Preferential Destruction of Metallic Single-Walled Carbon Nanotubes by Laser Irradiation

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Upon laser irradiation in air, metallic single-walled carbon nanotubes (SWNTs) in carbon nanotube thin film can be destroyed in preference to their semiconducting counterparts when the wavelength and power intensity of the irradiation are appropriate and the carbon nanotubes are not heavily bundled. Our method takes advantage of these two species' different rates of photolysis-assisted oxidation, creating the possibility of defining the semiconducting portions of carbon nanotube (CNT) networks using optical lithography, particularly when constructing all-CNT FETs (without metal electrodes) in the future.

Introduction

Owing to their exceptional electrical, thermal, and mechanical properties, single-walled carbon nanotubes (SWNTs) have been envisioned as one of the best candidates for many potential applications.[1,2] However, SWNTs are grown as a mixture of both metallic and semiconducting tubes by any production process currently available, and thus, their practical application to semiconductor electronics are largely hampered. Field effect transistors (FETs) made from the carbon−nanotube mixture show unsatisfactory device characteristics due to the electrical pass through metallic tubes.[3−4]

While still far from solving this problem, there have been several reported approaches. The first is to grow semiconducting carbon nanotubes preferentially.[5,6] Li et al. reported that semiconducting carbon nanotubes can be produced with a percentage of ∼89% relative to metallic tubes, while Hassaien et al. reported that metallic carbon nanotubes might be preferentially destroyed in hydrogen plasma.[7] While this approach has its advantages, improvement in growth selectivity and efficiency are needed.

The second approach relies on separation of metallic and semiconducting SWNTs. The reported separation methods include ac dielectrophoresis,[8] selective precipitation of metallic tubes using physical sorption of octadecylamine or bromine,[9,10] chromatography of DNA-wrapped carbon nanotubes,[11] and the recently reported selective attack by nitronium ions or adsorption by amine onto metallic carbon nanotubes.[12,13] In the best of these methods, s-SWNTs from batches yielding up to ∼90% relative to metallic tubes are still not usable. In addition, all of these separation methods involve complicated physical and/or chemical processes in which contamination and degradation of the carbon nanotubes can take place.

The third approach, first reported by an IBM group, is based on existing nanotube devices composed of metallic tubes bridging source-drain electrodes.[14] This approach utilizes the fact that the semiconducting carbon nanotubes can be tuned to the insulating (OFF) state by the application of a gate voltage. By ramping the drain-source voltage to a sufficiently high potential in the presence of oxygen, it is possible to burn off the metallic tubes. There are at least two disadvantages in this approach, however. The first is that the Joule heat generated by the high current passing through the metallic tubes may also burn the adjacent semiconducting tubes. Second, this approach is not efficient because the operation must be applied to each individual device. While metallic tubes may be selectively subjected to reaction in order to become insulating,[15,16] according to our study, thermal annealing well below 200 °C can easily cleave the functional groups and recover their metallic nature (see Supporting Information) as annealing at a much higher temperature is needed to obtain good contact between nanotubes and metal electrodes.

Clearly, a new approach is needed. Instead of the diameter-selective removal of carbon nanotubes observed during liquid-phase reaction,[17,18] we found that in SWNT thin films, particularly for the film in which metallic carbon nanotubes have been selectively reacted, metallic carbon tubes are more sensitive to light irradiation than their semiconducting counterparts, so a preferential oxidation of metallic carbon nanotubes can be induced. This method is straightforward and has the potential to position semiconducting portions of SWNTs using optical lithographic techniques, particularly in constructing all-CNT FETs (without metal electrodes) in the future.

Experimental Section

Three sources of commercially available purified SWNTs with different diameter distributions were used in this study. The first SWNTs were from Southwest Nanotechnologies (SWeNT, $d \approx 0.8 \pm 0.4$ nm). The second were HiPco SWNTs ($d \approx 1 \pm 0.3$ nm) purchased from CNI (Carbon Nanotechnologies Inc., CNI). The third were laser-ablation SWNTs (d averaged $\sim 1.3 \pm 0.3$ nm) also from CNI. The samples for irradiation were prepared as follows: SWNTs (∼5 mg) were dispersed in pure water (200 mL) with the addition of 1% Triton X-405 (Aldrich) via ultrasonication for 2−5 h followed by centrifugation at 50 000*g* for 10 h. Both supernatants and precipitates were collected. The supernatants (∼0.2 mL) were then dropped on quartz plates and dried at 200 °C, then washed thoroughly using ethanol and water. For comparison, the precipitates were also dispersed in water via a brief sonication and deposited on quartz plates. To study the sample history on the effect of optical irradiation, we used the samples in which metallic carbon nanotubes were selectively functionalized by

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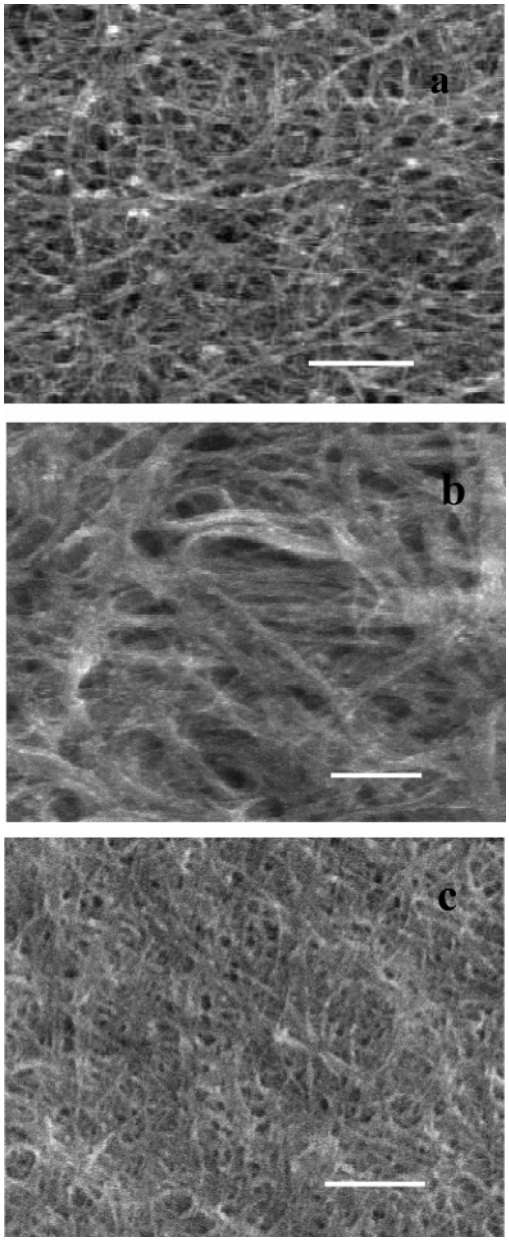

Figure 1. Scanning electron micrographs of HiPco SWNTs: (a) from the centrifuged supernatant, (b) from the centrifuged precipitate, (c) after selective reaction of metallic SWNTs using 4-brominebenzenediazonium. All samples were deposited on quartz plates and annealed at 650 °C. The bar scale is 200 nm.

4-brominebenzenediazonium, as described by Strano et al.[20,21] The chemically treated samples were dried and annealed at 650 °C in vacuum for 30 min. From the scanning electron microscope (SEM, JEOL JSM-6700FT) images shown in Figure 1 we can see that the samples from the supernatant and the chemically treated SWNTs are mainly in small bundles (<10 nm), while the tubes from the precipitate are in large bundles (10−50 nm).

The basic concept of laser irradiation induced preferential destruction of metallic tubes is simple and schematically illustrated in Figure 2. Laser irradiation and data collection were performed simultaneously using a micro-Raman system equipped with 514.5 (Ar^+) and 632.8 nm (He−Ne) lasers (Jobin Yvon, Horiba, HR800). The power of the 514.5 nm laser can be adjusted in the range of 0−100 mW, while that of the 632.8 nm laser is fixed at 20 mW. The diameter of the laser spots on

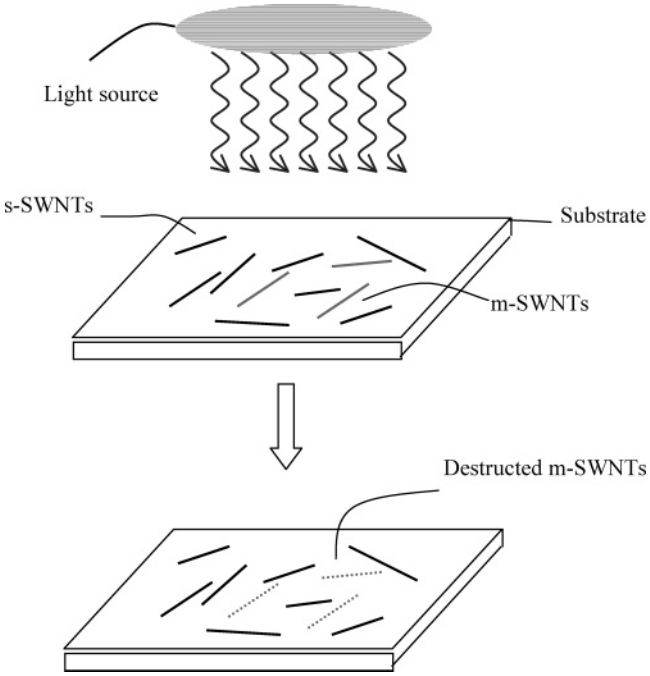

Figure 2. Schematic drawing of carbon nanotubes exposed to laser irradiation. Semiconducting carbon nanotubes (black) and metallic carbon nanotubes (grey) are illustrated.

samples is around 5 μm, and thus for a 20 mW laser, the power density is ~1 mW/μm^2.

Results and Discussion

Figure 3a shows Raman spectra around the radial breathing mode (RBM) region for the SWeNT SWNTs irradiated with the 514.5 nm laser operated at a power density of 3 mW/μm^2. For this laser, according to the correlation between energy E, RBM frequency ω, and tube diameter d (Kataura plot), Raman signals in the range of 150−215 cm^{-1} come from the third von Hove electronic transitions (S_{33}) of semiconducting carbon nanotubes, while Raman signals in the range of 230−300 cm^{-1} originate from the first von Hove electronic transitions (M_{11}) of metallic carbon nanotubes.[20] The major tube species for the peaks are indexed. Since all of the Raman signals decreased gradually upon laser irradiation, the Raman spectra are normalized to the G mode peak around 1590 cm^{-1}. It can be seen that upon irradiation the relative intensity of the Raman signal for semiconducting carbon nanotubes (16,0) remained almost constant, while those from metallic carbon nanotubes ((12,0), (8,5), (9,3)) decreased sharply. The decreasing rate of the metallic tube peaks was time dependent; it slowed gradually. After irradiation for a period of 80 min, the signals from metallic tubes decreased by ~85%.

Figure 3b shows the change of Raman spectra around the tangential mode (G and D) region for SWeNTs after the 514 nm laser irradiation. The spectra were recorded simultaneously with those in Figure 3a. The peak around 1542 cm^{-1}, the so-called Breit−Wigner−Fano (BWF) peak, which originates from electron−phonon interaction of metallic carbon nanotubes, also decreased after irradiation, which is consistent with the signals observed in the RBM region, indicating a preferential destruction of metallic carbon tubes. The increase in the D-band peak is indicative of the destruction of carbon nanotubes.

As seen in Figure 3, for the SWeNT SWNTs detected with the 514.5 nm laser, metallic carbon nanotubes with a small diameter (~0.9 nm) and semiconducting carbon nanotubes with

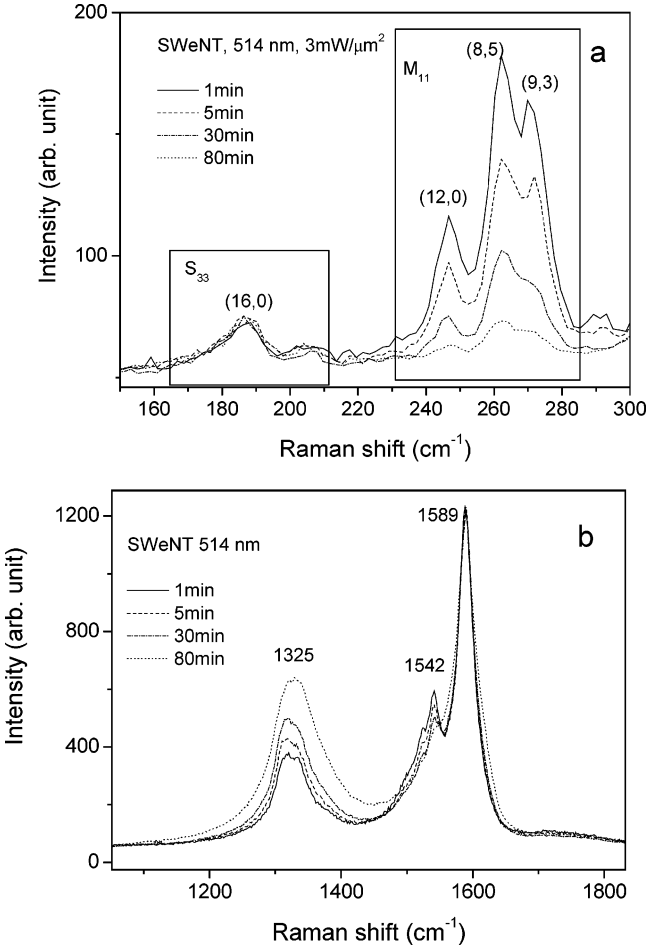

Figure 3. Change of Raman spectra for SWeNT SWNTs upon 514.5 nm laser irradiation: (a) around the radial breathing mode (RBM) region and (b) around the tangential mode (G and D) region. The laser power density is about 3mW/μm^2. The Raman spectra are normalized to the G mode peak around 1590 cm^{-1}.

a large diameter (~1.3 nm) were detected in the RBM region. One might argue that the change in the Raman signal might be due to the tube-size effect, as suggested by Banerjee et al.[18] To support our supposition that tube type rather than tube diameter dominates the irradiation effect, we performed irradiation with a 632.8 nm laser that detects large metallic and small semiconducting carbon nanotubes in the RBM region.

Shown in Figure 4 is the Raman spectrum in the RBM region for HiPco SWNTs upon 632.8 nm laser irradiation. Since few SWNTs in SWeNT sample match this laser energy, we choose HiPco SWNTs for the 632.8 nm laser irradiation. In this case, the signals in the range of 160−230 cm^{-1} originate from metallic tubes while those in range of 240−300 cm^{-1} are from semiconducting nanotubes. The diameters of the carbon nanotubes can be estimated using $d = 224/(\omega_{RBM} - 14)$, where d is the diameter and ω_{RBM} is the Raman shift. Therefore, the main components of carbon nanotubes detected by the 632.8 nm laser are metallic carbon nanotubes with a diameter of ~1.3 nm and semiconducting carbon nanotubes with a diameter of ~0.9 nm. While the changes in RBM Raman signals are complicated upon this irradiation compared to those upon 514 nm laser irradiation, as shown in Figure 3a, the general trend is the same: instead of SWNTs with small diameters being destroyed first, metallic carbon nanotubes are more easily destructed. The peak around 195 cm^{-1}, attributable to metallic tubes (13,4) ($d \approx 1.24$ nm), decreased by ~80%, while the peak at 257 cm^{-1} originating

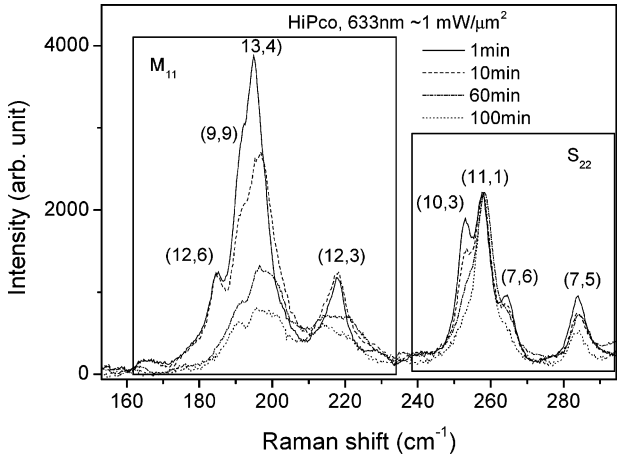

Figure 4. Change of Raman spectra around the radial breathing mode (RBM) region for HiPco SWNTs upon 632.8 nm laser irradiation. The laser power density is about 1 mW/μm^2. The Raman spectra are normalized to the G mode peak around 1590 cm^{-1}.

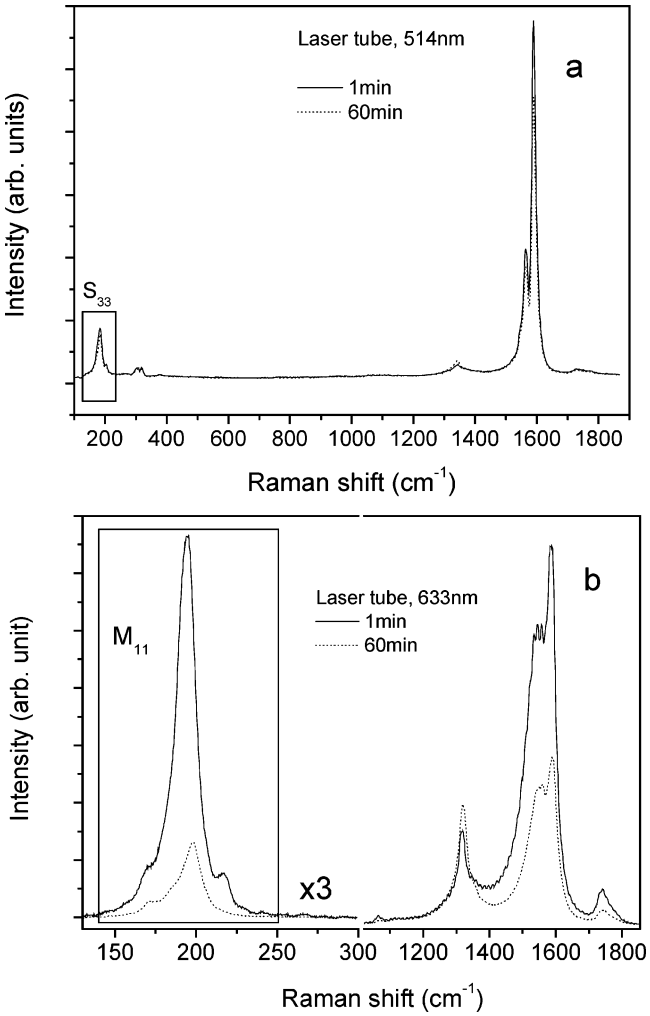

Figure 5. Change of Raman spectra for laser-ablation SWNTs upon irradiation using 514.5 (a) and 632.8 nm (b) lasers. The laser power density is 1 mW/μm^2 for both cases.

from semiconducting tubes (11,1) ($d \approx 0.92$ nm) remained essentially unchanged.

It is interesting to note that SWNTs with high chiral angles, such as semiconducting tubes (7,6) ($\theta = 27.5°$) and (10,3) ($\theta = 12.7°$), are more easily destroyed than those with low chiral angles (11,1) ($\theta = 4.3°$) upon laser irradiation. In this sense,

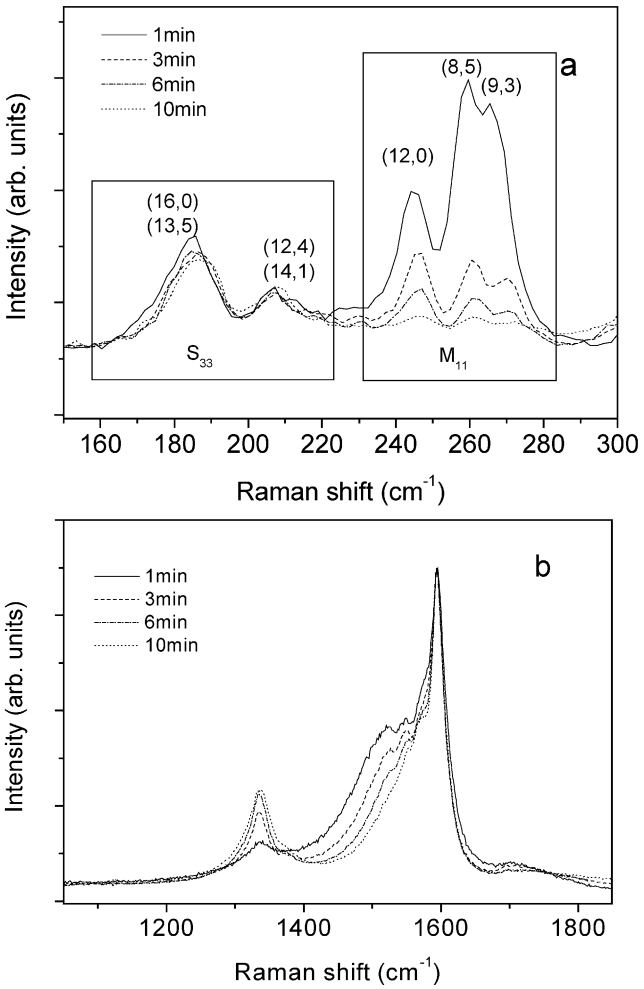

Figure 6. Change of Raman spectra for HiPco SWNTs upon 514.5 nm laser irradiation. The carbon nanotubes have been treated with 4-brominebenzenediazonium and annealed at 650 °C. The laser power density is about 1 mW/μm^2. The Raman spectra are normalized to the G mode peak around 1590 cm^{-1}.

laser irradiation may not only be useful for destroying metallic carbon nanotubes, but also be effective for fine tuning the electronic structure of the mixture of semiconducting carbon nanotubes. This finding extends the scope of laser resonance induced diameter-selective destruction of SWNTs.[17−19] Further study on this topic is under way.

As shown in Figure 5, the preferential destruction of metallic SWNTs is further supported by the observation that the Raman spectrum decreased remarkably (>80%) for laser-ablation SWNTs irradiated with a 632.8 nm laser for 1 h (Figure 5b). In this case the signals from metallic SWNTs dominate the spectrum. In contrast, the Raman spectrum of the SWNTs was not much changed when irradiated with the 514.5 nm laser under the same conditions, as shown in Figure 5a. In this case, semiconducting SWNTs dominate the Raman signal.

It should be noted that the optical destruction of SWNTs is very sample dependent. For the SWNTs from the supernatant, the selective destruction of SWNTs is much more apparent than those from the precipitate. This could be due to their difference in bundle size. The sample history also affects the result significantly. Shown in Figure 6 are Raman spectra of HiPco SWNTs treated with 4-brominebenzenediazonium and annealed at 650 °C. The functional groups are believed to be completely removed upon annealing. It can be seen that optical destruction of the chemically treated sample is much more efficient than that of the untreated SWNTs. The peaks from metallic tubes decreased by over 95% after irradiation for minutes instead of the 60+ min needed for a ~80% decrease for the untreated SWNTs. The change in the BWF peak around 1540 cm^{-1} is clear evidence that the metallic carbon nanotubes were preferentially destroyed. From SEM observations we noted that the bundles in the chemically treated sample are even smaller in size and more curved compared to those not subjected to the reaction. While the peaks from semiconducting SWNTs also decreased, we believe that the selectivity can be improved once the sample morphology and the incident-light power density are optimized. Importantly, the carbon nanotubes destructed by laser are not easily recovered by annealing (up to 650 °C), which is different from that subjected to selective reaction by chemicals.

We have also compared the ON/OFF ratio of carbon nanotube field-effect transistors (CNT-FETs) before and after laser irradiation. Depending on the irradiation wavelength, tube type, and irradiation duration, an up to five times enhancement of the ON/OFF ratio has been observed (see Supporting Information). While further improvement of the ON/OFF ratio is needed, we proved the concept of using external irradiation energy to destruct metallic carbon nanotubes preferentially.

Concluding Remarks

We conclude this work that upon laser irradiation in air metallic single-walled carbon nanotubes in carbon nanotube thin film can be destroyed in preference to their semiconducting counterparts. While it is still difficult to completely destroy all the metallic tubes with one or two lasers, in the future, however, when carbon nanotubes with fewer types of metallic components are synthesized, the finding presented in this work may find its practical applications, particularly in the construction of all CNT semiconductor devices (without metal electrodes) in which the portions subjected to irradiation act as FET channels while the portions without irradiation are used as source-drain electrodes. This may also pave the way for positioning and patterning semiconducting SWNTs, whose present unavailability is another huge barrier for application of CNTs to electronics.

Supporting Information Available: (1) Raman spectra showing cleavage of the functional group ($-C_6H_5Br$) from HiPco SWNTs at 160 °C; (2) comparison of $I_{DS}-V_g$ sweeps for HiPco SWNTs before and after 514.5 and 633 nm laser irradiations; (3) comparison of $I_{DS}-V_g$ sweeps for SWeNT SWNTs before and after 514 nm laser irradiation. This material is available free of charge via the Internet at http://pubs.acs.org.

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