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Electrical conductivity of individual polypyrrole microtube*

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Conducting microtubes (0.4–0.5μm in outer diameter) made of polypyrrole (PPy) doped with *p*-toluene sulfonic acid (PTSA) were synthesized by a self-assembly method. We report the electrical conductivity of an individual PPy microtube, on which a pair of platinum micro-leads was fabricated by focused ion beam deposition. The measured room-temperature conductivity of the individual PPy microtube was 0.29S/cm, which is comparable to that of template-synthesized PPy micro/nanotubes. The temperature dependence of conductivity of the individual microtube follows the three-dimensional variable-range hopping (3D VRH) model.

Keywords: conducting polymers, microtubes, self-assembly, conductivity, polypyrrole
PACC: 6146, 6140K, 8160J

1. Introduction

Conducting polymers such as polyacetylene, polypyrrole, and polyaniline have aroused great interest in both fundamental and applied research since the highly conducting polyacetylene was reported in 1977.[1] The common feature of conducting polymers is that the conductivity can be increased by a few orders of magnitude (10^{-10}–10^{4}S/cm) by doping.[1,2] Recently, conducting polymer nanostructures (e.g. nanotubes and nanowires) show potential applications in molecular electronics and nano-devices.[3] So far, various methods, such as template synthesis,[3−7] self-assembly,[8−10] electrospinning,[11] etc., have been widely used for the synthesis of polymer nanostructures. The template-guided synthesis proposed by Martin[4] is an effective method to synthesize micro/nanotubes and nanowires with controllable length and diameter by selecting micro/nanoporous templates.[4,6] The self-assembly method developed by Wan *et al*[8,9] is much simpler and cheaper without using an external template, and is well adapted to mass-produce polymer nanostructures. It has been proved that the essence of self-assembly is that the dopant acts as template in the process of forming micro/nanotubes.[8,9] It is noted that the size of tubes can also be controlled through changing synthesis conditions (e.g. the reaction temperature).[8]

By now, the electrical properties of compressed pellets composed of polymer nanostructures have been extensively reported.[12−17] However, there are only a few papers dedicated to the study of the electrical conductivity of individual polymer micro/nanotube, probably due to the difficulty in fabricating micro-leads onto the micro/nanotube. In general, the conductivity of individual polypyrrole (PPy) or polyaniline micro/nanotube is obtained based on the two-probe measurement of the bulk resistance across the host template after synthesis of the micro/nanotubes in this template.[3−6] Recently, Park *et al*[7] studied the electrical resistivity of template-synthesized PPy

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nanotube by using a conductive scanning probe microscope.

In this paper, the polypyrrole microtubes studied were synthesized by the self-assembly method. We have successfully fabricated a pair of platinum (Pt) micro-leads onto an individual PPy microtube using the focused ion beam technique. Here, we report the temperature dependence of electrical conductivity of the individual microtube. The room-temperature conductivity is 0.29S/cm.

2. Experimental

Pyrrole was distilled and stored under N_2 gas. The other reagents, including $FeCl_3 \cdot 6H_2O$ as an oxidant and *p*-toluene sulfonic acid (PTSA) as a dopant were used as received. PTSA doped PPy microtubes were synthesized by a self-assembly method in the presence of PTSA as the dopant.[18] In a typical synthesis procedure, appropriate ratio of pyrrole monomer and PTSA were mixed and dissolved in 10 ml of deionized water with stirring. The mixture was then cooled down to 0–5°C in an ice bath. A solution of $FeCl_3 \cdot 6H_2O$ of certain concentration was added slowly into the above mixture. After all the oxidant was added, the mixture was allowed to react for 15h in the ice bath. After filtering the mixture, the black precipitate was washed with deionized water, ethanol and ether several times, respectively, and finally dried at room temperature in a dynamic vacuum for 24h.

PPy microtubes, which were ultrasonically dispersed in ethanol, were placed on an insulating SiO_2 substrate. Then we found an individual microtube on the substrate; a pair of Pt micro-leads with 1.0μm in width and 0.5μm in thickness was fabricated by focused ion beam (FIB) deposition (Dual-Beam 235 FIB system from FEI Company, USA). The electrical resistance of the individual PPy-PTSA microtube was measured by a two-probe method using a KEITHLEY 220-programmable current source and a KEITHLEY 181-nanovoltmeter, which were auto-controlled by a computer.

3. Results and discussion

The structure of PPy-PTSA microtubes were identified by elemental analysis, infrared spectroscopy and x-ray diffraction. The morphology of microtubes was confirmed by a field-emission scanning electron microscope (SEM) and a transmission electron microscope (TEM). Figure 1 shows the typical SEM and TEM images of PPy-PTSA microtubes synthesized by the self-assembly method. It is noted that some of the microtubes are well aligned (see Fig.1 (a)). The average outer diameter of PPy microtubes is about 0.4–0.5μm and the average inner diameter is around 0.1–0.2μm. Figure 2 shows the SEM image of an individual PPy-PTSA microtube and a pair of attached Pt micro-leads with a cross section of $1.0 \times 0.5 \mu m^2$.

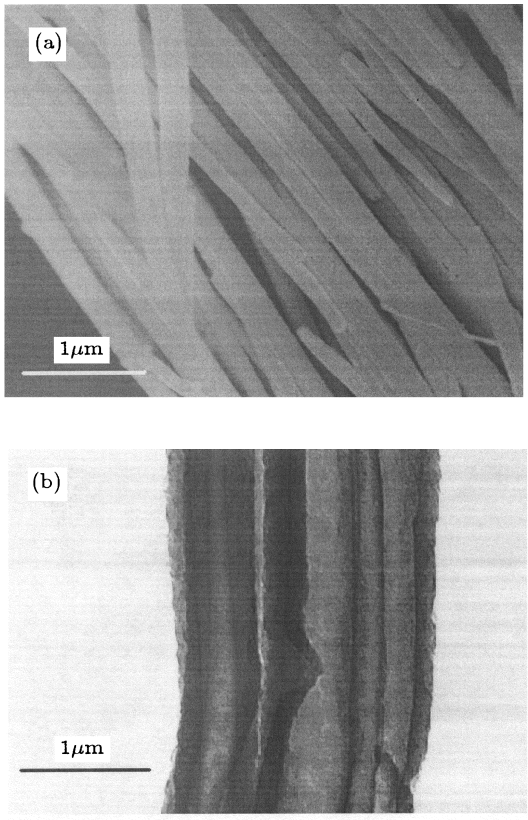


Fig.1. (a) Scanning electron microscope (SEM) and (b) transmission electron microscope (TEM) images of PPy-PTSA microtubes synthesized by self-assembly.

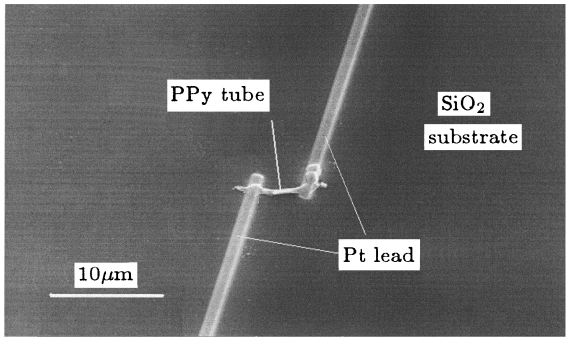


Fig.2. SEM image of an individual PPy-PTSA microtube and a pair of attached Pt micro-leads.

Figure 3(a) shows the temperature dependence of resistance of the individual PPy-PTSA microtube

measured by the two-lead technique. The room-temperature resistance is 1.6MΩ. The data represents almost the intrinsic resistance of the PPy microtube, since the resistance of the Pt micro-leads is only around 0.8kΩ which was estimated using the widely recognized resistivity of $5\times10^{-4}\Omega\cdot$cm for the focused ion beam deposited Pt lead.[19] The electrical conductivity of the PPy microtube can be obtained according to the following formula:

$$\sigma(T) = \frac{4L}{\pi(D^2 - d^2)R(T)},$$

where L=5.5μm is the length of the microtube between the two Pt micro-leads, D and d are the outer and inner diameters of the microtube, respectively, and $R(T)$ is the resistance of the measured tube. At room temperature, the conductivity of the measured individual PPy microtube is 0.29S/cm. For comparison, we briefly review the conductivity of template-synthesized PPy micro/nanotube. Park *et al*[7] reported that the conductivity of individual PPy nanotube measured by a conductive scanning probe microscope is about 0.83S/cm. Several groups[4−6] reported the conductivity based on a two-point measurement of the bulk resistance across the template after synthesis of PPy tubes within this template. In this method, the resistance of the template and the estimation of the number of tubes in the measurement area will decrease the accuracy of the results. It is found that the conductivity of the PPy micro/nanotube covers a wide range from 10^{-1} to 10^2S/cm.[4,5] For PPy microtube with 0.5μm in diameter, the room-temperature conductivity is about 10^0S/cm.[5] Recently, by using similar method, Mativetsly and Datars[6] studied the conductivity of template-synthesized PPy nanocylinders, which is about 0.1–0.6S/cm. It is obvious that the conductivity of template-synthesized PPy micro/nanostructures is comparable to that of our self-assembled PPy microtube. However, in our work, the conductivity of PPy tube was measured directly without the resistance of the template. So the result is more reliable and accurate.

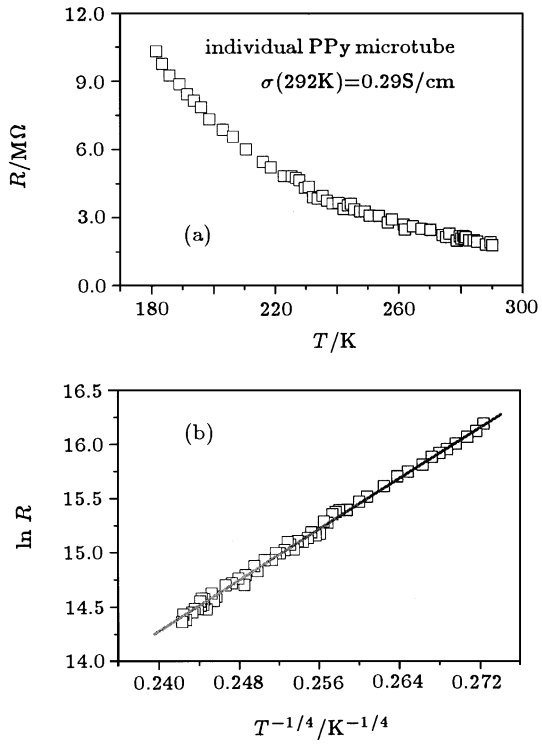


Fig.3. (a) Temperature dependence of resistance $R(T)$ of the individual PPy-PTSA microtube; (b) plotted as ln $R(T)$ versus $T^{-1/4}$.

Figure 3(a) also indicates that the temperature dependence of resistance of the individual PPy-PTSA microtube shows a semiconducting behaviour, namely, the resistance increases with the decrease of temperature. We point out that the resistance at lower temperature is not measured because the resistance is too large (R(180K)=11.3MΩ). For PPy bulk samples such as films and pressed pellets,[20,21] the temperature dependent resistivity is usually interpreted in terms of three-dimensional variable-range hopping (3D VRH) or one-dimensional (1D) VRH model:[22]

$$\rho(T) = \rho_0 \exp\,(T_0/T)^{1/(1+n)}$$

where T_0 is the characteristic Mott temperature and n=1, 2, or 3 for 1D, 2D, or 3D hopping. Figure 3(b) shows the ln $R(T)$ versus $T^{-1/4}$ plot, which indicates that the resistance data of the individual PPy-PTSA microtube follows 3D VRH model. We argue that this result is reasonable. From the view point of the electrons, the individual tube is still three dimensional because the localization length of electron of PPy (no more than 12nm[20]) is much smaller than the diameter of the microtube (∼450nm). This result confirms that 3D VRH is a more intrinsic conduction mechanism in PPy microtube, while the observed ln $R(T) \propto T^{-1/2}$ dependence for bulk samples is possibly due to the extensive disorder and inhomogeneity.[20]

4. Conclusion

In summary, by means of focused ion beam (FIB) deposition, we have measured directly the conductivity of an individual polypyrrole (PPy) microtube synthesized by self-assembly. It is interestingly found

that the room-temperature conductivity of the measured individual microtube is 0.29 S/cm, and the temperature dependence of resistance follows the three-dimensional variable-range hopping model. The results show that the FIB deposition is a reliable, practicable and effective approach to study the electrical properties of individual micro/nanostructure.

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