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 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 (C₅₉N@SWNTs). In contrast to C₆₀ 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 C₅₉N@SWNTs show an n-type behavior compared with p-type C₆₀@SWNTs, which is due to the electron donation property of azafullerene with a lower ionization potential, as compared with the case of C₆₀ fullerene. Our present study demonstrates that azafullerene molecules inside SWNTs make nanotubes very sensitive to light. The conductance of C₅₉N@SWNTs is mainly responsible for changes of conductivity. The syntheses of azafullerene and C₅₉N@SWNTs are performed by plasma irradiation and vapor diffusion methods, respectively.

The C₅₉N 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 SiO₂ 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/cm². 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 C₅₉N@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 C₅₉N@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. The same phenomenon is observed when we employ a metallic C₅₉N@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) C₅₉N@SWNT and a metallic (M) C₅₉N@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 C₅₉N@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 C₅₉N@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 C₅₉N@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...
molecules are found inside SWNTs, and therefore it is very active and can easily lose or gain an electron through regioselective reactions by binding to other atoms or molecules. According to previous works, this binding occurs 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 \( \Delta I_{DS} \) caused by incident light illumination to the original current \( I_{DS} \) 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\(^{\cdot}\)) is very active and can easily lose or gain an electron through regioselective reactions by binding to other atoms or molecules. According to previous works, this binding occurs via the nearest carbon atom (C\(^{\prime}\)) 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, 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 reaction mechanism between SWNT and encapsulated C\(_{59}\)N. This work was supported by the Global COE program in Tohoku University.

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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.

References