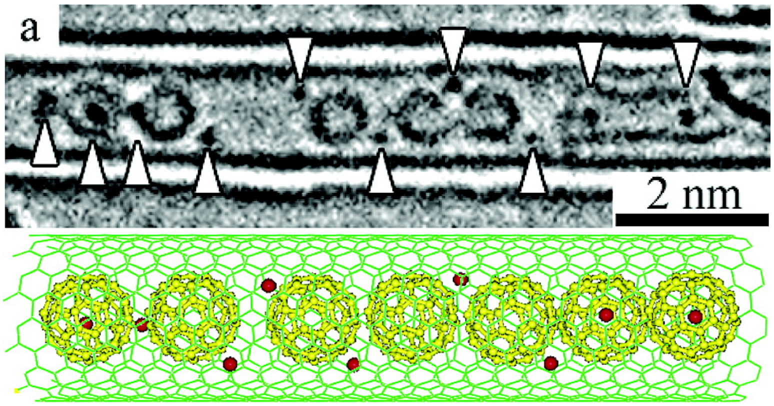
JOURNAL OF THE AMERICAN CHEMICAL SOCIETY

Communication

Entrapping of Exohedral Metallofullerenes in Carbon Nanotubes: (CsC)@SWNT Nano-Peapods

Bao-Yun Sun, Yuta Sato, Kazutomo Suenaga, Toshiya Okazaki, Naoki Kishi, Toshiki Sugai, Shunji Bandow, Sumio Iijima, and Hisanori Shinohara

J. Am. Chem. Soc., **2005**, 127 (51), 17972-17973• DOI: 10.1021/ja056238a • Publication Date (Web): 06 December 2005



J|A|C|S
COMMUNICATIONS

Entrapping of Exohedral Metallofullerenes in Carbon Nanotubes: $(CsC_{60})_n$@SWNT Nano-Peapods

Bao-Yun Sun,[†,‡] Yuta Sato,[§] Kazutomo Suenaga,[§] Toshiya Okazaki,[§] Naoki Kishi,[†] Toshiki Sugai,[†]
Shunji Bandow,[‖] Sumio Iijima,[‖] and Hisanori Shinohara*,[†,‡]

Department of Chemistry and Institute for Advanced Research, Nagoya University, Nagoya 464-8602, Japan, CREST, Japan Science Technology Corporation, c/o Department of Chemistry, Nagoya University, Nagoya 464-8602, Japan, Research Center for Advanced Carbon Materials, National Institute of Advanced Industrial Science and Technology (AIST), Tsukuba 305-8565, Japan, and Department of Materials Science and Engineering, Meijo University, Nagoya 468-8502, Japan

Received September 10, 2005; E-mail: noris@cc.nagoya-u.ac.jp

Single-wall carbon nanotubes (SWNTs) have a fascinating ability to encapsulate atoms or molecules into their one-dimensional nanospace. So far, a large number of different organic and inorganic species, such as fullerenes,[1] metallofullerenes,[2] single element,[3] ionic salt,[4] and H_2O,[5] have been demonstrated to be introduced into their cavity. Among those, the peapods encapsulating endohedral metallofullerenes[6] have exhibited the most intriguing behaviors in any filled SWNTs. For example, the band gap of SWNTs can be narrowed from 0.5 to 0.1 eV after inserting Gd@C_{82} metallofullerenes into SWNTs,[7] indicating that such peapods can become novel electronic devices, such as ambipolar field-effect transistors (FET).[8]

Potassium doping into C_{60} peapods can be achieved by introducing potassium vapor into the peapods.[9,10] In this case, K atoms were inserted randomly into CNTs and have two different kinds of positions, intratubular and intertubular positions, where the control of the doping level of potassium atoms was difficult.

Here, we report a high-yield synthesis of peapods encapsulating exohedral Cs metallofullerenes, $(CsC_{60})_n$@SWNTs, via a new chemical reduction method. High-resolution transmission electron microscopy (HRTEM) of the $(CsC_{60})_n$@SWNT peapods clearly shows that Cs atoms and C_{60} molecules jointly well align along the inner walls of SWNTs by forming CsC_{60} exohedral metallofullerenes. Furthermore, in situ electron energy loss spectroscopy (EELS) indicates that the formal charge state of encaged CsC_{60} is expressed as $Cs^{+1}C_{60}^{-1}$, similar to the reported bulk Cs fulleride.[11]

C_{60} was produced by the DC arc discharge method and isolated by HPLC separation.[12] C_{60} anions with the countercations of Cs were synthesized by a chemical reduction procedure in Ar atmosphere.[13,14] In brief, C_{60} was vigorously stirred with an excess Zn powder and aqueous CsOH in purified THF (Wako, 99.5%). The dark red THF layer containing CsC_{60} was separated from a colorless water layer. The observation of the typical sharp peak at 1075 nm in the NIR spectrum indicated that C_{60} existed as a monoanion in the THF solution.[11,14] In this study, Cs was chosen as the countercation because Cs has more electrons than potassium and is easier to see in the HRTEM. However, Cs could be replaced with other alkali metals by simply replacing CsOH with NaOH, KOH, or RbOH. They have similar behaviors as CsOH in the present reaction.

Prior to the doping, SWNTs, produced by the pulsed laser vaporization, were purified[15] and heated in dry air at 480 °C for 30 min to open the ends of the nanotubes. Since the present exohedral metallofullerenes, CsC_{60}, are very sensitive to oxygen and many oxidants, the SWNTs were exposed to H_2/Ar (3% H_2) gas flow at 400 °C for 3 h to reduce impurities (such as amorphous carbon materials) and kept in Ar atmosphere.

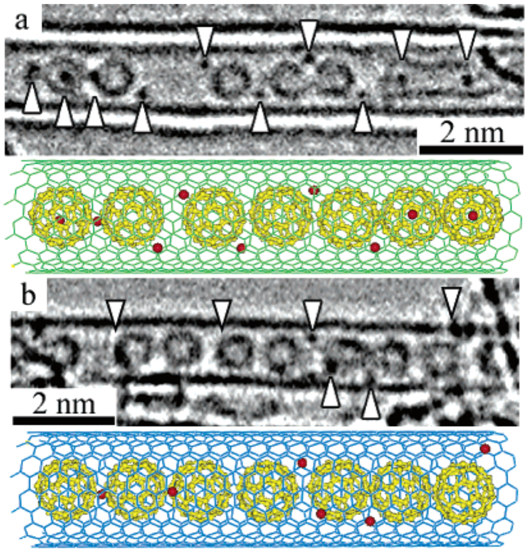


Figure 1. High-resolution TEM images of $(CsC_{60})_n$@SWNT peapods with the arrows indicating the Cs atoms (see movie 1) and schematics representing the TEM image (Cs, red; C_{60}, yellow) at 120 kV.

The dried CsC_{60} metallofullerene (0.5 mg) was sealed in a glass ampule under 10^{-6} Torr together with the open-ended SWNTs (1 mg), but they were separated with asbestos. The ampule was heated in a high-temperature oven at 500 °C for 2 days. The optimum doping temperature was 100 °C higher than the normal temperature for C_{60} peapods. All of these processes were carefully conducted under an Ar atmosphere. For TEM measurements, the sample was washed with THF, CS_2, and sonicated in acetone and dropped onto the grid. The structure of the peapods was examined with HRTEM operated at 120 kV (JEOL 2010F). The EELS spectra of Cs were obtained with an in situ electron energy-loss spectrometer (Gatan ENFINA).

In general, exohedral metallofullerenes, such as CsC_{60} and KC_{60}, are not stable in air and in solvents containing oxygen. In contrast, CsC_{60} metallofullerenes in the $(CsC_{60})_n$@SWNT peapods are totally stable even in organic solvents since these reactive fullerenes are protected from air by the walls of SWNTs.

Figure 1a and b (cf. the Supporting Information for the corresponding movie, movie 1) shows the typical HRTEM images of $(CsC_{60})_n$@SWNT. The filling yield is, in general, 10%. The two

---

[†] Nagoya University.
[‡] CREST.
[§] AIST.
[‖] Meijo University.

10.1021/ja056238a CCC: $30.25

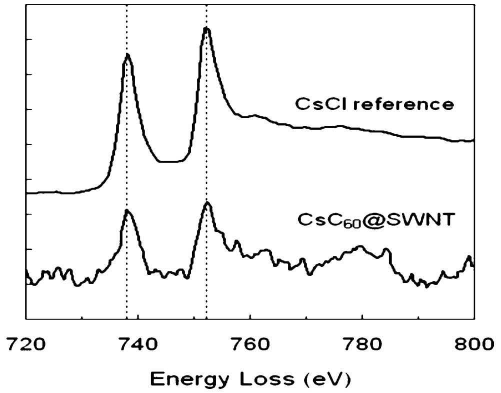


Figure 2. The EELS spectra of $(CsC_{60})_n$@SWNTs and CsCl.

parallel lines correspond to the walls of a SWNT, and the balls aligned within the nanotube are images of the entrapped C_{60} molecules. The overall appearance in the TEM image is similar to that of the normal C_{60} peapod,[1] except for dark spots seen adjacent to C_{60} molecules. The dark spots are seen outside the C_{60}, which should be the Cs metal atoms attached exohedrally to C_{60} molecules. Because of the electron beam irradiation during the TEM observation, some Cs atoms move between two C_{60} cages, suggesting that they are attracted by their two neighboring anions.

Figure 2 shows an in situ EELS spectrum of $(CsC_{60})_n$@SWNTs and its bundles at the Cs $M_{4,5}$ edges together with a reference spectrum of CsCl (Aldrich, 99.999%+). The peak positions of $(CsC_{60})_n$@SWNTs are exactly the same as those of CsCl, and the general features of these EELS signal peaks are also similar to each other. This suggests that the formal charge state of CsC_{60} in SWNTs is expressed as $Cs^{+1}C_{60}^{-1}$ as in the corresponding bulk Cs fulleride.[11]

A plausible mechanism for the formation of the exohedral Cs metallofullerene peapods is as follows. The Cs^{+1} and C_{60}^{-1} ion pair exists in the normal form of salt. If one C_{60}^{-1} anion entered the nanotube, it should be followed by a Cs^{+1} cation to maintain the whole system neutral. It is likely that a pair of $Cs^{+1}C_{60}^{-1}$ has no energy barriers of entering, and it eventually aligns within a SWNT with almost the normal bulk stoichiometric ratio ($Cs^{+1}C_{60}^{-1}$).

One of the most intriguing observations of the present study is the reaction dynamics of the encaged CsC_{60} metallofullerenes. Figure 3 shows time-dependent HRTEM images of a $(CsC_{60})_n$@SWNT peapod (cf. the Supporting Information for the corresponding movie, movie 2). Under the electron beam irradiation, a fullerene rearrangement in the nanotubes starts to occur (Figure 3b). The CsC_{60} molecules are already so close with each other as to form dimers, as seen in the HRTEM image. A sudden hopping of dark spots corresponding to Cs atoms (from Figure 3b and c) is clearly observable. Further exposure for ~21.2 s resulted in coalescence or fusion of the fullerenes, which generates dimers of CsC_{60} molecules (Figure 3d). The most important observation here is the fact that the Cs atom continues to attach to C_{60} molecules even after they form a dimer. This indicates that ionic bonding between Cs^{+1} and C_{60}^{-1} is fairly tight against electron beam irradiation.

Filling up carbon nanotubes by reactive species, such as the present exohedral CsC_{60} metallofullerenes, provides a brand new type of hybrid structure of peapods. The Cs metal atom can easily be replaced with other metal atoms (Na, K, Rb, etc.). Similarly, C_{60} molecules can be replaced with higher fullerenes and even endohedral metallofullerenes.[6] Furthermore, the ratio between metal atom and the fullerene can be varied by reducing fullerenes into different charge states by using chemical or electrochemical methods.

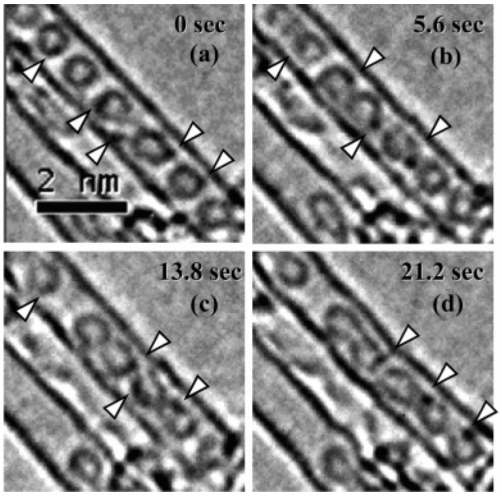


Figure 3. Time-dependent HRTEM images of $(CsC_{60})_n$@SWNT taken at 0, 5.6, 13.8, and 21.2 s (Δ: Cs, see movie 2, the movie speed is ca. 5 times faster than the real time).

Acknowledgment. We acknowledge the financial support by the JST CREST project on Novel Carbon Nanotube Materials and the Grants-in-Aid Scientific Research B (No. 16350071) of MEXT, Japan. The present study is partially supported by the NEDO Nano-Carbon Technology Project.

Supporting Information Available: Movies of the HRTEM images of $(CsC_{60})_n$@SWNT. This material is available free of charge via the Internet at http://pubs.acs.org.

References

(1) Smith, B. W.; Monthioux, M.; Luzzi, D. E. *Nature* **1998**, *396*, 323−324.
(2) Hirahara, K.; Suenaga, K.; Bandow, S.; Kato, H.; Okazaki, T.; Shinohara, H.; Iijima, S. *Phys. Rev. Lett.* **2000**, *85*, 5384−5387.
(3) Lee, R. S.; Kim, H. J.; Fischer, J. E.; Thess, A.; Smalley, R. E. *Nature* **1997**, *388*, 255−257.
(4) Meyer, R. R.; Sloan, J.; Dunin-Borkowski, R. E.; Kirkland, A. I.; Novotny, M. C.; Bailey, S. R.; Hutchison, J. L.; Green, M. L. H. *Science* **2000**, *289*, 1324−1326.
(5) Hummer, G.; Rasaiah, J. C.; Noworyta, J. P. *Nature* **2001**, *414*, 188−190.
(6) Shinohara, H. *Rep. Prog. Phys.* **2000**, *63*, 843−892.
(7) Lee, J.; Kim, H.; Kahng, S. J.; Kim, G.; Son, Y. W.; Ihm, J.; Kato, H.; Wang, Z. W.; Okazaki, T.; Shinohara, H.; Kuk, Y. *Nature* **2002**, *415*, 1005−1008.
(8) Shimada, T.; Okazaki, T.; Taniguchi, R.; Sugai, T.; Shinohara, H.; Suenaga, K.; Ohno, Y.; Mizuno, S.; Kishimoto, S.; Mizutani, T. *Appl. Phys. Lett.* **2002**, *81*, 4067−4069.
(9) Kalbac, M.; Kavan, L.; Zukalova, M.; Dunsch, L. *J. Phys. Chem. B* **2004**, *108*, 6275−6280.
(10) Guan, L. H.; Suenaga, K.; Shi, Z. J.; Gu, Z. N.; Iijima, S. *Phys. Rev. Lett.* **2005**, *94*, 045502.
(11) Reed, C. A.; Bolskar, R. D. *Chem. Rev.* **2000**, *100*, 1075−1120.
(12) Sun, B. Y.; Inoue, T.; Shimada, T.; Okazaki, T.; Sugai, T.; Suenaga, K.; Shinohara, H. *J. Phys. Chem. B* **2004**, *108*, 9011−9015.
(13) Sun, B. Y.; Luo, H. X.; Shi, Z. J.; Gu, Z. N. *Electrochem. Commun.* **2002**, *4*, 47−49.
(14) Wu, M. F.; Wei, X. W.; Qi, L.; Xu, Z. *Tetrahedron Lett.* **1996**, *37*, 7409−7412.
(15) Bandow, S.; Takizawa, M.; Kato, H.; Okazaki, T.; Shinohara, H.; Iijima, S. *Chem. Phys. Lett.* **2001**, *347*, 23−28.

JA056238A