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ORIGINAL PAPER

# Sensitive determination of adenine on poly(amidosulfonic acid)-modified glassy carbon electrode

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**Abstract** A novel and reliable direct electrochemical method was established for the detection of adenine, based on the differential pulse anodic stripping response at a poly (amidosulfonic acid) (poly-ASA)-modified glassy carbon electrode (GCE) fabricated by electropolymerization. The characterization of electrochemically synthesized poly-ASA film was investigated by atomic force microscopy, electrochemical impedance spectroscopy, and voltammetric methods. This poly-ASA-modified GCE could greatly enhance the detection sensitivity of adenine. At optimum conditions, the anodic peak exhibits a good linear concentration dependence in the range from $3.0\times10^{-8}$ to $1.0\times10^{-6}$ M ($r$=0.9994). The detection limit is $8.0\times10^{-9}$ M ($S/N$=3). The proposed method could be used to determinate the adenine in tablets of vitamin $B_4$ with satisfactory results.

**Keywords** Adenine · Poly-ASA-modified GCE · Differential pulse voltammetry · Enhanced sensitivity

## Introduction

Deoxyribonucleic acid (DNA) is a kind of important substance in living organisms. Adenine is an integral part found in DNA. Determining its concentration in DNA is important to the measurement of nucleic acid concentration itself. Nucleic acid plays a crucial role in the storage of genetic information and protein biosynthesis. Indeed, the presence of nucleic acid component in physiological fluids, tissues, and cells is related to the catabolism of nucleic acids, enzymatic degradation of tissues, dietary habits, and various salvage pathways [1, 2]. Therefore, the quantitative determination of adenine is a challenging and important task owing to the fact that it can be an indicator of important information on certain disease [3] and genetic diagnosis [4]. At present, a variety of analytical methods have been already developed for the detection and quantification of adenine in nucleic acids, which include high-performance liquid chromatography [2, 5–7], capillary electrophoresis [8–13], micellar electrokinetic chromatography [14], and chemiluminescence [3]. All the above methods require trained personnel and a well-equipped laboratory for their implementation. Therefore, there is a need for simple, inexpensive assays capable of measuring adenine. Recently, direct electrochemistry of DNA has attracted much attention among analytical chemist. Compared to the above methods, the electrochemical technique is practically suited for the analysis of adenine due to its high sensitivity and selectivity, fast response, inherent simplicity, and low cost. To date, many electrochemical protocols have been developed for the determination of the concentration of adenine [1, 15–21]. For example, Chen et al. reported the use of electrochemically pretreated glassy carbon electrode (GCE) for the simultaneous determination of adenine and guanine [1]. Farias et al. determine ultratrace adenine by adsorptive stripping voltammetry at a static mercury drop electrode [18]. Wang et al. reported the simultaneous determination of adenine and guanine using a β-cyclodextrin-incorporated carbon nanotubes-modified electrode [17]. However, it is still essential to

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develop a new and reliable method with high efficiency and convenience for the determination of adenine. To our knowledge, the direct electrochemical measurement of adenine at the poly(amidosulfonic acid) (poly-ASA)-modified electrode has not been reported.

Because of its enhanced sensitivity behavior, good electrocatalysis, and stability, polymeric film-modified electrodes have been widely used to construct biosensors [22–26], but have been little used for the direct determination of adenine. In this work, we present a sensitive voltammetric approach for the detection of adenine utilizing poly(amidosulfonic acid)-covered glassy carbon electrode (poly-ASA-GCE). The poly-ASA-modified GCE has the advantage of good affinity from PASA for adenine, and based on this, the electrochemical behavior of adenine on poly-ASA-modified GCE was studied. It was shown that the current peak of the oxidation of adenine could be enhanced in magnitude, and therefore, a simple, reliable, inexpensive, and sensitive electrochemical method was developed to determine trace level of adenine. And the poly-ASA-modified GCE exhibited good stability and reproducibility. The poly-ASA-modified GCE could have a significant attraction in biological and chemical researches.

## Experiment

Adenine were purchased from Sigma and the stock solution of $1.0\times10^{-2}$ M adenine was prepared by directly dissolving it in double-distilled water and then storing in a refrigerator at 4 °C. Amidosulfonic acid was obtained from Sinopharm Chemical Reagent Company (China). All other reagents (such as $K_3Fe(CN)_6$, $K_4Fe(CN)_6$, KCl, acetone, $NaH_2PO_4$, $Na_2HPO_4$, $H_3PO_4$, and NaOH) were purchased from Shanghai Chemical Reagents Company (China). All reagents were of analytical grade and used without any further purification. The double-distilled water was used for all experiments.

Electrochemical measurements were performed on a CHI 660A Electrochemical Workstation (CH Instruments, USA). A conventional three-electrode system was used throughout the experiments. The working electrode was a bare or poly-ASA-modified GCE (3.0 mm in diameter); the auxiliary electrode was a platinum wire and a saturated calomel electrode was used as the reference. All potentials in this paper refer to this reference electrode. Cyclic voltammetric experiments were carried out with a scan rate of 100 mV $s^{-1}$, unless otherwise stated.

Atomic force microscopy (AFM) images of the films were collected on a multimode Nanoscope III (a) scanning probe microscopy (Veeco Company, USA) in the tapping mode. A microfabricated silicon cantilever with a bending spring constant of 20–80 N $m^{-1}$ and a resonance frequency of 229–287 kHz was used to collect the images at a scan rate of 1.0 Hz in air.

Electrochemical impedance spectroscopy (EIS) was performed in 1.0 mM $K_3Fe(CN)_6/K_4Fe(CN)_6$ (1/1) mixture with 0.10 M KCl as supporting electrolyte, using an alternating current voltage of 5 mV within the frequency range of 0.1–$10^6$ Hz by Autolab Electrochemistry Instruments (Autolab, Eco Chemie, The Netherlands).

Prior to modification of poly-ASA, a bare GCE was polished successively with 0.3 and 0.05 μm $Al_2O_3$ slurry on silk. Then, it was rinsed with double-distilled water and sonicated subsequently in a 1:1 aqueous $HNO_3$ solution (volume ratio of water to $HNO_3$=1:1), acetone, and double-distilled water. After being cleaned, the electrode was immersed in pH 7.0 phosphate buffer solution (PBS) and was activated by cyclic potential scanning from −1.2 to 1.2 V at 100 mV $s^{-1}$ for 20 cycles.

Electrochemical modification of the activated GCE was performed using cyclic voltammetry in PBS (pH 7.0) containing 2.0 mM amidosulfonic acid in a potential range of −1.5 to +2.5 V at a scan rate of 100 mV $s^{-1}$ for 15 cyclic times. After the electropolymerization, the modified electrode was rinsed thoroughly with distilled water for further application.

Twenty tablets, each containing 10.0 mg/tablet adenine, were accurately weighed and finely powdered, respectively. To the accurately weighed amount of powder equivalent to approximately 70 mg of vitamin $B_4$, 50 mL of 0.01 M HCl was added. The mixture was shaken for 20 min and filtered into a 100-mL volumetric flask. The residue was washed several times with 0.01 M HCl and the solution was diluted to the mark.

## Results and discussion

### Fabrication of poly-ASA-modified GCE

Voltammograms of 2.0 mM amidosulfonic acid in 0.1 M PBS (pH 7.0) at the GCE are shown in Fig. 1. In the first scan, cathodic peak 1 was observed with a peak potential value at about −0.72 V. With a continuous increase of the number of cycles, anodic peaks 2 and 3 appeared at potentials of +0.05 and +1.46 V, respectively. Then, larger peaks were observed upon further potential cycling and trended to be stable after ten cycles, reflecting the continuous growth of the polymer film and the saturation of polymerization. These facts implied that poly-ASA membrane was deposited on the surface of GCE by electropolymerization. A homogeneous blue–black polymer film was formed on the GCE surface. After electropolymerization, the modified electrode was carefully rinsed with double-distilled water and then kept in pH 7.0 PBS.

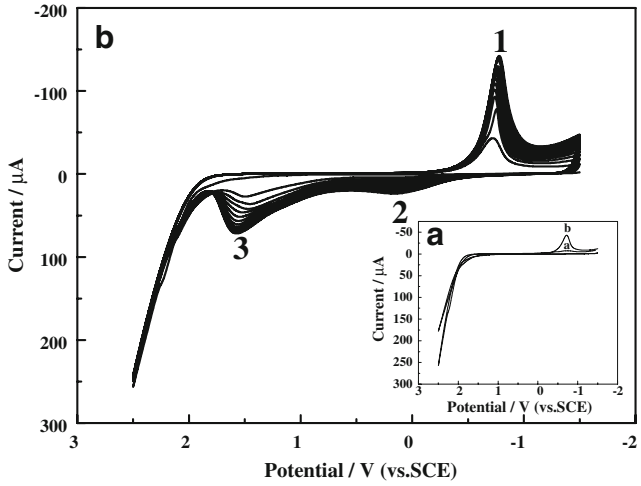



**Fig. 1** **a** The response of bare GCE (*curve a*) and the first CV scan of ASA (*curve b*). **b** Cyclic voltammograms of polymerization of poly-ASA (2.0 mM) on a bare GCE in the potential range from −1.5 to 2.5 V in a 0.1-M PBS (pH 7.0) at a scan rate of 100 mV $s^{-1}$. The cyclic time was 15

The formation and morphology of the poly-ASA film obtained on the GCE was characterized using AFM in air (Fig. 2). The AFM images showed that the bare GCE surface was relative smooth. After modification with poly-ASA, the surface morphology became very rough. This result demonstrated that poly-ASA film with mesoporous morphology was deposited on the GCE surface.

## Impedance characterization of the poly-ASA film-modified GCE and its electrochemical properties

The poly-ASA film-modified GCE was characterized by EIS (shown in Fig. 3a). From Fig. 3a, we can see that the redox process of the $[Fe(CN)_6]^{3-}/[Fe(CN)_6]^{4-}$ ions showed an electron transfer resistance of about 87 Ω (Fig. 3a, curve a) at a bare GCE. When a bare GCE was electropolymerized with ASA for different cyclic times, the electron transfer resistance increased signifi-

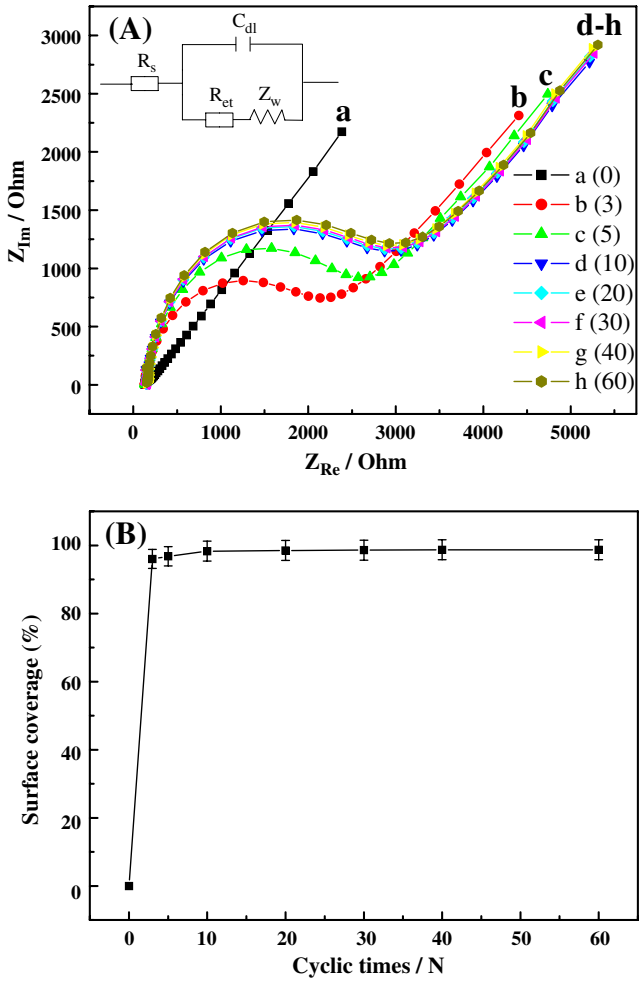



**Fig. 3** **a** Nyquist plots in impedance measurements of electrodes: *a* a bare GCE; *b–h* the poly-ASA film-modified GCEs with different electropolymerization cyclic times. Cyclic times: *b* 3; *c* 5; *d* 10; *e* 20; *f* 30; *g* 40; *h* 60. **b** Plot of the surface coverage ($\theta$) against the cyclic times. The data were obtained from **a**

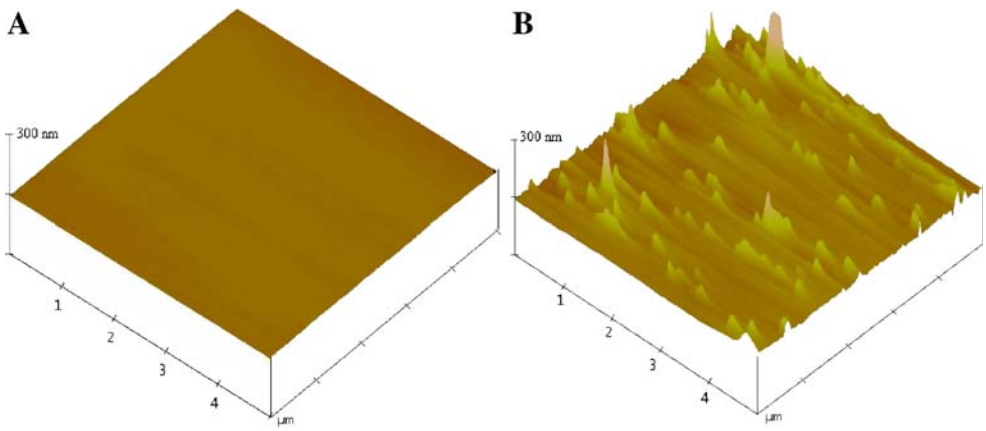



**Fig. 2** AFM images of a bare GCE (**a**) and a poly-ASA film-modified GCE with 15 cyclic times surface (**b**)

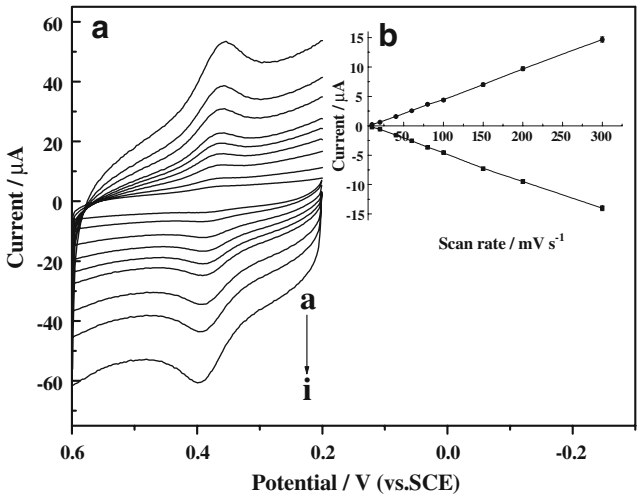



**Fig. 4** **a** Cyclic voltammograms of a poly-ASA-modified GCE in 0.05 M $H_2SO_4$ at various scan rates. From *a* to *i*, the scan rates are 10, 20, 40, 60, 80, 100, 150, and 200 mV $s^{-1}$, respectively. **b** Plot of the peak current as a function of the scan rate

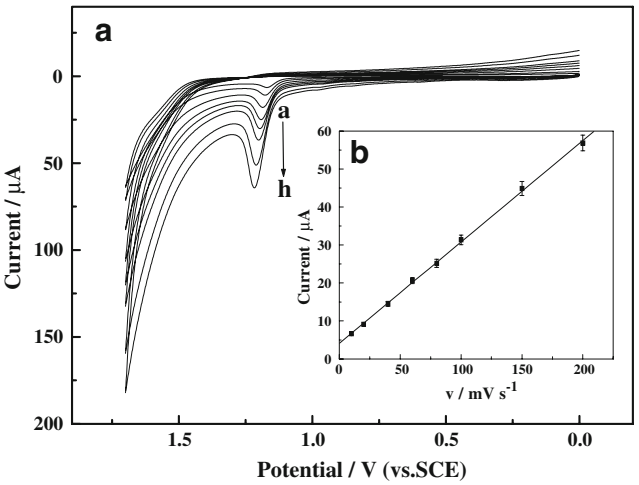



**Fig. 6** **a** Cyclic voltammograms of $1.0\times10^{-4}$ M adenine in 0.1 M PBS at various scan rates: *a* 10; *b* 20; *c* 40; *d* 60; *e* 80; *f* 100; *g* 150; *h* 200. **b** Plot of $I_{pa}$ vs. scan rate

cantly for the first ten cycles ($R_{ct}$=3,595 Ω), then did not increase with the electropolymerization times (Fig. 3a, curve d–h). The surface coverage ($\theta$) of poly-ASA film on a bare GCE can be evaluated from the EIS according to the equation [27, 28]:

$$\theta = 1 - R_{ct}^{Bare} \Big/ R_{ct}^{Poly-ASA} \quad (1)$$

where $R_{ct}^{Bare}$ denotes the charge transfer resistance of bare GCE, $R_{ct}^{Poly-ASA}$ is the corresponding resistance of the modified GCE by poly-ASA film with difference electropolymerization cyclic times. Figure 3b shows the

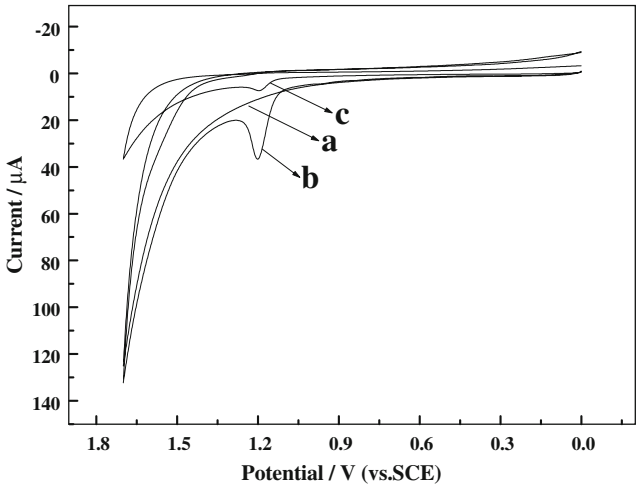
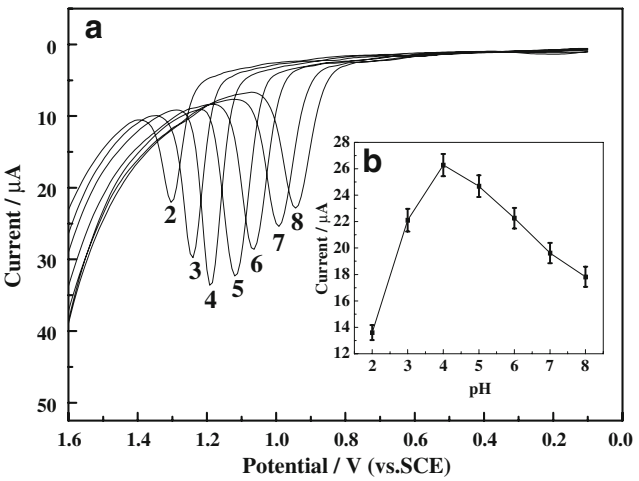



**Fig. 5** Cyclic voltammograms of poly-ASA-modified GCE in 0.1 M PBS (pH 4.0): Adenine *a* 0.0 M, *b* $1.0\times10^{-4}$ M, and *c* bare GCE with $1.0\times10^{-4}$ M adenine. Scan rate=100 mV $s^{-1}$



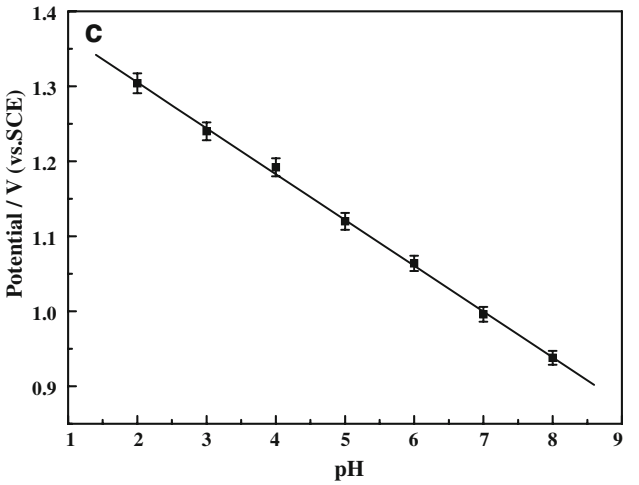
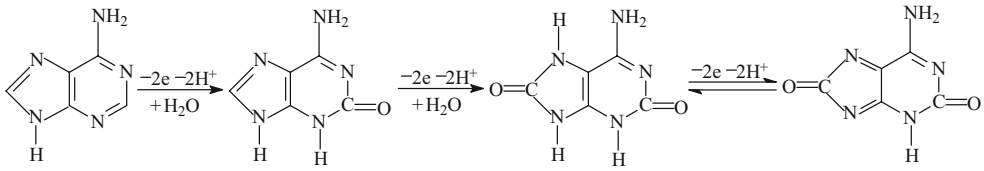




**Fig. 7** **a** Differential pulse voltammograms of $5.0\times10^{-5}$ M adenine in 0.1 M PBS at different pH values. **b** Plot of peak current vs. pH. **c** $E_{pa}$ as a function of pH

**Scheme 1** The reaction mechanism for adenine




poly-ASA film surface coverage ($\theta$) on bare GCE. It is evident that a saturated monolayer of poly-ASA film on the bare GCE surface was already formed after electropolymerization for ten cyclic times; then, the surface coverage ($\theta$) did not change with the increase of cyclic times.

Figure 4a shows the cyclic voltammograms of the poly-ASA film-modified GCE in 0.05 M $H_2SO_4$ solution at different scan rates ranging from 10 to 300 mV·s$^{-1}$. It can be seen that a well-defined redox couple appears and the peak current increases with increasing the scan rate. As shown in Fig. 4b, the anodic peak current ($I_{pa}$) is linearly dependent of the scan rate ($v$) with the equation: $I_{pa}$ (μA)=−0.048$v$+0.27 ($r$=0.9995), and the ratio of anodic peak current to the cathodic peak current ($I_{pa}/I_{pc}$) was almost equal to unity. The above results suggest that the electrochemical response of the poly-ASA-modified GCE corresponding to a surface-controlled process is reversible. The separation of the peak potentials ($\Delta E_p = E_{pa} - E_{pc}$) is 32 mV. Based on the formula ($\Delta E_p$ is close to $\frac{2.3RT}{nF}$ or 59/$n$ mV at 25 °C) [29], the number of electrons involved in the electrochemical process is two. Thus, the surface concentration of electroactive species ($\Gamma$) of the poly-ASA film could be evaluated according to the equation [30, 31]:

$$i_p = n^2F^2\frac{A\Gamma v}{4RT} \quad (2)$$

where $n$ represents the number of electrons involved in the reaction, $A$ is the geometric surface area (0.0225 cm$^2$) of the electrode, $\Gamma$ (mol cm$^{-2}$) represents the surface coverage, $v$ is the scan rate, $R$, $T$, and $F$ denote as usual for the gas constant, the temperature, and the Faraday constant, respectively. From the slope (0.048; Fig. 4b) of the anodic peak current versus the scan rate, the surface concentration of poly-ASA was calculated to be 5.68×10$^{-10}$ mol cm$^{-2}$, which further confirms the immobilized state of the poly-ASA.

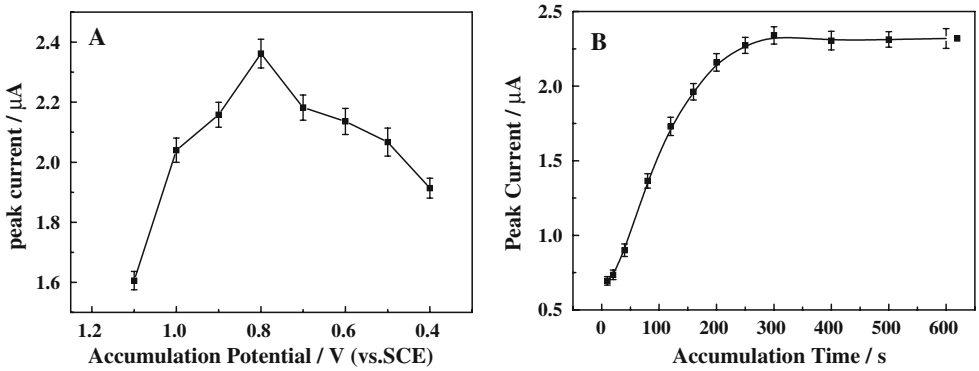
## Electrochemical behaviors of adenine at poly-ASA-modified GCE

The cyclic voltammograms of 1.0×10$^{-4}$ M adenine at a bare GCE (curve c) and a poly-ASA-modified GCE (curve b) in 0.1 M PBS (pH 4.0) are shown in Fig. 5. At poly-ASA-modified GCE, adenine exhibits a well-defined oxidation peak at about +1.2 V, while the peak current signal at the bare GCE is poor. This result is that, in ASA, there are electron-rich N atoms and high electron density of the sulfonic group, hence, the poly-ASA film is negatively charged in the condition of 0.1 M PBS (pH 4.0), while adenine is positively charged, which resulted in the adenine adsorbed from the bulk solution on the surface of poly-ASA-modified GCE by the electrostatic interactions. The peak potential of adenine at poly-ASA-modified GCE is almost same as that obtained at bare GCE. No reduction peak was observed on the cathodic scan, which indicated that the oxidation of adenine on poly-ASA-modified GCE is an electrochemically irreversible process.

## The influences of scan rate and pH on the oxidation of adenine at the poly-ASA-modified GCE

The cyclic voltammograms of 1×10$^{-4}$ M adenine in 0.1 M PBS (pH 4.0) at different scan rates are shown in Fig. 6a. The peak current increases with increasing the scan rate, while the peak potential shifts to a more positive

**Fig. 8** Effect of accumulation potential (**a**) and accumulation time (**b**) on the peak current of 1.0×10$^{-7}$ M adenine in PBS (pH 4.0)



value. As shown in Fig. 6b, the peak current of adenine is directly proportional to the scan rate ($v$) in the range of 10–200 mV $s^{-1}$ ($I_{pa}$=0.267$v$+4.074, $r$=0.9996). These results demonstrate that the electrode process was controlled by reactant adsorption and the electron transfer kinetics [1, 16].

The effect of solution pH (2.0–8.0) on the electrochemical responses of the poly-ASA-modified GCE toward the determination of adenine was studied. As shown in Fig. 7a and b, the anodic peak current of adenine reached the maximum at pH 4.0, then, the peak current decreased with the increase of solution pH. The pH dependence of oxidation peak potential of adenine is shown in Fig. 7c and obeys the equation, $E_p$=1.427−0.061pH ($r$=0.9994), respectively. The oxidation of adenine at solid electrode is expected to follow a three-step mechanism involving the total loss of six electrons (shown in Scheme 1) and the first two-electron oxidation is a rate-determining step [1, 16, 17, 32].

## The effect of accumulation potential and time on the current responses of adenine

The effects of accumulation potentials and accumulation time on the anodic stripping peak current responses of adenine were investigated. Figure 8a depicts the effect of accumulation potential on the anodic stripping peak currents after 300 s of accumulation time. It was found that the current–accumulation potential curve slightly increases from +0.4 to +0.8 V. As the accumulation potential shifted more positively, the current decreased. Thus, +0.8 V was elected as the optimal accumulation potential.

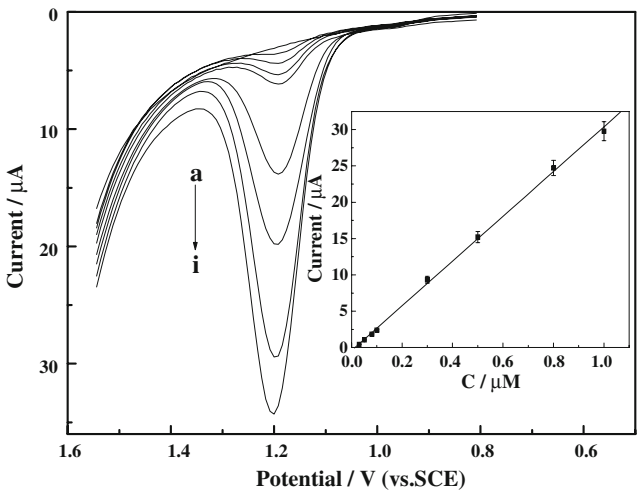



**Fig. 9** Differential pulse voltammograms of adenine at poly-ASA-modified GCE in 0.1 M PBS (pH 4.0). Adenine concentrations from *curve a* to *curve i* are 0.0, 0.030, 0.050, 0.080, 0.10, 0.30, 0.50, 0.80, and 1.0 μM, respectively. *Inset* calibration plots for adenine. Accumulation potential=+0.8 V; accumulation time=300 s

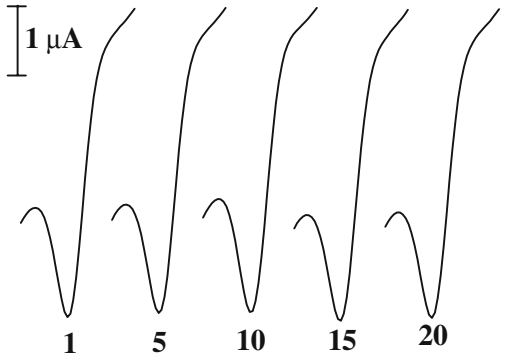



**Fig. 10** Repeatability at the identical surface of poly-ASA-modified electrode in 0.1 M PBS (pH 4.0). The *numbers* represent the times of successive measurement, which is 20. Adenine concentration=0.10 μM; accumulation time=300 s; accumulation potential=+0.8 V

At the same time, the study of the accumulation time was also carried out at the potential of +0.8 V. From Fig. 8b, it can be seen that the anodic stripping peak current of $1.0\times10^{-7}$ M adenine increases gradually with increasing accumulation time, whereas the peak current hardly changes as the accumulation time further increased. Here, the accumulation time of 300 s was selected.

## Determination of adenine

Under the optimum experiment conditions, the calibration plot for adenine detection in 0.1 M PBS (pH 4.0) was carried out by differential pulse voltammetry (DPV). As shown in Fig. 9, the electrochemical response of adenine increased linearly with the increase of the adenine concentration in the range of 0.030–1.0 μM. The linear regression equation was expressed as: $I_{pa}$ (μA)=−0.42+30.81$C$ (μM) with a correlation coefficient of $r$=0.9994. And the detection limit ($S/N$=3) is $8.0\times10^{-9}$ M.

The interference of foreign substances were investigated by analyzing a standard solution of 0.10 μM adenine into which increasing amounts of interfering analyte was added. If the tolerance limit was taken as the maximum concentration of the foreign substances (approximately 5% relative error), $Na^+$ (1,000 μM), glucose (1,000 μM), carbamide

**Table 1** Recovery test of adenine in tablet ($n$=5)

| Sample | Added ($\times10^{-8}$ M) | Found ($\times10^{-8}$ M) | Recovery (%) | RSD (%) |
|---|---|---|---|---|
| Adenine | 0.00 | 3.81 | / | 3.8 |
| | 3.00 | 6.93 | 104.00 | 4.2 |
| | 10.00 | 13.79 | 99.80 | 4.1 |
| | 30.00 | 34.48 | 102.23 | 3.9 |
| | 50.00 | 52.42 | 97.22 | 4.5 |

(800 μM), ascorbic acid (800 μM), $Ca^{2+}$ (300 μM), $Mg^{2+}$ (300 μM), $Cu^{2+}$ (250 μM), cucitric acid (200 μM), dopamine (100 μM), lysine (50 μM), and cysteine (50 μM) did not affect the determination of adenine.

### Reproducibility and stability

The repeatability was also evaluated by successively measuring the same 0.1 μM adenine for 20 times at the identical surface of poly-ASA-modified GCE and there was no electrode regeneration procedure necessary to apply between successive measurements. The average currents were 2.38 μA with the relative standard deviation (RSD) of 4.3% (shown in Fig. 10). Additionally, the reproducibility between multiple electrode preparations ($n$=10) was estimated by comparing the oxidation peak current of 0.10 M adenine and the average peak current was 2.32 μA with the RSD of 4.6%. The results indicated that the poly-ASA-modified film can prevent the adsorption of adenine and adenine oxidation products at the electrode surface which is observed at bare carbon electrodes, and the modified electrode has a good reproducibility.

The stability of the poly-ASA-modified electrode was investigated over a 2-week period. When the poly-ASA-modified electrode was stored in 0.1 M PBS (pH 7.0) at 4 °C in a refrigerator and was periodically removed from storage to measure the current response of 0.10 μM adenine, the anodic peak currents lost only 5.1% of the initial response after 2 weeks. It manifested that the poly-ASA-modified electrode showed good stability.

### Analytical application

The above-presented method was applied to the determination of adenine in tablets of vitamin $B_4$, which were prepared as described in the experimental section. The tablet samples of vitamin $B_4$ were diluted appropriately for determining and were analyzed by the standard addition method. The analytical result (10.29 mg/tablet) was in good agreement with the value indicated in the instruction booklet. Based on the above-presented method of measuring adenine by poly-ASA-modified GCE, the recovery of adenine for tablets was listed in Table 1. The satisfactory results showed that the above-presented method can be used to determine concentration of adenine in commercial tablets.

## Conclusions

In this work, we reported a novel method for the determination of adenine at low level by DPV at the poly-ASA-modified GCE prepared by electropolymerization method. The experimental results suggest that the poly-ASA film can enhance the sensitivity for determining adenine. In differential pulse voltammetric determination, the detection limit was evaluated to be $1.0\times10^{-7}$ M. And the proposed method could be applied to the detection of adenine in pharmaceutical formulations. In addition, after successive measurements, the modified electrode shows a stable response without fouling of the electrode surface by the adsorption of the oxidized product of adenine. The coexistence of other substances does not affect the property of the poly-ASA-modified GCE and the determination of adenine. The present new method for the determination of adenine proposed an excellent platform for expending the application of the polymer film in electrochemical field.

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