

Effects of Magnetic Field and Rare-Earth Ions on Properties of Polyaniline Nanoparticles

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ABSTRACT: The uniform polyaniline nanoparticles with the size of about 50 nm were electropolymerized using the method of constant potential of 0.8 V. The effects of rare-earth cations and magnetic field on the preparation and properties of polyaniline were investigated. It was found that the addition of rare-earth cations could enhance the effect of magnetic field on the properties of polyaniline. The resulting products were characterized by FTIR spectra, UV-vis spectra and scanning electron microscope (SEM); the conductivity and cyclic voltammetry (CV) were also investigated. The experimental results show that the magnetic

field has an orientation effect on polyaniline chain and there exists the interaction between rare-earth cations and polyaniline chain because of the electrostatic interaction. The addition of rare-earth cations can increase electrical conductivity, moreover, the effect of NdCl₃ and ErCl₃ on properties of polyaniline is more remarkable than LaCl₃ and SmCl₃. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 103: 2286–2294, 2007

Key words: polyaniline; nanoparticles; cyclic voltammetry; scanning electron microscope; FTIR spectra; UV-vis spectra

INTRODUCTION

Among all conductive polymers, polyaniline (PANI) has been the subject of intense investigations during the last two decades because of its desirable electrical, electrochemical, and optical properties coupled with excellent environmental stability.^{1,2} Low production cost and relatively simple to synthesize, high electrical conductivity and unique redox properties, it has immense industrial potential for a number of applications.^{3–5} However, since the strong rigidity and interaction between the PANI chains, its solubility and processability are very bad, which affect its applications deeply. To make it easily to be processed, it is very important to make tentative to improve synthesis conditions of PANI.

The problem of interaction of conductive polymers, especially PANI, and metal ions is of great importance, because of the fact that this may give rise to novel chemical and physical properties of the formed macromolecular complex. Recently, it was reported that PANI could interact with many heavy metal ions^{5,6} and rare-earth cations.^{7,8} Because of special electronic properties of rare-earth elements viz: their f–f electronic transitions of rare-earth elements are relatively insensitive to perturbations in their chemical

environment, complex formation of lanthanide ions with organic polymers is of particular interest. This aspect of rare earth–polymer complexes is important in respect to their potential applications in the field of research as well as industrial applications, for example, as using for emitting elements in organic light-emitting devices (OLEDs)^{9–11} as well as dopant additions to enhance quantum yield in OLEDs,¹² using for catalyst for some polymer reactions^{7,13}

The magnetic field can influence on the chemical reaction containing radicals and can induce orientation of most organic polymer molecules and biological macromolecules because of the magnetic susceptibility anisotropy.^{14,15} Some articles concerning the effect of magnetic field on the chemistry and electrochemistry reaction have been published.^{16,17} The existence of paramagnetic ions (for example, RE³⁺) in solutions can greatly increase the effects of magnetic alignment and improve the properties of a polymer,¹⁸ which may lead to the wider application foreground of complex of conducting polymer with RE³⁺. In electrochemical systems,¹⁹ a Lorentzian force will act on the valence electrons when magnetic field coupling with an electric field, this force leads to migration of ions and generates solution streaming, i.e., the magnetohydrodynamic (MHD) effect,²⁰ and then enhances mass transfer. However, because of the fact that the polymer cannot form a suitable ligand environment around the lanthanide ion,⁷ the articles concerning the effects of magnetic field as well as rare-earth cations on properties of PANI nanoparticles are few. So, lots of studies about the rare-earth–organic polymer com-

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plexes are needed. It was previously observed^{17,21} that the electropolymerization rate of PANI could be enhanced obviously under a magnetic field. Cai et al.²² investigated the effects of rare-earth cations on the training and properties of PANI obtained at magnetic field.

In this paper, we present new results about the effects of rare-earth cations (La^{3+} , Nd^{3+} , Sm^{3+} , Er^{3+}) and magnetic field on the electropolymerization of PANI. It was surprising for us to find that PANI nanoparticles with the size of about 50 nm can be prepared in a solution containing rare-earth cations in the presence of magnetic field using the method of constant potential. The cyclic voltammograms (CVs) for electrolysis of aniline and conductivity of the product were studied, and some properties of resulting product were characterized by scanning electron microscope (SEM), UV-vis, and FTIR spectra.

EXPERIMENTAL

The aniline (reagent grade) was distilled into colorless under reduced pressure prior to use. All rare-earth chlorides (LaCl_3 , NdCl_3 , SmCl_3 , and ErCl_3) were of 99.9% purity. Other chemicals were reagent grade and used as received without further treatment. All of the aqueous solutions were prepared with double distilled water.

The electrochemical polymerization of aniline was carried out in a classical three-electrode cell at ambient temperature, approximately 26°C. The gold-sprayed quartz glass (abbreviated to GQG) or the platinum sheet was used as working electrode, another a platinum sheet was used as counter electrode, and reference electrode was saturated calomel electrode (SCE). A vertical magnetic field was imposed with respect to the electrode surface unless otherwise stated. All potentials given here are referred to an SCE. A DH-1 potentiostat-galvanostat was used for electrochemical polymerization of aniline. PANI films were obtained using a method of constant potential (0.8 V) in a solution containing 0.2 mol dm^{-3} aniline, 1.0 mol dm^{-3} hydrochloric acid (HCl), and rare-earth cations in the absence and presence of magnetic field. After deposition, the films were rinsed with 0.5 mol dm^{-3} HCl. The cyclic voltammograms during polymerization of aniline were recorded using a YEW 3036 X-Y recorder, the sweep rate is 60 mV s^{-1} and the sweeping potential range is between -0.1 and 1.0 V versus SCE.

The morphologies of PANI films were observed using a scanning electron microscope (SEM XL-30 ESEM). The UV-vis electronic absorption spectra of all samples were obtained on UV-2550 spectrometer (Shimadzu) in the range of 300–900 nm. FTIR measurements of the samples were performed on a FTIR spectrometer (Bruker, model Tensor 27) in the 4000–400

cm^{-1} range with 4 cm^{-1} resolutions, pressed pellets were prepared of the powder samples ground with KBr for this purpose, and the powder samples were obtained using platinum sheet as working electrode at constant potential of 0.8 V. Conductivity of the resulting products were measured using conventional four-probe technique on pressed pellets of the powder samples prepared at 26°C. The magnetic field was applied by a home-made permanent magnet.

RESULTS AND DISCUSSION

Effect of magnetic field and rare-earth cations on cyclic voltammograms

Figures 1(a) and 1(b) show the cyclic voltammograms (CVs) for electrochemical polymerization of aniline in the solution containing 0.2 mol dm^{-3} aniline and 1.0 mol dm^{-3} HCl using platinum sheet as working electrode in the absence and presence of magnetic field. In Figure 1(a), with number of potential cycles, three pairs of redox peaks labeled as A/A'-C/C' are observable for the electropolymerization in the range of 0.05–0.80 V, and their peak currents increase, which means that autocatalytic polymerization occurs during electrolysis of aniline.²³ At anodic peak 0.18 V, the radical cation may be generated upon oxidation (polaron state),²⁴ or it can be assigned to the transport of proton into PANI chain.²⁵ While at anodic peak 0.79 V, diradical dications may be generated, which is attributed to the further oxidation of PANI to the form of quinoid (bipolaron state). And the "middle" peak at 0.48 V derives mainly from the redox reactions of oligomers and the degradation products including *p*-benzoquinone, quinoneimines, *p*-aminodiphenylamine, hydroquinone and *p*-aminophenol.^{26–28}

From a comparison of Figures 1(a) and 1(b), the polymerization behavior with magnetic field [Fig. 1(b)] is similar in shape to that without magnetic field [Fig. 1(a)], indicating that the mechanism of aniline polymerization is not remarkably affected by magnetic field. However, the potential and current of peaks increase with increasing potential cycles during electrolysis of aniline, and the color of the films becomes darker. Furthermore, the peak currents become bigger to the corresponding cycle, for example, the peak current of A on the final cycle in Figure 1(b) is approximately twenty-fold than that in Figure 1(a). This result indicates that the rate of aniline polymerization is undoubtedly enhanced by the presence of magnetic field. According to the previous literature,²⁹ the electropolymerization of aniline follows a coupling growth mechanism with the formation of radical cations. In the presence of magnetic field, the magnetic field coupled with the electric field can generate the MHD effect,²⁰ which enhances mass transfer and made the electropolymerization rate faster, this is the

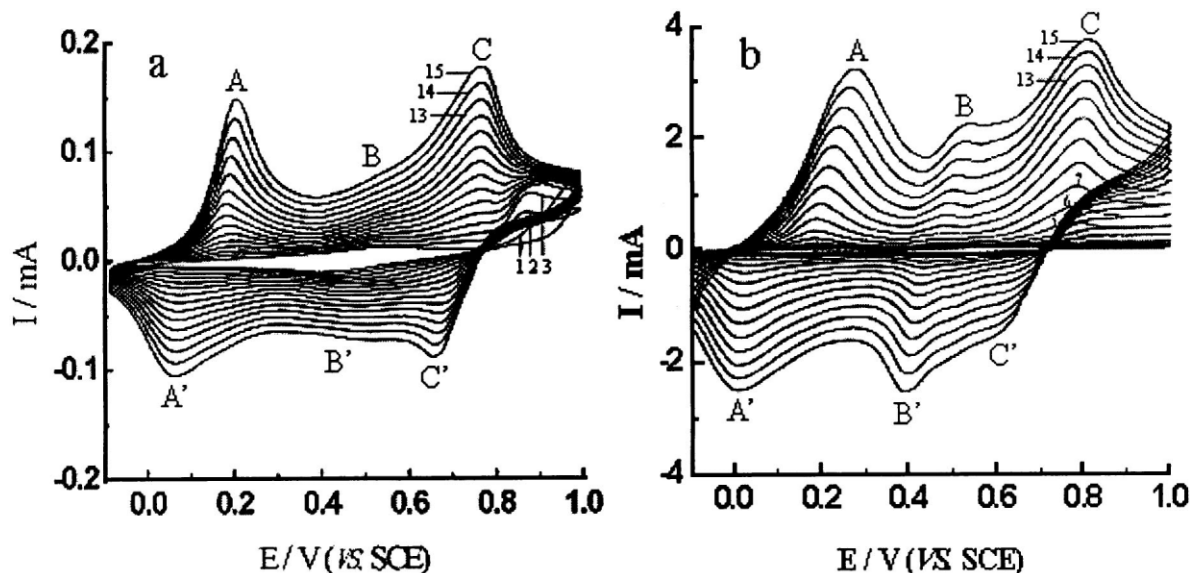


Figure 1 Cyclic voltammograms of PANI film growth on platinum sheet at 60 mV s^{-1} (a) 0.2 mol dm^{-3} aniline + 1.0 mol dm^{-3} HCl, 0 mT . (1) first cycle, (2) second cycle, . . . , (15) fifteen cycle (b) 0.2 mol dm^{-3} aniline + 1.0 mol dm^{-3} HCl, 760 mT , (1) first cycle, (2) second cycle, . . . , (15) fifteen cycle.

reason why the peaks current in Figure 1(b) are bigger than that in Figure 1(a).

Figure 2(a) shows the cyclic voltammograms of PANI film growth in the solution containing 0.2 mol dm^{-3} aniline, 1.0 mol dm^{-3} HCl, and 0.2 mol dm^{-3} ErCl_3 using platinum sheet as working electrode. Because of adding ErCl_3 in solution, the corresponding peak current in Figure 2(a) is bigger than that in Figure 1(a) and the anodic peak at 0.79 V shifts toward the

higher potential, 0.81 V . The effect of rare-earth cation Er^{3+} in solution on polymerization of aniline is considerable in the collaborative effects of counter ions and ion pairs in the electrolyte. Er^{3+} is doped into PANI films, followed by the equivalent number of anions in the electrolyte intercalated in the PANI layer²²; the increase of the amount of anions is advantageous to faster electron transfer and maintains the conductive state of the films,^{30,31} which results in in-

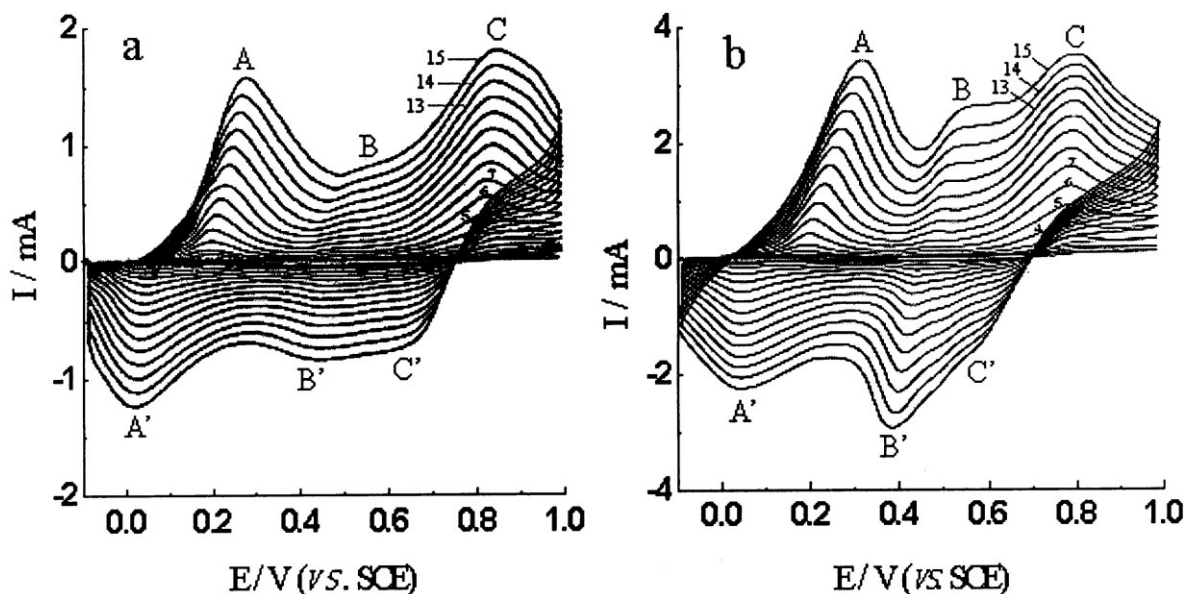


Figure 2 Cyclic voltammograms of PANI film growth on platinum sheet at 60 mV s^{-1} . (a) 0.2 mol dm^{-3} aniline + 1.0 mol dm^{-3} HCl + ErCl_3 , 0 mT . (1) first cycle, (2) second cycle, . . . , (15) fifteen cycle (b) 0.2 mol dm^{-3} aniline + 1.0 mol dm^{-3} HCl + ErCl_3 , 760 mT . (1) first cycle, (2) second cycle, . . . , (15) fifteen cycle.

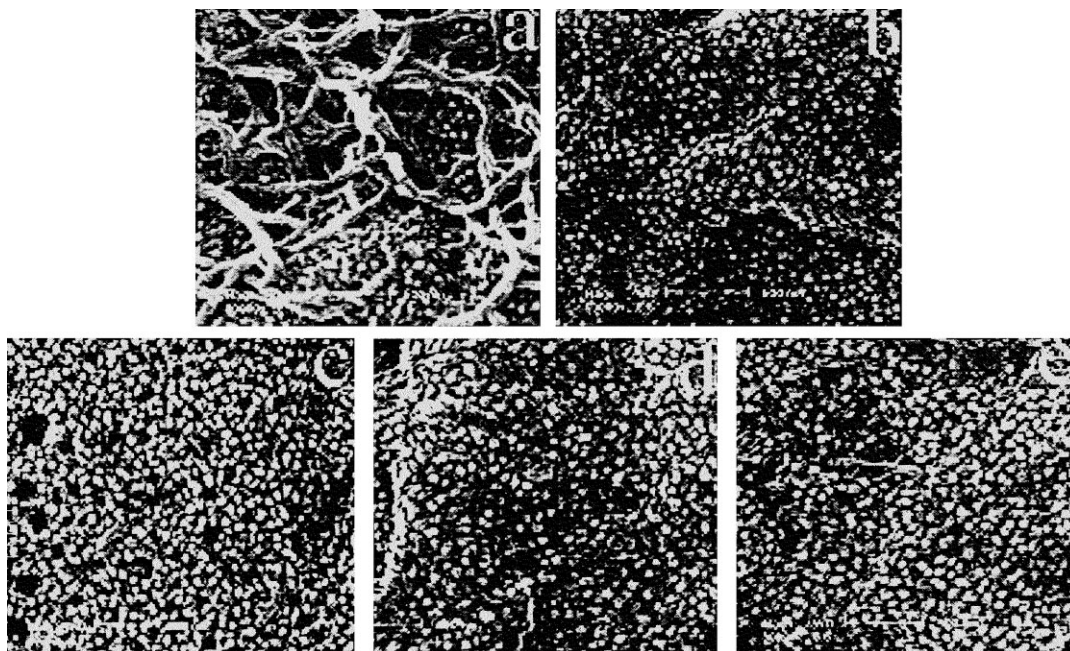


Figure 3 SEM morphologies of PANI films deposited onto GQG using the method of constant potential, 0.8 V. (a) 0.2 mol dm⁻³ aniline + 1.0 mol dm⁻³ HCl; (b) 0.2 mol dm⁻³ aniline + 1.0 mol dm⁻³ HCl + 0.2 mol dm⁻³ LaCl₃; (c) 0.2 mol dm⁻³ aniline + 1.0 mol dm⁻³ HCl + 0.2 mol dm⁻³ NdCl₃; (d) 0.2 mol dm⁻³ aniline + 1.0 mol dm⁻³ HCl + 0.2 mol dm⁻³ SmCl₃; (e) 0.2 mol dm⁻³ aniline + 1.0 mol dm⁻³ HCl + 0.2 mol dm⁻³ ErCl₃.

creasing of the polymerization rate. The shift of anodic peak from 0.79 to 0.81 V shows that the generation of diradical dications was more difficult to take place when the electrochemical polymerization was performed in the solution containing ErCl₃. This may be interpreted by the fact that there exists the interaction between Er³⁺ and intermediate corresponded by anodic peak at 0.48 V, then the formation of quinoid was inhibited. The corresponding peak current in Figure 2(b) are obviously bigger than that in Figure 2(a), it is suggested that the effect of magnetic field can be greatly enhanced in the presence of paramagnetic rare-earth cation. Moreover, in the presence of magnetic field, it is found that the effect of the Er³⁺ ion on CV is larger than that of the La³⁺, Nd³⁺, and Sm³⁺ ions (their CVs are not presented), the peak current A/A'-C/C' on the final cycle in Figure 2(b) is biggest. In view of the Nd³⁺, Sm³⁺, Er³⁺ are paramagnetic cations and their magnetic moment is 3.4 B.M, 1.74 B.M and 9.9 B.M, respectively, the Er³⁺ ion has a bigger magnetic moment, which is favorable for magnetic orientation effect in the presence of magnetic field. So, it is suggested that the larger the magnetic moment of the ion, the more obvious is the effect of magnetic field.

The SEM morphology of the PANI films

Figure 3(a) shows SEM morphology of PANI film deposited onto GQG in the solution containing 0.2 mol

dm⁻³ aniline and 1.0 mol dm⁻³ HCl using method of constant potential of 0.8 V, and the polymerization time is for 5 min. It is seen from Figure 3(a) that the PANI film presents interconnected network-like nanofibers morphology, moreover, there are some nanoparticles formed in the interspaces of nanofibers. Apparently, the diameters of nanofibers and nanoparticles of PANI film are <50 nm. When different rare-earth cation of same molar ratio as aniline was added into the solution, the PANI film presents pure nanoparticles morphology [Figs. 3(b)–3(e)], and the particles become distinct and uniform. Moreover, it is very interesting that the nanoparticles of PANI films obtained with rare-earth cations Nd³⁺ and Er³⁺ tend to more distinct and regular [Figs. 3(c) and 3(e)]. As mentioned earlier, the rare-earth cations are doped into the PANI film and they may coordinate with PANI chain, followed by the equivalent number of anions in the electrolyte intercalated in the PANI layer, the increase of the amount of anions is favorable for faster electron transfer,^{30,31} which results in increase of the polymerization rate. The mutual attraction, coordination, and stabilization of the anions for Nd³⁺ and Er³⁺ ions are much stronger than that of the La³⁺ and Sm³⁺ ion.²² So, the PANI chains doped Nd³⁺ and Er³⁺ would form a higher ordered structure.

Figure 4 shows SEM morphologies of PANI films obtained in the solution containing 0.2 mol dm⁻³ aniline, 1.0 mol dm⁻³ HCl and 0.2 mol dm⁻³ different rare-earth cations, using the method of constant po-

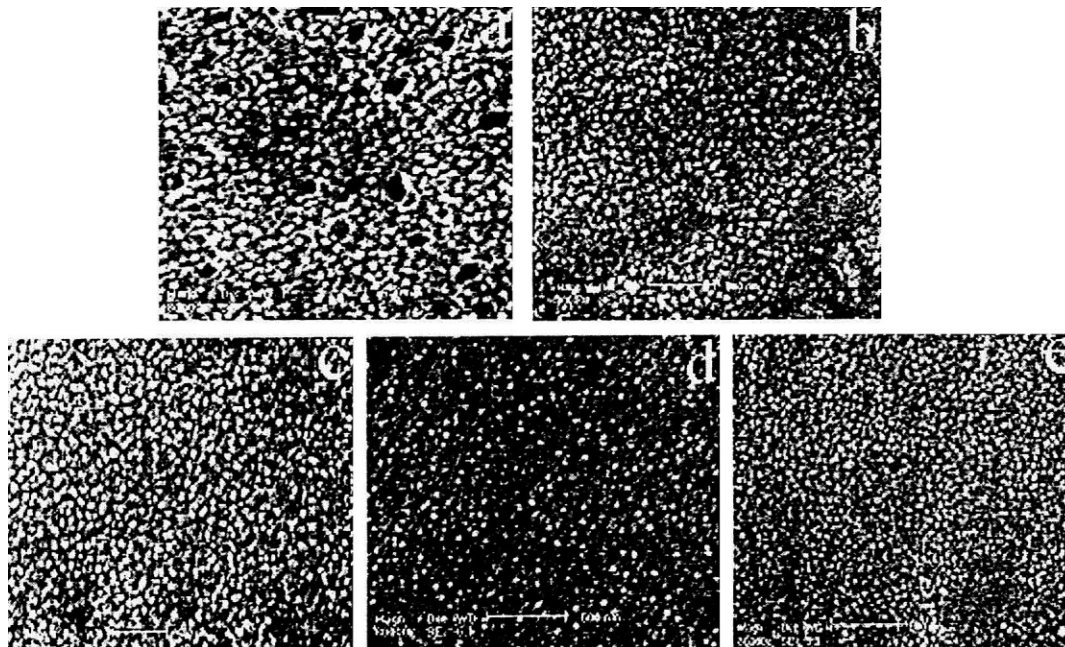


Figure 4 SEM morphologies of PANI films deposited onto GQG at magnetic field of 760 mT using the method of constant potential, 0.8 V. (a) 0.2 mol dm^{-3} aniline + 1.0 mol dm^{-3} HCl; (b) 0.2 mol dm^{-3} aniline + 1.0 mol dm^{-3} HCl + 0.2 mol dm^{-3} LaCl_3 ; (c) 0.2 mol dm^{-3} aniline + 1.0 mol dm^{-3} HCl + 0.2 mol dm^{-3} NdCl_3 ; (d) 0.2 mol dm^{-3} aniline + 1.0 mol dm^{-3} HCl + 0.2 mol dm^{-3} SmCl_3 ; (e) 0.2 mol dm^{-3} aniline + 1.0 mol dm^{-3} HCl + 0.2 mol dm^{-3} ErCl_3 .

tential of 0.8 V, which deposited onto GQG at magnetic field of 760 mT for 5 min. It is found that the PANI particles are all $<50 \text{ nm}$ in the five pictures of Figure 4. However, compared with Figure 3(a), Figure 4(a) presents pure nanoparticles morphology and nanofibers disappeared. It is suggested that an external magnetic field (B_p) imposed vertical to the electrode surface can affect the morphologies of PANI films. When the PANI films were prepared in the presence of different rare-earth cations and magnetic field of 760 mT, the PANI nanoparticles become more and more compact and uniform, and the nanoparticles besprinkle the whole PANI films, the particle sizes are relatively smaller than the others. As for Nd^{3+} -doped and Er^{3+} -doped PANI films, these phenomena are especially obvious. It was known that the magnetic field has the effects of orientation and stretching,³² the PANI chains can be arranged in a more regular and ordered way, leading to the oriented growth of PANI. In addition, when adding NdCl_3 and ErCl_3 in the solution, the Nd^{3+} and Er^{3+} are doped into the PANI film and they may coordinate with PANI chain.³³ Moreover, the Nd^{3+} and Er^{3+} are paramagnetic cations, and they have a bigger magnetic moment, which is favorable for magnetic orientation effect in the presence of strong magnetic field, the PANI chains doped Nd^{3+} and Er^{3+} would form a more ordered structure electro synthesized in the presence of magnetic field. The two factors earlier mentioned may be the reasons for obtaining more compact and uniform PANI nano-

particles shown in Figures 4(c) and 4(e). These results reveal the collaborative effects of rare-earth cations and magnetic field. The added paramagnetic ions interact strongly with the external magnetic field; they are trapped in the PANI chain or attach themselves loosely to the PANI backbone. When the growth of PANI is under the field's influence, the reactive molecules are aligned, and the insertion of paramagnetic ions greatly speeds up the alignment process.²² PANI chains are formed more regularly, and electron transfer is increased along the chains, which results in a more compact and uniform of morphology. The results also show that the effects of the larger magnetic moment ion on PANI nanoparticles are more obvious in the presence of magnetic field, which is consistent with the CVs.

Conductivity of resulting products

Table I gives the effects of rare-earth cations on the conductivity (σ) of the resulting products measured at 26°C . All samples were synthesized electrochemically in 1.0 mol dm^{-3} HCl aqueous solutions containing 0.2 mol dm^{-3} aniline and different rare-earth cations. By analyzing the conductivity values of all samples, it can be seen clearly that the conductivities of rare-earth cations-doped PANI enhanced, moreover, conductivities of doping Nd^{3+} and Er^{3+} PANI are bigger than that of the others. These results reveal the effects of rare-earth cation on the conductivity and the para-

TABLE I
Effects of Rare-Earth Cations on Conductivity of Resulting Products

Sample	σ (S cm ⁻¹)
PANI-HCl	2.74
PANI/La ³⁺	3.15
PANI/Nd ³⁺	4.37
PANI/Sm ³⁺	3.84
PANI/Er ³⁺	6.06

magnetic cations Nd³⁺ and Er³⁺ with larger magnetic moment induce higher conductivity, which is comparable with HCl-doped PANI. This may be due to the fact that the added rare-earth cations can interact with PANI chain,²² they are trapped in the PANI chain or attach themselves to the PANI backbone, then PANI chains are formed more regularly, and electron transfer is increased along the chains, which results in an increase of conductivity. In addition, according to literature,³⁴ the PANI subchains become more rigid and ordered under the influence of rare-earth cations, the Nd³⁺ and Er³⁺ ions with larger magnetic moment lead to a higher degree of chain orientation, which results in a more compact structure leading to a high degree of crystallinity. It has been known that PANI of high crystallinity has a higher conductivity than amorphous one,³⁵ that is to say, the higher crystalline order of the PANI chains causes a decreased separation of the chains and increased conductivity. So, it was understandable that the conductivity of PANI/Nd³⁺ and PANI/Er³⁺ powder is higher than that of the others.

UV-vis spectra of PANI films

Figure 5 shows UV-vis absorption spectra of PANI films deposited onto GQG, which were obtained in the solution containing 0.2 mol dm⁻³ aniline, 1.0 mol dm⁻³ HCl, with and without rare-earth cation. The PANI films formed at different conditions show three characteristic absorption bands at around 356–360, 421–426, and 807–842 nm, as exemplified in Figure 5. The absorption peak at ~356–360 nm corresponds to π - π^* transition of the benzenoid rings, while the peaks at ~421–426 nm can be assigned to the localized polaron bands which are the characteristics of protonated PANI together with extended tail at ~807–842 nm representing the conducting emeraldine salt phase of the polymer.³⁶ This suggests that the above-mentioned PANI films are in the doped state. According to literatures^{37–39}, the peaks at ~421–426 nm and ~807–842 nm are related to doping level and formation of polaron. Based on the previous research that the extent of doping can roughly be estimated from the absorption spectra of the PANI, in which the ratio of absorbencies at 807–842 nm (π -polaron) and 356–360

nm (π - π^* transition) indicated the doping level of PANI,⁴⁰ it was found that in the case of PANI salts the intensity ratio was smallest in PANI-HCl, which meant that the doping level of PANI-HCl was lower than that of PANI-rare-earth cations, and the doping level of PANI-ErCl₃ was highest.

Compared with the PANI films doped by only protonic acids [Fig. 5(a)], the absorption peaks because of π - π^* transition of the benzenoid rings and π -polaron transition of PANI films obtained with rare-earth cations [Fig. 5(b–e)] appear at the longer and shorter wavelength, respectively, and the peaks at about 421–426 nm because of the localized polaron bands are almost not shifted. The absorption peak at 356 nm [Fig. 5(a)] shifted to 360 nm when the PANI films doped by LaCl₃, NdCl₃, and ErCl₃, excepted for SmCl₃-doped shifted to 362 nm. The red shift may be due to the adding rare-earth cations made the conjugation chain enlarged, which made the energy for π - π^* transitions smaller. The absorption peak at 842 nm [Fig. 5(a)] shifted to 832, 811, 807, and 818 nm, respectively. The result indicates that there exists interaction between rare-earth cations and PANI chain,³³ which makes the energy transitions for π -polaron larger. In addition, the adding rare-earth cations diffuse into the PANI chain leading to increasing of the coordination of rare-earth cations with PANI chain and improve the doping degree of PANI.

Figure 6 shows UV-vis absorption spectra of PANI films deposited onto GQG, which were obtained in the solution containing 0.2 mol dm⁻³ aniline, 1.0 mol dm⁻³ HCl, with and without rare-earth cation, in the absence and presence of magnetic field. Compared to that of PANI films (Fig. 5) obtained without magnetic

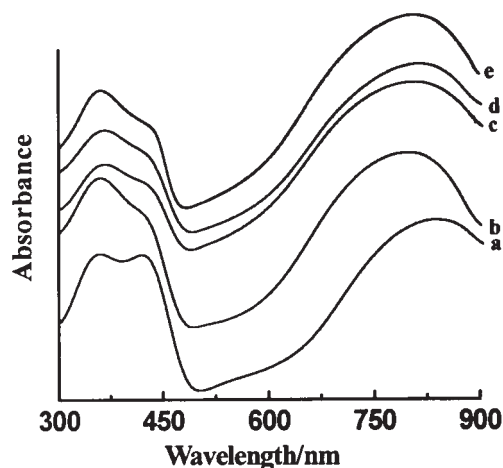


Figure 5 UV-vis absorption spectra of PANI films deposited onto the GQG at constant potential of 0.8 V. (a) 0.2 mol dm⁻³ aniline + 1.0 mol dm⁻³ HCl; (b) 0.2 mol dm⁻³ aniline + 1.0 mol dm⁻³ HCl + LaCl₃; (c) 0.2 mol dm⁻³ aniline + 1.0 mol dm⁻³ HCl + NdCl₃; (d) 0.2 mol dm⁻³ aniline + 1.0 mol dm⁻³ HCl + SmCl₃; (e) 0.2 mol dm⁻³ aniline + 1.0 mol dm⁻³ HCl + ErCl₃.

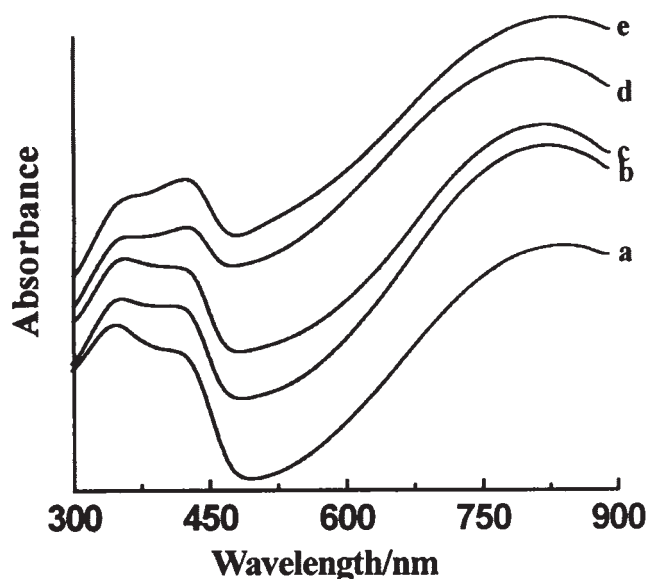


Figure 6 UV-vis absorption spectra of PANI films deposited onto the GQG at constant potential of 0.8 V, in the presence of magnetic field, 760mT. (a) 0.2 mol dm⁻³ aniline + 1.0 mol dm⁻³ HCl; (b) 0.2 mol dm⁻³ aniline + 1.0 mol dm⁻³ HCl + LaCl₃; (c) 0.2 mol dm⁻³ aniline + 1.0 mol dm⁻³ HCl + NdCl₃; (d) 0.2 mol dm⁻³ aniline + 1.0 mol dm⁻³ HCl + SmCl₃; (e) 0.2 mol dm⁻³ aniline + 1.0 mol dm⁻³ HCl + ErCl₃.

field, the UV-vis absorption peaks of PANI films obtained in the presence of magnetic field because of π - π^* transition and π -polaron transition are shifted apparently, as shown in Figure 6. The absorption peaks of π - π^* transition of PANI films appear at the shorter wavelength, and the absorption peaks of π -polaron transition shift to the longer wavelength. The phenomenon may be due to the effects of orientation and stretching by the magnetic field³² leading to the oriented growth of PANI, which results in the energy for π - π^* transition and π -polaron transition changed.

In Figure 6, compared with the HCl-doped PANI films (curve a), the absorption peaks of PANI films obtained with rare-earth cations and magnetic field because of π - π^* transition of the benzenoid rings shift to the longer wavelength, and the absorption peaks of π -polaron transition appear at the shorter wavelength, which is consistent with the above-mentioned. Compared the corresponding curves in Figure 5 and Figure 6, it is interesting to note that, the absorption peak of π - π^* transition of PANI film obtained with magnetic field [Fig. 6(a)] appears at the shorter wavelength than that of PANI film obtained without magnetic field [Fig. 5(a)], and when PANI films were prepared with rare-earth cations [Fig. 6(b-e)], the absorption peak of π - π^* transition shift to longer wavelength compared to that of HCl-doped PANI [Fig. 6(a)]. In addition, the absorption peaks due to π -polaron transition of PANI film obtained with rare-earth cations [Fig. 5(b-e)] ex-

hibit a blue shift and appear at the shorter wavelength, and when PANI films were prepared in the presence of magnetic field and rare-earth cations, the blue shift begin to decrease and tend to come back to that of the HCl-doped PANI film [Fig. 6(a)]. These results suggest that the effect of rare-earth cations is more obvious than that of the magnetic field and the effect of magnetic field can be enhanced in the presence of paramagnetic cations.

FTIR spectra of PANI powder

Figure 7 shows that the FTIR spectra of resulting products, which were prepared in 1.0 mol dm⁻³ HCl solution containing 0.2 mol dm⁻³ aniline and different rare-earth cations. It was found that the FTIR spectra of these PANI prepared are similar to each other, which indicates that the backbone structures of PANI are identical to each other. The main peaks at 1568 and 1489 cm⁻¹ in the spectrum of PANI-HCl correspond to quinone and benzene stretching-ring deformations, respectively. The absorption band at 1297 cm⁻¹ can be assigned to C-N stretching of the secondary aromatic amine. The band characteristic of the conducting protonated form is observed at 1242 cm⁻¹ and interpreted as C-N⁺ stretching vibration in the polaron structure.⁴¹ The 1137 cm⁻¹ band, assigned to a vibration mode of the -NH⁺= structure, is produced by the protonation of imine nitrogens.⁴² Out-of-plane bending vibration of C-H on benzene rings is located in

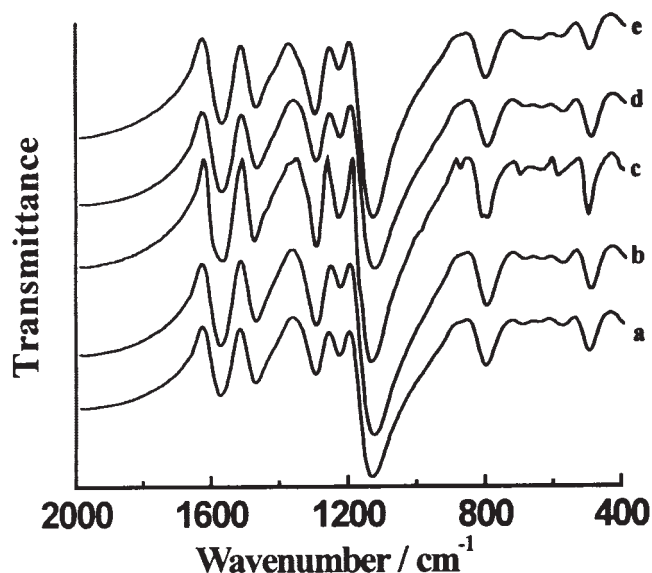


Figure 7 FTIR absorption spectra of PANI films deposited onto the GQG at constant potential of 0.8 V. (a) 0.2 mol dm⁻³ aniline + 1.0 mol dm⁻³ HCl; (b) 0.2 mol dm⁻³ aniline + 1.0 mol dm⁻³ HCl + LaCl₃; (c) 0.2 mol dm⁻³ aniline + 1.0 mol dm⁻³ HCl + NdCl₃; (d) 0.2 mol dm⁻³ aniline + 1.0 mol dm⁻³ HCl + SmCl₃; (e) 0.2 mol dm⁻³ aniline + 1.0 mol dm⁻³ HCl + ErCl₃.

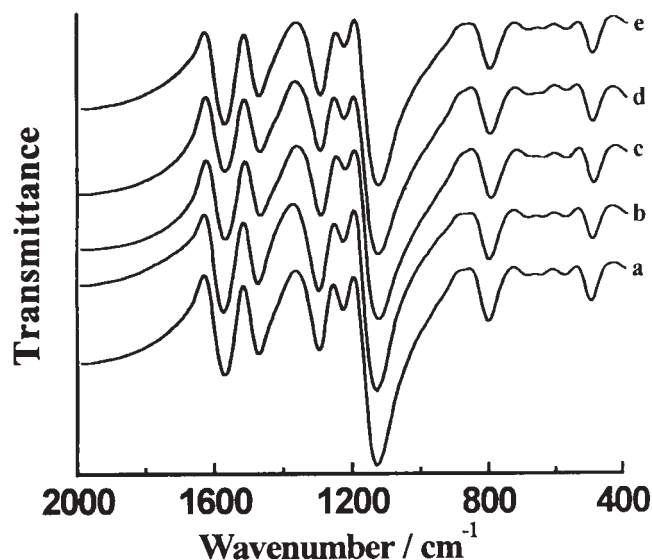


Figure 8 FTIR absorption spectra of PANI films deposited onto the GQG at constant potential of 0.8 V, in the presence of magnetic field, 760mT. (a) 0.2 mol dm⁻³ aniline + 1.0 mol dm⁻³ HCl; (b) 0.2 mol dm⁻³ aniline + 1.0 mol dm⁻³ HCl + LaCl₃; (c) 0.2 mol dm⁻³ aniline + 1.0 mol dm⁻³ HCl + NdCl₃; (d) 0.2 mol dm⁻³ aniline + 1.0 mol dm⁻³ HCl + SmCl₃; (e) 0.2 mol dm⁻³ aniline + 1.0 mol dm⁻³ HCl + ErCl₃.

the region of 800–880 cm⁻¹.^{42,43} These characteristic bands confirm that the PANI salts contain the conducting emeraldine salt phase.

When PANI were obtained in the solution containing rare-earth cations, some peaks present a few shifts in the wavenumbers. For example, when the PANI films doped by LaCl₃, NdCl₃, SmCl₃, and ErCl₃, compared with HCl-doped PANI, the peaks of the quinoid units shift from 1137 cm⁻¹–1128 cm⁻¹, 1133 cm⁻¹, 1134 cm⁻¹, 1135 cm⁻¹, and the stretching vibrations of benzoid ring shift from 1489 to 1486 cm⁻¹, 1484 cm⁻¹, 1485 cm⁻¹, 1488 cm⁻¹, respectively, other peaks are almost not shifted. While for PANI synthesized at magnetic field (Fig. 8), the peaks of FTIR spectra tend to appear at the higher wavenumber, such as the peaks of the quinoid units appear at 1139 cm⁻¹, 1144 cm⁻¹, 1135 cm⁻¹, 1136 cm⁻¹ and 1139 cm⁻¹, it can be found by comparing Figure 7 with Figure 8. The effects deriving from rare-earth cations and the magnetic field on FTIR spectra of PANI are different: the added rare-earth cations in solution could dope into the PANI and it may coordinate with nitrogen atoms in PANI chain,³³ which makes the peaks of FTIR spectra for PANI/rare-earth cations shift to the lower wavenumber comparing with that for PANI-HCl (curve a in Fig. 7); magnetic field because of its effects of orientation and stretching³² leads to the oriented growth of PANI, it is known that the reactive molecules of polymer are aligned under the field's influence. When the growth of PANI is in solution contain-

ing rare-earth cations in the presence of magnetic field, the paramagnetic ion Nd³⁺, Sm³⁺, and Er³⁺ interact with the imposed magnetic field and it can speed up the alignment process. Then PANI chains are formed more regularly leading to the peaks of FTIR spectra appear at the higher wavenumber, it can be found by comparing Figure 7 with Figure 8. This result means that the collaborative effect of rare earth cations and magnetic field exists, which is in consistent with the result drawn from UV-vis spectra.

CONCLUSIONS

In summary, a facile electrochemical method to synthesize the nanoparticles of PANI in the presence of rare-earth cations and magnetic field was introduced. The experiment results indicate that the electropolymerization rate and properties of PANI are greatly increased under the influence of rare-earth cations and magnetic field, which leads to the increase of chain order with concurrent increase in conductivity. The addition of paramagnetic rare-earth cations gives enhanced collaborative effects with external magnetic field, which leads to the PANI chain of PANI/rare-earth cations/Bp more ordered and regular. As for the Nd³⁺ and Er³⁺, they have a bigger magnetic moment, which is favorable for magnetic orientation effect in the presence of strong magnetic field, so, among rare-earth cations used in this study, the effects of Nd³⁺ and Er³⁺ ions on PANI properties are bigger than La³⁺ and Sm³⁺ in the presence of external magnetic field. The PANI films doped Nd³⁺ and Er³⁺ ions present a more compact and uniform of morphology, moreover, their conductivities are bigger than that of the others. This magnetic alignment process with paramagnetic ions is expected to improve a polymer's electrical, optical and mechanical properties so as to enlarge their fields of applications.

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