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Formation of conductive polyaniline nanoarrays from block copolymer template *via* electroplating

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ABSTRACT

Nanostructured thin films have drawn extensive attention because of their unique properties resulting from nanoscale features. One of the convenient ways to generate nanostructured thin films is to use pattern with nanoscale texture as a template for the reactions carrying out within the template. In this study, nanoporous thin film template was obtained from the self-assembly of degradable block copolymer, polystyrene-*b*-poly(L-lactide) (PS-PLLA) with PLLA cylinder nanostructure, at which the PLLA block can be hydrolyzed to form the nanopatterns with cylinder nanopores on conductive substrate (i.e., ITO substrate). The nanoporous PS thin film template was stabilized by modification of substrate using hydroxyl terminated PS so as to enhance the adhesion with substrate for following electroplating process. Combining a pulse electroplating method with the control of micro current, polyanilines can be successfully synthesized within the template to fabricate well-defined of conductive polymer nanoarrays.

1. Introduction

Nanoporous templates have been used for the fabrication of nanostructured materials that have potential applications in electronic, optical, magnetic, and energy storage devices. Both nuclear track etched polycarbonate and anodized aluminum oxide (AAO) membrane have been widely used as templates to prepare nanostructured materials [1,2]. The use of block copolymers (BCPs) as templates and scaffolds for the fabrication of nanostructured materials has also drawn significant attention [3–7]. BCPs that consist of chemically different components can self-assemble into various ordered nanostructures due to the incompatibility of constituent blocks [8,9]. Consequently, well-defined nanostructures with promising features for applications in nanotechnologies can be tailored by the molecular engineering of synthetic BCPs. By taking advantage of the degradable character of constituent block in BCPs, nanoporous polymeric materials could be fabricated by selective degeneration of self-assembled BCP phases composed of degradable block using UV [10], oxygen plasma [11], ozone exposure [12], and base aqueous solution [13–17].

Conductive polymers have emerged as a new class of materials because of their unique electrical, optical and chemical properties. With appropriate doping, the conductivity of the materials can be varied from semiconducting to metallic regime, offering new concepts of charge-transport mechanism. The synthesis of conductive polymer nanotubes and nanofibers has been fabricated by using various templates for the chemical and electrochemical reactions. Martin and co-workers pioneered the work in the synthesis of conductive polymer, such as polypyrrole, polythiophene, and polyaniline nanotubes and nanofibers in the pores of polycarbonate and AAO [18–20]. Polyaniline (PANI) is unique in the family of conjugated polymers; it is one of the most intensively investigated conductive polymers because of potential applications, such as electrochromic display devices, rechargeable batteries, sensors, and electrochemical capacitors [21–24]. One of the challenges in these electronic devices is the poor charge-transport rate due to slow diffusion of counter ions into/out of the conductive polymer film during redox processes [25,26]. Nanoarrays of conductive polymer is one of the ideal structures that can enhance the device performance by improving charge-transport rate and increasing surface area [27–29]. Stamm and co-workers reported that the fabrication of PANI nanorods using supramolecular assemblies of block copolymer as a scaffold material following by the electroplating of the PANI. Nevertheless, the PANI nanorods prepared by using this approach encountered the problems of the non-uniformity in height and the low aspect ratio [28].

Herein, we aim to create conductive polymer nanoarrays with uniform height and higher aspect ratio by using cylinder-forming nanoporous polymer as a template for electropolymerization. To

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demonstrate the feasibility of this approach, PANI is used as a representative material for the fabrication of conductive polymer nanoarrays *via* templated electroplating. Fig. 1 illustrates the fabrication processes of conductive polymer nanoarrays. A PS-PLLA BCP with a PLLA volume fraction of 25%, giving hexagonally packed PLLA cylinders in a PS matrix, resulting from BCP self-assembly, was synthesized [30,31], and used for the formation of nanostructured polymer thin films onto ITO glass. Hydroxyl terminated PS is used to modify the ITO glass so that the adhesion of PS-PLLA thin film on ITO glass can be significantly enhanced. PS-PLLA in chlorobenzene solution is spin-coated onto the modified ITO glass giving a thin film with thickness of ∼70 nm. Thin film samples with perpendicular PLLA cylinders can be obtained after spin-coating, and then hydrolyzed by using sodium hydroxide solution of methanol/water so as to create nanoporous PS with cylindrical nanochannels. Subsequently, the nanoporous PS thin films is used as a template for the polymerization of conductive polymer *via* electroplating. As a result, PANI cylinder nanoarrays with precisely controlled shape, size and orientation can be fabricated.

2. Experimental

2.1. Materials

PS-PLLA was prepared by a double-headed polymerization sequence. The synthesis of the PS-PLLA sample has been described previously [30,31]. The number-average molecular weight and the molecular weight distribution (polydispersity) of the PS were determined by GPC. The polydispersity of PS-PLLA was determined by GPC and the number of L-LA repeating units was determined as a function of the number of styrene repeating units by 1H NMR analysis. The number-average molecular weights of PS and PLLA, and the PDI of PS-PLLA are 38,300 g mol^{-1}, 15,600 g mol^{-1} and 1.33, respectively. The volume fraction of PLLA was thus calculated to be $f_{PLLA}v = 0.25$, by assuming that densities of PS and PLLA are 1.02 and 1.248 g cm^{-3}, respectively.

2.2. Sample preparation

An ITO glass slide was cleaned by using isopropyl alcohol, acetone solution, and then rinsed with deionized water. Molecular weights of 9000 g mol^{-1} hydroxyl terminated PS with a polydispersity of 1.25 was anchored to the ITO in order to increase the adhesion of PS-PLLA thin film on ITO glass for following hydrolysis process. The thin film sample was prepared onto the modified ITO substrate by spin-coating (1000 rpm) from a 1.0 wt % chlorobenzene dilute solution of PS-PLLA at 50 °C. Nanoporous template with well-oriented cylinder nanochannel arrays was then prepared after the hydrolysis of amorphous PLLA by treating with sodium hydroxide in a 40:60 v/v% solution of methanol/water [14].

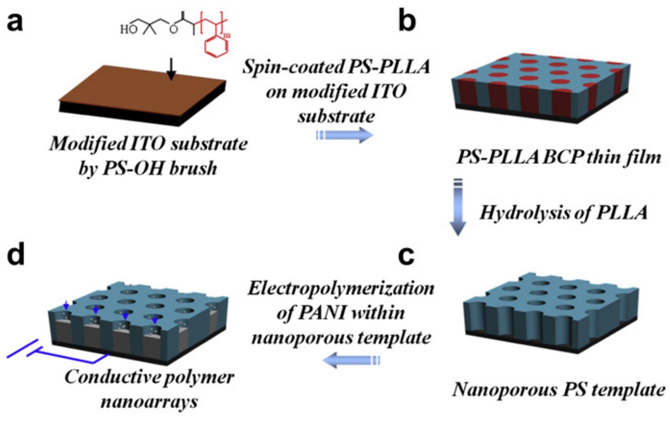

Fig. 1. Schematic illustration of the combination of block copolymer templating and electroplating for the formation of conductive polymer nanoarrays.

2.3. Electropolymerization of aniline

Aniline monomer was distilled under reduced pressure and stored under nitrogen prior to use. All experiments were carried out in a three-compartment cell. An Ag/AgCl (in 3 M KCl) was used as the reference, and a platinum foil was employed as the counter electrode. ITO was used as the working electrode for PANI deposition. PANI was electrochemically polymerized within the nanoporous PS template at an applied potential of 0.8 V versus the Ag/AgCl reference electrode in a methanol/water solution of 0.5 M H_2SO_4 containing 0.01 M aniline monomer.

2.4. Cyclic voltammetry

Cyclic voltammetry is a system of potentiodynamic electrochemical measurement. For the measurement of cyclic voltammetry, a voltage was applied to a working electrode in solution, and current flowing at the working electrode was plotted versus applied voltage to give the cyclic voltammogram. In this study, cyclic voltammogram was carried on CHI627C electrochemical workstation system. Cyclic voltammogram was examined in the voltage windows ranging from −0.2 to 1 V (vs. Ag/AgCl) at a scan rate of 100 mVs^{-1}.

2.5. Scanning probe microscope (SPM)

SPM imaging by tapping-mode was acquired from thin film samples. A Seiko SPA-400 AFM with a SEIKO SPI-3800N probe station was employed at room temperature in this study. A rectangle-shaped silicon tip was applied in dynamic force mode (DFM) experiments using a type of SI-DF20 with a spring force contact of 5 Nm^{-1} and scan rate of 1 Hz.

2.6. Transmission electron microscopy (TEM)

Thin film samples were stripped from the modified ITO glass by using 1% HF solution and floated onto the surface, and then recovered using copper grids. Staining was accomplished by exposing the samples to the vapor of a 4% aqueous OsO_4 solution for 3 h and the PANI can be stained by OsO_4 to increase the mass-thickness contrast. JEOL JEM-2100 transmission electron microscope was used (accelerating voltage: 200 kV).

3. Results and discussion

3.1. Templates from degradable BCP thin films

Fig. 2(a) and (b) shows the top- and bottom-view SPM phase images of spin-coated PS-PLLA thin films, suggesting the formation of perpendicular PLLA cylinders and the cylinders should span the thickness of the 70 nm thin film sample, consistent to the suggested mechanism of induced cylinder orientation for PS-PLLA *via* spin-coating [15]. Consequently, the constituent PLLA block in the PS-PLLA thin films was selectively degenerated by hydrolytic treatment to form nanoporous PS thin films with cylindrical nanochannels, as evidenced by the SPM height image (Fig. 2(c)). Furthermore, the thin film sample was observed by TEM (Fig. 2(d)) at which bright pore regions in contrast to the dark matrix can be

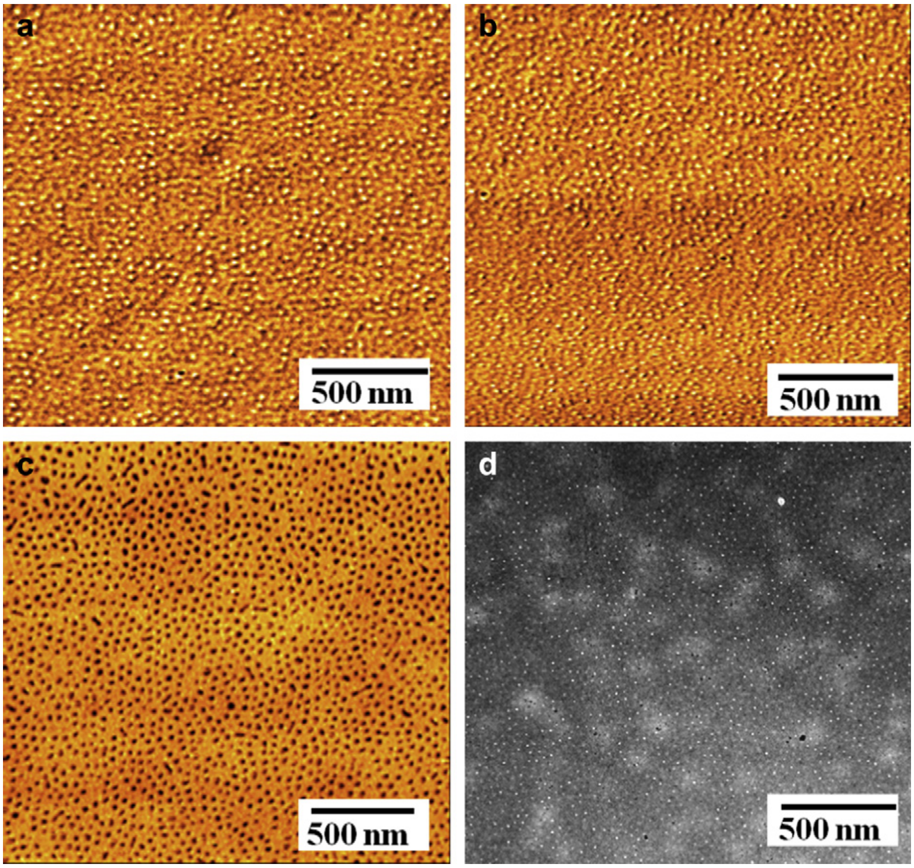

Fig. 2. Tapping-mode SPM (a) Top-view; (b) Bottom-view phase images of PS-PLLA thin film on modified ITO glass. (c) Tapping-mode SPM top-view height image and (d) TEM image of PS-PLLA thin film after hydrolytic treatment.

clearly identified, further confirming the formation of cylindrical nanochannels.

3.2. *Optimization of electrolyte solution for pore-filling*

For electropolymerization of aniline, the aniline monomer was dissolved into H_2SO_4 aqueous solution at a constant electrode potential. Cyclic voltammograms (CVs) of PANI on the modified ITO electrode, was recorded in an aqueous solution of 0.5 M H_2SO_4. As shown in Fig. 3(a), a couple of redox peaks (labeled as A1 and C1) near 0.25 and 0 V on the positive and negative sweeps, respectively, can be clearly identified. Those peaks are attributed to the conversion of PANI from leueoemeraldine into emeraldine form. Moreover, anodic current rises gradually with the positive shifting in electrode potentials (labeled as A2) at potentials above 0.6 V on the positive sweep while the corresponding reduction peak (labeled as C2) near 0.8 V on the negative sweep is observed. Peak A2 is attributed to the redox transition from the emeraldine form to form pernigraniline. As a result, PANI can be successfully synthesized by electrochemical method on the modified ITO glass regardless of the use of hydroxyl PS thin layer. For the electrochemical reaction of electrode surface, species in the electrolyte solution must be transported to the electrode so as to initiate the occurrence of the electrode reactions. Note that wetting is a key issue to drive the ions of aqueous plating baths diffuse into the nanochannels [14,32–34]. Accordingly, before electroplating within the nanoporous template, it is necessary to assure that the nanoporous PS template can be wetted by the electrolyte solution used. To evaluate the wetting degree of the electrolyte solution for the nanoporous PS template, contact angle measurement was carried out. To improve the wetting capability of electrolyte solution, methanol was used as co-solvent to dissolve aniline monomers, which ensures a large driving force to efficiently drive the electrolyte solution pore-fill into the nanochannels.

As shown in Fig. S1, the contact angle will decrease with the increase on the ratio of methanol in electrolyte solution, indicating

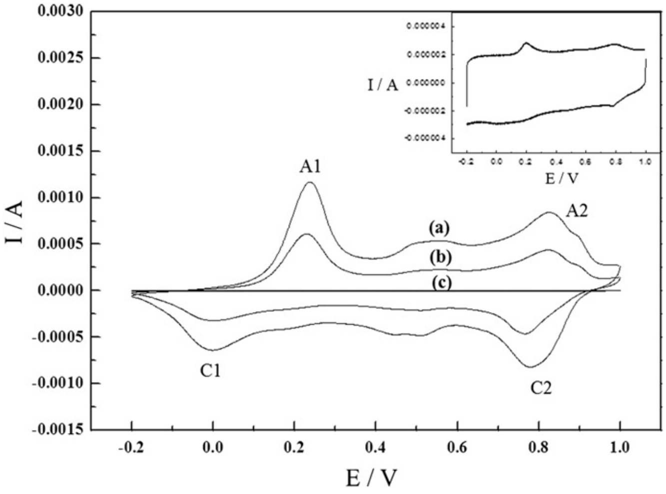

Fig. 3. CVs of PANI films synthesized from 0.01 M aniline aqueous solution containing (a) 0, (b) 25, and (c) 50 vol.% methanol recorded in an aqueous solution of 0.5 M H_2SO_4 with a scan rate of 100 mV/s. Inset shows the enlarge view for (c).

that increasing methanol content in electrolyte solution can give rise to the improvement on wetting capability. Furthermore, CVs of aniline polymerization in the electrolyte solution with different ratios of methanol were measured. As shown in Fig. 3, the voltammetric current decreases with increasing methanol content in electrolyte solution. No characteristic peaks of the PANI electropolymerization can be identified from the CVs while the electrolyte solution contains 75 vol.% methanol (not shown here). Note that the anodic and cathodic charge values resulting from the integration of I/E voltammetry is directly proportional to the growth rate of polyaniline. As a result, the polymerization rate will be reduced by adding methanol into electrolyte solution. As shown in Fig. S2(a), the oxide peak of methanol near 0.7 V can be clearly identified on the positive sweep, indicating that electric potential energy may be degenerated because of the methanol oxidation during electropolymerization of aniline at 0.8 V. Accordingly, the efficiency for the electropolymerization of aniline was reduced by the side reaction of methanol oxidation. By combining the results of contact angle and cyclic voltammetry experiments, the optimized electrolyte solution for the electroplating aniline within nanochannels is the electrolyte solution containing 25 vol.% methanol as solvent for following electropolymerization.

To investigate the formation of PANI nanoarrays, the PS/PANI nanocomposite was examined by TEM. Nevertheless, as shown in Fig. 4(a), the majority of nanochannels remains empty by using 25 vol.% methanol as solvent for electropolymerization. When the electrolyte solution contains 50 vol.% methanol, the wetting capability can be improved but the electroplating efficiency will be scarified. Consequently, no significant improvement in the formation of PANI nanoarrays can be achieved even with electroplating for 4 h, as shown in Fig. 4(b). Those experimental results indicate that the methanol is not a suitable surfactant in this system. For the oxidation of alcohol, it involves the loss of one or more hydrogen from the carbon bearing the —OH group. Methanol is not electrochemically stable, and it could be oxidized to formaldehyde or formic acid when used as co-solvent for electropolymerization of aniline. To solve this problem, tertiary alcohol was used since it contains no hydrogen so that no oxidation will occur. As demonstrated in Fig. S2(b), there is no oxide peak on the positive sweep in the CVs for tert-butanol. Furthermore, the electrolyte solution with tert-butanol indeed gives better wetting capability, as evidenced by the contact angle measurements (Fig. S1). As shown in Fig. S3, the voltammetric current is independent upon the tert-butanol concentration in the electrolyte solution, indicating that electropolymerization of aniline will not be affected by the introduction of tert-butaniol. Considering the improvement of wetting capability, the electrolyte solution containing 75% tert-butanol was thus used for templated electropolymerization.

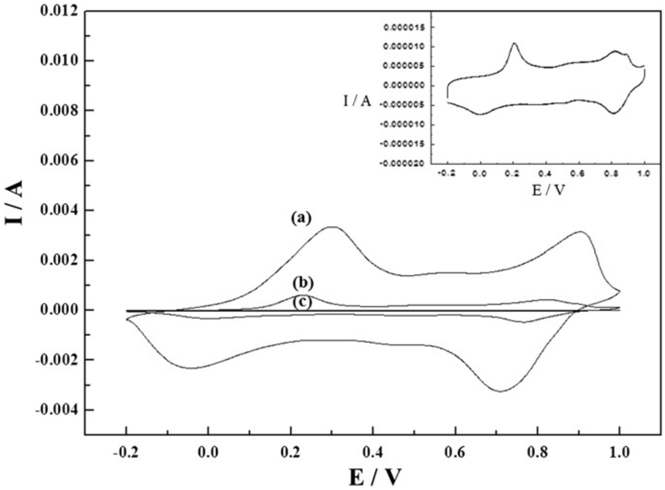

Fig. 5. CVs of PANI film synthesized from (a) 0.01, (b) 0.005 and (c) 0.001 M aniline aqueous solution containing 75 vol.% tert-butanol recorded in an aqueous solution of 0.5 M H_2SO_4 with a scan rate of 100 mV/s. Inset shows the enlarge view for (c).

3.3. Electropolymerization of aniline within BCPs templates

For electropolymerization of aniline within nanochannels, the formation of templated PANI nanorods can easily be overgrown because of the fast growth rate of electroplating aniline. As found, the forming PANI nanorods will grow out of the nanoporous PS template for only 30 s reaction. Since the polymerization rate is controlled by the reactant concentration, the concentration of aniline monomer was changed from 0.01 to 0.001 M in order to lower the growth rate. As shown in Fig. 5, the peak current from the CVs decreases with decreasing the concentration of monomer, indicating that polymerization rate can be successfully reduced by lowering the concentration of monomer.

Moreover, it is difficult to achieve uniform growth rate of PANI within each nanochannels by using traditional potentiostatic method due to non-uniformly diffused field of aniline monomers in the electrolyte solution. As a result, instead of using continuous electroplating, a pulse mode having a periodic electroplating and a diffused sequence was applied to equalize the concentration

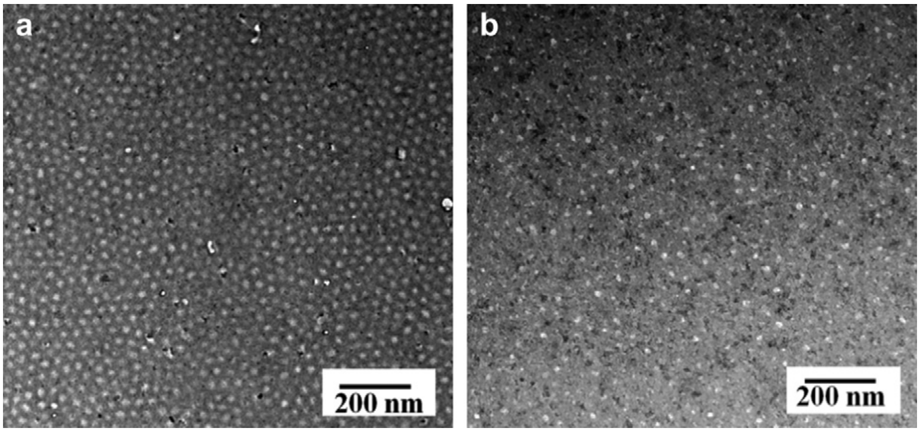

Fig. 4. TEM mass-thickness images of thin film samples after the electropolymerization of aniline within nanopores in 0.01 M aniline aqueous solution containing (a) 25 vol.% for 1 h and (b) 50 vol.% for 4 h.

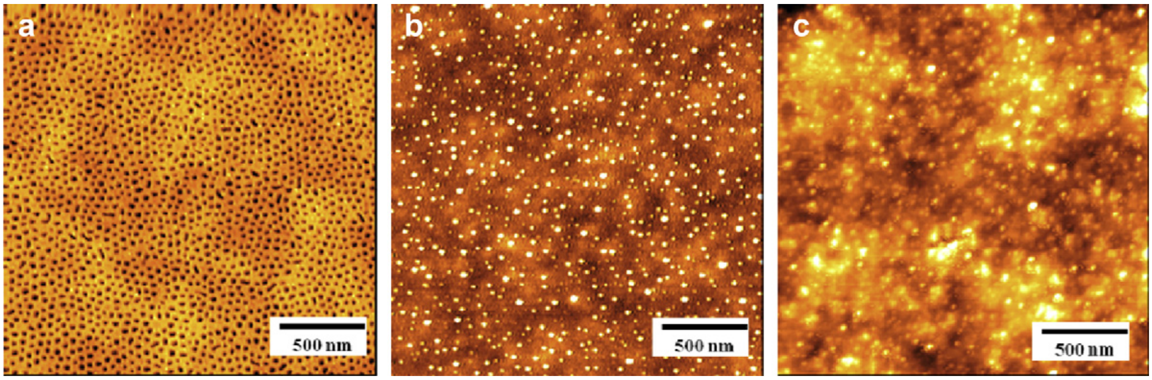

Fig. 6. Tapping-mode SPM height images of nanoporous PS template after electropolymerization of aniline within nanopores in 0.001 M aniline aqueous solution containing 75 vol.% tert-butanol for (a) 300, (b) 600, and (c) 1200 s.

gradient of aniline monomer within the nanochannels. The pulse plating of aniline within the nanochannels was carried out at 0.8 V. The duty cycle and the pulse frequency were 0.2 and 0.4 Hz, respectively. As a result, electropolymerization of aniline can be achieved in the electroplating conditions with micro current, as evidenced by chronoamperogram recorded in the pulse plating (Fig. S4). By combining the use of the electrolyte solution with low-concentration aniline monomer and the pulse plating, templated electropolymerization of aniline was carried out.

As shown in Fig. 6(a), the morphology of nanoporous PS template can still be recognized after electropolymerization for 300 s, indicating that the height of PANI should be smaller than the thickness of nanoporous PS template. CV result further demonstrates that PANI can be successfully synthesized within the nanochannels (Fig. S5). The shape of the CVs of PS/PANI nanocomposite is approximately equal to that of PANI, indicating the existence of the PANI within the nanochannels, and also no variation in the electrochemical properties of forming PANI can be found. By increasing the electropolymerization time to 600 s, a PANI-filled template can be formed, as evidenced by the formation of protruded nanorods (Fig. 6(b)). After 1200 s, the PS surface will be covered by the overgrown of PANI (Fig. 6(c)). Consequently, conductive polymer can be successfully synthesized so as to fabricate well-defined conductive polymer nanoarrays.

4. Conclusions

Nanoporous polymer thin films on ITO substrate was obtained from the self-assembly of degradable block copolymers followed by hydrolysis. By combining block copolymer templating and electroplating, a promising way to construct conductive PANI nanoarrays was developed. Those precisely controlled nanostructured thin films have appealing potentials for practical applications in nanotechnologies.

Acknowledgments

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Appendix A. Supplementary material

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.polymer.2012.04.031.

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