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Polyaniline Nanofibrils Array Synthesized within the Anodic Aluminum Oxide Template

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Abstract: Polyaniline (PANI) nanofibrils were prepared within the anodic aluminum oxide (AAO) template. The surface appearance of PANI nanofibrils and the structure of nanofibril array were observed by scanning electron microscopy (SEM). The diameter and the length of PANI nanofibrils are dependent on the pore diameter and the thickness of AAO template. X-ray photoelectron spectroscopy (XPS) supplies the surface analysis confidence on the PANI nanofibrils. Fourier Transmission Infrared (FTIR) was used to confirm the fibrils composed of PANI.

Keywords: Polyaniline, scanning electron microscopy, X-ray photoelectron spectroscopy.

Introduction

Many methods for the fabrication of nanoparticles have been developed ranging from lithographic techniques to chemical methods. The method termed template synthesis for preparation of a variety of micro- and nano-materials has been explored[1-3]. The template membranes employed contain cylindrical pores with mono-disperse diameters, that extend through the entire thickness of the membrane. The diameter of this nanocylinder is determined by the diameter of the pores of the template membrane. We have used template synthesis to synthesize nano-wires or nano-tubules of metals[4,5], semiconductors and carbons[6].

As electronically conductive polymers have interesting and useful electronic, optical and redox properties, many research groups have tried to apply the template synthesis method to synthesize the micro- or nano- structure of conductive polymers. C. R. Martin's group has synthesized electronically conductive polymers, such as polypyrrole[7,8], poly (3-methylthiophene)[8] and polyacetylene. J. W. Schultze's group[9] has also investigated the microstructure of conductive polymers. The template-synthesized electronically conductive polymer micro- or nano-fibrils can have electronical conductivities that are orders of magnitude higher than conventional forms (*eg*. powder or thin film). In this paper, we will report a convenient and feasible method to synthesize the PANI nanofibrils array based on the anodic aluminum oxide (AAO) template.

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Experimental Section

The starting monomer, aniline (Aldrich 99%) was twice distilled *prior* to use. Ammonium persulphate and H_2SO_4 were used as received.

Preparation of AAO Template

An aluminum foil (99.999% in pure, size $0.10\times20\times30mm^3$) was ultrasonically degreased for 10 minutes, then electropolished for 20 seconds and promptly rinsed with doubly distilled water. Afterward, the aluminum foil was anodized at 80 V_{DC} for 2hrs in 0.5mol/L phosphate acid solution. Each substrate was then exposed to a saturated $HgCl_2$ solution for 1 hour, the oxide section separated from the aluminum substrate as the result of amalgamation of underlying aluminum. The pore diameter of AAO used here is 200nm and the corresponding images could be seen in the references [4-6].

Synthesis of PANI Nanofibrils

AAO membrane is immersed in a precooled (5°C) solution of 0.5 mol aniline in 1 mol H_2SO_4. An equal volume of precooled (5°C) oxidant solution containing ammonium persulphate (0.25 mol) in 1 mol/L H_2SO_4 was added. The mixture was left for polymerization for 2 h at *ca* 5°C. During this period, polyaniline was produced from the monomer and deposited within the pores of the membranes.

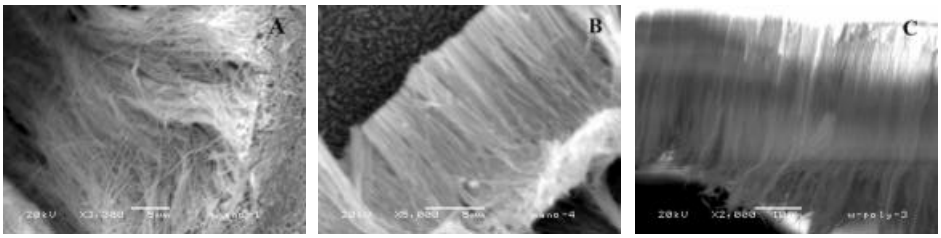
Results and Discussion

Morphology of PANI Nanofibril

Scanning electron microscopic (SEM) images were recorded with JSM-5600LV microscope. The samples were obtained as following: the membrane was glued using epoxy resin to a piece of glass. The surface of the membrane was partly polished carefully using a grit sandpaper to remove any polymeric surface layer. Then the surface of the membrane was placed in 3 mol/L NaOH to dissolve the aluminum oxide. *Prior* to characterization, the sample was attached to a SEM sample stub with carbon conductive paint, 10 nm of Au was sputtered onto the surface. **Figure 1** shows the characteristic images of PANI fibrils synthesized within the AAO template. From the **Figure 1(A)**, we can see that the PANI fibrils have the characteristics of highly ordered orientation and good mechanism. Few of the random fibrils are caused by immersing the samples in the NaOH solution to dissolve the alumina. When the PANI/AAO is partially dissolved in the NaOH, PANI nanofibrils still keep the original structure of AAO template. As indicated in *prior* correspondences[7,8], template synthesis yields conductive polymer fibrils, which run through the pores in the micro-porous membrane, and thin polymer films, which coat both faces of the membrane. **Figure 1(B)** shows that the PANI nanofibrils run through the AAO template, and thin PANI film that links the ends of fibrils. PANI nanofibrils reassembled the bristles of a “brush” is shown in

Figure 1(C). From **Figure 1**, we obtained that the diameter of fibrils is 200nm. The highly oriented uniform PANI array has a density of 5.3×10^{8} cm^{-2} and a length of about 60 μm, which have a similar morphology of the surface of the AAO template used.

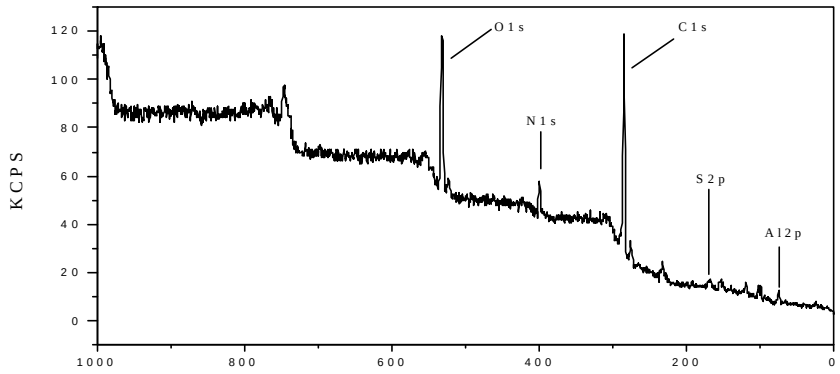
Figure 1 Scanning electron micrographs of the PANI nanofibrils doped by H_2SO_4. (A) the end of PANI nanofibrils links to the PANI film. (B) the characteristic image of an array of nanofibrils. (C) top view of an array of nanofibrils which is like the "fibrils brush"



X-ray Photoelectron Spectroscopy (XPS) and Fourier Transmission Infrared (FTIR)

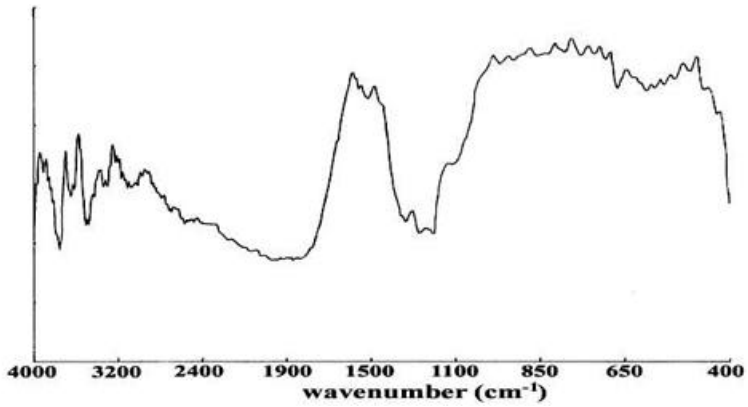
XPS measurements were carried out using an Escalab 220 iXL system (VG Scientific Inc.) with a monochromatic Mg Kα X-ray source (1284.6 eV). The pressure in the chamber during analysis was approximately 2×10^{-10} Torr. **Figure 2** shows the XPS survey scan from 0 to 1000eV of PANI/AAO composites. From **Figure 2**, it can be seen that PANI is deposited not only on the surface of AAO but also in the pores of AAO according to the peaks appearing in the chart. During the process of examination, we found that the binding energies of C, N, O and Al, are identical with the reported standard XPS and need not to carry out the "charge emendation". This result reveals that the surface of PANI/AAO composites is conductive due to conductive characteristics of the PANI. Fourier Transmission Infrared (FTIR) was use to confirm that the inner fibrils were composed of PANI. As indicated in **Figure 3** obtained from the dissolved inner fibril material showed the absorption band of N-H stretching vibration mode at

Figure 2 XPS survey scan for PANI/AAO composite membrane doped with H_2SO_4.



3247cm^{-1}, and the stretching vibration mode of benzene-N at 1124 cm^{-1}, and the benzene mode assignment at 1544 cm^{-1} and 1585 cm^{-1}.

Figure 3 FTIR spectra of PANI which was dissolved from the AAO membrane



Conclusion

We have successfully prepared the PANI nanofibrils within the AAO template, and also applied SEM, XPS and FTIR techniques to characterize the structure of PANI nanofibrils. The PANI nanofibrils are highly ordered and uniform that has good mechanism properties. As noted above, when conductive polymers are synthesized within the pores of the membranes, the polymer preferentially nucleates and grows on the pore walls. The diameter and the length of the nanofibrils are determined by the pore diameter and the thickness of AAO membrane template.

Acknowledgments

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