

Preparation and characterization of polyaniline nanostructures doped with oxalic acid

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In this article, Polyaniline(PANI) nanostructure was prepared at room temperature using oxalic acid(OA) as dopant and ammonium persulphate (APS) as oxidant by self-assembly method. The structure and property of polyaniline nanostructures were characterized by SEM, TEM, IR and X-ray diffraction(XRD) methods. These measurements prove the successful synthesis of polyaniline nanostructures. It is found that the molar ratio of OA to An(aniline monomer) affects the morphology of the PANI product.

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Conducting-polymer nanostructures have recently become the object of numerous investigations because of the potentially interesting electrical properties conferred to polymer morphology produced at the nano-scale level. They have an attractive prospect and potential applications in the field of microelectronics and medicine, because of their unique structures and excellent electrical, magnetic, optical properties. There are a variety of methods to synthesis polymer nanostructures. The template method [1] is usually an effective way to synthesis nanotubes and nanowires polymer. But we need to remove the template after the reaction and its post-processing is more complex. Wan Meixiang's group [2-5] has reported the preparation of polyaniline nanotubes through self-assembly method in their studies. Through the interaction between aniline monomer and hydrophilic groups from dopant, they can form tubular micelles, which play the role of the template during the formation of the nanotube structure. From the change of reaction conditions we can control the size of the PANI nanotubes (fiber or spherical).

Currently a lot of doping agents are available to prepare polyaniline through self-assembly method [6-10]. However, oxalic acid as dopant to prepare polyaniline nanostructures is still rarely reported in the literature. In this article we use oxalic acid as dopant and ammonium persulfate (APS) as oxidant, via self-assembly method to prepare polyaniline nanostructures. The product of polyaniline nanostructures have good electrical conductivity and we are trying to work out the best condition for the synthesis of polyaniline nanostructures. By means of infrared spectroscopy, ultraviolet spectroscopy, X-ray diffraction, electron microscopy and other testing methods, we measure the structure and performance of the product.

1. Experimental section

1.1 Reagent

Aniline (vacuum distillation), oxalic acid, ammonium persulfate, methanol, ether.

All the agents used are of analytical grade level.

1.2 Synthesis of polyaniline nanostructures

Polyaniline is prepared through self-assembly process, using oxalic acid as dopant and ammonium persulfate (APS) as oxidant. The experimental process is as follows:

Weigh certain amount of oxalic acid and dissolved it in 10 mL of deionized water. Then add 0.13 mL of aniline and put the mixture at room temperature for 30min to make aniline and acid fully react to form the corresponding salt. And then weigh 0.29g of ammonium persulfate and dissolve it in 5mL deionized water.

Control the molar ratio of [OA] / [AN] as 1, 1/2, 1/4 and 1/8. Then the above two solutions can be mixed at room temperature for 12 h. Filter the reactants, and then use distilled water, methanol, ether to wash the product several times. Finally make the product drying in vacuum at room temperature for 24 h.

1.3 Testing and characterization

XRD:Germany D8 Tools X-ray Diffraction is used to analysis the phase structure of the sample;

IR: Perkin Elme Fourier Infrared Spectroscopy is used to test the infrared absorption spectrum of the sample;

SEM/TEM: JEOL-JSM6700F Scanning and Transmission Electron Microscopy is used for the morphology characterization for the samples;

Conductivity Test: The Four-Probe method is used to test the current and voltage of the samples. According to the formula we can calculate the conductivity of the sample.

2. Results and discussion

2.1 The microscopic morphology of polyaniline

SEM images in Fig. 1 show the morphology of the product at different molar ratio of $[OA] / [AN]$, and the concentration of $[AN]$ is 0.13 M.

When $[OA]/[AN]$ is 1, the product aggregates into flocculent particles as Fig. 1 shows and conductivity is $1.11 \times 10^{-2} \text{ S/cm}$. Oxalic acid dopant anion contains two carbonyl group, and its ability to provide proton is very strong. It makes the hydrogen ion easy to inject into the polyaniline molecular chain. The degree of charge delocalization in the molecular chain increases, and the conductivity in chain also increases. Therefore polyaniline prepared by oxalic acid as the dopant has high conductivity.

When $[OA]/[AN]$ is 1/2, the product shows as interwoven mesh structure. The formation of the rod is short with diameter about 180nm. Fig. 2a transmission electron microscopy shows it is fibrous rods and the length of tubes is about $2 \mu\text{m}$. The conductivity is $1.7 \times 10^{-3} \text{ S/cm}$. Compared to the floc accumulation structure, the conductivity of the rod-like structure decreases.

When $[OA]/[AN]$ is 1/4, it forms mesh nanofibers with diameter about 170nm. The conductivity is $2.4 \times 10^{-4} \text{ S/cm}$.

When $[OA]/[AN]$ is 1/8, it still shows as interwoven mesh structure. Fig. 2b transmission electron microscopy indicates that the polyaniline shows the tubular structure. The diameter of the tube is about 160nm with conductivity $2.1 \times 10^{-4} \text{ S/cm}$.

From the electron microscope photograph we can see, when the ratio of $[OA] / [AN]$ ranges from 1/8 to 1/2, it can form nanofiber structure. Compared with the floc structure, electrical conductivity of the fibrous is not very high. This may be due to the fibrous interwoven mesh structure. The structure leads to the limited movement of carriers, which can produce conductive effect in the chain structure. As the doping concentration decreases, the doping level also decreases. This may result in lower conductivity.

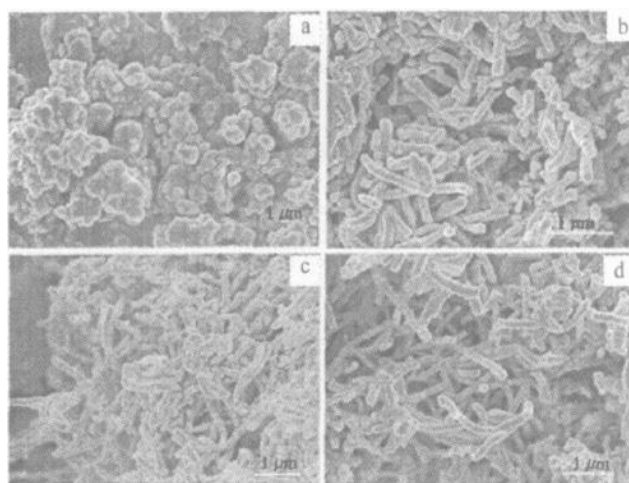


Fig. 1. Electron micrograph for different molar ratio of polyaniline nanostructures Molar ratio of $[OA] / [AN]$: (a) 1; (b) 1/2; (c) 1/4; (d) 1/8.

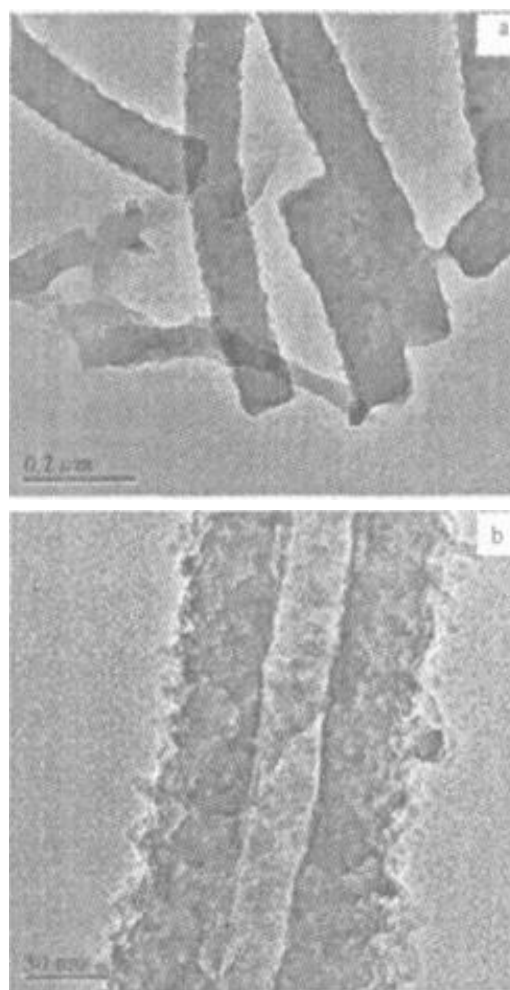


Fig. 2. Transmission electron micrographs of polyaniline Molar ratio of $[OA] / [AN]$: (a) 1/2; (b) 1/8.

2.2 UV and IR spectra of polyaniline

Fig. 3 shows the UV spectra of the doped polyaniline synthesis by oxalic acid when using N-methyl pyrrolidone as the solvent. Two peaks can be seen from the UV spectra figure, respectively at 320nm and 620nm. The peak at 320 nm is related to the π - π^* transition of benzene ring [11], while the peak at 620nm is related to the characteristic peaks of the quinone ring structure [12]. It can be seen from the UV spectra that oxalic acid has been well doped into the main chain of polyaniline.

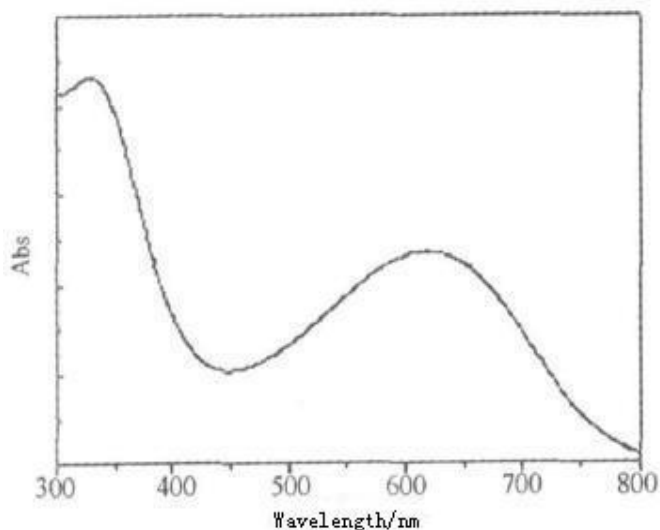


Fig. 3. UV spectra of polyaniline nanostructure.

Fig. 4 shows the infrared absorption spectra of self-assembled polyaniline nanostructures. The peak at 1577 cm^{-1} attributes to the absorption vibration peak of $\text{C}=\text{C}$ in quinone ring and at 1489 cm^{-1} attributes to the absorption vibration peak of $\text{C}=\text{C}$ in benzene ring. While peak at 1295 cm^{-1} is related to the stretching vibration peak of $\text{C}-\text{N}$ in quinone ring and 1141 cm^{-1} belongs to the vibration peak of quinone ring mode. The 801 cm^{-1} peak attributes to the plane bending vibration peak of $\text{C}-\text{H}$ in disubstituted benzene [13]. These above are characteristic peaks of polyaniline. The peak at 1141 cm^{-1} is known as the peak with electronic state [14]. It is a sign of the level of conductivity of polyaniline. It can be seen from the peak that polyaniline doped by oxalic acid has a strong peak with electronic state. 1242 cm^{-1} peak attributes to the absorb vibration of carboxyl in dopant. This further illustrates that the oxalic acid has doped well into the polyaniline chain.

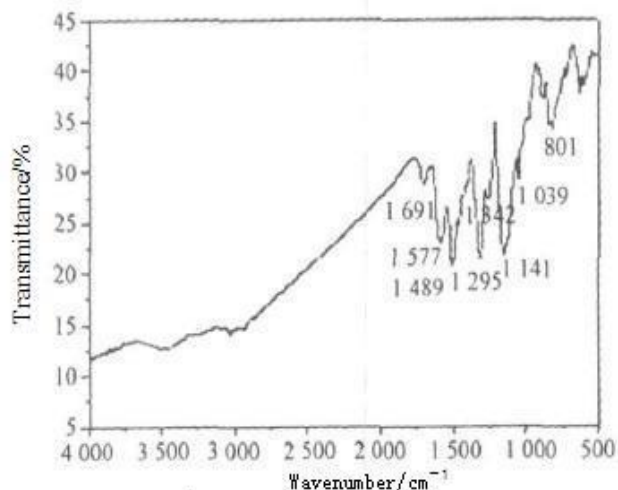


Fig. 4. IR spectra of polyaniline nanostructure.

2.3 X-ray diffraction analysis of polyaniline

Fig. 5 shows the X-ray Diffraction peaks of polyaniline nanostructure doped by oxalic acid. Characteristic diffraction peaks of polyaniline in the spectra are not as sharp as crystal. This is because polyaniline as a polymer can only be in a short-range order. From the figure can be seen when $2\theta = 6.46^\circ, 18.44^\circ$ and 25.7° there appears three strong low-angle diffraction peaks. Among these peak belts, peak at 6.46° is caused due to the periodic structure between the doping agent and N atoms close to the polymer main chain. The two peaks at 18.44° and 25.7° attribute to the periodic vertical and parallel structure in the polymer main chain [15-16]. They are consistent with diffraction peaks of polyaniline doped with other acids.

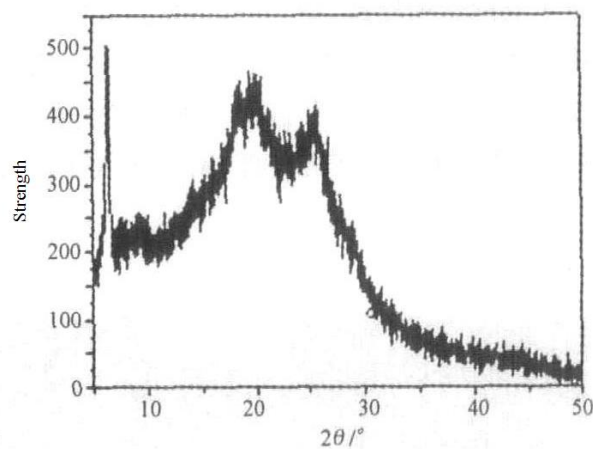


Fig. 5. X-ray diffraction pattern of polyaniline nanostructures.

3. Conclusions

In this paper, it is the first time to use dicarboxylic acids(oxalic acid) as dopant and ammonium persulfate as the oxidant to synthesis polyaniline nanostructures through self-assembly method. The study analyzes how the molar ratio of oxalic acid with aniline affects the morphology and properties of polymers. The results show that molar ratio of acid with aniline is influential to the product morphology and electrical conductivity. With the lower molar ratio, the diameter and conductivity of nanostructure is reduced accordingly. According to control the proper molar ratio, we can obtain polyaniline nanostructures with good electrical conductivity.

References

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