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Short communication

Patterning carbon nanotubes with silane by scanning electrochemical microscopy

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ABSTRACT

This work reports a novel approach of patterning carbon nanotubes (CNTs) with scanning electrochemical microscopy (SECM). The concept is based on the localized cathodic current flux, which induces the pH increase on the conductive surface confined under the microelectrode. The latter facilitates the local deposition of silane sol–gel films, which embed the CNTs from the dispersion. The patterns can be tuned by deposition potential, time and scan rate of the microelectrode, as characterized by optical microscopy, scanning electron microscopy (SEM), energy-dispersive X-ray analysis (EDX) and profilometry.

1. Introduction

Carbon nanotubes (CNTs) have unique properties, such as high electric conductivity, surface area, optical absorbance and mechanical strength and good permeability to small molecules, which allow their applications in energy, sensing, optical and other devices. The synthesis and assembly of CNTs have been thoroughly investigated and reviewed [1,2]. Yet, for fabricating CNT-based devices, patterns are highly desired. There are mainly three methods of patterning CNTs, *i.e.* lithography, ink-jet printing and laser etching. Lithography approach is the most commonly used, which can be divided into two directions. It can be used for either patterning of the catalyst layer, which serves as spatially selective growth sites for the chemical vapor deposition of CNTs [3,4], or for the local removal of CNTs that were formed previously [5,6]. Lithography is unique in yielding vertically or perpendicularly aligned CNT patterns, but it is sophisticated and expensive. As compared with lithography, ink-jet printing is much easier to operate providing a proper CNT ink. The inks are CNT dispersions consisting of surfactants and binders for improving the rheology [7]. Short CNTs are preferred to achieve high concentration in the ink and prevent blocking of the printing nozzle. However, the main limitation for ink-jet printing is the resolution, which is limited to *ca.* 100 μm due to the minimum size of the droplet [8,9]. Patterning CNTs by laser etching, which is based on locally burning CNTs under laser beam, was also reported [10,11]. But it is only applicable for local removal of CNTs that were pre-deposited.

Electrodeposition is also a promising technique for patterning. One approach is the selective electrodeposition of CNTs on conductive patterns. For example, Yang et al. [12] electrodeposited carboxylic functionalized CNTs (CNT-COOH) on ITO patterns based on the anodic generation of H^+, which drove the precipitation of CNT-COOH. Ogihara et al. [13] reported the electrophoretic deposition of single-walled CNTs (SWCNTs) on a pre-patterned electrode surface, where CNTs adsorbed better onto the electrode and those deposited on the patterns were later removed by sonication. These approaches were relatively simple but limited to electrostatically charged CNTs. Meanwhile, electrodeposition is also powerful for preparing bulk CNT films. For example, Walcarius et al. [14] reported the electrodeposition of vitamin K_3-modified CNTs with silane and enzymes for fabricating biosensors.

Patterning through electrochemistry has been widely carried out by scanning electrochemical microscopy (SECM). It is based on localizing the electrodeposition into a confined area on the substrate below a micro- to nanometer sized electrode tip. Patterns of various metals and conductive polymers have been successfully generated by SECM [15]. Recently, we also patterned graphene from graphene oxide using direct-mode SECM [16]. However, to the best of our knowledge, SECM has still not been applied for CNT patterning.

In this work, we report a novel method for patterning non-functionalized multi-walled CNTs (MWCNTs) with SECM. Patterns of MWCNTs with silane having resolution of *ca.* 30 μm were successfully generated by applying potential between Au or stainless steel substrate and a Pt microelectrode (25 μm diameter) which is positioned close to the substrate. The silane which was co-deposited with CNTs served as the binder. The patterning process was well controlled by the applied potential, time and lateral scan rate of the microelectrode.

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2. Experimental

Au samples (100 nm of Au vapor deposited on glass with a 10 nm Cr adhesive layer) were cleaned with EtOH and H_2O prior to use. Mirror-like polished stainless steel 304 plates were cleaned by sequentially sonicating in EtOH, 1 $\mathrm{mol \cdot L^{-1}}$ NaOH and H_2O for 10 min, respectively. All the chemicals used are of analytical grade. The water used is purified to 18.3 MΩ cm with Barnstead Easypure UV system. The CNT dispersion with silane consisted of 0.1 wt.% MWCNT (Cheap Tubes), 0.2 $\mathrm{mol \cdot L^{-1}}$ tetramethoxysilane (TMOS, Merck) and 2 wt.% cetyltrimethylammonium chloride (CTAC, Alfa Aesar). After mixing the chemicals, the dispersion was sonicated for 2 h in a bath before use.

The patterning was carried out with a commercial SECM (CHI920C, CH Instruments, USA). A 25 μm diameter Pt microelectrode was approached to *ca*. 12 μm above an Au or stainless steel surface using the feedback mode SECM in deoxygenated 1 mM $\mathrm{Ru(NH_3)_6^{3+}}$ redox solution. After positioning the microelectrode, the redox solution was replaced by the CNT dispersion with silane, and the electrochemical cell was switched to the direct mode. For patterning, a negative potential was applied to the Au or stainless steel surface *versus* the Pt microelectrode (E_{surf} *vs.* E_{tip}. Note: the potential is not comparable to that in three-electrode system *versus* a reference electrode [16].) which served as the counter electrode. The microelectrode was either kept for a few seconds, or scanned across the surface at a set rate. After patterning, the samples were dismantled from the cell, washed with DI water and blow-dried with N_2 flow.

The samples were examined by Olympus BX60 optical microscope and scanning electron microscopy (SEM, SIRION, FEI Co. Ltd.) with energy-dispersive X-ray analysis (EDX, X-Max 20, Oxford Instruments). EDX spectra were acquired with 5 kV acceleration voltage and spot size 5. The height of the patterned spots was measured with profilometry (Veeco Dektak 150).

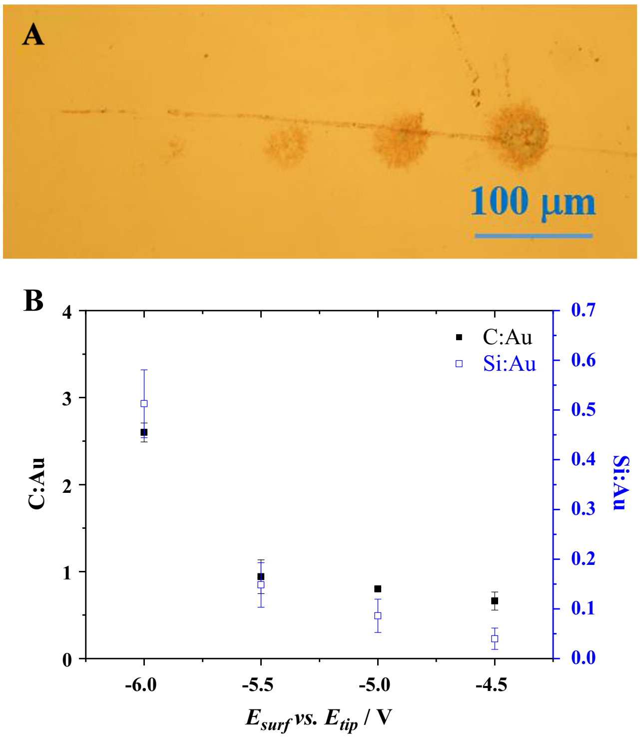

Fig. 1. Optical image of CNT/silane films locally electrodeposited on Au at different potentials for 2 s (A). From left to right: −4.5 V, −5.0 V, −5.5 V and −6.0 V (E_{surf} *vs.* E_{tip}). The C:Au and Si:Au atomic ratio of the local deposits as measured by EDX (B).

3. Results and discussion

Fig. 1A shows the optical image of locally electrodeposited CNTs with silane. The depositions were generated by applying different potentials between the Au surface and the Pt microelectrode. Black colored spots can be clearly seen when the potential on the gold surface was more negative than −4.5 V (*vs.* Pt microelectrode). This suggests that local depositions were formed, which originated from the current flux under the microelectrode. The latter caused the local pH increase on the gold substrate (cathode), catalyzing the sol–gel deposition which embedded the CNTs. Moreover, the spots are larger and darker as the potential of the gold surface was more negative. This is due to the increasing deposition current at more negative potentials, which facilitated the deposition, but increased the area of the pattern and might induce intensive hydrogen evolution. EDX measurements were further carried out to examine the spots. As compared with the substrate, the spots have much higher C and Si signals. This confirms that the depositions consisted of silane with CNTs. It should be noted that Au signals were also detected on the deposits, indicating that the electron beam penetrated to the substrate. Thus, the atomic ratio of C:Au and Si:Au reflects semi-quantitatively the content of CNTs and silane in the deposits. From Fig. 1B, it is seen that the ratios increase as the deposition potential was more negative, especially when it reached −6.0 V (*vs.* Pt microelectrode). This suggests that deposition is facilitated at negative potentials, which is in accordance with Fig. 1A. Furthermore, the C:Au and Si:Au have a similar trend as a function of deposition potential, indicating that the deposition of CNTs is driven by the entrapment in the electrodeposited silane films.

The effect of patterning time on the local deposition was also investigated. Fig. 2A demonstrates the optical image of CNT/silane locally electrodeposited at −5.0 V ($E_{surf.}$ *vs.* E_{tip}). It can be seen that the spots, which were deposited by applying potential for different durations, grow slightly larger and significantly darker upon prolonging the deposition time. The increase in the blackness of the spots suggests the increase in CNT content, which is confirmed by SEM and EDX. The SEM images show that the spot deposited for 2 s contains only a few CNTs (Fig. 2B), while much denser CNTs can be seen from the spot deposited for 10 s (Fig. 2C). The C:Au and Si:Au ratios of the spots as measured by EDX gradually increased as the deposition time increases (Fig. 2D), indicating that CNTs deposited with silane sol–gel films. It should be noted that deposition is fairly efficient indicated by the short time, *i.e.* a few seconds, that is required to clearly observe the deposited spots by optical microscopy. We further measured the height of the spots by profilometry. It is seen from Fig. 2E that the spots grew vertically almost linearly as a function of deposition time. All the results above suggest that prolonging the patterning time enhances the deposition of silane, which embedded the CNTs in the composite local depositions.

Moreover, lines of CNTs with silane were also patterned by laterally scanning the biased microelectrode. The width of the lines is *ca.* 50 μm, which is about two times the diameter of the microelectrode. As the scan rate increased, the lines became lighter colored, suggesting less deposition of CNTs. The EDX results show that the C:Au and Si:Au values decreased upon increasing the scan rate (Fig. 2F). This indicates that less CNTs and silane were deposited at higher scan rate, which is attributed to less deposition time per unit area.

The CNTs could also be patterned on the stainless steel surface. Fig. 3A depicts the SEM image of the CNT/silane spots locally electrodeposited at −4.5 V ($E_{surf.}$ *vs.* E_{tip}) for different durations. The spots look similar, but the magnified images show a significant increase in the density of CNTs as the deposition time increased (Fig. 3B and C). This suggests that prolonging the deposition time also facilitated the deposition of CNTs. Line patterns could also be generated, and the blackness of the lines decreased as the scan rate of the microelectrode increased (Fig. 3D). The line patterned at 20 $\mathrm{μm \cdot s^{-1}}$ is hardly seen. These trends