



Pure zinc sulfide quantum dot as highly selective luminescent probe for determination of hazardous cyanide ion



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ABSTRACT

A rapid and simple fluorescence method is presented for selective and sensitive determination of hazardous cyanide ion in aqueous solution based on functionalized zinc sulfide (ZnS) quantum dot (QD) as luminescent prob. The ultra-small ZnS QDs were synthesized using a chemical co-precipitation method in the presence of 2-mercaptoethanol (ME) as an efficient capping agent. The prepared pure ZnS QDs was applied as an optical sensor for determination of cyanide ions in aqueous solutions. ZnS nanoparticles have exhibited a strong fluorescent emission at about 424 nm. The fluorescence intensity of QDs is linearly proportional to the cyanide ion concentration in the range 2.44×10^{-6} to 2.59×10^{-5} M with a detection limit of 1.70×10^{-7} M at pH 11. The designed fluorescent sensor possesses remarkable selectivity for cyanide ion over other anions such as Cl^- , Br^- , F^- , I^- , IO_3^- , ClO_4^- , BrO_3^- , CO_3^{2-} , NO_2^- , NO_3^- , SO_4^{2-} , $\text{S}_2\text{O}_4^{2-}$, $\text{C}_2\text{O}_4^{2-}$, SCN^- , N_3^- , citrate and tartarate with negligible influences on the cyanide detection by fluorescence spectroscopy.

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1. Introduction

The recognition, separation and determination of anions have received considerable attention due to their important roles in biological, industrial, and environmental processes [1,2]. Cyanide ion (CN^-) is known as one of the most lethal poisons, and the mechanism of human toxicity for cyanide lies in its ability to suppress the transport of oxygen [3]. CN^- ion is widely distributed in the ecosystem and has been associated with toxic effects in humans and animals [4]. Cyanide is also commonly used worldwide in industrial applications such as metal mining, metal plating, and plastics manufacture [5]. Moreover, cyanide played an important role in the cause of death of fire cases, and thus the recognition and determination of cyanide amounts of human blood in fire victims are areas of active research [6].

There are many kinds of qualitative and quantitative methods for analysis of CN^- in wide fields, reflecting the great needs of its analysis. Detection of CN^- ion can be accomplished by various instrumental methods such as photometry [7], spectrofluorimetry [8], colorimetry [9], GC/MS [10], electrochemical [11], and flow injection [12] techniques. Among the various reported techniques, fluorescent sensors present many appealing advantages, including high sensitivity, low cost, easy detection, and remote control. While a number of synthetic organic luminescent probes for detection of CN^- anion have been

designed, a few of them are capable of displaying high selectivity over other anions. In addition, these organic fluorophores suffer from low quantum yield and poor photostability, which thus limits their practical applications [13].

In the recent years, semiconductor nanoparticles or quantum dots (QDs) have been developed as luminescent probes for sensing events [14]. QDs, as a brand new class of fluorescent receptors, have the three dimensions confined to 1–8 nm length scale. QDs possess an excellent photostability, high quantum yields, and long fluorescence lifetimes [15]. In addition, due to the unique and novel properties of the QD based luminescent sensors such as low cost fabrication, reliability, reproducibility, accuracy, high sensitivity and selectivity, expanding applications of QDs to develop inorganic anions, cations, drugs, organic dyes, explosive compounds and biomolecular sensors are a topic of current interest [16–20].

In the case of QDs, zinc sulfide, with wide band gap energy are so far most studied, due to their tunable emission in the visible range, the advances in their preparation, and their potential use for industrial and biomedical applications [21]. Moreover, coating the surface of these semiconductor nanoparticles with suitable ligands or capping agents has profound effects on the photoluminescence response of the QDs to some chemical species [22]. On the other hand, the surface modification of QDs may change their chemical, optical, and photocatalytic properties. It can give rise to effects, such as (i) an enhancement of their excitonic and defect emission, (ii) an improvement of the photostability of QDs, (iii) the generation of new traps on the QDs surface, leading to the appearance of new emission bands, (iv) an

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enhancement of the selectivity, sensitivity and efficiency of light induced reactions occurring on the surface of QDs, etc. [23].

Mehta et al. have reported the utilization of polyethylene glycol (PEG) capped ZnS nanoparticles (NPs) for cyanide ion detection [24]. PEG capped ZnS NPs were synthesized by microwave process in the range of 12–15 nm. In addition, higher than the amount of ZnS NPs was required for the analyses.

In another work, W.J. Jin and co-workers [22] have reported a turn-out cyanide sensor based on CdSe NPs functionalized with tert-butyl-N-(2-mercaptoethyl)-carbamate groups. This method also has limitations like the use of organic solvent (chloroform) and hazardous CdSe QDs. Because of the use of toxic, volatile organic solvents, the development of a practical and effective cyanide sensor is in infancy.

In this work, we have used a very simple, fast and reproducible process for the synthesis of ultra-small ZnS QDs by chemical co-precipitation method. Free-standing clusters of semiconductors can be easily formed in large quantities by relatively inexpensive means in aqueous media, at room temperature. Characterization of the prepared ZnS QDs was carried out with various techniques including transmission electron microscopy (TEM), X-ray diffraction (XRD), and UV–vis and fluorescence spectroscopy. In addition, an optical based on the fluorescence quenching of ZnS QDs in the presence of CN^- ions was developed for selective determination of trace amounts of CN^- ions in aqueous media.

2. Experimental

2.1. Apparatus and materials

All fluorescence spectra were recorded on a Cary Eclipse fluorescence spectrophotometer (Varian). The UV–vis absorption spectra of the ZnS QDs were also recorded using an Agilent 8453 UV–vis spectrophotometer. A digital pH meter, Metrohm model 692, equipped with a combined glass calomel electrode was used for the pH adjustments. The morphology of the prepared ZnS QDs was examined using a JEM-200CX transmission electron microscope. The X-ray diffraction pattern was obtained using German Bruker D8Advanced Diffractometer with $\text{Cu K}\alpha$ source ($\lambda = 1.5406 \text{ \AA}$).

Reagent grade sodium sulfide ($\text{Na}_2\text{S}\cdot 9\text{H}_2\text{O}$), 2-mercaptoethanol (ME), and zinc nitrate salt, and other anions used (all from Merck) were of the highest purity available and used without any further purification. All solutions were prepared using double distilled water.

2.2. Preparation of ZnS QDs

ZnS QDs were synthesized by a chemical co-precipitation method at room temperature, without using any organic solvent following the previous literature [17]. For this purpose, 50 mL aqueous solution of 0.01 M zinc nitrate was prepared in double distilled water. The solution was transferred to a three-necked flask, under N_2 inert gas with continuous magnetic stirring. Then, 50 mL aqueous solution of ME (0.01 M) as capping agent was added drop wise to the above solution under vigorous stirring. Then, 50 mL aqueous solution of 0.01 M sodium sulfide was added drop-wise to the solution. The reaction was completed for 1 h, and the precipitated nanoparticles of ZnS were separated in a centrifuge at 3000–4000 rpm within 10–15 min, and were washed by water. The resulting powders were dried in vacuum at room temperature for use in further studies.

2.3. Fluorescent detection of hazardous CN^- anions

An aqueous solution of ZnS QD capped with ME was prepared by dispersion of certain amount of ZnS in doubly distilled water. For the quenching studies, 2.5 mL of aqueous solution of phosphate buffer was placed in the quartz cell (4.0 cm \times 1.0 cm \times 1.0 cm) and 100 μL of ZnS QD with desired concentrations was added, and then titrated

by successive additions of 50 μL portions of 500 $\mu\text{g mL}^{-1}$ stock solutions of CN^- ion and the solution was mixed before any fluorescence measurement. The fluorescence spectra of ZnS QDs in the absence and presence of the CN^- anion were recorded at excitation and emission wavelengths of 265 and 423.9 nm, respectively. The scan speed was 1200 nm min^{-1} and the band-slits of both excitation and emission were set as 5.0 nm.

3. Results and discussion

3.1. Characterization of the synthesized ZnS QDs

3.1.1. TEM and XRD studies of ZnS QDs

The morphology and particle size of the prepared ZnS QDs were studied by the transmission electron microscopy. Fig. 1 indicates the TEM image of the synthesized ZnS nanoparticles capped by ME with almost spherical particles. TEM image shows that the particles are most rounds with the average particle size of 4 nm. However, it is worth noting that only a small percentage of the total particles showed a diameter size greater than 5 nm. Besides, some large particles are also apparent in Fig. 1, indicating aggregation of QDs. These aggregates may be formed at relatively high QD concentrations (most likely during the solvent evaporation process of TEM experiments) via interconnection of the ME capped ZnS QDs to form a three-dimensional ZnS QD network [19,22].

In addition, for investigation of the crystalline structure and purity of nanoparticles, X-ray diffractometry was performed on the ME capped ZnS Nanoparticles. Fig. 1 shows the XRD pattern of a typical ZnS nanoparticle sample. The crystal structure of the sample is cubic zinc blend with peaks indexed as (111), (220) and (311), which match well with the standard card, JCPDS NO 5-566 [25]. The XRD peaks of samples are broad due to the small crystalline domains in the nanoparticles. On the other hand, the average particle size of the ZnS QDs was obtained about $2.1 \pm 0.2 \text{ nm}$ using the Debye–Scherrer relation [26].

3.1.2. Optical characteristics of ZnS nanoparticles

The optical properties of ME capped ZnS QDs were characterized by UV–Vis absorption spectrometry and fluorescence spectroscopy. The results are shown in Fig. 2(a), wherein QDs exhibited a broad absorption spectrum and narrow emission band with a characteristic band at 271 nm and 423.9 nm, respectively.

Quantum confinement effects are expected in the colloids due to small particle size detectable as a blue-shift of nano-phase optical absorption edge caused by band gap widening in the UV region [27] and a corresponding blue-shift in photoluminescence (PL). In the corresponding fluorescence spectrum of ZnS QD, a narrow maximum emission band centered at 423.9 nm was observed when QDs were excited by the radiation of 265 nm. The narrow emission spectrum indicated that high degree of monodispersity of colloidal ZnS QDs is present [28]. The emission band in the PL spectra of ZnS nanocrystals at about 424 nm could be assigned to the radiative recombination involving defect states in the ZnS nanocrystals [29]. As in the bulk ZnS, the dominant defect involving the violet–blue emission in QDs is sulfur vacancies (VS), which form shallow donor levels below the conduction band (CB) [30]. The energy levels of defects VS become deeper in the band gaps of ZnS QDs than in the bulk counterpart because of quantum confinements. The electron-hole pairs created by ionization are possibly trapped at these defects, where they recombine and generate luminescence [14].

The UV–Vis optical spectrum of the synthesized ZnS in the presence of constant concentration of ME as capping agent is shown in Fig. 2. As can be seen, the absorption spectra revealed an absorption edge wavelength at 271 nm. UV–vis spectrum was used for evaluation of an approximate size of prepared ZnS nanoparticles [31].

The method developed by Swanepoel [32] was used to calculate the absorption coefficient α . An expression for the absorption coefficient,

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