Synthesis and Property Characterization of $C_{69}N$ Azafullerene Encapsulated Single-Walled Carbon Nanotubes

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ABSTRACT Our study demonstrates that the $C_{69}N$ azafullerene can be encapsulated inside single-walled carbon nanotubes (SWNTs), which is confirmed by TEM, UV—vis—IR spectroscopy, Raman spectroscopy, and UPS. The electrical transport properties of SWNTs are found to change drastically due to the encapsulated $C_{69}N$ azafullerene. Our experimental results indicate that $C_{69}N$ encapsulated SWNTs show the high-performance n-type behavior compared with p-type characteristics of pristine SWNTs and C_{70} encapsulated SWNTs. This n-type transport characteristic can be explained by the charge transfer effect between SWNTs and encapsulated $C_{69}N$, which can easily lose an electron. The unique electronic properties of $C_{69}N$ encapsulated SWNTs make them potentially useful in many applications in engineering functional nanodevices.

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The synthesis of functionalized single-walled carbon nanotubes (SWNTs) is becoming a central concern for the use of SWNTs in future device technologies. In particular, the hollow inner space of SWNTs makes them easily encapsulate various atoms or molecules, which leads to a new class of hybrid materials with novel electronic properties. The encapsulation of C_{60} fullerene in SWNTs, named peapod, has received great theoretical and experimental attention in the past years.[1] In addition, other fullerenes, such as C_{70}, C_{84}, and metallofullerenes such as $Gd@C_{82}$, have been encapsulated inside SWNTs,[2,3] producing a great variety of peapod nanostructures. Recent works have shown that the $C_{59}N$ azafullerene can also be encapsulated within SWNTs, and they display different morphologies in SWNTs such as dimers or oligomers compared with that of the C_{60} peapod.[4−6] The encapsulation of fullerenes inside SWNTs is found to strongly modify the electronic structure of SWNTs, which depends on the type of fullerenes. Therefore, the transport properties of different peapods differ from each other, which leads to various novel applications in nanoelectronic devices. Compared with the $C_{59}N$ peapod, it remains an open question so far as to synthesis and property of SWNTs encapsulating the $C_{69}N$ azafullerene, where one N atom replaces one C atom in the rugby ball shaped C_{70} fullerene. Moreover, it has been proposed that the C_{70} fullerene with asymmetric structure displays both lying and standing geometrical arrangements inside SWNTs, which is different from behaviors of C_{60} in SWNTs. Considering this, a unique morphology of $C_{69}N$ azafullerene inside SWNTs can easily be envisaged, and some interesting interactions are expected to take place between $C_{69}N$ and SWNTs.

In this study, we report the first synthesis and characterization of $C_{69}N$ azafullerene encapsulated SWNTs. The encapsulation is proven by transmission electron microscopy, Raman spectroscopy, and UV—vis—IR absorption spectroscopy. Moreover, we have systematically investigated the electronic properties of the $C_{69}N$ peapod in comparison with the C_{70} peapod. Our measurements indicate that the electronic structure of SWNTs is strongly modified upon insertion of $C_{69}N$ azafullerene in contrast to the case of the C_{70} peapod.

RESULTS AND DISCUSSION

The pristine SWNTs with diameter distribution of about 1.3−1.5 nm are prepared by an arc discharge using Fe/Ni as catalyst.[7] The synthesis of $C_{69}N$ azafullerene from the C_{70} fullerene is realized by a nitrogen plasma ion-irradiation method.[8] It is found that $C_{69}N$ can efficiently be formed by N atom bombardment during a plasma irradiation process. The C_{70} fullerene after plasma irradiation is dissolved in toluene,
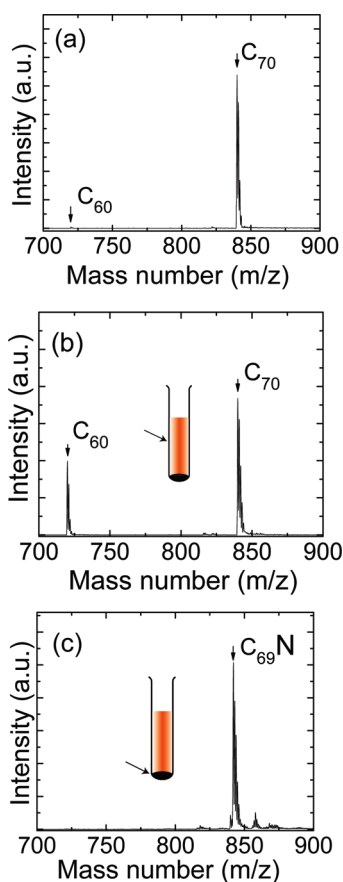
Figure 1. Mass spectra of C_{70} fullerene (a), dissolved fullerenes in toluene (b), and the residue in toluene (c). The insets in panels b and c schematically show the separation of fullerenes and azafullerene in toluene.

and its mixture is separated into a residue and a solution. All of the samples are examined by a laser-desorption time-of-flight mass spectrometer (LD-TOF-MS). Figure 1a shows the mass spectrum of original C_{70} fullerene, where its corresponding mass number of 840 is clearly indentified. Only a small amount of C_{60} fullerene as impurity is confirmed, and the relative peak intensity ratio of C_{60} to C_{70} is 0.003, indicating an extremely high purity of C_{70}. After nitrogen plasma irradiation, the major materials dissolved in toluene are composed of C_{60} and C_{70} fullerenes, as seen in Figure 1b. The increased signal of C_{60} fullerene demonstrates that most of the C_{70} fullerene is converted into $C_{69}N$, as shown in Figure 1c, in which the peak at $m/s = 842$ is dominant in the residue. Only trace amount of C_{70} is found in the residue in terms of the low peak intensity ratio of $C_{70}/C_{69}N = 0.07$, and this result indicates that $C_{69}N$ has a purity much higher than the purity of $C_{59}N$ azafullerene synthesized under the same experimental conditions (Supporting Information, Figure S1). This difference is possibly ascribed to high reactivity of N atom with C_{70}, rather than with C_{60}, during the plasma synthesis process.

The encapsulation of $C_{69}N$ azafullerene inside SWNTs ($C_{69}N$@SWNTs) has been realized by either vapor diffu-
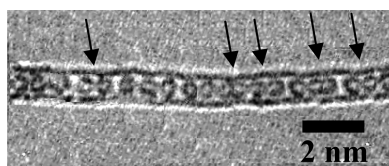

Figure 2. TEM image for a $C_{69}N$@SWNT.

sion method or plasma ion-irradiation method, and this procedure has been used previously for the preparation of other peapods.[4,9] A TEM image of the $C_{69}N$ peapod is shown in Figure 2, where monomers and dimers, $(C_{69}N)_2$, of azafullerene (as shown by arrows) are present inside the SWNT. This phenomenon is in agreement with the theoretical work in which $C_{69}N$ molecules are not stable and rather undergo dimerization reaction to $(C_{69}N)_2$.[10] Figure 3 gives the UV−vis−NIR absorption spectra of pristine SWNTs, C_{70}@SWNTs, and $C_{69}N$@SWNTs. The obtained spectra show characteristic peaks associated with interband transitions. The broad peaks in the range of 1500−2000 nm can be assigned as the first van Hove transition (E_{11}^S) in the semiconducting nanotubes based on their transition energy, whereas the peaks in the range of 900−1100 and 600−750 nm can be attributed to the second van Hove transition in the semiconducting SWNTs (E_{22}^S) and the transition in the metallic SWNTs (E_{11}^M), respectively. In our case, the decrease of the peak intensity for E_{11}^S is not obvious for $C_{69}N$ and C_{70} peapods, which is similar to the case of Cs (as strong electron donor) encapsulated SWNTs. Our results are somewhat different from previous descriptions by Kazaoui *et al.* who observed a significant reduction of absorption peaks due to doping organic molecules.[11] This difference can be possibly explained in terms where the charge transfer interaction between SWNTs and encapsulated molecules/atoms is relatively weak compared with that between SWNTs and dopants which modify the SWNTs' properties from both their inside and outside. However, the distinct shift of spectra upon C_{70} or $C_{69}N$ encapsulation is clearly observed in the E_{11}^S region. For instance, the absorption peak at ∼1765 nm in pristine SWNTs is red-shifted to ∼1800 and ∼1845 nm for the C_{70} peapod and $C_{69}N$ peapod, respectively, indicating that the encapsulated molecules substantially tune the electronic structure of
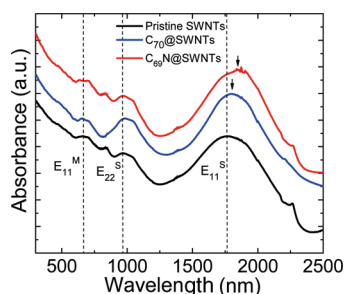

Figure 3. UV−vis−NIR optical absorption spectra of nanotube films for pristine SWNTs, C_{70}@SWNTs, and $C_{69}N$@SWNTs.

host SWNTs. This seems to be consistent with the band gap narrowing effect of fullerene peapods described in previous works.[12] In particular, such resulting band modulation in E_{11}^S of SWNTs upon $C_{69}N$ encapsulation is apparently stronger than the case by C_{70} encapsulation, in agreement with the observed Raman spectra of $C_{70}@SWNTs$ and $C_{69}N@SWNTs$ excited at 1.96 and 2.54 eV (Supporting Information). The intensities of the radial breathing mode (RBM) peaks for $C_{70}@SWNTs$ and $C_{69}N@SWNTs$ are reduced relative to those for pristine SWNTs, and also both encapsulated samples are found to exhibit a strong downshift of RBM modes (Supporting Information, Figure S2). Thus, significant influence of the encapsulated fullerene or azafullerene structure on electronic properties of the SWNTs is believed to occur, which induces a loss of resonance enhancement due to the quenching of optical transitions between van Hove singularities. There is a slight downshift of the RBM peaks in the $C_{69}N$ peapod relative to that found for the C_{70} peapod, which implies that the electronic structures of $C_{70}@SWNTs$ and $C_{69}N@SWNTs$ could be different due to the different charge transfer effects of C_{70} and $C_{69}N$. In addition, the encapsulated SWNT samples exhibit the reduced peak intensity in tangential displacement (TG) mode compared with that observed for pristine SWNTs (Supporting Information, Figure S3), as a result of loss of intertube interactions by encapsulation. A slight downshift is observed in TG mode excited at 1.96 eV for the $C_{69}N$ peapod, indicating evidence of charge transfer from SWNTs to the encapsulated $C_{69}N$. Therefore, the charge transfer interaction between $C_{69}N$ and SWNTs is considered to be stronger than that between C_{70} and SWNTs.

In order to analyze the electronic structure of $C_{69}N$ and $C_{69}N@SWNTs$, their work functions are investigated by ultraviolet photoemission spectroscopy (UPS). Figure 4a shows the photoelectron emission spectra of C_{70} and $C_{69}N$, in which the work function of $C_{69}N$ is determined to be about 5.0 eV, much smaller than that (5.5 eV) observed for C_{70}, suggesting evidently that the electronic property of $C_{69}N$ is significantly different from that of C_{70}. Namely, the nitrogen atom bonding with a C atom makes the release of electrons easier in the case of $C_{69}N$ azafullerene. Furthermore, the electronic properties of SWNTs are found to be significantly controlled by $C_{69}N$ encapsulation. In Figure 4b, the work functions of pristine SWNTs and $C_{69}N@SWNTs$ are estimated to be 4.85 and 4.70 eV, respectively. The result suggests that the work function of pristine SWNTs is reduced by 0.15 eV after $C_{69}N$ encapsulation, which is very similar to the case of alkali metal intercalations in SWNTs.[13] The reduction of work function can be understood by the charge transfer from $C_{69}N$ to SWNTs, which shifts the Fermi level toward the conduction band. In other words, the Fermi level of nanotubes is strongly modified by the interaction between SWNTs and $C_{69}N$ azafullerene.
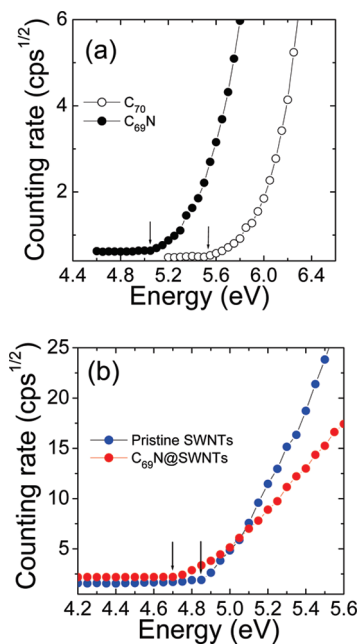

Figure 4. Photoelectron emission spectra: (a) C_{70} and $C_{69}N$, (b) pristine SWNTs and $C_{69}N@SWNTs$.

To prove the detailed band gap modulation effect of SWNTs by $C_{69}N$ encapsulation, we have measured the electrical transport properties of field-effect transistors (FETs) fabricated with different peapods as current channels. Figure 5 shows the typical electrical properties of SWNT−FET devices fabricated with a pristine SWNT and a C_{70} peapod, where the characteristics of source−drain current *versus* gate voltage (I_{DS}−V_G) curve are measured at room temperature for source−drain bias (V_{DS}) = 0.1 V. The typical transport properties of pristine SWNTs exhibit the well-known p-type semiconducting behavior. The threshold voltage (V_{th}) for hole conductance is −21 V in this device. In general, the V_{th} for most examined pristine SWNTs is less than −20 V, although it has a random distribution. In contrast, after C_{70} encapsulation, a positive shift of V_{th} up to 4 V is observed, which indicates that the hole density is greatly enhanced along the encapsulated SWNT in contrast to the p-type pristine SWNT. On the other hand, the electron transfer from the host SWNT to C_{70} is confirmed due to the electron accepting behavior of C_{70} fullerenes.
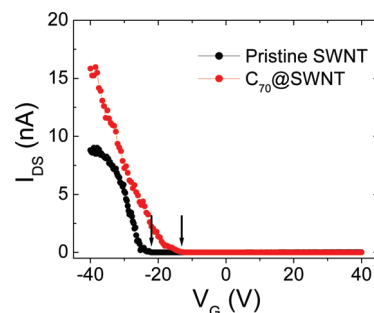

Figure 5. I_{DS}−V_G curves measured with V_{DS} = 0.1 V for a pristine SWNT−FET device and a C_{70} peapod FET device.
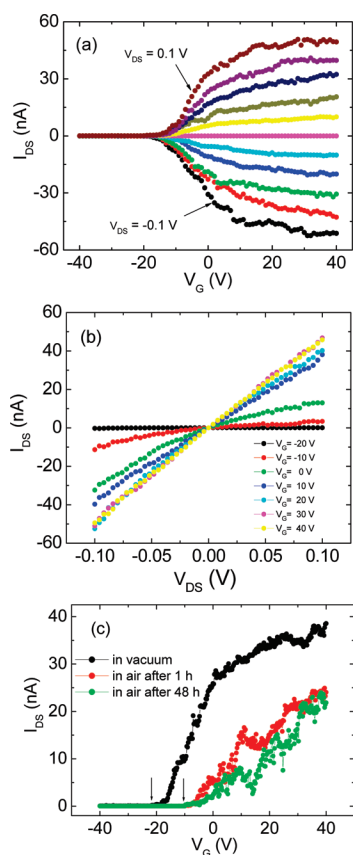
Figure 6. $I_{DS}-V_G$ **curves measured for n-type** $C_{69}N$ **peapod FET device at** $V_{DS} = -0.1-0.1$ V **(a),** $I_{DS}-V_{DS}$ **curves measured with** V_G **in the range of** $-20-40$ V **(b),** $I_{DS}-V_G$ **curves measured for an n-type** $C_{69}N$ **peapod with** $V_{DS} = 0.1$ V **in vacuum and after air exposure for 1 and 48 h (c).**

In contrast, the semiconducting properties of the $C_{69}N$ peapod turn out to be significantly changed, and an n-type characteristic is found as compared with the p-type C_{70} peapod. Figure 6a presents the $I_{DS}-V_G$ characteristics for the n-type $C_{69}N$ peapod with V_{DS} ranging from -0.1 to 0.1 V in steps of 20 mV. The transfer characteristics confirm that the conductance of the $C_{69}N$ peapod FET device can well be controlled by the electrostatic potential in the channel. The $I_{DS}-V_G$ curves display an almost symmetric feature at positive and negative V_{DS}, showing good reproducibility. Evidently, their n-type nature is attributed to the charge transfer between $C_{69}N$ and local parts of SWNTs, in agreement with the results in Figure 4b. Measurements made on more than 25 independent devices reveal that such n-type electrical transport behavior is similar to that found for the $C_{59}N$ peapod, but the threshold voltage generally shifts more negatively compared with the case of the $C_{59}N$ peapod, indicating that $C_{69}N$ represents a strong electron donor in contrast to $C_{59}N$.

The V_{th} necessary to deplete this n-type FET device is about -16 V at the 20 mV bias, and the carrier (electron) concentration along the nanotube is estimated to be 3.5×10^7/cm according to the ref 14. The mobility of carriers can be evaluated to be 2.9 cm²/(V·s) from the

slope $dI_{DS}/dV_G \sim 0.39 \times 10^{-9}$ A/V at $V_{DS} = 20$ mV, as determined from the linear region of $I_{DS}-V_G$ curves. This mobility is much higher than the average value of 1.5 cm²/(V·s) for most p-type pristine SWNTs measured under the same conditions, which means that the n-type $C_{69}N$ peapod exhibits a better performance in comparison with that of pristine SWNT–FETs in our experiments. To further estimate the performance of the n-type azafullerene peapod FET device, we have investigated the $I_{DS}-V_{DS}$ curves with V_{DS} ranging from -0.1 to 0.1 V by applying different gate voltages from -20 to 40 V, as shown in Figure 6b. As expected, the conductance of the sample is significantly suppressed by decreasing the gate voltages from 40 V until the gate voltage reaches about -20 V, which also exhibits a reproducible characteristic for n-type nanotube FETs.

Moreover, the air-stable ability for the n-type $C_{69}N$ peapod FET device has been investigated, which is of significant importance for their potential applications. Figure 6c gives the $I_{DS}-V_G$ characteristics for the n-type peapod measured at $V_{DS} = 0.1$ V in both vacuum and after air exposure for 1 and 48 h, respectively. Obviously, the n-type behavior remains even after 48 h exposure to air though noise-like fluctuations appear to exist in the $I_{DS}-V_G$ curve. In addition, a positive shift of V_{th} of 13 V together with a drop of current in the $I_{DS}-V_G$ curve is observed as the n-type FET device is exposed to air for both 1 and 48 h. The plausible explanation for these phenomena is due to absorption of oxygen, possibly reaching a saturation point after 1 h, on either the surface of the SWNT or the contact area between the nanotubes and electrodes, leading to the decrease of electron density in the azafullerene peapod. To confirm this, the FET device is measured again in vacuum and a recovered feature of threshold voltage and current is confirmed. This result indicates definitively that excellent air-stable n-type nanotubes are obtained by $C_{69}N$ encapsulation. On the basis of the above results, the observed n-type behavior of the $C_{69}N$ peapod is concluded to be due to the novel electronic structure of $C_{69}N$, which can easily lose one electron to form a single bond with materials.[10,15]

CONCLUSION

Our results present the first experimental demonstration that the $C_{69}N$ azafullerene is encapsulated inside SWNTs. The formation of $C_{69}N$ peapod has been confirmed by TEM, and their properties are characterized by UV–vis–IR spectroscopy, Raman spectroscopy, and UPS. Our findings indicate that the band structure modification of SWNTs upon $C_{69}N$ encapsulation is much stronger than that observed in SWNTs due to C_{70} encapsulation. We have compared the electrical transport properties of C_{70} and $C_{69}N$ encapsulated SWNTs by fabricating them as current channels of FET devices. Our experimental results demonstrate that the

$C_{69}N$ peapod shows high-performance n-type behavior compared with p-type characteristics of C_{70} peapods. This difference can be explained by the novel electronic structure of $C_{69}N$, which can easily lose an electron. Additionally, the n-type behavior of the $C_{69}N$ peapod remains stable even in air, suggesting that such a new material has great potential in engineering functional nanodevices.

EXPERIMENTAL SECTION

The azafullerene $C_{69}N$ was synthesized by a nitrogen plasma irradiation method.[8] A plasma was generated by applying RF power with a frequency of 13.56 MHz, and nitrogen ions in the plasma were generated and accelerated toward the substrate by a sheath electric field in front of the deposited C_{70} fullerene. The experimental time lasted for 1 h, and about 70 mg of C_{70} fullerene was sublimated. Detailed experimental conditions are given as follows: plasma density $n_p \sim 10^9 \, cm^{-3}$, electron temperature $T_e \sim 0.5$ eV, and nitrogen ion irradiation energy $E_i = 10-40$ eV. The fullerene C_{70} after plasma irradiation was dissolved in toluene, and its mixture was separated into a residue and a solution. The mass spectroscopy analysis of the formed $C_{69}N$ azafullerene was performed using a laser-desorption time-of-flight mass spectrometer (LD-TOF-MS, Shimadzu AXIMA-CFR+).

$C_{69}N$ azafullerene or C_{70} fullerene molecule encapsulated SWNTs were synthesized by a vapor diffusion method. The purified SWNTs together with azafullerene or fullerene powders were first sealed in a glass tube under the vacuum conditions at $\sim 10^{-5}$ Torr. After that, the sealed glass tube was heated at 500 °C for 48 h to encapsulate $C_{69}N$ azafullerene or C_{70} fullerene in SWNTs. The encapsulated samples were obtained after the above process and examined in detail by field emission transmission electron microscopy (FE-TEM, Hitachi HF-2000) operated at 200 kV and Raman spectroscopy with laser wavelengths at 488 nm (Seki Technotoron) and 633 nm (Horiba).

UV−vis−NIR spectra were measured with a V-7200 spectrophotometer in a wavelength range of 200−2500 nm. Quartz cells with a volume of 5 mL were used to support samples. UV−vis−NIR spectra were taken by directly depositing $C_{69}N$ azafullerene or C_{70} fullerene peapod samples on the surface of quartz cells, forming nanotube thin films with a thickness of 50−200 nm, and an empty quartz cell was used as a reference for the measurements.

In order to make field-effect transistor (FET) devices, azafullerene or fullerene peapods were first dispersed by supersonic treatment for over 9 h in the N,N-dimethylformamide (DMF) solvent. Then the nanotube solution was spin-coated onto an FET substrate, which consists of pairs of Au electrodes. An individual SWNT bridging the two Au electrodes on the substrate was confirmed by atomic force microscopy (AFM; JSPM-5400). Electronic transport properties of FET devices were measured using a semiconductor parameter analyzer (Agilent 4155C) in vacuum. The source−drain current (I_{DS}) was investigated as functions of gate bias (V_G).

Supporting Information Available: Comparisons of mass spectra between synthesized $C_{59}N$ and $C_{69}N$ azafullerenes. Raman spectra in RBM and TG modes of pristine SWNTs, C_{70}@SWNTs, and $C_{69}N$@SWNTs excited by lasers at 1.96 and 2.54 eV. This material is available free of charge *via* the Internet at http://pubs.acs.org.

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