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Simultaneous Detection of Hydroquinone and Catechol Using Platinum Nanoparticles Decorated Graphene/Poly-Cyclodextrin/Multiwalled Carbon Nanotubes (MWCNTs) Nanocomposite Based Biosensor

Xiaomei Huang[1,*], Xiang Deng[1], Wenjing Qi[2,*], and Di Wu[2]

[1] *Department of Chemistry and Chemical Engineering, Sichuan University of Arts and Science, Dazhou, Sichuan 635000, P. R. China*
[2] *Chongqing Key Laboratory of Inorganic Functional Materials, College of Chemistry, Chongqing Normal University, Chongqing 401331, P. R. China*

Graphene cyclodextrin prepolymer (pre-CD)-multiwall carbon nanotubes (Gr-CDP-MWCNTs) nanocomposites modified on glassy carbon electrode (Gr-CDP-MWCNTs/GCE) are prepared and then platinum particles (PtNPs) are electrodeposited on it. The simultaneous determination of hydroquinone (HQ) and catechol (CC) at PtNPs/Gr-CDP-MWCNTs/GCE is reported in the present work. Synergistic effect of nanomaterials, host-guest chemical reaction ability of CDP, the stacking interaction between detected molecules and Gr-MWCNTs surface are considered as the main reasons of successfully simultaneous detection of HQ and CC. Cyclic voltammetry (CV), scanning electron microscopy (SEM) and different pulse voltammetry (DPV) are employed to characterize the proposed PtNPs/Gr-CDP-MWCNTs electrochemical biosensor. The prepared PtNPs/Gr-CDP-MWCNTs sensor shows linear response ranges of 0.05–27.2 μM and 0.1–27.2 μM and have low detection limits (S/N = 3) of 0.015 μM and 0.03 μM for simultaneous electrochemical determination of HQ and CC, respectively. It is also applied for the measurement of HQ and CC in local river water samples with recoveries from 98.0 to 102.0% and from 99.3 to 101.5%.

Keywords: Graphene (Gr), Multiwall Carbon Nanotubes (MWCNTs), Hydroquinone (HQ), Catechol (CC), Electrochemical Biosensor.

1. INTRODUCTION

Hydroquinone (HQ) and catechol (CC) are two isomers of dihydroxybenzene which are important environmental pollutants due to their high toxicity and low degradability in the ecological system,[1] which are harmful to human health and ecological environment. They are mostly derived from various agricultural and industrial activities, including waste discharge from wood preservatives, coking, textiles, plastics, dyes, paper, herbicides industries and the partial degradation of phenoxy contaminants in remediation processes.[2,3] Since these two phenolic compounds isomers usually coexist and interfere with each other during their determination. It is necessary to establish a simple, fast and reliable analytical method for sensitive and selective determination of dihydroxybenzene isomers in various matrices. Up to now, various approaches have been exploited to meet the rising demand for the determination of dihydroxybenzene isomers, including liquid chromatography/ultraviolet spectrometry,[4,5] synchronous fluorescence,[6] chemiluminescence,[7,8] spectrophotometry,[9] gas chromatography/mass spectrometry,[10] and pH based-flow injection analysis.[11] The mentioned above procedures usually require specific equipment, laboratory conditions, and are not suitable for on-site analysis. However electrochemical methods have the merits of low cost, simple operation, automatic and fast analysis. The key point of electrochemical methods lies in the high sensitivity, good selectivity and potential applicability for the quantification of phenols (such as HQ and CC) in real samples.[12–19]

Graphene (Gr), a two-dimensional carbon material, has drawn tremendous attention from both experimental and theoretical communities because of its merits of high

*Authors to whom correspondence should be addressed.

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surface area, excellent conductivity, strong mechanical properties and unique electronic property arising from its strict 2D structure,[20,21] and its potential technical applications.[22,23] Due to its unique properties, Gr has been applied as an attractive material in designing novel sensors. However, pure Gr is hydrophobic and has no appreciable solubility in most solvents and owing to the π–π interaction between individual Gr. Therefore Gr easily tends to form irreversible agglomerates or even restocks to form graphite through Van der waals interactions,[24,25] which limits its chemical manipulation and wide applications. In order to scale up the production of Gr for technological applications, many methods have been reported, such as chemical modification,[26] acid oxidation[27] and non-covalent interactions.[28] Most of these methods are complex, difficult to control or sever, and may damage the structure of Gr and lose of the intrinsic properties of Gr-based materials. Gr can be hybridized with metallic nanoparticles, organic polymers, semiconductor nanostructures, carbon nanomaterials,[29] which can not only keep the graphene morphology, but also improve the utilization rate of the GR matrix composites.

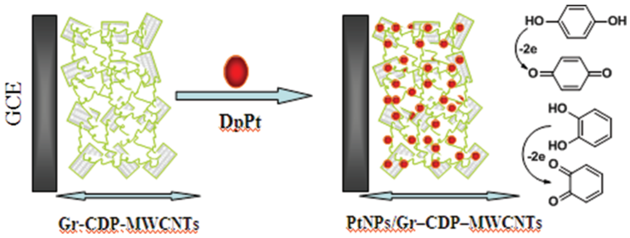
In this paper, Gr and MWCNTs are dispersed in the mixed solution of β-Cyclodextrin (β-CD) and prepolymer (pre-CDP), and then platinum particles (PtNPs) are electrodeposited on the Gr-CDP-MWCNTs modified glassy carbon electrode by constant potential stripping technique to simultaneous detect HQ and CC. The 1D MWCNTs and 2D Gr formed a 3D hierarchical structure in the present work. MWCNTs can effectively inhibit the stacking of individual Gr and enhance the utilization of Gr based composites.[30] PtNPs can increase catalytic activity and electrical conductivity. So PtNPs/Gr-CDP-MWCNTs are prepared and applied in as a novel electrochemical sensors for simultaneous determination of HQ and CC with high electrochemical sensitivity.

2. EXPERIMENTAL DETAILS

2.1. Instrumentation and Chemicals

Cyclic voltammetric (CV) measurement and differential puls voltammetry (DPV) measurement were carried out on CHI660D electrochemistry system (Shanghai CH instruments Co., China). The three-electrode system used in this work consisted of a modified electrode (GCE, $\Phi = 4$ mm) as working electrode, a platinum wire as auxiliary electrode, and a saturated calomel electrode (SCE) as reference electrode, respectively. Model PHSJ-3F laboratory pH meter (Leici Instrument, Shanghai, China) was used to test the pH value.

Chloroplatic acid (H_2PtCl_6) was purchased from Sigma Chemical Co. (St. Louis, Mo, USA). Multiwall carbon nanotubes (MWCNTs > 95% purity) were purchased from Chengdu Organic Chemicals Co. Ltd. Graphene oxide (Gr) was purchased from Nanjing Xianfeng Nano Co. (Nanjing,



Scheme 1. The schematic diagram of the fabrication of the prepared PtNPs/Gr-CDP-MWCNTs/GCE electrochemical biosensor.

China). β-Cyclodextrin (β-CD), Catechol (CC) and hydroquinone (HQ) were purchased from Aldrich. Mineral oil was obtained from Beijing Chemical Co. (China). All the other chemicals employed were analytical grade and used without further purification. Phosphate buffer solution (PBS) consisting of 0.10 M KH_2PO_4–Na_2HPO_4 was used as supporting electrolyte for electrochemical measurements. The supporting electrolyte was 0.1 M KCl. Ultrapure water was used throughout.

2.2. Fabrication of the Biosensor

The pre-CDP was prepared according to the previously reported method.[31] 1 mg Gr and 1 mg MWCNTs are dissolved in 1 mL 1% pre-CDP solution by ultrasonic dispersion to obtain a stable black suspension. 10 μL of the resulting suspension is dropped on a clean glassy carbon electrode ($\Phi = 4$ mm) surface and dried in the air. And then the electrochemical deposition of PtNPs is performed on Gr-CDP-MWCNTs/GCE to form PtNPs/Gr-CDP-MWCNTs/GCE in aqueous solution containing 1% H_2PtCl_6. The deposition time is 20 s and the potential is −0.2 V. For comparison, Gr-CDP-MWCNTs/GCE, PtNPs/Gr-CDP/GCE and PtNPs/MWCNTs-CDP/GCE are prepared by the same method. Scheme 1 shows the structure of the prepared PtNPs/Gr-CDP-MWCNTs/GCE and explains the electron mediating properties of PtNPs/MWCNTs-CDP/GCE toward the oxidation of HQ and CC.

3. RESULTS AND DISCUSSION

3.1. The Structure Characterization

The surface morphology of different nanocompsites modified electrodes is characterized by SEM in Figure 1. As expected, sheet structure belonging to Gr is covered by intertwined MWCNTs, resulting in the formation of the percolating network. And the rough and porous structure of Gr-CDP-MWCNTs modified film is observed in Figure 1(A). Pt nanoparticles are indeed electrodeposited on the Gr-CDP-MWCNTs nanocomposite surface as shown in the the white spots in Figure 1(B). They are equably adsorbed on the surface of Gr-CDP-MWCNTs nanocomposite and formed highly dispersed nanoparticles with large surface area, which may enhance the electron transport and catalytic activity of PtNPs/Gr-CDP-MWCNTs nanocomposite.

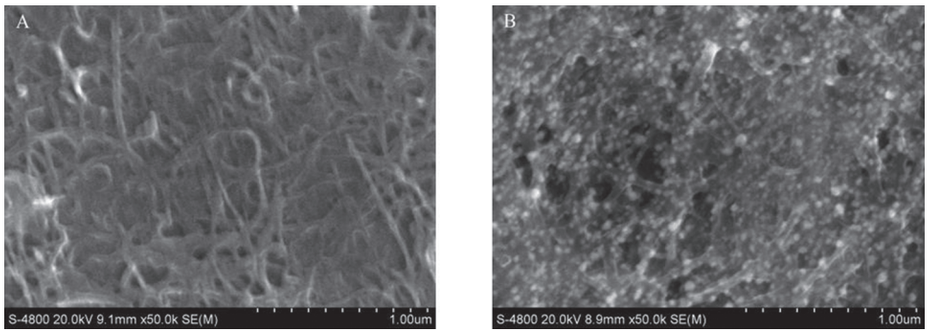


Figure 1. SEM images of the surface morphologies of (A) Gr-CDP-MWCNTs and (B) PtNPs/Gr-CDP-MWCNTs nanocompsite.

3.2. Electrochemical Characterization of the Modified Electrode

The feasibility of simultaneous electrochemical determination of HQ and CC using PtNPs/Gr-CDP-MWCNTs/GCE is studied. Figure 2(A) shows cyclic voltammograms (CVs) of Gr-CDP-MWCNTs/GCE, PtNPs/MWCNTs-CDP/GCE and PtNPs/Gr-CDP/GCE containing 50 μM HQ and CC, respectively. Although the Gr-CDP-MWCNTs/GCE, PtNPs/MWCNTs-CDP/GCE and PtNPs/Gr-CDP/GCE can also give well-separated anodic peaks for HQ and CC, the oxidation current densities for HQ and CC at three modified electrodes are much lower than those at PtNPs/Gr-CDP-MWCNTs/GCE. Figure 2(B) shows DPVs of Gr-CDP-MWCNTs/GCE, PtNPs/MWCNTs-CDP/GCE, PtNPs/Gr-CDP/GCE and PtNPs/Gr-CDP-MWCNTs/GCE containing 50 μM HQ and CC, respectively. The peak current density for each bimolecular at PtNPs/Gr-CDP-MWCNTs/GCE is much higher than those at three other modified electrodes, which is well consistent with the results of CVs. The biosensor PtNPs/Gr-CDP-MWCNTs/GCE shows the best catalytic performance, which is ascribed to synergistic action between Gr-CDP-MWCNTs and PtNPs. It enables large electrochemically active surface area, rapid electron transfer, and fast transport of analytes to electrode surface. The PtNPs/Gr-CDP-MWCNTs/GCE electrochemical biosensor

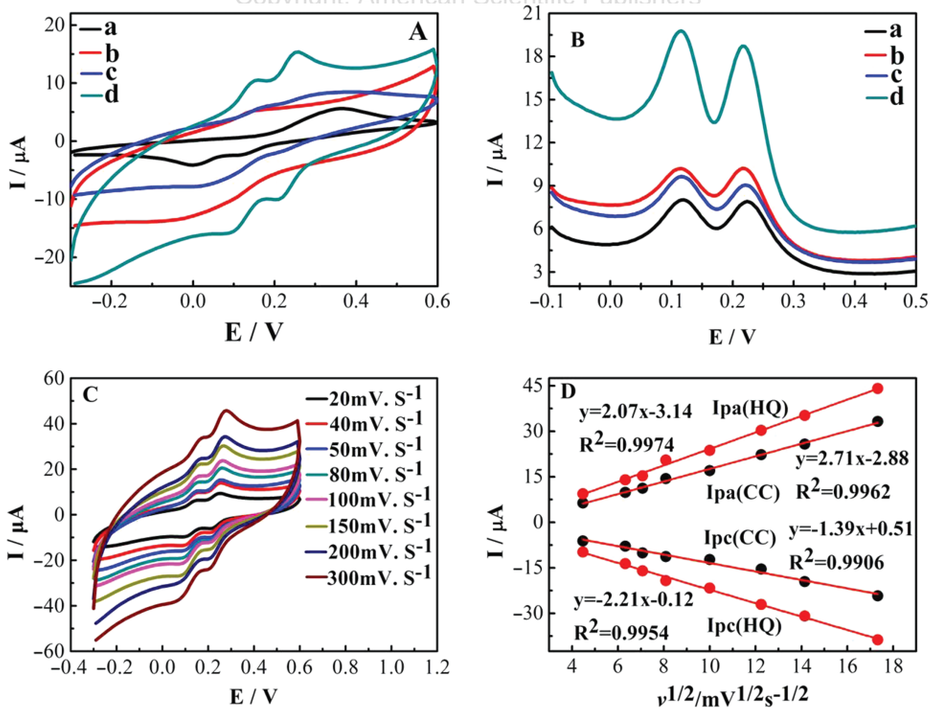


Figure 2. Cyclic voltammograms (A) and DPVs (B) of a mixture of 50 μM HQ and CC in 0.1 M PBS (pH 6.0) at different electrodes: (a) Gr-CDP-MWCNTs/GCE (black), (b) PtNPs/MWCNTs-CDP/GCE (red), (c) PtNPs/Gr-CDP/GCE (blue) and (d) PtNPs/Gr-CDP-MWCNTs/GCE (green). Scan rate: 50 mV/s. Cyclic voltammograms (C) and (D) of equimolar mixture (50 μM) of HQ and CC in pH 6.0 at PtNPs/Gr-CDP-MWCNTs/GCE at various scan rates. Scan rate (mV/s, from inner to outer): 20, 40, 50, 100, 150, 200, 300.

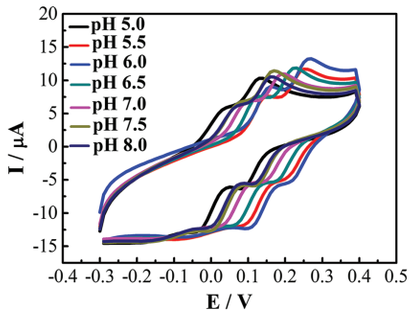


Figure 3. CVs of PtNPs/Gr-CDP-MWCNTs/GCE at scan rate 50 mV/s in different pH solutions. pH: 5.0, 5.5, 6.0, 6.5, 7.0, 7.5, 8.0.

is used for individual and simultaneous determination of HQ and CC in the following experiments.

Figures 2(C) and (D) shows CVs of PtNPs/Gr-CDP-MWCNTs/GCE containing 50 μM HQ and CC at different scan rates. The anodic peak current densities for HQ and CC are proportional to the square roots of scan rates from 20 to 300 mV/s, indicating that electro-oxidation of these two biomolecules at PtNPs/Gr-CDP-MWCNTs/GCE is a diffusion-controlled behavior.

3.3. pH Effect

The effect of solution pH on the electrochemical response of HQ and CC is investigated at different pH of PBS solution, over the range from pH 5.0 to pH 8.0 by CVs in Figure 3. The optimal response is at pH 6.0. Therefore, this pH 6.0 is chosen for the following analytical experiments.

3.4. PtNPs/Gr-CDP-MWCNTs/GCE for Electrochemical Determination of HQ and CC

The main aim of the present investigation is to determine HQ and CC simultaneously. In order to improve the sensitivity and the linear range, different pulse voltammetry (DPV) are employed to record the anodic peak currents. Under the optimal conditions, two clear and well-separated peaks are observed, and the peak currents increased linearly with the increasing concentration of HQ and CC (Fig. 4(A)) by adding HQ and CC mixture, Figure 4(B) shows HQ and CC could be determined in the ranges of 0.05–565 μM and 0.01–515 μM. The detection limits (S/N = 3) are 0.015 μM and 0.003 μM, respectively. The linear regression equations for HQ and CC are expressed as $I_{pa} = 12.25 + 0.18c$ (I_{pa}:μA, c:μM, $R^2 = 0.9952$), and $I_{pa} = 8.59 + 0.19c$ (I_{pa}:μA, c:μM, $R^2 = 0.9960$) respectively.

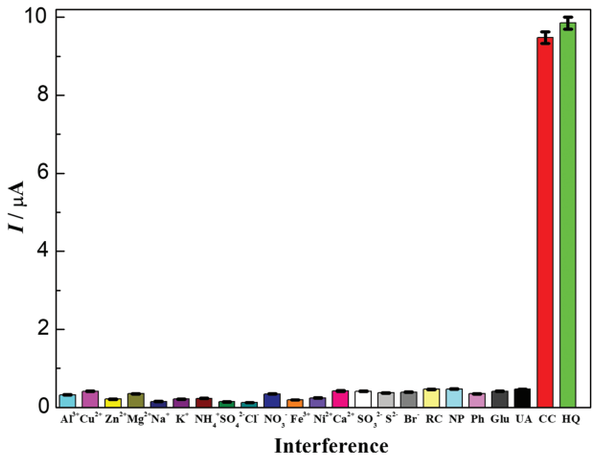


Figure 5. Selectivity of the proposed biosensor against different non-targets: 1000-fold Al^{3+}, Cu^{2+}, Zn^{2+}, Mg^{2+}, Na^{+}, K^{+}, NH_4^{+}, SO_4^{2-}, Cl^{-}, NO_3^{-}, 100-fold Fe^{3+}, Ni^{2+},Ca^{2+}, SO_3^{2-}, S^{2-}, Br^{-}, 10-fold resorcinol (RC), nitrophenol (NP), phenol (Ph), glucose (Glu) and uric acid (UA). All working buffer is 0.1 M PBS (pH 6.0) at scan rate of 50 mV/s. The concentration of hydroquinone (HQ) and catechol (CC) keeps the same at 50 μM.

All these experimental results show that the present work has provided a sensitive, and more importantly, simultaneous determination of two dihydroxybenzene isomers without interference for each other, which is advantageous over previous reports.[32–36] This can be attributed to the following aspects. First of all, MWCNTs can effectively inhibit the stacking of individual Gr and enhance the utilization of Gr based composites, which improves the electrochemical signal of the modified electrode. Secondly, the remarkable synergistic effects of the three components

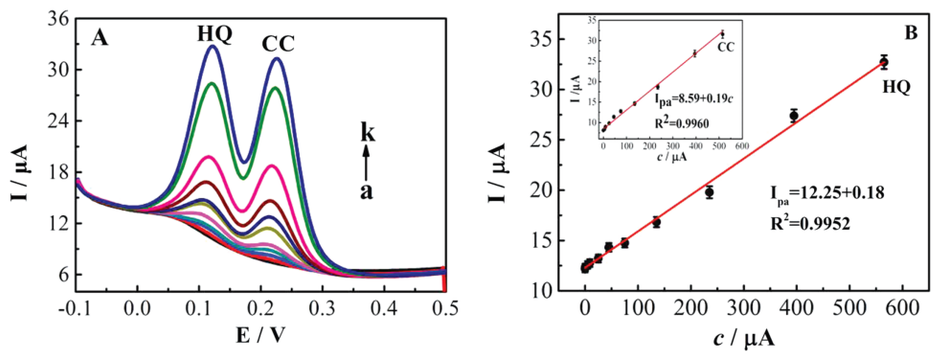


Figure 4. DPV of PtNPs/Gr-CDP-MWCNTs/GCE with CC and HQ mixtures (A) and the linear dependence of Ipc of CC and HQ with concentration (B).

Table I. Simultaneous determination results for HQ and CC in water (我把表格给你重新做了 必须是三线表, 不能有其他格式 缩进那些).

	Added (μM)		Found (μM)		RSD (%)		Mean recovery (%)	
Samples	HQ	CC	HQ	CC	HQ	CC	HQ	CC
1	20.0	20.0	19.8	20.3.	2.9	3.6	99.0	101.5
2	50.0	50.0	51.6.	50.7	2.1	2.8	103.2	101.4
3	100.0	100.0	104.5	96.4	2.9	3.6	104.5	96.4

of PtNPs, MWCNTs and Grs increase electrode conductivity, which sharply improves the sensitivity of PtNPs/Gr-CDP-MWCNTs/GCE for HQ and CC detections.

3.5. The Stability, Repeatability and Interference of the Determination

The PtNPs/Gr-CDP-MWCNTs/GCE shows no obvious current response decay after being stored in 0.1 M PBS at 4 °C for 30 days, indicating the good stability of the PtNPs/Gr-CDP-MWCNTs/GCE. The storage stability of the proposed biosensor is studied. The biosensor also shows good reproducibility for the determination of HQ and CC concentration. The relative standard deviations (RSD) are 3.25% and 4.36% for five successive assays of 50 μM HQ and CC, respectively. It is due to the fact that it is a none-enzyme electrochemical sensor.

The possible interferences of some common inorganic ions and organic compounds are also studied. It is found that 1000-fold Al^{3+}, Cu^{2+}, Zn^{2+}, Mg^{2+}, Na^{+}, K^{+}, NH_4^{+}, SO_4^{2-}, Cl^{-}, NO_3^{-}, 100-fold Fe^{3+}, Ni^{2+}, Ca^{2+}, SO_3^{2-}, S^{2-}, Br^{-}, 10-fold resorcinol (RC), nitrophenol (NP), phenol, glucose and uric acid (UA) have on interference in the determination of 50 μM HQ and CC (signals change below 5%) (Fig. 5). Thus, the proposed biosensor shows a high selectivity and good anti-interference ability.

3.6. Sample Analysis

To investigate the practical applicability of the proposed method for the simultaneous determinations of HQ and CC, local river water samples are tested. HQ and CC are not found in the real samples using the present method. The recovery experiments are performed by measuring the DPV responses. The amounts of HQ and CC in water sample are detected using the standard addition method, and the results are listed in Table I. The recoveries range from 99.0 to 104.5% and from 96.4 to 101.5% for HQ and CC, respectively. It suggests that this new sensor is applicability and reliability.

4. CONCLUSIONS

In summary, a novel PtNPs/Gr-CDP-MWCNTs/GCE electrochemical biosensor is developed to simultaneously determine HQ and CC in this work. The modified electrode not only shows high selectivity towards the oxidation of HQ and CC, but also resolves their overlapped oxidation peaks into two well-defined peaks, respectively. The improved the electrochemical signal of the modified electrode is ascribed to the fact that MWCNTs can effectively inhibit the stacking of individual Gr and enhance the utilization of Gr based composites. Meanwhile, the remarkable synergistic effects of Gr-CDP-MWCNTs and PtNPs increase electrode conductivity. The simple fabrication procedure, well stability, low detection limit, excellent sensitivity and high selectivity suggest that PtNPs/Gr-CDP-MWCNTs/GCE electrochemical biosensor is an attractive candidate for practical applications.

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