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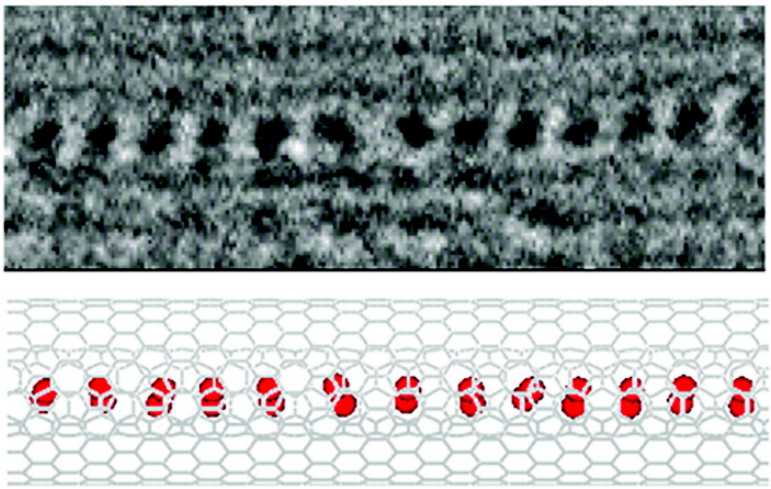

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Metallic Wires of Lanthanum Atoms Inside Carbon Nanotubes

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Atomic wires, whose structures and properties are completely different from those at large dimensions, are ideal subjects for investigating the quantum effect and thus attract much interest. It still remains a challenge to fabricate stable atomic wires. The reported examples mainly involved noble metals, for instance, a single gold atomic chain generated inside the transmission electron microscope (TEM).[1−3] Recently, we introduced molten iodine into single-walled carbon nanotubes (SWNTs) with a diameter of ∼1 nm, generating a single atomic chain of iodine longer than 10 nm.[4] Our results have the implication for the utilization of SWNTs as sheaths to stabilize atomic chains of metals, which are of potential applications in many fields but may be unstable alone. Recent theoretical calculations also pointed out that, if SWNTs were filled with ferromagnetic materials, they would demonstrate high potential in realizing the desired magnetic properties.[5] So it would be of great importance to fabricate metallic wires of metals inside SWNTs with a controlled manner. The first problem to be solved is how to introduce metals into SWNTs. In the case of some molten "heavy" metals that have high surface tensions (typical 400−600 mN m^{-1}) and thus could not wet the surface of SWNTs, spontaneous filling should not be possible.[6] To bypass these problems, we tentatively managed to use metallofullerenes (fullerene accommodating metals), which are easily introduced into SWNTs,[7] as starting materials to fabricate stable atomic wires of metals inside SWNTs. In this study, we choose $La_2@C_{80}$, in which C_{80} fullerene acts as a "molecular bag" to carry La atoms into SWNTs. After heating the $La_2@C_{80}$-encapsulated SWNTs, so-called $La_2@C_{80}$ peapods, we obtained metallic wires of La inside carbon nanotubes (CNTs) and revealed their structures by using high-resolution electron microscopy (HR-TEM) and electron energy loss spectroscopy (EELS).

The $La_2@C_{80}$ molecules were introduced into arc-discharged SWNTs with a mean diameter of ∼1.4 nm by heating the mixture of SWNTs and $La_2@C_{80}$ powder in an evacuated glass ampule at 823 K for 24 h.[7] A vacuum heat treatment at 1273 K was then performed on the so-obtained peapods to transform the encapsulated metallofullerenes. The peapods before and after the vacuum heat treatment were characterized by a field emission HR-TEM (JEOL, JEM-2010F with a post-specimen aberration corrector, operated at 120 kV) and a EELS spectrometer attached on the microscope.

The filling yield is estimated to be as high as 90%. Nearly all SWNTs with a diameter larger than 1.3 nm are fully encapsulated with $La_2@C_{80}$ molecules, which align linearly inside the host SWNTs. Figure 1a shows a typical HR-TEM image of an isolated $La_2@C_{80}$ peapod. The C_{80} cages are nearly stationary and not spinning in the tube; therefore, the isolated La atoms, which are restricted to the two furthermost positions within the C_{80} fullerene cage,[8] are clearly visible as dark spots. The state-of-art HR-TEM[9] enables us to directly visualize the atomic arrangement of the C_{80} cage, which has spheroidal I_h symmetry.[10] The measured La−La separation is not uniform, implying that the orientation of the $La_2@C_{80}$ dipole moment does not show any preference inside the SWNTs, while it arranges randomly.

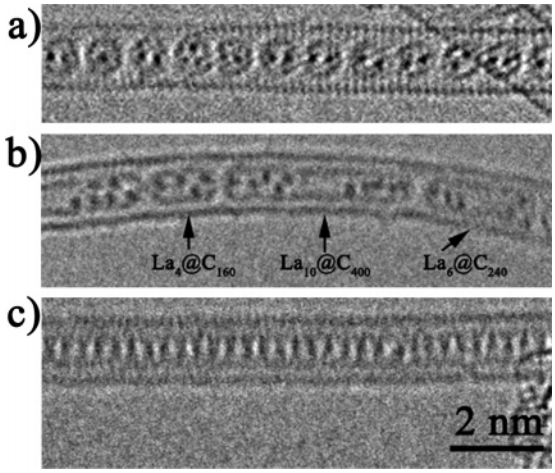

Figure 1. HR-TEM images of (a) original $La_2@C_{80}$ peapods, (b) an intermediate phase after the heat treatments for 1 h, and (c) final product, a metallic wire of La atoms inside double-walled carbon nanotubes, after the heat treatments for 48 h. Dark spots inside the fullerene cages and CNTs correspond to the encapsulated La atoms.

Previous results have proved that annealing C_{60} nanopeapods at high temperature resulted in the coalescence of the fullerene peas, eventually forming double-walled carbon nanotubes (DWNTs).[11,12] The coalescence of C_{60} fullerenes inside SWNTs was studied in detail very recently.[13] However, no attention has been paid to the metallofullerene peapods. Here we present the first study on the coalescence of the encapsulated $La_2@C_{80}$ and the growth of La atomic wires. After heating the metallofullerene peapods for 1 h, several nanocapsules, such as $La_4@C_{160}$, $La_6@C_{240}$, and $La_{10}@C_{400}$, appear inside the host SWNTs (Figure 1b), corresponding to the coalescence of two, three, and four metallofullerenes. When we increased the time for the heat treatment from 1 to 48 h, the C_{80} cages eventually transform to inner carbon nanotubes with a diameter of ∼0.7 nm, while the entrapped La atoms tend to form dimers and arrange linearly inside the inner tubes (Figure 1c). Each dark spot is ascribed to a La dimer (two overlapped La atoms). The La wires are not always continuous along the carbon nanotubes, but with typical length is ∼10 nm.

To our best knowledge, this is the first realization of the dimer chains of rare earth metals. Figure 2 shows the detailed HR-TEM images and the corresponding schematic representations of this novel structure. In Figure 2a, La dimers in the projection along the electron beam direction appear as heavy dark spots. Detailed analysis reveals that the La−La distance in a dimer and the dimer−dimer separation measured from the centers of the intensity maxima are 0.44 ± 0.02 and 0.48 ± 0.02 nm, respectively. Both are larger than the nearest-neighbor spacing (0.38 nm) of La atoms in the

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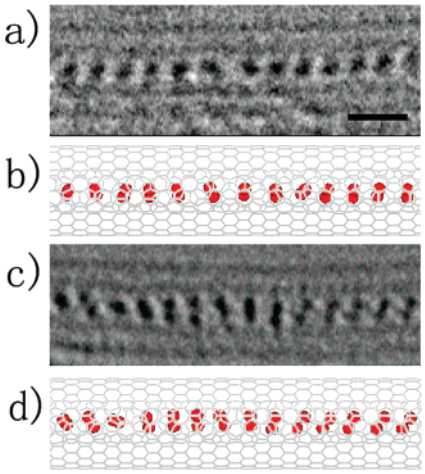

Figure 2. HR-TEM images and schematic representations of the La atomic chains inside the carbon nanotubes. Heavy dark spots correspond to two encapsulated La atoms, and light dark spots correspond to single La atoms in the projection along the incident electron beam. Scale bar = 1 nm; red: lanthanum, gray: carbon.

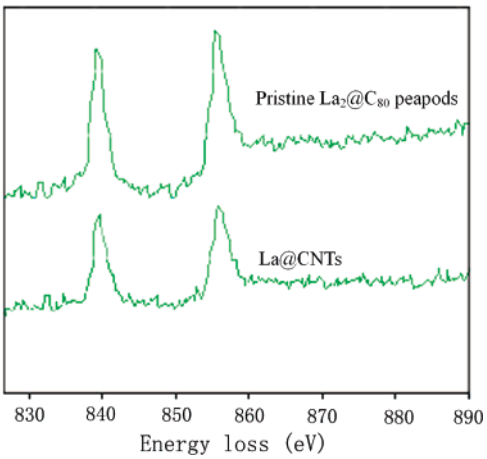

Figure 3. EELS spectra taken from the $La_2@C_{80}$ peapods and La@CNTs, showing the La $M_{4,5}$ edge. The peak positions for the $La_2@C_{80}$ peapods after the heat treatment are the same as those for the pristine $La_2@C_{80}$ peapods, indicating that the valence state of La in the CNTs remains +3, the same as that in $La_2@C_{80}$ peapods.

crystal. The La dimers are not immobile, while occasionally they rotate (keeping the center of the dimer stationary) inside the DWNTs under the electron beam irradiation. During the HR-TEM observation, two dark spots, corresponding to two La atoms in a dimer, altered to a heavier dark spot, corresponding to overlapped La atoms (see Movie 1 in Supporting Information). Physical properties of these La atomic wires should be more diversified than crystalline La or $La_2@C_{80}$ because of various atomic configurations and possible coordination inside the carbon nanotubes.

The valence state of La atoms was monitored by EELS taken from a bundle of the CNTs containing $La_2@C_{80}$ or La atomic wires (Figure 3). There may be a charge redistribution of metal after the heat treatment. Previous study reported that the valence state of Sm atoms transformed from +2 to +3 when $Sm@C_{82}$ inside SWNTs coalesced to nanocapsules under electron beam irradiation.[14] In our study, however, there is no shift of the La $M_{4,5}$ edge after the heat treatment compared with the pristine $La_2@C_{80}$ peapods, indicating a valence state of the encapsulated La atomic wires inside the CNT that is the same as that in the $La_2@C_{80}$ peapod, namely, trivalent (La^{3+}).[15] The La atoms are positively charged, implying that La may form carbide inside CNTs. The pristine lanthanide metallofullerene peapod is regarded as a one-dimensional chain of dipole and magnetic moments, and the distribution of metal atoms determines the physical properties of the peapods. In the case of the La atomic chains, the properties of these new structures of lanthanum are subjects for future study.

In summary, we introduced La atoms into carbon nanotubes with the help of fullerene cages as "carry bags" and then transformed them into atomic wires. Since the transition or lanthanoid metals have been successfully encapsulated in the fullerene cage to form metallofullerene, our method can be applicable for all the metallofullerenes, generating atomic wires of transition or lanthanoid series metals inside CNTs. Such one-dimensional materials are ideal for studying magnetic and transport properties of atomic-scale quantum wires.

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Supporting Information Available: A movie on the movement of the La dimers inside carbon nanotubes. This material is available free of charge via the Internet at http://pubs.acs.org.

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