*Int. J. Electrochem. Sci.*, 11 **(2016)** 7139 – 7149, doi: 10.20964/2016.08.65

**International Journal of ELECTROCHEMICAL SCIENCE**
www.electrochemsci.org

# An Electrochemical Hydroquinone Sensor with Nitrogen-Doped Graphene Modified Electrode

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*Received:* 10 May 2016 / *Accepted:* 19 June 2016 / *Published:* 7 July 2016

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In this paper a solvethermal synthesized nitrogen-doped graphene (NG) was used as modifier on carbon ionic liquid electrode (CILE) to get a novel modified electrode, which was denoted as NG/CILE. An electrochemical hydroquinone (HQ) sensor was constructed with NG/CILE as working electrode. Electrochemical behaviors of HQ on NG/CILE were investigated by cyclic voltammetry with a pair of redox peaks observed. Compared with that of CILE, electrochemical responses of HQ were enhanced greatly with the peak-to-peak separation reduced. The result indicated good electrocatalytic ability of NG/CILE to the redox reaction of HQ. Under the optimal conditions a wider linear response between the peak current and HQ concentration was established in the concentration range from 0.2 to 800.0 μmol $L^{-1}$ accompanied by a detection limit of 0.625 nmol $L^{-1}$ (3σ). Furthermore, the as-proposed HQ sensor exhibited high sensitivity and good selectivity toward HQ detection, which was successful applied to the synthetic water samples analysis.

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**Keywords:** Nitrogen-doped graphene; Carbon Ionic Liquid Electrode; Hydroquinone; Electrochemistry; Electrochemical sensor

## 1. INTRODUCTION

As a common used chemical regent, hydroquinone (HQ, 1,4-dihydroxybenzene) has been widely applied in various fields including food antioxidant, anthraquinone dye, blackwhite film developer, polymerization inhibitors and some other chemical processes [1, 2]. Also HQ is defined as a common environmental pollutant existed in environmental samples, which is toxicity to humans and difficult to be degraded [3,4]. So it is requisite to explore sensitive and efficient analytical approaches for HQ analysis. Various analytical approaches, including spectrophotometry [5], HPLC [6], fluorescence [7], chemiluminescence [8] and electroanalysis [9] have been proposed for HQ determination. Among them electrochemical methods have been reported with the merits of facile operation, high sensitivity and economic equipments [10,11]. To further improve the sensitivity and selectivity, chemically modified electrodes (CME) with different kinds of modifiers, such as nanomaterials, polymers and ionic liquid (IL), have been designed to achieve electrochemical determination of HQ. Zhang et al. reported an electrochemical approach for simultaneously analyzing HQ and catechol (CC) by using three-dimensional graphite carbon nitride nanosheets-carbon nanotube composite as electrode modifier [12]. Huang et al. developed a carbon nanocages-reduced graphene oxide composite modified electrode for HQ and CC with a detection limit of HQ as 0.87 [13]. Ribeiro et al. studied the electrochemical behaviors of HQ and CC on tetraruthenated oxovanadium (IV) porphyrin modified glassy carbon electrode [14]. Sun et al. also reported a poly(crystal violet) functionalized graphene (GR) modified electrode for HQ detection [15].

As the thinnest carbon nanomaterials with unique characters like good electrical and thermal conductivity, extremely mechanical strength and big surface area, GR is widely used in electrochemical biosensors and CME [16-18]. Recently chemical doping GR had been reported and reviewed [19]. By doping other atoms in the structure of GR, the property of GR can be modulated with new performances appeared. Wang et al. summarized recent research progress of GR doping and its potential applications [20]. Nitrogen atom has the similar atom size with carbon atom, which has been used to dope into different carbon materials including carbon nanotube and GR [21]. Putri et al. reviewed the advances of nitrogen-doped GR (NG) in synthesis, characterization and potential applications [22]. Deng et al generalized the preparations and applications of NG in supercapacitors [23]. In general three common bonding allocations of nitrogen atom are present within the carbon lattice, which is graphitic, pyridinic and pyrrolic nitrogen [24]. The presence of nitrogen atom in GR endores different properties such as better electron transfer efficiency, higher electrocatalytic activity with activation region on GR surface and excellent biocompatibility [25]. Feng et al. fabricated an ultrasensitive electrochemical dopamine sensor by means of three-dimensional NG [26]. Yang et al. constructed an electrochemical glucose biosensor using $Mn_3O_4$ nanoparticles/NG hybrid composite modified electrode [27]. Sheng et al. studied the electrocatalytic ability of NG to the reduction reaction of oxygen in alkaline solution [28]. Sun et al. synthesized NG with high nitrogen level and fabricated an advanced electrode in high performance supercapacitors [29]. Our group also explored a NG modified electrode to realize the direct electrochemistry of hemoglobin [30].

Herein NG was synthesized by a facile solvothermal method and further used as electrode modifier. By using IL as the binder and the modifier in the traditional carbon paste electrode, carbon ionic liquid electrode (CILE) has been proven to possess certain unique characteristics including high ionic conductivity, certain electrocatalytic ability with wide electrochemical windows [31]. Recently modified CILE has also been applied as the substrate electrode for fabricating electrochemical sensors, which show the synergistic effects of modifiers and CILE [32, 33]. In the present study NG modified CILE was constructed to study the electrochemical behavior of HQ. The presence of NG on the CILE surface resulted in the enhancement of the electrochemical responses of HQ. Based on the differential pulse voltammetric technique, a new sensitive electrochemical approach for HQ was explored with NG/CILE as the working electrode.

## 2. EXPERIMENTAL

### *2.1 Reagents and apparatus*

Graphite powder (particle size 30 μm, Shanghai Colloid Chem. Co., China), hydroquinone (HQ, Shanghai Chem. Reagent Ltd. Co., China) and 1-hexylpyridinium hexafluorophosphate ($HPPF_6$, Lanzhou Yulu Fine Chem. Co., China) were used as received. NG was synthesized based on a solvothermal method reported in our former work [34].

Electrochemical measurements were carried out on a CHI 750B electrochemical workstation (Shanghai CH Instrument, China) with a conventional three-electrode cell. CILE or NG/CILE was used as the working electrode. A saturated calomel electrode (SCE) and a platinum wire electrode were used as the reference and the counter electrodes. Transmission electron microscopy (TEM) measurement was performed on a JEM-2100 microscope (JEOL, Japan) at 200 kV acceleration potential.

### *2.2 Preparation of NG/CILE*

CILE was fabricated with graphite powder and $HPPF_6$ according to the procedure reported in reference [35]. Then 7.0 μL of 1.0 mg $mL^{-1}$ NG solution (with absolute ethanol as solvent) was pipetted onto CILE surface. After drying at the room temperature, NG/CILE was obtained.

### *2.3 Procedure*

HQ solution in 0.1 mol $L^{-1}$ pH 2.0 PBS was put into a 10 mL electrochemical cell and the three-electrode system was immersed in the solution during measurements. Cyclic voltammetry was performed for the electrochemical behavior of HQ within the potential range of -0.2~0.8 V at the scan rate of 100 mV $s^{-1}$. Chronocoulommetry was carried out in the potential range of 0.6~-0.2 V with parameters set as: pulse width of 0.1 s, sample interval $2.5\times10^{-4}$ s and quiet time of 2 s. Differential pulse voltammetric (DPV) measurements were recorded for the quantitative analysis of HQ with the instrumental parameters set as: step increment potential of 0.004 V, pulse amplitude of 0.05 V, pulse width of 0.05 s, ample width of 0.017 s and pulse period of 0.2 s.

## 3. RESULTS AND DISCUSSION

### *3.1 Characteristics of NG*

Typical TEM technique was employed to obtain the morphology of NG with image shown in Figure 1. It can be seen that NG was present as nanosheets with some folding, which was due to high surface energy. The dimension was about 20 to 100 nm. X-ray diffraction (XRD) was used to analyze the content and bonding status of nitrogen with the amount of nitrogen in NG as 10.5%. The types of bonding configurations of nitrogen dopant in carbon structures were pyridinic, pyrrolic and quaternary nitrogen. More detailed information and explanations about the synthesis and the formation mechanism of NG were discussed in our report [34].

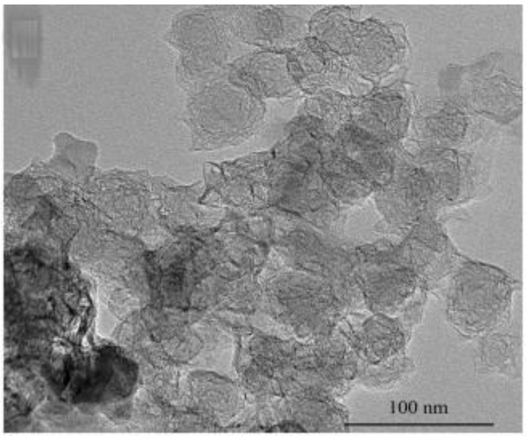


**Figure 1.** TEM image of NG.

### *3.2 Electrochemical behaviors of HQ on NG/CILE*

Figure 2 showed the voltammetric response on CILE (a) and NG/CILE (b) for $5.0\times10^{-4}$ mol $L^{-1}$ HQ in 0.1 mol $L^{-1}$ pH 2.0 PBS at the scan rate of 100 mV $s^{-1}$. On bare CILE a pair of broad redox peaks could be observed and on NG/CILE the peaks became sharper with higher currents. Electrochemical reaction of HQ can easily take place in the selected potential range because of the presence of hydroxyl group on HQ structure [10].

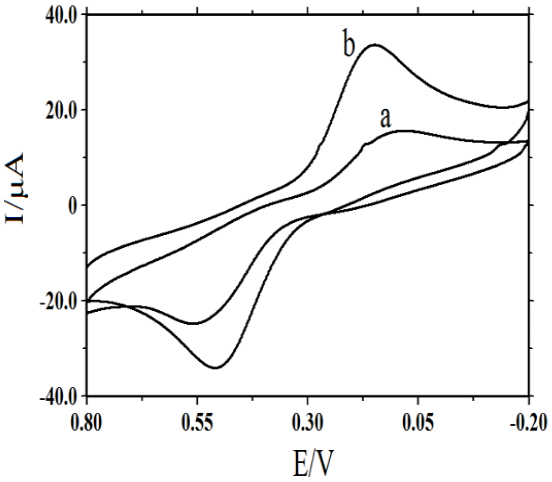


**Figure 2.** Cyclic voltammetric curves of $5.0\times10^{-4}$ mol $L^{-1}$ HQ on (a) CILE and (b) NG/CILE in pH 2.0 PBS.

**Table 1.** Voltammetric data of HQ on different electrodes.

| Electrode | $I_{pa}$ (μA) | $I_{pc}$ (μA) | $I_{pa}/I_{pc}$ | $E_{pa}$ (V) | $E_{pc}$ (V) | $\Delta E_p$ (V) |
|---|---|---|---|---|---|---|
| CILE | 15.92 | 7.65 | 2.08 | 0.561 | 0.113 | 0.488 |
| NG/CILE | 23.96 | 22.08 | 0.96 | 0.508 | 0.153 | 0.355 |

$\Delta E_p$ is the difference of $E_{pa}$ and $E_{pc}$.

All the electrochemical data of two cyclic voltammgrams were summarized and listed in Table 1. The ratio of anodic peak current to cathodic peak current ($I_{pa}/I_{pc}$) and the difference of peak-to-peak potential ($\Delta E_p$) on NG/CILE were smaller than that of CILE, indicating a more reversible electrochemical process could be got on NG/CILE due to the excellent electrocatalytic activity of NG [30]. The existence of nitrogen atom in GR nanosheet exhibited certain catalytic activity with the interaction of aromatic ring of HQ with GR, which enhanced the electron transfer of the analyte. Consequently, a new electroanalytical approach for HQ detection was further developed based on the relationship of $I_{pa}$ and HQ concentration with NG/CILE as the working electrode.

### *3.3 Influence of buffer pH*

The influence of buffer acidity on voltammetric behavior of $5.0\times10^{-4}$ mol $L^{-1}$ HQ at NG/CILE was studied in pH range from 1.5 to 5.5. As shown in Figure 3A, cyclic voltammograms were greatly influenced by the buffer pH with the gradually deformation. With the increase of buffer pH, the redox peak potentials shifted negatively, indicating that protons were participated in the electrode reaction. The relationships between formal peak potential ($E^{0'}$) and $I_{pa}$ with buffer pH were plotted and shown in Figure 3B and Figure 3C. The linear equation between $E^{0'}$ and pH was $E^{0'}(V) = -0.054\ pH + 0.444$ ($n = 8$, $\gamma = 0.998$). The slope value -54 mV $pH^{-1}$ was very close to Nernstian value (-59 mV $pH^{-1}$). So that the same amount of electron and proton were participated in the electrode process. As shown in Figure 3C the maximum $I_{pa}$ value was obtained at pH 2.0 in the pH range of 1.5~5.5. Hence, pH 2.0 was used for later experiments.

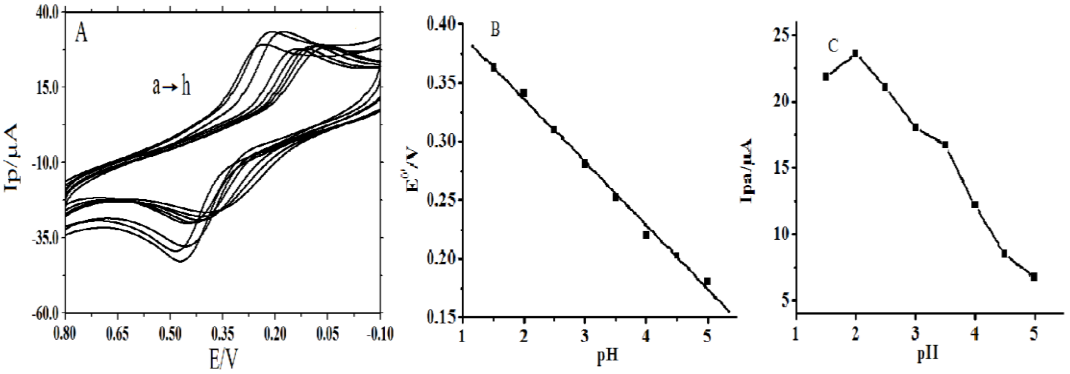


**Figure 3.** (A) Cyclic voltammetric curves of $5.0\times10^{-4}$ mol $L^{-1}$ HQ on NG/CILE with different pH PBS (from a to h: 1.5, 2.0, 2.5, 3.0, 3.5, 4.0, 4.5, 5.0); (B) The relationship between $E^{0'}$ and pH; (C) The relationship between $I_{pa}$ and pH.

### *3.4 Influence of scan rate*

The influence of scan rate on electrochemical responses of HQ at NG/CILE was studied in the range of 20~500 mV $s^{-1}$. As seen from Figure 4A, the currents of two peaks grown with the regular movement of redox potentials as with the scan rate increasing, which demonstrated a quasi-reversible electrode process.

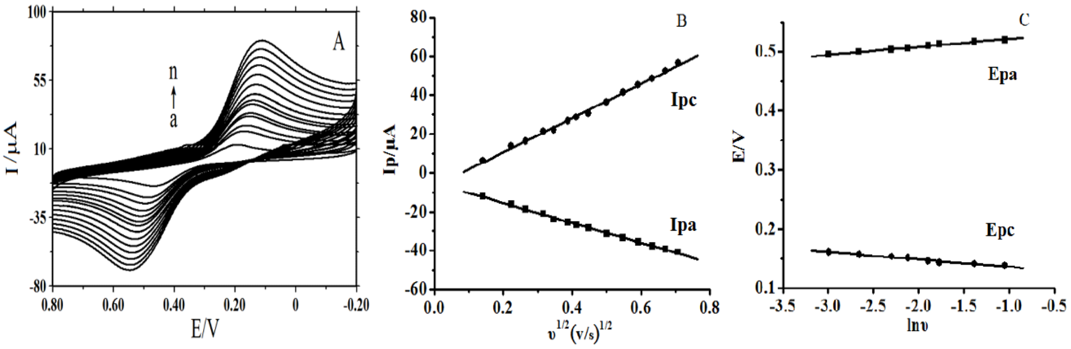
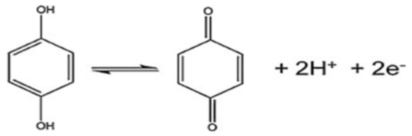


**Figure 4.** (A) Cyclic voltammetric curves of $5.0\times10^{-4}$ mol $L^{-1}$ HQ on NG/CILE in pH 2.0 PBS while changing scan rate (υ) as 20, 50, 70, 100, 120, 150, 170, 200, 250, 300, 350, 400, 450 and 500 m $V^{-1}$ (from a to n); (B) Linear relationships of $I_{pa}$ and $I_{pc}$ versus $\upsilon^{1/2}$; (C) Linear relationships of $E_{pa}$ and $E_{pc}$ with lnυ.

The linear relationship between the redox peak currents and the square root of scan rate ($\upsilon^{1/2}$) were plotted with the equations as $I_{pa}$ (μA) = -51.03 $\upsilon^{1/2}$ (V $s^{-1}$) -5.34 (n = 14, γ = 0.998) and $I_{pc}$ (μA) = 89.94 $\upsilon^{1/2}$ (V $s^{-1}$) - 6.99 (n = 14, γ = 0.998) (Figure 4B), which indicated the electrochemical process was controlled by diffusion. Simultaneously, the redox peak potentials also exhibited good linear relationships with lnυ and the equations were $E_{pa}$ (V) = 0.0133 lnυ + 0.535 (n=8, γ=0.993) and $E_{pc}$ (V) = -0.0125 lnυ + 0.124 (n = 8, γ = 0.987). According to the Laviron's electrochemical theory [36], the electrochemical parameters were calculated with charge transfer coefficient ($\alpha$) as 0.52, electron transfer number ($n$) as 1.97 and electrode reaction standard rate constant ($k_s$) as 0.128 $s^{-1}$. The value of $n$ (1.97) was almost equal to the theoretical data (2), indicating two electrons were involved in the electrode reaction. So the electrochemical oxidation of HQ on NG/CILE was a two-electron and two-proton process with the electrode reaction as follows:



### *3.5 Chronocoulometric curve*

As for the diffusion-controlled electrochemical reaction, the diffusional coefficient ($D$) could be obtained by recording the chronocoulometric curves of HQ on NG/CILE (Figure 5A). The plot between *Q* and $t^{1/2}$ was established with linear regression equation of Q ($10^{-6}$C) = 68.56 $t^{1/2}$ + 7.53 (n = 17, γ = 0.998) (Figure 5B). Based on Anson's equation [37]: $Q = 2\ nFAD^{1/2}ct^{1/2}/\pi^{1/2} + Qdl + nF\Gamma$, the *D* value of HQ was got as $2.82\times10^{-5}$ $cm^2\ s^{-1}$, which was larger than that on GCE ($2.26\times10^{-5}$ $cm^2\ s^{-1}$) [38], showing a faster electrochemical reaction of HQ on NG/CILE. This result could be contributed the presence of high conductive NG on the electrode that accelerated the electron transfer rate from reactant to substrate electrode.

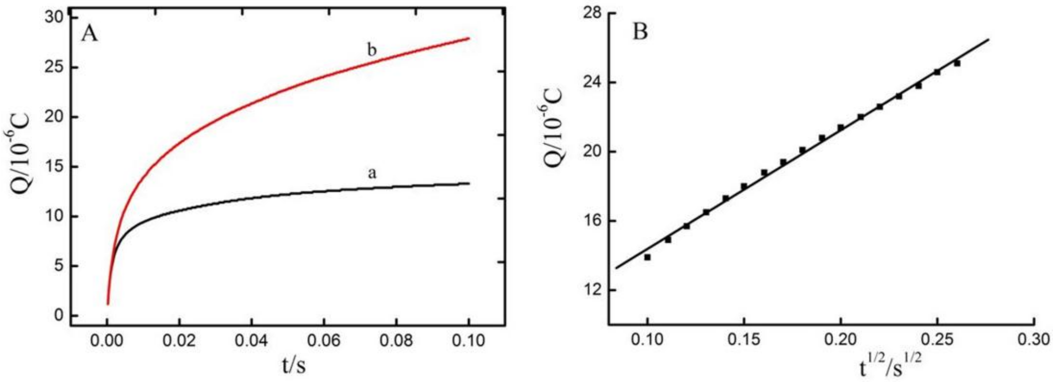


**Figure 5.** (A) Chronocoulometric curves of NG/CILE in (a) pH 2.0 PBS and (b) pH 2.0 PBS with $5.0\times10^{-4}$ mol $L^{-1}$ HQ; (B) Linear relationship of Q against $t^{1/2}$.

### *3.6 Analytical application*

Due to the catalytic effect of NG/CILE to the electrochemical reaction of HQ, DPV was adopted to quantitative determination of HQ with the results shown in Figure 6. A linear relationship could be got between $I_{pa}$ and HQ concentrations in the range of $2.0\times10^{-7}$ ~ $8.0\times10^{-4}$ mol $L^{-1}$ (as shown in insert of Figure 6).

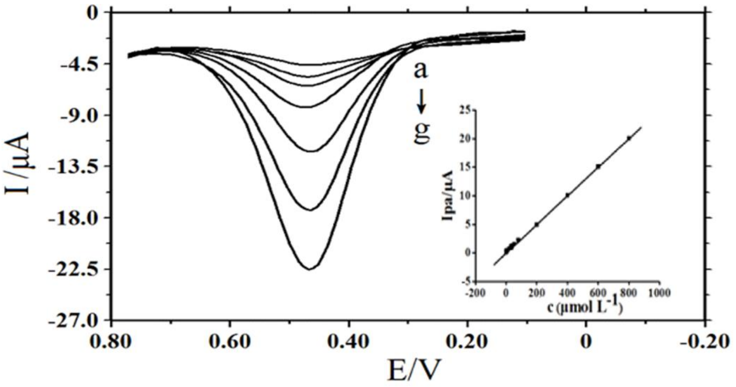


**Figure 6.** DPV curves of various concentrations HQ on NG/CILE (from a to g: 40.0, 60.0, 80.0, 200.0, 400.0, 600.0, 800.0 µmol $L^{-1}$). Inset is the relationship of $I_{pa}$ with the HQ concentration.

The linear regression equation was got as $I_{pa}$ (µA) = 0.025 C (µmol $L^{-1}$) - 0.0253 (γ = 0.997) accompanied by a detection limit of $6.25\times10^{-8}$ mol $L^{-1}$ (3σ). The reproducibility of NG/CILE was evaluated by recording 11 successive detections of $5.0\times10^{-4}$ mol $L^{-1}$ HQ. The relative standard deviation (RSD) of peak values was calculated as 2.8%. Five electrodes were prepared independently with the same procedure, which was used for the determination of $5.0\times10^{-4}$ mol $L^{-1}$ HQ and the RSD value was 3.7%, demonstrating good repeatability of the modified electrodes.

The analytical performances of NG/CILE for HQ detection were compared to those of previously published electrochemical HQ sensors with different modifiers. It was evident from Table 2 that the performance of the as-explored method showed a relatively wider linear range and lower detection limit for HQ analysis. The results could be ascribed to the synergistic effects of NG and CILE, which provided a fast electron transfer path for HQ electrochemical reaction.

**Table 2.** Comparision of analytical parameters for HQ analysis.

| Electrode* | Linear range (μmol $L^{-1}$) | Detection Limit (μmol $L^{-1}$) | References |
|---|---|---|---|
| CNCs-RGO/GCE | 1.0~300.0 | 0.87 | 13 |
| VOTPRu/GCE | 2.0~38.0 | 0.55 | 14 |
| GR-chitosan/GCE | 1.0~300.0 | 0.75 | 39 |
| GN-CN-MT/GCE | 0.1~600.0 | 0.01 | 40 |
| AuNPs/$Fe_3O_4$-APTES-GO/GCE | 3.0~137.0 | 1.1 | 41 |
| RGO-MWNTs/GCE | 8.0~391.0 | 2.6 | 42 |
| MWNT/GCE | 1.0~100.0 | 0.75 | 43 |
| BG/GCE | 5.0~100.0 | 0.3 | 44 |
| PASA/MWNTs/GCE | 6.0~100.0 | 1.0 | 45 |
| P-rGO/GCE | 5.0~90.0 | 0.08 | 46 |
| GMC/GCE | 2.0~50.0 | 0.37 | 47 |
| NG/CILE | 0.2~800.0 | 0.0625 | This work |

*CNCs-RGO: carbon nanocages-reduced graphene oxide, VOTPRu: {VOTPyP[$RuCl_3$(dppb)]$_4$} porphyrin, GN-CN-MT: graphene nanosheets and carbon nanospheres mixture, AuNPs: gold nanoparticles, APTES: (3-Aminopropyl) triethoxysilane, RGO: reduced graphene oxide, MWNT: multi-walled carbon nano tubes, BG: boron-doped graphene, PASA: polyamidosulfonic acid, P-rGO: porous reduced graphene oxide, CMC: graphitic mesoporous carbon.

### *3.7 Sample determination*

Under the optimal conditions the synthetic wastewater samples that contained HQ and metal ions were detected based on to the experimental procedure. HQ with certain concentration was mixed with different metal ions and diluted to 10 mL by 0.1 mol $L^{-1}$ pH 2.0 PBS, then the solution was put into electrochemical cell and detected by the three-electrode system. As shown in Table 3, the detection results were satisfactory with the RSD values of 1.59~2.46%. The recovery was achieved in the range of 99.6% ~102.5% by standard addition method. So NG/CILE could be effective to HQ detection in synthetic wastewater samples.

**Table 3.** Determination results of HQ in synthetic wastewater samples (n=3)

| Sample | Specified (μmol $L^{-1}$) | Found (μmol $L^{-1}$) | Added (μmol $L^{-1}$) | Total (μmol $L^{-1}$) | RSD (%) | Recovery (%) |
|---|---|---|---|---|---|---|
| 1 | 20.0 | 19.67 | 80.0 | 99.34 | 1.59 | 99.6 |
| 2 | 40.0 | 43.08 | 60.0 | 104.57 | 2.46 | 102.5 |

Sample 1 contains 5.0 μmol $L^{-1}$ of $Na^+$, $Ca^{2+}$, $Mg^{2+}$, $Cd^{2+}$ and 20.0 μmol $L^{-1}$ HQ;
Sample 2 contains 20.0 μmol $L^{-1}$ of $Na^+$, $Ca^{2+}$, $Cu^{2+}$, $Mn^{2+}$ and 40.0 μmol $L^{-1}$ HQ.

## 4. CONCLUSION

In this paper NG modified CILE was prepared by directly putting NG on the CILE surface, which showed the advantages such as easy preparation, good stability and excellent electrocatalytic activity. Cyclic voltammetric behaviors of HQ on NG/CILE were checked with electrochemical parameters of α, n and $k_s$ as 0.52, 1.97 and 0.128 $s^{-1}$, respectively. The linear detection range for HQ was from $2.0\times10^{-7}$ to $8.0\times10^{-4}$ mol $L^{-1}$ with the detection limit of $6.25\times10^{-8}$ mol $L^{-1}$ (3σ). Furthermore, this method showed good anti-interference ability, reproducibility and repeatability for the HQ detection in synthetic wastewater samples. Therefore NG had the potential applications in the electrode modification and electroanalysis.

ACKNOWLEDGEMENTS
This work was supported by the National Natural Science Foundation of China (21365010), the International S&T Cooperation Project of Hainan Province (KJHZ2015-13), the Taishan Scholar Overseas Distinguished Professorship program from Shandong Province Government and Natural Science Foundation of Hainan Province (20162031). L.F Dong thanks financial support from Malmstrom Endowed Fund at Hamline University.

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