Dynamical behavior of organic molecules encapsulated in single wall carbon nanotubes investigated by Aberration Corrected-HRTEM

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Despite the recent progress in nano-electronics with SWNTs as active material [1], such devices are limited to the near-infrared region due to the intrinsically small band gaps of SWNTs. The encapsulation of molecules (peas) makes SWNTs optically active in the visible spectra range and allows tuning the properties of new hybrids as well as keeping the physical properties of SWNTs. Recently, the very first peapods with photoluminescence (PL) emission in the visible spectral range have been demonstrated by our team [2, 3] by encapsulating α-sexithiophene (6T) inside SWNTs.

Aberration-corrected high-resolution transmission microscopy (AC-HRTEM) is the only direct technique to observe the nanotubes together with the encapsulated molecules. We used a FEI Titan 80-300 high-resolution transmission electron microscope equipped with a hexapole-based aberration corrector (COES company) for the image-forming lens operated at 80 kV. This way, the electron knock-on damage to the sample was reduced. We present images slightly under-focused (C_S=5µm, black atom contrast) in order to enhance the contrast of the molecule inside the SWNT. The results obtained were compared with HRTEM image simulations performed with a standard multislice procedure [4].

Following molecules were encapsulated inside the SWNTs – pyrene; benz [b] anthracene aka tetracene; coronene and α-sexithiophene (6T), see Fig.1. For the encapsulation of pyrene and tetracene samples NanoCarboLab (NCL) nanotubes were used. Coronene and 6T samples were encapsulated in nanotubes provided by Meiji University (SO) that are bigger in diameter (up to 1.6 nm) thus more convenient for larger molecule encapsulation. Peapods were obtained by following a vapor-phase method based on the sublimation of the molecules in the presence of purified SWNTs in a sealed quartz tube at low pressure. The resulting adducts were separated from the nonen-capsulated molecules by extensive washing with solvent and by treatment at reduced pressure to sublimate the molecules adsorbed on the external SWNT walls. The peapods were carefully characterized by mean of Raman, UV and fluorescence spectroscopy that confirmed the encapsulation of the molecules.

The AC-HRTEM images reveal successful encapsulation of all examined samples see Fig.2. However, even though low dose imaging conditions were used, it is intriguing to note that the molecules containing only carbon seems to react faster under the electron beam to form small structures that resemble a carbon nanotube. Further investigation should be done at lower voltage, although it is not very likely to improve the situation, as the damage is probably initiated by ionization more than by knock-on damage. Keeping the specimen at liquid nitrogen temperature might also help. Kinetics of the degradation process was recorded during the acquisition of image series. Reconstruction of tetracene accommodation inside the tube is presented in Fig.3. In the early stage of observation, round and line structures can be recognized. Those are marked with red color, Fig 3 (A). The size of the objects corresponds to the theoretical size of tetracene (9.7 Å, C-C distance). The 6T sample is more stable during the long time observation, most probably because it contains 6 atoms of sulphur. Two arrays of 6T molecules accommodated alongside the tube

sidewall are present. Molecules rotate and twist inside the tube. We can conclude that relatively long time of observation has destructive effect on peapods containing pure organic molecules, making them very difficult to investigate.

References

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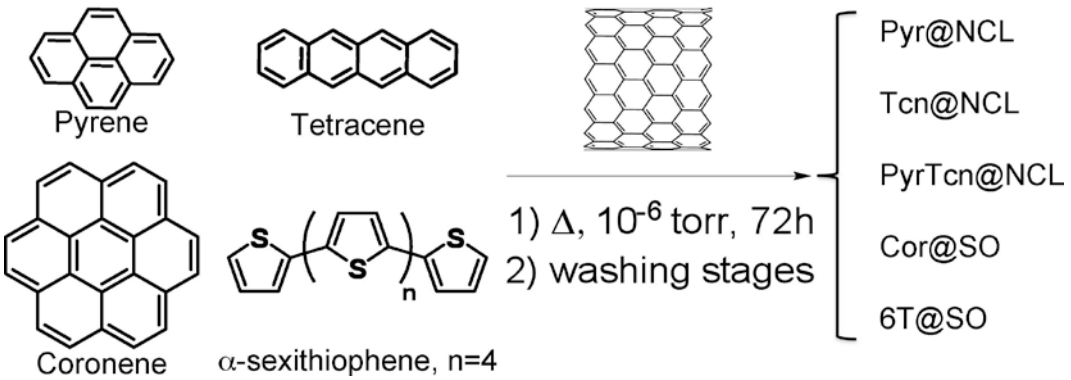

Figure 1. *Scheme illustrating the encapsulation of pyrene, tetracene, coronene and a-sexithiophene (6T) in SWNTs resulting in the corresponding peapods labeled Pyr@NCL, Tcn@NCL, PyrTcn@NCL, Cor@SO and 6T@SO.*

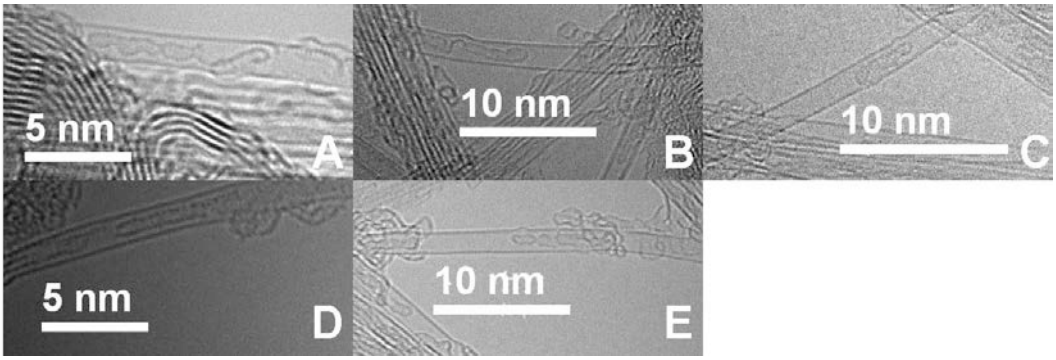

Figure 2. *High-resolution images of (A) Pyr@NCL,(B) Tcn@NCL, (C) PyrTcn@NCL, (D) 6T@SO and Cor@SO.*

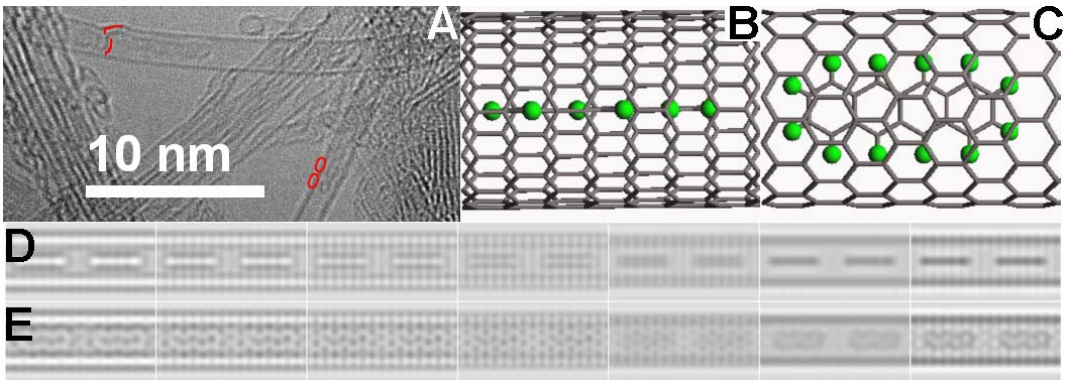

Figure 3. *(A) High-resolution image of Tcn@NCL. Atomic model of tetracene molecule inside a (16,0) SWNT (B, C) together with the corresponding simulation for the molecular plane parallel (D) and perpendicular (E) to the electron beam. The defocus varies from −6 to +6 in steps of 2 nm (from left to right).*