Encapsulating Nanoparticle Arrays into Layer-by-layer Multilayers by Capillary Transfer Lithography

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We introduce capillary transfer lithography for the fabrication of ordered microscopic arrays from nanoparticulate materials encapsulated into ultrathin (<100 nm) flexible polymer films. Well-defined polymer micropatterns have been fabricated by capillary transfer lithography and used as a protective template for guided assembly of nanoparticles on layer-by-layer (LbL) multilayers. Sequential removal of this template facilitates further assembly of a topmost polyelectrolyte film, hence completing encapsulation. The striped and chess-board arrays of a single layer of carbon nanotubes and gold nanoparticles were sandwiched between two polymer LbL multilayers of thickness 19 nm each.

Introduction

Functionalized organic and polymeric thin films containing optically active nanomaterials are of great importance in many emerging applications in sensors, photonics, and electronics.[1−4] Layer-by-layer (LbL) assembly, which is based on electrostatic assembly of oppositely charged species, is an effective and versatile approach to the creation of ultrathin organic multilayered films with well-defined internal structure.[5,6] This technique has been extended to incorporate a variety of functional materials such as colloids,[7,8] biomaterials,[9] inorganic nanoparticles,[10,11] quantum dots,[12,13] and carbon nanotubes[14] into LbL films. Microscopic patterning on polyelectrolyte films with high lateral resolution has been demonstrated by using chemical composition variation imposed by polymer-on-polymer stamping technique.[15,16] Subsequent selective attachment of functional materials on these patterned surfaces by electrostatic and other intermolecular interactions has been obtained. In this way, a variety of complex patterns from various materials such as colloids,[17,18] biological materials,[19,20] and nanoparticles[21,22] has been demonstrated on chemically patterned LbL films. However, strict control over the LbL surface morphology and pH or ionic strength of solution is required to achieve high selectivity over large areas, which can be a challenge. In addition, the pattern contrast in these cases is limited by the selectivity of site-specific deposition, which can be masked by strong nonspecific attractions for systems with weak chemical contrast.

Controlling the selectivity in the surface assembly by tuning the chemical affinity of the patterned surfaces and solution conditions is even harder for materials with low surface charge density and for materials with strong nonspecific interactions. One example is oxidized carbon nanotubes, which show modest-to-weak deposition selectivity onto chemical patterns of self-assembled monolayers[23,24] as well as onto positively charged poly(allylamine hydrochloride) (PAH) and negatively charged poly(sodium 4-styrenesulfonate) (PSS) polyelectrolytes widely used in LbL technology.[6] This weak selectivity is due to strong van der Waals attraction combined with weak specific chemical interactions of the few chemical groups available. Therefore, the reliable fabrication of precisely designed micropatterned arrays of carbon nanotubes or other weakly interacting materials on top of weakly interacting polymer multilayers with variable

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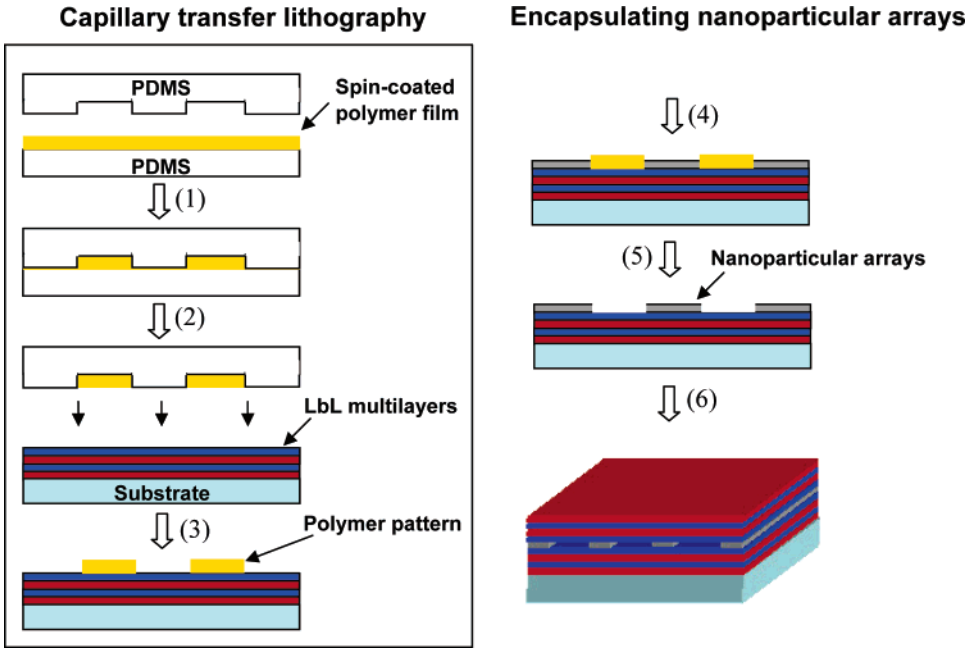

Figure 1. Schematic of patterning process by capillary transfer lithography and the subsequent assembly of encapsulated nanoparticular arrays: (1) PDMS mold contacting spin-coated polymer film. (2) Release of the PDMS mold. (3) Contacting the LbL multilayer and transferring the polymer pattern. (4) Selective deposition of nanoparticular arrays on unprotected surface areas. (5) Removal of sacrificial polymer pattern by rinsing with solvent. (6) Encapsulation of the nanoparticle array by the assembly of topmost LbL film.

surface composition[25] represents a great challenge. To overcome this challenge, a number of alternative fabrication methods have been recently suggested. For example, patterned LbL multilayers[26] or amphiphilic films[27] have been prepared by depositing target materials on a poly(dimethylsiloxane) (PDMS) stamp and then transferring them to LbL multilayers. Direct application of photolithography to LbL films has been recently suggested.[28] Selective buildup of three-dimensional (3D) structures of multiple quantum dots has been reported by modification of quantum dot surface coatings and choice of a proper assembly partner.[29] Although these approaches have shown high pattern contrast and good lateral resolution, there were some limitations for achieving high surface density of functional materials because of low reactivity of the PDMS surface.

Utilization of a polymer pattern as a sacrificial template or mask for subsequent assembly is widespread in microelectronic technology (photoresists for lift-off process).[30] A similar approach can be exploited to increase selectivity and contrast of patterned arrays while avoiding nonspecific adsorption on the protected surface areas. In fact, polymer nano- and microstructures have proven to be very successful in patterned etching of solid substrates or in selective deposition of functional materials.[31−33] Soft lithography, which uses PDMS elastomer as a stamp or a mold, has been an efficient technique to prepare 2D and 3D polymer nano- or microstructures on various solid surfaces including silicon, glass, and metal substrates.[32−35] For example, nanoscale patterns of 2D polymer have been prepared by microcontact printing and used as a scaffold for the deposition of gold nanoparticles.[36] Well-defined 3D polymer microstructures have been fabricated by modified molding methods including imprint lithography,[37,38] microtransfer molding,[39] micromolding in capillaries,[40,41] solvent-assisted micromolding,[42] and capillary force lithography.[43] In these processes, an elastomeric master is pressed into a compliant polymer film that has been softened by heat or solvent, enabling the polymer to fill the recessed areas of the master by capillary forces. In most cases, an additional dry etching process is needed to remove a residual film in the compressed areas.[43,44] Microcontact printing uses the protruding region of PDMS stamp to transfer a thin polymer layer onto target substrate.[45] In this method, lateral spacing is determined by the original stamp dimension, but control of the vertical dimension and

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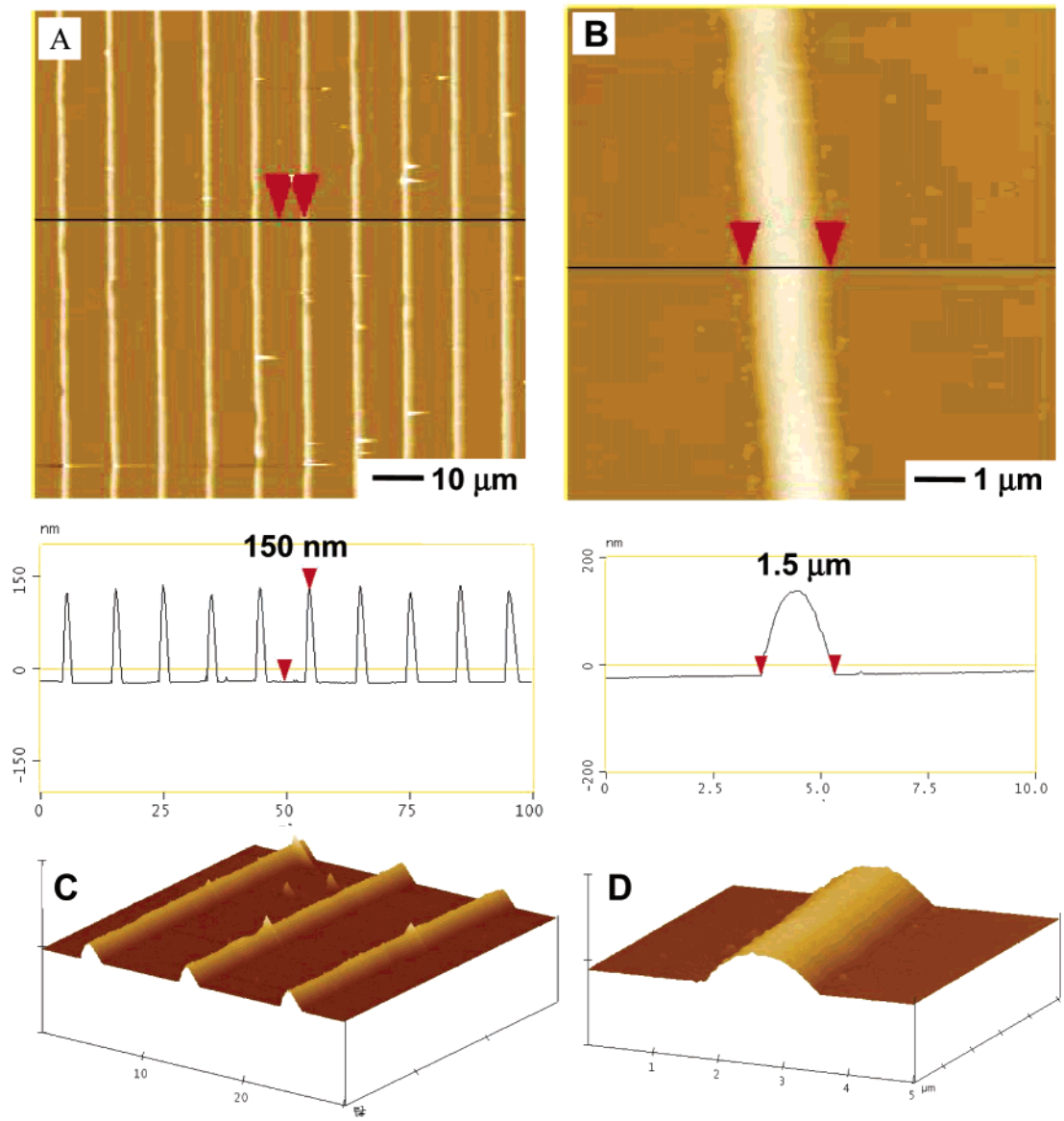

Figure 2. AFM images of PS micropattern prepared by microcontact printing on top of PAH-terminated LbL film on a silicon substrate: (A, B) topographical images and corresponding cross-sections at different scales; (C, D) 3D AFM images.

a 3D shape are limited by dewetting behavior of polymer solution confined between the stamp and the substrate.

Finally, although microcontact printing has been widely used for patterning polymer structures on the surface of LbL multilayers as we discussed above, it is usually limited in the formation of well-defined *open* 3D polymer microstructures. High-resolution patterning with the possibility for fabrication of *encapsulated arrays* by conformal coverage of these arrays with a topmost LbL multilayer is rarely demonstrated. In fact, we have preliminarily demonstrated that polymer microstructures prepared by microcontact printing can be used as a sacrificial template for patterned carbon nanotube arrays encapsulated into freely suspended films.[46]

Here, we demonstrate the extensive capabilities of polymer sacrificial templates for the encapsulation of organized arrays from both carbon nanotubes and gold nanoparticles within polyelectrolyte multilayers by introducing novel polymer patterning technique for the sake of well-defined, high-resolution 3D patterning. We suggest a variant of the soft-lithography technique, termed capillary transfer lithography (CTL), which is based on a capillary filling approach and transfer molding for the creation of 3D polymer open structures onto polyelectrolyte LbL multilayers. We demonstrated various sacrificial polymer microstructures onto LbL surfaces and the fabrication of the well-defined 2D arrays *encapsulated into LbL films*.

Experimental Section

Materials. Gold nanoparticles (13 nm in diameter) were synthesized by use of $HAuCl_4$ solution as described elsewhere.[47,48] The gold nanoparticles have modest negative charges under normal pH conditions and can be used for electrostatic surface deposition

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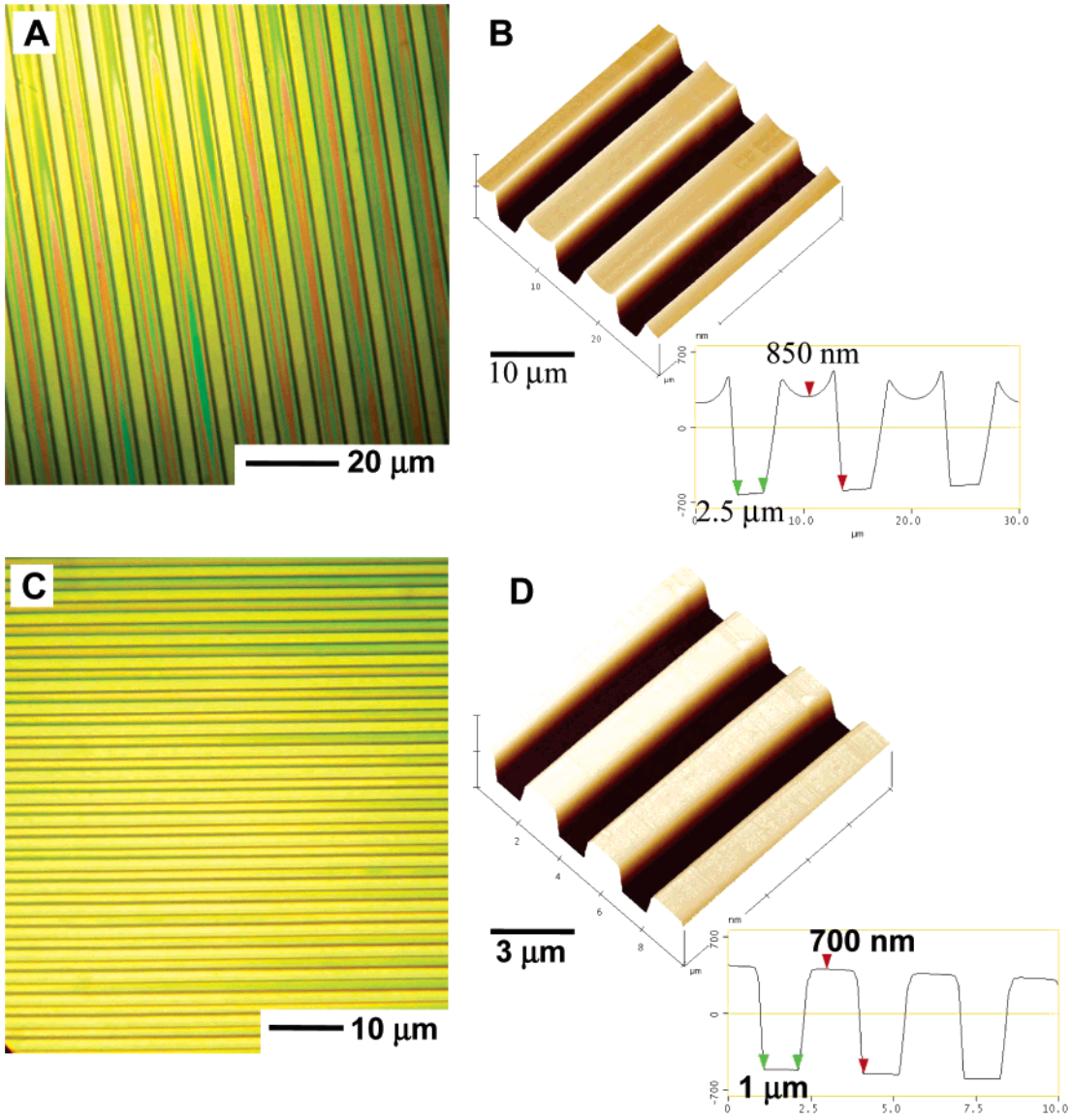

Figure 3. Optical (A, C) and AFM (B, D) topographical images and cross-sections for PS micropatterns prepared by capillary transfer lithography with two different PDMS molds on PAH-terminated LbL film.

without further modification. Single-walled carbon nanotubes (SWNT), produced by the arc discharge method, were purchased from Carbolex (Lexington, KY). Carbon nanotubes were purified by oxidation in dilute nitric acid (3 M, 45 h), filtration (0.4 μm pore size), and taking supernatant after high-speed centrifugation (18 000 rpm, 1 h).[23,24] A metastable dispersion of oxidized SWNTs in aqueous solution (without surfactant) was prepared by sonication (bath sonicator, 1 h) in Nanopure water (18 MΩ·cm). Due to the carboxylic acid groups on the walls and ends after oxidation, carbon nanotubes are negatively charged under normal pH conditions. Two polyelectrolytes, poly(allylamine hydrochloride) (PAH, MW = 70 000) and poly(sodium 4-styrenesulfonate) (PSS, MW = 70 000) were purchased from Aldrich and used as received. The (100) silicon wafers with a typical size 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. PDMS molds were prepared by curing liquid prepolymer (Sylgard 184, Dow Chemical) on top of corresponding silicon master at 60 °C for 1 h in a vacuum oven.

Capillary Transfer Lithography. The experimental procedures for patterning polymer onto polyelectrolyte multilayers, deposition of nanoparticulate materials, and their encapsulation are outlined schematically in Figure 1. LbL multilayers were prepared on silicon substrate by the spin-assisted LbL (SA-LbL) method, which is described in detail elsewhere.[4,49] For LbL deposition, PAH (0.2 wt %) and PSS (0.2 wt %) aqueous solutions were prepared. Sacrificial polystyrene (PS) micropatterns on top of LbL multilayers (PAH as a top layer) were obtained by use of capillary transfer lithography (Figure 1). For this process, PDMS substrate was soaked in toluene for 1−2 min before a thin PS film was prepared on a PDMS substrate by spin-coating of PS ink (MW = 200 000, 2% in toluene) at 3000 rpm for 20 s. A PDMS mold with the appropriate pattern was then brought into conformal contact with the PS film on the PDMS substrate and pressed for 1 min. When the PDMS mold was detached from the PDMS substrate, the patterned polymer layer was trapped inside the recessed regions of the PDMS mold. The polymer pattern formed in this way was then immediately transferred onto the LbL surface by conformal contact of the PDMS mold with the LbL film for 1 min.

Nanoparticle and Nanotube Arrays. For gold nanoparticle adsorption, a few drops of gold nanoparticle solution were evenly placed onto the patterned substrate and stored for 30 min at ambient laboratory conditions. The substrate was then washed with Nanopure water several times and dried with nitrogen gas. For CNT

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adsorption, a few drops of CNT solution were evenly distributed onto the patterned substrates and blow-dried with N_2 gas. This step was repeated several times to increase the surface density of CNTs. After adsorption of gold nanoparticles or CNTs, the sacrificial PS template pattern was gently rinsed away with toluene, leaving only the patterned array of gold nanoparticles or CNTs strongly attached to the PAH-terminated areas of LbL multilayers. The removal of PS templates exposed intact PAH-terminated surface areas, which were further used for encapsulating nanoparticular arrays into LbL multilayers by continuing SA-LbL deposition of the LbL film starting from PSS. The resulting topmost film conformably covered the complete specimen (Figure 1).

Characterization. Atomic force microscopy (AFM) scanning was performed in the tapping mode on a Dimension 3000 microscope (Digital Instruments) under ambient conditions according to a usual routine.[50,51] AFM images were acquired at scan rates in the range of 0.3−1.0 Hz and a set-point amplitude ratio of about 0.8−0.9, which corresponds to the light tapping regime. Silicon cantilevers with a spring constant of about 50 N/m and a tip radius of 10−20 nm were used in this study. These parameters were verified by resonance frequency measurements[52] and a gold nanoparticle reference sample.

Results and Discussion

Polymer Pattern Formation. Figure 2 shows topographical images of the PS micropattern obtained onto LbL film by this microcontact printing. The line spacing was 10 μm (Figure 2A) and the line width was 1.5 μm (Figure 2B), which all are close to original stamp dimensions. Figure 2C,D shows 3D PS microstructure with close to ideal, rounded, semicylindrical shape of PS layers with a width of 1.5 μm and a height of 150 nm. The sharp boundaries between protected and unprotected areas typically have a width of 50 nm or less (Figure 2B). This round shape is caused by the action of surface tension on transferred PS solution in the course of its evaporation.

PS microstructures prepared by the CTL method are slightly different from those prepared by conventional microcontact printing, reflecting different physical processes occurring. Figure 3A shows an optical image of the PS micropattern formed by CTL printing onto the PAH-terminated LbL multilayer surface, which demonstrates its high quality and sharp edges. An AFM image (Figure 3B) illustrates well-defined 3D PS microstructure with 2.5 μm spacing and 850 nm height, which is a replica of the PDMS mold. A meniscus edge at the top of polymer features was caused by incomplete filling the recessed regions of the mold.[43] Recently, this kind of meniscus edge has been used to generate a PDMS stamp for high-resolution soft lithography.[53]

CTL printing was also successful in preparing 3D PS microstructures with smaller lateral dimensions. As can be seen in Figure 3C, a smaller PS micropattern showed uniform parallel stripes with 1.5 μm width and perfect spacing. An AFM image (Figure 3D) clearly revealed the well-defined 3D structure of parallel lines with 700 nm height and 3 μm spacing (1.5 μm separation between polymer areas) with the width of the polymer−substrate transition zone below 50 nm. We observed no meniscus edges, which indicates that the softened polymer completely fills the recessed region of the mold. From these observations, we concluded that the softened polymer inside the recessed regions of mold can be effectively trapped by the PDMS mold and completely transferred to the PAH surface due to the compression elasticity of the PDMS mold and differences in surface energies between PDMS and PAH.[54]

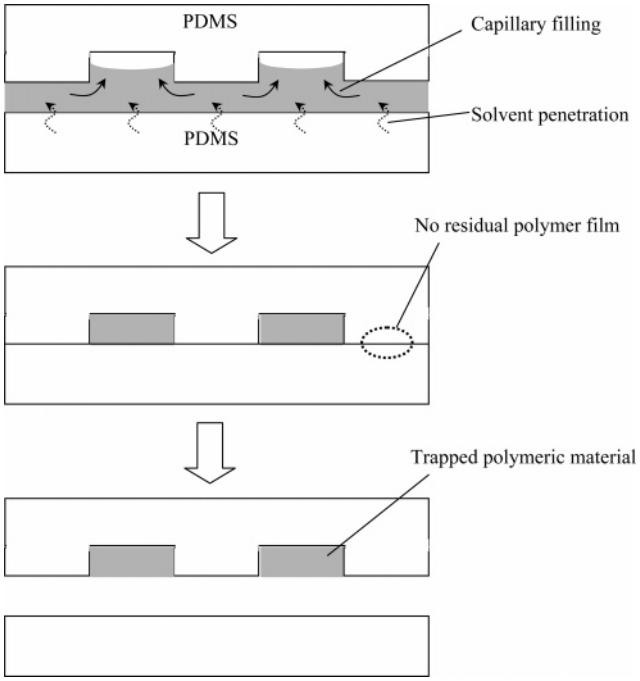

Figure 4. Schematic of interactions between PDMS mold, polymer layer, and PDMS substrate during capillary transfer lithography.

The basic principle of CTL printing, which uses capillary filling of polymers softened by solvent, is similar to capillary force lithography or solvent-assisted micromolding introduced recently.[42,43] First, as illustrated in Figure 4, the solvent can be constantly resupplied from the presoaked PDMS substrate to the polymer layer and soften the polymer. The resulting polymer solution fills the recessed region of the PDMS mold by capillary filling. Second, the low surface energy of the PDMS substrate decreases the interaction with polymer, enabling the formation of polymer open structure. Softened polymer film between two PDMS surfaces is repelled with no residual polymer film found between the PDMS mold and substrate (Figure 4).

Employment of the PDMS substrate in the molding process makes our process versatile. The use of PDMS in our CTL process has several advantages for preparing 3D polymer microstructures due to its low surface energy, elasticity, and swelling.[55,56] The elasticity and low surface energy of PDMS also enables the efficient transfer of this polymer microstructure to other substrates with higher surface energy. When this mold is immediately placed on the LbL film and pressed, the polymer inside the negative structure

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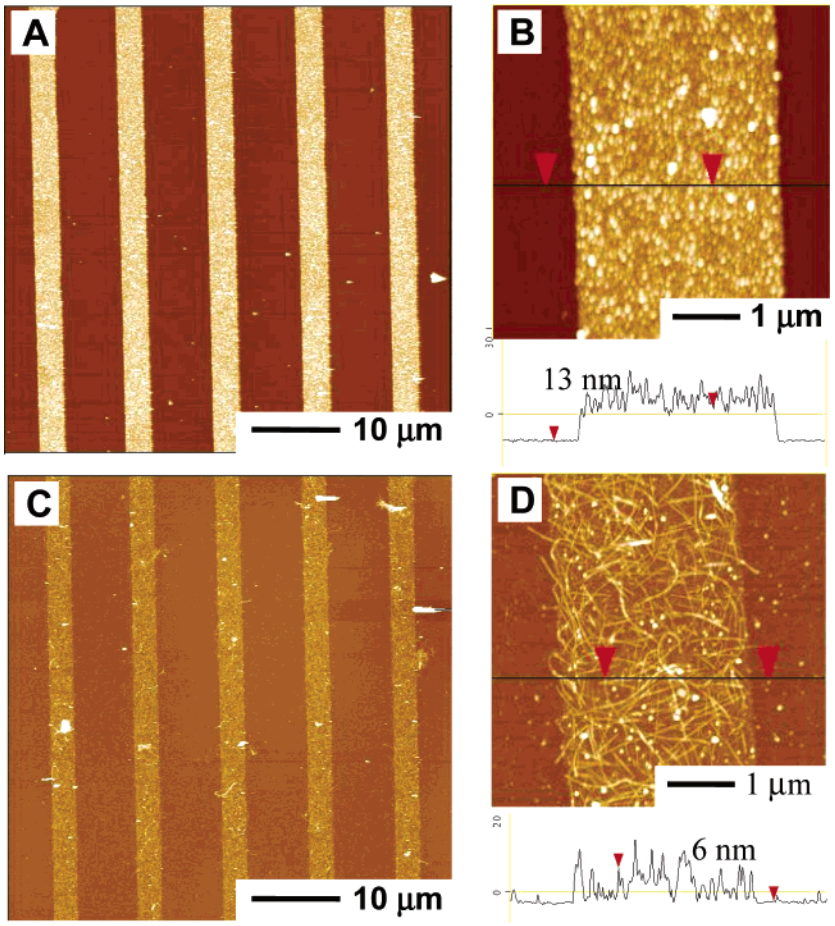

Figure 5. AFM topographical images at different scales and corresponding cross-sections of stripes of gold nanoparticle (A, B) and carbon nanotube (C, D) selectively deposited on LbL film.

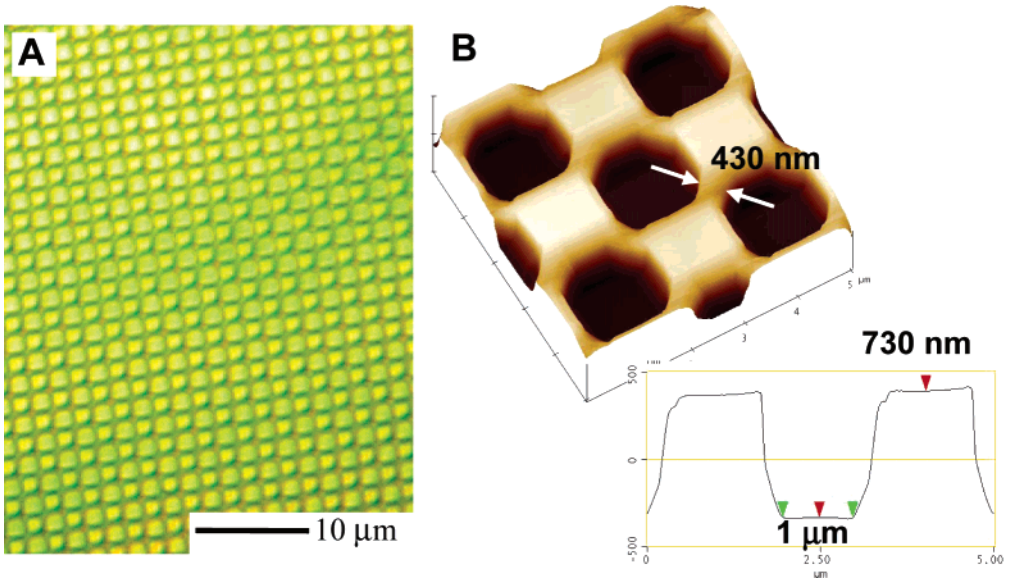

Figure 6. Optical (A) and AFM topographical (B) images at different scales and corresponding cross-sections of chess-board PS micropattern prepared by capillary transfer lithography on LbL film.

is transferred to the polyelectrolyte surface, resulting in a 3D patterned polymer microstructure with sharp boundaries that is complementary to the PDMS pattern.

Formation of Open Nanoparticulate Arrays. Next, we used these patterned polymer microstructures as sacrificial templates for the formation of carbon nanotube and gold nanoparticle arrays located on the surface of LbL films. After the selective deposition of these nanomaterials on the protected LbL surfaces, the PS micropattern was easily removed by rinsing with toluene, a good solvent for PS, leaving only the patterned array of carbon nanotubes or gold nanoparticles strongly attached to the LbL multilayers alternating with intact surface areas of LbL film (Figures 5−8).

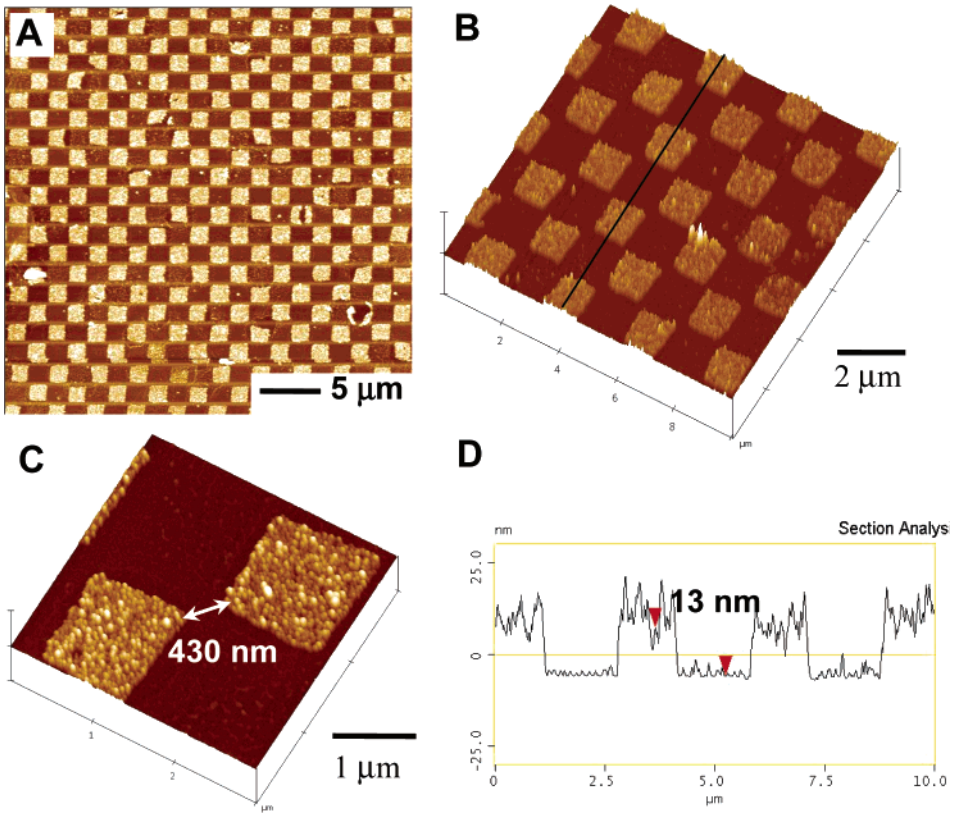

Figure 7. Topographical images at different scales (A−C) and corresponding cross-section for the chess-board array of gold nanoparticles (D).

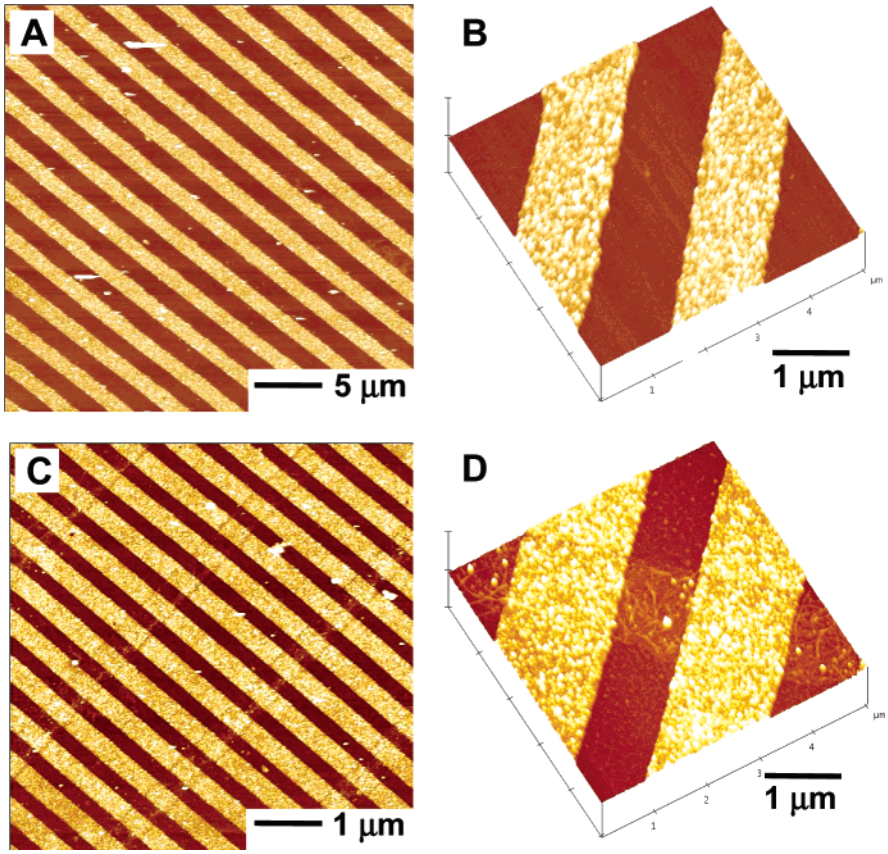

Figure 8. Topographical images of patterned gold nanoparticle array before (A, B) and after (C, D) sequential deposition of orthogonal carbon nanotube array (weaker stripes with larger spacing oriented perpendicularly to initial stripes).

Figure 5 shows the patterned arrays of carbon nanotubes and gold nanoparticles fabricated by using 10 μm PS micropatterns. Apparently dissolving the PS pattern did not damage the polyelectrolyte multilayers, because the thickness of multilayer did not change and the surface morphology appeared unchanged. The boundaries between areas remained

sharp as well (about 50 nm) (Figure 5). The height of gold nanoparticles of 13 nm indicated a monolayer of gold nanoparticles. The height of carbon nanotube layer was around 5 nm, which indicates a monolayer of carbon nanotube bundles.[24] We were able to achieve high-quality patterns complementary to PS patterns with good uniformity over the entire surface area. These observations indicate that the interaction between PS sacrificial structures and the PAH surface was strong enough to sustain solution treatment in the deposition step but weak enough to allow easily dissolution with a good solvent. This balance is a critical element for successful patterning and transfer suggested here.

We obtained similar results for different spacings and more complex shapes of PDMS molds. We prepared PS micropatterns using a PDMS mold containing a chess-board pattern with 430 nm distance from corner to corner and 1 μm distance from side to side of square surface areas (Figure 6). The optical image in Figure 6A shows a very uniform PS micropattern complementary to the PDMS mold over large surface areas. The AFM image in Figure 6B illustrates that the spacings in the PDMS mold have been successfully replicated by the PS micropattern. This kind of well-defined 3D polymer microstructure with sharp boundaries was not easily achievable by conventional microcontact printing on the LbL surfaces. The subsequent formation of gold nanoparticle arrays on these surfaces clearly showed that the original chess-board pattern has been replicated with good accuracy (Figure 7). Importantly, the edge sharpness remained high (below 50 nm), and the regular and alternating rectangular shapes were faithfully transferred from the original features of the PDMS mold.

Another application in which CTL printing has proven useful was the preparation of hierarchical multicomponent arrays by multistep CTL printing (Figure 8). The PS sacrificial template allowed for the sequential formation of two different microarrays on the intact surface areas of LbL film. We sequentially applied two different PDMS molds for the formation of the gold nanoparticle stripe pattern with 3 μm spacing as a first layer, followed by the formation of the carbon nanotube pattern with 10 μm spacing oriented perpendicularly to the gold nanoparticle stripes (Figure 8C). Figure 8C shows an AFM image of a large area of well-defined crossed stripes with each wide stripe containing gold nanoparticles and each perpendicular thinner and less visible stripe containing carbon nanotubes (Figure 8D). This demonstrates that the PS-protected LbL surface areas were intact after removal of PS and can be further modified. We observed that no carbon nanotubes appeared on the surface of gold nanoparticle areas, whereas they both have strong interaction with the intact PAH surface.

Formation of Encapsulated Patterned Arrays. The intact polyelectrolyte surface originally covered by the sacrificial PS template was further used for encapsulating nanoparticulate arrays into LbL multilayers as shown in Figure 1. To demonstrate the feasibility of this approach for the encapsulation of nanoparticle arrays into LbL multilayers, we further deposited nine bilayers of PAH/PSS on top of the patterned arrays formed by both gold nanoparticles and carbon nanotubes (see Figure 5 for their surface morphology).

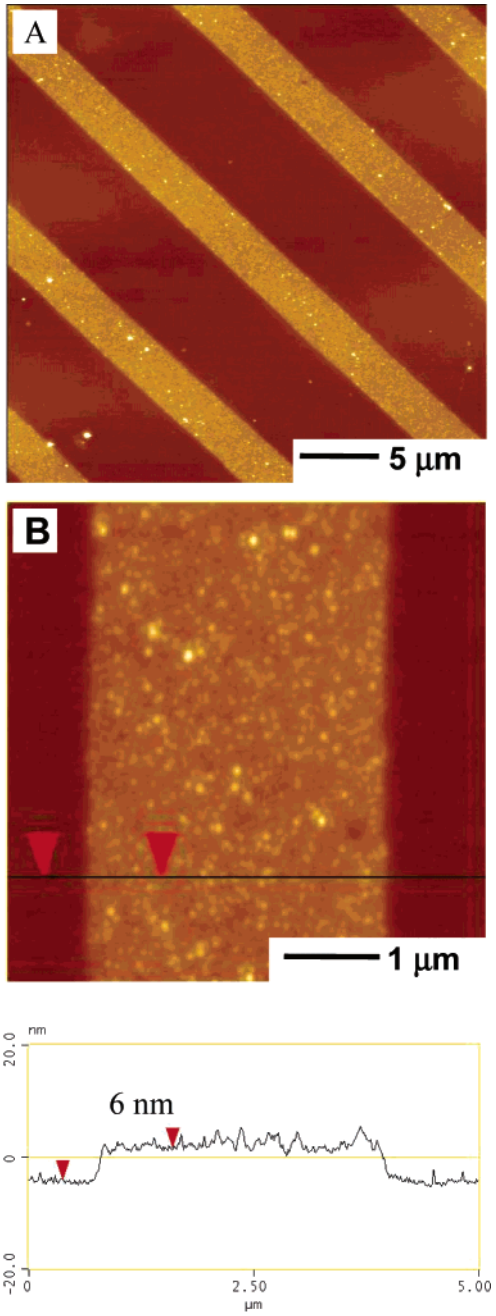

Figure 9. Topographical images at different scales (A, B) and corresponding cross-section of the gold nanoparticle array encapsulated into LbL film.

Figure 9 shows AFM topographical images of gold nanoparticle arrays encapsulated between two LbL multilayers. Well-defined stripes of the encapsulated gold nanoparticles are clearly visible on a large scale even after coverage with relatively thick LbL multilayers (19 nm[46]). High contrast is similar to that observed for an open array (Figure 5). However, the high-resolution AFM image shows relatively densely filled surface areas along the stripes and fuzzy boundaries, a significant difference from the initial gold nanoparticle array (Figure 9). A cross-section of these areas shows modest peak-to-value height variation, indicating deposition of the topmost LbL film in a conformal manner by filling open space between nanoparticles (surface coverage below 50%). This filling resulted in effective reduction of the apparent elevation of the gold nanoparticle areas from the original 13 nm (Figure 5B) to 6 nm (Figure 9A).

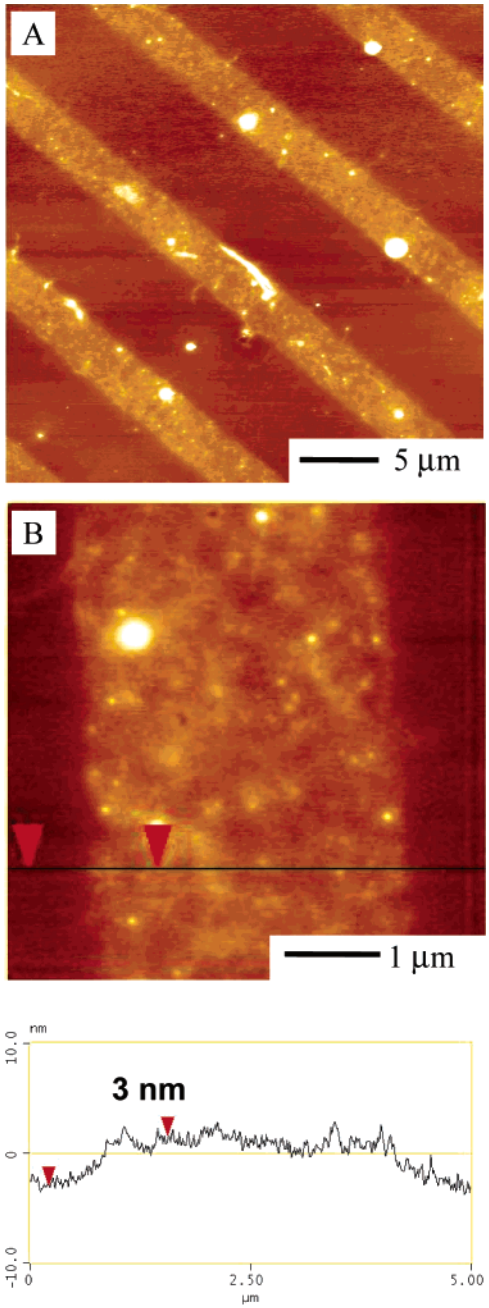

Figure 10. Topographical images at different scales (A, B) and corresponding cross-section of the carbon nanotube array encapsulated into LbL film.

Uniform coverage with the topmost LbL multilayer was achieved for carbon nanotube arrays as well. At medium resolution, we still easily observed parallel stripes of carbon nanotube arrays (Figure 10). However, at higher resolution, the original surface morphology of carbon nanotube arrays (Figure 5D) appeared smeared due to the coverage with the topmost LbL multilayered film (Figure 10). Details of carbon nanotube bundle packing within these areas became poorly visible. AFM cross-section showed the decrease of the height differences from initial 5−6 nm to 2−3 nm (Figure 10).

Conclusions

In conclusion, we demonstrated that capillary transfer lithography is a simple and efficient method of creating 3D polymer micropatterns on the surface of LbL multilayers by transferring polymer patterns from a PDMS mold onto the target substrate. The key elements of this method are creation of polymer microstructure and transferring it onto the polyelectrolyte surface. Most conventional molding methods for forming 3D polymer microstructures on the strongly interactive substrates result in residual polymer film on the compressed region, which needs to be etched away for further applications.[32] In contrast, the polymer microstructure fabricated here is easily transferred from the recessing regions of the PDMS mold to target substrate in a very controllable manner, resulting in 3D open microstructure.

We suggested that these polymer microstructures can be used as sacrificial templates for subsequent assembly of both carbon nanotubes and gold nanoparticles onto LbL films in the patterned manner. The advantages of this approach include highly selective patterning, greater control over the 3D structure, and the possibility of further modification of protected surface areas. We demonstrated that further modification of intact surface areas can be used to fabricate heterogeneous orthogonal arrays or to encapsulate nanoparticular arrays into LbL multilayers. While we limited our approach to PS micropatterns for the assembly of water-soluble nanomaterials, this method can be extended to micropatterning a wide range of polymers onto a range of substrates as long as the PDMS stamp is wetted with a polymer solvent.[56] The patterned nanoparticle or nanotube array could be used in many potential applications such as sensing elements in sensor arrays, functional components in electronic devices, and anisotropic structural materials.

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