JOURNAL OF THE AMERICAN CHEMICAL SOCIETY

Communication

pubs.acs.org/JACS

Single Chirality Extraction of Single-Wall Carbon Nanotubes for the Encapsulation of Organic Molecules

Masatoshi Kawai,[†] Haruka Kyakuno,[†] Takuya Suzuki,[†] Toru Igarashi,[†] Hironori Suzuki,[‡] Toshiya Okazaki,[‡] Hiromichi Kataura,[‡,§] Yutaka Maniwa,[†,§] and Kazuhiro Yanagi*[,†]

[†]Tokyo Metropolitan University, Hachioji 192-0397, Japan

[‡]National Institute of Advanced Industrial Science and Technology (AIST), Tsukuba 305-8565, Japan

[§]Japan Science and Technology Agency Core Research for Evolutional Science and Technology (JST-CREST), Gobancho, Chiyoda-ku, Tokyo, 102-0076 Japan

Supporting Information

ABSTRACT: The hollow inner spaces of single-wall carbon nanotubes (SWCNTs) can confine various types of molecules. Many remarkable phenomena have been observed inside SWCNTs while encapsulating organic molecules (peapods). However, a mixed electronic structure state of the surrounding SWCNTs has impeded a detailed understanding of the physical/chemical properties of peapods and their device applications. We present a single-chirality purification method for SWCNTs that can encapsulate organic molecules. A single-chiral state of (11,10) SWCNTs with a diameter of 1.44 nm, which is large enough for molecular encapsulation, was obtained after a two-step purification method: metal-semiconductor sorting and cesium-chloride sorting. The encapsulation of C_{60} to the (11,10) SWCNTs was also succeeded, promising a route toward single-chirality peapod devices.

The recent advancements in purification techniques for single-wall carbon nanotubes (SWCNTs) have enabled us to obtain high-purity metallic, semiconducting, and single-chiral state SWCNT samples.[1] The preparation of SWCNT samples with selected chirality is of great significance for understanding their properties and applications on a large scale. Various techniques, including polymers,[2] monomers,[3] DNA wrapping extraction,[4] density gradient sorting,[5,6] and gel chromatography,[7,8] have been proposed for single-chiral purification. As a result, obtaining single-chiral samples in high purity, such as (6,5), (8,6), are now possible. Notably, the diameters currently obtained single-chiral samples are approximately 1.0 nm or less. As a result, encapsulating organic molecules into the inner hollow spaces of SWCNTs is difficult. Recently, nearly single-chiral state SWCNTs with a diameter of 1.3 nm have been reported, but their extraction yield is significantly small.[9]

From the discovery of the encapsulation of fullerenes inside nanotubes,[10] SWCNTs with a diameter of approximately 1.4 nm have been shown to encapsulate various types of molecules. SWCNTs that can encapsulate organic molecules are termed peapods. Encapsulated molecules have exhibited unique properties inside of the SWCNT inner hollow space, including band gap modulation[11] and energy transfers.[12] The presence of molecules influences the physical properties of SWCNTs, and the encapsulation of molecules is an approach that is used to tune nanotube properties. In addition, unique chemical reactions have been observed inside the nanospace, such as the production of double-wall carbon nanotubes with the coalescence of encapsulated fullerenes.[13] Various fascinating physical and chemical phenomena have also occurred in peapods. Previous SWCNT samples used for the production of peapods have always existed in a mixed chirality state. Organic molecules have been encapsulated in metallic or semiconducting SWCNTs[14] but only in the mixed-chiral state. Such mixed states prevent the detailed understanding of interactions between the encapsulated molecules and nanotubes and prohibit the preparation of peapod samples with uniform electronic characteristics. Developing a technique to obtain a single-chiral state of SWCNTs that can encapsulate organic molecules (i.e., preparation of single-chiral SWCNTs with approximately 1.4 nm diameters, which is large enough for the encapsulation of C_{60}) is essential.

Herein, we report the successful extraction of single-chiral state of SWCNTs with (11,10) chirality (1.44 nm diameter). We achieved the single chiral extraction through the following two purification approaches: (a) Cesium chloride (CsCl) was used as a density medium during the density gradient ultracentrifugation for single-chiral extraction (CsCl sorting); and (b) the single-chiral extraction was achieved using a two steps purification process with CsCl sorting and metal-semiconductor sorting (MS sorting) by usual density-gradient ultracentrifugation.[6] In addition, we succeeded to encapsulate C_{60} to the (11,10) SWCNTs.

Figure 1 shows the optical absorption and photoluminescence spectra of (11,10) chirality SWCNTs. The purification process details are available in the Supporting Information (SI). As starting materials, we used SWCNTs that were produced by arc-discharge method (ArcSO, Meijyo Nano Co.). We sorted the metallic and semiconducting (Semi) types of SWCNTs through typical MS sorting. MS sorting was performed in a manner similar to a previous report.[15] The optical absorption bands caused by the S_{22}, M_{11}, and S_{33}/S_{44} transitions were identified in the starting sample (Mixture, Figure 1a), and an average diameter of approximately 1.4 nm was estimated.[15]

Received: February 10, 2012
Published: May 30, 2012

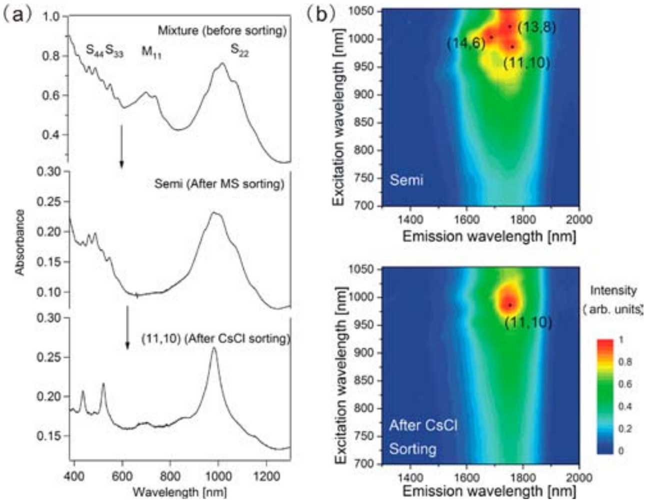

Figure 1. (a) Optical absorption spectra of Mixture (top, before sorting), Semi (middle, after MS sorting), and (11,10) SWCNTs (bottom, after CsCl sorting). (b) PL mappings of the Semi (top) and (11,10) SWCNTs (bottom, after CsCl sorting).

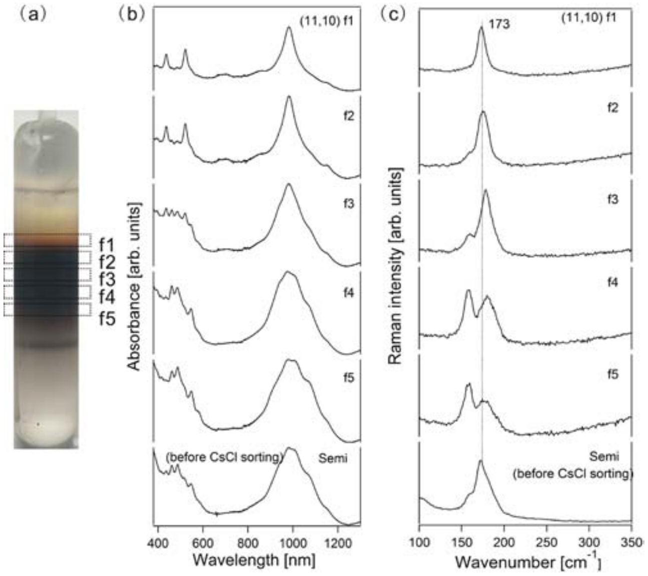

Figure 2. (a) An image of a centrifugation tube after CsCl sorting. (b) Optical absorption spectra of the fractions. (c) RBMs of the fractions. The modes are obtained at an excitation wavelength of 514 nm.

After MS sorting, high-purity semiconducting SWCNTs (Semi) were obtained. The purities were estimated to be >95% due to the lack of the M_{11} bands in the Semi. However, the optical absorption bands in the Semi were rather broad, indicating the presence of semiconducting SWCNTs with different chiralities. The photoluminescence spectrum of the Semi (Figure 1b) indicated that three main chiralities [(13,8), (11,10), (14.6)] existed in the sample, which were identified with reference to ref 16. A CsCl sorting procedure was applied to the Semi. After CsCl sorting, very steep optical absorption bands in S_{22}, S_{33}, S_{44} regions were obtained (Figure 1a). The photoluminescence spectrum of the sample clearly indicated the enrichment of (11,10). Contribution from other chiral SWCNTs, such as (13,8) and (14,6), cannot be identified in the photoluminescence (PL), suggesting a single-chirality state of the sample.

Detailed procedures for the CsCl sorting of Semi are further described (see also SI). The Semi sample was dispersed into a 2% sodium cholate (SC) (w/w) and 42.5% CsCl (w/w) solution, and the homogeneous solution was delivered to a centrifugation tube (the density gradient was not formed before centrifugation). The solution was centrifuged at 65 000 rpm for 9 h (P65NT rotor, Hitachi-koki Co.). After centrifugation, a density gradient was self-formed, and a band appeared around the central position of the centrifugation tube, as shown in Figure 2a. Small pieces of the band fractions, nearly 0.5 mL, were then carefully extracted from the top. SWCNTs were typically located in the density region from 1.42 to 1.50 g mL^{-1}. The optical absorption and Raman spectra (radial breathing modes, RBM) of the fractions are shown in Figure 2b,c. As shown in the figures, (11,10) chirality was selectively contained in the top layer of the fractions (f1). In the RBMs of the f1 fraction, only one peak at 173 cm^{-1} is observed, corresponding to a diameter of 1.43 nm,[17] which is in agreement with the tight-binding calculated diameter of (11,10) chirality (1.44 nm).[16] The RBM can be fitted with a single Lorenz function with half-width 5 cm^{-1}, confirming the single-chiral state of the sample. However, the lower regions of the fractions (f2 to f5) contained several other chiralities. The PL spectra of the fractions (Figure S1, SI) supported the fact. The PL signals from (13,8) and (14,6) appeared in the lower band region. Notably, a relative RBM peak intensity at 173 cm^{-1} decreased in the lower fraction regions (f4 and f5), as compared to that of the Semi. This result suggests that the (11,10) chirality was selectively extracted to the top fraction, and additionally the relative amount of (11,10) in lower fraction regions decreased compared to the initial sample. These results are also in agreement with the PL mapping of the lower fractions (Figure S1, SI), where the peak signal from (11,10) is relatively small when compared with that of Semi.

One of the reasons that the single-chirality state of 1.4 nm SWCNTs is achieved is that CsCl sorting has good sorting capability with respect to difference of densities. CsCl has been used as one of gradient materials in biology for the separation of DNA and proteins.[18] But typically, iodixanol is used as a gradient medium for the density gradient ultracentrifugation sorting of SWCNTs, as first proposed by Arnold.[6,19] The high-purity metal-semiconductor purification of SWCNTs with a diameter of 1.4 nm was achieved. However, the single-chirality purification of 1.4 nm SWCNTs has not yet been achieved using iodixanol. One of the advantages for using CsCl as a gradient medium is that the density gradient formed by CsCl after centrifugation is moderately curved (almost linear), as shown in Figure S2, SI. In the case of iodixanol, the density gradient becomes very steep after long centrifugation times, reducing the sorting resolution. Therefore, CsCl is more advantageous for gradient formation than iodixanol.

In the case of SWCNTs with diameters of approximately 0.8 nm, CsCl sorting tends to sort SWCNTs by diameters. Figure 3 shows results of CsCl sorting of approximately 0.8 nm SWCNTs (CoMoCAT SG65, Aldrich). The details of sorting are described in the SI. The optical absorption spectra indicate that the S_{11} peaks shifted to a lower energy region as the fraction number decreased (Figure 3b). As a result, extracting the large diameter tube [(7,5), diameter 0.83 nm] from initial (6,5) enriched sample [(6,5), diameter 0.76 nm] was possible (Figure 3c). This finding indicates that the densities of nanotubes with large diameters are smaller than those with small diameters (the densities of the (7,5) enriched and the

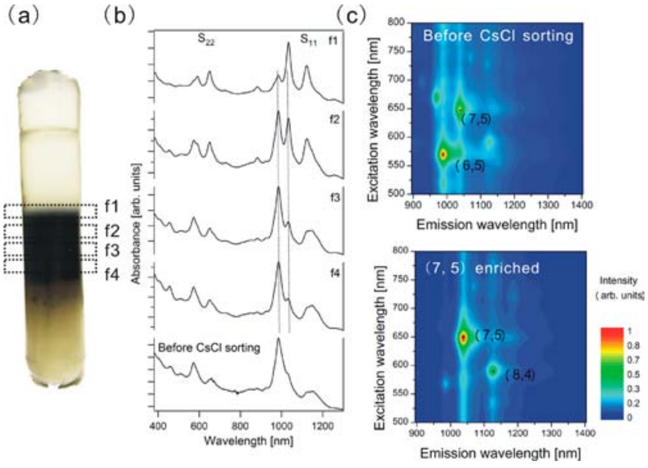

Figure 3. CsCl sorting of SWCNTs with diameters of approximately 0.8 nm, (CoMoCAT, SG65, Aldrich). (a) An image of a centrifuge tube after CsCl sorting. (b) Optical absorption spectra of the fractions. (c) PL spectra of the samples before sorting (top) and of (7,5) enriched by CsCl sorting (bottom).

(6,5) enriched fractions were 1.46 ± 0.01 and 1.48 ± 0.01 g mL^{-1}, respectively). This tendency is similar to that reported using iodixanol sorting [19] and can be explained by a simple buoyant density model written in the SI.

In the case of SWCNTs with diameters of approximately 1.4 nm, such simple relationships are clearly violated. The (11,10) chirality is not the largest nanotube diameter in the sample, as clearly shown in the optical absorption, RBM, and PL spectra. The (11,10) chirality was obtained in the lowest density region, 1.43 ± 0.01 g mL^{-1}. The packing structures of SC on the surface of the SWCNTs were predicted to influence the buoyant density.[20] To discuss the packing structure, we calculated the minimum potential energies of SC in its adsorption on the surfaces of the SWCNTs with approximately 1.4 nm diameters by using molecular dynamic (MD) simulations (Figure S3, SI). The details of MD simulations are described in the SI. The calculation indicates that the potential energy of the SC adsorption on the surface of (11,10) was the lowest among the other semiconducting SWCNTs, (14,6) and (13,8) (Figure S3, SI). Therefore, the calculation suggests the amount of the SC adsorbed on the surface of (11,10) would be larger than (13,8) and (14,6), and then the extraction volume of the (11,10)−SC complexes became larger, making the density of (11,10) smaller than the other chiralities.

From what is currently known, the CsCl sorting method cannot sort metal-semiconductor samples. In the case of CsCl sorting, only SC can be used as a surfactant for monodispersed SWCNTs. Other surfactants, such as sodium dodecyl sulfate (SDS), sodium deoxycholate, sodium benzene sulfate, cannot be used because the concentration of CsCl is 42.5%, and dispersions of SWCNTs in such high concentrations of CsCl are difficult. Thus, we cannot use SDS, which is usually a key surfactant used for metal-semiconductor sorting.[6−8] As a result we have not achieved metal-semiconductor sorting of 1.4 nm SWCNTs with CsCl. When CsCl sorting was performed on pristine SWCNTs (Mixture, Figure 1a), only (11,10) SWCNTs in a mixture state of metallic SWCNTs were extracted (Figure S4, SI). The MD calculation indicates that the minimum potential energies of the SC adsorption tended to be low as the chiral angles of SWCNTs approached 30° (Figure S3, SI). The minimum potential energies of the SC adsorption on the armchair metallic (chiral angle: 30°) and (11,10) SWCNTs (chiral angle: 28.4°) were lower than the other semiconducting SWCNTs with similar diameter size but smaller chiral angles. The above result demonstrates why we needed to apply a two-step purification process, MS and CsCl sorting, for the single chiral extraction of (11,10) SWCNTs. Notably, in the case of CoMoCAT sorting, the chiral angles of (6,5) and (7,5) are almost similar, 27.0° and 24.5°, but their diameters are significantly different, 0.76 nm and 0.83 nm, respectively. Therefore, the difference of their diameters would dominantly contribute to the difference of their densities, as shown in Figure 3.

The diameter of (11,10) SWCNTs is 1.44 nm, which is large enough for encapsulation of various kinds of organic molecules. For confirmation of molecular encapsulation, we encapsulated C_{60} to the (11,10) SWCNTs obtained by CsCl sorting. We prepared (11,10) SWCNTs encapsulating C_{60} [(11,10) peapod] using a typical sublimation method (see SI). The Raman spectrum of the (11,10) peapod (Figure 4a) clearly shows the presence of the Ag(2) mode of the encapsulated C_{60}, 1464 cm^{-1}. Figure 4b shows the shift of the RBM by encapsulation of C_{60} into (11,10). These results indicate the success of encapsulation of C_{60}.[21,22] For comparison, we encapsulated C_{60} to Semi (Semi peapod), which was in a mixed state of several semiconducting SWCNTs with different chiralities, and the changes of RBMs in the Semi are also shown (Figure 4b). In the case of the Semi, the changes of the RBMs by encapsulation of C_{60} were very complicated, and correct identifications of their shifts were rather difficult, because the RBMs were composed of several peaks due to the

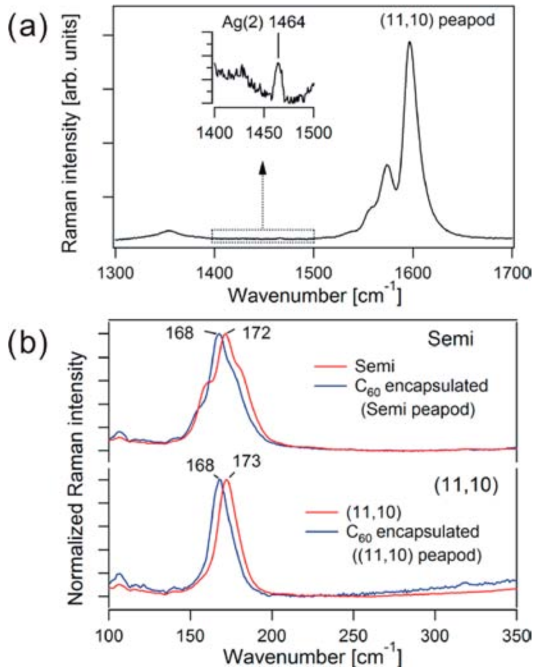

Figure 4. (a) The Raman spectrum of (11,10) peapod. The spectrum was obtained at an excitation wavelength of 488 nm. The Ag(2) peak of encapsulated C_{60} was enlarged and is presented in the inset. (b) The changes of the Raman peaks of the radial breathing modes caused by encapsulation of C_{60} into Semi and (11,10) SWCNTs (excitation wavelength of 514 nm). The Raman spectra were normalized at the peaks. Red and blue lines are before and after C_{60} encapsulation, respectively.

presence of the several different chiralities. However, in the case of the (11,10), a clear down shift of its RBM peak from 173 cm^{-1} to 168 cm^{-1} was identified. The down shift would be caused by the weak hybridization between the π states of SWCNTs and those of C_{60}.[23] The single-chirality state of (11,10) made the sharp single RBM peak and enabled the clear identification of its shift.

In summary, the single-chiral purification of (11,10) SWCNTs, whose diameter was 1.44 nm and sufficiently large for molecular encapsulation, was achieved after a two-step purification method using MS and CsCl sorting. Our results indicate the great potential of density-gradient sorting, the basic idea of which is first proposed by Arnold et al,[6] for the single-chiral purification of various types of SWCNTs. Moreover, single-chirality C_{60} peapods, (11,10) peapods, were also prepared. This method will contribute to the clarification of detailed physical/chemical properties of molecules inside nanospaces and will also serve an essential role in applications of peapod electronic devices due to their uniform surrounding electronic structures.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Details of purification methods, sample preparations and MD simulations, experimental setups for optical measurements, additional PL data, comparison of density gradient between CsCl and iodixanol, minimum potential energies of the SC adsorption on SWCNTs with approximately 1.4 nm diameter calculated by MD simulations, CsCl sorting results of initial SWCNTs, and a simple model for the relationships between diameter and density are included. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

yanagi-kazuhiro@tmu.ac.jp

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This work was partially supported by a Grant-in-Aid for Scientific Research on Innovative Areas (no. 21108523, "π-Space") and from the Ministry of Education, Culture, Sports, Science and Technology (no. 2365117) and by the Industrial Technology Research Grant Program in 2007 from New Energy and Industrial Technology Development Organization, Japan.

■ REFERENCES

(1) Hersam, M. C. *Nat. Nanotechnol.* **2008**, *3*, 387−394.

(2) Nish, A.; Hwang, J.; Doig, J.; Nicholas, R. J. *Nat. Nanotechnol.* **2007**, *2*, 640−646.

(3) Ju, S.; Doll, J.; Sharma, I.; Papadimitrakopoulos, F. *Nat. Nanotechnol.* **2008**, *3*, 356−362.

(4) Tu, X.; Manohar, S.; Jagota, A.; Zheng, M. *Nature* **2009**, *460*, 250−253.

(5) Ghosh, S.; Bachilo, S. M.; Weisman, R. B. *Nat. Nanotechnol.* **2010**, *5*, 443−450.

(6) Arnold, M. S.; Green, A. A.; Hulvat, J. F.; Stupp, S. I.; Hersam, M. C. *Nat. Nanotechnol.* **2006**, *1*, 60−65.

(7) Moshammer, K.; Hennrich, F.; Kappes, M. M. *Nano Res.* **2009**, *2*, 599−606.

(8) Liu, H.; Nishide, D.; Tanaka, T.; Kataura, H. *Nat. Comm.* **2011**, *2*, 309−316.

(9) Tange, M.; Okazaki, T.; Iijima, S. *J. Am. Chem. Soc.* **2011**, *133*, 11908−11911.

(10) Smith, B. W.; Monthioux, M.; Luzzi, D. E. *Nature* **1998**, *396*, 323−324.

(11) Lee, J.; Kim, H.; Kahng, S.; Kim, G.; Son, Y.; Ihm, J.; Kato, H.; Wang, Z. W.; Okazaki, T.; Shinohara, H.; Kuk, Y. *Nature* **2002**, *415*, 1005−1008.

(12) Yanagi, K.; Iakoubovskii, K.; Matsui, H.; Matsuzaki, H.; Okamoto, H.; Miyata, Y.; Maniwa, Y.; Kazaoui, S.; Minami, N.; Kataura, H. *J. Am. Chem. Soc.* **2007**, *129*, 4992−4997.

(13) Bandow, S.; Takizawa, M.; Hirahara, K.; Yudasaka, M.; Iijima, S. *Chem. Phys. Lett.* **2001**, *337*, 48−54.

(14) Yanagi, K.; Miyata, Y.; Liu, Z.; Suenaga, K.; Osamu, S.; Kataura, H. *J. Phys. Chem. C* **2010**, *114*, 2524−2530.

(15) Yanagi, K.; Udoguchi, H.; Sagitani, S.; Oshima, Y.; Takenobu, T.; Kataura, H.; Ishida, T.; Matsuda, K.; Maniwa, Y. *ACS Nano* **2010**, *4*, 4027−4032.

(16) Weisman, R. B.; Bachilo, S. M. *Nano Lett.* **2003**, *3*, 1235−1238.

(17) Dresselhaus, M. S.; Dresselhaus, G.; Saito, R.; Jorio, A. *Phys. Rep.* **2005**, *409*, 47−99.

(18) *Preparative Centrifugation*; Rickwood, D., Ed.; Oxford University Press: New York, 1992.

(19) Arnold, M. S.; Stupp, S. I.; Hersam, M. C. *Nano Lett.* **2005**, *5*, 713−718.

(20) Arnold, M. S.; Suntivich, J.; Stupp, S. I.; Hersam, M. C. *ACS Nano* **2008**, *2*, 2291−2300.

(21) Bandow, S.; Takizawa, M.; Kato, H.; Okazaki, T.; Shinohara, H.; Iijima, S. *Chem. Phys. Lett.* **2001**, *347*, 23−28.

(22) Kuzmany, H.; Pfeiffer, R.; Kramberger, C.; Pichler, T.; Liu, X.; Knupfer, M.; Fink, J.; Kataura, H.; Achiba, Y.; Smith, B.; Luzzi, D. *Appl. Phys. A: Mater. Sci. Process.* **2003**, *76*, 449−455.

(23) Okada, S. *Chem. Phys. Lett.* **2007**, *438*, 59−62.