A New Method of Carbon-Nanotube Patterning Using Reduction Potentials

By Jong Hak Lee, Jun Ho Shin, Yu Hee Kim, Sung Min Park, P. S. Alegaonkar, and Ji-Beom Yoo

Carbon nanotubes (CNTs) have attracted considerable interest as high-stiffness materials and for use in nanodevices, on account of their extraordinary mechanical, chemical, and electrical properties.[1] There have been several examples of CNTs being used to realize devices and composites.[2,3] However, several hurdles remain to be overcome before CNT-based technology can be deployed on a commercial scale. Among these hurdles are locating and patterning technologies. So far, films of CNT networks have been patterned in the micrometer regime by a variety of techniques, including using a poly(methyl methacrylate) (PMMA) or poly(dimethylsiloxane) (PDMS) stamp, CO₂ snow-jet etching, and O₂ plasma etching.[4] However, these methods have limitations in commercial applications, such as lack of scalability, low resolution, and low reliability. This paper reports that noble metals, such as Au, Pt, and Ag, can promote the oxidation of CNTs at a relatively low temperature (350 °C), because of the reduction potential of the CNTs (in this study, oxidation means decomposition to CO₂). Based on these phenomena, a nanometer-sized, patterned, random network of CNTs is fabricated. This study also examines the difference in the reduction potentials of single-walled and multiwalled CNTs (SWCNTs and MWCNTs, respectively).

Scheme 1 summarizes the experimental procedure used to determine the reduction potential of the CNTs and to obtain the novel nanometer-sized patterns of SWCNTs. In order to make a CNT–metal junction, very thin metal films were deposited on a CNT film using electron-beam evaporation. The samples were then annealed in a box furnace at 350 °C in ambient air. In a reactive environment, a material system can be considered a "galvanic cell" if there is electrical contact between two materials with different reduction potentials, and they are in the same electrolyte.[5] Under these conditions, the corrosion rate of the material with the lower reduction potential can be faster than that of the material with the higher reduction potential.[5] The novel method for patterning CNT films was developed by applying this phenomenon. In order to confine the CNTs to a selected area, lines and numbers were drawn with Ag (15 nm thick) using photolithography, before depositing the CNT film on the substrate. Figure 1a and b shows images of the patterned CNT films after annealing. The CNTs are confined to the areas without Ag. Only the CNT patterns remained after an aqua-regia treatment. The widths of the lines patterned by the CNTs were 560 and 750 nm. Photolithography and metal deposition are well-developed techniques, with which CNT patterns several tens of nanometers in size can be obtained.

Recently, several applications based on the interaction between CNTs and metal contacts were reported,[6] but there has been no concise explanation for the phenomenon. A better understanding of the interaction between CNTs and metals is needed, since metals are used as electrodes, substrates, and/or as the main components of CNT-based devices and composites. In particular, in nanoscale materials, a small degree of metamorphosis can cause serious problems, as these materials are quite small, containing very few atoms. Therefore, for practical applications of CNTs, it is very important to obtain information on their basic parameters, such as their reduction potential. The reduction potentials were estimated by producing galvanic coupling between various metals and CNTs.

Figure 2 shows scanning electron microscopy (SEM) images of metal-coated MWCNTs after annealing at 350 °C for 4 h. The density of the CNTs shown in Figure 2a was almost the same as that of the CNTs shown in Figure 2b. All CNTs were totally eliminated in Figure 2b; and only a few remained in Figure 2c. According to other reports, MWCNTs are thermally stable at 350 °C in ambient air.[7] It is well-known that CNTs have excellent thermal stability.[8] In some reports, in situ Raman spectroscopy
analysis of nanotube oxidation showed a decrease in the intensity of the D band beginning at approximately 370 °C, indicating oxidation of the amorphous carbon deposited on the CNTs. The temperature for the heating-induced purification of CNTs has been reported to range from 370 to 400 °C. The G band has been reported to increase or remain constant until 580 °C. This suggests that most CNTs are thermally stable, while a few that present some defects are eliminated below 400 °C. There is a distinct difference between MWCNTs (Fig. 2a) and MWCNTs coated with various metals, such as Au, Pt, Ag, Cu, and W (the results in the case of Pt, Ag, Cu can be seen in the Supporting Information). In the case of the metal-coated MWCNTs, there are many contacts between the CNTs and the metals, which have different reduction potentials from the tubes. Moreover, air can act as an electrolyte by supplying moisture.

Therefore, this structure can be called a "galvanic cell". Although its appearance is similar to that of the CNT-only films, some reactions, such as reduction or oxidation, take place in corrosive environments, such as high-temperature air. The oxidation rate of a material with a low reduction potential will be fast, being driven by the difference in reduction potential between the two materials. If the CNTs have a higher reduction potential than the metal, the state of the CNT will remain unchanged, while the metal will be oxidized. In the opposite case, the CNT will be oxidized and ultimately disappear. Therefore, the reduction potential of the MWCNTs can be estimated from these results. In the case of Ni, all nanotubes remained after annealing. This suggests that the Ni thin film was oxidized and the CNTs remained in their as-deposited state. This result was also observed in the case of Ti (the SEM images can be seen in the Supporting Information). Therefore, as shown in Figure 4, the reduction potential of the MWCNTs at 350 °C is located somewhere between that of W and Ni.

Different results were observed for SWCNTs. As shown in Figure 3, the SWCNTs with no metal contact and those with In remained intact. Only a few SWCNTs remained in the case of Ni, and they disappeared completely when in contact with metals such as Cu, W, and Ni after annealing at 350 °C for 4 h (SEM images can be seen in the Supporting Information). In the case of In and Ti, all the SWCNTs remained after annealing. Therefore, as shown in Figure 4, the reduction potential of the SWCNTs at 350 °C is located somewhere between those of Ni and In. This means that the reduction potential of SWCNTs is lower than that of MWCNTs. This higher reactivity can possibly be attributed to the increased strain on the aromatic structure of the nonplanar benzene subunits that make up the nanotubes.

MWCNTs are generally more stable on account of the steric hindrance of the outer walls, as well as the lower strain that exists on these outer walls because of their larger diameters. This steric hindrance affects the reduction potential, indicating why the burning temperature of SWCNTs is lower than that of MWCNTs despite the fact that the mechanical strength of the former is higher than that of the latter, and that SWCNTs have fewer defects than MWCNTs. Based on these experiments, it can be concluded that the oxidation of SWCNTs and MWCNTs is dependent on their reduction potentials. The reactions between the metal and the CNTs can be written as follows:

\[
\begin{align*}
\text{aM} + b\text{O}_2 & \rightarrow k\text{M}_x\text{O}_y : \Delta G_1 \\
k\text{M}_x\text{O}_y + b\text{CNT} & \rightarrow \text{aM} + b\text{CO}_2 : \Delta G_2
\end{align*}
\]
resulting in the overall chemical reaction

\[ aM + b\text{CNT} + bO_2 \rightarrow aM + b\text{CO}_2 \]  

These results can be theoretically explained using the Nernst equation. The Nernst equation can determine the reduction process and trends in a chemical reaction. Two solutions can be obtained using this equation. One is

\[ \Delta G = \Delta G_{\text{CNT}-\text{CO}_2} - nF\Delta E^0 \]

where \( \Delta G_{\text{CNT}-\text{CO}_2} \) is the Gibbs free energy of the CNT pyrolysis, \( n \) is the number of electrons in the reaction, \( F \) is Faraday’s constant, and \( \Delta E^0 \) is the difference in the standard reduction potentials between the metal and CNT (\( \Delta E^0 = E_{\text{red}}^{\text{M}} - E_{\text{red}}^{\text{CNT}} \)). In the case of the noble-metal–CNT system, \( \Delta E^0 \) has a positive value and the free energy of the reaction (\( \Delta G \)) is lower than that of the isolated CNT system. This suggests that a metal contact, which has a high reduction potential, can promote the oxidation of CNTs. The other equation is

\[ \Delta G = -\Delta S_{\text{CNT-\text{CO}_2}}dT - nF\Delta E^0 \]

where \( \Delta S_{\text{CNT-\text{CO}_2}} \) is the entropy of the reaction and \( T \) is the absolute temperature. At equilibrium, \( \Delta G \) approaches zero, and the equilibrium temperature can be affected by the difference in reduction potential. Consequently, pyrolysis or oxidation can be induced more easily with increasing difference in reduction potential and temperature. When two different materials are coupled together, the one with lower reduction potential has excess electron activity, where the electrons are transferred to the material with the more-positive reduction potential.

Figure 5 shows SEM images of elaborately patterned CNT films. In order to prevent aggregation and migration of Ag nanoparticles during the annealing process, a 5 nm Ti layer was deposited before the Ag film. This result indicates that CNT patterns several tens of nanometers in size can be obtained as long as this size of metal nanopatterens can be obtained.

In summary, a nanometer-sized pattern of a CNT film was successfully fabricated by employing the difference in reduction potential between the CNTs and different metals. Moreover, this study examined the reduction potentials of CNTs using a very simple method. Noble metals (such as Au, Pt, and Ag) can induce the oxidation of CNTs at a relatively low temperature in air. The reduction potential of MWCNTs is located between those of W and Ni, while that of SWCNTs are located between those of Ni and In. Overall, these findings can be used as guidelines for designing CNT-based devices.

**Experimental**

**Sample Preparation and Annealing Process:** MWCNTs and SWCNTs were obtained from ILJIN Nanotech Co., Ltd. (Korea). The CNTs were...
dispersed in a 1% sodium dodecylsulfate solution dissolved in water and sonicated using a tip-sonication instrument. In order to obtain a well-dispersed CNT solution, the sonicated solution was centrifuged at 12,000 g (g: 10 ms⁻²). A uniform CNT film was obtained by vacuum filtration; and transferred [14] to a silicon wafer with thermally grown SiO₂ (500 nm). All the metals were deposited onto the CNT films to a thickness of 3 nm to examine the elimination of CNT. With Au and Ag, nanoparticle formation began rapidly. Therefore, the thickness of the Au and Ag films was increased to 15 nm in order to completely remove the CNTs. After preparation, the samples were annealed at 350 °C for 4 h in air.

**CNT-Film Patterning:** Photoresists (PRs) were patterned using a Nikon stepper. Ag films 15 nm thick were deposited onto the nanometer-sized PR-patterned substrate. After a lift-off process to remove the PR, a uniform CNT film was transferred onto the substrate and annealed at 350 °C for 4 h in air. The Ag nanoparticles were removed by dipping the samples in aqua regia for 30 min; followed by rinsing with deionized water.

**Fine CNT-Film Patterning:** The photolithography process and annealing conditions were the same as those used in CNT-film patterning. The only difference was that a 5nm Ti film was deposited as a binding layer before Ag-film deposition.

**Acknowledgements**

This research was funded by the KOSEF through the CNNC (Center for Nanotubes and Nanostructured Composites) at Sungkyunkwan University; and the BK21 Project of the School of Advanced Materials Science & Engineering. Supporting Information is available online from Wiley InterScience or from the author.

Received: August 27, 2008
Revised: October 7, 2008
Published online: January 14, 2009

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