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High sensitive simultaneous determination of catechol and hydroquinone at mesoporous carbon CMK-3 electrode in comparison with multi-walled carbon nanotubes and Vulcan XC-72 carbon electrodes

Jingjing Yu, Wei Du, Faqiong Zhao, Baizhao Zeng*

Department of Chemistry, Wuhan University, Wuhan, Hubei 430072, PR China

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ABSTRACT

The simultaneous voltammetric determination of catechol (CC) and hydroquinone (HQ) has been achieved at a mesoporous carbon CMK-3 modified electrode in phosphate buffer solution (pH 7.0). At the electrode both CC and HQ can cause a pair of quasi-reversible and well-defined redox peaks and their peak potential difference increases. In comparison with multi-walled carbon nanotubes (MWCNTs) and Vulcan XC-72 carbon modified electrodes the CMK-3 modified electrode shows larger peak currents and higher adsorbed amounts for the two dihydroxybenzene isomers. This is related to the higher specific surface area of CMK-3. Under the optimized conditions, the linear concentration ranges for CC and HQ are 5×10^{-7} to 3.5×10^{-5} M and 1×10^{-6} to 3×10^{-5} M, respectively. In the presence of 5 μM isomer, the linear concentration range of CC (or HQ) is 5×10^{-7} to 2.5×10^{-5} M (or 5×10^{-7} to 2.0×10^{-5} M). The sensitivity for CC or HQ is 41 A M^{-1} cm^{-2} or 52 A M^{-1} cm^{-2}, which is close to that without isomer. The detection limits (S/N = 3) for CC and HQ are 1×10^{-7} M after preconcentration on open circuit for 240 s.

1. Introduction

Catechol (CC, 1,2-dihydroxybenzene) and hydroquinone (HQ, 1,4-dihydroxybenzene) widely exist in industrial effluents, such as the waste from oil refineries, coal tar, plastic, leather, paint, steel and pharmaceutical industries [1,2]. Because of their toxicity, their assay is generally required. So far various methods have been exploited for their determination, such as electrochemistry [3–5], high-performance liquid chromatography (HPLC) [6], pH based-flow injection analysis [7], synchronous fluorescence [8], biosensor [9,10], etc. However, their simultaneous determination is a challenge because they present similar property. For example, their voltammetric peaks are board and overlap with each other. To achieve their simultaneous voltammetric determination, many materials were used to modify electrodes, such as single-walled carbon nanotubes (SWCNTs) [11], mesoporous Pt [12], carbon-atom-wire [13], poly-bromophenol blue/carbon nanotubes [14], etc. Wang et al. [11] reported that CC and HQ could be simultaneously determined in NaAc–HAc buffer solution by using a SWCNTs electrode and a multiple semi-differential technique. The oxidation peak currents of HQ and CC were linear to their concentration in the ranges of 4.0×10^{-7} to 1.0×10^{-5} M and 4.0×10^{-5} to 1.0×10^{-4} M. Ghanem used a mesoporous platinum electrode to realize the simultaneous determination of CC and HQ in 1.0 M $HClO_4$ by differential pulse voltammetry (DPV) [12]. The oxidation peak currents and their concentrations showed linear relationship in the ranges of 0.05–2.0 mM and 0.02–1.0 mM. However, acidic solutions were used in these works, which cannot meet the demand of practical application.

As far as we know, mesoporous carbon materials modified electrodes have not been used for the electrochemical determination of CC or HQ. Actually, these materials are excellent adsorbents for phenolic compounds owing to their abundant porous structure and high specific surface area [15–17]. Thus, they present promising application in the preconcentration and determination of phenolic compounds. Unlike many other mesoporous materials, mesoporous carbon materials show high mechanical stability and electric conductivity [18], which is important for their application. They are generally used as adsorbent in environmental area [15–17,19], and as catalyst [20] or catalyst support [18,21] in battery field. Recently, their application in electroanalytical chemistry was reported. CMK-3, for instance, synthesized using mesoporous silica SBA-15 as template, possesses highly ordered mesopores with high specific surface area, large pore volume and narrow pore size distribution centered at about 4.5 nm [22]. It was used to modify electrode for the determination of some biological molecules, including epinephrine [23], L-cysteine [24] and dopamine [25]. In addition, it was adopted as protein immobilization material to

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* Corresponding author. Tel.: +86 27 87218704; fax: +86 27 87647617.
E-mail address: bzzeng@whu.edu.cn (B. Zeng).

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study the direct electrochemistry of hemoglobin (Hb) [26] and to fabricate glucose biosensor [27].

The purpose of this work is to explore the feasibility to determine CC and HQ simultaneously with a CMK-3 modified electrode. Multi-walled carbon nanotubes (MWCNTs) and Vulcan XC-72 carbon modified electrodes are studied for comparison since they possess high surface area [28,29] and are frequently used in electrochemistry field [30,31]. Carbon nanotubes (CNTs) are composed of cylindrical graphite sheets with nanometer diameter. CNTs are subdivided into two classes: SWCNTs and MWCNTs. SWCNTs consist of single hollow tube while MWCNTs are composed of multiple concentric nanotubes [28,32]. They have attracted enormous interest in electrochemistry because of their unique structure with large surface area, high electrical conductivity and remarkable mechanical properties [30,33]. Vulcan XC-72 carbon, known as a universal catalyst support in the field of electrochemistry [29,31], is a kind of carbon nanoparticle (diameter: about 30 nm) with high surface area [34]. It has been used as component for the fabrication of electrochemical biosensor [34]. In this work, result shows that in pH 7.0 phosphate buffer solutions (PBS) both CC and HQ give a pair of quasi-reversible redox peaks and their anodic peak potential difference is up to 125 mV at CMK-3 modified electrode. What's more, the electrode shows larger peak current and higher adsorbed amount than MWCNTs and Vulcan XC-72 modified electrodes due to its higher specific surface area.

2. Experimental

2.1. Reagents

CC and HQ came from Sinopharm Chemical Reagent Co. Ltd. (Shanghai, China). MWCNTs (Chengdu Organic Chemicals Co. Ltd., China) were refluxed for 16 h in concentrated HNO_3 before use. Vulcan XC-72 carbon was purchased from Cobot Co. (USA). Nafion solution was prepared by diluting 5% Nafion DE 520 solution (DuPont) with water. Other chemicals used were of analytical grade and the solutions were prepared with deionized water.

2.2. Electrode preparation

Mesoporous carbon material CMK-3 was prepared by using mesoporous silica material SBA-15 as template and sucrose as carbon source according to the literature [22]. Before modification, the bare glassy carbon electrode (GCE) was polished to mirror smooth with 0.05 μm Al_2O_3 slurry, rinsed with water, and then ultrasonicated in water bath. Five milligrams of CMK-3 material was dispersed in 1 ml 0.05% Nafion with the aid of ultrasonic agitation. Then 2 μl of the mixture was transferred onto the GCE surface, and the solvent was evaporated under an infrared lamp. Thus, CMK-3-Nafion/GCE was obtained. For comparison, MWCNTs-Nafion/GCE and Vulcan XC-72-Nafion/GCE were prepared through similar way.

2.3. Apparatus and methods

All electrochemical experiments were performed on a CHI 660A electrochemical workstation (CH Instru. Co., Shanghai, China) at room temperature (25 ± 2 °C). The working electrode was a modified GCE (2 mm in diameter). A saturated calomel electrode (SCE) served as the reference electrode, and a Pt wire served as the counter electrode. The supporting electrolyte was air-saturated 0.10 M PBS (pH 7.0). Cyclic voltammograms (CVs) and linear sweep voltammograms (LSVs) were recorded after preconcentration on open circuit for 240 s. After each measurement, the modified electrode underwent five successive cyclic potential scan between −1.0 V and 1.0 V in the mixture of 7.5 ml PBS (pH 7.0, 0.10 M) and 0.5 ml ethanol to refresh the electrode.

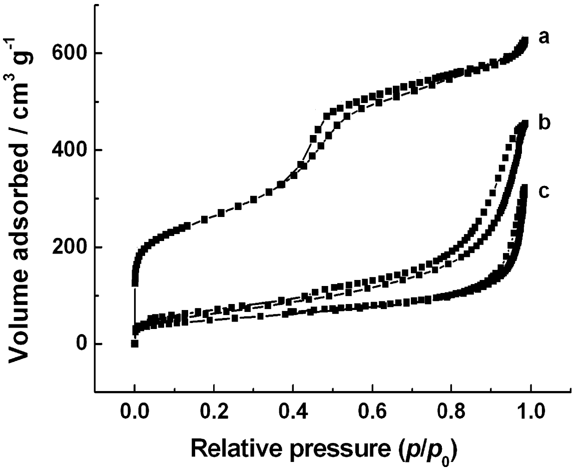

Fig. 1. N_2 adsorption/desorption isotherms for CMK-3 (a), MWCNTs (b) and Vulcan XC-72 carbon (c).

The adsorption and desorption experiments of nitrogen gas were performed on a SA 3100 surface area and pore size analyzer (Beckman Coulter INC., USA). The samples were outgassed under vacuum at 393 K for 2 h before the adsorption of nitrogen gas.

3. Results and discussion

3.1. N_2 adsorption/desorption isotherms of carbon materials

As shown in Fig. 1, the N_2.adsorption/desorption isotherm of CMK-3 is a type IV curve of mesoporous materials with a steep hysteresis loop. The sharp rise at relative pressure (P/P_0) of about 0.4 indicates the existence of mesopores with narrow pore size distribution. According to Brunauer–Emmett–Teller (BET) method [35,36], the specific surface area (S_{BET}) and pore volume are estimated to be 938.04 m^2 g^{-1} and 0.9557 m^3 g^{-1}, respectively. MWCNTs and Vulcan XC-72 show larger pores for the sharp rise occurs at higher relative pressure (near 1). This is mainly related to the hollow tube of MWCNTs and the hole of Vulcan XC-72 carbon particle aggregate. Their specific surface areas are ca. 227.78 m^2 g^{-1} (for MWCNTs) and 76.97 m^2 g^{-1} (for Vulcan XC-72). Thus, their surface areas follow such order as: S_{BET} (CMK-3) > S_{BET} (MWCNTs) > S_{BET} (Vulcan XC-72).

3.2. Voltammetric response of CMK-3-Nafion/GCE to CC and HQ

CVs of CC and HQ at CMK-3-Nafion/GCE and bare GCE are shown in Fig. 2. At CMK-3-Nafion/GCE, a pair of well-defined redox peaks is observed for both CC and HQ. The formal potential ($E^{0\prime}$, defined as the average of cathodic and anodic peak potentials) is 0.162 V for CC and 0.035 V for HQ. Compared with those at bare GCE, the peak currents increase greatly. The average peak current (i_{av}, defined as the average of cathodic and anodic peak currents) at CMK-3-Nafion/GCE for CC (or HQ) is 289 (or 477) folds of that at bare GCE. On the other hand, the peak potential differences (ΔE_p) between anodic and cathodic peak (i.e., 68 mV and 74 mV for CC and HQ, respectively) are smaller than those on bare GCE (i.e., 153 mV and 143 mV), indicating that the reversibility of electrochemical reaction is improved. Furthermore, their cathodic (i_{pc}) and anodic (i_{pa}) peak currents are near equal. Hence it can be proposed that the electrochemical processes of CC and HQ at CMK-3-Nafion/GCE are quasi-reversible [37]. Additionally, the cathodic (ΔE_{pc}) and