A Simple Approach for Fabricating Polypyrrole Nanowire Arrays

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Abstract. Highly ordered nanoporous anodic aluminum oxide (AAO) templates were prepared, which had 35 nm average porous diameter and $4.8 \times 10^{10}$ pores cm$^{-2}$ porous density. The AAO template was affixed tightly to the surface of glass carbon electrode (GCE). Cyclic voltammetry (CV) and direct current electrodeposits (DCED) method were utilized to fabricate polypyrrole nanowire arrays. Experimental results indicated that DCED methods were simpler and more efficient than CV. Furthermore, the prepared polypyrrole nanowire arrays were characterized by high-resolution scan electron micrograph (HRSEM).

1. Introduction

In the last few years, there has been considerable interest in one dimension nanostructure, such as nanotubes, nanowires, nanorods, and nanobelts, because of their potential for fundamental studies of the effect of dimensionality and size on a material’s physical properties and for their application on nanodevices [1]. Several fabrication approaches have been developed, but presently, difficulty and challenge still existed in preparing big area highly ordered nanoarray materials, which could be directly utilized in practical devices. Among available approaches, template-based synthesis was well suited for producing arrays with uniform diameters and high aspect ratio ratios [2]. Porous anodic aluminum oxide (AAO) templates especially attracted extensive interest because of its desirable characteristics, including highly ordered porous distribution, uniform and tunable pore diameters over a wide range (7 ~ 300 nm) and lengths (to > 100 µm), good mechanical and thermal stability and well-developed preparation methods.

Conductive polymer nanomaterials have attracted increasing attention, mainly due to their potential applications in catalysis, drug delivery, microelectronics, biological sensors, energy conversion and storage, light-emitting display devices and optical storage [3]. Martin and Demoustier-Champagne have reported numerous excellent studies range from fabricating of nanostructures to their properties and application [4]. Most of this work were carried out using commercially available Particle Track-etched Membranes (PTM) templates. However, porous distribution of these polymeric membranes is random and their porous density is relatively low. Herein, highly uniform nanoporous AAO templates were fabricated in our lab with two-step anodization method. SEM photograph indicated that porous distribution was very ordered and porous diameter was uniform. With these templates help, large-scale
uniform and uniform PPy nanowire arrays were directly grown on the surfaces of GCEs by DCED method. Compared with previous reports, our nanowire possessed less diameter and higher density, and the distribution was highly uniform in the whole reaction region.

2. Experimental
All the common chemicals were of analytical grade. The water used in all experiments is twice distilled with quartz heating tube. A WYK603 model direct current steady potential/current power provided constant potential. Cyclic voltammetry was performed on a LK98A model Microcomputer-based Electrochemical Analyzer. A model HITACHI S-5200 scanning electron microscope (SEM) was used in morphology analysis.

Based previous works [5], our AAO templates were fabricated by two-step anodizing approach in 1.0 mol/L sulfuric acid electrolyte with 20 V steady potential under 0 ~ 5 °C. The preparing procedures were described in detailed elsewhere [6].

3. Results and discussion
Systemic condition experiments indicated that the anealing and polishing procedures can be cancelled if two-step anodization method was used. Optimal experimental parameters have been obtained for fabricating large-area highly ordered AAO templates. The AAO template possessed closely packed hexagonal cylindrical monodisperse nanochannel with average porous diameter at 35 nm, channel length at about 30 ~ 70 µm and porous density about at 4.8 × 10^{10} pores·cm^{-2}. The representative SEM photograph of our template was shown in Figure 1.

The dry template was stuck to the surface of GCE with epoxy resins. After complete solidification through 12 h, the template was soaked in methanol with ultrasonic for 10 minutes. Then it was immersed in water under ultrasonic for about 10 minutes. This pretreatment assured that all nanochannels and interspace of template and the surface of GCE were fully occupied with water. In other words, all air bubbles must be driven out, which would ensure the PPy nanowires continuously formed.

CV and DCED polymerization reaction both were carried out under room temperature with mildly stirring. The 10.0 mL electrolyte contained 0.4mol/L pyrrole, 0.04mol/L toluene-4-sulfonic sodium and pH was modified to 4.0 with 0.01 mol/L sulfuric acid. Before reaction, the electrolyte was saturated with highly pure N₂ for 15 minutes. In CV, a GCE fixed with template working electrode, a platinum-disk auxiliary electrode, and a saturated calomel reference electrode was used in a three-electrode configuration. The scan potential ranged from 0 ~ 0.75 V and scan speed was 50 mV/s. After about 50 minutes, the black PPy began to form on the surface of template and reaction was stopped. In
contrast with CV. In DCED, the GCE equipped with template worked as anode and a platinum-slice electrode worked as cathode. 0.65 V constant potential was used under mildly stirring. After about 15 minutes, the PPy grew out of nanochannels and reaction could be stopped. The PPy on the surface of template was carefully removed. The surface was washed with twice distilled water. 6mol/L NaOH aqueous solution was dipped on the surface to dissolve template. Then the black PPy was washed again and again and soaked in water. The whole piece of PPy can be cut down and was washed with acetone. After dry, it was investigated by HRSEM. The result was shown in Figure 2. Photograph of microstructures (Figure 2a) showed that polypyrrole nanowire arrays were highly uniform in a large scale. For clarity of SEM, the amplificatory polypyrrole nanowires with 38 nm uniform diameters were shown in Figure 2b and 2c. Though some portions were collapsed, the high-resolution scan electron micrograph (HRSEM) photographs of PPy nanowire indicated that nanowire arrays had less diameter and higher density (figure 2b and 2c).

Figure 2. HRSEM photograph of polypyrrole nanowire array
4. Conclusions
Large area highly uniform and ordered PPy nanowire arrays have been fabricated by DCED method with the help of AAO templates. The contrasted experiments revealed that DCED was more efficient to prepare PPy nanowire arrays than CV. The diameter of single PPy nanowire was 40 nm, which was agreed well to the porous diameter of our prepared AAO template. This work gave significant explore in fabricating large-scale ordered conductive polymer 1-D nanomaterials arrays, which was very near to practical nanodevices.

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