Carbon Nanotube Arrays Encapsulated into Freely Suspended Flexible Films

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Introduction. Long-living freely standing organized micro- and nanostructures composed of nanowires and nanotubes are rarely demonstrated due to their extremely fragile nature. Instead, a vast majority of known nanostructures are fabricated and stay at solid surfaces which provide firm support but can severely alter their properties. Several rare examples of freely standing nanostructures include freely suspended carbon nanotubes (CNTs), nanotube forests, and multilayered films.[1−3] Here, we suggest a novel approach for the fabrication of free-standing microarrays of CNTs by encapsulating them into robust albeit compliant polymeric nanofilms. For such sandwiched structures only nanoscale compliant barriers (below 20 nm thick) stand between the sandwiched carbon nanotube arrays and the environment, which might expand the CNTs applications requiring robust elastic behavior, access (possibly controlled) to both sides, and in-plane anisotropic (e.g., conductivity) properties.

Freely suspended ultrathin (thickness of 100−1000 nm) films incorporating different functional nanomaterials have been recently suggested.[4−7] Freely suspended membranes containing nanoparticles have been fabricated by a number of approaches including layer-by-layer (LbL) assembly,[7] cast at air−water interfaces,[8] and spin-coating on sacrificial layer.[9] CNT-containing membranes have recently been demonstrated to show several interesting properties such as high tensile strength approaching that of hard ceramics,[7] electrical conductivity,[10] and controlled molecular transport.[11] On the other hand, freely suspended nanoscale (thickness below 100 nm) membranes containing gold nanoparticles with high elasticity and robustness have been recently fabricated.[12] These nanomembranes might serve as pressure or acoustic microsensors, replacing stiff silicon membranes.[13] Carbon nanotubes, with their excellent mechanical strength and unique electrical properties, represent excellent candidates for these multifunctional membrane sensors requiring high electrical conductivity and extreme robustness.[14]

Here, we demonstrate the successful fabrication of carbon nanotube microscopic arrays encapsulated into freely suspended LbL membranes by using spin-assisted LbL (SA-LbL) assembly and microcontact printing via sacrificial polymer patterning. Free-standing patterned polymer films have been fabricated by growth of polymer on a patterned self-assembled monolayer.[15] Patterned assembly on a polyelectrolyte multilayer has been previously demonstrated with colloids,[16,17] biological materials,[18−20] and nanoparticles.[21,22] These approaches involve patterning LbL multilayers by using polymer-on-polymer stamping or photolithography techniques or with subsequent selective adsorption controlled by electrostatic interactions.[23−25]

We show that the patterned array of carbon nanotubes can be incorporated in the freely suspended LbL membranes by using the micropatterned LbL surface as a template for subsequent nanotube assembly (Figure 1). In this method, the micropatterned surface composed of alternating open-protected surface areas was formed by the microcontact printing followed by CNTs selective adsorption onto the LbL multilayers. Removal of the protective polymer layer after the first step exposed electrostatically active surface areas, thus, allowing further deposition of LbL multilayers resulting in carbon nanotube arrays sandwiched between LbL films.

Experimental Details. *Materials.* Single-walled carbon nanotubes, produced by the arc discharge method, were purchased from Carbolex (Texas, U.S.A.). Stable dispersion of CNTs in aqueous solution (without surfactant) was prepared by oxidation in nitric acid (3 M, 45 h), filtration

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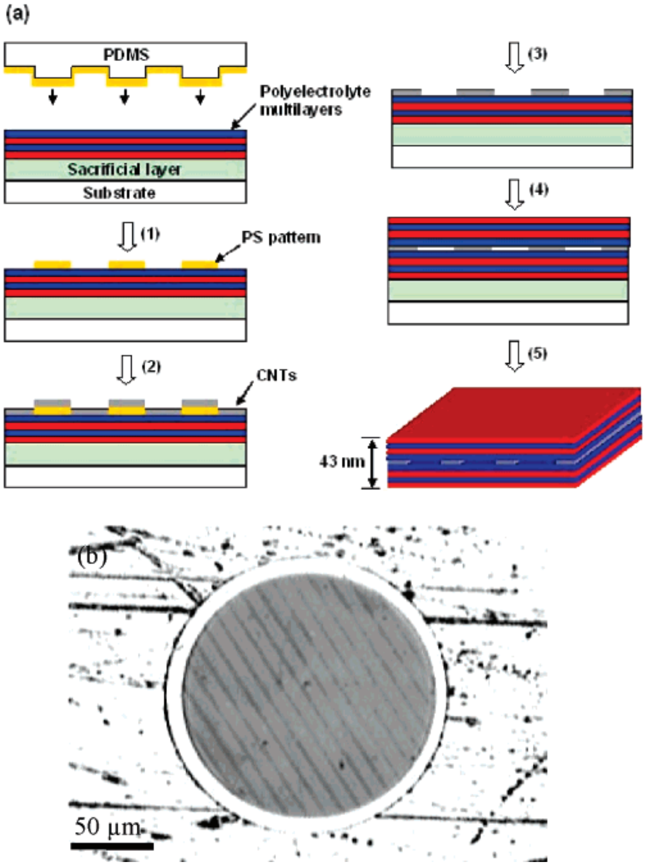

Figure 1. (a) Schematic illustration of the fabrication procedure of the freely suspended carbon nanotube arrays: (1) the microcontact printing of PS onto polyelectrolyte multilayers; (2) deposition of carbon nanotubes on the patterned substrates; (3) removing PS layers; (4) formation of topmost polyelectrolyte multilayers by LbL assembly; (5) releasing carbon nanotube arrays by rinsing away the supporting sacrificial film. (b) Optical image of freely suspended carbon nanotube array suspended over the 150 μm hole.

(0.4 μm pore size), and taking supernatant after high-speed centrifugation (18000 rpm, 1 h).[26,27] Poly(allylamine hydrochloride) (PAH, $M_w = 70000$) and poly(sodium 4-styrenesulfonate) (PSS, $M_w = 70000$) were purchased from Aldrich and used as received. PAH was chosen due to the fact that the amine groups in PAH polymer have strong interactions with carbon nanotubes with functional COOH groups.[7,28] For LbL deposition, PAH (0.2wt %) and PSS (0.2wt %) solutions were prepared with Nanopure water (18 MΩ cm). The (100) silicon wafers of 10 × 20 mm were cleaned in piranha solution (3:1 mixture of H_2SO_4/H_2O_2) for 1 h and then rinsed thoroughly with Nanopure water.

Fabrication of Freely Suspended Nanomembranes. For freely suspended nanomembranes, cellulose acetate (CA) was used as a sacrificial layer and LbL multilayers were prepared by the SA-LbL method as described in detail elsewhere.[12,29] The experimental procedure for patterned arrays of CNTs is outlined schematically in Figure 1. Sacrificial polystyrene (PS) micropatterns on LbL multilayer surfaces (PAH as a top layer) were obtained by microcontact printing of PS ink ($M_w = 200000$, 2% in toluene) with PDMS stamp.[30,31] Deposition of CNTs was accomplished by blow-drying CNT solution with N_2 gas on the PS patterned substrate. The sacrificial PS layer was rinsed away with toluene, leaving only the patterned array of the carbon nanotubes strongly attached to the LbL multilayer. On the other hand, this removal exposed intact PAH-covered surface areas. On top of this patterned surface, additional polyelectrolyte multilayers were deposited with SA-LbL assembly. By dissolving sacrificial supporting CA layer in acetone, we transferred the patterned nanomembranes on either a TEM grid or a copper substrate with a 150 μm opening. The overall microstructure is described as $(PAH/PSS)_9PAH/CNT/(PAH/PSS)_9PAH$. For confocal Raman mapping, the membranes were transferred on a glass surface.

Table 1. Mechanical Properties of Freely Suspended Membranes

name	thickness (nm)	CNT volume %	elastic modulus (GPa)	theoretical elastic modulus (GPa)
9CNT*9[a]	43	0.4−0.8	5.9 ± 0.9	5.5−9.5
9CNT9[b]	60	0.8−1.6	8.8 ± 2.1	9.5−13.5
9_9[c]	35	0	1.5 ± 1.0	NA

[a] $(PAH/PSS)_9/PAH/CNT/PAH(PAH/PSS)_9PAH$ with patterned carbon nanotube arrays. [b] $(PAH/PSS)_9/PAH/CNT/PAH(PAH/PSS)_9PAH$ with uniform carbon nanotube monolayer. [c] $(PAH/PSS)_{18}/PAH$.

Characterization. AFM scanning was performed in the tapping mode on a Dimension 3000 microscope (Digital Instruments) under ambient conditions. The micromechanical testing for the freely suspended nanomembranes was conducted according to the procedure described elsewhere.[12] Raman mapping and spectroscopy of the nanomembranes were conducted with a custom-designed confocal Raman instrument based on an Aurora-III near-field scanning optical microscope (DI).[32] A Nd:YAG laser (532 nm wavelength) was used as the light source.

Results and Discussion. The thickness of CNT nanocomposite films was about 43 nm (Table 1). The patterned nanotube array sandwiched between two LbL multilayers was transferred onto an opening in a copper substrate according to the usual routine and showed continuous parallel stripes with spacing of 10 μm (predetermined by a stamp spacing) extended over the whole opening area, which indicates intact carbon nanotube arrays after transfer (Figure 1b).

Figure 2a shows an optical image of the PS sacrificial micropattern on PAH-terminated LbL surface on a silicon wafer, which demonstrates its high quality across a whole view area (~400 μm). Actually, the patterned area was only limited by the physical dimensions of PDMS stamp (3 × 3 mm^2). The transfer of PS layers from PDMS stamp to PAH surface was efficient and driven by differences in surface energies between PDMS and PAH.[30,33] Figure 2b shows AFM topographical images of the PS micropattern with close to ideal, rounded, semi-cylindrical shape of PS layers with

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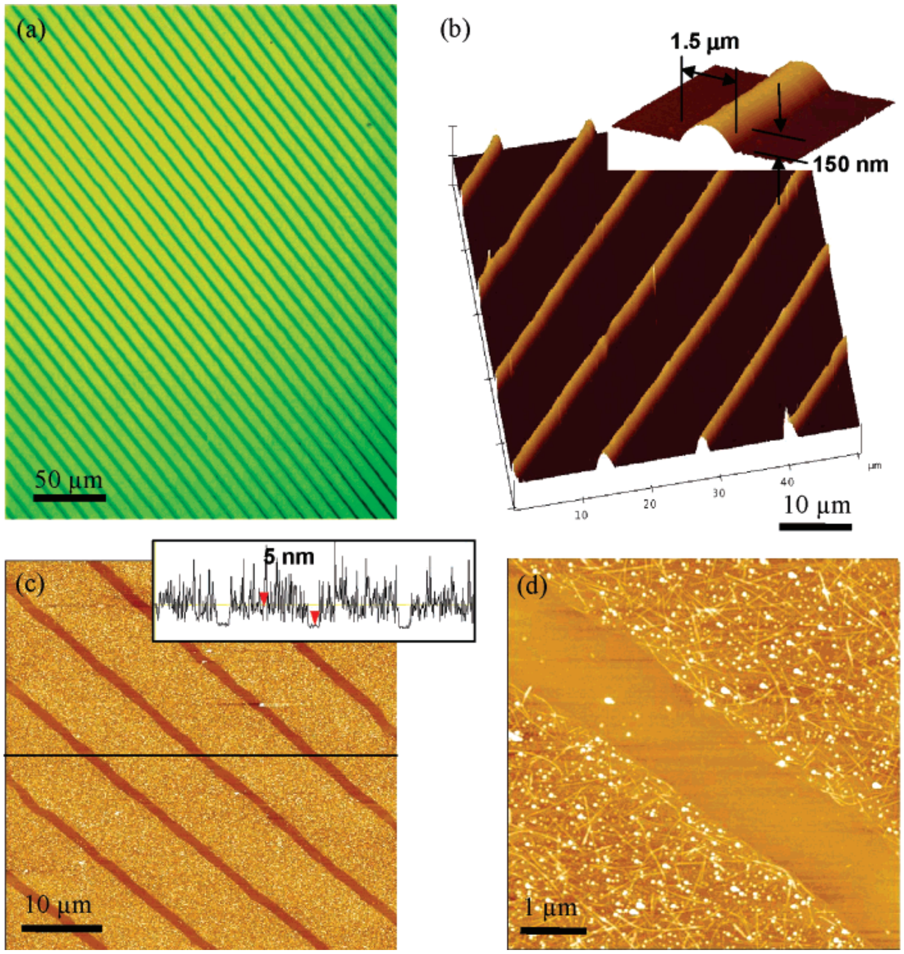

Figure 2. (a) Optical and (b) AFM images of polystyrene micropatterns on top of PAH surface on a silicon substrate; (c) and (d) AFM images of patterned carbon nanotubes after removal of the PS template.

a width of 1.5 μm and a height of 150 nm. This round shape is caused by the action of surface tension on transferred PS solution in the course of its evaporation.

We deposited carbon nanotubes on the patterned substrate and removed PS layer with toluene (Figure 2c). Dissolving of the PS layer did not damage the polyelectrolyte multilayers. The quality of selective adsorption was high: we found almost no carbon nanotubes on the regions protected by PS layers (Figure 2d). The height of carbon nanotube layer was close to 5 nm, which indicates a monolayer of carbon nanotube bundles (bundle diameter measured independently was within 3−5 nm).[27] The surface density of nanotubes was estimated to be 18 bundles/μm^2 and can be controlled by solution concentration. The orientation of carbon nanotubes in this design is random but the possibility to obtain uniformly oriented arrays or more complex patterns will be studied further.

Confocal Raman mapping of the freely suspended patterned CNT films demonstrated excellent optical contrast caused by strong resonance Raman scattering from carbon nanotube areas. Figure 3a shows the surface distribution of the Raman G-mode obtained by integrating intensity at 1590 cm^{-1} (a main resonance peak for carbon nanotubes).[34−36] Raman mapping shows clearly recognizable parallel lines separated by narrower dark stripes with 10 μm spacing. This Raman image clearly identifies the patterned carbon nanotube array inside the LbL membrane. Figure 3b shows representative Raman spectra on two different areas with (position 1, p1) and without (position 2, p2) carbon nanotubes (Figure 3a). Raman spectra at position 2 showed no signs of known Raman features of carbon nanotubes with several weak features originated from PSS/PAH matrix.[37] In contrast, Raman spectra at position 1 displayed all typical spectral features of carbon nanotubes including D, G, and G′-modes with peak positions close to that of well-known peaks for as-obtained carbon nanotubes.[34] This result indicates that neither oxidation process nor deposition routine affected significantly microstructure of carbon nanotubes encapsulated into LbL membranes. High optical contrast caused by the alternating layers into LbL membrane creates an efficient Raman grating with the variation of G-band intensity of 1:1000 and higher.

Finally, we tested how the encapsulation of the carbon nanotube array affects elastic properties of the freely

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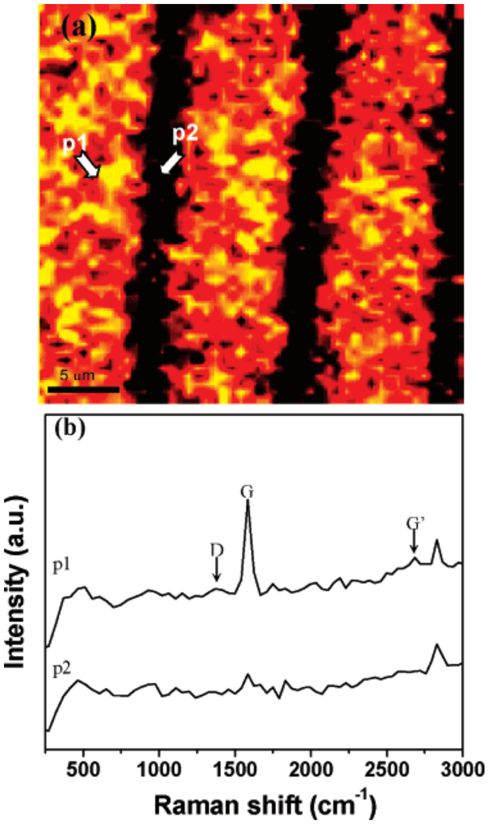

Figure 3. (a) Raman mapping of the LbL membrane with embedded carbon nanotube array; (b) Raman spectra of two different locations (with and without carbon nanotubes).

suspended films. As known, embedding uniform carbon nanotubes into LbL free-standing films enhances their mechanical properties due to the filler toughening phenomenon.[7] However, the question of the effect of the carbon nanotube encapsulation on the elastic properties of *patterned membranes* has been never addressed. Thus, we investigated the mechanical behavior of freely suspended membranes by using interferometry.[12] Figure 4a shows an example of interference pattern arising from membrane deflection under air pressure. By analyzing the interference pattern, we calculated the deflection vs applied pressure (Figure 4b). The deflection of the patterned membranes containing carbon nanotubes (9CNT*9) was much smaller than that for purely polymeric membranes (9_9) (Figure 4b). This difference indicates increasing bending stiffness and higher elastic modulus. Indeed, the analysis of the deflection vs pressure according to the theory of the membrane elasticity[12] showed the elastic modulus of the freely suspended films with nanotube array within 5−9 GPa, which is much higher than that for purely polymer membranes (Table 1). The elastic modulus measured here for films containing a single layer of carbon nanotubes is very high as compared to regular polymer composites with similar matrixes.[38] This result confirms that the filler toughening mechanism effectively enhances the elastic properties of the patterned nanomembranes similarly to that demonstrated for thick homogeneous LbL films.[7] The observed elastic moduli were close to the composite elastic moduli predicted by the Takayanagi model assuming the elastic modulus of carbon nanotubes of 1 TPa and the isostrain condition for two phases (Table 1).[38]

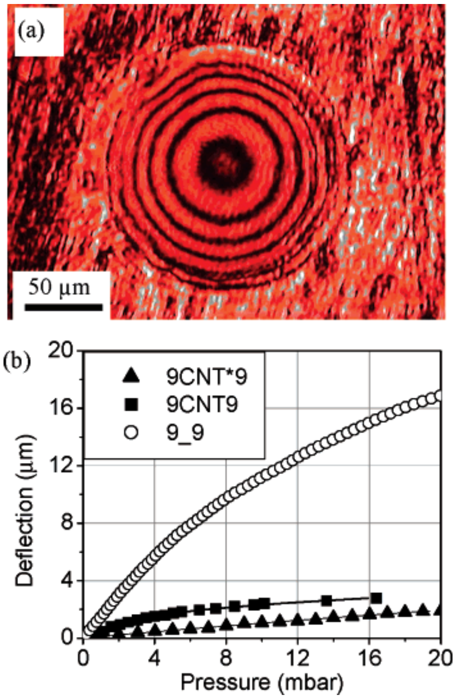

Figure 4. (a) An interference pattern of the deflected freely suspended carbon nanotube array under bulging test; (b) deflection of freely suspended membranes with different contents of carbon nanotubes determined from the bulging experiments.

These results suggest that the patterned geometry *does not prevent* the toughening of membrane elastic properties via encapsulation and can be used for fine-tuning of the micromechanical response. On the other hand, this result implies that we can fabricate freely suspended carbon nanotube arrays embedded in nanoscale polymer films without losing their excellent mechanical properties but bringing new anisotropic properties such as optical (Raman) gratings and potentially directional conductivity. These encapsulated carbon nanotube arrays are expected to show anisotropic mechanical and electrical properties, which can be explored for potential applications for directional sensing and anisotropic electrical conducting.[39] These anisotropic properties are currently under investigation.

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