High Resolution Electron Microscopy of Er@C-90 in Peapods

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- Advances in nanotechnology increasingly rely on **characterization tools with atomic resolution**.
- SWNT is an ideal nanometer-scale **sample cell** for direct imaging of molecular structures with TEM.
- The encapsulated molecules can modify the electronic structure of SWNTs, which means that we can perform '**band-gap engineering**' at sites where a fullerene is inserted.
- Endohedral metallofullerenes like Er@C-90 possess strong dipole moments, and the dipole ordering of these molecules in SWNT may provide a means for **information transmission.**

Introduction:

Carbon is a remarkable material showing a variety of stable forms. In particular, carbon nanotubes (CNTs) have attracted great interest because they are considered as prototypes of one-dimensional nanostructures in science and technology. **One of the most distinguishing features of CNTs is that they can encapsulate metal atoms or molecules into their central hollow space, which may lead to a new class of materials with novel applications.** The incorporation of molecules into the hollow space of single-walled nanotubes (SWNTs) has been called "peapods." They are expected to act us building blocks in future electronics because the mechanical and electrical properties of SWNTs undergo considerable modification upon encapsulation. This allows us to finely tune SWNTs by altering the encapsulated fullerenes. And since SWNTs are extremely thin and almost transparent to high-energy electron beams, they can act as an ideal sample cell at nanometer scale and thus allow transmission electron microscopy (TEM) to observe molecular structures encapsulated.

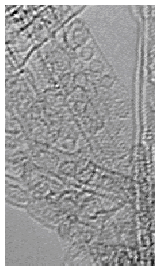

Figure 1. TEM image of peapod structures.

Sample Preparation:

We employ a bulk production method through the gas phase reaction to produce peapods. This method allows us to produce various fullerene peapods in high yield (> 80%). **In order to obtain high-purity and high-yield peapods, one should prepare isolated fullerene molecules and high-purity open-ended SWNTs**. Since Fullerenes are soluble molecules, we can purify them more than 99% with a well-established separation method, such as high performance liquid chromatography (HPLC). On the other hand, SWNTs can be purified by a combination of several methods. For example, we remove the amorphous carbon materials and metal catalyst particles by refluxing the as-produced SWNTs in acid solutions; the acid treatment also promotes cap-opening of SWNTs. This purification method strongly depends on the purity of the pristine SWNT material. It is extremely difficult to remove graphitic particles or sheets because they are more stable than SWNTs. Therefore, it is important to synthesize without such impurities from the beginning. Following the acid treatment, the SWNTs were heated in dry hair at 450˚C for 30 min to fully open the tube ends because amorphous carbons could clog them. Besides the gas phase reaction method, peapods can also be made through liquid phase reaction. This method involves immersing open-ended SWNTs in a saturated solution of fullerenes, yet unfortunately the doping yield can only reach as high as ~70%.

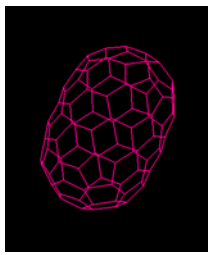

Figure 2. C-90 Fullerene

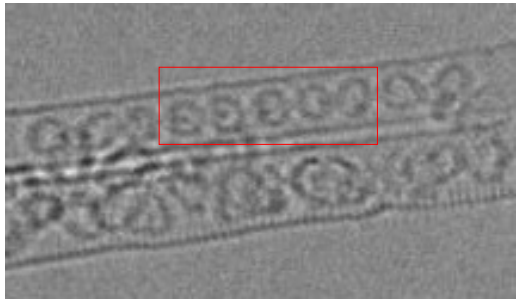

Figure 4. HR-TEM image of the Er@C-90 metallofullerenes inside SWNTs. Dark spots seen in each molecule correspond to the individual Er atoms. A JEOL 2010F electron microscope was operated for imaging.

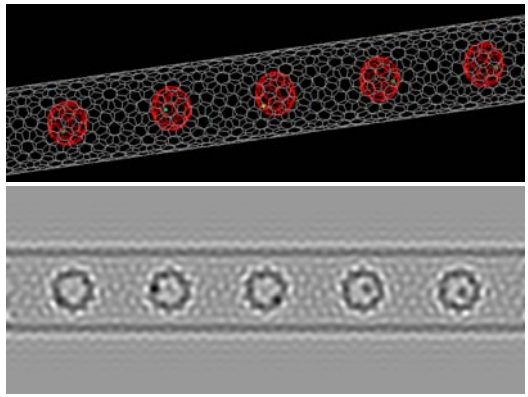

Figure 5. HR-TEM simulation for a Er@C-90 metallofullerene peapod.

- The estimated distribution of tube diameters for Er@C-90 endoheral metallofullerene encapsulation is between **1.6 – 2.0 nm**. The average intermolecular distance between each Er@C-90 is **1.82 nm**. This result is statistically analyzed by DigitalMicrograph and is based on our direct observation of Er@C-90 in peapods.

- Due to the difficulty in observing Er@C-90, which is easily damaged by the electron beam (it often coalesces within a few seconds) , the precise molecular structure has yet been determined. Thus, we have not been able to obtain atomic-resolution images on this structure. As a result, the preferred dipole orientation in peapods is not clearly understood.

- Based on theoretical studies, C-90 should be anti-symmetrical. However, in many of the images we obtained, Er@C-90 appears to be fairly symmetrical like C-60.

Figure 3. JEOL 2010F: A high-resolution TEM with single-atom sensitivity

Table 1. Critical Diameter for SWNTs to encapsulate C-60, C-70, C-78, and C-84

Fullerene	d/ nm
C-60	1.37
C-70	1.45
C-78	1.45
C-84	1.54

S. Bandow et al. *Chem. Phys. Lett.*, **347**, 23 (2001)

Conclusion:

Although the exact molecular shape of the Erbium metallofullerene (Er@C-90) has not been fully analyzed, direct observation of this metallofullerene in a peapod has led to successful determination of the critical tube diameter for encapsulation and the intermolecular distance between each metallofullerene in SWNTs. In addition, by a comparison of high resolution images with a simulation to extract the relative metal atom positions in C-90, the dipole orientations in metallofullere peapod can be revealed. Yet the preferred dipole orientation of Er@C-90 in peapods has not yet been confirmed due to insufficient high-resolution images.

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