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with Printed Monolayers of Alkylsiloxanes
as Templates**

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This paper describes the use of patterned self-assembled monolayers (SAMs) in area-selective deposition of conducting polymers (polypyrrole and polyaniline) on *insulating*, hydroxyl-terminated surfaces such as Si/SiO₂ and glass. Patterned SAMs of octadecylsiloxane were generated on the hydroxyl-terminated surfaces using microcontact printing; they defined and directed the deposition of conducting polymers. The rate of deposition on the hydrophobic surface is higher than that on the hydrophilic surface: immersion of a substrate patterned with a methyl-terminated SAM in an appropriate aqueous polymerization bath produced a "positive" pattern of the conducting polymer on the surface. The conducting polymer deposited on the hydrophobic region of a surface completely covered by the polymer could be readily removed by transferring it to adhesive tape to form a "positive" pattern on the tape, leaving a "negative" pattern on the surface of the substrate. The conducting polymer deposited on the hydrophobic surface had a more extended conformation, and thus a higher conductivity (approximately 3 orders of magnitude in difference) than that formed on the hydrophilic surface. The smallest features of conducting polymers generated using these procedures were $\sim 2 \mu\text{m}$ in lateral dimension. The edge roughness of these patterns was $\sim 0.5 \mu\text{m}$. These patterned microstructures of conducting polymers were conductive; they have been used as electrodes in display devices based on polymer dispersed liquid crystals.

Introduction

Conjugated organic polymers are increasingly important as active materials in optoelectronics,¹ microelectronics,² microelectromechanical systems (MEMS),³ sensors,⁴ and related areas.⁵ For example, the undoped, semiconductive forms of conjugated polymers are used in the fabrication of microelectronic devices such as diodes, light-emitting diodes (LEDs), and transistors.^{1,2} The doped, conductive forms of conjugated polymers are being evaluated as potential alternatives to metals as connecting wires and conductive channels, since the conductivity of these materials can be tuned over a wide range by changing the dopant and/or doping level. Flexible, all-plastic, microelectronic devices based on conjugated organic polymers are now appearing in prototype forms.^{6,7}

Many of these applications require the formation of patterns and structures of conjugated organic polymers

with feature sizes $\leq 100 \mu\text{m}$. A number of techniques have been successfully demonstrated for the formation of patterned microfeatures of these materials: for example, photolithography,⁸ e-beam writing,⁹ laser writing,¹⁰ and surface-templated deposition.¹¹ Here we wish to report another procedure for such application that combines microcontact printing (μCP)¹² and area-selective deposition.¹¹

Microcontact printing is a convenient, non-photolithographic technique that has been used to form patterned microfeatures of self-assembled monolayers (SAMs) on the surfaces of a variety of substrates.¹² Patterned features as small as $0.5 \mu\text{m}$ can be routinely generated on both planar and nonplanar surfaces.¹³ The capability of patterning a surface with different monolayers allows us to easily tailor the physical and/or chemical properties of this surface and thus allows us to define and control the nucleation and deposition of other materials on this surface. For example, we have been able to attach mammalian cells selectively,¹⁴ and Nuzzo and co-workers

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have deposited copper by chemical vapor deposition (CVD), exclusively,¹⁵ on certain regions of a surface by patterning this surface with appropriate SAMs. Here we demonstrated that patterned SAMs can serve as templates for area-selective deposition to form patterned microstructures of conducting polymers on surfaces of insulating substrates terminated with hydroxyl groups.¹⁶

The SAMs used in the present work were octadecylsiloxanes on Si/SiO₂ or glass. Polypyrrole (PPY) and polyaniline (PANI) were chosen in the present study for their ease of preparation and their excellent stability in air. This work demonstrates a convenient, low-cost method for forming patterned microstructures of conducting polymers on insulating substrates and provides a potential protocol for fabricating flexible, all-plastic, electronic or optoelectronic devices.

Experimental Section

Materials and Substrates. Octadecyltrichlorosilane (OTS, 95%), anthraquinone-2-sulfonic acid, sodium salt monohydrate (97%), 5-sulfosalicylic acid dihydrate (99+%), FeCl₃·6H₂O (98%), and pyrrole (98%) were purchased from Aldrich. Aniline (99.9%), (NH₄)₂S₂O₈ (99.4%), and hydrochloric acid (37.5%) were obtained from Fisher Scientific. All chemicals were used as received unless a purification procedure is mentioned in the text. Microscope slides (Gold Seal, precleaned) were obtained from Clay Adams Co. The poly(dimethylsiloxane) (PDMS) elastomer (Sylgard 184) was obtained from Dow Corning (Midland, MI). Polished Si(100) wafers (Cz, N/phosphorus-doped, 1–10 Ω cm, test grade, and SEMI standard flatness) covered by native oxide were obtained from Silicon Sense (Nashua, NH). Si/SiO₂ substrates and glass slides were cleaned by heating at ~70 °C for ~1 h in a freshly prepared piranha solution (a mixture of 98% H₂SO₄ and 30% H₂O₂, 7:3, v/v), followed by extensive rinsing with distilled water. They were dried under a stream of nitrogen and were used immediately. **Caution:** piranha solution is an extremely strong oxidant and should be handled with care.

Microcontact Printing of Octadecyltrichlorosilane. The stamps were fabricated by casting a liquid prepolymer of PDMS against appropriate masters according to published procedures.^{12,17} The masters were patterned relief structures in thin films of either photoresist or wax and were fabricated using photolithography and micromachining, respectively. The "ink" used for the present work was an ~0.2% (w/w) solution of OTS in hexane; it was prepared and stored in a nitrogen-filled glovebox and could be used up to 2 months if filtered through a nylon membrane (Spartan-25, 0.2 μm pore size) each time before use. The PDMS stamp was inked with a Q-tip cotton swab (Figure 1), and then brought into contact with the substrate for 15–30 s.¹⁸ SAMs only formed on those areas of the surface that were in contact with the stamp during printing.

Polymerization and Deposition of Conducting Polymers. Polymerization of PPY and PANI were carried out at room temperature (23–25 °C). In general, two solutions (one containing the monomer and the other containing the oxidant) were prepared separately and then mixed together to start the polymerization. The polymerization time was registered relative to the point when the two solutions were mixed together. When glass slide was used as the substrate, the side that had not been patterned with SAMs was covered with adhesive tape to block the polymerization and deposition of polymers on the surface of this side.

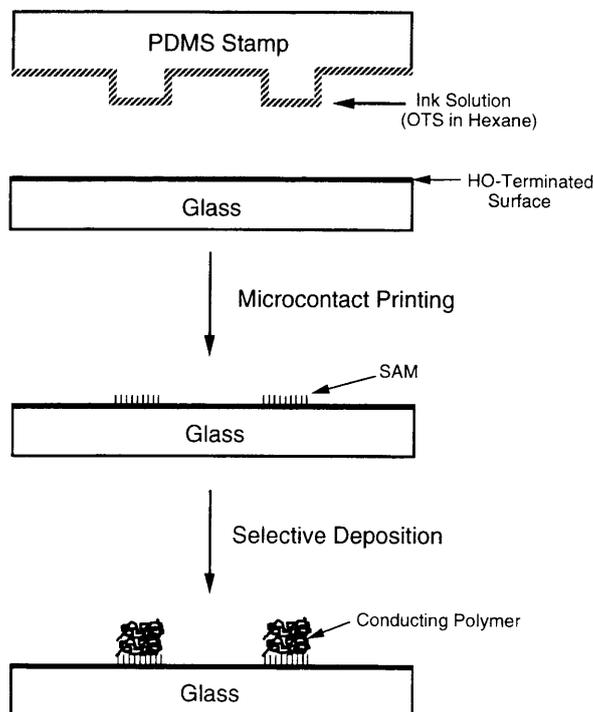


Figure 1. Schematic illustration of the procedure used for the formation of patterned microstructures of conducting polymers with printed SAMs as templates.

Polymerization and Deposition of Polypyrrole.¹⁹ Anthraquinone-2-sulfonic acid, sodium salt monohydrate (2.45 g), 5-sulfosalicylic acid dihydrate (13.35 g), and FeCl₃·6H₂O (8.75 g) were dissolved in 250 mL of distilled water. The substrates patterned with SAMs were placed in this solution using plastic clamps and were equally spaced. An aqueous solution of pyrrole (1.5 mL in 250 mL of distilled water) was then added slowly with mild magnetic stirring. After different periods of polymerization, the substrates were taken out, washed in distilled water for ~10 min, and then dried under a stream of nitrogen.

Polymerization and Deposition of Polyaniline.²⁰ The aniline was purified by distillation in vacuum. The substrates patterned with SAMs were placed in an aqueous solution containing aniline (4 mL) and 1 M HCl (200 mL) solution using plastic clamps and were equally spaced. Another solution containing (NH₄)₂S₂O₈ (2.3 g) and 1 M HCl (100 mL) was added to initiate polymerization. The substrates were taken out after ~5 min and placed in an aqueous solution of aniline (8 mL) in 1 N HCl (200 mL) for ~30 min to reduce the oxidation state of polyaniline from the pernigraniline to the emeraldine.²⁰ The substrates were then immersed in 1 M HCl for ~1 min and dried under a stream of nitrogen.

Adhesive Tape Test of Deposited Films. A piece of invisible tape (Highland, 3M) was placed on the deposited film, pressed gently to achieve a homogeneous contact between the tape and the film, and then peeled off quickly.

Fabrication of Polymer Liquid Crystal (PDLC) Display Devices. A display device can be easily fabricated by sandwiching a thin layer of PDLC between two electrodes. In our experiments, one electrode was a piece of glass slide coated with an interdigitated array of polypyrrole and the other was another piece of glass slide covered with a thin layer of indium-tin-oxide (ITO). The pattern of polypyrrole was fabricated using area-selective deposition with a polymerization time of ~10 min. Three drops of E7 liquid crystal fluid (BDH Ltd.), seven drops of NOA-65 optical adhesive (Norlands Products, New Brunswick, NJ), and ~20 mg of 15 μm polystyrene spacer (EM. Ind.) were mixed thoroughly in a watch glass. One or two drops of this homogeneous mixture were spread onto the glass slide patterned with

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polypyrrole and the ITO electrode was then carefully placed on the top of the liquid film. After the fluid was solidified by exposure to a UV light for ~ 20 min, copper wires were attached to the pads of the pattern of polypyrrole using silver paste (DuPont) and these pads were subsequently covered with epoxy glue.

Instrumentation. Ultraviolet–visible–near-infrared (UV–vis–near-IR) spectra were taken on a Perkin-Elmer Lambda 9 spectrometer supported with 7700 computer software. Scanning electron micrographs were taken on a JEOL JSM-6400 (or JSM-6300) scanning electron microscope. Ellipsometry measurements were done using a thin film ellipsometer (Type 43603–200E, Rudolph Research, NJ) with Si/SiO₂ as the substrate.

Results and Discussion

Area-Selective Deposition of Conducting Polymers. The success of area-selective deposition of a conducting polymer using a patterned template depends principally on the interfacial properties and the exposed molecular functionality of the surface. Figure 1 outlines the procedure that we have used. The SAM of octadecylsiloxane changed the wettability of a hydroxyl-terminated surface from hydrophilic to hydrophobic: the change in water contact angle was from $\sim 3^\circ$ to $\sim 110^\circ$. The polymerization and deposition of polypyrrole and polyaniline occurred more rapidly on the CH₃-terminated, hydrophobic regions than on the OH-terminated, hydrophilic regions.

Figure 2 shows SEM images of patterned microstructures of PPY and PANI deposited on glass slides with printed SAMs of OTS as templates. The smallest feature of the conducting polymer was $\sim 2 \mu\text{m}$ in lateral dimension. The quality of these patterns is obviously lower than that of patterns generated using e-beam writing and photolithography.^{8,9,21} The present procedure may, however, be useful for its convenience and low cost and for its ability to form micropatterns on nonplanar surfaces¹³ and/or over large areas.²²

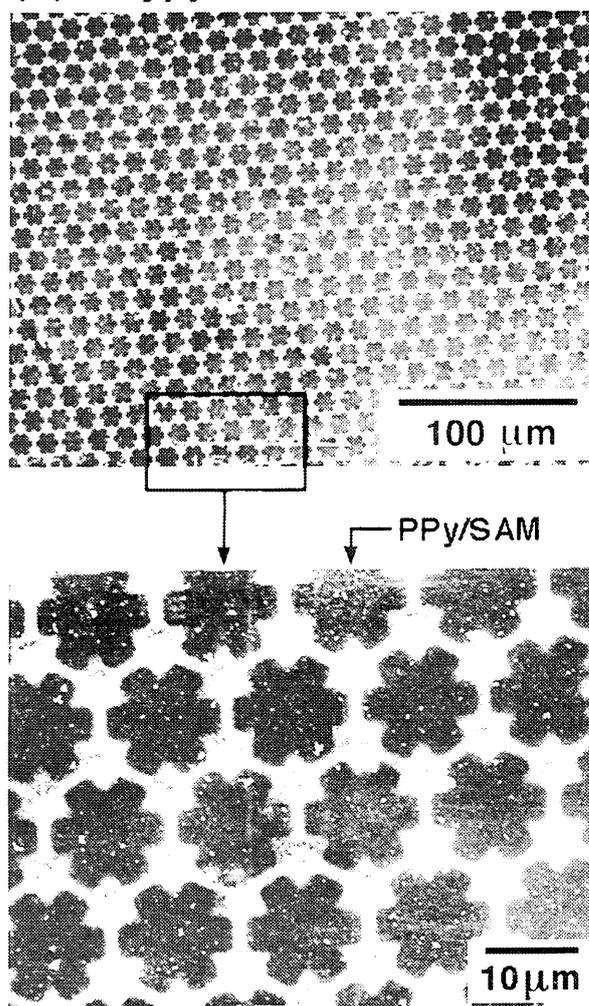
We also measured quantitatively the change of thickness of polypyrrole with the duration of the polymerization/deposition (Figure 3). Si/SiO₂ wafers ($\sim 1 \times 2 \text{ cm}^2$) were used as the substrate; half of the surface of each substrate had been derivatized with a SAM of OTS by printing with a flat PDMS stamp. Immediately after immersion in the polymerization bath, deposition occurred predominantly on the hydrophobic region. The selectivity decreased as polymerization proceeded. For example, deposition of polypyrrole on the hydrophobic region was greater than that on the hydrophilic region by a factor of ~ 6 when the deposition time was ~ 6 min, but was ~ 2 for a deposition time of ~ 15 min.

Electronic Structure of Polypyrrole Films Deposited with SAMs as Templates. The electronic structure of thin films of polypyrrole deposited using the present procedure depends strongly on the interfacial properties of the surface. Figure 4 shows UV–vis–near-IR spectra of thin films of polypyrrole selectively deposited on the SAM-derivatized (hydrophobic) region and the bare (hydrophilic) region, respectively. The substrates used here were glass slides; half of the surface of each slide had been derivatized with a SAM of OTS by printing with a flat PDMS stamp. The polymerization/deposition was allowed to proceed for ~ 15 min. The UV–vis–near-IR spectrum (Figure 4A) of the thin film of polypyrrole deposited on the hydrophobic region shows a steadily increasing “free-carrier-tail” starting from ~ 1000 nm to the IR region; the UV–vis–near-IR spectrum (Figure 4B)

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(A) Polypyrrole



(B) Polyaniline

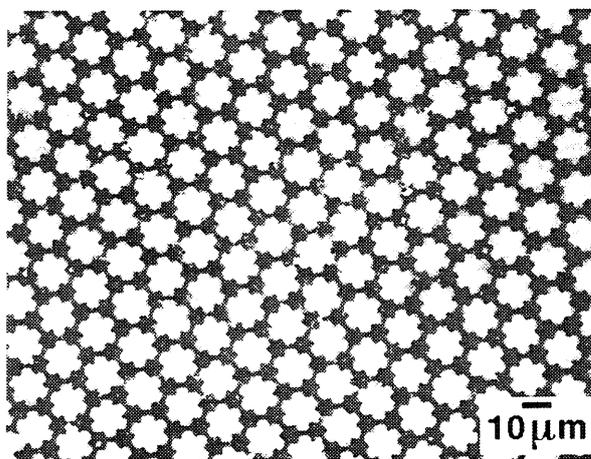


Figure 2. SEM images of patterned microstructures of (A) polypyrrole and (B) polyaniline deposited on glass slides with printed SAMs as templates. The polymerization time was ~ 10.5 min for polypyrrole and ~ 5 min for polyaniline. The dark regions are conducting polymers selectively deposited on the hydrophobic, SAM-covered regions; the bright regions are hydrophilic, bare regions. The stamps used for polypyrrole and polyaniline had complementary relief patterns on their surfaces.

of the thin film of polypyrrole deposited on the hydrophilic region shows a broad absorption band with a maximum at ~ 1182 nm.

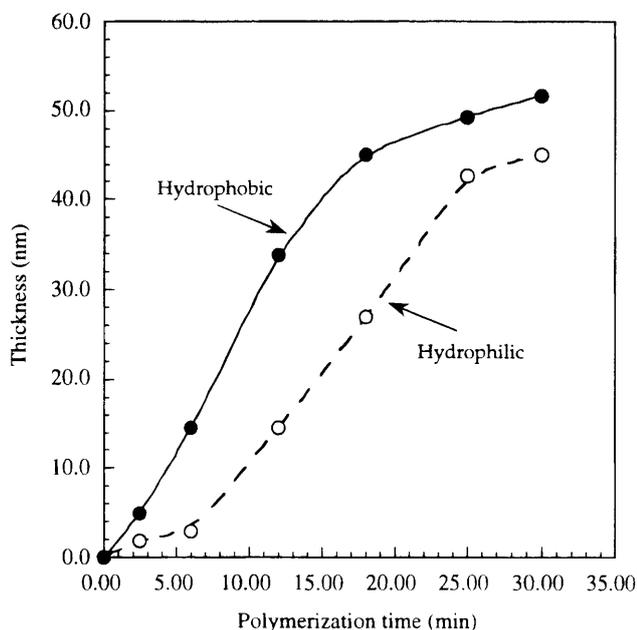


Figure 3. Dependence of thickness of deposited polypyrrole on the time elapsed during polymerization/deposition. The thickness of polypyrrole was measured using an ellipsometer. Si wafers covered with native oxide were used as the substrates; half of the surface of each substrate was printed with SAMs using a flat PDMS stamp.

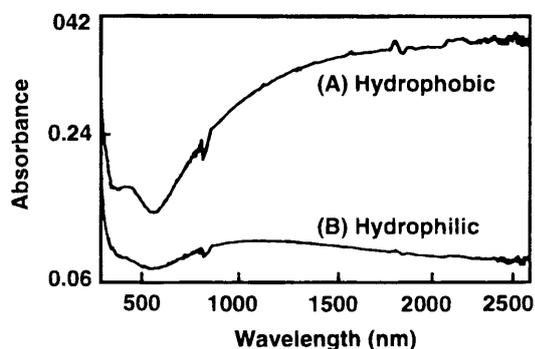


Figure 4. UV-vis-near-IR spectra of thin films of polypyrrole deposited (with a polymerization time of ~ 15 min) on different regions of a patterned surface: (A) hydrophobic region; (B) hydrophilic region.

The "free-carrier-tail" in the near-IR region is characteristic of mobility of conductive electrons.²³⁻²⁵ We have previously proposed from detailed studies of polyaniline films deposited from "good" and "poor" solvents that the presence of a well-developed "free-carrier-tail" is associated with an "expanded coil" molecular conformation while its absence and the appearance of a localized polaron peak is associated with a "tight coil" molecular conformation which reduces π conjugation along the polymer backbone and hence conduction electron mobility.²⁶ We believe that the presence of a "free-carrier-tail" in the UV-vis-near-IR spectrum of the PPY deposited on a hydrophobic surface may be associated with a more extended molecular conformation than the polymer deposited on a hydrophilic surface which only shows a localized polaron adsorption at ~ 1182 nm. The interfacial properties of a substrate probably only directly determine the properties of polymer

chains within the first several monolayers initially polymerized on the surface; these polymer chains may, however, influence the conformational properties of polymer chains polymerized afterward.

Electrical Properties of Conducting Polymers Deposited with SAMs as Templates. The most surprising and interesting feature of the present study (and possibly a feature of significant technological importance) was the discovery of enormous difference in sheet resistivity of the polymer films deposited on hydrophobic versus hydrophilic surfaces. The sheet resistivity of a polypyrrole film deposited (with a polymerization time of ~ 15 min) on the CH_3 -terminated, hydrophobic surface was $\sim 1.6 \times 10^3 \Omega/\square$ (the corresponding conductivity was $\sim 150 \text{ S/cm}$, based on a film thickness of $\sim 410 \text{ \AA}$ from Figure 3); the film deposited (with the same polymerization time) on the OH-terminated, hydrophilic surface had a sheet resistivity greater than the limit of the ohmmeter employed, i.e., $> 10^7 \Omega/\square$ (the corresponding conductivity was $< 0.5 \text{ S/cm}$, based on a film thickness of $\sim 20 \text{ \AA}$ from Figure 3). A similar electrical behavior was also observed for polyaniline films deposited with SAMs as templates: the sheet resistivity of a polyaniline film deposited (with a polymerization time of ~ 5.5 min) on the hydrophobic surface was $\sim 5 \times 10^3 \Omega/\square$ whereas that of a film deposited on the hydrophilic surface was $> 10^7 \Omega/\square$.

Lines of PPY (~ 1 cm in length, $\sim 200 \mu\text{m}$ in width, deposited on the hydrophobic regions of a SAM-patterned surface with a polymerization time of ~ 15 min) were prepared on glass slides and used for the measurement of conductivity. A conductivity of $\sim 100 \text{ S/cm}$ was measured using the two-probe method. An interdigitated array containing isolated lines ($\sim 500 \mu\text{m}$ in width, separated by $\sim 300 \mu\text{m}$) of PPY was also fabricated to test isolation. The measured resistance across this array was $> 10 \text{ M}\Omega$ (beyond the measurable range of the instrument). This value is more than 3 orders of magnitude higher than that measured on continuous regions of PPY films, confirming that PPY lines that are $\sim 300 \mu\text{m}$ in separation are electrically isolated from each other by a medium having much lower conductivity.

Adhesion Properties of Deposited Conducting Polymers. The adhesion between a deposited polymer and a substrate is mainly determined by the interfacial properties of the substrate. In many cases, the adhesion strength is related to the surface free energy of the substrate.²⁷ As a result, the patterned SAMs used here not only controlled the nucleation and deposition of a conducting polymer but also influenced the adhesion between the deposited film of this polymer and the substrate.²⁸ We found that the deposited thin films of polypyrrole adhered more strongly to the hydrophilic, bare region than to the hydrophobic region derivatized with SAMs of OTS. This property has been used in a different system to fabricate both "positive" and "negative" patterns of polypyrrole using a procedure similar to the adhesive tape test.²⁹ For example, we immersed a SAM-patterned substrate in the polymerization bath for ~ 18 min to cover the entire surface with a thin layer of polypyrrole, and then we removed the film on the hydrophobic region by transferring it to adhesive tape to form a "positive" pattern (that is, the pattern of the SAM on the original substrate) on the tape and to leave a complementary, "negative" pattern on the surface of the substrate. Figure 5 shows SEM images of the "positive" and "negative" patterns of polypyrrole prepared using this procedure. The adhesion

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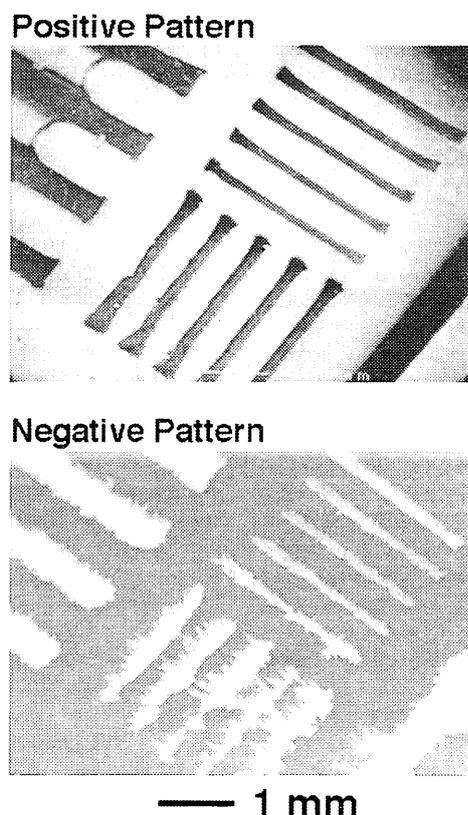


Figure 5. SEM images of a "positive" pattern (that is, polypyrrole deposited on the hydrophobic region) of polypyrrole and the corresponding "negative" pattern (that is, polypyrrole deposited on the hydrophilic region).

between polypyrrole and the bare, hydrophilic region was strong enough to pass the adhesive tape test. The adhesion between the polymer and the SAM-derivatized region was relatively weak, and the film was easily removed by using adhesive tape.

Patterned Thin Films of Polypyrrole as Electrodes in Liquid Crystal Display Devices. The surface resistivity of thin films of PPY deposited on the hydrophobic regions was more than 3 orders of magnitude lower than that of films deposited on the hydrophilic regions. As a result, we could directly fabricate display devices using as-deposited microstructures of PPY as the electrodes. Figure 6 shows photographs of a display device based on polymer dispersed liquid crystals (PDLC).³⁰ The interdigitated array of polypyrrole was deposited on the hydrophobic region of a glass slide with a polymerization time of ~ 10 min. This polymerization time, and therefore the thickness of the deposited film of polypyrrole, was chosen such that the optical transparency in the visible region and the resistance of the formed film were both optimized. A mixture of PDLC was sandwiched between two glass slides; one of them had been covered with the interdigitated array of polypyrrole and the other one had been coated with a thin film of indium-tin-oxide (ITO). A thin layer of PDLC is opaque because the incident light is scattered from the submicrometer-sized droplets of PDLC. This layer becomes transparent when a voltage is applied between the two electrodes and the droplets are oriented in the electric field to an orientation where their reflective index matches that of the polymer matrix. The procedure demonstrated here could also be extended to form patterned microstructures of conducting polymers

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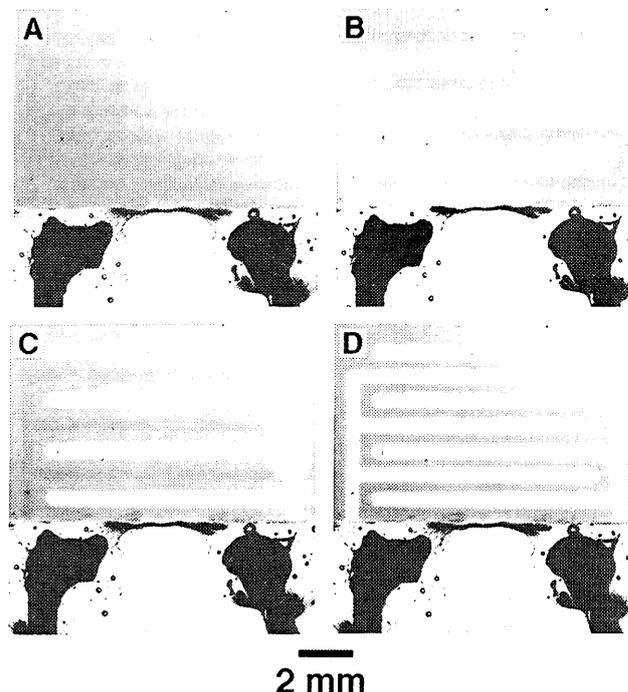


Figure 6. Photographs of a PLCD device with a micropattern of interdigitated pair: (A) no voltage was applied; (B) the left-half of the pair was turned on; (C) the right-half of the pair was turned on; (D) the whole pattern was turned on. The applied ac voltage was 110 V, 60 Hz. The bottom half in each small figure is Cu wires attached to the pads of the PPY pattern.

on insulating, polymeric films that could be subsequently used to fabricate flexible, all-plastic electronic and optical devices.

Summary

In summary, we have demonstrated a simple, convenient, and low-cost method for forming micropatterns and microstructures of conducting polymers (polypyrrole and polyaniline) on insulating substrates. The interfacial properties of a surface control the polymerization, deposition, and adhesion of conducting polymers on a substrate. The rate of deposition on the hydrophobic surface is somewhat higher than that on the hydrophilic surface; the sheet resistivity of the film deposited on the hydrophobic surface is several orders of lower than that of the film deposited on the hydrophilic surface. Using patterned SAMs of octadecylsiloxane (formed by μ CP) as templates, we have been able to form patterned microstructures of conducting on hydroxyl-terminated surfaces with a minimum feature size of $\sim 2 \mu\text{m}$. The substrates used here could be insulators and semiconductors (for example, glass slides, plasma-treated polymer films, and Si/SiO₂). The patterned microstructures of conducting polymers formed this way could be directly used as electrodes in display devices or sensors³¹ and as connecting wires in micro-electronic circuits. As a prototype example, we have fabricated PDLC display devices using patterned microstructures of PPY as the electrodes.

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