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Electrochemical fabrication of aligned microtubular heterojunctions of poly(*p*-phenylene) and polythiophene

Mingxiao Fu, Feng'en Chen, Jiaxin Zhang and Gaoquan Shi*

Department of Chemistry, Tsinghua University, Beijing 100084, People's Republic of China.
E-mail: gshi@tsinghua.edu.cn; Fax: 86-10-62771149

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Aligned microtubular heterojunctions of poly(*p*-phenylene) (PPP) and polythiophene (PTh) were fabricated by successive electrochemical oxidations of benzene and thiophene in freshly distilled boron trifluoride–diethyl ether (BFEE) solution and using a microporous alumina membrane with pores of 200 nm diameter as the template. The morphology and chain structure of the microtubular heterojunctions were studied by scanning and transmission electron microscopies and Raman spectroscopy. The current (*I*)–voltage (*V*) curves revealed that the aligned microtubular heterojunctions had a better rectification effect than that of the normal PPP/PTh bilayer heterojunction.

Introduction

Conducting polymer composites, which are an effective combination of two or more conducting polymers or a conducting polymer and other organic or inorganic materials, have attracted increasing attention. This is mainly due to the unique properties of such composites which make them technologically superior to or more cost effective than alternative materials. Since the first experimental results published decades ago, conducting polymer composites have been adapted to a variety of applications, such as electromagnetic interference shielding and electrostatic dissipation.[1] The design and understanding of a well-defined conducting structure with uniform dimensions is one of the most challenging goals of contemporary science.[2,3] Therefore, the synthesis and application of micro- and nanotubules of conducting polymers have been investigated widely in recent years.[4,5] Microtubules of conducting polymers are usually produced by the use of a template guided synthesis technique.[6–9] Much of this work has been carried out using a microporous polymeric filtration membrane as the template, and the tubules obtained are brittle and shorter than 20 μm. Furthermore, there have not been any publications concerned with the fabrication of microtubular heterojunctions of conducting polymers.

Very strong poly(*p*-phenylene) and polythiophene films (polythiophene film can be stronger than aluminium foil) can be prepared by electrochemical polymerization of the corresponding monomers in boron trifluoride–diethyl ether solution. The films are flexible and can be cut into a variety of desired structures, such as triangles, squares, circles and fibers, with a knife or a pair of scissors.[10–13] Therefore, we believe that high-quality composite microtubules of PPP/PTh can also be produced in the same medium. In this paper, we report an electrochemical approach to the fabrication of aligned microtubular heterojunctions with composite microtubules of PPP and PTh.

Experimental

Chemical pure grade thiophene was a product of Beijing University of Science and Technology (China) and was used after distillation. Analytical pure grade benzene (Beijing Yili Chemical Factory) was twice distilled before use. Boron trifluoride–diethyl ether (BFEE) was purchased from Beijing Changyang Chemical Factory. It is a colorless product and was used directly without further treatment.

Microporous alumina membranes (Anodisc 25) with a pore diameter 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.[14]

Electrochemical syntheses and investigations were performed in a one-compartment cell using a model 283 potentiostat-galvanostat (EG&G Princeton Applied Research) under computer control. The procedure for fabrication of the working electrode is as follows: first, a gold layer with a thickness of *ca.* 50 nm was evaporated onto one side of the host membrane. Then a stainless steel (AISI 304) sheet was used as a 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 in contact with the electrolyte was *ca.* 1.8 cm^2. The counter electrode was also a stainless steel sheet (1.8 cm × 6.0 cm). The distance between the working and counter electrodes was 1.5 cm. All potentials were referenced to an Ag/AgCl electrode (immersed directly in the solution). A correction of 0.069 V was needed to convert the potentials measured in BFEE originally *vs.* Ag/AgCl to potentials *vs.* the standard hydrogen electrode.[10] Two kinds of electrolytes were used successively. One was a BFEE solution containing 30 mmol L^{-1} thiophene, and the other was a BFEE solution containing 1.6 mol L^{-1} benzene. All solutions were deaerated by bubbling dry nitrogen through them and a slight nitrogen overpressure was maintained during the experiments. The aligned microtubular heterojunctions were fabricated by successive deposition of PPP and PTh into the micropores of the template. At first, poly(*p*-phenylene) microtubules were grown by direct oxidation of benzene in BFEE potentiostatically at 1.7 V (*vs* Ag/AgCl). Then a BFEE solution of thiophene replaced the initial electrolyte, and PTh tubules were grown potentiostatically at 1.3 V (*vs.* Ag/AgCl). These two steps were performed successively. The lengths of the tubules were controlled by the total charge passed through the cell. Linear sweep voltammograms of the aligned microtubular heterojunctions were recorded in air using the film of the composite microtubules without removing the aluminium template; thin gold layers were evaporated on both sides of the aligned microtubular heterojunctions before measuring the current (*I*)–voltage (*V*) curve which showed a rectification effect. Aligned composite PPP/PTh microtubules adhered to the gold layer were then

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obtained by dissolving the alumina templates with 1 M KOH for 24 hours and were then washed with distilled water repeatedly at room temperature.

The normal PPP/PTh bilayer heterojunction was fabricated by successive deposition of PPP and PTh films onto a plate electrode surface. The working electrode was a gold layer ($\sim$50 nm) coated stainless steel sheet and the counter electrode was also a stainless steel sheet (AISI 304). Other experimental conditions and procedures were the same as those used for fabrication of microtubular heterojunctions.

Raman spectra were recorded on a RM 2000 microscopic confocal Raman spectrometer (Renishaw plc, England) employing a 632.8 nm laser beam and a CCD detector with 4 cm^{-1} resolution. The spectra were recorded by using a 50 × objective lens and accumulated 3 times each for 10 s. The power was always kept very low ($\sim$0.1 mW) to avoid destruction of the sample. The samples used for the Raman study were as-formed composite films of the microtubules in which the aluminium templates were retained. The composite membrane was cut vertically into two pieces and the laser beam was focused on the newly formed cross-section. Scanning electron micrographs were taken using a KY2800 electron micrographer (Scientific Instrumental Plant of the Chinese Academy of Sciences). The transmission electron microscopy image was obtained using a Hitachi 800 electron microscope.

Results and discussion

Fig. 1A shows a scanning electron microscopy (SEM) image of a composite microtubules array after removing the aluminium template with 1 mol L^{-1} KOH. The length of the microtubules was about 40 μm, which was controlled by the total charge passed through the cell during the electropolymerization. The tubules were uniformly and firmly adhered to a thin gold layer. The microtubules are flexible and the skin of the tubules is smooth, which is largely due to the skin of the tubules being made of high-strength conducting polymers. Furthermore, the aluminium membrane template, having much higher pore densities, has much better pore uniformity than those of the widely used polycarbonate (PC) template. Microtubules as long as 60 μm could be obtained if sufficient charge is passed through the cell (about 7 C cm^{-2}). Fig. 1B and 1C are transmission electron microscopy images of the 60 μm long composite microtubules of PPP and PTh. It is clear from the images that the bottom parts of the microtubules changed into wires, and the upper parts kept their tubular morphologies.

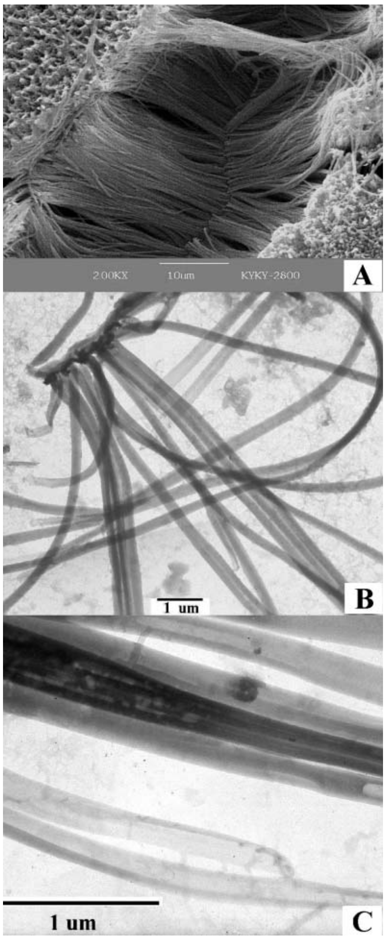

Fig. 1 A scanning electron micrograph (A) and transmission electron micrograph (B, C) of aligned PPP/PTh microtubular heterojunctions.

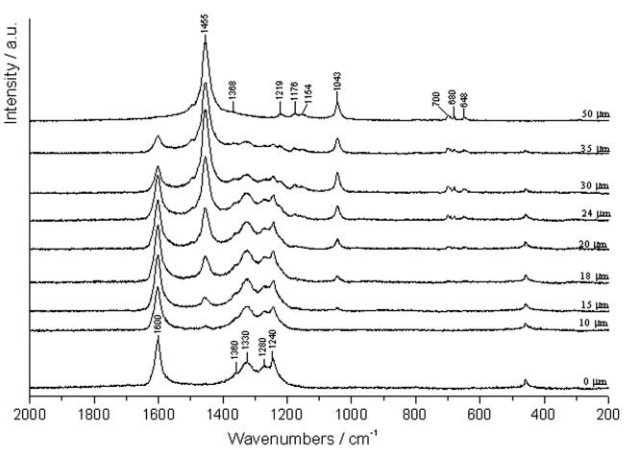

Fig. 2 Raman spectra of as-grown aligned PPP/PTh microtubular heterojunctions.

The 632.8 nm excited Raman spectra of the cross-section of an as-formed PPP/PTh composite microtubules film in which the porous alumina membrane has been retained is shown in Fig. 2. The tubules are 60 μm long and the total charge used for PPP and PTh growth was 3.5 C cm^{-2} each. A weak "fluorescence" background and high signal-to-noise (S/N) ratios were found in these spectra. We set the bottom of the composite microtubules as the start point. Raman spectra were recorded by focusing the laser spot (1 μm in diameter) at certain distances along the composite microtubules. In agreement with previous reports,[15–19] the assignments of the Raman bands of polythiophene and poly(*p*-phenylene) are listed in Table 1. Here the intensity of the 1455 cm^{-1} band, which is attributed to C=C symmetric stretching, can be regarded as a measurement of PTh content, and that of the band at *ca.* 1605 cm^{-1} as a measurement of PPP content in the skin of microtubules. The 1455 cm^{-1} band emerged in the spectra recorded at points more than 10 μm from the bottom, while the 1605 cm^{-1} band decreased gradually and finally disappeared as the laser spot moved to the top of the microtubules. The spectroscopic

Table 1 The assignment (cm^{-1}) of the bands in the Raman spectra of PPP and PTh

	PTh		PPP	
Assignment	R	O	R	O
C=C ring stretching	1455	1452	1605	1600
Quinoidic structure		1430		
C–C inter-ring stretching	1368	1362	1280	1330
C–C stretching	1219	1219	1220	1240
Kinks	1176	1176		
Kinks	1154	1154		
C–H bending	1043	1043		
Ring deformation C–S–C	700	700		
Kinks	680	680		
Kinks	648	648		

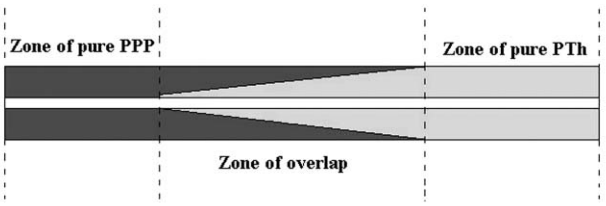

Fig. 3 Sketch of a PPP/PTh microtubular heterojunction.

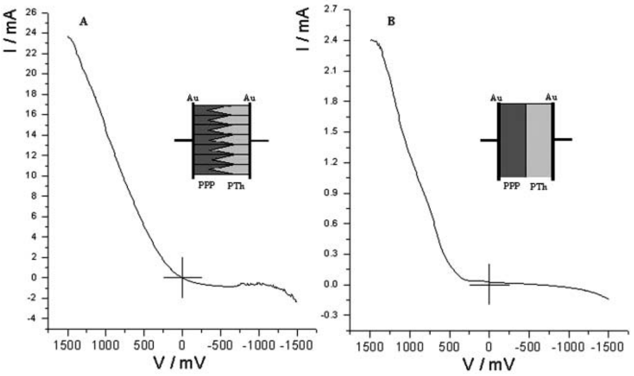

Fig. 4 Current (*I*)–voltage (*V*) of aligned PPP/PTh microtubular heterojunctions (A) and normal PPP/PTh film heterojunction (B).

phenomena described above implies that the composite microtubules could not be divided simply into a PPP part and a PTh part. As demonstrated in Fig. 3, the microtubules have three composition zones: a zone of pure PPP (about 10 μm long at the bottom), an overlap zone (has both PPP and PTh, about 35 μm long) and a zone of pure PTh (about 12 μm at the top).

Fig. 4 illustrates the current (*I*)–voltage (*V*) curves of aligned microtubular PPP/PTh heterojunctions (A) and normal PPP/PTh film heterojunctions (B). The two kinds of heterojunctions were fabricated by successive deposition of 3.5 C cm^{-2} PPP and 3.5 C cm^{-2} PTh each. It is clear from this figure that the aligned PPP/PTh microtubular heterojunctions shows a rectification effect. The peak potential of oxidation was 1.0 V for PPP and 0.4 V for PTh *vs.* Ag/AgCl in BFEE solution, respectively.[10,20] This indicates that the Fermi level of PPP (E_{PPP}) was lower than that of PTh (E_{PTh}). Therefore, carrier (e^+) flow from PPP to PTh, an increasing negative charge would build up at the PPP surface and an equal, opposite charge (positive) would also exist on the surface of the PTh.[21] As a result, an opposite electric field was produced, and at the same time, the inner electronic field, from PTh to PPP, hinders the flow of carrier (e^+) from PPP to PTh and a thermal equilibrium is produced. When a forward bias was applied at the PPP side, an external field formed, the direction of which is from PPP to PTh; the external field reduces the strength of the internal field, resulting in a decrease in the amount of space-charge. Therefore, the current increases exponentially as a forward voltage is applied and little current flows under a reverse applied bias. In comparison with the heterojunction made of bilayer films of PPP and PTh (Fig. 4B), the aligned microtubular heterojunctions have a lower conduction potential (close to 0 V) and a much higher conduction current (about 10 times at a given potential). These are possibly due to the microtubular heterojunctions having a much higher junction area and much lower resistance.

Conclusions

Aligned poly(*p*-phenylene)/polythiophene microtubular heterojunctions with tubule diameter of 200 nm can be synthesized by successive electrochemical oxidation of benzene and thiophene in boron trifluoride–diethyl ether solution using microporous aluminium membrane as template. Raman spectroscopy studies revealed that a microtubular heterojunction could be divided into three parts—a zone of pure PPP, an overlap zone and a zone of pure PTh. The *I*–*V* curve of the aligned PPP/PTh heterojunctions show a much better rectification effect than that of the normal film heterojunction.

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