

Graphene quantum dots modified glassy carbon electrode *via* electrostatic self-assembly strategy and its application



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ABSTRACT

An electrostatic self-assembly strategy for the preparation of graphene quantum dots (GQDs) attached to the surface of a glassy carbon electrode (GCE) has been developed. The GQDs were prepared by tuning the carbonization degree of citric acid and characterized by atomic force microscopy, transmission electron microscopy, Raman spectroscopy and UV–vis absorption spectroscopy. In addition, the electrochemical behaviours of hydroquinone (HQ) and catechol (CC) on the resulting modified electrodes were investigated. Under optimum conditions, the as-prepared GQDs modified electrode exhibited high electrochemical activity and good selectivity for the oxidation of HQ and CC, the linear ranges for HQ and CC were 4.0–600 μM and 6.0–400 μM respectively, and the detection limit was 0.40 μM and 0.75 μM , respectively. The modified electrode was also applied for the detection of real samples with satisfactory results.

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1. Introduction

Hydroquinone (HQ) and catechol (CC) are two isomers of phenolic compounds that are widely used in pharmaceuticals, cosmetics, antioxidants, photography and dyes. Unfortunately, these phenolic compounds are considered to be significant toxic airborne environmental pollutants. Therefore, the development and establishment of a reliable analytical method for the determination of HQ and CC is crucial. Various methods, such as high performance liquid chromatography (HPLC) [1], gas chromatography-mass spectrometry (GC-MS) [2], chemiluminescence [3], capillary electrochromatography [4], and electrochemical methods [5], have been used to determine HQ and CC in different samples. Among these methods, electrochemical methods have received considerable attention for HQ and CC detection due to high sensitivity, good selectivity and simplicity. However, improvement in the selectivity poses a major challenge for the electrochemical determination of HQ and CC, because these two isomers of phenolic compounds possess similar structures, electrochemical properties and coexistence of usual interference. Several advanced materials with superior electrocatalytic activity (i.e., graphene [6], $\text{g-C}_3\text{N}_4$, carbon nanotubes composites [7] and

several other metal-nanoparticles [8,9]) have been introduced on electrode interfaces to address these problems.

Graphene quantum dots (GQDs), which are a new member of the carbon nanomaterial family, have attracted considerable scientific attention due to their unique, excellent physical and chemical properties. Owing to better quantum confinement, more edge defects, high aqueous solubility, strong photoluminescence (PL) emission, desirable fluorescence properties and low cytotoxicity, GQDs have been developed for applications in various fields, such as photocatalysis [10], biosensing [11] and chemiluminescence analysis [12]. GQDs can be prepared using two strategies, including the top-down method and the bottom-up growth process. Most top-down methods include cutting graphene oxide (GO) by a hydrothermal method [13] and graphitic exfoliation by an electrochemical route [14]. However, the bottom-up process primarily involves carbonization of some special organic precursors, especially citric acid (CA) *via* thermal treatment [15]. In comparison, the bottom-up growth process is widely used in the characteristics of its simple operation, low environmental pollution, low cost, better purity and aqueous solubility.

Recently, much attention has been focused on electrostatic self-assembly for the preparation of electrochemical sensing interfaces due to the simple procedure and structural control [16–18]. The electrostatic self-assembly strategy is a versatile nanofabrication technique, which exhibits remarkable advantages over conventional methods in terms of versatility and simplicity. In addition,

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this method allows for molecular-level control over the structure and composition with simple benchmark operations [19].

To the best of our knowledge, the application of GQDs for electrochemical sensors has been rarely explored. In the current study, GQDs were prepared by tuning the carbonization degree of citric acid and followed by characterization using various techniques. Then, the GQDs were attached to the surface of a glassy carbon electrode (GCE) using an electrostatic self-assembly strategy. The GQDs modified electrode was used to investigate the electrochemical behaviour of HQ and CC. Benefiting from the advantages of GQDs, the GQDs modified electrode exhibited excellent performance, such as high electrochemical activity, good selectivity and high sensitivity for the simultaneous determination of HQ and CC. The main contribution of this study is the preparation of the GQDs modified electrode using an electrostatic self-assembly strategy.

2. Experimental

2.1. Chemicals and Apparatus

Citric acid (CA, A.R.), Hydroquinone (HQ, A.R.) and Catechol (CC, A.R.) were purchased from the Tianjin Kemiou Chemical Reagent Co., Ltd (Tianjin, China). Poly (diallyldimethylammonium chloride) (PDDA, MW < 100 000) was purchased from Aladdin (Shanghai, China). Phosphate buffer solutions with various pH values were prepared by mixing 0.10 mol L⁻¹ Na₂HPO₄ and NaH₂PO₄. All of the other chemical reagents were of analytical grade and used without further purification. Double distilled ultrapure water with an electric resistance >18.3 MΩ was used for the preparation of all the solution.

The electrochemical experiments were carried out with a CHI 660D (CH Instruments, Inc., Shanghai, China) electrochemical workstation and VMP2 potentiostat controlled by the EC-Lab software (Princeton, USA). A bare glassy carbon electrode (GCE) or the modified GCE were used as the working electrode (WE), a Pt wire was applied as the counter electrode (CE), and all of the potentials were referred to a saturated calomel electrode (SCE). Atomic force microscopy (AFM) was performed using a multi-mode nanoscope IIIa controller (Veeco, USA). Transmission electron microscopy (TEM) was performed with a Tecnai G220 (FEI, USA) operating at 200 kV. The Raman spectrum was recorded using laser confocal micro-Raman spectroscopy (LabRAM HR800, France). The light absorption properties of the samples were

recorded on an ultraviolet-visible (UV-Vis) spectrophotometer (UV-2450, Shimadzu Corporation, Japan)

2.2. Synthesis of GQDs

The GQDs were synthesized using pyrolysis CA method based on a previous study [15]. Briefly, 2.0 g of CA powder was placed into a 10 mL breaker and heated to 473 K for 30 min until the CA was liquated and the colour of the CA liquid changed from colourless to orange. Then, 100 mL of a 10 mg mL⁻¹ NaOH solution was added dropwise into the obtained orange CA liquid under vigorous stirring followed by adjustment of the pH value to 7. Finally, the aqueous GQDs solution was obtained.

2.3. Preparation of GQDs modified electrode

GQDs/GCE was fabricated using an electrostatic self-assembly strategy (Fig. 1). Prior to use, the bare GCE (3 mm diameter) was carefully polished by 0.3 μm and 0.05 μm Al₂O₃ powder slurries for several times to produce a mirror like finish. Then the electrode was ultrasonically washed with distilled water and ethanol for several minutes and dried in blowing N₂ prior to use. The activated GCE (record as OH⁻/GCE) was prepared according to the previously reported protocols [20]. The clean GCE was activated in 0.05 mol L⁻¹ H₂SO₄ by CV in a range from 0.0 to 2.0 V at a scan rate of 50 mV s⁻¹. Next, the OH⁻/GCE was washed with copious amounts of water and dried in flowing N₂. Then, the OH⁻/GCE was immersed in a 0.3 wt% solution of poly (diallyldimethylammonium chloride) (PDDA, MW < 100 000) for 10 min to prepare a positively charged surface. Finally, the electrode was immersed in the above-mentioned GQDs solution for 15 min, rinsed with deionized water and dried with N₂ to afford the GQDs/GCE.

3. Result and discussion

3.1. Preparation and characterization of GQDs

In the current study, the GQDs were prepared using the pyrolysis CA method based on a previous study [15]. Fig. 2A and 2B show the typical AFM images of the resulting GQDs. Based on these images, the as-prepared GQDs are highly dispersed on the substrate (Fig. 2A) with a typical topographic height distribution from 0.5~1.5 nm (1.1 nm average thickness), signifying that most of the GQDs typically consist of ca. 1~4 graphene layers (Fig. 2B) [21].

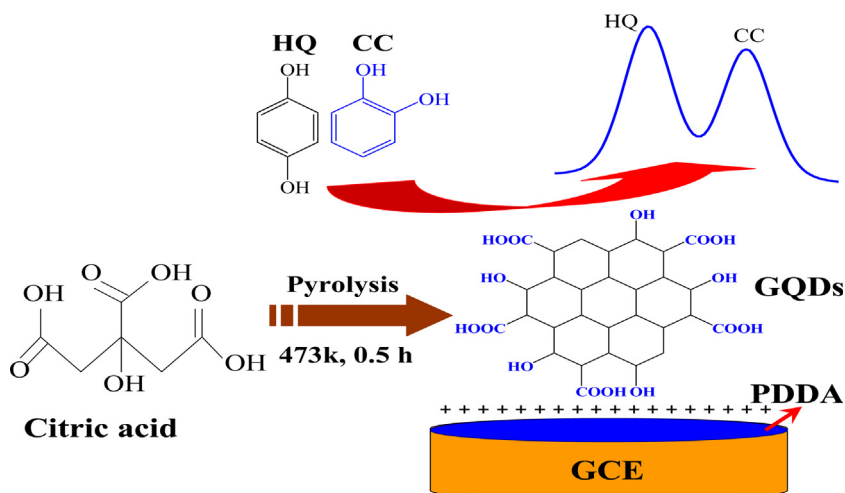


Fig. 1. Schematic drawing of the synthesis of GQDs from pyrolysis citric acid and electrochemical oxidize HQ and CC on GQDs/GCE.

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