Preparation of polyaniline nanostructures doped with different dicarboxylic acids through template-free method

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In this article nanoscaled polyanilines (PANI) were prepared based on template-free method in the presence of dicarboxylic acid dopants (e.g. *D*-tartaric acid, succinic acid, maleic acid and fumaric acid). The *trans-cis* isomerization of butenedioic acid played an important role in the formation of nanostructures from the plane-like to nanofibers, and the PANI doped with maleic acid (MA) had larger diameter, higher crystallinity and conductivity than PANI doped with fumaric acid (FA).

Keywords: polyaniline; nanostructures; dicarboxylic acid; *trans-cis* isomerization

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1. Introduction

Many studies have recently focused on polyaniline (PANI) nanostructures because their unique properties can be controlled by oxidation and protonation state [1], which makes them suitable for applications such as sensors, batteries, molecular electronic devices, corrosion inhibitors and separation membranes [2–4]. A variety of chemical methods have been applied to prepare one-dimensional (1D) nanostructures of PANI [5–7]. The effect of doping acid has been discussed in many reports [8–11].

In this work, dicarboxylic acids, such as *D*-tartaric acid, succinic acid, maleic acid and fumaric acid, were used as PANI dopants. Nanostructures of polyaniline (PANI) were prepared based on template-free method in the presence of dicarboxylic acids as dopants.

2. Experimental section

2.1. Reagents

Aniline monomer was distilled under reduced pressure.

Doping acids: *D*-tartaric acid (*D*-TA), succinic acid (SA), maleic acid (MA), fumaric acid (FA).

Oxidant: ammonium peroxydisulfate (APS).

All the reagents used were analytical grade, produced by Tianjin Institute of Fine Chemicals.

2.2. Synthesis of polyaniline nanostructures

The process was as follows: aniline monomer (2.5 mmol) and an appropriate amount of dicarboxylic acid were dissolved in 10 mL of deionized water to create a uniform solution under magnetic stirring in the ice-bath (0 to 4 °C) for 30 min. Then, an aqueous solution of (NH₄)₂S₂O₈ (APS, 0.54 g dissolved in 5 mL deionized water), was added to the above mixture, and the resulting solution was stirred for another 1 h. Finally, the reaction was left undisturbed at 4 °C for 24 h to produce PANI as dark-green powder.

The product was filtered and washed with deionized water and methanol several times. Finally, the product was dried in vacuum at room temperature for 24 h. A range of molar ratios of [*D*-TA]/[An] as 0.125:1, 0.25:1, 0.5:1 and 1:1 were introduced to investigate the influence of the molar ratio on the formation of the nanostructures, while keeping aniline concentration constant.

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2.3. Testing and characterization

The morphologies of the resulting PANI were measured with a JEM-200CX transmission electron microscope. Infrared spectra in the range of 400 to 4000 cm^{-1} were measured - by means of infrared spectrophotometer (AVATAR370, Nicolet) - on the PANI sample pellets made from KBr. The X-ray scattering study for the products was carried out on an X-ray diffraction instrument (D/max-2550, Rigaku Corporation). The room temperature conductivity of compressed PANI pellets was measured by a standard four-probe method using a resistivity measurement system, model RTS-9, and a probe, model S-2A.

3. Results and discussion

3.1. The microscopic morphology of polyaniline nanostructures

The morphologies of PANI nanostructures are shown in Fig. 1. When the *D*-TA/An molar ratio is 0.125, there is a coexistence of nanofibers and plate-like nanostructures; as the *D*-TA/An molar ratio changes from 0.25 to 0.5, the morphology also changes from network-like to dendritic nanostructures. When the *D*-TA/An ratio increases to 1, the branches of dendritic polyaniline are bald. Furthermore, the ratios also have an influence on the inner diameter of the resulting PANI, varying from 10 nm to 50 nm when the ratio changes from 0.25 to 0.5. However, the hollow structures could not be obtained at the molar ratios of 0.125 and 1. The molar ratio of 0.25 has been selected for further investigation of the effect of the dopant structure on the morphology and diameter of the resulting nanostructures.

Fig. 2 clearly shows that network-like and dendritic nanostructures could not be produced by doping with different dicarboxylic acids under the same synthesis condition. The morphology of the samples doped with SA represents nanofibers, but the images (c) and (d) in Fig. 2 indicate that the *trans-cis* isomerization of butenedioic acid plays an important role in the formation of nanostructures. PANI nanostructures doped with maleic acid self-assembled into the plane-like, while such occur-

Fig. 1. TEM images of PANI nanostructures synthesized at *D*-TA/An ratios of (a) 1:8, (b) 1:4, (c) 1:2, and (d) 1.

Fig. 2. TEM images of PANI nanostructures doped with different dicarboxylic acids: (a) PANI-D-TA, (b) PANI-SA, (c) PANI-MA, (d) PANI-FA. Synthesis conditions: [dopant]/[An] = 0.25; temperature from 0 to 4 °C.

rence could not be found in the product doped with fumaric acid. It is found that the diameter of PANI-MA is about 2 times larger than that of PANI-FA.

3.2. Crystallographic analysis of polyaniline nanostructures

Fig. 3 presents the XRD patterns of PANI doped with different dicarboxylic acids. The characteristic peaks at $2\theta = 20.1^\circ$ and 25.8° are observed in

Fig. 3. XRD patterns of PANI nanostructures doped with different dicarboxylic acids: (a) PANI-D-TA, (b) PANI-SA, (c) PANI-MA, and (d) PANI-FA. Synthesis conditions: [dopant]/[An] = 0.25; temperature from 0 to 4 °C.

Fig. 4. FT-IR spectra of PANI nanostructures doped with different dicarboxylic acids. Synthesis conditions: [dopant]/[An] = 0.25; temperature from 0 to 4 °C.

all PANI nanostructures, and are attributed to the periodicity perpendicular and parallel to the polymer chain, respectively [9].

3.3. Chemical structure of polyaniline

Typical FT-IR spectra of PANI-D-TA, PANI-SA, PANI-MA and PANI-FA are shown in Fig. 4. Approximately, the C=C stretching vibrations of the quinoid and benzenoid rings appear at 1574 and 1495 cm⁻¹, respectively. The C-N stretching mode

Fig. 5. The effect of the molar ratio of dopant to aniline on the conductivity of the PANI-MA nanostructures.

is at 1298 cm⁻¹, and the N=Q=N absorption peaks (Q represents the quinoid ring) at 1137 cm⁻¹ are observed.

3.4. Electrical properties of nanoscaled polyaniline

The change in [D-TA]/[An] ratio causes the room-temperature conductivity changing from 0.125 to 1, as shown in Fig. 5. The results indicate that polyaniline network has the highest conductivity. There are two possible reasons to explain this phenomenon: (1) it may be easier to form conductive network than with the others ones; (2) it may be contributed to its higher crystallinity.

4. Conclusions

In summary, the *D*-tartaric acid, succinic acid, maleic acid and fumaric acid doped PANI nanofibers with average diameter of 148 to 285 nm, could be prepared by template-free method. The effects of dicarboxylic acids with various structures and the molar ratios of dopant to aniline on conductivity, crystallinity, morphology were discussed. The network nanostructures showed the highest conductivity of 5.88 10⁻² S/cm. This may be contributed to their high crystallinity and preference to form a conductive network. FT-IR spectra indicated that the characteristic peaks shifted from

high wavenumber to low wavenumber if compared with others. This suggests that the electrons in the PANI-D-TA are less localized. Furthermore, the trans-cis isomerization of butenedioic acid plays an important role in the transformation of nanostructures from the plane-like to nanofibers.

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