



Short communication

Tunable electrochemiluminescence of CdSe@ZnSe quantum dots by adjusting ZnSe shell thickness

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ABSTRACT

CdSe quantum dots as cores capped with ZnSe shell (CdSe@ZnSe QDs) via a facile and eco-friendly strategy have been synthesized in aqueous solution for the first time. The electrochemiluminescence (ECL) of CdSe@ZnSe QDs was greatly enhanced compared to that of CdSe QDs. In particular, the ECL properties of the resulting CdSe@ZnSe QDs were found to be controllable by adjusting the thickness of ZnSe shells. Benefiting from the enhanced ECL intensity, the sensor based on CdSe@ZnSe QDs could accurately quantify dopamine from 10.0 nM to 3.0 μM with a detection limit of 3.6 nM.

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1. Introduction

CdSe quantum dots (QDs) are one of the most popular electrochemiluminescence (ECL) emitters due to their intrinsic properties such as unique luminescent properties [1,2] and relatively low cost. However, the ECL signal of pure CdSe QDs is lower than that of conventional luminescent reagents such as luminal or tris(2,2'-bipyridyl) ruthenium(II) complex ([Ru(bpy)₃]²⁺) which restricts their wide analytical applications. Thus, it is important to select effective methods to enhance ECL of CdSe QDs. Unlike fluorescence, the ECL emission is more sensitive and dependent on the surface properties and the presence of surface state [3] which can be changed by composition with other materials, passivating with capping agent or metal ion doping [4,5]. As a capping agent, ZnSe should in theory be a good candidate for CdSe QDs due to its lattice parameter good match, a wider band gap, and the type I band alignment to confine both holes and electrons in CdSe [6]. A large number of methods have been applied to synthesize core-shell CdSe@ZnSe QDs. However, most of them have been performed by the use of trioctylphosphine selenide (TOPSe) in organic solution as a source of selenium in combination with high boiling solvent, which are non-eco-friendly as well as time and energy consuming [6]. Therefore, a facile and eco-friendly method for synthesizing core-shell CdSe@ZnSe QDs in aqueous solution is urgently needed. In addition,

many efforts have been focused on the fluorescence of core-shell CdSe@ZnSe QDs [7–10]. The work concerning enhanced ECL emission from CdSe capped with ZnSe is very scarce, although Bard and co-workers firstly investigated the ECL of CdSe@ZnSe QDs in organic solution [11].

In this work, we have proposed a novel and efficient approach to prepare CdSe@ZnSe QDs and investigated its ECL behavior in aqueous solution for the first time. Especially, the effect of ZnSe amount in the CdSe@ZnSe QDs on ECL intensity was investigated. It was found that ECL behaviors of CdSe@ZnSe QDs can be tuned by varying the amount of ZnSe. The strong ECL intensity of the CdSe@ZnSe QDs provided a colorimetric, simple and sensitive assay strategy for dopamine detection, which could be further utilized in ECL imaging or biosensors for immune and DNA assays.

2. Experimental

2.1. Reagents and chemicals

Selenium metal powder (Se) with the purity of 99.95% was obtained from XingTa Chemical Plant Co., Ltd. (Shanghai, China). Sodium borohydride (NaBH₄) was purchased from Sinopharm Chemical Reagents Co., Ltd. (Shanghai, China). 3-Mercaptopropionic acid (MPA), dopamine hydrochloride (DA), uric acid (UA) and L-ascorbic acid (AA) were provided from Sigma-Aldrich. All other reagents were of analytical grade and were used without further purification. Double distilled water was used in all experiments.

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2.2. Apparatus

Electrochemical experiments were performed with a CHI 760C electrochemical workstation (CHI, USA), an MPI-ECL Analyzer (Xi'an Remax Electronic High-Tech Ltd.) and a PG2000-pro scientific class spectrometer (Shanghai, China). The morphologies were observed on high resolution transmission electron microscope (TEM) (Philip CM-120). UV-vis absorption spectra were recorded on a Shimadzu UV-2450 spectrophotometer (Tokyo, Japan). The fluorescence spectra (FL) were performed on a FluoroMax-4 fluorescence spectrophotometer (Horiba, USA).

2.3. Synthesis of CdSe QDs and CdSe@ZnSe QDs in aqueous solution

CdSe core quantum dots were synthesized according to the literature with a slight modification [12]. Se precursor, NaHSe, was prepared by the reaction between 15.8 mg Se and 15.1 mg NaBH₄ in 5 mL of water maintained at 0 °C and a N₂ atmosphere for 1 h. Meanwhile, 91.3 mg of CdCl₂·2.5H₂O and 87 μL of MPA were dissolved in 50 mL of H₂O. The pH of the resulting Cd-MPA complex was adjusted to 11 by adding 1 M NaOH solution in dropwise and purged for about 30 min with N₂ before further use. The aqueous colloidal solution of CdSe nanoparticles was synthesized through the addition of freshly prepared oxygen-free NaHSe solutions to N₂-saturated Cd-MPA solution refluxed at 100 °C for 4 h or another prolonged 4 h at 160 °C (only for control experiment) under vigorous stirring condition. The resultant was purified three times by isopropyl alcohol with centrifugation at 10,000 rpm. The purified CdSe QDs were kept in double-distilled water and stored in the dark at 4 °C for later use.

The purified CdSe QDs were used as core to directly grow ZnSe layer with various thickness to prepare CdSe@ZnSe QDs by controlling the molar ratio of Cd/Zn. Take the ratio of 1:1 as an example. Zn-MPA solution was prepared by mixing 54.5 mg ZnCl₂ and 87 μL MPA and the pH value was adjusted to 11 by the addition of 1 M NaOH. CdSe QDs prepared as described above were added to Zn-MPA solution with magnetic stirring and purged for about 30 min with N₂. Then N₂-saturated NaHSe was injected to mixture of CdSe core and Zn-MPA solution in N₂ atmosphere throughout the reaction time. The temperature of the above solution was maintained at 160 °C for the growth of the ZnSe for 4 h [13]. The resultant was purified three times by isopropyl alcohol with centrifugation at 10,000 rpm. The purified CdSe@ZnSe QDs were kept in double-distilled water and stored in the dark at 4 °C for later use. Similarly, the pure ZnSe QDs were also prepared in the absence of CdSe QDs as core.

2.4. Preparation of QD film modified GCE

The QDs include pure CdSe QDs refluxed at 100 °C for 4 h (CdSe-I QDs) or another prolonged 4 h at 160 °C (CdSe-II QDs), CdSe@ZnSe QDs with different core and shell molar ratios, CdSe QDs and ZnSe QDs mixture at the molar ratio at 1:3. The corresponding QD modified GCE electrodes were defined as CdSe-I QDs/GCE, CdSe-II QDs/GCE, CdSe@ZnSe QDs/GCE and CdSe + ZnSe QDs/GCE, respectively.

3. Results and discussion

3.1. Characterization of CdSe QDs and CdSe@ZnSe QDs

As shown in Fig. 1A, the average diameter of the CdSe QDs was about 3 nm. As expected, after the growth of ZnSe capping shell, the average size of the resulted CdSe@ZnSe QDs has been increased to 5 nm or so (Fig. 1B).

As depicted in Fig. 1C, the growth of the ZnSe caused a small bathochromic shift of absorbance in the UV-vis absorption spectra. Meanwhile, the typical UV-vis absorbance for CdSe QDs gradually decreased with the increasing ZnSe shell thickness, which means that the CdSe core has been strongly combined with the capping ZnSe

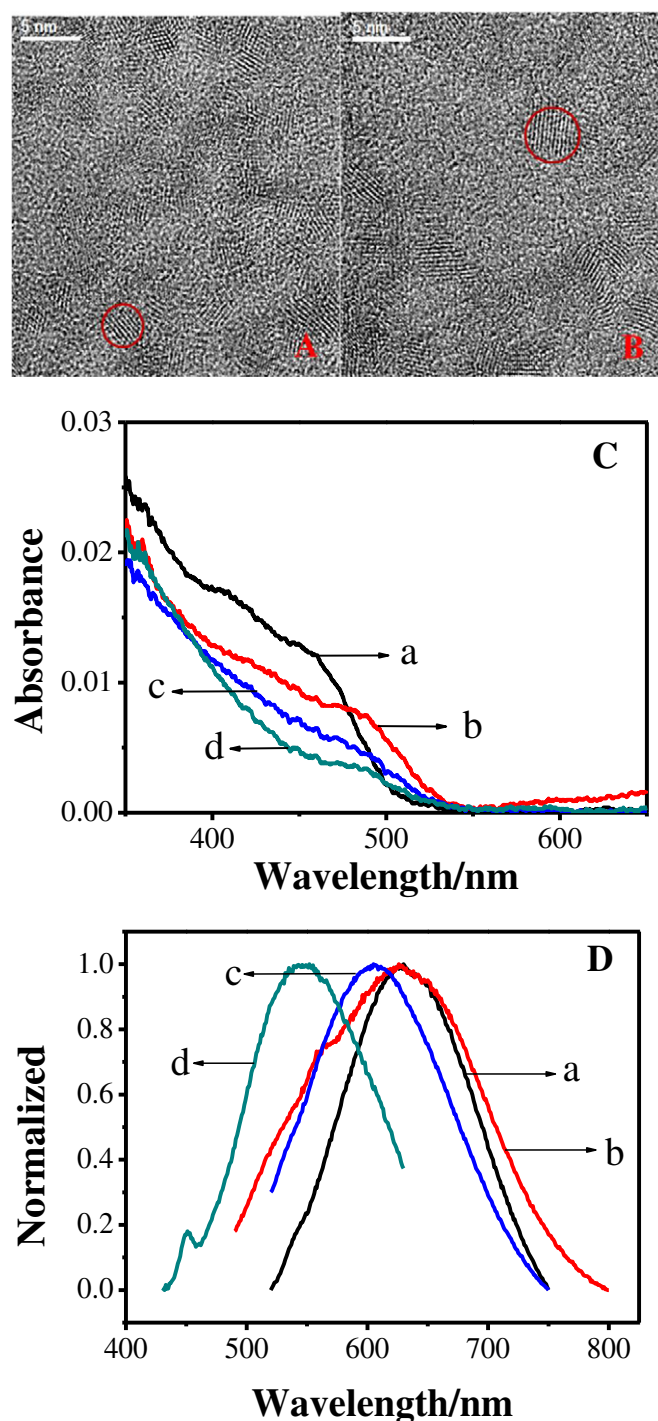


Fig. 1. TEM images of (A) CdSe QDs, (B) CdSe@ZnSe QDs, (C) the UV-Vis absorption spectra and (D) normalized photoluminescence spectra of CdSe QDs (a) and CdSe@ZnSe QDs with different core-shell molar ratios (b) 1:1, (c) 1:3 and (d) 1:5.

shell. The corresponding normalized photoluminescence spectra have been shown in Fig. 1D. Blue shift of the photoluminescence spectra was observed with continuous increasing the ZnSe shell thickness, which may be due to a result of the higher concentration of structural defects created within the thicker deposited shell [6].

3.2. ECL behaviors of CdSe@ZnSe QDs/GCE

As shown in Fig. 2A, it is worthy of pointing out that the threshold voltage and peak potential of ECL were negatively shifted along with

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