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Origin of the n-type transport behavior of azafullerene encapsulated single-walled carbon nanotubes

Nguyen Thanh Cuong,^{1,2} Minoru Otani,^{1,2} Yoko Iizumi,^{3,4} Toshiya Okazaki,^{3,4,5} Georgios Rotas,⁶ Nikos Tagmatarchis,⁶ Yongfeng Li,⁷ Toshiro Kaneko,⁴ Rikizo Hatakeyama,⁷ and Susumu Okada^{2,3,a)}

¹Nanosystem Research Institute (NRI), National Institute of Advanced Industrial Science and Technology (AIST), Tsukuba 305-8568, Japan

²Japan Science and Technology Agency, CREST, 5 Sanbancho, Chiyoda-ku, Tokyo 102-0075, Japan

³Graduate School of Pure and Applied Sciences, University of Tsukuba, 1-1-1 Tennodai, Tsukuba 305-8577, Japan

⁴Nanotube Research Center, National Institute of Advanced Industrial Science and Technology (AIST), Tsukuba 305-8565, Japan

⁵Japan Science and Technology Agency, PRESTO, 4-1-8 Honcho, Kawaguchi 332-0012, Japan

⁶Theoretical and Physical Chemistry Institute, National Hellenic Research Foundation, 48 Vass. Constantinou Avenue, 11635 Athens, Greece

⁷Department of Electronic Engineering, Tohoku University, 6-6-05 Aoba, Aramaki, Aobaku, Sendai 980-8579, Japan

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The transport properties of C₅₉N encapsulated semiconducting single-walled carbon nanotubes (SWCNTs) (C₅₉N-peapod) are investigated. Transport measurements of the peapods in field effect transistors (FETs) reveal that ~14% of the C₅₉N-peapod sample shows n-type behavior even though the electronic properties of the host SWCNTs are similar to those of C₆₀-peapods that exhibit only p-type property. First-principles electronic-structure calculations reveal that the unique transport behavior originates from the monomer form of C₅₉N encapsulated in SWCNTs. The singly occupied (SO) state of C₅₉N lies in the energy gap of the SWCNT and the energy of this state increases substantially when electrons are injected. Because of this shift to higher energy, the SO state acts as a shallow donor state for the conduction band of the nanotube, which leads to n-type behavior in FET measurements. © 2011 American Institute of Physics. [doi:10.1063/1.3619828]

Following the discovery of single-walled carbon nanotubes (SWCNTs) two decades ago,¹ much effort has been devoted to these carbon allotropes because of their unusual structural and electronic properties. An example is the variation of their electronic structure, which ranges from metallic to semiconducting depending on the arrangement of atoms along the circumference of the SWCNT.^{2,3} Because of these properties, carbon nanotubes (CNTs) are now keeping a premier position in the field of semiconductor device technology in the next generation as a constituent for conducting channel in switching devices. Indeed, it has been demonstrated that individual semiconducting CNTs can function as field effect transistors (FETs).⁴⁻⁶ It has been reported that such FETs exhibit different properties depending on the metal species of the electrode. While the fabrication technology of CNTs is advancing steadily, little is known of the fundamental properties of CNTs compared with the current stage of semiconductor technology.

Besides the atomic network in CNTs, the nanometer-scale tubular spacing inherent in CNTs also allows an interesting class of compounds comprised of host CNTs and encapsulated guest materials to be formed. Such materials possess a totally different structure from that in the bulk state. It has been demonstrated that high resolution transmission electron microscope (HRTEM) experiments revealed the encapsulation of C₆₀ in CNTs.^{7,8} In addition to

C₆₀, larger fullerenes⁹ and metallofullerenes¹⁰ have also been encapsulated in CNTs. These unusual nanometer-scale carbon networks have been coined “carbon peapods,” and their structures are characterized by an interesting combination of one- and zero-dimensional constituent units, i.e., CNTs and fullerenes. Recently, encapsulation of C₅₉N azafullerenes into CNTs has been achieved using plasma ion irradiation.¹¹ Azafullerenes exhibit several morphologies (monomers, dimers, and oligomers) inside SWCNTs, whereas only the dimer form, (C₅₉N)₂, is stable in solution.¹² Interestingly, encapsulated azafullerenes change the transport properties of SWCNTs from p-type to n-type in FET structures. Spectroscopic characterization of azafullerene peapods has also been performed using a sample that was synthesized by vapor-phase filling methods.¹³ The results suggest that azafullerene peapods may show p-type FET behavior similar to that of C₆₀ peapods. It was concluded that the discrepancy between these two reports may be caused by the different methods used to prepare the azafullerene materials.¹³

The production and spectroscopic characterization of the C₅₉N-peapods used here have been described in detail previously.¹³ Briefly, azafullerene peapods were synthesized by vapor-phase doping. The average tube diameter of the SWCNTs (Meijo Arc APJ-type) used was 1.4 ± 0.2 nm. UV-vis-near-infrared (NIR) absorption and PL spectroscopy revealed that the effects of encapsulation of C₅₉N on the electronic properties of SWCNTs are very similar to those of C₆₀ on C₆₀ peapods.¹³

^{a)} Author to whom correspondence should be addressed. Electronic mail: sokada@comas.frsc.tsukuba.ac.jp.

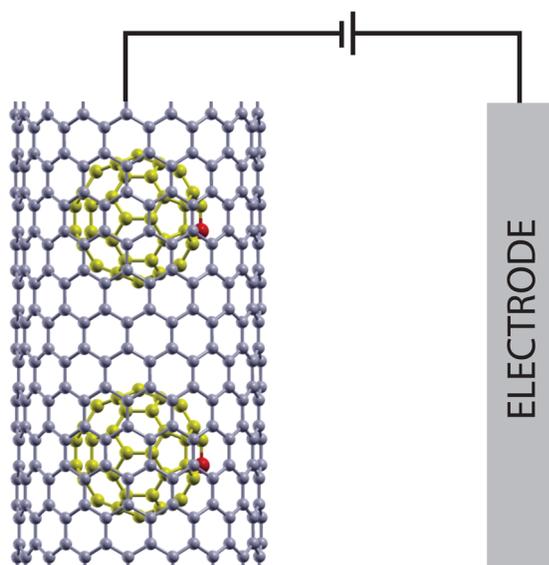


FIG. 1. (Color online) Geometric structure of a $C_{59}N$ -peapod FET. Pale gray (yellow and gray circles correspond with C atoms belonging into azafullerenes and SWCNT) and dark gray (red circle) circles denote C and N atoms, respectively. A gray panel on the right-hand side represents the electrode that is simulated by the effective screening medium with an infinite dielectric constant.

The procedure used to obtain FET transport measurements has been described in detail elsewhere.¹¹ $C_{59}N@SWCNTs$ are ultrasonically dispersed in *N,N*-dimethylformamide solvent and then spincoated on a FET substrate.¹⁴ The transport measurements ($V_{DS} = 1$ V) are carried out in vacuum (10^{-5} Pa) on a semiconductor parameter analyzer (Agilent 4155C).

All calculations were performed using the local density approximation (LDA) in the framework of density functional theory (DFT) (Refs. 14 and 15) with the effective screening medium (ESM) method.¹⁶ The structural model shown in Fig. 1 simulates a peapod FET where the top-gate electrode has been modeled by the effective medium with an infinite dielectric constant. A vacuum region of 1 nm was included between the wall of the nanotube and the electrode. Then, an electric field was applied between the peapod and electrode, leading to electron and hole injection into the peapod and electrode, respectively. During the ESM calculations, ultrasoft pseudopotentials were used to describe the electron-ion interaction¹⁷ in which the valence wave functions and charge density were expanded in terms of a plane-wave basis set with cutoff energies of 25 Ry and 225 Ry, respectively. The atomic geometry was fixed to the optimized structure under zero electric field.

Figure 2 shows the HRTEM image of $C_{59}N$ azafullerenes encapsulated SWCNTs. The azafullerenes packed into the SWCNTs with a high density. Our previous study revealed that a large portion of encapsulated $C_{59}N$ tends to form dimers.¹³ However, we also observed that isolated $C_{59}N$ monomers are stable in SWCNTs. By counting the number of molecules of encapsulated $C_{59}N$, it was found that 84% of $C_{59}N$ exists in a dimeric form, while 14% remains in an isolated monomers.¹³ Only a small portion ($\sim 2\%$) of azafullerenes forms oligomeric structures.

Spectroscopic characterization revealed that the effects of encapsulation of azafullerenes on the electronic structure of SWCNTs are almost identical to those of C_{60} peapods,¹³

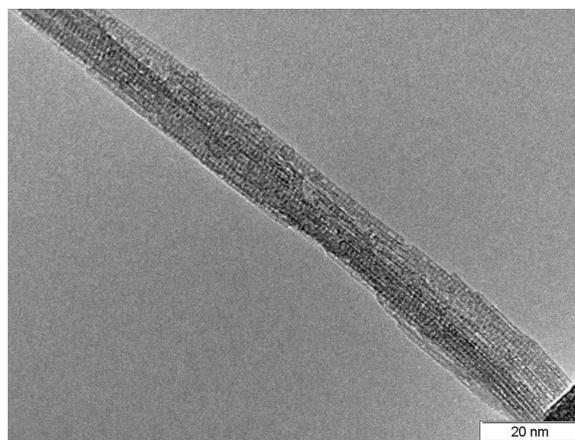


FIG. 2. Typical HRTEM images of azafullerenes encapsulated in SWCNTs (JEOL JEM-1010).

indicating p-type transport behavior for our FET configuration.¹¹ Indeed, 58% of the devices show p-type behavior. Typical current-voltage ($I_{DS}-V_G$) curves are shown in Fig. 3(a). However, surprisingly the conductance increases as V_G increases in 42% of the devices, indicating that these azafullerene peapods behave as a n-channel (15%) or ambipolar (27%) FET with normally off character [Figs. 3(b) and 3(c)]. Especially pure n-type behavior has not been observed for other fullerene peapods.¹¹ Spectroscopic results suggested that the electronic states of azafullerene peapods are almost identical to those of C_{60} peapods.¹³ Therefore, it is likely that increase of the conductance in positive V_G may be caused by an electronic state that is sensitive to the external electric field. Note that both the p and ambipolar transport properties may be ascribed to the dimerized and oligomerized forms of $C_{59}N$ encapsulated in SWCNTs by comparing the structural analysis based on the TEM images.

To understand the increase of the conductance in positive V_G , we next investigate the electronic structure of a

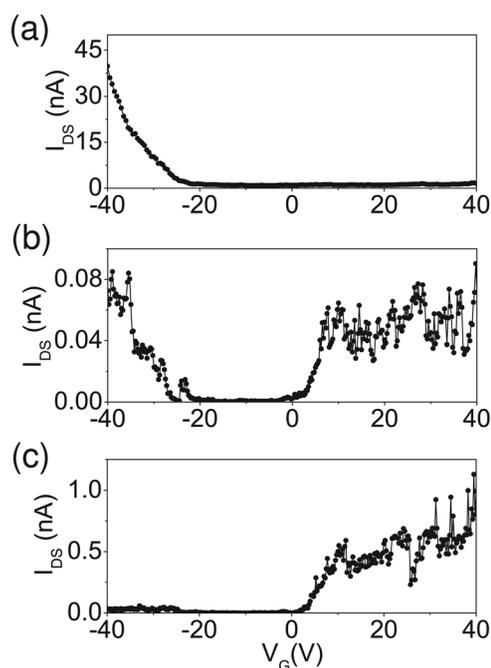


FIG. 3. $I_{DS}-V_G$ curves for azafullerene peapods ($V_{DS} = 1.0$ V). (a) p-type, (b) ambipolar, and (c) n-type transport behavior.

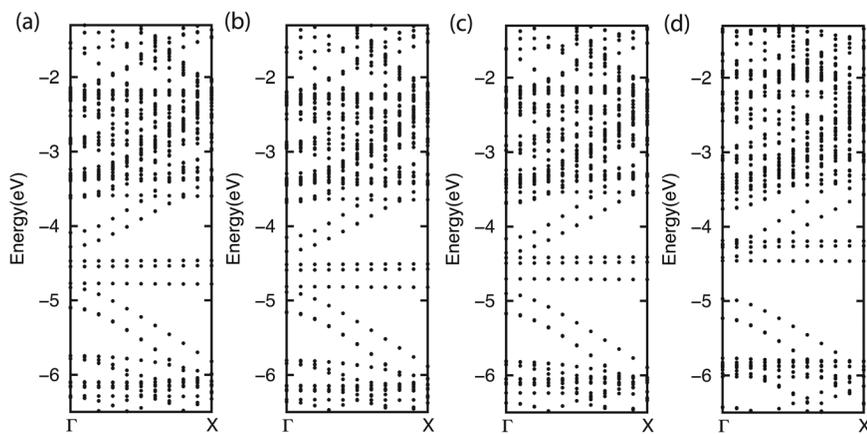


FIG. 4. Electronic structures of $C_{59}N$ encapsulated in a (17,0) nanotube under various applied electric fields of (a) zero, (b) 0.06 V/nm (0.01 electron doping), (c) 0.63 V/nm (0.1 electron doping), and (d) 3.20 V/nm (0.5 electron doping). Energies are measured from that of the vacuum level. The Fermi level under each electric field is -4.78 , -4.82 , -4.70 , and -4.41 eV for fields of 0.0, 0.06, 0.63, and 3.20 V/nm, respectively.

peapod consisting of a (17,0) nanotube containing a chain of monomeric $C_{59}N$ molecules under various electric fields as shown in Fig. 4. Under zero electric field, three bunched states emerge in the fundamental energy gap of the semiconducting nanotube. These three flat dispersion bands are ascribed to electronic states of $C_{59}N$ [Fig. 4(a)]. The electrons are accommodated up to the lowest branch of these three states. Furthermore, because $C_{59}N$ possesses 61 electrons in the 60 π states of a buckyball, the highest occupied state is occupied by single electron (single occupied state: SO state) leading to radical electrons in $C_{59}N$. It should be noted that the electronic structure of the $C_{59}N$ peapod near the Fermi level is qualitatively the same as that of the single electron-doped C_{60} peapod.^{18,19}

Application of an electric field leads to electron injection into the SO state. By increasing the electric field, the SO state shifts monotonically upward and finally crosses the bottom of the conduction band of the nanotube under an electric field of 3.20 V/nm, which corresponds to 0.5 electron-doping [Figs. 4(b)–4(d)]. According to this shift to higher energy, the SO state with excess charge should be a shallow donor level for the conduction band of the semiconducting nanotube. The SO state can donate electrons to the conduction band of the nanotube leading to the increase of the conductance in positive V_G for the $C_{59}N$ -peapod-FETs. In marked contrast to the SO and unoccupied states of $C_{59}N$, the occupied states of $C_{59}N$ and both valence and conduction energy bands of the nanotubes are unaffected by the application of an external electric field. This insensitivity to an electric field is ascribed to the valence electrons screening the electric field by modifying their distribution.

An unpaired electron in the SO state causes its eigenvalue to shift to higher energy by accommodating electrons under an applied electric field. Because the electrons are localized on a sphere with a diameter of about 0.7 nm, a significant Coulomb repulsive interaction, i.e., on-site U is expected to occur, leading to the shift to higher energy. Indeed, the calculated value of the on-site U is 0.8 eV, which was evaluated using the formula proposed by Anisimov.²⁰ This analysis corroborates the finding that strong electron-electron interactions on $C_{59}N$ cause the n-type conduction of its peapod FET, in which the SO state of $C_{59}N$ acts as a shallow

donor state for the conduction band of the nanotube. Thus, it is expected that peapods containing atoms or molecules with unpaired electrons exhibit n-type conduction properties because of the resulting large electron-electron correlation. A large on-site U also prevents the SO state from acting as a shallow acceptor state for the valence band of the nanotube. Because the SO state of $C_{59}N$ is located just above the valence band of the nanotube, hole injection is expected to take place by exciting valence electrons of the nanotube into the SO state of $C_{59}N$. However, such a process is not expected because the large on-site U makes the electron systems energetically unfavorable.

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