

Original Research

Influence of acetone on nanostructure and electrochemical properties of interfacial synthesized polyaniline nanofibers

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Abstract

The growth of polyaniline (PANI) nanofibers through interfacial polymerization can be well controlled by adding a small amount of acetone in the water/chloroform system. It was found that the polymerization rate became slower in the presence of acetone, yielding PANI nanofibers with larger aspect ratios. The influences of the acetone addition on the morphology, microstructure and properties of as-prepared PANI nanofibers were studied by scanning electron microscope (FE-SEM), ultraviolet–visible spectra (UV–vis), Fourier transform infrared (FT-IR) and Raman spectroscopy, X-ray diffraction (XRD), thermogravimetry analysis (TGA), and electrical and electrochemical measurements. The experimental results showed that PANI nanofibers prepared by using ammonium persulfate (APS) as an oxidant with acetone exhibited slower growth, the larger ratio of length to diameter, and higher crystallinity ($2\theta=6^\circ, 19^\circ, 26^\circ$) than that without acetone, meanwhile remained larger yield of 11.23% and higher conductivity 1.8×10^{-2} S/cm compared with that obtained by replacing APS with FeCl_3 . More importantly, these PANI nanofibers exhibited better electrochemical behaviors, which benefitted from their high crystallinity and good conductivity.

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Keywords: Polyaniline nanofiber; Interfacial polymerization; Acetone addition; Microstructure; Electrochemical behavior

1. Introduction

Polyaniline (PANI) as one of the most useful conducting polymers has attracted great research interests due to its facile preparation, low cost, reversible acid/base doping/dedoping chemistry, and good environmental stability [1,2]. In particular, nanostructured conducting polymers have offered unique opportunities for fabricating super-capacitors, batteries, chemical sensors, catalytic supports and functional nanocomposites, which mainly results from their beneficial characteristics at the nanometer scale. Among the various nanostructures, PANI nanofibers possess high surface area and large ratio of length to diameter and have drawn more and more attentions, furthermore

the properties of these materials become dependent on their size and shape when their dimensions decrease to the nanoscale [3].

Notably, interfacial polymerization without the templates as a facile synthetic strategy was exploited for generating high-quality PANI nanofibers [4,5]. Furthermore, it is observed that the structure of the oxidant, especially the oxidation/reduction potential, will affect the morphology and size of the nanostructured PANI. Usually, ammonium persulfate (APS) is used as an oxidant in the polymerization of PANI because a much higher conversion and yield can be obtained in comparison with other oxidants, such as FeCl_3 . However, when the APS was replaced by FeCl_3 , the as-prepared nanofibers not only were thinner in diameter, but also had higher crystallinity [6]. It is worth to point out that a slow polymerization rate was observed with FeCl_3 as an oxidant in the interfacial polymerization, implying that there was enough time for the self-assembly process of oligomers when a large number of oligomers produced or the oligomers could stay for a longer

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time at the interface [7]. Thus higher crystalline products can be obtained in the slower interfacial polymerization of PANI.

In this work, acetone is employed to provide a restrictive effect in the PANI chain growth which allows tailoring of microstructure of the resulting PANI nanofibers. In general, acetone was always used during the post-treatment of PANI. Therefore, a small amount of acetone as a co-solvent was added into the water/chloroform system to affect the growth of PANI nanofibers by using APS as the oxidant. It is expected that a novel and inexpensive approach is presented by introducing acetone into the interfacial polymerization for preparing high crystalline PANI nanofibers with higher yield. The influence of the acetone addition on the morphology, microstructure and properties of as-prepared PANI nanofibers was studied in the present investigation.

2. Experimental

2.1. Materials

Aniline, ammonium persulfate (APS), hydrochloric acid (HCl), chloroform (CHCl_3), acetone, and FeCl_3 were obtained from Guoyao Group Chemical Reagent Co. Ltd. and used as received without any further purification. The deionized water was used for all experiments.

2.2. Preparation

0.1 M aniline solution was prepared by dissolving aniline in 10 mL CHCl_3 as the organic phase in the interfacial polymerization. The water phase was APS (0.025 M) in 10 mL HCl

aqueous solution, APS (0.025 M) in 10 mL HCl aqueous solution with 5% acetone addition and FeCl_3 (1.2 M) in 10 mL HCl aqueous solution as the samples of a, b and c, respectively. Then the aqueous solution was carefully transferred alongside the wall onto the organic solution to form water/chloroform systems. Put the system quiet without any disturbance, and then the products were washed with deionized water and finally dried at 60 °C for 24 h under vacuum.

2.3. Characterization

The morphologies of PANI nanofibers were observed on HITACHI S-4800 Field Emission Scanning Electron Microscope (FE-SEM). The optical absorption measurements were carried out on a UV-2550 Ultraviolet–visible spectrophotometer in the wavelength region from 200 to 800 nm with a scanning speed of 400 nm/min. The microstructures of the PANI nanofibers were characterized on an Renishaw inVia-Reflex micro-Raman Spectroscopy System using a 532 nm He–Ne laser with the laser output power of 5.0 mW, and a Nicolet 8700 Fourier transform infrared spectrometer (FT-IR) at room temperature over a frequency range of 2000–400 cm^{-1} with a resolution of 4 cm^{-1} by a total of 100 scans for each sample. The crystal structures were characterized on a Philips PZ1200 X-ray diffractometer by using Cu $\text{K}\alpha$ X-rays with a voltage of 40 kV and a current of 30 mA. The thermal stability was studied using a NETZSCH TG 209 F1 thermogravimetric analyzer (TGA). The samples were heated from 30–900 °C at a heating rate of 20 °C/min under a nitrogen atmosphere with a flow rate of 20 mL/min.

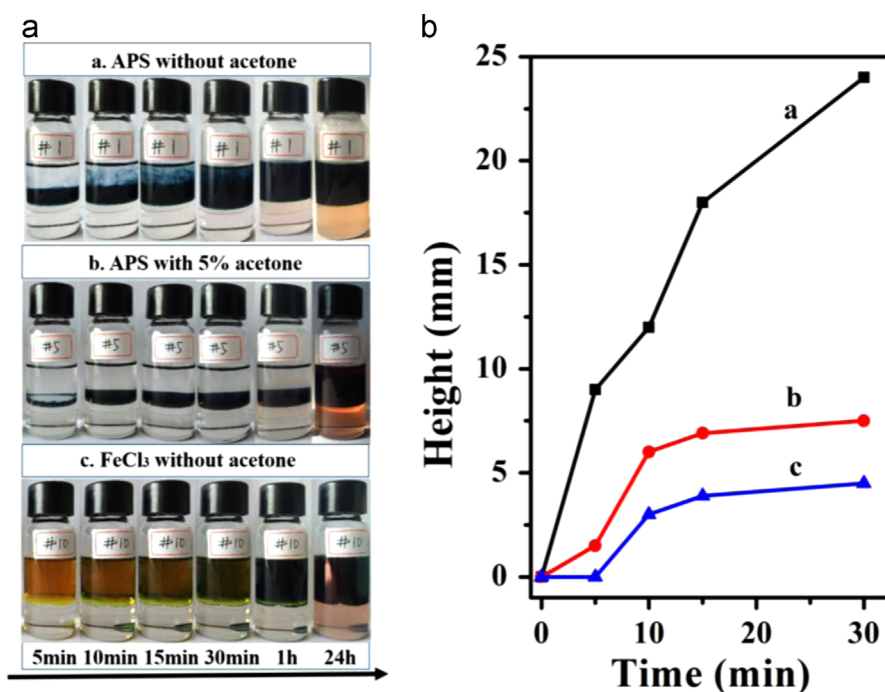


Fig. 1. (a) Observation of the formation and (b) the height of products with the reaction time in various water/chloroform systems: (a) APS without acetone, (b) APS with 5% acetone and (c) FeCl_3 without acetone.

All the samples were pressed into thin sheet under 5 MPa, and measured by a two-point probe method to test the electrical conductivity of the as-prepared PANI at room temperature by using an Agilent 34401A digital multi-meter. Electrochemical measurements were carried out in a three-electrode system. A glassy carbon electrode with a diameter of 3 mm served as the substrate to prepare the working electrode. A platinum sheet ($1 \times 1 \text{ cm}^2$) and Ag/AgCl with saturated KCl solution were used as the counter and reference electrodes, respectively. The working electrode was prepared by casting the sample onto the glassy carbon electrode surface. Typically, 10 mg PANI samples was ultrasonically dispersed in 10 mL deionized water. Then, 20 μL of the above suspension was dripped onto the glassy carbon electrode using a pipette gun and dried at room temperature. Cyclic voltammetry (CV) and galvanostatic charge/discharge (GCD) were measured on a CHI660D electrochemical workstation (Chenhua, Shanghai) at room temperature. An aqueous solution of 1 M H_2SO_4 was used as the electrolyte. CV tests were carried out from -0.2 to 0.8 V at different scan rates. GCD property was measured at the current density of 1 A/g .

3. Results and discussion

3.1. Effect of acetone on reaction

The interfacial polymerization process with time is shown in Fig. 1. Generally, small oligomeric intermediates such as dimers and trimers were produced in the beginning of chemical oxidation polymerization of aniline with ammonium persulfate. These oligomers continued to grow through reacting with each other or with monomers [3]. Once PANI nanofibers were formed at the water/chloroform interface, they would diffuse into aqueous phase due to the hydrophilic property of PANI, resulting in that the color of the polymerization system changed from transparent to blue and then deep green [8,9]. Importantly, the time when the color appeared to change depended on the synthesis conditions. As we can see from Fig. 1(a), in the system introduced APS without acetone, the products filled the interface after 5 min, and migrated into water phase after 10 min. For the sample b, PANI filled the boundary in 10 min. After 20 min, the aqueous phase was full of products whereas no apparent diffusion occurred with the acetone addition. The system with FeCl_3 as oxidant without acetone appeared green product until 15 min, and the product directly diffused into the water phase. This may be related to the kinds of oxidants. Whether there were any addition of acetone in water/chloroform system, the aqueous phase was filled with product after the reaction time of 24 h. Because the initial reaction speed had a great influence on the formation of PANI, we studied the relationship of the interfacial height of PANI nanofibers with time over the first 30 min, as shown in Fig. 1(b), in three systems. The interfacial heights of PANI nanofibers were 9, 12, 18, 24 mm for sample a, 0, 6, 6.9, 7.5 mm for sample b and 0, 3, 3.9, 4.5 mm for sample c, in 5 min, 10 min, 15 min and 30 min, respectively. It can be easily seen that a relative slow polymerization rate can be

observed when acetone addition was added into the aqueous phase, but it was still faster than that occurred in the system where the APS was replaced by FeCl_3 as the oxidant. This fact indicates that the polymerization rate could be efficiently adjusted by the addition of acetone. Moreover, the acetone has an important influence on the fields of PANI in different system, the fields of samples a, b and c are 10.92%, 11.23%, 9.86%. Owing to the extended reaction time, the sample b using APS oxidant with acetone addition tended to produce more products than that without. Meantime, the oxidation of APS is better than FeCl_3 , so the PANI with APS has a higher field than FeCl_3 . Therefore, the duration of the growth and diffusion of PANI nanofibers reflects the rate of the overall polymerization process [3].

3.2. Morphology

It has been demonstrated that the interfacial tension between the growing oligomer chain and the reaction medium and the polymerization kinetics significantly affect the morphology of the resulting polymer [3]. During the interfacial polymerization process, the lack of aniline monomers in the water phase effectively restricted the further growth of initial PANI nanofibers [10]. Therefore, the final products should be the nanofibrous morphology. Fig. 2 shows SEM morphology of PANI nanofibers synthesized by interfacial polymerization in different water/chloroform system: (a) APS without acetone, (b) APS with 5% acetone and (c) FeCl_3 without acetone. From Fig. 2(b) and (c), PANI nanofibers observed with good morphology were very regular and uniform. For the sample b, the diameter of PANI nanofibers was 80–120 nm and the length was 400–600 nm. However, due to the slower reaction rate and weaker oxidation ability, the diameter and length of PANI nanofibers were 60–80 nm and 600–700 nm for sample c. But in Fig. 2(a), the diameter of PANI nanofibers increased to 100–120 nm while its length decreased to 300–500 nm for that prepared without acetone addition for sample a. Besides, these nanofibers tend to agglomerate into a few amount of particles. Furthermore, the ratios of length to diameter were 2.5–5.5, 3.3–7.5 and 7.5–11.7 for samples a, b and c. In a word, PANI nanofibers with larger ratio of length to diameter and less entanglement can be produced in the water/chloroform system with acetone addition, which may be benefitted from the extended reaction time at interface [11]. The morphology indicates that PANI nanofibers can be synthesized in the presence of acetone addition. In conclusion, the acetone addition had an important effect on the morphology of PANI nanofibers.

3.3. Electronic structure

The electronic structure of PANI nanofibers was studied by UV–vis spectra and shown in Fig. 3. Clearly, the samples a and b exhibited similar characteristic bands. For PANI nanofibers prepared in APS oxidation system, there occurred three characteristic bands, around 338 nm, 425 nm and 667 nm, which can be assigned to $\pi-\pi^*$, polaron- π^* and π -polaron transition, respectively, indicating that the products were in the conducting emeraldine salt (ES) form [4,12–14].

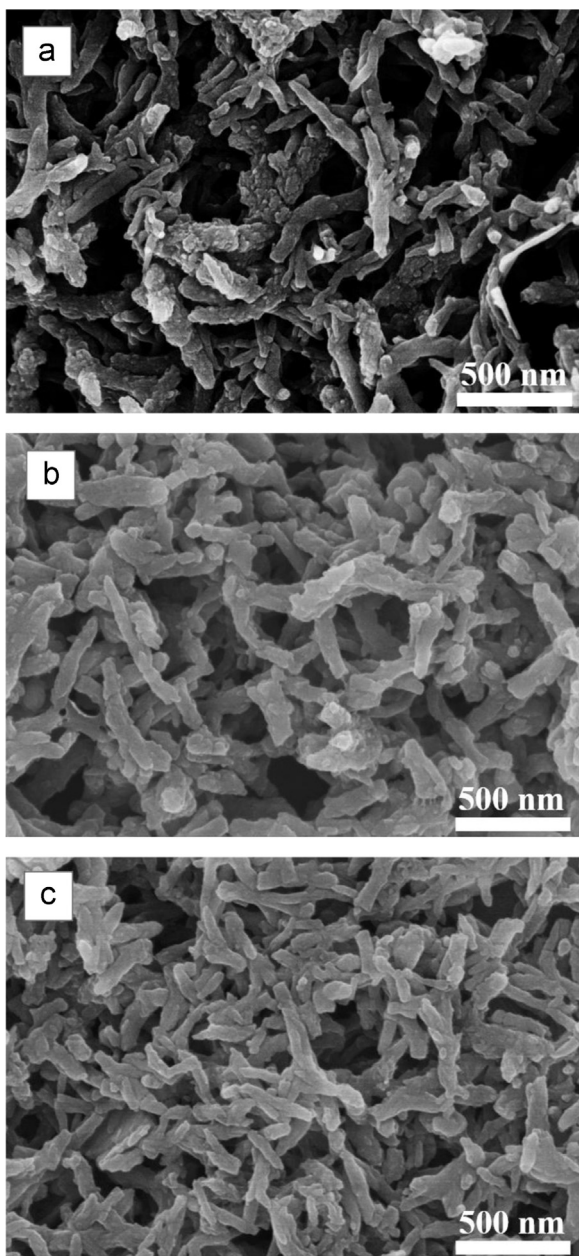


Fig. 2. SEM images of PANI nanofibers prepared by interfacial polymerization in water/chloroform system: (a) APS without acetone, (b) APS with 5% acetone and (c) FeCl_3 without acetone.

For the samples b and c, the blue-shift of the band for π - π^* transition to 336 nm and 304 nm could be observed, respectively, demonstrating larger energy gap [14].

The doping level can be roughly estimated from the absorption spectra of PANI at polaron- π^* in the length of 425 nm [3], which suggests all PANI nanofibers are in the doped state. From the spectra of UV-vis, the PANI nanofibers produced in FeCl_3 oxidation system have largest energy gap, which is consistent with the conductivity results. According to the conductivity results, the conductivities were 2.23×10^{-2} S/cm and 1.80×10^{-2} S/cm and 9.26×10^{-3} S/cm for PANI synthesized in a, b and c reaction condition.

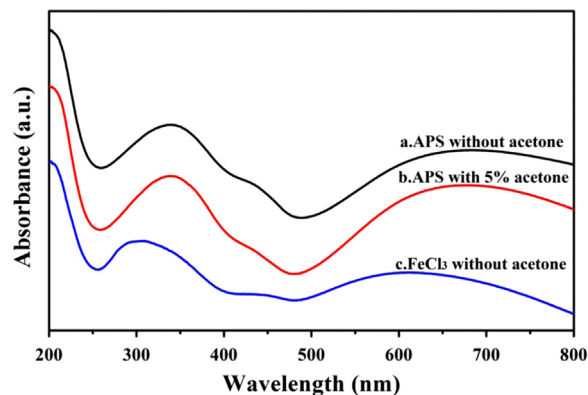


Fig. 3. UV-vis spectra of PANI nanofibers prepared by interfacial polymerization in water/chloroform system: (a) APS without acetone, (b) APS with 5% acetone and (c) FeCl_3 without acetone.

3.4. Chemical structure

Fig. 4(a) gives the FT-IR spectra of PANI nanofibers prepared by interfacial polymerization. The characteristic band at around 1299 cm^{-1} attributed to $\text{C}-\text{N}^+$ stretching vibration mode appears in all the samples, indicating that PANI prepared is in the doped state. The bands at 1133 and 821 cm^{-1} can be assigned to in-plane and out-of-plane bending vibration of C-H on the 1,4-desubstituted ring, respectively. More importantly, the typical bands at 1560 and 1490 cm^{-1} can be ascribed to the $\text{C}=\text{C}$ stretching vibration of quinoid and benzenoid rings, respectively [4,9,16,17]. The intensity ratio of 1560 and 1490 cm^{-1} represents the relative content of quinone and benzene structures in polymers, and the higher value means larger conjugation length along the molecular chains. In general, long conjugation is beneficial for the delocalization of electrons along the backbones, which means higher conductivity. The intensity ratio of PANI nanofibers obtained in the systems a, b and c is 0.79, 0.78 and 0.72, respectively. The result presents a good agreement with the UV-vis spectra and conductivity test, indicating that both acetone addition and oxidant have effects on the chain structure.

To have a better understanding of PANI nanostructures, we choose a green laser line excitation of 532 nm, rather than red or blue laser excitation on the ground that uniform intensity spectra from both reduced and oxidized form of PANI should be obtained [18]. Similar results consistent with former researches can be observed from Fig. 4(b). In the spectra of PANI prepared with acetone addition, bands at 1165 cm^{-1} , 1325 cm^{-1} and 1485 cm^{-1} represent in-plane vibration of C-H, stretching vibration in $\text{C}-\text{N}^+$ and vibration in $\text{C}=\text{N}$ on quinone ring, respectively, which suggest the PANI prepared is in the form of ES [15]. In addition, the strong peak at 1595 cm^{-1} and weak band at 1555 cm^{-1} mean the $\text{C}=\text{C}$ and $\text{C}-\text{C}$ stretching vibration in the quinonoid ring, respectively [15,18]. In the low frequency region, the two bands are located at 745 and 785 cm^{-1} , corresponding to imine deformation ($\text{C}-\text{N}-\text{C}$ bending) and quinone ring deformation, respectively [17]. Band at 415 cm^{-1} represents C-H out-

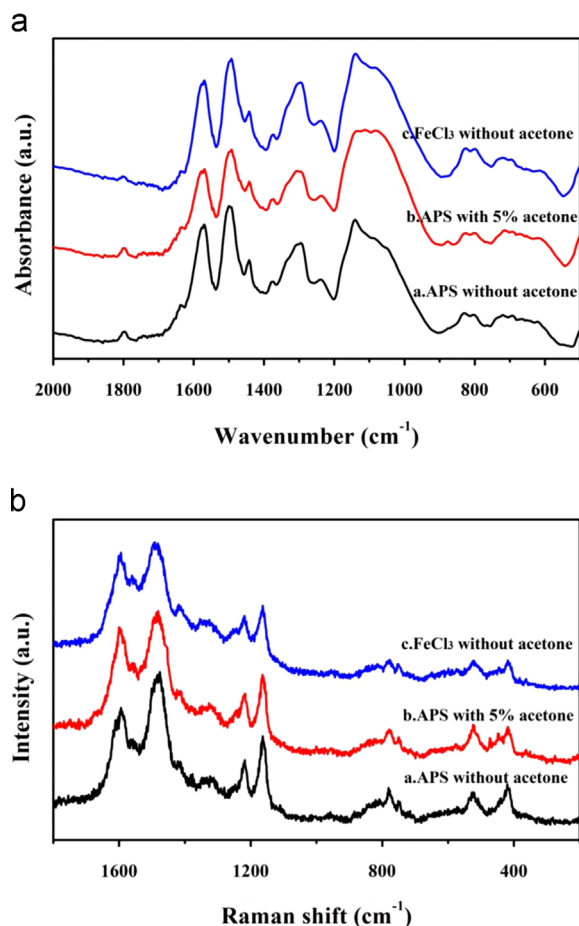


Fig. 4. (a) FT-IR and (b) Raman spectra of PANI nanofibers prepared by interfacial polymerization in water/chloroform system: (a) APS without acetone, (b) APS with 5% acetone and (c) FeCl_3 without acetone.

plane bending in bipolar. Briefly, all the samples exhibit the similar characteristic bands of PANI prepared whether by introducing different oxidants or adding acetone.

3.5. Crystalline structure

The PANI with higher crystallinity tends to display a metallic-like conductive behavior. To study the crystallinity of PANI nanofibers obtained in different system, XRD patterns were employed and shown in Fig. 5. For the samples b and c, there appear three diffraction peaks centered at 6° , 19° and 26° . The two peaks centered at $2\theta=19^\circ$ and 26° are ascribed to periodicity parallel and perpendicular to the polymer chains, respectively [3,13,16], showing that the samples were in crystalline structure. However, a strong peak at $2\theta=6^\circ$ assigned as the periodicity along the polymer chain is also observed [5], which indicates that the PANI nanofibers obtained with acetone addition are highly crystalline. Whereas PANI produced without acetone addition exhibited worse crystallinity, only one broad peak can be observed at higher degree. The amorphous structure of PANI prepared by interfacial polymerization without any acetone is similar with that obtained by conventional chemical oxidation reaction. The intensity of

$2\theta=6^\circ$ increased gradually from samples a to c, which suggested the PANI with FeCl_3 possessed best crystallinity, and PANI with APS without acetone was worst.

The acetone addition plays a vital role in producing the high crystalline PANI nanofibers by extending the reaction time. Compared with the traditional interfacial polymerization, the system with acetone addition can produce PANI with higher

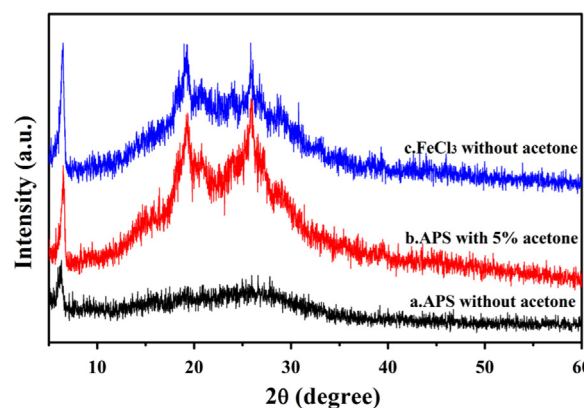


Fig. 5. XRD patterns of PANI nanofibers prepared by interfacial polymerization in water/chloroform system: (a) APS without acetone, (b) APS with 5% acetone and (c) FeCl_3 without acetone.

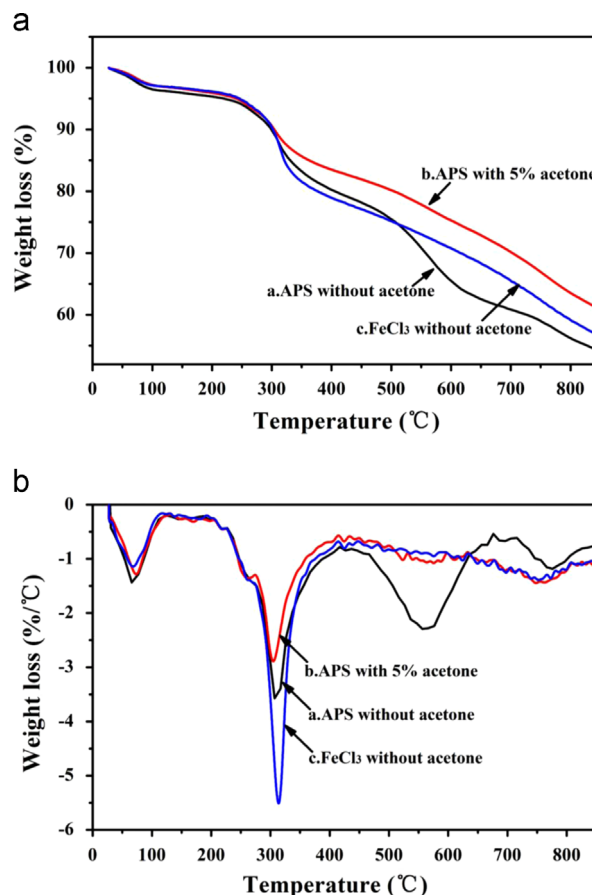


Fig. 6. (a) TGA and (b) DTG curves of PANI nanofibers prepared by interfacial polymerization in water/chloroform system: (a) APS without acetone, (b) APS with 5% acetone and (c) FeCl_3 without acetone.

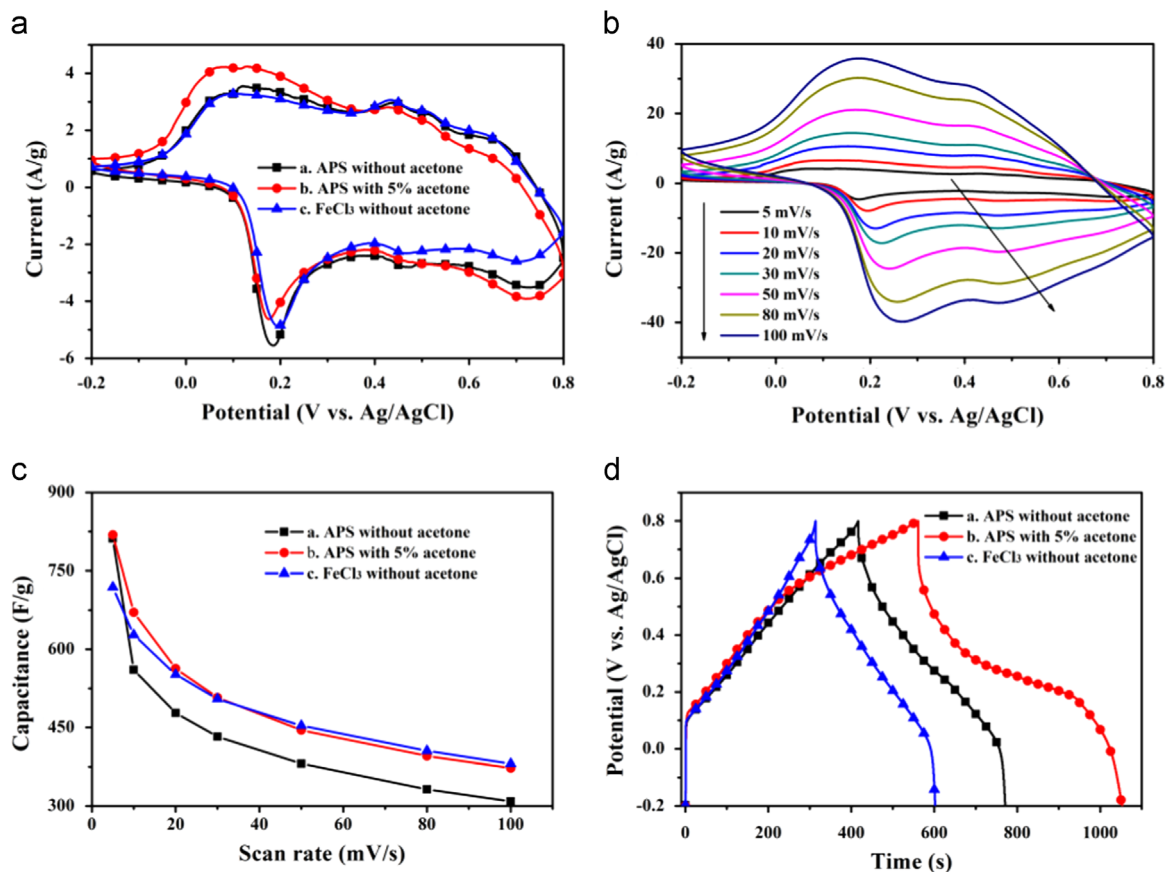


Fig. 7. (a) Cyclic voltammograms at the scan rate of 5 mV/s, (b) cyclic voltammograms at different scan rates, (c) capacitance as a function of scan rates, and (d) charge–discharge curves of PANI nanofibers prepared by interfacial polymerization in water/chloroform system: (a) APS without acetone, (b) APS with 5% acetone and (c) FeCl_3 without acetone as working electrodes in 1 M H_2SO_4 aqueous electrolyte.

crystallinity. Therefore, it is an effective route to improve the crystalline property of polymers. It is meaningful for interfacial polymerization to prepare PANI nanofiber with excellent crystalline property.

3.6. Thermal stability

Fig. 6 shows the TGA and DTG diagrams of PANI nanofibers obtained by interfacial polymerization in water/chloroform system, in which PANI made with acetone addition shows the better thermal stability. At first, the weight loss was about 3.7%, 4.4% and 2.9% of initial mass at 100 °C due to the evaporation of water for samples a, b and c, respectively [19]. After that, the samples showed a weight loss between 100 and 400 °C, which may be assigned to the weight loss of dopant molecule and oligomer. According to the DTG, the curve of PANI prepared using APS without acetone emerges a trend of constant decomposition in 550 °C, indicating a poor thermal stability due to its amorphous structure seen in Fig. 5. As regard to PANI obtained with acetone addition, a smaller weight loss arises from the crystalline structure which is revealed by XRD patterns [20]. The following weight loss is attributed to the decomposition of PANI backbone, and it causes weight loss near 600 °C. When arrived to 850 °C, the residual weights of samples a, b and c were 54.08%, 60.80%

and 56.46%, respectively. In conclusion, compared with different samples, PANI prepared with acetone addition exhibits the best thermal stability, which is mainly caused by its highly ordered molecule arrangement.

3.7. Electrochemical property

The morphology and chemical structure as well as the crystalline property certainly have much influence on the electrochemical behaviors of PANI. So as to evaluate the basic capacitive property of the obtained PANI nanofibers as the electrode material, cyclic voltammetry (CV) and galvanostatic charge–discharge (GCD) were studied by a three-electrode system in a 1.0 M H_2SO_4 electrolyte at a potential window of -0.2 to 0.8 V. Obviously, as can be seen in Fig. 7 (a), all the samples prepared with different oxidants or acetone addition exhibit three pairs of redox peaks at a scan rate of 5 mV/s, suggesting a typical pseudo-capacitive characteristic of PANI. The first pair of redox peaks is ascribed to the transformation between the leucoemeraldine base (LB) and emeraldine salt (ES) states of PANI, while the second pair is due to the transformation between ES and pernigraniline base (PB) states [21,22]. In addition, the first cathodic peak and corresponding anodic peak transfer to lower potential, it slightly decreases from 0.196 V to 0.184 V and 0.174 V for

the samples c, a and b, respectively, while the current density increases in the order of PANI nanofibers prepared with APS, FeCl₃ and APS with acetone. Moreover, the other cathodic peaks and corresponding anodic peaks hardly change. The result indicates that the redox transition and faradic transition of different samples take place during the electrochemical test, and PANI nanofibers prepared with APS as oxidant and with 5% acetone addition show the lowest ionic diffusion resistance [21,23].

In addition, the CV curves for all the samples at different scan rates are carried out to study the rate capacity of PANI as electrode material. For example, Fig. 7(b) gives out the diagram for sample b at the scan rates from 5 mV/s to 100 mV/s. Compared with that at low scan rate, the intermediate redox peaks disappear and only two pairs of redox peaks can be observed. Meanwhile, the peak current at cathodic and anodic increased with the improved scan rate, indicating a well rate capacity property. In general, high scan rates lead to either depletion or saturation of the protons in the electrolyte inside the electrode during the redox course due to slow proton transfer process occurred in the electrolyte and at the electrode interface. Therefore, the capacitive property becomes worse with the increase of scan rate. Therefore, the capacitance obtained at a relative slow scan rate is believed to be closest to that of full utilization of the electrode material [3,7]. At the scan rate of 5 mV/s, the values are 811.4, 818.7 and 719.0 F/g for the samples a, b and c, respectively. In details, the capacitance decreases for all the samples with the scan rate from 5 mV/s to 100 mV/s. As observed in Fig. 7(c), the values of PANI prepared with APS as oxidant and without acetone addition are smaller than those of the other two samples at the same scan rate. As regards to the samples b and c, the capacitance for PANI prepared with 5% acetone is better at lower scan rate less than 30 mV/s. However, the value of PANI prepared with FeCl₃ exceeds at higher scan rate more than 50 mV/s. The surprising phenomenon may be connected with the different conductivity and crystalline property, both of which play important roles in the electrochemical testing process [7,22].

In order to further investigate the capacitive property of electrode materials, GCD tests were carried out at the current density of 1 A/g. As shown in Fig. 7(d), all the samples exhibit similar triangle shapes during the charging and discharging process, indicating these electrodes to have a characteristic of capacitive behavior and excellent reversibility [5,7,22]. Obviously, the discharging time increases from 600, 780 and 1050 s for the samples c, a and b, respectively. Meanwhile, the discharging stage for PANI prepared with 5% acetone addition appears the largest initial potential drop at high potential values as well as the highest slope value, indicating that the highest capacitance among the samples consistent with the result in CV curves.

4. Conclusions

PANI nanofibers with different length-to-diameter ratios were prepared by interfacial polymerization using APS without acetone, APS with 5% acetone and FeCl₃ without acetone. From observation of the formation of products in aqueous phase, the addition of acetone can effectively decrease the reaction rate. Comparing with

each other, PANI nanofibers synthesized at different situations possessed similar optical and chemical structure. However, the sample prepared with acetone addition exhibited better crystalline property compared with that without acetone, the same as the thermostability property. Finally, the electrochemical property was also studied by the means of CV and GCD measurements. It was found that both the conductivity and crystalline property have a vital influence on the capacitive performance. PANI nanofibers obtained with acetone exhibited higher capacitance and excellent rate capacity property. This work is meaningful in studying the effect of acetone addition on the formation of PANI nanofibers, and it is promising in providing a new route to prepare conducting polymers with excellent electrochemical property.

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References

- [1] G. Ciric-Marjanovic, *Synth. Met.* 177 (2013) 1–47.
- [2] R. Ramya, R. Sivasubramanian, M.V. Sangaranarayanan, *Electrochim. Acta* 101 (2013) 109–129.
- [3] H.W. Park, T. Kim, J. Huh, M. Kang, J.E. Lee, H. Yoon, *ACS Nano* 6 (2012) 7624–7633.
- [4] A.A. Rakić, S. Trifunović, G. Ćirić-Marjanović, *Synth. Met.* 192 (2014) 56–65.
- [5] W. Yang, Z. Gao, N. Song, Y. Zhang, Y. Yang, J. Wang, *J. Power Sources* 272 (2014) 915–921.
- [6] L. Zhang, M.X. Wan, Y. Wei, *Rapid Commun.* 27 (2006) 366–371.
- [7] T. Li, Z. Qin, B. Liang, F. Tian, J. Zhao, N. Liu, M. Zhu, *Electrochim. Acta.*, 2015, in press, <http://dx.doi.org/10.1016/j.electacta.2015.03.169>.
- [8] J. Huang, B. Kaner, *Chem. Commun.* (2006) 367–376.
- [9] A. Abdolahi, E. Hamzah, Z. Ibrahim, S. Hashim, *Materials* 5 (2012) 1487–1494.
- [10] R. Li, Z. Chen, J. Li, C. Zhang, Q. Guo, *Synth. Met.* 171 (2013) 39–44.
- [11] N. Nuraje, K. Su, N. Yang, H. Matsui, *ACS Nano* 2 (2008) 502–506.
- [12] C. Su, G.C. Wang, F.R. Huang, X.W. Li, *J. Mater. Sci.* 43 (2008) 197–202.
- [13] S. Banerjee, J.P. Saikia, A. Kumar, B.K. Konwar, *Nanotechnology* 21 (2010) 045101.
- [14] P. Chutia, A. Kumar, *Physica B* 436 (2014) 200–207.
- [15] M. Bláha, M. Riesová, J. Zedník, A. Anžlovar, M. Zigon, J. Vohlídal, *Synth. Met.* 161 (2011) 1217–1225.
- [16] L. Zhang, G.I.N. Waterhouse, L. Zhang, *J. Nanomater.* 2011 (2011) 1–7.
- [17] S. Bhadra, D. Khastgir, N.K. Singha, J.H. Lee, *Prog. Polym. Sci.* 34 (2009) 783–810.
- [18] M. Trchová, Z. Morávková, M. Bláha, J. Stejskal, *Electrochim. Acta* 122 (2014) 28–38.
- [19] W. Qiu, L. Ma, M. Gan, J. Yan, S. Zeng, Z. Li, Y. Bai, *J. Nanopart. Res.* 16 (2014) 2370–2378.
- [20] X. Zhang, J. Zhu, N. Haldolaarachchige, J. Ryu, D.P. Young, S. Wei, Z. Guo, *Polymer* 53 (2012) 2109–2120.
- [21] W. Chen, R.B. Rakhi, H.N. Alshareef, *J. Phys. Chem. C* 117 (2013) 15009–15019.
- [22] D.S. Dhawale, A. Vinu, C.D. Lokhande, *Electrochim. Acta* 56 (2011) 9482–9487.
- [23] L. Ren, G. Zhang, J. Wang, L. Kang, Z. Lei, Z. Liu, Z. Liu, Z. Hao, Z. Liu, *Electrochim. Acta* 145 (2014) 99–108.