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Electrochemical fabrication of polythiophene film coated metallic nanowire arrays

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Metallic gold (Au) and silver (Ag) nanowire arrays coated with polythiophene (PTh) films were fabricated by successive electrochemical depositions of PTh and metal into the pores of a microporous alumina membrane. The diameter of the composite nanowires was 200 nm and that of the metallic nanowires was about 100 nm. They are adhered to a thin gold film and aligned in a high density of ca. 10^{10} wires/cm^2. The morphology of the composite nanowires has been characterized by an optical microscope, Raman spectroscopy, scanning and transmission electron microscopies. Their electrochemical property has also been investigated. © *2003 Kluwer Academic Publishers*

1. Introduction

There is an increasing interest in the fabrication of one-dimensional nanostructures, mainly due to they have potential applications in electronic, magnetic, optical, and micromechanical devices [1–3]. Metallic nanowires are also of importance in both science and technology [4, 5]. Highly ordered metallic nanowire arrays can be applied as microelectrodes, probes, and data storage devices [3, 6]. However, the metallic nanowires are sensitive to air and moisture, which degrades the performance of nano-devices [7]. C. R. Martin's group has been exploring a template method, which has been tested to be a versatile approach for preparing nanomaterials. This technique entails synthesizing the desired material within the pores of a nanoporous membrane [8]. Recently, we also prepared high-quality aligned polythiophene nanotubules by using nanoporous alumina membrane as template (AM) [9]. This array of PTh nanotubules with the alumina membrane can be used as a "second" template and the metallic nanowires enclosed in the PTh film may be protected from oxidation and corrosion. In this paper, we describe the fabrication of the composite nanowires arrays of Au (or Ag) and PTh.

2. Experimental

Microporous alumina membranes (Anodisc 25) with pore diameters of 200 nm were purchased from Whatman International Ltd. The membranes have a pore density of ca. 10^{10} pores/cm^2 and a thickness of 60 μm. Thiophene was a product of Beijing University of Science and Technology (Beijing, China), and it was used after distillation. Boron trifluoride diethyl etherate (BFEE) was a fresh product of Beijing Changyang Chemical Plant (Beijing, China), in which BF_3 concentration was 48.24% and water content was 0.24% (by volume).

Electrochemical syntheses and examinations were performed in a one-compartment cell with the use of a Model 283 potentiostat-galavanostat (EG&G Princeton Applied Research) under computer control. The procedure of working electrode fabrication is as follows: First, a gold layer with thickness of ca. 20 nm was evaporated on one side of the host membrane. Second, an indium tin oxide (ITO) glass electrode was used as current collector and contacted to the gold layer of the membrane. The membrane together with the current collector was fixed between two Teflon rings. The area of the membrane contacted to the electrodes was ca. 1.8 cm^2.

During the process of electrosynthesis of PTh nanotubule arrays, a stainless steel (AISI 304) sheet (1.8 cm × 6.0 cm) was used as the counter electrode and an Ag/AgCl wire (immersed directly in the solution) was used as the reference electrode. A correction of 0.069 V was needed to bring the measured potentials in BFEE originally vs. Ag/AgCl to potentials vs. the standard hydrogen electrode [10]. The electrolyte solution was freshly distilled BFEE containing 30 mmol/L thiophene. The solution was de-aerated by bubbling dry nitrogen gas for 5 min before electrochemical polymerization, and was maintained at a slight nitrogen overpressure during the experiments. PTh tubules were grown potentiostatically at 1.3 V (vs. Ag/AgCl). The lengths of the tubules were controlled by the total charges passed in the cell. The composite of PTh microtubules and the microporous alumina

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membrane was washed repeatedly by diethyl ether and distilled water after the electrochemical polymerization and served as the template for metallic wires growth.

The Au (Ag) nanowires were electrochemically deposited in the PTh tubules at a constant current density of 2.0 (3.0) mA cm^{-2}. The compositions of the electrolytes are listed in Tables I and II. The lengths of the metallic wires were controlled by the time of deposition. Aligned PTh nanotubules and Au (Ag) nanowires coated with polythiophene were obtained by dissolving the alumina templates with 1 M KOH for 24 h and then washed with distilled water repeatedly at room temperature.

Raman spectra were carried out on a RM 2000 microscopic confocal Raman spectrometer (Renishaw PLC.) with an excitation of 632.8 nm laser beam at 0.5 mW, and were accumulated 3 times for 30 s each. The spectra were recorded with a charge-coupled device (CCD) camera. Scanning electron microscopy images were taken out by the use of a KY2800 electron micrographer (Scientific Instrumental Plant of Chinese Academy of

TABLE I The solution used for Au nanowire deposition

Components	Unit	Amount
H_2O	ml	15.0
$AuCl_3 \cdot HCl \cdot 4H_2O$	g	1.0
Na_2SO_3	g	1.05
$(NH_4)_3C_6H_5O_7$ (tri-ammonium citrate)	g	1.2
$CoSO_4 \cdot 7H_2O$	g	0.01
EDTA (ethylenediamine tetraacetic acid)	g	0.9
pH		7.0

TABLE II The solution used for Ag nanowire deposition

Components	Unit	Amount
H_2O	ml	45.0
$C_7H_6O_6S \cdot 2H_2O$ (5-sulfasalicylic acid)	g	6.0
KOH	g	0.5
$AgNO_3$	g	1.5
CH_3COONH_4 (Ammonium acetate)	g	2.8
$NH_3 \cdot H_2O$	ml	4.5
pH		9.0

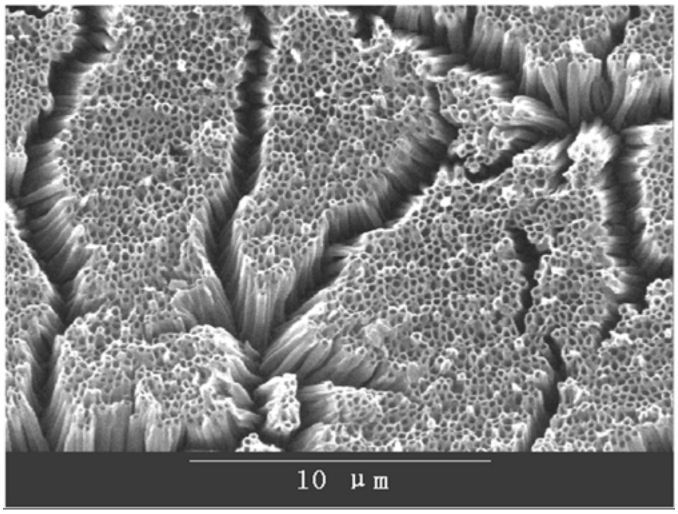

Figure 1 Scanning electron micrograph of aligned PTh nanotubules.

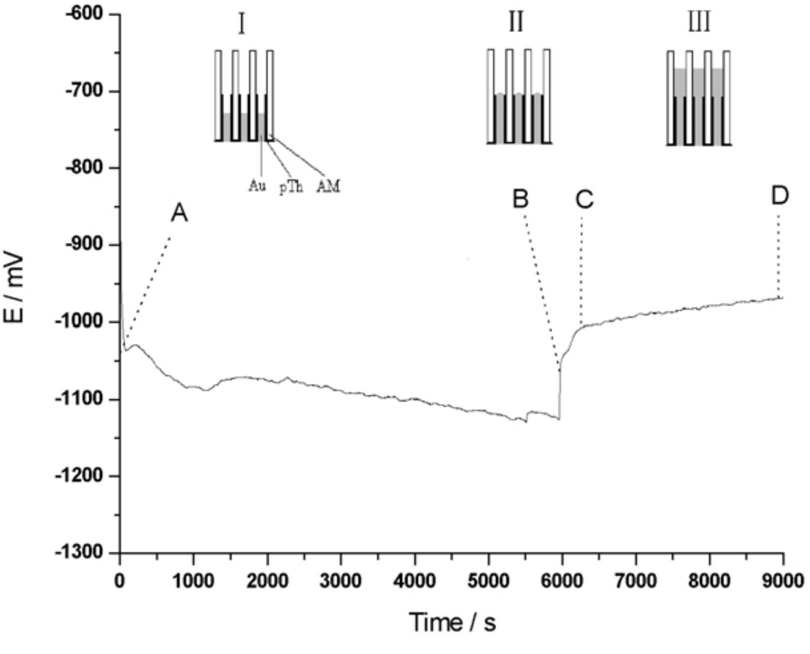

Figure 2 Potential versus time curve of the process of Au nanowire growth.

Sciences, Beijing, China). The transmission electron microscopy image was obtained using a Hitachi 800 electron microscope (Japan).

3. Results and discussion

Fig. 1 shows the scanning electron micrograph of the aligned PTh microtubules with length of ∼5 μm. The tubules are uniformly and firmly adhered to a thin gold film (see Experimental section). The tubular alignment shown here is much better than that of the conducting polymer tubules reported previously. This is mainly due to the alumina membrane templates having much high pore densities and much better pore uniformity than those of the widely used polycarbonate (PC) templates. The high strength of the PTh skin also supports the formation of high-quality tubules. The tubules are straight and stand upright on the gold layer. Their mouths are open and smooth, and the skin thickness of each tubule is about 20 nm. Accordingly, the aligned PTh nanotubules can be applied as the template for the growth of metallic nanowires.

In order to observe the metallic wires and their PTh coats clearly, the length of the metallic wires was controlled to be longer than that of the PTh coats. Actually, the length of the nanowires depends on the total charge passed in the cell or the electrolysis time at constant current density. The growing rate of Au nanowires was found to be about 1 μm/500 s. A typical potential-time curve for Au (Ag) nanowire growth is plotted in Fig. 2 (in this case the materiel is Au). Nanowires were grown in the PTh nanotubules during the course of A-B (I), and the length of Au nanowires was increased to be nearly the same to that of the PTh nanotubules (∼12 μm) during the course of B-C (II). After this period, the nanowires continued to grow in the pores of AM template (III). The diameters of the nanowires grown in "III" period were larger than those of the nanowires formed in period "I". This resulted in the increase of electrochemical deposition area or the decrease of the actual current density and also the decrease of the applied potential. As shown in Fig. 1, the transition period B-C was fairly short (about 250 s) in the Au nanowire growth curve due to the uniformity of the PTh nanotubule length.

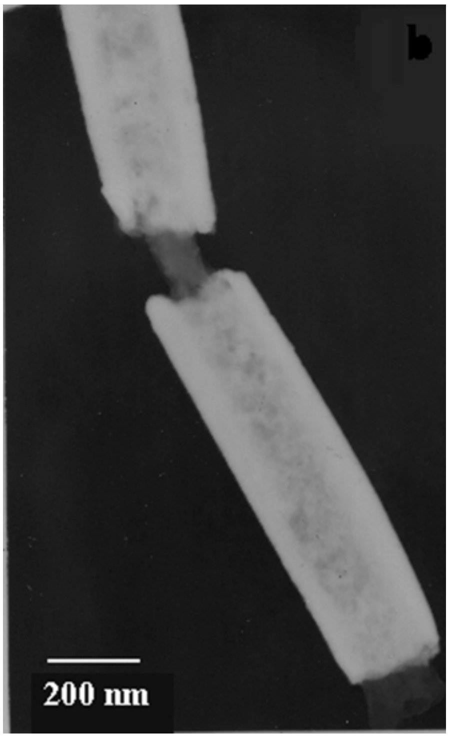

Figure 4 Transmission electron microscopy image of a Au/PTh composite nanowire.

Fig. 3 shows a representative SEM image of highly ordered Au/PTh composite nanowire arrays prepared in the AM templates with 200 nm diameter pores (Ag/PTh nanowires give a similar image). It is clear from this figure that the nanowires have equal height and a highly ordered tip array. The nanowires retain the size and shape of the template and arrange in a high density. However, the naked part and PTh coated part of the metallic nanowires cannot be distinguished clearly from this figure. This is mainly because the conductivity of the metallic wires is much higher than that of polythiophene films.

Although the fabricated Au/PTh nanowires are coated with PTh partly, there are only a few short

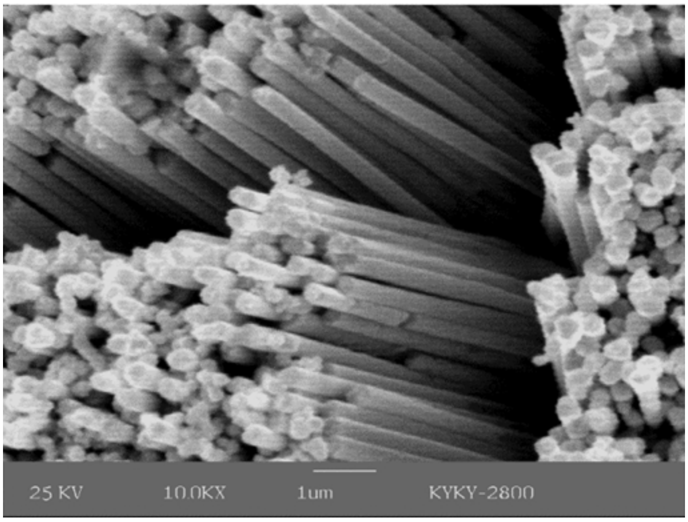

Figure 3 Scanning electron micrographs of aligned Au/PTh composite nanowires.

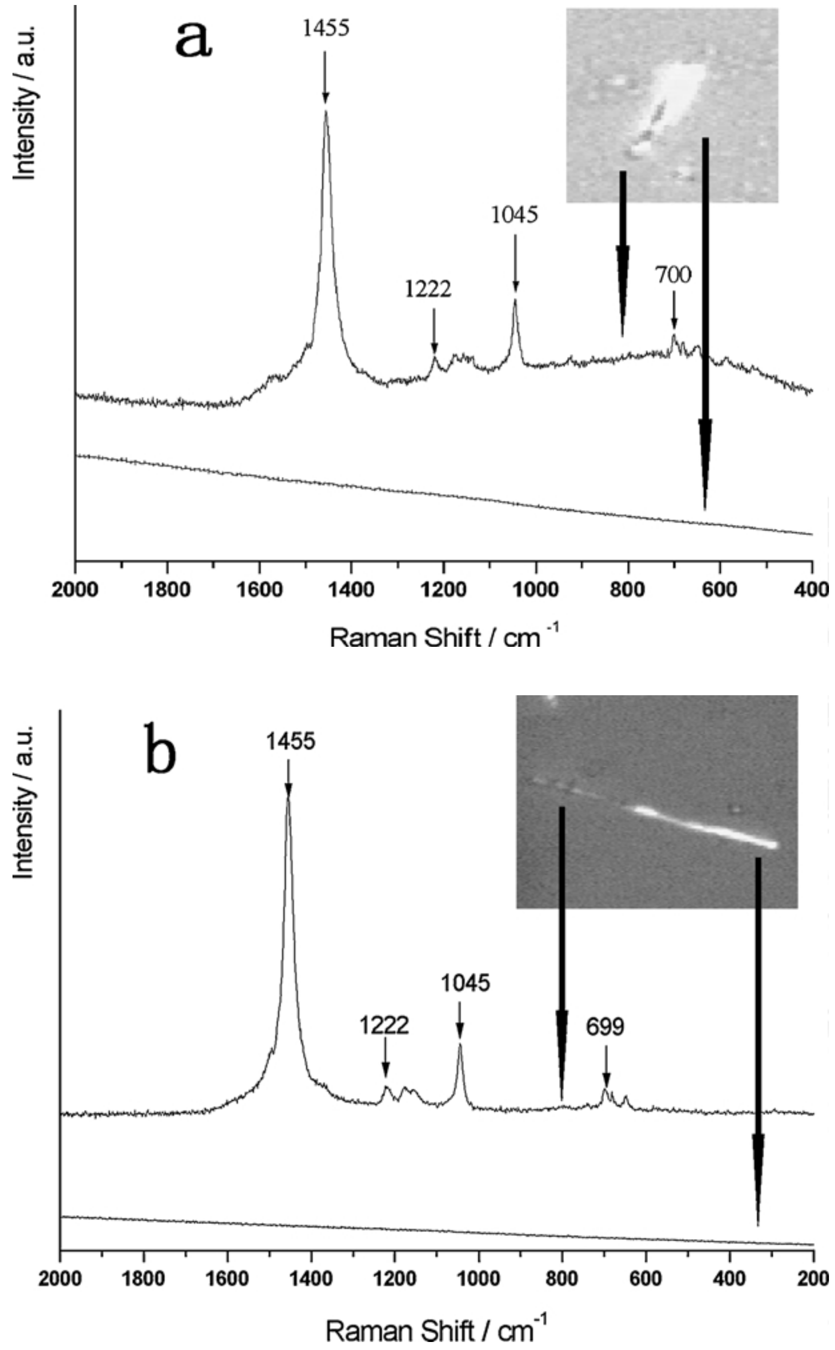

Figure 5 Raman spectra and optical microscope (insert) images of Au/PTh (a) and Ag/PTh (b) composite nanowires.

naked metal rods can be seen from their TEM images. It is possibly due to the naked metallic parts of the nanowires were destroyed by the ultrasonic vibration during the TEM sample preparing process. However, the PTh coated metallic wires have better mechanical stability than that of naked metallic nanowires and can be observed by TEM in the original state. It is mainly due to the good flexibility and the high strength of the PTh film synthesized in our system [9, 10]. Fig. 4 illustrates a TEM image of a special single Au/PTh nanowire. The coated PTh tube was separated into two parts and the Au nanowire was observed. The diameter of the Au nanowire was about 100 nm, which was approximately equal to the inner-diameter of the PTh tubules [9].

As can be seen from the insert of Fig. 5, under the optical microscope, the Au/PTh (a) and Ag/PTh (b) composite nanowire combined with a bright and a dim section, because the surfaces of PTh and metallic wire have differential reflectivity [11]. The image of naked metallic wire is bright and that of the PTh coated wire is dim. The Raman spectra of the two different sections were also shown in this figure. The spectrum of the dim section represents the characteristic features of polythiophene. For example, the band attributed to C=C symmetry stretching appears at 1455 cm^{-1} [9]. However, the bright section does not display any Raman signals. This indicates that the dim section is polythiophene, while the bright section is Au (Ag) nanowires, which are not coated with PTh and longer than the PTh nanotubules.

The cyclic voltammogram of a film of aligned Au/PTh composite nanowires showed broad and strong capacitive redox waves (Fig. 6b). Their wave currents

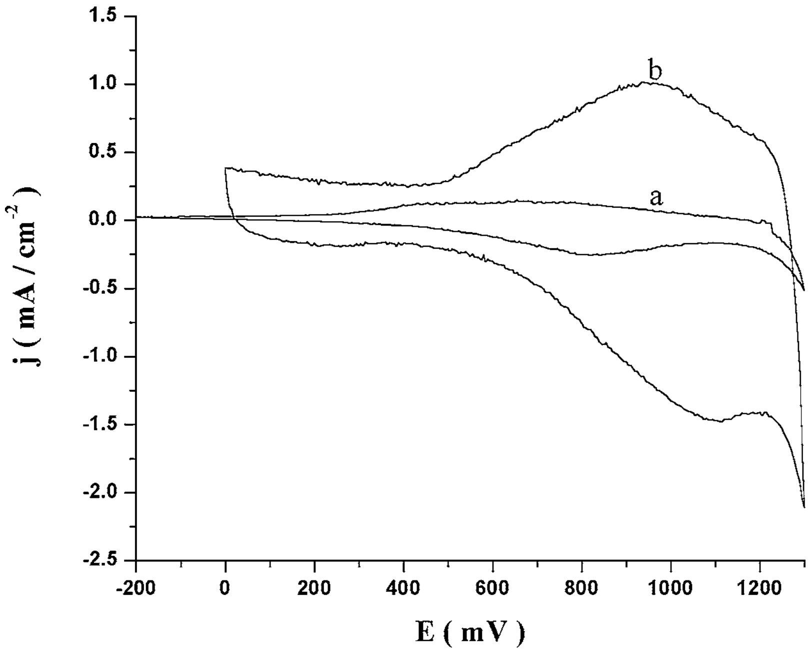

Figure 6 Cyclic voltammograms of a PTh (9×10^{-4} g cm^{-2}) film on a platinum electrode (a), and Au/PTh composite nanowire (5×10^{-4} g cm^{-2}) (b) in 0.1 M $LiClO_4$ acetonitrile solutions at a potential scan rate of 20 mV s^{-1}.

were much higher than those of the flat film deposited on the platinum electrode (Fig. 6a). This is mainly due to the fact that the surface area of aligned nanowires is much larger than that of a normal film, which results in much higher film/electrolyte double-layer capacitive charges.

4. Conclusions

Highly ordered Au and Ag nanowire arrays coated which polythiophene have been electrochemically fabricated within alumina membrane templates with pore diameters of 200 nm. This electrochemical fabrication method is simple and effective. It would also be applied to fabricate other metal and conducting polymer coating-composite nanomaterials. This kind of nanowire arrays would be useful for studying the composite material properties and have potential utilization in the future.

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