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Multilayer Transfer Printing of Electroactive Thin Film Composites

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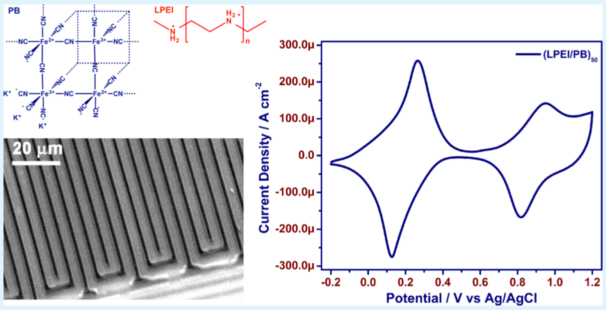
ABSTRACT: We demonstrate the high fidelity transfer printing of an electroactive polymer nanocomposite thin film onto a conductive electrode. Polyelectrolyte multilayer thin films of thickness ~200 nm containing 68 vol % Prussian Blue nanoparticles are assembled on a UV-curable photopolymer stamp and transferred in their entirety onto ITO-coated glass creating ~2.5 μm-wide line patterns with ~1.25 μm spacing. AFM and SEM are used to investigate pattern fidelity and morphology, while cyclic voltammetry confirms the electroactive nature of the film and electrical connectivity with the electrode. The patterning strategy presented here could be used to pattern electroactive thin films containing a high density of nanoparticles onto individually addressable microelectrodes for a variety of applications ranging from biosensor arrays to flexible electronics.



KEYWORDS: *surface patterning, stamping, layer-by-layer assembly, polyelectrolyte multilayers, polymer nanocomposite, Prussian blue nanoparticles, and electrical conductivity*

INTRODUCTION

The layer-by-layer (LbL) assembly of multilayer thin films[1] has opened up a completely new era of possibilities for creating functional and conformal coatings. Examples include superhydrophilic,[2] superhydrophobic,[3] and antireflective coatings,[4] electrochromic thin films,[5,6] and drug delivery coatings.[7,8] There has been particular promise in the generation of electrochemically active thin films, which can be used as components in devices ranging from energy storage/generation and displays to activated responsive surfaces.[9] Micro- and nanometer scale patterns[10,11] of these materials introduce new opportunities in areas such as flexible electronics,[12,13] organic transistors,[14] electrochromic optical diffraction gratings,[15] and biosensor arrays,[16] among others.

Micro- and nanofabrication of small features can be created using conventional techniques like photolithography[15] and scanning beam lithography, or soft lithographic methods like molding and embossing. All of these methods have been widely studied and successfully applied to produce patterned structures. Some of the main drawbacks of conventional techniques are their high cost, time-consuming processing procedures, and geometric limitations of the substrates.[17] Multilayer transfer printing (MTP),[18−22] wherein a multilayer film is assembled on a flexible stamp and directly transferred to a substrate, addresses many of these limitations. MTP is a simple process in which the flexibility of the stamp allows for conformal coatings over large areas at low cost. Microcontact printing methods using elastomeric PDMS stamps have been studied extensively in the last two decades.[23−25] The extension of these methods to a broader range of materials systems is particularly important, as it enables the generation of a larger number of applications and potential materials combinations.

The inclusion of polymeric films, including polyelectrolyte multilayer films, has required addressing certain challenges such as maintaining the integrity of ultrathin films, achieving precise features and resolution of the transferred thin film, and controlling adhesion interactions for complete transfer of the multilayer, some of which can be addressed by choosing different stamp materials[20] and patterning processes. When the film to be transferred is a nanomaterial composite, additional concerns involve maintaining the integrity, nanoparticle distribution, and materials function of the film.

In this study, we present a multilayer transfer printing approach that yields very well-defined positive patterns of electroactive inorganic nanoparticle-containing multilayer films. While previous works have demonstrated successful patterning of gold nanoparticle-containing thin films using traditional lithography[26] as well as imprinting and lift-off strategies,[27] here we demonstrate a successful example of electrical connection between a conductive substrate and the patterned thin film. Furthermore, the MTP approach presented here avoids common issues associated with surface patterning, including formation of a meniscus at the film surface and the presence of residual material between the patterns often created by imprinting[28] and capillary transfer[29] techniques. The thin films used in this study are polyelectrolyte multilayer films containing Prussian Blue (PB) nanoparticles (68 vol %) and linear polyethylenimine. PB nanoparticle-containing films have been investigated in our group previously for applications in electrochromic displays,[5] electrochemically activated controlled

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release,[30] and "mechanomutable" materials,[31] while other authors have explored PB materials for use in glucose sensors.[32] Given the multitude of applications for PB-based films as well as for LbL composite films in general,[33,34] a technique for high fidelity patterning while maintaining electrical connectivity between nanoparticles within the film, and to the underlying electrode, is crucial to realize these applications.

■ EXPERIMENTAL SECTION

Materials. Linear polyethylenimine (LPEI) (M_n = 25 000) was purchased from Polysciences (Warrington, PA). Iron(II) chloride tetrahydrate, potassium ferricyanide, potassium hydrogen phthalate (KHPh), and trichloro(1*H*,1*H*,2*H*,2*H*-perfluorooctyl)silane were purchased from Sigma-Aldrich (St. Louis, MO). All chemicals were used as received. Indium tin oxide (ITO)-coated glass slides (CD-50IN-CUV) were purchased from Delta Technologies, Limited (Stillwater, MN).

Synthesis of Prussian Blue (PB) Nanoparticles. Synthesis of PB nanoparticles was previously described elsewhere.[5] Briefly, 50 mL of aqueous 10 mM $FeCl_2 \cdot 4H_2O$ was added dropwise to an equivalent volume of aqueous 50 mM $K_3[Fe(CN)_6]$ and 50 mM KCl with vigorous stirring. The dark green mixture was immediately submitted to dialysis against a regenerated cellulose membrane with a 3500 Da molecular weight cutoff to remove excess $K_3[Fe(CN)_6]$ and KCl. The resulting blue nanoparticle suspension was adjusted to pH 4 with potassium hydrogen phthalate (KHPh) (final concentration of 1 mM) and hydrochloric acid.

Assembly of LPEI/PB Films. Films were assembled on NOA 63 stamps described below. LPEI solutions were prepared in deionized water at a concentration of 10 mM based on the polymer repeat unit. The solution pH was adjusted to the desired value with HCl. $(LPEI/PB)_{50}$ multilayer films (i.e., comprising 50 bilayers) were assembled by dip coating using an automated Zeiss HMS Series programmable slide stainer. Briefly, substrates were immersed in an LPEI solution for 10 min followed by three separate deionized water rinse baths (adjusted to pH 4 with HCl) for a total of four (2:1:1) minutes. Next, the substrates were immersed in a PB solution for 10 min followed by the same rinse cycle. This dip cascade was repeated for a total of n = 50 bilayers. Volume fraction of the PB nanoparticle inside the multilayer thin films was calculated as reported elsewhere.[5]

Polymer Stamps and Multilayer Transfer Printing (MTP). A commercial polymer (Norland Optical Adhesive (NOA) 63, Norland Products Inc., Cranbury Township, NJ) was employed for patterning. NOA 63 is a clear, colorless photopolymer, originally developed as an optical adhesive. It has excellent optical and mechanical properties making this polymer useful for the creation of submicrometer size patterns with a high aspect ratio. NOA 63 was cast onto a fluorinated silicon master with desired patterns. Fluorination was performed by vacuum deposition in a desiccator containing trichloro(1*H*,1*H*,2*H*,2*H*-perfluorooctyl) silane for 2 h. This step was followed by curing of the polymer (~5 mm thick layer) with a 100 W UV-lamp (λ = 365 nm) at a distance of 15 cm for 30 min. Following curing, the stamp and silicon master assembly was placed in an oven at 50 °C for 10 min. Immediately after removal from the oven, the stamp was peeled off the silicon master and excellent replication of the master was observed (Figure 1a). The stamp was then cleaned with air plasma (Harrick PDC-32G Plasma Cleaner at the low power setting (6.8W)) for 30 s and an $(LPEI/PB)_{50}$ multilayer thin film was assembled onto the stamp by dip coating. The $(LPEI/PB)_{50}$ film was transferred from the stamp to a conductive ITO-coated glass slide for pattern visualization and cyclic voltammetry measurements; before the transfer procedure, the ITO was dipped into LPEI for 10 min to create a positive charge on the negatively charged ITO, since the outmost layer of the $(LPEI/PB)_{50}$ film is the negatively charged PB. The film-coated NOA 63 stamp and the LPEI-coated ITO glass slide were brought into contact and firmly compressed together with a paper binder clip. Samples were placed into a dry crystallization dish, which was immediately placed into a larger preheated (at 60 °C) crystallization dish filled with 20 mL of deionized water to provide humidity to assist with the transfer printing. The secondary dish was covered with aluminum foil and kept in an oven at 60 °C for 2 h. After allowing the stamp and substrate to cool to room temperature, the stamp was peeled off the ITO-glass, revealing complete transfer of the film. The transferred film patterns on the ITO-glass slide were characterized without further processing.

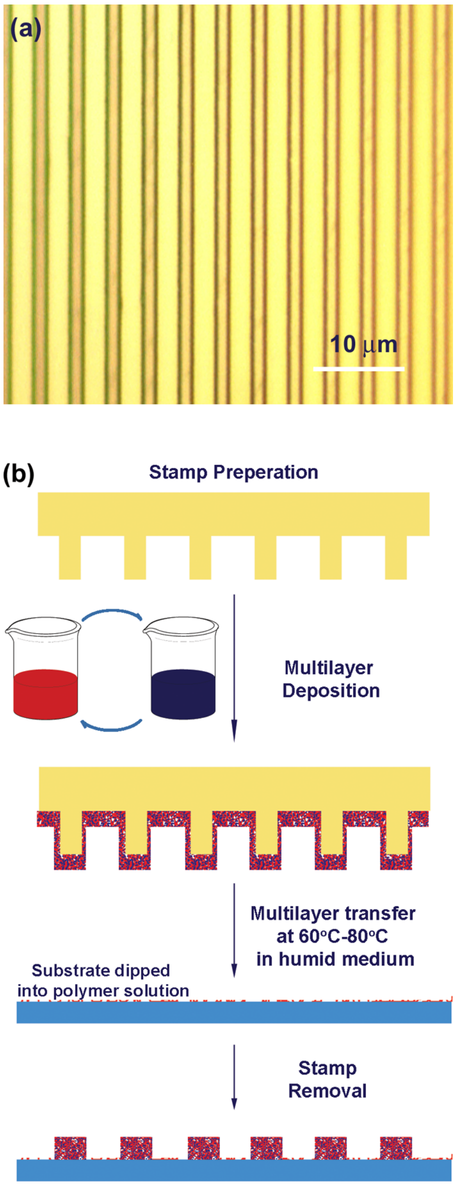

Figure 1. (a) NOA 63 stamp and (b) composite multilayer transfer printing process. Multilayers were directly deposited on an NOA 63 stamp and transferred onto an ITO-coated glass slide that was pretreated with LPEI polymer solution.

Atomic Force Microscopy (AFM). AFM-imaging of $(LPEI/PB)_{50}$ films on ITO-glass substrates was performed using a Nanoscope IV multimode microscope (Digital Instruments/Veeco Metrology Group, Santa Barbara, CA) in contact mode. A silicon nitride (Si_3N_4) cantilever with a nominal spring constant of 0.06 N/m carrying a tip with a nominal diameter of 2 nm was employed.

Scanning Electron Microscopy (SEM). The morphology of the transferred multilayer films was investigated with a field emission scanning electron microscope (FE-SEM) using a FEI/Philips XL30 FEG ESEM instrument at an acceleration voltage of 10 kV. Samples on ITO-glass were mounted on sample disk pucks and SEM images were taken without further surface treatment.

Cyclic Voltammetry (CV). Cyclic voltammetry was performed in a three-electrode electrochemical cell controlled by an EG&G 263A potentiostat/galvanostat. The cell volume was ca. 15−20 mL, and 0.1 M KHPh with pH 4.0 was used as the electrolyte. A silver/silver chloride (Ag/AgCl) electrode and a platinum wire were used as a reference electrode and counter electrode, respectively. A scan rate of 50 mV/s was employed.

■ RESULTS AND DISCUSSION

Electroactive multilayer thin film composites were patterned onto a conductive substrate using a multilayer transfer printing approach as shown schematically in Figure 1. In this process, a hard polymer stamp of NOA 63, which has been successfully introduced for submicron size patterning,[20] was first prepared on a fluorinated silicon master. Next, the NOA 63 stamp was subjected to air plasma to remove contaminants and render the surface negatively charged. Thereafter, a polyelectrolyte multilayer thin film containing 50 bilayers of positively charged linear polyethylenimine (LPEI) and electroactive, negatively charged Prussian Blue (PB) nanoparticles was assembled on the stamp using the layer-by-layer assembly method. Finally, the film on the stamp was brought into contact with a conductive ITO-coated glass substrate pretreated with LPEI and was heated above 60 °C, the temperature at which NOA 63 undergoes a softening point near its glass transition and becomes elastomeric, enabling it to make conformal contact with the substrate, and to be lifted off with ease, making the multilayer transfer process more favorable.[20]

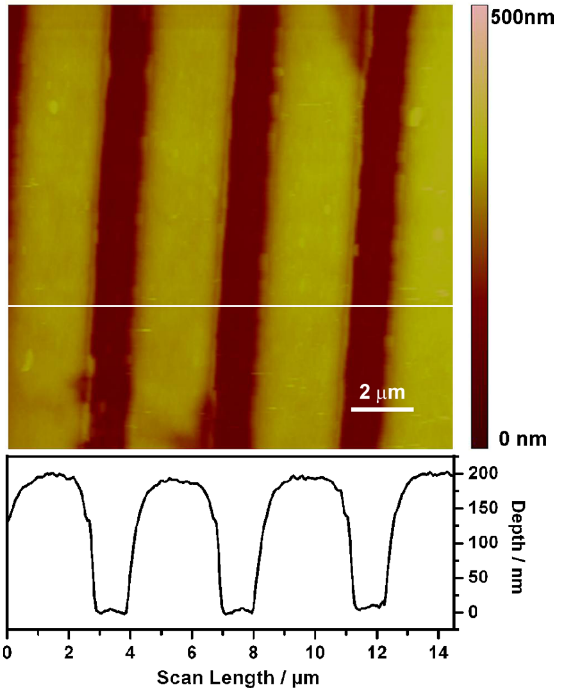

Figure 2. AFM height image (scan size is 14.5 *µ*m × 14.5 *µ*m) and corresponding cross-sectional profile of the transferred $(LPEI/PB)_{50}$ film.

Atomic force microscopy (AFM) was used to characterize the pattern fidelity and to measure the thickness and roughness of the transferred film. An AFM height image and the corresponding cross sectional profile of a transfer printed $(LPEI/PB)_{50}$ film are shown in Figure 2. The average film thickness was calculated to be 194 ± 4.8 nm as determined by averaging over 12 different locations based on AFM. The LPEI/PB multilayer system grows linearly with an average thickness per bilayer of 4.1 nm on ITO-glass slide slide.[5] This slight difference in thickness might arise from the intrinsic hydrophobic nature of the NOA 63 substrate. The root-mean-squared (rms) roughness of the films was calculated to be 6.6 ± 0.9 nm, as determined from measurements at 12 2 *µ*m × 2 *µ*m spots using Veeco NanoScope v614r1 software. This value is quite comparable to the rms roughness of a nontransfer printed film, which was calculated to be 4.2 ± 0.6 nm, matching the size of the PB nanoparticles (median diameter of 4−5 nm determined by TEM[5]). Cross-sectional profile analysis of the AFM images clearly reveals a high fidelity of pattern transfer since the line width and spacing match those for the NOA 63 stamp. Line width is the average of 20 measurements obtained from randomly selected locations on the transferred film from AFM images and was calculated to be 2.56 ± 0.07 *µ*m. Similarly, feature sizes of the lines and spaces from the stamp were estimated to be 2.52 ± 0.04 *µ*m and 1.25 ± 0.03 *µ*m, respectively.

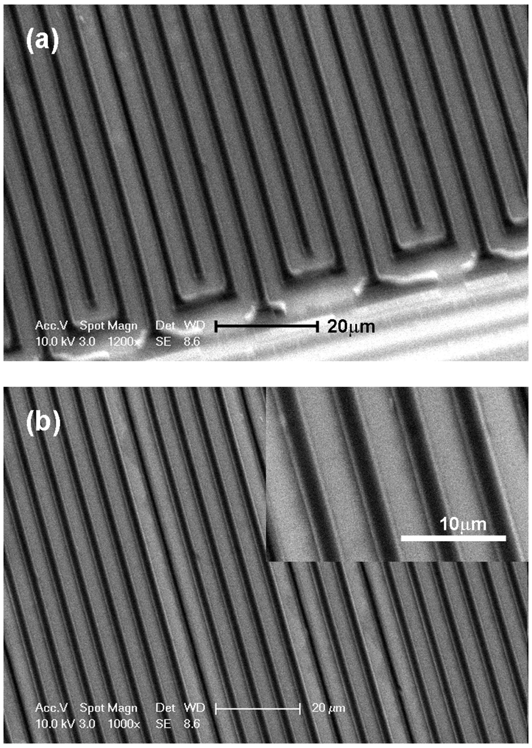

Figure 3. SEM images of the multilayer transfer printed films of $(LPEI/PB)_{50}$ on an ITO-glass slide showing an (a) edge view (scale bar reproduced from the original for better visibility) and a (b) large area view.

Furthermore, our approach to transfer multilayers does not drive formation of a meniscus on the film surface, a common problem observed by capillary force driven patterning techniques.[34] This result indicates that during the MTP process the film−substrate interaction is sufficiently dominant over the film-stamp interaction as dictated by the temperature of the MTP process, such that the film is uniformly released from the stamp. Moreover, AFM images show that the film does not spread to the spaces between the line features, a problem often associated with pressure or humidity driven methods.[19,26,27,34]

Scanning electron microscopy (SEM) was used to further assess the morphology and pattern fidelity of the transferred film over a larger area. Typical SEM images of the printed $(LPEI/PB)_{50}$ films are shown in Figure 3. Figure 3a shows well-

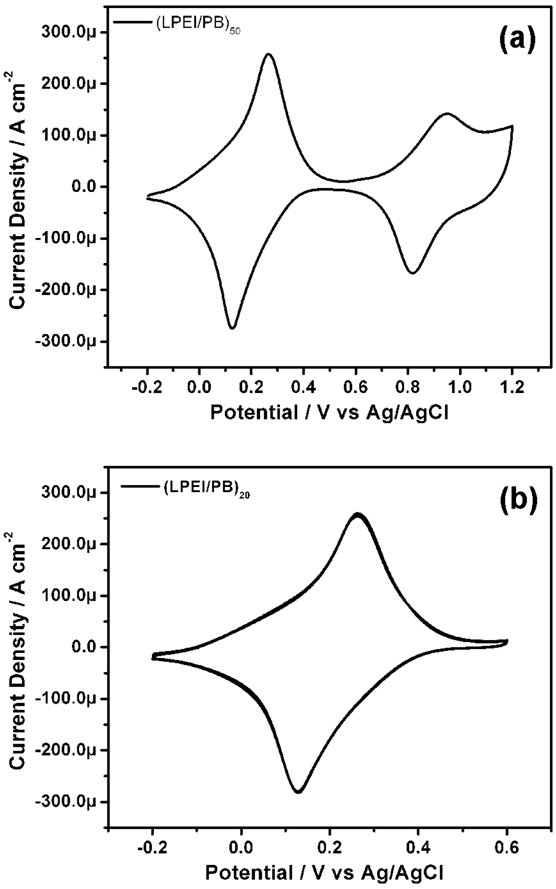

Figure 4. (a) Cyclic voltammogram of the stamped (LPEI/PB)$_{50}$ film on ITO-glass at a scan rate of 50 mV/s. The electrolyte was 0.1 M potassium hydrogen phthalate at pH 4.0. (b) CV behavior of the Prussian White−Prussian Blue redox couple after 100 cycles. Potentials are reported with respect to an Ag/AgCl reference electrode.

defined line space patterns including the edge of the features. Figure 3b shows a wide area presentation of line patterns with a close up image as the inset. The SEM images confirm that our method for multilayer transfer printing creates outstanding replication of the original patterns over a wide area without leaving residual film between line features.

Cyclic voltammetry (CV) was used to confirm electrical connectivity between the conductive substrate and the electroactive Prussian Blue (PB) nanoparticles in the thin film. PB, a mixed valence transition metal complex, possesses well-defined redox behavior in which the oxidation states of the iron centers can be modulated by an applied electric potential. Here, we immersed the patterned film on ITO-glass (electroactive film coverage on the substrate was around 0.5 × 1.0 cm) in a three-electrode electrochemical cell and swept the voltage between −0.2 V and +1.2 V (vs Ag/AgCl) to access all of the oxidation states. The cyclic voltammogram shows redox peaks with oxidation potentials at 0.196 and 0.880 V corresponding to Prussian White−Prussian Blue and Prussian Blue−Prussian Yellow, respectively, in agreement with those reported earlier.[5,35] This result confirms that an electrical connection has indeed been established between the substrate and film (Figure 4a), and that the film morphology still enables communication between nanoparticles and appropriate ionic and electronic conduction for film redox behavior. Performance, stability and integrity of the transferred films were further investigated. The cyclic voltammogram of the PW and PB redox couple (Figure 4b) remained almost the same after 100 cycles; less than a 1.5% (4 μA/cm^2) decrease in current density indicates the electrochemical stability of the transferred film.

■ CONCLUSIONS

In short, we have presented a facile approach to surface pattern multilayer thin films of organic−inorganic nanocomposite materials via transfer printing. We have confirmed the fidelity of the pattern transfer and have established an electrical connection between the substrate and redox-active Prussian Blue nanoparticles within the film. Given the broad range of applications of layer-by-layer films in general and for PB-based materials in particular, this method could be applied to the patterning of films on independently addressable microelectrodes. These microelectrode arrays contain individual regions of functional thin films that can be utilized for biosensor arrays, flexible electronic displays, electrically triggered drug delivery, or manipulation of cellular behavior on surfaces, among other applications.

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Notes

The authors declare no competing financial interest.

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