Journal of Colloid and Interface Science 472 (2016) 76–83

Contents lists available at ScienceDirect

Journal of Colloid and Interface Science

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

Dual-channel optical sensing platform for detection of diminazene aceturate based on thioglycolic acid-wrapped cadmium telluride/cadmium sulfide quantum dots

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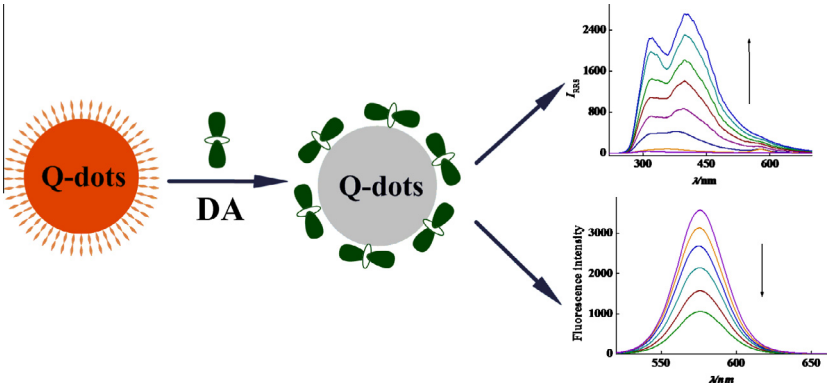
HIGHLIGHTS

- A dual-channel optical sensing platform has been designed for the detection of DA.
- The sensing platform combines the advantages of DWO-RRS and fluorescence.
- The possible mechanism of the sensing system was also explored.
- The proposed method has been successfully applied to the detection of DA in the milk samples.

GRAPHICAL ABSTRACT

We design a dual-channel optical sensing platform which combines the advantages of dual-wavelength overlapping resonance Rayleigh scattering (DWO-RRS) and fluorescence for the detection of diminazene aceturate (DA). The proposed method has been applied successfully to the detection of DA in milk samples.



ARTICLE INFO

Article history:
Received 12 November 2015
Revised 4 March 2016
Accepted 11 March 2016
Available online 11 March 2016

Keywords:
Quantum dots
Diminazene aceturate
Dual-wavelength overlapping resonance
Rayleigh scattering
Fluorescence

ABSTRACT

A dual-channel optical sensing platform which combines the advantages of dual-wavelength overlapping resonance Rayleigh scattering (DWO-RRS) and fluorescence has been designed for the detection of diminazene aceturate (DA). It is based on the use of thioglycolic acid-wrapped CdTe/CdS quantum dots (Q-dots). In the absence of DA, the thioglycolic acid-wrapped CdTe/CdS Q-dots exhibit the high fluorescence spectrum and low RRS spectrum, so are selected to develop an easy-to-get system. In the presence of DA, the thioglycolic acid-wrapped CdTe/CdS Q-dots and DA form a complex through electrostatic interaction, which result in the RRS intensity getting enhanced significantly with new RRS peaks appearing at 317 and 397 nm; the fluorescence is powerfully quenched. Under optimum conditions, the scattering intensities of the two peaks are proportional to the concentration of DA in the range of 0.0061–3.0 μg mL^{-1}. The detection limits for the two single peaks are 4.1 ng mL^{-1} and 3.3 ng mL^{-1}, while that of the DWO-RRS method is 1.8 ng mL^{-1}, indicating that the DWO-RRS method has high sensitivity. Besides, the fluorescence also exhibits good linear range from 0.0354 to 10.0 μg mL^{-1} with a detection limit of 10.6 ng mL^{-1}. In addition, the system has been applied to the detection of DA in milk samples with satisfactory results.

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http://dx.doi.org/10.1016/j.jcis.2016.03.017
0021-9797/

1. Introduction

The increasing concern about food safety issues, especially chemical residues in food animals, has stimulated active research in recent years [1–3]. Residues of these chemicals may enter the food chain and compromise human health, so the importance of ensuring food safety through the reduction of chemical residues in our food supply cannot be overemphasized. Diminazene aceturate (DA), which primarily consists of two amidinophenyl moieties linked by a triazene bridge, is one of the few treatment drugs for animal trypanosomosis in the market [4]. DA residues can lead to the emergence of bacterial resistance and the accumulation of residues in animal products [5]. To ensure wholesomeness of food of animal origin and protect consumers from exposure to the chemical residue, the Joint FAO/WHO Expert Committee on Food Additives have established maximum residue limits (mg/kg) for DA in edible animal tissues: muscle, 0.5; liver, 1.2; kidney, 6; milk, 0.15 [6]. In addition, a conservative acceptable daily intake of <100 μg/kg/day is set for human consumption [7].

In view of the importance of the detection of DA, some strategies have been proposed, such as capillary zone electrophoresis (CZE) [8], high-performance liquid chromatographic (HPLC) method [9,10], liquid chromatography-mass spectrometry (LC-MS) [11], enzyme linked immuno sorbent assay (ELISA) [12] and electrochemical method [13]. The CZE is rapid and effective, yet it commonly suffers from lack of stability and reproducibility. The HPLC and LC-MS methods, although sensitive and specific multi-analytical results, tend to be time consuming and dependent on highly skilled personnel and expensive equipments. ELISA provides relatively lower detection limit, but it involves several complicated procedures so as to obtain the antibody. Electrochemical method is attractive for DA detection because of its wide linear range and sensitivity, but the lack of stability and involving several complicated and tedious steps to fabricate functionalized electrodes cannot be neglected. Therefore, developing a rapid, simple, high sensitivity and low-cost method for quantitative detection of DA is urgently needed.

Multidimensional sensing devices such as dual- [14–16], triple- [17] and quadruple-channel [18] sensing have drawn significant attention, on account of they can offer more than one transduction channel and thereby enhance the accuracy and/or diversity. Nevertheless, most of these are based on the preparation of optical probes for target guest. Undoubtedly, the sophisticated molecular synthesis is technically complex and time-consuming. Q-dots, robust inorganic chromophores, often possess more than one-dimensional optical properties, which can provide vast potential for multichannel sensing. But thus far, Q-dots are still widely used as a fluorescent probe for ions, drugs and foods [19–21]. Particularly, dual-channel optical sensing based on Q-dots is rare in addition to the paper published by Wu et al. [16]. The system was developed through integration of the optical responses (phosphorescence emission and resonant light scattering) of Mn-doped ZnS Q-dots. The thioglycolic acid-wrapped CdTe/CdS Q-dots exhibit the high fluorescence spectrum and low resonance Rayleigh scattering (RRS) spectrum, are promising candidates for dual-channel optical sensing. RRS, a well-developed analytical technique in recent years, has been known for its sensitivity and simplicity. The assay is sensitive to the molecular interaction such as hydrophobic interaction, hydrogen bonding and intermolecular electrostatic attraction [22]. Recently, multi-response RRS has brought into focus due to much higher sensitivity and better flexibility than the single-wavelength method. For instance, Zhu et al. reported a dual-wavelength overlapping resonance Rayleigh scattering (DWO-RRS) method for the detection of doxycycline [23]. Hao et al. and Shi et al. developed a triple-wavelength overlapping resonance Rayleigh scattering (TWO-RRS) method for drug analysis [24,25]. Multi-response RRS as a novel and improved technique is a revolutionary milestone in the development of RRS.

Herein, we develop a dual-channel optical sensing platform for the detection of DA by utilizing simultaneously DWO-RRS and fluorescence based on thioglycolic acid-wrapped CdTe/CdS Q-dots. The dual-channel optical sensing platform combines the advantages of the DWO-RRS and fluorescence. More importantly, monitoring simultaneously the dual-channel optical signals can conduce to increase the accuracy for detection. Furthermore, the two optical signals can be achieved on a fluorescence spectrophotometer in different modes, thus experimental procedures are greatly simplified. Finally, the sensor has been applied to the detection of DA in milk samples with satisfactory results.

2. Experimental section

2.1. Reagents and apparatus

Cadmium chloride ($CdCl_2{\cdot}2.5H_2O$), tellurium powder (Te powder), thioglycolic acid and thioacetamide were supplied by Sinopharm Chemical Reagent Co. Ltd (Shanghai, China). Glutathione (GSH) and sodium borohydride ($NaBH_4$) were obtained from Aladdin Chemistry Co. Ltd (Shanghai, China) and Tianjin Huanwei Fine Chemical Co. Ltd (Tianjin, China), respectively. Diminazene aceturate (DA) was purchased from Sigma (St. Louis, MO, USA). All other chemicals not mentioned here were of analytical grade. All aqueous solutions were prepared with ultrapure water (18.2 MΩ cm).

The RRS and fluorescence measurements were recorded using an F-2500 fluorescence spectrophotometer (Hitachi, Tokyo, Japan, http://hitachi.shuoyi.com). The UV–vis absorption spectra were recorded with a UV-2450 spectrophotometer (Tianmei Corporation, Shanghai, China, http://www.techcomp.com.cn). The appearance and size of nanoparticles was obtained on a JEOL JEM-2100 transmission electron microscopy (TEM, Hitachi, Japan, http://www.hitachi.com). The acidity of the solution were measured with a pHS-3C pH meter (Leici, Shanghai, China). Magnetic stirring was performed with a SZCL-A magnetic stirrer (Zhengzhou, China).

2.2. Synthesis of thioglycolic acid-wrapped CdTe/CdS Q-dots

Synthesis of thioglycolic acid-wrapped CdTe/CdS Q-dots was carried out in aqueous solution according to the previously reported method [26]. Under argon atmosphere and magnetic stirring, Te powder (0.0192 g) reacted with excessive sodium borohydride in ultrapure water to produce the colorless solution of NaHTe. $CdCl_2{\cdot}2.5H_2O$ (0.1370 g), 80 μL thioglycolic acid and 150 mL ultrapure water were added to a 250 mL three-necked flask. Under argon atmosphere and magnetic stirring, the mixed solution was adjusted to 11.0 by using the dropwise addition of 1.0 mol L^{-1} NaOH solution. Subsequently, H_2Te gas generated by dropwise adding H_2SO_4 (0.5 mol L^{-1}) into NaHTe was introduced to the three-necked flask with a slow argon flow for 30 min. Then the resulting solution mixture was heated to 369 K and refluxed for 110 min. After that, 1 mL thioacetamide solution which concentration was 0.00405 g mL^{-1} was added into the three-necked flask. The solution was heated to 369 K and refluxed for another 60 min. Eventually, thioglycolic acid-wrapped CdTe/CdS Q-dots were obtained. The concentration of thioglycolic acid-wrapped CdTe/CdS Q-dots was 1.0×10^{-3} mol L^{-1} (determined by the concentration of Te^{2-}) [27].

2.3. General procedure

Thioglycolic acid-wrapped CdTe/CdS Q-dots (1 mM, 300 μL), Britton-Robinson buffer (5.2, 500 μL) and a series of different