Rapid Direct Nanowriting of Conductive Polymer via Electrochemical Oxidative Nanolithography

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The ability to rapidly pattern and write conductive polymers has been identified as one of the target areas for fabrication of organic electronic and optoelectronic devices.[1] Several different techniques, such as photochemical lithography,[2] micromolding,[3] electropolymerization using modified electrodes,[4] deposition using scanning electrochemical microscopy (SECM),[5] and printing techniques,[6] have been successfully applied to fulfill the micrometer and submicrometer dimension (>0.1 μm). However, there is increased demand for miniaturization of conductive polymers to the nanometer-size scale. Among current state-of-the-art techniques, scanning probe-based lithography (SPL) offers high spatial precision without complicated steps in comparison to other patterning techniques. SPL has been developed by many research groups to pattern metal,[7] metal oxides,[8] organic monolayers,[9] and biomolecules.[10] To our knowledge, SPL to pattern conductive polymers has been developed only by a few research groups. Using dip-pen nanolithography (DPN), Mirkin and co-workers[11] have reported the preparation of conductive polymer lines down to 290-nm width at writing speeds as high as 0.8 μm/s using ionically charged conducting polymers as the "ink" for writing on oppositely charged substrates. Noy et al.[12] have reported a combination of DPN and scanning optical confocal microscopy to write and image nanowires of luminescent conductive polymers. Grinstaff and Liu have reported true nanoscale (<100 nm) writing of a polythiophene down to 30-nm line width at writing speeds as high as 10 nm/s using electrochemical-DPN (E-DPN).[13] Within the scope of this work, rapid direct writing of conductive polymer at the defined nanoscale, <100 nm, on an insulator, glass, has been demonstrated via a novel SPL technique, electrochemical oxidative nanolithography (Figure 1). This technique combines electrochemical atomic force microscopy (ECAFM) with a novel process for making conductive polymers that we have termed solid-state oxidative cross-linking (SOC) (Figure 2).[14,15]

SOC is a procedure to convert a processible precursor polymer, **1**, in the solid swollen state to a cross-linked conducting polymer, **2**, as shown in Figure 2. The SOC technique provides solution processibility of the precursor and hence the conductive polymer, an attribute that is critical for low-cost fabrication.[1] We have demonstrated that conversion of **1** to **2** is nearly quantitative and that **2** has a conductivity approximately 1 order of magnitude higher[16] than that reported for electrochemically generated poly-(terthiophene).[17] We have also shown that conductive polymers prepared using SOC have a doping level of $\sim$30% and exhibit ion transport upon redox switching.[15]

With the electrochemical nanolithography process (Figure 1),[18] a conductive AFM tip serves as the working electrode and when
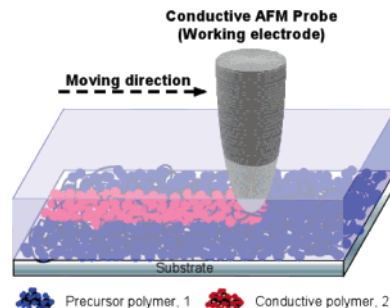
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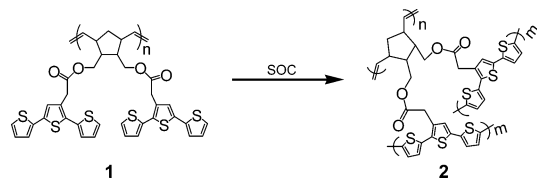**Figure 1.** Electrochemical oxidative nanolithography process.

Figure 2. Conversion of insulating precursor polymer, **1**, to conductive polymer, **2**, via solid-state oxidative cross-linking (SOC).
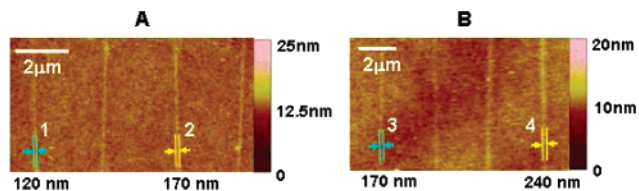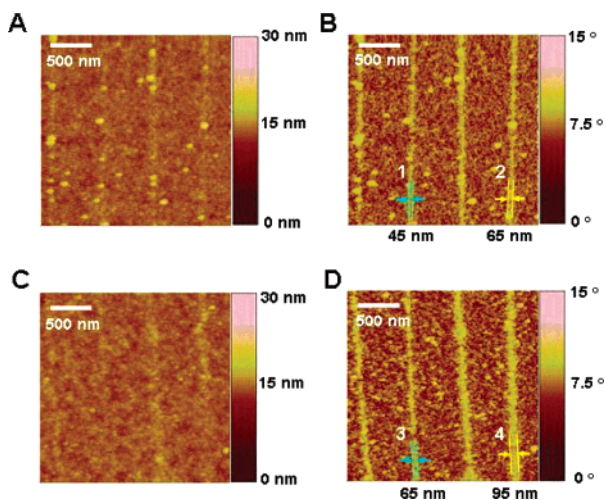

Figure 3. (A) Height image of conductive polymer nanolines written at 60 μm/s (1) and 30 μm/s (2) via contact mode. (B) Height image of conductive polymer nanolines written at 30 μm/s (3) and 15 μm/s (4). Performed in 0.1 M TBAP/PC at 1.4 V (vs SHE) using Au-coated SiN$_4$ AFM tips (average tip diameter = $\sim$40 nm).

brought in contact having a potential sufficient to initiate SOC with the swollen film, the cross-linking reaction ensues to produce conductive polymer. The conductive AFM tip can move in a programmed manner and, furthermore, the potential can be held constant, pulsed (square wave), or scanned (triangular wave). The entire procedure is a maskless, one-step process that does not contain any sophisticated steps of patterning and developing. Unlike other reported SPL techniques, with our technique there is no material transfer from tip to substrate, and the conductive polymer lines are patterned into a precursor plastic.

The height image obtained after contact mode (CM) writing to prepare **2** is shown in Figure 3. Conductive polymer lines of 120 (line 1), 170 (lines 2 and 3), and 240 nm (line 4) width were obtained at the writing speeds of 60, 30, and 15 μm/s, respectively, at a potential of 1.4 V vs standard hydrogen electrode (SHE). Writing without potential did not produce any observable grooves,

Figure 4. Height (A) and phase (B) image of conductive polymer nanolines written at 15 μm/s (1) and 10 μm/s (2) via tapping mode writing. Height (C) and phase (D) image of nanolines written at 10 μm/s (3) and 5 μm/s (4). Performed in 0.1 M TBAP/PC at 1.4 V (vs SHE) using Au-coated SiN$_4$ AFM tips.

confirming that the lines are not generated via scratching the polymer film surface with the tip. A writing speed of 60 μm/s is surprisingly fast compared to current SPL of conducting polymers.[11–13] Our rapid writing could be attributed to the fact that material transfer from tip to substrate is nonexistent and that there is no nucleation and growth required to form conductive polymer as there would be for E-DPN.[13] CM writing provided 2.5-D features in which ICP lines are raised from the polymer surface with an average height of ~1.6 nm (see Supporting Information). On the basis of previous work reported by Lyuksyutov et al.,[19] it can be hypothesized that the attractive electrostratic force between the charged tip and the electron-rich terthiophenes of the precursor polymer film, **1**, is strong enough to draw the softened polymer toward the tip.

The images obtained after tapping mode (TM) writing to prepare lines of **2** are shown in Figure 4. TM writing can be analogized to a nanostippling process. To our knowledge, the only other example of nanostippling was recently reported by Stone et al., in which short synthetic peptides were written via tapping mode DPN.[20] The smallest line width obtained using TM writing was 45 nm, close to the diameter of the AFM tips used (~40 nm). With the nanolines written by tapping mode, no significant height change was observed (Figure 4A,C); however, there is an obvious phase contrast (Figure 4B,D) between the insulating linear precursor polymer, **1**, and the cross-linked conductive polymer, **2**. This phase contrast has been attributed to the difference in material rigidities.[21]

The width of nanolines can be manipulated by controlling writing speed, writing mode, and applied potential. As shown in Figure 4B and D, the line widths of nanolines were controlled between 45 and 95 nm via manipulating the writing speed between 15 and 5 μm/s, respectively. The writing speed and writing mode dictates the duration of time that the AFM tip spends in contact with a specific location of the precursor polymer film. The propagation rate of **2** away from the AFM tip was calculated to be ~25 μm/s for CM writing at 1.4 V. This correlates to our earlier results for SOC micrometer-scale patterning of **2** in that propagation away from a gold surface was found to be ~30 μm/s.[16] Propagation of **2** away from the tip in TM writing was calculated to be ~2 μm/s at 1.4 V. This propagation speed, being approximately 13 times slower than that for CM writing, indicates that the tip in TM writing

spends ~8% of the time in contact with the film. Tapping mode writing at 1.5 V and 15 μm/s write speed resulted in nanolines of 85 nm width (see Supporting Information). Thus, the propagation speed at 1.5 V is calculated to be 4 μm/s, which is ~2 times faster than that at 1.4 V. Faster propagation at higher applied potential implies that it is possible to achieve faster writing speeds.

In conclusion, true nanometer-scale (<100 nm) writing of conductive polymer into an insulating polymer film at speeds of >5 μm/s was achieved by a novel SPL technique. To our knowledge, the writing speeds of this technique are 1500 times faster than the only other reported SPL technique for nanowriting of conducting polymers.[13] The feature size of conductive polymers can be controlled via writing speed, writing mode, and applied potential. Furthermore, conductive polymer lines are imbedded in an insulating film, and we have found no specific restriction in the choice of substrates. This technique is presently being applied to the fabrication of all plastic nanoscale electronic devices in our laboratories and will be reported at a later date.

Supporting Information Available: Experimental details for electrochemical oxidative nanolithography and images for tapping mode writing at 1.5 V. This material is available free of charge via the Internet at http://pubs.acs.org.

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