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Novel route to polyaniline nanofibers from miniemulsion polymerization

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Abstract A new synthesis approach for polyaniline (PANI) nanofibers with a yield of 95% was developed by using miniemulsion polymerization method. The nanofibers of 40 nm in diameter and 300 nm in length obtained had self-assembled to form a continuous conducting network, which induced a high conductivity of 1.23 S/cm. By investigating the morphologies and chemical structures of the PANI nanofiber by TEM, SEM, XRD, and FT-IR, a possible formation mechanism was proposed.

Introduction

Polyaniline (PANI) is one of the most prominent conducting polymers due to its facile synthesis, environmental stability, and reversibly tunable redox characteristics that allow the control of electrical and optical properties [1]. However, in order to exploit the fundamental properties of PANI further, more attentions should be paid to its processability since PANI does not melt and only presents very low solubility [2]. The preparation of PANI nanocomposites has proved to be an effective way for improving the processability of the intractable PANI [3]. Moreover, compared with granuled PANI synthesized by conventional chemical methods, nano-structured PANI, especially PANI nanofiber [4–6], exhibits superior chemical sensing and unique photothermal effect, which will bring potential applications in sensors and electronic devices. Typical strategies towards nano-PANIs comprise "hard and soft" template [7], water/oil interfacial polymerization [8], rapid-mixing method [9], and dilute polymerization technique [10]. Recently, how to improve the relatively low synthesis yield and increase the conductivity of PANI have been the great challenges [11], which determine whether the industrial applications can be realized. So that, a new route that soluble nano-structured PANI can be simply fabricated with high product yield and high conductivity is thirsty to be explored.

In recent years, miniemulsion polymerization has been found to be particularly attractive to obtain nanocomposite particles [12, 13]. In miniemulsion polymerization, the particle nucleation occurs primarily within the submicrometer monomer droplets and it is just an in-situ polymerization process [14]. On the other hand, the emulsifier needed to stabilize the miniemulsion is fewer compared with the conventional emulsion or microemulsion, although better system stability can be achieved [15]. To our knowledge, the unusual behavior of miniemulsion has not been applied to the preparation of soluble PANI nanofiber in literature. Whether the advantages of miniemulsion polymerization can be transferred to aniline system and obtain well-dispersed conductive PANI nanofiber with a high product yield is an interesting subject.

In this work, miniemulsion polymerization method had been utilized to fabricate PANI nanofibers. The morphologies of the reaction products were characterized by scanning electron microscope (SEM) and transmission electron microscopy (TEM), and their structural features had been demonstrated by X-ray diffraction (XRD) and

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FTIR spectroscopy. Based on the experimental results, the formation mechanism of nanofiber network was discussed.

Experimental

Materials

Aniline (Shanghai Chemical Reagents Co.) was distilled and stored in refrigerator before use. Hexadecane (HD) was bought from Aldrich and used as received. Sodium dodecyl sulfate (SDS), hydrochloric acid (HCl), ammonium persulfate (APS), ethanol, ethyl glycol, *N*,*N*-dimethyl formamide (DMF), and dimethyl sulfoxide (DMSO) were all bought from Shanghai Chemical Reagents Co. and used as received.

Synthesis of PANI nanofibers

In a typical procedure, an oil phase composed 5 g aniline and 0.1 g hexdecane was mixed with the aqueous phase containing 0.1 g SDS and 45 g water. The mixture was stirred for 15 min and then ultrasonicated for 10 min at 0 °C to form a stable miniemulsion system. Subsequently, 10 mL aqueous HCl with a concentration of 1 mol/L was added to the prepared miniemulsion, and then a solution of APS (aniline:APS = 1:1) in distilled water was added at once. After 6 h, the deep green reaction mixture were filtered and washed thoroughly, first with water and then with acetone. The whole experiment was conducted at room temperature.

Analytical methods

The product yield was determined by the gravimetric method. FTIR spectra were recorded on a NicoletMAGNA-IR 750 spectrometer using a KBr pellet. UV–vis spectra were recorded between 300 and 700 nm on a CARY-5E spectrophotometer (VARIAN) by dispersing the PANI powder in DMF by ultrasonication for 20 min. Transmission electron microscopy (TEM) analysis was performed with a Jeol 100CX II operating at 200 kV. The diluted samples were mounted on the copper grids and left to dry. FESEM images were obtained on a JEOL JSM-6700 field-emission scanning electron microanalyzer. Powder XRD patterns of as-synthesized samples were recorded with a PW1700 X-ray diffractometer. The dried powder of PANI was pressed into round pellet with a diameter of 2.5 cm and thickness of 1.5 cm, then its electrical conductivities were measured using a RTS-9 four-point probes resistivity measurement system (Four Probes Technology Co., China) in dry air at ambient temperature.

Results and discussion

TEM and SEM images of PANI nanofiber are given in Fig. 1. It can be concluded that the diameters of PANI nanofiber are about 30 nm and a continuous nanofiber network has been formed. As characterized by FT-IR spectra and shown in Fig. 2, the chemical structures of these PANI nanofibers are identical to the emeraldine salt form of PANI [16]. The main peaks are in good agreement with previously reported results [17]. The weak absorptions at 3054 cm^{-1} are attributed to the N–H stretching vibration. The major peaks at 1560 and 1480 cm^{-1} are ascribed to the stretching of the N–Q–N and N–B–N unit in the polymer chain, whereas Q and B represents the quinoide structure and the benzene ring, respectively. The band at 1120 cm^{-1} is associated with high electrical conductivity and a high degree of electron delocalization as reported in literature [15]. The peaks at 806 cm^{-1} can be assigned to the out-of-plane vibration in the 1,4-disubstituted benzene ring, respectively. The peaks at 760, 742, and 726 cm^{-1} are attributed to wagging vibrations of the five C–H groups of end phenyls in the PANI chains in nanometer-scale PANI samples, which indicates that PANI consist of a large number of terminating polymer chains. The UV–vis

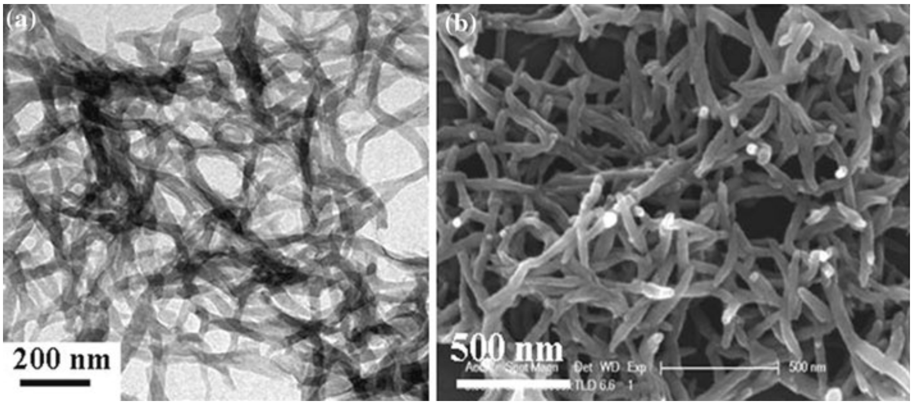

Fig. 1 TEM (**a**) and SEM (**b**) images of PANI nanofibers

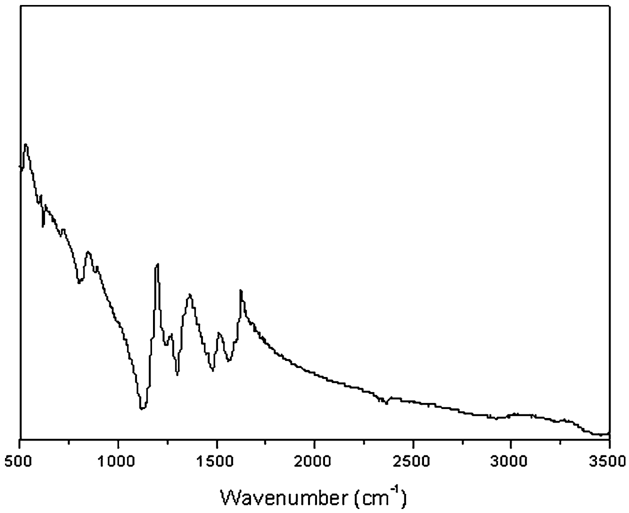

Fig. 2 FT-IR spectra of PANI nanofibers

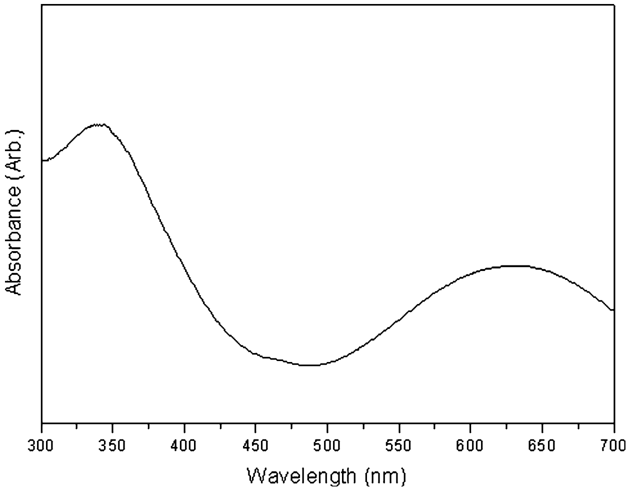

Fig. 3 UV–vis spectra of PANI nanofibers

absorption of PANI dispersed in DMF solvent (Fig. 3) shows two peaks at 344 nm and 632 nm, which are due to the π–π* (benzenoid) and n–π* (quinoid) transitions of the emeraldine salt of PANI, respectively [18, 19].

Figure 4 shows the XRD pattern of doped PANI nanofibers. In agreement with the reported results about conventional PANI powders or films [16], the diffraction pattern consists of three sharp peaks at $2\theta = 15.1$, 20.4, and 25.5, respectively. The peak centered at 15.1 is ascribed to periodicity parallel to the polymer chain and the peak centered at 25.5 is attributed to the periodicity perpendicular to the polymer chain.

During the chemical oxidative polymerization, it was reported that PANI nanofibers "naturally" form in solution via homogeneous nucleation at the initial stage of the polymerization, and these initial nanofibers elongate to nanofibers, if heterogeneous nucleation is suppressed during the polymerization [7, 11]. Therefore, the purpose of various methods for preparation of PANI nanofibers is, essentially, to suppress secondary growth. The purpose of this experiment is just taking advantage of in-situ miniemulsion polymerization method to suppress the overgrowth of PANI nanofiber. On one hand, miniemulsion polymerization facilitates the generation of particles with smaller size due to the ultrasonication homogenization effect [20, 21]. In this system, thinner nanofibers are obtained at the beginning of reaction, which means that much more increased nucleation sites compared with other conventional reactions are available at the interface. Therefore, the initiator molecules added are depleted quickly during the formation of nanofibers, disabling further polymerization leading to overgrowth. On the other hand, the costablizer HD can generate osmotic pressure and suppress the transfer of monomer between different reaction sites [12, 13]. As a result, aniline monomers nucleate independently leading to uniform PANI nanofibers. In addition, the concentration of emulsifier in miniemulsion system is relatively low compared with that of conventional emulsion or microemulsion polymerizations, which ensures that there is no redundant emulsifier to stabilize the aniline monomer dissolved or diffused in aqueous phase to polymerize. That is to say, the byproduct of spherical or granular PANI particles is avoided to a great extent, which leads to the uniform morphology and high yield of PANI nanofibers. In order to prove this expectation, an emulsion polymerization is performed, whose recipe is similar to that of our miniemulsion that the oil phase composed of 5 g aniline was mixed with the aqueous phase containing 0.25 g SDS and 45 g water. The mixture was stirred for 15 min. Subsequently, 10 mL aqueous HCl with a concentration of 1 mol/L was added to the prepared miniemulsion,

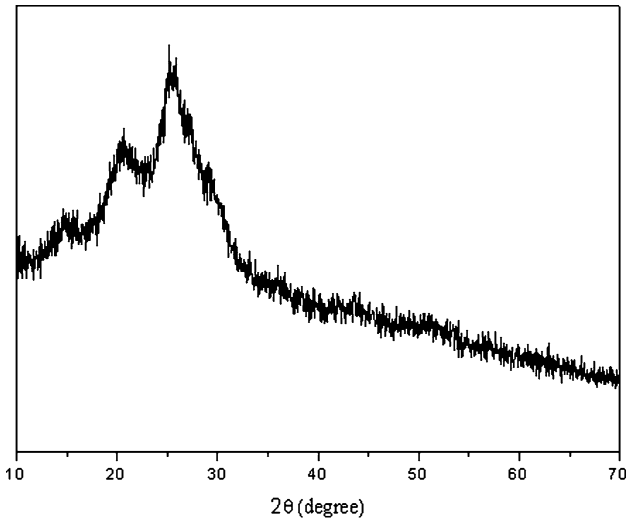

Fig. 4 XRD spectra of PANI nanofibers

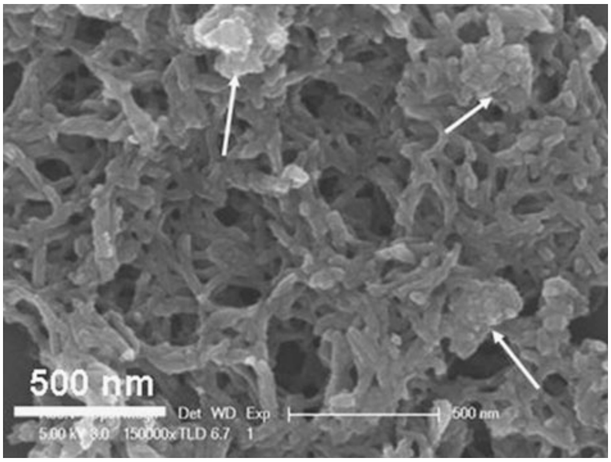

Fig. 5 TEM image of PANI obtained from emulsion polymerization, the *white arrows* instructs the spherical PANI particles which results from secondary nucleation

and then a solution of ammonium APS (aniline:APS = 1:1) in distilled water was added at once. After 6 h, the deep green reaction mixture were filtered and washed thoroughly, first with water and then with acetone. The whole experiment was conducted at room temperature.

As shown in Fig. 5, there appears many spherical PANI particles, owing to that the concentration of emulsifier is relatively high and the residual emulsifier besides stabilizing aniline chain structure leading to spherical micelle in aqueous phase, which allow the secondary nucleation of aniline and results in irregularly shaped PANI particles and granular agglomerates.

Based on the above discussions, the formation mechanism of uniform PANI nanofibers in this system can be concluded as follows. Amphiphilic aniline exists in forms of anilinium salt micelle and aniline monomer droplet at the initial state of polymerization. When water-soluble initiator APS has been introduced, the polymerization of aniline should proceed at the anilinium micelle/water and aniline monomer droplet/water interface. During the polymerization, the rigid chain structure of aniline and the π–π interaction between chains facilitate the nanofibers micelles merge and elongate at the chain direction, leading to high-yield PANI nanofibers, which self-assemble to the final network morphology. The conductivity measurements demonstrate the above discussions that well-conducted network has been built and a higher conductivity of 1.23 S/cm is exhibited by the samples.

The dispersibility of PANI nanofibers in common solvents has been improved. PANI nanofibers are stably dispersed in not only strong polar solvents such as DMF (0.08 g/20 mL) and DMSO (0.075 g/20 mL), but also weak polar solvents such as water (0.013 g/20 mL), ethanol (0.01 g/20 mL), and ethyl glycol (0.024 g/20 mL), bringing about their enhanced processability and broad application field.

Conclusion

In summary, we have demonstrated that stable, pure aqueous PANI colloids can be prepared by a simple, novel, cost-effective and environmentally benign miniemulsion polymerization strategy with a high yield of 95%. The formation of continuous network ensures a good conductivity of 1.23 S/cm. This method has the following advantages: (i) use of aqueous media, (ii) ease of operation, (iii) high yield and (iv) ability to increase the solubility of product in water and other solvent. In addition to enhancing the conventional applications of conducting polymers in chemical sensing, actuators, lightweight battery electrodes and anticorrosion coatings, the remarkable processability as well as ease of synthesis of PANI nanofibers make these nanostructures promising for use as a new class of functional building blocks for fabricating nano-scale electronic devices. Moreover, these well-dispersed nanofibers are also good sources or templates for fabricating other functional nanostructures and composites.

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