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Graphene enhanced electrochemiluminescence of CdS nanocrystal for H_2O_2 sensing

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ABSTRACT

Graphene-CdS (G-CdS) nanocomposites were successfully prepared by CdS nanocrystals (CdS NCs) formed in situ on the surface of graphene sheets, using graphene oxide (GO) sheets with rich negatively charged carboxylic acid groups as starting materials. Compared with pure CdS NCs, the presence of the graphene doped in G-CdS nanocomposites could facilitate the electrochemical redox process of CdS NCs; further, the as-prepared G-CdS nanocomposite can react with H_2O_2 to generate strong and stable electrochemiluminescent (ECL) emission, which not only enhances its ECL intensity by about 4.3-fold but also decreases its onset potential for about 320 mV. The as-prepared solid-state ECL H_2O_2 sensor shows acceptable linear response from 5 μM up to 1 mM with a detection limit of 1.7 μM (S/N = 3). The ECL H_2O_2 sensor exhibits excellent reproducibility and long-term stability. Such a property would promote the potential application of the graphene as enhanced materials in fabricating sensors for chemical and biochemical analysis.

1. Introduction

Graphene, a new two-dimensional carbon nanomaterial with outstanding physical and chemical properties, has become one of the most exciting topics of both fundamental science and applied research in the last three to four years [1]. As ideal electrode materials with high surface area [2], excellent conductivity [3], unique graphitized basal plane structure and low manufacturing cost [4], both graphene and its composites have made an impact in the field of electrochemical catalysis, sensing and biosensing [5–11]. Papakonstantinou and co-workers [5] demonstrated that multilayer graphene nanoflake for simultaneously determining dopamine, ascorbic acid, and uric acid. It was also found that the graphene-modified electrode could determine dopamine in a large excess of ascorbic acid, showing a better performance than multi-walled carbon nanotubes-modified electrode [6]. Furthermore, Niu's group [7] reported that the polyvinylpyrrolidone-protected graphene/polyethylenimine-functionalized ionic liquid nanocomposite exhibited great electrocatalysis toward the reduction of H_2O_2, and further the direct electron transfer of glucose oxidase (GOD) was achieved. These results indicate that graphene shows great potential as enhanced materials to fabricate the electrochemical sensing interface, and up to now, it is just the beginning of this fantastic topic.

Semiconductor CdS has generated enormous interests in electrochemiluminescence (ECL) analysis due to its ready preparation and good chemical stability [12]. Previous reports have proved electrochemical reduced and oxidized CdS nanomaterials could produce ECL with the coreactant H_2O_2 [13], and further studies indicated that CdS doped by the suitable substance within the certain content region, can not only enhance the ECL intensity, but also decrease the ECL onset potential [14–16]. Chen and co-workers [14] have demonstrated CdS nanocrystals (CdS NCs) doped with carbon nanotubes showed a 5-fold enhanced ECL than CdS film and the ECL starting voltage shifts positively from −1.15 to −0.85 V. Li and co-workers [15] have indicated that the ECL intensity of CdS-Ag nanocomposite arrays (CdS-Ag NCAs), prepared by 10-min electrodeposition time, is 5-fold of CdS hierarchical nano-arrays (CdS HNAs), and the ECL onset voltage shifts positively by 0.45 V. However, the ECL intensity of CdS-Ag NCAs decreased when the electrodeposition time was over 10 min, and even obviously less than that of CdS HNAs when the electrodeposition time is 30 min. Recently, Xu and co-workers [16] found that the MWCNT-CdS nanocomposite fabricated by an in situ synthesis method showed much more sensitive ECL responses compared with that of the MWCNT-CdS composite obtained under simple ultrasonication mix at a desired ratio.

To our best knowledge, there is scarce study to investigate the effect of graphene on CdS NCs ECL behaviors, and further explore the application of graphene/CdS NCs in the field of ECL analysis. Recently, Rajamathi and co-workers [17] demonstrated the synthesis of graphene-nanocrystalline metal sulphide composites by a one-pot reaction starting from Hummers' GO [18], but the exfolia-

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tion and aggregation phenomenon of the metal sulphide from the composites was very serious. In the present study, graphene oxide (GO) sheets with rich negatively charged carboxylic acid groups were prepared by the modified Hummers' method [19], and the as-prepared GO sheets were further adopted to in situ fabricate graphene-CdS (G-CdS) nanocomposite. And then the ECL behaviors of G-CdS nanocomposite were investigated in H_2O_2 solution, showing that the presence of graphene doped in G-CdS nanocomposites could decrease the onset potential of the ECL reaction between CdS NCs and H_2O_2 with greatly enhanced ECL intensity.

2. Experimental

2.1. Reagents

$Cd(NO_3)_2{\cdot}4H_2O$, H_2O_2 (30%, w/v, solution) and ethanol were purchased from Sinopharm Chemical Reagent Co., Ltd. Nafion (5%) was purchased from Sigma–Aldrich. Other reagents were of analytical grade and used as received without further purification. All solutions were prepared with twice-distilled water and 0.10 M pH 9.0 phosphate buffer solution (PBS) was used as electrolyte.

2.2. Apparatus

Transmission electron microscopy (TEM) images were taken with a JEOL 2100 transmission electron microscopy (JEOL, Japan) operated at 200 kV. The UV–vis diffuse reflectance spectra of the sample were measured by a Perkin-Elmer Lambda 18, UV–vis-NIR spectrometer (Perkin-Elmer, USA). The infrared spectroscopy (IR) spectra of the samples were obtained from Nicolet Nexus 470 FT-IR Spectrometer (Thermo Nicolet, USA).

Electrochemical signals were recorded using CHI660 B electrochemical analyzer (Chen Hua Instruments, Shanghai, China) and ECL curves were recorded by a Model MPI-A electrochemiluminescence 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 glassy carbon electrode (GCE, 3 mm in diameter) was used as working electrode, Ag/AgCl (saturated KCl solution) as reference electrode and platinum wire as counter electrode, respectively. The electrochemical measurements were performed in the potential range from −0.1 to −1.5 V with the scan rate of 100 mV s^{-1} under quiescent conditions.

2.3. Preparation of G-CdS

The in situ synthesis of G-CdS nanocomposite was done according to the literature with some modifications [17]. Briefly, 17 mg GO sheets (prepared by the modified Hummers' method [19]) were dispersed in 10 mL twice-distilled water by sonication for 30 min to give a brown solution and 50 mL 0.035 M $Cd(NO_3)_2$ solution was added drop-by-drop into the as-prepared solution under stirring for 3 h. And then H_2S gas was bubbled through this dispersion for 1 h to form a green G-CdS precipitation in situ. The resulting solids were centrifuged and washed three times with distilled water and acetone, and dried in vacuum at 45 °C for 24 h. In addition, G-CdS nanocomposite doped with different graphene amounts were prepared by the above procedure with various amounts of GO sheets and free CdS NCs was obtained in the absence of GO sheets.

2.4. Fabrication of modified electrodes

Prior to modification, the GCE was first polished with sand paper followed by 1.0, 0.3, and 0.05 μm alumina slurry, respectively, then sonicated in a water bath to remove any residues. 1.1 mg G-CdS nanocomposite was dispersed in 0.5 mL 0.3% Nafion/ethanol solution to make a G-CdS homogeneous suspension, and 6 μL of this suspension was cast on the pretreated GCE surface and dried in air at room temperature to form G-CdS nanocomposite modified GCE (denoted as G-CdS/GCE). The modified electrode was rinsed by water for several times prior to use. As a comparison, 6 μL of 2.0 mg/mL CdS (dispersed in 0.3% Nafion/ethanol) was used to fabricate CdS/GCE.

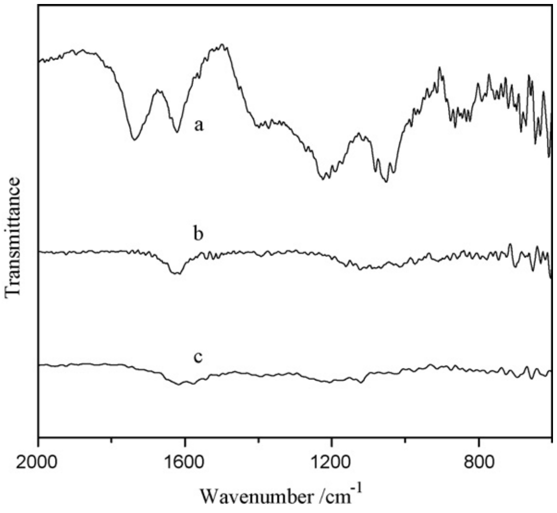

Fig. 1. IR spectra of GO (a), free CdS (b) and G-CdS (c).

2.5. Sample collection

Four different rainwater samples were collected in polyethylene containers in the same day and transported to the laboratory immediately after the rain. They were filtered through 0.45 μm filter membranes to remove insoluble particles.

3. Results and discussion

3.1. Characterizations of G-CdS nanocomposite

The as-prepared G-CdS nanocomposites with different graphene amount were characterized by elemental analysis with 2.4%, 4.6%, 10.7%, 30% and 64% graphene doped in the G-CdS nanocomposites, respectively. To ascertain the reduction of GO to graphene, the pristine GO, free CdS NCs and G-CdS were characterized by infrared spectroscopy (Fig. 1). Several characteristic peaks of GO can be observed in Fig. 1(a), in detail, the 1733 and 1631 cm^{-1} band belong to the stretching vibrations of C=O and H_2O molecules in GO, respectively. The bending vibration of O–H is observed at 1265 cm^{-1} and the stretching vibration of C–O is observed at 1052 cm^{-1} [17,20]. These characteristic peaks of GO are not observed in the case of G-CdS (Fig. 1(c)), indicating that GO has been reduced to graphene.

Furthermore, these G-CdS nanocomposites were compared with the pristine graphene sheets and CdS NCs by UV–vis diffuse reflectance absorption. As seen in Fig. 2, there is no absorption obtained from the pristine graphene sheets (Fig. 2(g)) in the visible light region [2], while a considerable absorbance at the wavelength less than 550 nm was observed from the CdS NCs (Fig. 2(a)). Also the absorption spectra of the G-CdS nanocomposites doped with different graphene amount (Fig. 2(b)–(f)) are similar to that of the pure CdS NCs, showing that the CdS NCs in the G-CdS nanocomposites basically maintain their original structural characteristics [21], and the strengths of the absorption are gradually weakened

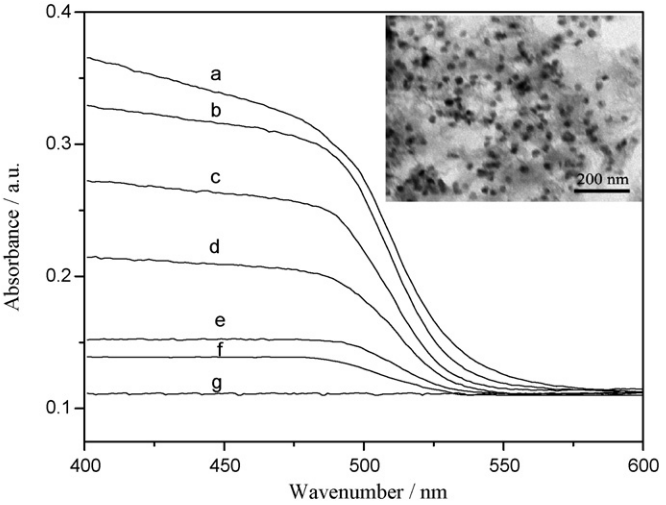

Fig. 2. Diffuse reflectance UV–vis spectra of CdS NCs (a) and G-CdS nanocomposites doped with different graphene amount: 2.4% (b), 4.6% (c), 10.7% (d), 30% (e), 64% (f) and the pristine graphene sheets (g). Inset: TEM image of G-CdS nanocomposite.

with the increase of the doping graphene amount. TEM image (Fig. 2 inset) shows that CdS sphere nanoparticles with an average diameter of 12 nm are uniformly dispersed on the surface of the graphene sheet without apparent exfoliation and aggregation, which reveals the modified GO sheets with rich carboxylic acid groups instead of Hummers' GO [18] can improve the structure and morphology of G-CdS nanocomposites.

3.2. Electrochemical and ECL characterization of G-CdS nanocomposite

Cyclic voltammetric (CV) curves were recorded in deaerated 0.10 M pH 9.0 PBS at bare GCE, CdS/GCE and G-CdS/GCE (fabricated by G-CdS doped with 4.6% graphene) between −0.1 and −1.5 V, as displayed in Fig. 3(A) inset, and the quantities of CdS NCs are equal in both films. For bare GCE (Fig. 3(A) inset curve (a), there are no obvious reduction currents resulting from the electrolysis of water [16]. Curves (b) and (c) in the inset of Fig. 3(A) show a pair of oxidation and reduction peaks appeared at ca. −0.85 and −1.25 V, respectively, which were ascribed to the oxidation and reduction of CdS NCs [16,22], confirming that the CdS NCs in the G-CdS nanocomposite still retain their electrochemical activity. The oxidation and reduction peak currents at the G-CdS nanocomposite film was enhanced much more than that of CdS NCs film, which manifests that the doped graphene could facilitate the electrochemical redox process of CdS NCs.

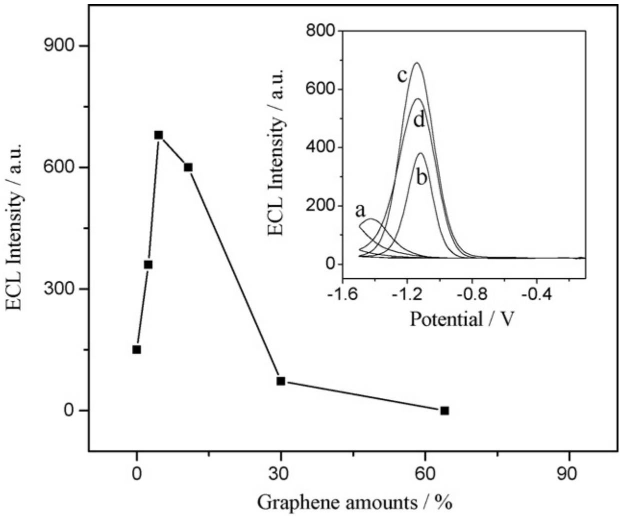

Fig. 4. The dependance of the doping graphene amount in G-CdS on ECL intensity. Inset: ECL-potential curves of CdS NCs (a) and G-CdS doped with different graphene amount: 2.4% (b), 4.6% (c), 10.7% (d) in 0.10 M pH 9.0 PBS containing 1.0 mM H_2O_2. Scan rate: 100 mV s^{-1}.

CdS NCs were reduced to generate nanocrystal species that could react with some coreactants (H_2O_2 or $S_2O_8{}^{2-}$) to produce excited states (CdS NCs*) and then to emit light in aqueous solution [12–14]. In this study, H_2O_2 was selected as the coreactant. Fig. 3(A) and (B) shows CV and ECL-potential curves in the 0.10 M PBS containing 1.0 mM H_2O_2. The reduction peak currents at both CdS NCs and G-CdS nanocomposites film increased greatly due to the electrocatalytic reaction between CdS NCs and H_2O_2 [16], and the ECL intensity and reduction peak current from the G-CdS nanocomposites film is about 4.3-fold and 5.5-fold higher than that observed from the CdS NCs film. As shown in Fig. 3(B), the ECL onset potential of the composite film (−0.75 V) was about 320 mV more positive than that of CdS NCs (−1.07 V), and one ECL peak was observed in both curves, resulting from the reaction between CdS NCs and H_2O_2. The results indicate that the presence of the graphene doped in G-CdS nanocomposites not only enhance the ECL intensity but also decrease the potential barriers of the ECL reaction obviously.

The ECL intensity of CdS nanocomposite was seriously influenced by the doped substance amount, and obviously decreased with high doped substance amount in the CdS nanocomposites [15,16]. The dependence of graphene amount on the ECL intensity is shown in Fig. 4. With the increase of graphene amount from 2.4% to 4.6%, the ECL intensity was enhanced 2.4- and 4.3-fold, respectively. However, the ECL intensity was decreased with the graphene

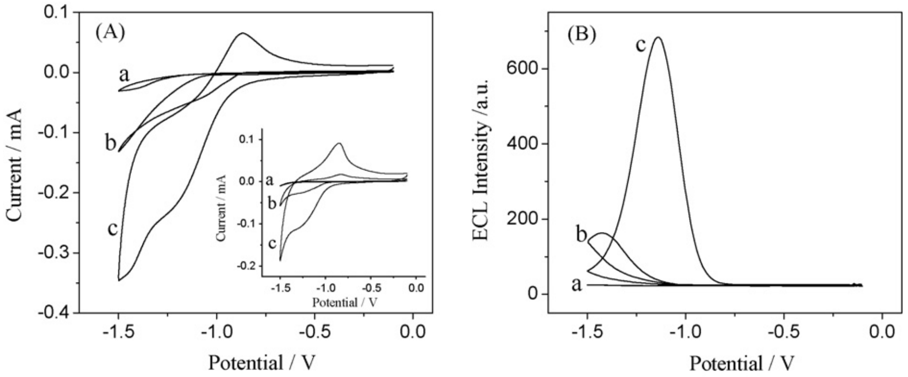

Fig. 3. CVs (A) and ECL-potential curves (B) of bare GCE (a), CdS/GCE (b) and G-CdS/GCE (c) in 0.10 M pH 9.0 PBS containing 1.0 mM H_2O_2. Inset: corresponding CVs of them in deaerated 0.10 M pH 9.0 PBS. Scan rate: 100 mV s^{-1}.

Table 1
H_2O_2 concentration in real samples tested by the ECL sensor.

Samples	Found (μM)	Added (μM)	Total found (μM)	Recovery (%)	Spectrophotometry [24] (μM)	RSD (%)
1	3.12	5.00	8.03	98.9	8.24	4.5
2	4.18	10.00	14.82	104.5	14.53	7.1
3	2.54	25.00	28.31	102.8	27.16	6.5
4	2.84	50.00	51.36	97.2	52.61	3.6

doped in G-CdS nanocomposite increased from 10.7% to 30% and it was hard to observe any ECL signal when the doping graphene amount was 64%. This result is accordance with the ECL behaviors of CdS-Ag nanocomposite [15] and MWCNT-CdS [16], which can be caused by the blackbody effect [16,23]. In order to achieve the best ECL response, the amount of graphene used in the experiment was chosen as 4.6%.

Under optimized conditions, H_2O_2 could obviously increase the ECL intensity of G-CdS nanocomposites, a linear relation between the ECL intensity and H_2O_2 concentration was obtained from 5 μM up to 1 mM (inset in Fig. 5) with a detection limit (S/N = 3) of 1.7 μM (R = 0.997). When consecutive scans from −0.1 to −1.5 V were performed for 13 circles in 0.1 M PBS containing 1.0 mM H_2O_2 (Fig. 6), no obvious change was observed, which implies that the as-prepared G-CdS nanocomposites film is stable.

3.3. Reproducibility and stability

The reproducibility of the H_2O_2 sensor (fabricated by the G-CdS nanocomposite containing 4.6% graphene) was examined at a H_2O_2 concentration of 0.2 mM. The mean ECL intensity is 94 a.u. with a relative standard deviation (RSD) of 3.5% for six determinations. The fabrication reproducibility of five H_2O_2 sensor shows an acceptable reproducibility with a relative standard deviation of 5.8% for the ECL intensity obtained in the H_2O_2 concentration of 0.2 mM. And the long-time storage stability of the fabricated H_2O_2 ECL sensor was examined by measuring the ECL response to H_2O_2 standard solution, and it retained about 87% of its initial ECL intensity after an intermitted use over the 5-week period, showing that the fabricated H_2O_2 ECL sensor modified electrode possesses an acceptable stability.

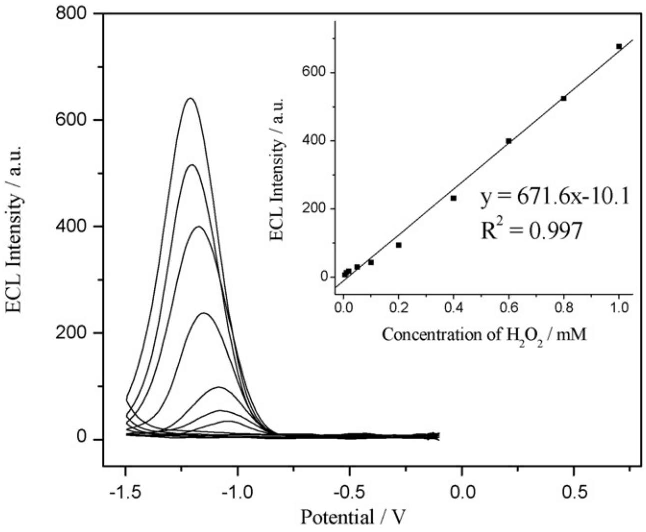

Fig. 5. Effect of H_2O_2 concentration on ECL intensity of G-CdS/GCE in 0.10 M pH 9.0 PBS containing: 0.05 mM, 0.1 mM, 0.2 mM, 0.4 mM, 0.6 mM, 0.8 mM and 1.0 mM H_2O_2 (from lower to upper). Inset: calibration curve for H_2O_2 detection. Scan rate: 100 mV s^{-1}.

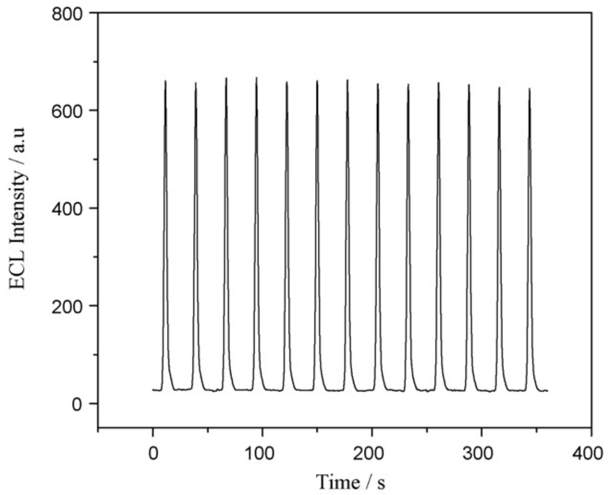

Fig. 6. ECL emission from the G-CdS/GCE in 0.10 M pH 9.0 PBS containing 1.0 mM H_2O_2 under continuous cyclic scans from −0.1 to −1.5 V for 13 cycles. Scan rate: 100 mV s^{-1}.

3.4. Sample analysis

Four different rainwater samples were determined and the standard addition method was used in the sample analysis procedure. Table 1 shows the determined values and the recovery values. Each sample was analyzed at the same time with both the ECL and the spectrophotometric methods [24] in order to avoid possible differences caused by degradation of the analyte in the sample. As can be seen, there is a good agreement between the two methods. The recovery rates were between 97.2% and 104.5% which is satisfactory for practical applications of the simple ECL device.

4. Conclusions

In summary, G-CdS nanocomposites with excellent distribution were successfully achieved based on the modified GO sheets as starting materials. Compared with pure CdS NCs, the as-prepared G-CdS nanocomposite not only enhances the ECL intensity by 4.3 times but also decreases the ECL onset potential from −1.07 to −0.75 V with the coreactant H_2O_2, and shows acceptable linear response from 5 μM up to 1 mM with a detection limit of 1.7 μM. Based on the sensitive detection of H_2O_2, which is a product in most oxidase reactions, with specificity of enzyme reaction, the proposed prototype sensor could become an alternative method to bioassays.

Acknowledgements

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