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Electrogenerated chemiluminescence from CdS nanotubes and its sensing application in aqueous solution

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Abstract

Electrogenerated chemiluminescence (ECL) of CdS nanotubes in aqueous solution and its sensing application were studied by entrapping the CdS nanotubes in carbon paste electrode. Two ECL peaks were observed at −0.9 V (ECL-1) and −1.2 V (ECL-2), respectively, when the potential was cycled between 0 and −1.6 V. The electrochemically reduced nanocrystal species of CdS nanotubes could collide with the oxidized species in an annihilation process to produce the peak of ECL-1. The electron-transfer reaction between the reduced CdS nanocrystal species and oxidant coreactants such as $S_2O_8{}^{2-}$, H_2O_2, and reduced dissolved oxygen led to the appearance of the ECL-2 peak. Based on the enhancing effect of H_2O_2 on ECL-2 intensity, a novel CdS ECL sensor was developed for H_2O_2 detection. The sensor exhibited a detection limit of 0.1 μM and a linear range from 0.5 μM to 0.01 mM. The relative standard deviations of five replicate determinations of 5 μM H_2O_2 was 2.6%. In addition, the ECL spectrum in aqueous solution also exhibited two peaks at 500 and 640 nm, respectively.

Keywords: Electrogenerated chemiluminescence; CdS nanotubes; H_2O_2 detection

1. Introduction

Semiconductor nanocrystals (NCs) have been extensively studied because of their unique size-dependent electronic, optical and electrochemical properties [1]. Highly luminescent semiconductor NCs have gained increasing attention in light-emitting devices and tagging applications [2–6]. Due to the controllable merits of electrochemical method, the spectroelectrochemical behavior of semiconductor NCs has been extensively carried out [7,8]. As reported, an electron injection by applying cathodic potential to the nanoparticle layers composing of CdSe or CdSe/CdS core-shell NCs can dramatically enhance the efficiency of chemiluminescence and allow the achievement of efficient and stable ECL from CdSe nanoparticle layers in aqueous solution [9]. Recent research indicated that the electrochemically reduced and oxidized Si NCs [10] or CdSe NCs [11] could react with coreactants to produce ECL. The electron-transfer reaction between electrochemically formed nanocrystal species and coreactants implies that NCs have great potential for developing novel ECL sensors.

ECL has many promising advantages such as simplicity, high sensitivity, rapidity and easy controllability, and it has been proved to be a useful technique for analytical applications including organic analysis, immunosensors, DNA-probe assays and enzymatic biosensors [12]. In this paper, following the ECL studies on CdS nanoparticles [13] and CdS nanotubes in the mixed solution of 0.1 M $K_2S_2O_8$ and 0.1 M KOH [14], an alternative approach to study the ECL properties of CdS nanotubes in pH 8.0 phosphate buffer solution (PBS) was proposed, which is more suitable for analytical applications in biological system. Based on the electron-transfer reaction between electrochemically reduced CdS nanocrystal species and coreactant H_2O_2, a new CdS ECL sensor for H_2O_2 determination was developed.

The accurate and rapid determination of H_2O_2 is of practical importance in chemical, biological, clinical and other fields [15,16] Although H_2O_2 can be detected by many enzyme-based biosensors [17,24], the enzymes cannot promise a complete long-term stability of the sensors due to their inherent instability. Here, a novel CdS-based ECL sensor for H_2O_2 detection provides a more effective way with better stability and higher

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sensitivity. As expected, the hydrophobicity of paraffin used for preparing the carbon paste resulted in the formation of a clear O/W interface between immobilized CdS nanotubes and aqueous solution, which suggested a new fabrication method to study the ECL behavior of nanocrystals in aqueous system. Using carbon paste to immobilize CdS nanocrystals not only provided an easy renewable modified electrode surface, but also could retain the ECL features of CdS for more than several months.

2. Experimental

2.1. Reagents

The CdS nanotubes were synthesized following the reference [14]. H_2O_2 (30%, w/v, solution) and $K_2S_2O_8$ were purchased from Shanghai Chemical Reagent Company (Shanghai, China). 0.1 M phosphate buffer solution (PBS) (pH 8.0) containing 0.01 M $K_2S_2O_8$ and 0.1 M KCl was used as the electrolyte in the measuring system. High-purity nitrogen was used for air-free condition. All other chemicals were of analytical grade. Doubly distilled water was used throughout.

2.2. Modified electrode preparation

The carbon paste electrode (CPE) was fabricated as follows: graphite powder (60 mg) and the CdS nanotubes (20 mg) were thoroughly mixed in ethanol solvent by ultrasonic dispersion. After drying under stirring, a homogenized graphite/CdS mixture was achieved. Subsequently, paraffin oil was added to the mixture (oil/mixture = 1:4, w/w) and mixed fully until a homogeneous paste was obtained. The prepared paste was packed into a glass tube with a 4 mm inner diameter and electrical contact was established with a copper rod through the back of the homemade electrode. Prior to each experiment, the electrode surface was polished with weighing paper and rinsed with redistilled water.

2.3. Instrumentation and measurements

Electrogenerated chemiluminescence studies were performed using a Model MPI-A from Electrochemiluminescence Analyzer Systems (Xi'An Remax Electronic Science & Technology Co. Ltd., Xi'An, China). The spectral width of the photomultiplier tube (PMT) used in Model MPI-A Electrochemiluminescence Analyzer was 200–800 nm and the voltage of the PMT was set at 800 V in the process of detection. A CHI 660 electrochemical analyzer (Shanghai Chenhua, China) was used for electrochemical experiments. A conventional three-electrode configuration was used. An Ag/AgCl reference electrode and a platinum wire counter electrode were used for all measurements, respectively. The CPE with the CdS nanotubes was used as the working electrode. The UV absorption spectra were acquired in a Ruili 1200 photospectrometer (Peking Analytical Instrument Co., Peking, China). Photoluminescence (PL) and ECL spectra were obtained on AMINCO Bowman Series 2 Luminescence Spectrometer (SLM Inc., USA).

3. Results and discussion

3.1. PL and UV characterizations for CdS NCs

As reported [14], the CdS nanotubes with diameter of about 100–140 nm are composed of numerous compacted nanocrystals. The average size of these nanocrystals is estimated to be about 7 nm. Fig. 1 shows the photoluminescence (PL) and UV (inset) spectra from the CdS in ethanol solution. The PL emission peak at 616 nm and the absorption peak at 490 nm indicated the existence of quantum size effect for the CdS nanoparticles [18].

3.2. Electrochemical and ECL behaviors of CdS nanotubes in CPE

Cyclic voltammograms (CVs) and ECL curves of the CdS nanotubes are shown in Fig. 2. In the CVs (inset A), the anodic and the cathodic peaks (curve c) were observed at −0.85 V (A1) and −1.2 V (C1), respectively, in pH 8.0 PBS containing 0.1 M KCl and 0.01 M $K_2S_2O_8$. In the curve b, the peak A1 did not appear at the blank carbon paste electrode, which implied that the peak A1 was attributed to the oxidation of CdS nanotubes. The peak C1 appeared in both curve a and curve b was assigned to the reduction of $S_2O_8{}^{2-}$, because this peak was not found in the absence of $S_2O_8{}^{2-}$ (curve a). In the ECL curves, upon the potential scan with an initial negative direction, two light emission peaks occurred at −0.9 and −1.2 V defined as ECL-1 and ECL-2, respectively, corresponding to the two CV peaks. No light emission was observed on bare CPE in the same condition, suggesting the ECL processes were due to the existence of CdS nanotubes. Therefore, the ECL peaks indicated that the CdS nanocrystals immobilized in CPE could be oxidized or reduced by charge injection during potential cycling and participated in relevant ECL processes. According to the previous report [13], electrogenerated reduced species ($CdS^{\bullet -}$) can col-

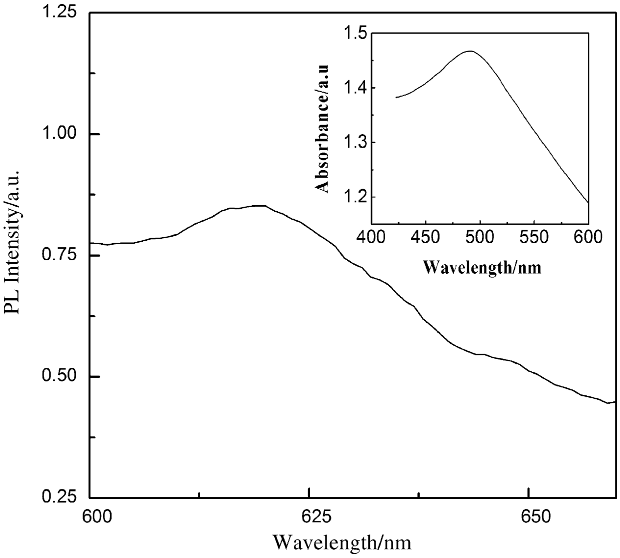

Fig. 1. Photoluminescence and UV (inset) spectra of CdS nanotubes in ethanol solution. Excitation wavelength: 350 nm.