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Determination of catechol and hydroquinone with high sensitivity using MOF-graphene composites modified electrode

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ABSTRACT

A composite (MOF-GO) of Cu-based MOF-199 (MOF) and graphene oxide (GO) was prepared by the solvothermal method and used as the modified material to fabricate an electrochemical sensor for the determination of catechol (CT) and hydroquinone (HQ). The modification was carried out through the electrodeposition of MOF-GO composites on the glassy carbon electrode and the transformation of MOF-GO to MOF-ERGO by an electrochemical reduction. Differential pulse voltammetry (DPV) was employed for exploring the electrochemical properties of the as-prepared electrode and the oxidation of CT and HQ at the modified electrode. Under the optimized experimental condition, the linear calibration curve was obtained in the range from 0.1 μM to 566 μM for CT ($R^2 = 0.997$) and 0.1 μM to 476 μM for HQ ($R^2 = 0.999$) with the same low detection limit of 0.1 μM ($S/N = 3$). The experimental results showed that the modified electrode was easily fabricated in control and exhibited the outstanding stability. The validity for practical samples detection of CT and HQ was also demonstrated with satisfactory results.

1. Introduction

Catechol (CT) and Hydroquinone (HQ), two isomers of dihydroxybenzene, are easily introduced into environment owing to their extensive use as raw materials and synthetic intermediates in chemical and pharmaceutical industries [1,2]. They are hazardous to both environment and human and difficult to be degraded in the ecological environment [3,4]. So they are considered as priority environmental pollutants and need to be monitored in the aquatic environment by the United States Environmental Protection Agency (EPA) and the European Union (EU) [5,6]. Therefore, it is necessary to develop a fast, simple and sensitive way to detect these two substances. Nowadays, there are some different ways to detect CT and HQ, including chromatography [7,8], fluorescence [9], spectrophotometry [10], chemiluminescence [11] and electrochemical method [12,13]. Unfortunately, most of them hold the requirements of the expensive instruments and the sample pretreatment, which possess the defects of the high cost and long time. For example, when spectrophotometry was employed to detect CT or HQ, the sample should be pretreated in order to make the sample have adsorption at a certain wavelength. Ni et al. [14] developed a spectrophotometric method to detect hydroquinone and phenol based on their inhibitory effect on the oxidation of Rhodamine B (RhB) in acid solution. Obviously, these methods are unfeasible for routine analysis. Compared to these methods, electrochemical method has a low requirement for the instrument and simple operation with the high sensitivity and good selectivity, indicating a more preferable way to the determination of CT and HQ. However, CT and HQ are difficult to be detected and distinguished at a commercial working electrode because their oxidation current peaks are overlapped. Therefore, many materials, such as carbon materials [15,16], conductive polymers [17], and metal and metal oxide nanoparticles [18–20], were employed to modify the electrode in order to distinguish these two peaks and enhance the current signals.

In recent years, metal-organic frameworks (MOFs) have aroused a lot of attentions for its large surface areas and tunable pore sizes, which have been applied widely in the fields of gas storage and separation, catalysis and clean energy [21–26]. Recently, MOFs were demonstrated as a novel material to modify the electrode for the electrochemical application because of the electrochemical activity of the metal ions and the well-ordered porous skeleton. MOFs have been reported as an effective electro-catalyst for the electrochemical reduction of CO_2 and O_2 [27–30]. MOFs also have been used to fabricate an electrochemical sensing platform to detect glutathione [31], ascorbic acid [32], hydrazine [33] and H_2O_2 [34]. Nevertheless, the electrochemical applications of pure MOFs still suffer from the intrinsic deficiency such as the instability in the aqueous solution and the low sensitivity. For solving these problems, the heterostructures of MOFs combined with other

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functional materials have been developed and performed the enhanced electrochemical performance and stability compared with the pure MOFs in different research areas [35–38]. Loh et al. [39] studied the electro-catalytic action of the composites of MOFs and graphene oxide (GO) on the hydrogen evolution reaction (HER), oxygen evolution reaction (OER), and oxygen reduction reaction (ORR). Their study showed that the composites exhibited the better electrochemical performance and stability in acid than that of pure MOFs due to the synergistic effect of GO and MOF. Wu et al. [40] also demonstrated the modification of MOFs-GO composites was able to increase the proton conductivity of Nafion based proton exchange membranes. Zhao et al. [41] reported that the composition of the copper-based metal-organic framework (Cu-MOF) and graphene led to an improving stability due to the multiple interactions, including hydrogen bonding, π-π stacking and Cu-O coordination between Cu-MOF and graphene. Moreover, the nanocomposites of Cu-MOF and graphene also showed an enhanced performance on the electrochemical detection of H_2O_2 and ascorbic acid because of the synergetic effect of these two materials.

Attracted by the reported advantages and the synergetic effect of MOFs and graphene, the copper-based MOF-199 and GO were selected to fabricate a modified electrode for the detection of CT and HQ. Recently we reported a modified electrode based on MOF-199 and single-walled carbon nanotubes (SWCNTs) for the simultaneous determination of CT and HQ. The modified electrode exhibited an excellent performance. However, the SWCNTs film easily peeled off with the increase of detection times. To avoid this kind of problems, the combination of MOF-199 and GO occurred in the synthetic stage of MOF-199 in this work. Then the MOF-GO modified glassy carbon electrode was fabricated by the electrodeposition method and an electrochemical reduction was subsequently carried out to transform GO into the reduced graphene oxide (ERGO). The combination way would not only make the electrochemical fabrication method very simple, but also make the modified electrode more stable in the actual detection. In the meanwhile, the electron transfer rate of the proposed modified electrode would increase because of the excellent conductivity of ERGO and the porous structure and large surface area of MOF. What's more, due to the π-π interactions between dihydroxybenzenes and benzenetricarboxylate (BTC) ligands of MOF-199, the electrochemical responses could be further improved due to the enrichment of dihydroxybenzenes on the electrode surface. With all the advantages above and the synergetic interaction of MOF and ERGO, the modified electrode exhibited the high performance for the determination of CT and HQ.

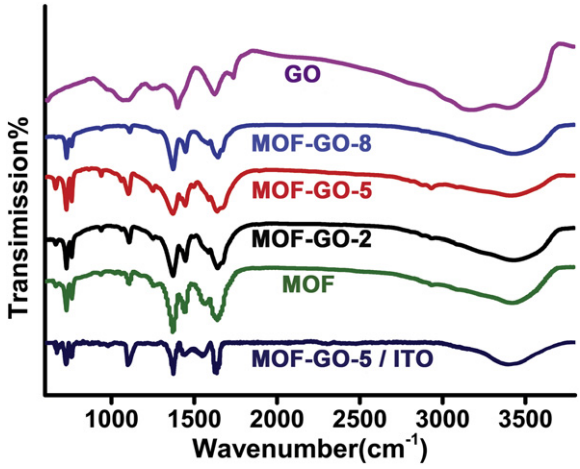

Fig. 2. FT-IR spectra of GO, MOF-GO-*n*, MOF and MOF-GO-5/ITO.

2. Experimental

2.1. Materials and reagents

The graphite powder was purchased from Nanjing Xianfeng Nano Co. (Nanjing, China). Copper nitrate hexahydrate ($Cu(NO_3)_2 \cdot 6H_2O$), sodium nitrate($NaNO_3$), sodium dihydrogen phosphate dihydrate ($NaH_2PO_4 \cdot 2H_2O$), dibasic sodium phosphate heptahydrate ($Na_2HPO_4 \cdot 7H_2O$), *N*,*N*-dimethylformamide (DMF), hydrogen peroxide(30%), dichloromethane and ethane were obtained from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). Trimesic acid (H_3BTC) was acquired from Aladdin. All these chemicals are analytical grade and used as-received without further purification.

2.2. Apparatus

FT-IR spectra were recorded on a NEXUS FT-IR spectrophotometer from 500 to 4000 cm^{-1}. Raman spectra were tested by a RENISHAW Raman spectroscopy. Powder X-Ray diffraction (XRD) was carried out using an X-ray diffractometer (RU-200B/D/MAX-RB) with Cu Kα (40 kV, 40 mA, λ = 1.54050 Å). Scanning electron microscopy (SEM) was carried out on A Hitachi S4800 scanning electron microscope. The pH values were measured on a PH-25 digital acidometer (PR China).

All the electrochemical experiments were performed on a CHI660D electrochemical analyzer (CH. Instruments, Shanghai Chenhua Instrument Corporation, China). A conventional three-electrode cell

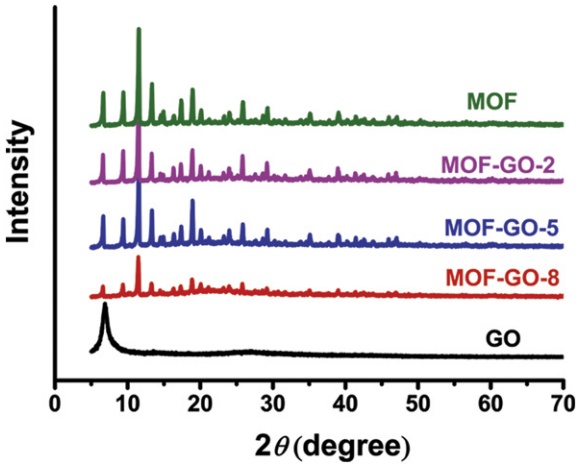

Fig. 1. XRD patterns of MOF, MOF-GO-*n*, and GO.

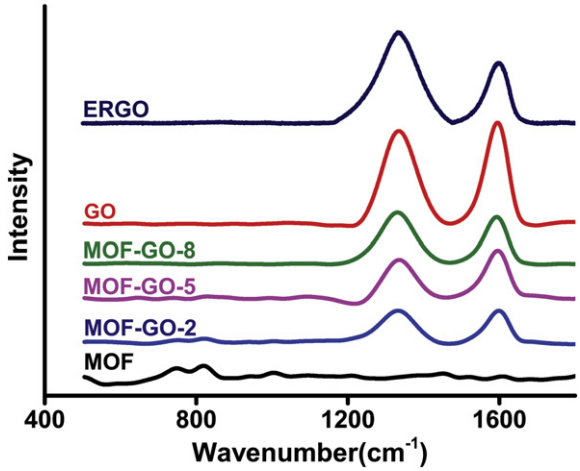

Fig. 3. Raman spectra of ERGO, GO, MOF-GO-*n* and MOF.