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Photoswitching in Azafullerene Encapsulated Single-Walled Carbon Nanotube FET Devices

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Single-walled carbon nanotubes (SWNTs) provide a promising material in building nanoelectronic devices due to their unique structure and electronic properties and thus are of great interest in science. Very recently, much research effort has been devoted to constructing optoelectronic devices such as a photoabsorber, emitter, and sensor[1−3] using modified SWNTs, since light may provide a convenient, precise, and simple tool for controlling the conductivity of SWNTs. In this communication, we report the photoinduced electrical transport properties of azafullerene encapsulated SWNTs ($C_{59}N$@SWNTs). In contrast to C_{60} fullerene, the structure and electronic properties of azafullerene are greatly modified due to incorporation of one nitrogen atom into the fullerene skeleton. Our previous studies have indicated that $C_{59}N$@SWNTs show an *n*-type behavior compared with *p*-type C_{60}@SWNTs,[4] which is due to the electron donation property of azafullerene with a lower ionization potential, as compared with the case of C_{60} fullerene. Our present study demonstrates that azafullerene molecules inside SWNTs make nanotubes very sensitive to light. The conductance of $C_{59}N$@SWNTs changes abruptly upon light illumination. Our experimental data suggest photoinduced charge transfer in $C_{59}N$@SWNTs is mainly responsible for changes of conductivity.

The syntheses of azafullerene and $C_{59}N$@SWNTs are performed by plasma irradiation and vapor diffusion methods, respectively.[4] The $C_{59}N$ inside SWNTs is characterized in detail by transmission electron microscope imaging (Hitachi HF-2000) (see Supporting Information). We fabricated carbon nanotube field-effect transistors (FETs) according to the reported procedures in refs 4 and 5, in which individual nanotubes ~1.4 nm in diameter (identified using atomic force microscopy (AFM)) bridge two Au electrodes with a gap of 500 nm. The Au electrodes with a thickness of 150 nm were used as source and drain electrodes, and they are fabricated on a 500 nm SiO_2 insulating layer by a lithography technique. A doped silicon wafer serves as a back-gate electrode for the samples. Electrical measurements are carried out both in the dark and upon light illumination in a vacuum ($10^{-4}-10^{-5}$ Pa) using a semiconductor parameter analyzer (Agilent 4155C). Light-induced conductance switching is observed under the exposure of light generated from a 150 W Xe lamp (LSX-2501) with a wavelength of 390−1100 nm and an intensity of ~50 mW/cm^2. Exposure at a particular wavelength is carried out using a monochromator.

The source−drain current is first measured as a function of gate voltage ($I_{DS}-V_G$) for $C_{59}N$@SWNT-FET devices. Figure 1a shows two typical samples, where either an *n*-type semiconducting or a metallic FET transport characteristic is observed without light illumination. The inset of Figure 1a shows an AFM image of a nanotube spanning two Au electrodes. Figure 1b shows the $I_{DS}-V_G$ behavior for a semiconducting FET under 400 nm light exposure in contrast to the behavior without light. It can be seen that *n*-type conductance is greatly reduced. Figure 1c gives the characteristics of I_{DS} as a function of time at $V_G = 40$ V and $V_{DS} = 1$ V for a semiconducting $C_{59}N$@SWNT without and with incident light (1 s) illumination. As a comparison, a sharp decrease in current is immediately observed at 130 s upon the UV light (400 nm) pulse. The light induced change persists after illumination has been removed; namely, the off-state current remains a constant value before recovering its initial level, which is similar to the phenomenon of the persistent photoconductivity observed elsewhere in many semiconductors.[6,7] The same phenomenon is observed when we employ a metallic $C_{59}N$@SWNT instead of a semiconducting one. Figure 1d depicts the transient photoinduced response of I_{DS} vs time for a metallic nanotube FET device which is illuminated three times (400 nm wavelength, exposure time is 1 s in each case), suggesting that the photoswitching behavior is independent of the type of the nanotube. And interestingly, photoresponses are observed each time. The off-state currents for both devices are found to recover automatically when I_{DS} vs time curves are measured again on the devices.

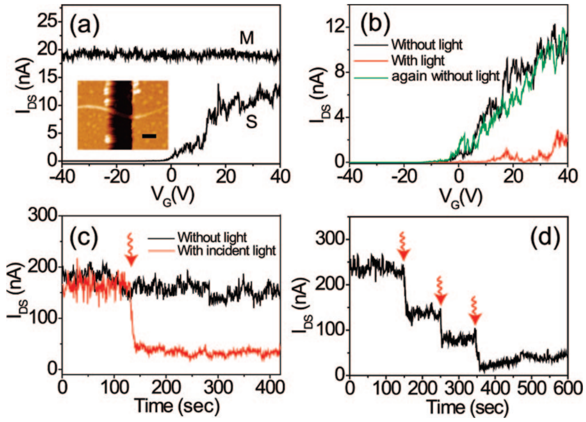

Figure 1. (a) $I_{DS}-V_G$ characteristics measured with $V_{DS} = 0.1$ V at room temperature for an *n*-type semiconducting (S) $C_{59}N$@SWNT and a metallic (M) $C_{59}N$@SWNT without Xe lamp light. The inset shows an AFM image of a nanotube FET device, scale bar, 300 nm. (b) Comparison of $I_{DS}-V_G$ characteristics for a semiconducting $C_{59}N$@SWNT with and without Xe lamp illumination. (c) I_{DS} characteristic measured as a function of time without and with incident light (400 nm wavelength) for a semiconducting $C_{59}N$@SWNT. (d) The time response of I_{DS} measured at $V_G = 40$ V and $V_{DS} = 1$ V with a 1 s light pulse (400 nm wavelength, 3 times) for a metallic nanotube.

During our measurements, it is found that a decrease in the source−drain current is caused under light illumination on all the fabricated $C_{59}N$@SWNT-FET devices, and they exhibit repeatable switching characteristics for many cycles.

To further investigate the photoswitching characteristics, we have exposed the devices to the 1 s light pulse while doing $I_{DS}-V_G$

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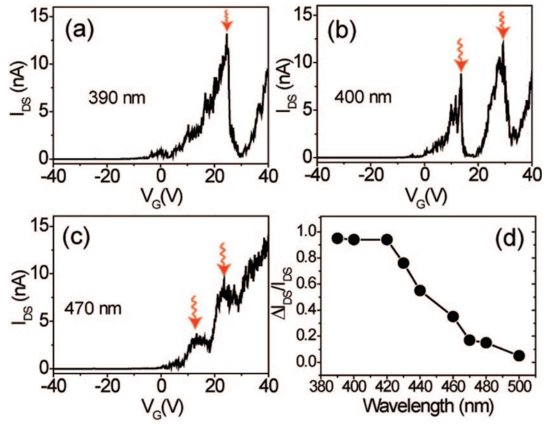

Figure 2. $I_{DS}-V_G$ characteristics measured with V_{DS} = 0.1 V at room temperature for an *n*-type $C_{59}N$@SWNT with incident light (390 nm wavelength), (b) with incident light at 400 nm 2 times, and (c) with incident light at 470 nm 2 times. (d) $\Delta I_{DS}/I_{DS}$ measured as a function of wavelengths.

measurements. A drastic decrease of current by over 95% is observed in Figure 2a when the device is measured under incident UV illumination (390 nm, 1 s), which is consistent with the time dependent behavior observed in Figure 1b. As the gate voltage is continually swept (with sweeping speed ~1.4 V/s), the current is restored gradually to its initial current during scanning to high positive gate voltages, indicating the recovery can be made by sweeping the gate voltage. Figure 2b gives the response during $I_{DS}-V_G$ sweeping for a 400 nm light pulse exposure two times. It can be seen that the recovery by the gate is reproducible. The photoresponse is also found to depend on the wavelength of light. The change of conductance gradually becomes less pronounced when increasing the wavelength of light. Figure 2c gives the $I_{DS}-V_G$ characteristic with a 1 s light illumination at 470 nm, where only an ~15% decrease of I_{DS} is observed. Figure 2d shows the ratio of the changed current ΔI_{DS} caused by incident light illumination to the original current I_{DS} ($\Delta I_{DS}/I_{DS}$) as a function of the wavelength. For wavelengths more than 480 nm, the change of current becomes negligible. Measurements made on more than 20 devices reveal that this threshold wavelength is quite similar to each other.

To clarify the photoswitching mechanism, comparative experiments were performed on the *p*-type pristine SWNTs and C_{60}@SWNTs under the same experimental conditions (see Supporting Information). We observe no big change in the conductance for those two types of samples. This further suggests that azafullerene is responsible for the decrease of conduction. Figure 3 presents our proposed mechanism. It is well-known that the $C_{59}N$ radical ($C_{59}N^•$) is very active and can easily lose or gain an electron through regioselective reactions by binding to other atoms or molecules.[8,9] According to previous works,[9−11] this binding occurs via the nearest carbon atom (C′) of N in the structure of $C_{59}N$, as it is very active and easily bound with other atoms such as C or H. In our $C_{59}N$@SWNT samples, both monomer and dimers of $C_{59}N$ molecules are found inside SWNTs,[4,10] and therefore it is very likely the *n*-type behavior is due to the charge transfer from encapsulated $C_{59}N$ to SWNT by such C′−C bonding (there is an unpaired electron in $C_{59}N^•$). This is presented in the left diagram of Figure 3, in which a radical-ion-pair is drawn, indicating the partial charge transfer to the SWNT. Although the bonding energy between the $C_{59}N$ and SWNT is not clarified, however, the interdimer bonding energy of $(C_{59}N)_2$ is well-known to be relatively weak, less than 1 eV, according to theoretical calculations,[11] and thus such a bonding can easily undergo homolysis under photolysis or thermolysis conditions, resulting in the formation of azafullerenenyl radical $C_{59}N^•$. Two possible reasons could be responsible for the wavelength dependence observed here: (1) the bonding between the $C_{59}N$ and SWNT requires a photon with a high enough energy to break; however, since the threshold is 480 nm, this means the bonding energy should be ~2.58 eV, which is considerably higher than the 1 eV for $(C_{59}N)_2$; (2) the absorbed photon energy results in heating of the sample which gives rise to thermolysis of the bond. The exact mechanism is still unclear at this stage. Nevertheless, when this occurs, the previously donated electron charges are transferred back to azafullerene, leading to less *n*-doping and a decrease in current, as shown in Figure 3. As the free radical $C_{59}N^•$ is active, the C′−C bonding can be easily brought back by perturbations in the system, such as gate sweeping, making such a process reversible.

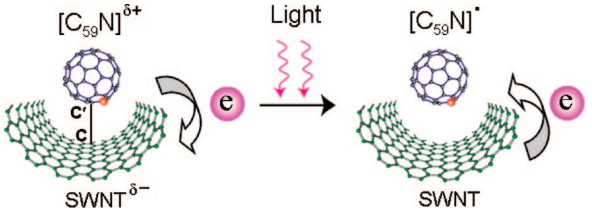

Figure 3. Schematic illustration of proposed photoinduced electron transfer reaction mechanism between SWNT and encapsulated $C_{59}N$.

In summary, we have investigated the photoinduced transport properties of $C_{59}N$@SWNTs. It is found that the conductance can repeatedly be switched by exposure to UV light when the azafullerene molecules are inside SWNTs. The photoswtiching characteristic is found to be dependent on the wavelengths, opening opportunities for SWNT-based photoswitches which are wavelength-selective. The specific sensitivity of electronic structure of $C_{59}N$ to light appears to be the main contribution to the observed photoresponse of $C_{59}N$@SWNTs. Our study suggests a new and promising path to making photoswitches or photodetectors by novel and interesting $C_{59}N$@SWNTs.

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Supporting Information Available: TEM images of $C_{59}N$@SWNTs, and photoinduced transport properties of *p*-type pristine SWNTs and C_{60}@SWNTs. This material is available free of charge via the Internet at http://pubs.acs.org.

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