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Electrogenerated chemiluminescence resonance energy transfer between luminol and CdS/graphene nanocomposites and its sensing application☆

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ABSTRACT

Electrogenerated chemiluminescence (ECL) behaviors of luminol were comparatively studied at CdS quantum dos, graphene, and CdS/graphene (CdS/GR) nanocomposites modified gold electrodes in neutral condition. The most intense anodic ECL signal was obtained at the CdS/GR nanocomposites modified gold electrode (CdS/GR/GE). The anodic ECL of luminol (ECL-1) located at ~0.50 V (vs SCE) was increased nearly 50-times compared with the bare gold electrode. Besides, two stronger anodic ECL peaks (ECL-2 and ECL-3) were observed at 1.0 V and 1.4 V (vs SCE), respectively. The fluorescence and the UV–vis absorption spectra revealed that resonance energy transfer between luminol and CdS/GR nanocomposites was possible. The ECL spectra further demonstrated the occurrence of ECL resonance energy transfer (ECL-RET), which resulted in strong ECL-2 and ECL-3. Cytochrome C could significantly inhibit the intensities of the anodic ECL peaks, and could be sensitively detected.

1. Introduction

Luminol is one of the most famous electrogenerated chemiluminescence (ECL) reagents and can produce strong anodic ECL at conventional solid electrodes in alkaline condition [1,2]. However, strong alkaline condition is not suitable for biosensing application. In the past few decades, many efforts have been done to improve luminol ECL in neutral condition, including the investigation of luminol ECL at various nanomaterials modified electrodes. It was found in our previous work that noble metal nanoparticles, such as gold and silver nanoparticles, can catalyze electro-oxidation of luminol and can significantly increase the anodic luminol ECL in neutral condition [3–5]. For example, luminol ECL can be enhanced nearly 2 orders of magnitude at gold nanospheres, gold nanorods, and silver nanoparticles modified gold electrodes [3–5]. As another important nanomaterials in ECL investigation, semiconductor quantum dots (QDs) have been extensively studied due to their excellent luminescent behaviors and have been widely used in the construction of biosensors since it was first reported in 2002 [6–11]. Except their famous cathodic ECL, catalytical behaviors of QDs have also been investigated. For example, CdSe QDs can catalyze the oxidation of tris(2,2′-bipyridyl)ruthenium ($Ru(bpy)_3^{2+}$) and act as coreactant to generate strong anodic ECL in neutral solution [12].

Graphene has recently attracted much attention in electrochemical applications owing to its particular electronic properties and large surface area [13]. Many novel luminescent behaviors of traditional ECL systems have been reported at the graphene modified electrodes [14–17]. Although graphene modified electrodes exhibit outstanding characters in electroanalytical chemistry, the restacking of graphene monolayer during electrode modification often inhibits its electrochemical response. The intercalation of nanoparticles into graphene sheets is proven to be very effective in preventing the agglomeration of graphene. Moreover, the hybridization of graphene with nanoparticles can not only provide an effective strategy for enhancing the functionality of materials but also further maximize high activity on the surface of graphene sheet. Therefore, numerous studies have been focused on the synthesis and applications of graphene/inorganic nanocomposite materials [18–24].

Recently, several electrogenerated chemiluminescence resonance energy transfer (ECL-RET) systems including QDs, luminol, lucigenin, and $Ru(bpy)_3^{2+}$ have been successfully applied in bioassay application, revealing that ECL-RET could occur between traditional luminescent reagents and quantum dots [25–29]. However, to the best of our knowledge, there have no reports on the ECL-RET between luminol and quantum dots/graphene nanocomposites.

Herein, luminol ECL was studied at a gold electrode modified with CdS quantum dots/graphene (CdS/GR) nanocomposites in neutral condition, and strong anodic luminol ECL was obtained without the need of coreactant. The ECL-RET between luminol and CdS/GR nanocomposites could generate two stronger anodic ECL peaks at more

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positive potential. The proposed ECL-RET system could be used in the sensitive detection of cytochrome C.

2. Materials and methods

2.1. Chemicals

Luminol and cytochrome C were purchased from Sigma-Aldrich. A luminol stock solution (0.01 mol L^{-1}) was prepared by dissolving luminol in 0.1 mol L^{-1} NaOH and stored in the refrigerator. The stock solution was used to prepare working standard solution by suitable dilution. All other chemicals were analytical grade and double distilled water was used throughout. 0.1 mol L^{-1} pH 7.4 phosphate buffer solution (PBS) was prepared by mixing the stock solutions of Na_2HPO_4 and NaH_2PO_4, and then adjusting the pH with 0.1 mol L^{-1} NaOH and H_3PO_4.

2.2. Instruments

The ECL emission measurements were conducted on a model MPI-M electrochemiluminescence analyzer (Xi'An Remax Electronic Science & Technology Co. Ltd., China) at room temperature, and the voltage of the photomultiplier tube (PMT) was set at −800 V in the process of detection. All experiments were carried out with three-electrode system, including a modified gold electrode (GE) as the working electrode, a platinum wire as the counter electrode and a saturated calomel electrode (SCE) as the reference electrode, respectively. A commercial 5 mL cylindroid glass cell was used as ECL cell and was placed directly in front of the PMT. The UV–vis absorption spectra were obtained on a Shimadzu UV-3600 spectrophotometer (Shimadzu, Japan). The fluorescence (FL) measurements were carried out on a RF-5301PC FL spectrophotometer (Shimadzu, Japan). The ECL spectrum was obtained by collecting the ECL data during cyclic potential sweep with 10 pieces of filter at 400, 425, 450, 475, 500, 525, 550, 575, 600, and 625 nm, respectively. The electrochemical impedance spectroscopy (EIS) was conducted on a CHI 760D electrochemical workstation (CH Instruments Co., China).

2.3. Fabrication of nanomaterials modified gold electrodes

CdS/GR nanocomposite was synthesized according to the previous work of our group [24]. In a typical procedure, GO and aqueous solution of sodium 1-pyrene sulfonate were mixed together, and ultrasonically treated for 30 min. Then, an aqueous solution of $CdCl_2 \cdot 2.5H_2O$ was added and treated by ultrasonication for another 30 min. Finally, an aqueous solution of thioacetamide (TAA) was added and kept at 80 °C for 2 h under constant stirring. The CdS/GR nanocomposites were finally separated by centrifugation at 9000 rpm for 10 min, washed with double distilled water for three times. 10 mg CdS/GR was then dispersed in 10 mL double distilled water to form 1 mg/mL suspension for further use. Suitable amount of CdS/GR suspension was spread on the working area of gold electrode (2 mm in diameter) and dried at room temperature to fabricate CdS/GR modified GE (denoted as CdS/GR/GE). For comparison, CdS QDs and graphene modified gold electrodes (denoted as CdS/GE and GR/GE) were also fabricated using the similar method without the addition of GO or $CdCl_2 \cdot 2.5H_2O$, respectively.

3. Results and discussion

3.1. Luminol ECL at different modified electrodes

It is well-known that anodic luminol ECL is extremely weak in neutral condition at bare gold electrode (GE). The anodic ECL can be greatly improved at nanomaterials modified GE due to the electrocatalytical behavior of nanomaterials [3,4]. Therefore, nanomaterials modified electrode was often used in luminol ECL to make it suitable for biosensing applications. Previous work revealed that QDs and graphene can catalyze luminol ECL [30,31]. Recently, it was found that CdS/graphene nanocomposites exhibited enhanced optoelectronic properties compared with CdS or graphene, revealing that QDs/graphene nanocomposites not only inherit the superior properties of graphene and QDs, but also lead to some special properties through the combination of graphene with QDs [24,32]. However, up to date, luminol ECL has not been investigated at the CdS/graphene nanocomposites modified electrode. Therefore, in the present work, luminol ECL was comparatively studied at CdS QDs, graphene, and CdS/graphene nanocomposites modified gold electrodes as shown in Fig. 1. In the neutral condition, a weak anodic ECL peak can be observed at ~0.50 V at the bare GE, which can be assigned to the light emission of luminol (the inset of Fig. 1). When CdS QDs were modified on the bare GE, the anodic ECL was slightly enhanced. When graphene was modified on the bare GE, the onset potential of the anodic ECL was negatively shifted, and the ECL intensity increased nearly 10-times, revealing that graphene has the electrocatalytic effect on the ECL reactions. When CdS/GR nanocomposites were modified on the bare GE, three strong anodic ECL peaks were obtained at 0.50 V (ECL-1), 1.0 V (ECL-2), and 1.4 V (ECL-3), respectively. ECL-1 should be result from luminol oxidation because its potential was the same as that of luminol ECL at the bare GE. The intensity of ECL-1 increased 50-times compared with the signal from the bare GE. The strong anodic luminol ECL make it possible to transfer its energy to other species. No electrochemical peak was obtained at cyclic voltammogram corresponding to the potential of ECL-2 revealing that ECL-2 should be result from energy transfer rather than electrochemical reaction. The intensity of ECL-2 increased 60-times compared with that at the CdS/GE. ECL-3 was obtained at 1.4 V where the oxidation of QDs occurred. Because the potential of ECL-3 is close to that of ECL-2, energy transfer still exists. Therefore, the synergistic effect of the energy transfer and the oxidation of QDs lead to stronger ECL emission.

3.2. Effects of the amount of nanocomposites and luminol on ECL

Since strong anodic ECL can be obtained at the CdS/GR nanocomposites modified electrode in luminol solution, the effects of the amount of modified nanocomposites and luminol concentration on ECL intensities were investigated. It can be found from Fig. 2 that ECL intensities increased with the increase of immobilized nanocomposites from 0.32 μg/cm^2 to 4.80 μg/cm^2. Further increase of the amount of loaded nanocomposites, the modified film became unstable and was easy to be stripped from the electrode. Therefore, 4.80 μg/cm^2 of nanocomposites suspension was chosen to modify electrode.

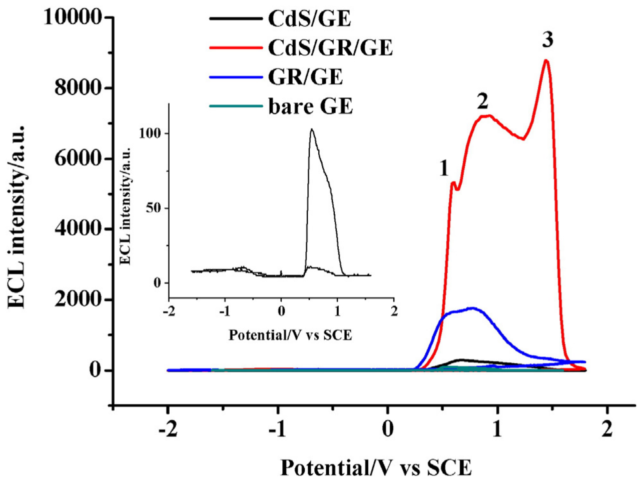

Fig. 1. Electrogenerated chemiluminescence of luminol at a bare GE, a GR/GE, a CdS/GE, and a CdS/GR/GE in neutral condition. The inset is the enlarged luminol ECL at a bare GE. Luminol, 1.0×10^{-4} mol L^{-1}; PBS, 0.1 mol L^{-1}; pH, 7.4; scan rate, 100 mV s^{-1}. If not mentioned additionally, all high voltages applied to the PMT were maintained at −800 V.

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