

Synthesis and Properties of Polyaniline Nanolayers in the Presence of Retinol in Aqueous Ethanol

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Received 10 December 2007; accepted 22 June 2008

DOI 10.1002/app.28868

Published online 8 September 2008 in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: Polyaniline (PANI) nanolayers were shown to form spontaneously during the chemical oxidation in the presence of retinol using pure water and aqueous ethanol as reaction media. The effects of the retinol, the volume fraction of ethanol, and the acidity of the polymerization medium on the D.C. conductivity of PANI were investigated through two-probe method at room temperature. The introduction of 0.2 g retinol improved the D.C. conductivity value of PANI to 3.0 S/cm in pure water and 4.46 S/cm in 50% aqueous ethanol when the H^+ concentration was 0.5M. The D.C. conductivity values were 5.1 and 5.49 S/cm when the concentration of H^+ was 1.0M in pure water and 2.5M in 50% aqueous ethanol, respectively. The products were also

characterized by Fourier transform infrared spectroscopy, ultraviolet–visible spectroscopy, scanning electron microscope, cyclic voltammetry, and X-ray diffraction techniques. Moreover, the resulting PANI nanolayers exhibited an unusual electromagnetic loss at the microwave frequency ($f = 8.2\text{--}12.4$ GHz) and it arose from order arrangement of polaron as charge carrier caused by nanolayers morphologies and the materials can be used for the potential application as microwave absorbing materials. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 110: 3162–3171, 2008

Key words: polyaniline (PANI); template polymerization; retinol; nanolayers; electromagnetic loss

INTRODUCTION

Polyaniline (PANI) has generated tremendous interests due to their potential applications in batteries,¹ electrochromic display devices,² sensors,³ electromagnetic shields,⁴ etc. It is under intensive research and developed world wide both in academic world and in chemical and electronic industries for its good environmental stability, easy synthesis, and the electronic properties can be reversibly changed over the full range from an insulator to a metallic conductor. PANI has been considered as one of the most promising microwave absorbing materials because the electromagnetic parameters can be adjusted by changing both oxidation and protonation state. Therefore, several papers concerning influence of dopant nature and protonation state on the dielectric properties of PANI at the microwave frequency ($f = 8\text{--}12$ GHz) has been reported.^{5,6} All experimental results showed that PANI only exhibited an electrical loss. In fact, microwave absorbing materials are required to have both electrical and magnetic loss at the microwave frequency to satisfy the requirement for the application. Thus, it is necessary to improve

its absorbency and to expand the absorbing band at the microwave frequency. In general, there are two ways to solve the above issues. One is to blend PANI with inorganic magnetic materials to prepare composites. Another is to synthesize PANI with particular morphology such as tubes, layers, fibers, rods, etc, because theoretical calculations reveal that these materials exhibit unique absorption character.

There are a lot of routes for synthesizing PANI such as emulsion polymerization,⁷ template polymerization,⁸ interface polymerization,⁹ dispersion polymerization,¹⁰ “seeding” polymerization,¹¹ etc. The template polymerization has been paid more attention because this method can be used to synthesize the micro or nano PANI with particular physicochemical properties. Compared with the “hard” template, the “soft” template polymerization often use microstructure which is formed by the surface active agents or the dopant acid itself as the surface active agents because of the structure diversity and the morphology stability.¹² Furthermore, the surface active agents could be easily removed by rinsing with water or ethanol. PANI with particular morphological structure such as nanolines and nanoparticles has been synthesized in the presence of “soft” template such as soybean peroxidase, chondroitin sulfate, and β -cyclodextrin.^{13–15}

During the progress of these areas, many functional dopants have been introduced in the

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polymeric matrix by *in situ* doping method, such as amino acid,¹⁶ dodecylbenzenesulfonic acid, camphor-sulfuric acid, poly(ethenesulfonic acid), poly(styrene sulfonic acid), poly(acrylic acid), and so on.^{17,18} Based on earlier interesting phenomenon, it was assumed that the functional group (i.e., $-\text{C}=\text{C}-$, $-\text{C}=\text{O}$, $-\text{OH}$) might play a key role in the results of novel conducting polymers.¹⁹ Therefore, a program to research PANI in the presence of such functional group was considered. In the molecular structure of vitamin A acetic ether hydrolysis products, retinol, there are several conjugated double-bonds and the hydroxyl functional group. So PANIs are synthesized in the presence of retinol in either pure water or aqueous ethanol. As for there are no acidic ions in the molecule of retinol, we choose HCl for offering the acidic ions in the reaction media. Effects of the retinol, the ethanol volume fraction, and the acidity of the reaction media on the properties of PANI are also studied.

EXPERIMENTAL

Materials

The monomer of aniline (Tianjin Kermel Exploit Center of Chemical Reagent, China), ammonium peroxydisulfate (APS) (Jinbei Fine Chemical, China), acetone, hydrochloric acid (Xi'an Industry of Chemical Reagents, China), methanol (Tianjin Industry of Chemical Reagents, China), and vitamin A acetic ester (Runde Bioengineering, China) were analytical grade and used without further purification.

Instruments

The room temperature D.C. conductivity is measured through two-probe method using the resistivity meter (DM 618, Vector Apparatus, China) at room temperature. Dry powdered samples were made into pellets using a steel die of 2.0 cm diameter in a hydraulic press under a pressure of 20 MPa. The re-

sistance was recorded and the D.C. conductivity values were calculated directly from the measured resistance and sample dimensions. The reproducibility of the result was checked by measuring the resistance three times for each pellet. Infrared spectra in the range of $400\text{--}4000\text{ cm}^{-1}$ are recorded at 32 scans per spectrum at 2 cm^{-1} resolution using a fully computerized (WQF-31 model, Rui Li, China), where the samples are prepared in pellet form using spectroscopic-grade KBr powder. UV-vis electronic absorption of PANI solutions are recorded on a shimadzu 2550 UV-vis spectrophotometer using *N*-methyl-2-pyrrolidone (NMP) as solvent. SEM photographs are obtained with an Amray 1000B scanning electron microscopy. The surfaces are gold sputtered prior to observation. The cyclic voltammetry (CV) experiments were carried out by an electrochemical workstation (CHI660 model, Chenhua, China) in a three-electrode arrangement using graphite electrode as the working electrode, platinum electrode as auxiliary electrode, and calomel electrode as the reference electrode. For electrochemical study, 5.0 mg PANI synthesized with or without retinol were dissolved by NMP and coated on graphite electrode underwent cyclic voltammogram between -0.2 and 1.0 V versus SCE at the scan rate of 10 mV/s in 1.0 M HCl solution, respectively. X-ray diffraction pattern were recorded for the structural characterization of PANI on powder samples by a X'Pert MPD PRO instrument (PANalytical, Holland) from 5° to 50° at room temperature. The relative permittivity (ϵ) and permeability (μ) of the nanolayers at the microwave frequency ($8.2\text{--}12.4\text{ GHz}$) at room temperature were measured by HP8510B vector network analyzer.

Hydrolysis of vitamin A acetic ether

Definite dosage of vitamin A acetic ether is hydrolyzed under alkaline condition at 50°C . The reaction equation is showed in Figure 1.

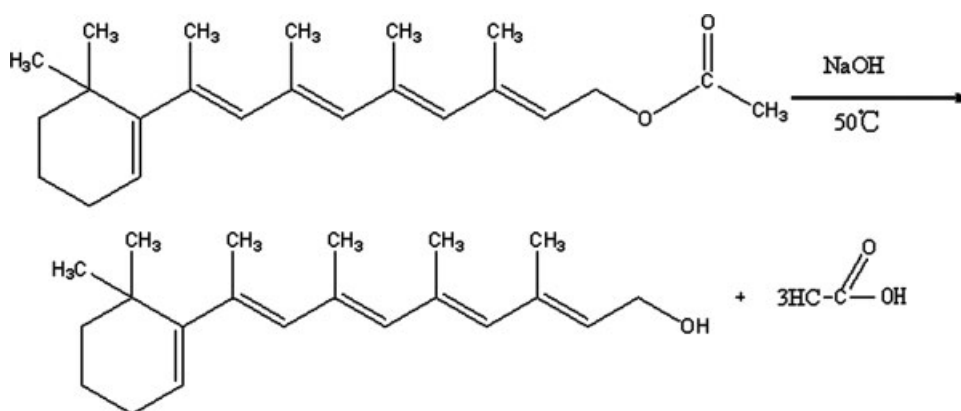


Figure 1 Reaction equation of the hydrolysis of vitamin A acetic ether.

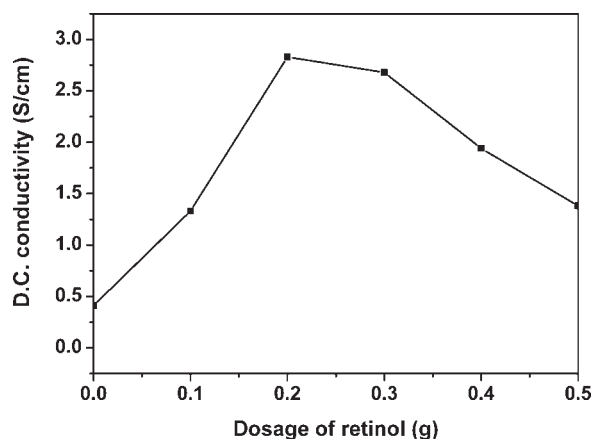


Figure 2 Effects of the dosage of retinol on the D.C. conductivity of PANI.

Synthesis of PANI in the presence of retinol

The chemical polymerization of aniline was carried out in the presence of retinol using HCl as acidic dopant, pure water and aqueous ethanol as reaction media, respectively. Aqueous solution of oxidant, APS at appropriate concentration was added to the reaction media in dropwise fashion in 1 h using a dropping funnel. The polymerization temperature was controlled at 0–5°C. The reaction time is 5 h after APS of aqueous solution is dropped wholly. Then PANI doped by HCl is collected on a filter and rinsed by acetone, ethanol, and deionized water to remove the oligomer and the retinol and dried in a vacuum oven at room temperature.

RESULTS AND DISCUSSION

Effect of the retinol dosage on the D.C. conductivity of PANI

Figure 2 shows the effect of the retinol dosage on the D.C. conductivity of PANI. As shown in Figure 2, the D.C. conductivity value of PANI synthesized in pure water without any retinol is 0.41 S/cm and then increases with increase in the retinol dosage. When the retinol dosage is 0.2 g the D.C. conductivity value reaches 2.83 S/cm, while the dosage increases to 0.5 g when the value decreases to 1.38 S/cm. The conjugated structure in the retinol molecule has a stronger effect on the polymerization of aniline and then induces the increase in the D.C. conductivity value of PANI.²⁰ The D.C. conductivity of PANI will decrease following sequentially increasing in the retinol dosage as the hydroxyl group in retinol is easy to nucleophilic invade the radical cation in the reaction intermediate, and has an accessory effect on the polymerization of aniline.

Effects of the ethanol volume fraction on the D.C. conductivity of PANI

The effects of the ethanol volume fraction in the reaction media on the D.C. conductivity of PANI are illustrated in Figure 3. From Figure 3 it is observed that the increase in the D.C. conductivity with the ethanol volume fraction seems to be significant at the lower ethanol volume fraction. In case of PANI synthesized in 50% aqueous ethanol, the value of D.C. conductivity reaches 4.46 S/cm. However, the D.C. conductivity value is found to decrease with sequential increase in the ethanol volume fraction. The increase in D.C. conductivity is due to the more regular structure of PANI caused by the H-bonding between the polymer chains and the ethanol molecule. The H-bonding affects the chain alignment of the polymer that leads to increasing conjugation length in PANI chains and brings about the increase in the D.C. conductivity.²¹ With the increase in the ethanol volume fraction, the decrease in the D.C. conductivity of PANI may be due to the hydroxyl group in ethanol, which has an accessory effect on the polymerization of aniline.

Effect of $[H^+]$ in the reaction media on the D.C. conductivity of PANI

As the hydroxyl group is easy to nucleophilic invading the radical cation in the reaction intermediate, the hydroxyl group in the retinol molecule also has an accessory effect on the polymerization of aniline. Some literature²² has reported that PANI with good electrical properties can be synthesized through reducing the ability of the nucleophilic invasion by turning $-OH$ to $-OH_2^+$ at the acidic condition. So PANIs are synthesized with different acidity in either pure water or aqueous ethanol with or without retinol as “soft template” in this work. The

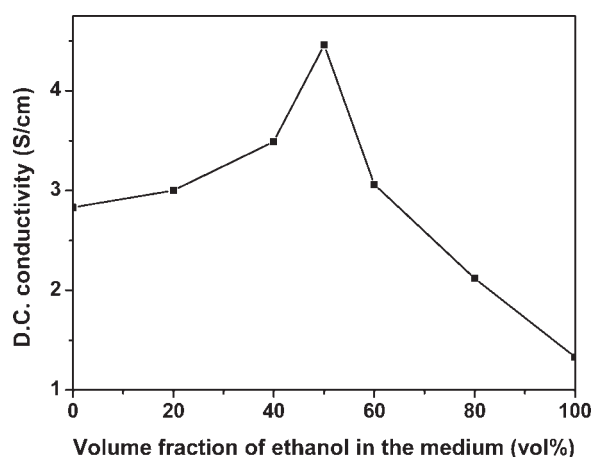


Figure 3 Effect of the ethanol volume fraction in the polymerization medium on the D.C. conductivity of PANI.

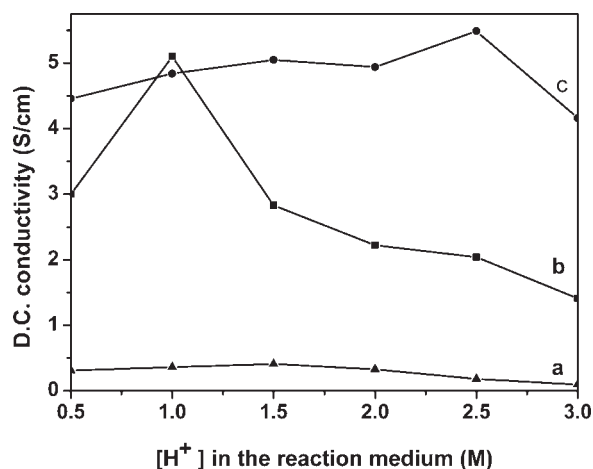


Figure 4 Effects of the $[H^+]$ on the D.C. conductivity of PANI synthesized in: (a) pure water without retinol; (b) pure water with retinol; (c) 50% aqueous ethanol with retinol.

results are showed in Figure 4. From Figure 4 it is observed that the D.C. conductivity value of PANI is 0.31 S/cm when the H^+ concentration is 0.5M in pure water without any retinol, and that of PANIs synthesized with retinol are 3.0 and 4.46 S/cm when the H^+ concentration are 0.5M in pure water and 50% aqueous ethanol, respectively. It increases to 0.41 S/cm when the concentration of H^+ in pure water is 1.5M for PANI synthesized without retinol. And for PANI synthesized with retinol the values are 5.1 S/cm when the concentration of H^+ is 1.0M in pure water and 5.49 S/cm when the concentration of H^+ is 2.5M in 50% aqueous ethanol. The optimal H^+ concentration in aqueous ethanol is higher than that in pure water, because the effective concentration in aqueous ethanol is lower than that in pure water at the same H^+ concentration. Following increasing concentration of H^+ , the D.C. conductivity value is reduced to 1.41 S/cm when the concentration of H^+ is 3.0M in pure water. The D.C. conductivity value of PANI synthesized in aqueous ethanol shows a slight decrease with increasing concentration of H^+ . The D.C. conductivity value of PANI reduces distinctly in the presence of excessive acid ions because the conjugate structure of PANI is demolished by the superfluous covalent bonds between PANI and the chlorine ion and this is no better for the transmission on the PANI molecular chains. In the PANI synthesized in the higher concentration aqueous HCl medium the proportion of the $-N-$ in amine structure is higher than 0.5 which means that the imine structure is changed to amine structure during the addition reaction of the quinonyl unit by HCl.²³ This is the reason that the D.C. conductivity value of PANI decreases following increasing concentration of H^+ in the reaction media.

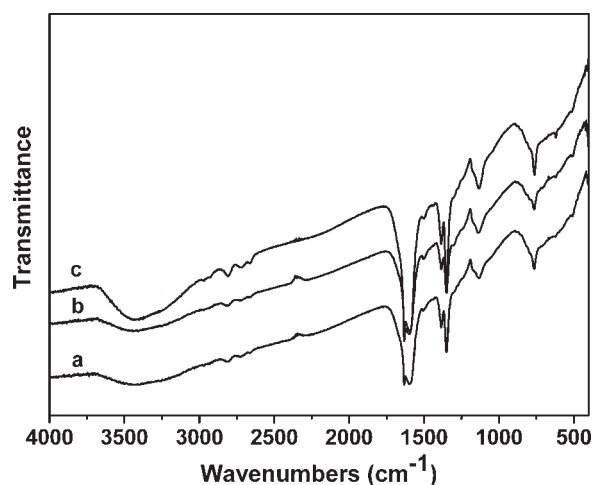


Figure 5 FTIR absorbance of PANI synthesized in pure water, aqueous ethanol in the presence of retinol, separately: (a) in pure water without retinol; (b) in pure water with retinol; (c) in aqueous ethanol with retinol.

FTIR analysis

The molecular structures of resulting PANI synthesized in the presence of retinol in pure water and aqueous ethanol were characterized by Fourier transform infrared (FTIR) spectra and shown in Figure 5. It can be seen that these spectra are in good agreement for PANI with previously reported results.²⁴ The single band at 766 cm^{-1} was reported for representing in plane C–H bending motions of benzenoid rings. 1385 and 1350 cm^{-1} for C–N stretching and 1631 and 1591 cm^{-1} consistent with the stretching vibrations of $N=Q=N$ rings, $N-B-N$ rings, respectively. The strong characteristic band appearing at 1140 cm^{-1} which was described as the “electron-like band” and is considered to be a measure of delocalization of electrons and, thus, it is a characteristic peak of PANI with excellent conductivity.

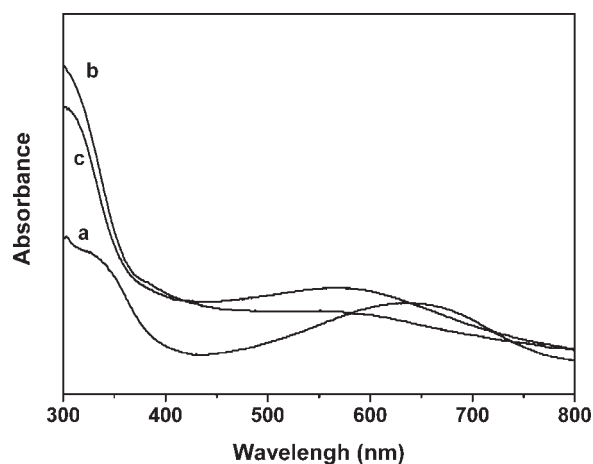


Figure 6 UV-vis absorption spectra of PANI synthesized in the presence of retinol: (a) 0.0 g; (b) 0.2 g; (c) 0.5 g.

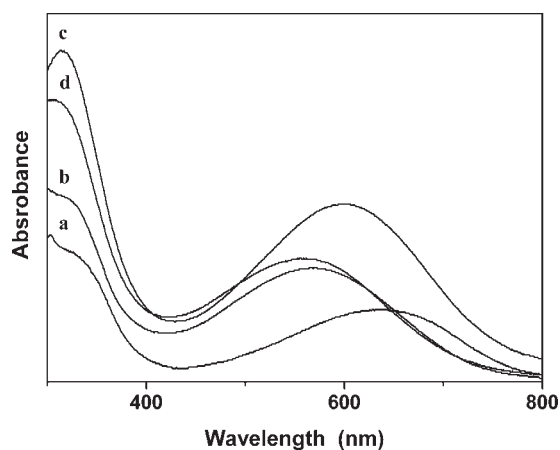


Figure 7 UV-vis absorption spectra of PANI synthesized in aqueous ethanol: (a) 0%; (b) 20%; (c) 50%; and (d) 80%.

UV-vis spectra

The electronic absorption spectra of PANI synthesized in the presence of 0 g [Fig. 6(a)], 0.2 g [Fig. 6(b)], and 0.5 g [Fig. 6(c)] retinol are given in Figure 6. All spectra show an absorption band at 330–400 nm. The bands are associated with the π - π^* tran-

sition of the aromatic rings. Compared with Figure 6(a), the absorption peaks between 330 and 400 nm are slightly blue-shifted in Figure 6(b,c). That means the π - π^* transition of the aromatic rings is affected by the conjugated structure in the retinol molecule. The characteristic peaks of PANI appearing at about 500–750 nm correspond to the transition from a localized benzenoid highest occupied molecular orbital, that is, a benzenoid to quinoid excitonic transition.^{25,26} This shows that the above-mentioned PANIs are in the doped state. Because of π -polaron transition of PANI the peaks shift from 650 to 600 nm. The blue shift implies that there exists interaction between PANI chains and the conjugated structure of the retinol molecule, which makes the energy gap of π -polaron narrower and the absorbance higher.

Figure 7 presents the UV-vis absorption spectra of PANI synthesized in aqueous ethanol with retinol, (a) 0%; (b) 20%; (c) 50%; and (d) 80%, respectively. Compared with pure water, the PANI synthesized in aqueous ethanol has two similar absorption peaks. It is interesting to note that by increasing the ethanol volume fraction in the reaction media, the

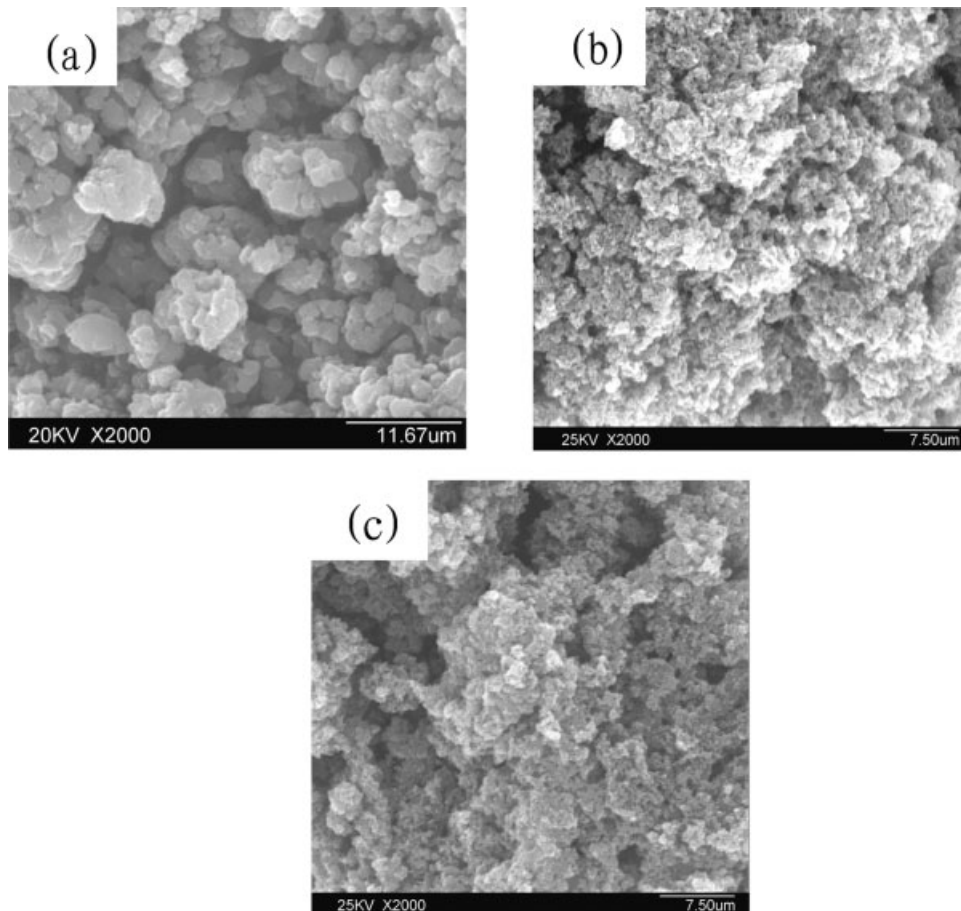


Figure 8 SEM photographs of PANI synthesized in the presence of retinol: (a) 0.0 g; (b) 0.2 g; (c) 0.5 g.

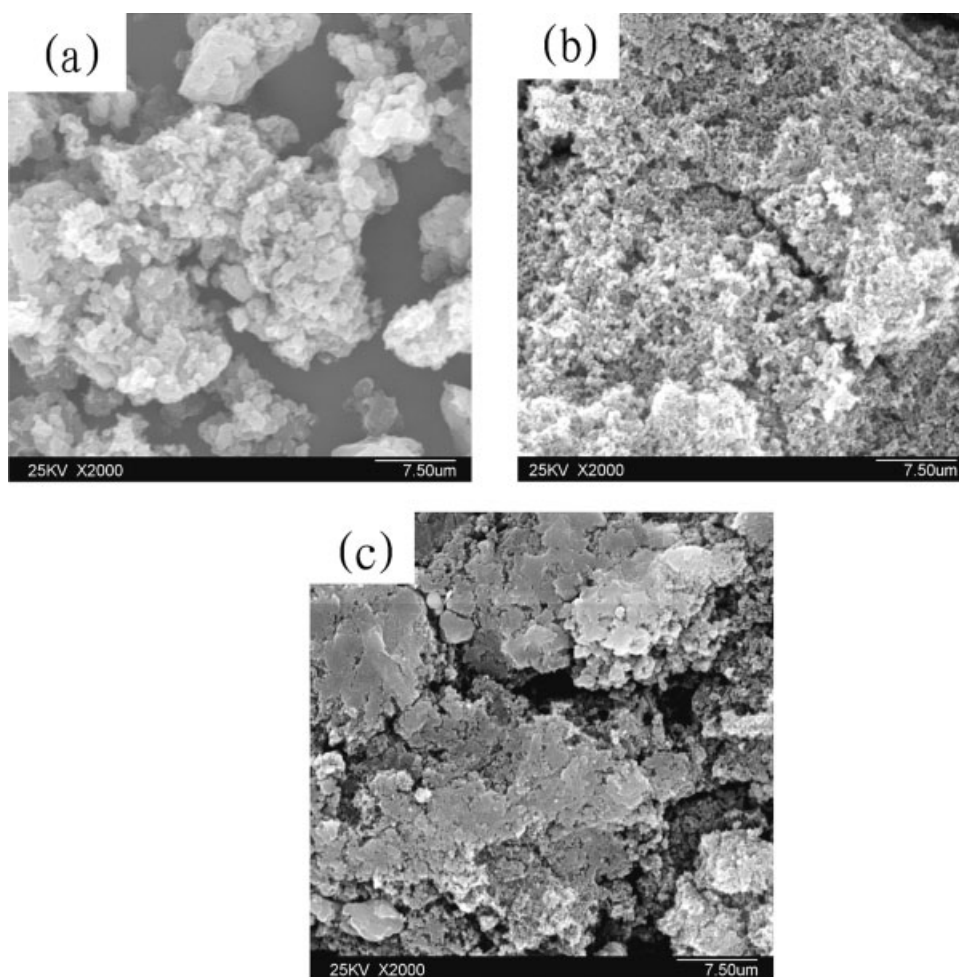


Figure 9 SEM photographs of PANI synthesized in aqueous ethanol in the presence of retinol: (a) 20%; (b) 50%; and (c) 80%.

polaron band exhibits a blue shift and appears at the lower wavelength. The blue shift of the peaks are much less obvious when the ethanol volume fraction is 50%, which indicates that the polarons in PANI synthesized under this condition are much less delocalized than that of others PANI. Owing to the addition of large amounts of ethanol, the PANI may become less compatible with excessive ethanol and the segments increase of PANI tend to decrease the contact with the ethanol by coiling the chains. It is deduced that excessive ethanol has negative effects on the synthesis of PANI.²⁷

SEM studies

The scanning electron microscopy (SEM) images of PANI synthesized in the presence of 0.0 g [Fig. 8(a)], 0.2 g [Fig. 8(b)], and 0.5 g [Fig. 8(c)] retinol are presented in Figure 8. From the SEM photographs, the order of the PANI particles size synthesized in the presence of retinol is following: (b) < (c) < (a). The result confirms that the smaller the particle size of

PANI the higher the D.C. conductivity value of PANI; due to the smaller particle size of PANI, the porosity and the contact resistance between the particles of PANI reduces.²⁸

The SEM images of PANI synthesized with different ethanol volume fraction: 20% [Fig. 9(a)], 50% [Fig. 9(b)], and 80% [Fig. 9(c)] are shown in Figure 9. From the SEM photographs, the order of the PANI particles size synthesized in aqueous ethanol is following: (b) < (c) < (a). That means that there are H-bonding between the polymer chains and the ethanol molecule, and the morphologies of PANI are affected by the ethanol volume fraction.

The nanolayer morphologies of the PANI synthesized with different concentration of H⁺ in pure water: (a) 0.5M, (b) 2.5M, (c) 3.0M and in aqueous ethanol: (d) 0.5M, (e) 2.5M, and (f) 3.0M were shown in Figure 10. The basic morphological units of the PANI synthesized in the pure water are microparticles and nanolayers [shown in Fig. 10(a–c)] while there are mainly nanolayers in the photograph of the PANI synthesized in aqueous ethanol [Fig. 10(d–f)].

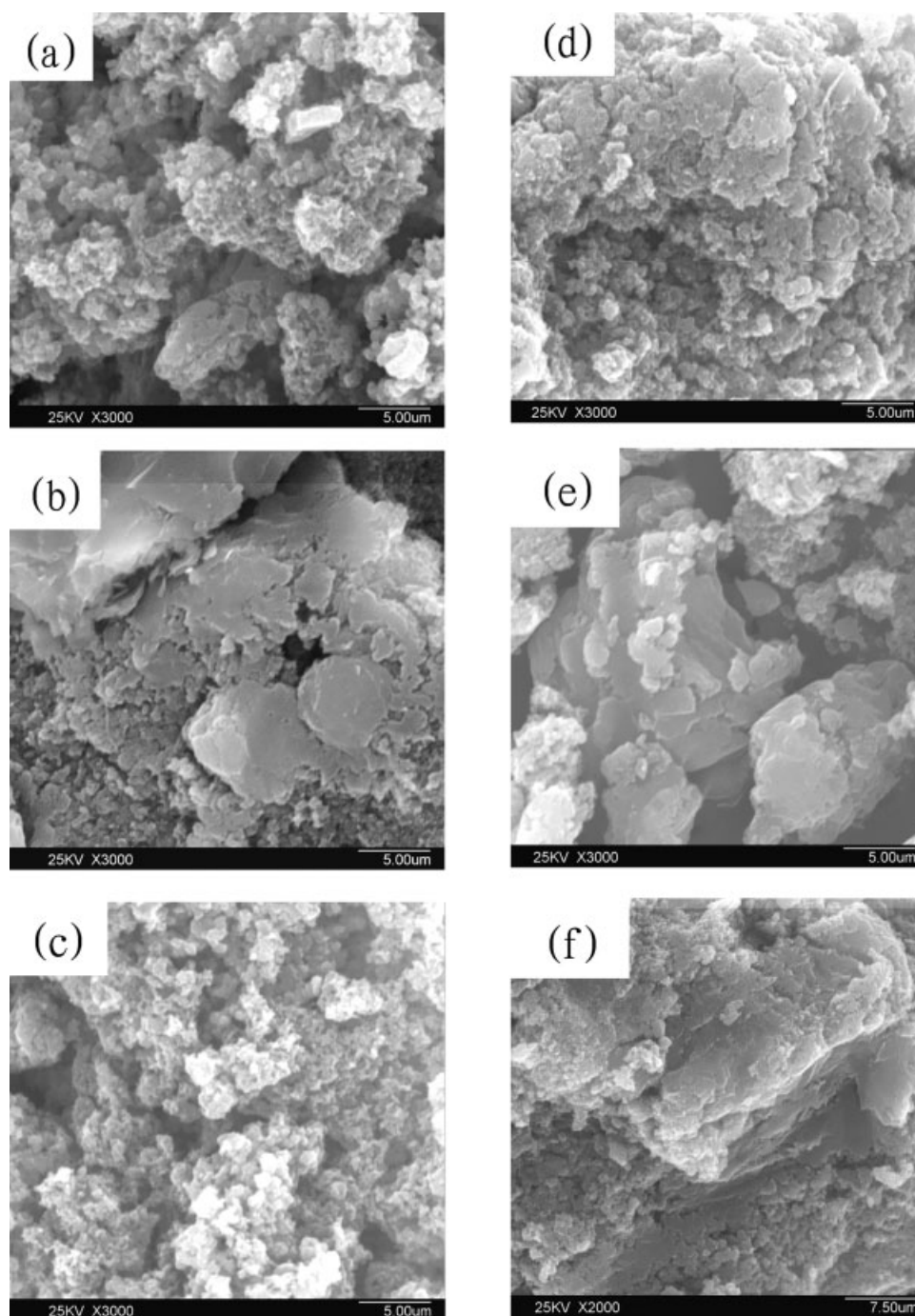


Figure 10 SEM photographs of PANI synthesized with different concentration of H^+ in pure water: (a) 0.5M, (b) 2.5M, (c) 3.0M and in aqueous ethanol: (d) 0.5M, (e) 2.5M, and (f) 3.0M.

It is illustrated that the nanolayers of PANI is easily synthesized in aqueous ethanol under the action of the H-bonding between PANI, ethanol molecule, and retinol.

Cyclic voltammetry

The redox behavior of PANI was studied using CV. As shown in (Fig. 11), the cyclic voltammogram of

PANI synthesized in pure water without retinol [Fig. 11(a)], PANI synthesized in pure water with retinol [Fig. 11(b)], and PANI synthesized in aqueous ethanol with retinol [Fig. 11(c)] exhibits two redox couples, respectively. The first redox couples could be attributed to the leucoemeraldine to emeraldine transition, and the second one is due to the transition from the emeraldine to pernigraniline state.²⁹ The CV curves of PANI synthesized with

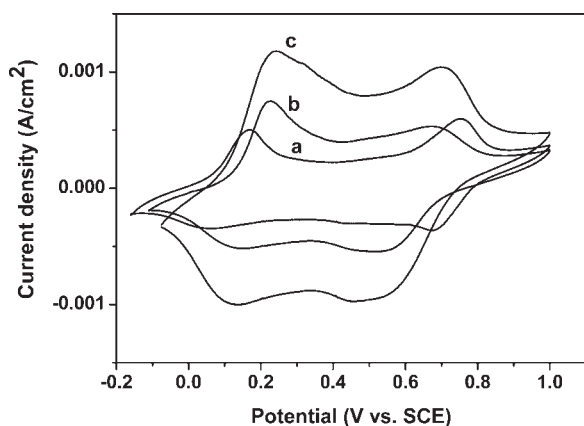


Figure 11 Cyclic voltammograms (recorded at 10 mV/s in 1.0M HCl) of PANI synthesized in pure water without retinol (a), in pure water with retinol (b), and in aqueous ethanol with retinol (c).

retinol in general resemble that of PANI synthesized without retinol, except that the first peak for PANI synthesized with retinol shifts to a more positive potential and the second peak shift to a more negative potential than that of PANI synthesized without retinol, which implies that the conversion of the leucoemeraldine to emeraldine state is slightly faster for PANI synthesized with retinol, and suggests that the reversibility of the redox process of PANI is apparently improved by retinol.

X-ray diffraction spectra

The X-ray diffraction spectra (XRD) pattern of PANI synthesized in pure water without retinol (a), in pure water with retinol (b), and in aqueous ethanol with retinol (c) are presented in Figure 12. As shown in Figure 12, PANI synthesized in aqueous ethanol with retinol showed unusual crystallinity. Three sharp peaks located at $2\theta = 30^\circ\text{--}40^\circ$, which are attributed to the periodicity perpendicular to the chain direction, were also observed.³⁰ It is noted that the intensity of these sharp peaks is induced when the PANI is synthesized in aqueous ethanol in the presence of retinol. It is apparent that the crystallinity of PANI synthesized in aqueous ethanol is higher compared with PANI synthesized in pure water, which is consistent with the D.C. conductivity of PANI.

ELECTROMAGNETIC PARAMETERS

As one knows, the relative permittivity (ϵ) and permeability (μ) are expressed as:

$$\epsilon = \epsilon' - \epsilon''j \quad (1)$$

$$\mu = \mu' - \mu''j \quad (2)$$

$$\tan \delta_e = \frac{\epsilon''}{\epsilon'} \quad (3)$$

$$\tan \delta_m = \frac{\mu''}{\mu'} \quad (4)$$

where ϵ' , ϵ'' , μ' , and μ'' are the real and ideal part of the permittivity and permeability, respectively. While $\tan \delta_e$ and $\tan \delta_m$ are the electrical and magnetic loss, respectively. It has been demonstrated that the doped PANI with HCl granules synthesized by a conventional method³¹ only exhibited an electrical loss at the microwave frequency ($f = 8\text{--}12$ GHz).³² However, the resulting nanolayers PANI synthesized in aqueous ethanol in the presence of retinol showed both electrical and magnetic loss at the microwave frequency ($f = 8.2\text{--}12.4$ GHz), as observed in Figure 13(b). The electrical and magnetic loss of the microparticles PANI synthesized in pure water without any retinol are also shown in Figure 13(a) as the reference. Compared with 1.79, the highest electrical loss, $\tan \delta_e$, of the microparticles PANI at 8.47 GHz and 0.72, the highest magnetic loss, $\tan \delta_m$ at 10.93 GHz, it was noted that the highest electrical loss, $\tan \delta_e$, of PANI nanolayers reached 1.98 at 10.4 GHz, and the highest magnetic loss, $\tan \delta_m$, was 2.24 at 9.67 GHz. The conducting PANI in its emeraldine base form, when protonated by HCl acid solution, possesses permanent electric dipoles. Therefore orientation (dipolar) polarization is the dominant polarization and the associated relaxation phenomena constitute the loss mechanisms. PANI with nanolayers morphology show unusual electromagnetic loss probably arose from partial order of

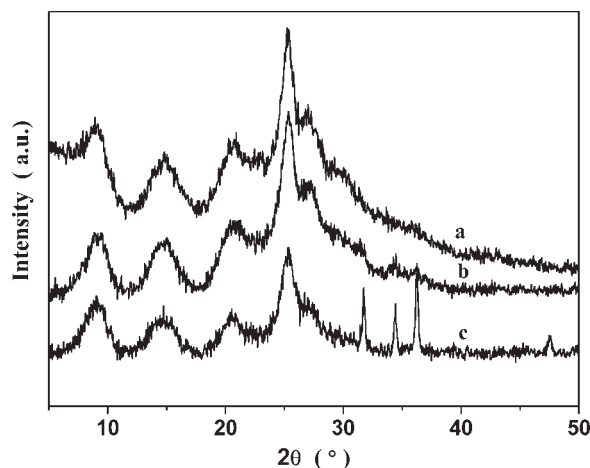


Figure 12 X-ray diffraction patterns for polyaniline synthesized in pure water without retinol (a), in pure water with retinol (b), and in aqueous ethanol with retinol (c).

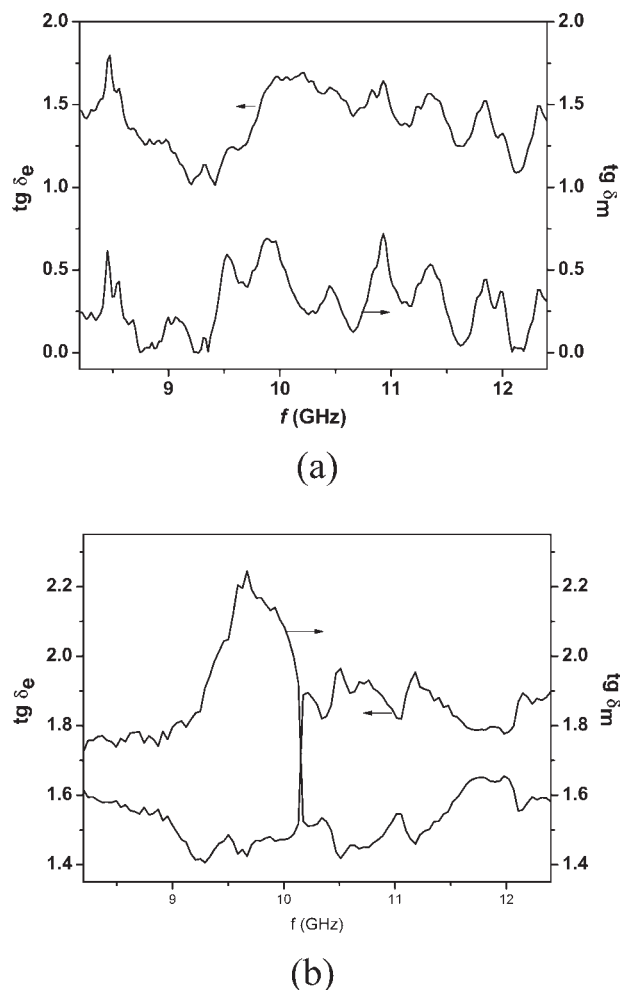


Figure 13 Dependence of the microwave frequency on the electromagnetic loss of the PANI synthesized in pure water without retinol (a) and in aqueous ethanol with retinol (b).

the polaron and charge carrier,³³ which shows paramagnetic behavior³⁴ caused by nanolayers morphology of PANI. We believe that the PANI nanolayers synthesized by a template method in the presence of retinol are useful for the potential application as microwave absorbing materials.

CONCLUSIONS

In summary, PANIs were prepared in the presence of retinol with different degrees of acidity in either pure water or aqueous ethanol via chemical oxidation method. The effects of retinol, the ethanol volume fraction, and the acidity on the D.C. conductivity of PANI are investigated through two-probe method at room temperature. The results imply that with increasing retinol dosage the D.C. conductivity value of PANI decreases first and then increases. With increasing ethanol volume fraction

and the acidity of the reaction media, the D.C. conductivity value of PANI increases first and then decreases. FTIR indicate that retinol slightly affect the molecular structure of PANI. UV-vis spectra illustrate that there are some H-bonding between the PANI chains and the ethanol molecule. The morphology of the PANI synthesized in aqueous ethanol in the presence of retinol is mainly nanolayers structure because of the H-bonding between the polymer chains, the ethanol molecule, and retinol. The cyclic voltammogram of PANI suggests that the reversibility of the redox process of PANI is apparently improved by retinol. It has been demonstrated that an unusual magnetic loss at $f = 8.2\text{--}12.4$ GHz for the resulting PANI nanolayers was observed and it arose from partial order of the polaron as charge carrier caused by a nanolayers morphology.

The authors appreciate the help of Ms. Li Liefeng for SEM photograph, and thank Mr. Liu Yuyang for the UV-vis tests. The authors are also thankful to the companies who kindly offered the materials.

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