Available online at www.sciencedirect.com
ScienceDirect
Bioelectrochemistry 72 (2008) 21–27
Bioelectrochemistry
www.elsevier.com/locate/bioelechem

A selective dopamine biosensor based on AgCl@polyaniline core–shell nanocomposites

Wei Yan, Xiaomiao Feng, Xiaojun Chen, Xinghua Li, Jun-Jie Zhu *

Key Laboratory of Analytical Chemistry for Life Science (MOE), School of Chemistry and Chemical Engineering, Nanjing University, Nanjing 210093, China

Received 19 September 2006; received in revised form 8 June 2007; accepted 19 July 2007
Available online 25 July 2007

Abstract

Silver chloride@polyaniline (PANI) core–shell (AgCl@PANI) nanocomposites were synthesized in the presence of polyvinylpyrrolidone (PVP). The obtained AgCl@PANI nanocomposites could be easily dispersed in aqueous media, which overcame the processible issues of PANI. Moreover, the nanocomposites showed excellent electrochemical behavior at pH neutral environment, and had inhibitive effect on oxidation of ascorbic acid. Fourier transform infrared spectrophotometry (FTIR) confirmed the existence of PVP in the nanocomposites. The C=O group of PVP is easy to form hydrogen bonding with the hydroxyl group of ascorbic acid, which can prevent ascorbic acid from oxidization. A selective dopamine biosensor was constructed based on the particular characteristic of the AgCl@PANI nanocomposites by the simple drop-coating. The biosensor could detect dopamine at its very low concentration in the presence of 5000 time concentration of ascorbic acid at neutral environment.

Keywords: Electrochemical; AgCl@polyaniline (PANI) core–shell nanocomposites; Dopamine; Ascorbic acid; Glassy carbon electrode

1. Introduction

Since the first report of electrical conductivity in a conjugated polymer in 1977 [1], conductive polymers have attracted much interest due to their high conductivity, ease of preparation, good environmental stability, and large variety of applications in light-emitting, electronic devices, chemical sensors, separation membranes, and antistatic coatings [2–4]. The most widely studied conducting polymers include polyanilie (PANI), polypyrole (PPy), and polythiophene (PTh). During them, PANI has been proven particularly useful in the development of biosensors, because of its low cost, ready film-forming ability, chemical and electrochemical stability, and scope for incorporation of functional groups [5]. However, the poor processability of PANI has greatly restricted its exploitation in commercial biosensors. Monomer aniline is carcinogen, and it is insoluble in common solvents [6]. The processability issues have been overcome by PANI nanostructure because they can be dispersed in aqueous media [7]. Moreover, since high surface area, PANI nanostructure allows fast diffusion of target molecules, resulting in the acceleration of electron transmission and the enhancement of current response[7–8].

Usually, acidic conditions (pH<4) are required for the formation of the highly conductive form of PANI, and this greatly restricts applications of PANI in bioelectrochemistry, which normally needs a neutral pH environment. It was reported that doping PANI with negatively charged units yielded a redox-active polymer at neutral and even basic aqueous solution. PANI nanoparticles doped with dodecyl-benzenesulfonic acid (DBSA) were used by Morrin et al. to immobilize horseradish peroxidase (HRP), thus H_2O_2 biosensors were fabricated [7,9]. Glucose biosensors were fabricated by immobilizing Glucose oxidase (GOx) on Au nanoparticles-conductive PANI nanocomposites, and this biosensor displayed high sensitivity for glucose sensing [8]. Sulfonate-functionalized Au nanoparticles (Au-NPs) were incorporated into PANI microrode through electropolymerization. The PANI/Au-NPs composites showed good electroactivity at neutral environment, despite that PANI is redox-active only under acidic condition by itself [10].

A kind of inorganic@conducting PANI nanocomposites, silver chloride@PANI core–shell (AgCl@PANI) nanocomposites, was synthesized [11]. Inorganic@conducting PANI nanocomposites

* Corresponding author. Tel./fax: +86 25 83594976.
E-mail address: jjzhu@nju.edu.cn (J.-J. Zhu).

1567-5394/$ - see front matter © 2007 Elsevier B.V. All rights reserved.
doi:10.1016/j.bioelechem.2007.07.003

with different combinations of the two components have attracted significant academic and technological attention because of their unique properties as well as extensive applications in diverse areas [12]. The AgCl@PANI nanocomposites exhibited excellent electrochemical behavior at neutral pH environment. Moreover, different with the PANI composites synthesized by Granot et al., which favored catalytic oxidation of ascorbic acid [10], AgCl@PANI nanocomposites have inhibitive effect on oxidation of ascorbic acid. Fourier transform infrared spectrophotometry (FTIR) confirmed the existence of PVP in AgCl@PANI nanocomposites [11]. The C=O group in PVP can form hydrogen bonding with ascorbic acid and prevents it from oxidation. A Biosensor, which could selectively determine dopamine in the presence of large excess of ascorbic acid, was successfully constructed based on the particular characteristic of AgCl@PANI nanocomposites.

Dopamine is a very important catecholamine neurotransmitter in the mammalian central nervous system. The change in the level of dopamine has been proved to be a very effective route toward brain functions, and the loss of dopamine-containing neurons may result in serious disease such as Parkinson's disease [13,14]. Selective and sensitive determination of dopamine has been a long-standing goal, and electrochemical techniques have been proved to be one of the most advantageous ways in the determination of dopamine [13–18]. A major problem in dopamine detection is the interference of ascorbic acid, which is also present in biological fluids at very high concentration (100–500 μmol L^{-1}), whereas dopamine levels are much smaller (<100 nmol L^{-1}) [19,20]. At bare electrodes, ascorbic acid is oxidized at a potential very close to that of dopamine [21]. Moreover, electrode surface can be easily fouled by the product of ascorbic acid oxidation, which results in rather poor selectivity and reproducibility in the determination of dopamine [22,23].

In this paper, a selective dopamine biosensor was developed by a very quick and simple drop-coating method. AgCl@PANI nanocomposites can be easily dispersed in aqueous media. Some dispersion solution was deposited on a glassy carbon (GC) electrode. The electrode was dried in air and then coated with a film of Nafion. The developing method involves no electrochemical steps, so it is easily amenable to mass production [10]. AgCl@PANI nanocomposites have inhibitive effect on oxidation of ascorbic acid, and Nafion film can suppress oxidative current of ascorbic acid further through charge discrimination [15,20]. The biosensor could determine dopamine in the presence of large excess of ascorbic acid at a neutral pH environment with great selectivity and sensitivity.

2. Experiment

2.1. Instruments and chemicals

Aniline, silver nitrate, Polyvinylpyrrolidone (PVP), hydrochloride (HCl), and ammonium persulfate ($(NH_4)_2S_2O_8$, APS) were purchased from Shanghai Chemical Reagent Co. Aniline was distilled under reduced pressure. Nafion, a 5 wt.% solution in a mixture of lower aliphatic alcohols and 20% water, was obtained from Aldrich. The 1% Nafion solution used in this study was prepared by diluting the 5% Nafion in ethanol. Ascorbic acid and dopamine chloride were purchased from Sigma Chemicals and used as received. Other chemicals used were of analytical reagent grade and used without further purification. Aqueous solutions were prepared with distilled water. Phosphate buffer solution (PBS) was prepared from NaH_2PO_4 (0.1 M) and Na_2HPO_4 (0.1 M) and adjusted the pH with 0.1 M H_3PO_4 and NaOH solutions. Freshly prepared ascorbic acid and dopamine were used for all experiments.

Electrochemical experiments were performed on a CHI630a electrochemical workstation (Chenhua Co., Shanghai, China) in a three-electrode configuration. A saturated calomel electrode (SCE) and a platinum electrode served as reference and counter electrode, respectively. All potentials given below were relative to the SCE. The working electrode was a modified GC electrode. Buffers were purged with highly purified nitrogen for at least 20 min prior to use and all electrochemical experiments were performed under nitrogen atmosphere.

Scanning electron microscopy (SEM) pictures were recorded on a JSM-5900 instrument.

2.2. Synthesis of AgCl@PANI nanocomposites

AgCl@PANI nanocomposites were synthesized according to reference [11]. $AgNO_3$ (0.012 M) and aniline (0.012 M) were added to 2% or 4% PVP aqueous solution. 5 mL of 1M HCl aqueous solutions of APS as oxidant were dropped into the above mixture under stirring at room temperature. The molar ratio of aniline to APS ([An]: [APS]) was 1:1. The reaction was allowed to proceed for 24 h. After that, the precipitate was centrifuged and washed several times with distilled water and ethanol. The final product was dried in vacuum at 40 °C for 24 h.

2.3. Preparation of the modified GC electrode

A GC electrode was polished to a mirror surface before each experiment with 0.05 μm α-Al_2O_3 slurry, and then ultrasonicated in distilled water and acetone successively. The cleaned electrode was dried with a stream of nitrogen immediately before use. AgCl@PANI nanocomposites were dispersed in distilled water to form a 1.0 mg/mL solution and ultrasonically treated for 30 min. The pretreated GC electrode was cast with 5 μL of the blue suspension of AgCl@PANI nanocomposites in water. The electrode was dried in air and then coated with 10 μL of 1% Nafion solution. The solvent was allowed to evaporate at room temperature. The modified electrode is denoted as Nafion–AgCl@PANI/GC.

PVP modified GC electrode was prepared by droplet evaporation of 20 μL of a 0.2% (wt/vol) methanolic PVP solution followed by drying for 12 min at room temperature.

3. Results and discussion

3.1. Physical characterization of Nafion coated AgCl@PANI film

The core–shell structure of AgCl@PANI nanocomposites has been verified by transmission electron microscopy (TEM).

Shell thickness and core diameter of the nanocomposites is of 20-70 nm separately [11]. Fig. 1 shows the SEM images of the AgCl@PANI (up) and Nafion coated AgCl@PANI (down) films on silicon wafers. Uniform films consisted of nanocomposites are observed. The subtle difference between the two images results from the membrane of Nafion, which was cast on one of the silicon wafers after they were coated with AgCl@PANI nanocomposites.

3.2. Cyclic voltammetric behavior of ascorbic acid and dopamine at AgCl@PANI nanocomposite modified GC electrode

Fig. 2 depicts the cyclic voltammograms obtained at a bare GC electrode in pH 7.0 phosphate buffer solution (0.1 M) (curve a), containing 1 mM ascorbic acid (curve b), 1 mM dopamine (curve c), and a mixture of 1 mM dopamine and 1 mM ascorbic acid (curve d). As shown in Fig. 2, the oxidation peak potential of ascorbic acid on the bare GC electrode surface is 0.175 V, which is close to that of dopamine (0.21 V). That oxidation of the two species occurred almost at the same potential would result in an overlapped voltammetric response. Actually, cyclic voltammogram obtained for the mixture of ascorbic acid and dopamine exhibits only one anodic peak. It is believed that oxidized dopamine acts as a catalyst for oxidation of ascorbic acid, which is also one of the reasons why only one oxidation peak with great peak current was obtained for

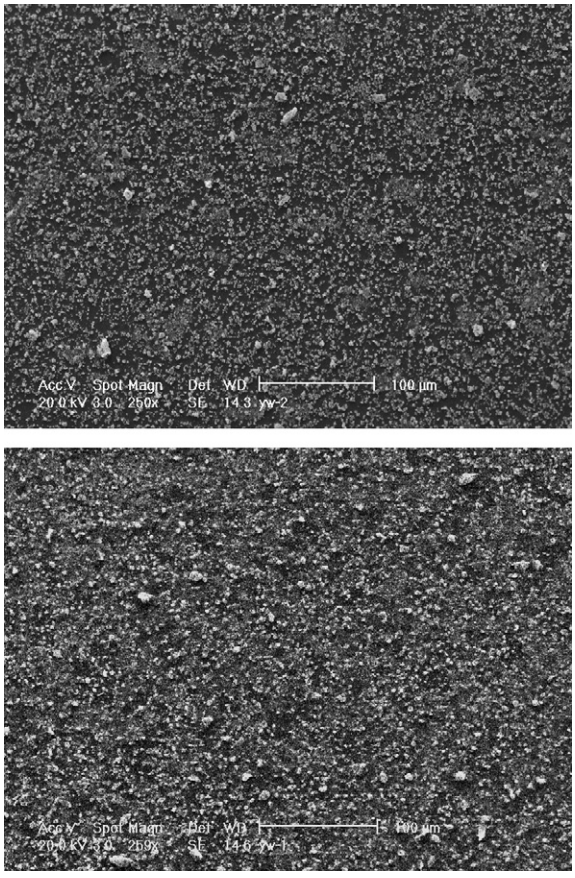

Fig. 1. SEM images of AgCl@PANI nanocomposite (up) and Nafion coated AgCl@PANI nanocomposite films (down) on silicon wafers.

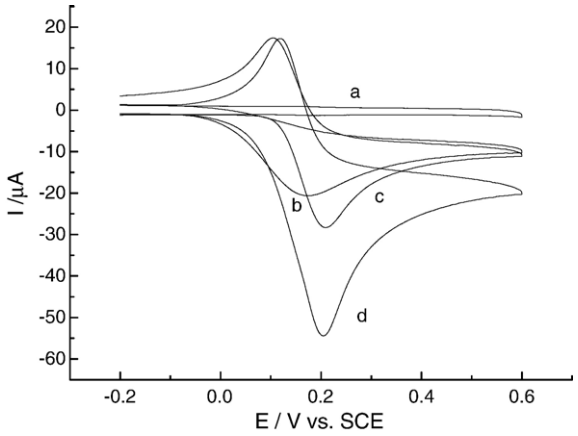

Fig. 2. Cyclic voltammograms of bare GC electrode. Curve (a): pH 7.0 phosphate buffer (0.1 M); Curve (b): (a) +1 mM ascorbic acid; Curve (c): (a) +1 mM dopamine; Curve (d): (a) + a mixture of 1 mM dopamine and 1 mM ascorbic acid. Scan rate: 0.1 V s^{-1}.

ascorbic and dopamine mixture. These observations clearly indicated that the existence of ascorbic acid had seriously interfered with the determination of dopamine at bare GC electrode [24–26].

The curve (a) of Fig. 3 shows the cyclic voltammetric behavior of the modified GC electrode in 0.1M PBS (pH 7.0). Only one pair of broad redox peaks was observed, which is the overlap of two redox processes normally found for the PANI system under acidic conditions. GC electrode modified with AgCl@PANI nanocomposites shows two pairs of redox peaks in solution with pH value below 4 [11]. It is well known that PANI exists in three well-defined oxidation states: leucoemeraldine, emeraldine and pernigraniline, and the two oxidation peaks are assigned to the transition of leucoemeraldine to emeraldine salt and the transition of emeraldine salt to pernigraniline separately [5, 27]. The two pairs of redox peaks of AgCl@PANI nanocomposites moved close with the increase of pH value and finally merged to show only one pair

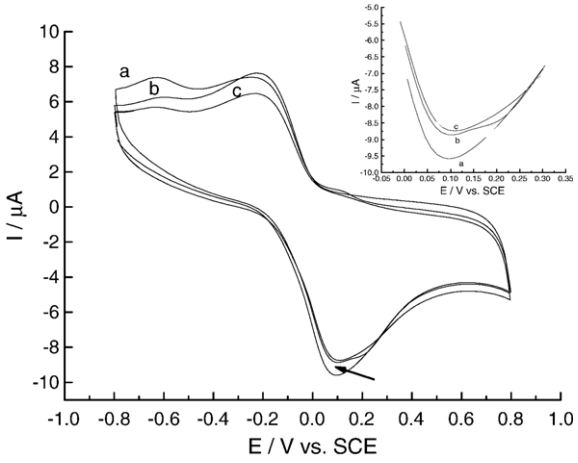

Fig. 3. Cyclic voltammograms of AgCl@PANI/GC electrode. Curve (a): pH 7.0 phosphate buffer (0.1 M); Curve (b): (a) +1 mM dopamine; Curve (c): (a) +1 mM ascorbic acid (Scan rate: 0.1 V s^{-1}). The insert shows the enlarged view of the region indicated by the arrow.

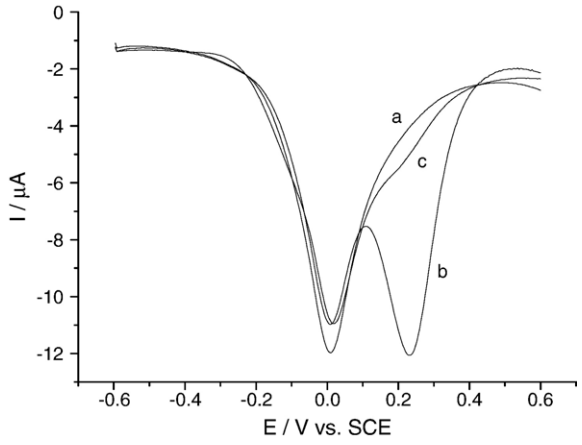

Fig. 4. Square-wave voltammograms of AgCl@PANI/GC electrode. Curve (a): pH 7.0 phosphate buffer; Curve (b): (a) +0.1 mM dopamine; Curve (c): (a) +1 mM ascorbic acid.

of broad redox peaks when pH value reached 4, and the redox peaks could still be observed even when pH value was 8 [11], indicating that AgCl@PANI nanocomposites could show excellent electrochemical behavior at pH neutral environment.

PANI is redoxactive only in acid media (pH < 4) by itself [5]. This greatly restricts its applicability in bioelectrochemistry, which normally requires a neutral pH environment. It was shown, however, doping PANI with negatively charged sulfonate units [28], or the incorporation of negatively charged poly (acrylic acid) [29] or DNA units [30], yields a redox-active polymer at neutral and even basic aqueous solutions. Although the mechanism why AgCl@PANI nanocomposites show good electrochemical activity in neutral media has not been clear yet, we believe that large amounts of negatively charged chloride ions have provided the anionic doping that made AgCl@PANI nanocomposites redox-active at neutral and even slightly basic aqueous solutions [31].

Certain amounts of AgCl@PANI nanocomposite dispersion solutions were dropped on the surface of GC electrode and then dried in air. The prepared modified GC electrode is referred as AgCl@PANI/GC electrode. The electrochemical behaviors of dopamine (curve b) and ascorbic acid (curve c) in pH 7.0 PBS at AgCl@PANI/GC electrode were examined using cyclic voltammetry. In curve b, there is a shoulder peak at 0.22 V, whereas no obvious shoulder peak appears in curve c. It can be seen in Fig. 2 that dopamine showed a couple of quasi-reversible redox peaks at bare GC electrode, but no reduction peak belonging to dopamine was observed in Fig. 3. In the mean time, both the oxidation and reduction peak currents of AgCl@PANI nanocomposites decreased. These observations suggest that there should be considerable interaction between the AgCl@PANI nanocomposites and dopamine or its oxidation products. Oxidation of ascorbic acid at bare GC electrode is believed to be totally irreversible, and at AgCl@PANI/GC electrode, no peak corresponding to reduction of ascorbic acid could be observed too. However, oxidation peak could not be observed at the same time, indicating that there are interactions between ascorbic acid and AgCl@PANI nanocomposites too.

3.3. Square-wave voltammetric behavior of ascorbic acid and dopamine at AgCl@PANI/GC electrode

Fig. 4 is the Square-wave voltammograms obtained at AgCl@PANI/GC electrode in pH 7.0 phosphate buffer (curve a), containing 1 mM dopamine (curve b), or 1 mM ascorbic acid (curve c). In curve a, oxidation peak at 0.02 V corresponds to the transition of leucoemeraldine to pernigraniline. When dopamine was added, a new oxidation peak at 0.22 V appeared. At the same time, the oxidation peak current of AgCl@PANI nanocomposites dropped due to the interaction between the nanocomposites and dopamine or its reduction products. A small broad wave at c.a. 0.22 V was observed when ascorbic acid was added into the buffer solution. It can be seen that although the concentration of ascorbic acid was ten times as much as that of dopamine, the oxidation peak current of ascorbic acid was much smaller. As we know, both PANI and dopamine carry positively charged amino groups at neutral

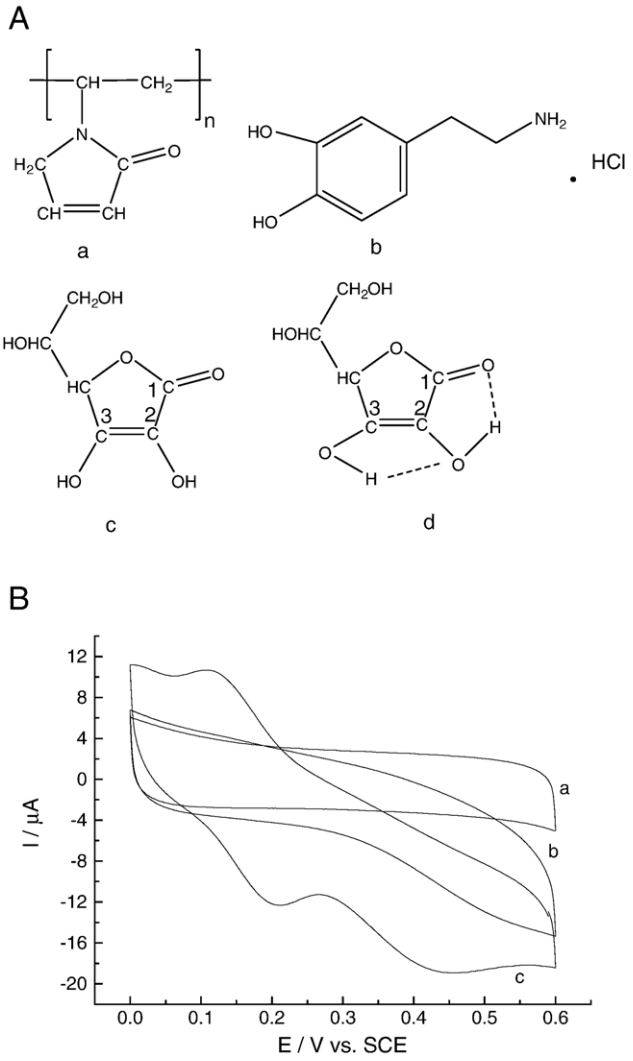

Fig. 5. Molecular structures of PVP (a), dopamine (b), ascorbic acid (c) and intramolecular hydrogen bonding of ascorbic acid (d) (A).Cyclic voltammograms of PVP modified GC electrode. Curve (a): pH 7.0 phosphate buffer (0.1 M); Curve (b): (a) +1 mM ascorbic acid; Curve (c): (a) +1 mM dopamine (Scan rate: 0.1 V s^{-1}) (B).

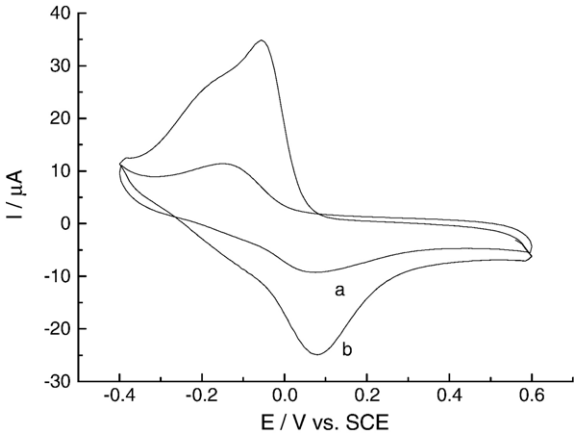

Fig. 6. Cyclic voltammograms of AgCl@PANI/GC electrode (a) and Nafion–AgCl@PANI/GC electrode (b) in pH 7.0 phosphate buffer (0.1 M). Scan rate: 0.1 V s^{-1}.

environment. The electrostatic repulsion between positively charged PANI shell of the AgCl@PANI nanocomposites and dopamine explains the reason why the oxidation peak current of dopamine at the electrode was much smaller than that at bare GC electrode. Ascorbic acid exists as a negatively charged ascorbate species in a neutral media, and the electrostatic attraction between ascorbic acid and PANI can enhance the surface concentration of ascorbic acid at the electrode. That is the reason why PANI is usually believed to favor catalytic oxidation of ascorbic acid. However, AgCl@PANI nanocomposites showed completely different characteristic. Although the surface concentration of ascorbic acid at the electrode had been improved through the interaction between positively charged PANI shell and negatively charged ascorbate, the oxidation of ascorbic acid at AgCl@PANI/GC electrode could hardly be decerned by cyclic voltammetry. Even by square-wave voltammetry, when the concentration of ascorbic acid reached 1 mM, only a small broad wave corresponding to oxidation of ascorbic acid could be observed. This indicates that not only does AgCl@PANI nanocomposites have no catalytic effect on oxidation of ascorbic acid, but also inhibit its oxidation. When ascorbic acid was added into the phosphate buffer solution, it can be observed that the redox peak currents of AgCl@PANI nanocomposites decreased (Fig. 3), indicating an unknown interaction between ascorbic acid and AgCl@PANI nanocomposites, which had hampered oxidation of ascorbic acid.

The molecular structure of AgCl@PANI nanocomposites was characterized by Fourier Transform infrared spectrophotometry (FTIR). The characteristic peak at 1651 cm^{-1} assignable to C=O could prove the presence of PVP in the nanocomposites [11]. Fig. 5A displays the molecular structures of PVP, dopamine hydrochloride and ascorbic acid. Ascorbic acid in aqueous solution, as in the crystal, exists exclusively as its enol tautomer (structure c) [32], and the tautomer can gain additional stability by the forming of intramolecular hydrogen bond (structure d). When pH value is over 5, however, the intramolecular hydrogen bond will break for the deprotonation of the hydroxyl group at C(3). PANI is positively charged at neutral environment, meanwhile ascorbic acid is negatively charged. Ascorbic acid can be adsorbed on the modified electrode surface through the electrostatic attraction. It has been proved that the C=O group in PVP is easy to form hydrogen bond with other atoms like oxygen, nitrogen and fluorin [33], thus the PVP in the nanocomposites can form intermolecular hydrogen bond with ascorbic acid, and prevents the hydroxyl group at C(2) from oxidization. Fig. 5B shows the cyclic voltammograms obtained at the PVP modified GC electrode in pH 7.0 phosphate buffer solution (curve a), containing 1 mM ascorbic acid (curve b), or 1 mM dopamine (curve c). A couple of redox peaks at 0.15V can be observed on curve b, whereas no redox peaks could be observed on curve c, indicating that PVP has prevented oxidation of ascorbic acid.

3.4. Square-wave voltammetric application for the determination of dopamine at Nafion–AgCl@PANI/GC electrode

In order to eliminate the interference of ascorbic acid with detection of dopamine completely, Nafion, a cation-exchange

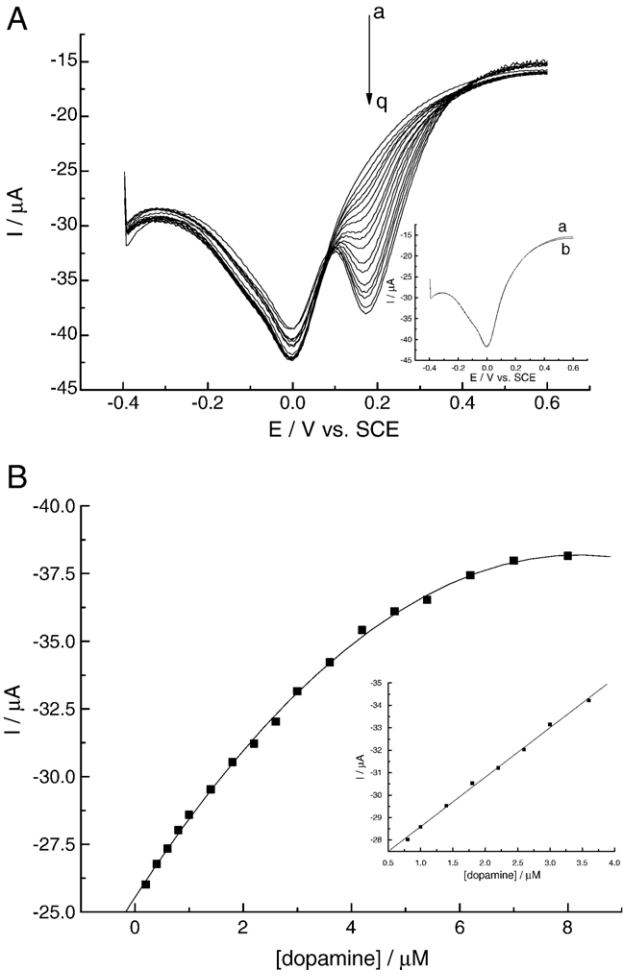

Fig. 7. (A) Square-wave voltammograms of ascorbic acid and dopamine at Nafion–AgCl@PANI/GC electrode in 0.1 M phosphate buffer solution (pH 7.0). [Dopamine] changed and [ascorbic acid] kept constant (i.e., [ascorbic acid]= 1 mM, [Dopamine]: (a) 0.2, (b) 0.4, (c) 0.6, (d) 0.8, (e) 1.0, (f) 1.4, (g) 1.8, (h) 2.2, (i) 2.6, (j) 3.0, (k) 3.6, (l) 4.2, (m) 4.8, (n) 5.4, (o) 6.2, (p) 7.0, (q) 8.0 μM). Inset is the square-wave voltammograms at Nafion–AgCl@PANI/GC electrode in 0.1 M phosphate buffer solution (pH 7.0) when [ascorbic acid] was 1 mM. (B) Relationship between the anodic peak currents and the concentration of dopamine.

polymer, whose films are highly permeable to cations but almost impermeable to anions, was used to coat AgCl@PANI nanocomposite modified GC electrode. Fig. 6 shows the cyclic voltammograms of AgCl@PANI/GC electrode (curve a) and Nafion–AgCl@PANI/GC electrode (curve b) obtained in pH 7.0 phosphate buffer solutions. At Nafion–AgCl@PANI/GC electrode, the peak separation between redox peaks (ΔE_p) was 136 mV, which was small than that at AgCl@PANI/GC electrode (332 mV). The decrease of ΔE_p might result from that Nafion film had provided enough negative charges for the PANI shell of nanocomposites, and then the conductivity of AgCl@PANI nanocomposites was improved [32]. In the meantime, the peak currents of PANI at Nafion–AgCl@PANI/GC electrode increased, which could be attributed to the fact that the membrane of Nafion had prevented AgCl@PANI nanocomposites at GC electrode from diffusing into the electrolytes.

Since dopamine exists in cationic form and ascorbic acid exists in anionic form at neutral environment, the Nafion membrane can strongly repulse anionic ascorbic acid and highly attract cationic dopamine. Fig. 7A represents the SWVs of different concentration of dopamine at Nafion–AgCl@PANI/GC electrode where the concentration of ascorbic acid kept the same (1 mM). From the insert of Fig. 7A, it can be seen that almost no response could be observed when 1 mM ascorbic acid was added into the phosphate buffer solution. This clearly indicates that Nafion film on the electrode surface have prevented anionic ascorbic acid from reaching the electrode surface, and made the electron exchange between ascorbic acid and the modified electrode almost impossible. Thus the selectivity of the AgCl@PANI/GC electrode towards dopamine was improved after it was coated with Nafion film. It was observed in Fig. 7 that with the increase of dopamine concentration, the peak currents for AgCl@PANI nanocomposites increased. The Nafion–AgCl@PANI/GC electrode can sense the increase in low level of dopamine (0.2 μM) in the presence of high concentration of ascorbic acid (1 mM), and the anodic peak currents for dopamine increased linearly with the increase of dopamine concentration with the correlation coefficient of 0.996 and sensitivity of 0.49 μA μM^{-1} (Fig. 7B).

3.5. Conclusion

AgCl@PANI nanocomposites have showed excellent redox-active behavior at neutral environment. Moreover, they had inhibitive effect on oxidation of ascorbic acid. The remaining PVP in the nanocomposites can form hydrogen bonding with ascorbic acid, and prevent it from oxidization. A highly selective dopamine biosensor was constructed based on the particular characteristic of AgCl@PANI nanocomposites. The biosensor could detect dopamine at its very low concentration in the presence of 5000 times concentration of ascorbic acid at neutral environment.

Acknowledgment

We greatly appreciate the support of the National Natural Science Foundation of China for the Key Program (20635020), Creative Research Group (20521503), General program (20575026, 90606016) and Jiangsu scientific foundation (BK2006114).

References

[1] H. Shirakawa, E.J. Louis, A.G. MacDiarmid, C.K. Chiang, A.J. Heeger, Synthesis of electrically conducting organic polymers: halogen derivatives of polyacethlene, $(CH)_x$. J. Chem. Soc., Chem. Commun. 16 (1977) 578–580.
[2] L. Liang, J. Liu, C.F. Windisch, G.J. Exarhos, Y. Lin, Direct assembly of large arrays of oriented conducting polymer nanowires, Angew. Chem. Int. Ed. 41 (2002) 3665–3668.
[3] J. Huang, S. Virji, B.H. Weiller, R.B. Kaner, Polyaniline nanofibers: facile synthesis and chemical sensors, J. Am. Chem. Soc. 125 (2003) 314–315.
[4] S.C. Huang, I.J. Ball, R.B. Kaner, Polyaniline membranes for pervaporation of carboxylic acids and water, Macromolecules 31 (1998) 5456–5464.
[5] W.S. Huang, B.D. Humphrey, A.G. MacDiarmid, Polyaniline: doping structure and derivatives, J. Chem. Soc., Faraday Trans. 82 (1986) 2385–2400.
[6] M. Cho, S. Park, J. Hwang, H. Choi, Synthesis and electrical properties of polymer composites with polyaniline nanoparticles, Mater. Sci. Eng. C 24 (2004) 15–18.
[7] A. Morrin, O. Ngamna, A.J. Killard, S.E. Moulton, M.R. Smyth, G.G. Wallace, An amperometric enzyme biosensor fabrication from polyaniline nanoparticles, Electroanalysis 17 (2005) 423–430.
[8] Y. Xian, Y. Hu, F. Liu, Y. Xian, H. Wang, L. Jin, Glucose biosensor based on Au nanoparticles-conductive polyaniline nanocomposite, Biosens. Bioelectron. 21 (2006) 1996–2000.
[9] A. Morrin, F. Wilbeer, O. Ngamna, A.J. Killard, S.E. Moulton, M.R. Smyth, G.G. Wallace, Novel biosensor fabrication methodology based on processable conducting polyaniline nanoparticles, Electrochem. Commun. 7 (2005) 317–322.
[10] E. Granot, E. Katz, B. Basnar, I. Willner, Enhanced bioelectrocatalysis using Au-Nanoparticle/polyaniline hybrid systems in thin films and microstructured rods assembled on electrodes, Chem. Mater. 17 (2005) 4600–4609.
[11] X. Feng, Y. Liu, C. Liu, W. Hou, J.-J. Zhu, One-step synthesis of AgCl/polyaniline core–shell composites with enhanced electroactivity, Nanotechnology 17 (2006) 3578–3583.
[12] R. Gangopadhyay, A. De, Conducting polymer nanocomposites: a brief overview, Chem. Mater. 12 (2000) 608–622.
[13] K. Pihel, Q.D. Walker, R.M. Wightman, Overoxidized polypyrrole-coated carbon fiber microelectrodes for dopamine measurements with Fast-Scan Cyclic Voltammetry, Anal. Chem. 68 (1996) 2084–2089.
[14] C.S. Cha, J. Chen, P.F. Liu, Improvement of the output characteristics of amperometric enzyme electrode by using the powder microelectrode technique, Biosens. Bioelecton. 13 (1998) 87–94.
[15] K. Wu, S. Hu, Electrochemical study and selective determination of dopamine at a multi-wall carbon nanotube-nafion film coated glassy carbon electrode, Microchim. Act. 144 (2004) 131–137.
[16] T. Selvaraju, R. Ramaraj, Simultaneous determination of ascorbic acid, dopamine and serotonin at poly(phenosafraniene) modified electrode, Electrochem. Comm. 5 (2003) 667–672.
[17] A. Salimi, K. Abdi, G.-R. Khayatian, Ameperometric detection of dopamine in the presence of ascorbic acid using a nafion coated glassy carbon electrode modified with catechin hydrate as a natural antioxidant, Microchim. Acta 144 (2003) 161–169.
[18] M. Zhang, K. Gong, H. Zhang, L. Mao, Layer-by-layer assembled carbon nanotubes for selective determination of dopamine in the presence of ascorbic acid, Biosens. Bioelecton. 20 (2005) 1270–1276.
[19] T. Zetterstrom, T. Sharp, C.A. Marsden, U. Ungerstedt, In vivo measurement of dopamine and its metabolites by intracerebral dialysis: change after D-amphetamine, J. Neurochem. 41 (1983) 1769–1773.
[20] P. Capella, B. Ghasemzadeh, K. Mitchell, R.N. Adams, Nafion-coated fiber electrodes for neurochemical studies in brain tissue, Electroanalysis 2 (1990) 175–182.
[21] L. Falat, H.Y. Cheng, Voltammetric differentiation of ascorbic acid and dopamine at an electrochemically treated graphite/epoxy electrode, Anal. Chem. 54 (1982) 2108–2031.
[22] P. Zhang, F.H. Wu, G.C. Zhao, X.W. Wei, Selective response of dopamine in the presence of ascorbic acid at multi-wall carbon nanotube modified gold electrode, Bioelectrochemistry 67 (2005) 109–114.

[23] S.M. Chen, W.Y. Chzo, Simultaneous voltammetric detection of dopamine and ascorbic acid using didodecyldimethylammonium bormide (DDAB) film-modified electrodes, J. Electroanl. Chem. 587 (2006) 226–234.
[24] F. Malem, D. Mandler, Self-assembled monolayers in electroanalytical chemistry: application of ω-mercapto carboxylic acid monolayers for the electrochemical detection of dopamine in the presence of a high concentration of ascorbic acid, Anal. Chem. 65 (1993) 37–41.
[25] C.R. Raj, K. Tokuda, T. Ohsaka, Electroanalytical applications of cationic self-assembled monolayers: square-wave voltammetric determination of dopamine and ascorbate, Bioelectrochemistry 53 (2001) 183–191.
[26] M.J. Giz, B. Duong, N.J. Tao, In situ STM study of self-assembled mercaptopropionic acid monolayers for electrochemical detection of dopamine, J. Electroanal. Chem. 465 (1999) 72–79.
[27] M.K. Park, K. Onishi, J. Locklin, F. Caruso, R.C. Advincula, Self-assembly and characterization of polyaniline and sulfonated polystyrene multilayer-coated colloidal particles and hollow shells, Langmuir 19 (2003) 8550–8554.
[28] P.N. Bartlett, J.H. Wang, Electroactivity, stability and application in an enzyme switch at pH 7 of poly(aniline)–poly(styrenesulfonate) composite films, J. Chem. Soc., Faraday Trans. 92 (1996) 4137–4143.
[29] P.N. Bartlett, E. Simon, Poly(aniline)–poly(acrylate) composite films as modified electrodes for the oxidation of NADH, Phys. Chem. Chem. Phys. 2 (2000) 2599–2606.
[30] Y. Xiao, A.B. Kharitonov, F. Patolsky, Y. Weizmann, I. Willner, Electrocatalytic intercalator-induced winding of double-stranded DNA with polyaniline, Chem. Commun. 13 (2003) 1540–1541.
[31] E. Granot, F. Patolsky, I. Willner, Electrochemical assembly of a CdS semiconductor nanoparticle monolayer on surfaces: structural properties and photoelectrochemical applications, J. Phys. Chem. B 108 (2004) 5875–5881.
[32] R.J. Morrison, R.N. Boyd, Organic Chemistry (5rd), Allyn and Bacon Inc., Boston, 1989, pp. 725–726.
[33] C. Barthet, M. Guglielmi, Aspects of the conducting properties of Nafion-doped polyaniline, Electrochim. Act. 18 (1996) 2791–2798.