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Short Communication

CdTe quantum dot-based fluorescent probes for selective detection of Hg (II): The effect of particle size

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ABSTRACT

Mercury ions-induced fluorescence quenching properties of CdTe quantum dots (QDs) have been studied using the fluorescence spectroscopic techniques. By using the hydrothermal method, the CdTe QDs with different particles sizes from 1.98 to 3.68 nm have been prepared, and the corresponding fluorescence emission wavelength is changed from 518 to 620 nm. The fluorescence of QDs is enhanced after linking Bovine serum albumin (BSA) onto the surface of the QDs. Experimental results show that the fluorescence intensity of BSA-coated CdTe QDs could be effectively quenched when Hg^{2+} react with BSA-coated CdTe QDs. Interestingly, both the sensing sensitivity and selectivity of this fluorescence probe could be improved when the particle size of the QDs decreases. Thus the BSA-coated CdTe QDs with green fluorescence emission have better advantages than the BSA-coated CdTe QDs with red fluorescence for Hg^{2+} detection. Interference experiment results indicate that the influence from other metal ions could be neglected in the detection, and the Hg^{2+} could be specifically detected. By using this BSA-coated CdTe QDs-based fluorescence probe, the Hg^{2+} could be detected with an ultra-low detection limit of nanomole level, and the linear range spans a scope from 0.001 to 1 μmol/L.

1. Introduction

As we know, heavy metals cause an immense danger to food safety and the environment. As a kind of toxic metallic ions, high level of Hg^{2+} in food and drinking water is detrimental to human health. Therefore, many analysis methods, such as electrochemical sensing [1], photoelectrochemical sensing [2], dye molecule–based or plasmonic colorimetric sensing [3,4], fluorescent sensor [5] and surface plasmon resonance (SPR) based fiber optic sensor [6], have been developed for the highly efficient, ultrasensitive and selective detection of Hg^{2+}.

Because of its simplicity and high sensitivity, quantum dots-based fluorescence probe for detection of chemical and biologic molecules have become a hot topic in nanoscience and analysis [7–11]. Recently, the fluorescence properties of QDs have also been used in the detection of Hg^{2+}. In the review of Vázquez-González et al., a detailed evaluation of the different approaches developed so far for the analysis of Cd^{2+}, Pb^{2+}, and Hg^{2+} by using various types of QDs has been provided [12]. Wang et al. report the synthesis of nitrogen-doped carbon nanodots with a high quantum yield of 38.4% [13]. These nitrogen-doped carbon nanodots could be used for mercury ion sensing with a detection limit of 80 nmol/L. By using the Cys-capped ZnS QDs, a highly sensitive and selective photoelectrochemical sensing method for Hg^{2+} detection was developed by Wang et al. [14]. The reported sensing method could be used for the detection of trace Hg^{2+} with a linear range of 0.01 to 10.0 μmol/L and a detection limit of 4.6 nmol/L. In the report of Liu et al., a green strategy for the production of fluorescent 2,3-diaminophenazine nanoparticles has been investigated by UV light irradiation [15]. The fluorescent nanoparticles can serve as a fluorescent sensor for sensitive and selective detection of Hg^{2+}. Jaiswal et al. reported the use of biopolymer-stabilized ZnS QDs for cation exchange reaction-based sensing of heavy metal ions including Hg^{2+}, Ag^{+}, and Pb^{2+} in water [16]. In the study of He et al., photo luminescent carbon dots have been synthesized using citric acid as the carbon source and diethylenetriamine as the surface passivation reagent [17]. This fluorescent probe could be used for selective detection of Hg(II) with a linear range of 0–80 μmol/L and a detection limit of 0.201 mmol/L

As a kind of important semiconductor nanocrystals, CdTe QDs exhibit unique photophysical properties due to their high quantum yield, excellent photo stability, narrow emission wavelengths and size-dependent fluorescence frequency. Idowu et al. reported the luminescent water-soluble CdTe QDs capped with different thiol carboxylic acids [18]. Fluorescence enhancement of CdTe QDs was observed when in the mixture with BSA. The MPA-capped CdTe QDs were used to detect the concentration of BSA and the size of them is 2.3 nm. In the report of Adegoke and Nyokong, MPA-capped CdTe QDs and CdTe@ZnS QDs have been employed as luminescent probes for the sensitive and selective sensing of peroxynitrite [19]. The size of MPA-CdTe QDs is 2.7 nm, and the size of GSH-TGA-CdTe@ZnS QDs is 3.0 nm. The

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limit of detection of 72.4 nmol/L was obtained. Li et al. developed a hydrothermal synthesis method of CdTe QDs with higher photoluminescence intensity [20]. The sizes of TGA-capped CdTe QDs are 2.0 ± 0.3 nm and 6.0 ± 0.9 nm. These CdTe QDs could be labeled with bovine serum albumin (BSA) for fluorescence probes without pretreatment.

CdTe QDs have also been used for Hg^{2+} detection. Xia and Zhu found that the denatured bovine serum albumin-coated CdTe QDs could be quenched effectively by Hg^{2+}, and the limit of detection for Hg^{2+} was 4.0×10^{-9} mol/L [21]. A highly selective and simple fluorescence sensor for Hg^{2+} detection based on cysteamine-capped CdTe QDs with size of 2.89 nm has been reported by Ding et al. [22]. They found the fluorescence quenching effect of cysteamine-capped CdTe QDs was linear with Hg^{2+} concentrations in the range of 6.0–450 nmol/L. Saikia et al. reported a simple and ultrasensitive sensing technique based on CdTe/ZnS QDs with the size of 5–6 nm for the detection of toxic Hg(II) [23]. Because of the interaction between QDs and Hg(II), the photo luminescence of QDs has been quenched via excited state electron transfer mechanism. The application of water-soluble *N*-acetyl-L-cysteine-capped CdTe QDs for Hg(II) detection has also been studied [24]. It has been found the presence of Hg(II) ions could quench the fluorescence of CdTe QDs with the size of 3 nm at 565 nm and produce new peak in 700–860 nm. Liu et al. reported the surface plasmon-coupled emission of CdTe QDs and developed a fluorescent sensor for Hg(II) ion sensing [25]. They found that this surface plasmon-coupled emission-based sensing enlarged the response range and has higher sensitivity.

Although many efforts have been developed to improve the sensing ability of the CdTe QDs-based fluorescence probe, the effect of particle size on the detection limit and selectivity for Hg^{2+} has seldom been reported. In this paper, BSA-coated CdTe QDs with different particle sizes have been prepared and been used in the Hg^{2+} detection. It has been found the fluorescence of BSA-coated CdTe QDs could be quenched greatly by Hg^{2+}. Furthermore, both the sensing sensitivity and selectivity of this fluorescence probe could be improved when the particle size of the QDs decreases.

2. Experimental

2.1. Materials and Chemicals

In this study, the following reagents were necessary, and all the solutions were prepared with double deionized water (DDW). Tellurium powder (~100 mesh, 99.99%), Cadmium chloride hemi (pentahydrate) ($CdCl_2 \cdot 2.5H_2O$, 99.95%), Sodium hydroxide (NaOH, AR, 96%), Mercuric chloride ($HgCl_2$, >99%) were purchased from Aladdin, China. Thioglycolic Acid (TGA, 98%) was acquired from ACROS ORGANIC Inc., Belgium. Sodium borohydride ($NaBH_4$, 99%) and *N*-Hydroxysuccinimide (NHS, 98%) were obtained from Sigma–Aldrich, America. Glycine (AR, >99%) was purchased from Shanghai ShanPu Chemical Company Ltd., China. Bovine serum albumin (BSA, >99%) was obtained from Bioreagent Inc., America.

2.2. The Preparation of CdTe QDs with Different Particle Sizes

The colloidal thioglycolic-acid (TGA)-capped CdTe QDs were synthesized based on the method [21,26] with minor modification. Firstly, 200 mL water to be used was boiled for 10 min to remove oxygen inside. Then, 63.8 mg Te powder and 60 mg $NaBH_4$ were added into a 50 mL three-necked flask. After bubbling nitrogen through the flask for 30 min, 4 mL oxygen-free water was injected into the above flask. Then, the temperature was adjusted to 0 °C by ice-bath and nitrogen gas was bubbled through the solution all the time. Meanwhile, the solution was stirred for 6 h to synthesize NaHTe. Next, 228 mg $CdCl_2 \cdot 2.5H_2O$ and 0.17 mL (14.1 mol/L) thioglycolic-acid were added into 100 mL oxygen-free water in a 500 mL three-necked flask. Last, adjusting the pH of the mixture to 10.5–11.0 with 1 mol/L NaOH solution, and adding the freshly prepared NaHTe solution into the above mixture under stirring, the orange CdTe precursors were formed. To form the different sizes of QDs, the precursors were heated up at 100 °C and refluxed for a certain period of time (5 min, 20 min, 40 min, 90 min, 3 h, 6 h, 8 h, 10 h, 24 h, 36 h, 48 h). The QDs were precipitated with excess isopropyl alcohol whose volume is triple that of QDs. By using a 10 mL centrifuge tube, the mixture was centrifuged at 8000 rpm for 5 min to remove unreacted substance. Afterwards, the precipitates can be redissolved in DDW the same volume as previous amount and stored in fridge under 4 °C for further use. The final concentration of prepared QDs was 1×10^{-2} mol/L, which was calculated according to the concentration of Cd^{2+}. The fluorescence emission spectra of the QDs solutions were recorded with the condition of excitation wavelength at 400 nm and the slit width of both excitation and emission at 5 nm.

2.3. Surface Modification and the Preparation of Fluorescent Probe

The surface modification is the process of linking BSA to CdTe QDs using the method reported by other group [20]. First, the as-prepared QDs with five sizes (2.34 nm, 2.85 nm, 3.29 nm, 3.5 nm and 3.68 nm, the corresponding emission wavelengths are 533 nm, 551 nm, 570 nm, 601 nm and 620 nm) were diluted to 1×10^{-3} mol/L. 100 μL QDs reacted with 100 μL NHS (4.3×10^{-5} mol/L) for 10 min to activate the carboxylic end of the QDs. Then the pH of the solution was adjusted to 7.4 by adding 4.7 mL phosphate buffer saline (PBS, 1×10^{-4} mol/L, pH = 7.4) solution followed by injecting 100 μL BSA (7.5×10^{-5} mol/L). Here, the concentration ratio of BSA and CdTe QDs is 0.075 ($C_{BSA} / C_{QDs} = 0.075$) and fixed. Then the solution was stirred for 30 min at 37 °C. After adding 100 μL Glycine (1.3×10^{-3} mol/L) without any purification into the reaction mixture as protective agent, the solution was shook for another 30 min. The same process was performed without addition of BSA solution, which can be made as blank control trial. The final concentration of the BSA-coated CdTe QDs is 2×10^{-5} mol/L according to the concentration of CdTe QDs. All the samples were stored in fridge overnight below 4 °C.

2.4. Detection of Hg^{2+}

The method was learned from the literature [21]. 5 mL BSA-coated QDs ($C_{QDs} = 2 \times 10^{-5}$ mol/L) with three different sizes (2.34 nm, 3.29 nm and 3.68 nm, the corresponding emission wavelengths are 533 nm, 570 nm and 620 nm) and 0.5 mL PBS (1×10^{-4} mol/L, pH = 7.4) buffer solution were added to the tubes. Different volume of 10 μmol/L Hg^{2+} stock solution (0 μL, 1 μL, 10 μL, 50 μL, 100 μL, 200 μL, 400 μL, 600 μL, 800 μL, 1 mL) were added to the above solution sequentially. The solution was diluted to 10 mL with ultrapure water and shook homogeneously for 5 min. The final concentrations of Hg^{2+} of these solutions are 0 μmol/L, 0.001 μmol/L, 0.01 μmol/L, 0.05 μmol/L, 0.1 μmol/L, 0.2 μmol/L, 0.4 μmol/L, 0.6 μmol/L, 0.8 μmol/L, 1 μmol/L. Finally, the fluorescence intensity of all solutions were measured with the condition the same as that of the CdTe QDs.

2.5. Equipment and Characterization

High Resolution Transmission Electron Microscopy (HRTEM) images of CdTe QDs were taken with a JEM-2100 instrument (JEOL, Japan). Centrifugation was carried out by using a 5810R centrifuge (Eppendorf, Japan). Absorption spectra were measured using a UV-3600 UV–Vis-NIR spectrophotometer (Shimadzu, Japan). All fluorescence spectra were collected using HORIBA JOBIN YVON fluorescence spectrometer (HORIBA, France) with the excitation of 400 nm and silt width of 5 nm. A Milli-Q water purification system (Millipore, USA) was used to acquire the deionized water.