

Transmission Electron Microscopy Imaging of Individual Functional Groups of Fullerene Derivatives

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Mobility and reactivity of the functionalized fullerenes with pyrrolidine (C_{60} - C_3NH_7) incorporated in single-wall carbon nanotubes were examined by high-resolution transmission electron microscopy. An individual functional group attached to each fullerene cage is unambiguously visualized. This provides a direct evidence for the functionalized structure on a single-molecular basis. A rotational motion of the incorporated molecules tends to occur during the observation and, consequently, each fullerene molecule is likely to stand facing its functionalized group towards the nanotube wall. A fine structure analysis of electron energy-loss spectra for the nitrogen $K(1s)$ edge shows a considerable change in the nitrogen chemical state and suggests a strong tube-fullerene interaction.

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Functionalizing or chemical modification of fullerenes is a promising approach to realize the fullerene-based devices such as organic photovoltaics or organic transistors and has attracted huge interest from both physicists and chemists [1]. Even though the nuclear magnetic resonance (NMR) and x-ray diffraction (XRD) techniques are generally used for the structural assignment of the functionalized fullerenes, a high-resolution transmission electron microscopy (HR-TEM) has been hardly used to characterize the fullerene derivatives because the individual functional groups are quite difficult to observe due to their very small scattering factors and their instabilities under the electron microscopes [2]. The structure of fullerene derivatives has therefore never been elucidated at the single-molecular basis. We demonstrate here for the first time the visualization of individual functional groups of fullerene derivatives and clarify their reactivity by *in situ* HR-TEM and electron energy-loss spectra (EELS).

The carbon nanotubes are also promising candidates for various potential applications. The physical and chemical properties of carbon nanotubes can be modified by doping, i.e., putting various molecules inside. It is known that the nanotubes can incorporate the fullerenes and their families inside the hollow, so-called “peapods,” and such encapsulations drastically alter the properties of the host nanotubes [3,4]. Especially the incorporations of endohedral metallofullerenes can alter the field-effect transistor (FET) properties of host nanotubes by robust interaction between fullerenes and nanotubes [5]. Using exofullerenes instead of endofullerenes as guest molecules should lead to more strong interactions between fullerenes and nanotubes, therefore a more effective doping could be achieved for realizing the nanotube devices. In this study, we have chosen the C_{60} - C_3NH_7 molecules as a typical fullerene

derivative and put them into the single-wall carbon nanotubes (SWNTs), in the hope of obtaining the direct evidence for the strong interaction between exofullerenes and nanotubes.

The fullerene molecules (C_{60}) with a functional group of C_3NH_7 [C_{60} - C_3NH_7 , N-methyle-3,4-fulleropyrrolidine, Fig. 1(a)] were prepared by following the Prato reaction [6]. They were then encased in the inner space of a SWNT by a reflux method using hexane as solvent [7]. For TEM measurements, the peapods [$(C_{60}$ - C_3NH_7)_n@SWNT] samples were suspended in ethanol (99.9 vol. %) by ultrasonication. The suspension was dropped onto a carbon microgrid for TEM observation. HR-TEM and EELS observations were performed at room temperature with JEM-2010F and JEM-2100F equipped with a Gatan CCD detector and a Tridium electron spectrometer at an accelerating voltage of 120 kV. A typical exposure time for imaging is ranging from 1 to 2 seconds and the electron total dose was kept as small as possible in order to minimize the irradiation effect. It turned out that the fullerene derivatives

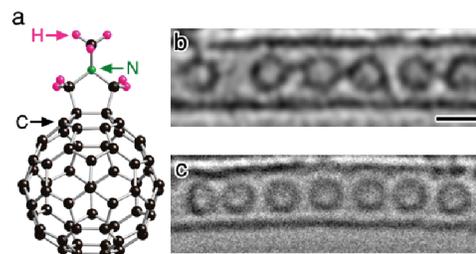


FIG. 1 (color). (a) A scheme of the used fullerene derivatives functionalized with a pyrrolidine (C_{60} - C_3NH_7 , N-methyle-3,4-fulleropyrrolidine). HR-TEM images of a functionalized fullerene peapod (b) and (c) the nonfunctionalized fullerene peapod.

are mostly resistive under the electron dose of $\sim 100\,000$ electrons/nm². However, some irradiation effect due to the incident electron beam can be particularly inevitable for the EELS fine structure analysis because we need quite longer exposure times to obtain the good signal-to-noise (SN) ratio from the low concentration elements such as nitrogen. The typical dose for the EELS analysis on the peapod materials is as much as 1 000 000 to 10 000 000 electrons/nm² in this experiment.

In order to visualize clearly the individual molecular structures with the functional groups, the contrast of nanotube walls overlapping the fullerene molecules must be minimized. For this purpose, we have optimized the microscopy imaging condition so that the interference from the nanotube graphene layer becomes minimum by adjusting the defocus value to get a zero amplitude in the contrast transfer function near the frequency of 0.214 nm (a distance between the neighboring zigzag chain in the graphene layer) [8]. Figure 1(b) shows a thus obtained HR-TEM image of a peapod of fullerene derivatives ((C₆₀-C₃NH₇)_n@SWNT). In comparison with a reference image of the nonfunctionalized C₆₀ peapod [Fig. 1(c)], the functionalized C₆₀ molecules exhibit some extra features outside the cage and therefore they are not spinning inside the SWNT.

Figure 2 shows a series of HR-TEM images of another (C₆₀-C₃NH₇)_n@SWNT taken under an interval of 2 seconds between each image. By carefully examining the obtained sequential images, one can notice that a line-shaped black contrast (approximately 0.25 nm long) can be seen at the outside of each fullerene molecule [indicated by the arrowheads in Fig. 2(b)], which correspond to the pyrrolidine-type functional groups. Although these contrasts of the functional groups can often appear in the

middle of the fullerene (marked by the arrows), it does not mean that they are inside the fullerenes. They actually locate between the nanotube and the fullerene in the projected HR-TEM image. And it is worth noting that the array of C₆₀-C₃NH₇ molecules does not appear aligned regularly in the tube axis because these functionalized fullerenes arrange in various directions relative to the axis of the SWNT. By inspecting the frame model attentively, it can be noted that almost all of the C₆₀-C₃NH₇ fullerenes align themselves with their functional groups extending toward the wall of the surrounding SWNT. In order to confirm the obtained HR-TEM images, the image simulations for the incorporated fullerene derivatives have been also made and will be discussed later.

By comparing the sequential HR-TEM images [Figs. 2(a)–2(c)], one can simply identify some rotational motions of the fullerene molecules inside SWNTs. The indicated fullerenes numbered 1, 2, and 3 and shown in Fig. 2(a) change their directions obviously compared with the corresponding ones in Fig. 2(b). The incident electron beam may transfer some energy to these fullerenes causing their rotations, although the incident electron density during the observation was substantially reduced comparing with that in the usual observation condition of “metal-fullerene” peapods [9]. A similar rotational motion of individual molecules can be more clearly seen in the movie provided through the supplementary material depository [10]. Note that the translational motions of fullerene molecules in SWNT are quite limited in the case of fullerene derivatives in comparison with the nonfunctionalized fullerenes, which show quite rapid translational motions in SWNTs [11]. This different behavior is suggestive of a strong interaction between the nanotube wall and the functionalized fullerenes. Also the functionalized fullerenes are more sensitive to the electron beam compared to the nonfunctionalized fullerenes and more easily fuse or coalesce with each other [12]. This is indeed a proof of the higher reactivity of the functionalized fullerenes. It is also worth noting that when two neighbor C₆₀-C₃NH₇ fullerenes begin to coalesce, they do not connect through their functional groups but the fullerene bodies themselves [indicated by arrows in Fig. 2(c)].

EELS fine structure analysis was also carried out in order to confirm the presence of nitrogen in the peapods and to detect the evolution of the chemical states of the incorporated nitrogen atoms of the functionalized fullerenes (C₆₀-C₃NH₇). Figures 3(a) and 3(b) show the EEL spectra of both the carbon *K* edge and nitrogen *K* edge obtained from a pure crystal of the functionalized C₆₀-C₃NH₇ fullerenes (intact) and the C₆₀-C₃NH₇ fullerenes inside SWNTs (peapods), respectively. The quantification of the carbon and nitrogen *K* edges by using a hydrogenic cross section with the convergence angle correction leads to the atomic ratios of N to C being 0.016 ± 0.003 for the functionalized C₆₀-C₃NH₇ fullerenes crystal while it is 0.0044 ± 0.0008 for the (C₆₀-C₃NH₇)_n@SWNT peapods. These values are in good agreement with the

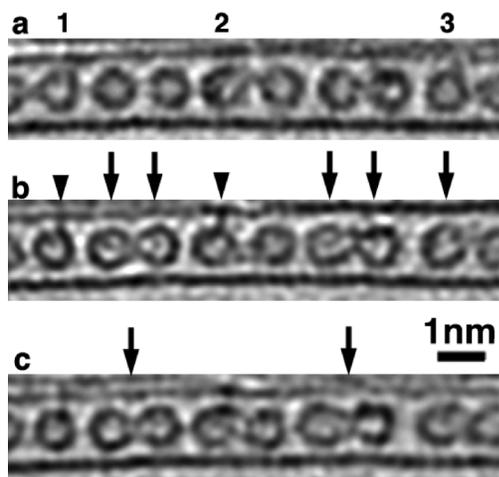


FIG. 2. A sequential HR-TEM image of (C₆₀-C₃NH₇)_n@SWNTs. The functional group attached to each fullerene cage is indicated by arrows and arrowheads. (a) 0 sec (b) 2 sec, and (c) 4 sec. Some of the fullerenes make rotations inside the SWNTs. Two of the adjacent fullerenes begin to fuse each other [(c)]. See also the provided movie file [10].

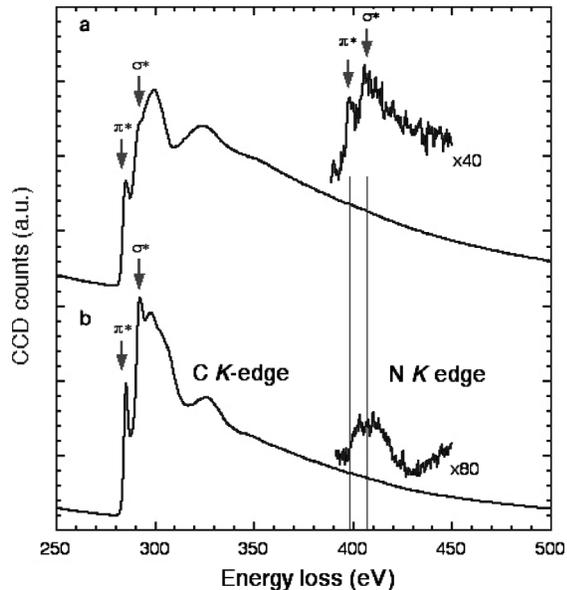


FIG. 3. (a),(b) EELS spectra taken from a crystalline particle of the fullerene derivatives (C_{60} - C_3NH_7) before being encapsulated and from the peapods, respectively. The fine structures of carbon represent for the fullerenes with degraded symmetry (a) and for the main contribution of SWNTs (b). The nitrogen K edge in (a) resembles that of nitrogen atoms in the pyrrolidine, but it completely evolves after the encapsulation in the peapod (b) because of the strong interaction with the tube wall.

calculated ones for the models [0.0159 (C_{60} - C_3NH_7) and 0.0038 (assuming that there are 200 atoms of C in SWNT per one C_{60} - C_3NH_7 molecule, for the fully packed peapods), respectively], and prove the presence of nitrogen. Therefore the effect of nitrogen atom loss due to the electron irradiation is negligible.

The fine structures of both carbon and nitrogen K edges look quite different for the two specimens. The clear π^* and σ^* peaks of the carbon K edge [Fig. 3(b)] from the peapods are attributed to the carbon atoms in nanotubes or the curved graphene layer [13], while the somehow dull peaks in the carbon K edge of intact fullerene derivatives [Fig. 3(a)] show quite a good agreement with those of the endohedral fullerenes and originate from the degraded symmetry of modified fullerenes [14]. Most interestingly the π^* and σ^* features of the nitrogen K edge of the C_{60} - C_3NH_7 fullerene peapods appear completely different from those of the intact C_{60} - C_3NH_7 fullerene derivatives. The nitrogen K edge of the intact fullerene derivatives shows the typical features of nitrogen in pyrrole [15,16], while a considerable core-level shift ($1 \sim 2$ eV) and relative intensity changes between π^* and σ^* can be obviously detected in the nitrogen K edge for the peapods. The alterations in the nitrogen K edge fine structure should be attributed to the changing of the environment around the nitrogen atoms for the C_{60} - C_3NH_7 fullerenes incorporated inside the SWNT compared with those for the intact C_{60} - C_3NH_7 fullerenes crystals during the longer acquisition time.

In order to investigate more detailed structure of the fullerene derivative in the peapods, careful simulations of the HR-TEM images were performed and compared with the experimental images [Figs. 4(a) and 4(b)]. The functionalized fullerenes of C_{60} - C_3NH_7 with their functional groups show very similar contrasts with the simulated ones. However, we should consider carefully some changes of the functional groups due to the electron irradiation. We have made the image simulations with the three different structures based on the described model [Fig. 4(c)], namely, (i) as is, (ii) without hydrogen atoms (lost 1–3 H atoms on the top of the methyl group), and (iii) without methyl group. If the fullerene derivatives retain the pyrrolidine groups as they are, the size of fullerene is too long to be encapsulated in standing alignment in SWNTs (in the radial direction of the SWNTs). Therefore the functional group should be deformed or maybe partly detached during the longer acquisition after a few exposure times. Indeed, the model without hydrogen (ii) or methyl (iii) fits fairly well with the experimental image [Fig. 4(a)] in terms of the distance between the tube wall and the molecular center. This result may suggest that the hydrogen atoms [or even the methyl group ($-CH_3$)] existing on the top of the pyrro-

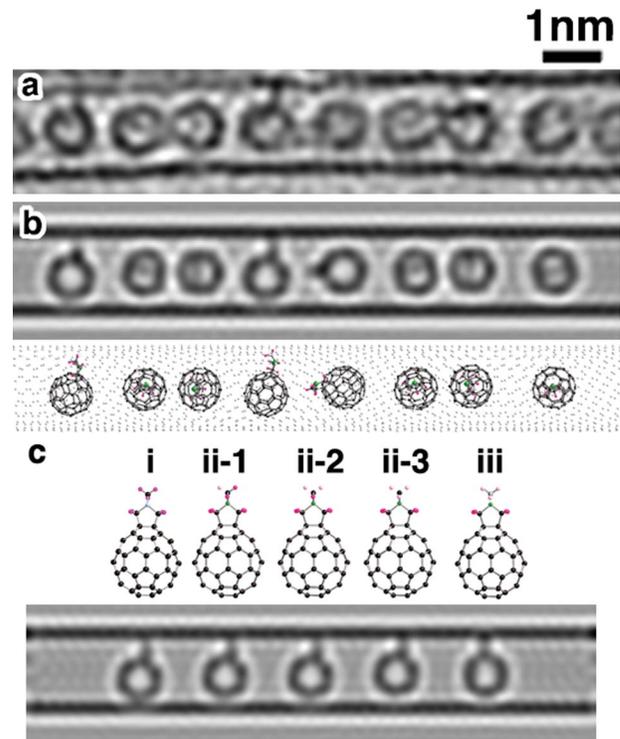


FIG. 4 (color). A comparison of the experimental HR-TEM image (a) with the simulated image (b). We have made several kinds of image simulations for the molecular structure: intact (i), with the detached hydrogen atoms (from 1–3 H atoms) (ii), or without the methyl group (iii). The latter two [(ii) and (iii)] fit reasonably well with the observed images. Note that most of the observed functional groups appearing to attach to the tube wall, suggesting the strong interaction between each functional group and the tube wall.

lidine may be lost under the incident electron beam. Consequently, the bared carbon or nitrogen atom should be likely to make new bonds with the carbon atoms in the SWNT. This explains well the strong interaction of the functional fullerenes with the carbon atoms of the SWNT's wall.

In order to corroborate the EELS fine structure analysis, the first principle calculations of the nitrogen $1s$ excitation level after the geometrical optimizations were performed for the defected structures described above [17]. The transition energy of the nitrogen $1s$ with a core hole for the intact C_{60} - C_3NH_7 was calculated around ~ 395 eV, which is reasonably close to (but a little smaller than) the experimental value of x-ray photoelectron spectroscopy (XPS) studies for the pyrrolidine [18,19]. Simply removing the hydrogen atoms or methyl group from the C_{60} - C_3NH_7 always leads to core-level shifts towards the lower energy, which disagree with our experiments. The upper shift as large as 2 eV can be well reproduced by approaching the nitrogen atom (after removing the methyl group) to the carbon nanotube until the C-N distance decreases to ~ 0.14 nm. The estimated core-level shift shows a good agreement with the observation and reasonably suggests a strong interaction between the nitrogen and the host nanotube.

The results presented here show direct evidence for a more robust interaction of the functionalized fullerenes with the host nanotubes than that of the nonfunctionalized fullerenes. The functionalized fullerenes cannot rotate freely in SWNTs. The functional groups are likely to couple with the host nanotube wall and become very reactive under the electron beam. Therefore the various functionalized fullerenes should act as efficient dopants for adjusting the properties of the host nanotube as it was recently shown for doping with the organic molecules [20].

This work is also important for the distinct visualization of individual functional groups. As it was recently demonstrated, even the light element (such as single carbon atoms) can be visualized by HR-TEM with atomic sensitivity [21]. There is, however, an intrinsic problem of electron irradiation damage due to the momentum transfer or inelastic scattering, therefore the constituent atoms are only visible when the individual molecules retain their structures under the electron microscopic observations. Using the nanotube as a specimen cell provides two advantageous conditions, i.e., the lowest background noise and the considerable specimen protection. Much lower dose imaging or decreasing the ambient temperature would be greatly beneficial for the future research aimed at analyzing individual molecular structures and/or chemical reactions.

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- [1] *The Chemistry of Fullerenes*, edited by R. Taylor (World Scientific, Singapore, 1995).
- [2] Y. Fujiyoshi, T. Kobayashi, K. Ishizuka, N. Uyeda, Y. Ishida, and Y. Harada, *Ultramicroscopy* **5**, 459 (1980).
- [3] J. Lee, H. Kim, S.-J. Kahng, G. Kim, Y. Son, J. Ihm, H. Kato, Z. W. Wang, T. Okazaki, H. Shinohara, and Y. Kuk, *Nature (London)* **415**, 1005 (2002).
- [4] D.J. Hornbaker, S.-J. Kahng, S. Misra, B. W. Smith, A. T. Johnson, E. J. Mele, D. E. Luzzi, and A. Yazdani, *Science* **295**, 828 (2002).
- [5] T. Shimada, T. Okazaki, R. Taniguchi, T. Sugai, H. Shinohara, K. Suenaga, Y. Ohno, S. Mizuno, S. Kishimoto, and T. Mizutani, *Appl. Phys. Lett.* **81**, 4067 (2002).
- [6] M. Prato, M. Maggini, C. Giacometti, G. Scorrano, G. Sandona, and G. Farnia, *Tetrahedron* **52**, 5221 (1996).
- [7] A. Mrzel (to be published).
- [8] Y. Sato, T. Yumura, K. Suenaga, H. Moribe, M. Ishida, D. Nishide, H. Shinohara, and S. Iijima (to be published).
- [9] K. Urita, Y. Sato, K. Suenaga, A. Gloter, A. Hashimoto, M. Ishida, T. Shimada, H. Shinohara, and S. Iijima, *Nano Lett.* **4**, 2451 (2004).
- [10] See EPAPS Document No. E-PRLTAO-96-050610 for a movie file (Movie1.gif) of rotating functionalized fullerenes. For more information on EPAPS, see <http://www.aip.org/pubservs/epaps.html>.
- [11] B. Smith, M. Monthieux, and D. Smith, *Chem. Phys. Lett.* **315**, 31 (1999).
- [12] D. A. Britz, A. N. Khlobystov, J. Wang, A. S. O'Neil, M. Poliakoff, A. Ardavan, and G. A. D. Briggs, *Chem. Commun. (Cambridge)* 176 (2004).
- [13] K. Suenaga, E. Sandre, C. Colliex, C. J. Pickard, H. Kataura, and S. Iijima, *Phys. Rev. B* **63**, 165408 (2001).
- [14] K. Suenaga, S. Iijima, H. Kato, and H. Shinohara, *Phys. Rev. B* **62**, 1627 (2000).
- [15] G. Rourillon, S. Raaen, T. A. Skotheim, M. Sagurton, R. Garrett, and G. P. Williams, *Surf. Sci. Lett.* **184**, L345 (1987).
- [16] K. Suenaga, M. Yudasaka, C. Colliex, and S. Iijima, *Chem. Phys. Lett.* **316**, 365 (2000).
- [17] The generalized gradient approximation with the pw91 and hct407 functionals was used for the geometrical optimization of the defected fullerene derivatives with a small piece of graphene layer. See the details in F. A. Hamprecht *et al.*, *J. Chem. Phys.* **109**, 6264 (1998).
- [18] S. Shimada, T. Hanai, O. Yamamoto, and H. Saitoh, *Thin Solid Films* **471**, 128 (2005).
- [19] S. Wallace, K. D. Bartle, and D. L. Perry, *Fuel* **68**, 1450 (1989).
- [20] T. Takenobu, T. Takano, M. Shiraishi, Y. Murakami, M. Ata, H. Kataura, Y. Achiba, and Y. Iwasa, *Nat. Mater.* **2**, 683 (2003).
- [21] A. Hashimoto, K. Suenaga, A. Gloter, K. Urita, and S. Iijima, *Nature (London)* **430**, 870 (2004).