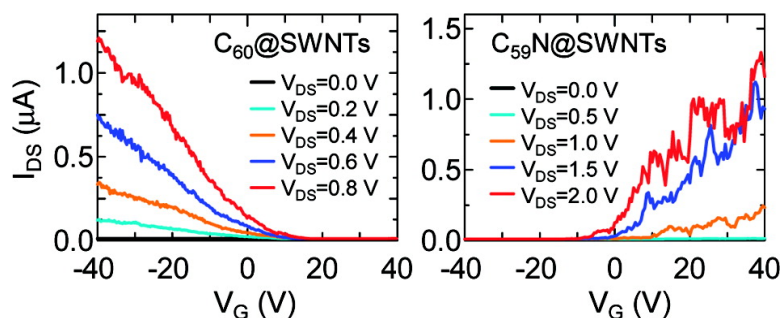## Communication

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Azafullerene Encapsulated Single-Walled Carbon Nanotubes with n-Type Electrical Transport Property

Toshiro Kaneko,* Yongfeng Li, Shohei Nishigaki, and Rikizo Hatakeyama

Department of Electronic Engineering, Tohoku University, Sendai 980-8579, Japan

Received September 25, 2007; E-mail: kaneko@ecei.tohoku.ac.jp

The azafullerene $C_{59}N$, i.e., a single carbon atom of the fullerene C_{60} cage replaced by a nitrogen atom,[1-3] has attracted special attention because of its interesting properties and applications in superconductivity, photoelectric devices, and organic semiconductors.[4] Although the theoretical study has indicated that the azafullerene has the property of an electron donor,[5] to our knowledge, there is no experimental verification of it. On the other hand, following the discovery of carbon nanotubes, carbon peapods, i.e., single-walled carbon nanotubes (SWNTs) encapsulating fullerenes, are recognized to be promising materials as potential building blocks for nanoelectronics. The presence of fullerenes inside SWNTs is expected to significantly modify the band structure of SWNTs and consequently affect their electrical transport properties. It has been reported experimentally that fullerene peapods can exhibit different transport properties, such as p-type, ambipolar, and metallic behaviors.[6] However, an n-type characteristic of the fullerene peapod has never been reported, which is indispensable for realizing SWNT-based electronic devices.

In this communication, we investigate synthesis, characterization, and electric transport properties of SWNTs encapsulating $C_{59}N$, which results in a clear-cut observation of the n-type behavior of the peapod. It is the first time that the azafullerene $C_{59}N$ is proven to be a good electron donor.

The azafullerene $C_{59}N$ is synthesized using a plasma irradiation method under the following conditions: plasma density $n_p \approx 10^9$ cm^{-3}, electron temperature $T_e \approx 0.5$ eV, and nitrogen-ion irradiation energy $E_i = 10-40$ eV.[7] The fullerene C_{60} after plasma irradiation is dissolved in toluene, and its mixture is separated into a residue and a solution. The mass spectroscopy analysis of the formed azafullerene is performed using a laser-desorption time-of-flight mass spectrometer (LD-TOF-MS, Shimadzu AXIMA-CFR+). Figure 1 shows mass spectra of (a) the residue and (b) the solution of the fullerene dissolved toluene in a positive ion mode of LD-TOF-MS. The peak at the mass number 722 is the most distinct in the residue, which originates from azafullerene $C_{59}N$. It is known that $C_{59}N$ is stable in the form of $(C_{59}N)_2$, but the mass number of $C_{59}N$ monomer (722) is detected here because the chemical bonding between $C_{59}N$ monomers is broken by the laser irradiation. In the solution, however, the peak intensity corresponding to $C_{59}N$ is much less than that of C_{60} (720) because $C_{59}N$ dissolves little in toluene. Therefore, $C_{59}N$ is dominant in the residue, although the quantitative abundance ratio of $C_{59}N$ to C_{60} is not determined from the results of LD-TOF-MS.

This $C_{59}N$ mixed with slight C_{60} is encapsulated into SWNTs[8] by either a vapor reaction method or a plasma ion-irradiation method. For the vapor reaction method, the purified SWNTs together with $C_{59}N$ fullerene powders, are sealed in a glass tube under a vacuum condition of $\sim10^{-5}$ Torr. After that, the sealed glass tube is heated at 420 °C for 48 h to encapsulate $C_{59}N$ in SWNTs. Raw samples are obtained after the above process and then purified via a washing process in toluene to remove most of
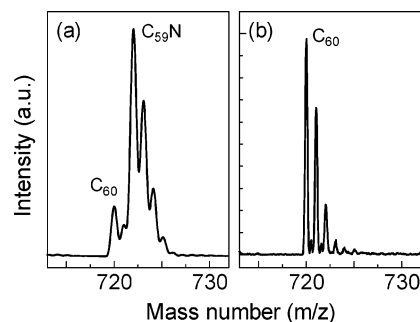

Figure 1. Mass spectra of (a) the residue and (b) the solution of the fullerene dissolved toluene in positive ion mode of LD-TOF-MS.
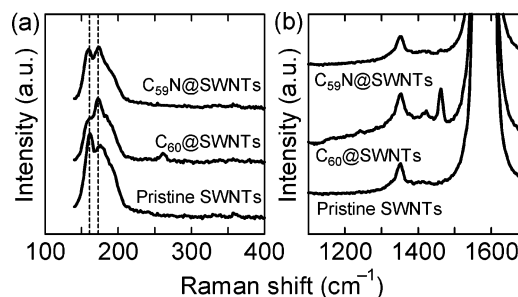

Figure 2. Raman spectra for the pristine, C_{60} encapsulated, and $C_{59}N$ encapsulated SWNTs in the ranges (a) 100−400 cm^{-1} (Radial breathing mode) and (b) 1100−1700 cm^{-1}. The Raman spectra are obtained at an excitation wavelength of 488 nm.

the excess fullerenes attached to the surface of SWNTs. The $C_{59}N$ encapsulated SWNTs purified are examined in detail by field emission transmission electron microscopy (FE-TEM, Hitachi HF-2000) operated at 200 kV and Raman spectroscopy (Jovin Yvon T-64000) with an Ar laser at 488 nm. The electronic transport properties of various SWNTs are investigated by fabricating them as the channels of field effect transistor (FET) devices. These SWNTs samples are ultrasonically dispersed in *N,N*-dimethylformamide first and then spincoated on FET substrates, each of which consists of Au drain−source electrodes on a SiO_2 insulating layer. A heavily doped Si substrate serves as a backgate. The detailed fabrication process for FET devices can be found elsewhere.[9,10] The transport measurements are performed at room temperature under vacuum conditions on a semiconductor parameter analyzer (Agilent 4155C).

Figure 2 shows Raman spectra for the pristine, C_{60} encapsulated (C_{60}@SWNTs), and $C_{59}N$ encapsulated SWNTs ($C_{59}N$@SWNTs) in the ranges (a) 100−400 cm^{-1} (Radial breathing mode) and (b) 1100−1700 cm^{-1}. The pristine SWNTs show Raman peaks at 161 and 178 cm^{-1}, which correspond to the SWNTs with diameters of about 1.54 and 1.40 nm, respectively. The spectrum shape in the C_{60} or $C_{59}N$ encapsulated SWNTs drastically changes in comparison with the pristine SWNTs, which is especially reflected in a decrease
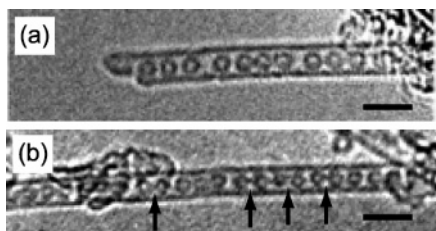
Figure 3. TEM images for (a) C_{60}@SWNTs and (b) C_{59}N@SWNTs (scale bar is 2 nm).
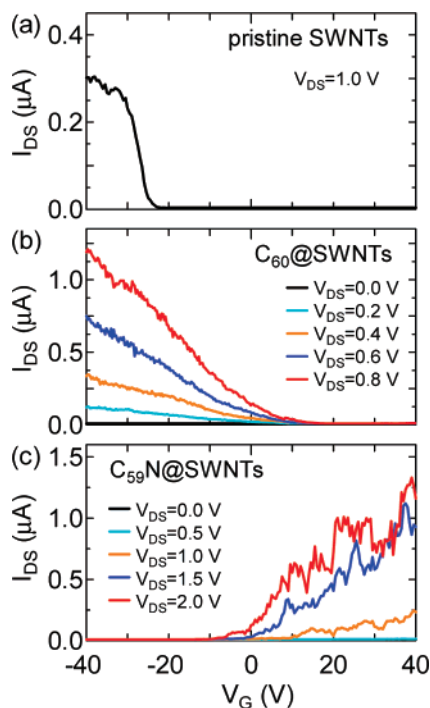

Figure 4. Source−drain current (I_{DS}) vs gate voltage (V_G) characteristics at room temperature for (a) pristine SWNT, (b) C_{60} encapsulated, and (c) C_{59}N encapsulated SWNTs.

in the peak intensity at 161 cm^{-1}. These results of Raman spectra in the RBM region give indirect evidence of the encapsulation of other materials, i.e., C_{60} or C_{59}N, inside SWNTs. In addition, it is found that the frequency of the G$^+$ mode (1591 cm^{-1}) slightly up-shifts and down-shifts in the cases of C_{60} and C_{59}N encapsulations, respectively (see Supporting Information).

To further verify the encapsulation of the fullerenes, Raman spectra in the range 1100−1700 cm^{-1} are measured in detail as shown in Figure 2b. The clear peaks at 1423 and 1469 cm^{-1} are observed in the C_{60}@SWNTs, corresponding to the modes Hg(7) and Ag(2) for C_{60}, respectively.[11] However, these peaks disappear in the C_{59}N@SWNTs because the peak intensities of Raman spectra of the modes Hg(7) and Ag(2) for C_{59}N are very weak compared with those for C_{60} (see Supporting Information).

A TEM observation result of C_{60}@SWNTs is shown in Figure 3a, which indicates that C_{60} molecules with spherical symmetry are filled into SWNTs, where C_{60} is isolated from each other. In the case of C_{59}N@SWNTs, on the other hand, paired C_{59}N dimers which are indicated by arrows in Figure 3b are observed along the tube axis. This means that C_{59}N is actually encapsulated into SWNTs and makes the dimer, forming a one-dimensional chain-like structure inside the SWNTs. The TEM images for C_{59}N

encapsulated SWNTs with lower magnification show the relatively high filling rate of the fullerenes (see Supporting Information).

The transport property of pristine semiconducting SWNTs is well-known to exhibit the p-type behavior as shown in Figure 4a, where a characteristic curve of source−drain current I_{DS} versus gate voltage V_G is described for source−drain voltage $V_{DS} = 1$ V. Figure 4b presents the transport property of C_{60}@SWNTs. The typical p-type characteristic is observed, but the threshold voltage (V_{th}) for hole conductance is found to shift from -28 V to $+20$ V compared with that of pristine SWNTs, indicating that the p-type behavior of the SWNTs is maintained by the C_{60} encapsulation. In contrast, the transport property of C_{59}N@SWNTs drastically changes to an n-type semiconductor [Figure 4c]. This n-type characteristic is attributed to the charge transfer between C_{59}N and local parts of SWNTs, suggesting that C_{59}N exert a strong electron donor effect on SWNTs. In addition, it should be noted that the above fullerene-induced characteristics have been observed in many independent SWNTs devices, and they have good reproducibility under measurements performed with different source−drain volt-ages.

In summary, we have investigated the electrical transport properties of C_{60} and C_{59}N encapsulated SWNTs by fabricating them as the channels of FET devices at room temperature. Their measurements indicate that C_{60}@SWNTs exhibit the enhanced p-type characteristics compared with the case of pristine SWNTs, whereas C_{59}N@SWNTs show the n-type behavior. The novel transport properties of these encapsulated SWNTs can be explained by the electron donor behavior of C_{59}N, which can modify the electronic structure of SWNTs.

Supporting Information Available: Raman spectra of fullerenes (C_{59}N and C_{60}) and fullerene encapsulated SWNTs and TEM images for C_{59}N encapsulated SWNTs with lower magnification in PDF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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