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Dual-signals electrochemiluminescence ratiometry based the synergic effect between luminol and CdSe quantum dots for direct detection of hydrogen peroxide

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ABSTRACT

In the present work, a dual signals electrochemiluminescence (ECL) ratiometric strategy was designed based on the synergic effect of the catalysis effect and ECL resonance energy transfer. It was found that CdSe quantum dots (CdSe QDs) can catalyze the oxidation of luminol to promote the signal intensity of luminol at 0.45 V. At the same time, a stronger cathodic ECL peak at −0.75 V from CdSe QDs was observed, which could be attributed to the resonance energy transfer between luminol as a donor and CdSe QDs as an acceptor. Moreover both signals from two different potentials increased with the increase hydrogen peroxide concentration. On the basis of the above results, an enzyme-free ECL sensor was fabricated by immobilization of coating CdSe QDs on Au-graphite oxide (GO-Au) composites modified glassy carbon electrode (GCE), and luminol solution as probe solution, which was used to detect rapidly and sensitively hydrogen peroxide in the range of 0.5–500 μM with a detection limit of 0.5 μM based on the ration of two signals. The sensor exhibited good reproducibility and sensitivity, suggesting that the simple method will be promising in the detection of active oxygen in environmental samples.

1. Introduction

It is well known that electrochemiluminescence (ECL) has been gained considerable attention due to outstanding characteristic such as simplicity, high sensitivity, easy controllability and low background [1–3]. Quantum dots (QDs), as a kind of luminescence specie, have been verified by Bard's group on the ECL properties of the silicon QDs [4]. Recently, QDs-based ECL analytical methods have been widely explored due to their unique size-dependent luminescence, high quantum field, optical, and electrochemical properties [5,6]. However, the ECL signal intensity of QDs is usually much lower than that of luminol or $Ru(bpy)_3^{2+}$, which limits their wide application. Therefore, it is necessary to develop effective approach to improve QDs ECL for a wider range of applications. Resonance energy transfer has been obtained growing attention as a powerful approach for enhancement of ECL in analysis of target detection, and three kinds of resonance energy transfer have been widely used, such as chemiluminescence resonance energy transfer [7], fluorescence resonance energy transfer [8], and bioluminescence resonance energy transfer [9]. However, in the past ECL resonance energy transfer has been paid less concern. Recently, searches have been gradually done based on the ECL resonance energy transfer involving $Ru(bpy)_3^{2+}$, quantum dots and luminol [10–13]. These searches indicated that ECL resonance energy transfer could happen between the traditional luminescent reagents and QDs. In addition to QDs have the ECL performance, they also could display a good catalytic property on chemiluminescence reactions [14], and the catalytic applications of QDs were relatively less reported on ECL studies [15]. Therefore, it's beautiful to use the catalytic property of QDs while in improving the ECL signals of them.

Hydrogen peroxide (H_2O_2), as a strong oxidant, which may make the body's antioxidant capacity decline by the loss of the body of antioxidants, and further lead to various diseases such as cancer, cardiovascular diseases, and Alzheimer's disease [16–18]. Therefore, it is necessary to detecting quickly and efficiently hydrogen peroxide. At present, several analytical methods have been designed for H_2O_2 detection, including the UV absorption [19], fluorescence [20], colorimetric assays [21,22], electrochemistry [23], chemiluminescence [24], and so on. However, these methods either time-consuming or require the expensive equipment and harmful fluorescence substance. Moreover, these approaches were mainly based on the variation of single signal, which may introduce false positive or negative errors due to the instrumental or environmental factors [25]. Therefore, developing a

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dual signals strategy requiring ordinary instrumentation yet detecting quickly H_2O_2 is very essential. Since Xu's group first reported the dual signals ECL ratiometric sensing approach based on CdS nanocrystal and luminol as two different ECL emitters [26], the ECL ratiometric sensors reply on the ratio of two ECL signals have been gotten more and more attention in chemical analysis, and most of them were designed based on the ECL resonance energy transfer between two different emitters such as peroxydisulfate/oxygen($O_2/S_2O_8^{2-}$) and amino-terminates perylene derivative (PTC-NH_2) [27], g-C_3N_4 nanosheets and Ag–PAMAM–luminol nanocomposites [28], CdS QDs and Ru(bpy)$_3^{2+}$ [12,29]. Herein, a dual-signals ECL ratiometry was built based resonance energy transfer between luminol and CdSe QDs.

Currently, nanocomposites have gotten promising application in different field. Graphene oxide (GO), as a kind of two-dimensional carbon material with a single atomic layer, can offer a platform for the fixation of organic and inorganic molecules due to its large surface area and high π-π conjunction. However, the surface of GO has oxygenated functional groups such as hydroxyl and carboxyl, so the conductivity of it is poorer. So graphene oxide can be decorated with mental nanoparticles to promote efficiently electrical conductivity. Au nanoparticles can greatly expedite the electron transfer and promote the ECL reaction, thus the GO-Au composites can act as a suitable substrate to load more labels.

In this work, we prepared the GO-Au composites to modify the glassy carbon electrode, then CdSe QDs fixed on the GO-Au composites modified electrode, luminol solution as probe solution in the presence of H_2O_2. It was observed CdSe QDs could effectively catalyze the reaction of luminol-hydrogen peroxide to enhance the luminol ECL signal, and a stronger cathodic ECL peak of CdSe QDs was obtained due to the resonance energy transfer between luminol and QDs. Both signals from two different potentials increased with the increase hydrogen peroxide concentration, thus a dual-signals ECL ratiometric strategy was developed for the detection H_2O_2 based on the collaborative effect of the catalysis effect and ECL resonance energy transfer.

2. Experimental

2.1. Reagents and materials

Selenium power (> 99.95%), Isopropyl alcohol and 30% H_2O_2, potassium per-manganate ($KMnO_4$), sulfuric acid (H_2SO_4, 95%–98%), hydrochloric acid (HCl, 36%–38%), graphite powder (≥99.85%), and sodium nitrate ($NaNO_3$, ≥99%) were purchased from Sinopharm Group Chemical Reagent Co., Ltd. Cadmium dichloride hemipentahydrate ($CdCl_2{\cdot}2.5H_2O$,99.0%), graphite power, sodium citrate and sodium sulfite (97.0%) were supplied from Aladdin Reagent Co., Ltd. (Shanghai, China). Luminol, gold chloride ($HAuCl_4$) and 3-mercaptopropionic acid were obtained from Sigma-Aldrich (St. Louis, MO, USA). All other reagents are of analytical grade or above and used without further purification.

0.1 M Carbonate buffer solution (CBS) was prepared using 0.1 M $NaHCO_3$ and 0.1 M $NaCO_3$, and the pH of which was 9.9 unless otherwise stated. Ultrapure water used for the solutions was purified by the Milli-Q system (≥18 MΩ, Milli-Q, Millipore, Billerica, MA, USA)

2.2. Apparatus

A laboratory-built ECL detection system was used. The ECL detection was performed with BPCL Ultra-Weak Luminescence Analyzer (Institute of biophysics, Chinese Academy of sciences, Beijing, China) and a CHI1110B Electrochemical Analyzer (Shanghai Chenhua Instrument Co., Ltd., Shanghai, China). A three-electrode system containing a bare or modified glassy carbon electrode (GCE, Φ = 3 mm) as working electrode, a platinum wire electrode as counter electrode and an Ag/AgCl (3 M KCl) electrode as reference electrode, was used. The voltage of the photomultiplier tube was −650 V. The morphologies of nanomaterials were characterized using Hitachi SU-70 scanning electron microscope (SEM, Hitachi, Tokyo, Japan) and Transmission electron microscopy (TEM, JEM-1011, Japan). The size distribution was obtained from the Zetasizer ZS90 (Malvern, Malvern, England). UV–vis spectra were measured with a TU-1901 (Beijing Puxi). The fluorescence spectra were measured with Hitachi F-4600 of Hitachi company. The UV lamp (365 nm). The dynamic light scattering (DLS) was taken on a Malvern Zetasizer Nano ZS 90 (UK).

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2.3. Preparation of the GO-Au composites

Graphene oxide was prepared from natural graphite power using a modification of Hummers method [30]. In a brief, 0.5 g graphite power, 0.5 g sodium nitrate and 23 mL concentrated sulfuric acid were injected into a round-bottomed flask placed in an ice bath, and the mixed solution was stirred vigorously. After the sodium nitrate was dissolved completely, 3 g solid potassium permanganate was added slowly to the solution and reacted for 2 h. When the solution was dispersed homogeneously, the mixture was transferred to a water bath (35 °C) and stirred vigorously for 1 h. When the temperature of suspension increased to 95 °C, adding 140 mL ultrapure water to the above solution kept the temperature blow 40 °C, followed by slow addition of 3 mL 30% H_2O_2 solution. After the color of the solution turned from dark brown to yellow, the solution was centrifuged and washed with 0.1 M HCl to dislodge metal ion, then the excessive acid was removed with ultrapure water. The suspension was repeatedly centrifuged and redissolved with ultrapure water until the pH was 6.0. The purified product was dried in a vacuum at room temperature. The resulted GO sample was dispersed in ultrapure water (1 mg/mL) by ultra-sonication for 1 h and centrifuged at 3000 rpm for 10 min and the upper solution was used.

GO-Au was prepared as follow. 2 mL 1 mg/mL GO dispersion, 4 mL 1% $HAuCl_4$ and 10 mL ultrapure water were added to a 50 mL round-bottom flask and ultra-sonicated for 1 h. Then sodium citrate (500 μL, 2 M) added to the above solution being refluxed for 4 h at 80 °C. Finally, the product was obtained by centrifugation washed with ultrapure water, and then GO-Au was dispersed in ultrapure water and stored in refrigerator for future use.

2.4. Synthesis of CdSe QDs

CdSe QDs were prepared referring to the reported literature procedures [31]. Firstly, 0.8 g sodium sulfite was added to a 100 mL round-bottom flask containing 50 mL ultrapure water. The solution was stirred under nitrogen atmosphere for 30 min, and heated to 90 °C. Then 0.08 g selenium power was added quickly to the above mixture, and refluxed for 5 h under nitrogen protection. When the selenium power was dissolved completely, the yellow clear Na_2SeSO_3 solution was received. Secondly, $CdCl_2$ solution was obtained by dissolving 37 mg $CdCl_2{\cdot}2.5H_2O$ in 50 mL ultrapure water, then 34.6 μL 3-mercaptopropionic acid was added to the $CdCl_2$ solution and adjusted pH to 9.0 with 0.1 M NaOH. Then Na_2SeSO_3 solution was injected into the mixture. After the solution was heated at 100 °C for 10 min, 3.70 mL $N_2H_4{\cdot}H_2O$ was added and refluxed for 10 h at 130 °C. The crude products were separated by centrifugation to obtain CdSe QDs, which were purified three times with Isopropyl alcohol and ultrapure water successively by centrifugation at 12000 rpm for 10 min. Finally, the resulted products were diapered in ultrapure water and stored at 4 °C for future use.

2.5. Measurement procedure

Firstly, the glassy carbon electrodes (GCE) were carefully polished to a mirror with 0.05, 0.3, and 1.0 μm α-Al_2O_3 power, and then cleaned ultrasonically with ethanol and ultrapure water successively. Next, GCE were rinsed thoroughly with ultrapure water and dried in nitrogen