Electrochimica Acta 56 (2011) 2748–2753

Contents lists available at ScienceDirect

Electrochimica Acta

journal homepage: www.elsevier.com/locate/electacta

Electrochemical behavior of catechol, resorcinol and hydroquinone at graphene–chitosan composite film modified glassy carbon electrode and their simultaneous determination in water samples

Huanshun Yin[a,b], Qingming Zhang[b,c], Yunlei Zhou[d], Qiang Ma[a], Tao liu[a], Lusheng Zhu[b,*], Shiyun Ai[a,*]

[a] *College of Chemistry and Material Science, Shandong Agricultural University, Taian, 271018 Shandong, China*
[b] *College of Resources and Environment, Shandong Agricultural University, Taian 271018, Shandong, China*
[c] *College of Chemistry and Pharmaceutical Sciences, Qingdao Agriculture University, Qingdao 266109, China*
[d] *College of Life Science, Beijing Normal University, 100875 Beijing, China*

ARTICLE INFO

Article history:
Received 5 October 2010
Received in revised form 8 December 2010
Accepted 18 December 2010
Available online 28 December 2010

Keywords:
Graphene
Catechol
Resorcinol
Hydroquinone
Simultaneous determination

ABSTRACT

Graphene–chitosan composite film modified glassy carbon electrode was prepared and characterized. The fabricated electrode showed excellent electrochemical catalytic activities towards the oxidation of catechol (CT), resorcinol (RS) and hydroquinone (HQ). The oxidation overpotentials of CT, RS and HQ decreased significantly and the corresponding oxidation currents increased remarkably compared with those obtained at the bare GCE and chitosan modified GCE. Some kinetic parameters, such as the electron transfer number (n), proton transfer number (m), charge transfer coefficient (α) and the apparent heterogeneous electron transfer rate constant (k_s), were calculated. Differential pulse voltammetry was used for the simultaneous determination of CT, RS and HQ in their ternary mixture. The peak-to-peak potential separations between CT and RS, RS and HQ, and HQ and CT were 0.388, 0.484 and 0.096 V, respectively. The calibration curves for CT, RS and HQ were obtained in the range of 1×10^{-6} to 4×10^{-4}, 1×10^{-6} to 5.5×10^{-4} and 1×10^{-6} to 3×10^{-4} mol L^{-1}, respectively. The detection limits were 7.5×10^{-7} mol L^{-1} ($S/N = 3$).

1. Introduction

Catechol (CT), resorcinol (RS) and hydroquinone (HQ) are three dihydroxybenzene isomers, which are widely used in cosmetics, tanning, pesticides, flavoring agents, medicines, antioxidant, dye and photography chemicals [1]. Due to their high toxicity and low degradability in the ecological environment, they are considered as environmental pollutants by the US Environmental Protection Agency (EPA) and the European Union (EU) [2]. During the manufacturing and application process of these compounds, some of them are inadvertently released into the environment to contaminate rivers and ground waters. Thus, it is easy for them to enter into the environments, and exists in industrial effluents and sanitary wastewater. Moreover, these isomers are often coexisting in environmental samples [3,4]. The allowable emission of phenolic compounds in the national standard of China (GB 8978-1996) is 0.5 mg/L (for dihydroxybenzene, 4.54×10^{-3} mol L^{-1}). Therefore, it is necessary to develop simple and rapid analytical method for dihydroxybenzene isomers determination.

Up to now, many analytical methods have been established to determine dihydroxybenzene isomers, such as high performance liquid chromatography [5], fluorescence [6], chemiluminescence [7], spectrophotometry [8], gas chromatography/mass spectrometry [9], capillary electrochromatography [10] and electrochemical methods [4,11–24]. Among them, electrochemical methods have attracted more and more attentions due to the advantages of fast response, cheap instrument, low cost, simple operation, time-saving, high sensitivity, and excellent selectivity. However, for electrochemical methods, more attentions are focused on the simultaneous determination of CT and HQ due to their redox peaks are overlapped at ordinary electrode [11–21]. In other words, the simultaneous determination of CT, RS and HQ by electrochemical methods is few reported. For instance, Yu et al. reported that CT and HQ can be high sensitive simultaneously determined at mesoporous carbon CMK-3 electrode with the peak-to-peak separation of the oxidation potential (ΔE_{pa}) of 125 mV [19]. Recently, though the simultaneous determinations of CT, RS and HQ have been performed at single-wall carbon nanotube (SWCNT) [23] and MWCNT [4] modified glassy carbon electrode (GCE), and MWCNT modified multielectrode array [24], it is still interesting to investigate novel

---

* Corresponding authors at: College of Chemistry and Material Science, Shandong Agricultural University, Daizong Street 61, Taian, 271018 Shandong, China. Tel.: +86 538 8247660; fax: +86 538 8242251.
E-mail addresses: lushzhu@sdau.edu.cn (L. Zhu), ashy@sdau.edu.cn (S. Ai).

0013-4686/$ – see front matter © 2010 Elsevier Ltd. All rights reserved.
doi:10.1016/j.electacta.2010.12.060

electrode material for the simultaneous determination of CT, RS and HQ.

In recent years, graphene nanosheets have attracted more and more attentions in the preparation of sensors and biosensors due to their large surface area, extraordinary electronic transport property, high electrocatalytic activity, good mechanical strength, high thermal conductivity and high mobility of charge carriers. However, the aggregation of graphene nanosheets limites their application [25]. In order to conquer this disadvantage, graphene nanosheets and chitosan are frequently used together because the positively charged chitosan can interact with the negatively charged graphene nanosheet to prevent their aggregation [26]. For instance, Li' group [27] reported the electrochemical determination of dopamine in the presence of ascorbic acid based on graphene nanosheets and chitosan modified GCE. Niu et al. proved that low-potential NADH detection can be achieved at an ionic liquid-functionalized graphene nanosheets and chitosan modified GCE [28]. It has also been reported that graphene nanosheets and chitosan can also be applied to investigate the direct electron transfer of glucose oxidase [29,30], cytochrome c [31] and horseradish peroxidase [32].

In this paper, a simple and fast method for the simultaneous determination of CT, RS and HQ at graphene–chitosan composite film modified GCE was presented using differential pulse voltammetry. The electrochemical behaviors of these isomers were investigated by cyclic voltammetry. The performance of the fabricated electrode, such as linear range and detection of limit, was evaluated and discussed.

2. Experimental

2.1. Reagents and apparatus

Catechol, resorcinol and hydroquinone were purchased from Aladdin (Shanghai, China). Chitosan was purchased from Sigma (USA). Graphene nanosheets were provided by Institute of Metal Research, Chinese Academy of Sciences [33]. 0.1 mol L^{-1} of three kinds of dihydroxybenzene stock solutions was prepared with double distilled deionized water and kept in darkness at 4 °C. Working solutions were freshly prepared before use by diluting the stock solution. Phosphate buffer solution (PBS, 0.1 mol L^{-1}) was prepared by mixing the stock solution of 0.1 mol L^{-1} NaH_2PO_4 and 0.1 mol L^{-1} Na_2HPO_4, and the pH was adjusted by NaOH or HCl. A 0.5% (mass ratio) chitosan solution was prepared by dissolving chitosan in 1.0% acetic acid solution with magnetic stirring for 1 h, and then the pH of the solution was adjusted to pH 5.0 with a concentrated NaOH solution. Other chemicals were analytical reagent grade and all solutions were prepared with double distilled deionized water from quartz. All the reagents were used without further purification.

Electrochemical experiments were performed with a CHI832A electrochemical workstation (Shanghai Chenhua Co., China) with a conventional three-electrode cell except electrochemical impedance spectroscopy, which was carried out at a CHI660C electrochemical workstation (Shanghai Chenhua Co., China). A bare or modified glassy carbon electrode (CHI104, d = 3 mm) was used as working electrode. A saturated calomel electrode (SCE) and a platinum wire were used as reference and auxiliary electrodes, respectively. All the measurements were carried out at room temperature (25 ± 0.5 °C).

2.2. Preparation of graphene–chitosan/GCE

Before modification, the bare GCE was polished to a mirror-like with 0.03 μm alumina slurry, then washed successively with anhydrous alcohol and double distilled deionized water in an ultrasonic bath and dried in N_2 blowing. 3.0 mg graphene was added into 1 mL 0.5% chitosan solution, followed by ultrasonication for 2 h to form a homogenous mixture of graphene–chitosan. Then, 5 μL of graphene–chitosan solution was deposited on the fresh prepared GCE surface. After the solvent evaporated, the electrode surface was thoroughly rinsed with double distilled deionized water and dried in the air. The obtained electrode was noted as graphene–chitosan/GCE. For comparison, chitosan/GCE was fabricated with the similar procedure.

2.3. Experimental procedure

A certain volume of diphenol stocking solution (or working solution) and 10 mL 0.1 mol L^{-1} PBS were added into an electrochemical cell, and then the three-electrode system was installed on it. The differential pulse voltammogram was recorded from −0.20 to 0.70 V with the parameters of increment potential, 0.004 V; pulse amplitude, 0.05 V; pulse width, 0.05 s; sample width, 0.0167 s; pulse period, 0.2 s; quiet time, 2 s. The cyclic voltammetry was scanned with scan arte of 100 mV s^{-1}, sample interval of 0.0001 V and quiet time of 2 s. The electrochemical impedance spectroscopy was performed in 5×10^{-3} mol L^{-1} $Fe(CN)_6{}^{-3/-4}$ (1:1) solution containing 0.1 mol L^{-1} KCl. The parameters were as follows: frequency range from 0.1 to 10^5 Hz; initative potential, 0.19 V; amplitude, 0.005 V and quiet time of 2 s.

3. Results and discussion

3.1. Characterization of electrochemical behavior of graphene–chitosan/GCE

The fabricated electrodes were characterized by cyclic voltammetry and electrochemical impedance spectroscopy in 5×10^{-3} mol L^{-1} $Fe(CN)_6{}^{-3/-4}$ (1:1) solution containing 0.1 mol L^{-1} KCl (Fig. S1 in Supplementary material). The results demonstrated that graphene–chitosan film was successfully immobilized on the GCE surface, which can effectively improve the conductivity of the electrode and increase the electron transfer rate.

3.2. Effect of pH on the electrochemical behavior of CT, RS and HQ

The effect of pH value on the electrochemical behavior of 2×10^{-4} mol L^{-1} CT, 2×10^{-4} mol L^{-1} RS and 2×10^{-4} mol L^{-1} HQ in the mixed solution at graphene–chitosan/GCE was carefully investigated by cyclic voltammetry in a wider pH range (pH 4.0–10.0). From Fig. 1A, it can be seen that the oxidation peak current of CT, RS and HQ increase with increasing pH value until it reaches 7.0, and then the oxidation peak currents decrease when the pH increases further. It has been reported that the pKa value of chitosan is between 6.39 and 6.51 [34]. The pKa values of CT, RS and HQ are 9.4, 9.4 [35] and 9.85 [36], respectively. When pH is between 4.0 and 6.0, the $-NH_2$ in chitosan will be protonated and the hydroxyl in dihydroxybenzenes will not ionized, which will decrease the adsorption capacity of the three dihydroxybenzene isomers. When pH increasing from 7.0 to 10.0, the increased hydroxyl ion in solution might also decrease the adsorption capacity of the three dihydroxybenzene isomers. Considering the determination sensitivity, pH 7.0 was chosen as the optimal experimental condition.

The relationship between the peak potential and pH was also investigated and the results were shown in Fig. 1B. For CT, two linear relationships were obtained with the regression equations of E_{pa} (V) = −0.055pH + 0.55 (R = 0.9957) for the oxidation process and E_{pc} (V) = −0.051pH + 0.44 (R = 0.9969) for the reduction process. For RS, a linear shift of E_{pa} towards negative potential with an increasing pH from 4 to 9 was observed. The linear regression