



Graphene–polyaniline composite film modified electrode for voltammetric determination of 4-aminophenol

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ARTICLE INFO

Article history:

Received 9 March 2011

Received in revised form 25 May 2011

Accepted 26 May 2011

Available online 2 June 2011

Keywords:

Graphene

Polyaniline

Nanocomposite

Aminophenol

Electrochemical sensor

ABSTRACT

An electrochemical sensor based on graphene–polyaniline (GR–PANI) nanocomposite for voltammetric determination of 4-aminophenol (4-AP) is presented. The electrochemical behavior of 4-AP at the GR–PANI composite film modified glassy carbon electrode (GCE) was investigated by cyclic voltammetry. 4-AP exhibits enhanced voltammetric response at GR–PANI modified GCE. This electrochemical sensor shows a favorable analytical performance for 4-AP detection with a detection limit of 6.5×10^{-8} M and high sensitivity of $604.2 \mu\text{A mM}^{-1}$. Moreover, 4-AP and paracetamol can be detected simultaneously without interference of each other in a large dynamic range.

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1. Introduction

Graphene-based nanomaterials have recently shown fascinating applications in electrochemical sensors and biosensors, which provide an effective sensing platform for small biomolecules [1,2]. Owing to the extraordinary electronic transport property and high electrocatalytic activity of graphene, the electrochemical reactions of analyte are greatly promoted on graphene film, resulting in enhanced voltammetric response [3,4]. Moreover, the electrochemical properties of graphene can be effectively modified by integration with other functional nanomaterials such as catalyst nanoparticles to produce versatile electrochemical sensing performance [5–9].

Polyaniline (PANI) is one of the most attractive conducting polymers, which has potential applications in electrochemical sensors and biosensors [10,11]. Owing to its good biocompatibility and inherent electroactivity, PANI can act as a suitable matrix for immobilization of biomolecules and mediator for redox and enzymatic reactions [12,13], which exhibits impressive signal amplification and antifouling properties [10]. Recent studies have demonstrated that integration of PANI with carbon nanotubes (CNTs) can significantly enhance the conductivity and electrocatalytic activity of the resultant electrode materials [14–17]. Comparing with carbon nanotubes, graphene has shown the advantages of high conductivity,

ease of production and function, good biocompatibility and abundance of inexpensive source material [2]. Therefore, it is highly desirable to explore graphene–polyaniline hybrid materials for applications in electrochemical sensors and biosensors. Recently, several groups reported the graphene–polyaniline nanocomposite prepared by in situ polymerization methods [18–20]. The doping of graphene with polyaniline remarkably enhances the conductivity and mechanical strength, which exhibit excellent performance as electrode material for supercapacitors. However, to the best of our knowledge, the electrochemical sensing properties of graphene–polyaniline nanocomposite have not been investigated.

4-Aminophenol (4-AP) is the primary hydrolytic degradation product of paracetamol [21]. As a widely used antipyretic and analgesic drug, paracetamol is an effective and safe agent to relieve mild to moderate pains [22]. However, 4-AP, with significant nephrotoxicity and teratogenic effect, can be detected in pharmaceutical preparations as a degradation product of paracetamol or as a synthetic intermediate. Due to its high toxicity, the maximum content of 4-AP in pharmaceuticals is limited to 50 ppm (0.005%, w/w) by the European [23] and United States [24] and Chinese pharmacopoeias. Therefore, it is essential to develop simple, sensitive and accurate analytical methods for 4-AP detection in pharmaceutical preparations. Since 4-AP is an electroactive compound, considerable interests have been focused on the development of chemically modified electrodes for 4-AP detection [25–30].

In this work, we prepared the graphene–polyaniline (GR–PANI) nanocomposite by in situ polymerization method. The electrochemical sensor was fabricated with the GR–PANI composite film

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modified glassy carbon electrode. The electrochemical behavior and voltammetric determination of 4-AP at the GR–PANI modified electrode was investigated in detail. The results show that the GR–PANI composite film can be used as an effective electrochemical sensing interface for 4-AP.

2. Experimental

2.1. Reagents and apparatus

Graphite powder (320 mesh, spectrographic pure) was purchased from Sinopharm Chemical Reagent Co., Ltd. Aniline, ammonium peroxydisulfate (APS), hydrazine hydrate (50%), 4-aminophenol and paracetamol were purchased from Aladdin Chemistry Co., Ltd. All other chemicals were of analytical reagent grade and used as received. Water used throughout all experiments was purified with the Millipore system.

Scanning electron microscopy (SEM) images were obtained on a Hitachi S-4800 scanning electron microscope. All electrochemical experiments were performed with a CHI 850C electrochemical workstation (CH Instruments, Shanghai, China). A conventional three-electrode system was used for all electrochemical experiments, which consisted of a platinum wire as counter electrode, an Ag/AgCl/3 M KCl as reference electrode, and a bare or modified glassy carbon electrode (3 mm diameter) as working electrode.

2.2. Preparation of GR–PANI nanocomposite

Graphene oxide was synthesized from graphite powder by the modified Hummers method [31,32]. Briefly, graphite was pre-oxidized in a mixture containing 15 mL concentrated H_2SO_4 , 5 g $\text{K}_2\text{S}_2\text{O}_8$ and 5 g P_2O_5 . The mixture was then diluted with deionized water, filtered and dried naturally. The preoxidized graphite was re-oxidized by Hummers method in a mixture of concentrated H_2SO_4 and KMnO_4 to produce the graphene oxide. GR–PANI nanocomposite was prepared by the literature method [18]. In a typical procedure, graphene oxide was dispersed in 1 M HCl containing 0.3 M aniline by ultrasonication for 1 h. Then, another solution of 0.075 M APS in 1 M HCl was rapidly added to the mixture under vigorous stirring. The color of the mixture changed into green after about 5 minutes, indicating polymerization of aniline. After stirring at room temperature overnight, the resulting mixture was diluted by 100 mL of water and collected by filtration. The resulting polyaniline-graphene oxide composite was then reduced by hydrazine in water at 95 °C. Finally, the composite was dispersed in 1 M HCl containing APS, and stirred at room temperature overnight. The resulting graphene–polyaniline nanocomposite was collected by filtration and dried in vacuum. Polyaniline nanofibers were prepared by the similar procedure according to the literature report [18].

2.3. Preparation of modified electrode

The as-prepared GR–PANI nanocomposite was dispersed in DMF with ultrasonication for 1 h to get a homogenous suspension (1 mg mL^{-1}). Then, 5 μL of the suspension was dropped onto the surface of freshly polished glassy carbon electrode (GCE) and dried at room temperature, resulting in the GR–PANI modified GCE (GR–PANI/GCE). For comparison, 5 μL of the homogenous suspension of graphene and PANI in DMF (1 mg mL^{-1}) was coated on bare GCE to obtain the GR and PANI modified GCE (GR/GCE and PANI/GCE), respectively.

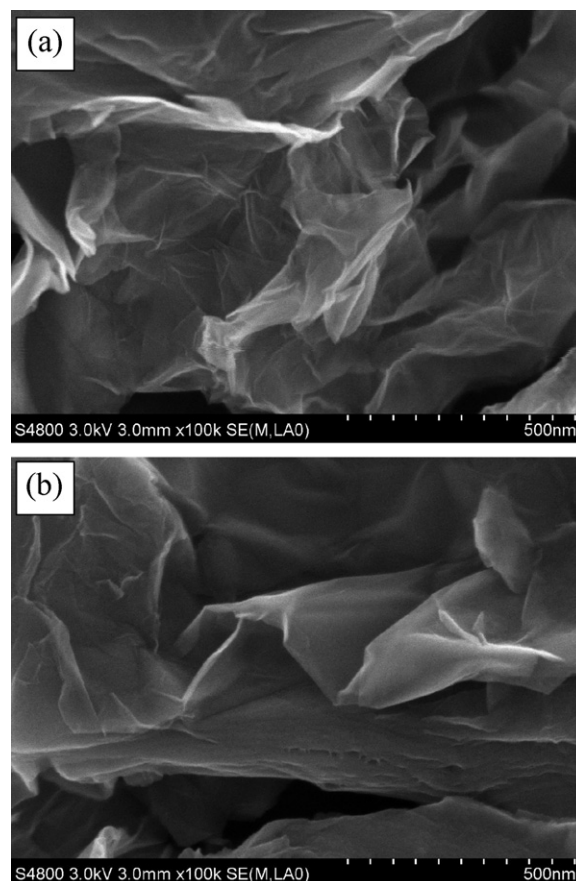


Fig. 1. SEM image of (a) GR and (b) GR–PANI nanocomposite.

3. Results and discussion

3.1. Preparation and characterization of GR–PANI nanocomposite

The GR–PANI nanocomposite was prepared by in situ polymerization according to the literature method [18]. In this method, the aniline monomer was first mixed with exfoliated graphene oxide sheets in water to form a homogenous suspension. Then, the in situ polymerization was initiated by APS to obtain the homogenous composite of graphene oxide–polyaniline. Finally, the composite was reduced to graphene by hydrazine and followed by reoxidation and reprotonation of the reduced PANI to produce the GR–PANI nanocomposite. To make graphene as the main component, the mass ratio of graphene oxide to aniline monomer in the starting materials was controlled at 4:1. The morphology of the as-prepared GR–PANI composite and graphene were characterized using scanning electron microscope (SEM). As shown in Fig. 1, GR–PANI exists in a layered and wrinkled form with PANI nanofibers distributed between and on the surface of graphene sheets. In the FT-IR spectra (figure not shown), the absorption peaks located at 1570 and 1135 cm^{-1} , and 1492 cm^{-1} represent the quinoidal and benzenoid structure of PANI, respectively [18,20]. The CV curves of GR–PANI composites in blank phosphate buffer solution (PBS) were featureless, which was consistent with the previous report [18]. This can be ascribed to the structure change of the polyaniline nanofibers during the reduction, reoxidation and reprotonation processes in the preparation of GR–PANI. The Nyquist plots at bare GCE, GR/GCE and GR–PANI/GCE were depicted in Fig. 2. It can be seen that GR–PANI has little higher interfacial charge-transfer resistance than GR; however, both of them are very low due to the good conductivity of GR. Moreover, the neglectable Warburg region on the Nyquist plot

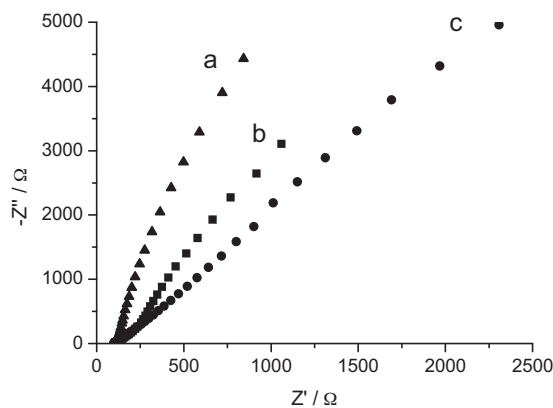


Fig. 2. Nyquist plots at (a) bare GCE, (b) GR-PANI/GCE and (c) GR/GCE in 5 mM $\text{Fe}(\text{CN})_6^{3-/4-}$ containing 0.1 M KCl. The frequency range is from 0.01 Hz to 100 kHz.

of GR-PANI indicates short and equal diffusion path length of the ions in electrolyte. This can be attributed to the homogenous morphology of the GR-PANI composite, in which the ions of electrolyte only access the surface of the nanocomposite [18].

3.2. Electrochemical behavior of 4-AP at GR-PANI/GCE

The electrochemical behavior of 4-AP was investigated in 0.1 M PBS (pH 7.0) by cyclic voltammetry. Fig. 3 depicts the cyclic voltammograms (CVs) of 4-AP at the bare GCE, GR/GCE, PANI/GCE and GR-PANI/GCE. At the bare GCE (Fig. 3a), 4-AP shows a quasi-reversible redox behavior with relative weak redox peaks at $E_{pa} = 0.314$ V and $E_{pc} = 0.116$ V. At GR/GCE (Fig. 3b), a pair of well-defined and quasi-reversible redox peaks corresponding to the electrochemical reaction of 4-AP were observed with $E_{pa} = 0.131$ V and $E_{pc} = 0.081$ V. The significantly increased redox peak currents and reduced oxidation potential at the graphene film can be reasonably ascribed to its good electrocatalytic activity. In the case of PANI/GCE, the redox peak currents were further increased with $E_{pa} = 0.181$ V and $E_{pc} = 0.057$ V. At GR-PANI/GCE, 4-AP exhibits remarkably enhanced voltammetric response comparing with GR and GR-PANI modified electrodes, with $E_{pa} = 0.162$ V and $E_{pc} = 0.078$ V. The net values of oxidation peak current of 4-AP obtained at the GR-PANI/GCE ($48.05 \mu\text{A}$) is about 1.7 and 1.4 times higher than that at the GR/GCE ($28.91 \mu\text{A}$) and PANI/GCE ($34.50 \mu\text{A}$), respectively. These results demonstrate that the electrochemical reactivity of 4-AP is remarkably promoted on the GR-PANI composite film. It is suggested that, with the synergistic

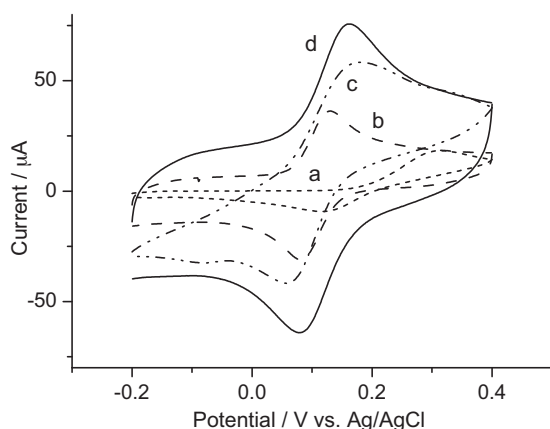


Fig. 3. CVs of 1.0 mM 4-AP at (a) bare GCE, (b) GR/GCE, (c) PANI/GCE and (d) GR-PANI/GCE in 0.1 M PBS (pH 7.0) at scan rate of 50 mV s^{-1} .

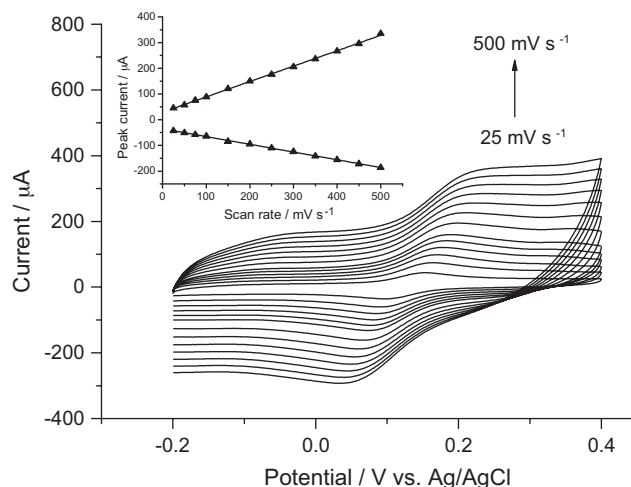


Fig. 4. CVs of 1.0 mM 4-AP at GR-PANI/GCE with different scan rates from 25 to 500 mV s^{-1} in 0.1 M PBS (pH 7.0). Insert, the plots of peak current vs. scan rate.

effects of graphene and polyaniline, the homogenous composite of GR-PANI provides an efficient microenvironment for the electrochemical reaction of 4-AP, resulting significantly enhanced voltammetric response.

3.3. The redox mechanism of 4-AP at GR-PANI/GCE

The effect of scan rate on the redox peak currents of 4-AP at the GR-PANI/GCE was investigated by cyclic voltammetry. As shown in Fig. 4, the anodic and cathodic peak currents increase with the scan rate, which are linearly proportional to scan rate in the range from 25 to 500 mV s^{-1} . The linear relationship between the peak current and scan rate can be expressed by the linear regression equation as: $I_{pa}/\mu\text{A} = 29.46 + 0.5909 \nu/\text{mV s}^{-1}$ ($R = 0.9973$) and $I_{pc}/\mu\text{A} = -35.34 - 0.3018 \nu/\text{mV s}^{-1}$ ($R = 0.9952$), respectively. This result indicates that the electrochemical reaction of 4-AP on the GR-PANI film is a surface-controlled process. At high scan rates ranging from 100 to 500 mV s^{-1} , the linear regression equations of E_{pa} and E_{pc} vs. the logarithm of the scan rates are expressed as $E_{pa} = 0.3127 + 0.06512 \log \nu$ ($R = 0.9910$) and $E_{pc} = 0.02670 - 0.04695 \log \nu$ ($R = 0.9951$), respectively. According to Laviron's equation [33], the slopes are equal to $2.3RT/(1-\alpha)nF$ and $-2.3RT/\alpha nF$ for anodic and cathodic peak, respectively. Thus, the electron transfer coefficient (α) and the electron transfer number (n) are calculated to be 0.58 and 2, respectively. The adsorbed amount of 4-aminophenol on the surface of GR-PANI/GCE was further calculated by the following equation: $i_p = n^2 F^2 A \Gamma \nu / 4RT$ [33]. Based on the relationship of i_p with ν , the value of the surface concentration of 4-aminophenol (Γ) was obtained with the results as $2.1 \times 10^{-9} \text{ mol cm}^{-2}$, indicating good adsorptivity of the GR-PANI composite film.

The effect of solution pH on the redox reaction of 4-AP at the GR-PANI/GCE was investigated in the range of pH 4.0–8.0. As shown in Fig. 5, a negative shift of both the cathodic and anodic peak potentials occurs when the pH value is increased. The formal potential E^0 changes linearly as a function of solution pH with the linear regression equation as: $E^0/\text{V} = 0.5110 - 0.05790 \text{ pH}$ ($R = 0.9973$). The slope value of -57.9 mV pH^{-1} is close to the theoretical value of -58.6 mV pH^{-1} according to Nernst equation, suggesting equal numbers of proton and electron are involved in the redox reaction. Thus, at the GR-PANI/GCE, the redox reaction of 4-AP is a two-proton coupled two-electron process (Scheme 1) [25].

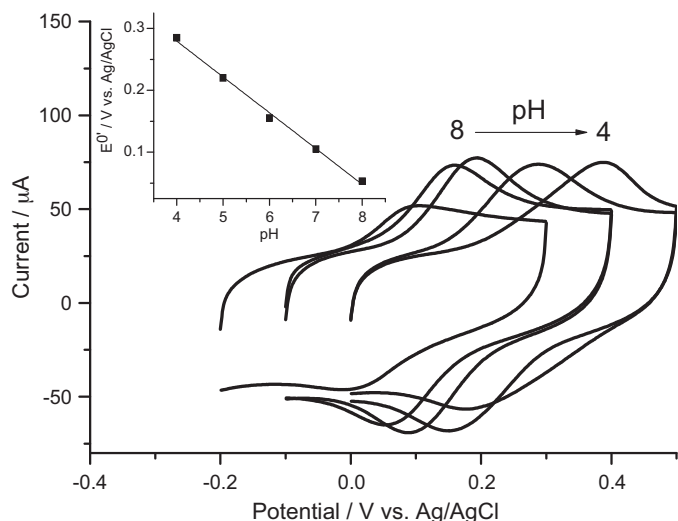
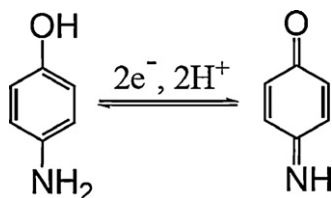


Fig. 5. CVs of 1.0 mM 4-AP at GR-PANI/GCE in 0.1 M PBS with different pH values of 4.0, 5.0, 6.0, 7.0 and 8.0. Insert, the plot of formal potential vs. pH values. Scan rate, 50 mV s^{-1} .



Scheme 1. The electrooxidation mechanism of 4-AP.

3.4. Voltammetric determination of 4-AP

The voltammetric determination of 4-AP was carried out in 0.1 M PBS (pH 7.0) using differential pulse voltammetry at the GR-PANI/GCE. Fig. 6 depicts the differential pulse voltammograms (DPVs) of various concentrations of 4-AP. The peak currents increase linearly against the concentration of 4-AP within the range of 0.2–100 μM . The calibration curve for 4-AP shows two linear segments: the first linear segment increases from 0.2 to 20 μM with the linear regression equation of $I_p/\mu\text{A} = 9.822 + 0.1776c/\mu\text{M}$ ($R = 0.9975$), and the second linear segment increases up to 100 μM with the linear regression equation of $I_p/\mu\text{A} = 1.489 + 0.6042c/\mu\text{M}$ ($R = 0.9990$). The detection limit ($S/N = 3$) is estimated to be $6.5 \times 10^{-8} \text{ M}$ and the sensitivity is 177.6 and $604.2 \mu\text{A mM}^{-1}$ for two linear segment, respectively. As can be seen from Table 1, the detection limit of 4-AP at the GR-PANI/GCE is lower than those obtained on p[NVCzVBSA1]/CFME ($1 \times 10^{-6} \text{ M}$) and carbon ionic liquid electrode ($1 \times 10^{-7} \text{ M}$), and is comparable to that of graphene–chitosan modified GCE ($5.7 \times 10^{-8} \text{ M}$) and SWNTs/POAPE modified GCE ($6 \times 10^{-8} \text{ M}$), indicating favorable analytical performance of this electrochemical sensor.

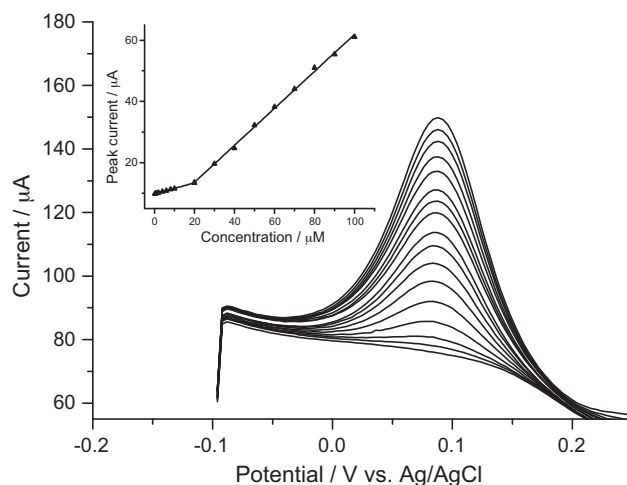


Fig. 6. DPVs of 0.2, 0.6, 1, 2, 4, 6, 8, 10, 20, 30, 40, 50, 60, 70, 80, 90 and 100 μM of 4-AP at GR-PANI/GCE in 0.1 M PBS (pH 7.0). Insert, the plot of peak current vs. 4-AP concentration.

Since 4-AP is a degradation product of paracetamol, it necessary for an electrochemical sensor to detect 4-AP in the presence of paracetamol. Simultaneous determination of various concentrations of 4-AP and paracetamol was carried out at GR-PANI/GCE in 0.1 M PBS (pH 7.0). 4-AP and paracetamol exhibit well-defined DPV waves with peak potentials at 0.087 and 0.376 V, respectively. The peak-to-peak separation of 4-AP and paracetamol is 0.311 V, which is large enough for their simultaneous determination. As shown in Fig. 7, 4-AP and paracetamol can be detected simultaneously without interference of each other. The calibration curve for 4-AP also exhibits two linear segments with regression equation as: $I_p/\mu\text{A} = 6.974 + 0.2317c/\mu\text{M}$ ($R = 0.9930$) and $I_p/\mu\text{A} = 1.233 + 0.5184c/\mu\text{M}$ ($R = 0.9987$) in the linear range of 1.0–20 μM and 20–100 μM , respectively. For paracetamol, the linear detection range is 10–100 μM with linear regression equation as: $I_p/\mu\text{A} = -3.762 + 0.3823c/\mu\text{M}$ ($R = 0.9987$). These results indicate the good selectivity of the GR-PANI based electrochemical sensing interface.

The long-term stability of the GR-PANI/GCE electrochemical sensor was investigated by examining its current response during storage in a refrigerator at 4 $^{\circ}\text{C}$. The electrochemical sensor exhibited no obvious decrease in current response in the first week and maintained about 95% of its initial value after two weeks. The relative standard deviation (RSD) of the GR-PANI/GCE electrochemical sensor in response to 50 μM 4-AP for ten measurements was 3.8%, indicating the good reproducibility.

The interference of some small biomolecules and phenol derivatives on the determination of 4-AP was investigated. The result showed that 50-fold of glucose, uric acid, tryptophan, tyrosine, cysteine, phenol, 4-nitrophenol and 4-chlorophenol did not interfere with the DPV signal of 50 μM 4-AP (peak current change $< \pm 5\%$).

Table 1

Comparison of the performances of some 4-AP electrochemical sensors.

Electrode	LOD (M)	Linear range (μM)	Sensitivity ($\mu\text{A mM}^{-1}$)	Reference
Graphene–chitosan/GCE	5.7×10^{-8}	0.2–550	33	[25]
CILE ^a	1.0×10^{-7}	0.3–1000	–	[26]
p[NVCzVBSA1]/CFME ^b	1×10^{-6}	–	–	[27]
SWNTs/POAPE/GCE ^c	6×10^{-8}	0.2–100	1800	[28]
GR-PANI/GCE	6.5×10^{-8}	0.2–2020–100	177.6; 604.2	This work

^a Carbon ionic liquid electrode.

^b Poly[N-vinylcarbazole-co-vinylbenzene sulfonic acid]/carbon fibre microelectrode.

^c Single-wall carbon nanotubes/poly(4-aminopyridine).

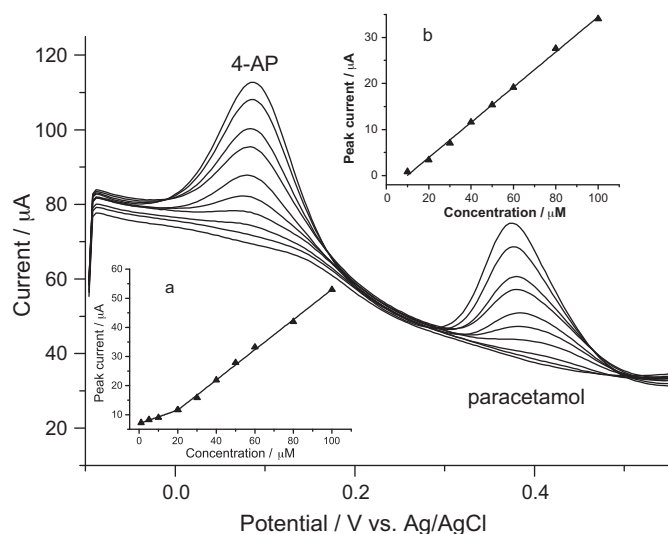


Fig. 7. DPVs of 1, 5, 10, 20, 30, 40, 50, 60, 80 and 100 μM of 4-AP and paracetamol at GR-PANI/GCE in 0.1 M PBS (pH 7.0). Insert, (a) the plot of peak current vs. 4-AP concentration, (b) the plot of peak current vs. paracetamol concentration.

4. Conclusions

In summary, GR-PANI nanocomposite was prepared and utilized as electrochemical sensing interface for 4-AP. The electrochemical behavior of 4-AP at the GR-PANI composite film modified electrode was studied. The results indicate that the GR-PANI nanocomposite can provide a favorable microenvironment for the electrochemical reaction of 4-AP, resulting in enhanced the voltammetric response. This GR-PANI based electrochemical sensor processes low detection limit, high sensitivity and long-term stability for the determination of 4-AP. Moreover, 4-AP and paracetamol can be detected simultaneously without interference of each other in a large dynamic range. The GR-PANI nanocomposite may offer a new approach for developing graphene-based electrochemical sensors and biosensors.

Acknowledgements

This work was financially supported by the National Natural Science Foundation of China (No. 21002082) and the Key Project of Chinese Ministry of Education (No. 210129), and the Specific Funding for the Technology centers of Henan Province (No. 102102313101).

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