Simultaneous voltammetric determination of dihydroxybenzene isomers at single-walled carbon nanohorn modified glassy carbon electrode

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ABSTRACT

The voltammetric behaviors of dihydroxybenzene isomers were studied at the single-walled carbon nanohorn modified glassy carbon (SWCNH-modified GC) electrode. Compared with the bare electrode, SWCNH-modified GC electrode has stronger electrocatalytic activity for the oxidation of dihydroxybenzenes with the increase in peak current and the decrease in peak separation (ΔE_p) between the anodic and cathodic peaks. Furthermore, the three isomers can be determined simultaneously and sensitively by using linear sweep voltammetry at the SWCNH-modified GC electrode. For hydroquinone, catechol, and resorcinol, the oxidation peak currents are linear with the concentrations in the range of 0.5-100 μM , 0.5-100 μM , and 1.0-100 μM , respectively. Their detection limits at a signal-to-noise ratio of 3 are 0.1 μM , 0.2 μM , and 0.5 μM , respectively. These results make SWCNH-modified GC electrode a promising candidate for the simultaneous determination of isomers.

Keywords: Single-walled carbon nanohorns; Dihydroxybenzene isomers; Electrochemistry; Simultaneous determination; Accumulation

1. Introduction

Catechol, resorcinol, and hydroquinone (*o*-, *m*- and *p*-dihydroxybenzene, respectively) are the isomers of dihydroxybenzene. They are widely used as important industry raw and synthetic intermediates in many fields such as tanning, dye, chemical, pesticide and some other fields closely relate with our life. They have been widely recognized as important environmental pollutants due to their vast scale distribution and difficulty in degradation [1]. Due to their similar structures and characteristics, they usually coexist and interfere with each other during their identification. Therefore, it is very necessary to develop fast and convenient methods for their simultaneous determination. So far, various techniques have been employed for the simultaneous determination of dihydroxybenzenes including chromatography [2,3], spectrophotometry [4], and synchronous fluorescence [5].

Electrochemical methods are one of the favored techniques in environmental and biological analysis because of their low cost, high sensitivity, rapid response and simple operation [6]. Nevertheless, the three dihydroxybenzene isomers have similar chemical structures, their peak potentials are too close to be identified at conventional electrodes. To overcome this problem, some novel material-based electrochemical electrodes for detection of the three dihydroxybenzene isomers have been reported [7-17]. Among various electrode materials, carbon nanotubes (CNTs) have gained great interest in analytical chemistry because of their excellent properties [18]. Especially, they have been widely used in electrochemistry due to their good

electrocatalytic properties. However, a high expectation for CNTs had to be lowered when some inspiring papers reported that the impurities within CNTs influenced their redox properties and even dominated their electrochemical responses [19,20]. So, it is necessary to develop new carbon electrode nanomaterials with high purity to avoid disputes.

Single-walled carbon nanohorns (SWCNHs), a new carbon allotrope within the family of elongated carbon nanotubes, were synthesized by laser ablation of pure graphite without using metal catalyst with high production rate, high yield, and high purity (95%) [21]. A single SWCNH is horn-shaped sheath composed of single-wall graphene sheets. The internal cone angle of the dahlia-like SWCNH is approximately 20°. Its diameter ranges from 2 to 5 nm and its length is about 40 to 50 nm. Typically, about 2000 of them assemble to form a spherical aggregate (diameters: 80-100 nm). Due to their unique properties, SWCNHs have been widely used for various applications, such as adsorption, drug delivery, fuel cells, super capacitors, biosensors and so on [22-25]. SWCNHs were essentially metal-free and can be used directly for electrochemical study. Moreover, SWCNHs may have many defect sites which facilitate electrochemical applications.

In this study, the electrochemical properties of dihydroxybenzene isomers at SWCNH-modified GC electrode are investigated. The peak potentials of the *o*-, *m*- and *p*-dihydroxybenzene isomers are well-separated, allowing the simultaneous determination of dihydroxybenzene isomers by using linear sweep voltammetry (LSV).

2. Experimental

2.1. Reagents

Professor S. Iijima generously offered dahlia-like SWCNHs that were prepared at room temperature by CO₂ laser ablation. Hydroquinone and resorcinol were purchased from Guangdong Xilong Chemical Co. Ltd (China). Catechol was purchased from Beijing Chemical Co. (China). All the chemicals used were of analytical grade purity and used as received. Aqueous solutions were prepared with doubly distilled water. 10 mM hydroquinone, catechol or resorcinol was prepared freshly and then the stock solution was diluted to various concentrations with doubly distilled water. Phosphate buffer solution (PBS, 0.1 M) was used as supporting electrolyte solution.

2.2. Apparatus

HRTEM measurements were performed on a FEI TECNAI G2 F20 microscope operated at an accelerating voltage of 200 KV. Cyclic voltammetry (CV) and linear sweep voltammetry (LSV) were performed on a CHI 830 electrochemical workstation (Shanghai, China). pH of the solution was controlled with pH meter (LEICI PHS-3C, Shanghai).

2.3. Preparation of SWCNH-modified GC electrode

Prior to the modification, bare GC electrode of 3 mm was polished with 1.0, 0.3, and 0.05 μm alumina slurry, respectively, and sonicated in double-distilled water. The cleaned electrode was dried with high-purity nitrogen steam. The procedure for the preparation of the modified electrode was as follows: 2.5 mg of SWCNHs were dispersed in 1 mL dimethylformamide with ultrasonic agitation to give a 2.5 mg/mL

black suspension, and then 2.5 μL of the SWCNH solution was dropped onto the GC electrode surface, dried, and thoroughly rinsed with water to make SWCNH-modified GC electrode.

2.4. Analytical procedure

A conventional three-electrode system was used for all electrochemical experiments, which consisted of a platinum wire as auxiliary electrode, an Ag/AgCl/saturated KCl as reference electrode, and a bare or modified GC electrode as working electrode. All experiments were conducted at room temperature. The pH of PBS was adjusted with 0.1 M NaOH or 0.1 M H_3PO_4 . 5.0 mL of PBS (different pH) was added into an electrochemical cell, and then dihydroxybenzene isomers standard solutions were added into the cell. The cyclic voltammograms were recorded in the range $-0.05 \sim 0.65$ V. The linear sweep voltammograms were recorded in the potential -0.2 to 0.8 V under open-circuit accumulation for 60 s with stirring the solution.

3. Results and discussion

3.1. Electrochemical behaviors of dihydroxybenzene isomers

Fig. 1 shows the voltammetric responses of the bare GC electrode and SWCNH-modified GC electrode towards the dihydroxybenzene isomers. At the bare GC electrode, the anodic and cathodic peaks of hydroquinone are at 0.304 V and 0.044 V, respectively (curve a, Fig. 1A). The potential separation (ΔE_p) of 260 mV indicates that hydroquinone exhibits a quasi-reversible electrochemical behavior. Catechol also shows a quasi-reversible electrochemical behavior with the anodic and cathodic peak potential at 0.426 V and 0.128 V, respectively (curve a, Fig. 1B). For resorcinol, a small anodic peak is observed at 0.744 V (curve a, Fig. 1C).

In contrast, a well-defined reversible redox pair for hydroquinone is obtained at the

SWCNH-modified GC electrode (curve b, Fig. 1A). The oxidation peak potential negatively shifts to 0.169 V and the reduction peak potential positively shifts to 0.117 V with ΔE_p of 52 mV. The reversibility of hydroquinone is significantly improved and the current signal is increased. The peak current at the SWCNH-modified GC electrode is 5.5 times higher than that at the bare GC electrode. Similarly, the oxidation peak potential of catechol negatively moves to 0.274 V and the reduction peak potential positively shifts to 0.222 V with a ΔE_p value of 52 mV at the SWCNH-modified GC electrode (curve b, Fig. 1B). Furthermore, the oxidation current of catechol at the SWCNH-modified GC electrode is about 6.78 times of that at the bare GC electrode and i_{pa}/i_{pc} is close to 1. The small ΔE_p indicates that the redox overpotential of catechol is significantly lowered at the SWCNH-modified GC electrode and the electrochemical redox activity of catechol is also improved. For resorcinol, the anodic peak potential shifts negatively to 0.557 V at the SWCNH-modified GC electrode (curve b, Fig.1C). Moreover, the oxidation peak current at the SWCNH-modified GC electrode is twice of that at the bare GC electrode. The electrocatalytic oxidation of resorcinol by SWCNHs is evidenced by the increase of the anodic peak current and the shift of the anodic peak potential compared to the bare GC electrode. The oxidation of resorcinol is complex and may generate mixed products, such as carbon dioxide and polymers [26]. The probable electrode reactions for hydroquinone and catechol are as follows [27]:

The results mentioned above mean that SWCNHs enhance the electron transfer during the electrochemical reactions of the three isomers. Fig. 2 shows high resolution transmission electron microscopy (HRTEM) image of the SWCNHs. The individual SWCNH structural unit is shown clearly. SWCNHs form dahlia-like assemblies with a diameter of about 100 nm. The unique nanohorn structure of SWCNHs may have plenty of edge plane-like defects. And the good electrocatalytic ability of SWCNHs may be ascribed to edge plane-like defects on the surface of SWCNHs, which may provide many favorable sites for electron transfer to molecules [25]. In addition, the effective surface area of the SWCNH-modified GC electrode was determined using chronocoulometry (Fig. 3) and the Anson equation [28], which at 25 °C is

$$Q=2nFCA\pi^{-1/2}D^{1/2}t^{1/2} + Q_{\text{ads}} + Q_{\text{dl}} \quad (1)$$

Where Q is the charge (μC), n is the number of electrons transferred, A is the electrode area (cm^2), D is the diffusion coefficient of the electroactive species ($\text{cm}^2 \text{s}^{-1}$), C is the bulk concentration of the electroactive species (mol cm^{-3}), t is the electrolysis time (s), F is the Faraday constant, Q_{dl} is double layer charge, Q_{ads} is Faradaic charge. 0.1 mM potassium ferricyanide in 1 M KCl aqueous solution of was used for this measurement. Potassium ferricyanide has a diffusion coefficient of $7.6 \times 10^{-6} \text{ cm}^2 \text{s}^{-1}$ at 25 °C. Here, we fitted a straight line ($t < 0.2\text{s}$) according to data and the linear regression equation is expressed as: $Q=12.75t^{1/2}+1.52$. The electrode area was calculated to be 0.424 cm^2 . The large surface area of the SWCNH-modified GC electrode may facilitate the accumulation of the dihydroxybenzene molecules. The above results suggested the SWCNHs possessed an excellent electrocatalytic activity to the dihydroxybenzene molecules, and thus is a good material for fabricating novel and sensitive electrochemical biosensing platform for detection the isomers.

3.2. Optimization of the experimental conditions

3.2.1. Effects of scan rate

The electrochemical behaviors of hydroquinone, catechol, and resorcinol were studied in 0.1 M pH 6.0 PBS at various scan rates. The oxidation peak currents of hydroquinone, catechol, and resorcinol at the SWCNH-modified GC electrode increase linearly with the scan rates in the range of 5-100 mV s^{-1} (Fig. 4). This suggested that the electrochemical oxidation of the each dihydroxybenzene is an adsorption-controlled process. Meanwhile, their oxidation peak potentials shift positively with the increasing scan rates. So, we chose a medium scan rate of 50 mV s^{-1} in the following experiments.

3.2.1. Effects of solution pH

Since proton takes part in the electrochemical reaction, the acidity of the electrolyte is considered to significantly affect the electrochemical behaviors of the dihydroxybenzenes [10, 11, 15]. Therefore, the CVs of hydroquinone, catechol, and resorcinol at different pH solutions in the range of 2.0-9.0 were investigated. The relationship between the pH of solution and the oxidation peak potentials of hydroquinone, catechol, and resorcinol was shown in Fig. 5. The oxidation peak potentials of the three isomers shift to lower values with the increase in pH values and these peak potentials decreases linearly with the rising pH values. The regression equations and correlation coefficients for these lines are $E_p = 0.514 - 0.057 \text{ pH}$ ($R = 0.998$) for hydroquinone, $E_p = 0.628 - 0.059 \text{ pH}$ ($R = 0.997$) for catechol, and $E_p = 1.009 - 0.063 \text{ pH}$ ($R = 0.999$) for resorcinol, respectively. The experimental results show that protons participate in the redox processes of dihydroxybenzene isomers at

the SWCNH-GC electrode. In addition, the three lines are almost parallel, which implies that the difference of the potential was constant. Therefore, the simultaneous determination of dihydroxybenzene isomers is possible in a broad range (pH 4.0-8.0) at the SWCNH-modified GC electrode. However, at low pH, the oxidation potentials were high and interference was serious. In view of the stability of the three isomers, a weak acidic solution was better for this experiment. In this study, pH 6.0 was chosen as the optimum pH.

3.2.2. Effect of accumulation time

Fig. 6 shows the effects of accumulation time on the simultaneous determination of 5 μ M hydroquinone, 5 μ M catechol, and 5 μ M resorcinol in 0.1 M pH 6.0 PBS. The LSV was recorded in solution after open-circuit accumulation. The oxidation peak currents of dihydroxybenzene isomers increased with increasing accumulation time and the maximum peak currents are obtained at 60 s for both catechol and resorcinol. For hydroquinone, the peak current at 60 s was close to the maximum peak current. Therefore, an accumulation time of 60 s was used in the following experiments. The peak currents of hydroquinone, catechol, and resorcinol at 60 s were 5.23, 2.46, and 2.79 times of that without accumulation, respectively.

3.2.3. Determination of hydroquinone, catechol, and resorcinol

LSVs for hydroquinone, catechol, and resorcinol in their mixture at the bare GC electrode and SWCNH-modified GC electrode are shown in Fig. 7. At the bare GC electrode (curve a), the oxidation peaks of hydroquinone and catechol completely overlap and show a broad overlapped peak at 0.387 V. The oxidation peak of resorcinol appears at 0.788 V. In contrast, the LSV peaks are well-resolved at the

SWCNH-modified GC electrode with the peak potentials at about 0.166 V, 0.269 V, and 0.621 V for hydroquinone, catechol, and resorcinol, respectively. The separation of the oxidation peak potentials for hydroquinone-catechol, catechol-resorcinol, and hydroquinone-resorcinol is 103 mV, 352 mV and 455 mV, respectively. The large separation of the peak potentials allows selective determination of hydroquinone, catechol, and resorcinol in the presence of the other two species.

To test the feasibility of SWCNH-modified GC electrode in the simultaneous and sensitive determination of dihydroxybenzene isomers, LSV was performed for different concentrations of one isomer at the SWCNH-modified GC electrode in the presence of a constant concentration of the other two isomers. As shown in Fig. 8, the peak current that corresponds to the oxidation of one isomer increases with the increase of its concentration. For other two isomers with constant concentrations, the oxidation peak currents change slightly, which does not influence the determination of the two isomers. It means that the oxidation of the three isomers at the presented electrode may take place independently. As shown in Fig. 9A, the peak current of hydroquinone increases linearly with the increase in hydroquinone concentrations from 0.5 μ M to 10 μ M (I (μ A) = $0.58 + 0.31 C$ (μ M), $R = 0.996$) and from 10 μ M to 100 μ M (I (μ A) = $2.61 + 0.15 C$ (μ M), $R = 0.995$). Similarly, the oxidation peak currents of catechol and resorcinol are also proportional to their concentrations in the range of 0.5-100 μ M for catechol (I (μ A) = $0.52 + 0.12 C$ (μ M) (Fig. 9B), $R = 0.995$) and 1-100 μ M for resorcinol (I (μ A) = $0.38 + 0.15 C$ (μ M), $R = 0.996$) (Fig. 9C). The detection limits ($S/N=3$) at a signal-to-noise ratio of 3 for hydroquinone, catechol, and resorcinol are 0.1, 0.2, and 0.5 μ M, respectively. Compared with other carbon materials-based electrodes, such as multi-walled carbon nanotube (MWCNT) [12] and single-walled carbon nanotube (SWCNT) [16], the electrochemical platform based

SWCNHs exhibited comparable detection limit. This demonstrated that SWCNHs could be an optional choice for dihydroxybenzene isomers detection.

The relative standard deviations (R.S.D.) of the same electrode are 4.41%, 4.07%, and 2.35% for 6 successive measurements of hydroquinone, catechol, and resorcinol in ternary mixture solution of 10 μ M hydroquinone, 10 μ M catechol, and 10 μ M resorcinol, respectively. The reproducibility of electrode to electrode was also assessed in above mixture solution. The R.S.D (n=6) of the peak currents were less than 5.0% for these three species. It is noticeable that the oxidation potential of resorcinol slightly shifts positively with the continual use of the same electrode. Maybe this is attributed to the adsorption of its electrochemical oxidation products onto the electrode surface that influences the electrooxidation of resorcinol. However, the peak current for resorcinol can keep steady with deviations below 5.0%. And the peak separation between catechol and resorcinol become a little larger with the continual use of the same electrode. So this does not affect the simultaneous determination of the three isomers.

3.3. Interference of coexisting substances

The possible interferences of some species in the wastewater were also tested with a mixed dihydroxybenzenes solution (10 μ M hydroquinone, catechol, and resorcinol for each). A great number of cations and anions, such as K^+ , Na^+ , Ca^{2+} , Zn^{2+} , Cu^{2+} , NO_3^- , Cl^- , SO_4^{2-} , and Mg^{2+} (each concentration is 10 mM), have no influence on the signals of dihydroxybenzenes with deviations below 5%. 5-fold of phenol almost has no effect on the determination of dihydroxybenzene isomers.

3.4. Determination of dihydroxybenzene isomers in water samples

This method was applied to the determination of dihydroxybenzene isomers in tap water sample. The results demonstrate that no dihydroxybenzene was detected in the tap water with the SWCNH-modified GC electrode, which means that dihydroxybenzenes contents were below the detection limits. Thus, the proposed method was applied to detect tap water samples spiked with dihydroxybenzenes at a certain concentration. The determination of dihydroxybenzenes concentration was performed by the standard addition method. The analytical results were shown in Table 1. The recovery was 92-110%.

4. Conclusions

The redox behavior of dihydroxybenzene isomers was demonstrated at the SWCNH-modified GC electrode. The SWCNH-modified GC electrode showed an excellent electrocatalytic activity and reversibility towards the oxidation of dihydroxybenzene isomers. Besides, in a mixed solution, the isomer oxidation peaks become well resolved at the modified electrode and are separated by more than 100 mV. This enables a selective and simultaneous determination of dihydroxybenzene isomers by using LSV technique at the SWCNH-modified GC electrode. The electrocatalytic enhancement and selectivity for dihydroxybenzene isomers oxidation demonstrated the potential application of SWCNH-modified GC electrode for further investigation and simultaneous determination of other isomer systems.

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Table caption and Figure captions

Table 1 Determination of dihydroxybenzene isomers in water samples.

Figure 1 CVs of 100 μM hydroquinone (A), 100 μM catechol (B), and 100 μM resorcinol (C) at the bare GC electrode (a) and SWCNH-modified GC (b) electrode in 0.1 M PBS (pH 6.0). Scan rate: 100 mV s^{-1} .

Figure 2 HRTEM image of SWCNHs.

Figure 3 The chronocoulometry curve of 0.1 mM $\text{K}_3\text{Fe}(\text{CN})_6$ in 1 M KCl aqueous solution at the bare GC electrode (a) and the SWCNH-modified GC electrode (b).

Figure 4 Effects of scan rate on the oxidation peak current of 100 μM hydroquinone (a), 100 μM catechol (b), and 100 μM resorcinol (c) in pH 6.0 PBS on the SWCNH-modified GC electrode. .

Figure 5 Influences of pH on the oxidation peak potentials. Scan rate: 50 mV s^{-1} ; 100 μM hydroquinone (a), 100 μM catechol (b), and 100 μM resorcinol (c). pH values are as follows: 2.0, 3.0, 4.0, 5.0, 6.0, 7.0, 8.0, and 9.0.

Figure 6 Effects of accumulation time on the LSV peak currents of 5 μM hydroquinone (a), 5 μM catechol (b), and 5 μM resorcinol (c) in pH 6.0 PBS on the SWCNH-modified GC electrode. The LSV was recorded in solution after open-circuit accumulation. Scan rate: 50 mV s^{-1} .

Figure 7 LSVs at the bare GC electrode (a) and SWCNH-modified GC electrode (b) in 0.1 M pH 6.0 PBS containing 100 μM hydroquinone, catechol, and resorcinol. Scan rate: 50 mV s^{-1} .

Figure 8 LSVs at the SWCNH-modified GC electrode in 0.1 M pH 6.0 PBS (A) containing 10 μM catechol, 10 μM resorcinol, and different concentrations of hydroquinone (from inner to outer): 0.5, 1, 2, 4, 7, 10, 20, 40, 70, 100 μM ; (B) containing 10 μM hydroquinone, 10 μM resorcinol, and different concentrations of

catechol (from inner to outer): 0.5, 1, 3, 5, 10, 20, 40, 70, 100 μM ; and (C) containing 10 μM hydroquinone, 10 μM catechol, and different concentrations of resorcinol (from inner to outer): 1, 2, 4, 7, 10, 20, 70, 100 μM . Scan rate: 50 mV s^{-1} .

Figure 9 The calibration plots for hydroquinone (A), catechol (B), and resorcinol (C).

Biographies

Shuyun Zhu received her PhD from Changchun Institute of Applied Chemistry in 2012. Then, she worked as a college teacher in the College of Chemistry and Chemical Engineering at Qufu Normal University. Her current research interests include electrochemical and fluorescent applications of single-walled carbon nanohorns, as well as biosensors based on aptamers, DNA, and enzymes.

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Table 1 Determination of dihydroxybenzene isomers in water samples.

Water sample	Compound	Added (μM)	Found (μM)	Recovery (%)
1	hydroquinone	5.0	4.8	96
	catechol	5.0	5.11	102.2
	resorcinol	5.0	5.45	109
2	hydroquinone	20.0	18.4	92
	catechol	20.0	20.5	102.5
	resorcinol	20.0	22.0	110

Figure 1a

Figure 1b

Figure 1c

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6

Figure 7

Figure 8a

Figure 8b

Figure 8c

Figure 9a

Figure 9b

Figure 9c