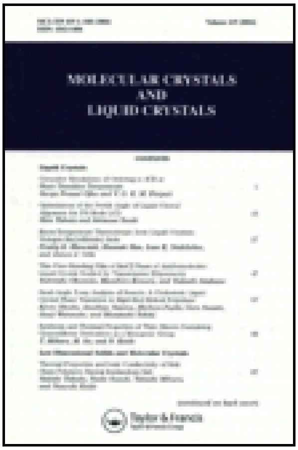

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# Electrochemical Fabrication of Conducting Polymer onto Selected Positions

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# Electrochemical Fabrication of Conducting Polymer onto Selected Positions

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*Conducting polymers such as polypyrrole and poly (3-hexylthiophene) have received particular interests because of easy preparation and relatively good stability. These polymers can be electrochemically synthesized in the form of thin film onto a working electrode. However, once the polymer film start to grow, all electrode surface contacted with deposition solution is to plated. The object of this research was to perform the selective electrodeposition of conducting polymers on the working electrode. This type of polymerization could be completed by adapting confined area electrolysis. Microstructures of conducting polymers were fabricated by using this method. The similar microstructures fabricated by electrochemical carving method.*

**Keywords:** carved pattern; confined area electrolysis; microstructure; P3HT; polypyrrole

## INTRODUCTION

In recent years, conducting polymers [1–4] with conjugated $\pi$-bond electron structure on their backbone have been extensively investigated because they have a wide range of useful applications such as solar cell, light weight battery, electrochromic device and sensors [5].

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Among them, polypyrrole [6] and polyaniline have received particular interest because of easy preparation into thin films having good conductivity and thermal and chemical stabilities. Substitution of long alkyl chains on the 3-position of thiophene ring produced modified poly(3-hexylthiophene) (P3HT) renowned for a good soluble conducting polymer [7–10]. Electrochemical polymerization of these conducting polymers generally induces thin films deposited on the working electrode [11]. However the deposited film spreads over the whole surface of working electrode, which is in contact with the electrolyte. Therefore, it is impossible to fabricate the nano/micro-scale structures by using electrochemical method. Even the fabrication of microstructures is important in microelectronic devices [12].

In this work, we performed confined area electrolysis to obtain microstructures of conducting polymer by using electrochemical method [13]. Two different methods were used. One is an electrochemical polymerization method by using very small counter electrode in two-electrode cell system as shown in Figure 1 [13,14]. This type of electrochemical polymerization occurred in the confined area of the working electrode confined with the counter electrode. This allowed us obtaining patterns of polypyrole by moving counter electrode on the working electrode [15–17]. The other type is electrocarving method. This method is to use the redox-dependent solubility of poly (3-hexylthiophene) [18].

## EXPERIMENTAL

Figure 1 shows a schematic diagram to illustrate the basic concept of the confined area electrodeposition. A potentiostat (potentiostat/galvanostat, Model 263 A, EG&G, USA) was used to apply the

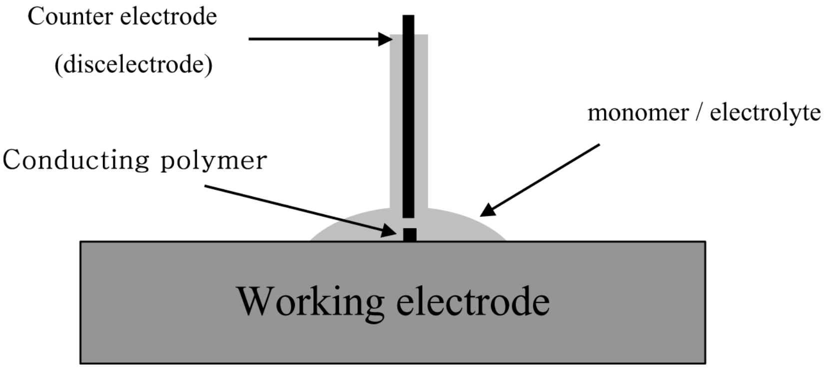

**FIGURE 1** Schematic diagram of electrochemical cell with two-electrode system.

necessary potential functions. Platinum disc electrodes of 500 and 76 μm diameter served as counter electrodes and indium tin oxide (ITO) glass (7 S/cm, Samsung Corning, Korea) was used as working electrode. Deposition solution was 0.1 M pyrrole in 0.1 M tetrabutylammonium tetrafluoroborate ($TBABF_4$)/propylene carbonate (PC). The potentials for polymerization were between 2.00 and 3.00 V and the polymerization durations were in 5–100 sec. Polymer patterns were characterized by using cyclic voltammetry (CV) method and optical microscope (Metallurgical microscope, Model XJZ-6A, Samwon, Korea). For CV tests, Pt plate counter electrode, Ag wire reference electrode and 0.1 M $TBABF_4$/PC electrolyte were used.

Figure 2 describes preparing methods for carved pattern of the conducting polymer. The deposition solution for P3HT synthesis was 0.1 M 3-hexylthiophene in 0.1 M $LiClO_4$/acetonitrile. For fabricating carved pattern, Pt wire as counter electrode in a glass capillary (of 100 μm) containing 0.1 M $LiClO_4$/PC as electrolyte was used. Electrocarving process involved the following steps; (1) Large poly (3-hexylthiophene) film was prepared by chronoamperometry method. (2) The P3HT film was reduced by applying reduction potential. (3) Micro dot of oxidized form

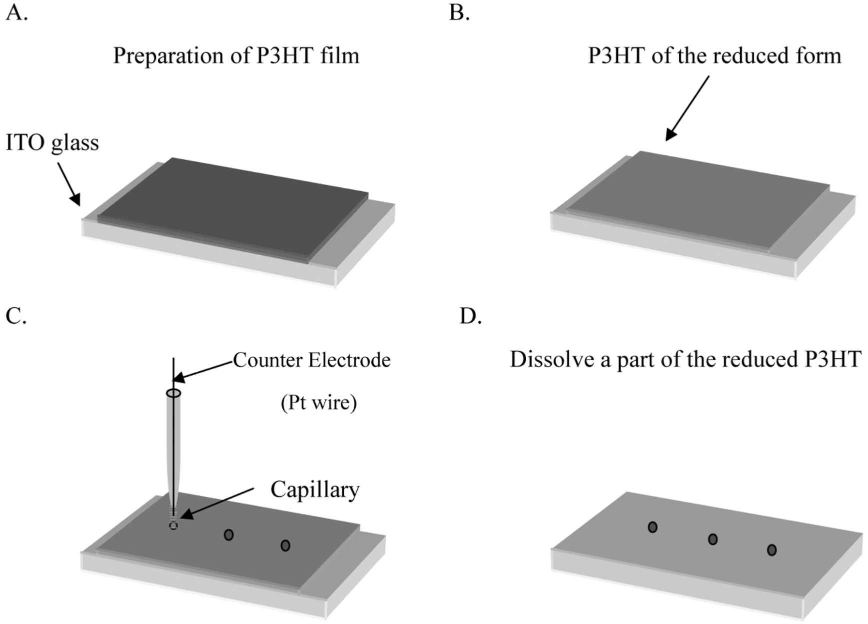

**FIGURE 2** Schematic diagram of the process for carved polymer pattern. (A)-(B)-(C)-(D).

was induced by applying constant oxidation potential. The counter electrode was moved to the next location and the same oxidation process repeated. (4) Dissolving the reduced P3HT using tetrahydrofuran (THF), the only oxidized P3HT was left [19]. The remained carved pattern was characterized by using cyclic voltammetry method and optical microscope.

## RESULTS AND DISCUSSION

Figure 3 shows a cyclic voltammogram of the polymerization of pyrrole on ITO glass with potential window of −2.00–3.00 V using Pt counter electrode only. The monomer oxidation current in the first anodic scan rapidly increased at 2.50 V. This rapid increase mainly due to the pseudo catalytic oxidative polymerization of monomer occurred at this potential and the polymers began to be deposited on the electrode as a thin film shape. Therefore, this potential is chosen for polymerization. Micro dots of polypyrrole were fabricated by chronoamperometry method using Pt disc electrodes of 500 and 76 μm diameters. When the deposition potential of 2.50 V was employed for Pt disc electrode with 500 μm, the anodic and cathodic peaks are well developed as shown in Figure 4(a). On the other hands, when the deposition potential of 2.00 V was applied, the redox peak didn't exist. For Pt disc electrode 76 μm, polymerization potential was 3.00 V. If the potential was

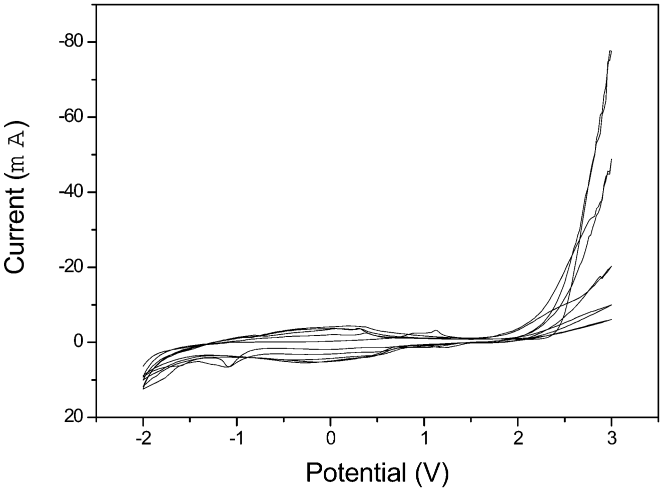

**FIGURE 3** CV of pyrrole electropolymerization with two-electrode system. In 0.1 M pyrrole in 0.1 M TBABF$_4$/ PC, Scan rate; 100 mV/s.

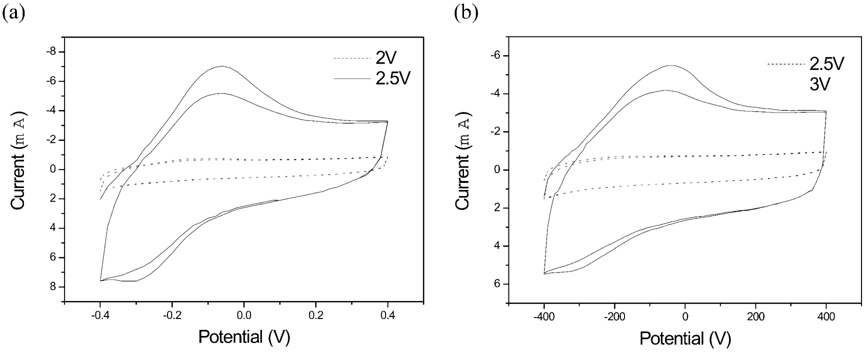

**FIGURE 4** (a) CV of six polypyrrole dots (500 μm Pt electrode used); (b) CV of ten polypyrrole dots (76 μm Pt electrode used).

decreased to 2.50 V, the polymerization didn't take place. Figure 4(b) shows no anodic and cathodic peaks of polypyrrole when 2.50 V was applied. Based on these results, electrochemical fabrication of micropatterns were performed. Figure 5(a) shows that Pt disk electrode of 500 μm diameter produced a 500 μm polymer dot and (b) is the same figure shows in the 76 μm Pt disk electrode can produce about 100 μm polymer dot was synthesized.

We also fabricated conductive dots and line using 76 μm Pt disk electrode. Figure 6 shows the images of polypyrrole patterns. After deposition of a dot, the counter electrode was moved to the next locations for making other dots on the working electrode and the same polymerization processes were repeated. For the polymer line, the counter electrode straightly and continuously moved along the

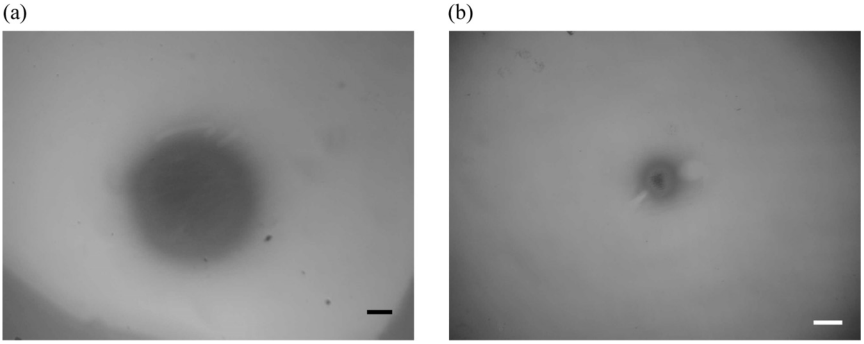

**FIGURE 5** Images of polypyrrole dot (scale bar; 100 μm): (a) 500 μm Pt electrode was used, and (b) 76 μm Pt electrode was used.

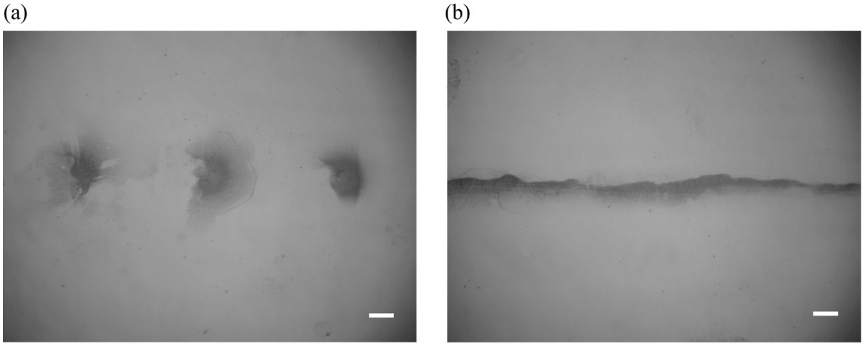

**FIGURE 6** Images of polypyrrole patterns (scale bar; 100 μm) (a) Image of three polypyrrole dots (a) and polypyrrole line (b).

working electrode surface during electrochemical polymerization. Each polymer dots have ca. 100 μm in diameter and polymer line has ca. 100 μm in width.

A large poly (3-hexylthiophene) film was prepared by using chronoamperometry method as in Figure 7(a). Polymerization condition of 3HT was 2.00 V (vs. Ag/AgCl (sat'd KCl)), 10 sec. Because reduced P3HT have a higher solubility compared to oxidized one, the synthesized P3HT was reduced by applying constant potential until reduction reaction was completed. Figure 7(b) shows that the reduction reaction dramatically occurred at the early stage and the reduction current was hardly observed after 25 sec. This fact indicates that reduction reaction was completed successfully. And then several micro parts of P3HT

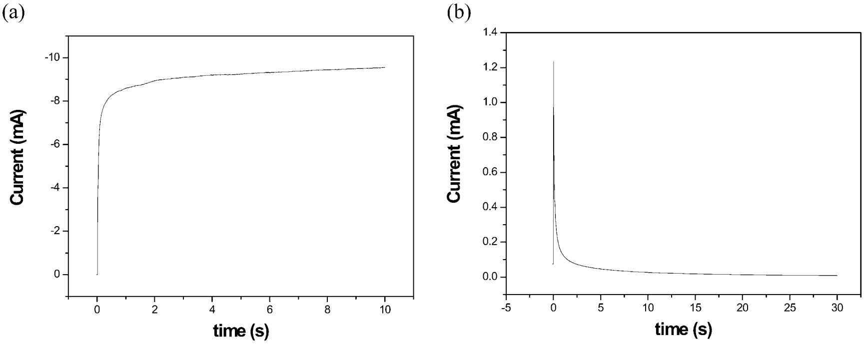

**FIGURE 7** Chronoamperograms of electropolymerization of 3HT(a) and for the reduction of P3HT(b).

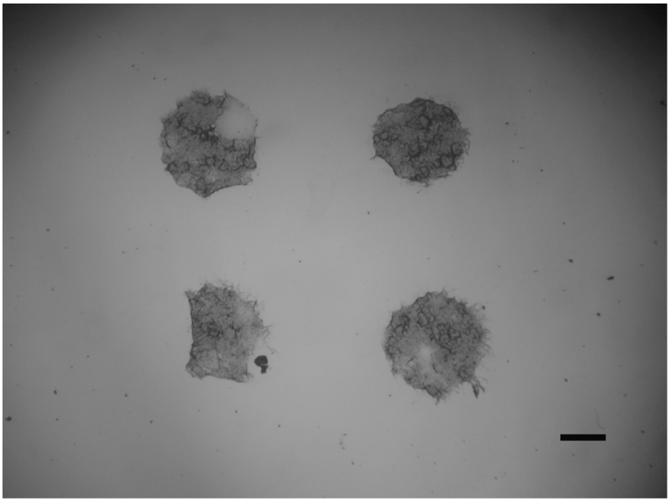

**FIGURE 8** Image of carved conducting polymer pattern after dissolving the reduced P3HT. Oxidation condition; 3.00 V 10 sec.

film were fabricated by oxidizing with the capillary electrode containing electrolyte. Oxidation potential of 3.00 V vs. Pt counter (or reference electrode) was applied for 10 sec. Then the oxidized polymer patterns were implanted in a large reduced polymer film. We dipped this working electrode into THF solvent for removing the unreacted area of the original P3HT. The THF solvent completely dissolved the area of the reduced P3HT [18]. The only oxidized polymer patterns were left on the ITO glass. Figure 8 shows the remaining conducting polymer pattern. The average size of the carved conducting polymer dots was ca. 120 μm diameter.

## CONCLUSION

Conducting polymers can be easily synthesized in the form of thin film onto a working electrode using electrochemical polymerization. When the thin film is formed, the polymers are deposited onto all electrode surface area contacted with deposition solution. In this study, electrochemical micro-pattern fabrications of polypyrrole and poly(3-hexylthiophene) were carried out using micro-scale counter electrode. For electrochemical deposition of polypyrrole with micro Pt disk electrode produced a polymer dot whose size is similar to that of the counter electrode. Also the size of the polymer dots was increased, as polymerization time was increased. This method also allowed us obtaining polymer lines by moving counter electrode along the working electrode surface. Based on this, we obtained polymer dots of 100 μm diameter and polymer lines of 100 μm width. We also obtained a carved pattern of the conducting polymer using the redox-dependent solubility of poly(3-hexylthionphene). The reduced form of P3HT is completely soluble to several kinds of organic solvents. So, we could get carved polymer dots of 120 μm diameter on the substrate.

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