



# Electrodeposition of graphene oxide doped poly(3,4-ethylenedioxythiophene) film and its electrochemical sensing of catechol and hydroquinone

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## ABSTRACT

A novel poly(3,4-ethylenedioxy-thiophene) (PEDOT)/graphene oxide (GO) hybrid film was directly electrodeposited on a glassy carbon electrode. The SEM and TEM images of the as-obtained film revealed that PEDOT grew well on the surface of GO sheets with high affinity. The chemical structure of the composite was characterized by FT-IR, and the result conformed the formation of PEDOT doped by GO, leading to the enhanced electrochemical performance of the modified electrode. The composite modified electrode was utilized as an electrochemical sensor for the simultaneous detection of hydroquinone (HQ) and catechol (CT). It showed well electrocatalytic activity toward the redox of HQ and CT. Under the optimized condition, the response peak currents of the modified electrodes were linear over ranges from 2.5 to 200  $\mu\text{M}$  for HQ and from 2 to 400  $\mu\text{M}$  for CT. The sensor also exhibited good sensitivity with the detection limit of 1.6  $\mu\text{M}$  for both HQ and CT, and good stability. This study provides a new kind of composite modified electrode for electrochemical sensors.

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## 1. Introduction

Hydroquinone (HQ) and catechol (CT) are two important isomers of dihydroxybenzene, which are widely used in dye, cosmetics, antioxidants, secondary coloring matters, and so on, and can easily be introduced into environment as pollutants due to their high toxicity and low degradability in the ecological environment [1]. Moreover, the dihydroxybenzene isomers often coexist and interfere with each other because of the similar structure and property. Therefore, the design and development of effective analytical methods are strongly demanded for the simultaneous determination of HQ and CT.

Several methods have been exploited for the determination of dihydroxybenzene analysis, such as chromatography [2], spectrophotometry [3], synchronous fluorescence [4], etc. Among these methods, chromatographic method is commonly employed as standard analytical methods, but it has the disadvantages of high cost, time-consuming and complicated pretreatment. Optical methods usually need some additional reagents for signal generation. Thus, it is still highly challenging but desirable to develop a quick, simple and sensitive method for simultaneous determination of HQ and CT.

Recently, an electrochemical method has received increasing great attention for the detection of such reagents due to its simple, sensitive, and more feasible analysis. And the use of chemically modified electrodes provides a tool for improving the performance of solid electrodes. More and more functional materials are used to fabricate the modified electrode for sensors. For instance, the simultaneous determination of HQ and CT at a glassy carbon electrode (GCE) modified with multiwall carbon nanotubes (CNTs) [5], polythionine (PTH) [6], and polyaniline (PAN) [7] have been reported with acceptable sensitivity, respectively.

In the recent years, graphene oxide (GO) has attracted more and more attentions for the construction of chemical modified electrode in the area of sensors [8,9], due to a similar structure of graphene with plenty functional groups. The oxygen-containing groups on GO sheets may protect carbon sheets from restacking and agglomeration, and allow it readily swell and disperse in water and some other solvents [10,11], and also act as the combining sites for graphene-based composites. Due to the poor conductivity of GO, conducting polymers are welcome to combine with GO to form a novel conducting composite for various applications [12]. Poly(3,4-ethylenedioxythiophene) (PEDOT) is one of the most studied conducting polymers in electrochemical sensors due to its good stability, high-speed electron transfer, and easy formation of the tenacious film. PEDOT modified electrodes are reported to have good electrocatalytic effect on the phenolic compounds, dopamine, uric acid and morphine [13–15]. However, the combination of GO or graphene with PEDOT for electrochemical sensors has been few reported, although their novel hybrid materials usually prepared

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via chemical or self-assembled approaches are widely studied in energy storage systems [16,17].

Herein, we firstly report a facile electrodeposition method to fabricate the GO doped PEDOT (PEDOT/GO) film for the simultaneous determination of HQ and CT as an electrochemical sensor. The novel PEDOT/GO modified GCE exhibited good electrochemical performance and good electrocatalytic activity to the redox reactions of HQ and CT, and the sensor based on PEDOT/GO showed good stability and acceptable sensitivity. The morphology and chemical structure of the hybrid film were well-characterized. The performance of the fabricated electrode and the electrochemical behavior of the isomers were investigated by cyclic voltammetry (CV), differential pulse voltammetry (DPV) and electrochemical impedance spectroscopy (EIS).

## 2. Experimental

### 2.1. Reagents and apparatus

Graphene oxide was prepared from natural graphite (12,000 mesh) by a modified Hummers method we described elsewhere [18]. 3,4-Ethylenedioxythiophene (EDOT) was obtained from Aladdin reagents. Catechol and hydroquinone were purchased from Sinopharm Chemical Reagent Beijing Co., Ltd. Disodium hydrogen phosphate, dihydrogen phosphate and citric acid were purchased from Nanjing Chemical Reagent Co., Ltd. All reagents were obtained as analytical grade and used without further purification. Millipore water from a Milli-Q water purifying system ( $18\text{ M}\Omega\text{ cm}^{-2}$ ) was used for all experiments.  $0.1\text{ mol L}^{-1}$  citric acid/disodium hydrogen phosphate buffer solution (CPS) was prepared from citric acid and  $\text{Na}_2\text{HPO}_4$ .  $0.1\text{ mol L}^{-1}$  phosphate buffer solution (PBS) was prepared from  $\text{NaH}_2\text{PO}_4$  and  $\text{Na}_2\text{HPO}_4$ . All experiments were performed at room temperature. ( $22 \pm 0.5\text{ }^\circ\text{C}$ )

Electrochemical experiments were performed with a CHI660D electrochemical workstation (Shanghai Chenhua Co., Ltd., China) coupled with a conventional three-electrode cell. A bare or modified GCE (CHI104,  $d=3\text{ mm}$ ) was used as the working electrode. A saturated calomel electrode (SCE) and a platinum wire electrode were used as reference and auxiliary electrodes, respectively. Field emission scanning electron microscope (SEM) and transmission electron microscopy (TEM) images were obtained with S-4800 (Hitachi Co., Ltd., Japan) and JEM-2100 (JEOL Co., Ltd., Japan), respectively. The Fourier-transform infrared spectroscopy (FT-IR) spectra were recorded with Nicolet IS-10 (Thermo Scientific Co., Ltd., USA).

### 2.2. Preparation of PEDOT/GO modified electrode

Prior to electro-deposition, the GCE was sequentially polished with  $1\text{ }\mu\text{m}$ ,  $0.3\text{ }\mu\text{m}$  and  $0.05\text{ }\mu\text{m}$  alumina/water slurry (Shanghai

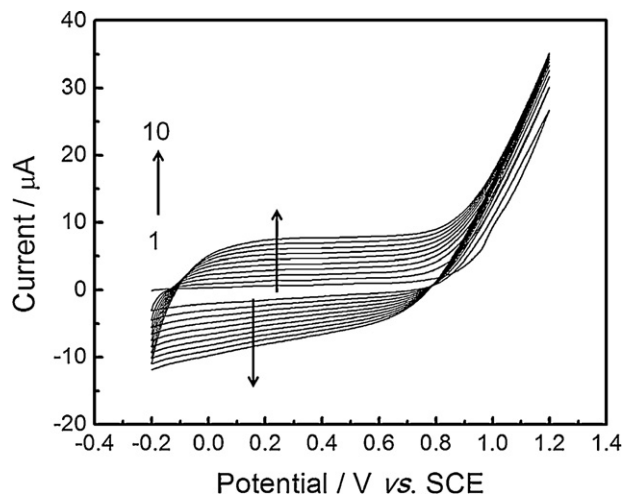


Fig. 1. CVs of GCE in  $0.01\text{ M}$  EDOT +  $1\text{ mg ml}^{-1}$  GO at a sweep rate of  $100\text{ mV s}^{-1}$  in the potential range between  $-0.2$  and  $1.2\text{ V}$  vs SCE.

Chenhua Co., Ltd., China) on a polishing cloth to a mirror-like finish. Then the polished GCE was rinsed with water and sequentially ultrasonicated in water, acetone,  $0.1\text{ M}$  NaOH and water for 5 min, respectively. After that, the GO doped PEDOT film was successfully generated on the surface of the clean GCE via the following electrochemical deposition procedure. GO ( $1\text{ mg ml}^{-1}$ ) and EDOT ( $0.01\text{ M}$ ) were dispersed in  $5\text{ ml}$  water and ultrasonicated for 30 min. The electrochemical polymerization of EDOT in presence of GO was performed by CV with potential scanning between  $-0.2$  and  $1.2\text{ V}$  at  $100\text{ mV s}^{-1}$ , under the condition of magnetic stirring and  $\text{N}_2$  bubbling.

### 2.3. Electrochemical measurements

CV and DPV were employed for examining the electrochemical signal of the as-fabricated PEDOT/GO electrode (PGE) and bare GCE to a certain amount of HQ or CT in  $0.1\text{ mol L}^{-1}$  CPS and  $0.1\text{ mol L}^{-1}$  PBS. The DPV conditions were as follows: potential increase,  $0.004\text{ V}$ ; amplitude,  $0.05\text{ V}$ ; pulse width,  $0.05\text{ s}$ ; pulse interval,  $0.2\text{ s}$ .

## 3. Results and discussion

### 3.1. Fabrication and characterization of PEDOT/GO film

The PEDOT/GO film was electropolymerized onto the GCE by CV as described in Section 2.2. The light blue film with metallic luster was formed slowly on the GCE. The cyclic voltammograms (CVs) of GCE in EDOT and GO solution are shown in Fig. 1. As revealed

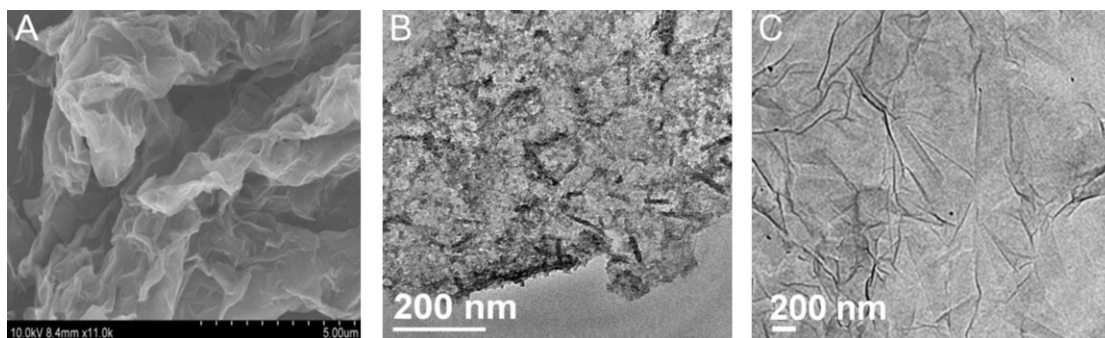


Fig. 2. SEM image of the PEDOT/GO modified electrode (A) and TEM images of the PEDOT/GO (B) and GO (C).

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