Synthesis of polyaniline nanotubes through UV light catalytic method

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In this study, nitrocellulose (NC) fiber blanket prepared by electrostatic spinning method has been used as a template, and copper nitrate ($\text{Cu}(\text{NO}_3)_2$) as an oxidant to synthesise polyaniline nanotubes doped with heteropolyacid ($\text{H}_4\text{SiW}_{12}\text{O}_{40}$, SiW_{12}) using UV light catalytic method. Infrared spectroscopy (IR), X-ray powder diffraction (XRD), scanning electron microscopy (SEM) and transmission electron microscopy (TEM) technologies were applied to characterize the prepared samples of polyaniline nanotubes. The results show that the external diameter of the tube is about 200 nm, and the internal diameter about 170 nm. We also give a reasonable speculation and explanation about the formation mechanism of the nanotubes.

Keywords: *UV irradiation; polyaniline; nanotubes; template; heteropolyacid*

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1. Introduction

Conducting polyaniline (PANI) has been widely investigated for thirty years due to its easy preparation, good environmental stability, low cost and unique doping mechanism. It has already become one of the focus in the conductive polymers family. In recent years, one-dimensional polyaniline nanotubes, as a new important branch of polyaniline materials, have caused great concern among scientists around the world and become a new hotspot of research. For example, Martin from United States, Greiner from Germany [1] and Wan Meixiang from China [2] have done a lot of studies on polyaniline nanotubes. Our group also used the template method to prepare polyaniline nanotube materials in the past years [3–6].

Electrospinning is a simple and common technology that has been widely studied for the use of spinning of a polymer solution. In a typical spinning process, the liquid polymer under electric field is extruded from a nozzle of a syringe, forming tiny droplets. When the electric field reaches a certain intensity, the charges gather on the surface of the droplets which allows them to overcome the

surface tension of the liquid, resulting in the formation of ejection stream from small droplets. The ejection stream is accelerated and sprayed towards a receiver. With the evaporation of the solvent, the jet length is elongated and becomes several times longer than its original length [7]. In this way continuous ultra-fine polymer fibers can be obtained. NC is a white and water-insoluble solid, and it has excellent solubility in a solution of acetone and ethylene. While in an acetone solution it also has very good adhesion ability, the mixed solution can be directly used for electrospinning. By changing the factors, such as applied voltage, the solution concentration, the distance between the receiving plate and injection port, and mixing time we can change the thickness of the fibers. The diameter of electrospun fibers generally varies between microscale to nanoscale dimensions.

Based on previous studies [8, 9], $\text{Cu}(\text{NO}_3)_2$ was used as an oxidant, SiW_{12} as a dopant and NC as a template. Polyaniline nanotubes doped with SiW_{12} were successfully synthesized under ultra-violet irradiation. We studied the relationship between the fiber diameter and the inner diameter of the nanotubes and also the formation mechanism of the nanotubes.

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2. Experiments

2.1. Reagents and instruments

Reagents

Aniline (after distillation treatment), $\text{SiW}_{12}\cdot\text{H}_2\text{O}$, $\text{Cu}(\text{NO}_3)_2$, acetone and nitrocellulose (NC), used in the experiment were of analytical grade.

Instruments and methods used for characterization

- Electrostatic high voltage device and a nozzle (self-assembly);
- UV light source (wavelength of 254 nm);
- FT-IR spectrum: Alpha-Centauri 650 spectrometer with a KBr pellet (Nicolet);
- Powder X-ray diffraction (PXRD): D/MAX-2200/PC X-ray diffractometer (Rigaku);
- Scanning electron microscopy (SEM): XL30 ESEM FEG (Philips);
- Transmission electron microscopy (TEM): JEM- 2010 (JEOL).

2.2. Preparation of nitrocellulose fiber blanket

1.0 g of nitrocellulose was dissolved in 5 mL of acetone. 1 mL of N, N-dimethylformamide (DMF) was added dropwise to the solution. The mixed solution was stirred at room temperature until its composition became homogeneous.

In our experiment, high voltage electrostatic DC device was applied at the testing voltage of 12 kV. The distance from the nozzle to the receiving plate was 22 cm. In order to ensure the fibers to be easily peeled off from the receiving plate, a 15×15 cm steel mesh with small holes was used as the receiving plate. Diagram of a system with a high voltage electrostatic device is shown in Fig. 1.

The prepared nitrocellulose solution was placed in a syringe, and the high-voltage DC device was applied for electrostatic spinning. Finally, the obtained fiber blanket was dried under vacuum for 4 h at temperature about 60 °C.

Fig. 1. Diagram of a system with a high voltage electrostatic device.

2.3. Synthesis of polyaniline nanotubes using nitrocellulose fiber as a template

0.5 g $\text{H}_4\text{SiW}_{12}\text{O}_{40}$ was dissolved in 20 mL of distilled water, the mixed solution was used as a doping acid. 0.1 g of nitrocellulose fibers were immersed in the solution under ultrasonic agitation for 30 min in an ice-water bath.

24.2 g $\text{Cu}(\text{NO}_3)_2$ was added to the acid solution, where the NC fibers were immersed. Under magnetic stirring, 0.08 mL of aniline as a monomer was slowly added drop by drop.

The whole reaction system was placed in an ice-water bath. Simultaneously, it was exposed to UV irradiation with a wavelength of 254 nm for 48 h. The fibers were removed after the reaction and washed with distilled water until pH reached a value of about 6 to 7. Then the fibers were placed in an acetone solution with ultrasonic washing for 10 min. The resulting precipitate, after centrifuging, was washed with distilled water and ethanol for several times. Finally, the product was dried under vacuum at 50 °C for 12 h.

3. Results and discussion

3.1. Infrared spectroscopy

The infrared spectrum of polyaniline nanotubes doped with heteropolyacid is shown in Fig. 2.

Fig. 2. Infrared spectrum of polyaniline nanotubes doped with heteropolyacid.

Fig. 3. X-ray powder diffraction pattern of polyaniline nanotubes doped with heteropolyacid.

In the figure, the characteristic absorption peaks of heteropolyacid have appeared in the range of 700 to 1100 cm^{-1} : $\nu_{as}(\text{M}-\text{O}_d)$: 967.15 cm^{-1} ; $\nu_{as}(\text{X}-\text{O}_a)$: 914.50 cm^{-1} ; $\nu_{as}(\text{M}-\text{O}_b-\text{M})$: 878.39 cm^{-1} ; $\nu_{as}(\text{M}-\text{O}_c-\text{M})$: 789.64 cm^{-1} , respectively. It indicates that the heteropolyacid has been doped in the polyaniline molecule [10]. The peaks at 1553 cm^{-1} and 1487 cm^{-1} represent the absorption peaks of quinonediimine and benzene diimine skeleton vibrations. The peak at 1143 cm^{-1} shows that the polyaniline is in the doped state [11]. In addition, a peak, which has occurred at 1304 cm^{-1} is attributed to the stretching vibration of C-N, related to benzene. This also indicates that the prepared product is indeed polyaniline in the doped state. The characteristic peak of nitrocellulose disappears at 1600 to 1655 cm^{-1} , which shows that the nitrocellulose fibers template has been removed from the product.

3.2. X-ray powder diffraction

X-ray powder diffraction pattern of the product is shown in Fig. 3.

An analysis of the XRD pattern shows that the product is in a semi-crystalline state. The polyaniline nanotubes prepared by using nitrocellulose fiber blanket as a template have a distinct broad peak at $2\theta = 7.4^\circ$ [4]. This indicates that the formation of the doped acid state led to the short-range ordering of anions along the polyaniline

chain [12]. The broad peak that appeared at $2\theta = 25^\circ$ shows that the structure of polyaniline nanotubes is amorphous. The weak broad peak at high angle is the peak, which is vertical to the polyaniline chain [13]. The results of above analysis indicate that the resulting polyaniline fibers are disordered in a long-range, while they are ordered in a short-range.

Fig. 4. SEM image of electro-spun NC fibers.

3.3. Scanning electron micrograph and transmission electron micrograph

A scanning electron microscope image of the nitrocellulose fibers and a diagram of an average fiber diameter distribution are shown in Fig. 4 and Fig. 5. The average diameter of the fiber is about 170 nm.

Fig. 5. The distribution diagram of fiber diameter.

Scanning electron micrograph and transmission electron micrograph of the prepared polyaniline nanotubes doped by heteropolyacid, using nitrocellulose fiber blanket as a template are shown in Fig. 6 and Fig. 7.

Fig. 6. Scanning electron micrograph of polyaniline nanotubes doped with heteropolyacid.

As can be seen from the figure, the resulting product is essentially regular in shape. The outer diameter of the tube is about 200 nm and the inner diameter is about 170 nm. Obviously, the inner diameter of the fibers depends on the thickness of NC. This is presumably due to the fact that nitrocellulose fibers have a large surface area, therefore, the heteropolyacid is mainly adsorbed on the wire around the nitrocellulose. Polymerization of aniline needs acidic environment, therefore, aniline mainly

Fig. 7. Transmission electron micrograph of polyaniline nanotubes doped with heteropolyacid.

takes fibers as a template and polymerization takes places on its surface [14].

The presented results show that the method of dissolving and removing the center template can be used to prepare polyaniline nanotubes with an intact morphology. Presumably, this method is also applicable for other soluble templates to prepare tubular polyaniline.

4. Formation mechanism

In our experiment, $\text{Cu}(\text{NO}_3)_2$ was used as an oxidizing agent and SiW_{12} as a dopant. The resulting products are not organic-inorganic composite materials, instead they are pure polyaniline. By analyzing the above experiments, we speculate that the formation mechanism is as follows: UV photons interact with the solution, and the aniline monomer is excited to its excited state. Thereby solvated electrons are produced. The solvated electrons can be transferred from aniline under excited state to Cu^{2+} , forming the aniline radical cation and Cu^+ (because the $\text{Cu}^{2+}/\text{Cu}^+$ electric potential of the electrode pair is 0.57 V, while Cu^{2+}/Cu electric potential of the electrode pair is 0.34 V, Cu^{2+} is more easily reduced to Cu^+ by a weak reducing agent). Polymerization and interactions of aniline radical cation lead to the formation of polyaniline. While Cu^+ is instable, it can be oxidized by SiW_{12} to Cu^{2+} and remains in the

solution. Therefore, we can obtain pure polyaniline, not composite materials.

5. Conclusions

Using NC fiber blanket as a template and $\text{Cu}(\text{NO}_3)_2$ as an oxidant, polyaniline nanotube doped with heteropolyacid can be prepared under UV irradiation. We have studied its morphology and characteristics by infrared spectroscopy, X-ray powder diffraction, SEM and TEM characterization. The results show that a specific form of polyaniline can be synthesized by using metal salt as an oxidant and catalysis by UV irradiation.

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