Electrosynthesis of Polyaniline/SiO₂ Composite at high pH in the Absence of Extra Supporting Electrolyte

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Summary

Electropolymerization of aniline was investigated in solutions of different pH from 1.0 to 12.1 without extra supporting electrolyte. FT-IR Spectra of the polymers display characteristic absorptions for polyaniline (PANI) including that for protonated PANI, although some of the polymers were obtained in solutions of high pH. PANI obtained from acidic solutions displayed the usual electroactivities in 0.5 mol·l^{-1} H₂SO₄, while those obtained from solutions of pH 6.0 to 12.1 showed an unusual redox pair additionally on cyclic voltammograms at 0.04 V *vs*. SCE. This redox pair can be ascribed to the redox of phenazine ring, originated from the attack of nitrenium cation to PANI chain in the *ortho*-position. Electrocodeposition of PANI and SiO₂ was conducted through electrophoresis of silica particles towards anode as aniline anodically electropolymerized. Energy dispersive X-ray diffraction (EDX) analysis and SEM inspection were performed on obtained PANI / SiO₂ to investigate the composite film.

Introduction

Conducting polymers are of great interest to researchers in many fields due to their various properties and numerous possible applications. Polyaniline (PANI) in particular, which is oxygen- and moisture-stable, is the subject of many recent studies. PANI has promising applications in variety of technologic fields, such as batteries, sensors, corrosion inhibitors and capacitors, *ect* [1]. Composition of PANI with other functional materials can offer new materials with many interesting properties. For example, PANI doped with polyanions displayed electrocatalytic activities towards reduction of oxygen and proton [2]. Neutral particles, including noble metals [3], ceramics [4] and Prussian blue type materials [5], can also be incorporated into PANI film. The composites obtained have potential applications in many fields.

Electrosynthesis is an effective way to afford PANI and its composite films with a large variety of tunable parameters and so the advantage of convenient film control. Electropolymerization of aniline in acidic aqueous solutions is a traditional method for PANI film deposition [6]. While the suitable electrodeposition media for most oxides is aqueous solutions of comparatively high pH, reports about electrodeposition of composite based on PANI and oxide are very limited [7].

Recently, some groups succeeded in electropolymerization of aniline in neutral or basic aqueous media [8−14]. This offers a possibility for incorporating oxides into PANI film through electrocodeposition. Electrodeposition of composites can proceed through electrolytic deposition (ELD), electrophoretic deposition (EPD) or by the incorporation of both [15]. EPD of negatively charged oxide particles combined with anodic electropolymerization of aniline will be an effective way for the electrocodeposition of PANI and oxide. In order to provide oxide particles more opportunities to electrophoresize towards electrode, other charged particles, including supporting electrolyte, in the media should be as less as possible. In this paper, we reported the electrosynthese of electroactive PANI in aqueous solutions of different pH from 1.0 to 12.1 in the absence of extra supporting electrolyte. The incorporation of silica particles into the polymer was conducted to afford PANI / SiO_2 composite film.

Experimental

All chemicals used were of analytical grade. Aniline was distilled before use. Silica particles (average 300 nm) were prepared by a literature method [16]. Solutions and oxide particle suspension were prepared from distilled water. The pH value of the media was adjusted by HNO_3 or KOH.

Electrochemical experiments were performed on Princeton Applied Research Model 273 potentiostat/galvanostat. Electrosynthese of PANI and PANI / SiO_2 composite were conducted on carbon cloth electrode. Potentials were measured and reported versus SCE. Prior to electrodeposition, the carbon cloth electrode was cleaned by acetone and distilled water. Electropolymerization of aniline was conducted in solutions of 0.1 $mol \cdot l^{-1}$ aniline at different pH, through 35 successive cyclic voltammetric scans in the potential range of $-0.3 \sim 0.9$ V at 50 $mV \cdot s^{-1}$. Electrochemical properties of PANI and PANI / SiO_2 composite were studied in 0.5 $mol \cdot l^{-1}$ H_2SO_4 by cyclic voltammetry in the potential range of $-0.3 \sim 0.6$ V at 50 $mV \cdot s^{-1}$. The particle size and zeta-potential of silica in the suspension for composite film deposition were measured by using Malvern NanoZS Nanosizer. FT-IR studies were carried out on Perkin-Elmer Spectrum One FT-IR spectrophotometer with KBr pellets. The morphology of the composite film and the existence of silica were inspected by SEM and Energy dispersive X-ray diffraction (EDX) on SHIMADZU SSX-550 scanning electron microscope.

Results and Discussion

Electropolymerization of aniline is conducted in aqueous solutions of different pH without extra supporting electrolyte. Figure 1 is the cyclic voltammograms (CVs) of the 35th scans for electropolymerization in aqueous solutions of different pH. Similar with those reported in acidic aqueous solutions [6], the CV for electropolymerization in the solution of pH 1.0 shows the characteristic redox peaks of PANI on the 35th scan. As the pH increases to 2.0, 3.0 and 4.1, the redox peaks overlap. There is nearly no peak on the CVs for electropolymerization in solutions of pH ≥ 5, especially those in solutions of pH 6 and upwards which display similar curves of low current. The characteristic redox peaks PANI films showed in acidic solutions should be ascribed to the exchange among the leucoemeraldine, emeraldine and pernigraniline states of PANI. The polymer is no longer conductive enough for these state

exchanges to occur as the pH value of the solution increases. So there is no corresponding redox peaks on CVs at high pH. This is in accordance with Macdiarmid's report that PANI is essentially non-protonated in the media of pH greater than *ca*. 4 and hence has very low conductivity [17]. The polymers are inspected by FT-IR, typical results for the polymers obtained at pH 1.0 (curve a) and 12.1 (curve b) are in Figure 2. The bands at 1640 and 1633 cm^{-1} for the film obtained at pH 1.0 and 12.1, respectively, are due to nitrogen quinone rings. The bands at 1572 and 1571 cm^{-1} are related to benzoid rings. Both of the curves display the characteristic bands for protonated PANI at 1130 and 1118 cm^{-1}, respectively [8]. The appearance of this peak indicated that PANI is protonated even in the media of comparatively high pH. During aniline polymerization, hydronium species are released and so the local pH of the electrode surroundings may shift to low values [8].
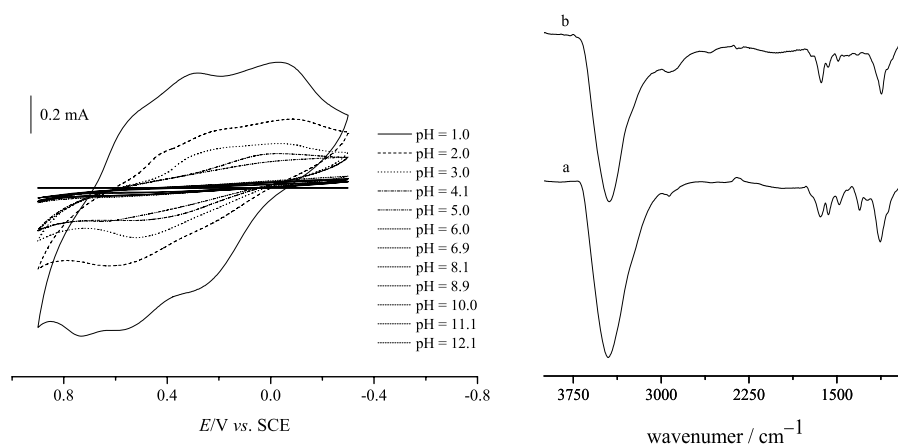

Figure 1. Cyclic voltammograms of the 35th scans for electropolymerization of aniline in aqueous solutions of different pH containing 0.1 $mol \cdot l^{-1}$ aniline; Scan rate: 50 $mV \cdot s^{-1}$.

Figure 2. FT-IR spectra of PANI made in solutions of pH 1.0 (a) and 12.1 (b).

The PANI obtained are potential scanned in 0.5 $mol \cdot l^{-1}$ H_2SO_4 to study its electrochemical activities. In this monomer free acidic solution, the CVs of all the films display characteristic redox pairs of PANI, showing that aniline has been successfully electropolymerized on carbon cloth in all the solutions. Figure 3 is the CVs of PANI made in solutions of pH 1.0 to 5.0 together with that of carbon cloth. The polymers obtained in nearly neutral solutions are less electroactive. As there is no extra supporting electrolyte in the solutions for aniline electropolymerization, the ionic strength should be less in these nearly neutral solutions. So the conductivity of the solution is not good enough and the polymerization is less effective. It was reported that counter ion facilitated the electropolymerization of aniline and the conductivity of the polymer can be modified as well [18]. The concentrations of NO_3^- should be larger in solutions of lower pH as more HNO_3 was added to adjust the pH. So the high electroactivity of films obtained in low pH media should be due to the comparatively high concentrations of both proton and counter ion. In the potential range of $-0.3 \sim 0.6$ V, the CVs of the films made in acidic solutions show

two redox pairs. The first one around 0.14 V should be ascribed to the exchange between the leucoemeraldine and emeraldine states of PANI. The second one around 0.45 V should be associated with the redox of other structures, such as hydrolysis products of PANI [8].
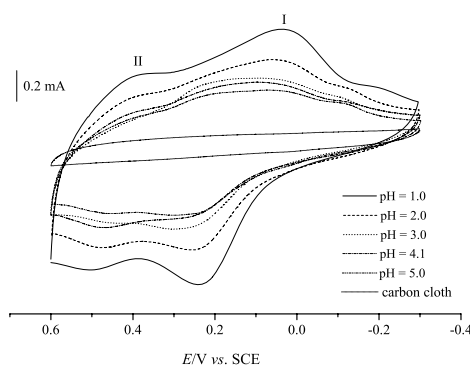

Figure 3. Cyclic voltammograms in 0.5 mol·l^{-1} H$_2$SO$_4$ of PANI made in solutions of pH 1.0 to 5.0; Scan rate: 50 mV·s^{-1}.
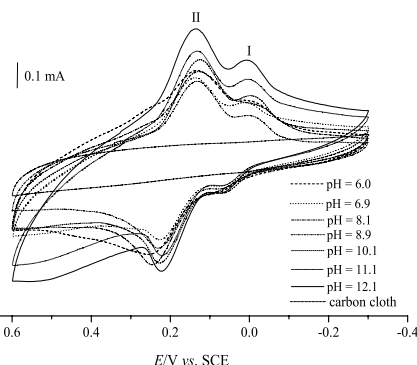
**Figure 4.** Cyclic voltammograms in 0.5 mol·l^{-1} H$_2$SO$_4$ of PANI made in solutions of pH 6.0 to 12.1; Scan rate: 50 mV·s^{-1}.

Figure 4 is the CVs of PANI made in solutions of pH 6.0 to 12.1 together with that of carbon cloth. The polymers obtained at pH 6.0 to 8.9 display similar electroactivities. The electroactivities of the films obtained in solutions of pH 10.1, 11.1 and 12.1 are higher and increase as pH increase. As cation has little influence on the electropolymerization of aniline [19], the high electroactivities of films obtained in high pH media may due to the increase of ionic strength of the media and the less protonation of aniline, oligoaniline and PANI as well, since less protonation of these species will facilitate the growth of the polymer [8, 20]. These CVs also show two redox pairs in the potential range of – 0.3 ~ 0.6 V, but appear in different potentials from those in Figure 3. The second redox pair in Figure 4 appeared around 0.18 V should be ascribed to the exchange between leucoemeraldine and emeraldine states of PANI as the first redox pair in Figure 3. There is no redox pair for the hydrolysis products on these curves, this is in accordance with the fact that PANI is difficult to hydrolysis in neutral or basic solutions. Instead, the CVs show a redox pair around 0.04 V. The films are rinsed with water and acetone several times and cyclic voltammetried after each rinse. There is little difference among these CVs for both of the redox pairs, indicating that both of them come from surface-immobilized electroactive species that are stable in water and acetone.

The electropolymerization of aniline can be envisaged to occur by several attack mechanisms [21] (Scheme 1). In high pH media, the low activity of PANI facilitates the existence of leucoemeraldine and so the fifth reaction route. The radical cation obtained in the first stage of aniline electrooxidation can lose a proton in these non-acidic media and then be electrooxided further to give nitrenium cation (Scheme 2). This will give phenazine ring by the attack of nitrenium cation to PANI chain in the *ortho*-position [22] (Scheme 3). The concentration of nitrenium cation and so the amount of phenazine ring in the polymer should be related with the pH of the reaction media. Figure 5 is the ratio of cathodic peak current of redox couple I (i_{cI}) to that of
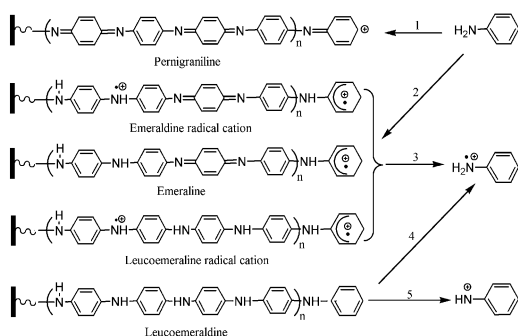
Scheme 1. Possible attack mechanisms between the growing polyaniline and the aniline monomer in various oxidsed states. Arrows show attack in the direction of species with higher electron density to species with lower electron density.
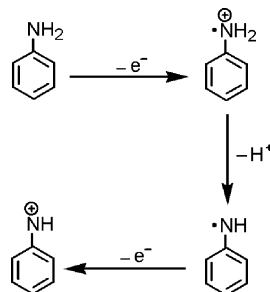
Scheme 2. Formation of nitrenium cation.

II (i_{cII}) in Figure 4 for PANI obtained at different pH. This ratio for the polymers made in solutions of pH 6.0 to 8.9 is not much influenced by pH. However, the ratio increases as the pH value of the electropolymerization media increases from pH = 8.9 to 12.1. This is in accordance with the fact that more basic media will facilitate the formation of nitrenium cation. The existence of phenazine ring in these polymers is evidenced as showed in Figure 6 by the similar potential of redox pair I in Figure 4 to that on the CV of phenazine in 0.5 mol·l^{-1} H$_2$SO$_4$ (dot line in Figure 6). Similar electrochemical behaviors of phenazine were reported in literatures [23, 24]. Vazquez and coworkers demonstrated a similar phenazine units containing conducting polymer obtained in electrochemical way [25].

The zeta potential of silica nanoparticles will be minus in basic solutions as the isoelectric point of silica is about 3.7 [26]. So the particles will electrophoresize towards anode and electrocodeposite together with PANI as the latter anodically electrodeposited. Electrocodeposition of PANI and SiO$_2$ is tried in suspension of pH 10.0 containing silica particles (300 nm average sized). The zeta potential of the silica particles is – 51 mV in this media. The CV of the obtained PANI / SiO$_2$ composite film in 0.5 mol·l^{-1} H$_2$SO$_4$ is in Figure 7 (solid line). There are two redox pairs on this
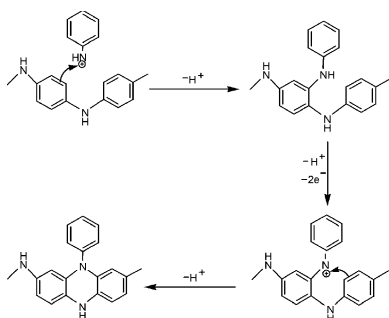
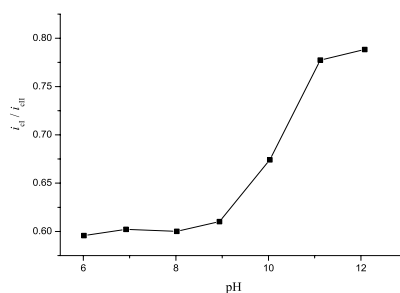**Scheme 3.** Attack of nitrenium cation to PANI chain in the *ortho*-position to give phenazine ring.

Figure 5. Ratio of cathodic peak current of redox couple I to that of II in Figure 4 for PANI obtained at different pH.
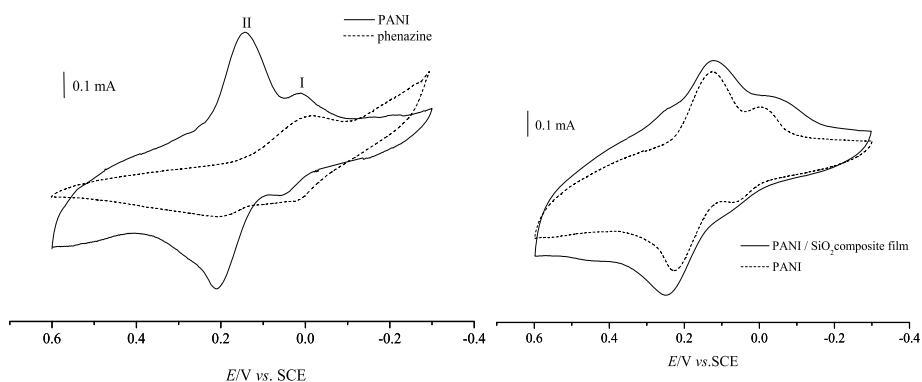
Figure 6. Cyclic voltammograms of phenazine (dot line) and PANI made in solutions of pH = 12.1 (solid line) in 0.5 mol·l^{-1} H$_2$SO$_4$; Scan rate: 50 mV·s^{-1}.

Figure 7. Cyclic voltammograms of PANI (dot line) and composite film of PANI / SiO$_2$ (solid line) in 0.5 mol·l^{-1} H$_2$SO$_4$; Scan rate: 50 mV·s^{-1}.

curve, similarly with that of the PANI made in the similar media but in the absence of silica (dot line). The currents of the peaks on the CV of the composite film are larger than those on the CV of PANI made in the solution of the same pH (Figure 7, dot line), indicating that more effective electropolymerization of aniline occurs in the presence of silica. The negative charged silica particles should work as charge-carriers in this media and so enhance the electropolymerization of aniline. The existence of silica in the composite film is confirmed by EDX analysis (Figure 8). A signal corresponding to sulfur also appears on the spectrum. This can be ascribed to SO$_4^{2-}$ doped in PANI during cyclic voltammetry of the film in H$_2$SO$_4$. Figure 9 is the SEM image of the composite film, on which silica particles are observed.
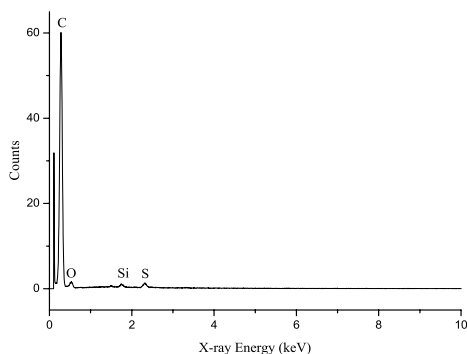

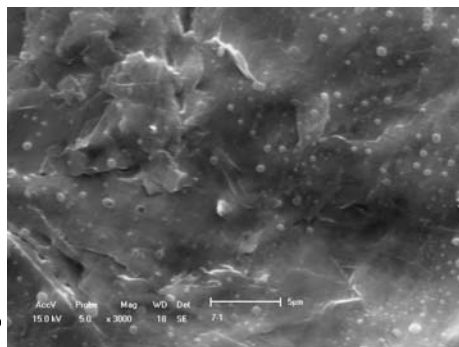**Figure 8.** EDX spectrum of PANI / SiO$_2$ (see Figure 9).

Figure 9. SEM image of composite film of PANI / SiO$_2$.

Conclusions

The traditional electropolymerization of aniline in acidic aqueous solution has limited the incorporation of oxides into polyaniline (PANI) through electrocodeposition, since most of the oxides electrodeposite more easily in media of high pH. To enquire the

possibility of incorporation oxide particles into PANI through electrophoretic deposition, electropolymerization of aniline is conducted in aqueous solutions of different pH from 1.0 to 12.1 without extra supporting electrolyte. Electroactive PANI films are obtained on carbon cloth that display characteristic vibrations in their FT-IR spectra. Usual redox peaks appear on cyclic voltammograms (CVs) in 0.5 mol·l^{-1} H$_2$SO$_4$ of the polymers obtained from acidic solutions. While an unusual redox pair at 0.04 V *vs*. SCE appears additionally on the CVs of the polymers obtained in solutions of high pH (from 6.0 to 12.1). This special behavior can be assigned to the redox of phenazine ring, originated from the attack of nitrenium cation to PANI chain in the *ortho*-position. The ratio of cathodic peak current of this redox couple to that of the characteristic redox pair for the exchange between leucoemeraldine and emeraldine at 0.18 V is higher in more basic solutions, in which the formation of nitrenium cation is facilitated. Silica particles are successfully incorporated into PANI in the media of pH 10.0 through electrophoresis of the particles towards anode as aniline anodically electropolymerizing. The existence of silica in the composite film is detected by EDX analysis and SEM investigation.

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