Fullerenes

Molecular Motion of Endohedral Fullerenes in Single-Walled Carbon Nanotubes**

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Spherical carbon cages of fullerene molecules interact by van der Waals forces to form close-packed arrangements in the solid state, such as the face-centered cubic lattice formed by C_{60} at room temperature.[1] Owing to the low directionality and low energy of the interfullerene interactions neutral fullerene molecules (such as C_{60}) are freely rotating in the crystal at room temperature.[2] Contrasting to the empty fullerene cages, metal-containing endohedral fullerenes are known to have large electric dipole moments of 3–4 Debye.[3] Therefore, it should be expected that intermolecular interactions in the solid $M@C_n$, (M = metal center) are dominated by strong dipolar interactions. For example, fullerene $Ce@C_{82}$ has a large dipole moment owing to the transfer of three valence electrons from the Ce atom to C_{82} cage.[4] This fullerene crystallizes in a hexagonal or a face-centered cubic close pack arrangement.[5] However, despite the dipole moment the fullerene $Ce@C_{82}$ has been shown to retain its rotational freedom in the crystalline state with an energetic barrier of only 1.3 kJ mol^{-1}.[6]

In contrast to bulk-fullerene crystals, fullerene molecules inserted in single-walled carbon nanotubes (SWNTs) form linear chains in which each fullerene has only two nearest neighbors[7] as compared to 12 neighbors in the crystalline bulk fullerenes.[1,5] As a result the intermolecular interactions in these self-assembled carbon nanostructures, designated as C_n@SWNT, and the dynamic behavior of the encapsulated molecules are expected to be different to those in solid fullerenes. C_n@SWNTs exhibit unique electronic properties and are currently attracting attention as building blocks for functional nanodevices.[8,9] C_n@SWNTs structures containing magnetically active mono-metallofullerenes $M@C_n$ are of interest as candidate materials for solid-state quantum computers.[10] We present herein for the first time a study on the molecular motion of mono-metallofullerene $Ce@C_{82}$ chains inside SWNTs demonstrating different modes of translational and rotational motion.

Raw SWNTs (Aldrich) were purified by a combination of standard techniques.[11] Only nanotubes with diameters 13.5 Å and 15.0 Å (as shown by Raman spectroscopy; Supporting Information) were present in the samples used for the experiments. The purified SWNTs were effectively filled with C_{60}, C_{70}, and $Ce@C_{82}$ (synthesized by DC arc-discharge method[12]) at 400–500 °C and 2×10^{-6} torr, which resulted in C_n@SWNT "peapod" structures in 60–90 % yields. The yield for inserting C_{82} in SWNTs was lower ($\approx$ 30 %) even when an excess of C_{82} was used.

High-resolution transmission electron microscope (HRTEM, JEOL 4000EX, LaB_6, information limit 0.12 nm) imaging conditions have been carefully tuned by lowering the accelerating voltage of the microscope to 100 kV and reducing the beam current density to a minimum to enable a direct observation of the molecular motion for the mono-metallofullerene inside SWNTs. Under these conditions the amount of the energy transferable from the electrons to the specimen is significantly reduced[13] compared to the standard TEM imaging conditions. No beam damage was observed in sp^2-carbon structures under these conditions over a period of 20 min. Most of the micrographs were obtained by using 2 s exposures of a charge-coupled-device (CCD) detector. Translational motion can be observed for all types of C_n in SWNTs (Figure 1 a), which indicates that the molecules are mobile inside the nanotube at room temperature and move independently of one another. This effect is particularly noticeable in the peapod bundles where several nanotubes are aligned parallel to each other. Observation of the ends of the nanotubes and side-wall defects confirms that there is no relative motion of nanotubes within the bundle. It is remarkable that the molecules continue their translational motion even inside apparently completely filled nanotubes (Figure 1 b, c).

In contrast to the independent translations observed for sparsely filled nanotubes, the chains of fullerenes with regular van der Waals separations between the molecules undergo collective translations, so that the entire chain shifts in a short time without changing the intermolecular separations. The motion of an isolated molecule in sparsely filled nanotube (Figure 1 a) is not continuous: the molecule performs abrupt jumps with irregular intervals of approximately 10 s.

In contrast to isolated fullerenes the motion of the chains is significantly slower and appears to be more continuous than abrupt: the rectangular (Figure 1 b) and zigzag (Figure 1 c) arrangements do not transform immediately into each other. Instead the rearrangement occurs through a series of states

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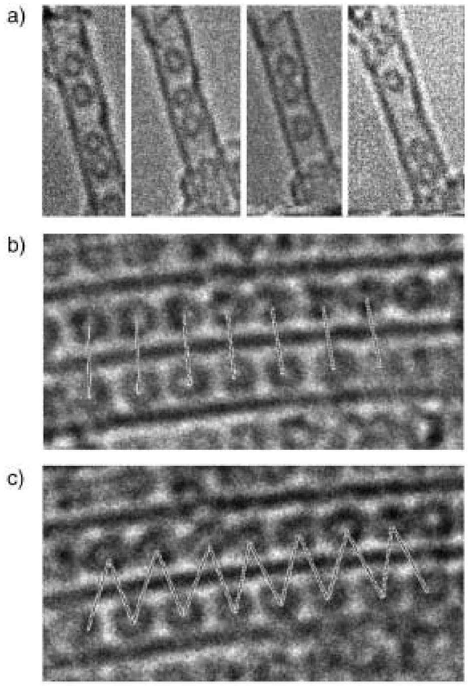

Figure 1. TEM micrographs showing translational motion of fullerenes in a) C_{82}@SWNT (time interval between photographs is 10 s) and b,c) in a bundle of ($Ce@C_{82}$)@SWNT structures (time interval is ≈1 min).

intermediate between the two extreme cases shown in Figure 1 b and c. The chain translates in both directions, and its motion resembles irregular collective oscillations involving large numbers of fullerene molecules. The observation of the collective motions in SWNTs indicates a low energetic barrier for translation and provides explanation for the mechanism of molecular transport along the nanotube during the filling process. A chain of fullerenes does not create a blockage in SWNT and, therefore, the nanotube can be effectively filled along the entire its length from just one entrance point, provided that there is a constant supply of fullerenes from the gas phase. This notion is supported by the HRTEM analysis showing that nearly all nanotubes in the samples are either completely filled or completely empty, whereas partially filled nanotubes are very rare.

Another type of molecular motion, rotation, can, in principle, be observed by HRTEM for endohedral fullerene molecules, because an individual lanthanide atom can be clearly seen as a dark spot at the edge of the fullerene cage as a result of the high single atom contrast,[14] which is related to $Z^{2/3}$ where Z is the atomic number. Previous work reported the continuous spinning of fullerene $Sm@C_{82}$ in SWNTs, so that the metal atom was not visible until the fullerene cages eventually became immobile as a result of beam damage.[15,16] A mixed dynamic behavior has been reported for $Gd@C_{82}$ in the "peapod"-type structure where some cages are stationary and some are spinning.[17,18] Similar to the mono-metallofullerenes, bis(metallo)fullerenes can exhibit a tumbling motion ($La_2@C_{80}$)[19] or total immobility ($Sc_2@C_{84}$)[20] inside nanotubes. Although systematic experimental data on the dynamics of C_n@SWNT systems is very limited, it is possible to conclude that different rotational behavior of fullerenes is related to the energy of the intermolecular interactions inside SWNT. For example, the difference in charge distribution for $Sm^{2+}@C_{82}{}^{2-}$ and $Gd^{3+}@C_{82}{}^{3-}$ results in the relative rotational immobility observed for $Gd@C_{82}$ as compared to $Sm@C_{82}$, which can be related to the stronger electrostatic intermolecular interactions for the latter, which restrict the free rotation.

Individual Ce atoms are visible as dark spots near the edges of the fullerene circles on the micrograph (Figure 2). Each $Ce@C_{82}$ experiences the local electric field owing to the dipoles of neighboring molecules. As the positive end of the dipole moment of $Ce@C_{82}$ coincides with the position of the Ce atom,[14] HRTEM reveals the orientation of $Ce@C_{82}$ dipole moments inside SWNTs. The distribution of angle θ (Figure 3 a,b) indicates a preferential orientation for $Ce@C_{82}$ with the dipole moment nearly parallel to the nanotube axis. Comparison of these angles (θ_1 and θ_2) for pairs of neighboring fullerenes shows a correlation between the orientations, thus, demonstrating that the dipole interactions influence the orientations of polar fullerene molecules in SWNTs (Figure 3 c). However, many fullerenes show significant deviations from the perfect order in SWNTs, as the impact of the electron beam and thermal motion at room temperature disrupt the order in the molecular chains.

A series of successive images with 2 s camera exposure time and with approximately 10 s interval between exposures revealed a discontinuous rotational motion of the fullerene molecules in isolated nanotubes (Figure 2 a–d): a particular $Ce@C_{82}$ molecule stays stationary at a certain position for several seconds before it abruptly jumps to a new stable orientation. Similarly to the translational motion of isolated molecules, the process of switching between different orientations is fast and irregular so that only orientations of

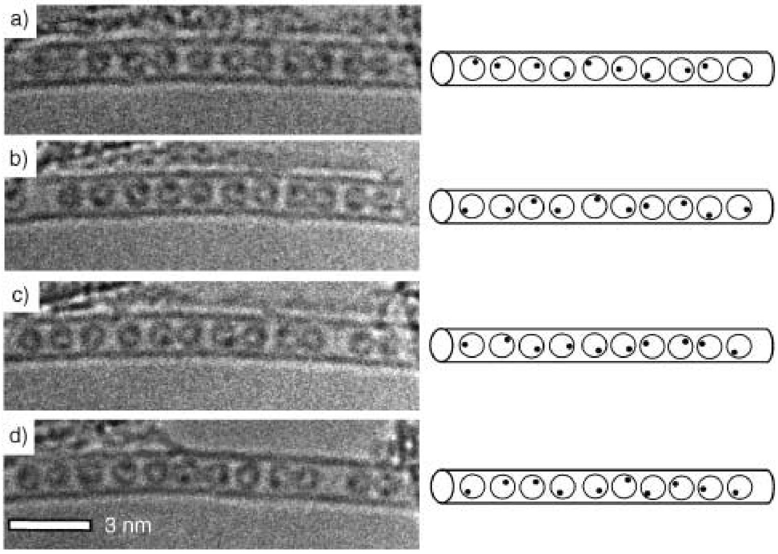

Figure 2. A series of successive HRTEM images of ($Ce@C_{82}$)@SWNT and their schematic representation (a–d).

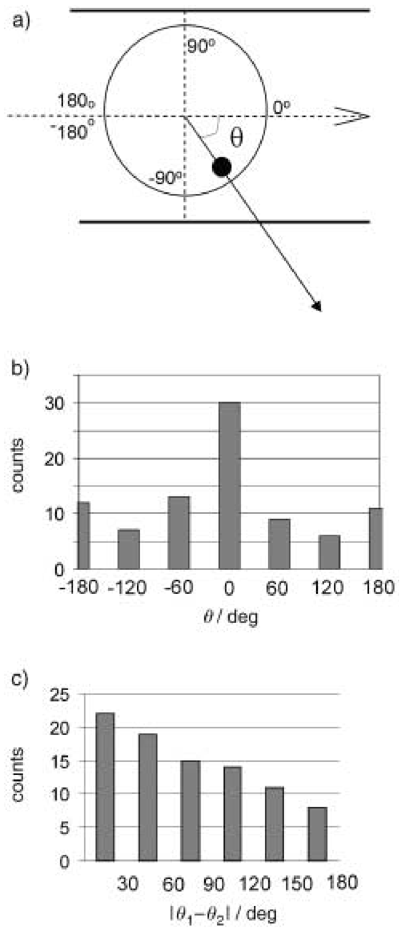

Figure 3. a) Schematic representation of Ce@C_n inside a nanotube: the nanotube direction is shown by a broken arrow, the dipole direction is shown by a solid arrow, θ is the angle between these directions. b) Experimental distribution of θ in (Ce@C_{82})@SWNTs. c) Distribution of $|\theta_1-\theta_2|$ for pairs of adjacent Ce@C_{82} molecules.

Ce@C_{82} corresponding to equilibrium positions can be captured on a CCD detector. The micrographs shown in Figure 2 represent a typical behavior of Ce@C_{82} observed for over 20 isolated nanotubes in different areas of the specimen dispersed on a 5 mm TEM grid. This motion is more likely to be associated with the molecular rotation than with a migration of the Ce atom within the fullerene, because a shift of the Ce atom with respect to the carbon cage requires the overcoming of a significant energetic barrier of 221 kJ mol^{-1}.[6] Thus, the relative energy required for metal rotation in a fixed cage is 170-times greater than that for the cage and metal rotating together in the crystal. The observed switching between equilibrium positions, as compared to a smooth continuous molecular rotation, indicates that the dipolar interfullerene interactions in the (Ce@C_{82})@SWNT system are significantly greater than in the crystal of Ce@C_{82} where molecules are freely rotating at temperatures above 80 K.[6] Each Ce@C_{82} in SWNT experiences the strong electrostatic field dominated by two nearest molecules (see Supporting Information), as compared to twelve nearest molecules in the close-packed crystalline Ce@C_{82}. Owing to the high symmetry of the electrostatic field in the crystal, each Ce@C_{82} molecule can exist in several energetically and geometrically equivalent orientations with a small barrier of 1.3 kJ mol^{-1} between them. However, the nearly free rotation in the crystal of Ce@C_{82} is substantially inhibited in the SWNT as a result of the lowering the symmetry of electrostatic potential for each fullerene.

We have also studied molecular rotation for peapods where each endohedral fullerene can interact with more than two neighboring molecules. (Ce@C_{82})@SWNTs structures spontaneously aggregate in small bundles with a distance of about 8 Å separating the molecules in adjacent nanotubes. Two or three spots appear on micrographs within each fullerene circle (Figure 4) that can be explained by fast switching orientations of Ce@C_{82} between two or three positions with a period shorter than the camera exposure time. At short camera exposures (≈1 s) during the HRTEM imaging the Ce atom appears delocalized between two positions (Figure 4b), whereas at longer exposures (2 s) the Ce atom appears delocalized over three sites (Figure 4a). This effect has been observed for several areas of the specimen where two or more nanotubes are positioned in a close proximity. Attempts to use exposure times shorter than 1 s or longer than 2 s did not produce images with sufficient resolution because of a too low electron dose on the detector or excessive specimen drift, respectively.

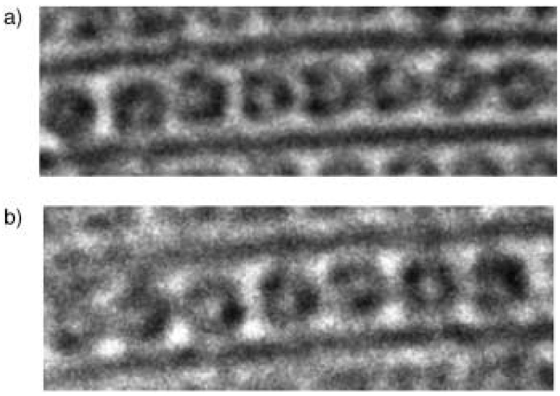

Figure 4. HRTEM micrographs of a bundle of (Ce@C_{82})@SWNT structures taken with a) 2 s and b) 1 s camera exposures.

The faster rate of discontinuous rotation for the endohedral fullerene in the bundle may be associated with dipolar interactions of each molecule with several molecules from adjacent nanotubes in addition to the interactions within the nanotube. This situation means the electrostatic potential around each fullerene has a complex symmetry, which causes orientational frustration for the Ce@C_{82} molecules. As a result, the molecular rotation in the bundle is less restricted than in the isolated nanotube. A bundle of (Ce@C_{82})@SWNTs can be viewed as an intermediate structure between a single "peapod" (Ce@C_{82})@SWNTs and the bulk crystal of the fullerene. Traditionally, bundles of C_n@SWNT are considered as "one dimensional" crystals[8] because of the molecular ordering within these structures, but our results indicate that they should in fact be considered to be "quasi-one-dimensional" or highly anisotropic three-dimensional structures.

In summary, we have synthesized a carbon nanostructure (Ce@C_{82})@SWNT containing isolated Ce atoms embedded in fullerenes. The molecules in nanotubes exhibit an unusual type of saltatory rotational motion visualized for the first time for mono-metallofullerenes. The alignment of the fullerene molecules and the rotational mode suggest the electrostatic dipole interaction influences the orientation of Ce@C_{82} in the nanotube. The nature and rate of the molecular rotation is affected by the external electrostatic fields, such as the field of a neighboring (Ce@C_{82})@SWNT structure within a bundle. In addition, cooperative translational oscillations have been observed for fullerene chains where the intermolecular separations are virtually unchanged as the entire molecular chain moves inside SWNT. It may be possible to exploit the dipolar interactions of this type to control the alignment of the molecular chains, thereby tuning the functional properties of the nanomaterials based on this type of carbon structures.

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