Journal of Luminescence 181 (2017) 433–438

Contents lists available at ScienceDirect

Journal of Luminescence

journal homepage: www.elsevier.com/locate/jlumin

Full Length Article

Chemiluminescence resonance energy transfer between CdS quantum dots and lucigenin and its sensing application

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ARTICLE INFO

Article history:
Received 15 May 2016
Received in revised form
6 September 2016
Accepted 5 October 2016
Available online 8 October 2016

Keywords:
Chemiluminescence
Resonance energy transfer
Lucigenin
Quantum dots
Ascorbic acid

ABSTRACT

Weak chemiluminescence (CL) of lucigenin was obtained in alkaline solution in the absence of H_2O_2, which could be apparently enhanced in the presence of CdS, CdSe, and CdTe quantum dots (QDs), and the most intense CL signal was obtained in the CdS QDs involved CL system. The CL spectrum revealed that the light emitter of lucigenin/CdS CL system is the excited state of CdS QDs. The overlap of the lucigenin CL spectrum and the UV–vis absorption spectrum of CdS QDs suggested that CL resonance energy transfer (CRET) could occur between them. The excited state of lucigenin can act as energy donor, and transfer its energy to CdS QDs, resulting in the strong CL emission. Ascorbic acid (AA) could further increase CL intensity, and the increased CL intensities were proportional to the concentrations of AA in the range of 1.0×10^{-10} mol L^{-1} to 5.0×10^{-6} mol L^{-1} with the detection limit of 6.7×10^{-11} mol L^{-1}. The proposed CRET system could be successfully applied in the sensitive detection of the level of AA in juice samples.

1. Introduction

Chemiluminescence (CL) has already been extensively applied in different areas of analytical chemistry due to its high sensitivity, wide linear range, and simple instrumentation. Generally, the study of CL was focused on several organic and inorganic molecular systems, including luminol, lucigenin, $Ru(bpy)_3^{2+}$ and Ce(IV) [1]. However, these traditional CL systems often suffered from low sensitivity and narrow application field. With the development of nanoscience and nanotechnology, metal nanoparticles involved CL has received considerable interest in the past few years, because of their unique catalytic properties and large surface area [2]. A number of researchers have indicated that the use of metallic nanoparticles in CL reactions can provide new avenues to enhance the inherent sensitivity and expand new applications of CL technique. Cui et al. reported that noble metal nanoparticles (NPs) can participate in CL reactions as reductants, catalysts, and nano-sized reaction platforms. For example, gold and platinum NPs can catalyze luminol-H_2O_2 CL reactions [3–5]. Gold and silver NPs could catalyze luminol-ferricyanide, luminol-$AgNO_3$, luminol-hydrazine, and $Ru(bpy)_3^{2+}$ CL systems [6–9]. Except metal NPs, quantum dots have been used in the CL reactions either as catalyst or as light emitter due to their good optical and electrical properties [10–15]. The advances of QDs based CL not only open a new field for the development of novel emitting species, but also expand the conventional optical utilizations of QDs.

Since it was first reported in 1934, chemiluminescent reaction of lucigenin has been used for the determination of trace metal ions and various organic reductants. The best-known CL reaction of lucigenin in alkaline aqueous media is that with hydrogen peroxide [16,17]. There are few reports about the nanoparticles involved lucigenin CL. Duan et al. found that Pt NPs can catalyze lucigenin CL to generate a visible light emission with autocatalytic property in alkaline solution [18]. Pt NPs could catalyze the reaction of lucigenin with hydrazine in alkaline solution, accompanying with a strong CL [19]. However, there has no report concerning QDs involved lucigenin CL.

Chemiluminescence resonance energy transfer (CRET) involves nonradiative transfer of energy from a CL donor to a fluorophore acceptor [10]. Since no external light is needed for the excitation in CRET approaches, the interferences caused by the light source can be eliminated, which will result in high sensitivity. However, compared with fluorescence RET, few studies had been reported on CRET due to the difficulty in finding an effective CL donor that can excite a fluorescent acceptor by energy transfer. In the most of pervious reported CRET work, luminol CL was often used as energy donor [20–25]. Meanwhile, QDs have already been proven as suitable materials for developing RET approaches, which can be used either as energy donors or as energy acceptors [26–28]. For example, Zhao et al. found that luminol-NaBrO CL can transfer its

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http://dx.doi.org/10.1016/j.jlumin.2016.10.004
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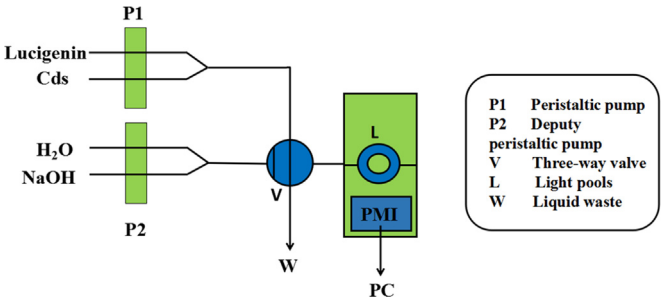

Fig. 1. Schematic diagram for flow injection-chemiluminescence system.

energy to CdTe QDs, revealing that CRET can occur between the traditional CL systems and QDs [22]. Up to date, CRET system involving lucigenin and QDs has not been reported.

Herein, lucigenin CL was investigated in the presence of CdS QDs in alkaline condition. CRET can occur between lucigenin CL and CdS QDs, resulting in the intense CL emission. The CL intensity can be further enhanced in the presence of ascorbic acid. As a result, ascorbic acid can be sensitively detected using the present CRET system.

2. Experimental section

2.1. Chemicals and solutions

A 1.0×10^{-2} mol L^{-1} stock solution of lucigenin was prepared by dissolving lucigenin (Sigma) in 0.1 mol L^{-1} sodium hydroxide solution. Working solutions of lucigenin were prepared by diluting the stock solution with double distilled water. All of other reagents were of analytical grade, and double distilled water was used throughout.

2.2. Synthesis of various QDs

CdS QDs were prepared as follows: 2 μL of mercaptoacetic acid (MPA) was added to 100 mL of 1.0 mM $CdCl_2$ solution under vigorous stirring. After adjusted the pH to 11 using 1.0 mol L^{-1} NaOH solution, the resulting clear solution was bubbled with highly pure N_2 for 30 min, and 50 mL of 1.34 mM Na_2S was added dropwise to the solution. The reaction was kept under bubbling nitrogen for 24 h [29].

CdTe QDs were synthesized according to the literature [30]. 26 μL of 6.0 mM MPA was first added into 50 mL of 2.0 mM $CdCl_2$ solution. After adjusted the pH to 11.0 using 1.0 mol L^{-1} NaOH solution, the resulting clear solution was bubbled with highly pure N_2 for 30 min, and 0.80 mL of 0.0625 mol L^{-1} NaHTe solution was slowly injected into the vigorously stirred and oxygen-free solution to obtain a yellow brown solution.

CdSe QD was synthesized following the literature procedures [31]. After 20 mL of 5.0 mM $CdCl_2$ was mixed with 20 μL of thioglycolic (TGA), 1.0 mol L^{-1} NaOH was added to adjust its pH to 10.0. The clear solution was diluted to 50 mL and bubbled with highly pure N_2 for 30 min. 0.5 mL of 0.1 mol L^{-1} Na_2SeO_3 was injected into this mixture to obtain a clear light yellow solution of CdSe QDs.

In order to purify QDs, the synthesized QDs were precipitated for three times by alcohol with centrifugation at 12,000 rpm for 10 min, and the resultant precipitates were re-dissolved in double-distilled water and kept under dark at 4 °C. The spectral behaviors of CdS, CdSe, and CdTe QDs were characterized by UV–vis absorption and fluorescence spectroscopy as shown in our previous work [32]. According to Peng's work, the average size of these QDs was 2.2 nm for CdSe, 3.5 nm for CdTe, and 3.2 nm for CdS, respectively [33].

2.3. CL measurements

The CL measurements were conducted on a model MPI-F flow-injection CL analysis system. The diagram of CL measurement was shown in Fig. 1.

Polytetrafluoroethylene tube (0.8 mm i.d.) was used to connect all components in the flow system. Two peristaltic pumps were used to deliver the solutions. The flow rates of lucigenin and CdS QDs solutions were 3.0 mL min^{-1}, which were mixed through a three-way piece. The flow rates of NaOH and ascorbic acid solutions were 1.5 mL min^{-1}, which were mixed by another three-way piece. The solutions from two three-way piece were mixed in a spiral flow CL cell, which was placed in front of the photomultiplier tube. The CL intensity was recorded as the peak height. The net CL intensity $\Delta I = I_s - I_0$ was used for the quantitative determination, where I_s and I_0 were the CL intensity of sample and blank solutions, respectively. The high voltage applied to the photomultiplier tube was maintained at −600 V throughout.

Juice samples were bought from the local supermarket. The samples were prepared by extracting the juices. The extracts were centrifuged until a clear liquid was obtained, which was diluted to a known volume with double distilled water. Then, the known amount of ascorbic acid standard solution was added, and the ascorbic acid contents in the final solutions were detected by the proposed method.

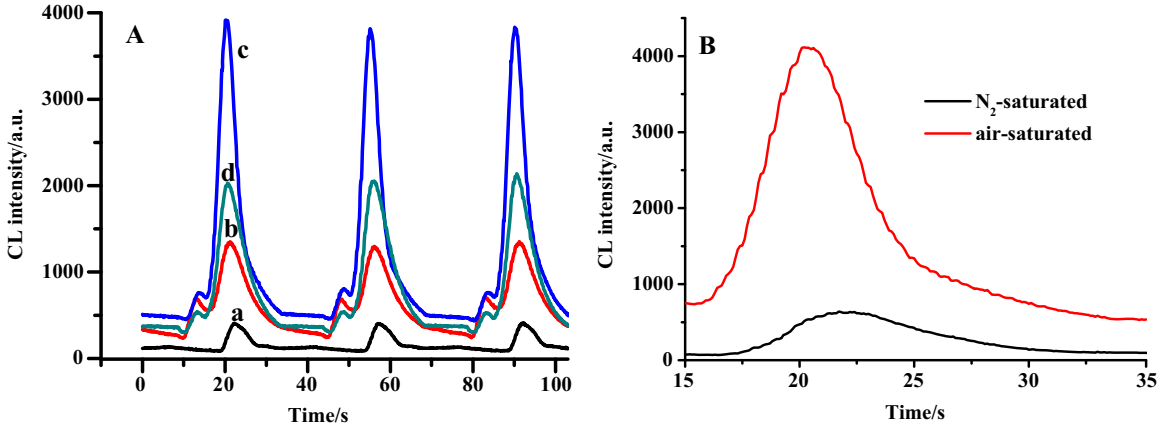

Fig. 2. (A) Enhancing effects of different QDs on lucigenin CL system. a. without QDs, b. CdSe QDs, c. CdTe QDs, d. CdS QDs. Lucigenin, 1.0×10^{-4} mol L^{-1}; NaOH, 0.1 mol L^{-1}. (B) Effect of different atmosphere on lucigenin/CdS CL system.