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Effect of methanol on morphology of polyaniline

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Abstract

Constant potential method is used to synthesize polyaniline (PANI) nanofibers in a solution containing methanol. According to shaping theory, the reasons about forming polyaniline nanofibers were suggested. The effects of the synthesis parameters, such as monomer concentration, methanol concentration, HCl concentration, electrode potential, polymerization time, and reaction temperature on the morphology of the PANI films have been investigated. Scanning electron microscopy results was used to characterize the morphology of PANI nanofibers. Both UV–vis absorption spectra and FTIR spectra indicate that there exists interaction between methanol molecules and polyaniline chains.

Keywords: Polyaniline; Nano-fibular structure; Alcohols; SEM

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1. Introduction

Conducting polyaniline is unique among conducting polymers on account of its excellent optical and electronic properties [1,2]. During the last decade, nanostructured (nanoparticles/-rods/-wires/-fibers) conducting polyaniline with unusual physical and chemical properties have attracted great research interests. Much research has been conducted on the nanostructure of polyaniline (PANI) because it exhibits enhanced performance in applications where a high surface contact area is needed between the nanostructures and its environment. Recently, various strategies including template synthesis, interfacial polymerization, self-assembly and stepwise electrochemical deposition have been developed for the preparation of polyaniline nanostructures [3–9]. For example, polyaniline nanostructures can be prepared by introducing "structural directing molecules" (such as surfactants [10] or polyelectrolytes [11]) into the chemical polymerization bath. Martin and Parthasarathy [12] proposed a method termed 'template synthesis' to prepare tubular conducting polymers, which has been successfully applied to synthesize microtubules of PANI [13,14], polypyrrole [15] and poly (3-methylthiophene) [16]. In recent years, Wan et al. [17,18] reported that the microtubes or nanotubes of PANI doped with various dopants could be obtained through a self-assembly process without using any external template. In addition, electrochemical polymerization such as electrospinning [11] and pulse galvanostatic method [19] can also produce conducting polymer nanofibers without templates. Although various methods of

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preparing PANI nanostructures have been reported, new simple and economical methods are still being explored.

Based on the facts [19,20] that there existed strong intermolecular H-bonding between PANI chains and alcohols and that the interaction may make PANI give rise to novel chemical and physical properties, we suggested a convenient and inexpensive electrochemical method for preparing polyaniline nanofiber in the presence of different alcohols in this paper. The results show that the PANI with nano-fibular morphology can be obtained under the proper preparation conditions. The effects of preparation conditions on the morphology of PANI films and the cause of forming polyaniline nanofibers were probed. The resulting products were characterized with scanning electron microscope (SEM), UV–vis spectroscopy and FT-IR spectroscopy.

2. Experimental

2.1. Chemicals

The monomer aniline (reagent grade) was distilled into colorless under reduced pressure prior to use. Other chemicals were reagent grade and used as received without further treatment. All of the aqueous solutions were prepared with double distilled water.

2.2. Synthesis

The electrochemical polymerization of aniline was carried out potentiostatically in a classical one-compartment three-electrode cell at ambient temperature, about 20 °C. An indium tin oxide conducting glass (abbreviated to ITO) or a platinum sheet was used as working electrode, another platinum sheet was used as counter electrode, and the reference electrode was saturated calomel electrode (SCE). All potentials given here are referred to the SCE. PANI films were obtained in a solution containing 0.2 mol dm^{-3} aniline, 1.0 mol dm^{-3} hydrochloric acid (HCl) with and without 0.5 mol dm^{-3} CH_3OH at 0.80 V, and the excellent cohesive films or product samples were formed on the ITO or platinum sheet. The films or product samples were rinsed with 1.0 mol dm^{-3} HCl, and latter was dried at 78 °C for 48 h. The films deposited onto electrode surfaces were directly characterized by SEM and UV–vis spectra.

2.3. Apparatus

A DH-1 potentiostat–galvanostat was used for electrochemical polymerization of aniline. The nanostructures were confirmed using a scanning electron microscope (SEM XL-30 ESEM). The molecular structures of resulting products were characterized by FTIR and UV–vis spectrometer. The UV–vis electronic absorption spectra of PANI films were obtained on UV-2550 spectrometer (Shimadzu) in the range of 300–900 nm. The FT-IR spectra of PANI powder samples were measured on a pressed pellet with KBr using an IFS66/S FTIR spectrometer (Bruker).

3. Results and discussion

3.1. Typical SEM images of PANI films

Fig. 1 shows SEM morphology of PANI film obtained in solution containing 0.2 mol dm^{-3} aniline and 1.0 mol dm^{-3} HCl with and without methanol deposited onto ITO, at 0.8 V, and the polymerization time is 15 min. From Fig. 1b, PANI nanofibers are observed obviously with diameter of approximately 150 nm, and the PANI nanofibers are very regular and uniform. Besides, these nanofibers tend to agglomerate into interconnected networks. Why does adding methanol favor the forming of fibular morphology? Whether does adding another alcohol into electrolyte solutions have similar effect? In order to confirm it, we add some different alcohols such as ethanol, propanol, and butanol during the polymerization process. The experiment results indicate that the PANI nanofibers can be synthesized in the presence of different alcohols, and PANI nanofibers containing different alcohols have similar microstructure.

The SEM morphologies in Fig. 2 indicate the PANI film synthesized in the presence of different alcohols present similar morphology. Why are different alcohols favorable for the shaping of polyaniline nanofibers? It has been reported [20] that methanol hydrogen bonds, via one of the lone pairs on its oxygen atom, with the sections of the polyaniline that are in the leucoemeraldine salt form (Fig. 3), or the methanol hydrogen also bonds directly to the emeraldine salt. The effect of the hydrogen bonding is to push the polymer chains apart. Al-Ghamdi and Al-Saigh also reported [21] that there existed strong intermolecular H-bonding between molecules of PANI and ethanol, and such interaction made the

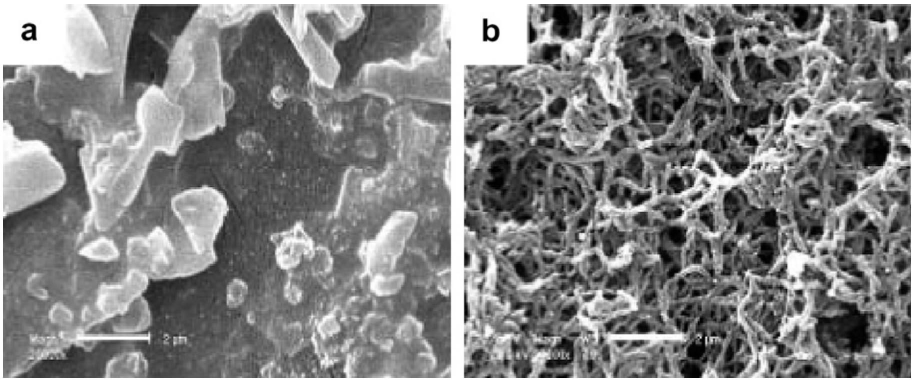

Fig. 1. The morphology of PANI films electrochemically synthesized under different conditions for 15 min: (a) 0.2 mol dm^{-3} aniline in 1.0 mol dm^{-3} HCl and (b) 0.2 mol dm^{-3} aniline in 1.0 mol dm^{-3} HCl with 0.5 mol dm^{-3} CH_3OH.

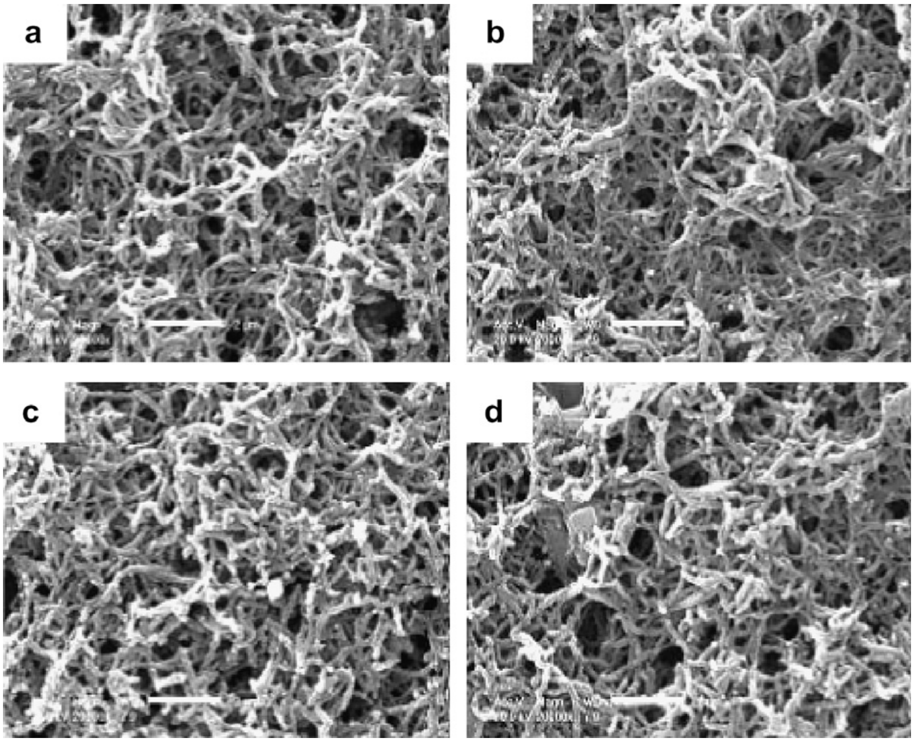

Fig. 2. The morphology of PANI films electrochemically synthesized under different alcohol solutions for 15 min: (a) 0.2 mol dm^{-3} aniline in 1.0 mol dm^{-3} HCl with 0.5 mol dm^{-3} CH_3OH, (b) 0.2 mol dm^{-3} aniline in 1.0 mol dm^{-3} HCl with 0.5 mol dm^{-3} C_2H_5OH, (c) 0.2 mol dm^{-3} aniline in 1.0 mol dm^{-3} HCl with 0.5 mol dm^{-3} C_3H_7OH and (d) 0.2 mol dm^{-3} aniline in 1.0 mol dm^{-3} HCl with 0.5 mol dm^{-3} C_4H_9OH.

PANI chains be wrapped by ethanol molecules. The intermolecular H-bonding interaction perpendicular to PANI chains is advantageous to the one-dimensional growth of PANI. In addition, because the alcohol is an amphipathic molecule, it may play the role of the surfactant molecule and wrap the PANI molecules. It has been resulted that the interactions between PANI chains and alcohol molecules may be much higher than the interaction between PANI chains and water molecules. Larger studies are needed to more thoroughly investigate the interaction between PANI chains and alcohol molecules. The radial growth of polymer nanowires overlaps and form 3D-interconnected polymer networks (Fig. 1b). Such morphologies are useful for applications such as electrode material of biosensor [22].

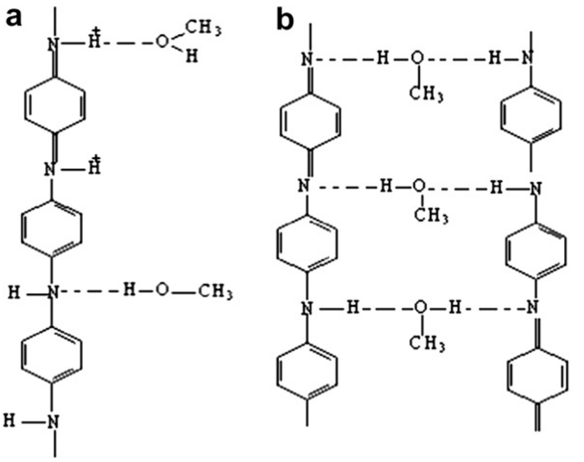

Fig. 3. Schematic representation of the proposed hydrogen bonding interaction between the methanol and the emeraldine salt (a) or its base (b).

3.2. Relationship between preparation conditions and morphology of PANI films

3.2.1. Effect of methanol concentration

Fig. 4 shows effect of methanol concentration on the morphology of PANI films deposited on the ITO in the solution containing 0.2 mol dm^{-3} aniline, 1.0 mol dm^{-3} HCl and methanol at 0.8 V. When the concentration of methanol is less than 0.3 mol dm^{-3} (Fig. 4a), the shaping PANI morphology tend to agglomerate into block, then PANI nanofibers prepared in higher methanol concentration (Fig. 4b) have more distinct morphology. It may be because that the polymer growth orientation is random because of the flexible chain structure of PANI. While the methanol concentration is too low, it does not prevent the PANI nanofibers agglomerating into together. The experiment results indicate that the content of methanol affected the growth of PANI nanofibers. Appropriate proportion methanol makes for the shaping of well-extended 1D nanofiber morphology.

3.2.2. Effect of hydrochloric acid concentration

The effect of hydrochloric acid concentration on the morphology of the PANI films synthesized at constant potential has been investigated. The corresponding morphologies of films are shown in Fig. 5. Compared Fig. 5b with Fig. 5a, the PANI film synthesized in 2.0 mol dm^{-3} hydrochloric acid shows the coexisting morphology of small particles and short fibers. According to shaping theory [23,24], the morphology of molecule is relevant to the corresponding size of polar group and alkyl group. So it may be because that the higher concentration hydrochloric acid affects the corresponding size of polar group and alkyl group of PANI, making them appear to the coexisting morphology of particles and fibers. The facts above-mentioned imply that too high concentration of HCl is disadvantageous to obtain the sole and regular PANI nanofibers.

3.2.3. Effect of electrode potential

Fig. 6 shows the effects of electrode potential on the morphology of PANI films, and the electrode potential was changed from 0.6 to 0.85 V. According to the experiment results, the fiber diameter increases from 80 to approximately 150 nm with increasing electrode potential. Apparently, the higher electrode potential can raise the rate of PANI polymerization and drop the wrapping rate of methanol, which is favorable for increasing PANI nanofiber diameter. So the diameter of nanofibers at 0.8 V is much larger

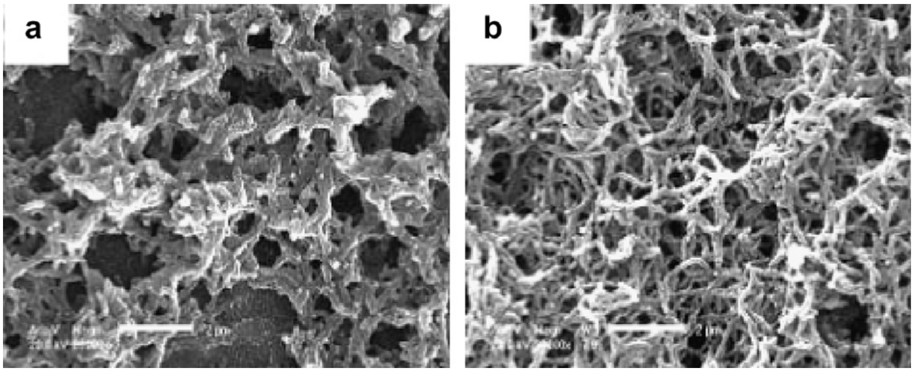

Fig. 4. SEM images of PANI prepared at various methanol concentration: aniline concentration = 0.2 mol dm^{-3}; HCl concentration = 1.0 mol dm^{-3}; 0.8 V potential; polymerization times 15 min; temperature = 20 °C. (a) 0.2 mol dm^{-3} and (b) 0.5 mol dm^{-3}.

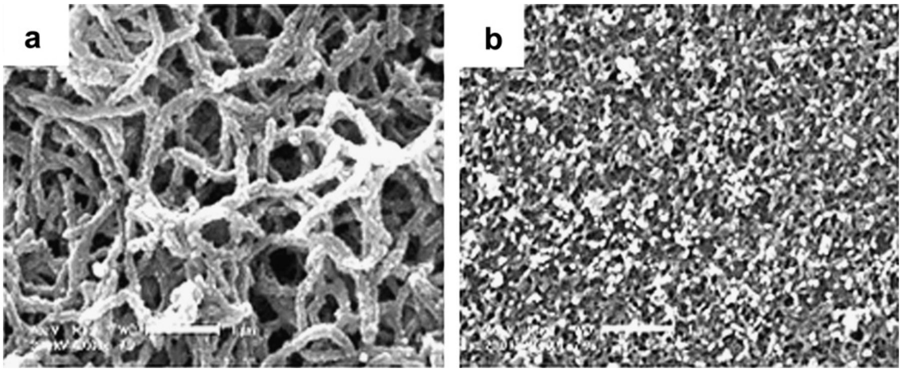

Fig. 5. SEM images of PANI prepared at various hydrochloric acid concentration: aniline concentration = 0.2 mol dm^{-3}; methanol concentration = 0.5 mol dm^{-3}; 0.8 V potential; polymerization times 15 min; temperature = 20 °C. (a) 1.0 mol dm^{-3} and (b) 2.0 mol dm^{-3}.

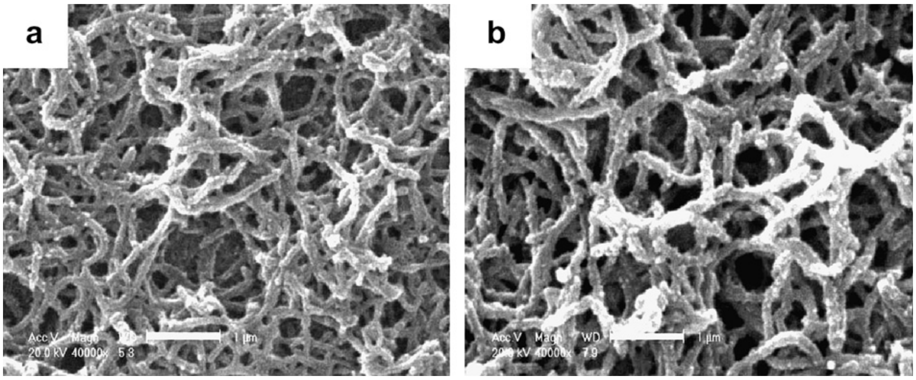

Fig. 6. SEM images of PANI prepared at various electrode potential: aniline concentration = 0.2 mol dm^{-3}; methanol concentration = 0.5 mol dm^{-3}; hydrochloric acid concentration = 1.0 mol dm^{-3}; polymerization times 15 min; temperature = 20 °C.

than that of nanofibers at 0.7 V. However, when the potential is less than 0.65 V or above 0.85 V, we cannot obtain uniform and regular PANI nanofibers. It may be due to that PANI cannot be synthesized when the potential is less than 0.65 V, while when the potential is above 0.85 V, PANI may be over-oxidized. So controlling potential the range from 0.65 to 0.8 V is favorable for shaping of uniform and regular PANI nanostructures.

3.2.4. Effect of temperature

The SEM images of PANI films prepared at various temperatures are shown in Fig. 7. It can be seen that the morphology of PANI film changes obviously with changing temperature. At the lower temperature (15–25 °C, Fig. 7a), the PANI film appears to regular and uniform nanofibers with diameter of approximately 150 nm. When the temperature is higher (⩾30 °C, Fig. 7b), the diameter of PANI nanofiber is above 200 nm, and in local region PANI tend to agglomerate into together. According to the literature [19], the electropolymerization and diffusion rates of monomer both increase with increasing temperature. And during low temperature range, the electropolymerization is the controlling step, which is good to the forming of nano-fibular PANI film. With the further increase of temperature, the diffusion of monomer may become the controlling process and monomer in the vicinity of electrode surface will be redundant, which is unfavorable for the growth of nanofiber.

Except for the effects of conditions mentioned above on morphology of PANI films, we also carried out the experiments about the effects of aniline concentration and polymerization time on PANI morphology. It has been found that aniline concentration controlling in the range from 0.15 to 0.4 mol dm^{-3} and polymerization time from 15 to 20 min are favorable for shaping of uniform and regular PANI nanofibers. Besides, during the electrochemical polymerization, slowly stirring is advantageous to the forming of uniform and regular

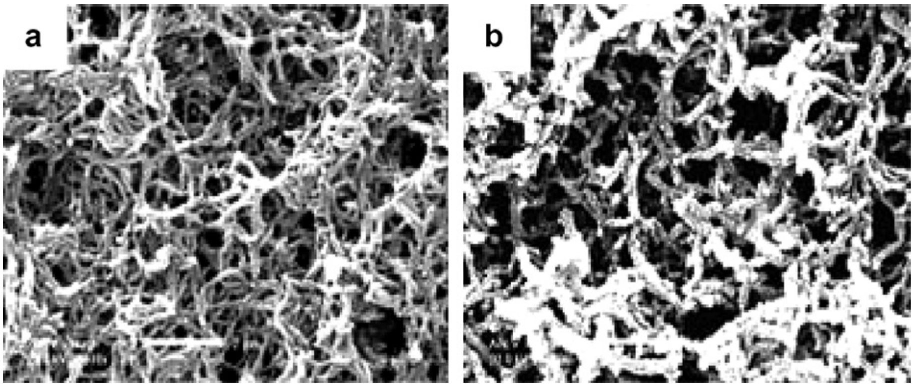

Fig. 7. SEM images of PANI prepared at various temperature: aniline concentration = 0.2 mol dm^{-3}; methanol concentration = 0.5 mol dm^{-3}; hydrochloric acid concentration = 1.0 mol dm^{-3}; polymerization times 15 min; 0.8 V potential. (a) 20 °C and (b) 30 °C.

PANI nanofiber, then quickly stirring is disadvantageous to that of PANI nanofibers.

3.3. UV–vis absorption spectra and FTIR spectra

3.3.1. UV–vis absorption spectra of PANI films

Fig. 8 shows UV–vis absorption spectra of PANI films deposited onto ITO, which were obtained in solution containing 0.2 mol dm^{-3} aniline, 1.0 mol dm^{-3} HCl with and without methanol. The PANI films formed at different conditions (Fig. 8) show three characteristic absorption bands at around 355, 430 and 815–825 nm. The characteristic peaks of PANI films appear at about 355 nm due to π–π* transition of the benzenoid ring and at about 430 nm and 815–825 nm due to polaron-π* and π-polaron band transitions [25], respectively. This shows that the above-mentioned PANI films are in the doped state. Compared with the PANI films doped by only hydrochloric acid (Fig. 8a), the absorption peaks (Fig. 8b) at 355 nm due to π–π* transition of the benzenoid rings and about 430 nm due to the polaron-π* bands are almost not shifted, and the peak due to π-polaron transition of PANI films obtained with methanol shift from 815 to 825 nm. The red shift implied that there exists interaction between PANI chains and methanol, which makes the energy gap of π-polaron narrower.

3.3.2. FTIR spectra of PANI products

Fig. 9 shows that the FTIR spectra of resulting products, which were synthesized electrochemically in the solution containing 0.2 mol dm^{-3} aniline, 1.0 mol dm^{-3} HCl with and without methanol. The

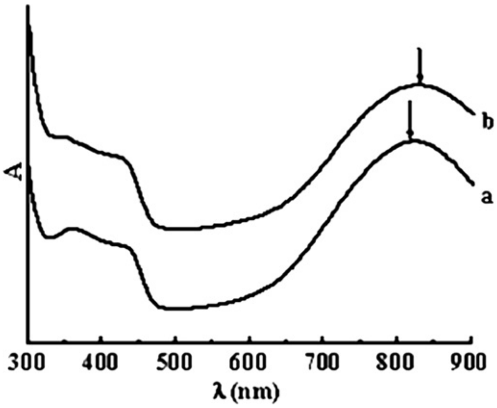

Fig. 8. The effect of methanol on the UV–vis spectra of PANI films deposited on the ITO: (a) 0.2 mol dm^{-3} aniline in 1.0 mol dm^{-3} HCl and (b) 0.2 mol dm^{-3} aniline in 1.0 mol dm^{-3} HCl with 0.5 mol dm^{-3} CH_3OH.

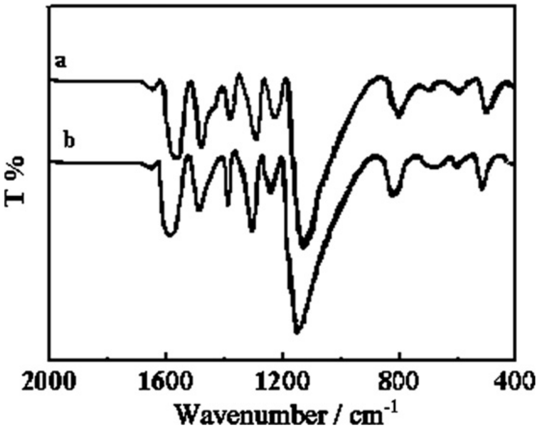

Fig. 9. FTIR spectra of PANI products deposited onto the platinum sheet at constant potential of 0.8 V: (a) 0.2 mol dm^{-3} aniline in 1.0 mol dm^{-3} HCl and (b) 0.2 mol dm^{-3} aniline in 1.0 mol dm^{-3} HCl with 0.5 mol dm^{-3} CH_3OH.

Table 1
FTIR band assignments of samples in Fig. 9

Sample	C=C quinoid ring (cm^{-1})	C=C benzoid ring (cm^{-1})	C—N (cm^{-1})	C=C quinoid ring (cm^{-1})	C—H (cm^{-1})
a	1576	1490	1298	1130	812
b	1582	1491	1302	1144	816

bands assignments of Fig. 9 are summarized in Table 1. The characteristic peaks at about 1576 and 1490 cm^{-1} correspond to the stretching vibrations of N=Q=N ring, N—B—N ring, respectively. The peak at 1300 cm^{-1} is attributed to C—N stretching vibration. The peaks at 1126 cm^{-1} and 808 cm^{-1} correspond to the characteristic of B—NH—Q or B—NH—B bonds, and out-of-plane bending vibration of C—H of benzene rings (where B refers to the benzenic-type rings and Q refers to the quinonic-type rings). The locations of these characteristic peaks present a good agreement with the literature [26,27], except for a few shifts in the wavenumbers. In addition, for all samples the bands located at about 3400 cm^{-1} and about 3200 cm^{-1} due to N—H bond stretching are not shown here.

When PANI was obtained in solution containing methanol, the peaks (curve (b)) of the quinoid unit shift to the higher wavenumber, other peaks are almost not shifted. Concretely, the existence of methanol makes the peak of the stretching vibrations of N=Q=N ring shift from 1576 cm^{-1} to 1582 cm^{-1}. In addition, the peak of B—NH—Q or B—NH—B bonds shifts 14 cm^{-1} towards higher wavenumber. According to the precision of TENSOR 27 FTIR spectrometer (4 cm^{-1}), the peaks shift of FTIR spectra may be caused by the H-bonding interaction between polyaniline chains and methanol. It is in agreement with the conclusions of UV–vis spectra.

4. Conclusion

In summary, a facile and economical electrochemical method of synthesizing the nanofibers of PANI with methanol was introduced. The reason about forming polyaniline nanofibers in the presence of alcohol was suggested. Synthetic conditions have great influences on the morphology of PANI. The high quality nano-fibular film can be obtained by constant potential method at the following conditions: 0.5 mol dm^{-3} methanol, 0.2 mol dm^{-3} aniline, 1.0 mol dm^{-3} HCl, polymerization time for 15 min, at 20 °C and 0.8 V. It is shown from UV–vis spectra and FTIR spectra that there exists interaction between methanol molecules and polyaniline chains.

Acknowledgement

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