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A fluorescent sensor based on thioglycolic acid capped cadmium sulfide quantum dots for the determination of dopamine

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ABSTRACT

A fluorescent sensor based on thioglycolic acid-capped cadmium sulfide quantum dots (TGA-CdS QDs) has been designed for the sensitive and selective detection of dopamine (DA). In the presence of dopamine (DA), the addition of 1-ethyl-3-(3-dimethylaminopropyl) carbodiimide (EDC) and *N*-hydroxysuccinimide (NHS) activates the reaction between the carboxylic group of the TGA and the amino group of dopamine to form an amide bond, quenching the fluorescence of the QDs. The fluorescence intensity of TGA-CdS QDs can be used to sense the presence of dopamine with a limit of detection of 0.68 μM and a working linear range of 1.0–17.5 μM. This sensor system shows great potential application for dopamine detection in dopamine drug samples and for future easy-to-make analytical devices.

1. Introduction

Dopamine (DA) is an especially important neurotransmitter of the catecholamines class, having roles in the function of the central nervous system [1,2]. DA is stored in the vesicles of the brain before its release [1]. Normal levels of DA are essential to maintain correct blood pressure, physical activity, motivation, learning, and awareness [3,4]. Abnormal levels of DA in the brain may lead to several serious neurological conditions such as Parkinson's disease, Psychosocial stress, Schizophrenia, and Alzheimer's disease [3,6]. Thus, elevated concentrations of DA in blood or in urine are important pathological indicators. As yet, however, there is no easily employed dopamine sensor available for clinical use. Various methods to determine the concentration of DA in human biofluids have been reported including using fluorescence spectroscopy [5–8,12], electrochemical method [9], colorimetric methods [3,10], HPLC [11], and flow injection analysis [13]. All these methods have advantages but also some limitations, for instance, complicated methods, pre-treatments with expensive reagents, and extensive times required to complete the assay. DA sensing using electrochemical techniques is particularly difficult as DA has a similar electrochemical potential to co-existing species such as ascorbic acid and uric acid [5,14,15].

Recently, developments in analytical chemistry have shown that nanomaterials could be ideal for building chemical sensors. These nanomaterials, such as quantum-dots, gold or silver nanoparticles, etc., show remarkable optical responses which are unique with respect to their bulk counterparts. Moreover, one can control the fine optical, electromagnetic, and other properties by size-tuning via the quantum confinement effect [16]. These nanomaterials can be further modified by making core-shell structures or by appropriate surface-bound capping molecules [17–18,30]. Quantum dots (QDs), semiconductor nanocrystals, have been investigated by many research groups for their excellent fluorescent properties [19–22]. One can use QDs in applications such as sensing [23–25,55], imaging [26,29], biological labeling [26], and photocatalysis [27,28].

In this work, a sensor for selective detection of dopamine is realised based on the fluorescence quenching of CdS QDs capped with thioglycolic acid (TGA). Covalent bonding between the TGA capping molecules of the fluorescent CdS QDs and the amino group of the dopamine occurs via activated carboxylic coupling, resulting in quenching of fluorescence and constituting the assay. The coupling agents are 1-ethyl-3-(3-dimethylaminopropyl) carbodiimide (EDC) and *N*-hydroxysuccinimide (NHS) giving the amide bonded product, as used extensively elsewhere, for instance for grafting to bioactive polyesters [31], sensing [32], or for protein-based materials for drug delivery and tissue engineering [33].

To the best of our knowledge, there are no examples of fluorescence sensors based on TGA-CdS QDs using EDC/NHS coupling for sensing of dopamine. Herein we describe the synthesis of TGA-capped CdS QDs (TGA-CdS QDs) via a very simple procedure. We then employ this

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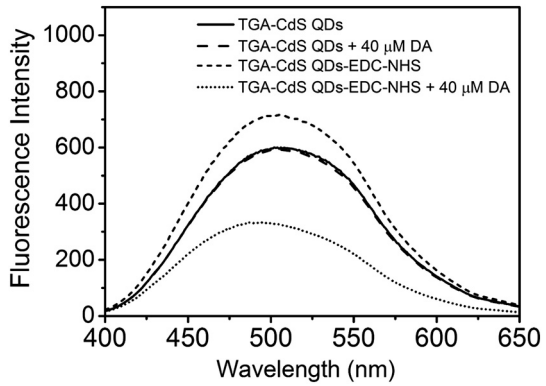

Fig. 1. The fluorescence emission spectra of TGA-CdS QDs, TGA-CdS QDs and 40 μM dopamine (reaction time is 45 min), TGA-CdS QDs in the presence of EDC/NHS only (reaction time is 20 min), and EDC/NHS and 40 μM dopamine (reaction time is 45 min). The final concentration of TGA-CdS QDs is 105 mg/L, EDC 1.612 mM, and NHS 0.806 mM in the ratio of 1:4:2.

nanomaterial as a fluorescence sensor for dopamine, assessing its selectivity and sensitivity in real world samples. The mechanism of TGA-CdS QDs fluorescence quenching by dopamine is attributed to a photoinduced electron transfer process.

2. Experimental

2.1. Materials

Cadmium chloride monohydrate ($CdCl_2 \cdot H_2O$, 99.5%) was purchased from Riedel-deHaen. Thioglycolic acid (98%), Dopamine hydrochloride (98%), and Norepinephrine (98%) were purchased from Sigma. Sodium sulfide ($Na_2S \cdot H_2O$, 30%) was purchased from Panreac. Hydrochloric acid (37%), acetic acid (glacial), and ethanol (99.9%) were purchased from QRëC™. Tris(hydroxymethyl)aminomethane (Tris, 99.8%) and potassium dihydrogen orthophosphate (99%) were purchased from Univar. *N*-Hydroxysuccinimide (NHS, 98%) and melamine (99%) were purchased from Aldrich. 1-Ethyl-3-(3-dimethylaminopropyl) carbodiimide hydrochloride (EDC, 98%), L-Valine (99%) and L-Tyrosine (99%) were purchased from Fluka. Dopamine HCl drug (INOPIN) (250 mg/10 mL) was purchased from Siam Bheasach Co., Ltd. (Thailand). Sodium hydroxide (97%) was purchased from Lobal chemie. L-Histidine (98%), L-(+)-lysine monohydrate (99%), L-Alanine (99%), L-Leucine (99%), L-Phenylalanine (98.5%) and L-Tryptophan (99%) were purchased from ACROS. L-Isoleucine (99%) was purchased from Fisher. All reagents were of analytical grade and used without further purification. All aqueous solutions were prepared with deionized water with specific resistivity of 18.2 MΩ cm from RiO_s™ Type I Simplicity 185 (Millipore water).

2.2. Apparatus

Fluorescence spectra were collected on a Shimadzu RF-5301PC and RF-6000 spectrofluorometer with slit widths on the excitation and emission monochromators affording 5 nm spectral resolution. Absorption spectra were recorded using a Cary60 Agilent Technologies spectrophotometer. Measurements of pH were carried out using a UB-10 UltraBasic pH meter (Denver Instrument). Transmission electron microscope (TEM) micrographs were recorded using a Tecnai G^2–20 TEM (FEI, Netherlands) under an accelerating voltage of 200 kV. The functional groups of the sensor were studied by Attenuated Total Reflection Fourier Transform Infrared spectroscopy (ATR-FTIR) with a Bruker TENSOR 27 spectrometer.

2.3. Analytical Methods

To study the fluorescence quenching of TGA-CdS QDs in the presence of dopamine following EDC/NHS binding, the following methods were carried out. A stock solution of 10 mM dopamine was prepared by dissolving dopamine hydrochloride in deionized water. To a 10 mL volumetric flask, 75 μL of the TGA-CdS QDs solution was added followed by the addition of solutions of DA, EDC, and NHS to a desired concentration level. Next, 0.50 mL of 1.0 M Tris buffer was added to adjust the solution pH. The mixture was made up to a final volume of 10.00 mL with DI water and incubated at room temperature for a desired time. For the most experiments, the mixture of TGA-CdS QDs/EDC-NHS was first mixed for about 20 min then, after adding DA, it was left to react for a further 45 min. The fluorescence intensity was then measured using $\lambda_{em}/\lambda_{ex} = 505/377$ nm.

2.4. Preparation of the TGA-Cadmium Sulfide Quantum Dots (TGA-CdS QDs)X

TGA-CdS QDs were synthesized based on methods described in the literature [7,34,35]. In brief, $CdCl_2 \cdot H_2O$ (0.5038 g, 2.502 mmol) was dissolved in 70 mL of DI water in a three-necked round bottom flask. Then, the solution of TGA 354 μL (0.459 g, 4.994 mmol) was added to the previous solution with stirring. After stirring the mixture under nitrogen atmosphere for 30 min, the solution pH was adjusted to 8–9 using 0.5 M aqueous NaOH. In another flask, $Na_2S \cdot H_2O$ (0.195 g, 2.499 mmol) was dissolved in 10 mL of DI water. Next, the Na_2S solution was slowly added to the reaction mixture. After refluxing at 65 °C under nitrogen atmosphere for 1 h, the colloidal quantum dots were left at room temperature. Then, the TGA-CdS QDs were purified by dispersing in ethanol and centrifuging at 3000 rpm for 20 min until a clear solution was obtained. Next, the supernatant was removed and the residual TGA-CdS

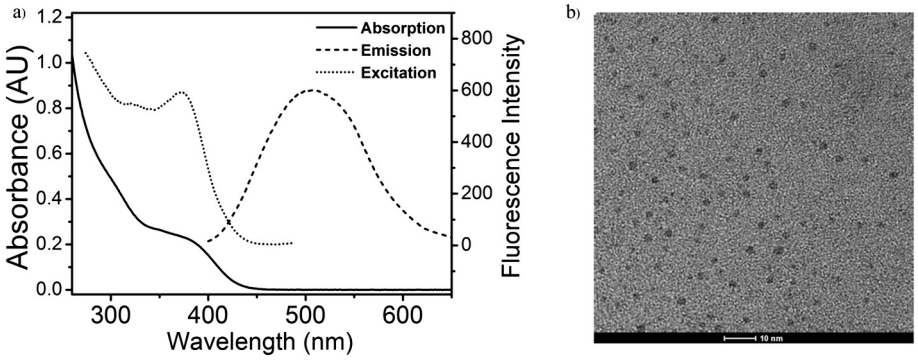

Fig. 2. (a) The absorption, fluorescence, and fluorescence excitation spectra of the synthesized TGA-CdS QDs ($\lambda_{em}/\lambda_{ex} = 505/377$ nm) (b) TEM image of TGA-CdS QDs (2.2 ± 0.3 nm; $n = 59$).