Solvent Effects on the Formation of Polyaniline Nanofibers in Dilute Polymerization System

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Abstract. Polyaniline (PANI) nanofibers were prepared in dilute polymerization system in the presence of organic solvents including acetone and ethanol. The as-prepared PANI nanofibers were characterized by field emission scanning electron microscopy, ultraviolet-visible absorption spectroscopy, Fourier transform infrared and Raman spectroscopy, X–ray diffraction analysis, thermogravimetric analysis and electrical measurements. The effects of the solvents on the morphology, microstructure, as well as thermal and conductive properties were discussed.

Introduction

Among the conductive polymers, polyaniline (PANI), owing to its environmental stability, relatively good processability, easily tunable electronic properties by changing the oxidation state and the degree of protonation, as well as low cost, has particular interest. [1] In the family of PANI micro/nanostructures, PANI nanofiber is one of the most intensively studied systems because of its high surface area, high carrier mobility, and remarkable propensity to form anisotropic structures, as well as can offer better performances or new properties compared with its conventional bulk counterparts. It is demonstrated that once the secondary growth could be effectively avoided, PANI would easily form nanofibrous structure. Moreover, aniline oligomers generated at the early stage of oxidation process play an important role in the formation of PANI nanostructure. [2] Dilute polymerization is a feasible route for the production of PANI nanofibers without using any surfactants and templates. To better understand the formation process of PANI nanofibers, acetone and ethanol would be added into dilute polymerization system in this work, respectively. Considerable attention has been paid to the effect of solvents on the formation of PANI nanofibers.

Experimental

Materials. Aniline monomers, ammonium persulfate (APS), hydrochloric acid (HCl), acetone and ethanol were purchased from Sinopharm Chemical Reagent Co. Ltd., herein aniline monomers were distilled under reduced pressure before use, and other reagents were analytically reagent and used without further purification. The deionized water was used to make up the solutions.

Preparation. 10 mL 0.008 M aniline monomer solution achieved by dissolving the aniline monomers in 1 M HCl was rapidly mixed with 10 mL APS in 1 M HCl solution with 1:2 molar ratio of aniline to APS in a beaker under mechanical stirring. After 1 min reaction, the reaction solution was rapidly diluted with 50 mL 10 % acetone and ethanol aqueous solution, respectively. Then 15 mL above-mentioned aniline monomer and APS solution were simultaneously added drop by drop into the diluted reaction solution. For comparison, aqueous solution of organic solvent was replaced by pure deionized water with the equal volume for diluting the reaction solution. After reaction for 12 h, the product was washed with deionized water and filtered for several times, and finally dried at 40 $^\circ$C for 48 h under vacuum.

Characterization. The morphologies of PANI nanofibers were observed on a HITACHI S–4800 field emission scanning electron microscope (FE–SEM). The ultraviolet-visible (UV–Vis) spectra of PANI solutions were recorded on a UV–2550 UV–Vis spectrophotometer. The chemical structures of

PANI nanofibers were characterized on a Nicolet 8700 Fourier transform infrared (FT–IR) spectrometer with a resolution of 4 cm^{-1} with a total of 100 scans, and a Renishaw inVia–Reflex micro–Raman Spectroscopy System using a 532 nm Nd: YAG laser with the laser output power of 25 mW at room temperature. X–ray diffraction patterns were obtained on a Philips PX1500 X–ray diffractometer by using Cu Kα X–rays with a voltage of 40 kV and a current of 30 mA. The thermogravimetric analysis (TGA) was studied on a NETZSCH TG 209 F1 thermogravimetric analyzer. The samples were heated from 30 to 900 °C at a heating rate of 20 °C min^{-1} under a nitrogen atmosphere with a flow rate of 20 mL min^{-1}.
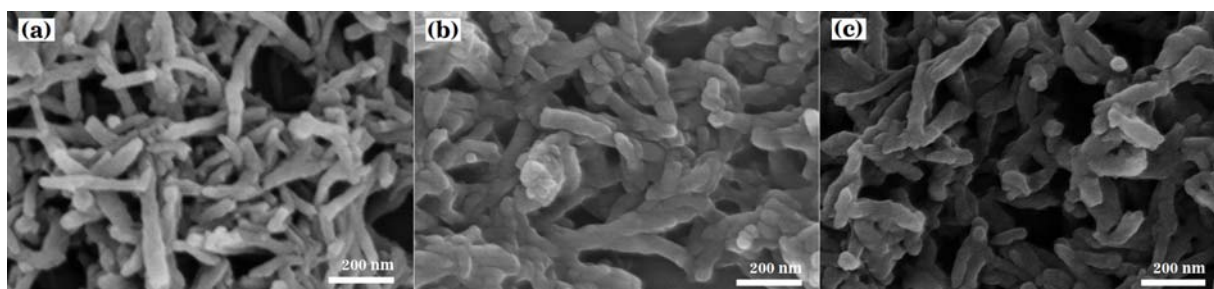
Results and Discussion

Fig. 1. The FE–SEM images for PANI nanofibers prepared in dilute polymerization without organic solvent (a) and with acetone (b) and ethanol (c).

Morphology. Fig. 1 depicts the morphologies of PANI nanofibers prepared in various reaction solutions. It clearly shows that all the products prepared in dilute polymerization system had similar nanofibrous morphology in appearance. For the system without organic solvent, PANI nanofibers exhibited relatively large aspect ratio (the average diameter of 30–40 nm, and length of 400–500 nm) and high dispersibility. In the presence of acetone, PANI nanofibers aggregated together and presented relatively large diameter and wide size distribution. As for the system with ethanol, PANI nanofibers aggregated slightly. The result implies that the introduction of organic solvent obviously affected the formation of PANI nanofibers, and more uniform PANI nanofibers with relatively large aspect ratio can be obtained in fully aqueous solution.
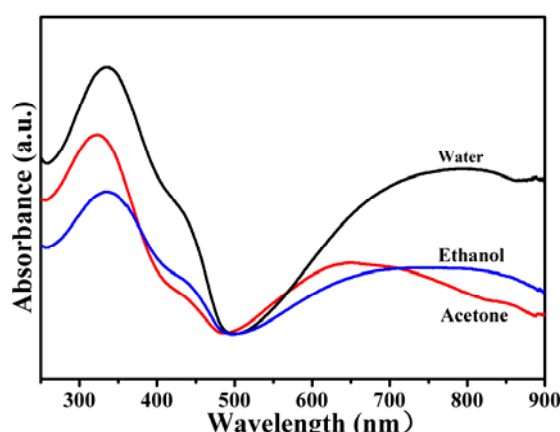

Fig. 2. UV–Vis absorption spectra for PANI nanofibers prepared in various reaction solutions.

Optical structure. The UV–Vis absorption spectra of PANI nanofibers prepared in various reaction solutions are shown in Fig. 2. The characteristic absorption bands at around 335 nm, 440 nm and 750 nm for PANI nanofibers are characteristic of emeraldine salt oxidation state. The band at around 335 nm was assigned to a π–π* transition in the benzenoid structure and at about 440 nm to the n–π* transition, representing the doping degree of polymer chains, while the longest wavelength band

was attributed to π–n transition in the quinonoid rings. [3] As shown in Fig. 2, among three kinds of PANI nanofibers, PANI nanofibers obtained in the presence of acetone exhibited an obvious blue shift for the lowest and longest wavelength band, indicating the existence of short conjugation length, low doping degree and large energy gap caused by the phenazine-like unites and aniline oligomers. [4]
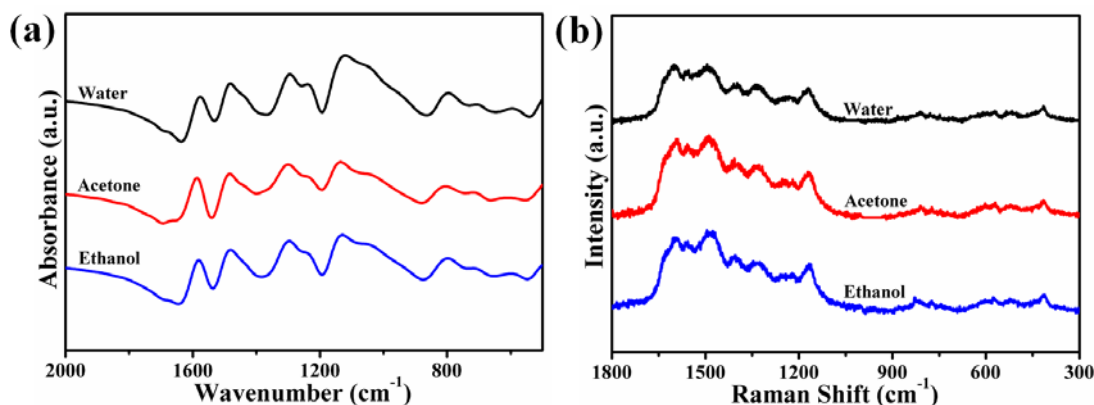
Fig. 3. FT–IR (a) and Raman (b) spectra for PANI nanofibers prepared in various reaction solutions.

Chemical structure. The FT–IR spectra of the PANI nanofibers prepared in various reaction solutions are presented in Fig. 3(a). It can be clearly seen that the main characteristic peaks of PANI appeared for all the PANI nanofibers. There are no obvious changes in the peak positions except the peak at around 1130 cm^{-1} that is considered to be a measurement for the delocalization degree of electrons. [5] The infrared peak of PANI nanofibers prepared in dilute polymerization system without organic solvent and with acetone and ethanol was appeared at 1124.3, 1137.8 and 1130.1 cm^{-1}, respectively. It implies low delocalization degree of electrons in the presence of acetone, that is to say, relatively low conductivity, which is consistent with the result from UV–Vis absorption spectra above.

Fig. 3(b) presents Raman spectra of the PANI nanofibers prepared in various reaction solutions. The characteristic peaks above 1000 cm^{-1} are sensitive to the oxidation state and protonated degree. It is found that the all the PANI nanofibers were the mixed structure of bipolarons and fully oxidized form. Meanwhile, the characteristic peaks appeared within the range from 1000 to 300 cm^{-1} were caused by the variation of the conformation of PANI molecular chains reflecting the crystallization property of PANI nanofibers, that is to say, they are dependent strong on the crystalline degree of PANI nanofibers. [6] It is noted that no obvious difference in these peaks for all the PANI nanofibers. Hence X–ray diffraction analysis was carried out to further study the crystalline structure.

Crystalline structure. Fig. 4 reveals the X–ray diffraction patterns of PANI nanofibers prepared in various reaction solutions. It is found that for fully aqueous solution, there are two sharp diffraction peaks appeared at around $2\theta = 25°$ and $19°$, whereas in the presence of organic solvents, especially for acetone, only one broad diffraction peak could be observed, implying these PANI nanofibers possessed poor crystalline property. This result shows that the introduction of organic solvents has an obvious impact on the growth of PANI nanofibers, which resulted in relatively low regularity of PANI molecular chains, as a result, more amorphous properties.
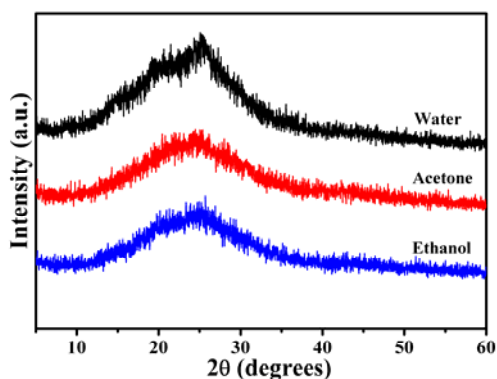
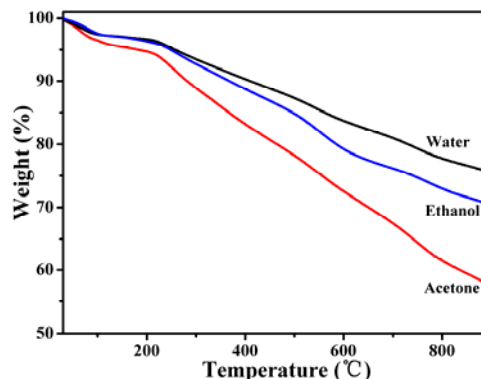Fig. 4. X–ray diffraction patterns for PANI nanofibers prepared in various reaction solutions.

Fig. 5. TGA curves for PANI nanofibers prepared in various reaction solutions.

Thermal stability. Fig. 5 shows the TGA curves of PANI nanofibers prepared in various reaction solutions. It can be seen that after undergoing a flat degradation process before 200 ^{o}C, PANI nanofibers began to rapidly degrade. Furthermore, PANI nanofibers prepared in fully aqueous solution possessed the highest thermal stability, whereas in the presence of acetone, the product held the lowest thermal stability and residual weight, resulting from its relatively amorphous structure. The residual weight was about 75.6, 70.6 and 57.5 % at 900 ^{o}C for PANI nanofibers in dilute polymerization system without organic solvent, and with ethanol and acetone, respectively.

Conclusions

Three kinds of PANI nanofibers were synthesized through dilute polymerization in various reaction solutions. The effects of organic solvent including ethanol and acetone on the morphology, chemical structure, crystal structure and thermal properties were discussed. It is found that the introduction of organic solvents especially for acetone has an obvious impact on the growth of PANI nanofibers. Although having similar nanofibrous structure in appearance, PANI nanofibers with relatively low regularity of polymeric chains formed in the presence of acetone possessed relatively small aspect ratio, poor dispersibility and uniformity, and low doping degree, as a result, more amorphous properties and weak thermal stability. In contrast, high quantity PANI nanofibers can be obtained in fully aqueous solution.

Acknowledgements

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