



Soluble polyaniline nanofibers prepared via surfactant-free emulsion polymerization



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ABSTRACT

Polyaniline nanofibers were successfully prepared using fumaric acid as the dopant and ammonium peroxydisulfate as the oxidant via surfactant-free emulsion polymerization. The influence of the polymerization parameters such as the oxidant–aniline molar ratio, the oxidant concentration, the molar ratio of fumaric acid and aniline and the fumaric acid concentration on the yield and conductivity of polyaniline was investigated on the basis of the orthogonal experimental method. The morphology, crystallinity, chemical structure and thermal stability of fumaric acid-doped polyaniline prepared under the optimal polymerization condition and the undoped polyaniline were characterized. The results demonstrated that fumaric acid-doped polyaniline has the morphology of nanofibers with a dense array of nodules, an excellent solubility in organic solvents, higher crystallinity, partially doping state and good thermal stability. But the undoped polyaniline formed granular particle agglomerations in a nearly amorphous state upon dedoping.

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1. Introduction

Conducting polymers are of interest due to their attractive features such as particularly room-temperature sensing property [1] as well as the wide range of controllable conductivity [2]. Among various conductive polymers, polyaniline (PANI) has received most interest because of its facile synthesis, good environmental stability, ease of conductivity control by changing the oxidation and protonation states, and the low cost of the monomer [3]. Particularly, one-dimensional nanostructured PANI combines the advantages of organic conductors with low-dimensional systems and thus creates interesting physicochemical properties [4]. Compared to the bulk PANI materials, the PANI nanofibers enhance the water processibility, improve the sensitivity and time response and also have unique advantages in other fields, including electric devices and flash welding [5]. Therefore, the PANI nanofibers have potential applications such as chemical and biological sensors, surface modified electrodes, biocompatible materials, artificial muscles, and anti-corrosion coatings [6].

PANI nanofibers with excellent performance have been fabricated by various methods and used for different applications.

For instance, Yin et al. [7] prepared the nano-fibrous PANI with 200 nm diameter and several micrometer lengths by rapid mixing polymerization and it exhibits larger electro-rheological effect and higher shear modulus when used as a new electro-rheological fluid. Du et al. [1] fabricated nanofibers with diameters of 50–100 nm and lengths varying from 500 nm to several micrometers by dilute polymerization method and found that their high sensitivity and fast response to ammonia gas are attributed to the large surface-to-volume ratio and interconnected network structures. By interfacial polymerization using hydrochloric acid (HCl) and camphor sulfonic acid (CSA) as dopants, Banerjee et al. [8] found that the PANI nanofibers possesses an enhanced antioxidant and haemolysis prevention activity as compared to the bulk PANI. Li et al. [9] synthesized high quality PANI nanofibers by a rapid mixing polymerization of aniline using ammonium peroxydisulfate (APS)/Fe²⁺ redox initiator as the oxidant without any hard or soft templates. And the influence of the concentrations of aniline, dopant and redox initiator and reaction time on the morphologies of the PANI nanostructures has been investigated for elucidating the formation of polyaniline nanofibers.

All in all, the approaches to the PANI nanofiber preparation consist of chemical oxidation method, electrochemical polymerization [10] and electrospinning [11] and mechanical stretching as well [12]. The chemical oxidation can be subdivided into “hard [13] and soft” template method [14] and template-free ways. Although the template method is considered as an effective way to preparing

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PANI nanofibers, the complicated post-processing [15] to remove template may destroy the PANI. Many template-free means adopted include nanofiber seeding polymerization [16], oligomer-assisted polymerization [17], dilute solution polymerization [18], interfacial polymerization [19], rapid mixing polymerization [20], radiolytic synthesis [21], sonochemical synthesis [22], photolithographic synthesis [23] and UV-irradiation of an aqueous precursor solution [24] together with the microwave-assisted synthesis [25]. All the above mentioned methods require a specific condition, except the rapid mixing polymerization, in which a relatively low aniline concentration is employed and may be an obstacle to prepare PANI nanofibers on a large scale.

Herein we adopt the surfactant-free emulsion polymerization method to prepare the PANI nanofibers, which has rarely been reported as a facile method to prepare the PANI nanofibers with a high yield, conductivity and solubility. And it can avoid the post-process of the template or surfactant. Compared with the conventional emulsion polymerization, surfactant-free emulsion polymerization is suitable for generating uniform, well-distributed nano- or microparticles without contaminating surfactants [26,27]. As functional protonic acid, fumaric acid can improve the solubility and conductivity of the PANI, because it makes the intramolecular and intermolecular conformation of the PANI more favorable for the charge delocalization on the molecular chain [28]. Using ammonium peroxydisulfate ((NH₄)₂S₂O₈) as the oxidant and fumaric acid as the dopant, PANI was successfully fabricated via surfactant-free emulsion polymerization under different polymerization conditions. The influence of the polymerization parameters on the PANI productivity and conductivity was investigated by the orthogonal experimental method. And the optimal synthesis condition was finally obtained based on the analysis of the comprehensive index. On this occasion, the fumaric acid-doped PANI with a nanofibers microstructure has the highest yield and conductivity, an excellent solubility in organic solvents. The characterization of the doped PANI was compared to the undoped one.

2. Experimental

2.1. Materials

(NH₄)₂S₂O₈ (analytical reagent) was obtained from Tianda Chemical Reagent Factory. Fumaric acid (analytical reagent) was purchased from Guoyao Group Chemical Reagent Co., Ltd. Aniline was obtained from Tianjin Kermel Chemical Reagent Co., Ltd.

2.2. Experimental procedure

2.2.1. Preparation of fumaric acid doped PANI

Firstly, (NH₄)₂S₂O₈ was dissolved in deionized water. Fumaric acid was then added to the deionized water and stirred for 30 min. 4 mL aniline, which was distilled twice in reduced pressure, was added to the acid emulsion and stirred for 30 min. Then (NH₄)₂S₂O₈ solution was dropwise introduced to the emulsion containing aniline and acid at a rate of 0.5 drop per second. And the polymerization reaction was carried on by mechanical stirring. All the operation was conducted at the room temperature. Subsequently, PANI doped by fumaric acid was filtrated using a core funnel, washed with deionized water until the filtrate was colorless and finally dried at 60 °C in a vacuum baking oven for 24 h. A series of 16 experiments were performed according to the orthogonal experiment designed in Table 1 by altering the molar ratio of (NH₄)₂S₂O₈ and aniline (A), the molar concentration of (NH₄)₂S₂O₈ (B), the molar ratio of fumaric acid and aniline (C), the molar concentration of itaconic acid (D) and the polymerization time (E). Based on the analysis result of the orthogonal experiments, fumaric acid-doped PANI under the optimal condition was prepared.

Table 1

The orthogonal experiment design of synthesizing fumaric acid-doped PANI.

Level	A	B (mol/L)	C	D (mol/L)	E (h)
1	0.5	0.25	0.25	0.25	6
2	1	0.5	0.5	0.5	13
3	1.5	0.75	0.75	0.75	20
4	2	1	1	1	27

2.2.2. Preparation of the undoped PANI

Ground fumaric acid-doped PANI prepared under the optimal condition was introduced into 20 mL aqueous ammonia with a concentration of 1 mol/L, oscillated by ultrasonics for 1 h, then filtered and washed with the deionized water until the filtrate was clear and colorless. The undoped PANI was obtained after being dried at 60 °C in the vacuum baking oven for 24 h.

2.3. Characterization

2.3.1. Yield calculation

The PANI yield was calculated by the formula:

$$y = \frac{m_2}{m_1} \times 100\% \quad (1)$$

where y is the yield, m_1 is the weight of aniline monomer and m_2 is the weight of fumaric acid doped PANI.

2.3.2. Conductivity measurement

0.25 g fumaric acid-doped PANI was ground, filtered by a sieve and then pressed into a disc with a diameter of 13 mm in a pressure of 15 MPa for 5 min by a powder pressing machine. The disc was tightly placed between two copper slices and then connected with an SD2002/3 digital ohmmeter to measure the resistance. The conductivity was calculated by

$$\sigma = \frac{L}{RS} \quad (2)$$

where σ is the conductivity (S/cm), L is the thickness of the PANI disc (cm), R is the value of resistance (Ω), S is the area of the PANI disc (cm²).

2.3.3. Solubility measurement

1 g fumaric acid-doped PANI prepared under the optimal condition was added to 10 mL N-methyl pyrrolidone (NMP) and oscillated by ultrasonics for 0.5 h at room temperature. The undissolved substance was separated by centrifugation, washed by water and weighed after being dried at 60 °C in the vacuum baking oven for 24 h to calculate the quality of the dissolved PANI. The solubility was recorded as the quality of PANI dissolved in 100 mL solvent with a unit of g/100 mL.

2.3.4. SEM

The morphology of the undoped PANI and fumaric acid-doped PANI prepared under the optimal condition was examined by cold field emission scanning electron microscope (Hitachi SU8020) after gold spraying.

2.3.5. XRD

The ground and filtered undoped PANI and the fumaric acid-doped PANI prepared in the optimal condition were placed in the sample cell. X-ray diffraction (XRD) experiments were carried out on Rigaku Dmax 2500 X-ray diffractometer (Japan Science Analysis Instrument Factory) in the range of 2–40°.

2.3.6. Infrared spectrum measurement

The undoped PANI and the fumaric acid-doped PANI prepared under the optimal condition were respectively ground with KBr

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