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Site-Controlled Application of Electric Potential on a Conducting Polymer “Canvas”

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Supporting Information

ABSTRACT: A novel patterning method for conducting polymer films was successfully demonstrated using the concept of bipolar electrochemistry. The local application of an anodic potential to poly(3-methylthiophene) (PMT) and poly(3,4-ethylenedioxythiophene) (PEDOT) on a bipolar electrode (BPE) realized local electrochemical doping and reaction depending on the supporting salt used. The potential applied on the BPE was measured and corresponded well to the patterns. The array-type driving electrode system was able to draw complex patterns in a site-controlled manner.

Bipolar electrochemistry has been receiving increasing attention among researchers in recent years.[1] In an electrolytic cell containing driving electrodes and an isolated conducting substrate, a bipolar electrode (BPE) is formed when the electric field is strong enough to induce both anodic and cathodic reactions. To exploit this phenomenon for material applications, many interesting approaches involving reactions of substrates being fixed[2] or deposited[3] on the BPE have been reported. We have attempted to create a composition gradient across the film via bipolar doping and reaction using a conducting-polymer thin film on the BPE.[4] In a consideration of the principles of bipolar electrochemistry, the shape and positioning of the driving electrodes as well as the cell design are important factors for controlling the potential distribution on the BPE. In our former work, we developed a U-type cell in which a “shielding wall” inserted between the driving electrodes played an important role in controlling the intensity of the potential gradient on the BPE.

This bipolar technique has shed light on electrochemical modification of conducting polymer films.[5] This may also be an efficient method for applying a local spot of electric potential on BPEs, thus providing a novel concept of electrochemical patterning and the invention of electrochromic devices that can be powered by indirect feeding of current from a power supply.

The spot-bipolar configuration is shown in Figure 1a. In the current study, the conducting polymer films were prepared on an indium tin oxide (ITO) electrode using the potential-sweep method in 0.1 M Bu_4NPF_6/MeCN containing thiophene monomers. After further dedoping of the film, the substrate was used as the BPE, which was placed into a container equipped with an external cathode wire and an anode ring separated by a plastic shielding cylinder. The device was filled with an electrolytic solution containing a low concentration of salt in order to induce BPE with a small current.[4] When a current flows via the

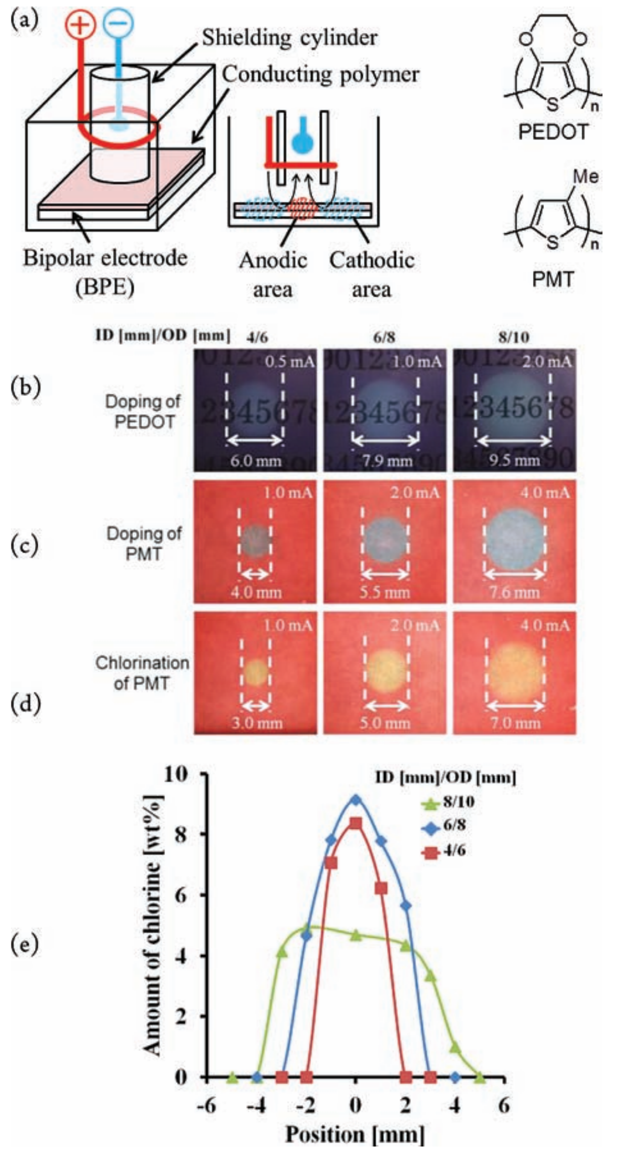

Figure 1. (a) Schematic illustrations of the setup used for bipolar patterning and the chemical structures of PEDOT and PMT. (b−d) Pictures of the conducting polymer films showing doped PEDOT, PMT, and chlorinated PMT. (e) EDX profile of the chlorinated PMT at each position.

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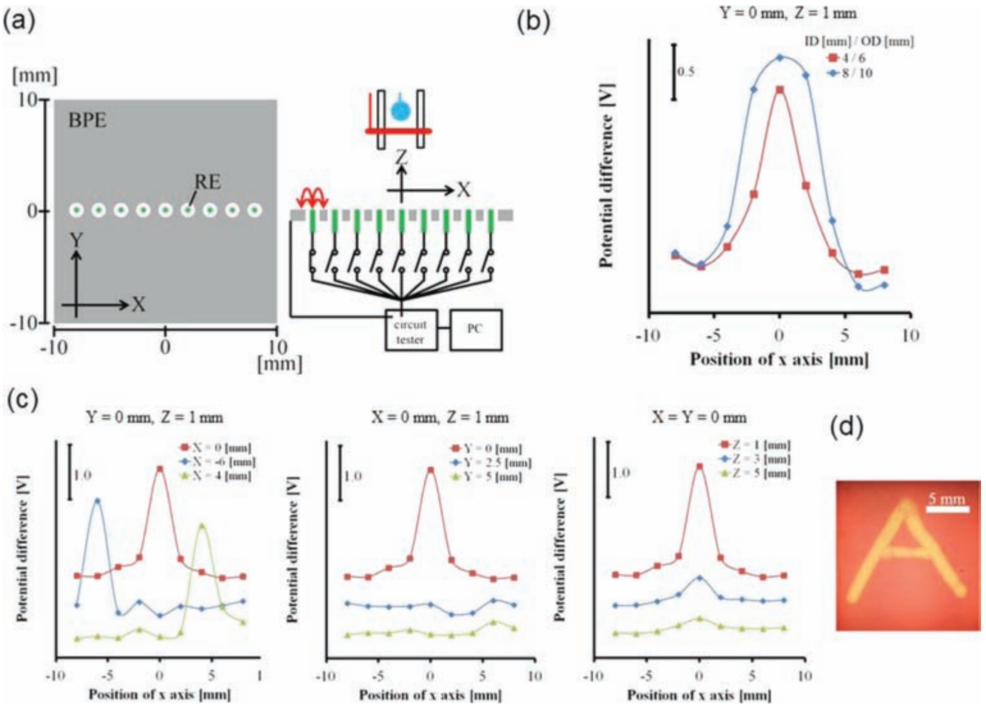

Figure 2. (a) Illutrations of the setup used for measuring the potential distribution on the BPE. (b) Plot of measured potential differences between the BPE and RE ($Y = 0$ mm, $Z = 1$ mm) using various cylinder sizes (ID/OD = 4 mm/6 mm and 8 mm/10 mm). (c) Plot of measured potential differences between BPE and RE obtained by setting the cylinder electrode (ID/OD = 2 mm/4 mm) at each position. (d) Picture of the PMT film after bipolar chlorination obtained by moving the cylinder electrode.

BPE, a new anodic area appears under the driving cathode wire together with a surrounding cathodic area with its interface gradient. The cylinders employed were 1 mm in thickness with internal diameter (ID)/outside diameter (OD) of 4 mm/6 mm, 6 mm/8 mm, and 8 mm/10 mm. The distance between the cylinder and the BPE was kept constant at 1 mm. Figure 1b,c shows pictures of poly(3,4-ethylenedioxy)thiophene (PEDOT)[6] and poly(3-methylthiophene) (PMT)[7] films doped with the bipolar device for 0.01 C in 5 mM Bu_4NPF_6/MeCN under a constant current. A clear spot appeared in the anodic pattern of the BPE. This local color change completely recovered when the whole substrate was treated with cathodic electricity (dedoping). When a nucleophilic supporting salt (5 mM Et_4NCl/MeCN) was used, a yellow circle on the PMT film was formed irreversibly as a result of electrochemical chlorination at the 4-position of the repeating thiophene unit (Figure 1d).[8] Interestingly, the spot size changed depending only on the diameter of the shielding cylinder. As for the chlorination patterning, the content of chlorine could be estimated by local elemental analysis using energy dispersive X-ray spectroscopy (EDX) at different positions of the polymer film (Figure 1e). The EDX results provided clear evidence that chlorine atoms were successfully introduced into the PMT film. The band width in the chlorination profiles corresponded well to the visible spot size. X-ray photoelectron spectroscopy (XPS) analysis of the surface of the chlorinated PMT revealed that the chlorine atoms introduced were covalently linked to the thiophene rings[9] (see Figure S1 in the Supporting Information).

When the shielding cylinder was split into three parts, anodic spots were induced on the corresponding position, resulting in three circle patterns with equal size in spite of the fact that only a pair of driving electrodes was used (Figure S2).

To provide a better understanding of the spot patterning mechanism, we measured the electric potential distribution applied at each position of the BPE using the setup shown schematically in Figure 2a. The voltage between a tip-modified reference electrode (RE) and the surface was measured at different positions.[10] A constant current (1 mA) flowed between the feeder electrodes in 5 mM Et_4NCl/MeCN, and the potential differences observed across the *x* axis of the BPE are shown in Figure 2b. The electric potential profile of the small-diameter cylinder (ID/OD = 4 mm/6 mm) peaked at the center of the cylinder and gradually decreased toward the border. In the case of the large-diameter cylinder (ID/OD = 8 mm/10 mm), the electric potential profile was broader. This direct observation of the potential difference on the BPE strongly supports the spot application of potential, which can realize patterned doping and chlorination on conducting polymer films.

According to the results, it may be possible to move the cylinder electrode over the BPE to supply a continuous electric potential to a polymer film. First, the potential difference distribution on the BPE was monitored by changing the position of the cylinder electrode (Figure 2c). The motions of the cylinder electrode along the *x* axis and *y* axis gave reasonable electric potential profiles depending on the location of the cylinder. When the distance between the cylinder electrode and the BPE was small ($Z = 1$ mm), the potential difference peak reached 1.5 V at the center of the BPE. As the cylinder electrode moved away from the surface, the potential difference induced on the BPE decreased gradually. This means that the potential supply to the BPE can be controlled by lifting the cylinder electrode. On the basis of this idea, we successfully drew a chlorination pattern on the conducting polymer "canvas" (Figure 2d).

To explore a more practical application of bipolar patterning, we prepared an array-type device in which feeder electrodes could be controlled independently. A 3 × 3 array device composed of nine independent cathodes and an anode split into four line segments was fabricated (Figure 3a). Electricity was fed to all of the anode lines, while the electricity supply to the individual cathodes could be manipulated independently. Figure 3b−e shows the results of chlorination patterning for the PMT film using the array of driving electrodes. When all of the feeder cathodes were active, nine corresponding yellow spots appeared, one under each cylinder (Figure 3b). In contrast, we obtained eight surrounding spots when the center feeder cathode was idle (Figure 3c). Similarly, other chlorination patternings were successfully demonstrated by the appropriate choice of active feeder cathodes (Figure 3d,e).

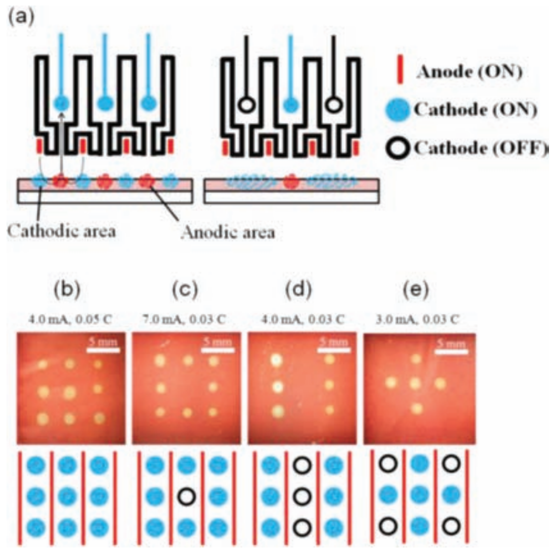

Figure 3. (a) Schematic illustrations of the array-type setup used for bipolar patterning. (b−e) Pictures of the PMT film after bipolar chlorination driven by independently controlled cathodes. The illustrations below the pictures represent the anode wires (red lines), active cathodes (blue ●), and idling cathodes (black ○).

In conclusion, we have successfully demonstrated a novel concept of bipolar patterning for a conducting polymer canvas without a connection to an external circuit. The local potential distribution on the BPE, which made it possible for pattern spot modification of conducting polymer films, was confirmed by measuring the potential difference. By extending the bipolar spot patterning, we have also demonstrated a drawing application and array-type patterning in a site-controlled manner.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Experimental section, Scheme S1, and Figures S1−S3. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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(6) The color of PEDOT was deep-blue in the neutral state. The film became transparent when anodically doped. The color change was derived from the formation of ionic states, namely, polarons (radical cations) and bipolarons (dications) in the polymer backbone. The cathodic reaction on the bipolar electrode is probably reduction of a trace of contaminating oxygen and/or water.

(7) The PMT in the neutral state showed a red color, and it turned blue in the doped state.

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(9) The covalently linked C−Cl and the dopant Cl^- can be observed by XPS. See: Soudan, P.; Lucas, P.; Breau, L.; Bélanger, D. *Langmuir* **2000**, *16*, 4362−4366.

(10) The potential difference measurement for the surface of the BPE was in accordance with a reported technique (see ref 2b).