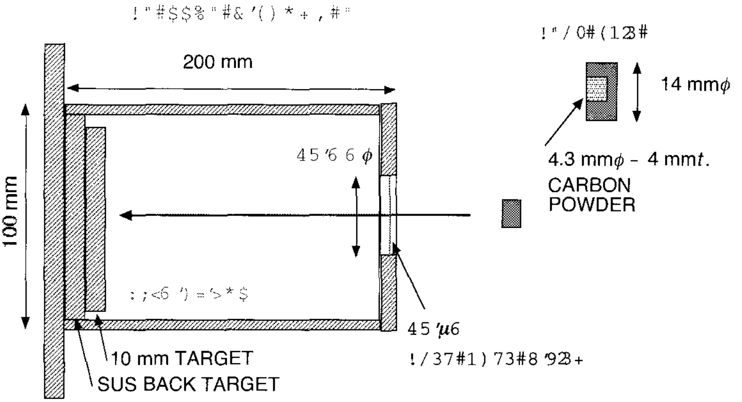

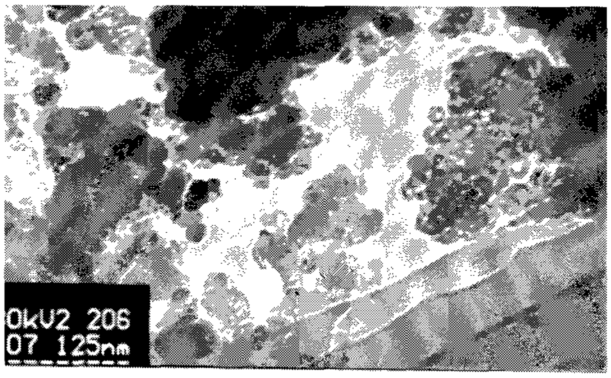

Fig. 1: Schematic of a cylindrical pressure chamber, where a bullet comes in, breaking the thin film and hit the target-plate.

Fig. 2: A TEM image of onion-fullerenes (right side) in the sample (x 80000).

2P-2

A single carbon fullerene's synthesis and control of fullerene's size by a STM tip inside TEM-STM system

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A single carbon fullerene attract much interest for a fundamental science and nanotechnology in molecular devices [1]. For such purposes, it is important to control and manipulate a single carbon fullerene to make a molecular-rink with the electrodes for the study of conductance behavior. Many attractive methods have been proposed for the synthesis of carbon fullerenes [2]. However, rather less attention has been paid for the synthesis of a single carbon fullerene and the control technique of the fullerene size for device geometry.

In this study, we exploited a new method to make a single carbon fullerene by using a scanning tunneling microscope (STM) tip, the synthesis process was observed by an UHV (ultra-high vacuum) transmission electron microscope (TEM-STM). A nanogap of about 1nm distance was made between two gold electrodes (one at the substrate and the other at the tip position of the STM) inside the electron microscope. A single carbon fullerene was synthesized from amorphous carbon at the gold electrode. We found that amorphous carbon which was sandwiched between two electrodes transformed into a single carbon fullerene by flowing the high current and/or voltage (more than ~0.5V, ~100 μ A).Furthermore approach-retraction procedure of the tip changed the size of this carbon fullerene.

Fig 1 (a) shows a single carbon fullerene made between the two gold electrodes. The diameter of 1.4±0.1nm suggests an icosahedral fullerene, C_{240}. After the repeat of being pinched of this single carbon fullerene changed the size of a carbon fullerene (Fig1(b),(c)).The flowing the current and pinching the fullerene while applying high bias voltage caused decrement of the diameter. 1.2±0.1nm (in (b)) and 1.0±0.1nm (in (c)).

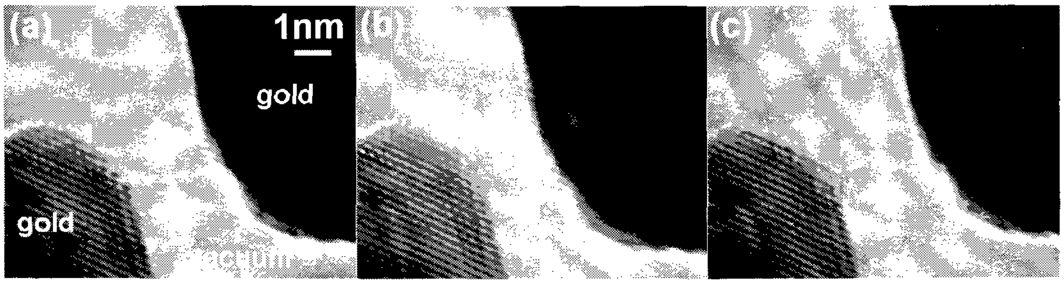

Fig1. Transmission electron microscope (TEM) images of a single carbon fullerene on gold electrode. Note the change of the single fullerene size and molecule transport from one to the other side of the electrode, while approach – pinching– retraction of the tip.

[1] H.Park et.al *Nature* **407**(2000)57, J.Taylor et al *Phys Rev B* **63** (2001)121104
[2] H.W.Kroto, R.E.Smalley *Nature* **318** (1985)162, W.Kratschmer, D.R.Huffman *Nature* **347** (1990)354
[3] A.Hashimoto,S.Iijima et al *Nature* 430 (2004)870

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2P-3

Light Emitting and Liquid Crystalline Functions of Functionalized Fullerenes

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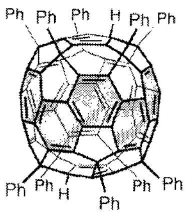
Organic and inorganic functionalization of fullerenes has attracted much interest in the area of chemistry and physics, because one can obtain useful materials by utilizing rich properties of both functional groups and fullerenes. A further interesting point to note is that successful molecular design of such functionalized fullerenes can provide novel functions that are unavailable from individual functional groups or fullerenes.

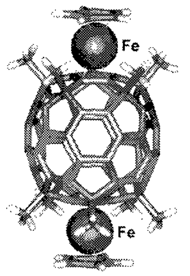
Fullerenes have been shown to be weakly fluorescent (C_{60}: $\Phi = 0.00032$). We found that selective ten-fold functionalization onto the 60π-spherical conjugation of [60]fullerene creates an novel cyclic π-electron conjugated system, [10]cyclophenacene, and that it shows strong fluorescence ($\Phi = 0.29$)[1]. Such high quantum yield suggests their applicability in electroluminescent devices. Next, we synthesized di-metal [60]fullerene complexes "double-decker buckyferrocene" which have two ferrocene moieties embedded on the top and bottom of [10]cyclophenacene[2]. These compounds may offer new opportunities in the molecular-level electronics.

Fullerene-containing liquid crystals are promising electro/photo active soft materials. However, taking into account the size and shape of the C_{60} unit, the elaboration of liquid crystalline fullerene derivatives have represented a conceptual and synthetic challenge. We synthesized shuttlecock-shaped fullerene liquid crystalline molecules, in which the C_{60} unit does not disturb liquid crystalline properties[3,4]. Installation of metal atoms into the shuttlecock molecules afforded novel mixed ferrocene-fullerene liquid crystals. Donor/acceptor characters and supramolecular columnar structure of these liquid crystals represents an important step towards the development of solar energy conversion devices.

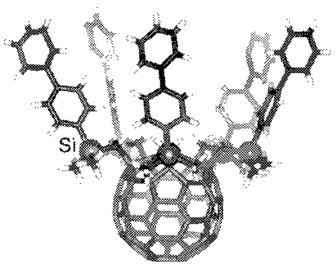
We successfully drew out some intrinsic value in fullerenes by the functionalization of fullerenes. We expect this study enhances the possibilities for the application of fullerenes.



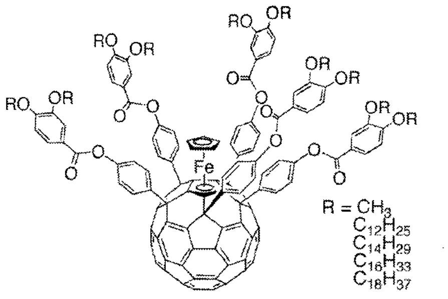
[10]Cyclophenacene



Double-Decker Buckyferrocene



Shuttlecock Molecule



Mixed Ferrocene-Fullerene Liquid Crystal

References: [1] Matsuo, Y.; Tahara, K.; Sawamura, M.; Nakamura, E. *J. Am. Chem. Soc.* **2004**, *28*, 8725. [2] Matsuo, Y.; Tahara, K.; Nakamura, E. *J. Am. Chem. Soc.* **2006**, in press. [3] Sawamura, M.; Kawai, K.; Matsuo, Y.; Kanie, K.; Kato, T.; Nakamura, E. *Nature* **2002**, *419*, 702. [4] Matsuo, Y.; Muramatsu, A.; Hamasaki, R.; Mizoshita, N.; Kato, T.; Nakamura, E. *J. Am. Chem. Soc.* **2004**, 126, 432.

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2P-4

Synthesis, Characterization, and 1,6-Asymmetric Induction of Chiral Ruthenium Allenylidene Complexes Bearing a Fullerene Cyclopentadienyl Ligand

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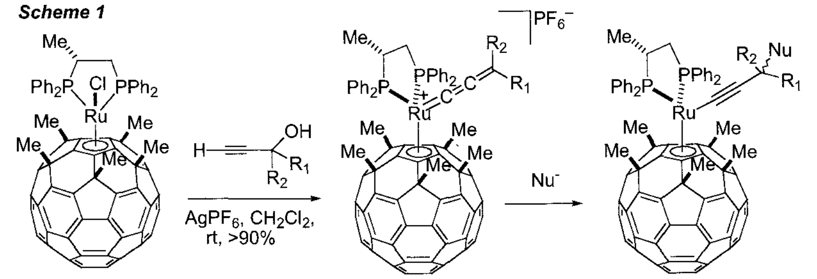
Following our recent study on the 1,3- and 1,4-chirality transfer by the use of a fullerene cyclopendadienyl ligand,[1] we report herein the preparation of ruthenium allenylidende complexes **2** – **6** and the 1,6-asymmetric induction in the nucleophilic addition to these allenylidenes (Scheme 1). These complexes enjoy rich chemical and physical properties from both the fullerene and allenylidene moieties, which are evidenced from the broad and intense absorption in their UV-Vis-NIR spectra (Figure 1) and the reversible multi-redox behavior in the cyclic voltammogram (Figure 2).

Scheme 1



Ru($C_{60}Me_5$)Cl((*R*)-prophos)
(**1**)

2: R_1 = Ph, R_2 = Ph
3: R_1 = H, R_2 = C_6H_4-OMe-4
4: R_1 = H, R_2 = C_6H_4-NMe_2-4
5: R_1 = H, R_2 = Fc
6: R_1 = H, R_2 = Ph

up to 95 : 5
diastereoselectivity

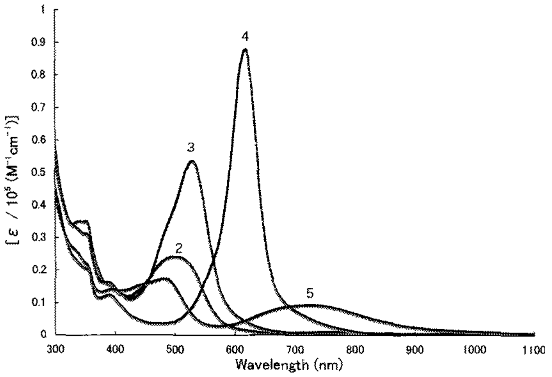


Figure 1. UV-Vis-NIR spectra of **2** - **5**.

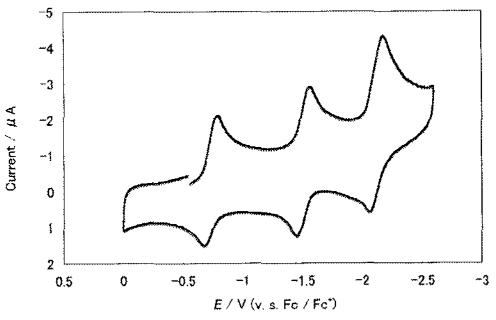


Figure 2. CV spectrum of **2**.

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Reference: [1] Matsuo, Y.; Mitani, M.; Zhong, Y.-W.; Nakamura, E. *Organometallics* **2006**, *25*, 2896.

2P-5

Unusual Water Permeability of Vesicles Made of Amphiphilic Fullerenes

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Bilayer membrane made of phospholipid is the fundamental structure in biology in that the membrane physically holds the biological machinery while keeping permeability to water at ambient temperature. Permeability of the membrane to water has therefore drawn much interest of scientists in various fields.

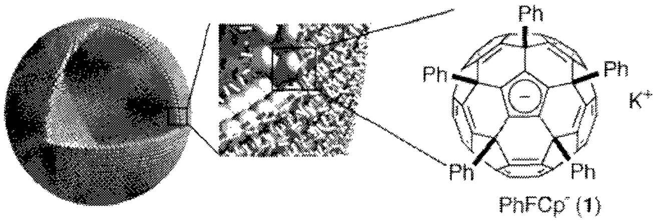

Fig 1. Bilayer vesicle made of amphiphlic fullrene (**1**)

In the present study, we found that a bilayer vesicle made of membrane of amphiphilic fullerene (PhFCp$^-$, **1**)[1] has extremely low permeability to water. The fullerene bilayer recorded permeability coefficient of 2.48 × 10^{-8} m/s (20 °C) which was 1,000,000~1,000 times smaller than common lipid bilayers. More interestingly, we found that the permeability coefficient decreased on warming and recorded the highest value of 1.24 × 10^{-8} m/s at 70 °C (Fig. 2). Thermodynamic analysis of the temperature-dependent permeability showed that the fullerene membrane acts as an entropy barrier to water permeation, which suggested a unique mechanism for the water permeation.

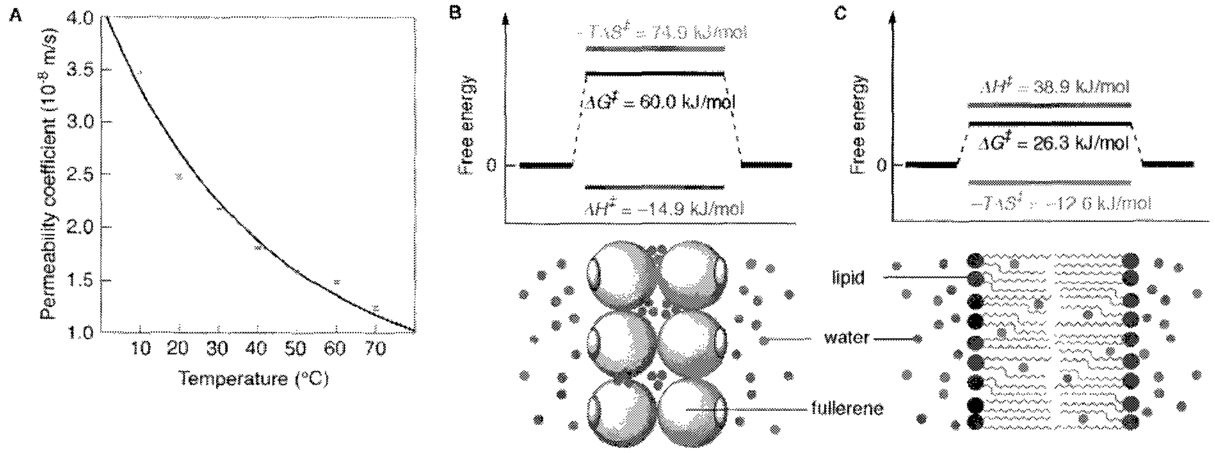

Fig 2. Water permeability of bilayer membrane. Temperature dependence of permeability of the fullerene vesicle to water (**A**). Energy diagrams and schematic representation of water permeation through fullerene

[1] S. Zhou *et al.*, *Science*, **291**, 1944 (2001); M. Sawamura *et al.*, *Chem. Lett.*, **9**. 1098 (2000).

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2P-6

Photochemical Reaction of C_{60} with Sulfilimines

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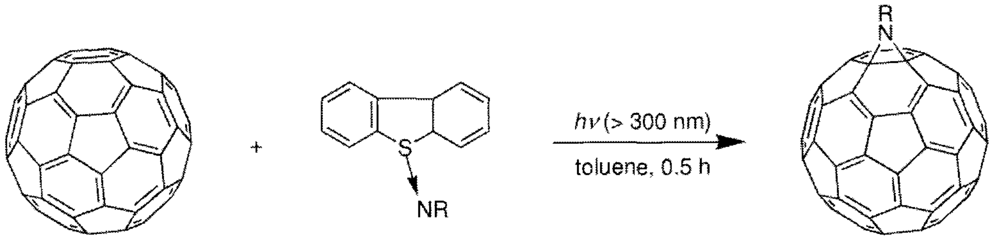
Takeshi Akasaka[1], Toshiaki Yoshimura[2], and Hiroyuki Morita[2]

[1]*Center for Tsukuba Advanced Research Alliance, University of Tsukuba, Tsukuba, Ibaraki 305-8577, Japan*
[2]*Department of Material Systems Engineering and Life Science, Faculty of Engineering, Toyama University, Gofuku, Toyama 930-8555, Japan*

In the chemistry of fullerene, the functionalization of fullerenes is one of the most interesting themes regarding to the development of the new material with the unique properties.

The aziridinofullerene, including an aza-bridged structure, is such an example of the modified fullerenes, which is obtained by the thermal and photochemical reaction of C_{60} with azides [1]. This method, however, affords two isomers with the different addition sites. To improve the regioselectivity in the addition, we carried out the generation of a nitrene by a photochemical cleavage of the S-N linkage in sulfilimine derivatives (1a-c). We found that the nitrene was trapped by C_{60} in a highly regioselective manner. The structure of the nitrene adduct (2a) was confirmed by the spectroscopic and X-ray crystallographic analysis.



1a: R = tosyl
b: R = benzyl
c: R = trifluoroacetyl

2

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References: [1] J. Averdung *et al., Tetrahedron.* **52**, 5407-5420 (1996).

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2P-7

Application of C_{60} as the photochemical probe

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Takatsugu Wakahara, and Takeshi Akasaka*

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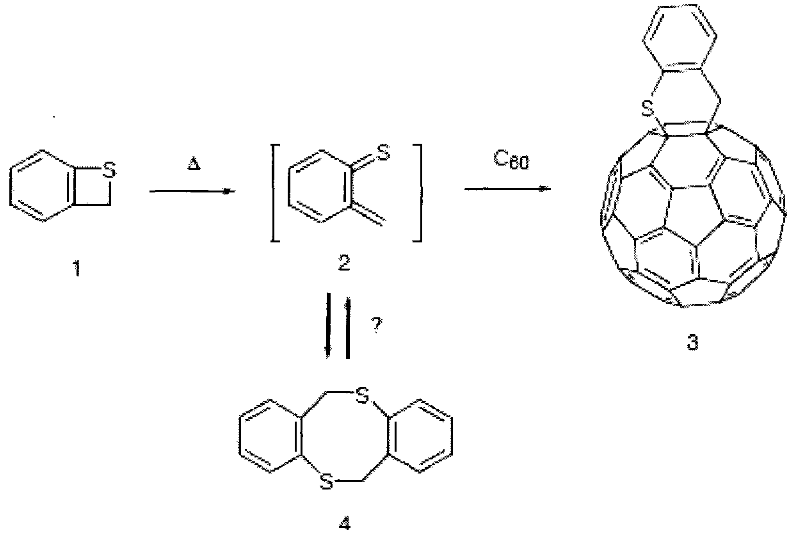
Tsukuba, Tsukuba, Ibaraki 305-8577, Japan*

Benzothiet (**1**), one of the heterocyclic organosulfur compounds has been known to generate *o*-thioquinonemethide (**2**) in a thermal heterocyclic ring opening process, which is a reactive diene-type intermediate. Ohno et. al. reported that diene **2** generated from thermolysis of **1** reacts with C_{60} to afford the corresponding 1:1 adduct (**3**)[1]. Although, it has been suggested that 6*H*,12*H*dibenzo[*b*,*f*]-1,5-dithiocin (4) is formed by the dimerization of **2** in a thermal manner[2], it has not been clarified so far whether **2** can be generated from **4**, photochemically. In this context, we have carried out the photolysis of **4** in the presence of C_{60} and found that **3** was obtained as a major product. The structure of the adduct **3** was confirmed by the spectroscopic analysis. The redox properties of **3** and its oxidized derivatives were also investigated.



#Present address: Department of Applied Chemistry and Molecular Engineering Institute, Kinki University, Kowakae, Higashi-Osaka 577-8502, Japan.

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[1] Ohno, M.;et.al., *Tetrahedron Letters* **1995**, *36*, 6899.
[2] Herbert, M.;et, al., *Angevandte, Chem.* **1987**, *99*, 1040

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2P-8

C_{60} as a Chemical Probe: Photolysis of Diazirine with C_{60}

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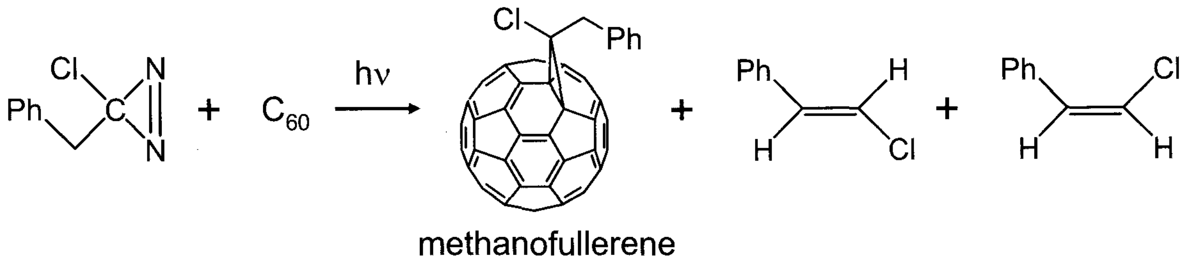
Photolysis of diazirine has been widely used to produce carbene. It has been reported that these reactions also yield a diazo compound as an intramolecular rearrangement product and the olefins coming through the rearrangement in the exited state (RIES) of diazirine. To know the photolytic pathway of diazirine is important for its chemical usage. Recently, we reported the use of C_{60} as a probe to distinguish carbene/diazo partition in the photolysis of diazirine [1]. C_{60} reacts with diazo compound to yield fulleroid and with carbene to methanofullerene.

Photolysis of benzylchlorodiazirine has been studied by mainly spectroscopic methods so far, but its decomposition process has not been clear yet. We carried out the photolysis of benzylchlorodiazirine in the presence of C_{60}, and found formation of methanofullerene and olefins. These suggest that the photolysis of benzylchlorodiazirine proceeds via pathways of carbene formation and RIES rearrangement.



Reference
[1] T. Akasaka, M. T. H. Liu, Y. Niino, Y. Maeda, T. Wakahara, M. Okamura, K. Kobayashi, S. Nagase, *J. Am. Chem. Soc.*, **2000,** *122*, 7134-7135. T. Wakahara, Y. Niino, T. Kato, Y. Maeda, T. Akasaka, M. T. H. Liu, K. Kobayashi, S. Nagase, *J. Am. Chem. Soc.*, **2002**, *124*, 9465-9468. M. O. Ishitsuka, Y. Niino, T. Wakahara, T. Akasaka, M. T. H. Liu, K. Kobayashi, S. Nagase, *Tetrahedron Lett.*, **2004**, *45*, 6321-6322.

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2P-9

Chemical functionalization of C_{60} with diazirine

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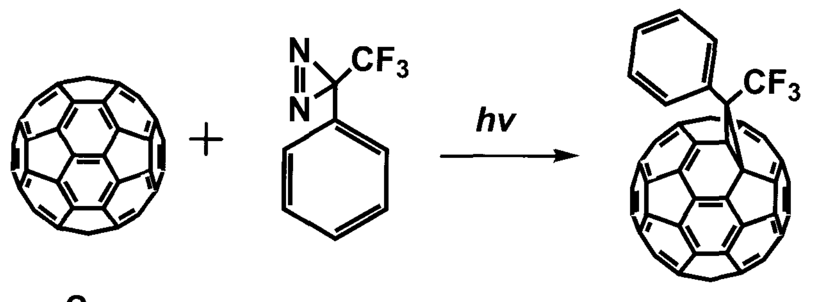
Studies on biological activity of organofullerenes are interesting because of several fundamental properties of fullerenes: photoactivity, ability to accept and release electrons, and relatively high reactivity that allows structural modifications. It is very important to attach the hydrophilic appendants to fullerenes, because it helps solubilization to physiological media.[1,2] Meanwhile, many bio-functionalized 3-trifluoromethyl-3-phenyldiazirine derivatives are synthesized and used as a photo affinity probe. These diazirines show favorable photochemical properties in addition to excellent chemical stabilities.[3,4] In this context, the reaction of fullerene with these diazirines may promise a versatile approach to many bio-functionalized fullerenes.

Herein, we report the synthesis and characterization of trifluoromethylphenyl carbene derivative [**1**]. The structure was determined by mass, absorption and NMR spectroscopic analyses. The redox properties of [**1**] were also investigated by cyclic and differential pulse voltammogram measurements.



C_{60}

1

References:

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(2) Bolskar, R. et al., *J. Am. Chem. Soc.* 2003, *125*, 5471.

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2P-10

Novel Aziridination of C_{60} Using *N*-Haloamides

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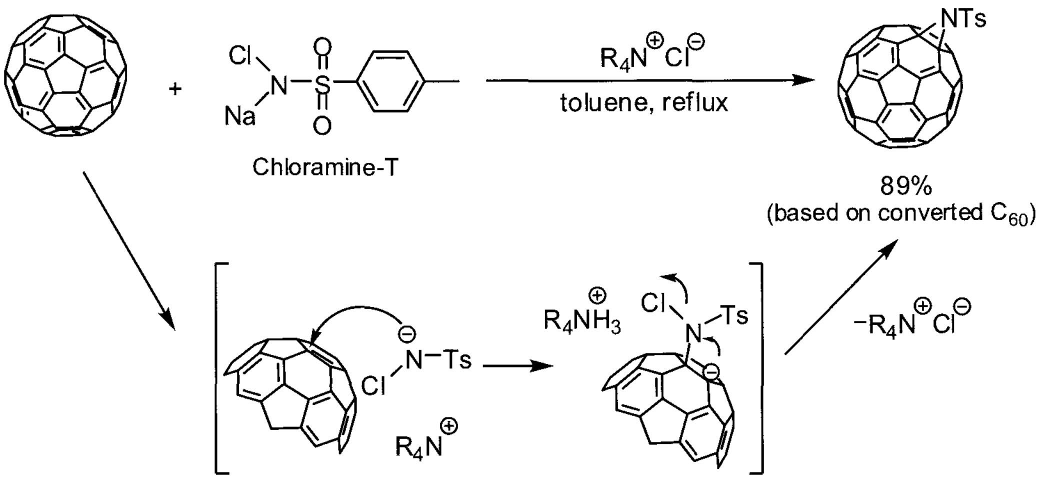
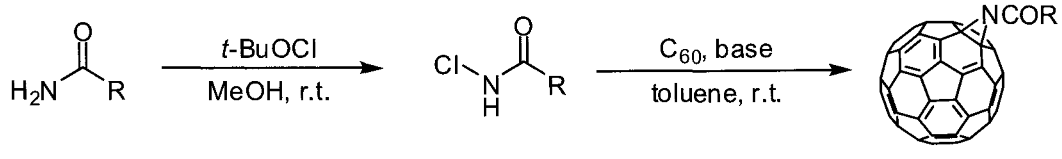
Functionalization of C_{60} is expected to induce fascinating chemical and/or physical properties. The development of a facile and efficient method for introduction of a nitrogen atom to C_{60} would not only be a significant subject but also directly connected to efficient synthesis of an azafullerene. Although the thermal reaction of organic azides with C_{60} provides azafulleroids and aziridinofullerenes[1], the method requires high temperature and explosive reagents, in addition, an aziridinofullerene were yielded as a minor product under the conditions. From these points of view, we will report on novel and practical synthesis of aziridinofullerenes by the reaction of C_{60} with *N*-haloamides. For example, the reaction of C_{60} with chloramine-T in the presence of phase-transfer catalyst gave the corresponding aziridinofullerene in high yield. Based on the method, other readily available amides were found to function as nitrogen sources for the Aziridination. When C_{60} was treated with *N*-chlorinated amides prepared by the reaction of amides and *t*-BuOCl, in the presence of a base, a variety of aziridinofullerenes were readily obtained.





R = OBn, $OC_{16}H_{33}$, $O(CH_2)_3Si(OEt)_3$, $N(C_{12}H_{25})_2$, etc.

[1] M. Prato, Q. C. Li, F. Wudl, and V. Lucchini, *J. Am. Chem. Soc.* **115**, 1148 (1993).

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2P-11

The Convenient Synthesis of Various [60] Fullerene Derivatives via Nitrofullerene Intermediate

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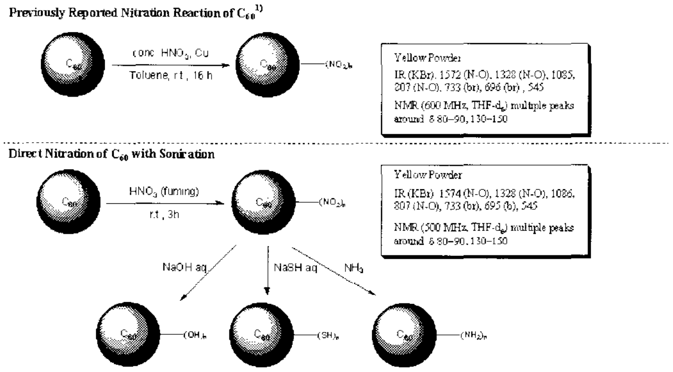
The effective methods for the surface modification of fullerene are necessary to develop next generation fullerene materials. However, the reaction of fullerene is quite limited because of its poor solubility in solvents. In this report we wish to demonstrate the effective methods to prepare various fullerene derivatives via nitrofullerene intermediate, which was synthesized by the heterogeneous reaction by using aq. HNO_3 (fuming) and fullerene.



The heterogeneous mixture of aq. HNO_3 (fuming) and fullerene was stirred for 3 hours at room temperature to give dark orange solution; the NO_2 radical dissolved in aq. HNO_3 (fuming) directly reacted with fullerene to give the nitrofullerene. After dilution with water the product was extracted with AcOEt and the obtained fullerene derivatives were purified by using silica gel column. The structure was determined by ^{13}C NMR and IR as a mixture of tetra- and hexanitrofullerene, which was reported by Chiang et. al.[1)] Since the above reaction was carried out under heterogeneous conditions at room temperature and no organic solvent was applied, it could be applied for large-scale synthesis of various fullerene derivatives. For example, OH, SH, and NH_2 groups were introduced by further substitution reactions to give the corresponding water-soluble fullerene derivatives. PEGylated fullerene was synthesized as well for the purpose of drug delivery.

References: 1) V. Anantharaj, J. Bhonsle, T. Canteenwala, and L. Y. Chiang, *J. Chem. Soc., Perkin Trans. 1*, **1999**, 31-36.

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2P-12

Control of the Motion of Encapsulated Atoms Inside Fullerene Cage

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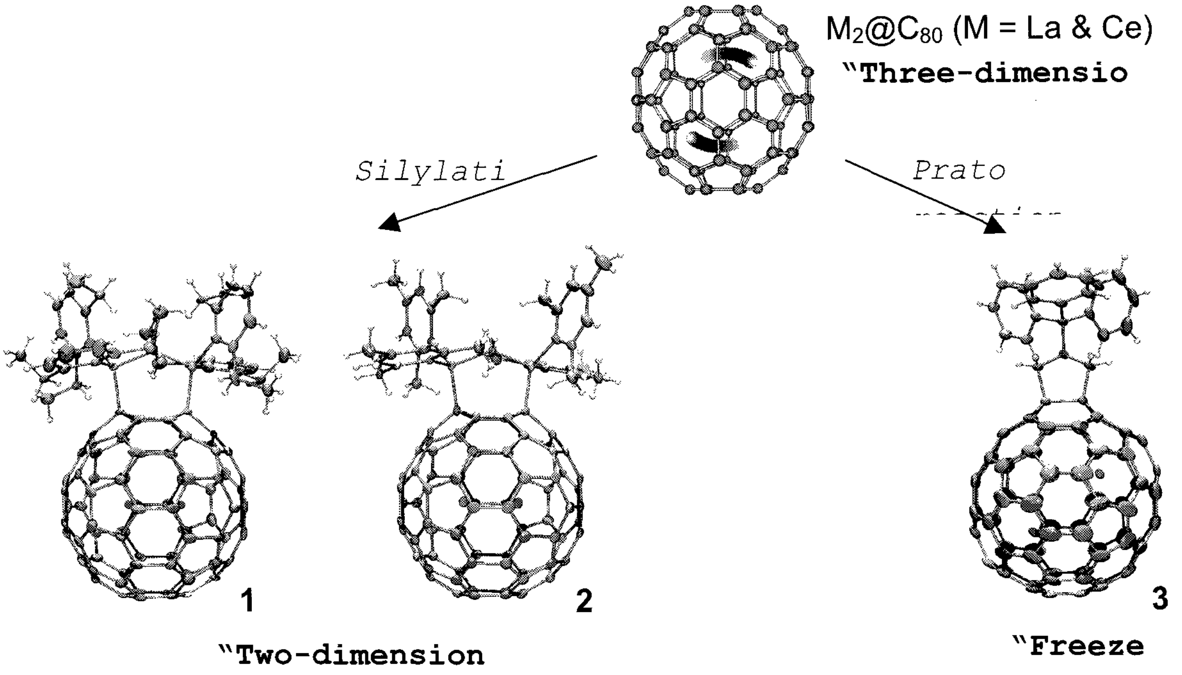
Among many kinds of metallofullerenes, $M_2@C_{80}$ has attracted special attention for the dynamics of the encapsulated metal atoms because of their three-dimensional random motion.[1] Control of motion of atoms within a cage is expected to be very valuable in designing functional molecular devices with new electronic or magnetic properties.

Herein we report the synthesis and full characterization of silylated $La_2@C_{80}$ (**1**),[2] $Ce_2@C_{80}$ (**2**),[3] and Prato adducts of $La_2@C_{80}$ (**3**).[4] In the case of **1** and **3**, ^{139}La NMR study clarified the dynamic behavior of the La atoms. In the case of **2**, paramagnetic NMR shift analysis[5] originating from the Ce atoms gave the information about the rotational position of the Ce atoms. These data reveal that the dynamic motion of the La and Ce atoms encapsulated inside the fullerene cage can be controllable by outside functionalization of the cage.



References: (1) Akasaka, T. et al. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 1643. (2) Yamada, M. et al. to be submitted. (3) Yamada, M. et al. *J. Am. Chem. Soc.* **2005**, *127*, 14570. (4) Yamada, M. et al. *J. Am. Chem. Soc.* **2006**, *128*, 1402. (5) Yamada, M. et al. *J. Am. Chem. Soc.* **2006**, *128*, 1400.

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2P-13

Chemical derivatization of Ce@C$_{82}$

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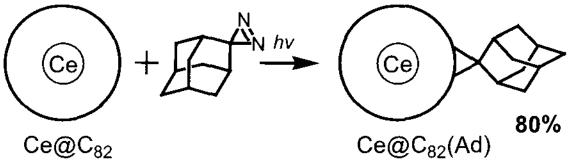
Ce@C$_{82}$ has the arbon cage (C_{2v}) and the formed electric structure (Ce^{3+}C$_{82}$$^{3-}$) similar to those of La@C$_{82}$. The difference between them is that Ce@C$_{82}$ includes the metal having *f* electron. It is interesting to know the reactivity of Ce@C$_{82}$ and the properties of its derivatives. Herein, we report the derivatization of Ce@C$_{82}$ with adamantandiazirine.

Ce@C$_{82}$ was functionalized in the similar way used for La@C$_{82}$ reported previously [1,2]. Major isomer (Ce@C$_{82}$Ad-A) and minor isomer (Ce@C$_{82}$Ad-B) were isolated from the reaction mixture by HPLC with a Buckyprep Column (Figure 1). Cyclic and differential pulse voltammograms reveal their characteristic redox potentials. Bulk controlled-potential electrolysis of Ce@C$_{82}$Ad was used to prepare their anions. The cage symmetries of Ce@C$_{82}$Ad-A and B have been verified as C_1 and C_s, respectively, by measuring the ^{13}C NMR spectra of their anions. The ^{13}C NMR spectrum of [Ce@C$_{82}$Ad-B]$^-$ clearly shows the temperature-dependent shifts caused by the *f* electron remaining on the Ce atom.

Scheme.



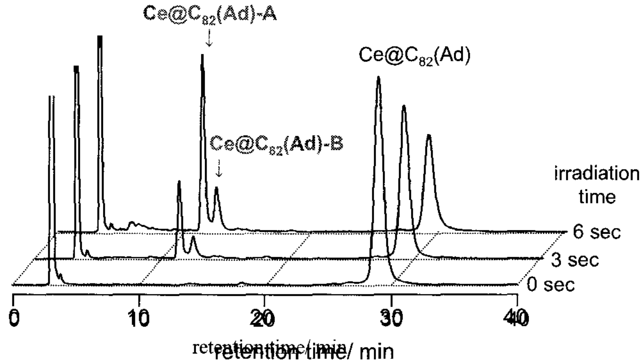


Figure 1. HPLC profiles of reaction mixture. Conditions: column, Buckyprep ϕ 4.6 × 250 mm; eluent, toluene 1.0 mL/min.

[1] Y, Maeda. et al. *J. Am. Chem. Soc.* **2004**, *126*, 6858-6859.

[2] Y, Matsunaga. et al. *ITE Lett.* **2006**, *7*, 43-49.

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2P-14

STM/STS studies of T_d-symmetric metallofullerene: $Lu_2@C_{76}$

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In the present study, we found that $Lu_2@C_{76}$ has T_d-symmetry[1], though the empty-C_{76} has been reported as having D_2 symmetry[2]. These differences can be interpreted as due to a charge transfer from the encaged Lu atoms to the carbon cage, which increases significantly the stability of the T_d-C_{76} cage. A combination of scanning tunneling microscopy (STM) and theoretical calculations is a powerful tool for obtaining structural and electronic information on fullerenes and metallofullerenes[3]. To determine the amount of the charge transfer and also to confirm the symmetry of the fullerene, we have investigated $Lu_2@C_{76}$ metallofullerenes by STM with DFT calculations.

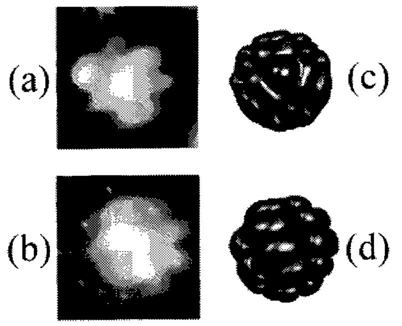

Figure 1: UHV-STM images (1.5×1.5 nm) of $Lu_2@C_{76}$ molecule observed at (a)V_s = +1.5 V, and (b)V_s = -1.5 V. DFT calculations (B3LYP/6-31G(d)) for C_{76}^{6-}, (c)LUMO+3, and (d)HOMO-3.

The samples were prepared by vacuum sublimation of $Lu_2@C_{76}$. All the sample preparation and STM measurements were performed in an UHV condition. Figure 1 shows the STM images of an individual $Lu_2@C_{76}$ molecule directly absorbed on Si(111) 7×7 surface at room temperature together with DFT calculations (B3LYP/6-31G(d)) for the local density-of-state of C_{76}^{6-}. Distinct intramolecular structures are observed (a, b), indicating the absence of free rotation similar to other fullerene cases[3]. The observed internal images and the corresponding DFT calculations(c, d) agree well with each other.

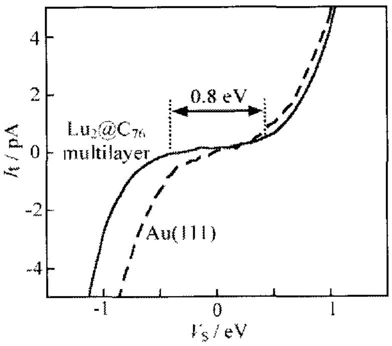

Figure 2: STS spectra of a $Lu_2@C_{76}$ multilayer on Au(111) and reference at room temperature. The $Lu_2@C_{76}$ spectrum shows the HOMO-LUMO gap of 0.8 eV.

Figure 2 shows scanning tunneling spectroscopy (STS) spectra for a multilayer of $Lu_2@C_{76}$ on Au(111) and on a bare Au(111) surface for a reference. The HOMO-LUMO gap of the $Lu_2@C_{76}$ was evaluated to be 0.8 eV. This is consistent with the DFT calculations (0.84 eV) and also is close to the value estimated from UV-Vis-NIR spectrum of $Lu_2@C_{76}/CS_2$ solution (0.69 eV)[1]. These results strongly suggest that $Lu_2@C_{76}$ has T_d-C_{76}^{6-} cage, i.e. 6 electrons are transferred from Lu atoms to the cage.

[1] H. Umemoto *et al.*, *J. Am. Chem. Soc.*, submitted.
[2] R. Ettl *et al.*, *Nature*, **353**, 149 (1991).
[3] A. Taninaka *et al.*, *Jpn. J. Appl. Phys.*, **44**, 3226 (2005).

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2P-15

Optical Properties of Erbium Dimetallofullerenes: $Er_2@C_{82}$ and $(Er_2C_2)@C_{82}$

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Lanthanide metallofullerenes might exhibit fluorescence from encapsulated metal atom(s). These may provide a potential application to organic fluorescence materials. Recently, we found that $(Er_2C_2)@C_{82}$, an di-Er-metal-carbide fullerene, exhibits much more enhanced photoluminescence (PL) than that of $Er_2@C_{82}$, a pure di-Er metallofullerene[2]. In this study, we measured the optical properties of these metallofullerenes and discuss the role played by a C_2 radical existing between the two Er atoms for the enhanced PL.

Figure 1 shows the emission spectra of $Er_2@C_{82}$-$C_{3v}(8)$ and $(Er_2C_2)@C_{82}$-$C_{3v}(8)$ in bisphenol-A polycarbonate thin films at 3.5 K[3]. We have obtained fine spectra whose origin is an electron transition of 4*f* orbital of Er^{3+}: $^4I_{13/2} \rightarrow {}^4I_{15/2}$, though the emission spectra at room temperature are broad. These spectra are very similar with each other. The presence of the C_2 radical does not affect so much for the observed spectral features. This is also indicated by the corresponding emission lifetimes and X-ray absorption spectra between $Er_2@C_{82}$-$C_{3v}(8)$ and $(Er_2C_2)@C_{82}$-$C_{3v}(8)$.

Emission lifetimes of $Er_2@C_{82}$-$C_{3v}(8)$ and $(Er_2C_2)@C_{82}$-$C_{3v}(8)$ are 0.47 μ sec and 0.48 μ sec, respectively. This result indicates that encapsulated C_2 radical does not affect the relaxation lifetime of the Er atoms. X-ray absorption spectra of $Er_2@C_{82}$-$C_{3v}(8)$, $(Er_2C_2)@C_{82}$-$C_{3v}(8)$ and Er_2O_3 are also similar, suggesting that the oxidation state of Er atoms in these metallofullerenes are the same (3+) and that the C_2 radical is in a neutral state. The transient absorption measurement of these metallofullerenres is now in progress.

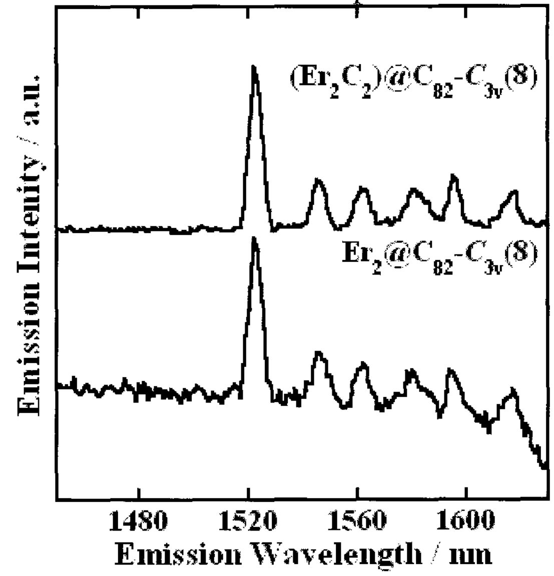

Figure 1 Emission Spectra of $Er_2@C_{82}$-$C_{3v}(8)$ and $(Er_2C_2)@C_{82}$-$C_{3v}(8)$ at 3.5 K.

Reference
[1] T. Inoue *et al., J. Phys. Chem.* B **108**(23), 7573 (2004).
[2] Y. Ito *et al., 29th Fullerene-Nanotube General Symposium,* **1P-40** (2005).
[3] V. K. Koltover *et al., Phys. of the Solid State,* **44**(3), 506 (2002).

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2P-16

Development of High-resolution Ion Mobility and Applications for Metallofullerenes

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[2]*Institute for Advanced Research, Nagoya University*
[3]*CREST, Japan Science and Technology Agency*

Structural studies have been a main issue on metallofullerenes, where NMR and X-ray diffraction have played important roles to clarify their unique structures and properties. These methods, however, require large amount of isolated samples, which prevent us from systematic studies and from discovery of new structures. In the previous work, we have measured an ion mobility of Sc metallofullerenes and have clarified universality of the carbide structures [1]. The measurement system, however, utilizes continuous ion detection with quadrupole mass filter, which limits the mass and mobility resolution and demands the large pumping system. To overcome these difficulties, here we developed a new high-resolution mobility measurement system with a pulsed ion detection system.

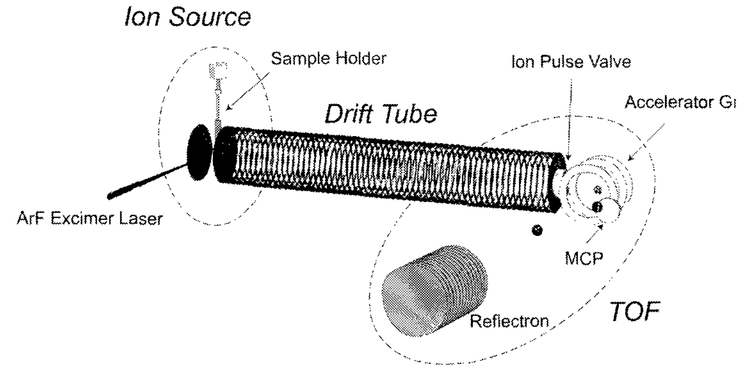

Fig. 1 Schematic diagram of apparatus

The new system consists of a laser vaporization ion source, a drift tube, an ion pulse valve (IPV), and a time of flight mass spectrometer (TOF) (Fig. 1). Fullerene ions from the ion source were introduced to the drift tube filled with He at 3 atm. The pressure was much higher than 1 atm of the conventional system expecting twice as higher mobility resolution [1]. The ions passing the drift tube exit through IPV and were detected by the TOF, where the mobility and the mass of the ions were simultaneously determined. IPV connects the high pressure drift tube and the high vacuum TOF with pulse mode, so that the new system vacuum pump (1200 l/s) is much smaller than the conventional ones (10,000 l/s) making it a handy and low cost system.

Now we are applying the system for metallofullerenes and exploring new structures.

References:

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

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2P-17

Formation Mechanism of C_{60} Polymer Rings Produced by Electron/Hole Injection from an STM Tip

○Ryo Nouchi[1,2], Yohei Ohta[2] and Yoshihiro Kubozono[1,2]

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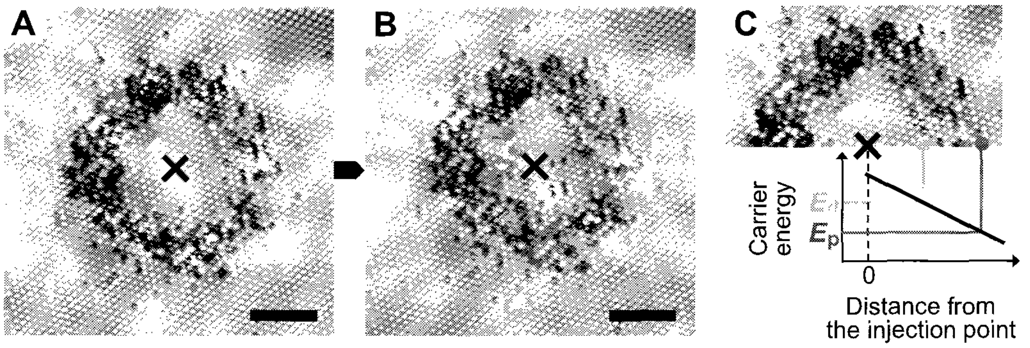
Carrier (electron/hole) injection from a scanning tunneling microscope (STM) tip into a close-packed layer of C_{60} induces the removal/movement [1] and polymerization [2] of C_{60} molecules. While the removal and movement are possible to be performed at single molecular scale, the polymerization is hard to be achieved at that precision. This is regarded as a consequence of the spatial spread of injected carriers. We previously reported that carrier injection into a close-packed multilayer of C_{60} induced polymerization with a ring-shaped distribution, and the polymer ring was enlarged by subsequent carrier injections [3]. In this study, we discuss about possible mechanisms for the ring formation, and propose a probable mechanism that the propagating carrier themselves produce the polymer ring.

Figure A shows a polymer pattern formed by hole injection at −3.3 V into the marked point. The scale bar is 10 nm. It should be noted that polymers are absent around the carrier injection point; a polymer ring is formed. Because the polymer ring is disappeared when we simply heat the sample, thermal field by the Joule heat generated by a tunneling current may induce depolymerization around the carrier injection point and produce a ring-shaped pattern. If it is the case, the thermal field should be unchanged for the carrier injection at the same condition. However, further injection of holes at the same bias voltage produced polymers around the center of the ring as shown in Fig. B. This implies that the ring formation does not originate from the induced thermal field. Here, we propose a probable mechanism that energies necessary for polymerization, E_p, and depolymerization, E_d, are supplied by injected carriers. Carriers with higher energies than E_p (E_d) can induce polymerization (depolymerization), and consequently the ring structure is formed as schematically shown in Fig. C. The proposed mechanism can well explain dependencies of ring diameters on the sample bias voltage and a type of injected carriers.



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2P-18

Fabrication of high-performance fullerene field-effect transistor devices and development to integrated circuits

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Field-effect transistor (FET) devices with thin films of organic molecules have attracted special attention for applications in flexible displays, smart cards, and radio-frequency identification tags. Especially, investigation and development of the *n*-channel organic FET devices are indispensable for progress of practical organic electronics. The FET devices with thin films of C_{60} showed *n*-channel normally-off FET properties with the highest field-effect mobility, μ, value of 0.56 - 0.65 cm^2 V^{-1} s^{-1} [1,2]. However, the μ values are still lower than those of the *p*-channel FET devices (e.g. 1.5 cm^2 V^{-1} s^{-1} in pentacene thin-film FET) [3].

Recently, it was found that the FET operation can be controlled by changing work function, ϕ, of source/drain electrodes in the organic single crystal FETs and the thin-film FETs [4-7]. In this study, we have succeeded in changing the output properties of C_{60} FET devices by use of metal electrodes with the ϕ value of 2.5 - 5.65 eV. The C_{60} FET device with Eu source/drain electrodes (ϕ = 2.5 eV) showed *n*-channel normally-on FET properties (Fig. 1). The values of μ and threshold voltage V_T were determined to be 0.50 cm^2 V^{-1} s^{-1} and 34 V, respectively. No energy barrier for electron exists between Eu electrodes and lowest unoccupied molecular orbital (LUMO) of C_{60} because the Fermi energy E_F of Eu is higher than the energy level of LUMO E_{LUMO}. Therefore, it has been concluded that high carrier injection from Eu electrode to LUMO causes the normally-on FET property. We have tried to reduce the off current by a doping of electron acceptor F_4TCNQ. The electron acceptor should disappear excess electrons injected from the source electrode without energy barrier, leading to the high-performance FET devices with high μ and on-off ratio. Furthermore, in the symposium, I will report complementary ring oscillator fabricated with C_{60} and pentacene FETs aiming at the development to integrated circuits.

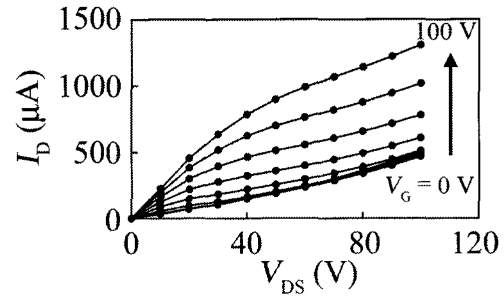

Fig. 1. I_D – V_{DS} plots for C_{60} FET device with Eu electrodes.

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2P-19

Synthesis of C_{60} polymers by free electron laser irradiation with a tunable wavelength

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Since the polymerization of C_{60} films was carried out by a phototransformation first, the possibility of a three-dimensional (3D) polymerized phase has been discussed. The purposes of this work are to develop a novel photon-assisted process for C_{60} polymerization and to synthesize 3D C_{60} polymers by free electron laser (FEL) irradiation. We have also noticed a “hole doping effect”, demonstrated in the synthesis of a diamond from a graphite.

FEL system we used generates a tunable near-infrared laser and the higher harmonics with a few tens microsecond macro-pulse including few hundreds pico-second micro-pulses. The power of the fundamental macro-pulse was 0.5 mJ/pulse with the repetition rate of 2Hz. The irradiation time was 120 min-180 min. The irradiated laser was the third harmonics 450 nm of the fundamental wavelength 1350 nm and ultraviolet laser, 345 nm, was also taken out as the fifth harmonics of 1700 nm. The irradiations through a quartz BK7 window were carried out under the pressure of 470 MPa in a vacuum chamber at around 10^{-6} Torr.

Figure 1 shows the typical Raman peaks of the $Ag(2)$-derived mode in the case of 453 nm FEL irradiation. The wave number of the peak of the non-irradiated pristine C_{60} was 1463 cm^{-1}, while that of the irradiated C_{60} and mixture of C_{60}+ I_2 changed to 1460 cm^{-1} and 1455 cm^{-1}. The half width of the Raman peak also increased corresponding to the amount of the peak shift. The ultraviolet rays (345nm) resulted in different changes of the Raman spectrum as show in figure 2. Double split of the peak was observed probably due to the strong absorbance in C_{60} and only sample surfaces were changed. The change of the Raman peak of C_{60}+ I_2 sample was definitely larger than that of pure C_{60} in both cases. These result insists that some additional mechanisms work for proceeding of the polymerization by addition of I_2.

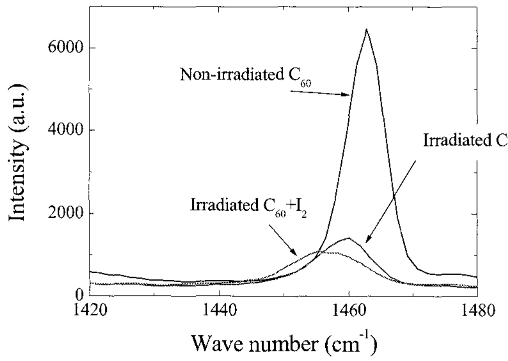

Figure 1

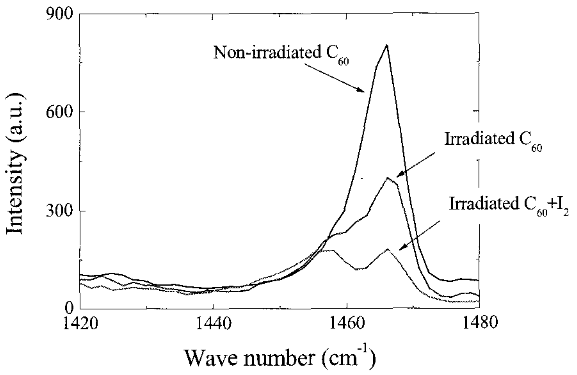

Figure 2

2P-20

Novel Functionalization of Fullerenes by Formation of Nanoparticles

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Fullerenes are currently of great interest in many areas of science and technology due to their unique chemical and physical properties. However, many of the potential applications are hampered because fullerenes are soluble in the limited range of solvents. Various attempts have been made to modify fullerenes chemically to surmount the limitations. One notable example is synthesis of water-soluble fullerene derivatives and their applications for medical, cosmetic, and biotechnological purposes. On the other hand, several groups including us found that the nanoparticles of fullerenes disperse stably in water even without the aid of dispersing agents such as surfactant. The finding holds promises for a totally new strategy for fullerenes functionalization.

Several different procedures have been developed for the preparation of the fullerene nanoparticles. We found that they can be obtained by recrystallization from a solution in tetrahydrofuran (THF).[1,2)] Our procedure is distinctly different from others in the sense that it does not employ highly toxic solvents such as benzene or toluene, and is suitable for biotechnological applications. Indeed, the procedure has been recognized as a standard protocol for studying biological activities of the fullerenes nanoparticles including the cytotoxicity, which attracts significant scientific interests and keen public attention at present. We found that negative surface charges of the fullerenes nanoparticles are responsible for the dispersion stability.

The obvious approach to prepare the nanoparticles in general is a top-down approach, in which bulk solids are reduced to small particles by mechanical forces, but it usually gives the particles no smaller than a few micrometers. In the case of fullerenes, however, we found that the nanoparticles, including the ones as small as 20 nm, are generated by simple hand-grinding of the bulk solids in an agate mortar.[3,4)] The nanoparticles thus obtained also disperse stably in water, and show the same surface characteristics as those prepared by bottom-up processes including recrystallization from solutions. Contrary to the previous reports, we found that the hand-ground nanoparticles do not inhibit aerobic growth of a model organism, *Escherichia coli*, suggesting that safe nanoparticles of fullerenes for biotechnological and/or medical applications can be obtained by an unexpectedly facile procedure.

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2P-21

Growth of Spiral Carbon Structures and Formation of Polyhedral Graphite Particles by Arc Discharge

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Carbon coils with helical/spiral structures, such as carbon nanocoils and microcoils, can be grown by the catalytic thermal decomposition of hydrocarbon gases, such as acetylene. Polyhedral graphite (PG) particles having highly graphitized spherical structures with diameters of 100–500 nm are formed by high-power laser irradiation on a graphite target in a high-pressure Ar atmosphere. Recently, we found that carbon coils were formed without a metal catalyst by arc vaporization using graphite electrodes in a high-pressure hydrogen atmosphere (hydrogen arc discharge), and we also succeeded in producing PG particles by arc discharge using cellulose char as a starting material (cellulose arc discharge). We investigated thermal graphitization via these two arc-vaporization processes by forming unusual carbon structures without using a metal catalyst.

Spiral carbon structures were formed by vaporizing a graphite anode by conventional DC arc discharge. Hydrogen gas was put into the arc chamber at a pressure of more than 0.1 MPa. The PG particles were produced by a modified DC arc discharge in Ar at a pressure of 0.1 MPa. A cellulose char pellet was introduced into the arc plasma between two electrodes during the arc discharge.

Figure 1 shows an SEM image of typical spiral carbon structures. Various spiral carbon structures, such as thin single coils, thick double-helix coils and twists, were obtained on the anode surface by hydrogen arc discharge. We found that the coiling chiralities and morphologies of the spiral carbon structures depended on the distance from the arc plasma. Figure 2 shows the PG particles obtained from the cellulose arc discharge. They are equivalent to those obtained from laser vaporization in that they have highly graphitized concentric structures with diameters of 150–500 nm. We will discuss why having high-density carbon species in the arc plasma is an important factor for the metal-free formation of these carbon materials.

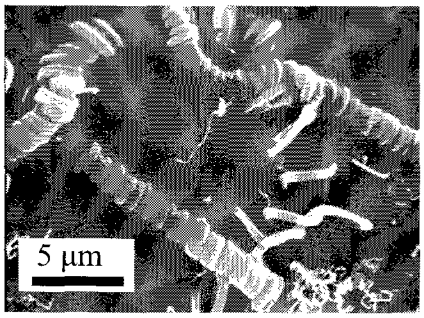

Fig. 1 SEM image of spiral carbon structures grown on anode surface by hydrogen arc discharge.

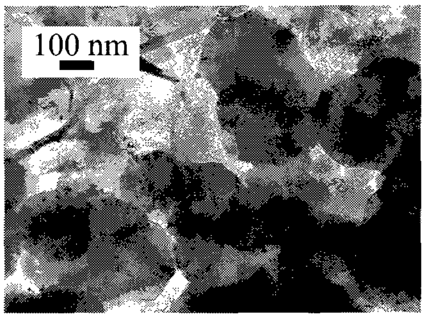

Fig. 2 TEM image of polyhedral graphite particles produced by cellulose arc discharge in Ar atmosphere.

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2P-22

Simulation of high-energy ion/atom impact on nano-carbons II: Collision of Ar multiple ions on graphite surface

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Abstract:

Collisions of highly charged ions on solid surfaces attract much attention from scientific and technological view points, since such collisions can raise significant structural change on the surfaces. Recently, possibility of nano-diamond formation upon irradiation of Ar^{+8} ions on graphite has been reported [1]. Upon collision, appearance of band-gap around 6 eV in scanning tunneling spectroscopy and a peak around 1350 $cm^{-1}$of infrared absorption are found. Both facts were interpreted as appearance of nano-diamond on the graphite surface.

Since the A^{r+8} ions have high Coulomb potential, the role of kinetic energy seems to be marginal. In contradictory, if neutralization of Ar^{+8} ions occurs prior to the collision, the kinetic energy becomes a key parameter. To understand intrinsic physics, computational tests including electron and ion dynamics are thus indispensable.

I performed the time-dependent density functional theory calculations being coupled with classical molecular dynamics simulations using the computer code FPSEID (éf-psái-dí:) which stands for First Principles Simulation tool for Electron Ion Dynamics [2]. I found that the structural change upon collision is dependent on the incident energy of Ar ions, which dress electrons during the collision on the graphite surface. In this paper, I'll discuss possibility of nano-diamond formation.

Acknowledgement:

All simulations in the present work have been performed using the Earth Simulator.

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2P-23

Dielectrophoretic Alignment of Carbon Nanocoils

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We have investigated the alignment of carbon nanocoils (CNCs) using dielectrophoresis.The cabon nanocoils synthesized by chemical vapor deposition weresuspended in iso-propyl-alcohol (IPA) using the ultrasonic dispersion. After the suspension was dropped on a pair of coplanar electrodes formed on glass substrate,AC or DC electric field was applied to the electrodes. After the evaporation of IPA, the surface between the electrodes was observed using a scanning electron microscope (SEM). In the case of DC electric field, most of all CNCs were moved toward the cathode. On the contrary, in case of AC electric field with the frequency higher than 100 Hz, CNCs were aligned along the electric field and connected each other. It is noted that the CNCs made bridges between the electrodes, when the CNC concentrations in IPA was high. At a higher electric field, the degree of the alignment was improved. The Debye length around the colloidal CNCs was estimated to be ~ 500 nm from the conductivity of the dispersion. This range is comparable to the coil diameters. As a result, the CNCs act as rods with a diameter of ~ 500 nm during the dielectrophoresis.

This work was carried out for Osaka Prefecture Collaboration of Regional
Entities for the Advancement of Technological Excellence, JST.

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2P-24

Novel Techniques for Continuous Growth of Carbon Nanotube

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It is known that the growth of carbon nanotube (CNT) is stopped by covering of unnecessary harmful carbon formed on a nanosized particle catalyst of metal in thermal CVD process. Therefore, it is necessary to remove the harmful carbon for the continuous growth. However, it is difficult to remove the only harmful carbon on the catalyst particle without destroy of CNT. We propose the novel techniques with the separated function of carbon supply and CNT growth as shown in Fig.1. The ionized carbon source gas is provided continuously into one side of the plate shaped catalyst, and then CNT is generated on nano-sized exposed catalyst at the preventive material in the other side.

For proof in principle, we attempted to separate the catalyst into the two fixed sites by using pure Fe foils. Thickness of the Fe foils was 20～50 μm. The carbon source gas was provided on one side of Fe foil in 850～900℃ and the other side was in Ar gas. The both sides of Fe foil surfaces were observed by SEM and Raman spectra. On the Fe foil surface in carbon source gas (CO, H_2, Ar), D-band peak was observed in Raman spectra as shown in Fig.2. On the other side of Fe foil surface in Ar gas, the large graphite grains grew with the thickness of about 5 μm without D-band peak. On the other hand, it was found that the carbon generation was prevented by an Ag mask on Fe foil. So, the carbon could be grown with the isolated island structure at pin-holes in the Ag film on the Fe foil. These data indicate the possibility that a high quality CNT without defect may grow on the exposed nano-sized catalyst (Fe) in the preventive material (Ag). Therefore, it is expected that high quality CNT would grow continuously if the carbon source supply could be kept on the exposed catalyst surface without covering of carbon by cleaning function of such a plasma etching process.

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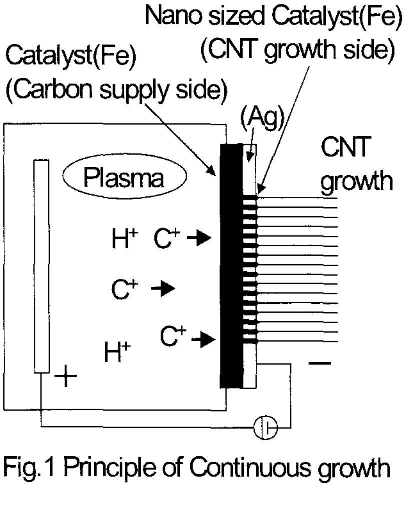

Fig.1 Principle of Continuous growth

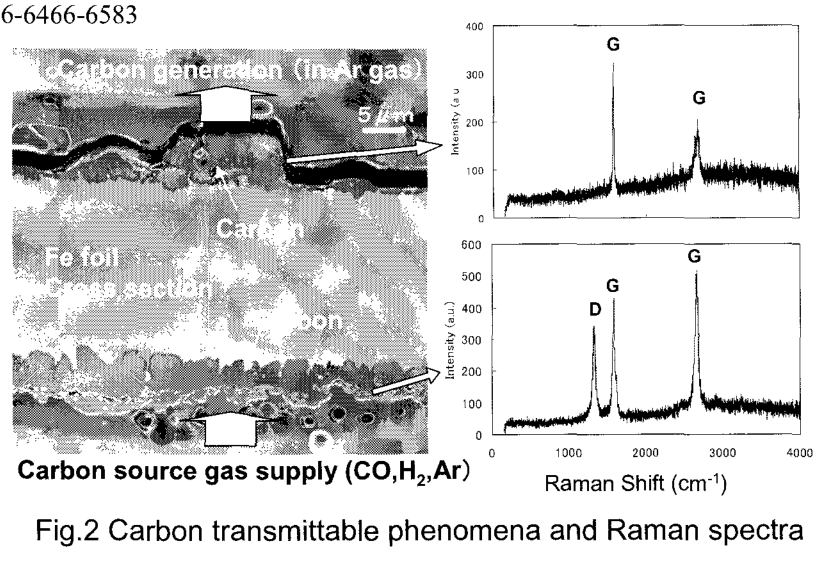

Fig.2 Carbon transmittable phenomena and Raman spectra

2P-25

Formation Mechanism of Single-walled Carbon Nanotubes on Natural Magnesite

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We have reported that single-walled carbon nanotubes (SWCNTs) can be grown on natural minerals by pyrolyzing methane gas, demonstrating the possibility of naturally occurring SWCNTs [1]. Our method to obtain SWCNTs using natural minerals is also interesting from the industrial point of view, because the method does not need the time and cost consuming preparation of the sophisticated catalysts. However, the detailed mechanism of the SWCNT growth on natural minerals is not well understood. In this paper, we report X-ray absorption fine structure (XAFS) study on growth mechanism of SWCNTs prepared with natural magnesite ($MgCO_3$).

A transparent single crystal of natural magnesite was purchased from Hori Mineralogy (Tokyo, Japan). X-ray fluorescence measurement revealed Fe to be a major impurity. The magnesite sample was crushed in an agate mortal and the resultant powder was placed in a Pt boat and set in the center of 25 mm-diameter SiO_2 reaction tube. The reaction tube was heated to 1173 K at a heating rate of 5 K/min with direct pumping, and then subjected to a 1 atm flow of a mixture of CH4 gas (5 cc/min) and Ar gas (100 cc/min) for 1 h.

XAFS measurements using synchrotron x-ray were done at a beamline BL-9C of KEK in Tsukuba. Si (111) crystals were used in the double-crystal monochromator of the beamline. Fe K-edge XAFS measurements were done at room temperature for four samples: (1) starting magnesite sample (abbreviated as Mag-S), (2) heat-treated magnesite sample at 1173 K in vacuum for 1 h (Mag-V), (3) CVD-treated sample (Mag-C), and (4) HCl washed sample after CVD treatment (Mag-H).

Fig. 1 shows the Fe K-edge XANES spectra of the above-mentioned four samples, comparing with those of Fe foil, Fe_2O_3 and Fe_3O_4. Structural characteristics of the iron states in CVD process will be discussed.

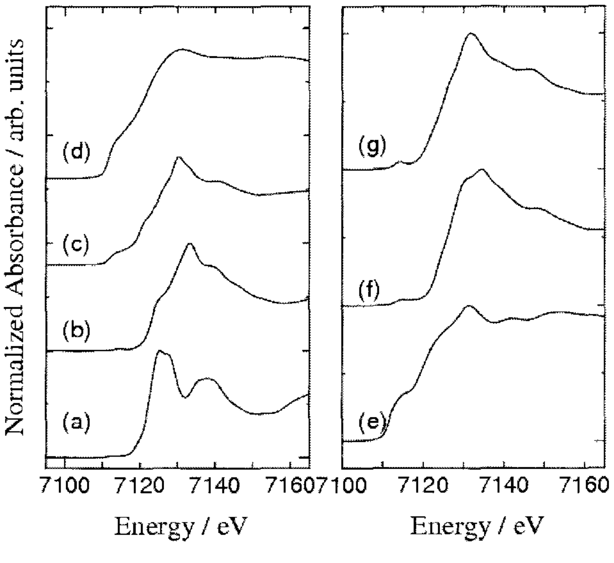

Fig.1 Observed XANES spectra of (a) Mag-S, (b) Mag-V, (c) Mag-C, (d) Mag-H, (e) Fe foil, (f) Fe_2O_3 and (g) Fe_3O_4.

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2P-26

Selective Growth of Carbon Nanotubes on pre-patterned 6H-SiC(000-1) using Ti mask

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It has been reported that well-aligned zigzag-type carbon nanotubes (CNTs) could be produced with fairly uniform tube diameters by surface decomposition of 6H-SiC(000-1) [2]. To fabricate CNT-based device, it is important to form selectively CNTs on SiC surface. However, an early study reported that, using conventional SiN mask, complete selective growth was difficult, since the mask was decomposed during the CNT growth on SiC [2]. In this study, we used high-melting temperature metal, Ti, as a mask for selective growth of CNT on SiC, since the melting point of Ti is higher than the decomposition temperature of SiC surface.

Equal line-and-space Ti patterns 10μm in width were fabricated on 6H-SiC(000-1) surface. The samples were heated at 1270°C for 30 min at 10^{-6} Pa, followed by annealing at 1700°C for 30 min at 10^{-2} Pa. After each treatment, the surfaces of the samples were investigated with SEM, STM, XPS and micro Raman spectroscopy.

After heating at 1270°C, carbon nanocaps were formed at the open areas, as shown in Fig.1. Strong G band peak was observed at these areas after annealing at 1700°C in micro Raman spectroscopy. Fig. 2 shows SEM images of the sample surface after heating at 1700°C. It was found that the shape of Ti mask was maintained even after annealing. In addition, XPS spectra showed that Ti was still present after annealing at 1700°C. From these results, the effectiveness of Ti mask was shown for the selective growth of CNT on SiC.

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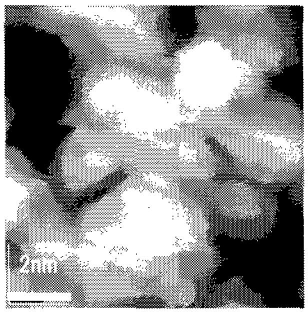

10 × 10nm

Fig. 1 STM images of an open area between the Ti masks after heating at 1270°C.

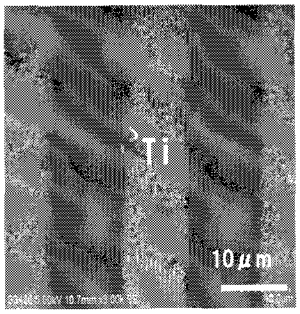

Fig. 2 SEM image of the sample surface after heating at 1700°C.

2P-27

Effects of oxygen pressure on carbon nanocap formation on 6H-SiC(000-1) by surface decomposition

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It has been reported that well-aligned zigzag-type carbon nanotubes (CNTs) could be produced by surface decomposition of SiC [1]. At the initial stage of the CNT growth, nanosized cap structure was observed on SiC surface. These carbon nanocaps are considered to determine the size and chirality of grown CNTs [2]. In this study, the effects of oxygen on carbon nanocap formation on SiC by the surface decomposition were investigated.

After HF etching, 6H-SiC (000-1) C-face samples were introduced into ultra-high vacuum (UHV) chamber. Then, they were annealed at 1270°C in the range from 5 to 30 min under various oxygen partial pressures (10^{-4} Pa, 10^{-3} Pa) by control of the supply of oxygen gas. For comparison, we also annealed several samples under UHV ($\sim 2\times10^{-8}$ Pa). The surfaces of the samples after annealing were investigated by STM and XPS.

After annealing for 30 min, STM observation showed that, irrespective of the oxygen pressure, carbon nanocaps were formed on SiC surface. Fig. 1 shows C1s XPS spectra for the samples after annealing under various oxygen pressures. It was found that the ratio of the peak intensity of the C sp^2 component to that of the SiC component became large, as the oxygen pressure increased. The thickness of carbon nanocap layers were estimated by angle-resoloved XPS, and the relation between the thickness and oxygen pressure is shown in Fig. 2. From these results, we conclude that oxygen enhances the decomposition of SiC surface, promoting the growth of carbon nanocaps on SiC surface.

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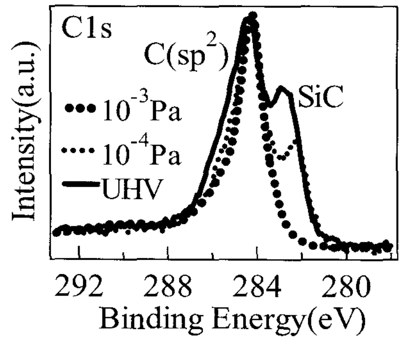

Fig. 1 C 1s XPS spectra of the samples after annealing under various oxygen pressures.

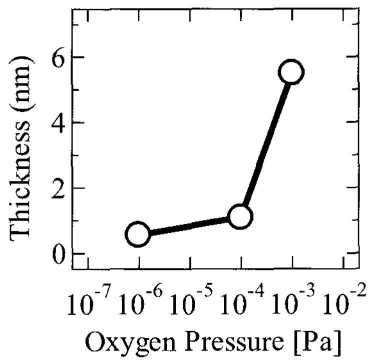

Fig. 2 The relation between carbon nanocap thickness and oxygen pressure.

2P-28

Toward the selective production of SWNT with a single chiral index

-Synthesis of SWNT with small and very narrow diameter distributions-

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Selecting of catalyst and ambient gas are well known to control diameters of SWNTs by laser ablation method. Actually, relatively narrow diameter distribution can be realized by laser ablation method with Rh/Pd catalyst. Laser ablation combined with N_2 gas, on the other hand, is known as the way giving rise to the smaller diameter distribution than that with Ar gas. Therefore, the combination of N_2 gas and Rh/Pd catalyst is safely expected to give the SWNTs with both the smaller and the narrower diameter distributions.

Figure 1a shows Raman spectrum of the raw soot, which was prepared under rapid flow rate condition with N_2 atmosphere and Rh/Pd catalyst. This spectrum indicates the presence of SWNTs with small diameter and narrow distribution, which is quite different from those prepared in Ar gas and Rh/Pd catalyst. The diameter distribution was also confirmed by examining the ω_G^- bands at the G mode frequencies as shown in the inset in Fig.1a.

Figure 1b shows the photoluminescence mapping of the sample after water-surfactant dispersions. From the spectral pattern, these SWNTs were found to have extremely narrow diameter distribution and also have very narrow chiral distribution.

These results suggest that the nanotube with the chiral index of (6,5) is a single major product. Furthermore,all these observations strongly suggest the potential capability of the present method for selective SWNT production with a single chiral index.

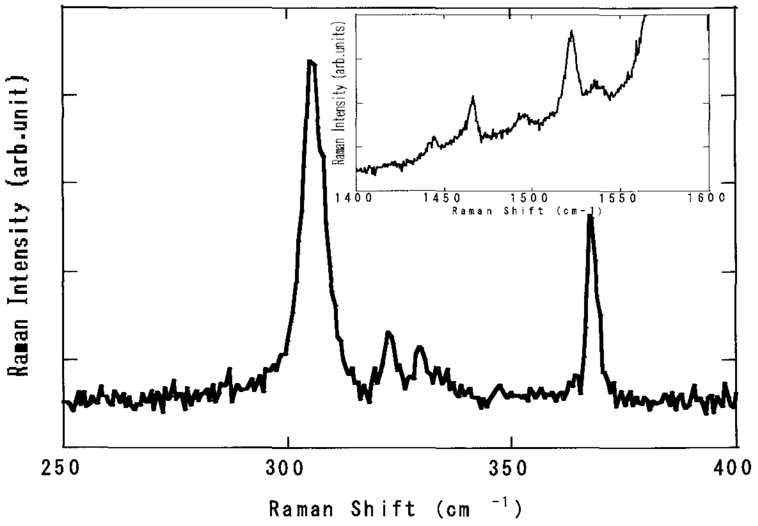

Fig.1a Raman spectra of deposited soot at 488nm

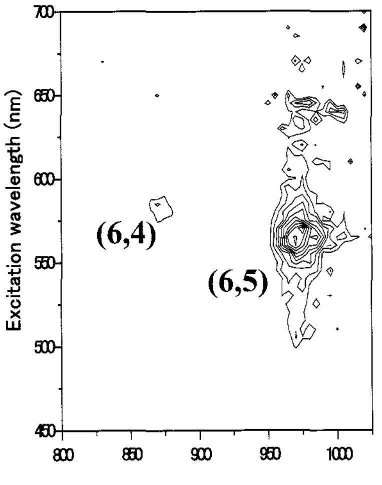

Fig.1b Photoluminescence mapping

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2P-29

Simple technique for controlling the diameter of SWNTs

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Our new experimental setup has been confirmed by synthesizing single-walled carbon nanotubes (SWNTs). We have investigated the relationships among catalyst species (molybdenum-cobalt, iron-cobalt, and rhodium-palladium) which are supported by USY-zeolite and carbon sources (methanol and ethanol) in the temperature range from 600 to 1000 °C. Regarding to the G/D ratio Mo-Co effects best as a catalyst for ethanol, however, it doesn't work well for methanol, and there is no remarkable difference in Fe-Co. Referring to the Kataura plot [1], one obvious fact becomes clear that Mo-Co gives the different SWNTs, the chiral indicies of which are completely different.

And furthermore, one reasonable growth mechanism is considered and this growth model gives us a simple way of controlling the diameter of SWNTs. In our experiment of ethanol CVD at 950°C, several transition metals are mixed with cobalt as a catalyst and RBM spectra indicate that diameter of SWNTs has been changed corresponding to the metal species, shown in Fig.1. Rh-Co and Pd-Co catalysts can synthesize narrower-diameter SWNTs comparing to the Fe-Co and Ni-Co catalysts, which can only synthesize SWNTs with slightly larger diameters. In ethanol CVD, Cobalt catalysts can synthesize SWNTs in itself, however iron catalysts cannot synthesize in itself since cobalt can resolve the ethanol and assist the seeds of SWNTs, on the other hand iron atoms cannot resolve the ethanol, however it can strongly assist the seeds because of the strong interaction between carbon atom and iron atom. This means that to control the catalysts composition can control the diameter of SWNTs, and referring to our results the order of this interactions are Pd ≅ Rh > Fe > Ni > Co.

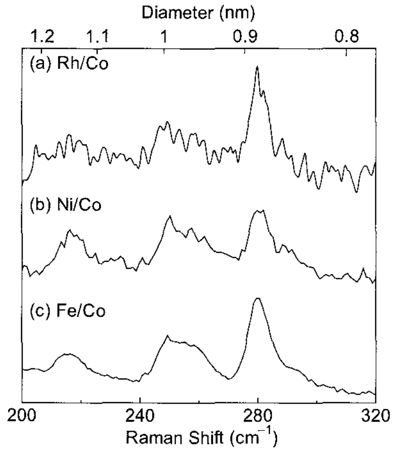

Fig.1 RBM of as grown SWCNT

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2P-30

Effective and Convenient Separation of Metallic Single-Walled Carbon Nanotubes

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Single-walled carbon nanotubes (SWNTs) have excellent mechanical and electrical properties that have led to the proposal of many potential applications. However, SWNTs are typically grown as the bundles of metallic and semiconducting tubes, this hindering the widespread applications. In the applications of SWNTs, it is extremely important to separate semiconducting and metallic SWNTs. We herein show a separation method involving a dispersion-centrifugation process in a tetrahydrofuran solution of amine, which makes metallic SWNTs highly concentrated in a simple way.

A typical dispersion procedure[1] is as follows: As-prepared SWNTs (AP-SWNTs) were added to a solution of a amine in tetrahydrofuran and then sonicated at room temperature followed by centrifugation of the suspension to remove non-dispersible SWNTs. Luminescence and AFM analyses of a supernatant solution showed that the SWNT are well exfoliated and highly dispersed in the solution. Theoretical calculations indicate that amines interact more preferably with as-prepared metallic SWNTs.[2,3] The selective decreasing of semiconducting absorption bands and the enhancement of metallic absorption bands were observed after repeating the dispersion-centrifugal process.[3,4] Raman spectra also shows the enrichment of the metallic SWNTs. The resistivity of the bucky paper made from the enriched metallic SWNTs is more conductive than that of AP-SWNTs. These results are also consistent with the NIR and Raman data.

This separation method is simple, convenient, and non-destructive suggesting a potential industrial utilization for widespread applications of SWNTs.

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2P-31

Effect of amphiphilic oligopeptides on dispersion of carbon nanotubes in water

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To develop a system useful to dispersion and solubilization of carbon nanotubes in aqueous and organic solutions, we have designed amphiphilic and linear oligopeptides. In the present design, Gly and Phe residues were introduced into the oligopeptides as the hydrophilic and hydrophobic regions, respectively (Fig 1). The number of Gly residues was changed to examine the effect of the hydrophilic property on the CNT-despersion in water. The effect of the hydrophobic property was also examined by changing the number of Phe residues. The dispersion of CNTs in water was estimated by means of UV-Vis absorption spectroscopy and TEM.

For dispersion of CNTs, each peptide was dissolved in water (about 0.5%) and CNT (1 mg) was added. After sonication, the obtained suspension was centrifuged, and then the supernatant was used for all experimental analyses. The UV-Vis spectra of the supernatants showed that the designed peptides can disperse CNTs in water and almost of CNTs exist as the bundled structure. The formation of the CNT-bundle was also confirmed by TEM images. These results demonstrated that amphiphilic linear oligopeptides can disperse CNTs in aqueous solutions as well as sodium dodecyl sulfate [1], cholic acid derivatives [2], DNA [3,4], polymers [5], and polypeptides [6,7]. We will discuss the effect of the amphiphilic properties of the oligopepttides on the dispersion of CNTs.

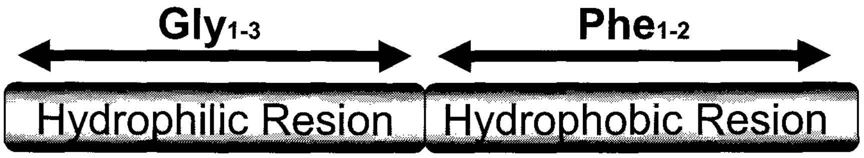

Fig. 1. Schematic representation of amphiphilic linear oligopeptides.

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2P-32

Effect of Surfactant Concentration on Length Distribution of Individually Dispersed Single-Walled Carbon Nanotubes

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Using appropriate surfactants, single-walled carbon nanotubes (SWCNTs) have been successfully debundled to individually dispersed tubes by ultrasonication methods. However, a major problem remains in the fact that most SWCNTs in the individually dispersed suspensions are shortened to the length less than several hundred nm [1].

In this study, to control the length of individual SWCNTs, effect of surfactant concentration on length distribution of individually dispersed SWCNTs was investigated by using surfactant sodium cholate [2]. SWCNTs produced by the HiPco process in purified form were dispersed in two kinds of aqueous sodium cholate solutions (10 and 40 mg/mL). The suspensions were ultrasonicated at a power level of 10W for 1 h by Branson Sonifier 450D and centrifuged at 21,800g for 3 h. The absorption spectra of the supernatant suspensions were measured using a UV-vis spectrophotometer. As shown in fig.1, both suspensions show similar spectra which are assumed to result from those dominated by individual tubes. Also the suspensions were spin-coated on cleaved mica substrates, and AFM images were acquired in air. As shown in fig.2, a clear difference of the average tube length is observed between (a) and (b). We estimated the length distribution of the tubes from Fig.2. As shown in fig.3, when the surfactant concentration is 40 mg/mL, many longer tubes than 1000 nm are observed.

These results indicate that an excess amount of the surfactant sodium cholate is effective to protect individual SWCNTs from breakage.

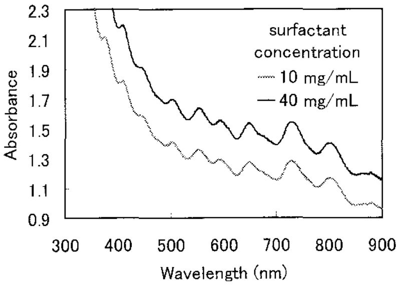

Fig.1. Absorption spectra of purified SWCNTs by HiPco process.

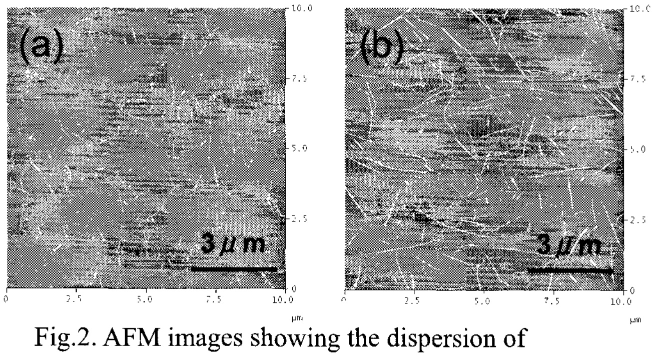

Fig.2. AFM images showing the dispersion of SWCNTs in aqueous sodium cholate solutions. Surfactant concentration : (a)10mg/mL, (b)40mg/mL.

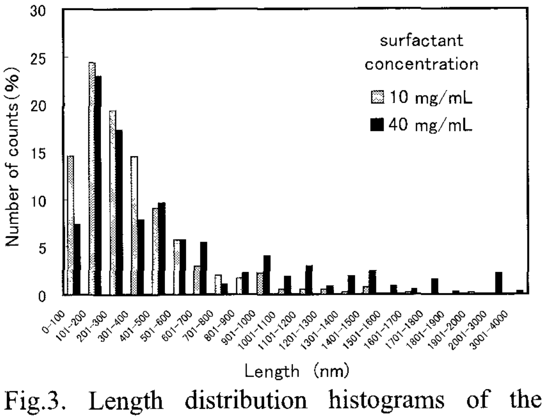

Fig.3. Length distribution histograms of the individually dispersed tubes estimated from fig.2.

Acknowledgement: We would like to thank Prof. H. Shinohara and Mr. M. Shiraishi of Nagoya University for their help and useful discussions to start this work.

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2P-33

New preparation method of carbon nanotube film for Photoluminescence Spectroscopy

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Photoluminescence (PL) spectroscopy has been developed as important technique for the characterization of semiconducting single-walled carbon nanotubes (SWNT). The dried film of DNA-wrapped SWNT hybrids was well characterized by using resonant Raman spectroscopy (RRS) and photoluminescence (PL) experiments [1]. Such stable solid-film of SWNT-polymer complex is good reference material for PL spectroscopy.

Carboxymethylcellulose (CMC) is known as a dispersion agent for SWNT [2]. We newly developed the thick film of SWNT-CMC complex. HiPco SWNT (Carbon Nanotechnologies, Inc.) was dispersed into the CMC aqueous solution of high concentration (2 wt %) by ultrasonic homogenizer (600 W). This dispersion liquid of SWNT-CMC complex was filtered using a filter of pore size 0.2μm for purification. Caused by high viscosity (~25mPa·s) of the CMC solution, we didn't use the conventional fractionation procedure by ultra-centrifugation with D_2O[3]. This fraction was dried into the film of the thickness 80μm on a metal plate gently heated under 100℃. We note that the elasticity of the film has increased by the filtration.

PL spectrum for SWNT-CMC complex in the film was similar to the results reported by Minami et al. [3]. These results show that the filtration for the extraction of the SWNT-CMC complex from the SWNTs dispersion liquid of high viscosity is effective technique for the preparation of the film for PL spectroscopy. The thin film on a quarts plate from the dispersion liquid of SWNT-CMC complex was also prepared by spin-coating for single-nanotube Raman spectroscopy. A number of the resonant Raman spectra of SWNT-CMC hybrids with a single RBM band were collected by micro Raman mapping. The laser excitation wavelength was 632.8nm. In the E22 region of semiconducting nanotubes, the RBM frequencies of the SWNT-CMC hybrids well corresponded to the results of sodium dodecyl sulfate (SDS) suspended SWNTs [3] by the difference of $2cm^{-1}$.

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2P-34

Light-harvesting function of carotenoid inside single wall carbon nanotubes

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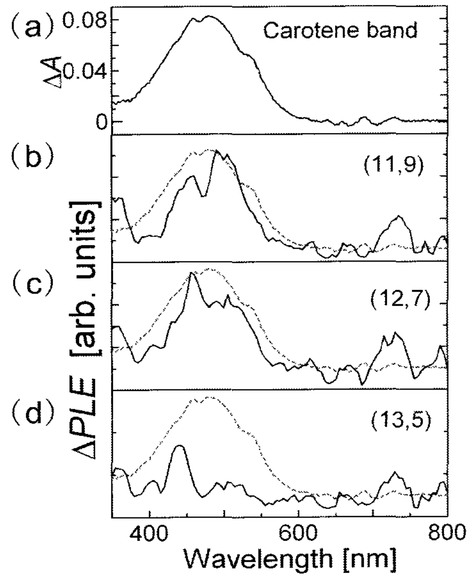
Abstract: Single wall carbon nanotubes (SWCNTs) are attractive components for nano-dimensional optoelectronic devices. Recently, the efficient generation and detection of light by a single SWCNT have been demonstrated. However, the spectral range of these unique devices is limited by the specific density of the states of semiconducting SWCNTs. Controllable modification of this spectral range is crucial for device application. There are two strategies to modify the optical properties of SWCNTs: one is to attach molecules outside the tube, the other is to encapsulate them inside the tube. It is inevitable to cause undesirable side effect by chemical reaction during the attachment of molecules. Thus the latter is a more gentle and elegant strategy. Carotenoids (Car) are very important natural pigments. They exhibit a light-harvesting function in photosynthetic pigment-protein complexes. Car absorbs light-energy where bacteriochlorophylls (Bchls) have a low extinction coefficient, and energy transfer from Car to Bchls is important for the efficient usage of solar light in photosynthesis. One might expect that if Car were encapsulated inside SWCNTs the similar light-harvesting function by encapsulated Car would occur. We investigated this possibility. In this study, β-carotene, a carotenoid, is encapsulated inside SWCNTs (We refer to the complexes produced in this fashion as Car@SWCNTs). We have clarified the detail structure of encapsulated β-carotene using X-ray diffraction, the polarization dependence of the optical absorption spectra, and Raman spectroscopy. The photoluminescence (PL) spectra revealed efficient energy transfer from the excited states of β-carotene to the SWCNTs. This novel observation will open the door for the fine-tuning, via the encapsulation of various molecules, of the optical properties of SWCNTs for numerous optoelectronic applications.



(a) Difference absorption spectrum ΔA between Car@SWCNT and SWCNT revealing the Carotene band. (b). (c) and (d) indicate the difference excitation spectra ΔPLE between Car@SWCNT and SWCNT for the (11,9), (12,7), and (13.5) tubes, respectively. The Carotene band is also shown with the dotted line for comparison. These figures clearly indicate the energy transfer from the excited states of Car to SWCNT.

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2P-35

NMR Study of Water Confined in SWNTs

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Single-wall carbon nanotubes (SWNTs) encapsulate many kinds of materials in their quasi-one-dimensional cavities with a typical diameter of one nanometer. Materials confined in such small cavities are expected to show novel features which cannot be observed in bulk materials. Water is one of such molecules in spite of a hydrophobic nature of the SWNT wall. The previous X-ray diffraction measurements have confirmed that water inside SWNT undergoes structural transitions from a "liquid" like state to "ice-nanotube; ice-NT" with lowering temperatures [1]. We have studied the molecular motions and proton dynamics of water inside SWNT by means of ^{1}H and ^{2}H NMR in a temperature range from 100 to 300 K across the ice-NT formation temperature, T_C. Above T_C, the motionally narrowed NMR spectra are observed due to the mobile water molecules. This indicates that water inside SWNTs is in a liquid state where the translational and rotational motions of water molecules are fast on the NMR time scale of $\sim 10^{-5}$ s. However, with lowering temperatures from 300 K, the molecular rotation slightly deviates from the complete isotropic rotation. This phenomenon was explained based on the existence of a preferential orientation of water molecules even in the liquid state. Below 220 K, we have observed the gradual decrease in ^{2}H NMR intensity according to the formation of the ordered ices, heptagonal and octagonal ice-NTs. All the protons in the ordered ices are found to be fixed at around each hydrogen bond or atomic site at the NMR time scale below around 120 K.

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2P-36

Chemical Modification of Carbon Nanohorns by Microwave

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High purity and higher order structures of carbon nanohorns (CNHs) are attractive for applications in fuel cells and drug delivery. Because CNH surfaces are made of single-walled carbon nanotubes, however, the surface properties of CNHs give rise to the same problems facing the nanotube applications. One of the problems is poor wettability. The surface of CNHs needs to be modified so that it wets better against common solvents and other materials. Unlike nanotubes where many chemical modifications have been reported, oxidation seems to be the only modification performed on CNHs so far. The oxidized CNHs wet better and have larger surface areas. Technically, CNHs have been oxidized by either treating with strong acids or heating in air. The acid treatment necessarily leaves unwanted acids behind and the heat treatment requires careful temperature controls. We have reported that carbon nanotubes are efficiently modified by using microwave radiation. Here, we examine if the same microwave technique can be applied to modification of CNHs.

As a model reaction, oxidation of CNHs in air was examined. A small amount of CNHs in a glass tube was placed in a microwave reactor (2455 MHz). The sample was irradiated with microwave of a controlled power for a certain time. A degree of oxidation was estimated by the dispersed amount in tetrahydrofuran. It was also examined by X-ray photoelectron spectroscopy. Both results indicate that only a small irradiance is enough to oxidize CNHs. We also used the microwave chemistry to attach Pt nanoparticles on CNHs. These studies demonstrate that the microwave irradiation is a highly efficient method for chemical modification that produces no unwanted chemicals, requires low power, and takes only a very short time.

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2P-37

Production of Hydrogen by Direct Decomposition of Methane using arc SWNHs

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Direct decomposition of methane ($CH_4 \rightarrow C+2H_2$) using carbon catalytic system is much of interest as a highly environment-friendly method for the production of high purity hydrogen due to absence of CO_x as byproducts. In previous research, SWNHs (by laser ablation and arc discharge) were used for catalyst of direct decomposition, and it was known that the lifetime of catalytic activity of SWNH by arc discharge is longer than that by laser ablation, and the activity of SWNH by arc discharge is larger than SWNH by laser ablation. So in this study, the decomposition of methane using several arc SWNHs was examined.

The decomposition of methane was examined at 1173K.

As seen in Fig.1, the catalytic activity of arc SWNHs depends on the arc discharge atmosphere. And the lifetime of SWNH by arc discharge reachs about 1week.

And It's also suggested that the activity of arc SWNHs is strongly concerned to the agglomerate size of SWNH and concentration of unpaired electrons in SWNH structure.

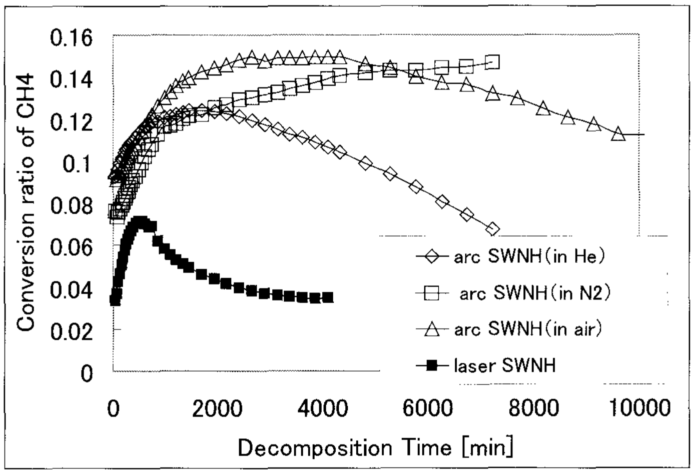

Fig.1 Catalytic Activity of SWNHs, on decomposition of methane (W/F=0.31 g-cat.h/mol, 1173 K)

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2P-38

Origin of graphite flakes including in SWNH sample prepared by pulsed arc discharge

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Single-wall carbon nanohorn aggregates (SWNHs) prepared by the methods based on pulsed arc discharge [1] and laser ablation [2] have a unique structure like a sea urchin. In this study, we analyze the morphological and structural features of SWNHs, and also impurity phase materials including in the as-prepared sample of SWNHs by the pulsed arc discharge. Morphological characteristic of arc-driven SWNHs is representative of the small diameters that are approaching to ~50 nm. This is a unique characteristic of arc-driven SWNHs. However, the collected sample includes both SWNHs and graphite flakes. Recently, we conducted pre-heating of carbon rod before arc-burning, and then prepared the sample. During the pre-heating, the smoke was given out from the rod, and small amount of soot (soot A) settled on the bottom of the chamber. Next, we conducted the arc-burning of pre-heated carbon rod and gathered the soot attached on the sidewall of the chamber (soot B). TGA results are in Fig.1, where the top TGA-trace was recorded for soot A and the bottom was for soot B. From these results, we can identify that the soot A mainly consists of graphite flakes, and soot B of SWNHs. We think that the graphite flakes were prepared during the pre-heating, and they were peeled off from the surface of the rod. Details of our experimental results will be described in the meeting.

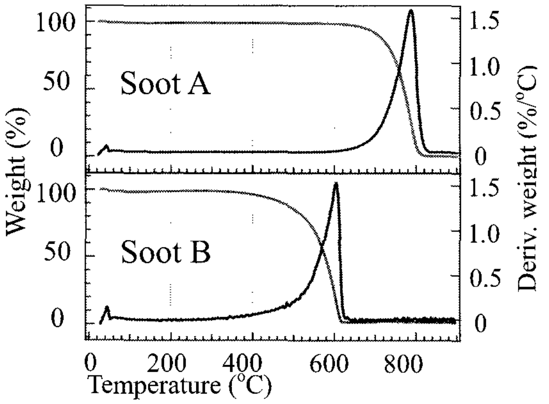

Fig. 1. TGA traces of soot A (top) and soot B (bottom)

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2P-39

Optimum oxidation condition to open holes on single-wall carbon nanohorns for CDDP incorporation and release

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We have been studying applications of single-wall carbon nanohorns (SWNHs) to drug delivery systems (DDS), and previously showed the incorporation of cisplatin (CDDP), anticancer drug, into SWNHs and the release of CDDP from SWNHs in solutions [1]. The quantity of CDDP released from CDDP@NHh and CDDP@NHox was 70% and 15%, respectively [2]. Here, NHh denotes SWNHs having holes with hydrogen-terminated edges [3], and NHox denotes those having holes with oxygen-containing functional groups (NHox). The small quantity, 15%, of CDDP released from NHox was caused by the sodium-plug effect [2]. Since dispersion of NHox in aqueous solutions is better than that of NHh, and it would be enhanced by the chemical modification of the hole edges, NHox is more preferable than NHh for the biological applications. To increase the releasable quantity of CDDP from NHox in phosphate buffered saline (PBS), we compensated for the sodium plug effect by enlarging the hole sizes without sacrificing the large incorporation quantity and slow release rate.

To enlarge the hole sizes of NHox precisely, we applied the slow combustion, in which temperature increased at 1°C/min in dry air up to a target temperature (T(target) = 450 ~ 580°C) and cooled down naturally [4]. CDDP was incorporated into these NHox using the nanoprecipitation method [1]. The quantities of incorporated and released CDDP were estimated from atomic absorption spectra. We also measured X-ray diffraction to confirm that there was no non-incorporated CDDP (crystal) outside NHox.

We found that the optimum T(target) was 500°C. CDDP@NHox(500°C) had the least amount of CDDP crystals located outside NHox, and the incorporated-CDDP quantity was 12 wt %. CDDP could be slowly released from NHox(500°C) in PBS, and about 80% of CDDP was released in 48 hours.

Acknowledgement: We thank Dr. T. Azami and Dr. D. Kasuya for preparing single-wall carbon nanohorns.

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2P-40

Size Effect of Nanowindows on Incorporation and Release of C_{60} in/from Single-Wall Carbon Nanohorns

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The sizes and numbers of nanowindows in single-wall carbon nanohorns (SWNH) can be controlled by the heating temperature and period in dry air, which was reported previously [1]. In this study, the relations of nanowindows' sizes and incorporation and release of C_{60} in/from SWNHs were investigated.

The SWNHs were oxidized in flowing air with a temperature rising speed of 1°C/min from room temperature to a target temperature (Ttg) of 400, 450, 475, 500, 525, 550 and 575 °C [1], which we denote as NHox. 0.2 mg of C_{60} per 1 g of NHox was incorporated in NHox by the nano-precipitation method [2]. The quantities of C_{60} incorporated in NHox (C_{60}@NHox) were analyzed with thermogravimetric (TG) and x-ray diffraction (XRD) measurements. C_{60}@NHox without any C_{60}-crystal contamination was obtained when Ttg was in a range of 475 and 550°C, and the incorporated-C_{60} quantity abruptly increased from 475 to 525 °C of Ttg, though their pore volumes measured with liquid nitrogen did not change greatly. This indicates that the holes with sizes of C_{60} increased in these Ttg ranges.

The release of the incorporated C_{60} was also examined. 2 mg of C_{60}@NHox were immersed in 300ml of toluene/ethanol (volume ratio, 8:2) solvent, and measured their UV/vis absorption spectra. The amounts of C_{60} released from C_{60}@NHox (Ttg=475-550°C) after immersing in toluene/ethanol for about 1 day increased from 50 to 80% as the Ttg increased from 475 to 550°C. The EELS analysis indicated that C_{60} remained near the core of NHox aggregates.

The release rates of C_{60} from C_{60}@NHox (Ttg=475~550°C) were fast for Ttg of 550°C and slow for 500 and 525°C, suggesting that the size of holes also influenced the release rate of C_{60}. When Ttg were 400, 450, and 575 °C, the release rates were extremely high due to the C_{60} crystals located outside of NHox.

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2P-41

Preparation, Purification, Characterization and Cytotoxicity of Water-soluble, Transition-metal Free Carbon Nanotube Aggregates

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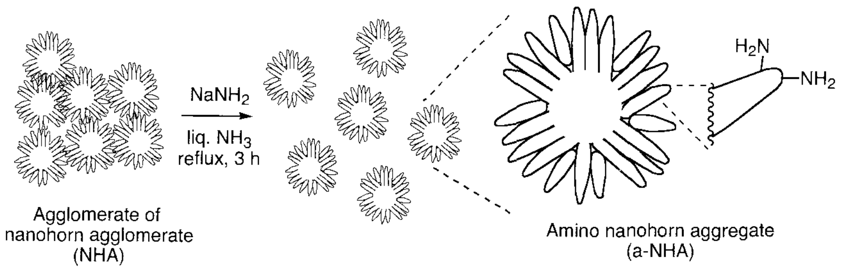
Risk assessment of carbon materials, inter alia, carbon nanotubes has surfaced as an important subject of nanomaterials research, which has however been hampered by the lack of characterization of sample materials. In this study, we have prepared water-soluble and metal-free carbon nanotube aggregate using carbon nanohorn aggregate and evaluated its cytotoxic effects.

We first prepared water-soluble carbon nanohorn aggregates by the reaction with sodium amide. Thus obtained amino carbon nanohorn aggregates were soluble in water up to 1 mg/mL. Dynamic laser light scattering studies on the aqueous solution showed that the solution contains isolated particles of ~1 × 10^2 nm.



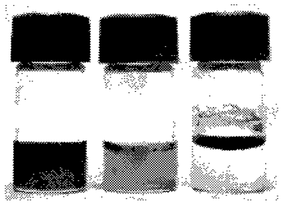


Figure. Aqueous solution of amino nanohorn aggregate. The concentration is 0.2 mg/mL, 0.02 mg/mL (left and middle, respectively). The right vial is untreated nanohorn aggregate in water.

With the physicochemical data in hand, we evaluated the toxic effect of carbon nanohorn on the mammalian cells. The amino nanohorn aggregates did not show significant cytotoxicity: The cytotoxicity was 1/10 of quartz micro-particles weight-wise. We, however, found that the particles were persistently taken up by the cells, which showed that certain care should be paid for the long-term biological effects.

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2P-42

Third-order Nonlinear Optical Response in Individual Double-Walled Carbon Nanotubes

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In double-walled carbon nanotubes (DWNTs), interactions between inner and outer tubes may modify optical transitions and nonlinear optical properties. We have reported the resonant behavior of nonlinear optical response and the ultrafast carrier relaxation [1]. In this presentation, we report on detailed studies of absorption spectra and nonlinear optical susceptibilities $\chi^{(3)}$ of DWNTs in comparison with single-walled carbon nanotubes (SWNTs).

DWNTs were produced by a chemical vapor deposition method using Fe nanoparticles and MgO powder as catalysts. DWNTs (SWNTs) were dispersed in D_2O-sodium dodecylbenzene sulfonate (SDBS) to obtain individual nanotubes. We carried out pump-probe measurements using a 150 fs-width pump pulse with the photon energy of 3.12 eV and a white continuum probe pulse.

Figure 1 shows absorption spectra of DWNTs (solid curve) and SWNTs (dashed curve) in D_2O/SDBS in the spectral range of 0.80–1.35 eV. Both spectra indicate similar structures corresponding to different diameters and chiral angles, and the absorption peaks observed for DWNTs are ascribed to the inner tubes. Small red shifts (1–9 meV) are observed in DWNTs compared with SWNTs, which suggests the existence of the inter-wall interaction in DWNTs. The figure of merit $\mathrm{Im}\chi^{(3)}/\alpha$ (α: absorption coefficient) is $-3.5\mathrm{x}10^{-14}$ esu cm for the (10,2) tube in DWNTs, and it is $-1.4\mathrm{x}10^{-14}$ esu cm for the same specific tube in SWNTs. Therefore, we have found that the optical nonlinearity in the E_{11} transitions for DWNTs is enhanced by a factor of ~2 compared with SWNTs.

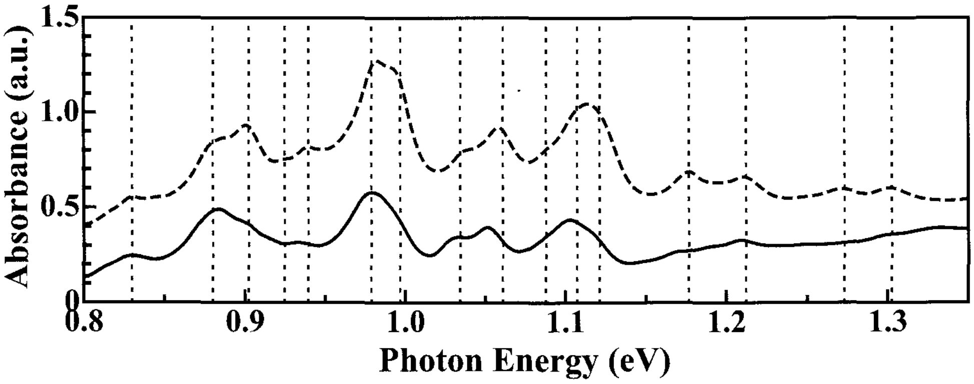

Fig. 1 Absorption spectra of DWNTs (solid curve) and SWNTs (dashed curve) in D_2O/SDBS

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2P-43

Diameter Dependence of Nonlinear Optical Susceptibilities in Individual Single-Walled Carbon Nanotubes

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We have recently reported that the third-order nonlinear optical susceptibility $\chi^{(3)}$ exhibits the resonant enhancement at the optical transitions between the valence and conduction bands in single-walled carbon nanotubes (SWNTs) thin films[1]. In the thin films, however, SWNTs form parallel bundles or ropes, and this bundling perturbs the electronic structure of the tubes. In this presentation, we report on the dependence of $\chi^{(3)}$ on the diameter/chirality in individually suspended SWNTs in solution.

HiPco (high-pressure CO conversion)-SWNTs were dispersed in D_2O-sodium dodecyl sulfate (SDS) to obtain individual nanotubes, each encased in a cylindrical micelle. Pump-probe measurements were made using an amplified Ti:sapphire laser system with the pump photon energy of 3.12 eV and the pulse duration of 150 fs. Values of Im $\chi^{(3)}$ in the nondegenerate configuration were measured in the spectral range of 0.85–3.00 eV.

Figure 1 shows absorption and $\chi^{(3)}$ spectra in the range of 0.85–1.40 eV. Absorption spectrum indicates sharp structures corresponding to different diameters and chiral angles of semiconducting nanotubes. Each optical transition was assigned to a specific (*n*,*m*) nanotube. The nonlinear susceptibility (closed circles) exhibits also a peak at each optical transition, indicating the resonant enhancement at the exciton peak.

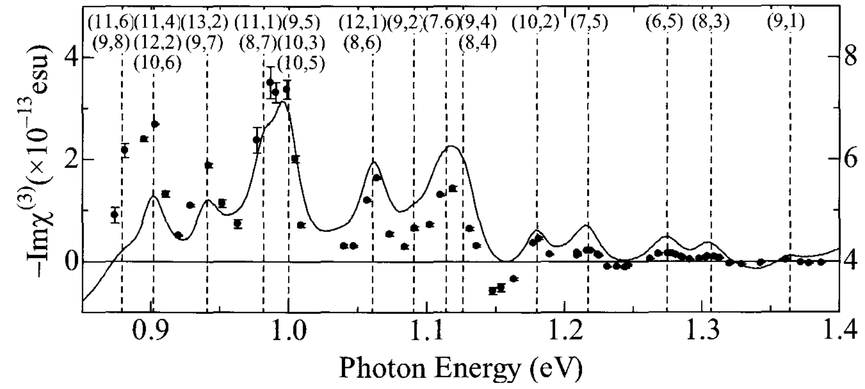

Fig. 1 Absorption and Im $\chi^{(3)}$ spectra of SWNTs in D_2O/SDS

The diameter (*D*) dependence of Im $\chi^{(3)}$ in semiconducting SWNTs was also investigated utilizing the assignment of the optical transitions in the absorption spectra. The figure of merit Im $\chi^{(3)}/\alpha$ (α: absorption coefficient) depends on $D^{6.1\pm0.9}$, and consequently the band gap dependence is -6.1 ± 0.9. We will discuss characteristic features of the nonlinear optical response in the 1D system.

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2P-44

Optical pH Response of Micelle-encapsulated and Polymer-wrapped Single-Wall Carbon Nanotubes

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It is known that optical properties of single-wall carbon nanotubes (SWNTs) are sensitive to their environment such as temperature or pH [1,2]. We investigated pH effect on optical characteristics of SWNTs dispersions. Typical surfactants such as sodium dodecylsulfate (SDS, anionic) and n-dodecyltrimethylammonium bromide (DTAB,cationic) and some polysaccharides such as carboxymethylcellulose (CMC) and chitosan with different charge features were used as dispersion agents. The spectroscopic properties of dispersed SWNTs prepared with these agents were probed by means of UV-vis-NIR absorption, NIR photoluminescence and Raman scattering under various pH condition.

The interband optical transitions originated from van Hove singularities were dependent on dispersion agent species and pH. The absorption peaks in the first semiconductive band range disappeared with decreasing pH in the case of SDS-SWNTs dispersion, whereas a small decrease in the peaks was observed in the case of DTAB. On the other hand, the CMC- and Chitosan-SWNTs dispersions did not show peak bleaching at low pH. The foregoing results implies that the discrepancy of the bleaching of interband transition induced by protonation between the surfactants and polysaccharides comes from the difference in the structural characteristics, that is micelle-like for the surfactants and wrapping for the polysaccharides.

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2P-45

Far-infrared absorption peak in single-walled carbon nanotubes and its correlation with tube lengths

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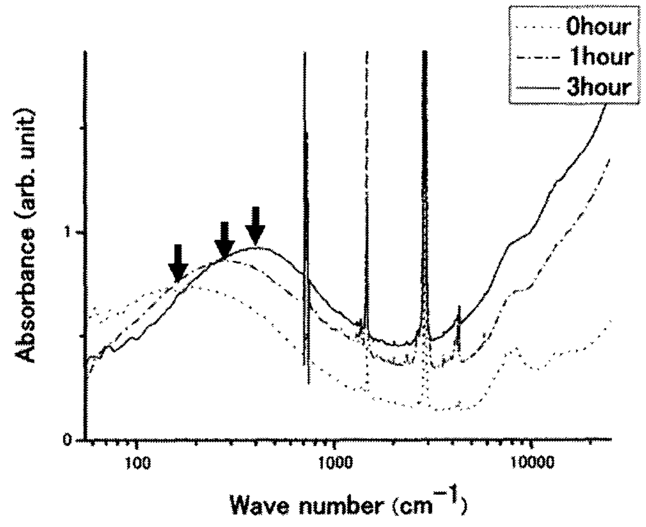
Recently, we have observed that the free carrier absorption in highly oriented films of single-walled carbon nanotubes (SWNTs) forms a well defined peak structure in the far-infrared region, which is attributable to the plasmon resonance of free carriers in the metallic tubes, presumably due to the finiteness in tube lengths [1]. This finding provides a new opportunity to determine the average length of SWNTs from the far-infrared (FIR) peak position. In this paper, we report our effort to prepare SWNTs with variable lengths and to establish a correlation between the length and the FIR peak position.

We dispersed the HipCo tubes in a mixture of concentrated sulfuric and nitric acids (3:1, 98% and 70%, respectively), and sonicated at room temperature [2]. The statistical length distribution using the AFM pictures revealed that the average lengths of untreated and three-hour sonicated tubes were 1.5 μm and 0.75 μm, respectively, indicating that the length is tuned by the sonication time in acid as expected. These nanotubes were mixed with in polyethylene, and stretched at elevated temperatures. Reasonable degree of alignment was obtained as in the previous report [1]. Figure shows the absorption spectra of untreated, one-hour treated, and three-hour treated HipCo tubes for polarization parallel to the stretching direction. The peak structure was observed in all samples, in fair agreement with the previous result [1]. Importantly, the peak position is moved to higher energy from 200 cm^{-1} to 400 cm^{-1}, being suggestive enough of the length dependence of the FIR peak position.



Figure

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2P-46

Dispersion Effect on high Field Magneto-optical Absorption Properties of Single-walled Carbon Nanotubes

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Single-walled carbon nanotubes (SWNTs) have cylindrical structure made of a graphene sheet, which leads to theoretical predictions of their novel properties, including the emergence of the Aharonov-Bohm (AB) effect when threaded with a magnetic flux. [1] Apart from the AB effect observed in nanometer-sized structures of semiconductors, the AB effect modifies the band structure of an SWNT itself. The modification of the first-subband gaps in semiconducting SWNTs has been demonstrated through magneto-optical strudies in magnetic fields to 45 T by Zaric et al. [2] We have investigated high field magneto-absorption properties of single-walled carbon nanotubes in the visible light region where absorption peaks originated from the second-subband gaps of semiconducting SWNTs and the first-subband gaps in metallic SWNTs, to 120 T using a single-turn coil system. In stretch-aligned SWNT/sodium dodecyl sulfate/gelatin films[3], an absorption peak corresponding to the first subband gap of (13, 1) SWNTs was observed to broaden and split into two peaks with applying magnetic fields in parallel to the alignment. The split width was 0.10 eV, which agrees quantitatively with the Ajiki-Ando theory[1]. By the application of magnetic fields in perpendicular to the alignment, no broadening was observed even at 120 T. These results suggest that the splitting observed in the former case was originated from the AB effect. However, those splittings were not observed to 120 T in stretch-aligned SWNT/ carboxymethylcellulose/gelatin films. This discrepancy suggests that interaction between dispersing agents and SWNTs could affect the manifestation of the AB effect.

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2P-47

The double resonance Raman intensity of carbon nanotubes and graphite

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In this paper, we calculate the double resonance Raman intensity (DRRI) of single wall carbon nanotubes (SWNTs) and graphite. In SWNTs, we consider such as the intermediate frequency modes (IFMs) which have the step-like dispersive peaks [1]. The negatively dispersive IFMs are considered the combination of the creation of an optic phonon and the annihilation of an acoustic phonon, and the positively IFMs are considered of the creation of both an optic and an acoustic phonon. In graphite, we calculate DRRI of the disorder-induced D-band as a function of the crystallite size L_a of the nanographite flake and as a function of the laser energy E_{laser}. Cançado *et al.* showed that the integrated intensity ratio I_D/I_G (I_D: D-band integrated intensity, I_G: G-Band integrated intensity) is proportional to E_{laser}^{-4} and L_a^{-1} [2]. The calculated results give I_D/I_G proportional to E_{laser}^{-4} and L_a^{-2} [3].

The double resonance Raman intensities and shifts are calculated by extended-tight-binding scheme [4,5]. The structure of spectra is understood by calculating electron-phonon and electron-photon matrix elements for possible combination of phonon modes and elastic scattering matrix elements. From the calculating results of DRRI of SWNTs and graphite, we determine the origin of IFMs and many other two phonon modes obtained in the experiment, the dependence of the chiral angle of DRRI of SWNTs and the excitation profile of Raman shifts.

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2P-48

Carbon Nanotube-Polyimide Composite Prepared through Water-Based Mixture of Nanotube and Polyamic Acid

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Composite materials of carbon nanotubes (CNT) and organic polymers are promising material forms for CNT applications. For preparing such materials, how to mix CNT into polymer matrixes is a key technology. Among the various mixing methods for CNT-polymer composites, the method using mixed solutions of CNT and polymers is becoming more promising because the dispersion techniques of CNT in solvents using strong ultrasonication with the aid of surfactant have been developed in these years. In such dispersion techniques water has been the most established solvent. However, the kinds of polymers are limited to water-soluble ones. This means most of major polymers are out of candidates because they are insoluble in water.

In this work, we extended the candidates of water-soluble polymers to polyimide, which is known as a super engineering plastic. Conventionally polyimides are not soluble in water in the final polyimide forms nor in the precursor polyamic acid (PAA) forms. In our approach we made a polyamic acid soluble in water by adding triethanolamine as shown in Fig. 1.[1]

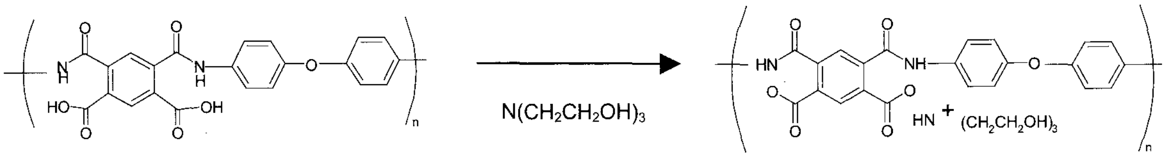

Fig. 1. Water-soluble PAA by addition of triethanolamine

CNT (CNI, X-grade) are sonicated in water with addition of a nonionic surfactant Triton X-100 in a strong ultrasonicator (Tosho Denki, Nano-Raptor), and mixed with the PAA water solution. The mixed solution was then cast on flat glass and heat-cured for imide conversion. Surface resistivity of the so-prepared films showed a drastic change at around 2 wt% concentration, indicating the formation of conductive networks by CNT.

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2P-49

Preparation and properties of liquid crystal-SWNT hybrid material

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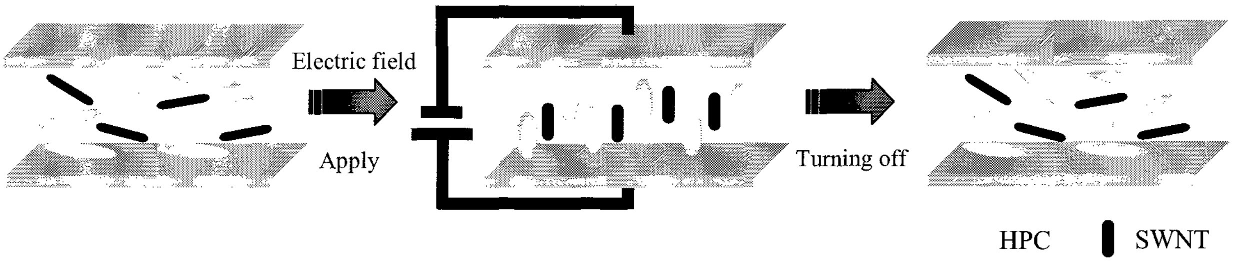
Single-Wall Carbon Nanotubes (SWNTs) are one-dimensional tubular carbon structures with different diameters and chiralities. Owing to their outstanding mechanical and electrical properties, many potential applications have been proposed. However, SWNTs bundled by van der Waals force between them are not dispersed in all solvents, which hinders their applications. Thus, we have investigated the novel dispersion and purification procedures of SWNTs using biopolymers1).

The liquid crystal (LC) exhibits very unique properties of crystal-like molecular alignment and liquid-like fluidity. In addition, the reorientation of LC is possible to be induced by applied electric or magnetic fields.

In this study, a new hybrid material composed of lyotropic LC, hydroxypropyl cellulose (HPC) and SWNTs dispersed with a biomaterial, such as carboxy methyl cellulose (CMC), was prepared.2) The effect of the electric field on the characterization of the LC-SWNT hybrid material was investigated by means of NIR-photoluminescence and Raman spectra. These results showed the evidence that SWNTs are individually dispersed in the LC material, regardless of whether or not in the electric field. Further, the electric field induced the reorientation of LC molecules, which was accompanied with the orientation of SWNTs. Then, on turning off the electric field, the alignment of both the SWNTs and LC molecules was collapsed. Consequently, the LC-SWNT hybrid material showed the response to the electric field.



Scheme Alignment of liquid crystal-SWNT hybrid materials induced by the applied electric field.

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[2] H.Yajima et al, Patent Appl. No. 2006-053998

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2P-50

Preparation and properties of chitosan film containing dispersed SWNTs

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Recently, the field of tissue engineering has developed rapidly, with much efforts being concentrated on the controlled attachment of cells to the artificial scaffolds. Additionally, recent studies have reported that the proliferation and differentiation of cells on their scaffolds are influenced by the surface roughness of scaffold materials, and the electric, magnetic, or mechanical stimulation.

In this paper, to introduce the outstanding mechanical and electric properties of single carbon nanotubes (SWNTs) into the scaffold material, the polymer film containing SWNTs dispersed by using a biopolymer, chitosan, was prepared[1]. Changes of the film property including the orientation of SWNTs into it by the mechanical stimulation were investigated.

SWNTs samples used in this study were HiPco SWNTs. SWNTs were mixed with 2% chitosan acetic acid solution and then treated using an ultrasonic disruptor for 1h. The obtained SWNTs dispersions were ultracentrifuged at 160,000g to remove large SWNTs' bundles. The supernatant solution after ultracentrifugation treatment was dissolved in gelatin solution. The SWNT/chitosan/gelatin films were obtained by casting the solution on glass substrates. Their films were peeled off from the substrate and soaked in 70% ethanol. Subsequently, these films were stretched until draw ratio 2. UV-vis-NIR absorption and emission spectra showed that SWNTs in the film were oriented for stretched direction. Further, the polarized-light microscope observation revealed that the orientation of the polymer film itself is induced by the stretching. The foregoing results and AFM observation showed that the orientation of SWNTs and the surface roughness of the film were grown with increasing SWNTs content in the film.

[1]T.Takahashi et al *Chem.Lett.***11** (2005) 1516

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2P-51

Shape Engineerable Single Walled Carbon Nanotube Bulk Solid

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In addressing the scientific and technological advantages of macroscopic forms of carbon nanotubes (CNT), we present a rational and general method to fabricate a highly densely packed and aligned single walled carbon nanotube (SWNT) solid material by utilizing a liquid-induced collapse of millimeter-scale tall, vertically aligned SWNT forests [1]. Characterization reveals that this "zippering" process packs the individual tubes to near ideal spacing thus creating a bulk CNT material, which we call the "SWNT solid." The solid enhances the bulk physical properties, such as mass density and hardness while retaining the intrinsic properties of SWNTs, such as electrical conductivity, flexibility, and surface area. Furthermore, by controlling the fabrication process, it is possible to fabricate a wide variety of solid structures from aligned solid sheets to high aspect ratios as well as a completely new solid/as-grown hybrid material. These unique characters make the SWNT solid a valuable material as flexible, conducting, high surface area applications, such as supercapacitor electrodes and flexible heaters. Moreover, the hybrid material opens new avenues for the robust mechanical and/or electrical attachment of as-grown material for the scientific studies of the physical properties of the SWNT forest, such as its tribology, and its applications toward low-wear electrical connections. For these reasons, the SWNT solid promises to open new frontiers in within the carbon nanotube field.

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2P-52

Electron transfer through single-walled carbon nanotube sheet

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We demonstrated electron transfer (ET) through single-walled carbon nanotubes (SWNTs) between two different redox reaction sites. In Fig. A, a possible mechanism is summarized. SWNT is reduced by a reductant at the one site, and the reduced SWNT provide an electron to an acceptor reagent at the other site. When redox proteins are employed as the reduced reagent, this ET system could function as efficient micro-reactor. We can expect that the hydrophobic interaction of the protein surface with SWNTs would facilitate the ET from SWNT.

In this study, the ET on the as-grown SWNT sheet was surveyed by the absorption spectral change of the reagent (1). We selected dithionite and $NaBH_4$ for the reductants, because of their low reduction potentials (Fig. B left). The reagents we used are ferricyanide ($K_3[Fe^{3+}(CN)_6]$) and heme protein cytochrome *c* (cyt *c*) in order to compare their surface interactions. The reduction potentials are higher than those of SWNTs that are previously reported (Fig. B right) (2).

As shown in Fig. C, we dropped the reductants and the reagents separately on the random-aligned SWNT sheet (Fig. D). After pipetting the solutions for several minutes, we recorded absorption spectra. Ferricyanide was not reduced by the process. We consider that the inorganic salt would not adsorb onto the SWNT surface (Fig. F(a)). On the contrary, the peaks of ferrous cyt *c* (Fig. E(c)) were observed, suggesting the reduction of the heme iron. We suppose that the ET pathway would be constructed by the contact of the hydrophobic domain of cyt *c* (Fig. F(b)). Thus, it was found that this ET system could be utilized for efficient catalysis by redox proteins.

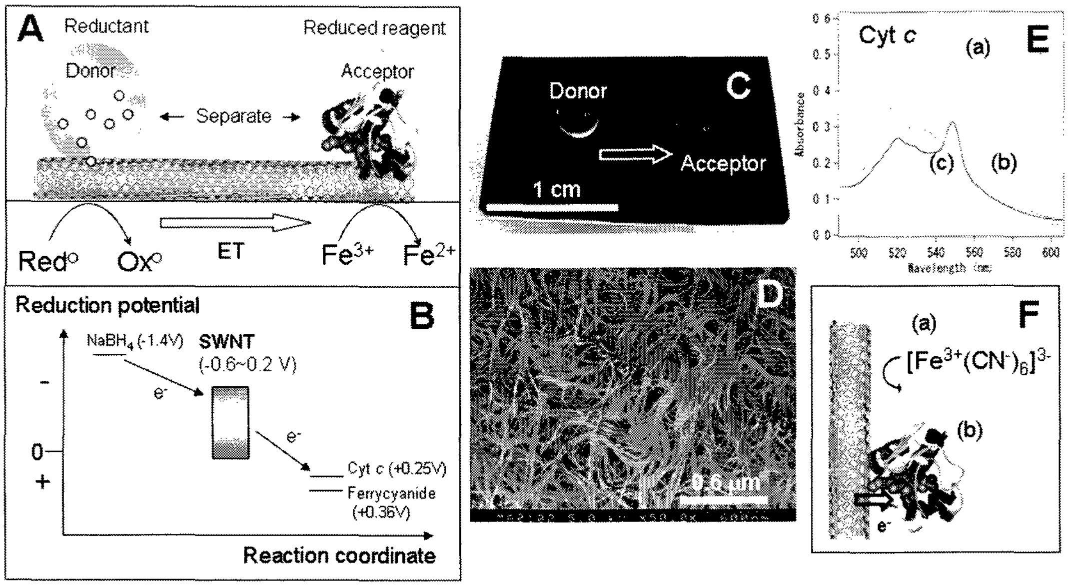

Figure (A) Schematic model of this ET system. (B) Reduction potentials of reductants, SWNT and the reagents. The reaction coordinate is the ET process through the system. (C) Experimental set up of the ET reaction from $NaBH_4$ to ferric cyt *c*. An arrow indicates the direction of ET. (D) SEM image of the SWNT sheet. The alignment of the SWNTs is random. (E) Absorption spectra of cyt *c*. (a) reduced, (b) oxidized, and (c) partially reduced on the sheet. (F) Schematic view of possible interactions of (a) ferricyanide and (b) cyt *c* on the sheet

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2P-53

Solvent Dependence of DC Electrodeposition of Carbon Nanotubes
- CNT Dielectric Constant -

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Applying DC electric field to the electrodes immersed in a carbon nanotube (CNT) dispersion in anhydrous solvents electrodeposites CNTs onto the anode surface. Prior to the electrodeposition, CNTs are treated in strong acids to afford a negative zeta-potential. So far, the following properties are known. (1) CNTs are strongly adhered to the anode surface. It requires scratching the anode to remove the CNTs. (2) All CNTs lie parallel to the anode surface, and form thin, straight bundles but not other forms of aggregates. (3) A trace amount of water in the dispersing solvents prohibits electrodeposition. (4) There is a high possibility that only semiconducting CNTs are deposited. DC electrophoresis moves CNTs toward the anode, but is not responsible for deposition. We speculate that van der Waals (VDW) interaction plays an important role in adhesion. In order to examine this hypothesis, CNTs were electrodeposited in various solvents and the results were analyzed by the Lifshitz theory.

The VDW interaction energies for pairs of colloidal bodies can be divided into a part that depends on geometry and another that depends on materials. The later is characterized by the Hamaker constant. According to the Lifshitz theory, the Hamaker constant is given by the differences of static dielectric constants of bodies and a medium as well as the dielectric permittivity of these materials at higher frequencies. If the contribution of the organic solvents at higher frequencies (i.e. absorbance) is much smaller than that of CNTs, the higher frequency term becomes independent of the solvent. In this case, the difference in VDW forces among various solvents is mainly determined by the static dielectric constants. The electrodeposited density was fitted by the Lifshitz theory and the dielectric constant of (semiconducting) CNTs was estimated.

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2P-54

Non-local 4-terminal Magnetoresistance Measurements using Single-walled Carbon Nanotubes

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Since Tsukagoshi et al. has reported magnetoresistance (MR) of multi-walled carbon nanotube (MWNT) in 1999 [1], carbon nanotubes (CNTs) attracts much attention as one of the pivotal molecules for novel molecular spin devices. However, in spite of many reports on MR in some molecular spin devices, it is still controversial that whether the observed MR was induced by magnetization reversal of electrodes or they were only spurious signals. To realize spin devices using CNTs, such a controversial problem should be solved, and we believe, so far, that this problem is ascribable to high contact resistance which can induce spurious signals between ferromagnetic electrodes.

A non-local 4-terminal MR measurement method, which provides highly reliable MR observation by bypassing above mentioned problems, has been originally proposed by Jedema *et al.* [2]. This method enables us to detect a difference of chemical potential of spin current (not electric current) between two electrodes because of decoupling of charge and spin, and we can bypass the problem of large contact resistance. Thus, we applied this method to our molecular spin-valve system, as follows.

Four ferromagnetic electrodes were deposited on SWNTs (Fig. 1). An electric current is injected from electrode 2 (el 2) to el 1. Whilst the charge current anisotropically flows from el 2 to el 1, spin current diffuses isotropically from el 2 to both el 1 and el 4. Hence, a voltage which corresponds to a difference of chemical potential of the spin current is generated. By applying a magnetic field (*B* in Fig.1), we can control the direction of magnetization of the electrodes (el 2 and el 3) because of a difference of coercive force in el 2 and el 3. As a result, el 3 can behave as a spin detector and the difference of the chemical potential of the spin current between el 3 and el 4 can be detected, which can be a direct proof of spin injection into the SWNTs. Fig. 2 shows the obtained result in this SWNT spin-valve, and a hysteresis of the resistance at around ±300 Oe was observed. The observed MR ratio was estimated to be about 3 % at 3.6 K. Detailed analyses will be implemented in the presentation.

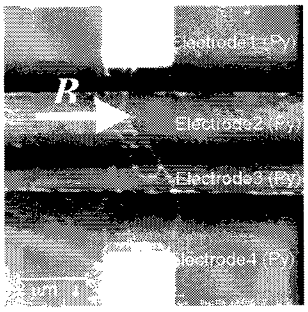

Fig. 1 An SEM image of a SWNT spin valve.

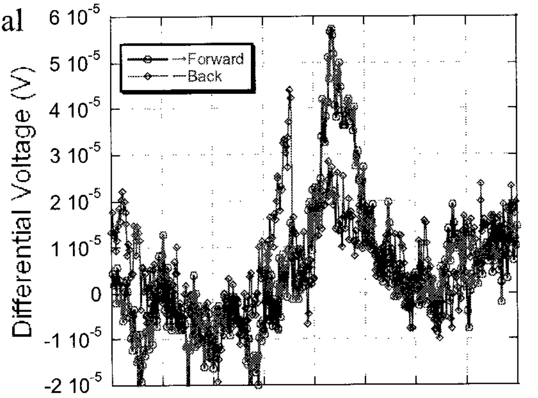

Fig. 2 An observed hysteresis in the spin valve at 3.6 K.

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2P-55

Formation of Secondary Thin Carbon Nanotubes on Thick Ones and Improvement in Field-Emission Characteristics

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The formation of many carbon nanotube (CNT) tips with small diameters on the surface of thick CNTs was investigated to improve the field-emission uniformity of a CNT emitter. A CNT layer was first grown on a metal substrate by thermal-chemical vapor deposition (CVD). CNTs in the layer were multiwalled nanotubes with diameters of 30-50 nm and formed a weblike network structure. A metal catalyst, iron, was then vacuum-deposited on the CNT layer, and secondary thin CNTs with diameters of 5-10 nm were formed from the catalyst particles attached to the surface of primary CNTs by thermal-CVD. The field emission from the low density CNT layer with the secondary CNTs showed an improvement in emission characteristics.

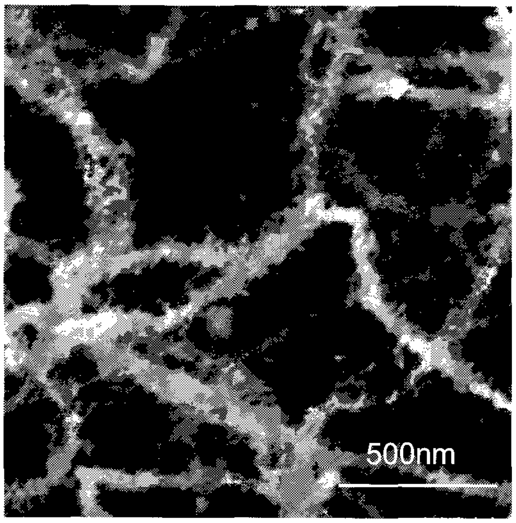

Fig.1 SEM images of CNT layer after second CVD with Fe catalyst deposition.

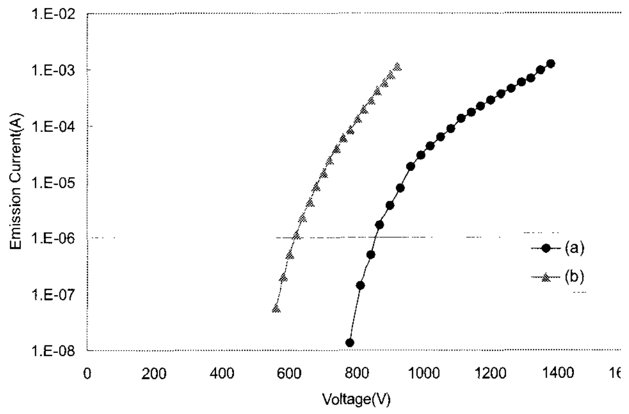

Fig.2 Field-emission characteristics of CNT layers. The spacing between the anode and CNT layer was 0.3 mm. The *I-V* curves for (a) high density CNT layer and (b) low density CNT layer, with secondary CNTs.

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2P-56

Development of Micro-focused X-ray Source with Carbon Nanotubes Field Emitter

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We have reported in the last Symposium about a micro-focused X-ray source with a carbon nanotube (CNT) field emitter and a simple electrostatic lens [1]. In this paper, we modified the electron optical system in order to improve a resolution of X-ray transmission image and penetrating power. As a focusing lens for electron beam emitted from CNT bundle field emitter, a new electrostatic lens of Butler type [2] was designed by taken into account a potential distributions and trajectories of electrons. Since a magnification of this lens was 1/5, a beam diameter on a Cu anode was expected a few micrometers. The maximum accelerating voltage of electron beam was increased up to 60 kV from 15 kV of before the modification. Figure 1 shows the X-ray transmission images of two LSIs with a polymer package taken at 23 kV. The fine structures, *e.g.*, the read flame pattern in Fig.(a) and the bonding wires with a diameter of 30 μ m in Fig.(b), were clearly resolved. It is suggested that the micro-focused X-ray source we developed is suitable for a high resolution X-ray radiography. This work has been supported by the Japanese Ministry of Education, Culture, Sports, Science and Technology for the Cooperation of Innovative Technology and Advanced Research in Evolution Area project, and for the foundation of Grant-in aid for Scientific Research (B), No. 18360023.

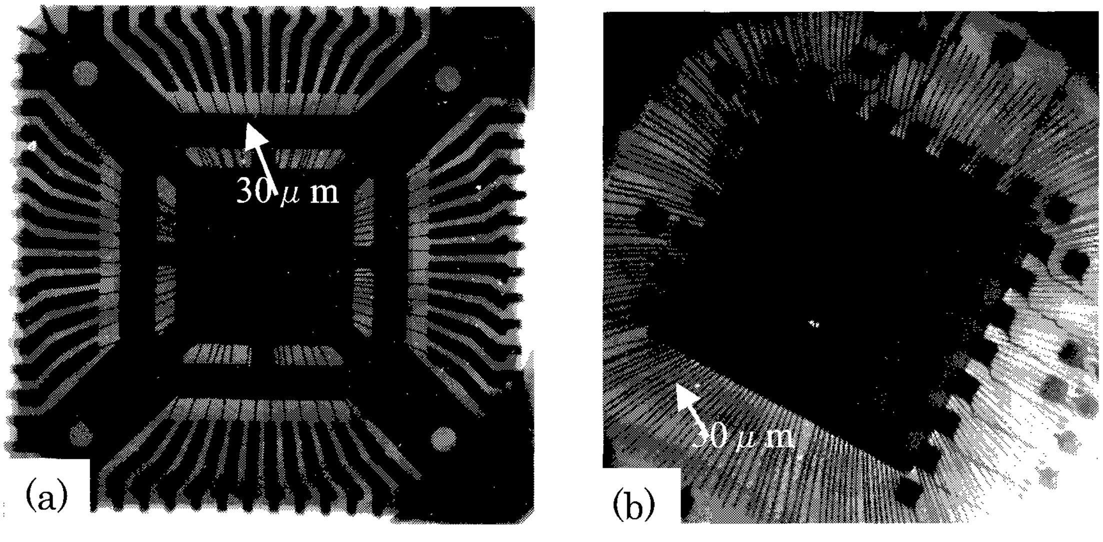

Fig. 1 X-ray transmission images of two LSIs with a polymer package taken at 23 kV

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2P-57

Development of compact FE-SEM equipped with carbon nanotubes bundle cathode

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FE-SEM equipped with carbon related material cathode such as carbon nanotubes and graphite nanoneedles have been reported by several authors [1]. We are developing a compact FE-SEM equipped with a multiwall carbon nanotubes (MWNTs) bundle cathode and a Butler electrostatic lens as a condenser lens. The preliminary results are reported in this paper. Figure 1 shows a schematic diagram of the compact FE-SEM. A MWNTs bundle cathode was produced by arc discharge in helium gas. A Butler lens consisted of an extraction and a focusing electrode was placed in front of the MWNTs bundle cathode. To obtain a fine probe beam, the electron beam passing through the Butler lens was focused by means of an objective lens made of a permanent magnet. The adoption of these two lenses brought about downsizing to our FE-SEM column, and a distance between cathode and sample stage was only 192mm. Figure 2 shows a SEM image of a Cu 200 mesh with 25μm line width taken at an acceleration voltage of 15kV. Whereas the order of base pressure was 10^{-5}Torr which was poor vacuum for field emission, lines of the Cu 200 mesh are perfectly resolved and a fiber-like object with ca. 2μm width indicated by an arrow can also be observed.

This work has been supported by the Japanese Ministry of Education, Culture, Sports, Science and Technology for the Cooperation of Innovative Technology and Advanced Research in Evolution Area Project, and for the foundation of Grant-in aid for Scientific Research (B), No. 18360023.

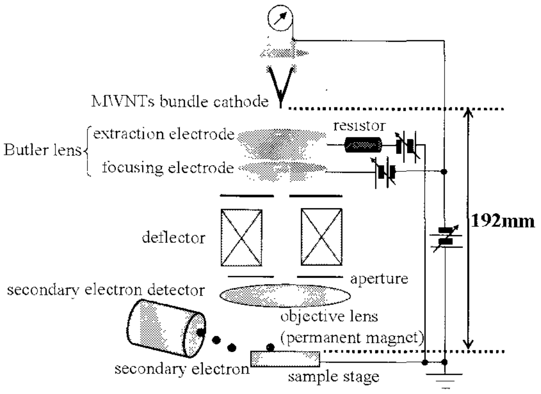

Fig. 1 Schematic diagram of our compact FE-SEM

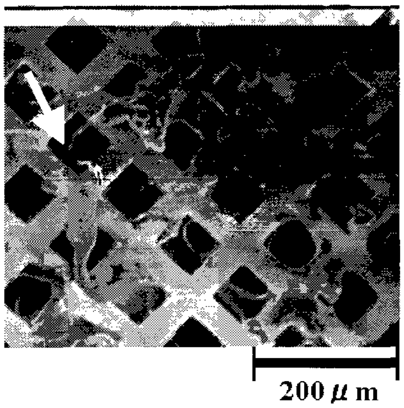

Fig. 2 SEM image of a Cu 200 mesh
Acceleration voltage: 15kV

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2P-58

Safety Evaluation of Fullerenes for Skin Application and Clinical Skin Lightning Effects of Fullerenes complex “Radical Sponge®”

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Basic safety testing results of Fullerenes (“BioFullerene®”, cosmetic grade) were reported [1]. Additional range of diverse safety studies of Fullerenes on the basis of Good Laboratory Practice (GLP: No.21, Mar/26, 1997), Standards for practical skin application and the succeeded clinical evaluation of Fullerenes complex (“Radical Sponge®”, water-soluble cosmetic ingredient) were carried out.

Primary Dermal Irritation Study: Fullerene was moistened with the propylene glycol, and it was exposed for 24 hour-occluded application) over the Japanese white rabbit skin. In the result, it is concluded that fullerene has no irritation potential under the condition. **14-Day Cumulative Skin Irritation Study**: 10w/v% fullerene suspended with propylene glycol was applied to rabbit skin once a day for 14 days. It is concluded fullerene induced no cumulative skin irritation. **Phototoxicity test**: When 25w/v% fullerene suspended with propylene glycol was applied and irradiated ultraviolet ray (UVA 11.2 J/cm^2) to guinea pigs, no contact phototoxicity was observed. **Adjuvant and Patch test**: 50 and 25w/v% fullerene suspended with propylene glycol were used for the induction treatments and challenge, respectively, using guinea pigs. Fullerene has no skin sensitization potential. **Adjuvant and Strip test**: On equal terms with Adjuvant and Patch test, added irradiation ultraviolet ray (UVA 11.2 J/cm^2). the results showed that fullerene was not considered to be skin photosensitization potential.

Clinical test: Fullerenes complex was applied to more than 30 patients for the evaluation of its skin lightning effects. The observation showed such as 94% of patients achieve fine and lighter skin tone after its 6 weeks application

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2P-59

Formation of Nitrogen Atom Encapsulated Fullerenes Using an Electron Cyclotron Resonance Discharge Plasma

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Fullerenes typified by C_{60} have hollow caged structure and can make compounds by trapping some atoms or molecules in the cages, which are called as endohedral fullerenes. Especially, the nitrogen atom encapsulated fullerene ($N@C_{60}$) has characteristic features as novel materials for quantum computer, and has been formed by using some methods [1,2]. However, $N@C_{60}$ formation efficiency is extremely low, and the $N@C_{60}$ formation mechanism has not been clarified in detail.

Here, the formation of $N@C_{60}$ is performed by using an electron cyclotron resonance (ECR) plasma as a nitrogen-ion source [3]. The nitrogen ions in the ECR plasma diffuse to a DC-voltage applied cupper substrate and are accelerated by an electric field in front of the substrate. C_{60} evaporated by an oven is deposited on the substrate. Thus, the nitrogen ions are continuously irradiated to the C_{60} thin film. Typical values of plasma density and electron temperature in a process region are 10^9 cm^{-3} and 0.5 eV, respectively.

The C_{60} thin film after nitrogen ion irradiation is analyzed by electron spin resonance (ESR), and indicates a very clear hyperfine-split electron paramagnetic resonance spectrum that seems to originate from $N@C_{60}$. It is found that the ratio of $N@C_{60}$ to C_{60} in the sample has a dependence on the energy of the irradiated ion and the optimum condition exists around the ion energy of 20-40 eV. The optimum ion energy for the $N@C_{60}$ formation is related to the energy barrier for kinetic penetration of the N atom through the fullerene framework, which has been estimated to be about 20 eV [4]. In addition, the ratio of $N@C_{60}$ to C_{60} can be improved by controlling an ion current flowing to the substrate, i.e., the amount of the irradiated nitrogen ions to the deposited C_{60} on the substrate. When the evaporated C_{60} is 600 mg per hour, the optimum ion current is found to be 6 mA.

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発表索引
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第３１回フラーレン・ナノチューブ総合シンポジウム
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営業品目

◎ 安定同位体 Si, S, V, Cr, Fe, Ni, Zn,---Pt, Hg, Tl など約 50 種類

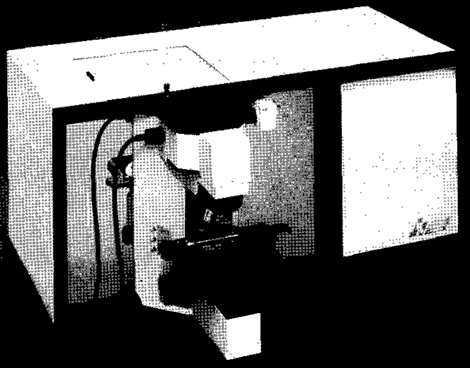
◎ ダイヤモンド粉末・その他の超硬材料

1. 爆発ダイヤモンド（DD）－黒鉛に爆薬の爆発による圧力をかけ、合成する。粒子は多結晶体で研磨に最適と言われている。
2. 超分散ダイヤモンド（UDD）－爆薬 TNT の分子中の炭素が爆発による高温・高圧下でダイヤモンドに変わったもの。粒径は30～50ナノのクラスターになっている。エレクトロニクス産業での高精度研磨・表面処理の用途が近年開発されている。
3. 静圧合成ダイヤモンド（工業用ダイヤモンド）－黒鉛に約5万気圧・1300℃以上の圧力をかけて合成したダイヤモンドを粉砕したもの。
4. その他研磨用ダイヤモンドペースト・BN・CBN など

◎フラーレン誘導体

No.3　水酸化フラーレン：$C60\ OH_{24}$
No.4　安定同位体置換フラーレン　C60：C60, 99%　C13,　20～30%
No.5　安定同位体置換フラーレン　C70：C70, 98%　C13,　20～30%
No.6　安定同位体置換フラーレン　C60 と C70 の混合物：　C13,　20～30%
No.9　フッ化フラーレン：$C60F_{36}$, 99%
No.10　高次フラーレン混合物：　C76, C78, C80, C84
No.16　メタフラーレンカルボン酸：
C60CHCOOH(1.2-methanbofullerenC60)-61-carboxylic acid
No.17 Bucky Fullerene – molecular hybrid C60 with Ferrocene:
$[\eta^5(C_5H_5)_2Fe]_2{*}C60$
No.18　Bucky Cobaltocene – ionic hybrid C60 with Cobaltocene:　$\eta^5(C_5H_5)_2Co{*}C60$
No.22　アミノカプロン酸 Na フラーレン
Type A: $C60HNH(CH_2)_3COONa$
Type B: $C60HNH(CH_2)_5COONa$
No.23　ビスマロン酸エチルフラーレン：$C60C(COOEt)_2$
No.24　ビスマロン酸ジエチルフラーレン：$C60[C(COOEt)_2]_2$
No.26　フラーレン・ブロマイド：$C60Br_{24}$
No.31　PCBM（mixture of isomeric 6,6-PhenylC71-butyl acid methyl esters）
〈For plastic solar cells〉
No.32　フッ化フラーレン：$C60\ F_{40}$

◎その他　翻訳〈英語・ドイツ語・フランス語・ロシア語など〉・技術調査




New

NANORUPTOR® ——バイオの技術をナノテクへ

密閉式超音波処理装置

実施例：燃料電池用触媒評価、カーボンナノチューブの分散。

特徴

●密閉処理

溶媒の蒸発・揮散がありません。
コンタミがありません。
ナノリスク対策に対応可能。

●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。

●多試料同時処理

最大24試料を同時に処理できます。

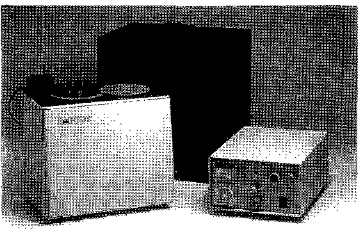
●多彩なラインアップ

汎用機からハイパワー機および連続処理機をご用意しています。

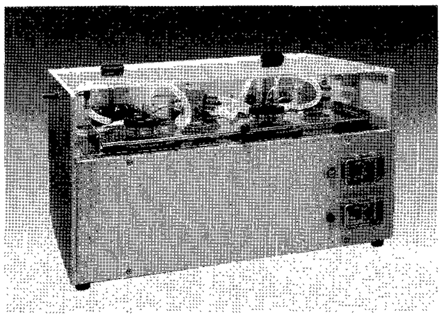
本商品は（独）産業技術総合研究所との共同研究により開発されました。

ハイパワーNANORUPTOR（NR-300）

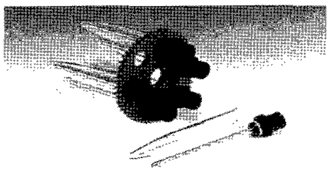
BIORUPTOR（UCD-250）



BIORUPTOR（UCW-201）



連続式NANORUPTOR（NR-2028）



密閉容器

用途

精製・分離・混合・分散・反応促進・触媒評価・各種スクリーニング

20余年培ってきたバイオのナノテクをご利用ください。

デモ機をご用意しております。どうぞお気軽にお問い合わせください。

お問い合わせ先

販売

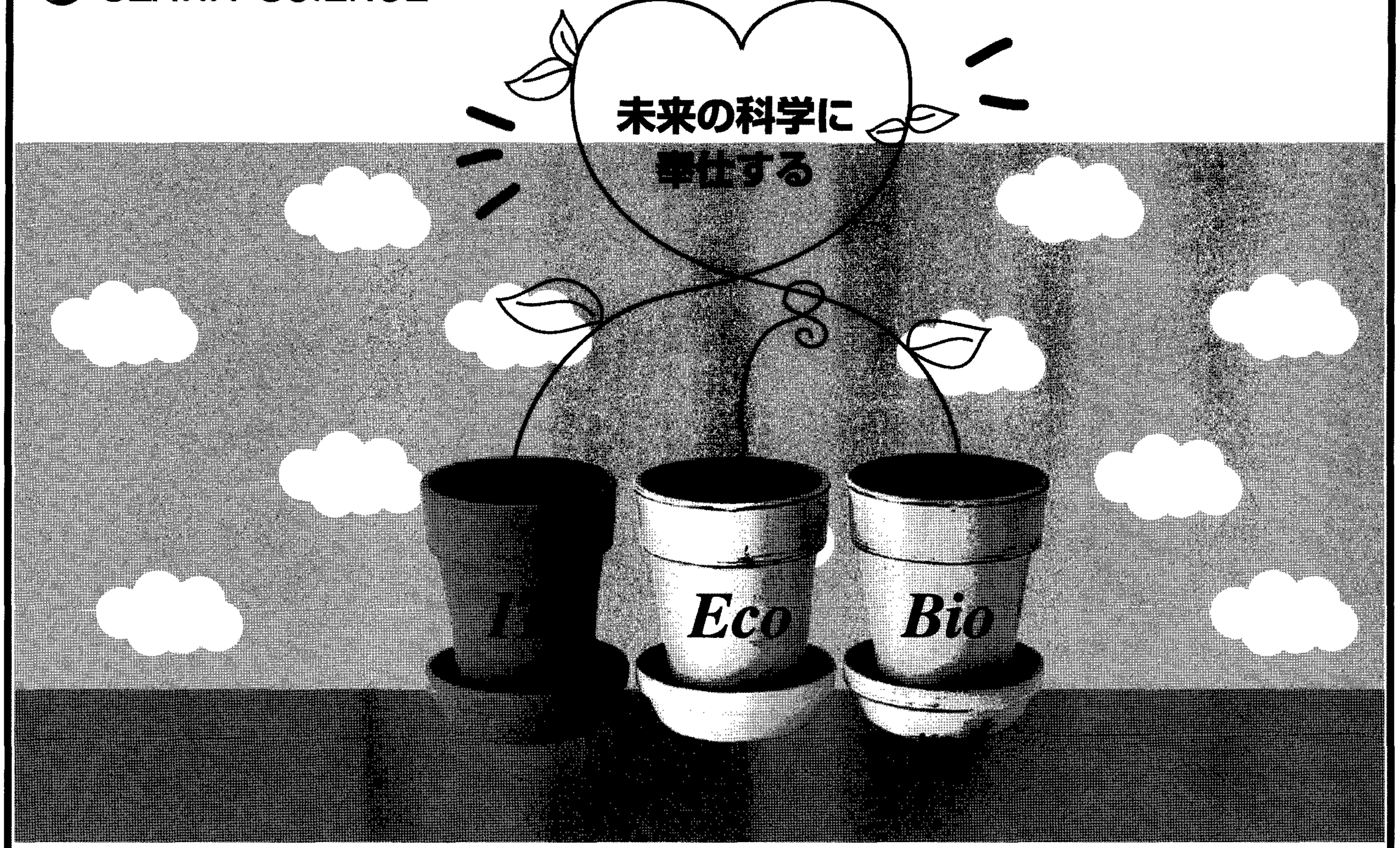
コスモ・バイオ株式会社

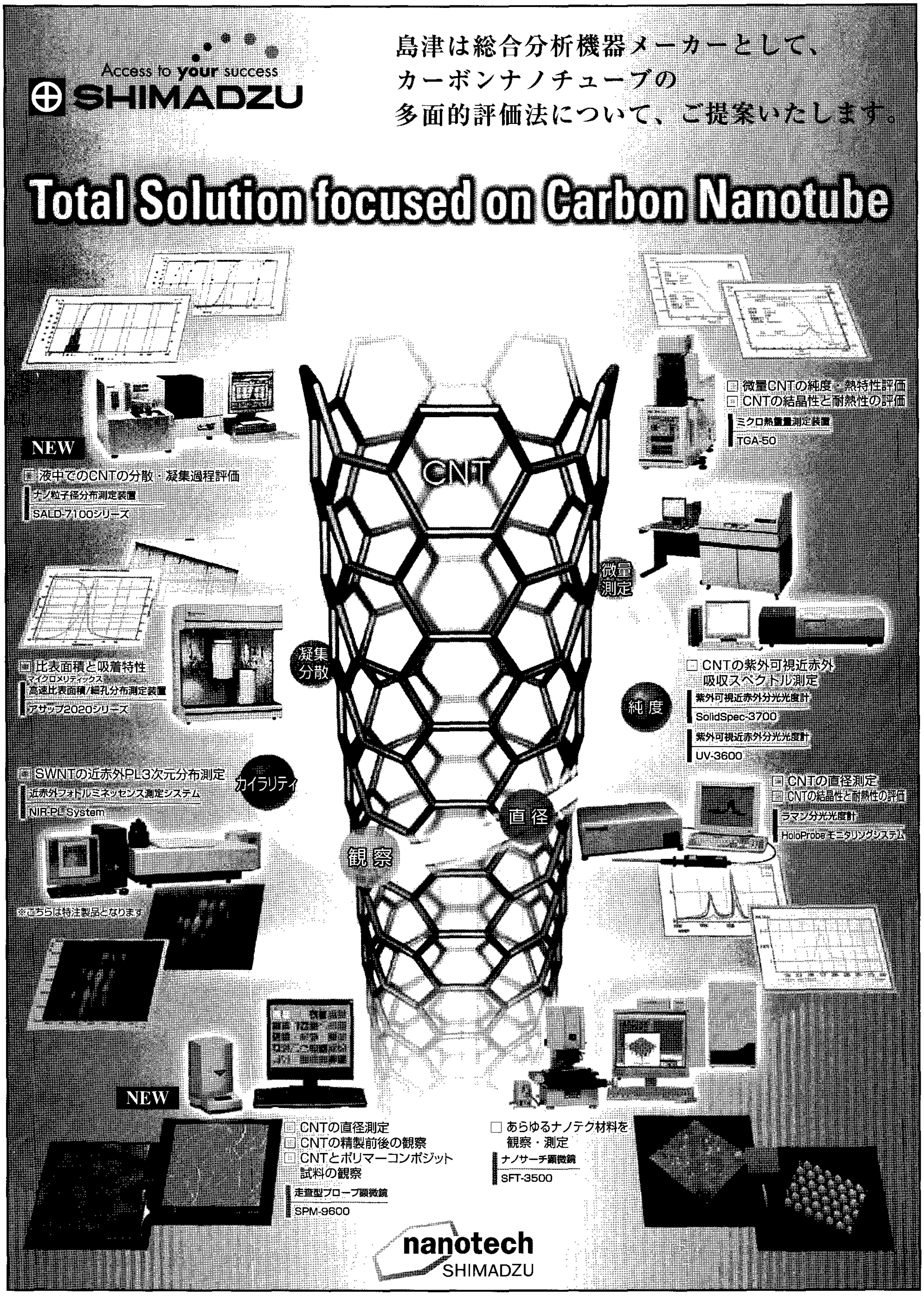
〒135-0016 東京都江東区東陽2-2-20 東陽駅前ビル
URL:http://www.cosmobio.co.jp
TEL（03）5632-9610　FAX（03）5632-9619
営業本部　栗原　mkurihar@cosmobio.co.jp
開発部　笹原　ksasahar@cosmobio.co.jp

製造

東湘電機株式会社

〒232-0027 神奈川県横浜市南区新川町5-29-2 新井ビル2F
TEL（045）261-8388　FAX（045）252-8935
技術部長　伊藤
e-mail:k-ito@bioruptor.jp


未来の科学に
奉仕する
I
Eco
Bio



住友商事のカーボンナノチューブ

Produced by Carbon Nanotechnologies Inc. (CNI)

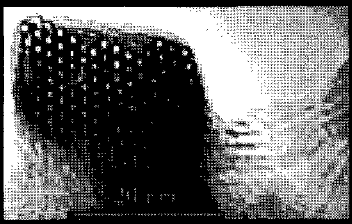
◆ 単層カーボンナノチューブ(SWNT)は、グラファイト構造の(グラフェン)シート一層で構成されている、直径約1nmの筒状分子です。ナノカーボン材料のなかでも、複数層からなる多層カーボンナノチューブ(MWNT)や、他のカーボン材料に比べて格段に優れた導電性・熱伝導性・構造的特性を有し、幅広い応用が期待されています。住友商事は、CNI社の日本・アジア地域での総代理店として、各種用途に適した製品のご提供に加え、共同開発の推進や事業化支援プロジェクトの実施など、カーボンナノチューブの応用製品開発を総合的に支援しています。

● HiPco® 単層カーボンナノチューブ

直径約1nmの単層カーボンナノチューブです。基礎研究や高機能用途向けに、触媒残留率の異なる下記3製品をご提供しております。

製品名	触媒残留率
HiPco® As Produced （未精製品）	< 35 wt%
HiPco® Purified （精製品）	< 15 wt%
HiPco® Super Pure （超高純度品）	< 5 wt%

＊ Bucky Plus™(フッ化カーボンナノチューブ)など修飾品も対応可能です。



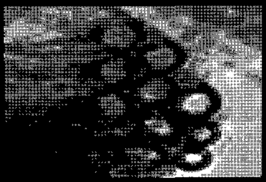
■ 単層カーボンナノチューブ ■

● CNI Xシリーズ

CNI社独自の製法で製造された、用途別産業応用向けカーボンナノチューブです。量産性に優れ、導電性樹脂複合材(EMI, ESD, Anti-Static)、フィールドエミッション用途などに、安定した製品供給が可能です。詳細につきましては、下記連絡先までお問合せください。

● 二層カーボンナノチューブ

CNI社独自の製法で製造された、直径約2nmの二層カーボンナノチューブです。



■ 二層カーボンナノチューブ ■

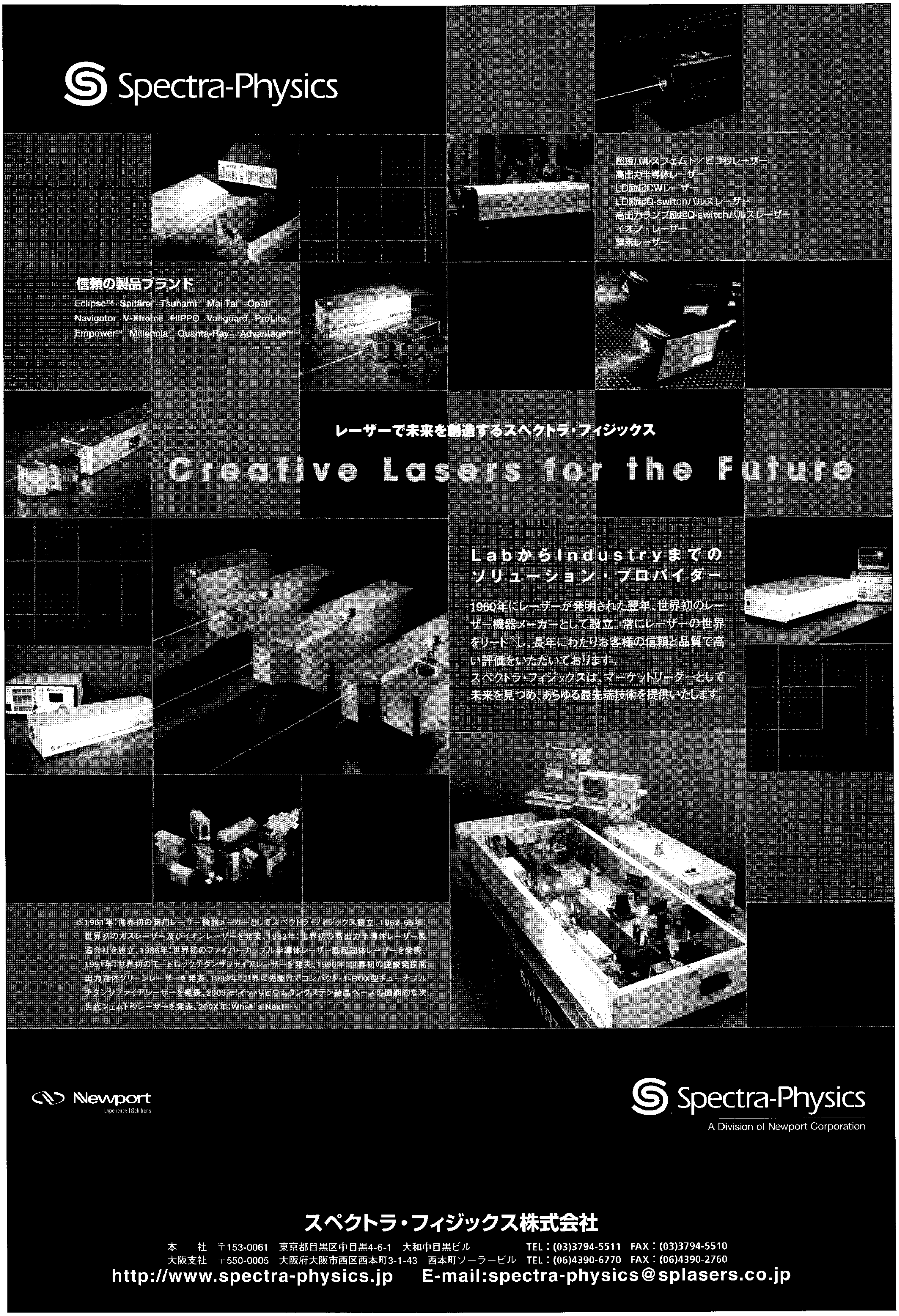
上記製品群を中心に、研究用から量産対応品、また共同開発によるカスタマイズ対応など、用途に応じたカーボンナノチューブの開発を進めています。弊社までお気軽にお問合せ下さい。

本件に関するお問合せ先

住友商事株式会社 電子材部 (担当:小野/青木)

E-mail : nano@em.sumitomocorp.co.jp
TEL : 03-5166-5857 FAX :03-5166-6234
住所 : 〒104-8610 東京都中央区晴海1-8-11
URL : www.sumitomocorp.co.jp/section/joho/nanotube.shtml

Sumitomo Corporation



コアテクノロジーからマーケットまで全てをカバー／ナノテクを分かりたい人、ビジネスにしたい人へのベストソリューションを提供／ナノテク国家プロジェクトからナノマテリアル、IT、バイオ、メディシン、エネルギー、MEMSに至るまで徹底取材

雑誌名：週刊ナノテク
発行日：毎週月曜日
発行予定部数：15,000部
予定頁数：16～32頁
体裁：A4変形、中綴じ
年間購読料：5万7,750円（本体5万5,000円）

産業タイムズ社
〒101-0021 東京都千代田区外神田5-5-4 第二日昌ビル
Tel.03-3834-5131 Fax.03-3834-5188
http://www.semicon-news.co.jp/ http://www.weeklynano.com

〒101-0021 東京都千代田区外神田5-5-4
第二日昌ビル
Tel.03-3834-5131㈹/Fax.03-3834-5188

産業タイムズ社の出版案内

詳細カタログ呈
Fax.での注文も承ります。定価は税・送料込み。

好評発売中！ **半導体工場ハンドブック2006**
ナノプロセスに本格突入した次世代ラインの全貌
A4変形判・143頁・定価3,150円（本体3,000円）

好評発売中！ **液晶・PDP・ELメーカー計画総覧2006年度版**
薄型テレビ向けで勝者をめざすFPDメーカー各社戦略
B5判・363頁・定価14,700円（本体14,000円）

好評発売中！ **アジア半導体/液晶ハンドブック2005**
台湾・韓国・中国・東南アジアのメーカー別プロフィール・設備投資を一覧
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新たな市場に向けて加速するコンパウンドセミコンダクタの最新動向
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日本で唯一の半導体産業ダイレクトリ“最新・大改訂版”
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2006年5月31日発刊予定 **プリント回路メーカー総覧2006年度版**
グローバル競争時代に勝ち抜く有力基板メーカーの最新戦略
B5判・約310頁・定価16,800円（本体16,000円）

好評発売中！ **半導体産業計画総覧2005年度版**
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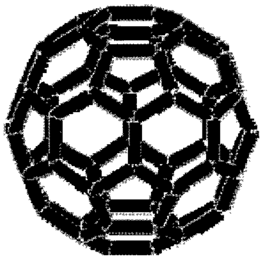
主要100社の最新事業計画・将来戦略を網羅
B5判・280頁・定価18,900円（本体18,000円）

米国・MTR社
フラーレン・ナノチューブ

株式会社マツボー
東京都港区虎ノ門3-8-21
電話 03-5472-1723
FAX 03-5472-1720
email: fulen@matsubo.co.jp

本ページ未掲載の種類のフラーレン・ナノチューブを
ご希望の場合はメーカーに問合わせますので
お申し付け下さい。

*C60, 70の純度はHPLCにより測定されています。



1. フラーレン混合物 （C60:70%, C70:25%, High Fullerene:5%)
2. フラーレンC60
   純度 >99%
   >99.5%
   >99.98%
   Sublimed
3. フラーレンC70
   純度 >99%
   >99%
   >99.5%
   Sublimed
4. SWナノチューブ(20-40%) クローズドエンド
5. SWナノチューブ(50%-70%) クローズドエンド
6. SWナノチューブ（70～80%）
   50～60%がオープンエンド
7. MWナノチューブ(95%)クローズドエンド
8. MWナノチューブ(70～80%)
   50～60%がオープンエンド
9. MWナノチューブ（85～90%）
   95%以上がオープンエンド

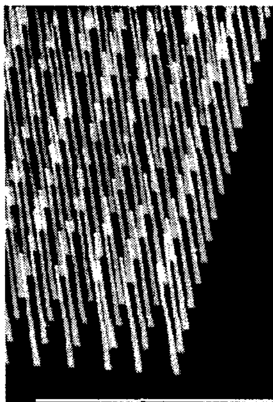
***High Fullerenes 95%**
C76
C78
C84>95%
C6099.9%(OH)n n=22-26
C6099.9%(OH)n n=22-26

***Bucky Ferrocene-molecular hybrid C60 w/ Ferrocene**
$\{\eta^5\text{–}(C_5H_5)_2Fe\}$ *C60
***Bucky Cobaltocene-ionic hybrid C60 w/ Cobaltocene**
$(\eta^5\text{–}C_5H_5)_2Co^2$*C60
***Complex C60 w/ Pt: (h2-C60)Pt(PPh_3)$_2$**
***Complex C60 w/ Fe: (h2-C60)Fe(Co)$_4$**
***Complex C60 w/ Ni: C60 (h3-C_5H_5)Ni(h5-C_5H_5)$_2$**
***Mixture of isomers C60F36**
***20-30%C13enrichedC60=99.0%**

***Higher Order Mixed Fullerenes(C76,78,84)**
***New Endohedral Metallofullerene Gd@C82**
***Halogenated Fullerenes**
1.C60Br24
2.C60C16
3.C60Br8Br2
4.Mixtures of isomers of C60F36

*水溶性 Amino Acids complexes of C60

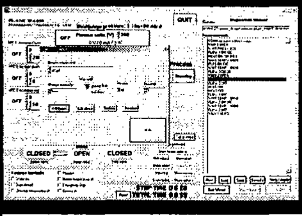
(w/Aminocapronic(A) and w/Aminobutyric(B) acids)w/unique solubility in water (50mg/ml)
(A)$C60(H)NH(CH_2)_5COO^-NA^+$
(B)$C60(H)NH(CH_2)_3COO^-NA^+$
***PCBM(6,6-Phenyl-C61-Butyl acid-Methylester)**

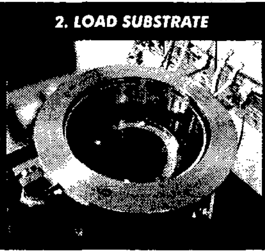


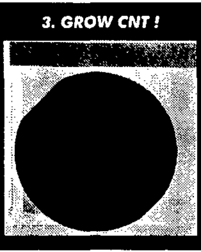
BLACK MAGIC

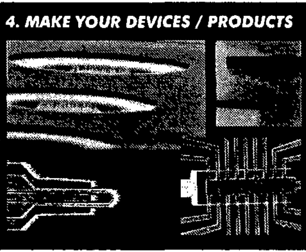
NANOINSTRUMENTS LTD

Advanced Carbon Nanotube Deposition Systems for Research and Industry


1. CREATE OR DOWNLOAD RECIPE


2. LOAD SUBSTRATE


3. GROW CNT !


4. MAKE YOUR DEVICES / PRODUCTS

Customer reviews

PORTLAND STATE UNIVERSITY (PORTLAND, OR, USA)

"Black Magic is a great system that enables us to use both thermal and plasma enhanced CVD for vertically aligned carbon nanotubes growth. We are impressed by the capabilities of the system - it can heat up to 1000C in less than a minute and cools down rapidly too. This allows us to manipulate the growth parameters in a more controlled fashion. The operation of the system is easy and user friendly. We are pleased to have this system in our lab." Prof. Jun Jiao, Director of Center for Electron Microscopy and Nanofabrication

NANYANG TECHNOLOGICAL UNIVERSITY (SINGAPORE)

"The 4-inch wafer PECVD tool provided by Nanoinstruments is fast and simple to use, easy to maintain and produces uniform vertically aligned carbon nanotubes - perfect for our electronic, mechanical and biological applica-tions." A/Prof Tay Beng Kang, Program Director, Nanoelectronics Research

COMPANY IN SILICON VALLEY, CA, USA

"The three 6-inch CNT reactors seamlessly operate with our robot to give round the clock production of wafer-scale carbon nanotubes. The fast response heater allows us to pre-treat, grow and anneal at different temperatures - giving us control of nanotube density, diameter, length and structure." President

Black Magic Carbon Nanotube Deposition Systems

COMBINED CVD+PECVD PLATFORMS

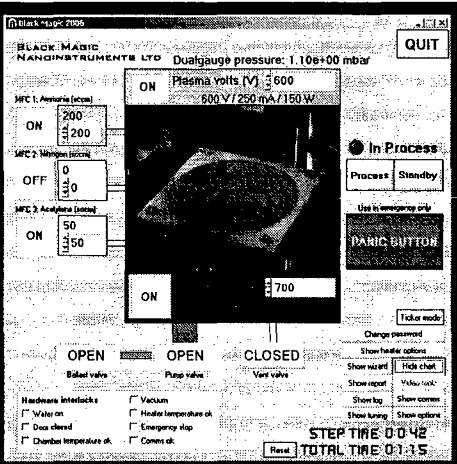
HIGH PERFORMANCE ISOLATED HEATER

AUTOMATIC RECIPE EXECUTION

ADVANCED SAFETY MANAGEMENT

FOR RESEARCH AND INDUSTRIAL PRODUCTION

LIVE VIDEO + DATA LOGGING/CHARTING
CONTROL/MONITORING OVER TCP-IP


Black Magic 2006

BLACK MAGIC
NANOINSTRUMENTS LTD

Dualgauge pressure: 1.10e+00 mbar

Plasma volts (V) 600 — ON
600 V / 250 mA / 150 W

MFC 1: Ammonia (sccm) — ON — 200 / 200

MFC 2: Nitrogen (sccm) — OFF — 0 / 0

MFC 3: Acetylene (sccm) — ON — 50 / 50

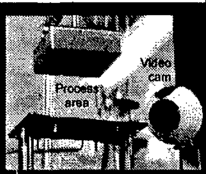
ON — 700

● In Process

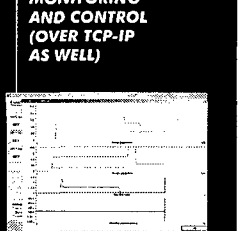
Ballast valve: OPEN
Pump valve: OPEN
Vent valve: CLOSED

Hardware interlocks
☐ Water on
☐ Door closed
☐ Chamber temperature ok
☐ Vacuum
☐ Heater temperature ok
☐ Emergency stop
☐ Comms ok

STEP TIME 0:0 42
TOTAL TIME 0:1 15



LIVE VIDEO, MONITORING AND CONTROL (OVER TCP-IP AS WELL)



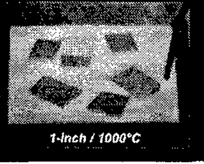
SPECIFICATION SUMMARY

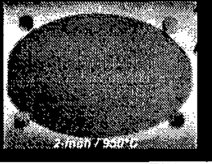
Black Magic version	*Standard*	*Pro*
Thermal CVD	✓	✓
Plasma CVD	✓	✓
User accounts	✓	✓
Heater zones	1	Up to 3
Temperature control	TC	TC+IR
Pressure control	-	✓
Safety interlocks	Up to 8	Up to 16
Automatic valves	Up to 3	Up to 8
Number of flow controllers	Up to 5	Up to 11
TCP/IP network operation	-	✓

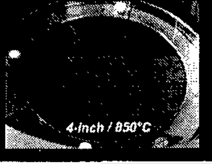
UL and CE approvals available on customer request

Deposition video at
http://www.nano-inst.com/videos

CVD+PECVD PLATFORMS


1-inch / 1000°C


2-inch / 950°C


4-inch / 850°C


6-inch / 850°C

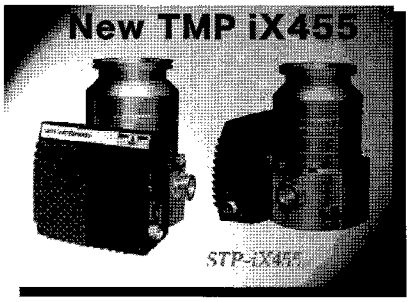
NANOINSTRUMENTS LTD
25 Badminton Close, Cambridge CB4 3NW, United Kingdom. Tel: +44 870 850 6497.

WEB: WWW.NANO-INST.COM
EMAIL: ENQUIRIES@NANO-INST.COM

CVD+PECVD カーボンナノチューブ成長装置 ***by Cambridge University***

日本総代理店 **アプリオリ 株式会社** Tel : 03-5296-5521•FAX: 03-5296-5525
E-Mail: info @apriori.co.jp http:// www. apriori.co.jp

aPRIORI



BOC EDWARDS

AILIN VACUUM

2005年 iX455 発売記念 キャンペーン

品番	品種	品名	定価	キャンペーン価格
PT640Z050	ターボ分子ポンプ	STP-iX455-300 ポンプ単体 (300L/s)	¥2,000,000	¥1,250,000
PT64W0Z00		iPS-240 電源ユニット	¥150,000	
PT64W1Z00		iDT-001 ディスプレイユニット	¥200,000	
PT64Y0A10		iPS-240 用プラグなしケーブル 3m	¥10,000	
PT64Y0B20		ケーブル 5m	¥25,000	
		合計金額	¥2,385,000	
PT640Z060		STP-iX455-450 ポンプ単体 (450L/s)	¥2,200,000	¥1,360,000
PT64W0Z00		iPS-240 電源ユニット	¥150,000	
PT64W1Z00		iDT-001 ディスプレイユニット	¥200,000	
PT64Y0A10		iPS-240 用プラグなしケーブル 3m	¥10,000	
PT64Y0B20		ケーブル 5m	¥25,000	
		合計金額	¥2,585,000	
		STP-H301CS	¥2,800,000	¥1,600,000
		STP-H451CS	¥3,000,000	¥1,700,000

品番	品種	品名	定価	キャンペーン価格
A65501904	ロータリーポンプ	RV12S 単相 100/200V	¥216,000	¥141,700
JZSSCB001		ケーブル	¥2,000	
		合計金額	¥218,000	

品番	品種	品名	定価	キャンペーン価格
A72601904	スクロールポンプ	XDS10S（ケーブル付）	¥600,000	¥390,000
A73001983		XDS35iS（ケーブル付）	¥1,100,000	¥700,000

品番	品種	品名	定価	キャンペーン価格
D39700000	表示器	TICS コントローラー	¥160,000	¥204,840
J40013120		電源ケーブル	¥5,000	
D02377000	ピラニゲージ	APGX-L-NW16 SS	¥62,000	
D14641000	マグネトロンゲージ	AIM-S NW25	¥99,200	
D40001030		ケーブル 3m	¥15,200	
		合計金額	¥341,400	

上記価格には消費税はふくまれません

［キャンペーン期間］ **～2006年9月30日**

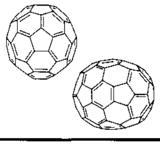
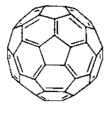
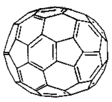
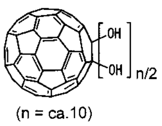
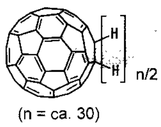
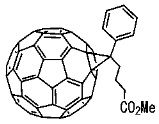
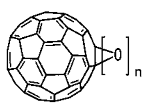
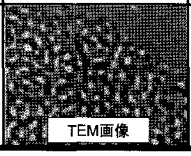
大変お買い得な価格になっておりますので　この機会に是非ご検討下さい。

AILIN VACUUM
株式会社アイリン真空
代表取締役　松井良憲
E-mail : info@ailin-va.com
関東営業所　〒349-0101 埼玉県蓮田市黒浜3393-1
TEL : 048-769-7011　FAX : 048-769-7483
本社　〒452-0961 愛知県西春日井郡春日町落合東出81
TEL : 052-401-2061　FAX : 052-401-6960

フロンティアカーボン株式
大量製造販売しているオン

nanom フラーレンサンプル価格一覧

2006年7月1日現在

銘柄	分子構造	主な組成・特性	取扱数量	販売価格
nanom mix 混合フラーレン		C60:約60% C70:約25% その他:高次フラーレン	50g	25,000円
			10g	6,000円
nanom purple フラーレンC60		C60:99%以上(HPLC面積%)	10g	30,000円
			5g	25,000円
			1g	8,000円
		C60:99.5%以上(HPLC面積%)	1g	10,000円
			500mg	8,000円
		昇華精製品	1g	15,000円
			500mg	12,000円
nanom orange フラーレンC70		C70:97%以上(HPLC面積%)	1g	40,000円
			500mg	30,000円
nanom spectra D100 水酸化フラーレン	 (n = ca.10)	C60(OH)n n=約10(MS)	2g	20,000円
			1g	12,000円
nanom spectra A100 水素化フラーレン	 (n = ca. 30)	C60(H)n n=約30(MS)	2g	24,000円
			1g	15,000円
nanom spectra E100 PCBM		PCBM:99%以上(HPLC面積%)	1g	80,000円
			500mg	65,000円
nanom spectra B100 酸化フラーレン	 (n = 1-2 が主成分)	$C60(O)_1$: 約40% $C60(O)_2$: 約30% その他 : C60, 三酸化体以上	1g	25,000円
			500mg	15,000円
nanom black		フラーレン類似構造を有する特殊な煤 炭素含有量 : 96.0%以上	100g	35,000円
			10g	4,000円

上記価格には消費税、送料は含まれておりません。別途申し受けます。

ナノテク材料は進化しつづけている。

C13安定同位体置換C60フラーレン(99%)
C13安定同位体置換C70フラーレン(98%)
水溶性C60CHCOOH、水溶性C60(OH)n　n=22～26
水溶性C60(H)NH(CH2)5COONA
C60H36フラーレン、C60F36フラーレン、Anti-HIVフラーレン
Gd@C82金属内包フラーレン、La@C82金属内包フラーレン
〔60〕PCBM〔Phenyl C61 Butyric Acid Methyl Ester 99.5%〕
〔70〕PCBM〔Phenyl C71 Butyric Acid Methyl Ester 99.0%〕
ハイブリッドC60フェロセン、ハイブリッドC60コバルトセン
C60･Ptフラーレン、C60･Feフラーレン、C60･Niフラーレン
Carbon Nano Paper, Aligned Carbon Nanotube Array
Carbon Nanotube based field emission X-ray tube
Vertical aligned MWCNT(3～30micron)
Electron field Emmission Cathode, C60 film
Triode Cathode ATC Series, C60C(COOE+)2
Carbon Nanotube AFM tip, C60(C(COOE+))2
Carbon Nanofiber, C60Br24, C76, C78, C84, C86

SWNT-COOH, purified(70-80%)
SWNT-NH_2, purified(70-80%)
SWNT-CONH-$C_{18}H_{37}$, purified(70-80%)
SWNT-COO-R-OH(2-5% rpynn)
Shorted SWNT-COOH, purity 90%, length 200-500 nm
Shorted SWNT-NH_2, purity 90%, length 200-500 nm
Shorted(200-500 nm) SWNT-COO-R-OH(5-10% group)
Solutions of functionalized SWNT in different solvents
Substituted pyrrolidinofullerene derivatives
Lower bulk density SWNT-COOH, purified(70-80%)
DWNT(double wall CNT), 20-30% purity, 3～5nm
DWNT(double wall CNT), 90% purity, 140nm

Compounds, Elements
Single-Metal Oxides
Multi-Metal Oxides
Nano-Wire Powders

Particles: MoS_2, CrO_3, HgI_2(alpha- & Beta-): Diamond Abrasive: <50nm, <100nm, <200nm, <250nm, <500nm, 200-400nm, <1um: Graphite: 15,000 mesh, 10,000 mesh.
Nanowires(Diameter ～100nm, L=～1-2um): Si, Ga, Bi, InP, GaP, II-VI compounds.
Composite particles: Dropped, shelled, & cored metals/oxides like Ag/SiO_2 core<100nm.
Coated particles: Surfacants on oxides, or Metals.
Shorter length CNTs: 0.5um(SWNTs, MWCNTs), 5um(more easily dispersible).
SWNTs, MWNTs surface funcationized with -COOH

SWNT

Closed SWNT 50-70%
Open SWNT 90%

MWNT (Aligned)

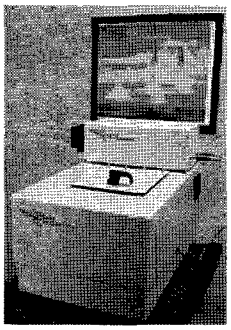
95%+OD: 10-20nm

Carbon Nano Fibers

OD: 240-500nm
OD: 80-200nm
OD: 40-80nm
OD: 240-500nm (graphitized)

ナノスペクトライザー

(Applied Nano Fluorescence社)
米国ライス大学ワイズマン教授が開発した単層カーボンナノチューブ測定器。



ナノチューブ／フラーレン

高純度95%多層カーボンナノチューブ
高純度95%単層カーボンナノチューブ
140nm大口径カーボンナノチューブ
2層カーボンナノチューブ
ナノホーン
SWNT−COOH
SWNT−NH_2
SWNT−CONH−$C_{18}H_{37}$
SWNT−COO−R−OH
Shorted　SWNT
水溶性SWNTアミノ酸
【60】PCBMフラーレン
【70】PCBMフラーレン
アミノC60誘導体フラーレン
Sc_3N@C80
Lu_3N@C80
Y_3N@C80
Er_3N@C80
La@C80

上記以外にも様々な理化学研究機器・材料を取り扱っております。詳しくは下記までお問い合わせ下さい。

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