

Electrochemical Preparation of Poly(*N*-acetylaniline)/Poly(4-styrenesulfonic acid-*co*-maleic acid) Composite Film Towards Ascorbic Acid Sensing

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Received 4 October 2007; accepted 14 February 2008

DOI 10.1002/app.28309

Published online 7 May 2008 in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: Poly(*N*-acetylaniline)/poly(4-styrenesulfonic acid-*co*-maleic acid) (PNAANI/PSSMA) composite film was prepared by cyclic voltammetry (CV), and was characterized by FTIR and X-ray photoelectron spectrum (XPS). The electroactivity of the composite film was high in neutral and basic solutions, and it had been used for amperometric determination of ascorbic acid (AA). Compared with pure PNAANI film, the catalytic activity of the composite film was much better. AA was detected amperometrically in sodium citrate buffer at a potential of 0.3 V (versus SCE). The response current was proportional to the concentration of

ascorbic acid in the range of 4.7×10^{-6} to 5.0×10^{-5} M and 5.0×10^{-5} to 2.5×10^{-3} M, respectively, with the detection limit of 1.9×10^{-6} mol L⁻¹ at a signal to noise ratio 3. In addition, the stability and reusability of the composite film were performed well, and it was satisfying to be used for determination of AA in real fruit juice samples. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 109: 2400–2407, 2008

Key words: poly(*N*-acetylaniline); poly(4-styrenesulfonic acid-*co*-maleic acid); composite film; electrochemical synthesis; ascorbic acid; amperometric determination

INTRODUCTION

The electroanalytical methods for determination of ascorbic acid (AA) have been an important topic for sensor research for decades. However, direct oxidation of this compound on a conventional electrode is almost impossible because of its large overpotential and its contamination by the oxidation products.^{1,2} To overcome these difficulties, a variety of active mediators immobilized at the electrode surface have been used for the oxidation of AA.^{3–5} The conductive polymer modified electrodes which often exhibited good catalytic effects due to their three-dimensional mediator distribution have been used for constructing AA sensors for a long time.^{6–9}

As a new class of advanced materials for numerous technological applications, conducting polymers hold tremendous promise,^{10,11} among which, polyaniline has attracted significant attention because of its high conductivity, good redox reversibility and stability.^{12,13} Polyaniline can be electrochemically polymerized easily and shows good electroactivity in acidic media. However, polyaniline has little electrochemical activity when pH > 4.^{14–16} To improve the chemical and physical properties of polyaniline, acidic groups, such as sulfonic and carboxyl groups,

are often inserted into the polymer chain which seems to change the microenvironment of the nitrogen atoms and shift the local pH. One approach in this way is the synthesis of self-doped sulfonated polyaniline;^{17–23} another approach is the introduction of electroactive dopant into the matrix of polyaniline.^{24–26} Besides, the composite films based on polyaniline and other macromolecules such as nafion have also been studied. Sung and Huang²⁷ prepared the polyaniline/nafion composite film and the properties of the resulting material are different from those of the pure polyaniline. Zheng et al.²⁸ reported that the PNAANI/nafion composite film shows good electrochemical activity in neutral and basic solutions. However, the catalytic activity of these composite films has seldom been studied. PSSMA anion had been doped into polyaniline to improve the properties of polyaniline.²⁹ Herein, a new composite film PNAANI/PSSMA is prepared and used to catalyze the oxidation of AA. Compared with nafion, the content of PSSMA in composite film is more easily controlled and optimized to meet the requirements for AA sensing. Furthermore, the price of PSSMA is much cheaper. The anion PSSMA^{m-} can be easily codeposited with PNAANI and an excellent stability of the PNAANI/PSSMA composite film is obtained. Plentiful carboxyl and sulfonic groups in PSSMA promise the enhancement of electrochemical activity and catalytic ability of the composite film. As a consequence, such a modified

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electrode can be used to develop AA sensor with a high sensitivity in wide pH range. Moreover, it can also be utilized for immobilization of biomolecule (e.g., enzymes) to develop applicable biosensors.

EXPERIMENTAL

Materials and equipment

N-acetylaniline (Shanghai Chemical Works, China) was used after recrystallization from absolute ethanol. Sodium salt of poly(4-styrenesulfonic acid-*co*-maleic acid) (PSSMA, $M_w = 20,000$) was purchased from Aldrich. Water used for preparation of solutions was doubly distilled in an all-quartz apparatus. Other chemicals used were of AR grade. Fresh oranges and tomatoes used for analysis were purchased from a supermarket. All experiments were carried out at room temperature.

Electrochemical measurements were performed on a LK2005 Electrochemical Analysis System (LAN-LIKE, Tianjin, China). A standard three-electrode single-compartment cell was used for preparation of the composite film and for other electrochemical measurements. A 3 mm in diameter glassy carbon disk electrode (GCE) was used as the working electrode, a platinum wire as the counter electrode and a saturated calomel electrode (SCE) as the reference electrode. GCE was polished before each experiment with 1, 0.3, and 0.05 μm α -alumina powder, respectively, and rinsed thoroughly with doubly distilled water between each polishing step, sonicated in 1 : 1 nitric acid, acetone and doubly distilled water successively and then allowed to dry at room temperature.

The X-ray photoelectron spectra (XPS) were recorded on a VG ESCALAB MKII X-ray photoelectron spectrometer, using nonmonochromated Mg K α radiation as the excitation source. Fourier transform infrared (FTIR) spectra were recorded on a VECTOR22 (Bruker, Germany) spectrophotometer using a KBr disk containing about 1.0 wt % sample.

Procedure

Electrochemical polymerization of PNAANI film was carried out by the method mentioned in literature.³⁰ Like PNAANI, the PNAANI/PSSMA composite film was also obtained when the prepared GCE was immersed in a solution containing 0.1M *N*-acetylaniline, 1.0M HClO₄ and a certain amount of PSSMA by sweeping the potential between -0.20 and 0.9 V (versus SCE) with a scan rate of 50 mV s^{-1} for 10 cycles. The composite film modified electrodes were characterized by FTIR, XPS and electrochemical method. Amperometric determination of AA was performed in sodium citrate buffer at a constant potential of 0.3 V (versus SCE).

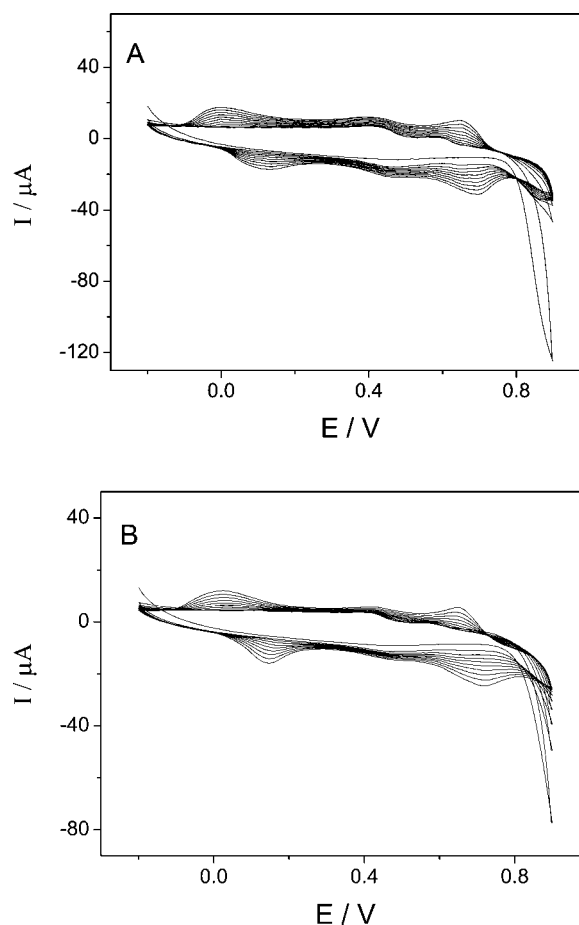


Figure 1 CVs of the growth of PNAANI film (A) and PNAANI/PSSMA film (B) at the GCE in 1.0M HClO₄ containing 0.1M *N*-acetylaniline (A), and 0.1M *N*-acetylaniline with 1.0 wt % PSSMA (B) scan rate 50 mV s^{-1} .

RESULTS AND DISCUSSION

Electropolymerization of PNAANI/PSSMA composite film

The CVs obtained during the electropolymerization of PNAANI and PNAANI with PSSMA on GCE are depicted in Figure 1(A,B), respectively. In both cases, the peak currents increase regularly with the successive scan cycles, indicating that the conductive polymer films have been formed. It is proved by XPS and FTIR that the anion PSSMA^{m-} can be codeposited with *N*-acetylaniline due to the strong electrostatic interactions between PSSMA^{m-} and the nitrogen atoms of *N*-acetylaniline in PNAANI.

Physical characteristics of PNAANI/PSSMA composite film

The wide scan XPS of PNAANI/PSSMA is shown in Figure 2. The peak of S2p appears at 168.0 eV , which is in agreement with that of the XPS spectrum of the

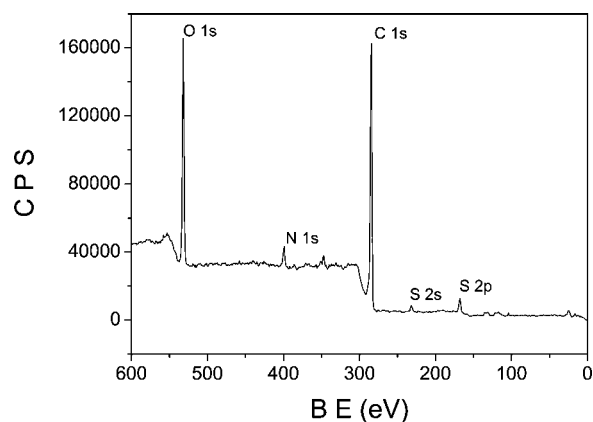


Figure 2 X-ray photoelectron spectrum (XPS) wide scan of PNAANI/PSSMA composite film (CPS: counts per second; BE: binding energy).

sulfonated polyaniline,^{31,32} in which a peak with binding energy of 167.2 eV is attributed to sulfur in the $-\text{SO}_3\text{H}$ group.

Narrow scans of S2p, C1s, and N1s (Fig. 3) show that the XPS signal of N1s of the PNAANI film can

be deconvoluted into three components: imine N (398.0 eV), amine N (399.8 eV) and positively charged N (402.3 eV). However, when the PSSMA^{m-} is codeposited with PNAANI, the binding energy of N1s has changed, the XPS signal can be deconvoluted into two Gaussian peaks, the peak at 399.5 eV can be assigned to the uncharged N ($-\text{N}<$) and the peak at 401.6 eV can be assigned to the positively charged N ($-\text{NH}^+=$). The percentage of positively charged N in PNAANI/PSSMA film (32%) is a little higher than that in pure PNAANI film (29%). Moreover, the XPS peak of imine N disappeared. These characters of XPS were also reported in the earlier works of sulfonated polyaniline,^{28,32,33} which are possibly due to the strong interaction between the sulfonic groups and cationic radical nitrogen atoms.³⁴

The FTIR spectra of PNAANI³⁵ (curve a) and PNAANI/PSSMA (curve b) are shown in Figure 4. In both cases, the absorption peaks at 1568 and 1489 cm^{-1} are due to the stretching of benzenoid and quinoid structures, respectively. A strong aromatic C—N stretching is responsible for the peak at

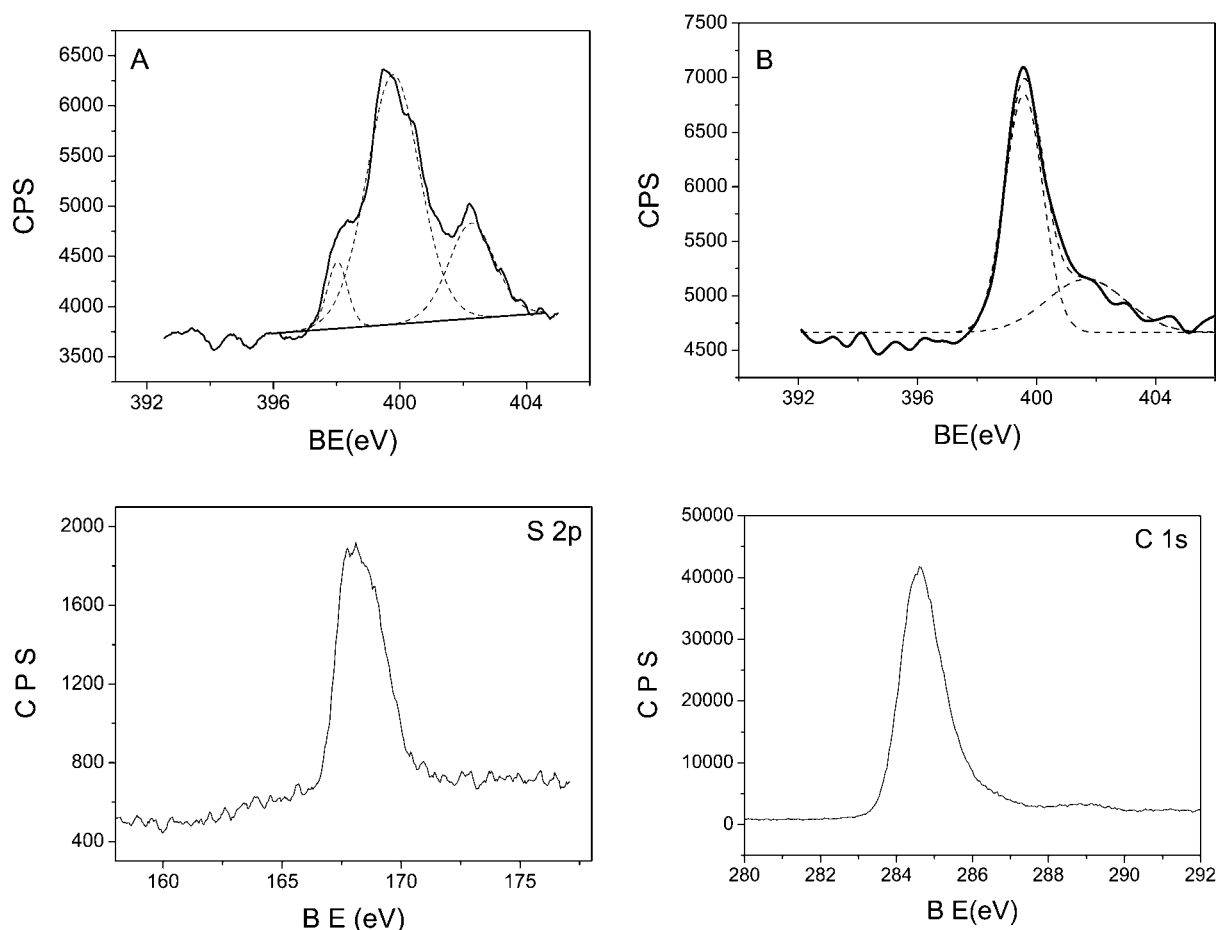


Figure 3 S2p, C1s, and N1s XPS spectra of PNAANI film (A) and PNAANI/PSSMA composite film (B) (CPS: counts per second; BE: binding energy).

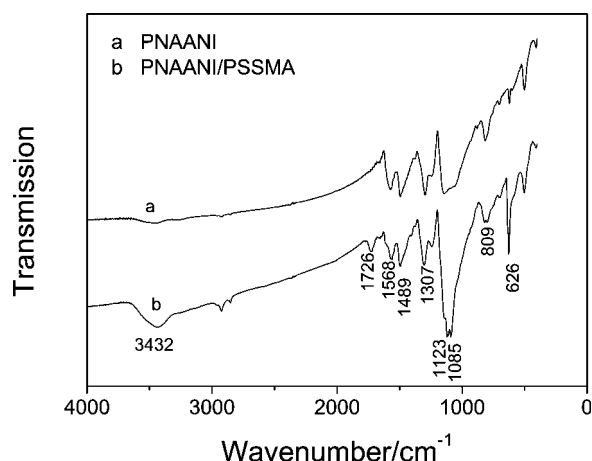


Figure 4 FTIR spectra of PNAANI (a) and PNAANI/PSSMA (b).

1307 cm^{-1} . The peak at 1123 cm^{-1} is due to the C—H in-plane deformation, which is used to evaluate the electron delocalization in polymers,¹² and the peak at 809 cm^{-1} can be attributed to the C—H out-plane bending vibration. The characteristic stretching vibration peaks of O—H and C=O of COOH at 3432 and 1726 cm^{-1} are only found in curve b. The symmetric O=S=O stretching appears at 1085 cm^{-1} in curve b, and the peak at 626 cm^{-1} is for the C—S stretching.^{36,37}

The XPS spectra and the differences between two FTIR spectra indicate that as an interesting dopant the PSSMA anion has been immobilized into matrix of PNAANI successfully.

Electrochemical characteristics of PNAANI/PSSMA composite film

The electrochemical activity of PNAANI film and PNAANI/PSSMA composite film is compared in buffer solutions at pH 7.0 and pH 10.0 respectively. As shown in Figure 5, PNAANI film shows no redox peak in pH 7.0 and pH 10.0 while the PNAANI/PSSMA composite film displays a pair of redox peak ($E_{\text{pa}} = -0.1$ V and $E_{\text{pc}} = -0.06$ V versus SCE) at pH 7.0 as well as at pH 10.0 ($E_{\text{pa}} = -0.52$ V and $E_{\text{pc}} = 0.23$ V versus SCE). Obviously, the composite film maintains a good electrochemical activity in neutral and even in basic solutions while PNAANI film loses, so that the electrochemical activity of PNAANI can be enhanced remarkably by the doping of PSSMA anions.

The polymeric PSSMA anion contains rich carboxyl and sulfonic groups, which can combine with protons to form weak acids. Like SPANI, the conductivity of PNAANI/PSSMA composite is independent of external protonation in a broad pH

range.³⁶ The environmental stability of the parent PNAANI is further improved by the insertion of acidic groups ($-\text{SO}_3^-$ and $-\text{CO}_2^-$) due to their strong electron withdrawing properties.³⁷ The PNAANI doped with PSSMA can maintain an acidic micro environment at the interface of polymer and solution. Since the redox reactions of PNAANI itself as well as the most redox reactions of organic compounds are proton involved, the acidic microenvironment could provide rich protons for these electrode processes. So PSSMA can enhance the electroactivity of PNAANI in weak acidic even in weak alkaline media.

The stability of the composite film

In Figure 5, on continuous electrochemical cycling between -0.7 and 0.5 V at 100 mV s^{-1} for 50 cycles, the decrease of the peak current of PNAANI/PSSMA film is at the level not exceeding 5% in pH 7.0 and pH 10.0 solutions respectively, and the electrochemical activity loses less in the neutral media. In fact, the composite film is more stable in acidic conditions. The electroactivity of the composite film has almost no loss in pH 5.0 buffer solution after 50 cycles. When the electrode is stored in pH 5.0 sodium citrate buffer solution at 4°C for a month, the peak current and potential have no change, too. Therefore, the composite film has good stability and reusability in a wide range of pH value.

Electrocatalytic oxidation of AA at the modified electrode

Figure 6(A,B) gives the cyclic voltammograms of different modified electrodes in the buffer solution con-

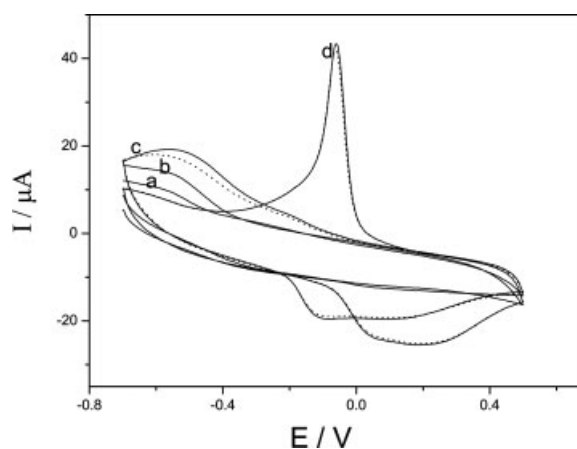


Figure 5 CVs of PNAANI film at pH 7.0 (0.1M sodium citrate buffer) (a), pH 10.0 (0.1M carbonate buffer) (b) and the CVs of PNAANI/PSSMA composite film at pH 10.0 (c), pH 7.0 (d). The first cycle (solid line) and the 50th cycle (dotted line). Scan rate: 100 mV s^{-1} .

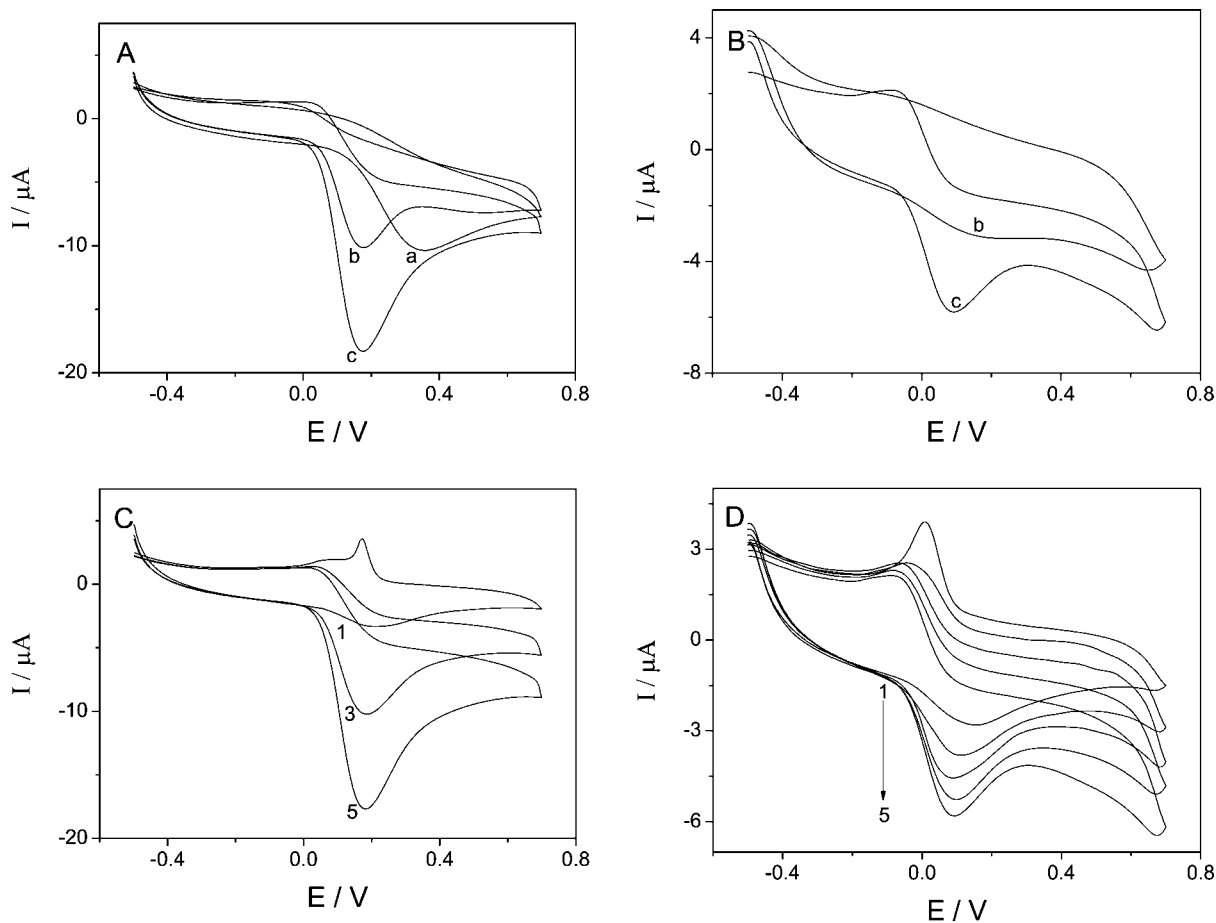


Figure 6 The CVs at the GCE (a), PNAANI (b), PNAANI/PSSMA (c) electrode in pH 5.0 (A) and pH 7.0 (B) sodium citrate solutions containing 2 mM AA, and the CVs at the composite modified electrode in sodium citrate buffer (pH 5.0 (C) and pH 7.0 (D)) containing AA from (1) to (5): 0.0, 0.5, 1.0, 1.5, 2.0 mM. Scan rate 10 mV s^{-1} .

taining 2 mM AA. It can be seen that the anodic overpotential shifts negatively more than 180 mV at the PNAANI (curve b in [Fig. 6(A,B)]) and PNAANI/PSSMA (curve c in [Fig. 6(A,B)]) modified GCE compared with that obtained at bare GCE [curve a in Fig. 6(A)]. However, the peak shape is well-defined at PNAANI/PSSMA modified electrode at pH 7.0 but it is not at PNAANI modified electrode. And the oxidation current at PNAANI modified electrode has almost no increase at pH 5.0 and is small at pH 7.0, which may be due to the loss of electroactivity of PNAANI film at $\text{pH} > 4$. It is obvious that the peak current increased about one time at PNAANI/PSSMA composite modified electrode at pH 5.0, and the electroactivity of PNAANI/PSSMA composite film still retains high at pH 7.0.

The cyclic voltammograms of the composite film modified electrode in different concentration solutions of AA are given in Figure 6(C,D). The oxidation peak current has a linear relationship with the AA concentration in the range from 0.5 to 2.0 mM at pH 7.0, which implies that the composite film can detect AA at physiological pH. However, the peak

current at pH 7.0 is much lower than that at pH 5.0, therefore, the effects of pH on catalytic oxidation of AA have also been discussed below.

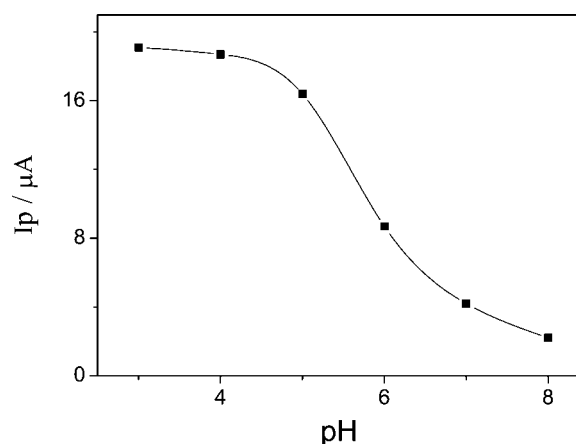


Figure 7 The dependence of peak currents on pH in 2 mM AA sodium citrate buffer solution, scan rate 10 mV s^{-1} (I_p : peak current).

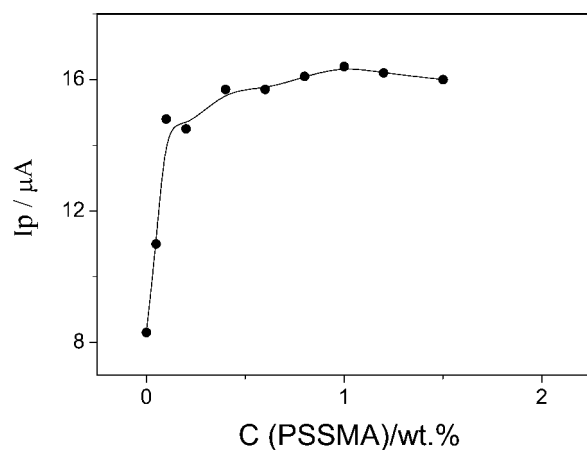


Figure 8 The dependence of peak currents on the PSSMA concentration in 2 mM AA sodium citrate buffer solution, scan rate 10 mV s^{-1} (I_p : peak current).

The effect of pH on catalytic oxidation of AA

Figure 7 depicts the dependence of peak currents on pH of the media. It is shown that the composite film has a high response to AA when $\text{pH} < 4.0$ and a good response from $\text{pH} 4.0$ to $\text{pH} 6.0$, and maintains its catalytic activity to a certain extent even in the neutral and weak alkaline media. To obtain a sensitive detection of AA, the buffer solution of $\text{pH} 5.0$ was chosen in the experiments. It should be noticed that the peak current is seriously influenced by the acidity of the buffer solution, so the pH value of the media has been controlled carefully in the measurements.

The effect of PSSMA concentration on catalytic oxidation of AA

A series of PNAANI/PSSMA composite films were prepared by changing the concentration of PSSMA in the electrolyte solution. The effect of PSSMA concentration on the response of composite film modified electrode was investigated in the presence of 2 mM AA at $\text{pH} 5.0$. As is shown in Figure 8, the current response increases with the concentration of PSSMA increasing, and reaches its maximum response while the concentration of PSSMA achieved about 0.8 wt % (the doping of PSSMA might be saturated). This can be interpreted as the electroactivity of the composite film is influenced by the amount of PSSMA containing in the composite film.

Amperometric detection of AA

Amperometric detection of AA was performed by using the composite film modified electrode at a constant potential. The effect of applied potential on the response of the modified electrode is shown in

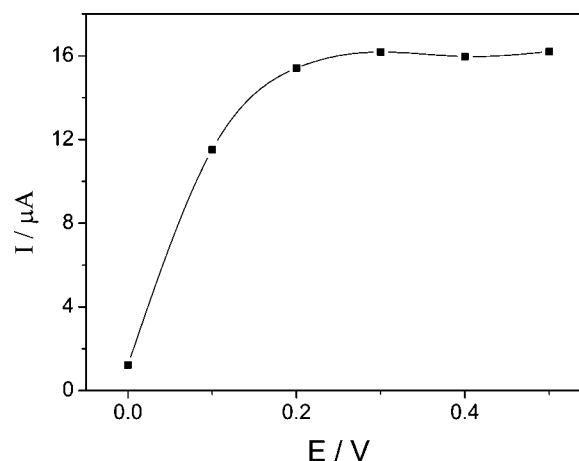


Figure 9 The dependence of response currents on constant potential in 0.1M citrate solution ($\text{pH} = 5.0$) containing 2 mM AA.

Figure 9. For the stationary case, at an applied potential of 0.3 V (versus SCE) a limiting current was achieved when the PNAANI/PSSMA/GCE was immersed in 0.1M sodium citrate solution containing 2 mM AA.

Under the optimum conditions, good linear relationships between the response current and the concentration of AA were obtained in citrate solution at $\text{pH} 5.0$, as shown in Figure 10. There are two linear relationships between the oxidation current and the concentration of AA with regression equations of $I(\mu A) = 1.14 + 12.6c(M)$ ($r = 0.9914$) in the range of 4.7×10^{-6} to $5.0 \times 10^{-5} \text{ M}$ and $I(\mu A) = 1.26 + 7.53c(M)$ ($r = 0.9990$) in the range of 5.0×10^{-5} to $2.5 \times 10^{-3} \text{ M}$, respectively, with a detection limit estimated $1.9 \times 10^{-6} \text{ M}$ at a signal to noise ratio 3.

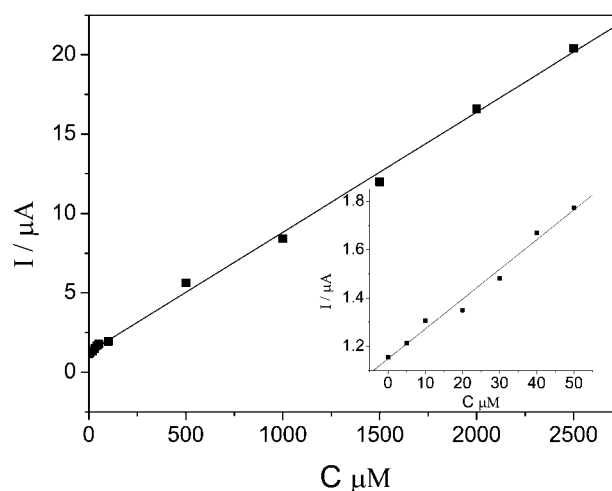


Figure 10 The relationship between response current and the concentration of AA from 5.0×10^{-5} to $2.5 \times 10^{-3} \text{ M}$ and insert from 4.7×10^{-6} to $5.0 \times 10^{-5} \text{ M}$, in 0.1M citrate buffer solution ($\text{pH} = 5.0$).

TABLE I
Ascorbic Acid in Orange and Tomato Juice Samples Detected by PNAANI/PSSMA-Modified Electrode

| Sample | Detected value ^a (mg/100 g) | Spike (mg/100 g) | Detected value after spike ^a (mg/100 g) | Recovery (%) | Detected by iodimetry ^a (mg/100 g) | Relative error (%) |
|--------------|---|---------------------|--|--------------|---|-----------------------|
| Orange juice | 50.3 | 50.0 | 99.2 | 97.8 | 51.8 | -2.9 |
| Tomato juice | 17.1 | 15.0 | 32.6 | 104.0 | 16.7 | 2.4 |

^a Average value of three measurements.

Thus, the composite film electrode can be used to determine AA at the level of micromole concentration. Compared with other modified polyaniline for the detection of AA, the detection limit is much better. Maybe the doped PSSMA provides an acidic microenvironment for the oxidation of AA at the surface of PNAANI/PSSMA/GCE, so that the detection sensitivity is highly improved in weak acidic media.

The PNAANI/PSSMA composite film modified electrode was used to measure the concentration of AA in fresh fruit juice samples (orange and tomato) which were obtained using a hand squeezer and then filtered into a beaker and diluted to 10 times with 0.1 mol L⁻¹ citrate buffer solution (pH 5.0). As is shown in Table I, the good recoveries are obtained and the detected values of the proposed method are comparatively close to that obtained by iodimetry. The possible interferences, which often exist in fresh fruits such as citric, tartaric, oxalic, malic and lactic acid and glucose, maltose, levulose and sucrose, were investigated in the test solutions which contain 2.0 × 10⁻³ M of AA. It is shown that the presence of 100-fold excess of the above compounds do not significantly influence the determination of AA at the applied potential of 0.3 V. Therefore the proposed method used to detect AA in real fruits is feasible.

CONCLUSIONS

The PNAANI/PSSMA composite film was prepared by electrochemical copolymerization of *N*-acetylaniline and PSSMA on GCE. Physical characteristics show that the PSSMA anion was doped into the matrix of PNAANI by intermolecular or electrostatic force between PSSMA and PNAANI. The electroactivity of PNAANI/PSSMA film retains high in neutral and basic solutions while PNAANI film loses its electroactivity. Compared with PNAANI, the catalytic activity of PNAANI/PSSMA composite film is enhanced remarkably by the doping of PSSMA anions. The amperometric determination of AA was performed in citrate buffer solution (pH 5.0) at an applied potential of 0.3 V (versus SCE). The high

sensitivity of this composite polymer modified electrode might be useful in developing AA sensors for detection at a low concentration level in weak acidic even in physiological pH solution.

References

- Ijeri, V. S.; Jaiswaland, P. V.; Srivastava, A. K. *Anal Chim Acta* 2001, 439, 291.
- Li, T. A.; Chen, L.; Liu, L.; Lu, N.; Song, W. B.; Xu, H. D. *Sens Actuators B* 2006, 113, 150.
- Zhang, L.; Lin, Q. X. *Analyst* 2001, 126, 367.
- Fernandez, L.; Carrero, H. *Electrochim Acta* 2005, 50, 1233.
- Raof, J. B.; Ojaniand, R.; Kiani, A. *J Electroanal Chem* 2001, 515, 45.
- Zhang, L.; Jia, J. B.; Zou, X. Q.; Dong, S. *J Electroanal* 2004, 16, 1413.
- Komsiyska, L.; Tsakova, V. *Electroanalysis* 2006, 18, 807.
- D'Eramo, F.; Sereno, L. E.; Arevalo, A. H. *Electroanalysis* 2007, 19, 96.
- Malinauskas, A.; Garjonyte, R.; Mažeikiene, R.; Jureviciute, I. *Talanta* 2004, 64, 121.
- MacDiarmid, A. G.; Mu, S.; Somasiri, N. L. D.; Wu, W. *Mol Cryst Liq Cryst* 1985, 121, 187.
- Kanungo, M.; Kumar, A.; Contractor, A. Q. *Anal Chem* 2003, 75, 5673.
- Chiang, J. C.; MacDiarmid, A. G. *Synth Met* 1986, 13, 193.
- Cao, Y.; Li, S.; Xue, Z.; Guo, D. *Synth Met* 1986, 16, 305.
- Diaz, A. F.; Logan, J. A. *J Electroanal Chem* 1980, 111, 111.
- Huang, W. S.; Humphrey, B. D.; MacDiarmid, A. G. *J Chem Soc Faraday Trans* 1986, 82, 2385.
- Hirai, T.; Kuwabata, S.; Yoneyama, H. *J Chem Soc Faraday Trans* 1989, 85, 969.
- Wen, T. C.; Huang, L. M.; Gopalan, A. *J Electrochem Soc* 2001, 148, D9.
- Lin, H. K.; Chen, S. A. *Macromolecules* 2000, 33, 8117.
- Lukachova, L. V.; Shkerin, E. A.; Puganova, E. A.; Karyakina, E. E.; Kiseleva, S. G.; Orlov, A. V.; Karpacheva, G. P.; Karyakin, A. A. *J Electroanal Chem* 2003, 544, 59.
- Karyalin, A. A.; Strakhova, A. K.; Yatsimirsky, A. K. *J Electroanal Chem* 1994, 371, 259.
- Fusilba, F.; Be'langer, D. *J Phys Chem B* 1999, 103, 9044.
- Mazeikiene, R.; Niaura, G.; Malinauskas, A. *Synth Met* 2003, 139, 89.
- Zhang, L. *J Solid State Electrochem* 2007, 11, 365.
- Tsutsumi, H.; Fukuzawa, S. *J Electrochem Soc* 1995, 142, 168.
- Hu, Z. A.; Shang, X. L.; Yang, Y. Y.; Kong, C.; Wu, H. Y. *Electrochim Acta* 2006, 51, 3351.
- Zhang, W. Z.; Kan, X. W.; Jiao, S. F.; Sun, J. G.; Yang, D. S.; Fang, B. *J Appl Polym Sci* 2006, 102, 5633.

27. Sung, J. Y.; Huang, H. *J Anal Chim Acta* 1991, 246, 275.
28. Zheng, L. Z.; Wu, S. G.; Lin, X. Q.; Shi, C. H.; Nie, L.; Rui, L. *Electroanalysis* 2003, 15, 191.
29. Luo, Y. C.; Do, J. S. *Sens Actuators B* 2006, 115, 102.
30. Zheng, L. Z.; Wu, S. G.; Lin, X. Q.; Nie, L.; Rui, L. *Analyst* 2001, 126, 736.
31. Wei, X.; Epstein, A. J. *Synth Met* 1995, 74, 123.
32. Mu, S. L. *Macromol Chem Phys* 2005, 206, 689.
33. Yang, C. H.; Wen, T. C. *J Electrochem Soc* 1994, 141, 2624.
34. Kilmartin, P. A.; Wright, G. A. *Synth Met* 1997, 88, 153.
35. Zheng, L. Z.; Xiong, L. Y.; Liu, C. F.; Jin, L. H. *Eur Polym Mater* 2006, 42, 2328.
36. Sahin, Y.; Pekmez, K.; Yildiz, A. *J Appl Polym Sci* 2002, 85, 1227.
37. Yue, J.; Wang, Z. H.; Cromack, K. R.; Epstein, A. G.; MacDiarmid, A. G. *J Am Chem Soc* 1991, 113, 2665.