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Synthesis and Electrical Transport Properties of $C_{59}N$ Encapsulated Single-Walled Carbon Nanotubes

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The azafullerene $C_{59}N$ is synthesized by a nitrogen plasma irradiation method, which has been confirmed by the analysis of mass spectroscopy. The encapsulation of $C_{59}N$ inside single-walled carbon nanotubes (SWNTs) is practiced via a vapor diffusion method. Electrical transport properties of C_{60} and $C_{59}N$ encapsulated SWNTs are investigated by fabricating them as the channels of FET devices at room temperature. It is found that the electrical transport properties of 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 peapods can be explained by the charge-transfer effect, which can modify the electronic structure of SWNTs.
Key words: plasma, fullerenes, carbon nanotubes, electronic property

1. INTRODUCTION

Single-walled carbon nanotubes (SWNTs) have various interesting chemical and physical properties, and as a result, they are regarded as one of the most promising candidates for future device fabrication. Recent studies indicate that SWNT based electronic devices have potential to surpass the silicon based electronics. However, the SWNT-based FET shows only p-type transport characteristics in general [1]. Therefore the physical or chemical modification of SWNTs is required to diversify the electronic properties of SWNTs. Two methods have been developed to modify the electronic properties of SWNTs, one of which is the outside modification [2,3], and the other is the inside modification using other functional materials [4,5]. The outside modification, i.e., intercalation of other materials between SWNTs mostly forming bundles, can change the electronic properties of SWNTs, which does not require so complicated procedure. However, intercalation is inevitably beset with problems for future applications, for example, air-stability of the intercalated SWNTs is one of the most fatal issues for the realization of SWNT based electronics because the intercalated materials are exposed to the air. On the contrary, the inside modification has some advantages, for example, functional-material encapsulated SWNTs are expected to ensure this air-stability, because the functional materials are inserted inside SWNTs and are isolated from the air.

Among various materials to be encapsulated in SWNTs, the azafullerene $C_{59}N$, i.e., a single carbon atom of the fullerene C_{60} cage is replaced by a nitrogen atom [6-8], has attracted special attention because of its interesting properties and applications in superconductivity, photoelectric devices, and organic semiconductor [9]. Although the theoretical study has indicated that the azafullerene has the property of electron donor [10], to our knowledge, there is no experimental verification of it up to now. In addition, it has been reported experimentally that fullerene peapods can exhibit different transport properties such as p-type, ambipolar, and metallic behaviors [11]. However, an n-type characteristic of the fullerene peapod has never been reported, which is indispensable for realizing SWNT-based electronic devices. In this work, we investigate synthesis, characterization, and electric transport property of SWNTs encapsulating $C_{59}N$, which results in a clear-cut observation of the n-type behavior of peapod. It is the first time for us to prove that the azafullerene $C_{59}N$ is a good electron donor.

2. EXPERIMENTAL

The azafullerene $C_{59}N$ is synthesized by a plasma irradiation method [12]. An experimental apparatus is schematically shown in Fig. 1, where nitrogen gas is input from the top of device, and a plasma is generated by applying RF power with a frequency of 13.56 MHz to a spiral-shaped RF antenna located at z = 27 cm (z = 0: bottom end of the device). C_{60} particles are sublimated from an oven around z = 25, and deposition takes place on a cylindrical stainless substrate at z = 25-39 cm. Nitrogen ions in the plasma are accelerated toward the substrate by a sheath electric field in front of the deposited C_{60} on the substrate. The experimental time lasts for 1h and about 80 mg C_{60} is sublimated. Plasma parameters are

measured by a Langmuir probe at z = 30 cm in the process area and at z = 53 cm in the plasma production area. 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.

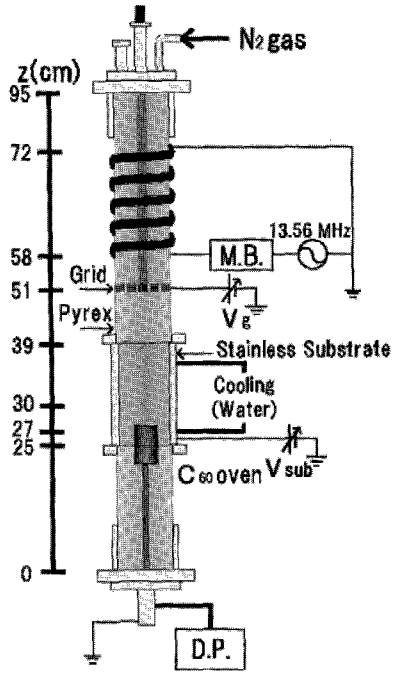

Fig. 1. Schematic of an experimental apparatus for the formation of $C_{59}N$ fullerene.

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 2 shows the mass spectrum of the residue in a positive ion mode of LD-TOF-MS, which does not dissolve in toluene. The peak at the mass number 722 is the most distinct in the residue, which originates from the 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. Thus, $C_{59}N$ is dominant in the residue, although the quantitative abundance ratio of $C_{59}N$ to C_{60} is not determined from the result of LD-TOF-MS.

The azafullerene $C_{59}N$ mixed with slight fullerene C_{60} is encapsulated into SWNTs [13] 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 the vacuum condition ~10^{-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 the excess fullerenes attached to the surface of SWNTs. $C_{59}N$ 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 [14, 15]. Transport measurements are performed at room temperature under vacuum conditions on a semiconductor parameter analyzer (Agilent 4155C).

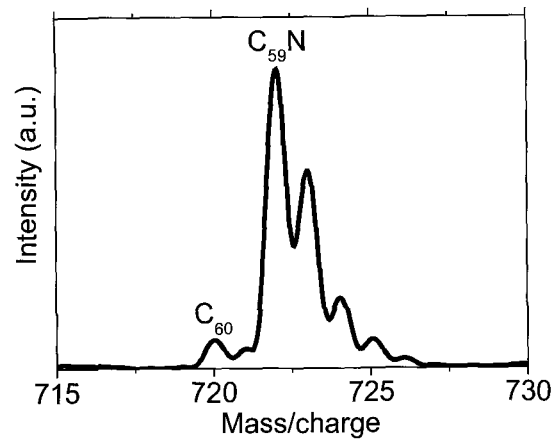

Fig. 2. Mass spectrum of $C_{59}N$ in positive ion mode of LD-TOF-MS.

3. RESULTS AND DISCUSSION

Figure 3 shows the Raman spectra for the pristine, C_{60} encapsulated (C_{60}@SWNTs), and $C_{59}N$ encapsulated SWNTs ($C_{59}N$@SWNTs) in the range of 100-500 cm^{-1} (Radial breathing mode) and high frequency mode of 1200-1700 cm^{-1}. The pristine SWNTs give 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 in the peak intensity at 161 cm^{-1}. These results of Raman spectra in the RBM region give evidence of the encapsulation of other materials, i.e., C_{60} or $C_{59}N$, inside SWNTs. The Raman spectra in the range of

1200-1700 cm^{-1} show significant difference between C_{60} and $C_{59}N$ encapsulated SWNTs, which further verifies the encapsulation of the azafullerene $C_{59}N$. 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 [16].

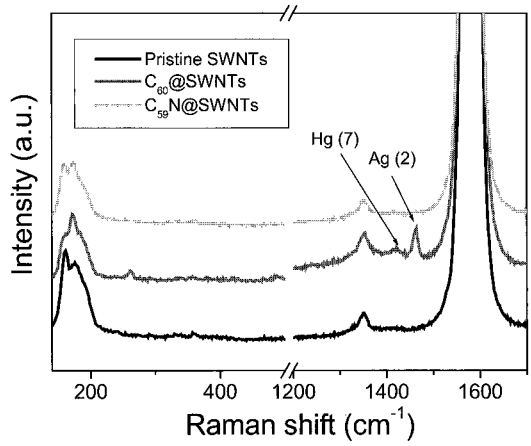

Fig. 3. Raman spectra of pristine, C_{60}@SWNTs, and $C_{59}N$@SWNTs.

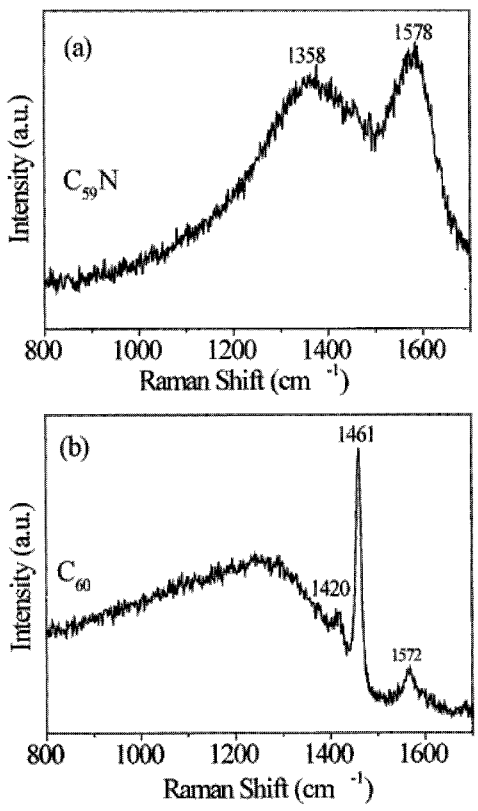

Fig. 4. Raman spectra for (a) $C_{59}N$ and (b) C_{60}

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}, as shown in Fig. 4, where the Raman spectra for $C_{59}N$ (a) and (b) C_{60} are further measured. In both the cases, the Raman lines in the frequency regions of 1350 cm^{-1} ~1600 cm^{-1} can be identified as Hg (7) and Hg (8) derived modes [16]. By comparison, the strongest peak in the case of C_{60} at 1461 cm^{-1}, corresponding to Ag (2) mode, is not detected in the case of $C_{59}N$, which is in agreement with the observations in Fig.3. This result reveals evidently that the Ag (2) mode (pentagonal inch mode) of C_{60} possibly becomes weak after one carbon atom is replaced by a nitrogen atom.

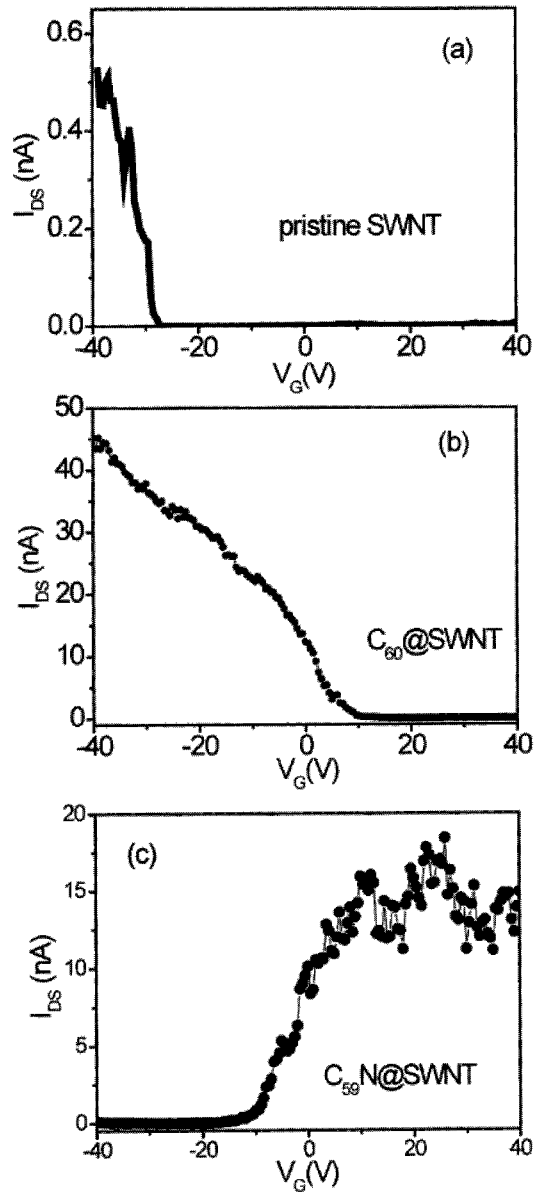

Fig. 5. Source-drain current (I_{DS}) vs gate voltage (V_G) characteristics at room temperature for (a) pristine SWNT, (b) C_{60} encapsulated, and (c) $C_{59}N$ encapsulated SWNTs.

The transport property of the pristine semiconducting SWNTs is well known to exhibit the p-type behavior as shown in Fig. 5(a), 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 5(b) presents the transport characteristic of C_{60}@SWNT. The typical p-type characteristic is still observed, but the threshold voltage (V_{th}) for hole conductance is found to show an upshift from -28 V to 15 V compared with that of pristine SWNTs, indicating that the p-type behavior of the SWNT is enhanced by the C_{60} encapsulation. In contrast, the transport property of $C_{59}N$@SWNT drastically changes to an n-type semiconductor, as seen in Fig. 5 (c). This n-type characteristic is possibly attributed to the charge transfer between $C_{59}N$ and local parts of SWNTs, suggesting that $C_{59}N$ exerts a strong electron donor effect on SWNTs, which is well in consistent with the theoretical predication [7]. 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 voltages.

4. SUMMARY

The azafullerene $C_{59}N$ has successfully been synthesized by a nitrogen plasma irradiation method, and its encapsulation inside SWNTs is confirmed by Raman spectra. 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. Our 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. Our results may pave the way for making high performance n-type semiconducting SWNTs which are anticipated to be a promising candidate for future nanodevices

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