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Carbon Nanotubes

Observations of Chemical Reactions at the Atomic Scale: Dynamics of Metal-Mediated Fullerene Coalescence and Nanotube Rupture**

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Single-walled carbon nanotubes (SWNTs), which are graphitic tubular structures with single-atom-thick sidewalls and varying diameters, are effective containers for a wide variety of molecular species.[1–4] They are particularly suitable for study by transmission electron microscopy (TEM).[4] Chemical reactions between molecules inside nanotubes can be triggered by external stimuli (for example, the TEM electron beam), with the nanotube acting as a miniature reactor vessel,[5] thus potentially steering a chemical reaction along a new pathway towards new products.[6,7] Nanotubes are often viewed as chemically inert containers. Although their surfaces can be involved in some chemical reactions,[8] the chemical reactivity of their interior has been considered to be very low.

TEM is the only method that allows direct visualization and study of the molecules inside nanotubes. We are currently exploiting the capabilities of an aberration-corrected TEM, which can record atomic resolution images in a time much shorter than needed for the electron beam to promote structural transformations inside SWNTs. Under our imaging conditions, these transformations usually occur on a timescale of seconds, which enables us to capture atomic images of the intermediates. These images can then be combined into a movie to follow the chemical transformations as they happen. Both walls and interiors of SWNTs can be seen on TEM micrographs, such that the positions and orientations of the encapsulated molecules can be readily determined from the images (Figure 1c). Accelerated electrons interact with the specimen and transfer their energy and momentum to the atoms of the specimen, causing knock-on damage, ionization, and/or heat-induced damage, the extent of which depends on the nature of the material. With this in mind, we carried out our TEM studies with an accelerating voltage of only 80 kV, which is well below the threshold for knock-on damage in carbon nanotubes (86 kV).[9] Under these conditions, the electron beam acts as an energy bath, promoting chemical transformations but not destroying the specimen, so that molecular dynamics and interactions can be observed in direct space at the atomic scale. It is not possible to measure the temperature of our nanotubes directly in TEM; however, provided that the nanotube has a good contact with the rest of the specimen (Supporting Information, Figure S2) the upper limit of heating by the electron beam is estimated to be 11 K above the temperature of the surroundings,[10] which is in good agreement with previous observations for nanotubes.[11]

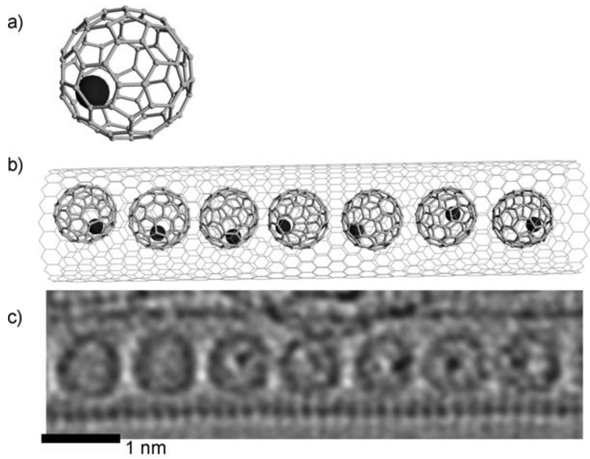

Figure 1. a) A single atom of dysprosium is encapsulated within a C_{82} fullerene. The Dy^{3+} atom interacts with the negatively charged carbon cage. b) Fullerenes inserted in the carbon nanotube line up in a chain. c) Aberration-corrected TEM image of $Dy@C_{82}$ inserted in the carbon nanotube. The dysprosium atoms can be seen as dark spots within the cages of fullerenes (except in the first and the second fullerenes, owing to fast rotation of these fullerenes).

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Ionization is less important for graphitic carbon owing to its high conductivity. A hole created when a valence electron is knocked out will be refilled by an electron from the π-electron system before the carbon atoms shift significantly from their equilibrium positions. However, ionization is more important for the molecular species inside the nanotube, as they possess poor conductivity and become more chemically reactive in their ionized form.

In an endohedral Dy@C_{82} fullerene molecule (Figure 1 a), a heavy atom of dysprosium is incarcerated in a spheroidal fullerene cage built from 82 carbon atoms. The metal atom is positively charged (stable oxidation state +3) and positioned off-center in the negatively charged cage (−3) so that the Dy@C_{82} molecule as a whole is neutral.[12] The fullerenes can spontaneously enter carbon nanotubes and form molecular chains, thereby interacting with the SWNT interior by low directional but very effective van der Waals forces.[1–4] The fullerene cages[13] and also the metal atoms inside fullerene cages exhibit dynamic rotational and translational motion inside nanotubes, confirming that no covalent bonding takes place between the molecules and SWNT.[14]

Figure 2 shows the first stages of reaction of Dy@C_{82} in a SWNT (see also the movie in the Supporting Information). Structural changes in the Dy@C_{82} molecules gradually accumulate and become strikingly apparent: an opening appears in one C_{82} cage at the location adjacent to the dysprosium atom, so that the metal atom is released from the fullerene (Figure 2 b).

The release of endohedral gadolinium and terbium atoms from fullerenes has been reported under standard TEM conditions with much higher accelerating voltages of 120 kV, which is significantly above the knock-on damage threshold. The cation release was attributed to the direct knock-on damage of fullerene cages by the electron beam.[15,16] Our observations were carried out at 80 kV and with atomic resolution and clearly indicate that the breakage of the C_{82} cage is specifically associated with the dysprosium atom. The energy of incident electrons transferred to the dysprosium atom may in turn be transferred to carbon atoms of the fullerene, thereby facilitating the rupture of the C−C bonds in the vicinity of dysprosium atoms. An additional important factor may arise from the changes in the oxidation state of the dysprosium atoms that are caused by interactions with the electron beam (similar to a well-known effect causing secondary electron emission in scanning electron microscopy). As for most lanthanides, the oxidation state +3 is the most stable for dysprosium. However, unlike the majority of lanthanoids, dysprosium can also attain the extremely reactive Dy^{4+} state[17,18] under specific conditions. Dy^{4+} can act as a strong oxidant towards most compounds, including both fullerene cages and carbon nanotubes [Eq. (1)].

$$\begin{tikzcd}
\mathrm{Dy}^{3+} \arrow[r, "\text{e-beam}"] & \mathrm{Dy}^{4+} + \mathrm{C}_n \arrow[r] & \mathrm{Dy}^{3+} + [\mathrm{C}_n]^{+} \arrow[ll, bend left]
\end{tikzcd} \qquad (1)$$

Even a transient increase of the oxidation state of dysprosium by the electron beam would create a catalytic center that is capable of destabilizing the molecules and triggering a chemical reaction. Neighboring C_{82} cages would thus join together (Figure 2 c,d) and eventually coalesce into a single molecule (Figure 2 f). The most likely mechanism for this process under the TEM conditions is expected to take place by radical cation intermediates formed on the fullerene cage (Figure 3). This mechanism can be very complex and involve many consecutive fast steps. The recent advances in the ultrafast TEM imaging,[19–23] electron diffraction,[24] and the electron energy-loss spectroscopy[25] applied for the molecular structures in nanotubes may help to unravel the

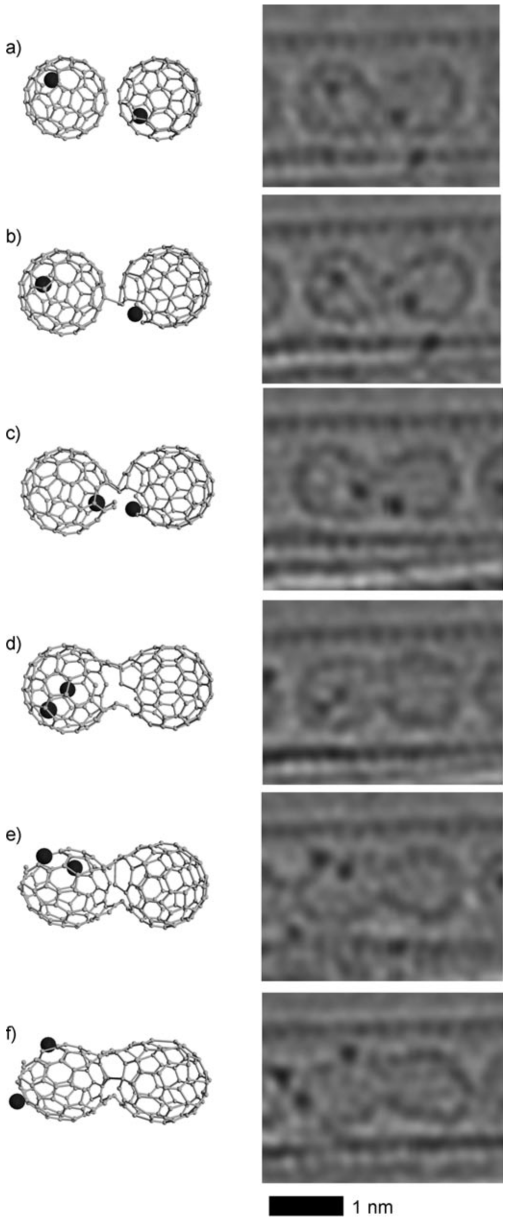

Figure 2. Aberration-corrected TEM showing dynamic processes in nanotubes with atomic resolution. A time series of images shows the fusion of two fullerene molecules. Carbon–carbon bonds of initially intact fullerene cages (a) break one by one in the vicinity of a dysprosium atom (b), until it leaves the C_{82} cage (c), and, combined with a dysprosium atom of the neighboring molecule, breaks the bonds of the second fullerene cage (d–f).

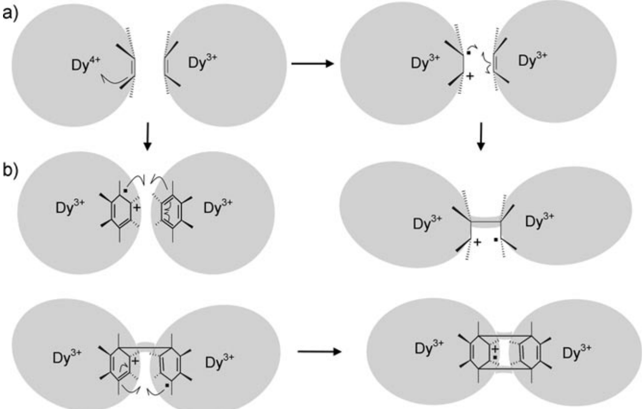

Figure 3. Proposed mechanisms for the initial stages of fullerene coalescence: a) Dy^{4+} withdraws an electron from one of the C=C bonds of fullerene, forming a radical cation that attacks another fullerene cage, which leads to the formation of sp^3 carbon atoms in the fullerene structures that cause the fullerene cages (gray) to distort. b) Alternatively, migration of the radical center may occur. The initial step is followed by a cascade of bond breaking and rearrangement of the fullerene cages driven by greater thermodynamic stability of the newly formed carbon nanotube.

precise mechanisms of these transformations in the future. At higher accelerating voltages and higher electron-beam current densities, the fullerene radical cation may also emerge from the direct impact of the electron beam on the fullerene cage, causing coalescence of molecules on the timescale commensurate with TEM measurements.

The coalescence of fullerenes continues until they form a new nanotube inside the original SWNT. This process is similar to a thermally induced coalescence of fullerenes in SWNTs, which takes place at temperatures above 1000 °C and yields double-walled nanotubes.[26] However, in contrast to the thermally induced transformation, the electron-beam-induced coalescence of molecules results in a structurally imperfect, corrugated internal nanotube, which does not anneal into a straight and coherent nanotube structure even after prolonged exposures to the electron beam, because all structural transformations stop as soon as the dysprosium atoms leave the fullerene cages. The fact that no further observable rearrangements take place without dysprosium atoms confirms the catalytic role of dysprosium in carbon structures.

Dysprosium atoms leave the fullerene cages during the coalescence process and are eventually positioned in the cavity of the SWNT. It is surprising that the dysprosium atoms liberated from fullerenes do not remain separate from each other as expected for positively charged ionic species, but instead they aggregate into pairs (Figure 2 e,f) and then to larger clusters of up to seven or eight atoms (Figure 4). As can be seen from a movie,[14] the metal cluster inside the SWNT remains very dynamic as the dysprosium atoms are tumbling and constantly changing their positions but still remain part of the cluster (Figure 4 a–d).

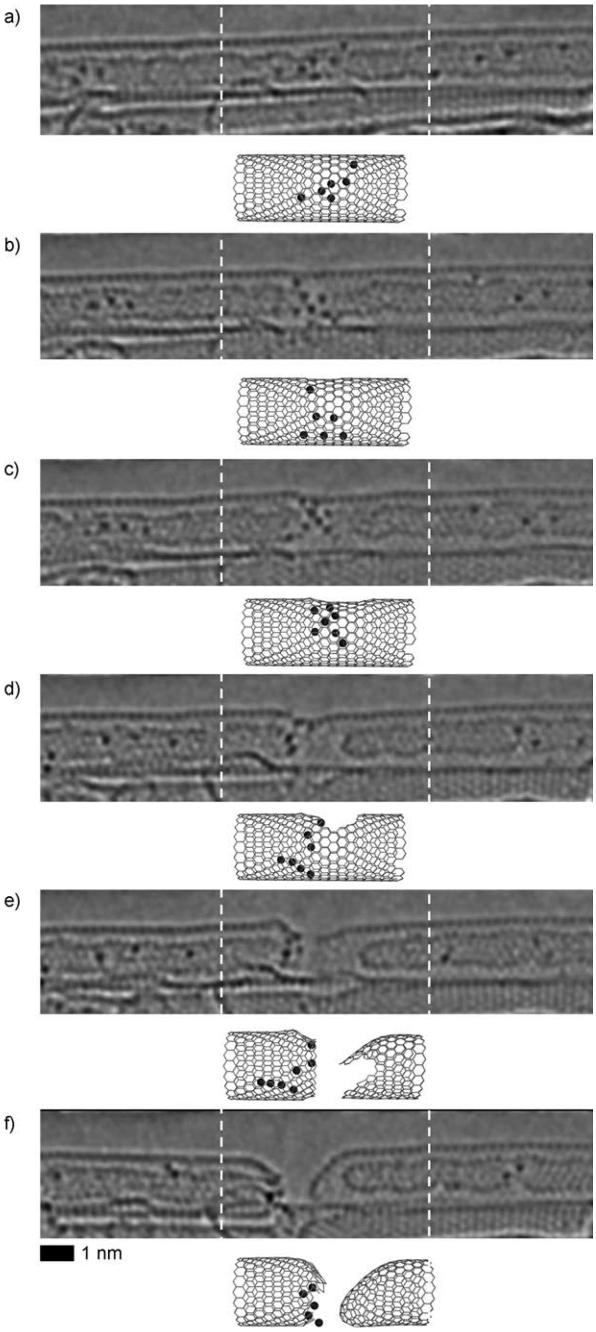

Figure 4. After complete polymerization of the fullerenes, dysprosium atoms move freely within the internal cavity of the newly formed carbon nanotube. a) After a period of time, discrete dysprosium atoms aggregate into a cluster. b,c) The cluster is very dynamic, and the metal atoms are constantly tumbling and changing their positions. c,d) Once the cluster reaches a critical size (about 7 dysprosium atoms), it starts interacting with the inner surface of the nanotube, producing a small kink on the upper side of the SWNT. e) After a prolonged interaction with the dysprosium cluster, the nanotube sidewall breaks, and the cluster retreats into the left part of the nanotube. f) Shortly after the rupture carbon atoms at the nanotube ends rearrange to seal the openings.

This behavior is quite different from previous examples of liberation of metal atoms from fullerene cages within carbon nanotubes after a high-temperature treatment[27,28] or under electron-beam irradiation.[29] In those cases, atoms of lanthanum or gadolinium would form highly ordered, stable nanocrystals within a carbon nanotube, so that the nanotube acting as a simple inert container, as expected. In contrast, the cluster of dysprosium atoms does have a defined structure, but when it reaches a critical size of five to eight atoms, the dysprosium cluster starts interacting with the sidewall of the SWNT (Figure 4e,f). The cluster initially creates a small defect in the nanotube sidewall, and eventually completely ruptures the nanotube into two parts. Interestingly, the cluster of dysprosium atoms stays intact after the breaking of the SWNT and retreats back into the nanotube cavity, thus indicating strong, persistent interactions between dysprosium atoms forming the cluster, which is possibly due to the presence of negatively charged pairs of carbon atoms $[C{\equiv}C]^{2-}$ (a typical structural unit in metal carbides; Supporting Information, Figure S2) which can bridge positively charged dysprosium atoms. The highly reactive nature of the dysprosium atoms is possibly a result of the electron-beam-induced transient switching from Dy^{3+} to Dy^{4+}, which is not possible for lanthanum and gadolinium, and thwarting the formation of an ordered dysprosium carbide nanocrystal.[17]

The metal-catalyzed nanotube rupture[14] finishes with structural rearrangements of dangling bonds. When the SWNT breaks, all of the dysprosium atoms remain in the left part. In the other part, the newly formed nanotube termini are re-sealed through a rapid rearrangement of the C−C bonds in the nanotube structure to achieve a thermodynamically stable closed-end nanotube. By contrast, the chemically active dysprosium atoms keep the end of the left part of the nanotube open (Figure 4 f).

We have observed a four-stage chemical transformation process promoted by metal atoms: 1) the fusing of adjacent fullerenes caused by dysprosium atoms in SWNTs; 2) the formation of a cluster of about seven dysprosium atoms; 3) the reaction of the metal cluster with the walls of the SWNT until both the inner and outer nanotube are completely severed; and 4) the formation of a cap sealing off the open tip of the nanotube. To our knowledge, this is the first time that such a complex reaction process has been observed in such detail. Our observation of these reactions shows that a SWNT cannot be viewed as a simple inert container for reactive species.[30] This work may open new avenues for modifications of the inner surface of carbon nanotubes through insertion of strong oxidants into nanotube cavities and their subsequent activation by external stimuli, such as electron beams, a UV laser, or heat.

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