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Rapid polymerization initiated by redox initiator for the synthesis of polyaniline nanofibers

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ABSTRACT

High quality polyaniline nanofibers have been synthesized by a rapid polymerization of aniline using ammonium peroxydisulfate (APS)/Fe^{2+} redox initiator as the oxidant without any hard or soft templates. The addition of Fe^{2+} in conventional polymerization system plays an important role in changing the bulk morphologies of polyaniline from irregular particle agglomerates to nanofibers. Open-circuit potential measurements indicate that the rate of polymerization of aniline with the aid of Fe^{2+} ions has a substantial increase. The influences of synthetic parameters, such as the concentrations of aniline, dopant, and redox initiator, and reaction time, on the sizes and morphologies of polyaniline nanostructures have been investigated for elucidating the formation of polyaniline nanofibers. Fourier transform infrared spectrum, UV–vis spectrum, and cyclic voltammograms reveal that the molecular structures and electrochemical properties of polyaniline nanofibers do not differ significantly from that of conventional polyaniline.

1. Introduction

Conducting polymers have been widely investigated because of their fascinating electrical and optical properties derived from their conjugated π-electron system. Among them, polyaniline is unique due to its easy synthesis, remarkable environmental stability, and simple and reversible acid doping/base dedoping properties, which possesses many potential applications including sensors, anticorrosion coating, electromagnetic shielding, and transparent flexible electrodes [1,2]. It can be synthesized easily through either chemical polymerization or electrochemical polymerization. However, conventional bulk chemical synthesis of polyaniline including aniline, an oxidant and a strong acid dopant produces a large amount of irregular particle agglomerates and a small amount of nanofibers [3,4].

In recent years, one-dimensional (1D) polyaniline nanostructures, such as nanorods, nanowires, nanofibers, nanotubes, and nanobelts, have received intensive interest because they possess the advantages of both low-dimensional system and organic conductors and have potential applications in polymeric conducting molecular wires [5], superhydrophobic and superhydrophilic devices [6], chemical sensors [7,8], actuators [9], and biosensors [10]. Several different routes have been developed to synthesize 1D polyaniline nanostructures with or without the aid of templates. Hard templates such as zeolites [5] and porous alumina [11], and soft templates such as surfactants and bulk dopant acids [12–16], can be used to confine the growth of polyaniline chain to prepare polyaniline nanofibers or nanotubes. As reported previously, nanofibers appear to be the intrinsic morphology of polyaniline even in conventional synthesis of polyaniline, and the hard or soft templates seems to be unnecessary for the formation of 1D polyaniline nanostructures [17,18]. Some new technologies without any hard or soft templates, such as interfacial polymerization [3,19], oligomer-assisted polymerization [20], rapidly-mixed reaction [21], seeding polymerization [22], falling pH polymerization [23–29], and dilute polymerization [30], have been exploited as promising synthetic method for 1D polyaniline nanostructures. Of these methods, suppressing secondary growth mechanism in low pH solution and self-assembly mechanism in high pH solution have been proposed. The synthetic conditions, such as concentration of monomers, pH values, mechanical agitation, types of oxidants and dopants, temperature, and reaction medium, have profound influences on the sizes, morphologies, and molecular structures of 1D polyaniline nanostructures. Recently, Kaner et al. [31] and Manohar et al. [32] have reported that the introduction of aniline dimer and other structurally related additives can accelerate the rate of polymerization of aniline, which changes the bulk morphology of polyaniline from irregular particle agglomerates to nanofibers. In the chemical synthesis of polyaniline, although ammonium peroxydisulfate (APS) is the most widely used oxidant, other oxidants, such as chloroaurate acid [33,34], ferric chloride [35], vanadium oxide [4,36], and the co-use of APS and sodium hypochlorite [37], have been employed for the oxidative polymerization of aniline. In traditional radical chain polymerization, redox initiators involving direct

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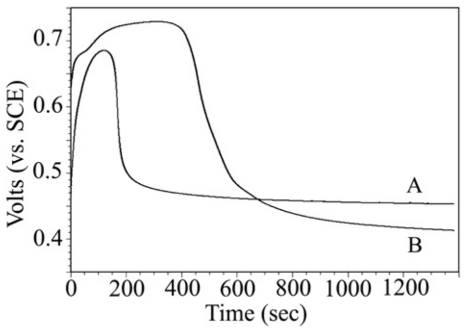

Fig. 1. Potential-time profile of aniline polymerization in aqueous 0.1 M HCl with (A) or without (B) Fe^{2+} ions. Conditions: [aniline] = 0.05 M, [aniline]/[APS] = 4: 1, [APS]/[Fe^{2+}] = 3: 2, and [HCl] = 0.1 M.

electron transfer between reductant and oxidant, can produce radicals at reasonable rates to initiate radical vinyl polymerization at low temperature due to their low activation energy as compared with that for thermal initiation [38], which inspires us to find a new oxidant for rapid polymerization of aniline. Herein, we report a facile rapid polymerization route to the synthesis of high quality polyaniline nanofibers initiated by APS/Fe^{2+} redox initiator. The APS/Fe^{2+} redox initiator plays an important role in the bulk naofibrillar morphologies of polyaniline.

2. Experimental

2.1. Synthesis of polyaniline nanofibers

In a typical synthesis, aniline (0.19 g) and $FeSO_4 \cdot 7H_2O$ (0.09 g) were dissolved in 20 mL of 0.1 M hydrogen chloride (HCl) solution with magnetic stirring to form a transparent aqueous solution. A fresh solution of APS (0.12 g) in 20 mL of 0.1 M HCl solution was rapidly transferred to the above solution containing aniline and $FeSO_4$. Upon the addition of APS, a series color change is observed with the naked eye: yellow, blue, and dark green. The polymerization reaction was carried out for 6 h at room temperature without any disturbance. The dark green precipitate was filtered off, washed with deionized water and ethanol several times, and dried at room temperature for 24 h.

2.2. Characterization

The morphologies and sizes of polyaniline samples were determined by field-emission scanning electron microscopy (FE-SEM, JSM 6700F) and transmission electron microscopy (TEM, JEM 2000EX). Samples for SEM were deposited onto Si wafer substrates and sputtered with a thin layer of Pd. Sample dispersed in deionized water are transferred to copper grids for TEM observation. Electrochemical properties of polyaniline were obtained on CHI660C electrochemical workstation. To monitor the polymerization of aniline, open-circuit potentials of the reaction solutions were measured as a function of time on a single-component two-electrode cell: Pt/reaction solution/reference electrode. A saturated calomel electrode (SCE) is used as the reference electrode. The cyclic voltammograms of polyaniline sample were determined in 0.1 M HCl aqueous solution with a scan rate of 0.05 V/s. The molecular structures of polyaniline sample were measured by Fourier transform infrared (FTIR, Nicolet Magna IR–750 spectrophotometer) spectroscopy and UV–vis spectroscopy (Cary 500 UV–vis–NIR spectrophotometer). The conductivity of the resulting products obtained using APS and APS/Fe^{2+} redox initiator is measured by the four point technique using a Jandel four point probe head. The samples are firstly compressed to 100 μm thick films and then measure the resistance.

3. Results and discussion

When APS is added into the solution containing aniline and $FeSO_4$, APS can react with Fe^{2+} ions instantaneously to produce sulfate radical anions because Fe^{2+} ions have a lower oxidation than aniline. The classical chemical formulais expressed as follows: $S_2O_8^{2-} + Fe^{2+} \rightarrow SO_4^{2-} + SO_4^{-\bullet} + Fe^{3+}$ [38], which can be demonstrated by an intermediate yellow solution upon the addition of APS. The polymerization of aniline is initiated by sulfate radical anion (Eox = 2.6 V) immediately rather than APS (Eox = 2.01 V), as evidenced by the immediate color change from a yellow solution to a blue solution, which is characteristic of the formation of polyaniline in its pernigraniline oxidation state. Open circuit potential measurements are used to monitor the polymerization of aniline with and without the addition of Fe^{2+} ions (Fig. 1). The potential–time profiles reveal that the polymerization reaction proceeds by three distinct stages: an induction period, the formation of the pernigraniline oxidation state, and the reduction of pernigraniline to the emeraldine oxidation state. The duration of the induction period and the formation of the pernigraniline oxidation state of the polymerization reactions with or without Fe^{2+} ions are about 150 s (Fig. 1A) and 400 s (Fig. 1B), respectively, indicating that a much faster polymerization of aniline happens with the aid of Fe^{2+} ions [31,32,39].

Fig. 2 shows typical SEM and TEM images of the as-synthesized polyaniline nanofibers. SEM images in Fig. 2A and Fig. S1 reveals that the dark green precipitate is composed of a large quantity of high quality polyaniline nanofibers. It is clear that these polyaniline

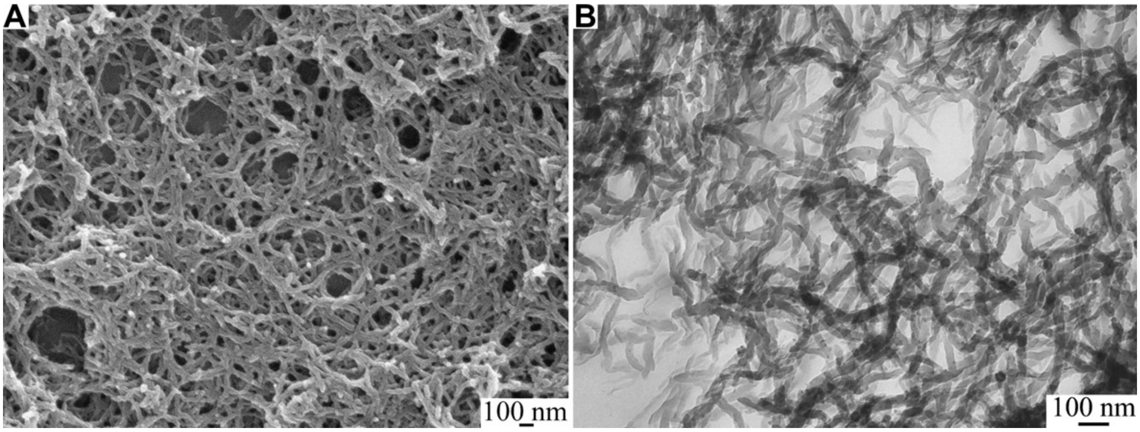

Fig. 2. SEM (A) and TEM(B) images of the as-synthesized polyaniline nanofibers. Synthetic conditions: [aniline] = 0.05 M, [aniline]/[APS] = 4: 1, [APS]/[Fe^{2+}] = 3: 2, [HCl] = 0.1 M, and 6 h.

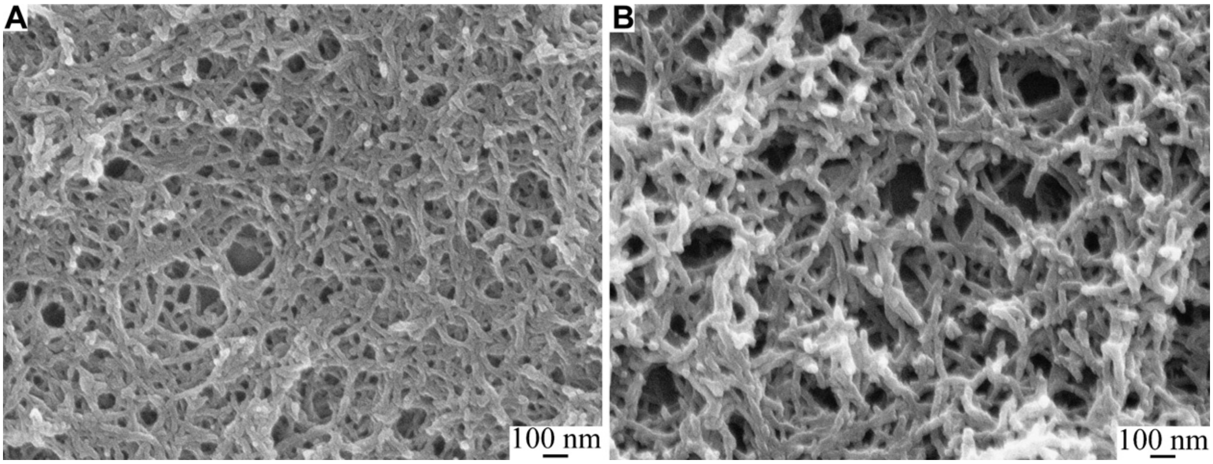

Fig. 3. SEM images of polyaniline nanofibers. (A) [aniline] = 0.05 M, 7 min; (B) [aniline] = 0.025 M, 6 h. Synthetic conditions: [aniline]/[APS] = 4: 1, [APS]/[Fe^{2+}] = 3: 2, and [HCl] = 0.1 M.

nanofibers with smooth surfaces have diameters in the range of 15–30 nm and are interconnected into network structures, which can be demonstrated by TEM observation (Fig. 2B).

To investigate the importance of redox initiator, synthesis of polyaniline by use of APS or co-use of APS and $FeCl_3$ was carried out, respectively. As shown in Fig. S2A and B, the polyaniline samples consist of a portion of nanofibers, and coral-like and granular agglomerates. In comparison with Fig. 2, secondary growth of polyaniline leads to the broad diameter distribution of nanofibers, indicating that APS/Fe^{2+} complex used as redox initiator plays an important role in suppressing the secondary growth to form high quality polyaniline nanofibers.

The influences of synthetic parameters, such as reaction time, concentrations of aniline, dopant, and redox initiator, on the sizes

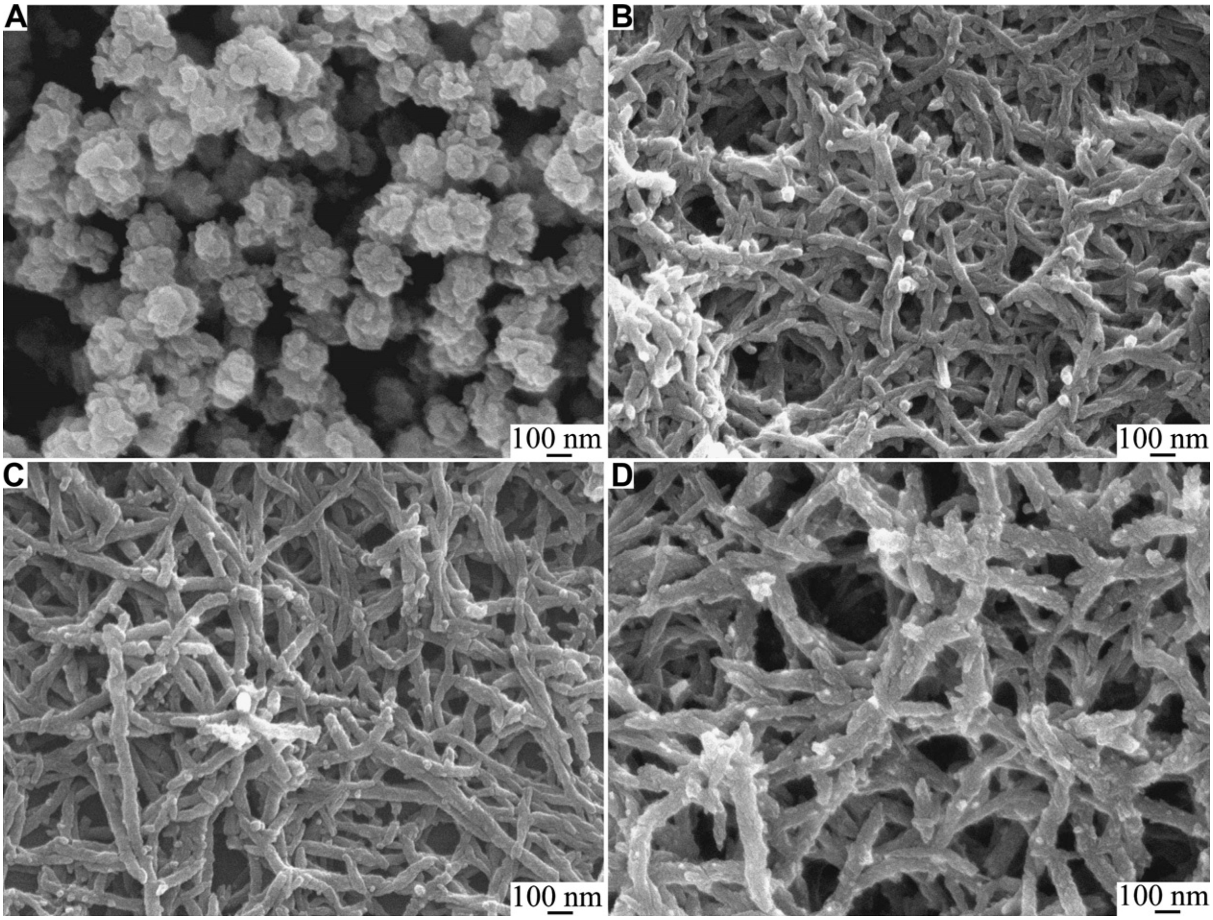

Fig. 4. SEM images of polyaniline nanofibers synthesized with different concentrations of HCl. (A) 0.01 M; (B) 0.2 M; (C) 0.5 M; (D) 1 M. Synthetic conditions: [aniline] = 0.05 M, [aniline]/[APS] = 4: 1, [APS]/[Fe^{2+}] = 3: 2, and 6 h.

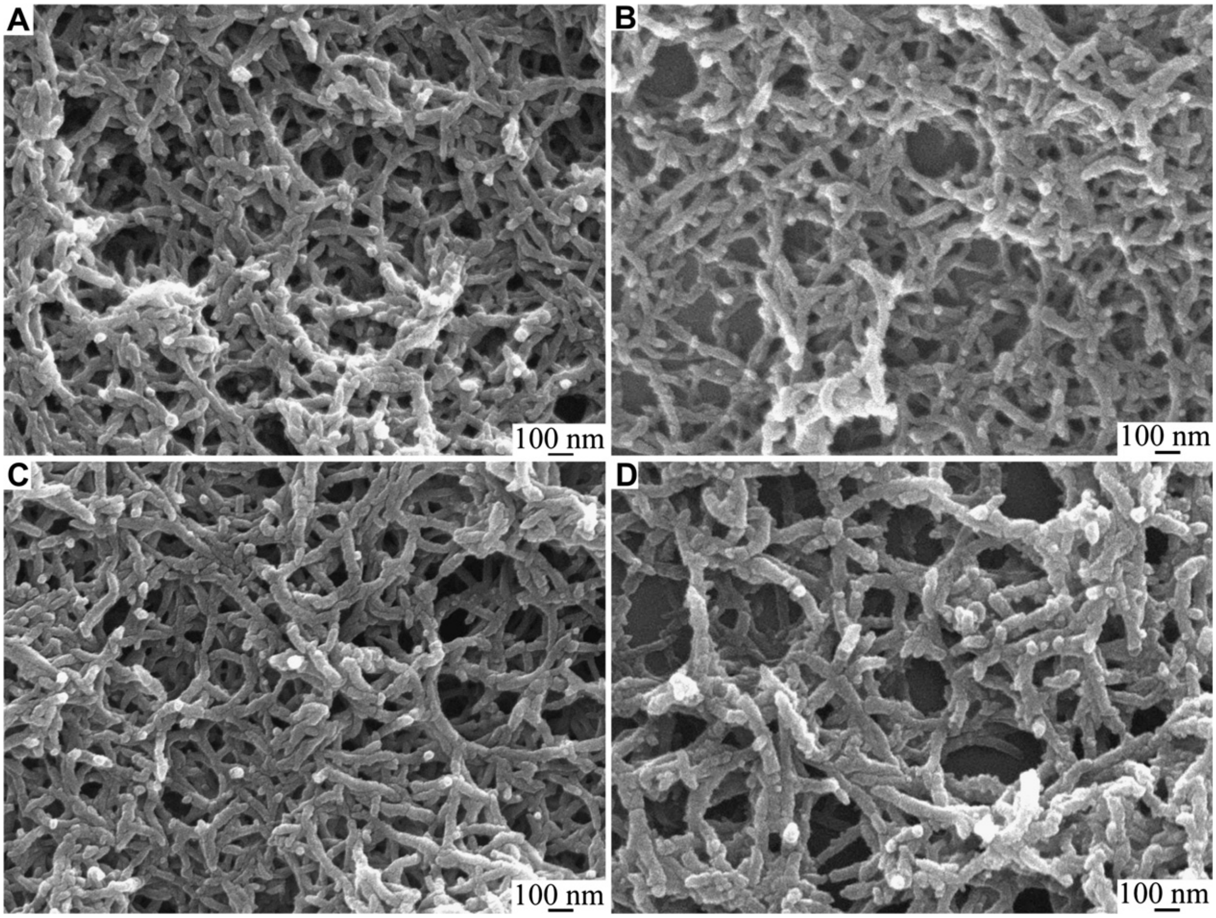

Fig. 5. SEM images of polyaniline nanofibers synthesized under different conditions. (A) [aniline]/[APS] = 4: 1, [APS]/[Fe^{2+}] = 10: 1; (B) [aniline]/[APS] = 4: 1, [APS]/[Fe^{2+}] = 3: 1; (C) [aniline]/[APS] = 3: 1, [APS]/[Fe^{2+}] = 3: 2; (D) [aniline]/[APS] = 2: 1, [APS]/[Fe^{2+}] = 3: 2. Other conditions: [aniline] = 0.05 M, [HCl] = 0.1 M, and 6 h.

and morphologies of polyaniline nanostructures have been investigated for elucidating the formation mechanism of polyaniline nanofibers. According to the open-circuit potential measurements, the rate of polymerization of aniline with the aid of Fe^{2+} ions is much faster than that without the aid of Fe^{2+} ions. After the reaction is performed for 7 min, as shown in Fig. 3A, polyaniline nanofibers with diameters of 10–25 nm and rough surfaces are obtained, revealing that polyaniline nanofibers are formed in a short time. As the concentration of aniline is decreased to 0.025 M (Fig. 3B), the diameters of polyaniline nanofibers are similar to that in Fig. 2, indicating that the concentration of aniline has no obvious influence on the diameters of polyaniline nanofibers. However, the concentration of HCl is important for adjusting the sizes and morphologies of polyaniline nanostructures as shown in Fig. 4 and Tab. S1. As the concentration of HCl is 0.01 M, no polyaniline nanofibers are found, and only granular aggregates with sizes of 100–200 nm are formed in the product (Fig. 4A and Fig. S3A). As the concentration of HCl is increased to 0.2 M (Fig. 4B and Fig. S3B), 0.5 M (Fig. 4C and Fig. S3C), and 1 M (Fig. 4D and Fig. S3D), the diameters of polyaniline nanofibers are in the range of 25–40 nm, 30–55 nm, and 50–90 nm, respectively. This indicates that the diameters of polyaniline nanofibers can be controlled directly by the concentration of the dopants. In addition, Fig. S1 and S3 reveal that the length of polyaniline nanofibers increases from 0.5 to 3 μm to 2–7 μm with the concentration of HCl increased from 0.1 M to 1 M. Interestingly, as the concentration of HCl is lower than 0.2 M, the surfaces of polyaniline nanofibers are very smooth (Figs. 2 and 4B), however, increasing the concentration of HCl (>0.5 M) results into small white spots on the surfaces of nanofibers (Fig. 4C and D), which may serve as surface active sites for heterogeneous nucleation [30].

The composition of redox initiator and the molar ratio of aniline to redox initiator have also important influences on the sizes and morphologies of polyaniline nanofibers as shown in Fig. 5 and Tab. S1. When the molar ratio of aniline to APS is kept to 4: 1 and the molar ratios of APS to Fe^{2+} are 10: 1 (Fig. 5A and Fig. S4A), and 3: 1 (Fig. 5B and Fig. S4B), the diameters of polyaniline nanofibers are 15–45 nm, and 15–40 nm, respectively, which is a litter larger than that in Fig. 2. However, when the molar ratio of APS to Fe^{2+} is kept to 3: 2, the molar ratios of aniline to APS are adjusted to 3: 1 (Fig. 5C and Fig. S4C), and 2: 1 (Fig. 5D and Fig. S4D), the diameters of polyaniline nanofibers are 25–50 nm, and 40–70 nm, respectively. It is clear that some nanoparticles grow on the surfaces of polyaniline nanofibers, indicating the increase of the concentration of APS can induce the heterogeneous nucleation on the surfaces of polyaniline nanofibers to form nanoparticles.

The formation process of polyaniline nanofibers is free of any templates and surfactants. As reported previously, polyaniline nanofibers can be formed under homogeneous nucleation conditions owing to the chemical oxidative polymerization process itself and the linear nature of polyaniline molecular chains [3]. Open-circuit potential measurements (Fig. 1) demonstrate that the rate of polymerization of aniline using redox initiator has a substantial increase compared with that without the aid of Fe^{2+} ions, indicating that sulfate radical anion with a standard redox potential of 2.6 V is used as a substantial oxidant for the polymerization of aniline.

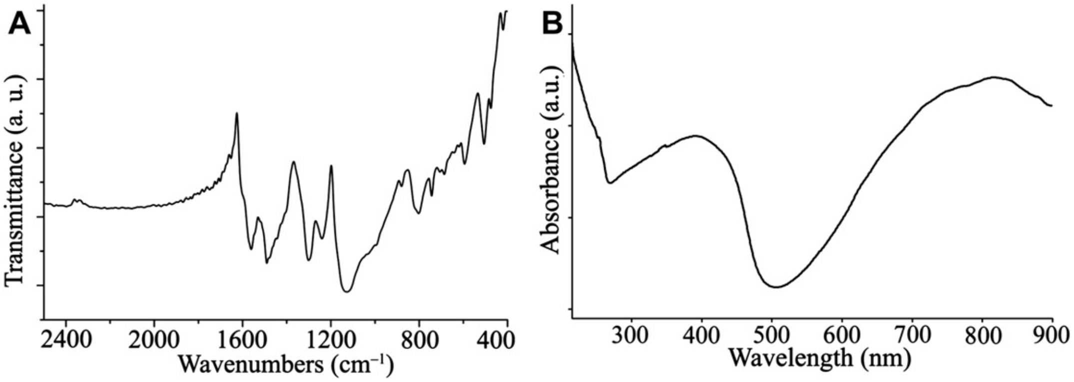

Fig. 6. FTIR (A) and UV–vis (B) spectra of the as-synthesized polyaniline nanofibers.

Accelerating the rate of polymerization will rapidly produce high oligomer concentration to favor homogeneous nucleation, which reduces the secondary nucleation sites on the preexisting nanofibers [31,32]. The decrease of the molar ratios of APS to Fe^{2+} may create much more sulfate radical anions to increase the polymerization rate, so homogeneous nucleation is achieved. However, the increase of HCl concentration will enhance the hydrophilicity of oligomers, and excessive APS will produce oligomers at a low polymerization rate, which may induce heterogeneous nucleation to form surface active sites on the surfaces of polyaniline nanofibers.

The molecular structures of the as-synthesized polyaniline nanofibers were characterized by FTIR and UV–vis spectroscopies. Typical FTIR spectrum of the as-synthesized polyaniline nanofibers is shown in Fig. 6A. The characteristic peaks at 1564 cm^{-1} and 1493 cm^{-1} are assigned to the C=C stretching of quinoid rings and benzenoid rings, respectively. The characteristic peaks at 1300 and 1126 cm^{-1} are attributed to the C–N stretching vibration of the secondary aromatic amine and aromatic C–H in-plane bending, respectively [12–16]. Fig. 6B presents typical UV–vis spectrum of the as-synthesized polyaniline nanofibers. The peaks at about 400 nm and 820 nm are attributed to polaron band $\rightarrow \pi^*$ transition, and the π to the localized polaron band of doped polyaniline, respectively [19,30]. Both FTIR and UV–vis spectra reveal that the as-synthesized nanofibers are doped polyaniline in its emeraldine salt form. The conductivities of the resulting products obtained using APS and APS/Fe^{2+} redox initiator are 0.67 S/cm and 0.37 S/cm, respectively, indicating that the molecular structures of polyaniline are not significantly affected by the APS/Fe^{2+} redox initiator. The cyclic voltammograms of the as-synthesized polyaniline nanofibers performed in 0.1 M HCl aqueous solution with a scan rate of 0.05 V/s are shown in Fig. 7. Two redox peaks characteristic can be seen clearly, which are similar to that of the parent polyaniline, indicating that the molecular structures and aqueous electrochemistry of polyaniline are not significantly affected by the nanofibrillar morphology [22,40].

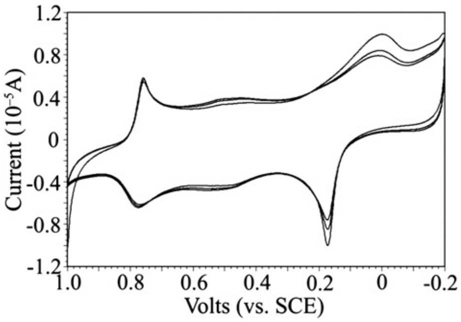

Fig. 7. The cyclic voltammograms of the as-synthesized polyaniline nanofibers performed in 0.1 M HCl aqueous solution with a scan rate of 0.05 V/s.

4. Conclusions

In summary, we describe a rapid polymerization route to the synthesis of high quality polyaniline nanofibers using APS/Fe^{2+} redox initiator as the oxidant without any hard or soft templates. Accelerating polymerization rate of aniline resulting from the redox initiator plays a critical role in the formation of polyaniline nanofibers. The reaction parameters, such as the concentrations of dopant, and redox initiator, and reaction time, have profound influences on the diameters and morphologies of polyaniline nanofibers. The molecular structures and electrochemical properties of polyaniline nanofibers do not differ significantly from that of conventional polyaniline, although the APS/Fe^{2+} redox initiator is used as an oxidant.

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Appendix. Supplementary material

Supplementary data associated with this article can be found in the online version, at doi:10.1016/j.polymer.2010.03.004

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