Directed Electrodeposition of Polymer Films Using Spatially Controllable Electric Field Gradients

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We report a method for the directed electrodeposition of polymer films in various patterns using spatially controllable electric field gradients. One- and two-dimensional electric field gradients were produced by applying different potential values at spatially distinct locations on an electrode surface. Variations in the resulting local electrochemical potentials were used to spatially manipulate the rate of electrodeposition of several polymers. By controlling the electric field gradient in the presence of sequentially varying deposition solutions, complex polymer patterns could be produced. One-dimensional structures consisting of alternating bands of polyaniline and either poly(phenylene) oxide or poly(aminophenylene) oxide were produced, as well as more complex two-dimensional structures. Film characterization was achieved through optical imaging, UV–vis spectroscopy, and ellipsometry. Results indicate that this directed deposition technique is a simple strategy to create complex, millimeter-sized surface patterns of electrodeposited materials.

Introduction

The ability to direct the deposition of materials onto surfaces into well-defined structures or patterns has wide-ranging application and is exploited in microelectronics, optics, sensors, and a host of other technologies. Typically, photolithography is used to guide the deposition or etching of materials at precise surface locations. Although less able to create specific local patterns or complex geometries, there has been increasing interest in the development and use of techniques that exploit gradients for the directed deposition of materials at surfaces with tailored and spatially controllable properties,1,2 for the design of dense combinatorial libraries,3 and for novel analytical testing methods.4

A variety of gradient-based fabrication methods have been developed, including free diffusion,5–7 diffusion in microfluidic networks,8 scanning tunneling microscopy (STM)-based replacement lithography,9 physical vapor deposition,10 and imposed electrochemical11,12 or electric field gradients.13 Electrochemical gradients represent a particularly appealing method for the construction of surfaces as well as for the local control of electrodes. The appeal of electrochemical gradients results partly from the flexibility and reversibility of the control they provide. This technique permits the fabrication of substrates with spatially controllable components with varying compositions and thicknesses. Electrochemical gradients have been used to fabricate self-assembled monolayer gradients,11,15,16 gradients in electrodeposited polymers,17 model surfaces for cell and protein adhesion studies,18–20 composition gradients of various metals,21–23 and spatially controllable pH gradients.24

In this work, we demonstrate the use of electric field gradients to direct polymer electrodeposition and generate spatially patterned films. A nonuniform electric field is applied to a resistive electrode surface to locally vary the deposition rate of either a conducting or insulating polymer film derived from aniline, phenol, or aminophenol monomers. At locations where the electrode potential is less than the deposition potential, no polymer is deposited, while at potentials exceeding this potential, a thin polymer film grows on the surface. By varying the magnitude of the applied potential values through a sequence of monomer-containing solutions, a variety of one- and two-dimensional film patterns were created. A combination of optical and electrochemical measurements was used to characterize the polymer structures. Scanning UV–vis spectroscopy was used to determine the location of particular polymers with respect to distance along the surface. Null-ellipsometry mapping was performed to monitor the change in thickness along the different polymer regions. This maskless deposition strategy produces...
structures of alternating conducting and insulating polymers that are spatially controllable in thickness, location, and shape.

Experimental Section

Materials and Reagents. Polymer electrodeposition was performed in solutions containing either 0.5 M sulfuric acid (Fisher Scientific, Fair Lawn, NJ) and 0.1 M aniline (Aldrich, Milwaukee, WI) or 0.1 M monobasic sodium phosphate (Fisher) and 10 mM phenol (Aldrich) or aminophenol (Aldrich), with the pH adjusted to ~7.0 with 1 M NaOH (Fisher). All experiments were performed in deionized water (NANOpure, Barnstead, Dubuque, IA).

Substrate Fabrication. Slides of indium tin oxide (ITO) coated float glass (Delta Technologies, Inc., Stillwater, MN) with a surface resistance of $R_s = 100 \, \Omega \, \text{square}^{-1}$ were cut to size (10 mm × 25 mm or 25 mm × 25 mm), rinsed in DI water, sonicated in a 50:50 solution of DI water and ethanol, sonicated in pure DI water, and dried under nitrogen. Electrical contacts to the ITO electrode were made by attaching copper wires with silver epoxy (H2OE parts A and B, Epoxy Technologies, Billerica, MA) and then coating the connections with an insulating epoxy (QuickSet Epoxy Gel, Henkel Consumer Adhesives, Inc., Avon, OH).

Electrochemistry. Electrodeposition was achieved in a cell consisting of the ITO electrode as the working electrode, a Hg/HgSO$_4$ reference electrode, and a Pt–Ir on Ti mesh counter electrode. For one-dimensional patterns, the electrode potentials were controlled with a bipotentiostat (AFRDE5 Bipotentiostat, Pine Instrument Co., Grove City, PA), with the two working electrodes ($E_1$ and $E_2$) connected to opposite ends of the substrate electrode. Polymer bands were formed by applying different potential values to the edges of the ITO electrode to create a potential gradient along the surface. Two-dimensional patterns were created by controlling the potential at four different locations on the ITO substrate using a multielectrode potentiostat (CH1030, CH Instruments, Austin, TX). Four electrode potentials ($E_1$, $E_2$, $E_3$, and $E_4$) were applied at the corners of a 25 mm × 25 mm square of the ITO substrate.

Imaging. Images of the various samples were acquired with a high-resolution charge-coupled device (CCD) camera (Model VCC 3972, Sanyo) equipped with a variable zoom lens (Zoom 7000, Navitar). The camera was interfaced to a computer through a frame grabber card (Pinnacle Systems, Inc., Mountain View, CA), and images were captured using commercially available software (Studio 8, Pinnacle Systems). Image analysis was performed with Image J (National Institutes of Health).

Optical Spectroscopy. A fiber optic spectrometer with a reflectance probe (S2000 Miniature Fiber Optic Spectrometer, Ocean Optics, Inc., Dunedin, FL) and deuterium tungsten light source (DT-LS, Zaber Technologies Inc., Richmond, BC) was used to move the cell to the desired position beneath the optical fiber probe with a resolution of ~0.1 mm. Both the positioning motor and data collection were controlled via a custom LabView program (National Instruments Corp., Austin, TX).

Ellipsometry. Ellipsometry measurements were performed using an automated, multifunctional optical system (Multiskop, Optrtx Gbr, Berlin, Germany) with spatial mapping capabilities. Ellipsometric data were obtained at a single-wavelength (632.8 nm beam with ~0.6 mm diameter) in the PCSA configuration at a 70° angle of incidence. Film calculations were performed using a commercial software package (Elll, Optrtx Gbr, Berlin, Germany). The refractive index, $n$, and absorption coefficient, $k$, of the substrate (ITO: $n = 1.7$, $k = 0.0$; float glass: $n = 1.5$, $k = 0.153$) were determined using a three-phase model (air/ITO/float glass). Ellipsometric angles $\Delta$ and $\Psi$ were recorded with respect to position by translating the sample using an integrated stepper motor. The thicknesses of the polymer films with respect to position were calculated using a four-phase model (air/polymer/ITO/float glass).

Results and Discussion

In this work, we have exploited the spatial control provided by surface electric field gradients to perform directed surface patterning with electrodeposited polymers. Patterns were constructed with a combination of the conducting polymer polyaniline (PANI) and insulating polymers poly(phenylene oxide) (PPO) and poly(aminophenylene oxide) (PAPO). The electrodeposition and growth behavior of these polymers is fairly well understood. 25–28 PANI films are frequently grown by potential cycling or constant potential methods in acidic solutions. 25–28 The resulting films form a dense, fibrous network with potential application in sensing, controlled delivery,30–32 corrosion prevention, 33–35 and electrochromic displays. 25,36 Figure 1A shows a typical cyclic voltammogram for PANI during a growth cycle on an ITO electrode from a solution containing 0.5 M H$_2$SO$_4$ and 0.1 M aniline. Film growth occurs while cycling the

![Figure 1](Image 378x410 to 497x453)

Figure 1. Cyclic voltammograms of polymer film growth on ITO at a scan rate of 5 mV/s. (A) Polyaniline (PANI) film growth from 0.5 M H$_2$SO$_4$ and 0.1 M aniline. (B) Poly(phenylene oxide) (PPO) film growth in 0.1 M NaH$_2$PO$_4$ and 10 mM phenol (pH = 7). (C) Poly(aminophenylene oxide) (PAPO) film growth in 0.1 M NaH$_2$PO$_4$ and 10 mM aminophenol (pH = 7). Arrows indicate increasing scan number.

Scheme 1. Voltage Scale Depicting Peak Potential Values Where Polymer Deposition Occurs

![Scheme 1](Image 382x556 to 493x744)
potential between −0.3 and 0.9 V versus Hg/HgSO₄ at 5 mV/s. The large anodic peak centered at \( E_{\text{PANI}} = 0.7 \text{ V} \) (Scheme 1) corresponds to aniline monomer oxidation, while the pair of peaks at −0.2 and 0.0 V reflects oxidation/reduction of the deposited polymer and the transition between the yellow, fully reduced leucoemeraldine state and the green, half-oxidized emeraldine state. Growth of the polymer is indicated by the increasing current with each potential cycle. The thickness of the PANI film has been shown to increase in relation to the total charge passed during cycling.²⁸,²⁹,³⁷

While oxidation of the aniline monomer forms conductive PANI films, oxidation of phenol³⁸–⁴¹ and aminophenol⁴² at an electrode surface produces insulating films of poly(phenylene oxide) (PPO) and poly(aminophenylene oxide) (PAPO), respectively. An example of the electrodeposition of a film of PPO on ITO in 0.1 M phosphate buffer (pH 7) containing 10 mM phenol is shown in Figure 1B. During the first anodic scan, a large peak appears at \( E_{\text{PPO}} = 0.5 \text{ V} \), corresponding to the oxidation of the phenol monomer. Subsequent cycles show significantly reduced currents. This behavior is consistent with the formation of a thin, compact, and insulating film of PPO on the electrode surface.⁴¹

The self-limiting growth of these films has prompted their use as thin insulators for the fabrication of microelectrodes and organic devices.³⁸,⁴⁰,⁴²,⁴³

Poly(aminophenylene oxide) (PAPO) growth follows a similar mechanism to that of PPO, although it has been suggested that both the hydroxyl and amino groups participate in the electropolymerization.⁴² The electrodeposition of PAPO on ITO in 0.1 M phosphate buffer (pH 7) containing 10 mM aminophenol is shown in Figure 1C. An oxidation peak is observed at \( E_{\text{PAPO}} = 0.3 \text{ V} \) during the first anodic cycle, with subsequent cycles showing a decrease in the current. This behavior is also consistent with the formation of a compact, insulating film.

The electrochemical behavior depicted in Figure 1 for these three polymer systems illustrates the fact that film formation proceeds at a potential where monomer oxidation occurs. Therefore, in addition to potential cycling,³⁹,⁴¹,⁴² films may be formed by constant potential deposition at potential values near or above the onset of monomer oxidation. For aniline, monomer oxidation begins near −0.5 V, with a peak at \( E_{\text{PANI}} = 0.7 \text{ V} \) (Scheme 1). For phenol and aminophenol, oxidation begins at −0.0 and 0.1 V, with peak potentials of \( E_{\text{PPO}} = 0.5 \text{ V} \) and \( E_{\text{PAPO}} = 0.3 \text{ V} \), respectively. At potentials below the onset values, monomer oxidation does not occur, while at and above these potentials, monomer oxidation results in polymer growth. Thus, each monomer exhibits a potential where the onset of polymerization occurs.

One can exploit this behavior to spatially localize deposition and direct deposition on surfaces using a surface electric field. A simple example of polymer patterning is shown in Figure 2, where two distinct regions of PANI and PPO have been electropolymerized onto ITO. A 25 mm long strip of ITO was placed in a solution of phenol, and a potential gradient was applied between the two edges, \( E_1 \) at the left of the sample was held at a potential of −0.1 V, while \( E_2 \) at the right edge of the sample was held at 0.6 V, which created a linear potential drop across the electrode (Figure 2A, curve i). This potential profile was held for a period of 10 min, and a PPO film grew on the right half of the electrode where the surface potential exceeded the monomer oxidation potential (\( E > E_{\text{PPO}} \)). Subsequently, the substrate was placed in an aniline solution and the entire substrate was held at 0.7 V near the deposition potential for PANI (\( E \sim E_{\text{PANI}} \)) for 2 min (Figure 2A, curve ii). This resulted in a PANI film being deposited on regions free of PPO, which served as a barrier to deposition. In the absence of the PPO film, PANI deposition would have been uniform over the surface of the ITO. This procedure resulted in a surface with an alternating region of PANI on the left and PPO on the right.

The presence and location of PANI and PPO films were verified using scanning UV-vis spectroscopy. A reflectance probe was scanned across the surface using a micropositioning system, and absorbance data were collected every 1 mm at a wavelength of 750 nm. The 750 nm band corresponds to absorbance from the conducting emeraldine state of PANI,⁴⁴–⁴⁶ Absorbance with respect to position is plotted in Figure 2B for the PANI-PPO sample and for bare ITO. For the bare ITO curve, the surface is featureless due to the transparency of the ITO sample in this wavelength region. In the presence of the polymer film, there

is a strong absorbance on the left side of the sample, corresponding to the PANI film, and a weak absorbance on the right where the PPO is located. At ~10 mm, there is a sharp decrease in absorbance, consistent with the sharp boundary between the PANI and PPO films.

Scanning null-ellipsometry was used to further quantify the thicknesses of the PANI and PPO films. Complete details of the ellipsometry measurements can be found in the Supporting Information. Film thicknesses were estimated by fitting the ellipsometry results to a four-layer interface model, which included the substrate glass, a thin ITO film, the polymer, and then air. The polymer film thickness and refractive index were used as fitting parameters. Notably, previous ellipsometry studies of PANI films have shown that both the refractive index and extinction coefficient vary with film thickness and polymer oxidation state.26–28

As noted in Figure 2C, PANI film thickness was found to vary from ~180 nm on the far left of the sample down to ~140 nm near the center. Although the PANI film appeared to decrease in thickness across the sample, the PPO film maintained a consistent thickness near ~120 nm. This PPO film was found to be somewhat thicker than previous literature values of 10–100 nm.30,42 The authors suspect that the difference in film thickness from that reported in previous studies is related to the film growth technique. In this study, the PANI film was grown at a constant potential as opposed to cycling, which is the method typically used for growth. A constant potential deposition might lend itself to thicker film growth due to a lower efficiency in the filling of the pin holes in the film. A schematic for the proposed surface containing the PANI and PPO regions is depicted in Figure 2D.

The ability to manipulate surface electric fields to localize polymer growth can readily be extended to more complex patterns. Figure 3 depicts a series of samples in which an increasing number of polymer bands are created by sequential deposition of PANI and PPO or PAPO layers. The potential profiles used to construct these samples are described in detail in the Supporting Information. The various polymers present on these samples are noted on the images. Notably, the dark regions correspond to PANI deposits, while the white regions correspond to areas of PPO or PAPO.

Figure 3. Optical images of four different polymer band constructions possessing alternating regions of insulating (PPO and PAPO) and conducting (PANI) polymer films. (A) Two band, PPO-PANI; (B) three band, PANI-PAPO-PANI; (C) four band, PANI-PAPO-PANI-PAPO; and (D) five band, PANI-PPO-PANI-PPO-PANI.

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Figure 4. Construction of a two-dimensional PANI surface pattern. (A) Contour plot of the computed surface electric field generated by holding $E_1$ and $E_3$ at $-0.2$ V and $E_2$ and $E_4$ at 0.7 V. (B) Sample image of a PANI film formed using the potential profile described in (A), with deposition at the top right and bottom left corners of the sample.

The ability to control deposition via surface electric field gradients can be further extended to two-dimensions to create more complex patterns. Examples of various two-dimensional polymer patterns are shown in Figures 4–6. In this system, four working electrodes are independently controlled to produce a variety of two-dimensional patterns. Figure 4 depicts two-dimensional potential profiles and an optical image of a simple pattern created with this four-electrode system. A PANI film was electrodeposited at the top right and bottom left corners by holding $E_1$ and $E_3$ at $-0.2$ V and $E_2$ and $E_4$ at 0.7 V for 30 s in an aniline-containing solution. Figure 4A is a contour plot of the calculated electric field on the two-dimensional surface. Figure 4B depicts the sample following deposition, with dark regions in the upper right and lower left corners corresponding to regions of PANI deposition. There is good agreement between the modeled potential profile and the sample structure, with PANI being thickest in areas with applied potentials near and above the value required for monomer oxidation ($E \sim E_{\text{PANI}}$) and a
decrease in thickness as the applied surface potential drops below that value. The film extends only to the region of surface potential values near 0.5 V, which corresponds to the onset of oxidation as seen in Figure 1A.

More complex surface patterns can also be created. Figure 5 is an example of a three-step pattern resulting in five different polymer regions, with PPO deposited in the four corners and PANI deposited in the center. To create this surface, PPO is first deposited at the top left and bottom right corners by holding $E_1$ and $E_3$ at 0.6 V and $E_2$ and $E_4$ at 0.25 V for 10 min in a solution containing phenol. Figure 5A is a contour plot of the applied electric field. The PPO film only forms on regions of the surface with an applied potential greater than 0.4 V, corresponding to the upper left and lower right sample regions. The deposition of PPO in these two corners is followed by the deposition of PPO in the upper right and lower left corners by holding $E_1$ and $E_3$

Figure 5. Construction of a two-dimensional surface pattern of PPO and PANI films. (A) Contour plot of the electric field used to deposit PPO at the top left and bottom right corners. (B) Contour plot of the electric field used to deposit PPO at the top right and bottom left corners. (C) Contour plot of the electric field used to deposit PANI at the center of sample. (D) Optical image of a sample containing PPO in four corners and PANI in the center.

at $-0.25$ V and $E_2$ and $E_4$ at 0.6 V for 10 min in a phenol-containing solution. Figure 5B is a contour plot of the associated electric field on the surface. The final deposition step involves directing PANI growth to the center of the sample. This is achieved by holding all four corners at 0.7 V in the presence of aniline. The surface electric field under these conditions is illustrated as a contour plot in Figure 5C. The PPO films deposited in the first and second steps are insulating, and they prevent PANI deposition at the corners of the sample. The PANI film only deposits on the exposed ITO surface in the center of the substrate. Figure 5D is an optical image of the resulting polymer surface, where the dark regions near the center correspond to PANI and the light regions at the sample edges are covered with PPO.

A variety of other two-dimensional surface patterns were created by changing the potential profile along the surface and the sequence of the deposition steps. Figure 6 is a compilation of patterns produced with this four electrode system. The simplest pattern is shown in Figure 6A, with PANI deposited at $E_2$ and $E_4$ following the procedure outlined for Figure 4. Figure 6B is continuation of Figure 6A, with all four corners having PANI deposits. Figure 6C is a replica of Figure 5, with PPO films in the four corners and a PANI film in the center. Figure 6D demonstrates a more complex, two-dimensional pattern formed by combining results from Figure 6B and C. In this sample, PANI was initially coated at the upper left and lower right corners by holding $E_1$ and $E_3$ at 0.7 V with $E_2$ and $E_4$ at $-0.25$ V in an aniline-containing solution. An insulating layer of PPO was then formed over this PANI deposit and extended toward the sample center by holding $E_1$ and $E_3$ at 0.6 V and $E_2$ and $E_4$ at $-0.3$ V. The process was repeated for the remaining two corners by holding

Figure 6. Examples of two-dimensional patterned films containing PPO and PANI films. Details of the samples and construction methods are provided in the text.
$E_2$ and $E_4$ at 0.7 V and $E_1$ and $E_3$ at $-0.25$ V in the presence of aniline and then holding $E_2$ and $E_4$ at 0.6 V and $E_1$ and $E_3$ at $-0.3$ V in a phenol solution. This produced a sample with PANI deposited at the four corners and a layer of PPO extended in a ring away from the corners toward the center of the sample. In the last step, the entire sample was held at 0.7 V, resulting in PANI deposition over the remaining bare surface at the sample center. The result of this deposition procedure is a complex, two-dimensional polymer pattern containing both PANI and PPO films. A variety of additional patterns with increasing complexity can be readily envisioned.

Conclusions

This paper describes a method for the directed deposition of polymer films onto electrode surfaces. Spatially controllable surface electric fields are used to localize the electrochemical deposition of several polymer films at desired sample locations. This provides an ability to construct a variety of surface patterns, ranging from simple one-dimensional bands to more complex, two-dimensional patterns. This technique requires no prior surface treatments and involves relatively simple, benchtop instrumentation. Furthermore, this directed deposition technique has potential for application in parallel processing and high-throughput fabrication. Patterned polymer films are applicable to a variety of technologies, including polymer light-emitting devices, organic electronics, analytical sensors, as well as for fundamental studies of surface and thin film properties.

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Supporting Information Available: Detailed null-ellipsometry results for a two band sample, characterization of a three band sample using UV—vis spectroscopy and null-ellipsometry, and recipes for the construction of various one-dimensional patterns shown in Figure 3. This material is available free of charge via the Internet at http://pubs.acs.org.

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