

One-Dimensional Metallofullerene Crystal Generated Inside Single-Walled Carbon Nanotubes

K. Hirahara,¹ K. Suenaga,¹ S. Bandow,¹ H. Kato,² T. Okazaki,² H. Shinohara,² and S. Iijima^{1,3,*}

¹*Japan Science and Technology Corporation, Faculty of Science and Technology, Meijo University, Tenpaku-ku, Nagoya 468-8502, Japan*

²*Department of Chemistry, Nagoya University, Nagoya, 464-8602, Japan*

³*Japan Science and Technology Corporation, NEC Corporation, Miyukigaoka, Tsukuba 305-8501, Japan*
(Received 7 June 2000)

Electron microscope imaging for gadolinium metallofullerenes encapsulating in single-wall carbon nanotubes [(Gd@C₈₂)_n@SWNTs] identifies the single Gd atom encaged in each. The intermolecular distance between Gd@C₈₂ is extremely regular, regarding the chains of Gd@C₈₂ as novel one-dimensional crystals. Chemical state analysis of Gd atoms suggests evidence for charge transfer from Gd to either a fullerene cage or a nanotube. The slopes of the temperature dependence of electric resistance for the matlike films of (Gd@C₈₂)_n@SWNTs and (C₆₀)_n@SWNTs are much steeper than that for empty SWNTs, suggesting the electron scattering due to the electrostatic potential from inside fullerenes playing an important role.

PACS numbers: 71.24.+q, 81.05.Tp, 81.70.Jb, 82.80.Pv

Single-wall carbon nanotubes (SWNTs) [1,2] have cylindrical empty space inside the tubes. It is an intuitively natural idea that one may try to introduce atoms or molecules into this empty space, since the endohedral doping of these may drastically alter the electronic, transport, and mechanical properties of SWNTs. C₆₀ molecules have been found to be encaged in SWNTs [3,4]. A more intriguing class of hybrid materials can be found when one can dope SWNTs with the so-called endohedral metallofullerenes [5] because the metallofullerenes are known to be narrow-gap semiconductors unlike C₆₀ and the band gap varies depending upon the kind and the number of atoms encaged. Here we report the high-yield synthesis of SWNTs encapsulating gadolinium endohedral metallofullerenes and the temperature dependence of electric resistance for the matlike film of (Gd@C₈₂)_n@SWNTs.

Soot containing Gd@C₈₂ and other gadolinium metallofullerenes [6] was generated in direct-current (500 A, 21 V) arc discharge of Gd/graphite composite rods (15 × 15 × 300 mm³, 0.8% atomic, Toyo Tanso Co.) under a 17 l/min flow of helium at 55–65 Torr [5]. The soot was Soxhlet extracted by carbon disulfide for 60 h. The isolation of Gd@C₈₂ metallofullerene was achieved by the multistage high-performance liquid chromatography (HPLC) technique [7] with two complementary types of HPLC columns of a Buckyprep column and a Bucky-clutcher column. The purity (99.9% and up) of the isolated Gd@C₈₂ was confirmed by both positive and negative laser-desorption time-of-flight mass spectrometry. The SWNT bundles were generated by a pulsed-laser vaporization of Fe-Ni (0.6%-0.6% atomic) containing composite carbon target [8], and the residual amorphous carbon materials and catalyst particles were removed by refluxing in HNO₃ for 8 h at 160 °C. The doping of Gd@C₈₂ into the inner hollow space of SWNTs was carried out in a sealed glass ampoule at 500 °C for 24 h. Prior to the introduction of SWNTs to the ampoule, the SWNTs

were heated in dry air at 420 °C for 20 min. The sample for electron microscopy was dispersed in hexane by conventional sonication and the suspension was dropped onto the electron microscope specimen microgrid. A transmission electron microscope (JEOL 2010F) equipped with an electron energy loss spectrometer (Gatan, GIF) was operated at 120 kV for imaging and at 117 kV for spectroscopy.

In the present study, we found that the doping reaction using unheated SWNTs at 420 °C in dry air resulted only in a very small amount of (C₆₀)_n@SWNT (the so-called pea pods) [9], based on the HRTEM (high resolution transmission electron microscopy) observation. This suggests that the heat treatment opens the tube ends, and therefore the fullerene dopants were easily able to creep in the nanotube. The result was supported by an additional experiment in which unpurified as-grown SWNTs were found to be fully doped with C₆₀ when heating at 420 °C. We therefore conclude that the acid treatment is just for purifying the SWNTs. Only the process of heating in dry air is essential to create *windows* for doping inside the SWNTs. According to a preliminary observation for (C₆₀)_n@SWNTs, yield of (C₆₀)_n@SWNTs was ~50%–60% for 12 h reaction at 400 °C. Further extended reactions for 50 h at 400 °C yielded almost ~100% of (C₆₀)_n@SWNTs, suggesting that the doping mechanism is dominated by thermal diffusion of fullerenes.

Figure 1(a) shows HRTEM images of the aligned Gd@C₈₂ chains encapsulated in SWNTs. The diameter of the SWNTs that contain these metallofullerenes ranges from 1.4 to 1.5 nm. The dark spots seen on most of the C₈₂ molecules correspond to the Gd atoms in the metallofullerene cages. Such dark spots have never been recognized in HRTEM images of empty C₆₀ molecules [10]. Hence, the experiment truly demonstrates that the fullerene contains a single metal atom inside each cage. The Gd atoms are off center in each C₈₂, which is a

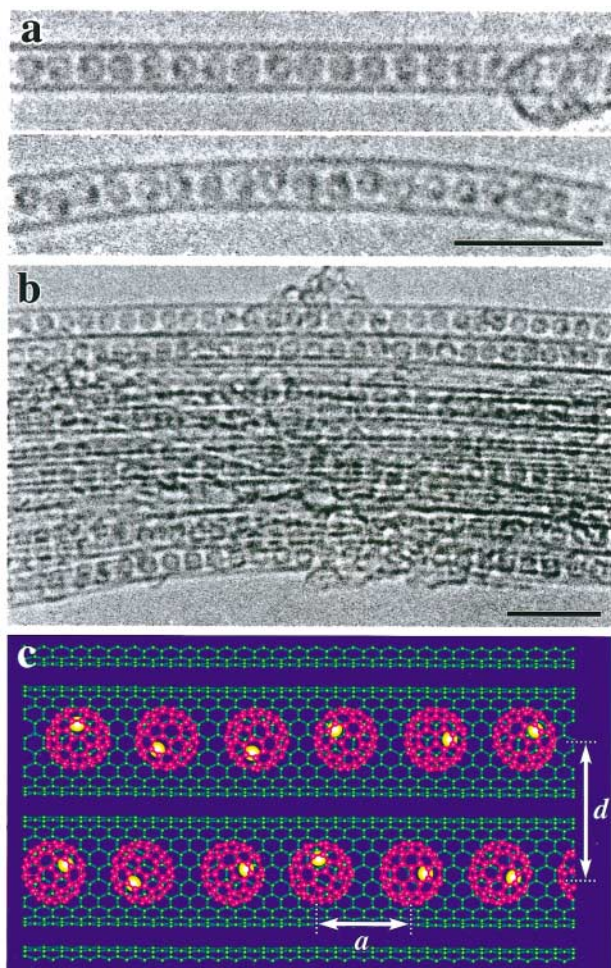


FIG. 1 (color). (a) and (b) HRTEM images of the isolated and bundled SWNTs containing the Gd@C₈₂ fullerenes. Dark spots seen on most of the fullerene cages correspond to the encapsulated Gd atoms that are oriented randomly in respect to the tube axis (bar = 5 nm). (c) A schematic representation of the metallofullerene containing SWNTs: (Gd@C₈₂)_n@SWNTs.

common characteristic for crystalline monometallofullerenes [5,11]. Being able to see the metal atoms means that the fullerene cages are not spinning even at room temperature. However, missing dark spots imply that some of the cages are spinning. These nanotubes used in the present experiment frequently form bundles [Fig. 1(b)] with an average intertubule spacing (d) \sim 1.89 nm [see the model in Fig. 1(c)].

The overall yield of the nanotubes encapsulating Gd@C₈₂ is quite high as will be demonstrated later. Although the bundles of empty SWNTs are also existing, almost all SWNTs in a bundle fully encapsulate Gd@C₈₂ for the doped bundles [Fig. 2(a)], which can be detected in their electron diffraction pattern. Such an example is shown in Fig. 2(b). Sharp streaks perpendicular to the bundle axis indicate that the intermolecular spacing between the adjacent Gd@C₈₂ is extremely regular within

each tubule as was expected from the HRTEM images. This is supported by a Fourier transform of the HRTEM image of the bundle [Fig. 2(a)] showing a similar streaked pattern. These chains of Gd@C₈₂ are therefore regarded as one-dimensional crystal with a constant intermolecular spacing.

The intermolecular spacing (a) measured is 1.10 ± 0.03 nm which is slightly smaller than that of the three-dimensional molecular crystal of M@C₈₂ (1.124 nm for

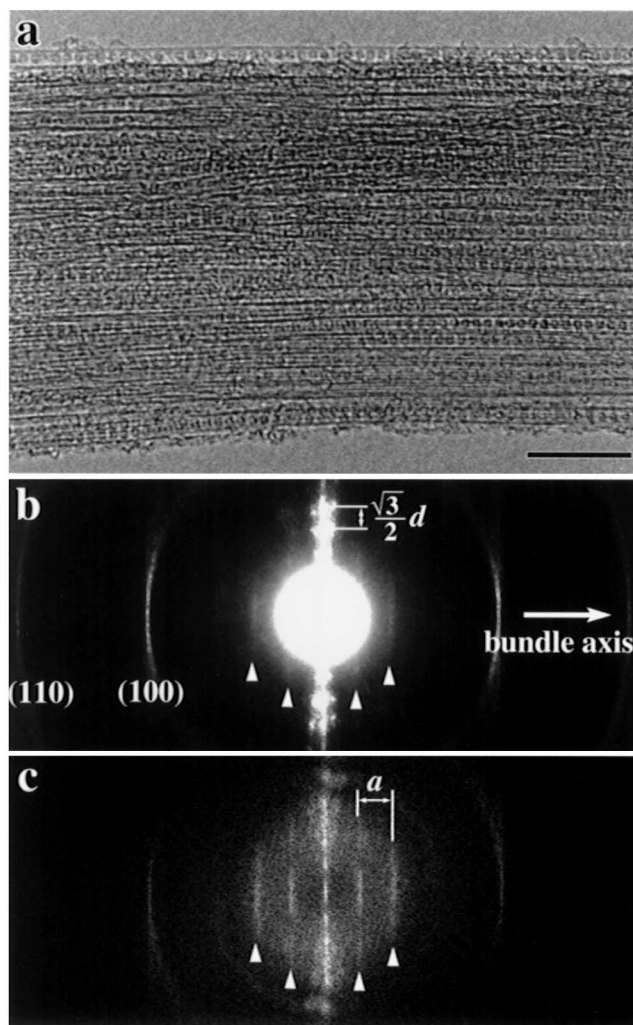


FIG. 2. (a) HRTEM image of a bundle composed of a few hundreds of SWNTs. Almost all SWNTs are fully packed with the Gd@C₈₂ fullerenes and the intermolecular spacing among them is constant (bar = 10 nm). (b) An electron diffraction pattern from the bundle and (c) a Fourier transform of the HRTEM image. A ring shown in both patterns corresponds to the (100) graphite reflection (\sim 0.214 nm). Spots aligned perpendicular to the bundle axis correspond to the intertube spacing (d) for the hexagonally close-packed SWNTs. The intertube spacing measured is not uniform but has an average value of 1.89 nm. Sharp streaks perpendicular to the bundle axis are a clear proof that the encapsulated Gd@C₈₂ are perfectly aligned and therefore regarded as one-dimensional crystal with a constant intermolecular spacing ($a \sim 1.10 \pm 0.03$ nm).

M = Sc) [11], having C_{2v} molecular symmetry based on previous synchrotron x-ray diffraction studies [5,11]. Similar one-dimensional crystals of C_{60} and C_{70} in SWNTs have the intermolecular spacings of ~ 0.97 and ~ 1.02 nm, respectively [12]. The nearest intermolecular distance of face-centered-cubic (fcc) phase of C_{60} solid is 1.00 nm [13], and that of fcc phase of thermally rotating C_{70} solid ($T > \sim 340$ K) is 1.06 nm [13,14]. In our HRTEM observation, the C_{70} molecules inside the SWNTs take random orientation, but not rotating. The intermolecular spacing obtained for a linear chain of C_{70} molecules inside SWNTs is a spatially averaged value and is comparable with that for the fcc phase of C_{70} solid. Hence we conclude that the intermolecular spacing obtained for one-dimensional crystals of C_{60} and C_{70} are smaller by $\sim 3\%$ and $\sim 4\%$, respectively. The shrink of the intermolecular spacing of inside fullerenes is perhaps associated with the small amount of electron charge transfer from fullerene cage to SWNTs.

The doping will take place from uncapped ends of SWNTs, which is supported by the fact that tubules located in the central portion of a bundle are doped equally to those at the surface of the bundle. There should be no diffusion path for large fullerene molecules from the outer bundle surfaces to the inner bundle.

A typical electron energy-loss spectrum recorded from several bundles of the $(Gd@C_{82})_n@SWNTs$ is shown in Fig. 3(a) with the Gd $N(4d)$ absorption edge (~ 145 eV) and the carbon $K(1s)$ absorption edge (~ 285 eV). The carbon K edge involves both contributions of the fullerene cage and SWNTs and therefore exhibits a sharp π^* peak and a large hump in σ^* around 299 eV. The normalization of the two edges using the relevant cross sections [15] gives the Gd/C atomic ratio of about 0.0025 (± 0.00047). This value is very close to the Gd/C atomic ratio calculated (0.0037) for a close-packed $(Gd@C_{82})_n@SWNTs$ (1.4 nm in diameter tube and 1.1 nm for intermolecular spacing). This suggests the packing rate of the $Gd@C_{82}$ is close to 68% in the examined SWNT bundles.

Figure 3(b) shows the Gd $M(3d)$ absorption edge obtained in the same region. The peak positions of the M edge of the lanthanoids metals are generally used to determine the valence state and consequently the amount of charge transfer [16]. The highest peak positions for the M_5 and M_4 edges for the $(Gd@C_{82})_n@SWNTs$ are experimentally measured as 1184 and 1214 eV, respectively. These peak positions perfectly fit with a reference spectrum for the Gd_2O_3 [16] and therefore are clear proof that the encaged Gd atoms are in a trivalent state. Since the same spin state ($^8S_{7/2}$) has been already confirmed for the encaged Gd in a bulk $Gd^{3+}@C_{82}^{3-}$ crystal [17], the valence state for the encaged Gd atoms of $Gd@C_{82}$ remains unchanged upon encapsulation by the SWNTs, i.e., $(Gd^{3+}@C_{82}^{3-})_n@SWNTs$. Although, at present, the charge state of the C_{82} fullerene cage of $(Gd@C_{82})_n@SWNTs$ is not clear, there might be

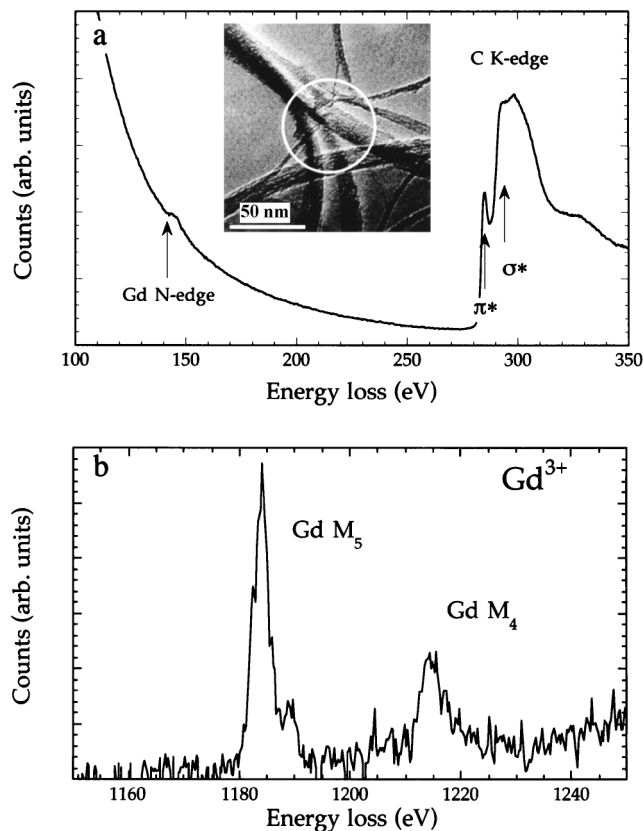


FIG. 3. (a) A typical EELS spectrum recorded from several bundles of the $(Gd@C_{82})_n@SWNTs$ (inset), involving the Gd N (~ 145 eV) and the carbon K -absorption edges (~ 285 eV). The normalization of the two edges using the relevant cross sections gives the Gd/C atomic ratio about 0.0025 (± 0.00047). Estimated Gd/C atomic ratio for close-packed $(Gd@C_{82})_n@SWNT$ is ~ 0.0037 (1.4 nm in diameter tube and 1.1 nm for intermolecular distance), suggesting the packing rate for the $Gd@C_{82}$ in SWNTs is about 68%. (b) The Gd M absorption edge from the same region. The highest peak positions for the M_5 and M_4 edges perfectly fit with the reference spectrum for Gd^{3+} and therefore are clear proof that the encaged Gd atoms are in a trivalent state as in the intact $Gd@C_{82}$ fullerene.

a possible charge transfer from the fullerene cage to the SWNTs. We noticed during the TEM observation that $(Gd@C_{82})_n@SWNTs$ are more fragile against the electron beam irradiation than the other SWNTs containing hollow fullerenes such as $(C_{60})_n@SWNTs$ and $(C_{70})_n@SWNTs$. This is suggestive of a considerable evolution in chemical properties of the nanotubes involving the metallofullerenes.

The direct-current electric resistance measurements were carried out by the four-probes method using the matlike films of $(Gd@C_{82})_n@SWNTs$, $(C_{60})_n@SWNTs$, and empty SWNTs (before doping of fullerenes) down to 5 K, and the results are shown in Fig. 4. The resistances in logarithmic scale for all samples indicate linear temperature dependence when the abscissa is represented by $T^{-1/4}$ (see inset of Fig. 4), suggesting the electron transport associated with three-dimensional variable

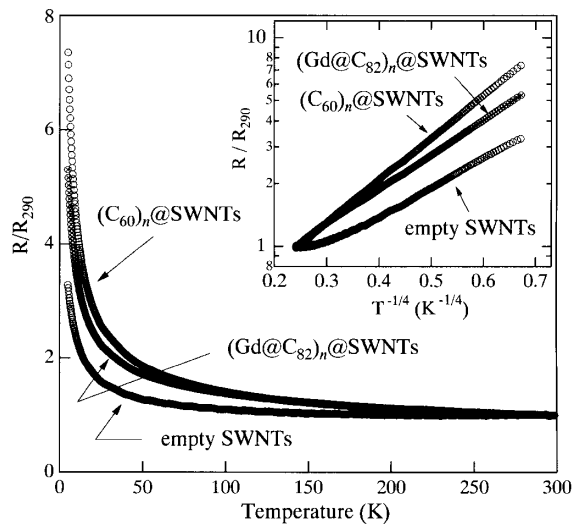


FIG. 4. Temperature dependence of electric resistance measured for the matlike films of $(\text{Gd}@C_{82})_n@SWNTs$, $(C_{60})_n@SWNTs$, and empty SWNTs. The ordinate is normalized with the electric resistance at 290 K ($\sim 10 \Omega$ for $\sim 1.5 \times \sim 4 \times \sim 0.2 \text{ mm}^3$ samples). The inset is the semilogarithmic plot of the electric resistance against $T^{-1/4}$. The measurements were carried out by the four-probes method with a constant current of $10 \mu\text{A}$.

range hopping [18]. The electric resistances are proportional to $\exp[(215/T)^{1/4}]$ for $(\text{Gd}@C_{82})_n@SWNTs$, $\exp[(475/T)^{1/4}]$ for $(C_{60})_n@SWNTs$ between the temperature range $5 < T < 300 \text{ K}$, and $\exp[(116/T)^{1/4}]$ for SWNTs between $5 < T < \sim 50 \text{ K}$. The larger temperature dependence on electric resistance observed for SWNTs encapsulating fullerenes is most probably a result of the scattering of conduction electrons due to the local electrostatic potential from inside fullerenes.

The significance of the present investigation follows. A substantial amount of fullerenes and endohedral metallofullerenes are doped in SWNTs through gas phase reaction. The gas phase doping into the SWNTs is a direct evidence for gas absorption inside the tubule hollows, giving a clear image of an absorption site in molecular level. In condensed matter physics, the doped SWNTs with regularly spaced dopant molecules will provide an ideal one-dimensional crystal expressed as a general form $(\text{metal}_l@C_m)_n@SWNTs$, where l , m , and n are integers (usually l is 1–3 and n infinite), and m is the number of carbon atoms in a fullerene. Here the doped molecule is not limited to one type of metallofullerenes but more than two types of them, or their combination with another type of molecules. The latter type doping gives rise to novel one-dimensional superstructures within a tubule.

H. S. thanks the JSPS Future Program on New Carbon Nano-Materials for the financial support of the study. A part of the work at Meijo University was supported by the Grant-in-Aid for Scientific Research on the Priority Areas “Fullerenes and Nanotubes” from the Japanese Ministry of Education, Science, Sports and Culture.

*Author to whom correspondence should be addressed.
Electronic address: ijjimas@meijo-u.ac.jp

- [1] S. Iijima and T. Ichihashi, *Nature (London)* **363**, 603 (1993).
- [2] D. S. Bethune *et al.*, *Nature (London)* **363**, 605 (1993).
- [3] B. W. Smith, M. Monthieux, and D. E. Luzzi, *Nature (London)* **396**, 323 (1998).
- [4] Y. Zhang, S. Iijima, Z. Shi, and Z. Gu, *Philos. Mag. Lett.* **79**, 473 (1999).
- [5] M. Takata, B. Umeda, E. Nishibori, M. Sakata, Y. Saito, M. Ohno, and H. Shinohara, *Nature (London)* **377**, 46 (1995).
- [6] H. Shinohara, M. Kishida, T. Nakane, T. Kato, S. Bandow, Y. Saito, X.-D. Wang, T. Hashizume, and T. Sakurai, in *Recent Advances in the Chemistry and Physics of Fullerenes and Related Materials*, edited by K. M. Kadish and R. S. Ruoff (The Electrochemical Society, Inc., New York, 1994), p. 1361, and references therein.
- [7] E. Yamamoto *et al.*, *J. Am. Chem. Soc.* **118**, 2293–2294 (1996).
- [8] A. Thess *et al.*, *Science* **273**, 483–487 (1996).
- [9] B. W. Smith and D. E. Luzzi, *Chem. Phys. Lett.* **321**, 169 (2000).
- [10] S. Iijima, T. Wakabayashi, and Y. Achiba, *J. Phys. Chem.* **100**, 5839 (1996).
- [11] E. Nishibori *et al.*, *Chem. Phys. Lett.* **298**, 79–84 (1998).
- [12] H. Kataura and K. Hirahara (unpublished).
- [13] M. S. Dresselhaus, G. Dresselhaus, and P. C. Eklund, *Science of Fullerenes and Carbon Nanotubes* (Academic Press, San Diego, 1996), in Chap. 7, and references therein.
- [14] As freezing the rotation of C_{70} molecules, the C_{70} solid indicates two types of hexagonally close-packed structures as a function of temperature; the nearest intermolecular distance of C_{70} in the basal plane is first 1.06 nm and finally falls into 1.01 nm with decreasing temperature.
- [15] The Hartree-Slater cross section with convergence angle correction provided by the Gatan ELP3.0 software were used for the normalization. The error is due to the uncertainty for the cross sections.
- [16] B. T. Thole, G. van der Laan, J. C. Fuggle, G. A. Sawatzky, R. C. Karnatak, and J.-M. Esteve, *Phys. Rev. B* **32**, 5107 (1985).
- [17] K. Suenaga, S. Iijima, H. Kato, and H. Shinohara, *Phys. Rev. B* **62**, 1627 (2000).
- [18] Y. Yoshida and I. Oguro, *J. Appl. Phys.* **86**, 999 (1999).