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# Simultaneous determination of bisphenol A and hydroquinone using a poly(melamine) coated graphene doped carbon paste electrode

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Abstract The authors describe an electrochemical sensor for simultaneous determination of bisphenol A (BPA) and hydroquinone (HQ). It is based on a carbon paste electrode doped with graphene and coated with poly(melamine) (PME/ GR-CPE). The modified electrode exhibits excellent conductivity, electrooxidative activity and adsorptive capability. The differential pulse voltammetric peaks for HQ and BPA are separated by around 300 mV. Amperometric responses (at 0.5 V for HQ and 0.8 V for BPA; both vs. SCE) are linear for BPA in the 9.0  $\mu$ M to 1.0 mM concentration range, and for HQ in the 7.0 μM to 1.0 mM concentration range. The respective detection limits are 10.5 nM and 74.0 nM. The sensor is reproducible, highly stable and sensitive. It was applied to the simultaneous determination of HQ and BPA in spiked tap water and waste water.

Keywords Sensor . Cyclic voltammetry . Differential pulse voltammetry . Electropolymerization . Water analysis

# Introduction

Phenol compounds are the essential raw materials and byproducts of numerous chemical industries. Some of these compounds can accumulate in the human body through food chain and cause abnormal sexual development and decrease the

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 $\boxtimes$  Zuo-Ning Gao gaozn@nxu.edu.cn average number of human spermatozoa [[1](#page-6-0)]. Bisphenol A (BPA) is a typical endocrine disruptor, which can mimic the body's own hormones and induce the negative health effects [[2](#page-6-0), [3](#page-6-0)]. It is widely used in the production of plastics, food containers and packing materials. The release and migration of BPA into the environment or the food are mainly attributed to the leakage of residual monomers or hydrolysates from polycarbonate plastics and epoxy resins or PVC products, under heat and acidic or basic conditions. Exposure to BPA through food and drinking water is potentially detrimental to human health, even at very low concentrations [[4](#page-6-0)]. BPA has been related to chronic diseases and fertility problems [\[5\]](#page-6-0). Based on the results generated from toxicological evaluation of the BPA, the specific migration limit (SML) of BPA (from mg⋅kg<sup>-1</sup> to sub-mg⋅kg<sup>-1</sup> levels), has been set for plastic materials or food containers and packages in different countries [\[6,](#page-6-0) [7](#page-6-0)]. Hydroquinone (HQ) can cause fatigue, headache, tachycardia, and kidney damage in humans [[8\]](#page-6-0). These two compounds usually coexist in our living environment or foods with high toxicity due to their similar chemical structure and properties. Thus, it is essential to develop a rapid, reliable and sensitive method for the simultaneous determination of HQ and BPA in the food and environment.

Several analytical techniques including high performance liquid chromatography (HPLC) [\[9](#page-6-0)], liquid chromatography– mass spectrometry (LC–MS) [\[10\]](#page-6-0), gas chromatography–mass spectrometry (GC–MS) [\[11\]](#page-6-0), chemiluminescence [[12](#page-6-0)], and fluorescence [[13](#page-7-0)] had been used for the determination of phenol compounds. However, these methods suffered from some problems such as requiring time-consuming sample pretreatment, expensive equipment and low sensitivity. Electrochemical method has some advantages of fast response speed, simple operation, time saving, high sensitivity and feasibility of miniaturization [\[14\]](#page-7-0). However, HQ or BPA exhibits slow electron transfer at bare electrodes, which leads to low sensitivity for their detection [\[15\]](#page-7-0). Therefore, various nanomaterials including

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gold nanodendrites [\[16\]](#page-7-0), carbon nanotubes [[17\]](#page-7-0),  $Bi<sub>2</sub>WO<sub>6</sub>$ nanoplates [\[18](#page-7-0)], molybdenum disulfide/polyaniline nanocomposite [\[19](#page-7-0)], Pt/graphene-carbon nanotubes nanocomposite [\[20\]](#page-7-0), carbon naocages/reduced graphene oxide composites [\[21\]](#page-7-0), layered tungsten sulfide-graphene nanocomposite [[22](#page-7-0)] were used to fabricate BPA or HQ sensors with lower detection limit. Pd nanoparticle $@TiO_2$  functionalized SiC was also fabricated to constructed electrochemical sensor for simultaneous determination of hydroquinone and bisphenol A [\[23](#page-7-0)].

Graphene (GR) has exhibited wide applications in electrochemical sensors due to its superior properties such as large surface, high electrical conductivity, remarkable electrocatalytic activity [\[24](#page-7-0), [25\]](#page-7-0). Previous works have also demonstrated the excellent electrocatalytic activity of graphene towards BPA oxidation [\[26,](#page-7-0) [27\]](#page-7-0). Here, graphene was doped in carbon paste electrode to improve the electrode conductivity and electrocatalytic activity. Conducting polymers have attracted intense attention owing to their good stability, reproducibility, more active sites, homogeneity in electrochemical deposition, and strong adherence to electrode surface [\[28\]](#page-7-0). The polymer such as polypyrrole  $[29]$ , polyaniline  $[30, 31]$ , poly $(3, 4$ ethylendioxythiophene) (PEDOT) [[32](#page-7-0)], poly(dopamine) [\[33\]](#page-7-0) and polypropylene [\[34\]](#page-7-0) have been used for biosensor application. Poly(melamine) (PME) with high stability and abundant nitrogen functional groups has been fabricated and used in electrochemical sensors [\[35](#page-7-0)–[37](#page-7-0)]. PME film modified glassy carbon electrode has been fabricated for the sensitive determination of guanine, adenine and epinephrine. [\[35\]](#page-7-0) PME modified pyrolytic graphite or screen-printed carbon electrode was constructed for sensitive detection of serotonin and gallic acid [\[36,](#page-7-0) [37\]](#page-7-0). PME contains amine groups and a benzene ring so it is supposed to provide binding sites for the adsorption and accumulation of hydroquinone and bisphenol and improve the sensitivity.

In this paper, a sensor based on PME coated on graphene doped carbon paste electrode (PME/GR-CPE) was fabricated for simultaneous determination of BPA and HQ. The fabrication schedule of this sensor was illustrated in Fig. [1.](#page-2-0) The PME/ GR-CPE exhibited superior performance such as high conductivity, electrocatalytic activity and adsorptive capability to BPA and HQ. Differential pulse voltammetry was used to simultaneously quantify HQ and BPA in a wider concentration range with high sensitivity under optimal conditions. The sensor showed good stability and reproducibility. The practical application of the sensor was demonstrated by detection of HQ and BPA in tap water and wastewater samples.

HQ and BPA were from Chemical northern suburb of Beijing (China, <http://11687545.mmfj.com>/) and Suzhou Kai-Fu

# Experimental

## Reagents

Chemical Co., Ltd. (China, <http://www.szkfc.com.cn>), respectively. Melamine was purchased from Aladdin Reagent Company (Shanghai, China, [www.aladdin-e.com\)](http://www.aladdin-e.com). All chemicals were of analytical grade and used without further purification. All solutions were freshly prepared with double deionized water.

#### Apparatus

The prepared composites were characterized by scanning electron microscopy (SEM) (JSM-6700F, JEOL, Japan) and Fourier transform infrared spectroscopy (FTIR) (Lumos, Bruker, UK). Raman spectrum was collected in a Renishaw InVia Raman microscope system with exciting laser wavelength of 514 nm, and the laser output power was 20 mW. Electrochemical experiments were performed with a CHI 660C electrochemical workstation (Chenhua, Shanghai, China) with a conventional three-electrode cell. The working electrode was bare carbon paste electrode or modified carbon paste electrode, reference and counter electrode used were a CHI150 saturated calomel electrode (SCE) and a CHI115 (CH instruments Inc.) platinum wires, respectively. All the measurements were carried out at room temperature.

# Fabrication of carbon paste electrode and graphene doped carbon paste electrode

Graphene was prepared by reduction of GO with references' method [[38](#page-7-0), [39](#page-7-0)]. The unmodified CPE was prepared by mixing 1.8 g of graphite powder and 0.60 mL of paraffin oil thoroughly in a mortar to form a homogeneous carbon paste. A portion of the carbon paste was pressed into the end of a poly (tetrafluoroethylene) (PTFE) cylindrical electrode body while a copper wire was inserted through the opposite end to establish an electrical contact. The graphene doped CPE was fabricated using the same procedure except the 0.6 mL of GR (0.2 mg mL−<sup>1</sup> ) into the carbon paste. Appropriate packing was achieved by pressing the surface against a bond paper until a smooth surface was obtained.

# Electrochemical deposition of poly(melamine) on graphene doped carbon paste electrode

The poly (melamine)/graphene doped CPE was obtained by cyclic voltammetry using graphene doped CPE as working electrode in  $0.1$  M  $H<sub>2</sub>SO<sub>4</sub>$  containing 1.0 mM melamine in the potential range of  $-0.1$  to  $+1.5$  V at 100 mV·s<sup>-1</sup> for 10 cycles.

## Electrochemical measurements

The electrochemical impedance spectroscopy was performed in 5 ×  $10^{-3}$  M [Fe(CN)<sub>6</sub>]<sup>3-/4−</sup> (1:1) solution containing 0.1 M

<span id="page-2-0"></span>Fig. 1 Illustration scheme of fabrication process of the electrochemical sensor



KCl. The parameters were as follows: frequency range from 1 to  $10^5$  Hz; initiative potential, 0.193 V; amplitude, 0.005 V and quiet time of 2 s. The differential pulse voltammogram was recorded from −0.2 to 1.2 V with the parameters of increment potential, 0.004 V; pulse amplitude, 0.05 V; pulse width, 0.0167 s; pulse period, 0.2 s; quiet time, 2 s. The cyclic voltammetry was scanned with scan rate of 50 mV·s<sup>-1</sup>, sample interval of 0.001 V and quiet time of 10s.

# Results and discussion

#### Characterization of the sensor

Raman spectroscopy was used to prove the presence of graphene on the electrode. As shown in Fig. [2](#page-3-0)a, three featured peaks located at 1369 cm<sup>-1</sup> (D-band), 1590 cm<sup>-1</sup> (G-band), and 2713 cm<sup> $-1$ </sup> (2D-band) can be observed for graphene sheets. The D-band corresponds to the  $A_{1g}$  mode breathing vibration of carbon atoms in planar terminations of disordered graphite. The G-band is assigned to  $E_{2g}$  mode of 2D graphite, which is related to vibration of  $sp^2$ -bonded carbon atoms in the 2D hexagonal lattice [[40\]](#page-7-0). The value of  $I_G/I_D$  is calculated to be 1.9, suggesting the quite high graphitization degree of few-layer graphene. The surface of PME/GR-CPE was also characterized by FTIR (Fig. [2](#page-3-0)b). This result showed N-H stretching  $(-NH<sub>2</sub>)$ , N-H bending, and C-N stretching bands of the PME at the wave numbers of 3606 cm<sup>-1</sup>, 1500–1600 cm<sup>-1</sup>, and

1019 cm−<sup>1</sup> , respectively. This confirmed the formation of PME particles on the GR-CPE.

The surface morphologies of GR-CPE, PME/GR-CPE were characterized by using scanning electron microscopy (SEM). As shown in Fig. [2](#page-3-0)c, the multiple layers of graphene flakes were observed on the electrode surface. The SEM image (Fig. [2d](#page-3-0)) of PME/GR-CPE confirmed the presence of PME particles on the electrode surface. The resulting PME/GR-CPE with a three-dimensional structure showed a higher surface area  $(0.0805 \text{ cm}^2)$  than that of GR-CPE  $(0.0975 \text{ cm}^2)$ , which offered a beneficial interface for electrochemical sensing.

The CVs of potassium ferricyanide on the different electrodes are shown in Fig. [3a](#page-3-0). A large peak-to-peak potential separation ( $\Delta E_p$ ) value of 217 mV was observed at the bare CPE, indicating the poor electron-transfer kinetics. The  $\Delta E_p$ value reduced to 175 mV (curve b) and 68 mV (curve c) for GR-CPE and PME/GR-CPE, respectively. Both the cathodic and anodic peak currents significantly enhanced after modifying with graphene due to the good conductivity and electrocatalytic activity of graphene. The cationic, nitrogen-rich PME surface was thought to concentration more anionic ferricyanide than that of the GR-CPE due to the electrostatic attraction. Thus, higher current responses were observed at PME/GR-CPE (Curve c in Fig. [3](#page-3-0)a). Electrochemical impedance spectrum (EIS) was employed to monitor the impedance changes in the sensor fabrication process. The impedance spectrum includes a semicircle portion and a linear part. The diameter of the semicircle is equivalent the electron-transfer resistance (R<sub>et</sub>), corresponding to the electro-transfer limited

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process. The linear part corresponds to the diffusion-limiting electrochemical process. Figure 3b displayed the nyquist plots of different electrodes in 0.1 M KCl solution containing 5 mM  $[Fe(CN)_6]^{3-/4-}$  probe. A large R<sub>et</sub> with a value of about 38.0 kΩ was obtained (curve a), indicating an inefficient electrontransfer process of redox probes at the surface of CPE. The R<sub>et</sub> value decreased to 18.3 kΩ after doping of graphene (curve b), which was mainly attributed to the high conductivity of graphene. A much lower  $R_{et}$  (6.4 kΩ) at the PME/GR-CPE surface was obtained, indicating the PME accelerated the electron communication between the redox couple  $[Fe(CN)_6]^{3-/4-}$  and the electrode surface. The fast electron-transfer kinetics demonstrated the potential of modified CPE for sensing applications.

#### Electrochemical behavior of BPA and HQ

The cyclic voltammetric behaviors of BPA and HQ on different electrodes were investigated. Figure [4](#page-4-0) showed the CV curves of 3.0  $\times$  10<sup>-4</sup> M BPA and 3.0  $\times$  10<sup>-4</sup> M HQ in 0.1 M phosphate buffer (pH 7.0). The current responses of both BPA and HQ were improved on GR-CPE compared with that on bared CPE. The improvement indicated that graphene promotes electron transport and communication between the solution and electrode due to the excellent conductivity. This result also confirmed the good electrocatalytic activity of graphene towards to BPA and HQ. On the PME/GR-CPE, the peak currents of BPA and HQ significantly increased compared with those on the bare CPE and GR-CPE, which was

Fig. 3 (a) CVs of a CPE, b GR-CPE, c PME/GR-CPE in 0.1 M KCl solution containing 5.0 mM  $K_3Fe(CN)_6$ . (b) Nyquist plots of a CPE, b GR-CPE, c PME/GR-CPE in 0.1 M KCl solution containing 5.0 mM  $[Fe(CN)_6]^{3-/4-}$ 





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attributed the high surface area and adsorptive capacity of PME/GR-CPE. The nitrogen-rich and aromatic features of PME are believed to interact with BPA or HQ through hydrogen bonding and  $\pi$ - $\pi$  interactions, respectively. The combination of the both effects is suggested to be responsible for the enhanced current responses.

The CVs of the mixture of  $3.0 \times 10^{-4}$  M BPA and  $3.0 \times 10^{-4}$  M HQ at different electrodes were shown in Fig. 5. The oxidation peak of HQ overlapped with that of BPA at CPE (curve a) and GR-CPE (curve b). However, the two well-defined peaks at 0.35 and 0.65 V were clearly shown on PME/GR-CPE, corresponded to the oxidation of HQ and BPA, respectively. These peaks were well separated and showed a potential difference of about 300 mV, which was an adequately large window for simultaneous detection of BPA and HQ in the mixed solutions. The oxidation currents of both HQ and BPA on the PME/GR-CPE are higher compared to a plain CPE and a GR-modified CPE. The high current responses were beneficial for the following sensing applications.

#### Optimization of method

The effects of pH and scan rates on the peak currents were investigated. Respective data and figures are given in the



Fig. 5 Cyclic voltammograms of mixture of  $3.0 \times 10^{-4}$  M HQ and  $3.0 \times 10^{-4}$  M BPA at a CPE, b GR-CPE, c PME/GR-CPE

Electronic Supporting Material (Fig. S1). The electrolyte with pH 2.5, scan rate of 50 mV  $S^{-1}$  were chosen for the following experiment. The oxidation peak currents of BPA and HQ were linear with the square root of scan rate  $(\gamma^{1/2})$  in the range of 100–700 mV·s<sup>-1</sup>. The regression equations were  $I_{pa}(\mu A) = -2.809 + 1.233 \nu^{1/2}$  $(mV^{1/2} \cdot s^{-1/2})$   $(R = 0.997)$  for BPA,  $I_{pa}$  $(\mu A) = 0.168 + 0.970 \sqrt{1/2}$   $(mV^{1/2} \cdot s^{-1/2})$   $(R = 0.992)$ for HQ, respectively, indicating that the electrode reactions of HQ and BPA at PME/GR-CPE are diffusioncontrolled processes [[18](#page-7-0)].

#### Simultaneous determination of HQ and BPA using DPV

For simultaneous determination of BPA and HQ using PME/ GR-CPE sensor, differential pulse voltammetry (DPV) was carried out under the optimized conditions. Figure [6a](#page-5-0) showed the DPV curves for different concentrations of BPA coexisting with HQ. The peak currents of BPA increased with increasing the concentration with two linear parts. The linear equations (inset of Fig. [6a](#page-5-0)) were  $I_{pa} (\mu A) = 0.371 + 23.269$  C (mM)  $(R = 0.998)$  in the range of  $9.0 \times 10^{-6} \sim 1.0 \times 10^{-4}$  M and  $I_{\text{pa}}$  $(\mu A) = 2.355 + 3.062$  C (mM) ( $R = 0.999$ ) in the range of  $1.0 \times 10^{-4}$  M ~  $1.0 \times 10^{-3}$  M with a detection limit of  $1.05 \times 10^{-8}$  M, respectively. As shown in Fig. [6](#page-5-0)b, the peak currents of HQ enhanced linearly with increasing the concen-tration of HQ. The linear equation (inset of Fig. [6b](#page-5-0)) was  $I_{pa}$  $(\mu A) = 0.343 + 12.541$  C (mM) ( $R = 0.998$ ) in the range of  $7.0 \times 10^{-6}$  M ~  $1.0 \times 10^{-3}$  M with a detection limit of  $7.4 \times 10^{-8}$  M. It was found that the presence of another substrate had no effect on the peak currents and potentials on the target analyte. Compared with other HQ or BPA electrochemical sensors with DPV techniques listed in Table [1,](#page-5-0) the sensor exhibited a lower detection limit and wider linear range. This result can be attributed to the synergistic effect between the graphene and PME. The remarkable conductivity, electrocatalytic activity of graphene and the adsorptive capability of PME may be the main contribution that can amplify the current signals and lowered the detection limit. Therefore, the PME/GR-CPE

Fig. 6 a DPV curves of various concentrations of BPA in the presence of  $3.0 \times 10^{-4}$  M HO, Inset is the relationship between concentrations of BPA and peak currents. b DPV curves of various concentrations of HQ in the presence of  $3.0 \times 10^{-4}$  M BPA, Inset is the relationship between concentrations of HQ and peak currents

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sensor is a competitive candidate for simultaneous detection of HQ and BPA.

#### Reproducibility, stability and interference study

To evaluate the fabrication reproducibility of the sensor, the oxidation peak currents of  $3.0 \times 10^{-4}$  M HQ and  $3.0 \times 10^{-4}$  M BPA on six PME/GR-CPE sensors with same fabrication procedures were measured. All of the sensors exhibited similar current responses with a relative standard deviation (RSD) of 2.8% and 3.5% for HQ and BPA, respectively. When the sensor was not in use, it was stored in a refrigerator at 4 °C. Initial responses of over 95.6% and 88.4% were maintained after storage for 15 and 30 days, respectively, indicating the good stability of the sensor.

In order to evaluate the selectivity of the sensor, the influences of various possible interferences on the determination of  $3.0 \times 10^{-4}$  M HO and  $3.0 \times 10^{-4}$  M BPA was investigated by DPV, as shown in Fig. [7](#page-6-0). It was found that  $10 \text{ mM } Zn(\text{NO}_3)_{2}$ , KCl, MgCl<sub>2</sub>, CaCl<sub>2</sub>, Na<sub>2</sub>SO<sub>4</sub>, catechol, 2-nitrophenol, 3-nitrophenol, 4-nitrophenol, aniline, humic acid and hydroxyflavonoids did not interfere with the determination of HQ and BPA in the present system (signal change below 5%). However, 10 mM resorcinol and paracetamol coexisting





MoS2/SPAN/GCE: molybdenum disulfide/self-doped polyaniline modified glassy carbon electrode.

β-CD/IL CPE: β-cyclodextrin (β-CD) modified ionic liquid based carbon paste electrode.

PGA/MWCNT-NH2/GCE: polyglutamate acid (PGA) and amino-functionalised carbon nanotubenanocomposite modified glassy carbon electrodes. BG/GCE: boron-doped graphene (BG) modified glass carbon electrode (GCE).

CNCs-RGO/GCE: carbon nanocages (CNCs)-reduced graphene oxide (RGO) modified glass carbon electrode.

PEDOT/NGE/GCE: poly(3,4-ethylenedioxythiophene) /nitrogen-doped graphene composites modified glassy carbon electrode (GCE).

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Fig. 7 The currents of  $3.0 \times 10^{-4}$  MHO and  $3.0 \times 10^{-4}$  M BPA in the absence a and presence of 10 mM various interferences (from b to (j)):  $\text{Zn}^{2+}$ , Na<sup>+</sup>, Ca<sup>2+</sup>, Mg<sup>2+</sup>, K<sup>+</sup>, 2-nitrophenol, 3-nitrophenol, 4-nitrophenol, catechol

with 3.0  $\times$  10<sup>-4</sup> M HO and 3.0  $\times$  10<sup>-4</sup> M BPA have some effects on the current response due to the similar oxidation peak potential. While the concentration of resorcinol and paracetamol below 1.0 mM, it did not interfere with the determination of HQ and BPA. The selectivity of this sensor was attributed to the adsorption and accumulation of BPA and HQ due to the interaction between amine groups of PME and the phenolic groups of BPA and HQ.

#### Real sample analysis

To evaluate the practical application of the PME/GR-CPE sensor for real sample analysis, the concentration of BPA and HQ in tap water and wastewater samples was determined with the standard addition method. Results showed recoveries ranging from 97.25% to 103.5% and RSDs ranging from 0.10% to 2.10% (Table 2), indicating the practical applicability and reliability of the sensor.

# **Conclusions**

A sensor based on PME/GR-CPE was fabricated through a facile doping and electro-polymerization method. Utilizing

Table 2 Determination of HQ and BPA in tap-water and wastewater samples  $(n = 3)$ 

Sample			$\text{Added}(\mu M)$ Founded $(\mu M)$ RSD $(\%)$				Recovery $(\% )$	
	<b>BPA</b>	HO	BPA	HO			BPA HO BPA	HO
Tap -water	40.0	60.0	40.8	59.5	1.17		$0.42 \quad 102.1$	99.14
	70.0	80.0	68.7	82.1	0.87		1.02 98.19	102.7
	20.0	30.0	20.3	29.9			0.92 2.10 101.7	99.68
Wastewater	40.0	60.0	38.9	62.1	1.21		0.72 97.25	103.5
	70.0	80.0	68.6	79.5	0.85		1.19 97.94	99.37
	20.0	30.0	19.9	29.3	0.89	0.10	99.50	97.68

the excellent conductivity and electrocatalytic activity of graphene, the adsorptive capability of PME, the sensor exhibited superior performance such as high sensitivity and stability to the simultaneous detection of HQ and BPA. The sensor was applied in detection of HQ and BPA in tap water and wastewater samples. Furthermore, PME based sensor can be implemented as a promising method for detection of phenol compounds in food and environment.

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Compliance with ethical standards The author(s) declare that they have no competing interests.

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