



Electrochromic response and electrochemiluminescence of CdS nanocrystals thin film in aqueous solution

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ABSTRACT

The enhanced visible absorbance related to electrochromic response (ECR) of CdS nanocrystals (NCs) thin film in aqueous solution was firstly investigated to elucidate the detailed electrochemiluminescence (ECL) mechanism of semiconductor NCs/H₂O₂ system. The recovery efficiency of ECR was found as the key factor to affect the intensity of ECL. This preliminary study between ECR and ECL of semiconductor NCs in aqueous solution can provide the profound guidance to fabricate enhanced “signal-off” kind ECL sensors to widen its application in analytical field.

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1. Introduction

Arising from their “artificial atom” character, semiconductor NCs are one of the most striking nanomaterials with unique optical and electronic properties [1]. Due to its special application in bioassay and bioimaging, investigation of semiconductor NCs in aqueous solution has attracted great attention, especially NCs have a great potential application in the development of novel ECL sensors and biological labels for ECL detection [2–10]. Unfortunately, the ECL mechanism of semiconductor NCs in aqueous solution with their co-reactants such as H₂O₂ is still not very clear due to the absence of convinced discovery.

Electrochromic response (ECR) is another characteristic for semiconductor NCs. The injection of electrons into the quantum-confined states of the nanocrystal leads to an ECR, including a strong, size-tunable, midinfrared absorption corresponding to an intraband transition, a bleach of the interband exciton transitions adsorption, and a quench of the narrow band-edge photoluminescence [1,11,12]. To cast a new light on the detail mechanism of ECL for semiconductor NCs, herein the concomitant ECR of CdS NCs are innovatively investigated to provide more powerful information in aqueous solution. In present work, enhanced visible absorbance (i.e. darkening of the color) of CdS NCs thin film was observed, even with naked-eyes, after electron injected. Most interestingly, the ECL intensity was found to be related to

the recovery efficiency of their ECR. Based on the above discovery, a reasonable ECL mechanism of semiconductor was convincingly elucidated.

2. Experimental

2.1. Reagents

All reagents were of analytical grade, and doubly distilled water was used throughout. CdS NCs with an average size of 4–5 nm used in this work were synthesized according to our previous work [2].

2.2. Apparatus

All electrochemical studies were performed with a conventional three-electrode system. A saturated calomel electrode (SCE) was used as reference electrode, and a Pt wire as counter electrode. An optically transparent conducting glass (FTO, Fluorine-doped tin oxide coated glasses, area 1 cm × 3 cm, sheet resistance 15 Ω/sq, transmittance 90% in the visible range) and glassy carbon electrode (GCE, ϕ = 3 mm) modified by CdS NCs thin film were used as substrate working electrodes for the ECR and ECL measurement, respectively. A CHI 760C electrochemical workstation (CH Instruments, USA) was used for all the electrochemical experiments. It combined with a UV-2550 Spectrophotometer (Simadzu Co., Japan) to construct an *in-situ* spectroelectrochemical system for the ECR measurement. ECL was conducted by a homemade ECL system, as reported previously [13]. High voltage applied to photomultiplier tube (PMT) was – 550 V, unless noted otherwise. CdS

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NCs thin film modified FTO was characterized by field emission scanning electron microscopy (FE-SEM, XL-30E).

2.3. Preparation of the CdS NCs thin film on GCE and FTO

The CdS NCs colloidal suspension (0.5 mg mL^{-1}) was prepared by dispersing CdS NCs in doubly distilled water with the help of ultrasonication. The working electrodes were modified by CdS NCs films with the same density ($42 \mu\text{g cm}^{-2}$) by casting the above prepared CdS NCs colloidal suspension on the surface of GCE or FTO. The coatings were dried in desiccator at room temperature. The morphology of the coating on FTO reveals a porous structure with the aggregated cluster comprised of small NCs (Fig. 1A). The thickness was determined to be $200 \pm 30 \text{ nm}$ (inset of Fig. 1A), which can provide the appropriate electrochromic response time in the order of minutes [14].

3. Results and discussion

3.1. Spectroelectrochemical properties of CdS NCs thin film

In order to explore the optical changes and the ECR properties of CdS NCs thin films, spectroelectrochemistry studies were performed. CdS NCs thin films were coated on FTO and spectral changes were investigated by UV-Vis spectrometer in 0.1 M PBS (pH 9) containing 0.1 M KCl. Simultaneously, the CdS NCs film modified FTO was biased at -1.2 V vs SCE. The films show multichrome (yellow–grey–black) with continuous electron injection. At the original state, CdS NCs thin film has yellow color (Fig. 1Ba). Following successive electron injection

for 1 min at -1.2 V , intensities of visible absorption increase, and the thin film has black color (Fig. 1Bb), which shows that the reduced CdS NCs thin film has a wide-spectrum enhanced absorbance property from 700 nm to 390 nm wavelength range (as shown in Curve b in Fig. 1C), compared to the original CdS NCs (Curve a in Fig. 1C). Meanwhile, the interband absorbance of CdS NCs to less than 500 nm decreased, namely, a bleach effect after electron injection [15]. More interestingly, after resetting to open circuit potential (OCP) within 45 min, the CdS NCs thin film in aqueous solution returns to yellow (Fig. 1Bc). It indicates that the injected electrons are extracted by the oxidant O_2 dissolved in aqueous solution.

3.2. Electrochromic response behavior of CdS NCs thin film

Since hydrogen peroxide is generally used as a coreactant in the ECL process of semiconductor NCs thin film, the effect of the oxidant H_2O_2 on the electrochromic behavior of CdS NCs thin film in aqueous solution was investigated by the well-designed time trace UV-Vis absorbance spectra. The optical signals were measured at 550 nm, which corresponds to the maximum enhanced visible absorbance wavelength of reduced CdS NCs from Fig. 1C. Fig. 1D shows the differential enhanced absorbance-time spectra of CdS NCs/FTO electrodes, which were recorded in 0.1 M PBS (pH 9) with various concentrations of H_2O_2 after biased at -1.2 V for 1 min then resetting to OCP. At the low concentration of H_2O_2 , 1 mM (Curve a in Fig. 1D), the enhanced visible absorbance of CdS NCs thin film increases dramatically for 1 min electron injection into CdS NCs, due to the low recovery efficiency. With the increase of the concentration of H_2O_2 from 5 mM to 20 mM, the enhanced visible absorbance got smaller

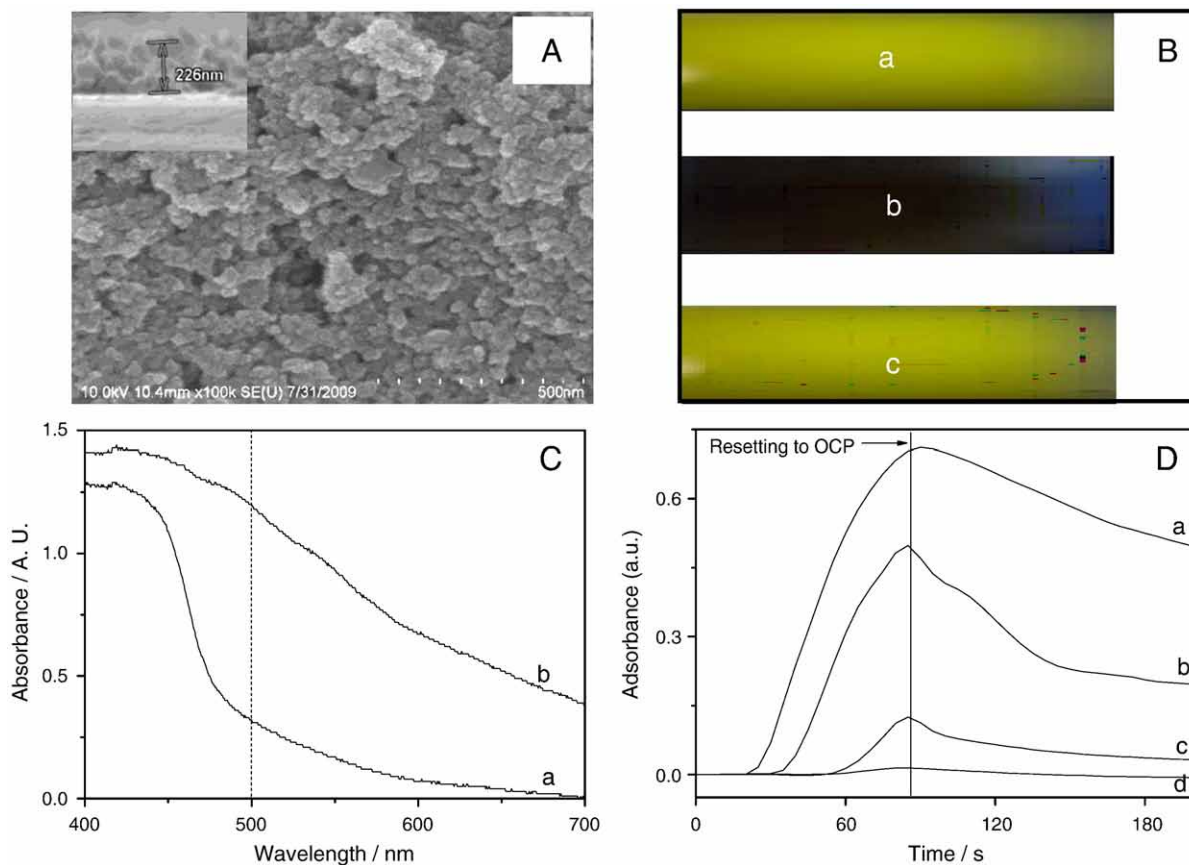


Fig. 1. (A) SEM (surface and cross-sectional) images of the CdS NCs films modified FTO. (B) Reversible electrochromic photographs of the CdS NCs films modified FTO electrodes in 0.1 M phosphate buffer with $1 \text{ mmol L}^{-1} \text{ H}_2\text{O}_2$ at open circuit potential (a), 1 min after applying a potential of -1.2 V vs SCE (b), and 45 min after resetting to open circuit potential (c). (C) Spectroelectrochemistry of CdS NCs thin film on FTO in 0.1 M PBS (pH 9), at open circuit potential (a) and after applying a potential of -1.2 V vs SCE for 1 min (b). (D) Time trace UV-visible absorbance spectra of CdS NCs thin film modified FTO electrodes in 0.1 M PBS (pH 9) with 1 mM (a), 5 mM (b), 10 mM (c), and 20 mM H_2O_2 (d) after applying a potential of -1.2 V vs SCE for 1 min then resetting to open circuit potential. The optical signal is measured at 550 nm.

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