

Short Communication

Nanoscale Morphology Control of Conducting Polymers by Cathodic Polymerization Route

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Polypyrrole films with three-dimensional nanoscale morphologies were synthesized on copper substrates by a novel cathodic deposition using in situ generated nitrosyl ions. Effect of deposition potential on the morphology of polypyrrole films was studied. It was found that the morphology of polypyrrole deposits depended significantly on the deposition potential. The polypyrrole films deposited at -0.5 and -0.6 V versus Ag/AgCl reference electrode contained spherical particles and mesopores. On the other hand, the polypyrrole films deposited at -0.7 and -0.8 V versus Ag/AgCl reference electrode showed nanorod- and dendrite-type morphology, respectively. All the synthesized polypyrrole films exhibited a unique three-dimensional mesopore structure depending on the deposition potential. As a result, it was found that growth pattern and morphology of conductive polymer can be controlled easily by the deposition potential applied to working electrodes.

Keywords: Polypyrrole, Morphology Control, Cathodic Polymerization, Conducting Polymer, Deposition Potential,

1. INTRODUCTION

Organic conducting polymers with fine-tunable electronic properties are attractive for applications such as energy storage devices, electronic circuits, flexible transparent displays, light-emitting diodes, actuators, chemical sensors and biosensors[1-4]. In general, conducting polymers have been made by chemical or electrochemical polymerization methods. Oxidizing agents such as FeCl₃ and ammonium peroxodisulphate have been used for chemical polymerization which provides granular conducting polymers[5,6]. On the other hand, electrochemical polymerization on a conducting substrate has been performed to make film-type conducting polymers under anodic deposition conditions[7-10]. In general, inert materials such as Pt and Au which are electrochemically stable

under the same anodic conditions have been used as substrates to avoid the anodic dissolution of working electrodes.

For the first time, we have reported a new electrochemical polymerization method to make porous film-type conducting polymers on a common substrate such as copper under cathodic deposition conditions[11]. The strong oxidizing agents (NO^+) generated in situ only on the working electrode allows the cathodic deposition of conducting polymers with nanoscale morphology through oxidative polymerization route[11].

Recently, many studies have attempted to control the morphologies of the conducting polymers which have strong effect on its properties[6,12-14]. To achieve it, templating technologies using polymer beads, emulsion or self-assembly of surfactant have been utilized. In the template method, conducting polymers were synthesized by the chemical polymerization on the surface of the template. So far, no work controlling morphology of conducting polymers by electrochemical polymerization has been reported. In this study, we report a facile and effective method for controlling the nanoscale morphology of polypyrrole using the novel cathodic electrodeposition route.

2. EXPERIMENTAL SECTION

An aqueous solution containing 0.4 M HNO_3 (Aldrich), 0.5 M NaNO_3 (Aldrich, 99%) and 0.2 M pyrrole (Aldrich, 98%) was used as a plating solution for cathodic deposition. Copper and platinum foils were used as the working electrode and the counter electrode, respectively while Ag/AgCl in 4 M KCl solution was used as the reference electrode. Before cathodic electrodeposition, linear sweep voltammetric (LSV) curves were obtained in an aqueous solution of 0.4 M HNO_3 and 0.5 M NaNO_3 to get information on electrochemical behavior of nitrate ions. The initial potential was set to 0.0 V and the potential was scanned to -0.8 V versus the Ag/AgCl reference electrode with a scan rate of 0.1 V/s. Cathodic electrodeposition to fabricate polypyrrole films was performed at 45°C for 2 min using chronoamperometric technique. Various step potentials (E_s) of -0.5, -0.6, -0.7 and -0.8 V were applied to the copper foil working electrodes with the fixed initial potential (E_i) of 0.0 V. The as-deposited polypyrrole films were washed with triply-distilled water and dried at 60°C for 12 h. For all electrochemical measurement and synthesis, VMP3 multi-channel potentiostat (BioLogic Science Instruments) was used. All the potentials of copper working electrodes were measured versus the Ag/AgCl reference electrode.

To examine the effect of deposition potential on the morphology of polypyrrole films deposited on the working electrodes, the surface of the resultant polypyrrole films were analyzed by field emission scanning electron microscopy (FE-SEM, JEOL JSM-7500F) using acceleration voltage of 15 kV. Chemical structure of the polypyrrole films was examined by Fourier transform infrared spectroscopy (FTIR, Perkin Elmer 100).

3. RESULTS AND DISCUSSION

It was recently revealed that electrochemical reaction of nitrate ions in an acidic environment proceeds via the EC mechanism composed of Eq. (1) and Eq. (2)[11].



As a result, in situ generated nitrosyl ions (NO^+), a strong oxidizing agent, on the electrode surface allow the cathodic deposition of polypyrrole[11]. The conducting polymers formed by cathodic deposition showed particular morphologies with a three-dimensional porous network, while the conducting polymers prepared during anodic deposition were reported to have two-dimensional morphologies[7,8].

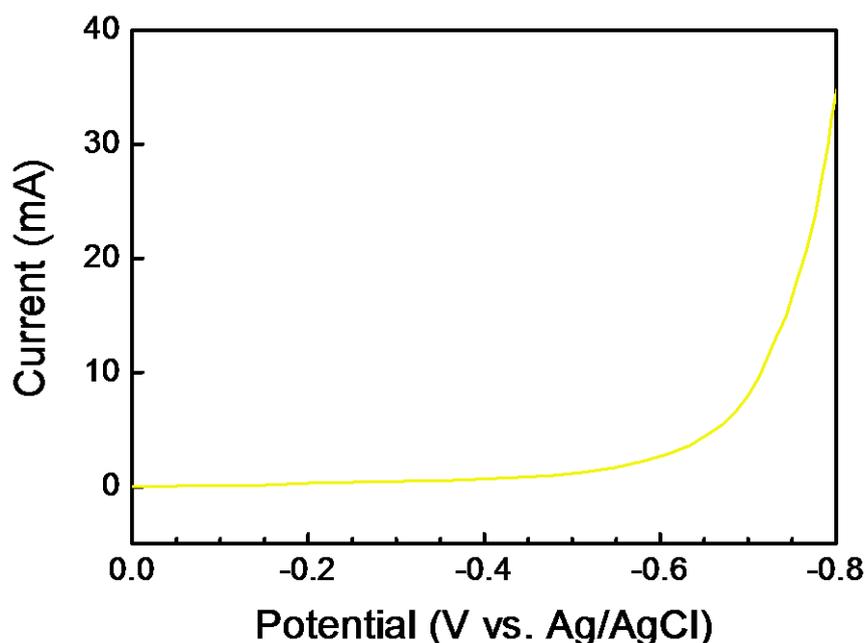


Figure 1. Linear sweep voltammetric curve for the reduction of nitrate ions at copper electrodes in an aqueous solution of 0.4 M HNO_3 and 0.5 M NaNO_3 .

It was postulated in the present work that nanoscale morphology of conductive polymers may be effectively controlled by applying different potentials to the working electrode since they have significant influence on the concentration of generated nitrosyl ions. Electrochemical reduction of nitrate ions at copper electrodes was monitored by linear sweep voltammetric (LSV) technique. Fig. 1 shows that the reduction rate of nitrate ions very sharply increased as the potential decreased below -0.5 V versus an Ag/AgCl reference electrode. Actually, efficient cathodic deposition of polypyrrole was achieved when the step potential less than -0.5 V was applied, where an appreciable amount of NO^+ species can be produced on the electrode surface. So, the following step potentials were chosen for the cathodic deposition of polypyrrole: -0.5, -0.6, -0.7 and -0.8 V versus Ag/AgCl.

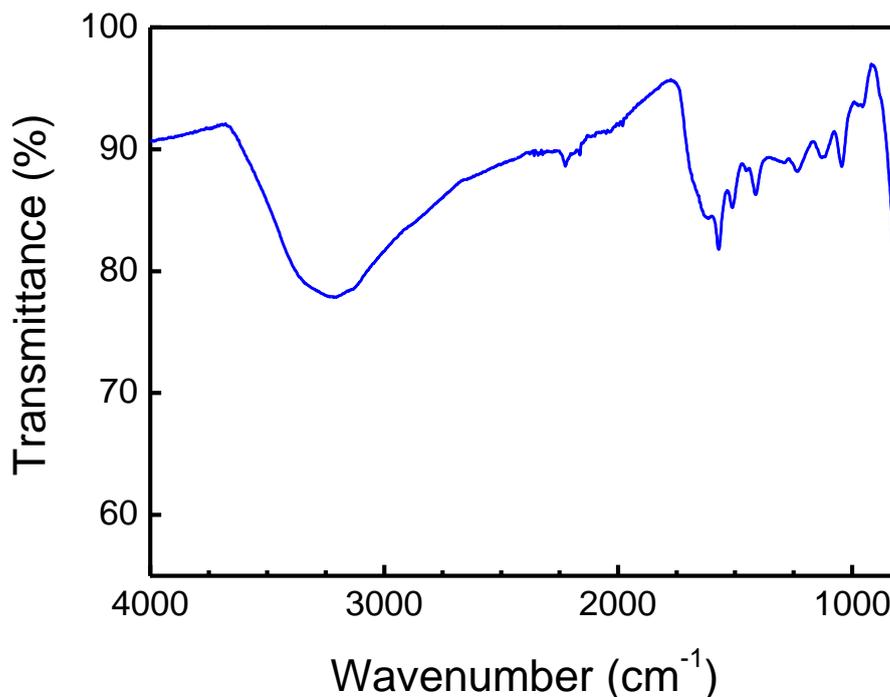


Figure 2. FT-IR spectrum of polypyrrole films deposited at -0.8 V versus the Ag/AgCl reference electrode.

Fig. 2 shows FTIR spectrum for the polypyrrole films deposited on the copper substrate at -0.8 V. The complex characteristic peaks observed in the region of 900~1600 cm^{-1} showed a good agreement with the ones reported in the literatures, confirming the formation of polypyrrole[5,15].

Fig. 3 shows SEM images of the polypyrrole films synthesized by cathodic deposition at various step potentials. The polypyrrole film deposited at -0.5 V contained spherical particles with a three-dimensional porous framework as shown in Fig. 3a. The size of polypyrrole particles ranged from 50 to 200 nm in diameter. In general, such a mesoporous network with large surface area is very helpful for electrochemical applications because of providing fast kinetics due to high accessibility of molecules or ions to the electrode surface[1,10,11]. The polypyrrole deposits prepared at -0.6 V showed very similar morphologies to those at -0.5 V, except that the particle size was relatively bigger (Fig. 3b). This feature directly indicates that the particle size of conducting polymers can be controlled effectively by changing applied potentials. Very surprisingly, nanorod-type polypyrroles with diameter of about 200 nm were created at -0.7 V in a form of a three-dimensional porous network (Fig. 3c). It is thought that the remarkable change may be closely related to the rate of reduction of nitrate ions. Further, dendritic growth of polypyrroles was observed at -0.8 V, showing film morphologies with a three-dimensional mesopore structure (Fig. 3d). It is thought that the remarkable morphological change may be closely related to the kinetics of polymerization. The growth rate of polypyrrole can depend on the concentration of generated nitrosyl ions, since the polymerization is initiated by the chemical oxidation of pyrrole by the nitrosyl ions[11,16]. It is estimated at higher current densities that the formation of rod- or dendrite-type conducting polymers may be more favorable than spherical particles which are prepared under mild conditions[11]. Overall results indicate that growth pattern of the

conducting polymers depend significantly on the applied potential under cathodic deposition conditions, resulting in different three-dimensional morphology with mesopores.

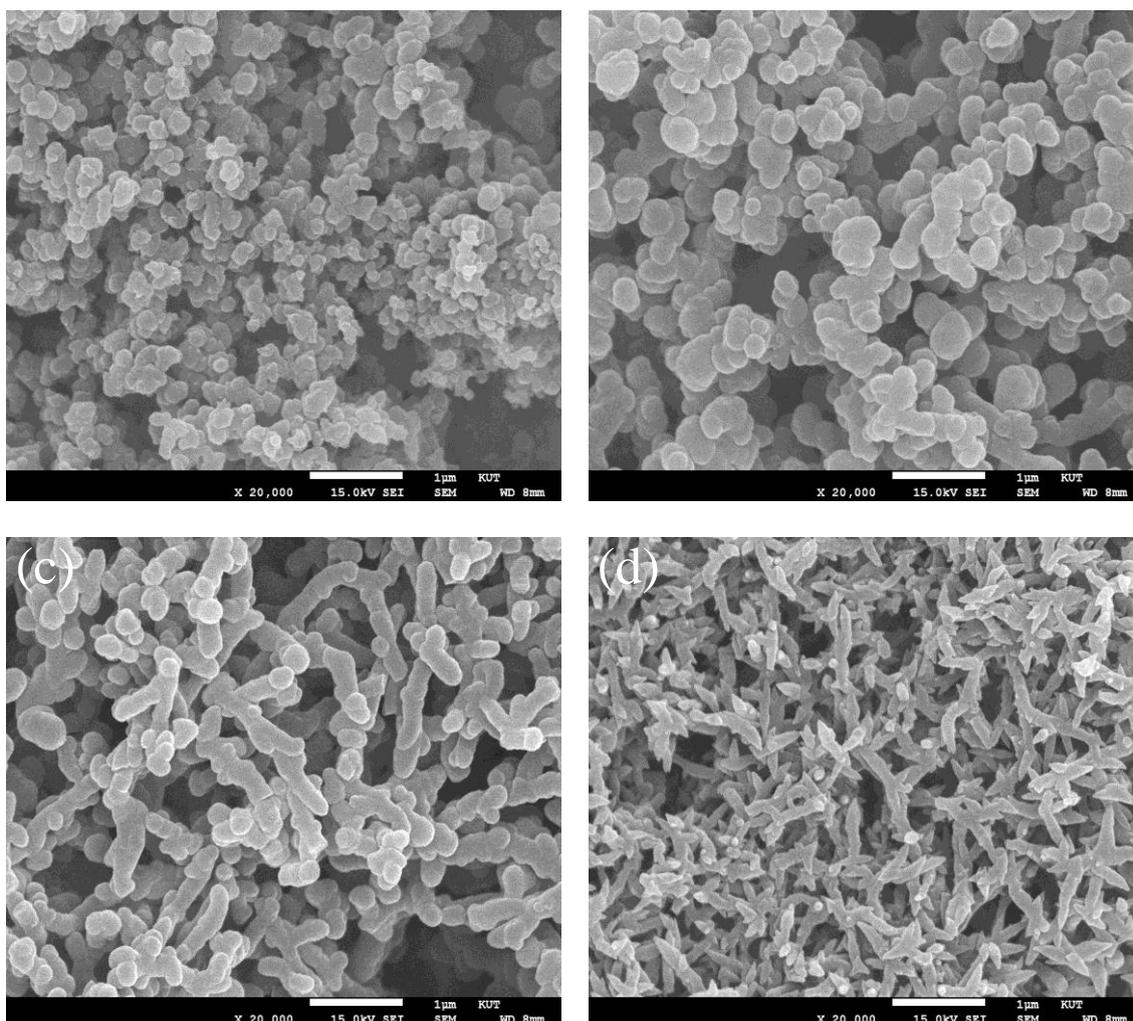


Figure 3. SEM images of polypyrrole films synthesized by cathodic polymerization at various deposition potentials: -0.5 V (a), -0.6 V (b), -0.7 V (c) and -0.8 V (d) versus the Ag/AgCl reference electrode.

4. CONCLUSION

Polypyrrole films with new nanoscale morphologies were synthesized by using a novel cathodic polymerization which proceeded through the oxidation of pyrrole monomers by in situ generated nitrosyl ions on the surface of copper electrodes. It was found that the morphology and growth pattern of the polypyrrole films depended significantly on the potential applied to the copper electrodes. The polypyrrole films deposited at -0.5 and -0.6 V contained spherical particles with three-dimensional porous morphologies. On the other hand, the polypyrrole films deposited at -0.7 and -0.8 V showed nanorod- and dendrite-type morphologies, respectively. All the polypyrrole films exhibited

three-dimensional mesopore structure which is very advantageous to chemical or electrochemical applications.

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