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Defect-Induced Atomic Migration in Carbon Nanopeapod: Tracking the Single-Atom Dynamic Behavior

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ABSTRACT

We demonstrate here the single-atom migration of Tb, Gd, or Ce metal from cage to cage through an intentionally induced atomic path within a carbon nanopeapod. The atomic path is actually an atomic defect (vacancy) induced at the fullerene cage during TEM observation. It is therefore proved that the atomic cage can be punctured by electron irradiation so that the imprisoned metal atoms can break out. The results definitively indicate the possibilities for an alternative method to transfer single atoms without using SPM tips but by using an "atomic carry-bag" such as fullerene.

Progress in nanotechnology relies on the atom craft techniques in a matter. Behavior of individual atoms is therefore more and more crucial in designing any atomic-scale nanodevice. A carbon nanopeapod is a one-dimensional nanostructured material that contains aligned fullerene molecules in single-walled carbon nanotubes (SWNTs).[1] Especially with the lanthanide metallofullerene, the peapod is regarded as a one-dimensional chain of dipole and magnetic moments, and the distribution of metal atoms essentially governs the physical properties of the peapods.[2−4] Unveiling the dynamical behavior of those atoms is quite important for predicting the functions of the peapod-based nanodevices. Recently, the atomic defects in carbon nanostructures have been elucidated by high-resolution transmission electron microscopy (HR-TEM).[5] Linking the migration of specific metal atoms with the existence of such atomic defects in carbon nanopeapods is challenging and important to clarify the well-known idea that atomic movement in solids should be connected to the lattice defects in the matrix. Here we show a successful detection of atomic defects in a carbon nanopeapod and track the individual atoms migrating through them, in order to investigate the solid-state diffusion on an individual-atom basis as well as to identify the atomic path for diffusion in this ideal test object.

To obtain direct evidence for defect-mediated atomic migration, we first show an experimental proof for the opening and closing of the atomic pathway on a fullerene cage as well as for the breakout of an imprisoned atom through it. Three phenomena proven by our in-situ HR-TEM observations of the carbon nanopeapod structures will be presented in this paper: (i) opening and closing of atomic paths on the fullerene cage, which are actually the vacancy-type defects on the fullerene induced by electron beam irradiation, (ii) breakout of one of the imprisoned Tb atoms through such induced atomic pathway on the encaging fullerene molecule, and (iii), most importantly, migration of the imprisoned Gd atoms from one cage to the next through another pathway interconnecting two adjacent fullerene cages.

The peapod specimens were dispersed in *n*-hexane and then fixed on the holey carbon grid for electron microscopy. HR-TEM observation has been performed by a JEOL 2010F microscope at the accelerating voltage of 120 kV. The CCD-based detector was used for image acquisition. The typical dose is around 60 000 electrons/nm^2 for one second exposure, and the cross-section for defect induction is estimated around 160 barn.[5] The sequential HR-TEM images have been stored

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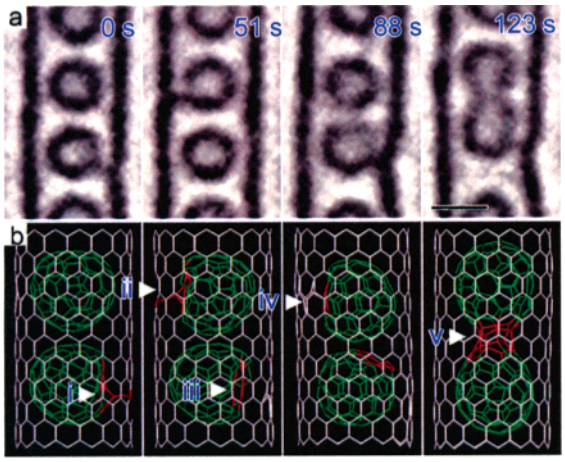

Figure 1. (a) A series of HR-TEM images for the atomic pathways opening and closing on the fullerene cage (C_{92}). In this case all the cages were originally empty. The arrows (a and b) in the schematic presentations (b) indicate the formation of interlayer couplings. An atomic path, or the vacancy-type defect, is clearly seen at the fullerene cage (arrows (i) and (ii)). These interlayer couplings dissociate after (arrows (iii) and (iv)) and one of the paths obviously closes (arrow (iv)). Then two fullerenes begin to coalesce ($t = 123$ s) and another kind of path is definitively induced to interconnect two adjacent fullerenes (arrow (v)). Scale bar, 1 nm.

at 0.3 to 1 Hz including the readout time. During the readout, the electron beam was blanking to reduce the irradiation damage. Under such a condition, the confidence level to capture a Gd atom ($Z = 64$) in a single HR-TEM image is around 95%.

Induction of an atomic defect on fullerene cage has first been made by taking advantage of the knock-on effect of carbon atoms during the HR-TEM observation. In the case of fullerenes aligned in a SWNT, a knocked-on carbon atom leads to a vacancy formation on the fullerene cage and then can be trapped at an interstitial (or an interlayer) site between the fullerene cage and the nanotube wall. This consists of a sort of the Frenkel pair.[6] In our previous study, the knock-on frequency has been already estimated in a similar observation with a high current flux of a high energy electron beam.[5] We can roughly expect irradiation-induced atomic defects on three of ten fullerenes in a five-minute observation under the employed experimental conditions. A preliminary experiment has confirmed the introduction of atomic defects on empty C_{92} fullerenes aligned in a SWNT. A series of sequential HR-TEM images with schematic presentations are shown in Figure 1 (see also Movie 1 in Supporting Information). At the beginning of HR-TEM observation, the interlayer coupling between nanotube and fullerene has been frequently detected and the examples are shown at $t = 0$ s and 51 s (shown by arrows (i) and (ii), respectively). An opening pathway at the fullerene cage is clearly visible at the indicated region (arrow (ii)). Figure 1b shows reasonable atomic models expected for the observed interlayer couplings. Because the exact positions for carbon atoms cannot be derived from the HR-TEM pictures, a most stable atomic configuration based on a semiempirical potential calculation has been employed for each model to achieve a better fit with the HR-TEM image simulations. Thus induced atomic vacancy on fullerene cage is definitively a junction from the inner space to the outer and would act as an atomic pathway through which the imprisoned metal atoms, if any, could escape.

At $t = 88$ s, two of the interlayer couplings dissociate and the defects seem to be mended (indicated by arrow (iii) and (iv)). Afterward, the two defected fullerenes (probably turn around to face its once defected area to each other and then) start to coalesce ($t = 123$ s). Such a coalescence of fullerene molecules has been already reported for C_{60} or C_{82} cages.[7−9] Here, assuming the coalescence of two defected C_{92} molecules with vacancy (actually C_{91}), a stable structure for C_{182} peanut-like fullerene is predicted (Figure 1b, right). Both the predicted model and the observed HR-TEM image clearly indicate that an atomic path has been obviously induced between the two adjacent fullerene cages and a junction has been formed to interconnect two inner spaces. Such a coalescence of fullerenes is not a particular phenomenon under the electron beam irradiation but can be more generally found in a Raman study of the peapods with careful heat treatments.[10,11] It should be mentioned that the presence of many pentagons (or a consequent higher curvature) of the fullerene cage is one of the important reasons why the defect is more likely to be induced at the fullerene site although the nanotube wall is more resistive.

We next show experimental evidence that an atom (non-carbon element) can definitively go through these atomic paths. A carbon nanopeapod encapsulating Tb dimetallofullerene ($Tb_2@C_{92}$) was used for this experiment. A detailed procedure for the specimen synthesis can be found in our previous reports.[12,13] Each fullerene carrying two Tb atoms in carbon nanotube is clearly visible at the initial state of the observation (Figure 2a, top: $t = 0$ s). The same exposure as mentioned above was employed for the observation condition. As more clearly seen in Movie 2 in Supporting Information, a series of sequential HR-TEM images successfully captured the moment for one of the Tb atoms breaking out from the metallofullerene indicated by an arrow ($t = 64$ and 99 s) in their schematic presentation (Figure 2b). This breakout of Tb atom clearly proves that the atomic pathway has been definitively induced on the fullerene cage as a consequent of the vacancy formation as suggested above. The atomic defect on the fullerene cage is likely to be induced near the encapsulated metal atom because of a localized charge predicted by theory.[14] Because the size of Tb^{3+} ion is larger (0.185 nm) than a mono- or even possibly di-vacancy of carbon, some rearrangements of the carbon atoms at the defected area should occur to transfer the Tb atom. At the moment of breakout, the fullerene cage surely undergoes a considerable deformation ($t = 64$ s). The metallofullerene cage seems to fix its defect after ejecting the Tb atom ($t = 99$ and 143 s) and the Tb atom starts to wander among the fullerenes inside the tube wall after breaking out (see also Figure S1 in Supporting Information).

Our electron spectroscopy study has already confirmed that the Tb atoms in the $Tb_2@C_{92}$ metallofullerene exhibit the trivalent state (Tb^{3+}).[15] A strong Coulombic repulsive force must, therefore, be exerted between the two imprisoned Tb

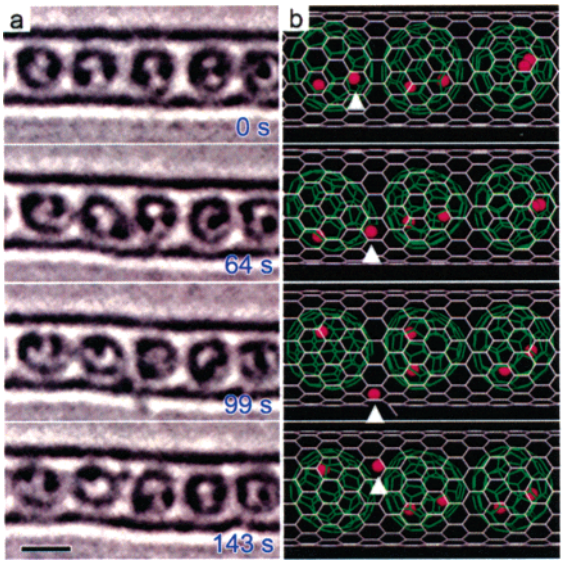

Figure 2. (a) A series of HR-TEM images showing the break out of the imprisoned Tb atoms from $Tb_2@C_{92}$ peapod. Each fullerene carries two Tb atoms at the initial stage ($t = 0$). One of the Tb atoms goes out through an atomic path induced between fullerene cage and tube wall (indicated by arrows). The fullerene cage undergoes a considerable deformation ($t = 64$ s) and the tube wall also shows some defects ($t = 99$ s). The escaped Tb atom wanders after inside the tube ($t = 143$ s). See also the provided movie file (Movie2.mov in Supporting Information) for the sequential HR-TEM images. The encapsulated Tb atoms appear in red and the migrating atom is indicated by a white arrow in the schematic presentation (b). Scale bar, 1 nm.

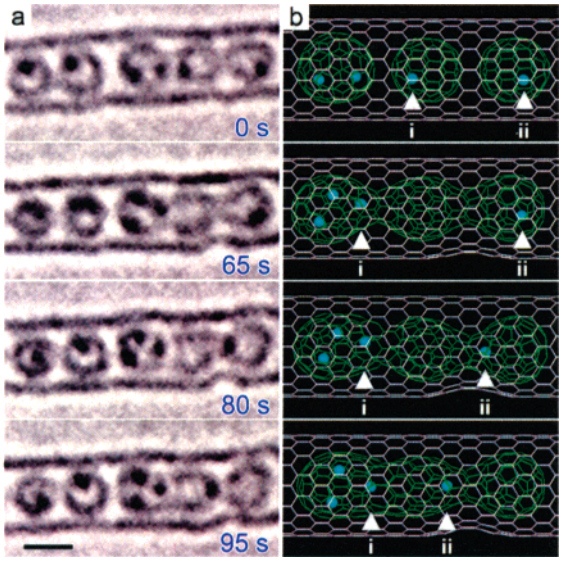

Figure 3. (a) Sequential HR-TEM images showing the migrating Gd atom from cage to cage. This SWNT is codoped with monometallofullerenes and dimetallofullerenes ($Gd@C_{82}$ and $Gd_2@C_{92}$). The numbers of Gd atoms in each cage deduced from the initial HR-TEM image ($t = 0$ s) are 1, 1, 2, 1, 1 (from left). One of the Gd atoms in $Gd@C_{82}$ (arrow (i)) moves into the adjacent cage ($t = 65$ s) and a trimetallofullerene is obviously formed ($t = 80$ s), followed by the migration of another Gd atom (arrow (ii); $t = 95$ s). The evolution of the number of Gd atoms in each cage is expressed as (1, 1, 2, 1, 1), (1, 1, 3, 0, 1), and then (1, 1, 3, 1, 0) ($t = 95$ s). See also the provided movie file (Movie3.mov in Supporting Information) for the sequential HR-TEM images. The migrating Gd atoms are indicated by white arrows in the schematic presentation (b). Scale bar, 1 nm.

cations in each cage. In contrast, the Tb atoms and fullerene cage should exhibit robust interaction with an ionic character ($(Tb^{3+})_2@C_{92}^{6-}$). Judging from the considerable deformation observed on the fullerene cage at the moment of breakout, there must be also a strong interaction exerted between the escaping Tb atom and the defective area of the carbon cage. These three different interactions mainly cooperate with each other and lead to the breakout of Tb atom, as far as there is little influence of the outer tube and of the adjacent fullerenes.

Transferring the imprisoned atoms from one cage to another through a path between two inner spaces of adjacent fullerenes has been also studied. To obtain clear proof of this atomic transfer from cage to cage, a heteropeapod which contains two kinds of fullerenes within a unique SWNT was synthesized. The Gd mono- and dimetallofullerenes ($Gd@C_{82}$ and $Gd_2@C_{92}$) were chosen. Despite the different affinity of two kinds of fullerenes, both can surely be encapsulated within a SWNT and lead to a codoped peapod. The atomic path interconnecting two different types of fullerenes is then expected to be induced during the observation.

Figure 3a shows two kinds of fullerenes aligned next to each other in a SWNT. The numbers of Gd atoms in each cage deduced from the initial HR-TEM image ($t = 0$ s) are 1, 1, 2, 1, 1 (from left). During the observation the three molecules began to coalesce as expected ($t = 65$ s); see also Movie 3 in Supporting Information. Then one Gd atom moved into the left cage ($t = 80$) (Figure 3b) through the induced atomic path interconnecting the two cages. A peanut-like fullerene which carries three Gd atoms at one chamber has been eventually generated ($t = 95$ s). This again is clear proof of the anticipated atomic path induced to interconnect two nanospaces by electron beam irradiation and does demonstrate the atomic transfer from cage to cage through it (see also Figures S2, S3, and S4 in Supporting Information).

This observation has other important implications. It is direct evidence of the weak coupling between the imprisoned metal atoms and the encapsulating cage, which allows the intramolecular motion of metal atoms inside a metallofullerene.[16,17] Also it indicates a new route to synthesize gigantic fullerenes with specific metal atoms inside. We observed up to four cations that can be included in one cage (See Figure S5 in Supporting Information). It does prove the clustering of metal atoms[9] with an interatom distance of as small as 0.4 nm. Most interestingly, this technique opens a new way to mix heteroatoms in a confined space if two different metallofullerenes are employed (see Figure S6 in Supporting Information).

The atomic transfer demonstrated here is quite important from the viewpoint of a possible bottom-up process to create a new material. One can endeavor to construct a desired molecule atom-by-atom or even to design a chemical reaction with an atomically controlled stoichiometry in such a confined nanospace. The phenomena shown here are basically induced by the "nonselective electron beam irradiation." It is therefore less controllable in comparison with the single-

atom manipulation by SPM tips.[18,19] It is more intriguing, however, to induce such an atomic path selectively on a desired molecule because a modern electron microscopy technique can allow us to make electron irradiation at an angstrom-scale region. Then we can expect the atomic transfer in a more controllable fashion.

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Supporting Information Available: HR-TEM images of the metallofullerenes in nanopeapods. This material is available free of charge via the Internet at http://pubs.acs.org.

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