



The immobilization of graphene quantum dots by one-step electrodeposition and its application in peroxydisulfate electrochemiluminescence



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ABSTRACT

This work reports a facile approach to achieve the immobilization of graphene quantum dots (GQDs) by one-step electrodeposition and the electrochemiluminescence (ECL) behaviors of the graphene quantum dots-chitosan (GQDs-CHIT) film was investigated with peroxydisulfate ($K_2S_2O_8$) solution as coreactant. Compare with the traditional dispensing method, the GQDs-CHIT/Au electrode by one-step electrodeposition showed more stable ECL signal. And the ECL signal of GQDs-CHIT modified electrode in $K_2S_2O_8$ solution was about 11-fold enhanced than that of bare electrode with the ECL onset potential positive shifted from -1.03 V to -0.82 V. Based on the above, an ECL sensor for $K_2S_2O_8$ determination was fabricated. The as-prepared ECL $K_2S_2O_8$ sensor shows wide linear response of 0.01–150 mM with the detection limit 3.3 μ M ($S/N = 3$). Moreover, we expect this method for the immobilization of GQDs can open up new prospects for the utilization of GQDs in electrochemical sensors.

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1. Introduction

As a valuable analytical technique, electrochemiluminescence (ECL) has aroused great interests in analytical chemistry owing to its distinct advantages of simplicity, rapidity, sensitivity, controllability and low background [1,2]. Thus, a number of ECL systems have been discovered and studied, including Ru complex [3–5], luminol [6,7], semiconductor quantum dots [8,9] and peroxydisulfate system [10]. Among these different ECL reactions that have been classified, quantum dots (QDs) [11–13] have been accepted as ECL indicators for their effective and valuable ECL behavior. However, these heavy metals have raised serious health and environmental concerns [14,15]. Thus, it is very necessary to search for novel nanomaterials with good ECL activities.

Graphene quantum dots (GQDs), as a new type of QDs, have attracted broad attention due to their unique electro-optical properties. Unlike traditional semiconductor QDs, GQDs possess superior properties like good biocompatibility, excellent solubility, high electrical conductivity and low toxicity. In recent years, GQDs [16–21] and GQDs based nanomaterials [22] are starting to be used in ECL due to their excellent ECL properties. For example, Li and co-workers [16] developed a facile microwave-assisted approach for the preparation of stabilizer-

free two-color GQDs, whose ECL behaviors were observed with $K_2S_2O_8$ as coreactant at the first time. And furthermore, a novel ECL sensor for Cd^{2+} was proposed. Due to the low cytotoxicity and excellent biocompatibility, GQDs are demonstrated to be an eco-friendly material as well as excellent ECL for sensors [17]. Chen's group found that L-cysteine (L-Cys) could serve as a new coreactant of ECL reactions of single-layer GQDs [18] and the possible ECL mechanism was investigated. The newly developed CQD/L-Cys ECL system has been applied in the selective and sensitive detection of lead (II) ions. However, in these ECL sensors, GQDs were put in the detection solution instead of immobilized on the electrode. Compared with putting GQDs in the detection solution, immobilizing GQDs on the electrode has fascinating advantages such as saving reagents, extending the application of GQDs, even improving the ECL efficiencies of GQDs. Thus, it is necessary to provide a method for achieving the immobilization of GQDs.

Persulfate, as a stable and powerful oxidant, has attracted increasing attention and been used for many applications [23–25]. However, it has been reported that persulfate may cause or aggravate diseases such as asthma [26] and skin reactions [27]. Until now, several impressive techniques have demonstrated the feasibility for the assay of persulfate [28, 29] including reductometric [30], polarographic [31], spectrophotometric [29,32] and electrochemical [27]. However, the above techniques have been criticized for time consumption, sample pretreatment, and complicated procedure. Thus, considerable efforts have been devoted to overcoming these problems.

Here, we provide a method for achieving the immobilization of GQDs. Chitosan, as a soluble polysaccharide compound, has been used

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as stabilizer and dispersing agent for QDs. So, GQDs-chitosan (CHIT) membrane was fabricated on the surface of Au electrode by a one-step electro-deposition method. The results showed that the electro-deposition membrane showed better distribution and stability than the traditional dispersing method. Based on the immobilization of GQDs, a novel ECL sensor for detection of $K_2S_2O_8$ was constructed. We hope this method for the immobilization of GQDs can open up new prospects for the utilization of GQDs in electrochemical sensors, which will further extend the application of an ECL detection method to construct biosensors.

2. Experimental

2.1. Reagents

CHIT was obtained from Sigma–Aldrich. Pitch carbon fibers directly purchased from Zhenjiang Hengshen Co. Ltd. PBS (0.1 M, pH 7.4) was used as the supporting electrolyte, which was prepared by mixing stock standard solutions of NaH_2PO_4 and Na_2HPO_4 , and adjusted the pH with 0.1 M H_3PO_4 or NaOH solution. Other reagents were of analytical grade and used as received without further purification, and all solutions were prepared with twice-distilled water.

2.2. Apparatus

Transmission electron microscopy (TEM) image was taken with a JEOL 2100 transmission electron microscopy (JEOL, Japan) operated at 200 kV. Atomic force microscopy (AFM) measurements were carried out using Bruker Innova Microscope instrument in tapping mode using antimony n-doped Si tip of 10 nm resolution. X-ray photoelectron spectroscopy (XPS) was surveyed with an X-ray photoelectron spectrometer (PHI 5000 VersaProbe, Japan). UV–vis absorption spectra were measured by UV-2450 spectrophotometer (Shimadzu, Japan). Fluorescence spectra were recorded on a Hitachi F-4500 fluorescence spectrophotometer (Tokyo, Japan). The photographs were taken using a Canon digital camera (IXUS 230 HS, China) under the illumination of a 365 nm UV lamp.

Electrochemical signals were recorded using CHI660 B electrochemical analyzer (Chen Hua Instruments, Shanghai, China) and ECL curves were recorded by a Model MPI-A ECL analyzer system (Xi'an Remax Electronic Science and Technology Co., Ltd., Xi'an, China). The photomultiplier tube (PMT) was biased at 800 V in the process of detection. All electrochemical and ECL curves were recorded by a conventional three-electrode system where a gold electrode (Au, 2 mm in diameter) was used as working electrode, a Ag/AgCl (saturated KCl solution) as reference electrode and platinum wire as counter electrode, respectively. The electrochemical measurements were performed in the potential range of 0 to -1.6 V with a scan rate of 100 mV s^{-1} .

2.3. Preparation of GQDs

According to the previous literature [33], 0.15 g pitch carbon fibers was added into a mixture of concentrated H_2SO_4 (98%, 30 mL) and HNO_3 (65%, 10 mL). The solution was sonicated for 2 h and then stirred for 24 h at 100 °C. The mixture was cooled and diluted with twice distilled water. Then, the pH was adjusted to 8.0 with Na_2CO_3 . The final product solution was further dialyzed in a dialysis bag (retained molecular weight: 2000 Da) for 3 days.

2.4. Fabrication of the modified electrodes

Prior to modification, the gold electrode was firstly polished with sand paper followed by 1.0, 0.3, and 0.05 μ m alumina slurry, respectively, and then sonicated in water to remove any residues.

The deposited nanocomposite solution was prepared as follows: CHIT solution of 0.5 wt.% was prepared by dissolving CHIT in 0.5 vol.%

aqueous acetic acid solution. The GQDs solution (10 mL, 0.4 mg mL^{-1}) was added into the CHIT solution (10 mL) and the mixture was sonicated for 5 min to obtain a GQDs-CHIT colloidal solution (0.2 mg mL^{-1}). Electrochemical deposition process was performed by dipping the Au electrode in the GQDs-CHIT solution at a constant negative potential of -2.3 V at 50 mV s^{-1} for 180 s. The electrode was then removed from the solution and rinsed with water to obtain a GQDs-CHIT film modified electrode (GQDs-CHIT/Au electrode). And the mechanism of electrodeposition is as follows [34] (Scheme 1): During the process of electrodeposition, the H^+ in GQDs-CHIT colloidal solution could be reduced to H_2 at the applied potential of -2.3 V, resulting in gradually increased pH value at the electrode surface. As the solubility of CHIT is pH-dependent, when the pH was higher than the pKa of CHIT (about 6.3), dissolved CHIT flocculated to form an insoluble hydrogel network due to the deprotonation of its amine groups. As a result, CHIT hydrogel incorporated with GQDs was electrodeposited on the cathode surface. Because of the generation of a CHIT gradient above the cathode surface, more CHIT would diffuse to the cathode from the distance, and continuous electrochemical reduction of H^+ produced more insoluble hydrogel to be deposited onto the cathode surface. Finally, GQDs-CHIT architecture was formed on the electrode surface.

GQDs/Au electrode and CHIT/Au electrode were also prepared with the same procedure as described above, respectively. As comparison, 6 μ L of 2.0 mg mL^{-1} GQDs-CHIT solution was casted onto the surface of pretreated Au electrode to form GQDs-CHIT/Au electrode. All of the modified electrodes were rinsed with water for several times prior to use.

3. Results and discussion

3.1. Characterization of the GQDs and GQDs-CHIT film

The FT-IR result of the as-prepared GQDs is displayed in Fig. 1A. The characteristic peak observed at 1421 cm^{-1} illustrated the presence of C–OH, and the peak located at 1640 cm^{-1} showed the existence C=O in carboxylic acid and carbonyl moieties. Fig. 1B shows the UV–vis absorption of GQDs, a typical absorption peak at ca. 300 nm can be observed. The emission spectra of the GQDs showed a strong peak at 500 nm. The inset of Fig. 1B showed the optical images of the GQDs with green emission under UV illumination.

XPS measurements were performed to further prove the composition of GQDs. The dominant graphitic C1s peak at 285 eV and O1s peak at ca. 532 eV for GQDs were showed in Fig. 1C. The high resolution C1s XPS spectra deconvoluted into three peaks were showed in Fig. 1D. And the peaks located at the binding energy of 284.7 eV were attributed to the C–C and C=C bonds. 286.2 and 287.5 eV could be assigned to the C–OH and C=O oxygen-containing carbon bands, respectively. The result indicated the prepared GQDs were functionalized with hydroxyl, carbonyl, and carboxylic acid groups.

The morphology of the as-prepared GQDs was displayed in Fig. 2. As shown in Fig. 2, the resulting GQDs was uniformly distributed with about 1–5 nm in size. The inset was the related TEM image in higher magnification. The 2D features and thicknesses of the GQDs were further characterized by the corresponding AFM (Fig. 2B), which revealed an average typical topographic height of 3 nm, suggesting that most of the GQDs consisted of few layers.

3.2. Electrochemical and ECL characterization of GQDs-CHIT/Au electrode

The ECL behaviors of bare Au electrode, CHIT/Au electrode, GQDs/Au and GQDs-CHIT/Au electrode were compared in 0.1 M PBS containing 0.05 M $K_2S_2O_8$ (Fig. 3A). It is clearly that the ECL signal of GQDs-CHIT/Au electrode (curve d) was much higher than that of bare Au electrode (curve a) and CHIT/Au electrode (curve b), suggesting that the immobilization of GQDs by the one-step electrodeposition. In addition, the ECL signal of the GQDs-CHIT/Au electrode was about 3-fold enhanced

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