



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.

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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).

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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⁻¹ 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 H₃PO₄. 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 -0.05–0.65 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.

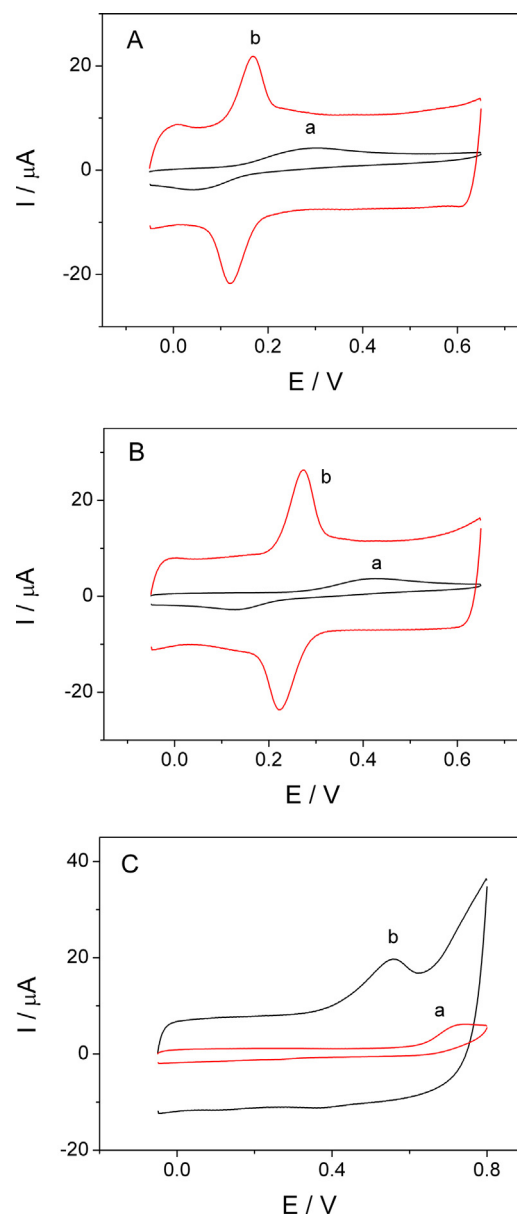


Fig. 1. CVs of 100 μM hydroquinone (A), 100 μM catechol (B), and 100 μM resorcinol (C) at the bare GC electrode (a) and SWCNH-modified GC (b) electrode in 0.1 M PBS (pH 6.0). Scan rate: 100 mV s⁻¹.

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 toward 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

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