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ORIGINAL PAPER

Soft template method to synthesize polyaniline microtubes doped with methyl orange

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Abstract A soft template method for fabrication of polyaniline (PANI) microtubes is presented in this paper. It was found that methyl orange in acidic solution can be effectively self-assembled into supramolecular aggregates like flake and dendrite and they were used as soft templates to prepare PANI microtubes in the present of aniline monomer and ammonium peroxydisulfate. The morphology and chemical structure of the PANI microtubules were characterized by means of transmission electron microscopy, scanning electron microscopy, Fourier transformed infrared spectra, UV–vis absorption spectra (UV–vis) and elemental analysis. The results showed prepared PANI microtubes were in conductive emeraldine state.

Keywords Polyaniline · Microtube · Soft-template · Methyl orange

Introduction

Recent years, nano/microstructure conducting polymers have received great interest due to their promising applications in nanodevices [1], molecular electronics [2], microsensors [3], microactuators [4]. Among all the conducting polymers, polyaniline (PANI) has attracted extensive attention because of its many outstanding electrical and optical properties [5], as well as its ease of preparation, remarkable processability, excellent environmental stability and special electronic properties [6].

Nano/microstructure conducting polymer can be prepared by some methods such as template-synthesis [7], interfacial polymerization [8], electrospinning [9] and electrochemical polymerization [10]. Generally, the template synthesis, which

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involves hard template and soft template, is considered to be the most effective route to prepare nano/microstructure conducting polymers. The diameter of conducting polymer nanostructures was determined by the diameter of the pores in hard template [11]. Although inorganic aluminum oxide [12], zeolite with channels [13], and polymer membranes with porosity [14] were commonly used as the hard-templates, their preparation and the post processing for removing template was rather tedious, especially the oriented structures would be disturbed during the post-processes. The soft-template method is advantageous because an external template and post-treatment can be omitted [15].

Low-dimensional nanostructures of PANI in various shapes and forms such as nanoparticles [16], nanowires [17], nanotubes [18], nanofibers [19] and even spheres [20] have been successfully synthesized by soft-template method. However, there are few reports on the preparation of PANI microtubules by soft-template method, Micro-structure polymers have broad application prospect in mimetic enzyme, molecular reactor, smart capsule, load and release of drugs, biotic motor, through research on micro-structure of polymers can made great breakthrough in more fields. Here we report a facile approach to synthesize PANI microtubes in this article.

In past reports, researchers mostly used amphiphilic structure materials which contain alkyl hydrophobic group as dopant to prepare micro-structure polyaniline, amphiphilic structure material which contains azobenzene hydrophobic group was rarely reported. It was found that azo dye can form rodlike swarms at low azo dye concentrations in previous studies [21, 22]. Our previous experiment results showed polyaniline micro/nanotubes doped with novel dopant-acid mordant yellow GG were prepared by soft template method in the presence of ammonium persulfate (APS) as an oxidant. It was found that the [HCl]/[An] molar ratios and method of washing of the products played a key role in the formation of micro/nanotubes. Changing the molar ratio of HCl to aniline, the typical morphology of PANI could be changed from nanotubes to microtubes. By using the different method of washing of the products, there were significant changes in morphology of PANI micro/nanotubes.

In this experiment, it was found methyl orange (MO) in acidic solution could effectively self-assembled into supramolecular aggregates. By adjusting the molar ratio of MO to hydrochloric acid, supramolecular aggregates like flake and dendrite were obtained. Using them as soft templates in the polymerization, PANI microtubes were prepared with the inner diameter and outer diameter of about 800 nm and 1.5 μm respectively. The length of PANI tubes ranges from about 5–15 μm. The structural characters and the formation mechanism of PANI microtubes were also discussed.

Experimental

Materials

Aniline monomer (An) (Tianjin KRS Chem. Co.) was distilled under reduced pressure before using. APS, MO, hydrochloric acid were purchased from East China Chemical Reagents Factory and were used as received.

Characterization

The morphologies of products were investigated with a Philip XL-30E field emission scanning electron microscope (SEM) and a Philip Tecnai-20 transmission electron microscope (TEM). UV–vis spectra were measured in *N*,*N*-dimethyl formamide (DMF) on a Varian Cary-300 UV–vis spectrophotometer. Infrared spectra of PANI samples were conducted by means of a Bruker Vector-22 FT-IR spectrophotometers in the range of 4,000–400 cm^{-1}. Elemental analyses of PANI samples were performed on a Thermo Flashea-1112 elemental analyzer. For conductivity measurements, the PANI samples were pressed into a round pellet 1 cm in diameter and analyzed using a four-probe instrument by applying a constant current.

Polymerization

A typical synthesis for the microstructure of PANI was as follows: aniline (5 mmol), MO (0.3 mmol) and a content hydrochloric acid was dissolved in 150 ml de-ionized water by supersonic stirring for 1 h at room temperature. Then, 50 ml aqueous solution of APS (5 mmol) was added to the above solution and the reaction was allowed to proceed in an ice bath with magnetic stirring for 12 h. Finally, the product was filtered and washed with distilled water, methanol, and ether each for several times and dried in vacuum at 40 °C for 24 h.

Results and discussion

In the experiment, the effect of the molar ratio of MO to hydrochloric acid was studied on morphology of the resulting PANI. It was found that the morphology of PANI was irregular grains (Fig. 1a) when the molar ratio was 0.1. But the morphology of PANI turned to regular rodlike (Fig. 1b) when the ratio was 0.06. In fact, typical TEM image (Fig. 2a, b) revealed that the rods were PANI microtubes. The inner and outer diameter of PANI tubes were about 800 nm and 1.5 μm respectively, the length of PANI tubes ranged from about 5–15 μm. Interestingly, in the absence of aniline monomers and APS, a little mixture from reaction system was taken and the morphology of the mixture was found different. When the molar ratio of MO to hydrochloric acid is 0.1, the morphology of mixture is flake (Fig. 3a). The morphology of mixture is dendrite (Fig. 3b) when the molar ratio is 0.06. It suggests that MO in acidic solution can effectively self-assembled into supramolecular aggregates. The morphology of PANI could be easily controlled by adjusting the molar ratio of MO to hydrochloric acid. It seemed that the ratio is a key factor for the formation of different supramolecular aggregates.

Although MO is not a typical surfactant, MO has a built-in amphiphilic design with hydrophilic sulfonic group and hydrophobic long alkyl chain. MO in different system may exist in more than one form of supramolecular aggregates like flake and dendrite. The polymerization will proceed with the addition of APS. In addition, APS as oxidant is water-soluble, polymerization would take place at the interface of template/water [23]. So these formed supramolecular aggregates like flake and

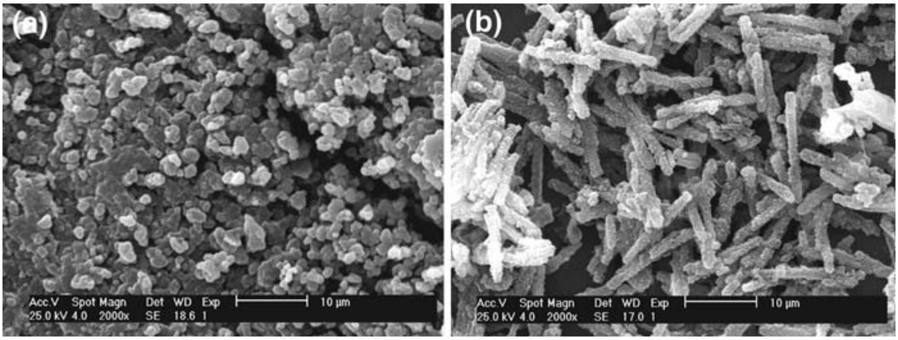

Fig. 1 Influence of the molar ratio of MO to hydrochloric acid on the morphology of PANI: **a** 0.1, **b** 0.06

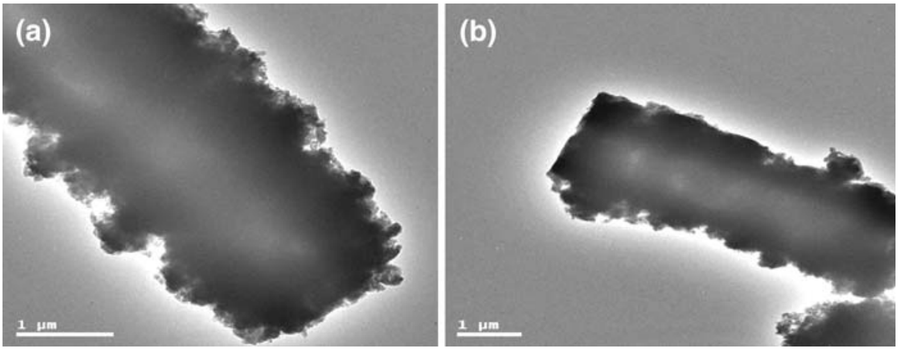

Fig. 2 TEM image of PANI microtube

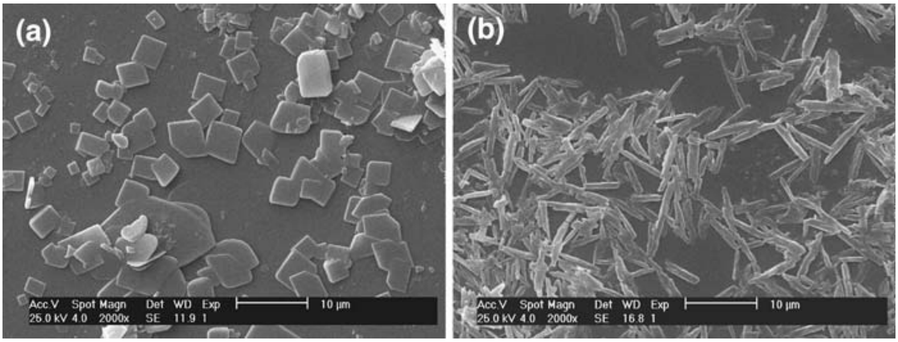

Fig. 3 Influence of the molar ratio of MO to hydrochloric acid on the morphology of supramolecular aggregates: **a** 0.1, **b** 0.06

dendrite may act as soft templates in polymerization. Finally, oxidative polymerization of aniline is confined by the supramolecular aggregates. Then PANI tubes were obtained by an elongation process [24].

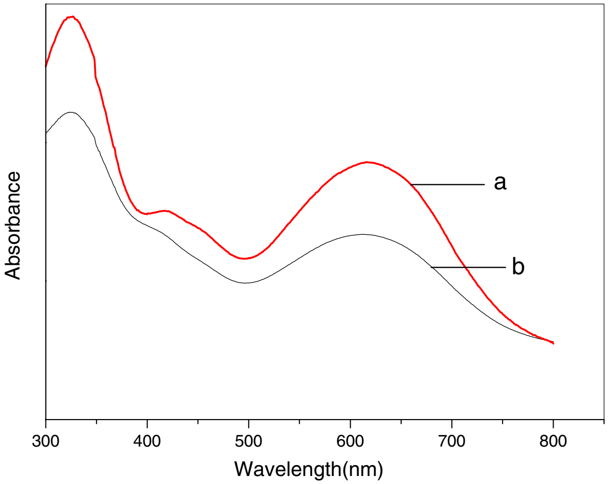

Fig. 4 UV–vis spectra of PANI with different morphologies: **a** microtubes, **b** irregular grains

Figure 4 is the UV–vis absorption spectra of PANI irregular grains and PANI microtubes. In spectra, three peaks were observed around 330, 420 and 620 nm. The peak at 330 nm can be attributed to a π–π^* benzenoid transition in the leucoemeraldine segments [25]. The broad peak at 620 nm corresponds to π–π^* quinonoid transition in the pernigraniline segments [26].The peak at 420 nm is related to the polaron band–π^* transition [27]. The polaron band transition around 420 nm is a typical absorption peak of doped PANI, this result reveals that prepared PANI is in doped state [28]. Compared to PANI irregular grains, absorption peak around 420 nm of PANI microtubes is broader and shifts to a higher wavelength which due to higher doping level of PANI microtubes.

The FTIR spectra of PANI irregular grains and PANI microtubes are shown in Fig. 5. For PANI microtubes, the peaks in the 3,450 cm^{-1} correspond to the N–H vibrations of the leucoemeraldine component [29]. The strong peaks at 1,584 and 1,495 cm^{-1} correspond to the C=C stretching modes of the quinonoid rings and benzenoid rings in the polyaniline chain, respectively [30]. The peaks at 1,251 and 1,304 cm^{-1} can be assigned to the C–N stretching mode of the polaron units [31]. And the peak at 509 cm^{-1} ascribed to the C–N–C torsion is also observed [32]. The benzene C–H bending deformation band at 1,142 cm^{-1} is characteristic of the semiquinone structure [33]. The band at 813 cm^{-1} is related to the C–H deformation, the band at 618 cm^{-1} is attributed to the benzenoid ring deformation [34]. The peaks at 1,042 and 699 cm^{-1} are relative to the S=O and S–O stretching vibration modes of the sulfonate groups attached to the aromatic rings [35]. For PANI irregular grains, similar result can be observed. But some differences between PANI microtubes and irregular grains are also observed. For PANI microtubes, the band at 1,142 cm, assigned as the doped state of PANI, is stronger than that of the PANI irregular grains. The results indicated that the doped level of PANI microtubes is higher and which were accord with the results of UV–vis spectra.

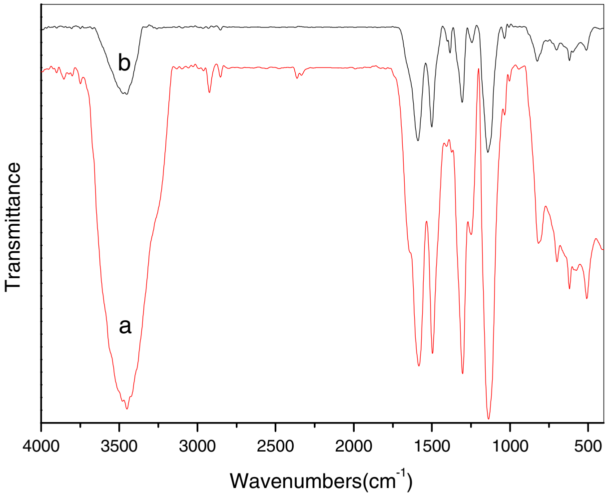

Fig. 5 FTIR spectra of PANI with different morphologies: **a** microtubes, **b** irregular grains

Table 1 Elemental analyses for PANI samples

Sample	C (wt%)	H (wt%)	N (wt%)	S (wt%)
PANI microtubes	61.29	7.80	12.23	2.99
PANI irregular grains	61.88	8.16	12.69	2.63

The results of elemental analysis for PANI samples are shown in Table 1. The S:N molar ratios of PANI microtubes and irregular grains are 0.11 and 0.09, respectively, which also indicated the doped level of PANI microtubes is higher. The result is consistent with its conductivity, UV–vis spectra and FTIR spectra. Due to the low doping level of the products, the conductivities of the as-prepared PANI are not high.

Conclusion

A facile method to synthesize PANI microtubules was reported. It was found that MO in acidic solution can form different supramolecular aggregates. By simply changing the molar ratio of MO to hydrochloric acid, supramolecular aggregates like flake and dendrite could be obtained. Two different morphologies of PANI with microtubes and grains were obtained by a polymerization process in the presence of supramolecular aggregates as soft templates via self-assembly process. The proposed method provides a novel route to design and synthesize PANI microstructures by soft template strategy, which may be applied to the synthesis of other nano/microstructures polymer.

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