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Chemiluminescence of CdTe nanocrystals catalyzed by sodium hexametaphosphate and its sensitive application for determination of estrogens

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ABSTRACT

A novel flow injection nanocrystals (NCs) chemiluminescence (CL) analysis method has been established for the determination of estradiol, estriol and estrone based on the enhancement of CdTe NCs–$KMnO_4$ CL reaction catalyzed by sodium hexametaphosphate. Glutathione (GSH)-capped CdTe nanocrystals were synthesized in aqueous medium, and the CdTe NCs emitted at around 555 nm was selected as the light emitter in CdTe NCs–$KMnO_4$ chemiluminescence (CL) system. It has been found that sodium hexametaphosphate (SHMP) enhanced the CL of the CdTe NCs–$KMnO_4$ system and estrogens increased these CL signals again in near neutral solution. UV–visible spectra, photoluminescence (PL) spectra, transmission electron microscopy (TEM) and CL spectra were used to characterize CdTe nanoparticles and investigate the mechanism of the CL reaction. On the basis of the enhancement, a novel flow-injection CL method has been established for the determination of estrogens. Under the optimum experimental conditions, three linear relationships were obtained. The method described is simple, sensitive, and has been successfully utilized for the determination of estrogens in tap water samples.

1. Introduction

Estradiol (E2), estriol (E3) and estrone (E1), three essential natural steroid hormones, play a very important role in the human body. Estradiol, secreted by the mature follicle of the ovary, can promote and adjust the feminine reproductive organ and the secondary sexual characteristic growth. Estriol, the estradiol metabolite, has the vital function in the medicine and could be used in the cervicitis on clinical. In addition, estrone has also potential uses in the medicine, treating the womb hypoplasia, menstruation being out of balance and the menopause barrier. However, they adjust feminine growth mature process normally in the low concentration. Herein, some analytical methods which have low detection limits and wider linear range are needed to monitor and control the reasonable use of estrogens.

Many analytical methods have been reported for the determination of estrogens, for example high performance liquid chromatography (HPLC) [1,2], electrocatalytic method [3], enzyme-linked immunosorbent assay (ELISA) [4], surface plasmon resonance (SPR) [5], gas chromatography–mass spectrometry (GC–MS) [6–8], HPLC–MS [9,10], and surface-assisted laser desorption/ionization mass spectrometry (SALDI-MS) [11]. Although most of these methods are sensitive and specific, they are also expensive, complicated and time-consuming. Due to the advantages of rapidity, high sensitivity, wide linear range, no background scattering light interference and relatively cheap instruments and reagents, chemiluminescence (CL) detection has also been used in determination of estrogens recently. In 2005, Schneider et al. developed the CL enzyme-linked immunosorbent assay for detection of ethinylestradiol [12]. Zhao and Lin used a micro-plate magnetic chemiluminescence enzyme immunoassay (MMCLEIA) for the determination of 17β-estradiol in water samples [13]. Wang et al. reported a tetrasulfonated manganese phthalocyanine (MnTSPc) catalyzed luminol–H_2O_2 CL system for the determination of estradiol, estrone and estriol in 2006 [14]. Li et al. also reported the measurement of estradiol, estrone and estriol by a novel luminol chemiluminescent method catalyzed by gold nanoparticles in 2007 [15]. Herein CL has its unique superiority in detecting estrogens.

Recently, the study of CL has been extended to nanoparticle systems. Colloidal semiconductor nanocrystals (quantum dots, QDs) have attracted much attention as fluorescence biological probes [16,17], donors or acceptors of fluorescence resonance energy transfer [18,19] and in bioimaging [20], because of their remarkable size-dependent optical, narrow emission peak and electronic properties. The incorporation of QDs has opened up new ways in the field of novel applications with enhanced sensitivity. Wang et al. reported the CL of CdTe NCs directly oxidized by some oxidants, such as H_2O_2 and $KMnO_4$, and its size-dependent and surfactant-sensitized effects [21]. Li et al. have reported the enhancement of the CL intensity using gold nanoparticles [22]. Jie et al. developed a novel label-free ECL biosensor based on CdS NCs for the detection of low-density lipoprotein by using self-assembly and

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gold nanoparticle amplification techniques [23]. Recently, the as-prepared luminol/antibody labeled Au NPs conjugates (LAAu NPs) were used as the chemiluminescent probe for the detection of carcinoembryonic antigen (CEA) in serum [24]. Kanwal et al. proposed polystyrene microspheres based sandwich immunosensor using CdTe nanoparticles amplification and ultrasensitive flow-injection chemiluminescence detection [25]. Thus, it would be of great significance to explore the novel CL behavior of semiconductor quantums for developing novel CL sensors. In our work, we employed CdTe NCs as emitter in CL reaction.

Most CL reactions have low quantum efficiencies and thus show weak luminescence. The weak emission can be greatly enhanced by sensitizers. In the present work, it was found that the addition of sodium hexametaphosphate into CdTe NCs–$KMnO_4$ system could increase CL signals. When in the presence of estrogens, these CL signals induced a great of enhancement in near neutral pH solution. Based on this, sensitive determination of trace levels of estrogens has been developed and applied for the determination of estrogens in tap water samples.

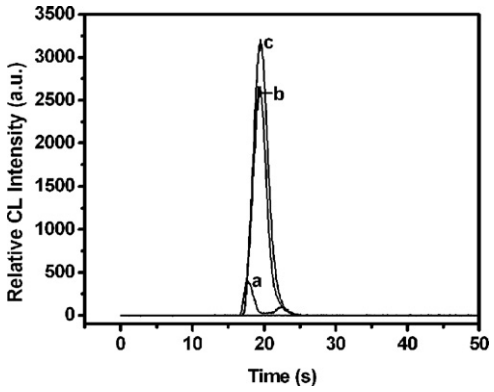

Fig. 1. The chemiluminescence kinetic curves of the CdTe–$KMnO_4$ CL reaction, without SHMP (a) and with SHMP in the absence of estradiol (b) and in the presence of 5.0×10^{-7} mol L^{-1} estradiol (c). Conditions: CdTe, 1.25×10^{-3} mol L^{-1}; $KMnO_4$, 3.0×10^{-4} mol L^{-1}; SHMP, 4.0×10^{-3} mol L^{-1}; PBS, 6.0; flow rate, 3.43 mL/min.

2. Experimental

2.1. Reagents

All the chemicals used were of analytical reagent grade or better. $CdCl_2 \cdot 2.5H_2O$ (99%), tellurium powder (99.999%) and β-estradiol were purchased from Alfa Aesar. $NaBH_4$ (98%) was obtained from Aladdin. Sodium hexametaphosphate (SHMP), estriol and estrone were from Sigma–Aldrich. L-Glutathione reduced (GSH) (≥99%) was purchased from Beijing Biodee Biotechnology Co. Potassium permanganate was from Sinopharm Chemical Reagent Co. Ltd.

Potassium permanganate stock solution (1.0×10^{-2} mol L^{-1}) was prepared by dissolving solid in doubly distilled water. The working solution was prepared daily by diluting the stock solution with water. SHMP solution was prepared daily in water. Stock solutions of estrogens were firstly prepared in 0.01 mol L^{-1} NaOH solution and stored in refrigerator and the working standard solution was diluted with water. All water used was doubly distilled water.

2.2. Preparation of CdTe NCs

GSH-capped CdTe NCs were synthesized as the procedure achieved by several groups [26,27], and we made little modification. Briefly, Cd precursor solutions were prepared by mixing a solution of $CdCl_2$ and GSH solution, and adjusted to pH 8.0–8.5 with 1 M NaOH. Then NaHTe solution, prepared by the reaction between Te powder and $NaBH_4$, was added to N_2-saturated $CdCl_2$ solution in the presence of GSH. The molar ratio of Cd^{2+}:Te:GSH was fixed at 4:1:10. After mixing, the reaction solution was heated to 90 °C and refluxed at different times to prepare GSH-capped CdTe NCs with different sizes. CdTe NCs samples used in the present work were purified by selective precipitation with isopropanol and re-dispersed in doubly distilled water.

2.3. Apparatus

The schematic diagram of the flow system employed in this work is shown in Fig. S1. It has two peristaltic pumps and an injection system synchronized by a microprocessor.

PTFE tubing (0.8 mm i.d.) was used as connection material in the flow system. Injection was worked using a six-way injection valve and finally reached the flow cell to produce chemiluminescence emission. The flow cell was made of colorless glass tube (0.5 mm i.d.) connected to a photomultiplier tube. The CL signals were detected and recorded with a computerized ultraweak luminescence analyzer (Xi'an Remex Analysis Instrument Co. Ltd., Xi'an, China). Date acquisition and treatment were performed with Remax software running under Windows XP. The CL spectra were recorded with a Hitachi F-2500 spectrofluorimeter (Tokyo, Japan) with the light source switched off. The PL spectra of CdTe NCs were performed on a model F-4500 spectrofluorometer (Hitachi, Japan) and the UV–visible absorption spectra were performed on a model UV-3010 spectrophotometer (Hitachi, Japan). All pH values were measured with a pHS-3C digital pH meter (Analytical Instruments Co., Tianda, Shanghai, China). The transmission electron microscopy (TEM) images of the nanocrystals were acquired using a high-resolution transmission electron microscopy (JEOL, JEM-2010, Japan).

2.4. Procedures

To obtain good mechanical and thermal stability of the flow-injection CL system, the instruments were run for 30 min before measurement. One peristaltic pump (two channels) was used to carry estrogen/PBS solution (or sample solution) and CdTe NCs, and another pump (two channels) was used to carry SHMP solution and $KMnO_4$ solution, respectively. The flow rate was fed at 3.43 mL/min for all lines. The pumps then started to inhale the whole system until a stable baseline was recorded. As shown in Fig. 1, the CdTe NCs–$KMnO_4$ system could emit weak CL in PBS buffer solution. However, when 4×10^{-3} mol L^{-1} SHMP was injected into the stream, the CL signal was enhanced greatly. Therefore, it could be assumed that SHMP strongly catalyzed the CdTe NCs–$KMnO_4$ CL reaction. When 5×10^{-7} mol L^{-1} β-estradiol was added to this system, the CL intensity enhanced. The similar phenomena could be observed for E1 and E3. It had no CL signal in the absence of CdTe NCs.

3. Results and discussion

3.1. Characterization and CL spectra of CdTe NCs

Fig. 2 shows the absorption and PL spectra of the different sizes of GSH-capped CdTe NCs. These CdTe NCs had an absorption maximum of the first electronic transition. And the PL peak and absorption maximum (Fig. 2) shifted to longer wavelengths with increasing NCs sizes, which can be calculated by the expression [28]:

$$D = (9.8127 \times 10^{-7})\lambda^3 - (1.7147 \times 10^{-3})\lambda^2 + (1.0064)\lambda - 194.84$$