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Communications to the Editor

Real Time Reaction Dynamics in Carbon Nanotubes

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The inner hollow spaces of single-wall carbon nanotubes (SWNTs) will provide ideal fields for chemical reactions. Molecules and atoms trapped inside SWNTs are completely isolated from the surroundings, and their chemical reactions can be externally triggered by energetic beams such as photons and electrons. Since SWNTs are extremely thin and almost transparent to high-energy electron beams, the modern analytical techniques based on transmission electron microscopy (TEM) can allow the direct observation of chemical reactions occurring within SWNTs. Here we present the first real-time observation of the formation of elongated nanocapsules through a coalescence of Sm metallofullerenes ($Sm@C_{82}$)[1] within SWNTs, which has been observed by in situ high-resolution TEM (HRTEM) coupled with electron energy loss spectroscopy (EELS). A transition of the valence state of the Sm atoms has been revealed by TEM/EELS as a result of electron beam irradiation on the SWNTs encapsulating the $Sm@C_{82}$ molecules, $(Sm@C_{82})_n@SWNTs$. The transition is associated with preferred coalescence reactions of the $Sm@C_{82}$ molecules.

The starting material, $(Sm@C_{82})_n@SWNTs$, were prepared by the gas-phase reaction.[2,3] Details of the synthesis and isolation of $Sm@C_{82}$ were described previously.[4,5] The purity of the $Sm@C_{82}$ was >99% as revealed by LD-TOF mass spectrometry.[4] The SWNT bundles were generated by a pulsed-laser vaporization of Fe−Ni (0.6−0.6 at. %) containing a carbon target at 1200 °C in 500 Torr of pure Ar stream.[2] The resulting SWNTs were directly introduced to a second furnace set at 500 °C by an Ar stream mixed with 5% of pure O_2 to burn amorphous carbons. The residual amorphous carbon materials (which remained even after the burning) and catalyst particles were removed by refluxing in HNO_3. The doping of $Sm@C_{82}$ into the inner hollow space of SWNTs was carried out in a sealed glass ampule at 500 °C for several days. Prior to the introduction of SWNTs to the ampule, the SWNTs were heated in dry air at 420 °C for 20 min.

The SWNT samples were examined with a transmission electron microscope (JEOL 2010F) equipped with an electron energy loss spectrometer (Gatan, GIF) operated at 120 kV.[6] The beam current density in the present experiment was kept at $\sim 5 \times 10^{-15}$ A/nm^2 both for imaging and spectroscopy to directly compare the time evolution of the HRTEM images and the EELS spectra.

Figure 1a shows HRTEM images of an individual $(Sm@C_{82})_n@$SWNT at the beginning of the observation (before the reaction). The $Sm@C_{82}$ molecules are perfectly aligned in a one-dimensional way with a constant intermolecular spacing. The encapsulated Sm atom can be seen as a dark spot inside the circle. This spot locates near the fullerene cage rather than the center of the cage, which is consistent with the known “off-centered” structure of monometallofullerenes.[7] Following the irradiation for a period of 4 min, a molecular rearrangement in the nanotubes starts to occur (Figure 1b). Some $Sm@C_{82}$ molecules are already so close to each other as to form dimers or clusters as seen in the HRTEM image. A sudden increase in the number of dark spots by Sm atoms in Figure 1b suggests that the rotational motion of Sm metallofullerenes was frozen due to the formation of intermolecular covalent bondings. Further exposure for ∼10 min resulted in coalescence or fusion which generates the dimers and clusters of the Sm metallofullerenes (Figure 1c). These were finally converted to much longer nanocapsules after ∼20 min irradiation (Figure 1d). The dark spots observed near the wall of the newly produced capsules correspond to the Sm atoms.

Further information on such reaction dynamics can be obtained by simultaneous in situ EELS measurements (Figure 2). The EELS spectrum observed from the bundles of the intact $(Sm@C_{82})_n@$SWNTs is shown Figure 2a together with the reference spectra of Sm^{2+} in $Sm@C_{82}$ and Sm^{3+} in Sm_2O_3.[8] A somewhat poor experimental signal-to-noise ratio for the EELS spectra of $(Sm@C_{82})_n@SWNTs$ is due to the extremely small amount of the Sm atom in this structure and the remarkably weak irradiation condition adopted in the present experiment. The peak positions of Sm M_{45} edges for $(Sm@C_{82})_n@SWNTs$ before the reaction are the same as those for the intact $Sm@C_{82}$. After electron beam irradiation for a period of ∼10 min, the peak widths of M_{45} edges became broader, showing additional intense peaks overlaping with the main peaks (Figure 2b). At the same time, the intensity of the divalent Sm^{2+} peaks decreased with the irradiation, and finally new M_{45} peaks appeared (Figure 2c). In particular, the M_5 edge at ∼1080 eV can be clearly seen in the spectrum; the peak position for this M_{45} edge corresponds to that of the trivalent Sm^{3+}.[8]

At this point, the valency of the Sm atoms has transformed from +2 to +3 with a time scale of ∼10 min, and the conversion was completed within ∼20 min irradiation. The time-dependent

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(1) Throughout this experiment, $Sm@C_{82}$ isomer I was used as a reactant molecule. For simplicity, “$Sm@C_{82}$” stands hereafter for $Sm@C_{82}$ isomer I.

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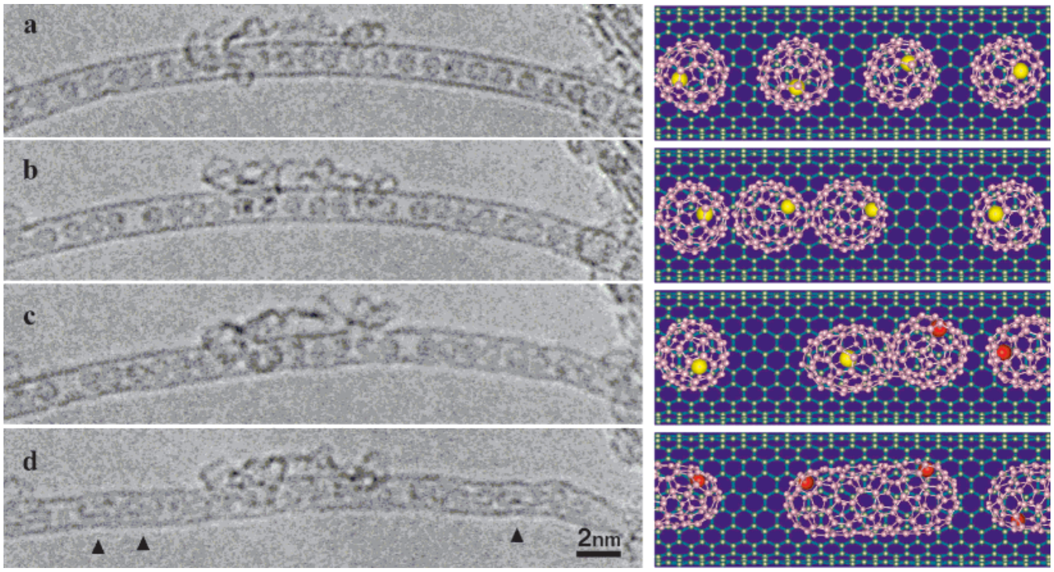

Figure 1. Time evolution of the HRTEM images of $(Sm@C_{82})@SWNTs$ (top) and schematic illustrations (bottom). The HRTEM images were observed after (a) ~0, (b) ~4, (c) ~10, and (d) ~20 min irradiations, respectively. Some of the produced nanocapsules can be clearly seen inside the SWNT (arrows). The yellow and the red balls in the illustrations denote the divalent Sm^{2+} and the trivalent Sm^{3+} atoms, respectively.

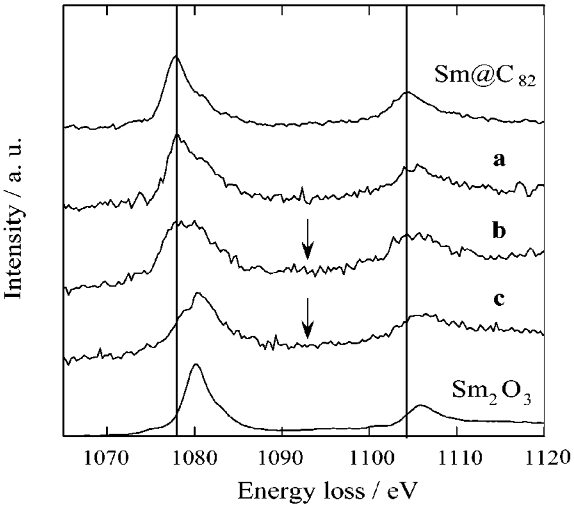

Figure 2. Time evolution of the EELS spectrum for $(Sm@C_{82})_n@SWNTs$, together with reference spectra for the divalent Sm^{2+} in the intact $Sm@C_{82}$ molecule and the trivalent Sm^{3+} in Sm_2O_3. The EELS spectra were taken at ~10 min intervals.

HRTEM and EELS measurements indicate that the valence state of Sm has transformed from +2 to +3 as a result of a new chemical bond formation due to Sm carbide upon coalescence of the fullerene cages (Figure 2c). Sm atoms may not be encaged in the nanocapsule but should at least be incorporated into the cage network, since the valence state of the Sm carbides (SmC_2) is +3[9] and those of various Sm metallofullerenes are +2 irrespective to the fullerene size.[8] The Sm atoms tend to be incorporated into the carbon networks to form more stable carbide bonds and do not form Sm clusters.

The present study demonstrated that chemical reaction dynamics in SWNTs can be directly monitored by the in situ HRTEM and EELS measurements with an atomic resolution. The inner hollow space of SWNTs can provide an excellent field for a variety of further nanoscale chemical reactions.

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Supporting Information Available: Mass and absorption spectral characterizations of $Sm@C_{82}$, and further HRTEM images of the bundle of $(Sm@C_{82})_n@SWNTs$ (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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