

Room-temperature fabrication of high-resolution carbon nanotube field-emission cathodes by self-assembly

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In this letter, we report a process for *room-temperature* assembly of patterned and periodic structures of carbon nanotubes (CNTs). Well-defined patterns with less than a 10- μm linewidth and variable thickness were readily deposited. The CNTs show long-range in-plane orientation ordering and adhere strongly to the substrates. The self-assembled macroscopic structures emit electrons under applied electrical field with the emission characteristics comparable to those from the high-temperature or/and low-resolution deposition processes. This room-temperature self-assembly method can be utilized for assembly and integration of nanostructured materials for a variety of devices, including the field-emission displays. © 2003 American Institute of Physics.

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Carbon nanotubes (CNTs)¹ have recently emerged as a promising class of electron field-emission materials² with a low-threshold field for emission and sustainable high-emission current.^{3–7} They are being actively investigated as the next generation of electron sources for a variety of vacuum electronic devices.^{8–10} For CNTs to become a viable engineering material for device applications, efficient assembly and integration processes are required that are currently lacking. Among the synthesis methods developed to date, chemical vapor deposition (CVD) is the only one capable of directly depositing CNT and CNT-like materials on device surfaces. However, the requirements of high temperature (typically $>800^\circ\text{C}$) and reactive environment have prevented its application from devices with limited thermal and/or chemical stability, such as field-emission displays (FED), which use low-melting-temperature glass substrates¹¹ and polymeric systems. Several techniques have been developed to assemble/integrate preformed nanostructures into functional hierarchical structures under mild conditions.¹² Screen-printing is currently used to fabricate CNT cathodes for FEDs.⁸ Among other issues, this approach suffers from low resolution and inefficient use of material.

We have recently shown that functionalized CNTs can self-assemble into uniform and ordered forms.¹³ Here we demonstrate that patterned and periodic CNT structures can be assembled on various substrates by a dip-coating process^{14,15} at *room temperature*. Structures with a less than 10- μm linewidth were obtained using template substrates. The emission characteristics of these self-assembled struc-

tures are characterized. The threshold field for 10 mA/cm² current density was found to be 6 V/ μm .

Purified single-walled carbon nanotube (SWNT) bundles produced at UNC¹⁶ were used as the starting material. They were chemically processed to be hydrophilic with controlled aspect ratios¹⁷ and were then vacuum annealed before use. A representative transmission electron microscope (TEM) image of the SWNT bundles after processing is shown in Fig. 1(a). The chemical treatment did not alter the basic structure of the SWNTs: the vibration frequencies of the Raman-active breathing and tangential modes remain the same [Fig. 1(b)]. Fourier-transform-infrared (FTIR) spectroscopy showed a strong C=O stretching mode at 1727 cm⁻¹, suggesting that defects were created and the dangling bonds were terminated by COOH groups, as previously reported.¹⁸

Substrates to be deposited with CNTs were first patterned with alternating hydrophobic and hydrophilic regions that are 10–100 μm in linewidth, as illustrated in Fig. 2. Two types of substrates were prepared for the CNT deposition. All the substrates were first coated with a thin layer of photoresist (Shipley 1813). In the first case, the pattern was created on a hydrophilic substrate, such as glass, by the standard photolithography method, using a printed polymer foil as the photomask (Fig 2, step 2a). In the second case, to provide a better electrical conduct, the hydrophilic substrates were metallized by thermal evaporation and photoresist lift-off (Step 2b). After UV ozone cleaning, solution silanization by 1 mM octadecyltrichlorosilane (OTS) in the mixed solvent of hexadecane and tetrachlorocarbon was performed in a dry box (step 3b).¹⁹ The processed substrate was then sonicated in chloroform and ethyl alcohol before use.

A homogeneous suspension of the SWNTs was stabilized in deionized water at a nanotube concentration up to

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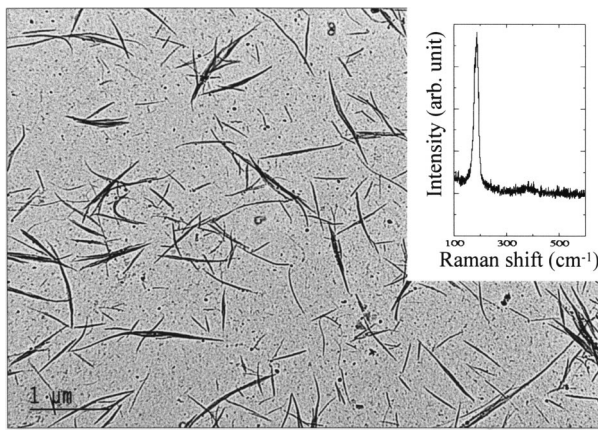


FIG. 1. Transmission electron micrographs of the processed SWNTs with average bundle lengths of 1–2 μm . Inset: Raman spectrum of the processed SWNTs showing the characteristic breathing mode.

1.0 g/L. The patterned substrate was submerged vertically into the SWNT/water suspension at room temperature. The nanotubes assembled along the water–substrate–air triple line on the hydrophilic regions of the substrate. As the triple line moved downward when the water gradually evaporated, a continuous SWNT film formed. The nanotubes adhered strongly to the hydrophilic substrate and cannot be removed by washing in solvents such as methanol, ethanol, and buffered hydrofluoric acid. This enabled the removal of the photoresist after CNT deposition. The bonding is attributed to the interaction between the -OH groups on the glass substrate and the functional groups that terminate the CNT defect sites.

As shown in Fig. 3, well-defined CNT patterns with a linewidth as small as 10 μm were obtained by this dip-coating process. At present, the linewidth is limited by the resolution of the printed polymer photomask rather than by the deposition method. The SWNT stripes have stepwise sharp edges at the interfaces and are smooth and continuous. The electrical conductivity of the self-assembled film deposited on an insulating surface was measured to be 0.2 S/cm at

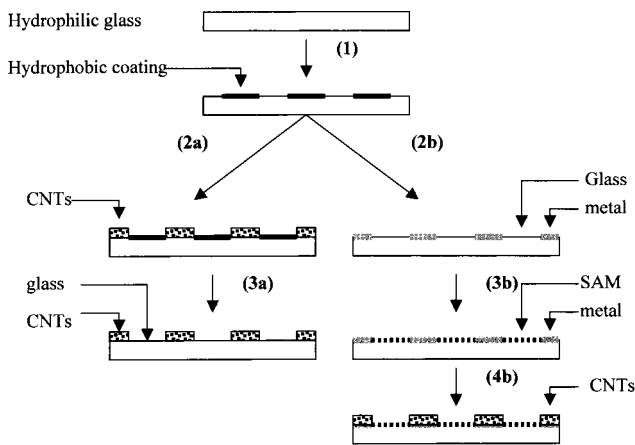


FIG. 2. A schematic illustration of the fabrication process: (1) a hydrophilic glass substrate is patterned with a layer of hydrophobic photoresist by photolithography. (2a) SWNTs are deposited on the hydrophilic regions of the substrate (exposed glass surface) by the self-assembly process. (3a) Removal of the hydrophobic polymer coating by washing the SWNT coated substrate in acetone. (2b) Metallization of metals (Cr/Al) and photoresist lift-off. (3b) Attachment of OTS molecules on hydroxyl terminated glass surface. (4) Deposition of CNTs on metal strips.

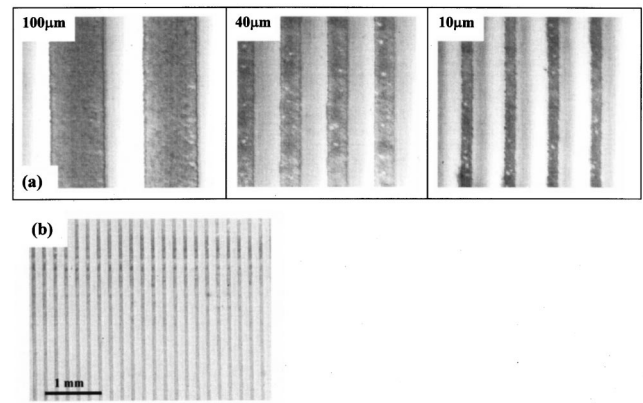


FIG. 3. Optical microscope images of the SWNTs deposited on glass (a) and aluminum (b) surfaces. The linewidths of the SWNT stripes in (a) are 100, 40, and 10 μm , respectively. The shadows in (a) are due to reflections from the surface underneath the glass substrate. The films were obtained at a deposition rate to 15 mm/day.

room temperature. For comparison, the conductivity of the freestanding SWNT membranes fabricated in our lab is ~ 0.3 S/cm.

The film thickness and the uniformity depended on the concentration of the suspension and the evaporation rate. Thick films were obtained at high concentration and low evaporation rate. In the case of water the thickness of the CNT film decreases with increasing temperature. The film became discontinuous when the temperature was raised above 40 $^{\circ}\text{C}$. The same phenomenon was observed when water was replaced by another fast-evaporating solvent, such as ethyl alcohol. Temperature fluctuation during deposition resulted in variations in the film thickness due to change in the solvent evaporation rate. Films of short SWNTs tend to be more uniform than those of long tubes, which is related to the difference in the quality of the suspension. In some cases streaks running parallel to the deposition direction were observed on the CNT films. This is attributed to the instability of receding fluid at the interface.^{20,21}

Similar to the CNT films assembled on chemically homogeneous structures reported previously,¹³ the SWNT bundles within each stripe are aligned in-plane along the water/substrate/air triple line direction. However, for the patterned substrate, the triple-line changes from parallel to the deposition direction at the interface between the hydrophobic

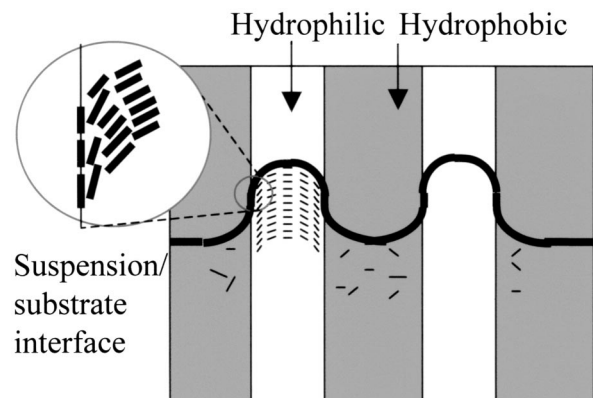


FIG. 4. An illustration of the gradual change of the CNT orientation on the patterned substrate.

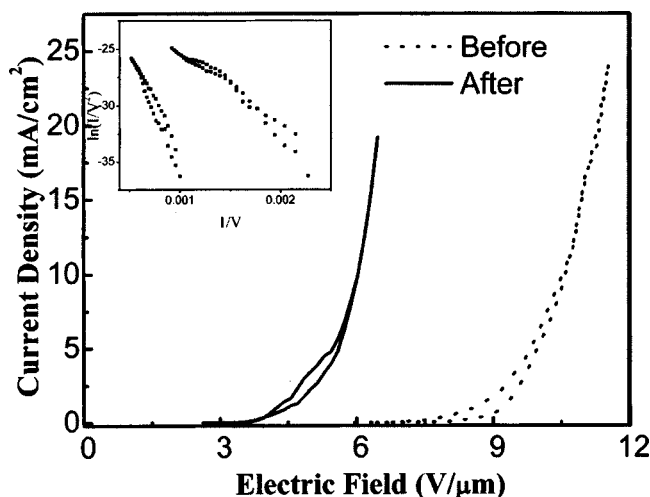


FIG. 5. Field-emission characteristics of a self assembled CNT film. The data was collected with a hemispherical tip (5-mm radius) as the anode and a cathode-anode distance of 168 μm . Solid line plot is after the conditioning process. Inset is the Fowler-Nordheim plot of the same data. After the first measurement, a relatively high electrical field was applied between the anode and the cathode for a short time. The threshold field for emission was substantially reduced after the conditioning process.

and hydrophilic region to perpendicular to the deposition direction in the middle of the hydrophilic region for each strip, as illustrated in Fig. 4. As a result, the orientation of the SWNT bundles changes gradually from parallel to perpendicular to the deposition direction between the edge and the middle point of each stripe. This is confirmed by TEM images of the SWNT film carefully removed from the substrates. The overall orientation of the SWNTs depends on the width of the stripes. For relatively large stripes, the preferred direction is perpendicular to the deposition direction.

The electron field-emission characteristics of these self-assembled SWNT films were measured in a vacuum chamber at 5×10^{-7} Torr base pressure. To provide electrical contact to the SWNTs, two Cr strips were evaporated on the edges of the SWNT strips. Figure 5 shows the emission $I-V$ characteristics of a patterned film (100- μm linewidth, 300- μm pitch), with 5- μm -length SWNT bundles. The data were collected with a hemispherical tip (5-mm radius) as the anode and a cathode-anode distance of 168 μm . In the first measurement, the threshold electric field for 10 mA/cm^2 current density was found to be 11 $\text{V}/\mu\text{m}$. It was substantially reduced after an electrical conditioning process.²² For the same sample, the threshold field was lowered to 6 $\text{V}/\mu\text{m}$ after the treatment, which is comparable to what we previously reported for free-standing membranes of long SWNT bundles (4–7 $\text{V}/\mu\text{m}$ for 10 mA/cm^2).⁶

In these self-assembled cathodes, the SWNTs are aligned in-plane on the surface of the substrates. Similar to the previous report of field-induced alignment of an isolated SWNT,⁷ we believe that when the applied field is high enough, the SWNT bundles first bend and protrude along the field direction, and then emit electrons from the tips. As a result, the threshold field depends on both the aspect ratio of the nanotubes and the interaction between the CNTs and the substrates. The activation process is believed to remove the “hot” spots on the cathode and to make it easier for the

CNTs to protrude along the field direction thus reduces the threshold field.

The electron field-emission characteristics of these self-assembled structures compare favorably with those from the CVD-grown CNTs^{23,24} and cathodes by the screen-printing methods.²⁵ Emission cathodes with a much higher pixel resolution can be obtained from the self-assembly process compared to what is afforded by the thick-film technique. The process is versatile, and similar results have been obtained from both SWNTs and multiwalled carbon nanotubes on a variety of substrates, such as Si, glass, ITO-coated glass, Al, and Cr. It is potentially a viable process for assembly and integration of nanostructured materials for device applications, including field-emission displays. Work is in progress to increase the deposition rate and the uniformity over large areas.

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