



Simultaneous voltammetric determination of nitrophenol isomers at ordered mesoporous carbon modified electrode



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ABSTRACT

In this paper, ordered mesoporous carbons (OMCs) modified glassy carbon electrode (GCE) (OMCs/GCE) was employed to investigate the electrochemical behavior of *o*-nitrophenol (*o*-NP), *m*-nitrophenol (*m*-NP) and *p*-nitrophenol (*p*-NP) in ambient-N₂ phosphate buffer saline. Compared with bare GCE, the OMCs/GCE exhibited obvious electrocatalytic activity towards nitrophenol isomers. The electrochemical reaction mechanism of nitrophenol at the modified electrode was also studied. At OMCs/GCE, the three nitrophenol isomers could be identified and separated successfully and the simultaneous determination was realized by detecting the reduction peaks of their intermediate products (at 0.209 V vs. saturated calomel electrode for *p*-NP, 0.020 V for *m*-NP and -0.201 V for *o*-NP) with differential pulse voltammetry. Under the optimized experimental conditions, the linear ranges of the calibration curves were 2–90 μM for *p*-NP, 1–100 μM for *m*-NP and 0.5–90 μM for *o*-NP with limits of detection of 0.1 μM, 0.06 μM and 0.08 μM for *p*-NP, *m*-NP and *o*-NP, respectively (*S/N* = 3). Therefore, the proposed method is simple, rapid, stable, sensitive, specific, reproducible and cost-effective, which can be applicable for real samples detection.

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1. Introduction

It has been reported that *o*-nitrophenol (*o*-NP), *m*-NP, and *p*-NP are three important environmental pollutants and they are classified as the hazardous wastes and priority toxic pollutants by Environmental Protection Agency of America [1,2]. These compounds are poisonous to human and animals, which would result in severe diseases, such as methemoglobinemia, fever, damage of liver and kidney [3–6]. Nitrophenol isomers are also harmful to plants, for instance, irrigating crops with water which contains nitrophenol isomers over 0.7 mM will lead to the reduction of output [7]. The three isomers are widely used in industrial production of pharmaceuticals, dyes and pesticides [8–10], therefore, they broadly distribute in soil and aquatic environment, and are difficult to degrade because of high stability [11–14]. For above-mentioned reasons, their detection becomes one of the important projects for environmental analysis. On the other hand, due to their

similar structures and properties, the three isomers usually coexist and interfere with each other during determination. At present, many experimental methods have been developed for the simultaneous determination of nitrophenol isomers, for example, flow injection analysis [15], spectrophotometry [16,17], high performance liquid chromatography [18], capillary electrophoresis [19]. However, these approaches are complex in sample preparation and generally need expensive instrumentation. Moreover, the on-site inspection is very difficult. Therefore, it is very important to explore a simple, rapid and cost-effective method for their simultaneous determination.

The emerging nanotechnology has opened up new exciting avenues for offering great opportunities for analytical applications, mostly due to the extraordinary physical and chemical properties of nanostructured materials [20–27]. In recent years, electrochemical method has attracted much attention due to its high-efficiency, low-cost, and easy-to-operation. Up to now, several kinds of nanomaterial-modified electrodes for simultaneous determination of nitrophenol isomers have been reported, for instance, multiwalled carbon nanotubes (MWNTs) modified glassy carbon electrode (GCE) (MWNTs/GCE) using linear sweep voltammetry (LSV) [28], nano-gold (nano-Au) modified GCE (nano-Au/GCE) using semi-derivative voltammetry (SDV) [5], β-cyclodextrin (CD)

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functionalized reduced graphene oxide (RGO) modified GCE (CD-RCO/GCE) using differential pulse voltammetry (DPV) [12], and CD functionalized mesoporous silica (SBA) modified carbon paste electrode (CPE) (CD-SBA/CPE) [2]. However, these methods either lack sensitivity, or are complicated in preparation of the electrodes.

Since the discovery of ordered mesoporous carbons (OMCs) in 1999, many scientists have paid great attention to the development of this kind carbon material due to its large surface area, well-defined pore size, and flexible framework [29–31]. It has been reported that largely due to the existence of the edge plane-like defective site and oxygen-containing functional groups on the surface of OMCs, they can provide a great deal of favorable sites to transmit electrons for electroactive substances [3,32]. At present, this ordered carbon material has been widely used in sensing, energy storage, bioreactor construction and catalytic application [32]. The advantages of fast electron transfer, high thermal stability and excellent electrocatalytic activity suggest that the OMCs will be a promising candidate for electrode modified material.

In this paper, we systematically studied the electrochemistry of nitrophenol isomers at OMCs-modified electrode. It turned out that the OMCs-modified electrode exhibited excellent electrocatalytic activity towards nitrophenol isomers. Well-separated voltammetric peaks were observed in their mixture solution, which could be applicable to simultaneously detect the three nitrophenol isomers.

2. Materials and methods

2.1. Chemicals and reagents

Triblock copolymer of Pluronic (P123) and Nafion (perfluorinated ion-exchange resin, 5 wt% solution in a mixture of lower aliphatic alcohols and water) were purchased from Aldrich Corporation. Tetraethoxysilane (TEOS) was purchased from Sinopharm Chemical Reagent Corporation. *o*-NP, *m*-NP and *p*-NP were purchased from Xiya Reagent Corporation, China and used without further purification. The solid nitrophenol isomers should be stored in the cool and dry place to avoid direct sunlight and their solutions should be prepared immediately before used. Phosphate buffer saline (PBS) was used as the supporting electrolyte. All other reagents were of the highest grade and all solutions were prepared with ultrapure water.

2.2. Synthesis of ordered mesoporous carbons

OMCs were synthesized according to the literatures with modification [29–31]. Initially, 2.0 g of P123 was added into 80 g of distilled water containing 60 g of 2 M HCl, and then the mixture was adequately stirred at 35 °C until P123 was completely dissolved. Following that, 4.2 g of TEOS was injected into the mixture, and stirred for 20 h at 35 °C. Subsequently, the mixture was aged at 100 °C overnight. The products were obtained by filtration and dried in air for 2 h. Next, the as-prepared precipitate was added into a mixture containing 1.5 g sucrose, 0.17 g H₂SO₄ and 10 g H₂O. After adequately stirring, the suspension was heated for 6 h at 100 °C in an oven, followed by continuously heating for 6 h at 160 °C. Afterwards, the brown product was calcined in a tubular furnace for 5 h at 550 °C and for 3 h at 900 °C under the protection of nitrogen gas in turn. Finally, OMCs was formed via the addition of 1.0 M NaOH into the resulting suspension. The obtained OMCs by centrifugation was washed, dried at 80 °C, and stored in a drier.

2.3. Preparation of OMCs modified electrode

The glassy carbon electrode (3 mm in diameter) was polished successively with 0.3 and 0.05 μm alumina slurry and sonicated in anhydrous ethanol and ultrapure water for 3 min, respectively [33].

Then, the electrode was thoroughly rinsed with ultrapure water. Nafion-OMCs composite was prepared by mixing 1.0 mL Nafion (0.05 wt%) with 2.0 mg OMCs powder and sonicated until a homogeneous aqueous dispersion resulted. 8.0 μL of the mixture was dropped onto the inverted electrode and dried under room temperature to acquire OMCs film modified GCE. At last, 4.0 μL of Nafion (0.05 wt%) was syringed onto the surface of modified electrode. Before use, the modified electrode was immersed into ultrapure water to remove any loosely bound modifiers.

2.4. Apparatus and methods

The wide-angle X-ray diffraction (XRD) patterns were recorded on a PANalytical X'Pert spectrometer using the Co Kα radiation ($\lambda = 1.789 \text{ \AA}$), and the data would be changed to Cu Kα data. Transmission electron micrograph (TEM) was taken on a FEI F20 S-TWIN instrument. N₂ adsorption-desorption analysis was measured on a Micromeritics ASAP 2020 instrument, pore volumes were determined using the adsorbed volume at a relative pressure of 0.99, multipoint Brunauer-Emmet-Teller (BET) surface area was estimated from the relative pressure range from 0.06 to 0.3. The pore size distributions of the as-prepared samples were analyzed using the Barrett-Joyner-Halenda (BJH) method. The electrochemical experiments were performed with CHI660D electrochemical workstation (CH Instruments, Chenhua, Shanghai, China). All electrochemical experiments were carried out in a conventional three-electrode system using a bare GCE or a modified GCE as working electrode, a platinum wire as counter electrode and a saturated calomel electrode (SCE) as reference electrode. All potentials in this article were recorded versus this reference. All measurements were performed at room temperature (~23 °C). The PBS solution was deaerated with high purity nitrogen for 20 min previously and kept on feeding nitrogen through the whole experimental process.

3. Results and discussion

3.1. Characterization of prepared OMCs

The TEM image of the prepared OMCs along the [001] direction demonstrates the regular pattern of carbon particles in the mesopore channel structure (Fig. 1). For mesoporous carbon, the BET surface area and pore volume are 1158 m² g⁻¹ and 1.26 cm³ g⁻¹, respectively. N₂ adsorption-desorption isotherm showed the pore with an average pore diameter of approximately 3.9 nm (Fig. 2).

3.2. Electrochemical behavior and reaction mechanism of nitrophenol isomers at OMCs/GCE

The cyclic voltammograms (CVs) of *p*-NP, *m*-NP and *o*-NP (each 10 μM) at bare GCE and OMCs/GCE in 0.1 M PBS (pH 4.8) buffer under saturated-N₂ are shown in Fig. 3. At bare GCE, *p*-NP, *m*-NP and *o*-NP gave a reduction peak at -0.731 V, -0.669 V and -0.623 V, respectively (curves a of Fig. 3A–C), which related to the irreversible reduction of nitryl [34,35]. Meanwhile, at OMCs/GCE, *p*-NP, *m*-NP and *o*-NP exhibited a clear nitryl reduction peak at -0.639 V, -0.582 V and -0.573 V, respectively (curves c of Fig. 3A–C). After modified with OMCs, the background current increased obviously, furthermore, the current signal increased significantly and all the reduction peak potentials positively shifted. To illustrate the other features at OMCs/GCE, *p*-NP was taken as an example. Besides the clear reduction peak of nitryl, a new pair of well-defined redox peaks appeared with oxidation and reduction peak at 0.239 V and 0.209 V at OMCs/GCE (Fig. 3A, curve c). Compared to the blank controlled trial (Fig. 3A, curve b), this new pair of peaks are attributed to the electrochemical behavior of *p*-NP rather than OMCs. Similarly,

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