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Room-temperature phosphorescence sensor based on manganese doped zinc sulfide quantum dots for detection of urea

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ABSTRACT

In this work, a simple scheme was proposed to prepare a urea-sensing system, which was composed of water-soluble Mn-doped ZnS phosphorescent QDs and urease. It allows for effective and quantitative detection of urea. The phosphorescence properties of MPA-capped Mn-doped ZnS QDs were explored to develop an RTP method for facile, rapid, cost-effective and selective detection of urea. This method does not need any deoxidant or other inducers and detects urea in biological fluids without being interfered from autofluorescence or the scattering light of the matrix. The new RTP sensor for urea detection has a detection limit of 0.014 mM and two linear ranges from 0 to 10 mM and from 10 to 60 mM. The precision for 11 replicate detections of 0.1 mM urea was 4.7%. The recoveries on spiked urine samples are 95–103%. It was successfully applied to the determination of urine without any complicated sample pretreatment.

1. Introduction

Urea is widely distributed in nature. Analysis and detection of urea are very important in some special fields, because urea is an important monitor of public health in water (especially in swimming pools) and soil productivity, a NH_3 pollution source in gas, a controlled substance in food security, and a standard factor of clinical diagnostics [1]. Urea also plays a strategic role in the marine nitrogen cycle [2,3]. Urea is the main end-product of human protein metabolism, so it is very important in clinical chemistry where urea nitrogen is used as an indicator of kidney dysfunction [4–6]. Urea detection is also necessary in medical care. Urea can be detected by electrochemical sensor [1], spectrophotometry [7], flow-injection spectrophotometry [8], gas chromatography [9], and so on. However, some methods are time-consuming, toxic, expensive and requiring complicated pretreatment, which hamper their further application. Biosensors may overcome some of these problems [10,11]. For example, an assay system with urease as catalyst and CdSe/ZnS quantum dots (QDs) as indicators was developed for quantitative analysis of urea [11]. However, the background fluorescence from biological fluids is severe [12,13]. Room-temperature phosphorescence (RTP) sensor based on Mn-doped ZnS quantum dots may overcome these disadvantages.

Previous studies on QDs for biosensing focus on the use of fluorescent QDs [11,14–16], but the short-lived autofluorescence and scattering light from biological matrices will bring errors. Recently, the $^4T_1(4G)$-$^6A_1(6S)$ transition of Mn^{2+} in Mn-doped ZnS QDs utilized into room-temperature phosphorescence (RTP) detection has attracted much attention, and is widely studied for developing sensors with great success, thus becoming a hotspot [12,13,15,17–24]. In this way, the interferences from biological matrices can be avoided by phosphorescent QDs because the long-lived phosphorescence has a suitable delay time [12,13,15]. The selectivity is also enhanced because phosphorescence is less common than fluorescence [17]. Reportedly, Mn-doped ZnS QDs exhibit promising phosphorescence emission (~590 nm) [25], which is produced by the energy transfer from the band gap of ZnS to Mn^{2+} dopant and the subsequent transition from the triplet state ($^4T_1$) to the ground state ($^6A_1$) of the Mn^{2+} involved in the ZnS host lattice [26]. The utilization of phosphorescent QDs in optical sensing is still at the initial stage but has been proven to be very prospective [12,25,18,27]. Biosensors do not need any complex sample pretreatment [13,28].

In this paper, a simple scheme was proposed to prepare the urea-sensing system, which was composed of water-soluble Mn-doped ZnS phosphorescent QDs and urease. It allows for effective and quantitative detection of urea. Colloidal Mn^{2+}-doped ZnS nanoparticles showing RTP emission were synthesized and then water-dissolved by capping mercaptopropionic acid (MPA) onto the surface of QDs. Such coating of the nanoparticles did not change their emission properties, but realized effective and quantitative detection of urea.

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2. Experimental

2.1. Materials and chemicals

Urease (208 U mg^{-1}, Anil Ax, USA) MPA was obtained from J&K Scientific, Beijing, China; urea, $Zn(Ac)_2 \cdot 2H_2O$, $Mn(Ac)_2 \cdot 4H_2O$, and $Na_2S \cdot 9H_2O$ were purchased from Tianjing Kermel Chemical Reagent Co., China. Ultrapure water (18.2 MΩ cm) was obtained from a Water Pro water purification system (Labconco Co., Kansas City, MO).

Apparatus: The surface morphology and microstructure of QDs were characterized by a JEM-2100F (Japan) transmission electron microscope (TEM). The samples for TEM were obtained by drying sample droplets from water dispersion onto a 300-mesh Cu grid coated with a lacey carbon film, which was then allowed to dry prior to imaging. Phosphorescence was measured on a Cary Eclipse fluorescence spectrophotometer (Varian American Pty Ltd., American), a high-performance R928 photomultiplier detector and an R 928PMT are used as reference signal and horizontal transmission, equipped with a plotter unit and a quartz cell (1 cm × 1 cm) in the phosphorescence mode. The slit width was 10 nm and 20 nm for excitation (295 nm) and emission (590 nm), respectively, with a scanning wavelength range from 200 to 700 nm. pH was measured with a pH meter (Jinpeng Analytical Instruments Co. Ltd, China).

2.2. Synthesis of Mn-doped ZnS QDs

Synthesis of Mn-Doped ZnS QDs was carried out in aqueous solution based on a published method with minor modification [13,29]. Briefly, 10 mL of 0.1 M $Zn(Ac)_2$, 4 mL of 0.01 M $Mn(Ac)_2$, and 100 mL of 0.04 M MPA were added to a three-neck flask. The solution was mixed and adjusted to pH 11 with 1 M NaOH. After air was removed with argon bubbling for 30 min at room temperature, 10 mL of 0.1 M Na_2S was immediately injected into the solution. After stirring for 20 min, the solution was aged at 50 °C under open air for 2 h to form MPA-capped Mn-doped ZnS QDs. The QDs were purified by precipitation with ethanol, separation by centrifuging, washing with ethanol, and drying in vacuum. The obtained QDs powder was highly soluble in water.

2.3. Assay conditions and RTP measurement

Assay conditions were set on the basis of a publication with minor modifications [11]. In order to study the effect of pH on the RTP intensity of the prepared QDs, samples with varying basicity (pH 8.0, 8.5, 9.6,10.5, 11.0 and 11.5) were prepared by adding different volumes of NaOH (0.1 M) to a phosphate buffered solution (PBS, pH 8.0, 20 mM). The prepared QDs were dissolved in water to 5.0 mg mL^{-1}, and 80 μL of the QD solution was added to each of the above solutions, followed by RTP detection at an excitation wavelength (λ_{ex}) of 295 nm and an emission wavelength (λ_{em}) of 590 nm. For urea detection, solutions containing urease (8.32 units mL^{-1}), MPA-capped Mn-doped ZnS QDs (5 mg mL^{-1}, 80 μL), and varying concentrations of urea (0–120 mM) were prepared each in 10 mL of PBS (20 mM, pH 8.0). Reactions lasted for 10 min (37 °C) before spectrophotometric analysis and pH measurement.

2.4. Sample collection and pretreatment

Eight human urine samples were collected from healthy volunteers. All samples were subjected to a 100-fold dilution before analysis and no other pretreatments were used.

2.5. Measurement procedures

To a 10-mL calibrated test tube, PBS (0.2 M, 1.0 mL), MPA-capped Mn-doped ZnS QDs (5 mg mL^{-1}, 80 μL), urine sample (0.1 mL), and urease (2080 units mL^{-1}, 40 μL) were successively added. The mixture was diluted to volume with ultrapure water, mixed thoroughly, and incubated in a water bath (37 °C) for 10 min. Then, the mixture was taken to phosphorescence measurement at λ_{ex}=295 nm.

3. Results and discussion

3.1. Characterization of the MPA-capped Mn-doped ZnS QDs

The size of MPA-capped Mn-doped ZnS QDs was detected by TEM to be ~3.5 nm (Fig. 1A). The QDs exhibited a maximum

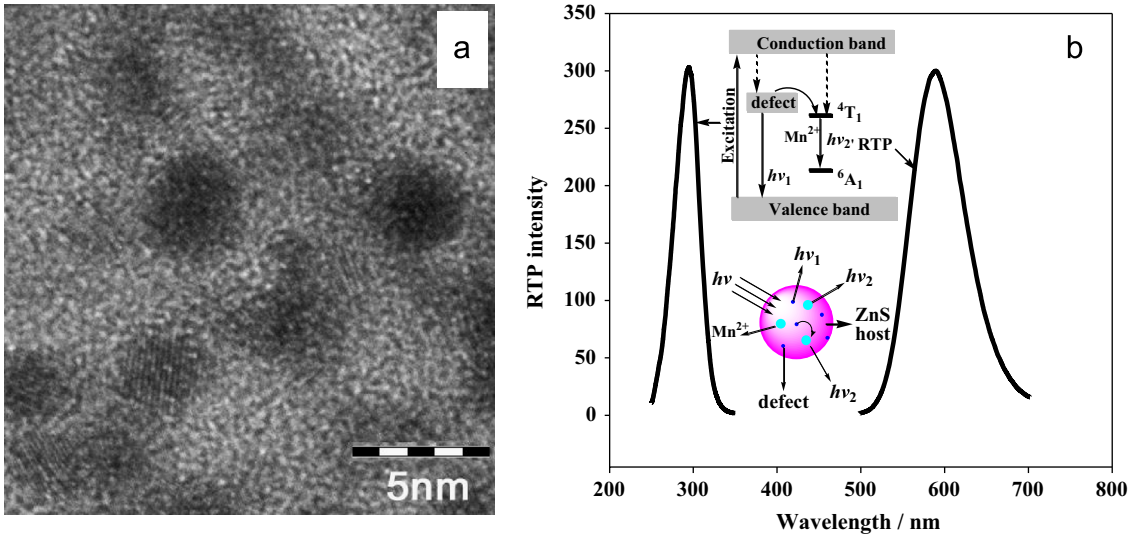

Fig. 1. (A) TEM image of MPA-capped Mn-doped ZnS QDs (B) The excitation (curves a) and RTP emission (curves b) spectra of Mn-doped ZnS QDs (40 μg mL^{-1}). Solutions were prepared in PBS (20 mM, pH 8.0).