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# Sulfidative Purification of Carbon Nanotubes Integrated in Transistors

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Carbon nanotubes (CNTs)[1] have been intensively investigated due to their unique one-dimensional structure with adjustable electronic conductivity and unusual mechanical strength.[2,3] To obtain any intrinsic properties from CNTs, they should be pure without carbonaceous impurities such as amorphous carbons on their surface. However, the growth of CNTs is inevitably accompanied by carbonaceous impurities, some of which still remain after purification procedures.[4] Here, we show a simple purification method using the sulfidation reaction of carbon, $C + 2S \rightarrow CS_2$, to selectively remove carbonaceous impurities from CNTs. It is demonstrated that the sulfidative purification of *CNTs integrated in* field-effect transistors (FET) results in a dramatic improvement of switching characteristics due to removal of carbonaceous impurities.

Regardless of the preparation method of CNTs, which is mainly arc-discharge, laser ablation, chemical vapor deposition (CVD), or high-pressure CO (HiPco) process, the carbonaceous materials on their surface are the most common impurities formed during growth.[5] Therefore, the separation of pure nanotubes is essential for fundamental research and for device applications. Since the carbonaceous particles are more susceptible to oxidation, in contrast to the perfect nanotube walls,[6] CNTs have been purified by oxidative treatments in gas phase or liquid phase.[4,7−10]

Nowadays, nanotubes for device applications are directly grown on a prepatterned catalyst by CVD due to its compatibility with conventional integration processes and capability on large areas.[11] However, the oxidative treatments are not suitable for the purification of CNTs integrated in a device because CNTs can be lost and deformed during the oxidation process. Therefore, CNTs grown by CVD are generally used without the subsequent purification process to avoid damage from the oxidative treatment. Recently, several groups have grown CNTs without surface carbon impurities by using water vapor, ammonia, or hydrogen gas or by using rapid growth process.[11−14] Nevertheless, the appearance of carbonaceous impurities is inevitable during CVD. Although many purification methods have been intensively studied, to our knowledge, there is no report regarding the removal of carbonaceous impurities from *CNTs integrated in a device*.

It is well-known that the sulfidation reaction of charcoal gives carbon disulfide. Until about 1950, the primary industrial production method of carbon disulfide was by heating charcoal to 750−900 °C in the presence of vaporized sulfur.[15] In this work, we chose sulfidation reaction to selectively remove carbonaceous impurities from CNTs because sulfidation is less reactive to carbon than oxidation, considering that molar Gibbs free energies of formation of gaseous $CO_2$ and $CS_2$ are −394.4 and 67.1 kJ/mol at room temperature, respectively.[16] Furthermore, sulfur shows high volatility in elemental form, and the reaction product ($CS_2$) is easily removable. Carbon disulfide is a colorless liquid that evaporates at room temperature.

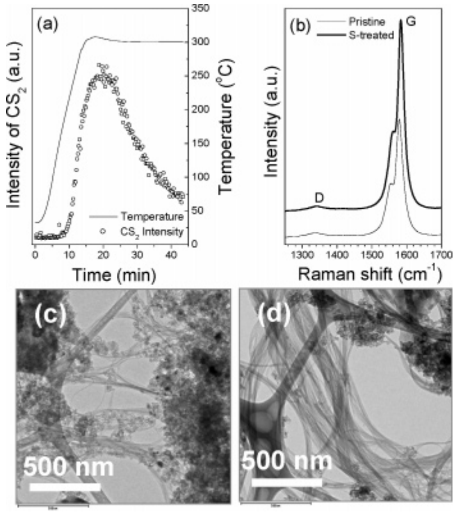

***Figure 1.*** Sulfidation of carbon nanotubes with carbonaceous impurities. (a) Mass intensity variation of $CS_2$ (76 amu) evolved during the heating of a mixture of nanotubes and sulfur. (b) Raman spectra of nanotubes before and after the sulfidation. TEM images of nanotubes (c) before and (d) after the sulfidation.

The sulfidation of carbonaceous impurities was performed at 300 °C to enhance the reactivity difference between carbonaceous impurities and CNTs. At first, the occurrence of sulfidation reaction at lower temperatures was proven with simultaneous thermogravimetry-differential scanning calorimetry-mass spectrometry (TG-DSC-MS) analysis. A mixture of single-walled carbon nanotubes (NanoCarb Inc., arc-discharge, purity 60%, diameter of 1.2−1.4 nm) and elemental sulfur (Aldrich, 99.998%) was loaded in an alumina crucible and heated to 300 °C with a heating rate of 20 °C/min. The temperature was maintained at 300 °C for 30 min in a vacuum (∼0.01 Torr). During the heating (see the temperature profile in Figure 1a), TG-DSC-MS was simultaneously analyzed with a Netzsch STA-MS-Skimmer instrument. In the DSC curve (data not shown), two endothermic peaks attributable to the melting and vaporization of sulfur are observed at 120 and 250 °C, respectively, and an exothermic peak from the sulfidation of carbonaceous impurities appears at 290 °C. The open circles in Figure 1a show that the mass intensity of carbon disulfide (76 amu) synchronously increases from 150 to 290 °C with the exothermic peak and subsequently reaches its maximum intensity at 306 °C. It then decreases due to the exhaustion of sulfur. This reveals that sulfur reacts to carbonaceous impurities on the surface of CNTs by the sulfidation reaction, $C + 2S \rightarrow CS_2$, at 300 °C in a vacuum (∼0.01 Torr).

The selectivity of the sulfidation of the carbonaceous impurities is evaluated with Raman spectroscopy (514 nm laser) by comparing the spectra before and after the sulfur treatment as shown in Figure 1b. Spectra were obtained at 10 positions and averaged. The overall tendency of the Raman spectra of the sulfur-treated CNTs is nearly the same as that of the pristine. However, the ratio ($I_D/I_G$) of the disorder-induced D-band to the tangential G-band (derived from

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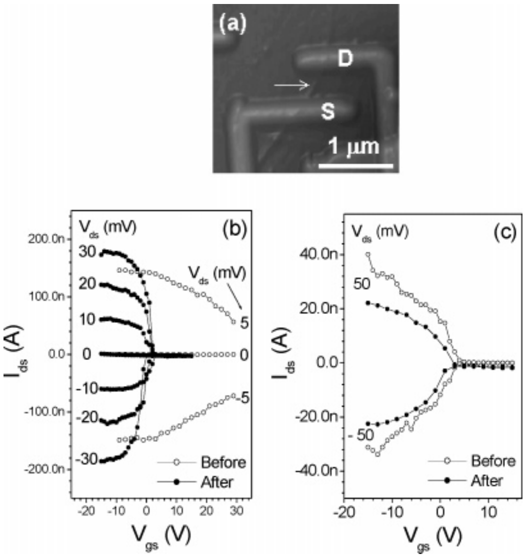

***Figure 2.*** (a) AFM image of a back-gated CNT-FET. S and D denotes source and drain, respectively, and CNT is designated by the arrow. (b,c) Drain−source current ($I_{ds}$) versus gate−source ($V_{gs}$) voltage characteristics of CNT-FETs before and after sulfur treatment. (b) The transistor with high off-state current before the sulfur treatment turns on and off at 3 V after treatment. (c) The normally operating transistor before the sulfur treatment shows the same threshold voltage at 3 V after the treatment.

the graphite-like in-plane mode) decreases from 0.05 to 0.035 after the sulfur treatment.[17] This means that the nanotube walls are not sulfidized and not deformed, but carbonaceous impurities are selectively removed by the sulfur treatment at 300 °C. Transmission electron microscopic (TEM) images before (Figure 1c) and after (Figure 1d) the treatment prove that the carbonaceous impurities were removed by sulfidation.

The purification method by sulfidation can be applied to *CNTs integrated* in devices since nanotube walls are impervious to the sulfidation as proven by Raman spectroscopy. We compared electrical properties of CNTs integrated in a FET before and after the sulfur treatment. Figure 2a shows a typical atomic force microscopic (AFM) image of CNT-FET studied in this work (see Supporting Information for the detailed procedure of FET fabrication).

Among the CNT-FETs fabricated, we selected a transistor that shows poor switching characteristics as shown in the drain−source current ($I_{ds}$) versus gate−source voltage ($V_{gs}$) curve of Figure 2b (○). The transistor with a resistance of 40 kΩ does not show a clear threshold voltage ($V_{th}$), which indicates the transition voltage from off-state to on-state. There are two possibilities for the transistor to show such poor switching performance. First, if the CNT integrated in the transistor is metallic or semiconducting with a narrow band gap, high off-state current can appear.[18] Second, the carbonaceous impurities on the outer surface of the CNT may act as a conduction path between source and drain, consequently increasing the off-state current in the transistor.[14]

Sulfur treatment for the nanotube integrated in the FET was as follows. The CNT-FET specimen was placed on a vacuum chamber with a base pressure of 11.7 mTorr, together with sulfur contained in an Al crucible. The specimen was then heated at 300 °C for 30 min without any carrier gas. During the sulfur treatment, working pressure gradually decreased from 15.3 mTorr to the base pressure as sulfur was evaporated and exhausted. After being cooled, the specimen was unloaded from the chamber.

The solid circles in Figure 2b show $I_{ds} - V_{gs}$ characteristics after sulfur treatment. Different from the device before the sulfidation, the sulfur-treated CNT-FET shows clear on/off switching with a threshold voltage ($V_{th}$) of 3 V and with an on-/off-state current ratio of two orders (see Supporting Information). For comparison, we investigated another CNT-FET, which had normally operated as a transistor before sulfur treatment. As shown with open circles in Figure 2c, the FET shows a typical p-FET $I_{ds} - V_{gs}$ curve with a threshold voltage of ∼3 V. After sulfur treatment, the FET still operates as a p-FET with the same threshold voltage.

If the sulfur treatment gave rise to the sulfidation of nanotube walls, the threshold voltage should shift due to the widened band gap by the deformation of the nanotube wall. However, as expected from the Raman spectra, there is no shift in $V_{th}$ with sulfur treatment. This reveals that the high off-state current is due to the carbonaceous impurities on the surface of the nanotube, which provide conduction paths between source and drain, and the impurities were selectively removed from the nanotube through the sulfidation reaction.

The purification of CNTs by sulfidation can be used to remove carbonaceous impurities that may remain after initial purifying procedures by other methods and can be more useful for *nanotubes integrated in devices* for fundamental characterizations or industrial applications.

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**Supporting Information Available:** FET fabrication procedure and $I_{ds} - V_{gs}$ curves in a log scale. This material is available free of charge via the Internet at http://pubs.acs.org.

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