

## Direct Imaging of the Alkali Metal Site in K-Doped Fullerene Peapods

Lunhui Guan,<sup>1,2</sup> Kazu Suenaga,<sup>2,\*</sup> Zujin Shi,<sup>1</sup> Zhennan Gu,<sup>1,†</sup> and Sumio Iijima<sup>2</sup>

<sup>1</sup>Department of Chemistry, Peking University, Beijing 100871, People's Republic of China

<sup>2</sup>National Institute of Advanced Industrial Science and Technology (AIST), Tsukuba 305-8565, Japan

(Received 27 September 2004; published 2 February 2005)

The structure of K-doped fullerene peapods has been investigated by means of high-resolution transmission electron microscopy and electron energy-loss spectroscopy (EELS). It is proven that the potassium atoms can be doped at the intermolecular sites within C<sub>60</sub> peapods. The EELS spectrum of potassium (K) *L* edge clearly exhibits the feature of K<sup>+</sup> in the doped peapod and consequently suggests *n*-type doping. These results encourage the realization of a one-dimensional superconducting wire based on the nanotube peapods.

DOI: 10.1103/PhysRevLett.94.045502

PACS numbers: 61.48.+c, 81.05.Tp, 81.70.Jb, 82.80.Pv

Molecular arrays of fullerenes can be encapsulated in single-walled carbon nanotubes (SWNTs) to form wirelike rows, as demonstrated for the first time by Smith *et al.* [1]. Since their discovery, fullerene-filled SWNTs, known as fullerene peapods, have been studied theoretically [2] and experimentally [3] due to their anticipated unique electronic properties and potential applications, e.g., in high temperature superconductors [4]. Recently, there have been several studies reported on the chemical doping of fullerene peapods, such as with FeCl<sub>3</sub> and potassium (K) [5–8]. By an *in situ* spectroelectrochemical study, it was suggested that doping peapods with potassium leads to an insertion of the alkali metal not only between the tubes in a bundle but also into the interior of the peapods [7]. Clarification of the dopant site is quite important in the analogy to the alkali-doped fullerite, e.g., the K<sub>x</sub>C<sub>60</sub> crystal [9,10], because the *n* doping into the lined-up fullerene molecules should cause an excess charge state and therefore may lead to its superconducting feature. However, the potassium atom site of the doped peapods has been so far unclear. Herein we report clear evidence for the intermolecular site of potassium atoms in K-doped fullerene peapods (C<sub>60</sub>@SWNTs) by means of high-resolution transmission electron microscopy (HR-TEM) and electron energy-loss spectroscopy (EELS).

In this study, SWNTs were prepared by an arc-discharge method and purified up to 95%. The typical diameters of the SWNTs are in the range of 1.3 to 1.4 nm, which is larger than the threshold for filling fullerenes (~1.2 nm) [11]. The SWNTs were first filled with fullerene molecules (C<sub>60</sub>) in a gas phase method [12] by mixing SWNTs with excess C<sub>60</sub> and heating the mixture at 773 K in 1 × 10<sup>-3</sup> Pa vacuum over 48 h. The filling ratio is estimated over 90% by HR-TEM observation. Then the peapod was degassed at 573 K in 1 × 10<sup>-3</sup> Pa vacuum and subsequently exposed to potassium vapor at 473 K over 50 h. Thus obtained K-doped peapods were dispersed in ethanol and a droplet of the suspension was deposited on a TEM grid coated with a holey carbon film. A field emission TEM (JEOL, JEM-2010F operated at 120 kV) equipped with an

electron energy-loss spectrometer (Gatan ENFINA) was used for the experiments. The observations were performed at a range of the temperature varying from 300 K up to 473 K. We also employed optimized parameters for imaging to minimize the electron beam induced modification of the material [13].

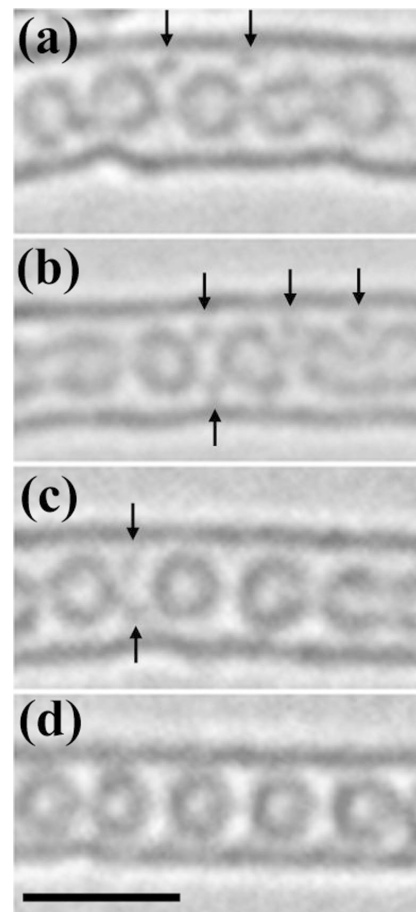


FIG. 1. HR-TEM images for the potassium-doped C<sub>60</sub> peapods (a)–(c) and the intact (undoped) C<sub>60</sub> peapod (d). The arrows indicate the potassium atom positions. Scale bar = 2 nm.

Figure 1 shows the typical HR-TEM images of the fullerene peapods ( $C_{60}$ @SWNTs) acquired at room temperature after (a)–(c) and before (d) doping with potassium. For the doped peapods with potassium, some dark spots clearly appear inside nanotubes and are allocated at the interfullerene sites (indicated by arrows) [Figs. 1(a)–1(c)]. They are ascribed to the individual potassium atoms in comparison with the undoped peapod where no extra dark spots can be detected [Fig. 1(d)]. It should be noted that even in the K-doped peapods, the doping with potassium has taken place inhomogeneously in the examined peapods because the potassium atoms cannot be seen at all in the interfullerene sites but are frequently absent. The number of potassium atoms among two adjacent fullerene molecules is typically one or two.

The above images are the first evidence for the encapsulation of potassium as doping ions inside SWNTs. The intermolecular distance of the intact peapods is approximately 0.99 or 0.97 nm [8,14] and does not show a dramatic change after the doping with potassium here. Also the potassium atoms are not totally immobile but occasionally move inside the peapods even at room temperature [15].

More importantly, the K-doped peapod has proven to be quite stable in the ambient condition. We successfully observed the potassium atoms at the intrapeapod sites even after the exposure to air or to ethanol. This is a stark contrast to the alkali-doped fullerite which easily decomposes in air so that the practical use of this superconducting material has not been taken seriously. Kalbac *et al.* have also suggested that exposure to air and humidity deactivates the potassium only outside the peapods, but it does not affect the potassium held inside the peapod and charged fullerene state [7]. The SWNTs definitively prevent the encapsulated potassium, which is very reactive, from oxidation during the sample preparation process. However, the potassium atoms in the doped peapods become quite unstable when heated. During our *in situ* TEM observation, the potassium atoms quickly disappeared when the specimen temperature is elevated to over  $\sim 373$  K. We assume that raising the temperature might cause a rapid movement of potassium atoms, which will lead to the escape of the potassium atoms from the SWNTs.

To confirm the presence of potassium atoms, a chemical analysis by means of EELS has been performed on the K-doped peapod as well as the intact (undoped) peapod and a KCl crystal. The spectra have been recorded on several bundles of peapods, but not on an individual peapod. Comparing the EELS spectrum of the K-doped peapod (Fig. 2 top) with those of the undoped peapod (middle) and the KCl crystal (bottom), one can clearly see the features of both the carbon  $K(1s)$  edge and potassium  $L_{23}(2p)$  edge of the three specimens. The carbon  $K$  edge of the undoped peapod involves the sharp  $\pi^*$  ( $\sim 285$  eV) peak and  $\sigma^*$  with a small bump feature starting around

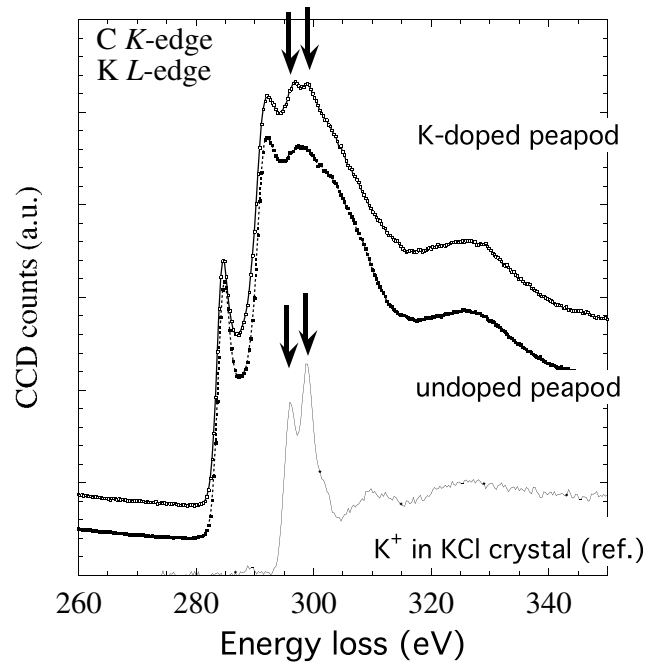


FIG. 2. EELS spectra of the K-doped peapod and the undoped peapod. A spectrum of KCl is also shown as a reference.

292 eV as reported in previous Letters [13,16], whereas the spectrum of the K-doped peapod clearly indicates some extra features just after the first  $\sigma^*$  peak (indicated by arrows). The two additional peaks obviously come from the potassium  $L_{23}$  edge as seen in the reference KCl spectrum (Fig. 2 bottom). Because there is no apparent core-level shift of the potassium  $L_{23}$  edge between the K-doped peapod and KCl, the oxidation state of potassium in the doped peapod should be +1 as so in the KCl. This is, therefore, a clear proof that the  $n$ -type doping should be realized in the peapod by potassium insertion as previously suggested by Raman studies [5–8]. However, the quantification of EELS spectra by using a simple hydrogenic cross section with the convergence angle correction leads to an extremely high K/C atomic ratio (6 at. % potassium), which means the ratio of potassium atoms per  $C_{60}$  fullerene is around  $x = 10$ – $15$  (in the form of  $K_xC_{60}$ ). This suggests that K doping has taken place also at the interpeapod sites in bundles [17].

A previous Raman study has shown that the doping with potassium starts with a charge transfer to the SWNT and the excess charge state of  $C_{60}$  fullerenes can be found only in heavily doped peapods [5]. Our observation also confirms the two different doping sites for K-doped peapods [7]; one is the intrapeapod site and the other is the interpeapod site (between the bundles). The potassium atoms outside the peapods do not survive the specimen preparation process and are probably washed out during the ultrasonication in ethanol. Therefore only the potassium atoms at the intrapeapod sites are visible in our HR-TEM images.

In order to determine the positions of potassium atoms inside the peapods, we performed a series of TEM image simulations with different potassium positions. In Fig. 1, the K- $C_{60}$  distance apparently ranges from 0.6 to 0.8 nm and the interfullerene distance shows up  $0.95 \pm 0.05$  nm in the projected TEM images. Liu *et al.* claimed by an electron diffraction study a decrease of the intermolecular distance from 0.99 to 0.96 nm with a heavier K-doping peapod [8], which cannot be confirmed by the present experiment. A reasonable fit with one of the experimental images was obtained when the K- $C_{60}$  distance is 0.6–0.8 nm and the potassium atom to tube-wall distance is set to 0.3 nm. The (10, 10) nanotube was chosen for the typical diameter of SWNT used in this experiment. Figure 3 shows one of the best fits between TEM image (a) and a simulation (b) with its schematic model (c). Thus the K- $C_{60}$  distance has a wide distribution, but a typical value (0.62 nm) has been chosen and schematized in Fig. 4(a). It is noted that the potassium atoms are not always in the same plane of fullerene molecules normal to the observation axis.

We should compare the position of potassium in the peapod with that in the classical superconducting fullerenes. The determination of the structure is of great interest in connection with the known structure of superconducting  $K_3C_{60}$ . The  $K_3C_{60}$  has a face center cubic lattice (lattice constant is 1.424 nm) with potassium atoms occupying both the interstitial tetrahedral and octahedral sites [9]. The most important feature of the K-doped  $C_{60}$  peapod is that it owns some structural similarity with  $K_3C_{60}$ . When potassium atoms occupy the tetrahedral sites with the two

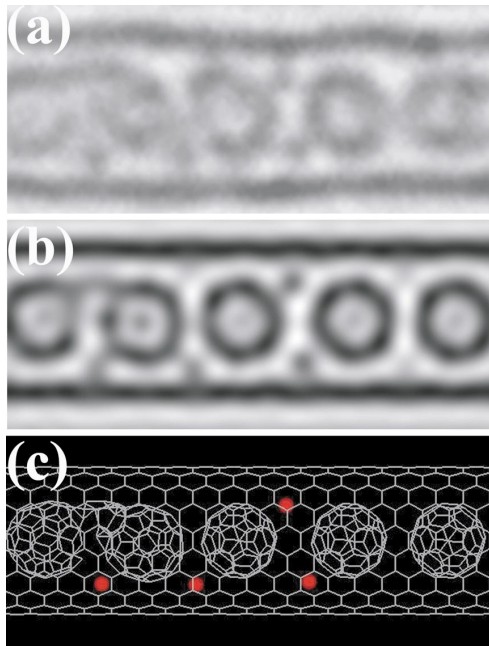


FIG. 3 (color). (a) A typical HR-TEM image of the K-doped  $C_{60}$  peapod, (b) a best fit simulation, and (c) its schematic model. (Red: potassium; gray: carbon).

neighboring  $C_{60}$  distance  $\sim 1.00$  nm, the shortest distance between a potassium atom and the nearest  $C_{60}$  molecule center is 0.61 nm. The angle between two  $C_{60}$  fullerenes and the interstitial potassium atom is  $109^\circ$  [Fig. 4(b)]. For the octahedral site, the K- $C_{60}$  distance is 0.71 nm and the  $C_{60}$ -K- $C_{60}$  angle is  $90^\circ$  [Fig. 4(c)]. Compared with those values, the position of potassium atom in the peapod is regarded within the range between tetragonal and octahedral sites in fullerenes.

Although our measurements do not provide any information on the charge state of the fullerene molecules, the typical doping rate of potassium for the intrapeapod sites can be  $x = 1$  or 2 in  $K_xC_{60}$  in SWNT for our experiments or  $x = 6$  at most with a simple calculation based on the ionic radius of potassium atom and the parameters obtained above. Because one electron from each potassium atom should also be shared with the tube wall as well as the two adjacent fullerenes, the charge state of each fullerene molecule cannot exceed  $-6$  unless extra electrons can be provided from outside the peapods. In the previous work Pichler *et al.* reported the  $-6$  charge state of fullerenes in their heavily doped peapods [5], a large part of which should be induced by potassium atoms outside the peapods, i.e., at the interpeapod sites between their bundles. These results positively suggest that tuning the charge state might be therefore possible by controlling the different dopant site and species.

In summary, we have demonstrated that the potassium atoms can be definitively doped at the intrapeapod sites by means of HR-TEM and that the  $n$ -type doping has been confirmed by EELS analysis, whereas a portion of potassium atoms remains outside or interpeapod sites. This is direct experimental evidence for the complex molecular chain synthesized within SWNT ( $K_xC_{60}@SWNT$ ). Also

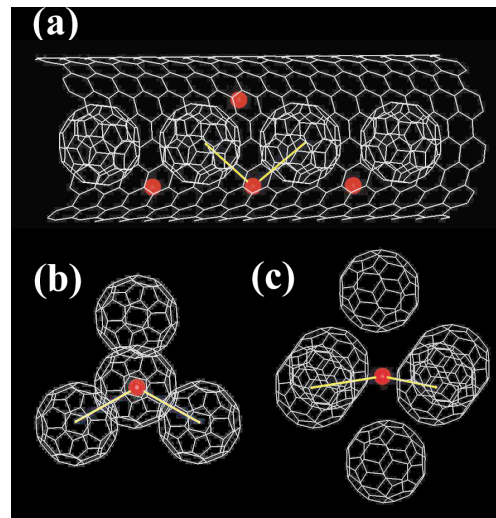


FIG. 4 (color). (a) A schematic model for the potassium sites in the K-doped  $C_{60}$  peapods and (b),(c) a partial structure of  $K_3C_{60}$  with potassium atoms at the tetrahedral and the octahedral sites (respectively). (Red: potassium; gray: carbon).

the structural similarities of the K-doped peapod to the superconducting fullerite ( $K_xC_{60}$ ) have been strongly suggested.

The work of electron microscopy and spectroscopy is supported by NEDO Nano-Carbon Technology project. The authors from Peking University thank NSFC and NKBRP (2001CB6105) for financial support. We thank Dr. T. Okazaki for fruitful discussions.

---

\*Electronic address: [suenaga-kazu@aist.go.jp](mailto:suenaga-kazu@aist.go.jp)

†Electronic address: [guzn@pku.edu.cn](mailto:guzn@pku.edu.cn)

- [1] B.W. Smith, M. Monthieux, and D.E. Luzzi, *Nature* (London) **396**, 323 (1998).
- [2] S. Okada, M. Otani, and A. Oshiyama, *Phys. Rev. B* **67**, 205411 (2003).
- [3] M. Monthieux, *Carbon* **40**, 1809 (2002), and references therein.
- [4] R. F. Service, *Science* **292**, 45 (2001).
- [5] T. Pichler, H. Kuzmany, H. Kataura, and Y. Achiba, *Phys. Rev. Lett.* **87**, 267401 (2001).
- [6] T. Pichler, A. Kukovec, H. Kuzmany, H. Kataura, and Y. Achiba, *Phys. Rev. B* **67**, 125416 (2003).
- [7] M. Kalbac, L. Kavan, M. Zukalova, and L. Dunsch, *J. Phys. Chem. B* **108**, 6275 (2004).
- [8] X. Liu, T. Pichler, M. Knupfer, J. Fink, and H. Kataura, *Phys. Rev. B* **69**, 075417 (2004).
- [9] P. W. Stephens, L. Mihaly, P. L. Lee, R. L. Wheten, S. M. Huang, R. Kaner, F. Deiderich, and K. Holczer, *Nature* (London) **351**, 632 (1991).
- [10] See, e.g., M. S. Dresselhaus, G. Dresselhaus, and P. C. Eklund, *Science of Fullerenes and Carbon Nanotubes* (Academic Press, San Diego, 1996).
- [11] A. Rochefort, *Phys. Rev. B* **67**, 115401 (2003).
- [12] H. Kataura, Y. Maniwa, T. Kodama, K. Kikuchi, K. Hirahara, K. Suenaga, S. Iijima, S. Suzuki, Y. Achiba, and W. Kratschmer, *Synth. Met.* **121**, 1195 (2001).
- [13] K. Suenaga, T. Okazaki, C. R. Wang, S. Bandow, H. Shinohara, and S. Iijima, *Phys. Rev. Lett.* **90**, 055506 (2003).
- [14] K. Hirahara, S. Bandow, K. Suenaga, H. Kato, T. Okazaki, H. Shinohara, and S. Iijima, *Phys. Rev. B* **64**, 115420 (2003).
- [15] See EPAPS Document No. E-PRLTAO-94-052506 for movie files of potassium atoms moving inside the peapods. A direct link to this document may be found in the online article's HTML reference section. The document may also be reached via the EPAPS homepage (<http://www.aip.org/pubservs/epaps.html>) or from <ftp.aip.org> in the directory /epaps/. See the EPAPS homepage for more information.
- [16] K. Hirahara, K. Suenaga, S. Bandow, H. Kato, T. Okazaki, H. Shinohara, and S. Iijima, *Phys. Rev. Lett.* **85**, 5384 (2000).
- [17] Therefore it does not directly prove that the dark spots in the peapod TEM images (Fig. 1) correspond to the K atoms. However, it should be mentioned that no trace of elements other than potassium and related oxygen has been found in the chemical analysis. There is indirect but enough convincing proof that the dark spots in Fig. 1 correspond to the potassium atoms.