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Communications

Selective Attachment of Multi-Walled Carbon Nanotubes on Poly(dimethyl siloxane) Substrates

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Introduction

Carbon nanotubes (CNTs) possess exceptional structural, mechanical, and electrical properties. Significant research effort in both scientific and technological fields has been devoted to the realization of the unique potential of CNTs into materials for practical applications such as polymeric composites, electronic sensing devices, field emission display, filter media, and hydrogen storage.¹ In the promising field of nanoscale electronic devices and materials, it is essential to place CNTs on a designed substrates or fabricate patterned CNT structures with a high surface coverage in a controlled manner. It was reported that patterned structures with CNTs could be achieved by the growth of aligned CNT arrays from pre-patterned substrates using conventional high temperature CVD processes, the pyrolysis of catalyst precursors, the self-assembly of monolayers on substrates and the self-assembly of CNTs.²⁻¹³ On the other hand, functionalized CNTs can be produced by controlled deposition within chemically modified regions.^{14,15} Despite the successful

implementation of CNTs into lateral device configurations, better control of the conventional process of nanotube assembly onto various substrates through simpler and more efficient ways is essential.

Among the many substrates, the patterning of CNTs onto polymeric films has many advantages on account of their high flexibility and good processibility. A variety of patterned polymeric films have been prepared using poly(dimethyl siloxane) (PDMS) and poly(ethylene terephthalate) as well as azo-type polymers.¹⁶⁻¹⁹ In particular, the formation of patterned CNT layers on PDMS substrates is a desirable configuration for further applications in microfluidic and field-emission devices.

This paper describes the controlled deposition of multi-walled carbon nanotubes (MWNT) onto PDMS substrates using a CNT dispersed water droplet without further modification and additional steps. The mechanism for the pattern formation is also discussed.

Experimental

Preparation of Patterned Films. The multi-walled carbon nanotube, MWNT (purity > 95 wt%) was purchased from Iljin Nanotech Co., Korea and used without further treatment. The PDMS polymer (Sylgard 184) was supplied by Dow Corning. The polymeric substrates were prepared by mixing two components followed by curing at 80 °C for 1 hr.

Prior to selective deposition, a solution containing 0.1 g of the pristine MWNT in 100 mL deionized water was dispersed using a sonicator (Branson 5510) for 1 hr. The solution was then centrifuged at 15,000 rpm for 40 min in order to remove the agglomerated CNT bundles as well as other contaminants. After treatment, 10 μ L of an aqueous MWNT solution was dropped onto the film and a copper grid (200 mesh, GLIDER) was carefully placed on top the droplet, as shown in Figure 1. This was then irradiated with UV light (wavelength; 254 nm) at 5.7 mW/cm² with an exposure time of 12 hrs in air. After exposure, the composite films were stirred for 3 hrs in deionized water to remove the impurities and physically adsorbed CNTs. The films were then dried for 1 day in a vacuum oven at room temperature.

Characterization. The FTIR measurements were per-

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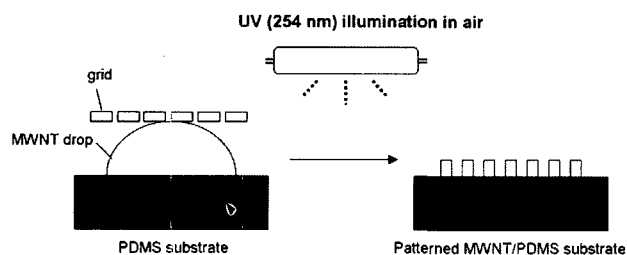


Figure 1. Schematic illustration for the preparation of the patterned MWNT/PDMS composite films.

formed on a Varian 2000 FTIR spectrometer in attenuated total reflectance (ATR-FTIR) mode using a Ge crystal detector with an incident angle of 45° . For each sample, 20 scans were signal-averaged at a resolution of 4 cm^{-1} . The baseline corrected infrared spectra of the composite films were obtained in absorbance mode at room temperature. Some of the spectra were also recorded using a KBr pelletized disk. The Raman spectra were obtained using a Jobin Yvon T64000 Raman spectrometer equipped with a 5.0 W Argon laser source for 513 nm excitation and a multichannel CCD detector. The optical microscopic measurements (OM) were carried out using a Nikon OPTIPHOT2-POL in reflection mode. Scanning electron microscopy (Hitachi, S-3500N) was used to investigate the surface texture of the films. The composite films were fixed horizontally on a sample holder to analyze the surface structure. A palladium-platinum alloy was sputtered onto the thin films to minimize film damage due to the electron beam as well as to obtain clear images. Thermal gravimetric analysis (TGA) was performed using a TA model 2050 TGA instrument under N_2 flow at a heating rate of $10^\circ\text{C}/\text{min}$. The solid samples were scratched off the composite films and heated from 50 to 900°C . The weight loss of the samples (TG curves) was then recorded.

Results and Discussion

Figure 2 shows the optical microscopy images of the patterned CNT surface structures formed on the PDMS films after UV irradiation for 12 hrs through copper grids (200 mesh). Clear contrasts could be observed between the areas exposed (squares) and the protected areas (lines), indicating the formation of CNT patterned surface structures. Figure 3 shows SEM images of the patterned MWNT layers formed on the PDMS matrix. Well-arranged CNT patterns were formed on the $10\ \mu\text{m}$ scale with a large surface coverage. In the high magnification images, some of the CNTs within each layer protruded with a significant number of individual nanotubes with an average diameter of $10\sim 20\text{ nm}$. The other CNTs appear to be entangled around some of the protruded CNTs. The extent of the agglomeration of the carbon nanotube bundles was reduced significantly by the ultrasonic treatment, as has been reported previously.^{20,21} In addition,

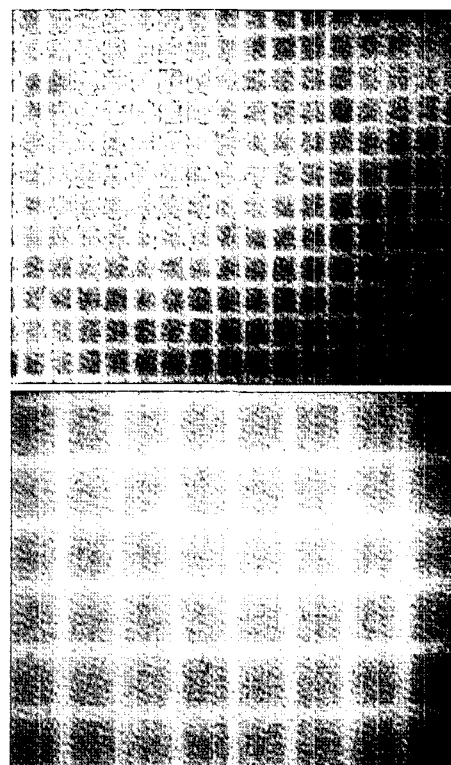


Figure 2. Optical microscopic images of the surface of the patterned MWNT/PDMS composite film.

there was no significant shortening in tube length, which is due to CNTs not being treated with acid. It should be noted that the convective evaporation during irradiation influences on the surface coverage of the CNTs. For example, at low CNT concentrations, the CNT coverage was driven to around the protected areas as a result of Marangoni convection at the liquid/air interface. In contrast, the surface coverage could be improved at high CNT concentrations.

The pattern formation of the MWNTs onto PDMS surfaces was further examined in detail by investigating the molecular structure of the patterned PDMS composite films using FTIR spectroscopy (Figure 4). A comparison of curve (b) with curve (a) of the pristine MWNTs, new peaks were observed at approximately 2885 cm^{-1} , which were assigned to the asymmetric C-H within the irradiated regions. This suggests that the carbon nanotubes were modified by the methyl radicals generated from the exposed PDMS surfaces during photo-oxidation.²² Moreover, the peak intensity of 795 cm^{-1} associated with $-\text{CH}_3$ rocking and Si-C stretching was significantly lower than that shown in curve (c) for the unmodified PDMS surface. This indicates the occurrence of methyl radicals from PDMS as a result of photodecomposition. In addition a new peak related to the oxidation of CNTs was also found at 1384 cm^{-1} but the detailed peak assignment is still unclear.²³ It is well known that PDMS interacts with UV light to give rise to various reactive species and excited molecules, inclu-

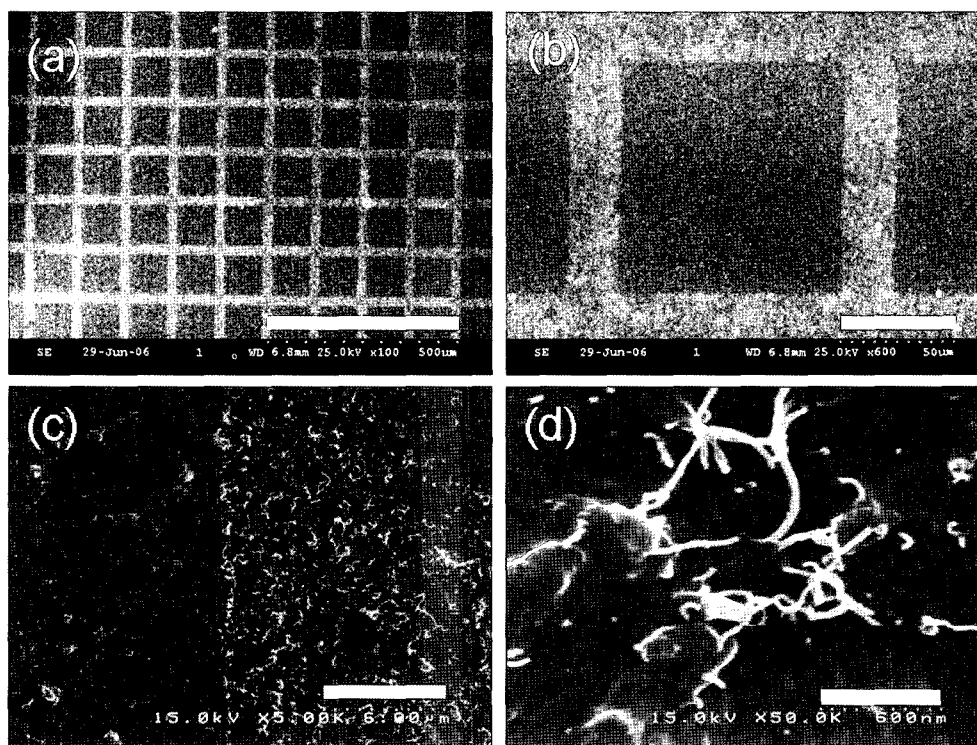


Figure 3. SEM micrographs of the patterned MWNT/PDMS surfaces. Scale bars denote (a) 500 μm , (b) 50 μm , (c) 6 μm , and (d) 600 nm.

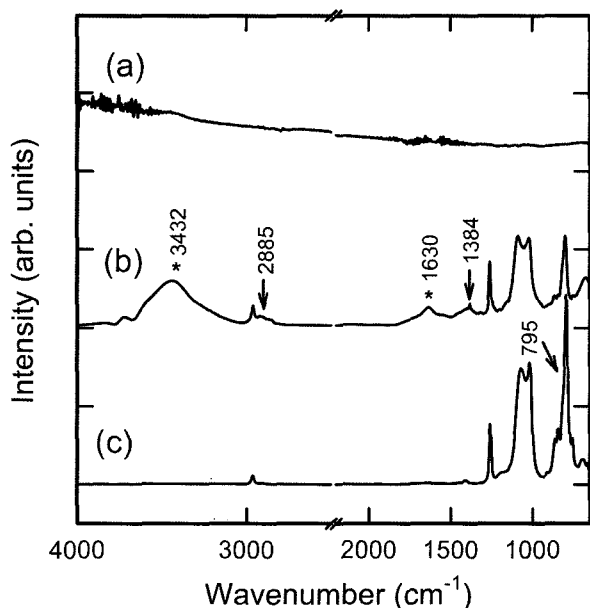


Figure 4. FTIR spectra of (a) pristine MWNT, (b) modified MWNT, and (c) PDMS. Asterisks at 1630 and 3432 cm^{-1} denote the peaks due to the -OH groups and adsorbed water, respectively.

ding methyl and hydroxyl radicals.²⁴⁻²⁶ Therefore, one possible mechanism involves the photo-dissociation of the mainly Si-CH₃ groups that then react with the CNT surface to give

the patterned surface structures in the chemically grafted CNTs. On the other hand, the peaks at around 1630 and 3432 cm^{-1} were assigned to the vibrational bands due to the stretching vibration of -OH groups as well as bending vibration of adsorbed water, respectively.²⁷

Raman spectroscopy was performed to investigate the chemical attachment of CNTs on PDMS, and the result is illustrated in Figure 5. All the spectra showed the typical D- and G-bands of MWNT at 1287 and 1600 cm^{-1} , respectively. After irradiation, the peak intensity became significantly weaker than that of the pristine MWNT, as evidenced by the change in the relative peak ratio of D to G band. This is in good agreement with previous results, and confirms that the surface of the CNTs was covalently modified through chemical attachment on the PDMS surface.^{27,28}

Such photo-grafting of MWNT onto the PDMS surface was further investigated using thermogravimetric analysis (TGA), as shown in Figure 6. The pure PDMS starts to decompose above 200 °C due to depolymerization of the polysiloxane backbone leading to formation of cyclosiloxanes, remaining about 68% of total weight after 700 °C.²⁹ On the other hand, for the pristine CNTs, there was no significant weight loss until 600 °C. For the comparison with MWNT scraped off the PDMS surface, the physically blended sample was prepared by mixing of MWNT and PDMS and its TGA behavior was also tested. As reflected by a significant interaction between nanotubes and PDMS, the thermal

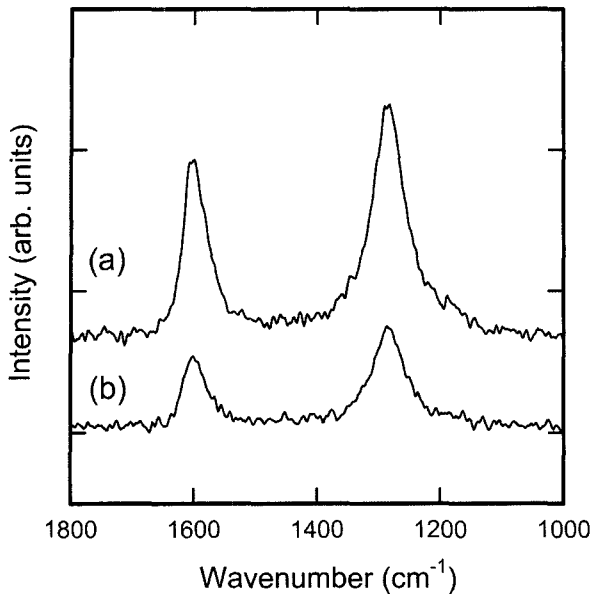


Figure 5. Raman spectra of (a) pristine MWNT and (b) modified MWNT.

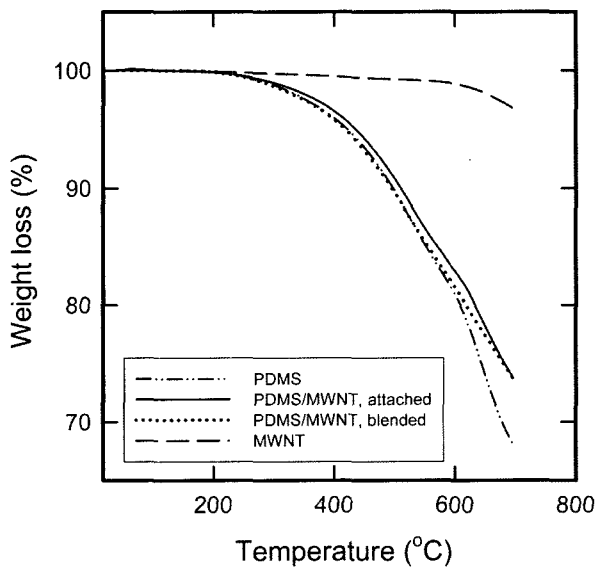


Figure 6. TGA scans of the various samples measured at a heating rate of 10°C/min under N₂.

decomposition behavior of attached sample is slightly different from that of blended PDMS. For instance, at 95% of weight loss, the decomposition of sample with the attached nanotubes is shifted to a higher temperature (436.3°C) relative to that of blended sample (422.6°C) and pure PDMS (422.6°C), which indicates that the incorporation of chemically modified nanotubes increases the thermal stability of PDMS.

Conclusions

In summary, multi-walled carbon nanotubes were selectively deposited on the PDMS surface to give patterned PDMS composite films using UV induced photo-grafting method. The spectroscopic evidence suggests that the nanotubes were chemically attached to the PDMS surface through covalent bonding with the mainly methyl radicals generated by the photodecomposition of methyl groups in the PDMS during photooxidation. This simple and efficient patterning method with carbon nanotubes can allow the patterning of CNTs onto diverse substrates and provide practical and potential applications in a variety of CNT based transistors and sensing devices.

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