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A novel flow-injection chemiluminescence method for determination of baclofen using L-cysteine capped CdS quantum dots

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ABSTRACT

L-Cysteine capped CdS quantum dots (QDs) were synthesized through a facile hydrothermal method and characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM), photoluminescence (PL), and UV–vis spectroscopy. The L-cysteine capped CdS QDs sample displayed chemiluminescence (CL) emission in reaction with $KMnO_4$ in acidic medium. It was found that the CL intensity of $KMnO_4$–L-cysteine capped CdS QDs CL system was remarkably enhanced in the presence of $Na_2S_2O_3$. Furthermore, the possible CL mechanism was presented for this CL reaction according to results of the kinetic curves of CL systems, the spectra of CL, PL and UV–vis. The CL intensity of $KMnO_4$–L-cysteine capped CdS QDs–$Na_2S_2O_3$ was strongly inhibited in the presence of baclofen. Based on this inhibition, a novel and sensitive flow-injection CL method was developed for the determination of baclofen. Under optimum conditions, the CL intensity was inversely proportional to the concentration of baclofen in the range of 0.012–24.0 mg L^{-1}, with a detection limit (3σ) of 0.0035 mg L^{-1}. The analytical applicability of the proposed CL system was assessed by determining baclofen in spiked environmental water samples and pharmaceutical formulation. The analytical performances of proposed flow-injection CL method for the determination of baclofen were compared with those obtained by corona discharge ionization ion mobility spectrometry (CD-IMS) method. The proposed CL system had a higher sensitivity than the CD-IMS method for the determination of baclofen.

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1. Introduction

Baclofen (4-amino-3-*p*-chlorophenylbutyric acid) is a gamma-aminobutyric acid (GABA) agonist that extensively uses as a skeletal muscle relaxant and antispastic agent in the treatment of spasticity caused by neurological disorders [1,2]. Development of new analytical approaches for determination of baclofen in environmental water samples and pharmaceutical products is of importance. Because the occurrence of different pharmaceuticals in the aquatic environment results from direct release from their production plants, as a source of much higher environmental discharges, human and animal excretion of unchanged pharmaceuticals and their metabolites and incorrect disposal of expired medicines [3,4]. In past decades, trace levels of these compounds have been detected in water resources. This is a major concern and a potential threat to human health, as well a threat to aquatic organisms [5]. Therefore, it is essential to detect the amounts of pharmaceuticals such as baclofen in environmental water samples. Moreover, the determination of baclofen in the pharmaceutical products is very important in the efficacy in the therapy of various diseases and in the quality control of baclofen preparations in the pharmaceutical industries.

To date, variety of analytical methods have been exploited for the determination of baclofen, including spectrophotometry [6–8] high-performance liquid chromatography (HPLC) [9–14], gas chromatography (GC) [15–17], liquid chromatography–tandem mass spectrometry (LC/MS/MS) [2,18–20], capillary electrophoresis (CE) [21–24], and potentiometry [25,26]. Although these methods are extensively used for the determination of baclofen in the diverse matrix, they suffer from some imperfections such as expensive instrumentation, tedious extraction procedures, need for toxic and costly organic solvents, derivatization, and considerable processing time [2,27].

Chemiluminescence (CL) methods have attracted extensive interest in various fields of analytical chemistry due to their

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simplicity of operation, high sensitivity, wide linear range, low detection limits, speed and low background signals [28]. In addition, the incorporation of a flow-injection analysis technique with CL-based detection provides high analytical throughput [29]. Nowadays, flow-injection CL method has been extended to be a powerful and important tool in a wide range of fields including clinical diagnosis [30], environmental [27,31,32], pharmaceutical [29] and food analysis [28,32].

Recently, CL studies have been developed from traditional molecular reactions for applications in nanomaterial-based systems; this has which have extended the field of applications of CL detection. Nanomaterials with the unique chemical and physical properties and high surface area have amplified the CL signal, which improved the sensitivity and stability of various CL systems [27,31,33,34]. Colloid semiconductor nanocrystals, quantum dots (QDs), owing to their extremely small sizes, tunable photoluminescence (PL) and their interesting electro-optical properties, have attracted tremendous consideration in many areas and possible applications such as bio-labeling and bio-imaging [35,36]. They can be produced readily as water-soluble forms by proper capping with hydrophilic ligands [37]. In most cases, the thiol-based ligands such as, mercaptoacetic acid, thioglycolic acid, glutathione and L-cysteine, were used as capping agents [35,38]. QDs are also applied in CL reactions as the CL emitting species or as catalysts of redox CL reactions. QDs have been employed as enhancer or sensitizer of Ce(IV)-sulfite [39,40], luminol–$KMnO_4$ [41] and luminol–$K_3Fe(CN)_6$ [42] HCO_3^-–H_2O_2 [43] CL systems. Direct CL of QDs occurs when an electron is injected into the conduction band and a hole is injected into the valence band of QDs after direct oxidation. When the excited state of the QDs returns to its ground state, CL emission is produced [35,38]. Talapin et al. [44] reported the first observation of the CL emission of QDs in which H_2O_2 was added into a solution containing dispersed CdSe/CdS nanocrystals. Li et al. [45] and Wang et al. [46] pointed out that CdTe and CdS QDs could be directly oxidized by H_2O_2 in basic conditions. In another work, Li et al. [47] reported that CdTe QDs modified with three different thioalkyl acids (mercaptoacetic acid, cysteine, and glutathione) could be directly oxidized by $K_3Fe(CN)_6$ generated CL emission in alkaline media.

It should be pointed out that the quantum yield of QDs–H_2O_2 CL systems is considerably low in comparison with the traditional CL systems such as luminol-oxidant systems [20]. Furthermore, in the reported QDs–H_2O_2 CL systems, high concentration of H_2O_2 (1 mol L^{-1} [45] or 0.8 mol L^{-1} [46]) was utilized as the CL oxidant. The decomposition of high concentration of H_2O_2 is very fast in the strong basic media, which would produce unstable CL signals [48]. These shortcomings may impede further extension of applications of QDs–H_2O_2 CL systems. Accordingly, optimizing CL reaction condition is of importance to improve the analytical performance of QDs CL systems.

In the present work, sensitive and novel flow-injection CL method has been developed for the determination of baclofen in spiked environmental water samples and pharmaceutical formulation. The possible mechanism of CdS QDs CL system was studied. Also, the obtained analytical results from the proposed CL and CD-IMS methods for the determination of baclofen were compared. To the best of the authors' knowledge, $KMnO_4$–L-cysteine capped CdS QDs–$Na_2S_2O_3$ CL system for the determination of baclofen has not been investigated yet.

2. Materials and methods

2.1. Materials and solutions

All the chemicals and reagents used were of analytical reagent grade and purchased from Merck Co. (Germany). Baclofen was supplied by Zahravi Pharmaceutical Co. (Tabriz, Iran). Doubly distilled water was used overall the experiments. The working solutions of H_2O_2 were freshly prepared from 30% (w/v) H_2O_2 reagent. A 100 mg L^{-1} stock standard solution of baclofen was freshly made by dissolving 10 mg baclofen in 100 mL of doubly distilled water, which was then stored at 4 °C in a refrigerator and kept away from light.

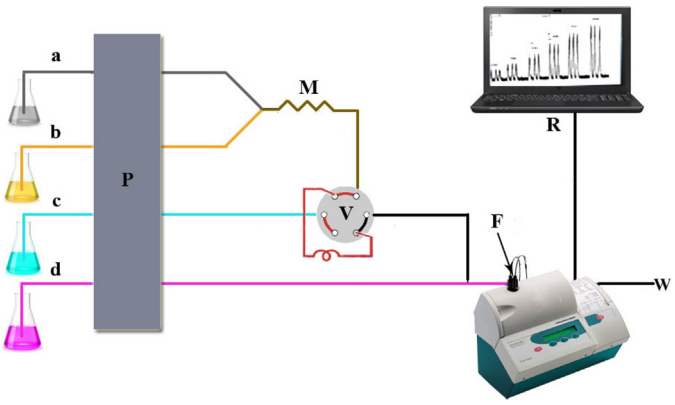

Fig. 1. Schematic diagram of flow-injection CL system: (a) acid solution; (b) sample or standard solution of mixture of baclofen and L-cysteine capped CdS QDs; (c) H_2O as the carrier; (d) $KMnO_4$ solution. P: peristaltic pump; M: mixing tube; V: injection valve; F: flow cell; W: waste; D: detector (luminometer); R: recorder (personal computer).

2.2. Apparatus

The CL signals produced from the CL reaction in the flow cell were detected with a FB12 luminometer (Berthold Detection Systems, Germany). The output from the luminometer was captured by the computer for data acquisition. Ultraviolet–visible (UV–vis) spectra of samples were recorded on a UV-Vis spectrophotometer (WPA Lightwave S2000, England). The X-ray diffraction (XRD) patterns were recorded to determine the crystal phase composition of synthesized CdS QDs using a Siemens X-ray diffractometer D5000 (USA), with Cu Kα radiation source of 1.54065 Å, the accelerating voltage of 40 kV and emission current of 30 mA. The average crystalline size of the samples was calculated according to the Debye–Scherrer formula [49]. The surface morphology and size of the synthesized QDs samples were characterized by scanning electron microscopy (SEM) via Mira3 FEG SEM (Tescan, Czech Republic), transmission electron microscopy (TEM) images and the selected area electron diffraction (SAED) patterns of synthesized sample were taken by a Cs-corrected TEM (JEM-2200FS, JEOL, Japan) operating at 200 kV. Fourier transform infrared (FT-IR) spectra were recorded with an IR-spectrometer (Tensor 27, Bruker, Germany). The photoluminescence spectra were measured on a spectrofluorometer (FP-6200, Jasco, Japan). Ion mobility spectrometry (IMS) apparatus (model 200, TOF Tech. Pars Co., Iran) with the corona discharge ionization source in the positive mode were used in this study. This instrument consisted of various parts such as IMS cell, a thermostatic oven, a needle for generating the corona, power supplies, a pulse generator, an analog-to-digital converter (PicoScope, UK), and a computer for data processing. The IMS cell includes ionization and drift regions separated by shutter grid. A Faraday cup detector was applied for ion current collection.

2.3. Procedures for chemiluminescence assay

Fig. 1 depicts a schematic diagram of the laboratory-made flow-injection CL detection system utilized in this work. All the

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