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COMMUNICATIONS

Imaging the Structure of an Individual C_{60} Fullerene Molecule and its Deformation Process Using HRTEM with Atomic Sensitivity

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The diversified properties of carbon nanostructures are related to their local configuration of pentagons and hexagons.[1] Therefore, the arrangement of the carbon network is of great interest in both scientific and technological viewpoints. In order to analyze the molecular structure of fullerenes, the X-ray diffraction and the nuclear magnetic resonance are generally used. These techniques, however, require a macroscopic amount of molecules, and the obtained structure is the average of all the molecules investigated (typically $\sim 10^{20}$ molecules). If one needs to identify individual molecular events, such as deformation or reaction involving rearrangement of pentagon/hexagon configurations, a new characterization technique with both high resolution and high sensitivity is required.

Transformation of the fullerene structure under the energetic particle irradiations has been an important issue since it is surely associated with the rearrangement of the carbon network and can lead to the creation of new structures.[2,3] However, no experimental investigation of such a fullerene transformation has been reported on an atomic scale so far. In order to visualize the individual molecular structure of fullerenes, higher spatial resolution is definitively required. Since the spatial resolution of the conventional TEM is limited by the spherical aberration coefficient (C_s) of its objective lens and the wave length (λ) of incident electron beam, the C_s must be minimized to achieve the best performance because the reduction of the λ is detrimental to the high sensitivity to visualize individual carbon atoms. A high-resolution transmission electron microscope (HRTEM, JEM-2010F) equipped with a C_s corrector (CEOS)[4] was operated at a moderate accelerating voltage (120 kV). The C_s was set to 0.5−10 μm in this work. We need a finite value of C_s, otherwise no contrast can be obtained. The HRTEM images were digitally recorded under a slightly underfocus condition ($\Delta f = -2$ to -7 nm).[5] For this microscope, the point resolution of 0.14 nm was obtained; however, HRTEM simulations were necessary in order to investigate the images of fullerenes taken under different projections.

In this communication, we first report the visualization of the molecular structure of the individual C_{60} fullerene with the icosahedral symmetry (I_h). For the past TEM observations, the cage structure of fullerene molecules appears only in a ring-shaped contrast,[6] and its intramolecular structure, such as pentagons and hexagons, has never been observed (Supporting Information, Figure S1). Single-wall carbon nanotube (SWNT) is used as a specimen support in this experiment. We observed the fullerene molecules which were located on the surface of the SWNTs perpendicular to the incident electron beam (not the ones inside the SWNTs), so that the carbon network of the SWNT does not interfere in the direct imaging of the fullerene intramolecular structures by HRTEM. For this purpose, the C_{60} fullerenes were chemically functionalized with pyrrolidine[7] so that the functional groups attached to each fullerene molecule should act as anchors,[8] and the functionalized C_{60} fullerenes are relatively stabilized on the surface of SWNT during the TEM observations.

Figure 1a−c shows a set of HRTEM images. Each figure shows one fullerene molecule located at the surface of SWNTs in different orientations. As one can see, each fullerene molecule does not appear in a simple ring-shaped contrast but does exhibit some intramolecular features. To corroborate the observed HRTEM images, the image simulations for the C_{60} fullerene molecules were systematically performed in more than 30 different orientations considering the I_h symmetry. Comparing with the simulated images shown in Figure 1d−f, the molecular orientation can be unambiguously assigned for these experimental images. The molecule showing a six-membered ring contrast inside Figure 1a is identical to the simulated one in Figure 1d which corresponds to the C_{60} molecule aligned parallel to the 6-fold symmetry axis (as shown in Figure 1g). Similarly, the image in Figure 1b corresponds to the simulation in Figure 1e, in which two pentagons are overlapped in projection (Figure 1h) and thus give rise to a small circle contrast in the middle of the C_{60} fullerene. The image in Figure 1c is nearly equivalent to the simulated image (Figure 1f) for the projected image shown in Figure 1i. It should be noted that the C_{60} fullerenes could be moving around during imaging since they are loosely anchored to the CNT substrate, and thus the images may represent an average of several orientations. Here we took the images as the snap of movies and made the exposure time (1 s for each frame) as low as possible in competition with the S/N ratio.

As well as the intact C_{60} molecules on which the symmetry and orientation of individual molecules can be easily identified by the current HRTEM, the deformed C_{60} fullerenes are often found after a longer irradiation time (roughly more than 30 s) or a high dose of electron irradiation (higher than 100 000 electrons/nm^2) during the TEM observations. Figure 2a−c gathers the HRTEM images of fullerenes which we were unable to convincingly identify with any orientations in the simulated images of C_{60} with I_h symmetry. These three images in Figure 2a−c clearly show the deviated structures from the spherical shape expected for the intact C_{60} molecules. This is a clear proof that the C_{60} fullerenes can be degraded from the I_h symmetry during the electron microscopic observations.

This fact strongly suggests that the observed molecules could have suffered a considerable deformation, and its carbon network has been reorganized (due to the electron irradiation), which should certainly deviate the molecule from its original structure. Three possible deformation processes were considered: (i) the Stone−Wales transformations,[9] (ii) introduction of vacancies,[10,11] and (iii) the relaxed C_{58} molecular structures after removing two carbon atoms.[10,11] Smalley et al. found that laser irradiation can fragment C_{60} into C_{58}, C_{56}, and other even smaller clusters via the loss of C_2 fragments.[12] From the stability considerations, losing C_2 units is more favorable than losing single C atoms from the C_{60} cage.[10,13]

10.1021/ja068516r CCC: $37.00

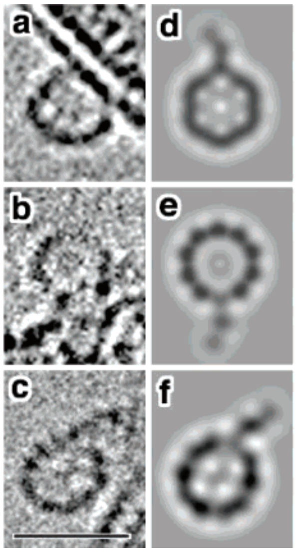

Figure 1. (a−c) HRTEM images of functionalized fullerene molecules with pyrrolidine ($C_{60}-C_3NH_7$) attached to the surface of SWNTs. The intramolecular structures are clearly visible for each fullerene. (d−f) Image simulations of C_{60} fullerene derivatives for various orientations to be compared. Corresponding atomic models are also shown in (g−i).

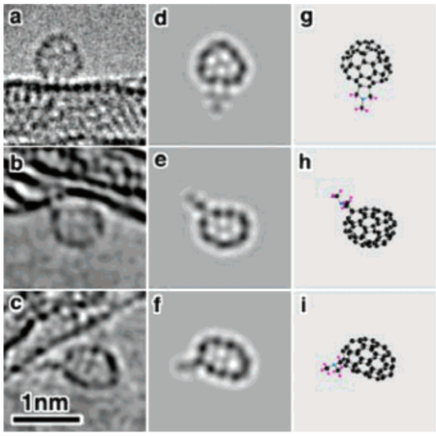

Figure 2. (a−c) HRTEM images of the degraded (or deformed) fullerene structures. (d−f) The simulated images are based on the assumption that C_{58} molecules probably formed after losing two carbon atoms (or a carbon dimer). Three C_{58} molecules with C_1 symmetry are depicted as reasonably well-fitted models. Corresponding atomic models are also shown in (g−i). The pyrrolidine type functional groups are attached arbitrarily in the image simulations.

In this study, the HRTEM image simulations based on the structural models of C_{60} molecules with the Stone−Wales transformations or with the vacancies (one to four) have been made to a large extent, however, neither of them fits with the experimental images. Since our observation voltage (120 kV) is larger than that of the knock-on damage threshold of the fullerene, which is between 40 and 80 kV,[14] the loss of C atoms is possible. We have therefore suggested the C_{58} molecules as the possible candidates by assuming that the two C atoms (or a carbon dimer) have been removed from the C_{60} due to the knock-on effect. Then the whole molecular structure could have been relaxed after. Three structures of C_{58} (shown in Figure 2g−i) were chosen among the 1205 isomers of C_{58} (disregarding the isolated pentagon rule) after the geometrical optimization,[15] which fit reasonably well (as shown by the simulated images in Figure 2d−f) with the experimental images in Figure 2a−c. Note that the knock-on effect generally produces the defective fullerene cage with various structures and the C_{58} is not the unique molecule formed after the irradiation. Because of the possible structural instability or continuous deformations of the molecules, and also the moving around of the molecules during the imaging, the simulated images cannot give the complete match to the detailed structures experimentally observed. This may reflect the intrinsic difficulty in imaging single molecules.

This work demonstrates that the carbon network of individual molecules can be visualized by using a C_s-corrected HRTEM. Even though this is successful only in limited cases, this type of approach is of great consequence toward the atomic resolution analysis of noncrystalline materials, particularly those made of light elements such as organic or biological molecules, which has been believed to be quite difficult to visualize by HRTEM. Keeping the accelerating voltage of TEM as low as possible is quite beneficial to minimize the knock-on damage of soft matters provided that the resolution can be compensated by the C_s correction. Surprisingly, the pyrrolidine functional groups do not suffer severe damage and are quite stable during the observations. The HRTEM study on the single organic molecules also demonstrates the stability of the single carbon chain under the electron beam.[16]

The deformation of C_{60} fullerene due to the electron beam is also observed. Although the simulations suggested the reasonable candidate of the transformation from C_{60} to C_{58}, the intrinsic difficulty in imaging single molecules gives rise to the limitation of the study. Further recording media with higher sensibility or lower accelerating voltage which may lessen the recording time are being anticipated.

Acknowledgment. Work on HRTEM is supported by CREST. Drs. S. Okubo and C. Ewels are gratefully acknowledged for their fruitful discussions. We thank Drs. H. Kataura and A. Mrzel for the specimen preparation.

Supporting Information Available: A typical HRTEM image of C_{60} functionalized fullerene with pyrrolidine ($C_{60}-C_3NH_7$) attached to the surface of SWNTs taken under 120 kV without C_s correction. This material is available free of charge via the Internet at http://pubs.acs.org.

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JA068516R