



An electrochemical sensor based on copper-based metal-organic frameworks-graphene composites for determination of dihydroxybenzene isomers in water



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ARTICLE INFO

Keywords:

Metal-organic framework
HKUST-1
Graphene
Hydroquinone
Catechol

ABSTRACT

A highly and simply sensitive electrochemical sensor was presented for the simultaneous determination of hydroquinone (HQ) and catechol (CT) in the water based on copper centered metal-organic framework-graphene composites (Cu-MOF-GN) [Cu-MOF = Cu₃(BTC)₂ (BTC = 1, 3, 5-benzenetricarboxylic acid)] modified glassy carbon electrode (Cu-MOF-GN/GCE). The modification procedure was carried out through casting metal-organic framework-graphene oxide composites (Cu-MOF-GO) on the bare glassy carbon electrode and followed by the transformation of Cu-MOF-GO to Cu-MOF-GN by an electrochemical reduction. The electrochemical behavior of HQ and CT at Cu-MOF-GN/GCE was investigated by cyclic voltammetry (CV), differential pulse voltammetry (DPV) and electrochemical impedance spectroscopy (EIS). Under the optimized conditions, the modified electrode had excellent electrocatalytic activity and high selectivity toward HQ and CT. The electrochemical sensor exhibited a linear response in the same range of 1.0×10^{-6} to 1.0×10^{-3} M with the detection limits of 5.9×10^{-7} M for HQ and 3.3×10^{-7} M for CT (S/N = 3). Four samples of tap water spiked with different concentrations of HQ and CT were considered. The method has been applied to the analysis of these isomers in spiked tap water with recoveries from 99.0 ~ 102.9% and relative standard deviations (RSDs) for 5 successive measurements less than 5% were also acceptable. This method was successfully applied to detect target analytes in the real samples with satisfying results. The MOFs-based sensors in the field of electrochemical sensing held a great promise for routine sensing applications.

1. Introduction

Hydroquinone (HQ) and catechol (CT) are two typical dihydroxybenzene isomers (DBIs) of phenolic compounds which widely coexist in environment, such as cosmetics, dye, pesticides, and pharmaceutical industries. They have great pollution because of their high toxicity and difficult to degrade property in the ecological environment [1,2]. It is significant to develop rapid and accurate analytical ways for the determination of them. Up to now, there have been many analytical methods to quantitatively determine HQ and CT, such as high-performance liquid chromatography [3], chemiluminescence [4] and electrochemical methods [5,6]. Among them, the electrochemical method has been widely concerned due to its fast response, low cost, high sensitivity and good selectivity. However, because of their similar structures and properties, they are difficult to separate and determine

simultaneously of the analyte. To resolve this problem, various materials have been used to manufacture the surface of working electrodes or as electrode materials, such as carbon nanotubes, metal sulfides and quantum dots [7–10]. But the production of appropriate materials is expensive, complex manufacturing and limited yield. So we urgently need a new kind of material to detect HQ and CT. Recently, metal-organic frameworks (MOFs) have been considered as a kind of rising-star materials with attracting enormous interests.

Metal-organic frameworks (MOFs) are a class of hybrid materials which possess unique chemical and physical properties with unprecedentedly large and uniform cavities. Recently, functional MOFs have attracted a great of research interest for their versatile applications in gas storage [11], drug delivery [12], catalysis [13,14], optical imaging [15] and sensing [16–19]. MOFs-based sensors have significant potential for developing powerful analytical techniques for the

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determination of biomolecules in environmental and industrial applications [13,20–22]. However, most of the MOFs are insulators and their electrochemical sensing applications are limited by the poor conductivity. Achieving effective electrochemical signal transduction as an important direction of MOFs biosensing research is how to prepare MOFs with redox activity and electrical conductivity while preserving its unique pore structure. An efficient way to resolve the problems is combining MOFs with other functional materials which have better electronic conductivity or make MOFs more stable [23]. Carbon materials have good electrical conductivity and stability. Cu-MOF [Cu-MOF = HKUST-1 = $\text{Cu}_3(\text{BTC})_2$ (BTC = 1, 3, 5-benzenetricarboxylic acid)], a copper-based MOF, is one of the most cited MOFs. The HKUST-1 has a large surface area, high pore volume, high chemical stability and the ability to combine water by coordinating to the unsaturated Cu(II) sites in other molecules [24–26]. Because of these properties, it is applied in the field of gas storage, catalysis and sensing applications [27]. For this purpose, GN and Cu-MOF composite materials stand out as a good partner to enhance the electroconductivity and the stability. Zhao et al. [28] combined Cu-MOF and GN with one-step synthesis to determine H_2O_2 and ascorbic acid with good performance.

In this work, the Cu-MOF has been synthesized using hydrothermal method and characterized by scanning electron microscopy (SEM) and X-ray diffraction (XRD). And the Cu-MOF-GN composite materials have been used to prepare the modified electrode, which is characterized by electrochemical methods, including of cyclic voltammetry (CV), differential pulse voltammetry (DPV) and electrochemical impedance spectroscopy (EIS). The GN not only can increase the electron transfer rate, but will also improve the stability of Cu-MOF. Then the Cu-MOF-GN modified glassy carbon electrode (Cu-MOF-GN/GCE) has been used for the simultaneous determination of HQ and CT with excellent electrochemical performance and extended linear ranges and lower detection limits. The method has been applied to the simultaneous analysis of these isomers in spiked tap water with great recoveries and relative standard deviations (RSDs). The MOFs-based sensors in the field of electrochemical sensing hold a great promise for routine sensing applications.

2. Experimental

2.1. Reagents and apparatus

Graphite was provided by Qingdao Fujin graphite Co., Ltd. friendly. Graphene was synthesized by using the modified Hummers method. Hydroquinone (HQ, purity $\geq 99.0\%$), catechol (CT, purity $\geq 99.0\%$) and 1, 3, 5-Benzenetricarboxylic acid (H_3BTC , purity $\geq 98.0\%$) were obtained from Aladdin (Shanghai, China). $\text{Cu}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (purity $\geq 99.0\%$), $\text{NaH}_2\text{PO}_4 \cdot 2\text{H}_2\text{O}$ (purity $\geq 99.0\%$) and $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$ (purity $\geq 99.0\%$) were obtained from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). N, N-dimethylformamide (DMF, purity $\geq 99.5\%$) and anhydrous ethanol (EtOH, purity $\geq 99.7\%$) were purchased from Tianjin Fuyu Fine Chemical Co., Ltd. Nafion D-521 dispersion (5% w/w in water and 1-propanol, ≥ 0.92 meq/g exchange capacity) was purchased from Alfa Aesar (Shanghai, China). 0.1 M phosphate buffer solutions (PBS) with different pH values (from 6.0 to 8.0) were prepared by mixing the $\text{NaH}_2\text{PO}_4 \cdot 2\text{H}_2\text{O}$ and $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$ in proper proportion. All chemicals were of analytical grade and used as received. The water used in all the experiments was double distilled water.

SEM images were obtained by JEOL JSM-6390LV (Japan). X-ray diffraction (XRD) data was obtained by Rigaku Ultima IV diffractometer (Japan). Filters (Tianjin Jinteng Instrument Factory, China). The electrochemical measurements were performed using a CHI-660C electrochemical workstation (Shanghai Chenhua Instrument Co., Ltd., China) with a conventional three-electrode cell.

2.2. Synthesis of Cu-MOF

The Cu-MOF was synthesized according to the previous literature with some modifications [29]. Firstly, 0.25 g of $\text{Cu}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and 0.25 g of H_3BTC were dissolved in 7.1 mL of deionized water and 7.1 mL of ethanol, respectively. The solution was mixed in a Teflon liner and placed in an autoclave. The autoclave was heated at 150 °C for 24 h, and then slowly cooled to room temperature. The blue powder was obtained by centrifugation and washed with water and DMF, and finally dried under vacuum at 80 °C for 24 h for further use.

2.3. Synthesis of graphene

To prepare GN from graphite, graphite oxide was first synthesized with graphite using a modified Hummers method [30]. In an ice-water bath, 0.6 g of graphite and 1.0 g of NaNO_3 were slowly added to 35 mL of ice H_2SO_4 with stirring. After that, 3.0 g of KMnO_4 was added slowly with the temperature under the 20 °C. And then, the temperature was raised to 35 °C and stirred for 30 min. 150 mL of deionized water was added to the system and the temperature was raised to 98 °C. After stirring for 15 min, the system was transferred to 200 mL of deionized water at 60 °C. The precipitate was washed by 5% HCl and the precipitate was placed in a freeze-oven for 5 h to obtain graphene oxide. The graphene oxide was coated on the surface of the glassy carbon electrode (GCE). The graphene oxide was electrochemically reduced to graphene by cyclic voltammetry (CV).

2.4. Preparation of the modified electrode

Prior to use, the GCE was polished with slurry of alumina oxide powder (0.3 μm and 0.05 μm) to obtain a mirror-like surface. Then the GCE was ultrasonically cleaned in absolute alcohol and distilled water for 2 min and dried by nitrogen for further use. 2 mg prepared Cu-MOF and 2 mg graphene oxide was ultrasonically dispersed in 2 mg of deionized water with 5 μL of nafion for 15 min to obtain a uniform dispersion. Then 6 μL of the dispersion was dropped on the electrode surface and dried under the room temperature. The Cu-MOF-GO composite was electrochemically reduced by cyclic scan between -1.6 and 0.6 V in 1 mM PBS (pH 7.0) until constant curves were achieved. The Cu-MOF-GN modified electrode was obtained, and the modified electrode was denoted as Cu-MOF-GN/GCE.

2.5. Sample pretreatment

Four tap water samples were collected from indoor in our college (Qingdao University, P. R. China). All water samples were collected in glass bottles and filtered through 0.45 μm filters to remove suspended particles. The filtrates immediately passed through strong acidic cation and strong alkaline anion ion-exchange resin, and then the samples after different addition of HQ and CT were determined by the proposed method [31]. The spiked recoveries were 99.0 ~ 102.9% and the RSDs for 5 successive measurements less than 5%, which indicated that this method was successfully applied to detect target analytes in the real samples with satisfying results.

2.6. Electrochemical measurement

All electrochemical experiments were performed at room temperature with a standard three-electrode system. The bare and modified glassy carbon electrode as the working electrodes. A platinum wire was used as the auxiliary electrode. All the potentials quoted here were referred to a saturated calomel electrode (SCE) electrode as the reference. DPV and CV measurements were used for electrochemical determination of HQ and CT. CV experiments were performed in the potential range of -0.4 – 0.8 V at a scan rate of 100 mV/s. The

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