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Study on the fluorescence resonance energy transfer between CdTe QDs and butyl-rhodamine B in the presence of CTMAB and its application on the detection of Hg(II)

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Abstract

The thioglycolic acid-functionalized CdTe quantum dots (QDs) were synthesized in aqueous solution using safe and low-cost inorganic salts as precursors. Fluorescence resonance energy transfer (FRET) system was constructed between CdTe QDs (donor) and butyl-rhodamine B (BRB) (acceptor) in the presence of cetyltrimethylammonium bromide (CTMAB). CTMAB micelles formed in water reduced the distance between the donor and the acceptor significantly and thus improved the FRET efficiency, which resulted in an obvious fluorescence enhancement of the acceptor. Several factors which impacted the fluorescence spectra of the FRET system were studied. The energy transfer efficiency (E) and the distance (r) between CdTe and BRB were obtained. The feasibility of the prepared FRET system as fluorescence probe for detecting Hg(II) in aqueous solution was demonstrated. At pH 6.60, a linear relationship could be established between the quenched fluorescence intensity of BRB and the concentration of Hg(II) in the range of 0.0625–2.5 μmol L^{-1}. The limit of detection was 20.3 nmol L^{-1}. The developed method was proved to be sensitive and repeatable to detect Hg(II) in a wide range in aqueous solutions.

Keywords: Fluorescence resonance energy transfer; CdTe quantum dots; Butyl-rhodamine B; Hg(II); Detection

1. Introduction

Fluorescence resonance energy transfer is a process by which excitation energy is transferred from an excited donor to an acceptor (which happens due to long-range dipole–dipole interactions between the donor and acceptor) and takes place without appearance of photon [1–3]. The process is generally experimentally manifested in simultaneous quenching of the donor fluorescence and electronic excitation of the acceptor [4–6]. According to Forster's theory, the rate of energy transfer depends mainly upon the following factors [1–4,7]: (1) the extent of spectral overlap between the donor emission and the acceptor UV–vis absorption, (2) the quantum yield (Φ) of the donor, (3) the relative orientation of the donor and acceptor transition dipoles, and (4) the distance between the donor and acceptor transition dipoles. As FRET is sensitive to molecular rearrangements in the 1–10 nm range, researchers have long used this photophysical process to monitor intracellular interactions and binding events [8,9]. The fluorophores of donor and acceptor can be entirely separated [10] or attached to the same macromolecule [11]. FRET technology provides a fast, sensitive and non-destructive way of measurement by its nano-scale study [5,6].

Quantum dots are generally composed of II–VI and III–V elements. They own unique excellent optical properties, such as broad excitation spectrum, narrow emission spectrum, precise tunablity of their emission peak, longer fluorescence lifetime and negligible photobleaching [12–14]. In recent years, with their water-soluble problem solved, the QDs are being widely used in a variety of biological applications [14]. Luminescent QDs applied to FRET has also been investigated extensively by several groups [10,11,15,16]. Alphandery et al. [10] and Chen et al. [17] have constructed FRET systems related to QDs either in mixed solid films or in water solution. This method provides a new way of thinking to extend the FRET applications in

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nucleic acid detection [15], protein interactions [16] and other biomedical researches.

Our motivation for constructing the FRET system of QDs (donor)–BRB (acceptor) is severalfold: (1) suitable size of CdTe QDs could be selected to maximize the extent of spectral overlap with BRB because of its precise tunable spectrum characteristics. Excitation wavelength could also be conveniently chosen to reduce the direct excitation of acceptor due to the broad excitation spectrum of CdTe QDs and narrow excitation spectrum of BRB, (2) the excited state lifetimes of CdTe QDs is longer than that of BRB in the same magnitude order (ns) [10,18], which makes it possible for very efficient energy transfer to occur, and (3) the efficiency of the transfer is expected to be high. This is not only due to the relatively high-fluorescence quantum yields of both CdTe QDs and BRB, but to the function of the CTMAB micelles, which minishes the distance between them. Therefore, CdTe QDs with suitable size and BRB with long emission wavelength were chosen for the FRET system.

Mercury ion is a well-known highly toxic environmental pollutant because of its accumulative and persistent nature in the environment and biota. It represents a major toxicity to microorganisms and environment even at low concentrations. Therefore, the rapid and sensitive detection of Hg(II) in the environment is of great importance. In recent years, several methods for Hg(II) detection have been reported [19–21]. Fluorescence method is particularly a suitable spectral method for monitoring low-level heavy metal ions because of its sensitivity, facility and rapidness [22,23]. Detection of Hg(II) in aqueous solution by FRET system in this work proved to be sensitive and repeatable.

2. Experimental

2.1. Apparatus

The transmission electron microscopy (TEM) image of the nanoparticles was acquired on a Philips Tecnai G^2 F20 field emission transmission electron microscope (Philips, Holand). All fluorescence spectra and intensities were measured with a F-4500 spectrofluorometer (Hitachi, Japan) with a 1 cm quartz cell. All UV absorption spectra were recorded with a UV-2450 UV–vis spectrophotometer (Shimadzu, Japan). The pH values were measured with a model Orion 420+ pH meter (Thermo Electro Corporation, USA). All optical measurements were performed at room temperature under ambient conditions.

2.2. Reagents

The chemicals were of A.R. grade or the best grade commercially available. All stock solutions of chemicals were prepared in doubly distilled water (DDW). Tellurium powder was a product of Beilian Fine Chemical Factory, China. $CdCl_2{\cdot}2.5H_2O$, $NaBH_4$, thioglycolic acid (TGA), cetyltrimethylammonium bromide (CTMAB) and butyl-rhodamine B (BRB) were purchased from Guangfu Fine Chemical Research Institute, China. A Hg(II) standard stock solution was prepared by dissolving 16.7 mg of $Hg(NO_3)_2{\cdot}0.5H_2O$ in 50 mL DDW containing three drops of HNO_3 (2.0 mol L^{-1}). A series of Tris–HCl buffer solution (0.05 mol L^{-1}) were used in the experiments.

2.3. Experimental procedures

The water-soluble CdTe QDs were synthesized by adding freshly prepared sodium hydrogen telluride (NaHTe) solution to a N_2-saturated $CdCl_2$ solution at pH 10.00 in the presence of thioglycolic acid (TGA) as a stabilizer [24,25]. Tellurium powder was chosen as a starting material to prepare the NaHTe aqueous solution. Briefly, it was reduced by excessive $NaBH_4$ in water under stirring and N_2 bubbling. After Te was completely reduced, a certain volume of the NaHTe solution was injected into a $CdCl_2$–TGA solution, which was deaerated by N_2 for 20 min. The molar ratio of Cd^{2+}/HTe^-/TGA was set as 1:0.5:2.4. Then, it was heated until boiling. Under refluxing, fluorescence of the solution appeared and could be tuned in color by prolonging the refluxing time. After being refluxed for a certain time, 0.001 mol L^{-1} (here and elsewhere, referring to Cd^{2+}) TGA-stabilized CdTe QDs exhibiting strong fluorescence at 536 nm were obtained. A luminescence quantum yield of 30.0% was measured for the CdTe QDs at room temperature by comparing with the fluorescence emission of rhodamine 6G in ethanol [26]. The full width at half maximum (FWHM) was about 38 nm.

The FRET system was constructed by mixing BRB and CTMAB in 1 mL of 0.05 mol L^{-1} Tris–HCl buffer solution first, and then a certain volume of CdTe colloidal solution was added. The as-prepared solution was diluted to 10.0 mL with DDW, stirred thoroughly and incubated for 20 min at room temperature for assay. The FRET system was used to detect Hg(II) via the quenching of the fluorescence intensity of the acceptor BRB. All the fluorescence spectra were obtained with the excitation wavelength of 447 nm. The excitation and emission slits were set to 2.5 nm.

3. Results and discussion

3.1. TEM image of the prepared CdTe QDs

The TEM image (Fig. 1) shows that the CdTe QDs are spherical morphology, homogeneously distributed and well proportional.

3.2. Absorption and fluorescence spectra of CdTe QDs (donor) and BRB (acceptor)

Fig. 2 shows absorption and fluorescence spectra obtained from CdTe QDs and BRB, respectively, dispersed in Tris–HCl buffer solution (pH 7.40). All spectra have been normalized for clarity of presentation. The appropriate size of CdTe QDs was chosen so as to maximize the overlap of the emission spectra of the donor and absorption spectra of the acceptor while still maintaining good resolution of their emission spectra. It can be seen that the maximal absorption and emission peaks of the QDs are at 524 and 536 nm, respectively, while those of BRB are at 558 and 576 nm, respectively. So there is appreciable over-