A selective fluorescence probe for mercury ion based on the fluorescence quenching of terbium(III)-doped cadmium sulfide composite nanoparticles

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ABSTRACT

A fluorescent probe for mercury(II) ions, based on the quenching of fluorescence of terbium(III) ions doped in CdS nanoparticles, has been developed. The terbium(III)-doped cadmium sulfide composite nanoparticles were successfully synthesized through a straightforward one-pot process, with the biomolecule glutathione (GSH) as a capping ligand. In addition, the terbium(III) ions were observed an enhancement of emission intensity, owing to fluorescence energy transfer from the excited CdS particles to the emitting terbium(III). Because of a specific interaction, the fluorescence intensity of terbium(III)-doped CdS particles is obviously reduced in the presence of mercury(II) ions. The fluorescence quenching phenomenon of terbium(III) can be attributed to the fact that the energy transfer system was destroyed by combining with mercury(II). Under the optimal conditions, the fluorescent intensity of terbium(III) ions at 491 nm decreased linearly with the concentration of mercury(II) ions ranging from $4.5\,\text{nmol}\,\text{L}^{-1}$ to $550\,\text{nmol}\,\text{L}^{-1}$. The limit of detection for mercury(II) was $0.1\,\text{nmol}\,\text{L}^{-1}$. This method is simple, practical, relatively free of interference from coexisting substances and can be successfully applied to the determination of mercury(II) ions in real water samples. In addition, the probable mechanism of reaction between terbium(III)-doped CdS composite nanoparticles and mercury(II) was also discussed.

1. Introduction

Heavy metals, as one of the most hazardous classes of pollutants in water sources due to their nonbiodegradability, have caused widespread water endangerment, contamination of fish, and serious health problems [1]. Mercury is one of the most dangerous and widespread global pollutant. Moreover, mercury(II) ions derivatives can accumulate in the organs of living things through food chain, doing huge harm to human being and the nature [2,3]. The cases in Minamata Bay in Japan in 1953 [4] were particularly disastrous. Concerns over toxic exposure to mercury provide motivation to explore new methods for monitoring aqueous Hg^{2+} from biological and environmental samples [5]. Current techniques for mercury determination have been established, such as spectrophotometry [6], atomic absorption/emission spetroscopy [7,8], inductively coupled plasma-mass spectroscopy (ICP-MS) [9], inductively coupled plasma-atomic emission spectrometry (ICP-AES) [10] and so on. These methods have low limits of detection and wide linear ranges. However, these analytical methods need expensive and sophisticated instrumentation or complicated sample preparation process. Therefore, there is a need for analytical methods for the selective,

sensitive, and rapid detection of Hg(II) ions. Recently, fluorescence detection with Hg^{2+}-responsive chemosensors offers a promising approach for simple and rapid tracking of mercury ions for biological, toxicological, and environmental monitoring [11–13]. These probes and sensors with small molecules [14], DNAzymes [15] and protein [16] or oligonucleotide platforms [17] for mercury reported so far generally exhibits long response time, narrow working concentration range or moderate selectivity. Therefore, searching for new fluorescence probe with high selectivity and good photochemical property is still a challenge for the analytical chemistry research efforts [18].

Semiconductor nanoparticles have attracted a lot of attentions in the past few decades due to their unique optical properties such as broad excitation band, size- and composition-tunable emission wavelength and excellent anti-photobleaching [19–21]. Recently, quantitative detection of heavy metal ions with semiconductor nanoparticles via spectra changes in photoluminescence has been widely reported. With regard to Hg(II), Chen et al. [22] reported mercaptoacetic acid (MAA)-coated CdTe quantum dots as luminescent probes for mercury ions. The first practical uses of CdS quantum dots capped with different organic ligands were employed as chemical sensor to determine zinc and copper ions in aqueous media [23]. Recently, Yan et al. [24] developed functionalized CdS nanoparticles as a fluorescence probe for the detection of Hg^{2+} with high sensitivity. More recently, a novel fluorogenic sen-

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sor to probe mercury ions based on L-cysteine-capped CdS quantum dots [25] was reported. These reports reveal that CdS nanoparticles utilized as luminescent probes and sensors were widely studied. However, searching for new fluorophores with high selectivity as well as good photochemical property including excellent photostability, large Stoke's shifts, high quantum yield and long fluorescence lifetime is still a challenge.

Recently, numerous papers on the luminescence of semiconductor nanoparticles doped with rare earth (RE) ions have appeared, such as Tb^{3+}-doped functionalized CdS and ZnS nanocrystals [26,27], Sm^{2+}-doped ZnS nanocrystals [28], Eu^{3+}-doped ZnS and CdS nanocrystalline [29] or Er^{3+}-doped glass matrix containing CdS QDs [30]. It is known that the absorption bands of nanoparticles are broader than those of RE which ensures the accordability in wavelength of the pump sources for the achievement of optical components such as amplifiers. Direct or indirect band-gap semiconductors could be good sensitizing centers since their excitation cross sections are very high due to the efficient band-to-band absorptions [31]. Compared to the surface-modified semiconductors nanoparticles, the RE-doped II–VI semiconductors nanocrystals exhibit a very narrow emission line, a large excitation–emission separation and a long fluorescence lifetime. In various articles it was concluded that the RE-doped II–VI semiconductors nanocrystals "form a new class of luminescent materials" [29]. Considering this, the Tb^{3+}-doped cadmium sulfide composite nanoparticles used as a fluorescence probe for determination of mercury ions was researched.

In our work, we report a new and simple method for creating water soluble Tb^{3+}-doped CdS composite nanoparticles with GSH as the capping ligand. This method is simple, sensitive, low cost and requires only room temperature conditions. Under the optimal conditions, the fluorescent intensity of Tb^{3+} with maximum band at 491 nm doped in CdS nanoparticles can be quenched gradually by mercury ions and the quenching of fluorescence fluorescent intensity is proportional to mercury ions concentration. This quenching can be attributed to the fact that the energy transfer system with CdS nanoparticles as donor and Tb^{3+} ions as accepter was destroyed upon combining with Hg^{2+}. Based on the quenching of fluorescence of Tb^{3+} ions, a sensitive and identified fluorescence probe for mercury(II) ions in aqueous solution was developed. The preliminary research reports showed that this method will enable us to construct efficient RE-doped CdS nanoparticles for heavy metals detection based on fluorescence quenching effect.

2. Experiment

2.1. Apparatus and reagents

The fluorescence spectra were performed using a Hitachi F-2500 spectrofluorometer (Hitachi, Japan) equipped with a plotter unit and a quartz cell (1 cm × 1 cm). The transmission electron microscopy (TEM) images were obtained using a JEM-2100 transmission electron microscope (JEOL, Japan). The UV spectra were acquired on a U-3010 spectrofluorometer (Hitachi). All pH values were measured with a pHS-3C digital pH meter (Analytical Instruments Co., Tianda, Shanghai, China).

All chemicals were of analytical-reagent grade or better. The stock solutions of $CdCl_2 \cdot 2.5H_2O$ (Alfa, USA), thioacetamide (CH_3CSNH_2, Alfa), NaOH (Alfa), $HgCl_2$ (Shanghai Reagent Company, China), sodium hexametaphosphate (Alfa), $Tb(NO_3)_3 \cdot 6H_2O$ (Sigma) and glutathione (GSH, Alfa) were prepared by dissolving them in ultra pure water without further purification. The phosphoric buffer solutions (PBS) were prepared by adjusting $0.067 \, mol \, L^{-1}$ KH_2PO_4 with $0.067 \, mol \, L^{-1}$ Na_2HPO_4. Ultra pure water was used throughout.

2.2. Synthesis of Tb^{3+}-doped CdS composite nanoparticles

The Tb^{3+}-doped CdS nanoparticles were prepared according to the scheme reported in literatures [32,33] and our previous work for mercaptoacetic acid capped CdS nanocrystals reported by Liang and co-workers [34] with a little change. Briefly, 30 mL $0.01 \, mol \, L^{-1}$ $CdCl_2 \cdot 2.5H_2O$, 45 mL of $0.1 \, mol \, L^{-1}$ sodium hexametaphosphate, 30 mL $0.01 \, mol \, L^{-1}$ GSH and 75 mL $0.01 \, mol \, L^{-1}$ Tb^{3+} were mixed in a 500 mL three-necked round bottomed flask and purged with N_2 in room temperature. Under vigorous stirring, 120 mL $0.01 \, mol \, L^{-1}$ CH_3CSNH_2 were added drop-wise and then 30 mL $0.1 \, mol \, L^{-1}$ NaOH solutions were added drop-wise to the flask. After stirring for 1.5 h, the composite nanoparticles were obtained. The as-prepared solutions are stable for one month at room temperature, no visible coacervation or precipitation was observed.

2.3. Procedure of determination of Hg^{2+}

In a series of 10 mL volumetric flasks, 4 mL of as-prepared Tb^{3+}-doped CdS solution, 2 mL of PBS (pH 5.29) and various amount of Hg^{2+} were added, then the mixture was diluted to the mark with water and mixed thoroughly. After incubating for 10 min at room temperature, the fluorescence spectrum of the F-2500 spectrofluorometer was recorded within the wavelength region from 390 to 650 nm. The excitation and emission wavelengths were 368 and 491 nm, respectively.

3. Result and discussion

3.1. TEM image of nanoparticles

The morphology of the Tb^{3+}-doped CdS nanoparticles was studied by TEM is shown in Fig. 1. The TEM image shows that the observed diameter of the nanoparticles was about 10 nm or so.

3.2. Spectral characteristics and reaction between nanoparticles and Hg^{2+}

The fluorescence emission spectra of (1) CdS nanoparticles, (2) Tb^{3+}–CdS, (3) Tb^{3+}–CdS–Hg^{2+}, (4) Tb^{3+} systems are shown in Fig. 2. As shown in Fig. 2, it can be seen that at the excitation of 368 nm, the Tb^{3+} system emits the characteristic fluorescence of Tb^{3+} with the weak emission peaks of 491 and 546 nm, which correspond to the transition of $^5D_4 \rightarrow {}^7F_6$ and $^5D_4 \rightarrow {}^7F_5$. The weak characteristic fluorescence may due to the fact that rare-earth ion Tb^{3+} has low absorption (molar absorption lower than 10). From curve 1 in Fig. 2, we can see the strong emission wavelength of CdS nanoparticles without Tb^{3+} occurs at 515 nm. After doping with Tb^{3+} ions, the fluorescence of Tb^{3+} ions can be enhanced remarkably. This indicates that CdS nanoparticles have the enhancement effect on the luminescence of Tb^{3+}. Chowdhury and Patra [35] founded that upon excitation of the CdS host, the energy from non-radiative recombination of electron–hole pairs can be transferred to the high-lying energy levels of the lanthanide's ion. Similarly, it may be explained that the electron trapped in the surface levels of CdS particles recombines with a valence band free hole and the energy is non-radiatively transferred to the Tb^{3+} ions. According to this suppose, an efficient energy transfer system with CdS nanoparticles as energy donor and Tb^{3+} ions as energy accepter was built.

When trace amounts of Hg^{2+} were added to the Tb^{3+}-doped CdS nanoparticles solution, the wavelength of excitation and emission were unchanged, but the intensity of the peak decreased (curve 3). The experimental phenomenon can be explained in the terms of strong affinity of mercury onto the surface of CdS nanoparti-