



Simultaneous electrochemical determination of dihydroxybenzene isomers using electrospun nitrogen-doped carbon nanofiber film electrode



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ABSTRACT

Nitrogen-doped carbon nanofibers (NCNFs) were prepared by a simple and efficient method which associated the electrospinning with the aborative designed carbonization process. Compared with electrospun CNFs, nitrogen-doping effect greatly reduced the diameter of nanofibers and changed the existing forms of nitrogen atoms. The free-standing NCNF film could be immediately used to prepare NCNF film modified glassy carbon electrode (NCNF-GCE). NCNF-GCE exhibited high electrocatalytic activity towards the oxidation of hydroquinone (HQ), catechol (CC), and resorcinol (RC). The excellent electrochemical performance of NCNF-GCE was ascribed to the large surface area, abundant defective sites, and unique nitrogen existing forms. Differential pulse voltammetry was used for the simultaneous determination of HQ, CC and RC in their ternary mixture. The separation of peak potentials is 104 mV and 400 mV for HQ–CC and CC–RC, respectively. The oxidation peak currents of HQ, CC and RC are linear to the concentrations over the range of 1–400 μM , 1–400 μM and 2–500 μM with the detection limits of 0.3 μM , 0.4 μM , and 0.8 μM ($S/N = 3$), respectively. The proposed method was applied to the simultaneous determination of the three dihydroxybenzene isomers in tap water and lake water samples, and the recoveries of 96.0–104.4% were obtained.

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1. Introduction

It is a great challenge to simultaneously discriminate and determine the isomers of organic compounds in organic and analytical chemistry [1,2]. Hydroquinone (HQ), catechol (CC), and resorcinol (RC) are three dihydroxybenzene isomers, and are widely used as fundamental chemical compounds and synthetic intermediates in many fields, such as dye, cosmetic, tanning, pharmaceutical and other chemical industries [3,4]. Due to their low degradability and high toxicity to humans and animals, these isomers have been included in the lists of priority pollutants to be monitored in the aquatic environment by US Environmental Protection Agency (EPA) and the European Union [5]. Ministry of Environmental Protection of the People's Republic of China has prescribed that the concentration of phenols should not exceed 0.009 mg/L in surface water samples, which is on the basis of the total phenols without chloric substituted group (GB 3838-2002). It has been reported that catechol and hydroquinone could act as promoters and cocarcinogens to increase tumor cell invasion and metastasis [6,7]. Catechol also

can induce DNA and protein damage through the oxidative pathway [8]. In addition, catechol also widely exists in plants such as vegetables, green teas, fruits, tobaccos and some traditional Chinese medicines, showing the biological importance such as antiviral, antioxidant, and regulator of the activities of some enzymes [9]. Therefore, it is important to develop a sensitive and efficient method for the determination of these isomers for environmental protection and food safety.

To date, various methods have been employed for the determination of dihydroxybenzene isomers, which can be classified into two kinds of strategies. One kind of strategy is based on the structural difference of these isomers, and utilized separation techniques to achieve the simultaneous determination, including high-performance liquid chromatography [10], and capillary electrophoresis [5]. These methods have minimal cross-interference, but are limited by the complicated operation, sample pretreatment and long analysis time [2]. Another type of strategy exploited the subtle discrepancy in their physicochemical properties, especially the redox activity, to simultaneously detect these isomers, including spectrophotometric method [11], colorimetric detection [12], room-temperature phosphorescent method [2], fluorescent quenching method [13], chemiluminescence [14], electrochemiluminescence [15], and electrochemical method. Due to the

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low maintenance costs and excellent sensitivity, electrochemical method has been widely explored for the simultaneous detection of dihydroxybenzene isomers. However, at bare electrode, the oxidation of catechol and hydroquinone usually exhibits overlapped oxidation peak, and resorcinol shows low response signal and high overpotential. Therefore, the activation or pretreatment of the bare electrode is required [16,17]. A chemically modified electrode was an excellent alternative to solve the signal separation problem by introducing a modifier, such as polymers [18] and nanomaterials [19–22]. Because of the unique electronic structures, high specific surface area, and abundant active sites, carbon nanomaterials have been extensively studied for the simultaneous determination of the three dihydroxybenzene isomers, including multi-walled carbon nanotubes (MWCNTs) [1,3,23–25], single-walled carbon nanotubes [26], carbon nanoparticles [27], graphene [4,28–32], single-walled carbon nanohorn [33], or multiple carbon nanomaterial hybrids [34–37]. Moreover, chemical doping of carbon materials with heteroatom, e.g. nitrogen, is an efficient way to tailor their electronic and chemical properties, thus greatly improved their electrocatalytic performances [38–40]. For example, nitrogen-doped (N-doped) carbon nanomaterials have been employed for the simultaneous determination of dihydroxybenzene isomers, showing improved analytical performance compared with non-doped counterparts [41–44]. However, the preparation of materials and/or modified electrodes needs sophisticated skills to obtain high sensitivity and selectivity. Therefore, it is necessary to prepare a high sensitive electrode without any complicated modification process.

Carbon nanofibers (CNFs) have been extensively used for sensor development due to good electrical conductivity, high surface area, and ease of surface functionalization [45]. Electrospinning is an interesting and promising technique to prepare carbon nanofibers using various carbon precursors [46]. One of the merits of electrospinning technique is that free-standing nanofiber membranes can be easily fabricated through mechanical or chemical peel-off from the collector, which facilitated their further applications. Free-standing electrospun CNF membranes have been used as electrode materials in energy conversion and storage devices [47], which greatly simplified the electrode preparation procedure. Recently, we developed a simple strategy for the preparation of free-standing N-doped CNF (NCNF) film using electrospinning and subsequent carbonization process [48]. Due to the high flexibility, the as-prepared NCNF film could be immediately used to modify the substrate electrode, and hence found promising applications in analytical and energy-related devices [48,49].

In this study, NCNFs were fabricated and used to simultaneously determine three dihydroxybenzene isomers. Compared with traditional electrospun CNFs, nitrogen doping process greatly reduced the diameter of nanofibers, and changed the existing form of nitrogen atoms in the as-produced nanofibers. Due to the flexibility and easy-processing property, the obtained NCNF film can be directly applied as electrode material, and the NCNF film modified glassy carbon electrode (NCNF-GCE) showed excellent electrocatalytic activities towards the oxidation of HQ, CC and RC. Furthermore, the NCNF/GC electrode was successfully used to determine dihydroxybenzene compounds in local tap water and lake water samples, and satisfactory results were obtained.

2. Experimental

2.1. Reagents and materials

Polyacrylonitrile (PAN, average Mw 150 000) and hydroquinone were purchased from Sigma–Aldrich. Catechol was supplied by

Alfa Aesar. Resorcinol was obtained from Sinopharm Chemical Reagent Co. Ltd. Phosphate buffer solution (PBS, 0.1 M) was prepared by mixing stock solutions of Na_2HPO_4 and NaH_2PO_4 . All chemicals were used without further purification. The water used throughout the experiments was deionized water with resistivity $\geq 18.2 \text{ M}\Omega \text{ cm}$.

2.2. Apparatus

The scanning electron microscopy (SEM) images were obtained using FEI XL-30 ESEM with an accelerating voltage of 20 kV. The transmission electron microscopy (TEM) images were acquired on Philips-TECNAI F20 microscope with an accelerating voltage of 200 kV. X-ray photoelectron spectra (XPS) were recorded on Escalab-MKII spectrometer with $\text{MoK}\alpha$ X-ray as excitation source. Raman spectra were performed on Renishaw RM-1000 with 514.5 nm laser as the exciting radiation. Electrochemical impedance spectroscopy (EIS) was performed on AUTOLAB PGSTAT 302N in 5 mM $[\text{Fe}(\text{CN})_6]^{3-/4-}$ containing 0.1 M KCl as supporting electrolyte within the frequency range of 0.01– 10^5 Hz. All other electrochemical measurements were performed with a CHI 832 electrochemical analyzer. A conventional three-electrode system was used, including a Ag/AgCl (saturated KCl) electrode as the reference electrode, a Pt wire as the counter electrode, NCNF-GCE as working electrode (2.0 mm in diameter). The parameters of differential pulse voltammetry (DPV) experiments were as follows: pulse amplitude, 0.05 V; pulse width, 0.05 s; pulse period 0.2 s.

2.3. Preparation of NCNFs

The NCNFs were prepared by the electrospinning and subsequent carbonization process, as reported in previous work [48]. Briefly, the electrospinning solution was composed of 10 wt.% PAN in DMF. The electrospinning process was carried out in the electric field of 100 kV/m with a flow rate of 1.0 mL/h. The obtained PAN nanofiber membrane was placed in mutual covered two combustion boats for the stabilization and carbonization. The steps were as followings: (1) 300 °C annealing for 60 min in N_2 to stabilize PAN nanofibers, (2) heating to 900 °C and kept for 120 min in N_2 to carbonize the PAN nanofibers, (3) cooling down to room temperature in N_2 . The entire thermal treatment procedure was performed with a heating rate of 10 °C/min. The pristine CNFs were prepared via the same procedures as NCNFs, except that the thermal treatment was conducted in one combustion boat and the stabilization step was performed in air.

2.4. Preparation of NCNF film modified electrode

Before modification, glassy carbon electrode (GCE) with a diameter of 2 mm was polished successively using 0.3 μm and 0.05 μm alumina slurry on a polishing cloth to a mirror-like finish. Then, the polished GCE was rinsed ultrasonically with anhydrous alcohol and double distilled water each for 5 min, and dried at room temperature. For the preparation of NCNF-GCE, the NCNF films were cut to the disk shape with the diameter of 2 mm using a hole-puncher. Then NCNF-GCE was obtained by directly adhering NCNF film to the surface of GCE by 0.5 μL of chitosan solution (0.05 wt.%). For comparison, CNF film modified GCE (CNF-GCE) was prepared using the same procedure as that of NCNF-GCE except using the cut CNF film. The chitosan modified GCE (CS-GCE) was prepared by spreading 0.5 μL of chitosan solution (0.05 wt.%) on GCE surface, and dried at room temperature.

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