

Dip-pen nanopatterning of photosensitive conducting polymer using a monomer ink

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Controlled patterning of conducting polymers at a micro- or nanoscale is the first step towards the fabrication of miniaturized functional devices. Here, we introduce an approach for the nanopatterning of conducting polymers using an improved monomer “ink” in dip-pen nanolithography (DPN). The nominal monomer “ink” is converted, *in situ*, to its conducting solid-state polymeric form after patterned. Proof-of-concept experiments have been performed with acid-promoted polymerization of pyrrole in a less reactive environment (tetrahydrofuran). The ratios of reactants are optimized to give an appropriate rate to match the operation of DPN. A similar synthesis process for the same polymer in its bulk form shows a high conductance and crystalline structure. The miniaturized conducting polymer sensors with light detection ability are fabricated by DPN using the improved ink formula, and exhibit excellent response, recovery, and sensitivity parameters. © 2004 American Institute of Physics. [DOI: 10.1063/1.1737469]

Conducting polymers are attractive alternatives for microelectronic materials that can be used in interconnection,¹ fabrication,² and panel display³ due to the unique combination of lightweight, structural and property flexibility, and certain processability. For these applications, the controlled patterning of conducting polymers at a desired location is essential.^{4,5} Dip-pen nanolithography (DPN) is suited for nondestructive, low cost, direct, and serial patterning.^{6–8} Lim and Mirkin⁹ has shown the patterning of polypyrrole on a self-assembled monolayer via electrostatic attraction. However, the low solubility of conducting polymers prevents the preparation of concentrated inks for a reliable and practical patterning. A simultaneous synthesis and patterning protocol is developed in electric DPN by using *in situ* electric-field-induced polymerization of thiophene between a conductive surface and a conductive atomic force microscope (AFM) tip.¹⁰ However, the structures that are produced cannot be used directly as components in electronic devices because such devices have to be made on insulating substrates. In addition, these DPN approaches generate pristine conducting polymers that cannot be easily doped to enhance conductance. Therefore, so the conductance of patterned structures is low and no device performance is reported. On the other hand, most conducting polymers produced by usual methods are intractable, insoluble films or powders. Many attempts have been made to improve the processability of the polymer without compromising its properties. Among these, an efficient method is to copolymerize two types of monomers to make copolymers. Some of them show interesting electrical and electrochromic properties, improved solubility and processability,^{11,12} and potentially open a multitude of possibilities in obtaining materials with varied structure and property.

Here, we describe an acid-promoted polymerization

method for DPN patterning of conducting polymers. The reactive liquid precursors polymerize to generate solid products after patterning as in sol-gel transitions.¹³ The ink composition has been optimized in regard to typical DPN practice, controlled reaction, processability, conductance, and generality. It is found that conducting polymers formed by pyrrole and tetrahydrofuran satisfy the patterning criteria and can be patterned successfully. The as-made conducting polymers are simultaneously doped by the acid that is added to the system as a catalyst. Upon solidification, conducting polymers show high conductance and crystalline structures. Then miniaturized conducting polymer devices capable of light sensing are fabricated by DPN patterning using the proposed monomer ink.

Pyrrole (99.9%), tetrahydrofuran (99.9%), and perchloric acid (70% analysis grade) were obtained from Aldrich and mixed in a right sequence. Usually, pyrrole was added to the mixture of tetrahydrofuran and acid in an appropriate ratio. The as-made ink shows low viscosity and can be patterned immediately. Depending on the degree of the reaction, the ink darkens and its viscosity increases until a black solid is formed in several weeks, which leaves a considerable time window for patterning. Ink coating is performed by dipping the tip in an ink for 30 s. All experiments were done on a ThermoMicroscope AFM in an ambient environment with the contact force between the tip and substrate of 0.5 nN. The measuring electrodes were made on silicon (100) with 600 nm oxide by photolithography, then by electron-beam depositing 5 nm chromium and 40 nm gold. After wiring out *via* a chip carrier, transport properties of the patterned conducting polymer structures were measured in a two-probe configuration on a Keithley sourcemeter in ambient conditions.¹⁴ The photoresponse of patterned conducting polymers was studied by illuminating with an incandescent light source (25 W). The relative intensity is adjusted by varying the distance between the light source and the sensor.

The reaction between pyrrole and perchloric acid imme-

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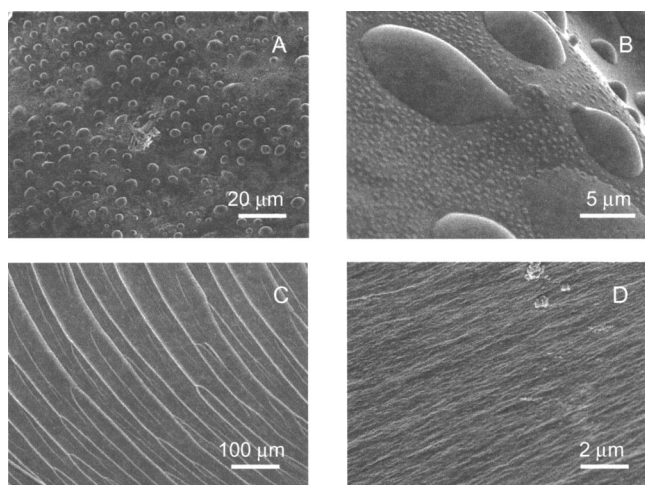


FIG. 1. SEM images taken from the surface and cross section of the polymer solid, showing hierarchal dots (a) and (b), and linear structures (c) and (d) at different length scales.

diately yields a black-colored solid. By diluting pyrrole and the acid in a less reactive environment (i.e., tetrahydrofuran), a steady reaction can occur with adjustable reaction rate. The UV-visible absorbance spectrum of an as-made ink (figure not shown) shows two peaks at 460 and 570 nm, which correspond to the $\pi-\pi^*$ transition in conjugated double bonds, and a polaron that is the combination of a charge site and a radical.^{15,16} The ink becomes dark and can be shaped in a desired mold until it changes to a black solid with bulk density of 1.0 g/cm³ in several weeks. Fourier transform infrared (FTIR) spectrum (figure not shown) shows the N-H stretch at 3470 cm⁻¹ and the CH₂ stretches (2872 cm⁻¹ and 2921 cm⁻¹), confirming the existence of pyrrole and tetrahydrofuran. The absence of a remarkable ketonic mode at 1700–1740 cm⁻¹ suggests most tetrahydrofuran rings are not open.

The transport properties of the conducting polymer are inextricably linked to molecular organization, such as morphology and chain arrangement. The conducting polymers produced in the process have crystalline regions as reflected in x-ray diffraction (XRD) (figure not shown). The sharper peaks reflect a more rigid and ordered packing and chain orientation. A maximum at 2θ of 25.3° (3.5 Å) is associated with the closest distance of face-to-face pyrrole rings,¹⁷ or pyrrole-furan rings. The lower angle peak in the 2θ range of 20.4° (4.3 Å) may be due to the scattering from side-to-side pyrrole or furan rings. The diffraction peak at 2θ from 8° to 14° is related to the counteranions (ClO₄⁻).¹⁸ From the XRD results, two mutually dependent forms of solid order are present: the first is in the polymer backbone and generates sharp peaks at a high angle range (15°–30°), and the second is with incorporated counteranions and generates low angle peaks (below 14°). As a result, the bulk conductance is measured to be 3.84×10^{-3} S.

Figure 1(a) shows a low magnification scanning electron microscope (SEM) image of the polymer pellet, where micro-sized dots can be discerned. At high magnification, large quantities of nanosized dots are observed around micro-sized dots [Fig. 1(b)]. The hierarchical structure suggests an ordered structure of the polymer solid. A SEM image collected from the cross section surface of the pellet shows millimeter

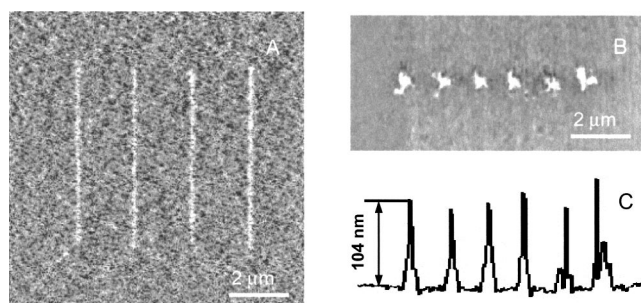


FIG. 2. Topographic AFM images of DPN-generated conducting polymer structures. (a) Four parallel lines produced at the moving speed of 2 μm/s using as prepared ink; (b) a dots array produced by holding the ink-coated tip for 1 s per dot using a 3-week-old ink; (c) a line profile of the dot array.

length lines with bifurcated structures [Fig. 1(c)]. The higher magnification image shows linear structures with a similar orientation [Fig. 1(d)], suggesting that the polymer chains are aligned. (Such alignment could be the result of a mechanical fracture, but the directional fracture is also evidence for the existence of energetically favorable directions.) It is possible that two different phases are present in the polymer solid, analogous to those in block copolymers: one is well crystalline with a more ordered structure, the other is less crystalline with a less ordered structure.¹⁹ In any case, such structures would enhance the conductance by transporting charge carriers along the chains or between multiple domains.

From our previous DPN practice, several criteria could be derived for a good ink for solid-state materials: a homogeneous solution, good flow ability, slow drying, and a specific affinity to the substrate. Due to its reactive nature, the monomer ink demonstrates different colors and viscosities at different stages. Thus it is necessary to find an appropriate time window that can produce polymer structures in a reliable way. DPN patterning is performed at different stages of the ink before it is completely solidified. If the ink is used within 1 week after preparation, repeated nanostructures can be produced in a controlled fashion. Figure 2(a) shows the topographic image of four parallel lines prepared by moving an ink-coated AFM tip across a SiO₂ substrate at the speed of 0.2 μm/s. The heights of the lines are ~3 nm and remain constant in the continuous imaging. However, some time after its preparation, or when using an ink with a high ratio of acid, the ink becomes sticky and DPN patterning becomes difficult. Meanwhile, the stickier ink produces dots with increased height and uneven shapes. For example, patterning ink that is 3 weeks old by holding the ink-coated tip for 1 s per dot produces a uniformly distributed dot array [Fig. 2(b)] the height of each dot is above 100 nm [Fig. 2(c)]. Although no detailed characterization is done on the “as-patterned” structures, owing to a lack of local probes at such dimensions, it is reasonable to believe that they share similar structural properties as bulk materials studied before.

Conducting polymers can be potentially used to make visible light detectors, which is important to transmit signals in communication. One major effort is to make miniaturized detectors and shrink the system by integration with the microelectronic platforms. Patterned conducting polymer structures can give a suitable response to visible light. Figure 3(a)

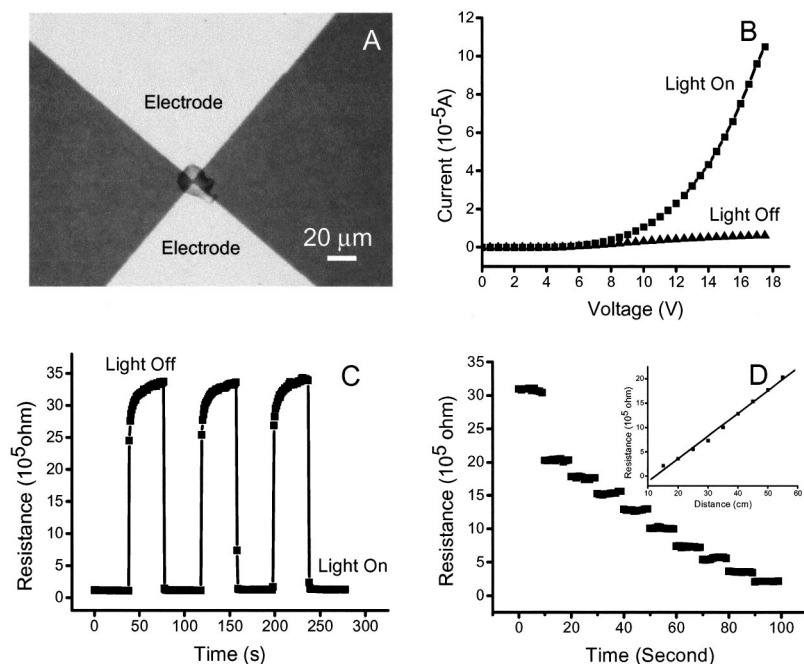


FIG. 3. (a) Optical micrograph of a patterned conducting polymer structure between a $2 \mu\text{m}$ electrode gap; (b) I - V curve of the patterned structure in dark and illuminated states; (c) repeated photoresponses of a patterned structure; (d) the dependence of resistance to the relative light intensity.

shows an optical micrograph of a patterned polymer disk, which is produced by holding an ink-coated tip between a $2 \mu\text{m}$ electrode gap for 30 s. When stimulated with visible light, the resistance reduces sharply. Figure 3(b) shows the current versus voltage (I - V) curves in both the dark and illuminated states. The conductance of the disk is estimated to be 0.04 S. Repeated resistance change is observed on a similar sensor by alternatively switching the light on and off [Figure 3(c)]. Further, at the illuminated state, the resistance is dependent on the illumination intensity: increasing the intensity leads to respective decrease in the resistance. The resistance is stable in measurements (a typical measurement scan period is 10 s) at specific illuminations, and reduces stepwise when the distance between the light source and the sensor is reduced [Fig. 3(d)]. A linear relation exists between the distance (d) and the resistance of the conducting polymer (R) [Fig. 3(d) inset], suggesting a relation of $R \propto d$. As the light intensity (E) depends on the distance (d) between the light source and the sensor by $E \propto d^{-2}$, we can deduce that the resistance of the photosensor depends exponentially on the intensity of light, $E \propto R^{-2}$. Based on these results, a miniaturized artificial light sensing system can be constructed to fulfill similar functions as those in a visual system or a circadian sunflower.²⁰

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