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Functional graphene-gold nano-composite fabricated electrochemical biosensor for direct and rapid detection of bisphenol A

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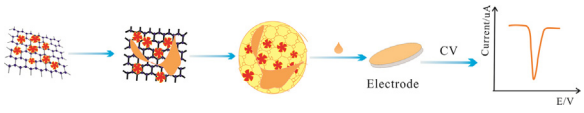
HIGHLIGHTS

- A novel graphene was fabricated via gold nanoparticle to separate individual sheets.
- Various techniques are adopted to characterize the prepared nanocomposites.
- A tyrosinase biosensor based on graphene-gold nanocomposites was developed.
- The proposed biosensor for BPA detection exhibited excellent performance.

GRAPHICAL ABSTRACT



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ABSTRACT

In this research, the graphene with excellent dispersity is prepared successfully by introducing gold nanoparticle to separate the individual sheets. Various techniques are adopted to characterize the prepared graphene and graphene-gold nanoparticle composite materials. This fabricated new composite material is used as the support material to construct a novel tyrosinase based biosensor for detection of bisphenol A (BPA). The electrochemical performances of the proposed new enzyme biosensor were investigated by differential pulse voltammetry (DPV) method. The proposed biosensor exhibited excellent performance for BPA determination with a wide linear range (2.5×10^{-3}–3.0 μM), a highly reproducible response (RSD of 2.7%), low interferences and long-term stability. And more importantly, the calculated detection limit of the proposed biosensor was as low as 1 nM. Compared with other detection methods, this graphene-gold nanoparticle composite based tyrosinase biosensor is proved to be a promising and reliable tool for rapid detection of BPA for on-site analysis of emergency BPA related pollution affairs.

1. Introduction

The plastic monomer and plasticizer bisphenol A (BPA) is one of the highest yield chemicals produced worldwide, with over six billion pounds produced each year [1]. BPA is mainly used in the production of polycarbonate plastics, epoxy resins and thermo plastics, and is found in food and beverage containers, glues, some dental sealants and composites under normal conditions of use which is due to the incomplete polymerization and to the

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degradation of polymers by exposure to high temperatures, occurring under normal conditions of use [2–5]. As one kind of endocrine disrupting compounds (EDCs), BPA is suspected of interfering with the normal function of the endocrine system causing adverse effects for humans and wildlife [6]. Toxicological studies on cells and animals have shown that BPA is estrogenic and affect the reproductive system after exposure to high doses [7,8]. However, these low doses effects of BPA have been of continuous conflicts [9,10]. Therefore, concerns about health risks of exposure to BPA have led to increased and urgent need for monitoring the trace amount of BPA.

Traditional analytical techniques can achieve BPA detection with high sensitivity and good precision. But these methods could only be carried out in the specific labs and operated by highly trained technicians no matter requiring the time-consuming sample pretreatments and expensive instruments, making them unsuitable for on-site and rapid monitoring. For these reasons, these highly instrument-depended detection methods can not completely meet the demand of rapid and on-tie monitoring of numerous samples. Alternatively, biosensors are the ideally analytical tools for on-site monitoring of BPA-contained environmental pollutants [11–13]. Compared with the instrument methods, electrochemical biosensors, on the contrary, represent a kind of rapid and economic detection methods with the advantage of high sensitivity, potential for miniaturization, and the possibility of in situ analysis [14].

It is well known that biosensing materials plays a vital role in the development of enzyme biosensor [15]. Graphene, which has been characterized as “the thinnest material in this world” [16], attracted great attention owing to some displayed excellent properties. The structural integrity of the graphene is a single layer of carbon atoms with extremely stable six-membered ring in two-dimensional crystal. The unique properties of graphene include fast electron transportation, high thermal conductivity, excellent mechanical stiffness and good biocompatibility [17], which result in wide application prospects in electronics, information, energy, materials and bio-medicine and other fields. However, the strong van der Waals effect between the single graphene sheets could induce the aggregation of graphene, leading to the insoluble in water and common organic solvents. These drawbacks limit the further applications of graphene in various fields. In order to fully show its excellent properties and to improve its processability (such as increased solubility, dispersibility, etc.), graphene usually should be effectively functionalized to avoid the adverse effects for sensing. Stankovich et al. obtained isocyanate functionalized graphene by modification with small organic molecules [18]. Meanwhile, long chain alkyl functionalized graphene was obtained by the chemical reaction between the amino groups of octadecylamine (ODA) and the carboxyl group of graphene oxide [19]. Besides, Shen et al. reported the preparation of functionalized amphiphilic graphene by copolymerization [20]. All these reported researches realized the excellent and uniform dispersibility in both polar and non-polar solution, supplying the directing techniques and strategies for application of graphene materials. Besides, sulfonated graphene has been prepared and applied in the field of electrochemical biosensors due to the significantly improved solubility and conductivity of grapheme [21]. Of note, all these previously reported results demonstrate that graphene is an eximious electrode material and can significantly enhance the performance of related biosensors.

In this research, firstly, we successfully prepared neoteric modified graphene. For the introduction of gold nanoparticles, compared with the traditional graphene, the properties of conductivity, adsorption and biocompatibility of the as-synthesized graphene were observably enhanced, which gave it unparalleled electrochemical performance. The novel graphene were further combined with chitosan and tyrosinase tightly to improve the activity of tyrosinase. Following, based on the unique properties of graphene, we assembled an unprecedented tyrosinase biosensor for BPA. Meanwhile, the performances of the novel biosensor were systematically compared with other traditional graphene based tyrosinase biosensors. Achieved results demonstrate that the novel tyrosinase based biosensor exhibited faster response, better operation repeatability, higher sensitivity, lower background current for BPA sensing than traditional graphene-based tyrosinase biosensor.

2. Materials and methods

2.1. Materials

BPA and graphite flakes were obtained from Sinopharm Chemical Reagent China (Beijing) Co., Ltd., tyrosinase (from mushroom, >1000 units mg^{-1}, pI 5.92) were purchased from Sigma. Acetonitrile and Methanol were HPLC grade from Dikma-pure Technologies Inc. All other chemicals (analytical grade) were purchased from Sinopharm Chemical Reagent China (Beijing) Co., Ltd., 0.1 mol L^{-1} phosphate buffer solutions (PBS, pH 7.0) were prepared by mixing standard solutions of K_2HPO_4 and KH_2PO_4. Unless otherwise mentioned, PBS (0.1 mol L^{-1}, pH 7.0) was used as the electrolyte in all experiments. Milli-Q water (18.25 MΩ cm^{-2}) was used throughout all experiments.

2.2. Apparatus

Transmission electron microscope (TEM), Scanning electron microscopy (SEM) and energy dispersive spectrometer (EDS) images were obtained with a transmission electron microscope JEOL2100HR (JEOL, Japan) with an accelerating voltage of 200 kV LaB6. Before the measurements, the samples were degassed at 180 °C for 6 h. And all the electrochemical experiments were carried out at room temperature. Electrochemical impedance

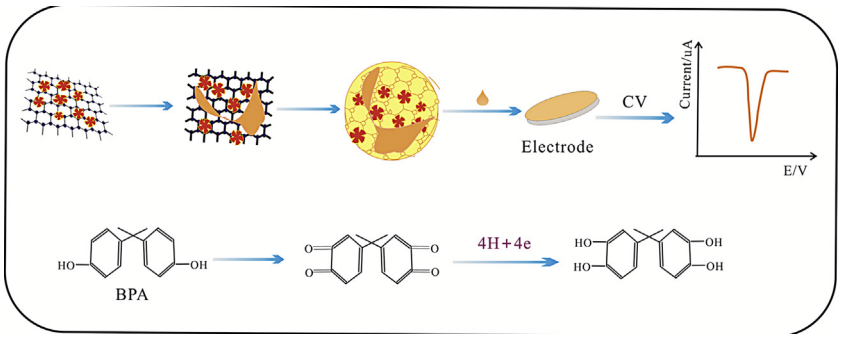

Fig. 1. The schematic diagram of biosensor preparation and the BPA sensing mechanism.

spectroscopy (EIS) measurements were performed in 2 mmol L^{-1} $K_3[Fe(CN)_6]/K_4[Fe(CN)_6]$ (1:1) solution containing 0.1 mol L^{-1} KCl, and the results were plotted in the form of complex plane diagrams (Nyquist plots) with a frequency range from 0.1 Hz to 10 kHz. Cyclic voltammetry, current–time curve (I–t) and differential pulse voltammetry (DPV) were carried out on glassy carbon (GCE) electrodes (diameter, 3 mm) using an Electrochemical CHI 1030B Workstation (CHI instruments, Chenhua, Shanghai, China). A three-electrode system was employed, consisting of a modified glassy carbon electrode (diameter, 3 mm) serving as the working electrode, saturated calomel electrode and platinum wire serving as the reference and counter electrodes respectively.

2.3. Preparation of graphene/gold composite nano material

Graphite oxide (GO), prepared from natural by an improved Hummer's method, was used as the starting material to prepare graphene/gold nano-composite materials [22]. In a typical procedure, 100 mg of graphite oxide was dispersed in 100 g of water. After sonication for 30 min, a clear, brown dispersion of graphene oxide was formed. Then, 4 mL 1% chloroauric acid ($HAucl_4$) situation was added into the dispersion of graphene oxide with repeated sonication for 30 min. The mixed solution was put in microwave and heated for 2 min. Then, the mixture was transferred to the three necked bottle and then kept at 80 °C for 20 min under constant stirring. After filtering and washing with water and alcohol thoroughly, graphene/gold composite nano material was stored after vacuum drying. Finally, the composite nano material was stored.

2.4. Preparation of biosensor

The whole synthesis protocol is shown in Fig. 1. The graphene/gold nano-composite material modified tyrosinase biosensor was prepared by the simple classic casting method. Firstly, the surface of GCE electrode was ultrasonically by Milli-Q water and ethanol, and was mechanically polished by alumina powder with a diameter of 0.05 μm. Then, the surface of electrode was dried with purified nitrogen stream. To obtain good performance, the mass ratios of graphene/gold nano-composite material, tyrosinase and chitosan in solution were optimized in control experiments. The final compositions of graphene/gold nano-composite material, tyrosinase and chitosan in solution were 3 mg mL^{-1}, 4.5 mg mL^{-1} and 1.5 mg mL^{-1}, respectively. The preparation process was as follows: 10 μL tyrosinase (4.5 mg mL^{-1}) was added into 10 μL aqueous solution (3 mg mL^{-1}) of graphene/gold nano-composite material, and the mixture solution was shaken for another 1 h. Then, 10 μL 1.5 mg mL^{-1} chitosan (chitosan, a linear polysaccharide with good film-forming ability) was injected into the above solution. Finally, 10 μL of the above mixture was casted onto the freshly polished surface of GCE electrode. A beaker was covered over the electrode so that water could be evaporated slowly to form a uniform film on the electrode. The dried electrode (denoted as GR/Au-Tyr-CS/GCE) was stored at 4 °C in a refrigerator until using.

Other enzyme electrodes were prepared with the similar procedures as described above. The suspension containing 1 mg mL^{-1} graphene, 1.5 mg mL^{-1} tyrosinase and 0.5 mg mL^{-1} chitosan was used to prepare the GR-Tyr-CS/GCE electrode; the Tyr-CS/GCE electrode were prepared by the suspension containing 1.5 mg mL^{-1} tyrosinase and 0.5 mg mL^{-1} chitosan; The suspension, containing 1.0 mg mL^{-1} graphene and 0.5 mg mL^{-1} chitosan, was used to prepare the GR/Au-CS/GCE electrode. Before electrochemical measurements, all types of the tyrosinase-based electrodes were stirred in 0.1 mol L^{-1} PBS (pH 7.0) for 30 min to remove residual mixtures.

3. Results and discussion

3.1. Characterization of graphene and graphene/gold nano-composite material

In order to avoid the agglomeration of graphene sheets, we introduced a small number of negatively charged gold

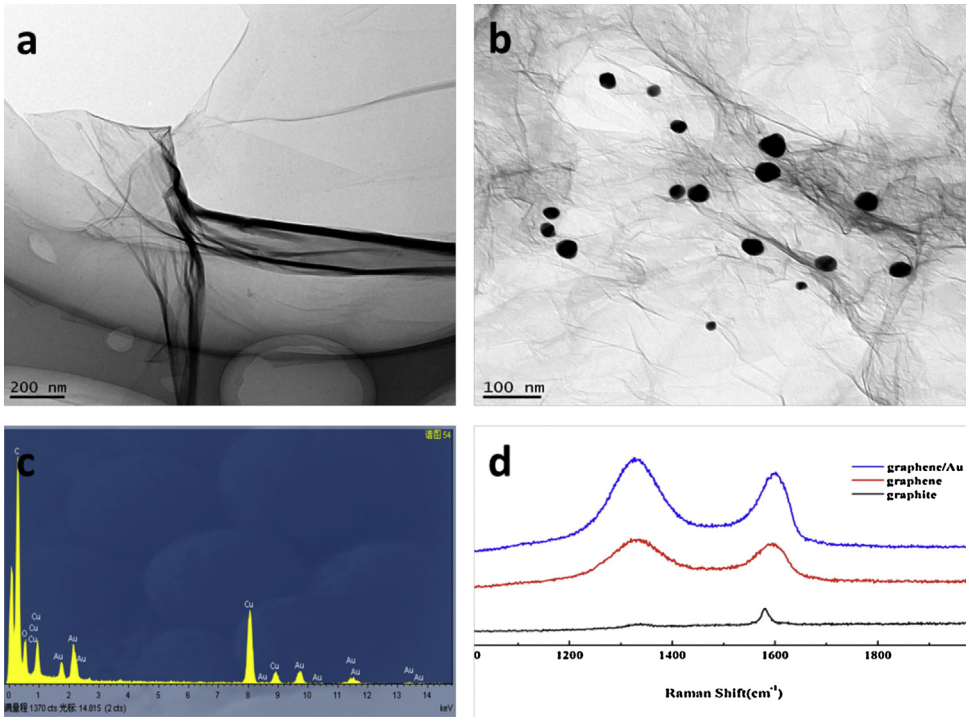

Fig. 2. Characterization result of graphen/Au composite materials. (a) TEM image of graphene; (b) graphene/Au composite; (c) EDS element analysis results and (d) Raman results.

nanoparticles into the system before it was finally reduced by hydrazine. The presence of negatively charged gold nanoparticle kept the graphene sheets separated by the electrostatic repulsion. Fig. 2a shows the high-resolution transmission electron microscope (HRTEM) image of prepared graphene. An obvious layered or even single layered structure is easily observed, which indicates that high-quality graphene obtained by our method. The representative TEM image of graphene/gold composite nanomaterial is also displayed in Fig. 2b, clearly illustrating that the homogeneous-dispersed small gold nanoparticles adhered on the surface of the transparent graphene sheets in flake-like shapes with wrinkles. In order to further confirm the gold nanoparticle-graphene composite material, EDS is adopted to characterize the element component. As shown in Fig. 2c, the three main elements are carbon, copper and gold, indicating the successful modification of graphene with gold nanoparticles. Collectively, the combined results of TEM and EDS results indicate that the reduction of graphene oxide and gold nanoparticle imported procedures do not cause the obvious change or damage of the characteristic single layered morphology of graphene. As the unique properties of graphene/gold nano-composite material are highly dependent on the individual sheet structure and dispersion of gold nanoparticles, the preservation of the original morphology of graphene and imported gold nanoparticles play the important role in the performance of graphene gold nano-composite based biosensors.

Extensive researches have been carried out using Raman scattering to monitor the structural changes of carbon based materials including graphene, providing additional evidence of the structure variations. In Fig. 2d, it is easily to observe the characteristic peak at 1528 cm^{-1}, which is defined as the G band of the pristine graphite and corresponds to the first-order scattering of the E_{2g} mode. Compared with that of the pristine graphite, the G band of GO is broadened due to the oxidation. And with the further reduction with hydrazine, the ratio of D/G (1353 cm^{-1}/1592 cm^{-1}) peak intensity of graphene is further increased. More importantly, the sharply enhanced of Raman signal is observed after the importation of gold nanoparticle to graphene. Anyway, all there results of characterization demonstrate that successful preparation of graphene/gold nanoparticle composites and the well properties for further sensing use.

3.2. Electrochemical behaviors of the fabricated biosensor

EIS is a very powerful and useful technique to monitor the formation and change of the adsorption layer on the GCE electrode. The obtained Nyquist plot of impedance spectra always includes a semicircle portion and a linear portion. The semicircle portion corresponds to the electron transfer limited process while the linear portion corresponds to the diffusion process. And the diameter of the semicircle portion in accordance with the electron transfer limited process equals to the electron transfer resistance (Rct) [23]. In the case of a very fast electron transfer process, the Nyquist plot contains only an obvious line portion, while an extremely slow electron transfer process includes a large semicircle portion. Based on these rules, the modification of the GCE electrode with different materials were measured and compared. EIS results shown in Fig. 3 clearly demonstrate the impedance difference of different material modified electrode. Firstly, the straight line shaped impedance spectrum of the bare electrode indicates the lowest Rct and fastest transfer of electron on the interface of the bare electrode. After the modification with tyrosinase-chitosan, the diameter of the semicircle of the impedance spectrum is much larger than that of the bare electrode. This increased impedance is induced by the formation of tyrosinase-chitosan film and hindered the transfer of electrons. When the graphene was spiked into the tyrosinase-chitosan and

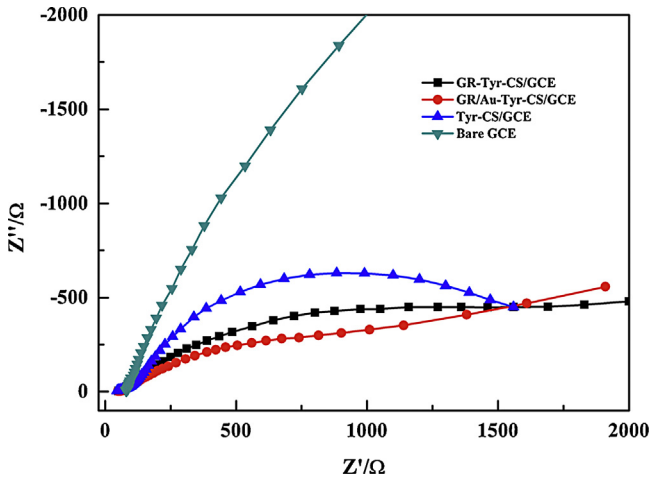

Fig. 3. Nyquist plots of bare GCE, Tyr-CS/GCE, GR/Au-Tyr-CS/GCE, GR-Tyr-CS/GCE modified electrodes in 2 mmol L^{-1} $K_3Fe(CN)_6/K_4Fe(CN)_6$ (1:1) containing 0.5 mol L^{-1} KNO_3.

used for modification of GCE electrode, the diameter of the semicircle of the impedance spectrum is further decreased, which could be attributed to the enhanced electron transfer ability by graphene on the surface of the electrode. Finally, the gold nanoparticle decorated graphene is used for modification of the electrode and the smallest Rct and the best electron transfer property is achieved based on the GR/Au-Tyr-CS/GCE. Therefore, these results prove that the GR/Au-Tyr-CS modified GCE has the best electrochemical performance for sensing.

The cyclic voltammogram technique (CV) is also adopted to further confirm the electrochemical performance of the modified sensing interface. Similar results of EIS are obtained as shown in Fig. 3. When using (a) bare electrode and (b) CS modified electrode, there is no redox current of the testing, indicating no catalytic activity for BPA with above mentioned two electrodes. As expected, when GR/Au-CS/GCE (c in Fig. 4) and GR/Au-Tyr-CS/GCE (d in Fig. 4) are used for the sensing, the apparent redox peaks all occur and the current intensity of the GR/Au-Tyr-CS/GCE is much better than that of GR/Au-CS/GCE, indicating the good maintained catalytic ability of tyrosinase in the composite materials for BPA reduction (Fig. 5).

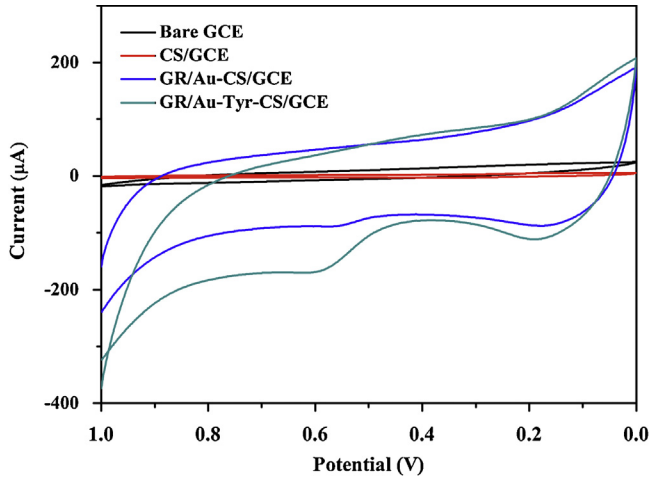

Fig. 4. Cyclic voltammograms of bare GCE, CS/GCE, GR/Au-Tyr-CS/GCE, GR/Au-CS/GCE modified electrodes in 0.1 M PBS (pH 7) at scan rate of 0.1 V s^{-1}.

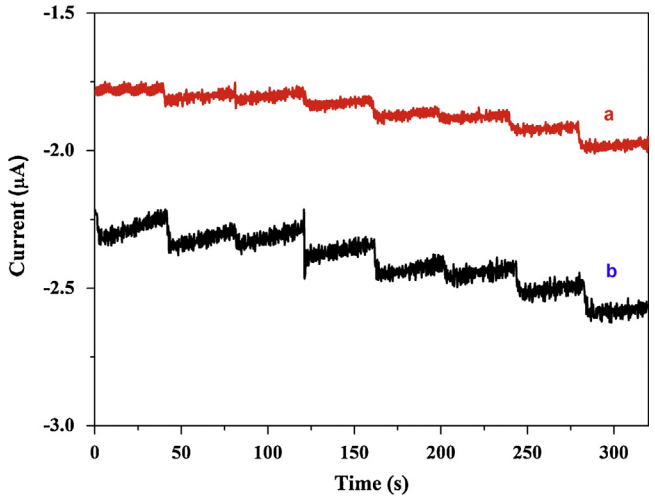

Fig. 5. Current response of successive addition of BPA of GR/Au-Tyr-CS/GCE, GR-Tyr-CS/GCE electrodes in 0.1 mol L^{-1} PBS (pH 7).

3.3. Study of tyrosinase based electrochemical biosensors for BPA sensing

Based on the optimized conditions for electrode modification, the decorated functional electrode was adopted for direct BPA sensing. BPA standard solution was successively added into the 0.1 mol L^{-1} PBS with continuous stirring and the instant current response was recorded at the same time. From the results shown in Fig. 6, it could easily be observed that the GR/Au-Tyr-CS/GCE could sense the addition of BPA in the system based on the intensity change of reduction current. Meanwhile, it is also noted that the sensing current variations of GR/Au-Tyr-CS/GCE is obviously enhanced by integration with tyrosinase for catalytic reduction of BPA. These results demonstrate the unparalleled electrochemical performance of the fabricated composite electrode in BPA sensing. Furthermore, the DPV was used as a powerful technique for BPA detection. BPA standard solutions with different concentrations in 0.1 mol L^{-1} PBS were detected with the fabricated GR/Au-Tyr-CS/GCE biosensor and corresponding peak currents were recorded for quantitative analysis. From the DPV sensing results in Fig. 6, it is observed that with the increase of BPA concentration, the DPV current is increased accordingly at the characteristic reduction potential of BPA at about 0.47 V. Meanwhile, the

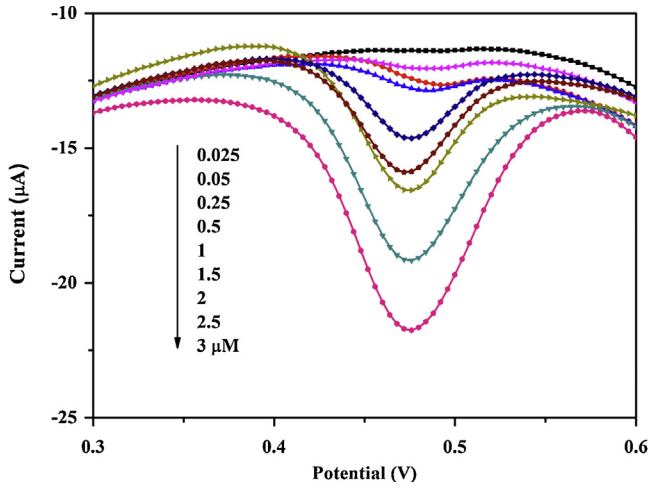

Fig. 6. The DPV signal response of GR/Au-Tyr-CS/GCE electrodes in 0.1 mol L^{-1} PBS (pH 7) with successive addition of BPA.

Table 1
Recoveries of BPA in disposable plastic cup and milk carton samples.

Samples	Added (μg/g)	Detected (μg/g)	Recovery (%)	RSD (%)
Disposable	3	2.94	98.0	5.1
Plastic cup	15	15.87	105.8	4.3
Milk carton	3	3.31	110.3	6.1
	15	14.79	98.6	5.9

calibration curve for BPA detection with this fabricated composite biosensor is developed based on the variations of peak current of DVP. The results showed that in the range of 0.025–3 μM, the concentration of BPA is in a highly linear relationship with the current intensity of DPV. And the final limit of detection was as low as 1 nM (S/N = 3). The sensitivity and correlation coefficient could be as low as 3.59718 μA mM^{-1} and 0.9966, respectively. We also tested the preservability of the fabricated biosensor which was prepared 90 days ago. The electrochemical behaviors showed that the RSD of current intensity was within 7.3%, which indicated that the biosensor has good preservablity. Comparatively, this sensing sensitivity and linear range for BPA detection of the fabricated graphene/Au composite biosensor are of great advantages for the usually reported contaminated concentration of BPA reported in the previous studies [24].

3.4. Superiority discussion of the graphene/Au composites biosensors

The good biosensing performance of the GR/Au-Tyr-CS/GCE composite biosensor for BPA detection can be attributed to the following aspects: firstly, the large surface area of graphene could dramatically enlarge the active surface area of the GCE electrode available for enzyme immobilization and catalytic electrochemical sensing; Meanwhile, compared with conventional graphene based biosensor, the introduction of gold nanoparticles to form the graphene/gold nanoparticle composite is attribute to the unparalleled electrochemical performance for the enhanced conductive ability of accelerating electron transfer rate. It was well known that the close distance between the catalytic active center of enzyme molecules and the underlying electrode could facilitate the electron transfer. Considering the enhancement effect of the gold particles for conductivity, we presume that the immobilized tyrosinase molecules may have a close contact with the graphene. Furthermore, the functional groups (i.e. hydroxyl and carboxyl) on the surface of graphene and the "LBL" like architectures of Tyr-GR nano-composites could provide a biocompatible microenvironment for the immobilized tyrosinase molecules to retain their secondary structure, which further improved their enzymatic stability and bioactivity.

3.5. Real sample analysis

In order to evaluate the analytical reliability and application potential of the proposed GR/Au-Tyr-CS/GCE biosensor, two kinds of blank disposable plastic cup and milk carton samples were diluted ad analyzed. Recovery experiments were carried out by the standard spiked method in these real samples. The results showed that the recovery ranged from 98.2% to 110.7%, and that the corresponding RSD ranged from 4.3 to 6.1% (Table 1), which revealed that the feasibility of the developed biosensor could be applied to the detection of ultra-trace level of BPA in disposable plastic cup and milk carton samples.

4. Conclusions

In summary, graphene sheets were successfully prepared by the introduction of gold nanoparticle to form the nano composite

structures. The integrated gold nanoparticles improved the biocompatibility and conductivity of graphene. This graphene-gold nanoparticle composite was used as the support to immobilize the tyrosinase on the surface of the electrode with the help of chitosan. This fabricated electrochemical biosensor was adopted for BPA detection. The EIS and CV results demonstrated that the biosensor could effective enhance the electrochemical performance and exhibit the typical catalytic reduction of BPA compared with other traditional sensors. Final sensing results indicated that this fabricated electrochemical biosensor could greatly improve the sensitivity for BPA detection. In addition, this fabricated biosensor revealed some other excellent characteristics such as wide linear range and long-term stability. This electrochemical biosensor with easy fabrication, low cost and good performance proposed in this paper provides a new strategy for the construction of BPA biosensors and can be applied in practice for continuous and rapid monitoring of BPA.

Acknowledgments

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