Diethyldithiocarbamate functionalized CdSe/CdS quantum dots as a fluorescent probe for copper ion detection

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ABSTRACT

A new fluorescent probe for copper ion detection is reported that it is based on the quenching of the fluorescence of the diethyldithiocarbamate (DDTC)-functionalized quantum dots (QDs) in the presence of copper ions. DDTC was bound to the QDs via the surface ligand exchange to form DDTC–QDs conjugates following the capping of 2-mercaptoacetic acid on the core–shell CdSe/CdS QDs. It was found that the fluorescence intensity of the conjugates was quenched after coordinated with Cu^{2+}. A linear relationship existed between the extent of quenching and the concentration of copper in the range of 0–100 $\mu g\,L^{-1}$, with a detection limit of 0.29 $\mu g\,L^{-1}$ (3σ). The DDTC-functionalized QDs showed excellent selectivity for Cu^{2+} over other metal cations. The fluorescent probe was successfully used for the determination of copper in environmental samples.

1. Introduction

It is well known that heavy metals can cause adverse health effects on humans and animals due to environmental and occupational exposure [1,2]. Monitoring of heavy metals in environment is of great importance because of their implications in health. A variety of methods, including atomic/molecular absorption spectroscopy [3], inductively coupled plasma emission/mass spectroscopy [4], electrochemical methods [5], and ion chromatography [6], have been reported and used successfully for the determination of heavy metals in environmental samples. Yet, there are still strong demands for developing simple, sensitive, selective and rapid methods for the measurement of heavy metals using inexpensive instrumentation and consumables.

Quantum dots (QDs) are semiconductors whose opto-electronic characteristics are closely related to the size and shape of the individual crystal [7]. They are highly luminescent and photostable fluorophores with unique photophysical properties, including broad absorption and narrow emission spectra, large extinct coefficients, resistance to photobleaching, long fluorescence lifetime, and size-tunable emission [8]. These properties provide important advantages over organic dyes and lanthanide probes in fluorescent applications, resulting in the increased use of QDs as the fluorescent probe in analytical chemistry [9].

Several review papers [8,10,11] have been published on the QDs-based analytical applications. The concentration of an analyte of interest can be measured based on the change of QDs' fluorescence intensity caused by the interaction between QDs and the analyte. Chen and Rosenzweig [12] reported for the first time that metal ions such as Zn^{2+} and Cu^{2+} could be determined by utilizing luminescent CdS QDs capped by different ligands, i.e., polyphopate, L-cysteine and thioglycerol. From then on, analytical methods for various metal ions [13–15] and small molecules [16] have also been established with the same principle. Zheng et al. [17] synthesized the peptide-coated CdS QDs for optical detection of Cu(II) and Ag(I). QDs capped with different mercaptoalkyl acids, such as mercaptopropionic acid [18], 2-mercaptoethane sulphonic acid [19], 2-mercaptoactic acid, mercaptosuccinic acid [20], and L-cysteine [21,22], aminonaphthol [23] and azamacrocycle [24] were reported for the detection of Cu(II) and other ions [25]. QDs including CdS and core–shell CdSe/ZnS and CdSe/CdS were used as the luminescent probe. It has also been demonstrated that QDs are the good indictors for enzymatic reactions [26–31] and used to develop specific analytical methods for urea [27], glucose [32], and some pollutants [33] with the combination of enzymatic reactions.

In the present study, core–shell CdSe/CdS QDs functionalized by *N,N*-diethyldithiocarbamate (DDTC) were synthesized and used as a fluorescence probe for the determination of trace amount of copper in environmental samples. DDTC is often used as the *copper reagent* in molecular absorption spectrophotometry [34] due to its specific and strong Cu^{2+} binding capability. The objective of this study is to develop a sensitive and selective method for the detec-

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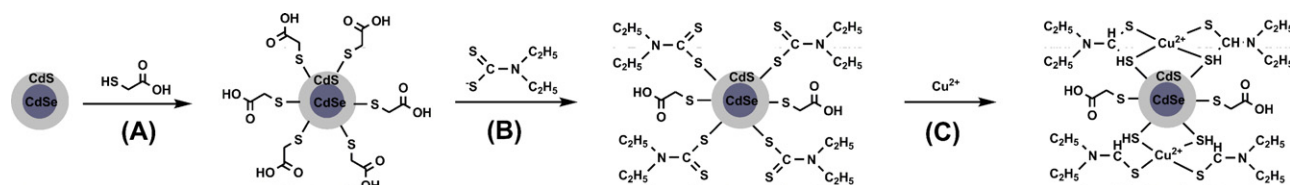E-mail address: taogh@suda.edu.cn (G. Tao).

Fig. 1. Scheme for the preparation of DDTC–QDs conjugates (A and B) and the coordination of Cu^{2+} and DDTC–QDs conjugates (C).

tion of copper ion by exploring the unique properties of QDs and specificity of DDTC.

2. Experimental

2.1. Apparatus

Fluorescence signals were acquired on an F-2500 fluorescence spectrophotometer (Hitachi, Japan). A U-2810 spectrophotometer (Hitachi, Japan) was used to obtain ultraviolet–visible absorption spectra. An AXIS Ultra[DLD] X-ray photoelectron spectroscopy (Kratos Analytical, UK) was used to characterize the nanoparticles. An Allegra 64R high-speed refrigerated centrifuge (Beckman, USA) was used to separate particles from solution. pH values were measured by a Delta 320 pH-meter (Mettler Toledo, Switzerland,). An AA240FS atomic absorption spectrometer (Varian, USA) was used for the verification test.

2.2. Reagents and standards

Sodium DDTC was purchased from Guangzhou Chemical Reagent Factory, China. Other chemicals used were obtained from Sinopharm Group, Shanghai, China. All chemicals were of analytical-reagent grade, except for nitric acid which was of MOS grade. Phosphate buffer solution was prepared by dissolving appropriate amount of disodium hydrogen phosphate and monosodium orthophosphate in water. Deionized water produced by a Milli-Q system (Millipore, USA) was used for preparing solutions.

2.3. Synthesis of DDTC-functionalized QDs

The synthesis procedure is schematically shown in Fig. 1(A) and (B). Firstly, the core–shell CdSe/CdS QDs capped by 2-mercaptoacetic acid (MPA) were prepared according to a previously reported method [35]. Secondly, the DDTC-functionalized QDs were synthesized by mixing DDTC with the prepared MPA-capped QDs (Fig. 1(B)). The procedure was as follows. 5 mL of 800 μmol L^{-1} DDTC were added to 5 mL of 0.25 g L^{-1} MPA-capped QDs solution. The mixture was stirred for 2 h, allowing DDTC to attach to the QDs through the binding between the mercapto groups of DDTC and the Cd atoms on QD surface. The DDTC-functionalized QDs were isolated from the bulk solution via acetone precipitation and centrifugation. The precipitate was re-dissolved in deionized water. The isolation steps were repeated three times to remove the contaminants. The resulting DDTC-functionalized QDs were re-dissolved in 10 mL of 20 mmol L^{-1} phosphate buffer (pH 8.23) for further use.

2.4. Analytical procedure

100 μL of standard or sample solution and 100 μL of the prepared DDTC-functionalized QDs were added into 800 μL of 20 mmol L^{-1} phosphate buffer (pH 8.23) and mixed thoroughly for 10 min. The reaction involved is shown in Fig. 1(C). The fluorescence spectrum of the mixture was then recorded under an excitation wavelength of 370 nm. The excitation and emission slits were set

at 5 and 5 nm for QD characterization, and 10 and 10 nm for copper detection, respectively. The maximum emission wavelength of 557 nm was used for quantitative analysis. A quartz cuvette with an optical path length of 10 mm was used for the measurement.

2.5. Sample preparation

Environmental samples were collected in a local industrial area. Water samples were filtered through Whatman filter paper (no. 42). 5 mL of nitric acid and 1 mL of hydrogen peroxide solution were then added into 100 mL filtered sample. The samples were heated and boiled for 30 min. Soil samples were prepared according to the Chinese National Standard for the determination of copper in soil [36]. All samples were adjusted to pH 8.23 with 20 mmol L^{-1} phosphate buffer, and stored in opaque polyethylene bottles at 4 °C prior to analysis.

3. Results and discussion

3.1. Synthesis and characterization of QDs functionalized by DDTC

After the core–shell CdSe/CdS QDs were synthesized, attempts were made to bind DDTC directly to the QDs surface via the surface–ligand exchange. However, the mixture turned to be milky with the addition of DDTC to the QDs suspension. It was probably because the exposed tertiary amine groups of DDTC attached to the QDs were hydrophobic, resulting in the formed DDTC-capped QDs being water-insoluble. Therefore, MPA was used to modify the synthesized QDs prior to the DDTC binding. The polar carboxylic acid group of MPA rendered the nanoparticles water-soluble.

After capped with MPA, the water-soluble QDs were reacted with DDTC to form DDTC–QDs conjugates. DDTC was bonded to the QDs based on the same ligand exchange mechanism as MPA was. As shown in Fig. 1(B), MPA capped on QDs were substituted by DDTC to a certain extent. The remaining MPA on the nanoparticles ensured them water-soluble. With the binding of DDTC, the quenching of the QDs' luminescence was observed. As shown in Fig. 2(B), a linear relationship was observed between the DDTC amount and $\ln(I_0/I)$, where I and I_0 are the luminescence intensity of QD with and without the addition of DDTC. The relationship revealed that a static Perrin-type quenching mechanism was involved. The quenching was caused by the charge transfer (or electron tunneling), which indicated that DDTC had been bonded to the surface of the QDs [37].

The partially quenched DDTC–QDs conjugates provided the basis of detection as it was observed that the fluorescence intensity of the conjugates decreased upon the coordination of the mercapto groups of DDTC with Cu^{2+}. The more DDTC bound on the surface of QDs, the more complexation sites for Cu^{2+} and thus the higher sensitivity. However, as shown in Fig. 2, increasing the amount of DDTC could cause more quenching of fluorescence intensity and less solubility of QDs. When the concentration of DDTC reached 1 mmol L^{-1}, precipitation was observed in the solution of DDTC–QDs conjugates. Therefore, 5 mL of 800 μmol L^{-1} DDTC was added to 5 mL of 0.25 g L^{-1} QD–MPA as a compromise.