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An electrochemical bisphenol A sensor based on one step electrochemical reduction of cuprous oxide wrapped graphene oxide nanoparticles modified electrode

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ABSTRACT

Bisphenol A (BPA), as an important industrial material, has been widespread concerned in recent years as its endocrine disrupting effect. This study reported a novel bisphenol A sensor via a facile one step electrochemical reduction of graphene oxide (rGO) and cuprous oxide (Cu_2O) nanocomposite modified glassy carbon electrodes. The characterization of the fabricated sensor was performed by scanning electron microscopy and X-ray spectroscopy. The prepared Cu_2O-rGO electrode presented fast response, high sensitivity and low background current. The response of BPA on prepared electrode was 2.15 times higher than reduced graphene modified electrode. Under the optimized experimental parameters, the detection range of the modified electrode was from 1×10^{-7} to 8×10^{-5} M and the limit of detection was 5.3×10^{-8} M (S/N =3). The prepared Cu_2O-rGO modified electrode has been successfully used for detecting BPA in environmental water samples.

1. Introduction

Bisphenol A (BPA) is a monomeric compound for producing plastics and resins, but also is an important environmental hormone due to its strong interference to the normal working hormones and metabolisms [1]. BPA is highly resistant to chemical degradation and it has been frequently detected in lots of environmental samples. Although European Food Safety Authority (EFSA) panel asserted that there is no health concern for any age group from dietary exposure and low health concern from aggregated exposure [2], the potential health risk of BPA are still a unresolved disputation between related toxicological researchers [3,4]. Recently, BPA has been found widely in natural waters, not only from the migration of BPA-based products, but also through effluent of wastewater, e.g., 568 ng/L of BPA in bottled water [5], 16 µg/L of BPA in the wastewater from an industrial park located in southern Taiwan [6]. From 2008, in order to avoiding the potential toxic effects of BPA to infants, Canada, European Union, most states of America and China successively impose restrictive measure on production and sale of milk bottles containing BPA. The dissolved BPA from food contact materials in the European Union (EU) should follow Regulation 10/2011/EU, i.e., specific migration limit (SML)≤0.6 mg/kg [7]. The oral reference dose (RfD) for BPA proposed by United States Environmental Protection Agency (EPA) is 50 µg/kg body weight day. Therefore, accurately and efficiently detecting BPA is particularly important.

In recent years, a large number of methods have been developed for detecting BPA, such as chromatography [8], spectrophotometry [9], immunoassay [10,11] and electrochemical sensor, etc. These methods have provided variously alternative strategies for studying environmental behaviors and physiological toxicities of BPA. Because BPA is an electrochemical active compound, and the advantages of electrochemical sensors, e.g., the high sensitivity, simple operation and on-site detection, developing and applying of electrochemical methods for BPA detection are attractive for the researchers. However, the signal to noise of bare electrode is insufficient to determine the trace level of BPA. Therefore, lots of efforts have been done by modifying the surface of bare glassy carbon electrode using various types of nanomaterials to improve the sensitivity of the electrode [12,13].

The reduced graphene oxide (rGO) characterized as the thinnest material in the world, and showed a bright future owing to its excellent properties [14–16]. The structural integrity of graphene is a single layer of carbon atoms with extremely stable six-membered ring in two-dimensional crystal. The unique property of graphene results in fast electron transportation, high thermal conductivity, excellent mechanical stiffness and good biocompatibility. The electrodes modified with rGO have been proposed and prepared for detecting BPA. Generally,

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these materials are often dominated by noble metal particles, such as Ag [17], Au [18], Pt [19], and Pd [20]. These modified electrodes usually suffered from high cost, multiple-step and time-consuming processes. Therefore, it is necessary to seek novel candidates to improve the properties of rGO-based modified electrodes.

Cu_2O is an important *p*-type transition-metal oxide semiconductor with a low cost and a high hole mobility. It has already been widely used as the electrode because of its superior performance in heterogeneous catalysts sensors [21]. As a potential alternative of noble metals, Cu_2O has been employed for attempting to prepare graphene-based electrodes. Zhang et al. [22] have prepared an electrochemical sensor of Cu_2O/graphene by solvothermal reactions for detecting dopamine. Liu et al. [23] have synthesized cubic Cu_2O nanocrystals and graphene hybrid by chemical reduction method at low temperature. Its electrochemical stability was highly improved as a non-enzymatic amperometric sensor for H_2O_2 and glucose. Murugan et al. [24] using facile two-step chemical methods have successfully synthesized $Co(OH)_2$ enfolded Cu_2O nanocubes on rGO for cafferne sensing. These composite nanoparticles are generally prepared by chemical reduced method, but their morphologies (e.g. cubic and porous) and electrochemical properties show differently due to their specific synthesized procedure. To date, the Cu_2O-rGO nanocomposite has not been used for the detection of BPA. In this paper, a novel electrochemical sensor based on sphere structure of Cu_2O nanospheres wrapped by rGO (Cu_2O-rGO) was prepared using electrochemical reduced method, which was carried out by one pot synthesis of Cu_2O nanocomposites and rGO by cyclic voltammetry (CV). The sensor was successfully evaluated to detect BPA in real environmental water sample.

2. Experimental

2.1. Chemicals and reagents

Bisphenol A (BPA), graphite powders, cupric sulfate ($CuSO_4 \cdot 5H_2O$), sodium hydroxide (NaOH), polyvinylpyrrolidone (PVP), potassium permanganate ($KMnO_4$), sulfuric acid (H_2SO_4, 98%), sodium nitrate ($NaNO_3$) and phosphoric acid (H_3PO_4) were purchased from Sinopharm Group Chemical Regent Co. Ltd. (Shanghai, China). BPA was dissolved in ethanol (5×10^{-5} M) and kept at 4 °C. Phosphate buffer solution (PBS, 0.1 M, pH=6.5) was used as reduced and supporting electrolyte. All chemicals used were at least analytical grade. Ultrapure water (18.2 MΩ·cm,

obtained by Milli-Q water purification system, Billerica, USA) was used for preparing of all buffers and standard solutions.

2.2. Instrumentation

Electrochemical measurements were performed on a CHI 660e electrochemical workstation (CH Instrument, Shanghai) in a conventional three-electrode system. The working electrode was a glass carbon electrode, the reference electrode was an Ag/AgCl electrode and the auxiliary electrode was a platinum wire. The morphology of nanocomposite was examined by scanning electron microscope (SEM) (Hitachi S-4800, Tokyo, Japan). The X-ray diffration (XRD) of the samples were carried out by using Bruker D8 Advance X-ray diffractometer.

2.3. Preparation of Cu_2O-rGO composite

The Cu_2O nanoparticles (Cu_2O NPs) were synthesized following a hydrothermal method [25]. Typically, 50 mg $CuSO_4 \cdot 5H_2O$ and PVP were dissolved in 20 mL H_2O to form a uniform solution under ultrasonic assistance. After 20 min, 2 mL of 0.2 M NaOH was added into the solution. Then, $N_2H_4 \cdot H_2O$ was introduced for reducing $Cu(OH)_2$. When the mixture turned to brick red suspension, the Cu_2O NPs was successfully prepared. The precipitates were washed with ethanol and ultrapure water for several times to remove the impurities, and then dispersed into water to form an aqueous solution of 1 mg/mL (Cu_2O NPs) for further use.

The graphite oxide was synthesized from graphite according to previous reports [26]. Graphite (0.5 g) and $NaNO_3$ (0.5 g) were successively added into concentrated H_2SO_4 (23 mL) in an ice bath. Then, another 3 g of $KMnO_4$ was added into the solution slowly, heated to 35 °C and kept for two hours. 40 mL of H_2O was thereafter added into the solution and heated to 95 °C. After 30 min, 100 mL H_2O and 20 mL of H_2O_2 was added sequentially into the solution. The final suspension was filtered, washed with 1 M of HCl and ultrapure water for three times. The product was dried at 60 °C to obtain graphene oxide (GO). Then, appropriate GO was dispersed into water to prepare 1 mg/mL GO solution.

2.4. Fabrication of Cu_2O-rGO nanocomposite based electrode

The details of the preparation of the Cu_2O-rGO composite are given as Fig. 1. The surface of glassy carbon electrode (GCE) was ultrasonically cleaned by ultrapure water and ethanol, and was mechanically
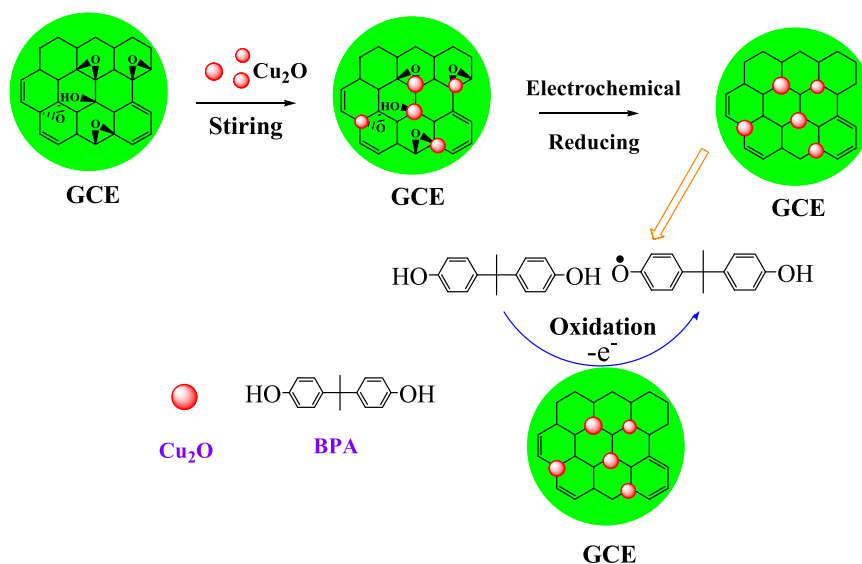

Fig. 1. Schematic diagram for one step electrochemical synthesis of Cu_2O-rGO electrode, and electrochemical oxidation process of BPA at Cu_2O-rGO/GCE.
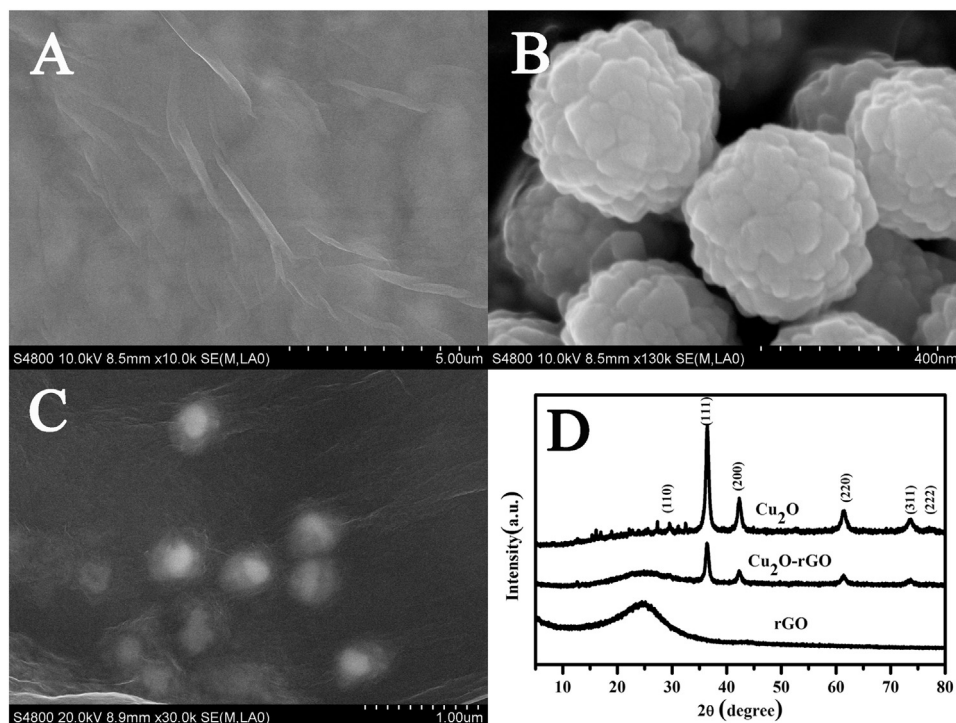
Fig. 2. The SEM images of rGO (A), Cu$_2$O NPs (B), Cu$_2$O-rGO composites nanoparticles (C), and the XRD spectroscopy of these materials (D).

polished by alumina powder (diameter 0.05 µm). Then the surface of electrode was dried with purified nitrogen stream. The synthesized Cu$_2$O nanoparticles (0.25 mg) was mechanically mixed with 10 mL GO solution (1 mg/mL) for 2 h. 5 µL of this Cu$_2$O and GO mixed solution was pipetted to coat the freshly polished surface of GCE electrode. After the electrode surface drying in air, the electrochemically reduced Cu$_2$O-rGO nanoparticles films were prepared at reduced potential of −1.2 V and reduced time of 120 s by cyclic voltammetry in phosphate buffer solution. The electrode was washed thoroughly to remove any unbound Cu$_2$O nanoparticles. The other electrodes such as rGO were also prepared using the similar method.

3. Results and discussion

3.1. Characterization

The morphologies and structures of prepared Cu$_2$O and Cu$_2$O-rGO composite nanoparticles were characterized by SEM and XRD respectively. Fig. 2A displays the pure electrochemical rGO, which exhibits typical silk fold, suggesting high surface area and abundant attach sites. Cu$_2$O NPs presents a uniform spherical structure with diameter of 400 nm (Fig. 2B). For the composite of Cu$_2$O-rGO, Cu$_2$O nanoparticles is wrapped by GO (Fig. 2C), and homogeneous attached onto the graphene successfully. The XRD spectra of Cu$_2$O, rGO and Cu$_2$O-rGO nanoparticles were studied and recorded (Fig. 2D). For rGO, the characteristic (002) reflection of graphite locate date disappears at 2θ=28.4° (JPPDS no.75−1621). Cu$_2$O nanoparticles with the diffraction peaks at 29.5°, 36.4°, 41.1°, 60.2°, 73.8° and 77.8° were well indexed to the (110), (111), (200), (220), (311), (222) crystal planes of Cu$_2$O (JCPDS No. 05−0667), corresponding to the cubic crystal structure of Cu$_2$O. The XRD pattern of Cu$_2$O-rGO presents almost all the characteristic peaks of Cu$_2$O and rGO, revealing the formation of crystal Cu$_2$O on graphene. The disappearance of diffraction peak of Cu$_2$O (110) in the Cu$_2$O/rGO nanocomposite can be attributed to Cu$_2$O had been successfully wrapped by rGO. Overall, because of GO's functional group coordinated with the Cu$_2$O nanoparticles stably, and graphene prevent the Cu$_2$O aggregation, the stability of Cu$_2$O could be

highly improved. Moreover, graphene provides more effective area and conduces to higher electron transfer efficiency of Cu$_2$O, the catalytic activity of hybrid Cu$_2$O/rGO nanocomposites for oxidation of BPA would be significant increased. Therefore, Cu$_2$O-rGO nanocomposites were selected to modify the electrode for BPA sensing in this study.

3.2. Electrochemical measurements

The electrochemical properties of the bare GCE and modified electrode were characterized by CV. Fig. 3A shows the cyclic voltammograms of bare GCE and modified electrode in 1 mM K$_3$[Fe(CN)$_6$]$^{3-/4-}$ solution (containing 0.1 M KCl). The electrochemical response of ferricyanide was a reversible process. For bare GCE (curve a), a pair of redox peaks was obtained with the peak-to-peak separation (ΔE_P) of 0.227 V. After modification with rGO (curve b), ΔE_P was 0.075 V and the redox peak currents increased which caused by its excellent conductivity and large specific surface area of reduced graphene oxide. For Cu$_2$O-rGO/GCE (curve c), the ΔE_P was 0.077 V and the redox peak currents continue to increase. The increasing redox peak currents were closely related to the good synergistic effect of Cu$_2$O nanoparticles and graphene. The CVs of the prepared electrodes in 5×10^{-5} M BPA solutions were also studied for comparison (Fig. 3B, C). There was only a small oxidation peak current at 0.510 V for the GCE electrode owing to the irreversibility of the electrochemical reaction of BPA. For Cu$_2$O/GCE, the Cu$_2$O nanoparticles were dispersed non-uniformly on the surface of electrode, which prevents the electronic transfer without peak current. For rGO/GCE, the oxidation peak current of BPA increased to 150 µA and no other peak had been observed. For Cu$_2$O-rGO/GCE, the current increased to 320 µA, 2 times higher than rGO/GCE. The significant currents increasing might be the increased conductive area of the Cu$_2$O-rGO modified electrode and the enhanced electron transfer rate between BPA and the electrode surface.

3.3. Effects of pH

The electrochemical responses of the prepared electrochemical sensor under different pH values are shown in Fig. 4. When vary the
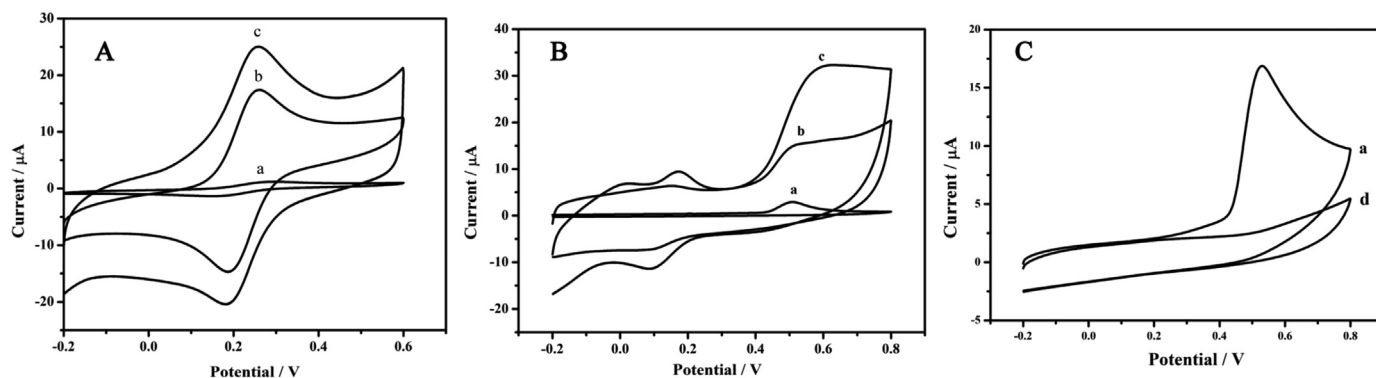
Fig. 3. (A) The cyclic voltammograms of 1 mM $K_3[Fe(CN)_6]^{3-/4-}$ (0.1 M KCl) and (B, C) 5×10^{-5} M BPA in phosphate buffer solution (pH=6.5) with bare GCE (a), rGO/GCE (b), Cu_2O-rGO/GCE (c) and Cu_2O/GCE (d) (scan rate: 0.1 V/s).

pH value from 5.0 to 6.5, the oxidation peak currents of BPA increased, and further increased the pH range from 6.5 to 8.0, the oxidation peak currents of BPA gradually decreased (Fig. 4A). The relationship between the oxidation peak potential (E_{pa}) and pH was also studied (Fig. 4B, curve b). It was found that the value of peak potential shifts to negative with the increase of pH. The relationship can be described by the equation of E_{pa}(V)=−0.0586 pH +0.966 (R^2=0.990). The shift of 0.0586 V/pH was approximately close to the theoretical value of 0.0576 V/pH, indicating that the electron transfer was accompanied by an equal number of protons in electrode reaction.

3.4. Effects of scan rate

To investigate the catalytic activity and the possible kinetic mechanism of Cu_2O-rGO modified electrode toward BPA (5×10^{-5} M), the influence of the scan rate (10–300 mV/s) on the current response was evaluated by CV (Fig. 5). The anodic peak currents (I_{pa}) increased linearly with the square root of scan rate. The linear relationship could be expressed by a regression equation of I_{pa}(μA)=3.9947$v^{1/2}$((mV s)$^{-1/2}$)+0.0325 (R^2=0.996) (Fig. 4B). This indicated that the oxidation of BPA was a typical diffusion controlled electrode process. Additionally, a linear relationship between the peak potential (E_{pa}) and the natural logarithm of the scan rate (ln$v$) was also obtained and it could be expressed by a regression equation of E_{pa}(V)=0.0511ln$v$ +0.3562 (R^2=0.996) (Fig. 5C).

The Laviron's equation is a useful tool for studying the kinetic mechanism of the electrode toward analytes. And it can be expressed as Eq. (1):

$$\mathrm{E}pa = E^0 + \left(\frac{RT}{\alpha nF}\right)In\left(\frac{RT\kappa^0}{\alpha nF}\right) + \left(\frac{RT}{\alpha nF}\right)Inv \tag{1}$$

Where α was the transfer coefficient, k^O was the standard rate constant of the reaction, n was the electron transfer number involved in the rate determining step, v was the scanning rate, E^O was the formal redox potential, R was the gas constant, T was the absolute temperature and F was the Faraday constant. According to the linear correlation of E_{pa}, the slope of the line was equal to $RT/\alpha nF$. In our study, αn was calculated to be 0.502. In general, α was assumed to be 0.5 in the irreversible electrode process. Therefore, the electron transfer number (n) was approximately 1. In addition, the electron transfer was accompanied by an equal number of protons in the electrode reaction. Therein, the calculated n (1.004) in our study indicated that the electrochemical reaction of BPA could be described as a process consisting of one electron and one proton transfer (Fig. 1).

3.5. Amperometric response

The influence of the applied potential on the amperometric response of the Cu_2O-rGO/GCE toward BPA was studied (Fig. 6A). When the applied potential ranged from 0.4 to 0.6 V, a maximum response could be obtained at 0.55 V. Therefore, 0.55 V was the preferential condition in this study. The amperometric signal of different electrodes had been tested upon the successive of BPA (1×10^{-7} M) and shown in Fig. 6B. There was no obvious current change for the bare glassy carbon electrode (curve a), indicating the weak response of GCE to BPA. For rGO/GCE (curve b), there was an obvious oxidation current, indicating better electronic transform activity of the rGO. As for the synthesized Cu_2O-rGO modified electrode (curve c), it presented the strongest signals of oxidation current with fast response. The large surface of graphene and outstanding electrochemical catalytic properties of Cu_2O contributed to the enhanced currents, as well as the oxidation efficiency of BPA.
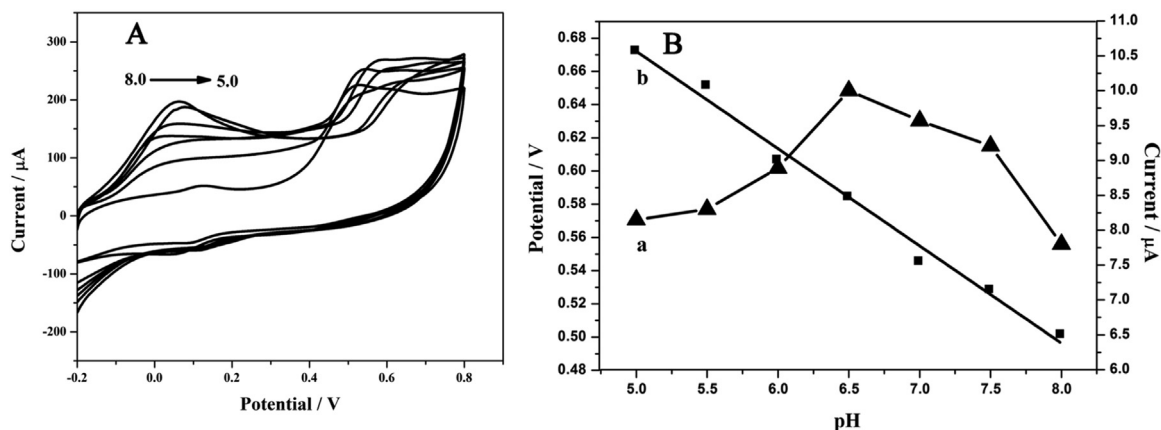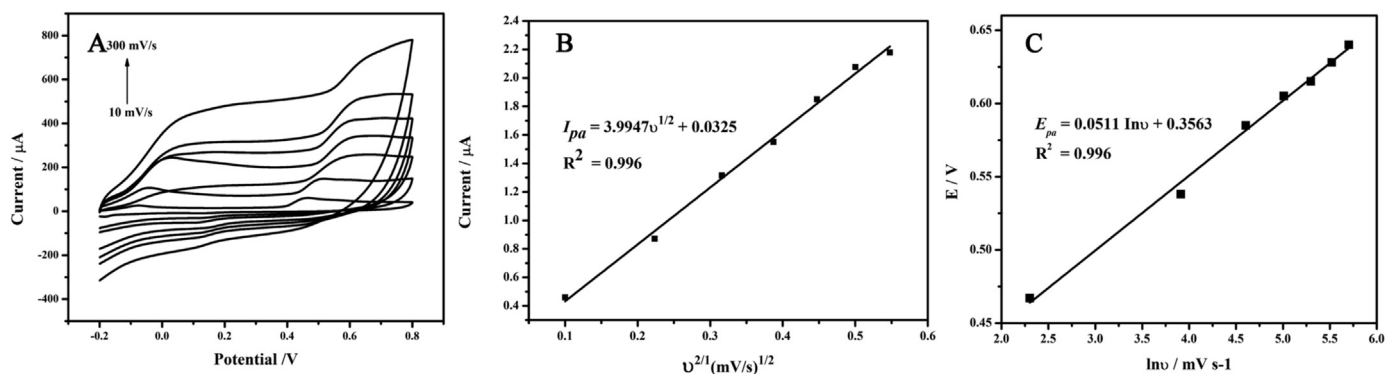

Fig. 4. (A) The cyclic voltammgrams of 5×10^{-5} M BPA at Cu_2O-rGO/GCE in 0.1 M PBS with different pH (from 5.0 to 8.0); (B) The effects of pH on the peak current (a) and potential (b) (scan rate: 0.1 V/s).

Fig. 5. (A) The cyclic voltammograms of BPA (5×10^{-5} M) on Cu$_2$O-rGO/GCE in 0.1 M PBS (pH 6.5) with scan rates of 10, 50, 100, 150, 200, 250 and 300 mV/s, respectively; (B) The linear relationship of plot of peak currents with scan rates; (C) The relationship between the peak potential and natural logarithm of scanning rates for BPA.
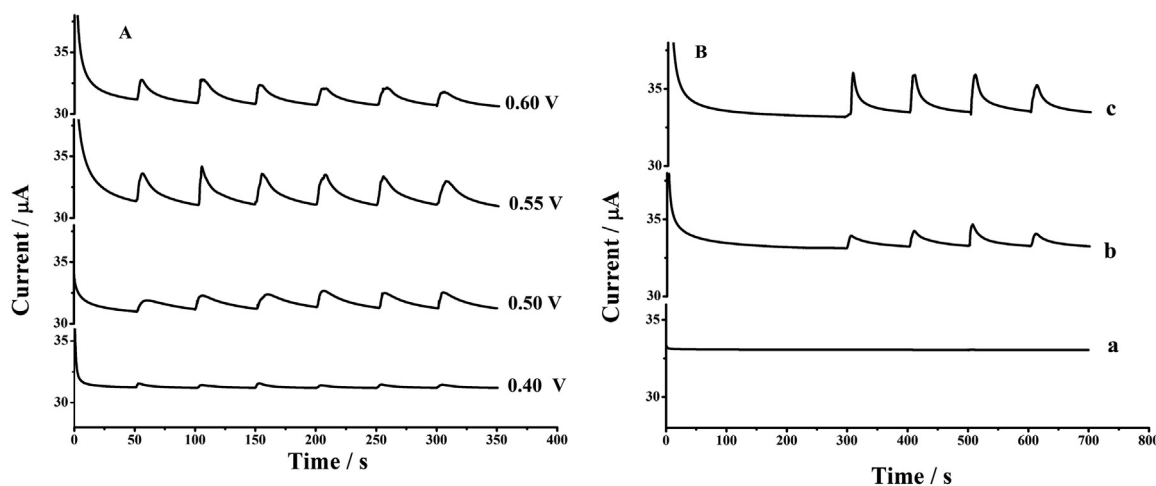

Fig. 6. The amperometric responses with different applied potential (A) and modified electrode (B) upon successively added of 1×10^{-5} M BPA under a constant potential of −0.55 V into stirring PBS (0.1 M, pH=6.5), (a, GCE; b, rGO/GC; c, Cu$_2$O-rGO/GCE).
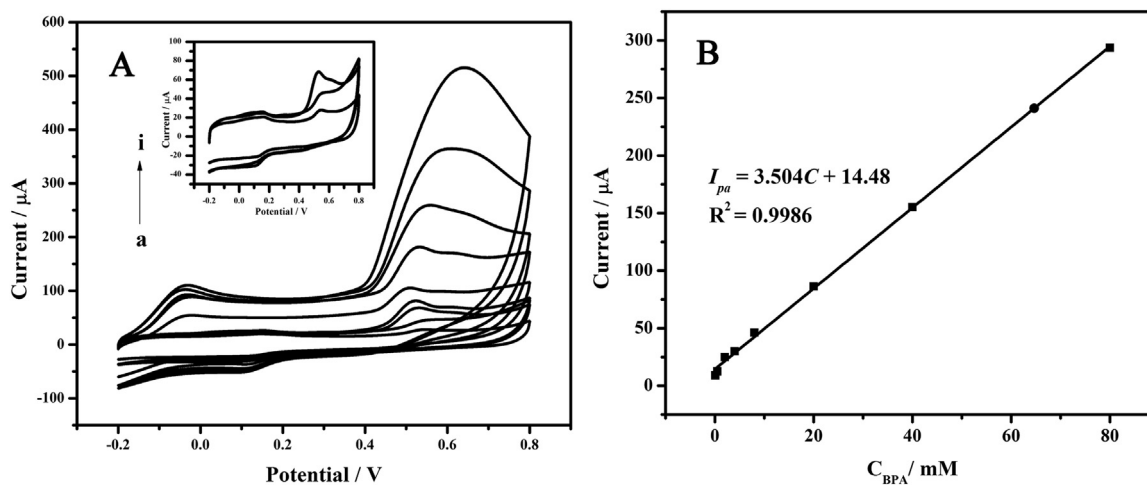

Fig. 7. (A) The CVs of the different concentrations of BPA (a-i: the concentrations of BPA are 0.1, 0.5, 2, 4, 8, 20, 40, and 80 μM); (B) The Linear relationship between the peak current (I_{pa}) and the concentrations of BPA.

3.6. Analytical performance

The performance of the Cu$_2$O-rGO based sensor for detecting BPA was performed using the cyclic voltammetry under the optimized conditions. As shown in Fig. 7A, the anodic peak currents (I_{pa}) was observed in CV curves with different amount of BPA. The linear relationship between I_{pa} and C was in the range from 1×10^{-7} to 8×10^{-5} M BPA solution, the linear regression equation was expressed

as I_{pa} (μA)=3.504 C (μA)+14.48 (R^2=0.9986) (Fig. 7B), and the limit of detection was 5.3×10^{-8} M (S/N=3). Compared with some other modified electrodes, the Cu$_2$O-rGO modified electrode presented comparable performance (Table 1), indicating it had the potential for detecting BPA in real samples.

The stability, reproducibility and interference of the modified electrodes were evaluated. In order to test the stability of the modified electrode, three parallel prepared electrodes were deposited at 4 °C in

Table 1
The comparison of the Cu_2O-rGO and other sensors for BPA determination.

| Sensors	Linear range (µM)	LOD (µM)	Reference
Ordered mesoporous carbon electrode	0.2–150	0.05	[27]
gold nanoparticles supported carbon nanotubes electrode	0.87–87	0.13	[28]
Molecularly imprinted chitosan-acetylene black eletrode	0.005–10	0.002	[29]
Gold nanoparticles dotted graphene elereode	0.01–10	0.005	[30]
Pt-graphene and carbon nanotubes electrode	0.06–80	0.042	[31]
Copper oxide-graphene nanocomposite electrode	0.0043–43.8	0.0024	[32]
Cuprous oxide and graphene electrode	0.1–80	0.053	This work
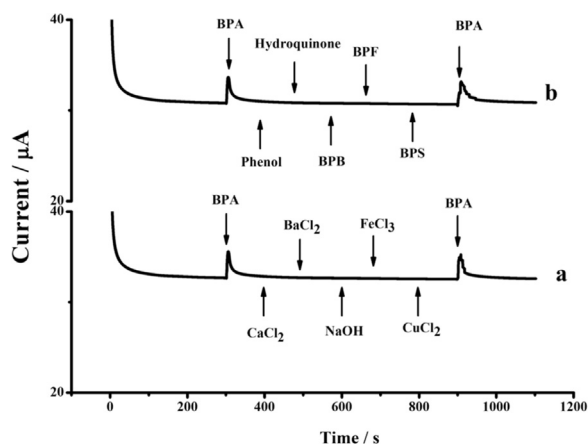
Fig. 8. The amperometric responses of Cu_2O-rGO modified electrode upon successive addition of organic substances (0.1 mM phenol, hydroquinone, bisphenol B, bisphenol F and bisphenol S) and coexisting metal ions (0.1 mM of Ca^{2+}, Ba^{2+}, Na^+, Fe^{3+}, Cu^{2+} was added, respectively).

Table 2
The results of BPA in practical water.

Water sample	Added (µM)	Found (µM)	Recovery (%)
Lake water	0	N.D.[a]	–
	0.5	0.53 ± 0.05[b]	106
	1.0	0.98 ± 0.02	98
	1.5	1.55 ± 0.04	103
Bottled water	0	N.D.	–
	0.5	0.51 ± 0.04	102
	1.0	1.00 ± 0.04	100
	1.5	1.54 ± 0.05	103
Tap water	0	N.D.	–
	0.5	0.49 ± 0.04	98
	1.0	0.98 ± 0.02	98
	1.5	1.52 ± 0.03	101

[a] N.D., not detected;
[b] Average ± Standard deviation.

refrigerator for 14 days. The response currents were still up to 90% of the original currents after 14 days, indicating the good stability of the prepared electrode. The relative standard deviation (RSD) for 7 times successively detection of 1×10^{-5} M of BPA was 5.8%, suggesting that the prepared electrode possesses a high precision. The interferences of some common inorganic ions (Ca^{2+}, Ba^{2+}, Na^+, Fe^{3+}, Cu^{2+}, OH^- and Cl^-, etc) has no obvious interference (Fig. 8a). These inorganic ions have no effect for detecting BPA after adding fresh BPA (1 µM) solutions. Potential organic interferences (e.g. phenol, hydroquinone, bisphenol B, bisphenol F and bisphenol S) were also studied. The results show there is no interference for BPA sensing (Fig. 8b). These results demonstrate that the proposed sensor is relatively selective for the determination of BPA.

3.7. Sample analysis

To testify the feasibility of prepared electrode, the environment water samples were analyzed. Prior to analysis, no pretreatment had been performed to the water sample except filtrating through 0.45 µm filter membrane. Under the optimized experimental conditions, certain amounts of BPA were added into the water samples. The results are shown in Table 2. The high recovery (98–106%) indicates that the prepared Cu_2O-rGO modified electrode is appropriate for the analysis of real water samples.

4. Conclusion

In summary, the Cu_2O-rGO nanopartical film modified glassy carbon electrodes have been prepared by the electrochemical reduced of GO, and the electrochemical catalytic properties of the electrode toward BPA have been evaluated. Wide linear range, high sensitivity and stability for detecting BPA have been obtained. The excellent properties of the electrode can be attributed to the high electrical conductivity of graphene and the outstanding electrochemical catalytic properties of Cu_2O. This modified electrochemical sensor shows further potential applications for detecting BPA in water samples.

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