

Pattern Transfer Printing of Multiwalled Carbon Nanotube Multilayers and Application in Biosensors

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We developed a simple, versatile technique to pattern multiwalled carbon nanotubes on any substrate. This approach involves the multilayer assembly of multiwalled carbon nanotube (MWNT) suspensions with opposite charges onto the patterned poly(dimethylsiloxane) via layer-by-layer assembly, followed by the pattern transfer onto various substrates, including silicon wafer, transparent glass slide, flexible and conducting polymeric substrate. The transferred MWNT pattern was precisely tunable with the thickness and exhibits a capacitor behavior that increases with growing film thickness. By taking advantage of patterned electrodes with high surface functionality within a MWNT network, we demonstrate the potential application of patterned MWNT electrodes as sensitive biosensor for glucose. Because of the characteristic electronic properties of carbon nanotubes, we anticipate this approach would provide a new route to integrating an active MWNT matrix for advanced electronic, energy, and sensor applications.

With their unique physical, chemical, and mechanical properties, carbon nanotubes (CNTs) offer promising opportunities in the design of functional thin films including catalytic membranes, biosensors, energy and electronic devices, and mechanical thin film applications. As these and other applications of CNT films become more sophisticated, it is critical to develop efficient strategies for controlling the architecture, geometry, and positioning of CNT arrays at the micrometer- and nanoscale to tailor film properties and functionality. Recent progress in patterning CNT thin films includes patterned catalysts for CNT

growth,^{1–4} adsorption onto a chemically modified surface,^{5–7} or manipulation with external fields and flows;^{8–11} however, patterning CNT films over large areas in a simple, reliable, and convenient manner continues to be a challenging endeavor.

Alternatively, the development of a new CNT thin film fabrication technique that relies on solution-based processing is particularly attractive because of the associated mild conditions and the ability to produce well-defined nanostructures with precisely controlled positions. Layer-by-layer (LbL) assembly is well-suited to these purposes, as it can create highly tunable, conformal thin films with nanoscale control over the film composition and structure.^{12,13} There have been approaches in coupling the unique properties of CNTs with the versatility of LbL assembly for electronic and biomaterial surfaces.^{14–16} For example, we have recently demonstrated a new method for the generation of all-MWNT multilayers.¹⁴ Moreover, the direct pattern transfer of multilayer films built on poly(dimethylsiloxane) (PDMS) has recently been shown to be a facile means to fabricate

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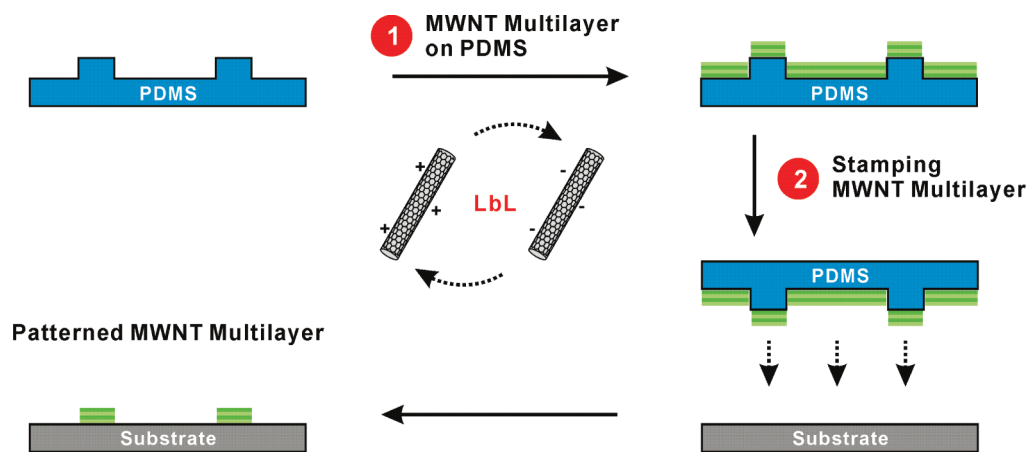


Figure 1. Schematic representation of MWNT multilayer pattern transfer process. Layer-by-layer assembled MWNT multilayer directly on top of patterned PDMS was stamped onto the receiving substrate.

patterned films with desired functionality onto various substrates.^{17–20}

With the combination of the unique features of CNTs for electronic components, multilayer self-assembly techniques, and soft lithography, herein, we present a simple and versatile method for fabricating and positioning micrometer-scale porous all-CNT structures with controlled nanoscale thickness. Specifically, multilayer thin films consisting *exclusively* of multiwalled carbon nanotubes (MWNTs) are assembled directly atop patterned PDMS stamps and transferred onto various substrates. This is important in that we can take advantage of the unique properties of MWNTs without incorporation of other organic materials that can potentially sacrifice the intrinsic electrochemical or electronic properties of MWNTs; we can also generate patterned MWNT networks without any prior surface templating, thus avoiding issues of selective deposition, masking, or etching while using minimal process steps. Finally, we demonstrate the use of this approach to generate microscale devices by stamping a patterned biosensor that can selectively and quantitatively detect the glucose.

Initially, a stable aqueous solution of chemically modified MWNTs was prepared based on a previous report. Negatively charged MWNTs with carboxylic acid (MWNT-COOH) groups were prepared by oxidation in strong acids.^{14,21} Further reaction with excess ethylenediamine afforded the positively charged MWNTs with free amine groups (MWNT-NH₂).^{14,22} X-ray photoelectron spectroscopy (XPS) confirmed the presence of the reactive functional groups on the surface of MWNTs (See Supporting Information). According to the zeta potential measurement, both chemically functionalized MWNT suspensions have a sufficient colloidal stability with a respective zeta potential of +43 mV (MWNT-NH₂, pH 2.5) and –35 mV (MWNT-COOH, pH 3.5) under the pH conditions examined (See Supporting Information). The

solutions remained clearly dispersed for more than a month following pH adjustment at a concentration of 0.50 mg/mL of MWNTs. It is worth noting that the negatively charged MWNT-COO[–] preserves a high degree of ionization even in low pH condition (pH 3.5), whereas common poly(carboxylic acid)s do not retain sufficient charges under similar pH conditions. This could be attributed to a considerably lower pK_a value of the MWNT-COOH because of the sp² characteristics of conjugated carbon nanotube backbone and the shift in pK_a often observed with polyvalent ionic species such as polyelectrolytes as a function of charge density.¹⁴

With these stable MWNT suspensions, MWNT films are constructed via LbL assembly directly on a micrometerscale patterned PDMS stamp based on the electrostatic interactions between positively charged MWNT-NH₃⁺ and negatively charged MWNT-COO[–] (Figure 1).

To achieve a complete transfer of MWNT film onto a desired substrate, it is critical to tailor the adhesion of the MWNT multilayer film between the PDMS surface (where it is assembled) and the substrate (where it will be transferred). Even though the PDMS interface with the multilayer is weak because of the low surface energy of PDMS (19.8 mJ/m²),²³ the fine control over the weak hydrophobic interactions of the PDMS interface with the multilayer compared to strong attractive electrostatic interactions between the MWNT top layer and the substrate is a prerequisite to ensure the successful pattern transfer upon contact. Unlike our previous reports that employed the adsorption of a hydrophobic weak polyelectrolyte, poly(allylamine hydrochloride) (PAH), on a PDMS stamp as a priming layer,^{17,18} we found that the affinity of MWNT-NH₃⁺ to hydrophobic PDMS was sufficient to create the initial deposition of MWNTs onto the PDMS. Following the deposition of a MWNT-NH₃⁺ priming layer, the MWNT multilayer was created by sequential deposition of MWNT suspensions with opposite charges in an architecture of PDMS/MWNT-NH₃⁺/(MWNT-COO[–]/MWNT-NH₃⁺)_n (typically, *n* = 5, 10, 20, and 30 bilayers),

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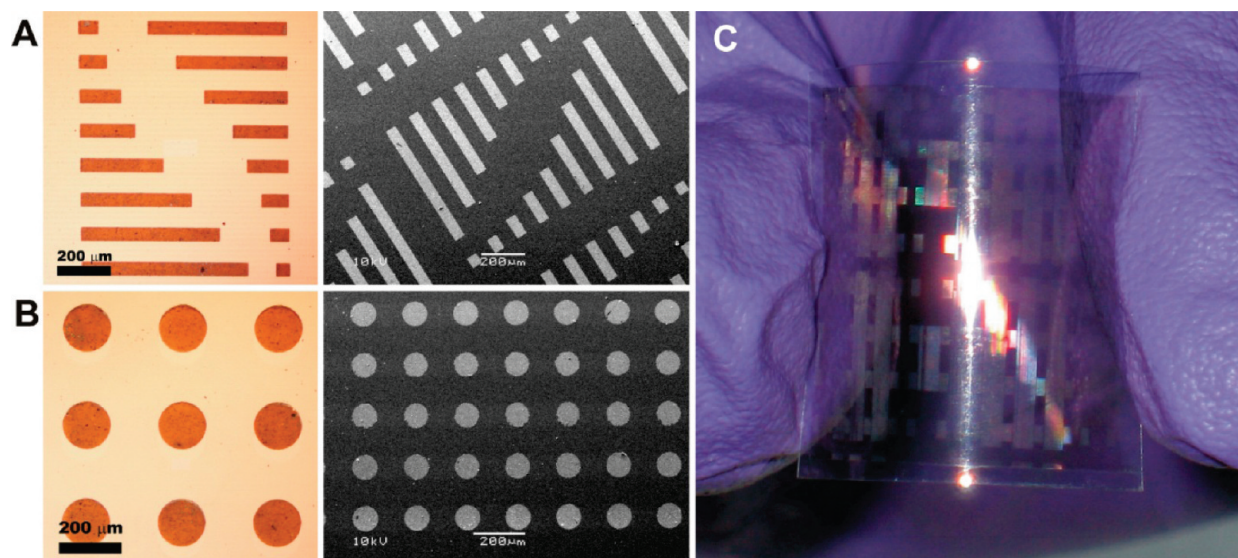


Figure 2. (a, b) Representative (left) optical microscope and (right) SEM images of patterned MWNT multilayer film on a silicon wafer, (c) photograph of MWNT pattern transferred on a flexible ITO-coated PET film. All are 5 bilayers of MWNT film.

with a positively charged MWNT-NH₃⁺ as a final top layer. The build-up of the MWNT film was also confirmed with a control experiment in which MWNT multilayers were deposited on a non-patterned silicon wafer; the control film exhibited a gradual linear growth of multilayers with an average bilayer thickness of 9.8 nm under the same LbL conditions (pH 3.5 (−)/2.5 (+)). This average bilayer thickness is comparable to our previous report describing 13.8 nm per bilayer with similar LbL conditions but with a longer deposition time (30 min per each layer).¹⁴

The patterned MWNT film on a PDMS was stamped onto various substrates such as a glass slide, indium tin oxide (ITO)-coated glass, silicon wafer, and ITO-coated poly(ethylene terephthalate) (PET), which were pre-treated with O₂ plasma for the development of negative surface charged groups (Figure 2). We observed that the quality of pattern transfer dramatically improved by addition of a drop of water on the MWNT film surface prior to stamping, to enhance the flexibility of the multilayer film and the contact between the film and the substrate. Moreover, a slight pressure of a few bars was essential for conformal contact during the pattern transfer. Pressure was applied via a pair of paper clips, and held for 3 h prior to release of pressure and removal of the stamp. Insufficient time or pressure during the transfer leads to a partial transfer of the film with a residual film remaining on the PDMS stamp. With the optimum conditions, the MWNT multilayer is transferred entirely to the substrate, resulting in a patterned multilayer thin film on the substrate with high fidelity. Successful pattern transfer was achieved irrespective of the pattern size or shape, as shown in Figure 2. The MWNT multilayer transfer printing was reproducible over a 2 × 2 cm² area (the entire area of the PDMS patterned stamp) and could possibly extend to even larger areas. Interestingly, a 5-bilayer MWNT multilayer was successfully transferred onto a flexible ITO-coated PET substrate, proving the generality of this method to any substrate (Figure 2c).

This result also demonstrates the possibility to design flexible CNT devices that can utilize LbL assembled MWNT multilayers as flexible electrodes, electrical circuits, and current collectors. Independent of our report, it is worth noting that Rogers and co-workers have demonstrated a similar pattern transfer of single-walled carbon nanotube (SWNT) multilayer onto various target substrates by depositing a thin layer of Au and polymers as a carrier layer to transfer as-grown SWNT multilayers.²⁴ Also, Zhou and co-workers have recently reported the fabrication of aligned SWNTs with a pattern transfer method for application in transparent thin film transistors.²⁵ Unlike these systems, which used additional materials such as gold or polymeric systems, we can directly transfer MWNT porous thin films to a number of electrode surfaces without introduction of additional materials that might hinder electrochemical and/or electronic performance, limit conditions of operation for the resulting device, and/or require additional processing steps for removal. Furthermore, the MWNT systems described here create highly porous networks with unique capacitive¹⁴ and catalytic capabilities.²⁶ Finally, the LbL method can be extended to a range of thicknesses with a great deal of control, and does not require extreme process conditions to generate the MWNT array.

In comparison to the pattern transfer printing approach we employed here, we also considered the concept of directly stamping a single MWNT layer onto a neutral surface, and using it as a template for directed and selective deposition of additional MWNTs via LbL assembly. Control experiments of direct contact printing using MWNT as an ink (a suspension of MWNT-NH₃⁺) on a silicon wafer, followed by additional LbL deposition

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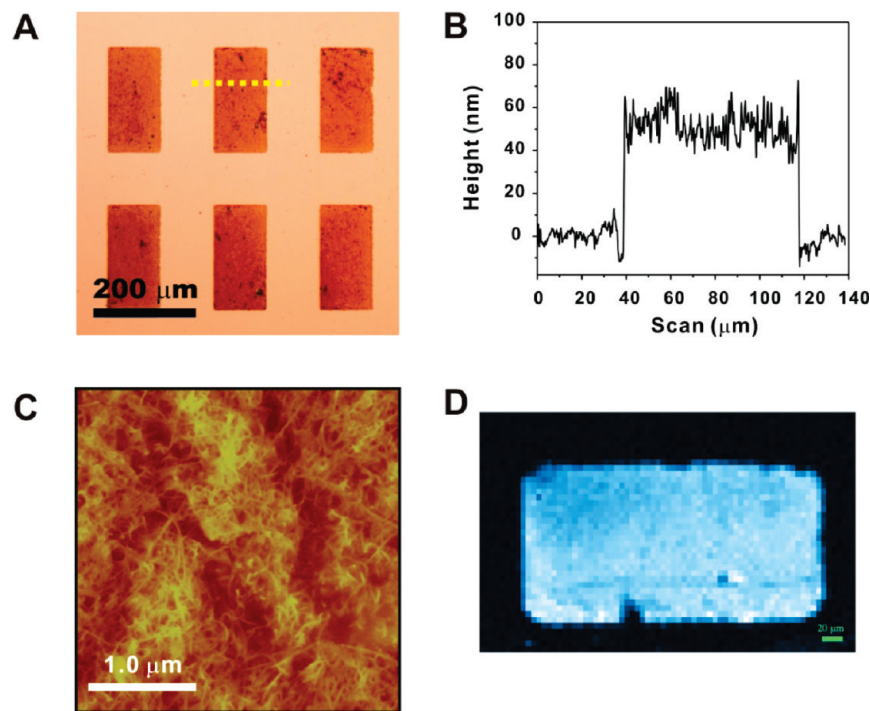


Figure 3. (a,b) Optical microscope image and corresponding surface profile of pattern transferred 5 bilayer MWNT film on a silicon wafer. (c) Height-mode AFM image of pattern transferred 30 bilayer film (scan size of $3 \times 3 \mu\text{m}^2$, Z-scale of 100 nm). (d) Raman mapping of pattern transferred 30 bilayer film on a silicon wafer (rectangular pattern of $100 \times 200 \mu\text{m}^2$ with a scale bar of $20 \mu\text{m}$). The surface profile was collected with a surface profilometer (Tencor P-16). The Raman mapping was based on baseline-subtracted integration of the D (1334 cm^{-1}) and G (1592 cm^{-1}) peaks from MWNTs.

of MWNT atop resulted in poorly defined pattern formation possibly because of the low degree of surface coverage of the initial layer and the lack of surface charge difference (See Supporting Information).

As mentioned, a unique feature of this pattern transfer method over other conventional means can be further demonstrated by controlling the average thickness of films on the substrate with the number of bilayers initially deposited on a PDMS stamp before pattern transfer (Figure 3). As shown in Figure 3, the thickness of the pattern transferred MWNT multilayers increased linearly with increasing numbers of bilayers, which is in close accordance with thicknesses measured on silicon for non-transferred films of the same number of bilayers. For example, the 5 bilayer film deposited on a silicon wafer was 45 nm, which is similar to the thickness of the transferred film ($51 \pm 7 \text{ nm}$). Additional evidence is presented with the 10 and 30 bilayer films transferred, showing a good agreement of film thickness with the directly adsorbed non-patterned control films (See Supporting Information). One interesting observation is that the thicker 30 bilayer film is considerably rougher than the thinner 5 and 10 bilayer films because of an increase in surface roughness with increased film thickness. The morphology of the top surface of the transferred pattern of 30 bilayer films exhibits an intertwined network structure of MWNTs under the examination with AFM (Figure 3c) (root-mean-squared roughness is 14 nm). This is in clear contrast to that of MWNTs cast on a plain substrate, which produces aligned MWNT structures without much of pore generation. We have also observed a clearly recognizable pattern by taking a baseline-subtracted

area map of D (1334 cm^{-1}) and G (1592 cm^{-1}) Raman modes of MWNTs (Figure 3d). The Raman spectra (See Supporting Information) displayed characteristic features of chemically functionalized MWNTs including high D (disorder due to sp^3 carbon bonds) and G (C–C stretching in graphitic lattice) modes with a clear contrast to the background free of any MWNTs.

The electrochemical properties of patterned MWNT films (rectangular patterns of $100 \mu\text{m} \times 200 \mu\text{m}$) on ITO-coated glass was investigated after heat treatments ($150 \text{ }^\circ\text{C}$ in vacuum, and $300 \text{ }^\circ\text{C}$ in H_2) with cyclic voltammetry in oxygen free 1.0 M KCl solutions by bubbling ultra high-purity argon gas for at least 30 min. Thermal cross-linking of the MWNT films not only prevents swelling from electrolytes but also provides mechanical strength to prevent delamination of the patterns from the substrate during the electrochemical measurement. Cyclic voltammograms of stamped MWNT films were obtained as a function of the number of bilayers at 50 mV/s (Figure 4). In these studies, the microcapacitor films were of the size of $100 \times 200 \mu\text{m}^2$ size, and the patterned films covered approximately 45% of the ITO electrode area of $2.5 \times 7.5 \text{ cm}^2$ in width and length, thus about a thousand of the MWNT microstructures were examined at once. The thickness dependent voltammetry curves showed considerably rectangular shapes, which is indicative of the capacitive behavior of carbon materials as reported in the case of the non-patterned all-MWNT multilayer thin film.¹⁴ In addition, these patterned electrodes can sustain capacitor behavior at various scan rates (10–100 mV/s), as shown by the rate-dependent cyclic voltammograms of the 30 bilayer film (Figure 4d). Integrated surface charges

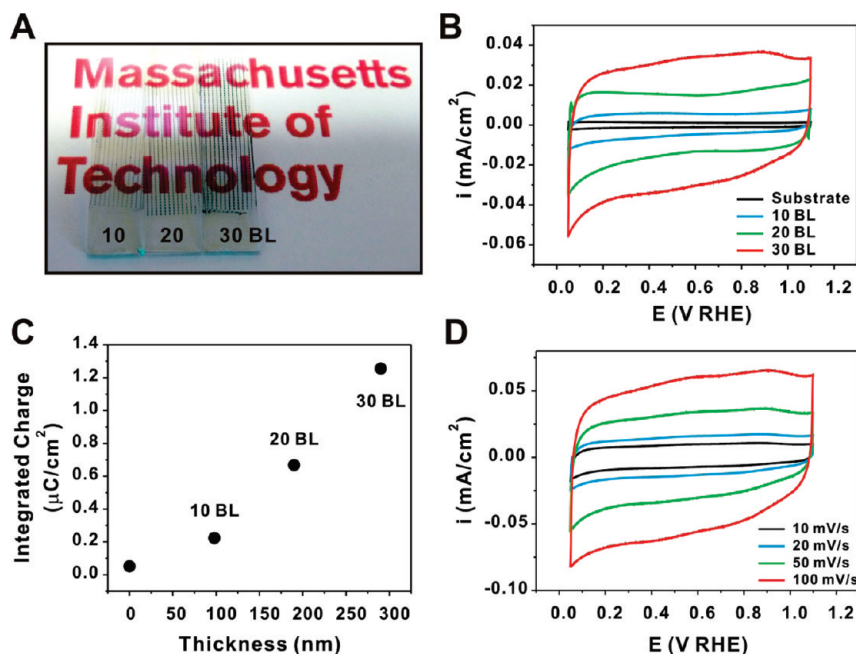


Figure 4. (a) Photograph of MWNT patterns transferred on ITO-coated glass electrodes (10, 20, and 30 bilayers) (rectangular pattern of $100 \times 200 \mu\text{m}^2$). (b) Cyclic voltammograms obtained from MWNT thin films from (a) in 1.0 M KCl at room temperature after heat treatments (150°C in vacuum and 300°C in H_2). A scan rate of 50 mV/s was used. (c) Integrated charge per geometric area of MWNT thin films from cyclic voltammograms vs thickness of film. (d) Cyclic voltammograms of 30 bilayer film with various scan rates.

per geometric area from adsorbed and desorbed ions on the MWNT thin film electrodes were also found to scale linearly as a function of film thickness (Figure 4c), showing a linear increase in the capacitance of the patterned electrodes with film thickness. Volumetric capacitance of $\sim 100 \text{ F}/\text{cm}^3$ was obtained on non-patterned MWNT film in neutral electrolyte (1.0 M KCl), and this is slightly lower than previously reported $\sim 130 \text{ F}/\text{cm}^3$ in acidic electrolytes (1.0 M H_2SO_4). The precise control of the energy capacity of the patterned electrodes, combined with the controlled shape and the thickness of the pattern on various substrates, shows the potential to design the electrodes for micrometer-scale energy devices and sensors.

To test the potential of the pattern transfer and the electrochemical properties of the MWNT multilayer as a platform for biological sensors and analytical tools, we have demonstrated the MWNT film as a biosensor for glucose detection (Figure 5). First, a MWNT multilayer pattern (5 bilayer) was transferred onto an interdigitated microelectrode array (IDA), and then glucose oxidase (GOx) enzyme was covalently immobilized to the surface carboxyl groups of MWNTs via an *N*-ethyl-*N'*-(3-dimethylaminopropyl)carbodiimide methiodide (EDC) mediated reaction (Figure 5a,b). According to the colorimetric assay with *o*-dianisidine, we found the amount of GOx on the film is 2.1×10^4 units per gram of MWNT (See Experimental Section for details). After GOx immobilization, the patterned MWNT film on IDA exhibited ohmic contact, as observed in current–voltage characteristics, without significant loss in conductivity (ca. 72% conductivity compared to the original) (Figure 5c). This result indicates that the pattern transfer enabled the MWNT multilayer to make reliable electrical contact with the electrodes. Considering that most CNT biosensors have

depended on the use of sophisticated lithographic techniques to integrate CNTs to an electrode substrate, our approach is straightforward and enables a fine control over the position and thickness of CNT films. As illustrated in Figure 5a, the glucose-GOx interaction on the electrode surface yields reaction products such as hydrogen peroxide that can affect the charge transport property of CNTs.^{27,28} A liquid-gated field-effect transistor (FET) configuration was constructed using the IDA to monitor the glucose-GOx interaction.^{29,30} The two gold electrode bands of the IDA (Figure 5b) served as source (S) and drain (D) electrodes, respectively. The MWNT film on IDA was immersed in a phosphate-buffered solution (10 mM, pH 7.0), and the gate potential (E_G) was applied between the Ag/AgCl reference electrode and the source electrode through the buffer solution. Figure 5d shows the response of an enzyme-MWNT film upon a serial addition of glucose with varying concentrations that are in the ranges of biological significance. The I_{SD} was monitored in real time at $V_{\text{SD}} = 1 \text{ mV}$ and $E_G = 1 \text{ mV}$. Upon each addition of glucose analyte (except buffer solution), the I_{SD} increased gradually and reached a saturated value. The modulation in I_{SD} was directly dependent on the concentration of glucose, as shown in the calibration curve (Figure 5e). A control experiment was further performed using patterned MWNT film without GOx attached. In this case, no remarkable response was measured under the same condition described above. The performance of this sensor is superior to what

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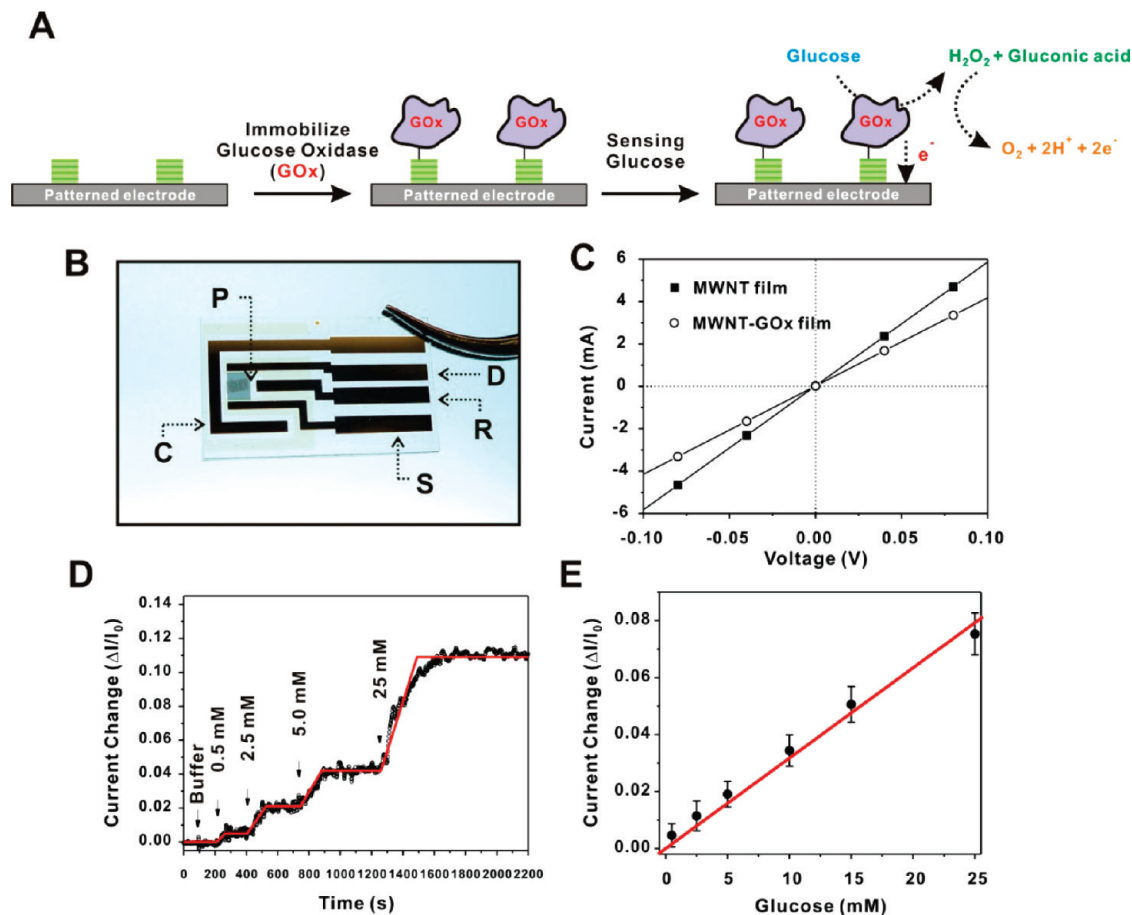


Figure 5. (a) Schematic illustration of patterned enzyme-MWNT film for glucose sensor. (b) Photograph of patterned enzyme-MWNT film on IDA (the patterned MWNT film (P), source (S), drain (D), reference (R), and counter (C) electrodes are individually labeled). (c) Characteristic $I-V$ curve of (■) MWNT film and (○) MWNT-GOx film measured on IDA. (d) Real-time response of the sensor upon a serial addition of 0.5–25.0 mM glucose (the arrow indicates the addition of analyte solutions), and (e) calibration curve of the sensor (The sensitivity was determined as the current change measured when the saturated value is reached after the addition of glucose).

has been reported in the case of GOx-coated SWNTs biosensor, which did not have a quantitative reproducibility because of a high signal-to-noise ratio.³¹ This proof-of-concept biosensor of MWNT multilayer thin film provides several unique advantages, including the following: (1) the large numbers of MWNT network films in a microarray enables excellent device-level performance characteristics and good device-to-device uniformity, and overcomes the fluctuations that can be found with individual CNT device; (2) the direct incorporation of functional groups that are available for further functionalization with other molecules; and (3) the potential of selective positioning and fabrication of multisensing arrays onto various substrates. However, it should be also noted that we do not attempt to optimize the various parameters in the glucose biosensor application, which will be subject of our ongoing investigation.

In summary, the work presented here illustrates a simple, versatile technique to pattern MWNT multilayer devices on various substrates. Stable suspensions of MWNTs with oppositely charged surface groups were sequentially deposited onto a patterned PDMS stamp via

electrostatic layer-by-layer assembly. The resulting MWNT multilayer on a PDMS stamp was successfully transferred onto the receiving substrate with controlled thickness and shapes. The transferred MWNT film preserved the intrinsic capacitive and electronic properties of MWNTs. We have also demonstrated the potential application of patterned MWNT electrodes as sensitive glucose biosensors. Because of the highly versatile and tunable properties of LbL assembled thin films combined with a soft patterning technique, we anticipate that the general concept presented here offers a unique potential platform for integrating active nanomaterials for advanced electronic, energy, and sensor applications.

Experimental Section

Materials. Multiwalled carbon nanotubes (MWNT, 95% purity, length 1–5 μm , outer diameter 15 ± 5 nm) were purchased from NanoLab (Newton, MA) and chemically functionalized according to the published protocol¹⁴ to prepare the stable suspensions of MWNT-COOH and MWNT-NH₂. Poly(dimethylsiloxane) (PDMS) stamps were created by curing Sylgard 184 (Dow Chemical) on a patterned silicon wafer master at 60 °C for 8 h. Gold-patterned interdigitated array (IDA) electrode was purchased from Bio-Logic (Knoxville, TN). All other reagents and solvents were purchased from

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Aldrich and used as received. Silicon wafer, glass slide, and ITO-coated PET were cleaned extensively prior to the deposition.

Multilayer Build-up onto PDMS Stamps. All MWNT multilayer films were assembled with a modified Carl Zeiss DS50 programmable slide stainer. Typically, films were constructed on a patterned PDMS with approximate size of $2 \times 3 \text{ cm}^2$. The substrate was first dipped into a MWNT-NH₃⁺ solution (pH 2.5, 0.50 mg/mL) for 30 min and rinsed three times with water (pH 2.5) for 1 min each. Subsequently, the substrate was introduced into aqueous solution of MWNT-COO⁻ (pH 3.5, 0.50 mg/mL) for 10 min, washed again three times with water (pH 3.5) for 1 min each. The same protocol was repeated for the suspension of MWNT-NH₃⁺ (pH 2.5, 0.50 mg/mL, 10 min dipping) to afford one bilayer of MWNT-COO⁻ and MWNT-NH₃⁺ with a notation of PDMS/MWNT-NH₃⁺/(MWNT-COO⁻/MWNT-NH₃⁺)₁. The dipping process was repeated until the desired number of bilayers (*n*) was obtained (typically, *n* = 5, 10, 20, 30).

Pattern Transfer Printing. The receiving substrates were treated with O₂ plasma (Harrick, Plasma Cleaner PDC-32G) for 2–5 min to develop the negative surface charges. After the plasma treatment, a 50 μL portion of water (pH 3.5) was spread onto the substrate, and MWNT film coated onto a PDMS stamp was placed directly on top with an additional silicon wafer to sandwich the PDMS stamp. A pair of paper clips was used to exert a pressure of a few bars to ensure the complete pattern transfer and was detached from the substrate after the complete drying of the water droplets (typically 3–6 h).

Patterned MWNT Film Characterizations. The surface morphology of patterned MWNT thin films were investigated using a scanning electron microscope (JEOL 6320 SEM) operating at 3.0 and 5.0 kV. Optical images were collected by using an Olympus microscope (IX51). Thickness and surface profile of MWNT thin films on silicon wafer was determined using a Tencor P-16 profilometer. Surface topology of MWNT thin films was examined using a Nanoscope IIIa AFM microscope (Digital Instruments, Santa Barbara, CA) in tapping mode in air. The root-mean-squared (rms) roughness of the films was examined from AFM images with a size of $5 \times 5 \text{ μm}^2$. Raman spectra were collected using LabRam HR800 Raman microscope (Horiba JY) with 632.8 nm HeNe laser excitation through a 10x objective (NA 0.25). A three-electrode cell was employed for electrochemical measurements, where a saturated calomel electrode (SCE) (Analytical Sensor, Inc.) and Pt wire were used as the reference and counter electrodes, respectively. MWNT thin films on ITO-coated glass slides were used as the working electrode. Cyclic Voltammetry was performed between -0.61

and 0.44 V (SCE) at room temperature in 1.0 M KCl solution using a bipotentiostat (PINE instrument).

Patterned MWNT Film Biosensor. The patterned MWNT film (5 bilayer) on IDA was treated with *N*-(3-dimethylaminopropyl)-*N'*-ethylcarbodiimide (EDC)/*N*-hydroxysuccinimide (NHS) (1.1 mmol/1.1 mmol) in distilled water. Subsequently, 0.20 mL of GOx (10 wt %) solution was reacted with the activated MWNT film on IDA. The terminal amine groups in lysine residues of GOx reacted with the carboxyl groups of the MWNT-COOH. For the glucose sensing experiment, a cylindrical solution chamber was designed and used for solution-based measurements. The gold IDA (65 fingers, 10 μm width, 2 mm length, 5 μm interfinger gap) substrate was immersed into a phosphate-buffered solution. Ag/AgCl ink was applied to a reference electrode. The current change measured was normalized as $\Delta I/I_0 = (I - I_0)/I_0$, where *I*₀ is the initial current and *I* is the measured real-time current.

Loading Amount of Glucose Oxidase (GOx) in MWNT Film. The patterned enzyme-MWNT film on IDA substrate was immersed in a 4.0 mL aqueous solution chamber and then 1.0 mL of glucose solution (0.10 M) was added into the chamber for the enzymatic reaction. The enzyme-MWNT substrate was removed from the reaction solution after 10 min, and 0.10 mL of peroxidase solution (0.20 wt %) and 0.20 mL of *o*-dianisidine solution (0.20 mM) were added into the solution. The mixture solution was incubated for 5 min, and the absorbance of the solution was measured at 416 nm by an UV/vis spectrometer (Perkin-Elmer Lambda 20). A standard curve of absorbance versus H₂O₂ concentration was plotted and used to determine the loading amount of GOx. All reactions were tested in a pH 7.0 phosphate-buffered solution at 25 °C. From the QCM measurement, the patterned MWNT film (5 bilayer) contained 4.4 μg MWNT, and the loading amount of GOx on the film was calculated to be 2.1×10^4 units per gram of MWNT. One unit of enzyme oxidizes 1.0 μmol of β-D-glucose to D-gluconolactone and H₂O₂.

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Supporting Information Available: Additional characterization data of XPS, Zeta-potential, SEM, AFM, and Raman spectra. This material is available free of charge via the Internet at <http://pubs.acs.org>.