Direct Imaging of $Sc_2@C_{84}$ Molecules Encapsulated Inside Single-Wall Carbon Nanotubes by High Resolution Electron Microscopy with Atomic Sensitivity

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Intramolecular structure of the scandium dimetallofullerene ($Sc_2@C_{84}$) has been clearly revealed by high resolution transmission electron microscopy with the single-atom sensitivity. Direct observation of two Sc atoms inside each fullerene molecule has led to a successful determination of the molecular symmetry among the three possible structural isomers for the $Sc_2@C_{84}$. The present work introduces a new electron microscopic approach to investigate individual molecular structures and demonstrates the possibility for determining the molecular isomer on a single-molecular basis.

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Fullerene, a cage-shaped molecule made of carbon, is able to accommodate many kinds of atoms (such as transition or lanthanoid series) in its hollow space. One of the central topics for studies on this new class of material is to determine the metal positions encapsulated inside the fullerene cage. Particularly the dimetallofullerene, that contains two metal atoms inside each cage, is intriguing because its chemical and physical properties are strongly dependent on its molecular symmetry, i.e., the relative positions of encapsulated atoms. Interests are focused on a scandium dimetallofullerene (a fullerene containing two Sc atoms, namely, $Sc_2@C_{84}$) because both covalent and ionic characters cause a strong interaction between the encapsulated atoms and the cage. Therefore the scandium metallofullerenes are expected to show more complicated behavior of the encapsulated atoms inside the fullerene cage than the lanthanoid metallofullerenes, in which the ionic character exclusively dominates the interaction between the encapsulated metal atoms and the fullerene cage.

Three different isomers (*I*, *II*, *III*) of $Sc_2@C_{84}$ were successfully isolated [1] and characterized by ^{13}C-nuclear magnetic resonance (NMR) and Raman spectroscopy in a previous report [2]. A theoretical study suggested three possible molecular isomers and predicted the possible Sc atom positions (Fig. 1) [3]. One of the three isomers (isomer *III*) was identified as D_{2d} symmetry with the two Sc atoms sitting on the symmetry axis (0.391 nm apart) by a powder synchrotron x-ray diffraction (XRD) study [4]. Although the theoretical calculation predicted one of the three isomers having C_s symmetry with two Sc atoms at the nonpolar positions inside the carbon cage [3], no experimental evidence has been reported for this peculiar endohedral atomic configuration. In order to corroborate this intramolecular structure by high resolution transmission electron microscopy (HR-TEM), we put the $Sc_2@C_{84}$ (isomer *I*) molecules into the single-wall carbon nanotubes (SWNTs). The open-ended SWNTs were exposed into the vapor of the metallofullerenes at 823 K so that the molecules filled the tubes (see the detailed preparation process in Ref. [5]). The SWNT can be regarded as an ideal specimen support for the HR-TEM investigations, because it is made of an extremely thin (single-atomic thick) graphite layer and exhibits an electron transparency with the lowest background level [6–9].

Since the single-atom contrast in a HR-TEM image depends on the power of 2/3 of Z (Z: the atomic number), the contrast of a single Sc atom ($Z = 21$) is, therefore, a fraction of the heavier atoms (La: $Z = 57$, for example) that have been successfully imaged in the previous experiments [6,8,9]. To visualize single atoms of the light elements in a HR-TEM with a high confidence level, a high performance CCD (1000×1000) detector with an efficiency of 2 counts per electron is used for the image acquisition. A high signal-to-noise ratio of 3, corresponding to the confidence level of ~80% for the single-atom imaging of the light elements (for example, Ca: $Z = 20$; Sc: $Z = 21$; Ti: $Z = 22$), has been realized with the background noise level $\sigma \sim 4.9$ when the acquisition time for each image is reduced down to 0.9 sec, reducing substantially the electron beam irradiation damage of the specimen.

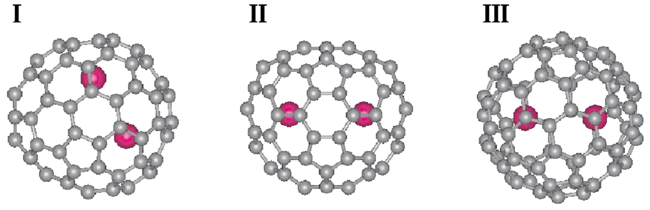

FIG. 1 (color). Three possible isomers (*I*, *II*, *III*) of $Sc_2@C_{84}$ suggested by NMR and theoretical studies (Refs. [2,3]) (C_s, C_{2v}, D_{2d}, respectively). The exact Sc atom positions were unknown except for (*III*).

Figure 2 shows a number of HR-TEM images of the $Sc_2@C_{84}$ molecules (isomer I) linearly aligned inside SWNTs. The $Sc_2@C_{84}$ molecules are seen like peas with the hollow structure. Two Sc atoms within each molecule are clearly visible as dark spots near the cage wall. The fullerene molecules are therefore stationary and not spinning in the nanotubes due to the strong interactions between fullerene-fullerene and/or nanotube fullerene. It is obvious that the two Sc atoms are not at the polar positions, i.e., the nonfurthermost positions inside the cage. In order to determine the Sc atom positions inside the cage as exactly as possible, numerous simulations for HR-TEM images of postulated metal positions have been performed. The C_s symmetry for the C_{84} cage (isomer I) was suggested by the ^{13}C-NMR study, and thus two Sc atoms must be encapsulated in C_{84} without breaking the C_s symmetry [3]. The interior positions of Sc atoms are supposed to be nonequivalent because two ^{45}Sc-NMR peaks were found for $Sc_2@C_{84}$ (isomer I) [10]. These suggest that two Sc atoms locate on the C_s plane. The HR-TEM images have been simulated for various atomic configurations under this assumption. Importance of two parameters has been eventually found by optimizing the simulations in comparison with the numerous HR-TEM images; one is the distance between two Sc atoms and the other is the distance of the Sc atom from the cage center. Note that the atomic arrangement of the C_{84} carbon cage could not be identified by the HR-TEM image due to the unresolved C-C distance. A best fit for the simulations to the observed images in various molecular orientations was obtained when the two Sc atoms are located at the positions of 0.20 ± 0.02 nm from the molecular center with the Sc-Sc distance of 0.35 ± 0.02 nm (Fig. 1). Legends (a)–(e) in the simulated image (Fig. 3) represent different molecular orientations in SWNT and correspond to those in Fig. 2. Note that the Sc atoms appear at the two poles in a certain orientation [(d), for example] because the two Sc atoms can be observed in projection parallel to the C_s plane. Also the relative Sc atom positions are apparently much closer to the cage in the simulated and observed images compared to the model structure. This is due to a finite spherical aberration (1 mm) of the microscope and a relatively large convergence angle (~ 2 mrad) employed for the experiments.

The results shown above clearly prove that the two Sc atoms are not located in axis through the molecular center. Consequently, the isomer (I) of $Sc_2@C_{84}$ unambiguously corresponds to one of the three possible isomers (Fig. 1) proposed by the NMR study and theory [2,3], which has C_s symmetry with the two Sc atoms at the off-axis positions (Fig. 1 left). The other two possible isomers can be excluded because they should have two Sc atoms at the furthermost positions inside their cages, where the two Sc atoms must show up in axis in the HR-TEM images for any orientation. The determined Sc atom

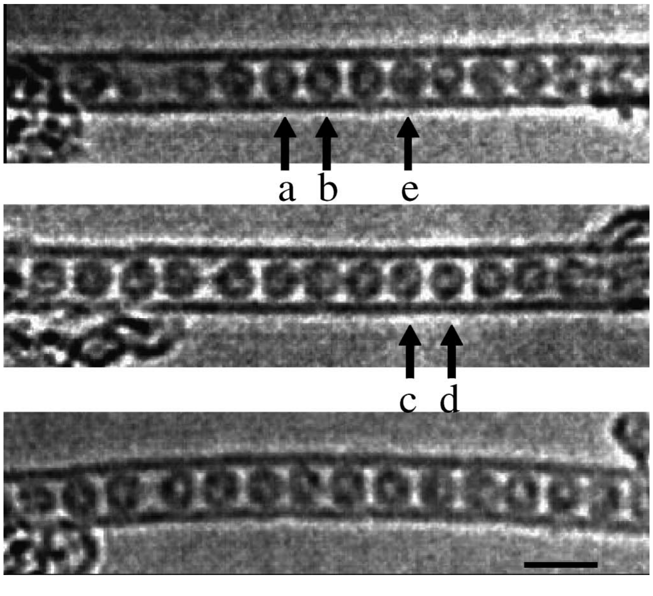

FIG. 2. HR-TEM images of the $Sc_2@C_{84}$ metallofullerenes inside SWNTs. Dark spots seen in each molecule correspond to the individual Sc atoms. Legends (a)–(e) correspond to the simulated image in Fig. 3. A JEOL 2010F electron microscope was operated at 117 keV for imaging. Bar = 2 nm.

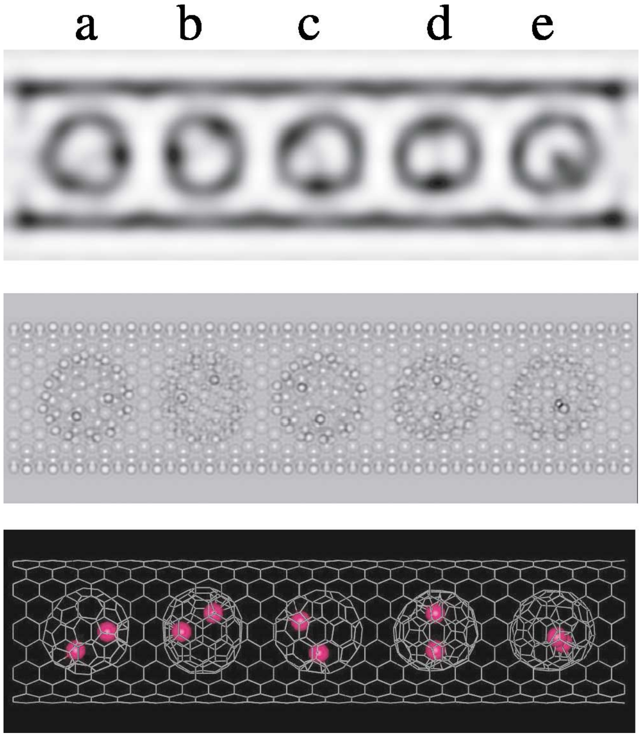

FIG. 3 (color). Simulated HR-TEM image (top panel) for various orientations of $Sc_2@C_{84}$ molecules inside SWNT. Projected atomic potential (middle panel) and models used for simulations (bottom panel) are also presented. Legends (a)–(e) correspond to those in the observed images in Fig. 2.

positions are in good agreement with the ones theoretically predicted (0.3486 nm for the Sc-Sc distance) [3].

The presence of Sc atoms was confirmed by an electron energy-loss spectrum (EELS) taken from a bundle of the SWNTs [Fig. 4(*a*)]. The zero shift of the Sc *L*-edge peaks proves the same valence state for the encapsulated Sc atoms as in the intact $Sc_2@C_{84}$ [Fig. 4(*b*)], namely, divalent (Sc^{2+} [11], referring to a spectrum for the trivalent Sc^{3+} in Sc_2O_3 [Fig. 4(*c*), inset] [12]. Consequently there must be a strong repulsive force exerted between the two cations in each cage, which tends to put the two Sc atoms far apart from each other. However, the present results show that the two Sc atoms are much closer within the cage. This proves that the interaction between the cage and encapsulated atoms overcomes the repulsive force between the two Sc^{2+} cations. In the lanthanide dimetallofullerenes, in contrast, the two lanthanide atoms should be restricted to the two furthermost positions in the cage [9,13,14], because of a fully ionic interaction between the positively charged cations and a rather homogeneously distributed negative charge on the cage. Physical properties of the transition metallofullerences should be much diversified than those for the lanthanide metallofullerenes because more variable atomic configurations of the encapsulated metals can be expected inside the cage.

Figure 5 represents the determined Sc atom positions in $Sc_2@C_{84}$ (isomer *I*) and a model for its aligned structure in a SWNT, namely, peapod. The verified structure of $Sc_2@C_{84}$ (isomer *I*) is consistent with the one suggested by NMR and theoretical studies [2,3]. One of the advantages of the HR-TEM technique is its capability to analyze the molecular structure on an individual basis, even though it is not yet possible to determine the symmetry of the carbon cage itself. This method may eventually become a routine tool to visualize any unknown molecule by using the SWNTs as containers for HR-TEM imaging. Although the scanning tunneling microscope is a powerful tool to provide a morphological image of an individual molecule and to analyze a local electronic structure for such a material [15,16], it is not yet suited to investigate the intramolecular structure for such as metallofullerenes in the peapods presented here.

The techniques like the NMR or XRD have been generally used to determine molecular symmetry among a series of possible isomers. These methods, however, require a mass quantity of the identical molecules and are unable to determine the symmetry on individual molecules among the isomer mixtures. The present HR-TEM technique successfully visualizes the intramolecular structure and its constituent single atoms and the isomer determination is consequently made possible on a single-molecular basis.

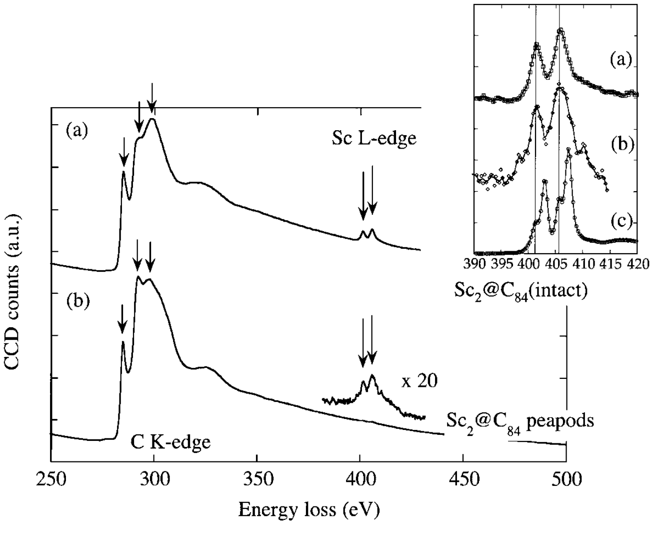

FIG. 4. EELS spectra taken from the intact $Sc_2@C_{84}$ (*a*), $Sc_2@C_{84}$ in SWNT (*b*), and Sc_2O_3 for reference (*c*). Compared with the spectrum for the Sc^{3+} in Sc_2O_3 (inset), the same valence state of the encapsulated Sc atoms (Sc^{2+}) is suggested for (*a*) and (*b*). Gatan imaging filter was used during the TEM operation for electron spectroscopy. The arrows indicate the peak positions assigned for the C *K*-edge including π^* and σ^* and the Sc L_{23}-edge.

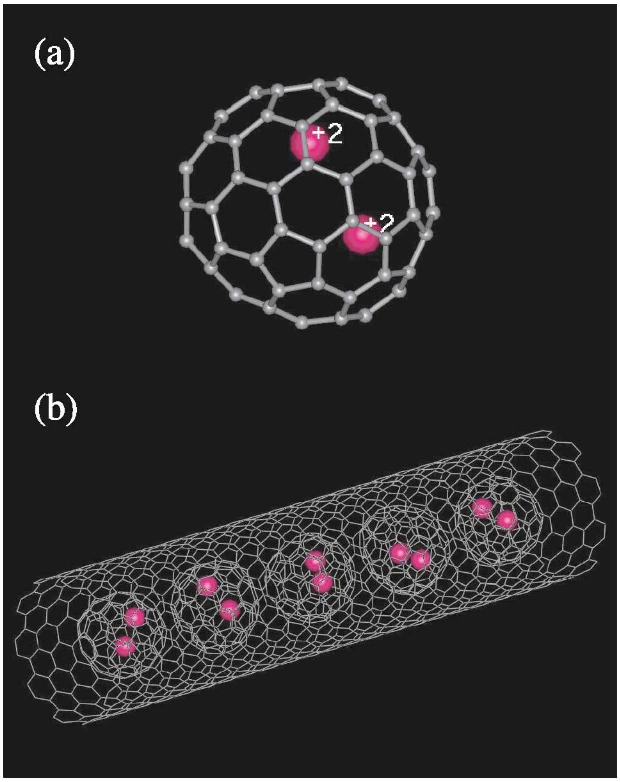

FIG. 5 (color). (a) The determined atomic positions in $Sc_2@C_{84}$ (isomer *I*). Two divalent Sc atoms are located at 0.20 ± 0.02 nm to the molecular center and at the nonpolar positions with the Sc-Sc distance 0.35 ± 0.02 nm. (b) A schematic presentation of the peapod, the $Sc_2@C_{84}$ molecules aligned in SWNT.

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