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The Cu-MOF-199/single-walled carbon nanotubes modified electrode for simultaneous determination of hydroquinone and catechol with extended linear ranges and lower detection limits

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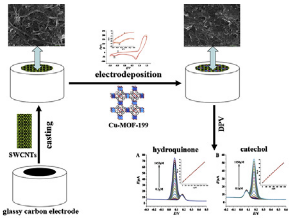
HIGHLIGHTS

- Cu-MOF-199/SWCNTs/GCE was facilely fabricated by the electrodeposition on SWCNTs/GCE.
- An electrochemical sensor for detecting HQ and CT was constructed based on this modified electrode.
- The proposed electrochemical sensor showed an extended linear range and lower detection limits.
- The proposed electrochemical sensor had an excellent stability and reproducibility.

GRAPHICAL ABSTRACT



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ABSTRACT

A novel electrochemical sensor based on Cu-MOF-199 [Cu-MOF-199 = $Cu_3(BTC)_2$ (BTC = 1,3,5-benzenetricarboxylicacid)] and SWCNTs (single-walled carbon nanotubes) was fabricated for the simultaneous determination of hydroquinone (HQ) and catechol (CT). The modification procedure was carried out through casting SWCNTs on the bare glassy carbon electrode (GCE) and followed by the electrodeposition of Cu-MOF-199 on the SWCNTs modified electrode. Cyclic voltammetry (CV), electrochemical impedance spectroscopy (EIS) and scanning electron microscopy (SEM) were performed to characterize the electrochemical performance and surface characteristics of the as-prepared sensor. The composite electrode exhibited an excellent electrocatalytic activity with increased electrochemical signals towards the oxidation of HQ and CT, owing to the synergistic effect of SWCNTs and Cu-MOF-199. Under the optimized condition, the linear response range were from 0.1 to 1453 μmol L^{-1} ($R_{HQ} = 0.9999$) for HQ and 0.1–1150 μmol L^{-1} ($R_{CT} = 0.9990$) for CT. The detection limits for HQ and CT were as low as 0.08 and 0.1 μmol L^{-1}, respectively. Moreover, the modified electrode presented the good reproducibility and the excellent anti-interference performance. The analytical performance of the developed sensor for the simultaneous detection of HQ and CT had been evaluated in practical samples with satisfying results.

1. Introduction

Hydroquinone (HQ) and catechol (CT) are two isomers of

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dihydroxybenzene which widely exist in industrial wastes, such as cosmetics, dye, pesticides, and pharmaceutical industries. They are considered as crucial environmental pollutants because of their high toxicity and the degradation-resistant properties in the ecological environment [1]. Hence, the rapid and accurate detection of HQ and CT is a significant issue for the environmental analysis. However, these two isomers are often coexisting [2], and it is difficult to separate and determine them due to their similar structures and properties. Therefore, the development of a rapid, accurate, and simple analytical method for the simultaneous detection of the two dihydroxybenzene isomers is highly desirable.

To date, various techniques, including spectrophotometry [3], chromatography [4], mass spectrometry [5], pH-based flow injection analysis [6], fluorescence [7] and electrochemical methods [8–14], have been applied to the detection of HQ and CT. Among those methods, the electrochemical method has attracted more attention since it posses the merits of simple operation, fast response and low cost, which offers the opportunity for portable, cheap and rapid methodologies. The simultaneous determination of HQ and CT is a special interest in electrochemistry system because those species exhibit overlapped oxidation peaks at conventional solid electrodes and are difficult to be distinguished. Thus, electrochemical detection approaches for those two substances must be developed with suitable modification materials that can provide complete resolution of their electrochemical signals, or determination the selective of at least one substance without influence from the other. For this purpose, various kinds of electrodes modified with graphene, carbon nanotubes and gold nanoparticles [15–18] have been constructed to improve the electrochemical performance of the sensing platform. Among them, metal-organic frameworks (MOFs) have received extensive interest by virtue of their exciting properties including large surface areas, ordered pore structure and multiple coordination sites. MOFs are composed of repeated metal complex units with a three-dimensional crystal lattice constructed from metal ion nodes linked together by organic linkers [19]. By the rational choice of metal ions and organic ligands, the structure of MOFs with the various pore size and framework topology can be tailored to meet the requirement of the specific application [20]. These characteristics have made MOFs develop quickly in many research fields including catalysis [21,22], ion exchange [23], gas storage and separation [24] and drug delivery [25]. Recently, a few studies have demonstrated the promise application of MOFs for the electrochemical sensing. Yuan et al. [26] reported a new 2-dimensional (2D) Co-based MOF which exhibited the electrocatalytic oxidation of reduced glutathione (GSH). The Co-MOF modified carbon paste electrode also showed a wide linear range from 2.5 μmol L^{-1} to 0.95 mmol L^{-1} with the detection limit of 2.5 μmol L^{-1} for the determination of GSH. Deep et al. [27] presented the surface assembly of a nanometal organic framework $[Cd(atc)\ (H_2O)_2]_n$ (atc = 2-aminoterephthalic acid) on a 2-aminobenzylamine (2-ABA) modified indium tin oxide (ITO) slide by sequential dipping. The pesticide sensor based on this modified electrode was designed for the electrochemical determination of parathion by the electrochemical impedance spectroscopy and its sensitivity was better or comparable to the reported sensors.

However, the application of pure MOFs in electrochemical researches is still faced with some problems because of their intrinsic deficiency such as the poor electronic conductivity and instability in aqueous environment [28–30]. An efficient way to resolve the problems is combining MOFs with other functional materials which have better electronic conductivity or make MOFs more stable [31,32]. For this purpose, carbon materials stand out as a good partner to enhance the electroconductivity and the stability. Zu et al. [33] incorporated the graphite oxide into a typical MOF, namely HKUST-1 or MOF-199 $[Cu_3(BTC)_2$ (BTC = 1,3,5-benzenetricarboxylicacid)], to improve hydrothermal stability and catalytic activity. Zhang et al. [34] synthesized a MOF-macroporous carbon hybrid material. The composites modified electrode showed an increase of the electrocatalytic ability for the oxidation of NADH and the reduction of H_2O_2 in neutral solution. Zhou et al. [35] also synthesized a Cu-bipy-BTC/MWCNTs hybrid composite. The electrode modified by the hybrid composite had a good performance for the H_2O_2 detection with a wide linear range. Therefore, the combination of carbon materials with MOFs for the electrochemical sensing platforms is highly desirable.

Inspired by these reports, we combined the advantages of MOFs and the single-walled carbon nanotubes (SWCNTs) to prepare Cu-MOF-199/SWCNTs modified electrode for the simultaneous determination of HQ and CT in this work. The combination of SWCNTs and Cu-MOF-199 could not only increase the surface area but also form a conductive interconnection network which may be favorable for the charge transfer. Moreover, the incorporation of SWCNTs could also make Cu-MOF-199 more stable. The Cu-MOF-199/SWCNTs modified electrode exhibited excellent electrochemical performance with extended linear ranges and lower detection limits for the simultaneous determination of HQ and CT.

2. Experimental

2.1. Reagents and materials

Hydroquinone, catechol, $Cu(NO_3)_2 \cdot 3H_2O$, 1,3,5-benzenetricarboxylic acid (H_3BTC), N,N-dimethylformamide (DMF), ethanol and other common chemicals were purchased from Sinopharm Chemical Reagent Co., Ltd. Single-walled nanotubes (SWCNTs) were obtained from Nanjing Xianfeng Nano Science and Technology Co., Ltd, China. All the chemicals were of analytical grade and used without further purification. Aqueous solutions were prepared with doubly distilled water.

The 0.2 mol L^{-1} phosphate buffer solutions (PBS) with different pH, including 0.1 mol L^{-1} KCl as a supporting electrolyte, were prepared by mixing the stock solutions of 0.2 mol L^{-1} NaH_2PO_4 and 0.2 mol L^{-1} Na_2HPO_4 and then adjusting the pH with H_3PO_4 or NaOH.

2.2. Apparatus and instruments

All electrochemical measurements, including cyclic voltammetry (CV), differential pulse voltammetry (DPV), and electrochemical impedance spectra (EIS), were carried out on a CHI660D electrochemical workstation (Shanghai Chenhua Co., China). A standard three-electrode cell was used for all the electrochemical experiments. A bare or modified glassy carbon electrode (GCE, 3 mm in diameter) was used as working electrode. A platinum wire was served as the counter electrode. A saturated calomel electrode (SCE) was applied as the reference electrode and all potentials reported in this paper were referenced to the SCE.

The modified materials were characterized by field emission scanning electron microscopy (Zeiss Ultra Plus, Germany) and Fourier transform infrared spectroscopy (Thermo Nicolet, USA).

2.3. Preparation of the modified materials

2.3.1. The preparation of the single-walled nanotubes (SWCNTs) suspension

The SWCNTs suspension (0.1 mg mL^{-1}) was prepared as described previously [36]. First, SWCNTs were mixed with a mixture solution of the concentrated H_2SO_4/HNO_3 ($V_{98\%H2SO4}:V_{65\%HNO3} = 3:1$) in a ice-water bath and then refluxed for 3 h at 80 °C in