Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy 157 (2016) 88–95

Contents lists available at ScienceDirect

Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy

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

Flow-injection chemiluminescence analysis for sensitive determination of atenolol using cadmium sulfide quantum dots

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ARTICLE INFO

Article history:
Received 26 October 2015
Received in revised form 11 December 2015
Accepted 13 December 2015
Available online 15 December 2015

Keywords:
Atenolol
CdS quantum dots
CTAB
Chemiluminescence
Flow injection

ABSTRACT

A sensitive, rapid and simple flow-injection chemiluminescence (CL) system based on the light emitted from $KMnO_4$–cadmium sulfide quantum dots (CdS QDs) reaction in the presence of cetyltrimethylammonium bromide (CTAB) in acidic medium was developed as a CL probe for the sensitive determination of atenolol. Optical and structural features of CdS QDs capped with L-cysteine, which synthesized via hydrothermal approach, were investigated using X-ray diffraction (XRD), scanning electron microscopy (SEM), photoluminescence (PL), and UV–Vis spectroscopy. The CL intensity of $KMnO_4$–CdS QDs–CTAB was remarkably enhanced in the presence of trace level of atenolol. Under optimum experimental conditions, there is a linear relationship between the increase in CL intensity of $KMnO_4$–CdS QDs–CTAB system and atenolol concentration in a range of 0.001 to 4.0 mg L^{-1} and 4.0 to 18.0 mg L^{-1}, with a detection limit (3σ) of 0.0010 mg L^{-1}. A possible mechanism for $KMnO_4$–CdS QDs–CTAB-atenolol CL reaction is proposed. To prove the practical application of the $KMnO_4$–CdS QDs–CTAB CL method, the method was applied for the determination of atenolol in spiked environmental water samples and commercial pharmaceutical formulation. Furthermore, corona discharge ionization ion mobility spectrometry (CD-IMS) technique was utilized for determination of atenolol.

1. Introduction

Atenolol, [4-[2-hydroxy-3-isopropyl-aminopropoxy]-phenyl-acetamide], is a β_1-receptor antagonist belonging to the category of β-blockers that is widely used in the therapy of diverse cardiovascular disorders such as angina pectoris, cardiac arrhythmia, and systematic hypertension [1]. It has been added to the list of banned drugs because of misuse as doping agents in sports, due to its soothing effect. The antihypertensive effect of atenolol means that a single dosage of 50 or 100 mg must be administered daily. An excessive dosage can lead to bradycardia, severe hypotension with shock, aggravation of cardiac failure, sinus pause, hypoglycemia, and bronchospasm [2]. Hereupon, development of simple and sensitive analytical techniques to determine the presence of atenolol in many fields, including doping control, forensic analysis, toxicology, and pharmacokinetic study, is of importance.

Moreover, pharmaceuticals can be accumulated in aqueous systems through inappropriate disposal and discharge of hospital and chemical industry wastes to the wastewater treatment plants [3–5]. Most of these compounds are resistant to natural removal, so they can remain in the environmental water resources for a long time and cause serious health problems [6]. Due to the aforementioned considerations, monitoring of atenolol in environmental water samples is very significant. As a result of the widespread use of atenolol, several analytical techniques have been used for the determination of atenolol in recent years, including liquid chromatography (LC) [7], high performance liquid chromatography (HPLC) [8–11], reverse-phase HPLC [12,13], spectrophotometry [14,15], liquid chromatography–tandem mass spectrometry (LC–MS–MS) [2], voltammetry [16], and chemiluminescence (CL) [1,17]. Although each reported analytical method has its advantages, the chromatography methods still involve expensive instrumentation, the need for toxic and costly organic solvents, tedious and time-consuming procedures [1,14,15]. Also, spectrophotometric methods lack sensitivity and selectivity [18].

CL has attracted considerable attention as a useful detection tool in wide variety of analytical applications due to its simplicity of operation, rapid response, high sensitivity, and wide dynamic range [18]. In addition, the incorporation of a flow-injection analysis technique with CL-based detection provides high analytical throughput [19]. Over the past several years, in order to improve the sensitivity and the stability of diverse CL reactions, nanomaterials have drawn considerable interest as signal amplifier in CL-based systems, due to their unique size and physicochemical attributes [18–20]. Among nanomaterials, quantum dots (QDs) have attracted substantial attention due to their exceptional photophysical properties and well-controlled nanosurface which result

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http://dx.doi.org/10.1016/j.saa.2015.12.015
1386-1425/

in probable application in a broad range of fields such as bio-labeling, bio-imaging, and multicolored photoluminescent probes [21]. Since traditional CL systems have low quantum yield, incorporation of QDs because of their brightness and continuous band gap tunability can improve the quantum yield of some CL reactions [22]. Direct CL of QDs occurs when an electron is injected into the conductive band and a hole is injected into the valence band of QDs after direct oxidation. The returning excited state of QDs to its ground state results in producing direct CL emission [21,23,24]. QDs-catalyzed CL systems were also studied, and their applications in detection of some analytes were demonstrated [22,25–27]. Talapin et al. [24] pointed out the first observation of QDs as an emitting species in CL system which was induced during direct oxidation of CdSe/CdS (core/shell) nanocrystals.

It should be noticed there are some restrictions in the utilization of QDs-H_2O_2 CL system due to drawbacks such as, low quantum yield, high concentration uses of H_2O_2, and relatively unstable signals which may be the result of fast decomposition of high concentration of H_2O_2 in basic condition [28,29]. Consequently, developing the QDs-based CL reaction is of importance for improving their analytical application in different fields [28].

Regarding to our knowledge, there is no previous report in the literature describing the enhancing effect of atenolol on $KMnO_4$–CdS QDs and $KMnO_4$–CdS QDs–CTAB CL systems in acidic media. In the present work, trace atenolol could enhance the CL emission of $KMnO_4$–CdS QDs and $KMnO_4$–CdS QDs–CTAB systems. $KMnO_4$–CdS QDs–CTAB CL system is more appropriate for determination of atenolol which led to the development of a sensitive and simple flow-injection CL method. The possible mechanism of the CdS QDs CL system in the presence of atenolol was investigated. Meanwhile, feasibility of the proposed CL method for determination of atenolol in spiked environmental water samples and pharmaceutical formulation was also proved. In addition, corona discharge ionization ion mobility spectrometry (CD-IMS) was employed for the determination of atenolol. Then, the obtained analytical features from the proposed CL and CD-IMS methods for the determination of atenolol were compared.

2. Experimental

2.1. Materials and solutions

All used chemicals and reagents were of high purity, analytical grade, or equivalent and purchased from Merck Co. (Germany). Atenolol was provided from Hakim pharmaceutical Co. (Tehran, Iran). All aqueous solutions were prepared with double-distilled water. Fresh stock standard solution of 100 mg L^{-1} atenolol was daily prepared by dissolving 10 mg of atenolol into 100 mL of double-distilled water, which was then maintained at 4 °C in a refrigerator and kept away from light.

2.2. Apparatus

The generated CL signals in the flow cell were determined via a CL analyzer, luminometer (FB12, Berthold detection systems, Germany). The generated signals were imported to the computer for data acquisition. Ultraviolet–visible (UV–Vis) spectrophotometer (S2000, WPA Lightwave, England) was utilized to implement scan spectrum of the samples. Crystal structure characterization was carried out by X-ray diffraction (XRD) analysis performed with a Siemens X-ray powder diffractometer (D5000, Siemens, Germany) with Cu Kα radiation (λ = 1.54056 Å) at room temperature. The average crystalline size of the prepared samples was calculated using the Debye–Scherrer formula [30]. The general morphology and surface structure of the prepared CdS QDs sample were recorded on a Mira3 FEG scanning electron microscopy (SEM) (Tescan, Czech Republic) and a Cs-corrected transmission electron microscopy (TEM) (JEM-2200FS, JEOL, Japan). The photoluminescence (PL) spectra were performed with a spectrofluorometer (FP-6200, Jasco, Japan). Furthermore, an ion mobility spectrometry (IMS) equipment (model 200, TOF Tech. Pars Co., Iran) by source type of corona discharge ionization was implemented in the positive mode. This device was equipped with an IMS cell, a thermostatic oven, a needle to produce the corona, power supplies, a pulse generator, an analog to digital converter (PicoScope, UK), and a computer for processing of the data.

2.3. Procedures for chemiluminescence assay

The configuration of the laboratory-made flow-injection CL detection system used in this work is represented in Fig. 1. All the solutions were continuously propelled into the flow cell by a peristaltic pump and the flow rate was set at 2.0 mL min^{-1} for all lines. A six-port injection valve with a 100 μL loop (Cheminert C22, Valco Instruments Co, Houston, USA) was employed for sample injection into the flow cell. The flow cell that is used for the present work was made by winding the length of glass tubing (0.8 mm i.d) to form coil of 100 μL volume. All flow lines were in polytetrafluoroethylene (PTFE) tubing (1.0 mm internal diameter (i.d.)). The solution streams were merged in the Y-pieces. As shown in Fig. 1, the acid solution (a), sample or standard solution of the mixture of atenolol, CTAB and CdS QDs (b), double-distilled

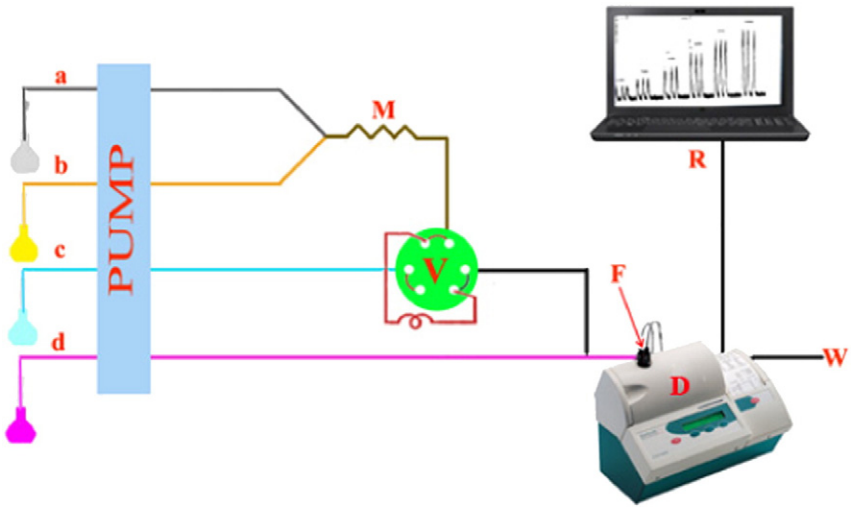

Fig. 1. Schematic diagram of flow-injection CL system; (a): acid solution; (b): sample or standard solution of mixture of atenolol, CTAB, and CdS QDs; (c): H_2O as the carrier; (d): $KMnO_4$ solution; P: peristaltic pump; M: mixing tube; V: injection valve; F: flow cell; W: waste; D: detector (luminometer);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