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Study on electrical conductivity of single polyaniline microtube

Shanxin Xiong^a, Qi Wang^{b,*}, Yinghong Chen^b

^a Temasek Laboratories of Nanyang Technological University, 50 Nanyang Drive, Singapore 637553, Singapore

^b State Key Lab. of Polymer Materials Engineering (Sichuan University), Polymer Research Institute of Sichuan University, Chengdu 610065, China

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Abstract

The PANI microtubes with diameter of 200 nm were synthesized by the template synthesis technique. The electrical conductivity of individual PANI microtube was measured directly in the template channel using scanning probe microscope (SPM). The average conductivity of the microtube is 5.81 S/cm, which is higher than that of bulk PANI (1.75 S/cm). The higher average conductivity is due to the enhancement of electrical conductivity caused by the confined environment and ordered structure of the template channels. Moreover, most of the conductivities of the microtubes are in the range of 10^{0} S/cm magnitude, which suggests that the SPM method possesses good reproducibility and feasibility for conductivity measurement of individual microtubes.

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1. Introduction

Since the conductive polyacetylene (PA) was reported in 1977 [1], the nanostructures of conductive polymers have attracted considerable interests [2–4]. Template synthesis [5–7] and self-assembly [8] are effective methods for the preparation of conductive polymer nanostructure. The one-dimensional conductive polymer (nanotube, nanowire) exhibits enhanced electrical conductivity [7]. Hence, it is essential to study the electrical property of an individual conductive polymer nanostructure. However, the tiny size and difficulty of manipulation are two main obstacles for this study.

In recent years, various measurement methods including experimental techniques and new testing equipment have been developed and applied. Plating electrode [9], as an effective approach, was used to measure the electrical properties of individual CNT bundles or "ropes". However, the random sedimentation of nanostructure caused the manipulation and measurement to be more complicated. An in-situ testing method was designed by K. Ramanathan et al. [10] and Yun et al. [11] to study the I-V characteristics of single nanowire through the direct synthesis of conductive polymer wires by electrodeposition within channels between two electrodes on the surface of silicon wafers. Also, a manipulator-equipped scanning electron microscope [12] was applied to characterize the electrical property of the carbon nanocoils. As a powerful and unique tool, scanning tunneling microscope (STM) can be utilized to understand the surface structure and morphology at the nanometer scale. A. Hassanien et al. [13] obtained the I-V characteristic of aligned coaxial nanowires of PANI passivated carbon nanotubes with STM. The multi-tips STM technique [14] is also a utilitarian means to directly map the surface scale. SPM was successfully applied for the studies of the electrical property of PPy nanotube [2].

For all the above mentioned work, the first step is to obtain a dispersed single nanostructure for plating the electrodes or other manipulations. Unfortunately, this stage is the key process, and also a difficult one. Are there any other methods that can work without this stage? Actually, the template synthesis method can provide well-dispersed and highly ordered nanostructure array. Herein, the PANI microtubes were prepared by the template synthesis method. An extra circuit uses the tip and sample stage of SPM as positive and

^{*} Corresponding author. Tel.: +86 28 85405133; fax: +86 28 85402465. *E-mail address:* qiwang@scu.edu.cn (Q. Wang).

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Fig. 1. Schematic process for the measurement of the electrical property of PANI microtube.

negative electrodes, respectively. The electrical conductivity of individual PANI microtube was measured easily by moving the position of the SPM tip.

2. Experimental

2.1. Materials

Analytic reagent grade aniline ($C_6H_5NH_2$), ammonium peroxydisulphate ((NH_4)₂ S_2O_8 , APS) and hydrochloric acid (HCl) were employed in the experiment. Aniline was distilled under reduced pressure, and stored at low temperature prior to use. APS and HCl were used as received. Anodic Aluminum Oxide (AAO) with pore diameter of 200 nm was obtained from Whatman International Ltd.

2.2. Template synthesis of PANI microtubes

PANI microtubes were prepared through in-situ polymerization of aniline in the template channels [15]. As a contrast, the aniline was polymerized simultaneously without the template under the same condition. The morphologies of the microtubes were observed through JEOL JSM-5600LV scanning electron microscope (SEM) and JEM-100CX transmission electron microscope (TEM). The template was partially and fully removed for SEM and TEM observations, respectively.

2.3. Measurement of electrical conductivity

Four probe resistance and SPA400 SPM were used to measure the electrical conductivities of bulk PANI and PANI microtube, respectively. The schematic diagram of I-V measurement is shown in Fig. 1. Details of the experimental procedures are given as follows: Firstly, the surface of template was treated with 1% (w/w) NaOH solution to partially remove the template and expose the PANI microtubes from the template. Then, Aurum film was sputtered onto the lower surface of the template. Finally, SPM was used to test the I-V characteristics. Here, the SPM tip and Aurum film acted as positive and negative electrodes, respectively. In the entire circuit, the resistance of the Aurum film can be neglected compared to the microtube. Hence, the I-V characteristics of individual microtubes were obtained.

3. Results and discussion

3.1. Template synthesis of PANI microtubes

As expected, the nanochannels of the template confine the geometry shape of PANI during the polymerization process. The resultant material possesses similar shape and size as those of template channels. Fig. 2a shows the typical SEM image of PANI microtubes, which is the duplicate of the template channels. The diameter of the microtubes is close to the pore diameter (200 nm) while the length of the microtubes is close to the thickness ($60 \mu m$) of the template. PANI microtubes can form a uniform and ordered array. However, some microtubes are randomly distributed after the template is removed. As shown in the



Fig. 2. Morphologies of PANI microtubes. (a) SEM image; (b) TEM image.

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