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Doped zinc sulfide quantum dots based phosphorescence turn-off/on probe for detecting histidine in biological fluid

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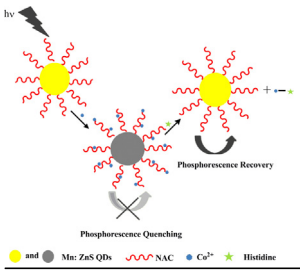
HIGHLIGHTS

- A turn-on phosphorescence quantum dots probe for histidine is fabricated.
- High sensitivity, good selectivity and low interference are achieved.
- Histidine in urine samples can be easily detected by the phosphorescence probe.

GRAPHICAL ABSTRACT



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ABSTRACT

We report a turn-on phosphorescence probe for detection of histidine based on Co^{2+}-adsorbed *N*-acetyl-L-cysteine (NAC) capped Mn: ZnS quantum dots (QDs) which is directly synthesized by the hydrothermal method. The phosphorescence of NAC-Mn: ZnS QDs is effectively quenched by Co^{2+} attributing to the adsorption of Co^{2+} onto the surface of QDs with a concomitant in suppressing the recombination process of hole and electron of QDs. The phosphorescence of Co^{2+}-adsorbed NAC-Mn: ZnS QDs can be recovered by binding of Co^{2+} with histidine. The quenching and regeneration of the phosphorescence of NAC-Mn: ZnS QDs have been studied in detail. The as-prepared QDs-based probe is applied to determine histidine with a linear range of 1.25–30 μM and a detection limit of 0.74 μM. The relative standard deviation for eleven repeat detections of 20 μM histidine is 0.65%. Co^{2+}-adsorbed NAC-Mn: ZnS QDs show high sensitivity and good selectivity to histidine over other amino acids, metal ions and co-existing substances. The proposed QDs probe has been successfully applied to determination of histidine in human urine samples with good recoveries of 98.5–103%.

1. Introduction

Histidine, an essential amino acid in humans and other mammals, dominates the transmission of metal elements in biological systems, and also acts as an important neurotransmitter or neuromodulator in the mammalian central nervous system [1–3]. Its overexpression is associated with a number of diseases such as AIDS [4], chronic kidney disease [5], Alzheimer's disease [6] and cancer [7]. The detection of histidine has thus received

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considerable attention in recent years. Numerous methods have been developed for determination of histidine including high-performance liquid chromatography [8,9], capillary electrophoresis [10–13], electrochemistry [14,15], spectrofluorimetry [16–20], and spectrophotometry [21,22]. All of these methods have some basic limitations with respect to their selectivity, equipment cost, complexity, sample processing, and long analysis time. Optical sensors have attracted increasing interests over the past decades owing to their high sensitivity, selectivity and simplicity. Among these, the luminescent probes mainly focus on studying small-molecule dyes and nanoparticles. But they, to a certain extent, suffer from high toxicity, low photostability or complicated synthetic procedures. As such, the development of an efficient and applicable luminescent probe for histidine is desirable.

It is well known that transition metal complexes and amino acid residues play important roles in many biological processes such as electron transfer, redox and catalysis [23]. In fact, transition metal ions are essential cofactors for many enzymes and proteins that have some important functions [24]. In these metalloproteases, the enzymes' active sites are highly specific and often involve histidine residues interacting with divalent transition metal cations such as Co^{2+}, Ni^{2+}, Cu^{2+}, and Zn^{2+}. Especially, Co(II) and Ni(II) are distinguished by their good histidine coordination ability [25]. The three coordination sites (*i.e.*, amino nitrogen (N), imidazole N and carboxylate oxygen) of histidine and the oxygen from water molecule can readily bind with metal ions in solution. In addition, the lower pK_a of the imino group of histidine (6.0) permits double coordination of Co^{2+} with the histidine amino and imino N. Other substituent histidine compounds including carnosine and anserine behave similarly; however, Co^{2+} is hard to coordinate with substituent histidines [26]. Iwig et al. mutated five histidine residues in *E. coli* RcnR and found three of the histidine residues are required for binding to Co(II) [27]. All these studies imply the potential use of the Co^{2+}-histidine affinity pair in chemical and biochemical analyses.

Since quantum dots (QDs) possesses advantages of high photoluminescence efficiency, excellent photostability, size-dependent emission wavelength, and sharp emission profile over conventional organic fluorophores, they are classified as promising fluorescence probes for detecting inorganic ions, small molecules and biological macromolecules in chemical and biological assays [28–32]. As an important class of nanomaterial, Mn-doped zinc sulfide quantum dots (Mn: ZnS QDs) have been widely studied in different fields attributing to their low toxicity, stable wide band gap semiconductor, and strong phosphorescence at 590 nm [33–35]. Moreover, the room temperature phosphorescence (RTP) of doped QDs affords several outstanding merits including large Stokes' shift between excitation and emission wavelengths, long emission lifetime, and immune of interference from the short-lived autofluorescence and scattering light over fluorescence. Hence, the use of RTP of doped QDs has drawn considerable attention in optosensing in recent years [36–51]. For instances, the analytical exploration of Mn: ZnS QDs as a phosphorescent probe was primarily brought out for detecting enoxacin in biological fluids [36]. Wang et al. [37] developed a turn-on RTP probe based on the enhancement of phosphorescence emission of sodium tripolyphosphate capped Mn: ZnS QDs by ascorbic acid and it was then applied to measure ascorbic acid with a detection limit of 9 nM. Ren and Yan [38] engineered ATP capped Mn: ZnS QDs for selective recognition of arginine and methylated arginine. The QDs permit phosphorescence detection of arginine in biological fluids with a detection limit of 0.23 mM. Wu et al. [39] prepared glucose oxidase functionalized Mn: ZnS QDs for phosphorescence sensing of serum glucose with a detection limit of 3 mM. Wang et al. [40] developed a surface molecular imprinting strategy for 3-mercaptopropyl trimethoxysilane capped Mn: ZnS QDs for the specific recognition of pentachlorophenol without any inducers and derivatization. The electrostatic interaction of methyl violet and 3-mercaptopropionic acid (MPA) capped Mn: ZnS QDs permitted the design of a turn-on RTP sensing of DNA with a detection limit of 34 mg mL^{-1} [41]. Similarly, a nanohybrid composed of octa(3-aminopropyl) octasilsequioxane octahydrochloride (OA-POSS) and MPA capped Mn: ZnS QDs was fabricated for RTP sensing of double-strand DNA with a detection limit of 55 nM, owing to the stronger interaction between OA-POSS and DNA with a concomitant quenching effect on the phosphorescence of Mn: ZnS QDs [42]. Wang et al. discriminated catechol from resorcinol and hydroquinone by RTP of sodium tripolyphosphate capped Mn: ZnS QDs [43]. The detection of intracellular Zn^{2+} has achieved by using silica-coated S^{2-} enriched Mn: ZnS QDs [44]. A multidimensional sensing device based on simultaneous utilization of the triple-channel optical properties (light scattering, phosphorescence, fluorescence) of MPA capped Mn: ZnS QDs for the discrimination of proteins was constructed [45].

To our knowledge, RTP can operate in phosphorescence quenching or turn-on modes. In comparison with the phosphorescence quenching mode, where a variety of factors can induce the ultimate phosphorescence "off" state, the phosphorescence "turn-on" mode appears to be more reliable and attractive because it can reduce the chance of false positives and is more amenable to multiplexing [52]. Herein, a Co^{2+}-adsorbed Mn: ZnS QDs probe for phosphorescence turn-on detection of histidine is proposed. The phosphorescence of the Mn: ZnS QDs is initially quenched by Co^{2+} and then the phosphorescence is regenerated by reacting with histidine, attributing to the removal of surface-adsorbed Co^{2+} from QDs by histidine. Finally, a phosphorescence turn-on probe based on Co^{2+}-adsorbed Mn: ZnS QDs for rapid and selective detection of histidine in biological fluid is developed. The proposed phosphorescence probe possesses high selectivity for histidine over other amino acids.

2. Experimental

2.1. Reagents

N-acetyl-L-cysteine (NAC), 4-(2-hydroxyethyl)-1-piperazineethanesulfonic acid (HEPES), $PdCl_2$, $PtCl_4$, $RhCl_3{\cdot}3H_2O$, $RuCl_3{\cdot}xH_2O$, $YCl_3{\cdot}6H_2O$, and $ZrCl_4$ were purchased from Aladdin Chemicals (Leonard, TX, USA). $ZnSO_4{\cdot}7H_2O$, $MnCl_2{\cdot}4H_2O$ and $Na_2S{\cdot}9H_2O$ were obtained from Tianjin Chemical Reagent Company (Tianjin, China). DL-histidine was received from Shanghai Reagent Factory (Shanghai, China). Cobalt standard stock solution (1000 mg L^{-1}) was purchased from Acros Organics (Geel, Belgium). Other analytical grade reagents were purchased from Beijing Chemical Reagent Company (Beijing, China). High purity water from a Milli-Q-RO_4 water purification system (Millipore, Bedford, MA, USA) with a resistivity higher than 18 MΩ cm was used to prepare all solutions. 0.10 M phosphate buffer solution (PBS) was prepared by mixing appropriate volumes of standard solutions of 0.10 M Na_2HPO_4 and 0.10 M NaH_2PO_4. The buffers were adjusted to the required pH with 0.10 M H_3PO_4 or 0.10 M NaOH.

2.2. Apparatus

The absorption and phosphorescence measurements were carried out on a Shimadzu UV-265 UV–vis absorption spectrophotomter (Kyoto, Japan) and a Hitachi F-4500 spectrofluorometer (Tokyo, Japan), respectively. Excitation and emission bandwidths were set at 10 nm. A 150 W xenon arc lamp was used as the excitation light source. A standard 1.0 cm quartz cell was used. pH measurements were taken on a Shanghai Rex Instrument Factory pHS-3C pH meter (Shanghai, China). Phosphorescence lifetime