Encapsulation of Molecules in Single-Walled Carbon Nanotube
- A Novel Nanodevice Material -

Single-walled carbon nanotube (SWNT) is the most promising material for molecular electronics because of its unique structural and electronic properties. Molecular electronics is an emerging area in which the goal is using molecular materials as core device components. An advantage of molecular electronics is obviously the small size of the core components, surpassing structures attainable by top-down lithography, and could therefore be essential for miniaturization. SWNTs are wires with molecular-scale diameters (~1 nm), and individual semiconducting SWNTs have been actively explored in order to construct nanotube field-effect transistors (FETs). For the further advancement of molecular electronics, the ability to obtain both p- and n-type FETs is important for constructing complementary electronics whose performance is better (for example, low power consumption) than that of devices consisting of unipolar p- or n-type transistors. SWNT-FETs built from as-grown tubes are found to be unipolar p-type. Several doping methods have been developed for nanotubes, although stability in air was not sufficient for the n-type doping.

On the other hand, due to their size and geometry, SWNTs also provide a unique opportunity for nanoscale engineering of novel one-dimensional systems, created by self-assembly of molecules inside the SWNT's hollow core. It has been experimentally shown that fullerenes can be inserted into SWNTs, forming a peapod-like structure [1]. The composite nature of peapod materials raises an exciting possibility of a nanoscale material having a tunable structure that can be tailored to a particular electronic functionality. In this work, we clarify the structure of organics/SWNT compounds, and investigate the charge transfer between SWNT and organic molecules. Since organic molecules predominantly occupy the inner space of SWNTs, the doping state is rather stable in air.

SWNTs were manufactured by laser vaporization of carbon rods doped with Co/Ni in an atmosphere of Ar and subsequently purified with H_2O_2, HCl and NaOH [2]. SWNTs were reacted with vapor of organic molecules, which are shown in Fig. 1, in a manner similar to the case of the C_{60}-peapod [3]. For structural characterization, synchrotron X-ray powder diffraction data were obtained at room temperature at beamline **BL02B2**. Figure 2 shows typical diffraction profiles for pristine, TCNQ-doped and TMTSF-doped SWNT materials. The most obvious difference between doped and undoped SWNTs is the strong reduction of peak intensity at approximately $Q \sim 0.4$ (Å^{-1}), which is indexed as (10) reflection. Such a behavior provides evidence of encapsulation of organic molecules inside SWNTs, as observed in several peapod materials and gas-adsorbed SWNTs [4].

Intensity reduction of the (10) peak allows us to estimate the chemical concentration ratio of encapsulated organic molecules to carbon atoms of SWNT. First, the parameters of pristine SWNTs were determined so as to reproduce the observed diffraction pattern shown in Fig. 2(a), taking the Gaussian distribution of the tube diameter into account. By using the obtained parameters, the intensity distributions of the diffraction pattern for the organic/SWNT compounds were well accounted for by inserting an uniform rod of charge with the diameter of 7 Å inside the tubes. From the density of uniform charge, the carbon number of SWNT per organic

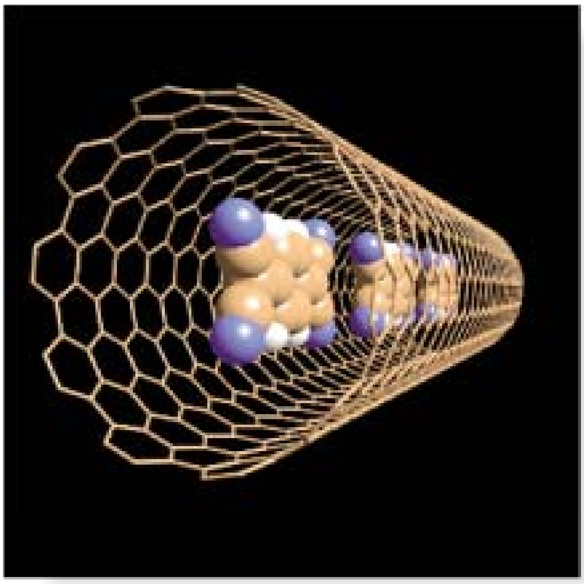

Fig. 1. Single walled carbon nanotube encapsulating TCNQ molecules.

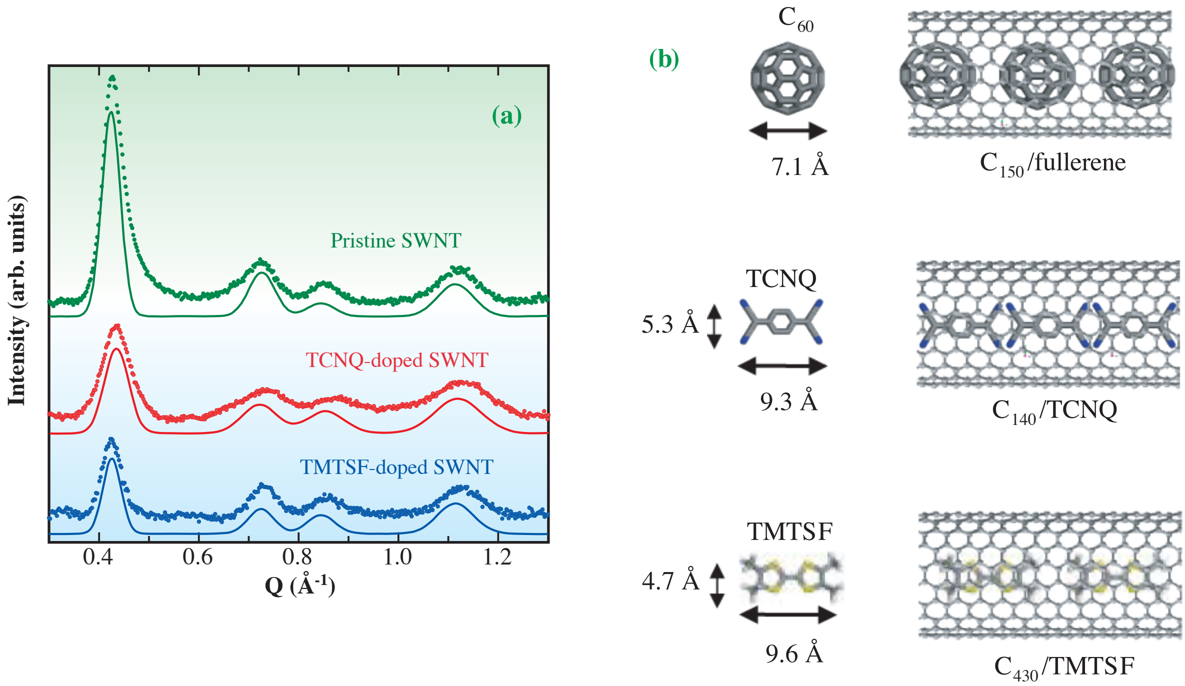

Fig. 2. X-ray diffraction pattern and a schematic structure model of organics/SWNT materials. **(a)** Observed and simulated X-ray diffraction patterns of pristine, TCNQ-reacted and TYMTSF-reacted SWNT. Dotted and solid lines represent observed and simulated patterns, respectively. **(b)** Schematic stacking patterns of C_{60}, TCNQ and TMTSF molecules inside (10, 10) SWNTs.

molecule was derived as $C_{140(10)}$/TCNQ and $C_{430(10)}$/TMTSF. A possible configuration of encapsulated organic molecules inside (10, 10) SWNT is described in Fig. 2(b) and compared with that of C_{60} peapods. The intensity reduction of the (10) peak was observed in all organics/SWNT compounds investigated (Fig. 1). Doping properties have been investigated by Raman and optical absorption spectroscopy. Both measurements clearly provide direct evidence of the charge transfer between SWNTs and organic molecules in SWNTs doped with TCNQ, F4TCNQ, TDAE, TTF, and TMTSF, while no appreciable change was detected in SWNTs doped with C_{60}, anthracene, tetracene, and pentacene [3]. TDAE-, TTF- and TMTSF-doped SWNTs were n-type semiconductors. We have investigated the air stability of organics/SWNT compounds through measurements before and after exposure to air. Spectra were unchanged for one week under ambient conditions, except for TDAE/SWNT compounds, providing evidence of air stability of organics/SWNT materials. Encapsulation of organic molecules in SWNTs is one of the possible reasons for the stability, since the outer wall of SWNTs will protect the molecules from oxygen.

In summary, we have synthesized SWNTs encapsulating organic molecules, and investigated the charge transfer between SWNTs and organic molecules. Since organic molecules predominantly occupy the inner space of SWNTs, the doping state is rather stable in air.

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