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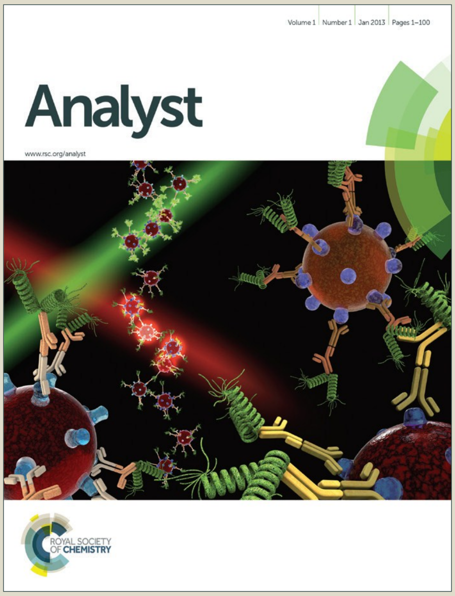

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ARTICLE

Electrochemically aminated glassy carbon electrode for simultaneous determination of hydroquinone and catechol†

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In this contribution, a very simple and reliable strategy based on the easy modification of glassy carbon electrode (GCE) by pre-electrolyzing GCE in ammonium carbamate aqueous solution was employed for the simultaneous determination of hydroquinone (HQ) and catechol (CC). Compared with bare GCE, the incorporation of nitrogen into the GCE surface structure improved the electrocatalytic property of GCE towards the electrooxidation of HQ and CC. The nitrogen-introduced GCE (N-GCE) was evaluated for the simultaneous detection of HQ and CC and the linear ranges for HQ and CC were both from 5 to 260 μM. Their detection limits were both evaluated to be 0.2 μM (S/N = 3). The present method was applied to the determination of HQ and CC in real river water samples with recoveries of 95.0–102.1%. In addition, a possible detection mechanism of HQ and CC was discussed.

Introduction

Electrochemical modification of carbon electrodes is an effective method to tailor the properties of electrodes intrinsically and manipulate their surface chemistries.[1, 2] The surface structures of electrodes are significantly changed during these electrochemical modification processes and consequently the interactions between materials with analytes are tuned.[3-6] Glassy carbon electrodes (GCEs) which consist of disordered carbon materials that are derived from polymers have been extensively utilized in electrochemistry. The rich surface chemistries of GCEs play an important role in good electrocatalysis, which make GCEs potential candidates for sensing applications.[7-10]

Dihydroxybenzene, including hydroquinone (HQ) and catechol (CC) is widely used chemicals and ubiquitous in biological systems and ecological environment.[11, 12] However, these compounds have been considered as the priority environmental pollutants by the US Environmental Protection Agency (EPA) and the European Union (EU) due to their high toxicity and low degradation.[13, 14] In addition, they are linked to diseases such as tachycardia and decompensation, and they have genotoxicity and carcinogenicity effect on human.[15-17] Therefore, the selective discrimination of one dihydroxybenzene compound from its isomers is of significant importance due to its significance in identifying the origin of contamination and some diseases.[18-20]

The development of efficient electrochemical techniques has received significant interest for the detection of these compounds because of their advantages such as simplicity and sensitivity.[21-30] However, the direct determination of dihydroxybenzene isomers is still a significant challenge owing to the adjacent potentials of their redox peaks at unmodified conventional solid electrodes, thus resulting in very poor resolution for simultaneous detection of them.[23-26] Many strategies have been proposed for detecting the two dihydroxybenzene isomers simultaneously. In these methods, the incorporation of nanostructured composite is of particular interest to enhance catalytic activity.[27-30] Nevertheless, in spite of the synthesis of the nanomaterial, the stable immobilization of the composite is also a challenge.

On the basis of our previous work,[31] the electrooxidation of GCEs in ammonium carbamate aqueous solution was an effective method to intrinsically modify the properties of GCEs by the introduction of amino groups into the surface structures of GCEs, and the corresponding aminated GCEs showed surprising electrocatalytic behaviour towards oxygen and some inorganic compounds.[31-35] Herein, we further employ the simple and general method for simultaneous electrochemical determination of dihydroxybenzene isomers. Based on the different electrocatalytic properties of the aminated GCEs towards HQ and CC, an alternative and simple protocol for simultaneous determination of these two isomers was established. This simple strategy based on the mild electrochemical oxidation of GCEs does not require any immobilization of films or composite and good reproducibility can be obtained by controlling the electrolysis time. The proposed N-GCE was further used in real sample analysis and good recoveries were acquired.

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Experimental

Reagents and chemicals

Ammonium carbamate obtained from Energy Chemical (China), HQ, CC and the other chemicals were purchased from Aladdin (Shanghai, China). All the chemicals were of analytical reagent grade and used as received. Phosphate buffer solution (PBS) was prepared by mixing the solution of 0.1 M K_2HPO_4 and 0.1 M KH_2PO_4.

Characterizations of different modified electrodes

Electrochemical measurements were performed with CHI 830C and CHI1030 electrochemical workstation (Chenhua, Shanghai, China) employing a conventional three-electrode system, which consisted of a bare or a modified GCE as working electrode, a platinum wire as counter electrode, and a saturated calomel electrode (SCE) as reference electrode. Electrochemical impedance spectra (EIS) were measured in 0.1 M KCl solutions containing 5 mM $[Fe(CN)_6]^{3-/4-}$ with ac amplitude of 5 mV in the frequency range of 0.01Hz to 100 kHz. XPS spectra measurements were conducted using a Physical Electronics Industries model 5500 multi-technique surface analysis system equipped with a hemispherical analyzer, a monochromator and a multichannel detector. Monochromatic Al Ka radiation (1486.6 eV, 300 W) was employed for excitation.

Preparation of Electrodes

Prior to each electrode modification, GCE (3 mm diameter) was first polished with fine wet emery paper (grain size 2000) and then with 0.3 μm and 0.05 μm alumina slurries, then sequentially ultrasonically cleaned with absolute alcohol and distilled water. To introduce nitrogen-containing functional groups into the polished GCE surface[31] (i.e., amination of GCE surface), the polished GCE was electrooxidized at a constant potential of + 1.1 V (vs. SCE) for 20 min in 0.1 M ammonium carbamate aqueous solution (pH ca. 9) at room temperature (22-24℃). The treated GCE was washed with doubly distilled water, and used as the working electrode in the following work. The resulting aminated GCE was designated as N-GCE.

Results and discussion

Characterization of N-GCE

The electrochemical behaviours of HQ, CC and their mixture at different electrodes have been characterized using cyclic voltammetry. Firstly, a comparison of the electrocatalytic oxidation of the two dihydroxybenzene isomers was investigated. Fig. 1A and Fig. 1B display the cyclic voltammograms (CVs) of the individual electrochemical behaviours of HQ and CC (each 300 μM) at bare GCE and N-GCE in 0.10 M PBS (pH 7.0), respectively. It can be observed that the anodic peak potentials of HQ and CC are at +400 mV (curve a in Fig. 1A) and +450 mV (curve a in Fig. 1B) at the bare GCE, respectively. However, their anodic peak potentials are 200 mV for HQ (curve b in Fig. 1A) and 300 mV for CC (curve b in Fig. 1B) at the N-GCE. Compared with the bare GCE, the anodic peak potentials of HQ and CC obtained at the N-GCE are about 200 mV and 150 mV negatively shift, indicating improved electrocatalytic performance of the N-GCE towards the electrooxidation of the two dihydroxybenzene isomers. Besides, the potential differences between the redox peaks of HQ and those of CC were determined to be 450 mV and 325 mV at the bare GCE, while those were determined to be 80 mV for both HQ and CC at the N-GCE, suggesting improved reversibility at N-GCE, which is highly desirable for the selective discrimination of HQ and CC. In addition, the redox peak currents of HQ and CC are approximately two times the height of those at the bare GCE, suggesting an increased electroactive surface area (ESA) of the N-GCE surface. In order to determine the ESA of the N-GCE and the bare GCE, cyclic voltammetry was employed in 0.1 M KCl using 5.0 mM $Fe(CN)_6^{4-/3-}$ as a probe at different scan rates. As shown in Fig. S1A and Fig. S1B, both the peak currents of GCE and N-GCE increased linearly with the square root of scan rate, indicating quasi-reversible diffusion controlled processes. Thus the following Randles-Sevcik equation was used to

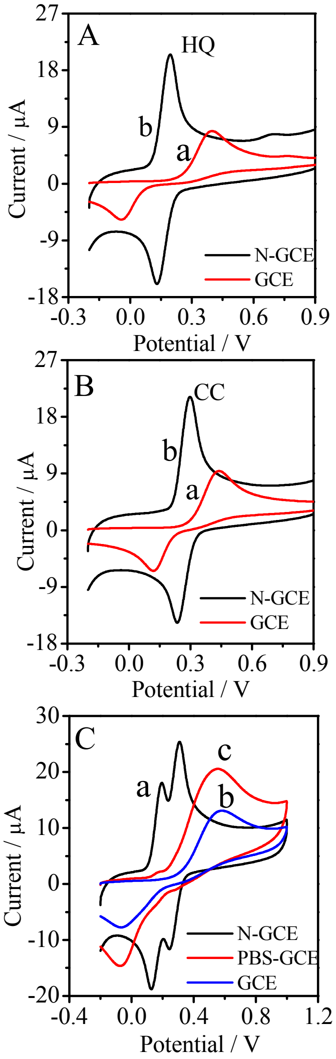


Fig. 1 Typical CVs at bare GCE (a) and N-GCE (b) for HQ (A) and CC (B), each 300 μM. (C) CVs of N-GCE (a), bare GCE (b) and PBS-GCE (c) in 0.1 M PBS (pH 7.0) containing the mixture of HQ and CC (each 300 μM). Scan rate, 0.1 V s^{-1}.

calculate the ESA:

$$i_{pa} = 2.69\times10^{5} n^{\frac{3}{2}} A C_0 D_0^{\frac{1}{2}} v^{\frac{1}{2}}$$

where i_{pa} refers to the anodic peak current (A), n the electron transfer number (n=1), D_0 the diffusion coefficient of 5 mM $Fe(CN)_6^{4-/3-}$ in 0.1 M KCl (7.6×10^{-6} cm^2 s^{-1}), C_0 the concentration of $Fe(CN)_6^{4-/3-}$ (mol cm^{-3}), v the scan rate (V s^{-1}), A the ESA, then from the slope of the i_{pa} versus $v^{1/2}$ linear regression equation, the ESA of the N-GCE was calculated to be 0.07cm^2, which was 1.77 times as large as the bare GCE.

The ability of N-GCEs to promote the voltammetric resolution of HQ and CC was investigated in their mixture. Fig. 1C shows the CVs of a mixture of HQ and CC (each 300 μM) at different modified electrodes. It can be observed that only one pair of redox peaks appears at the bare GCE (curve b). Obviously, the redox peaks of HQ and CC are overlapped at the bare GCE. In contrast, two pairs of distinctly well-defined peaks corresponding to the redox of HQ and CC are observed at the N-GCE with anodic peak potential difference of ac. 100 mV (curve a), demonstrating that the redox peaks of HQ and CC can be clearly resolved. Overall, the N-GCE exhibits excellent electrochemical behaviour towards the electrooxidation of HQ and CC, resulting in the separation of oxidation peaks and promising the potential application of N-GCE to the simultaneous detection of the two isomers.

Additionally, Electrochemical behaviour of the N-GCE was further characterized by electrochemical impedance spectroscopy (EIS), which could provide the interface information of the modified electrode surfaces. Fig. S2 shows the Nyquist plots of a GCE before and after amination in a 0.1 M KCl solution using 5.0 mM $[Fe(CN)_6]^{3-/4-}$ as a probe. Before amination (i.e., bare GCE), the redox process of the $[Fe(CN)_6]^{3-/4-}$ showed an electron transfer resistance (Ret) of about 100 Ω (curve b). When the GCE was aminated, it showed a higher Ret of about 200 Ω. The variation in AC impedance indicated the change of the surface structure of GCE. The increase of the Ret could be attributed to the higher defect content of the N-GCE. Although the Ret of N-GCE was bigger than bare GCE, the defects led to abundant active sites. Thus, the electrochemical activity was improved after amination.

Typically, both oxygen-containing groups and nitrogen-containing groups are introduced into the surface structures of GCEs during the amination process. The XPS spectra results shown in Fig. 2A and Fig. 2B reveals signals for N 1s and O 1s, which are consistent with our previous studies.[31] It confirms the incorporation of both nitrogen atoms and oxygen atoms into the surface structure of GCE. In order to identify the key factor responsible for the good electrocatalysis behaviour, control experiments were performed using PBS instead of ammonium carbamate aqueous solution as the pre-electrolysis solution. During this electrochemically active process, only oxygen-containing functional groups were introduced

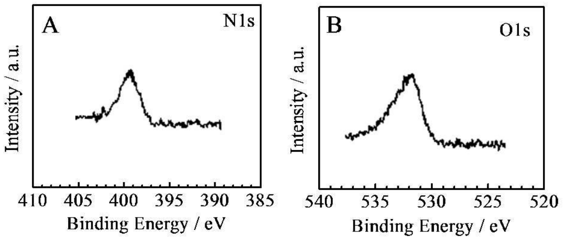
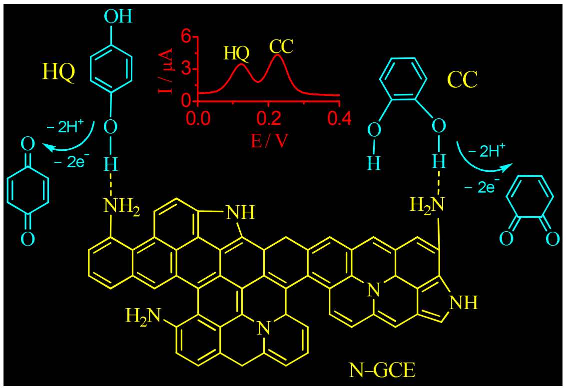


Fig.2. (A) XPS N1s spectra and (B) XPS O1s spectra of N-GCE.



Scheme 1. Schematic representation of interaction between the —OH groups of dihydroxybenzene and the amine groups of N-GCE and the electrooxidation of HQ and CC at N-GCE.

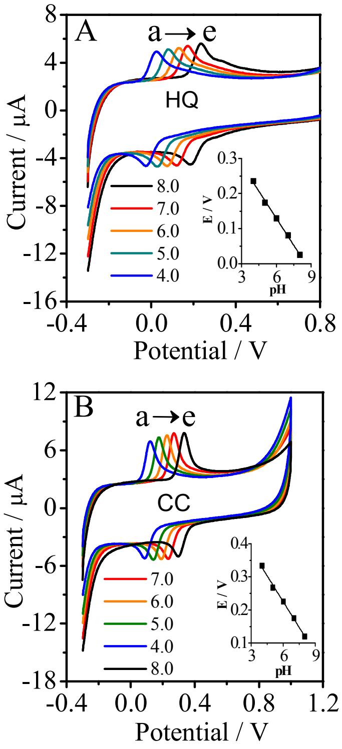


Fig.3. CVs of 50μM HQ (A) and 50μM CC (B) at N-GCE in 0.1 M PBS with different pH values (a-e): 4.0, 5.0, 6.0, 7.0 and 8.0. Insets: the corresponding plots of their peak potentials vs. pH values.

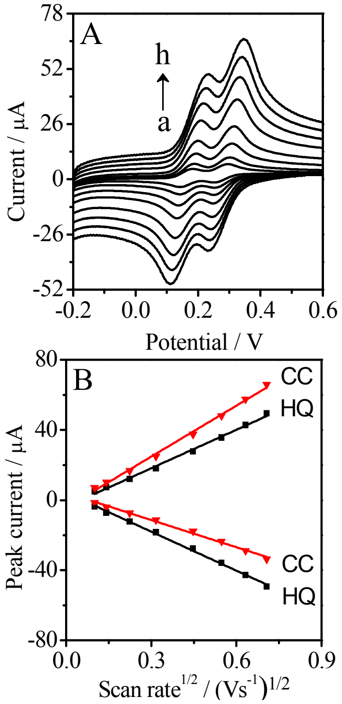


Fig. 4（A）: Typical CVs at N-GCE for the mixture of 300 μM HQ and 300 μM CC in 0.10 M PBS (pH 7.0) at different scan rates (a-h): 0.01, 0.02, 0.05, 0.1, 0.2, 0.3, 0.4 and 0.5 Vs^{-1}. (B) The corresponding plots of redox peak current vs. square root of scan rate for HQ and CC.

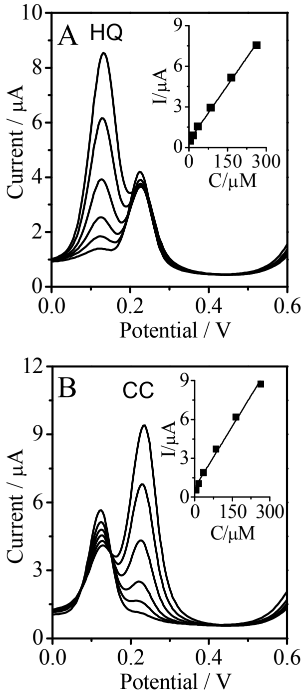


Fig.5. (A) DPVs of N-GCE in PBS containing 80μM CC and various concentrations of HQ in the range from 5 to 260 μM. (B) DPVs of N-GCE in PBS containing 80μM HQ and various concentrations of CC in the range from 5 to 260 μM. 0.1 M PBS (pH 5.0). Insets are their calibration plots.

into the resulting PBS-GCE.[4-6] It can be observed that the obtained PBS-GCE shows similar electrochemical performance to the bare GCE (curve c in Fig. 1C). Therefore, it can be concluded that the good electrocatalytic response of HQ and CC at the N-GCE are ascribed to the introduction of nitrogen-containing groups. In our previous study, we have revealed that three types of bonding configurations of nitrogen-containing groups existed within an aminated GCE (i.e., N-GCE) surface structure which were pyrrolic N, graphitic N and aniline-like N.[36]

The good electrocatalytic performance of N-GCE towards HQ and CC is considered to be attributed to the following two probable reasons: One is the introduction of nitrogen into GCE can create new active sites for the electrochemical reaction and can contribute high electrocatalytic performance of the GCE towards the redox reactions of HQ and CC.[28, 37, 38] The other is the amine groups could form intermolecular H-bonds with the –OH groups of HQ and CC, which can activate the –OH groups and essentially facilitate electron transfer between the N-GCE and dihydroxybenzene molecules through O–H···N.[2, 3, 23, 27, 38] Scheme 1 shows the possible detection mechanism of HQ and CC through hydrogen bonding between the –OH groups of dihydroxybenzene and the amine groups of the N-GCE. The formed hydrogen bonds could enhance the electron transfer kinetics of the redox reaction of HQ and CC at N-GCE.

Effect of pH and scan rate

The influences of solution pH on the peak currents and peak potentials of HQ and CC at N-GCEs were investigated by CVs as shown in Fig 3A and Fig. 3B. A shift of the oxidation peak potentials of both compounds towards more positive values were observed as the solution pH value was increased from 4.0 to 8.0, indicating that the proton-transfer process involved in the oxidation of these compounds. Good linear relationships between peak potential and pH value were obtained with the slope values of –51.2 and –51.8 mV/pH for HQ (E_{pa}(V) = 0.4368 – 0.0512 pH, R = 0.9961), and CC (E_{pa}(V) = 0.5358 – 0.0518 pH, R = 0.9943), respectively (insets in Fig. 3 A and Fig. 3B). These slope values suggested a two-electron coupled two-proton transfer electrode process.[23, 24] Moreover, the two regression lines were almost parallel, implying that the peak-to-peak separation between them was constant at different pH solutions. Considering the selectivity as well as HQ and CC easily undergo deprotonation at high pH, pH 5.0 was chosen for the subsequent experiments.

The effect of scan rate on the redox peaks of the mixture of HQ and CC at the N-GCE was investigated by CVs (Fig. 4A). The peak currents of both compounds increased linearly with square root of scan rate from 10 to 500 mV s^{-1}, while their oxidation peak potentials shifted positively (Fig. 4B). The result indicates that the electrode reactions of these compounds are all typical diffusion-controlled processes.

Table 1 Comparison of the N-GCE with other reported modified electrodes for the simultaneous detection of HQ and CC.

Electrodes	Linear range (μM)		LOD (μM)		Ref.
	HQ	CC	HQ	CC	
NA-COGH	0.4 – 600	0.8 – 500	0.019	0.034	13
Poly(thionine)-modified GCE	1 – 120	1 – 120	0.030	0.025	14
Nafion/MWCNTs/CDs/MWCNTs	1 – 200	4 – 200	0.070	0.060	16
GCE/Pt-MnO_2	3 – 481	15 – 447	—	—	20
THPP/CNTs/GCE	0.2 – 12	0.4 – 10	0.070	0.010	21
SiCNb electrode	0.8 – 500	39.8 – 980	1.2	0.80	22
PTH-modified GCE	39.8 – 980	1 – 120	0.030	0.025	23
MWCNTs-PDDA-GR	0.5 – 400	0.5 – 400	0.020	0.018	24
CNCs-RGO/GCE	1 – 300	1 – 400	0.40	0.87	25
RGO-MWNTs/GCE	8 – 391	5.5 – 540	2.6	1.8	26
BG	5 – 100	1 – 75	0.30	0.20	27
PEDOT/NGE	1 – 10	1 – 10	0.26	0.18	28
Au/$_L$-lysine/OMC-Au/Tyr/GCE	0.4 – 80	0.4 – 80	0.050	0.025	30
Pyridinic-NG/GCE	5 – 200	5 – 200	0.38	1.0	38
N-GCE	5 – 260	5 – 260	0.20	0.20	This work

Simultaneous determination of HQ and CC

In order to obtain a much higher current sensitivity and a better resolution, voltammetric response was investigated for the simultaneous and quantitive determinations of HQ and CC at N-GCE. Fig.5 shows the DPVs of HQ (Fig. 5A) and CC (Fig. 5B) in their mixtures varying the concentration of one compound while remaining the other compound constant. The linear ranges for HQ (Ip_{HQ} (μA) = 0.02731 C (μM) + 0.4986, R = 0.9966) and CC (Ip_{CC} (μA) = 0.03159 C (μM) + 0.7171), R = 0.9906) were both from 5 to 260 μM. Their detection limits were both evaluated to be 0.2 μM (S/N=3). A comparison of the proposed N-GCE with other modified electrodes developed for simultaneous detection of HQ and CC is listed in Table 1. It can be observed that the proposed method shows rational linear range and acceptable detection of limit. It obviously demonstrates that the proposed N-GCE obtained by simple pre-electrolysis in ammonium carbamate aqueous solution can be employed for a sensitive and reliable electrochemical sensing to the simultaneous and quantitative detection of HQ and CC.

Reproducibility, stability and interference

Reproducibility is one of the important factors to evaluate the feasibility of N-GCEs for real sample analysis. The reproducibility of N-GCE was tested by determining a mixture of HQ and CC (each 100 μM) in PBS (pH 5.0) for ten times. The relative standard deviation (RSD) of anodic peak current was 1.4% for HQ and 2.3% for CC. The reproducibility of ten independently prepared N-GCEs was also examined by recording the DPV signals of these two isomers. The RSD for the determination of HQ and CC was found to be 2.0% and 3.1%, respectively, indicating the good reproducibility of N-GCE.

The long-term stability of the N-GCE was investigated by measuring a mixture of 300 μM HQ and 300 μM CC in PBS (0.1M, pH 7.0) intermittently (Fig. S3). The electrodes were stored at room temperature by immersing them in PBS (0.1 M, pH 7.0) when it was not in use. The DPV responses of both HQ and CC retained about 90% of their initial response values to the N-GCE after 5 days of storage, indicating the good stability of N-GCE towards the simultaneous detection of HQ and CC.

Additionally, the possible interferents that may interfere with the detection of these two isomers were evaluated. 100-fold concentrations of K^+, Na^+, Ca^{2+}, Mg^{2+}, Cl^-, NO_3^-, Fe^{2+}, SO_4^{2-} and same concentrations of resorcinol, phenol, hydroxybenzoic acid, hydroxyl benzaldehyde, hydroxybenzyl alcohol, acetaminophen, ascorbic acid and uric acid showed no obvious influence on HQ and CC detection (signal change below 5%) at the N-GCE (Table. S1). These results reveals that the present method is promising for simultaneous determination of HQ and CC with good reproducibility, acceptable stability and excellent selectivity.

Sample analysis

In order to evaluate the validity of the developed method in analyzing real samples, the N-GCE was applied for the simultaneous determination of HQ and CC in river water (Lingshui-River, Dalian, China) without any pretreatment. The results were listed in Table 2. The average recoveries of five times detections were 100.2% and 95.0% for HQ and CC, respectively, which suggested the feasibility of the proposed strategy for simultaneous determination of HQ and CC in real samples analysis.

Conclusions

In this work, a simple and reliable method has been demonstrated for the simultaneous determination of dihydroxybenzene isomers using the electrochemically aminated N-GCE. The N-GCE showed much improved electrocatalytic oxidation behaviour and very good resolution towards the selective oxidation of HQ and CC. The easy processing method and the outstanding electrocatalytic property probably make the N-GCE a promising candidate for sensitive and selective electrochemical sensing of other phenolic compounds. It can be anticipated that this N-GCE can provide wide applications in the field of electrochemical sensors and fuel cells.

Table 2 Determination of HQ and CC in real river water sample (n = 5).

Water sample	Added (μM)	Found (μM)	Recovery (%)
HQ	40	40.07	100.2%
CC	40	36.40	95.0%

Acknowledgements

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