Nanopatterned Polythiophenes Films for Electrochormic Imaging

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Abstract

Electrochromic polymer films were patterned by a soft lithography technique using a nanopatterned PDMS mold to generate submicron size gratings. The redox currents ($\boldsymbol{i}_p$) were significantly increased due to the facilitated diffusion of counter ions associated with redox processes at the EC polymer electrode as analyzing cyclic voltammetry (CV) performed at different scan rates (v). As a result of such facilitated charge transport, the electrochromic (EC) properties of the patterned electrode were greatly enhanced to give high EC efficiency, including the coloration (E_c) and bleaching efficiencies (E_b).

Introduction

Electronic displays and imaging based on conducting polymers (CP) have attracted considerable attention since conjugated polymers can be easily processed with inexpensive technologies at low temperatures.[1-8] However, current technology toward practical applications are rather limited due to the problem of slow response time. In electrochromic devices (ECDs), electrons are injected or extracted under an applied electric field while charge balancing counter ions are simultaneously transported into or out of the EC layer.[9,10] Therefore transport of electrons and ions is directly related to EC properties such as coloration efficiency and response time.[9-12] Recently, fast response times and high color contrast have reportedly been achieved with EC devices fabricated with a nanostructured EC electrode since the nanostructures can provide a large surface area. Such a nanostructured EC electrode can be prepared through layer by layer (LBL) deposition[11,13] or by adopting nanotemplates such as anodized aluminum oxide (AAO),[14] TiO_2 nanoparticles,[8] Si nanowires,[10] and block copolymer templates.[15] As the charge transport in an EC device occurs vertically between the working and counter electrode, the design of a vertical EC nanostructure is indeed a challenge.

In this study, an EC device based on a nanopatterned polythiophene (PTH) film electrode was fabricated. The PTH electrode was prepared by directly nano-imprinting a conductive polymer film with a nanopattern replicated PDMS mold.

Experimental Section

The template consisted of nano-gratings in a 1 cm x 1 cm area with a width of 250 nm and a height of 90 nm. The gap between the gratings was 15 nm. The nanopattern transfer from the PDMS stamp to the composite films was carried out using Nanoimprint (HIS-400U, Hutem Inc.). The thickness of the polymer films was deetermind via profilometry measurements performed with an Alpha Step profilometer (Tencor Instruments, Alpha-Step IQ). The accuracy of the profilometer was 1 nm.

A liquid electrolyte containing 0.1 M lithium perchlorate ($LiClO_4$) in acetonitrile was isolated between the two electrodes by a spacer. The electrochemical properties were studied using an electrochemical analyzer (CH Instruments Inc, CHI624B). Electrochromic properties were determined by an in situ spectro-electrochemical setup.[8-12] The coloration efficiency and response time of the ECDs were determined at the absorption max under a square-wave switching potential using a chronocoulometry in liquid electrolyte having an EC window size of 1.0 x 1.0 cm^2. The EC response time for coloration and bleaching was determined at a 70 % absorption change[11,12] under the given step potentials. The electrochromic efficiency (EE) including the coloration and decoloration efficiency was determined by dividing the Δabs by the injected/ejected charge per unit area. The UV-Vis spectra were recorded for chloroform solutions with a AvaSpec (AvaSpec-2048. light source: AvaLight-DHS).

A 635 nm diode laser with an intensity of 3.3 mW was used to measure the diffraction from the patterned electrochromic devices at colored and bleached states. The intensities of the reflected (I_r), transmitted (I_t) light and I_a ('I_d+I_r' or 'I_d+I_t') were determined using a photodetector. I_d was obtained from a difference between the I_a and I_t or I_r. UV-Vis spectra were attained with an Avaspec-2048 fiber optic spectrometer. Atomic force microscopy (AFM) was carried out in tapping mode at room temperature with a Dimension 3100 SPM equipped with a Nanoscope IVa (Digital Instruments, Santa Barbara, CA, USA).

Patterning of PTH film by PDMS Imprinting.

PTH films were nanopatterned via soft lithography performed at room temperature. A PDMS mold consisting of periodic lines was employed in the nanopatterning process. Nano-gratings (1D) were first patterned on a PTH film by a single imprinting at room temperature. The average roughness (Ra) values and surface areas were increased upon patterning. The nano-gratings on the PTH film were wider in period and shallower in depth than those of the PDMS master, as determined from AFM (Figure 1).

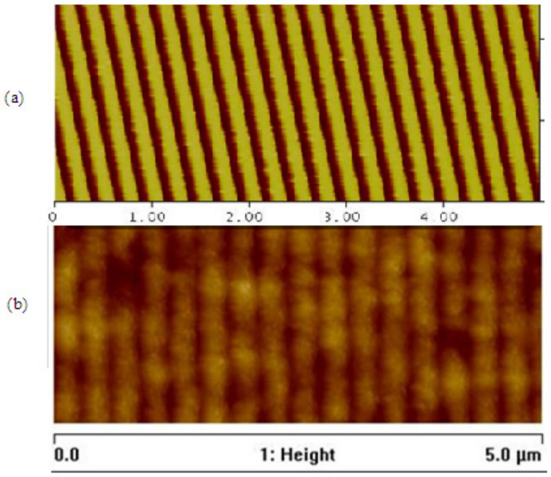

Figure 1. *AFM images of (a) PDMS master and (b) patterned PTH film by imprinting at RT .*

Electrochemical properties of nanopatterned PTH film.

Cyclic voltammetry measurements for the and patterned PTH films were performed in a three-electrode system using a solution of 0.1 M $LiClO_4$ in acetonitrile. All films exhibited several redox peaks characteristic of the polaronic and bipolaronic states of CP according to the following reaction:

$$\underset{\text{(neutral)}}{CP^{0} + ClO_4^-} \underset{\text{red}(+e^-)}{\overset{\text{ox}(-e^-)}{\rightleftharpoons}} \underset{\text{(polaron, radical cation)}}{CP^{+?}\,ClO_4^-} \underset{\text{red}\ (+e^-)}{\overset{\text{ox}\ (-e^-)}{\rightleftharpoons}} \underset{\text{(bipolaron, dication)}}{CP^{2+}\,2ClO_4^-} \qquad (1)$$

In eqn (1), ClO_4^- is a counter anion and e^- denotes an electron. The redox peaks of the patterned films were shifted with a much higher intensity than those of the unpatterned film. The current increase could be mainly attributed to the increased surface area in the patterned films. Both the anodic and cathodic currents were linearly correlated to $v^{1/2}$, which indicates that electrochemical doping of the entire PTH film occurred with no irreversible electrochemical reaction. The diffusion coefficient (D_f) for the patterned electrodes were determined from the slope of the plot for the current vs $v^{1/2}$. Interestingly, the diffusion coefficient for the patterned electrode was much larger than that of the unpatterned electrode. Therefore, as discussed in the literature, the electronic response of a conductive polymer-based device may improve as charge transport through the nanostructured electrode is enhanced due to fast diffusion at the electrode.

Electrochromic (EC) properties of nanostructured P3HT electrodes.

Transmissive-type EC devices were prepared with PTH films as a working electrode and ITO glass as a counter electrode. The EC devices exhibited a reversible color change from red to transparent-blue when -2 to 2 V was applied. The EC response required a larger potential step than was expected from the solution CV. This reflects the fact that the CV of the 2-electrode system exhibited broad redox peaks at +2 and -2 V for oxidation and reduction, respectively, for the patterned EC electrode. The UV-Vis absorbance changes of the EC cells was observed as the applied potential was changed from -2 V to 2 V as shown in Fgiure 2(a). High optical reversibility and coulommetric reversibility were observed with a switching time of 20 s (Figure 2(b)). The optical contrast (Δabs) and coloratioamperometric plot of $\boldsymbol{i}_p$ against time under a step potential exhibited typical 1st order differential decay. The $\boldsymbol{i}_p$ drops faster so as to reach saturation in the atterned films, suggesting improvement in charge transport through nano-patterning. As a result, the response times for both coloration and bleaching were significantly reduced in the patterned PTH films. Furthermore, the electrochromic efficiency (E_e) including the coloration (E_c) and bleaching efficiency (E_b), was higher in the patterned film. These results could be attributed to facilitated charge transfer through the nanostructured EC electrode. It is consistent with observations when the diffusion coefficient was determined (described above). The bleaching (p-doping) process was faster than the coloration process (de-doping), which matched to the results on diffusion coefficients. The E_e increased as the diffusion coefficient (D_f) was increased.

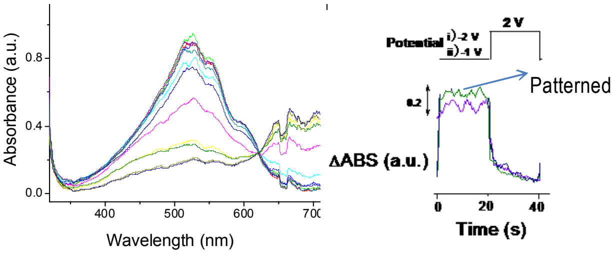

Figure 2. *(a) UV-Vis absorbance spectral change of the ECD with patterned PTH from neutral to oxidation state at the applied potential; -2 V, -1.5 V, -1.2 V, -1 V, -0.5 V, 0 V, 0.3 V, 0.6 V, 0.9 V, 1.2 V, 1.5 V, 1.8 V, and 2.0 V (from top to bottom). (b) Optical response of the ECD in response to the potential change of -2/+2 V.*

Switching times are dominated by the diffusion of counter ions through the films during the redox step. Fast optical response times (in seconds) were observed in the patterned systems because the patterned morphology of the polymer promotes the mobility of charge compensating counter ions. The response time for decoloration is faster when compared to that for coloration, which agrees well with the larger D_f associated with the decoloration.

Reversible electrochromic diffraction from a nanostructured EC window.

The diffraction light intensity and thus, the efficiency (DE) of a grating depend on the optical properties (the absorptivity *k* and the refractive index *n*) of the grating material. Therefore, it is possible to use an electrochemical stimulus to modulate the DE of a redox-active grating. Light diffraction was examined by in-situ detection of the diffracted light (I_d) from the cell under a 635 nm laser, by both transmittive and reflective mode. Photographs of the diffracted light image from a patterned ECD at -2 V (colored) and +2V (bleached) are shown in Figure 3. The EC diffraction cells showed fast and reversible light modulation within a second as shown in Figure 3.

A more thorough account of EC diffraction is forthcoming. However, a key aspect of note is that the overall redox behavior of the patterned P3HT electrode could be applied to an electrically driven diffraction lighter, where ion diffusion is accompanied by a redox process control. This would allow for control over both color change and the refractive index.

Figure 3. *Photographs of the diffracted light image from the patterned ECD, showing reversible diffraction modulation at -2 V (colored) and +2V (bleached).*

Conclusion

We prepared PTH nanopatterns by imprinting technology. The charge transport characteristics of PTH films were examined with the nano patterns. Due to the increase in surface area, the charge transport was facilitated in the patterned films with an increased diffusion coefficient (D_f) for counter anion. This resulted in an improved response time and higher coloration and bleaching efficiencies for the P3HT-based electrochromic devices. In the patterned cell, diffraction modulation using an electrochromic operation was achieved. Optimization and mechanism of the EC response at the nano patterned PTH films will be discussed.

Acknowledgment

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Biography

Eunkyoung Kim received her BS degree in chemistry from Yonsei University in Seoul (Korea) in 1982, a master’s degree in chemistry from Seoul National University in Seoul (Korea) in 1984, and PhD in chemistry from University of Houston in 1990. She worked for Korea Research Institute of Chemical Technology in Daejeon (KRICT) from 1992 to 2004. Since 2004, she has been a professor of chemical engineering at Yonsei University, Seoul, Korea. Her work has primarily focused on the development of functional polymers, including chromogenic polymers, photopolymers, and charge transport issues in polymeric media. She is an editorial committee (Macromolecular Research), committee member (Korea Polymer Society), and general manager (Korean Society for Imaging Science and Technology). (Send correspondence to: 82-2-2123-5752 (tel.) or 82-2-361-6401 (fax)).