NJC

Accepted Manuscript

This is an *Accepted Manuscript*, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this *Accepted Manuscript* with the edited and formatted *Advance Article* as soon as it is available.

You can find more information about *Accepted Manuscripts* in the Information for Authors.

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard Terms & Conditions and the Ethical guidelines still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this *Accepted Manuscript* or any consequences arising from the use of any information it contains.

ROYAL SOCIETY OF CHEMISTRY

www.rsc.org/njc

Highly sensitive fluorescent determination of sulfide using BSA-capped CdS quantum dots

Weidan Na, Xiaotong Liu, Tianyu Hu and Xingguang Su *

Department of Analytical Chemistry, College of Chemistry, Jilin University, Changchun, 130012, China

*Corresponding author, Tel.: +86-431-85168352, E-mail address: suxg@jlu.edu.cn

This work presented a novel nanosensor for rapidly detection of sulfide，which was based on the fluorescence “turn off-on” of bovine serum albumin-capped CdS quantum dots (BSA-CdS QDs). Cd^{2+} could react with S^{2-} to generate fluorescent CdS QDs in the presence of BSA. When Pb(II) was added to the BSA-CdS QDs solution, the fluorescence of CdS QDs would “turn off” due to the coordination of the Pb(II) and BSA presented on the CdS QDs surface. The quenched fluorescence of CdS QDs could be “turn on” upon the addition of sulfide by forming the stable PbS compound. Quantitative analysis was performed by monitoring the fluorescence intensity variation of CdS QDs. Under the optimum conditions, a good linear range for sulfide detection from 0.16-4.8 μmol/L was realized. With the detection limit down to 5.0×10^{-8} mol/L, the nanosensor exhibited good selectivity for sulfide in the presence of other anions.

Key words sulfide anions; fluorescence detection; CdS quantum dots

1. Introduction

Sulfide is widely present in many environments, as sulfide anions are generated not only as a byproduct from industrial processes but also in bio systems.[1] Sulfide is widely used in different fields, for instance, conversion into sulfur and sulfuric acid, dyes and cosmetic manufacturing, production of wood pulp.[2] Exposure to a high level of sulfide can cause adverse effects on human health including loss of consciousness, irritation of mucous membranes, and respiratory paralysis. Once protonated, sulfide anions turns into HS^- or H_2S which are more toxic and caustic. Recent studies have shown that protonated sulfide is involved in multiple physiological processes. For example, cause a reduction in blood pressure, inhibition of insulin signaling and regulation of inflammation.[3-5] In addition, it is related to several diseases, such as Alzheimer's disease, Down's syndrome, diabetes, and liver cirrhosis.[6,7] Because of the widely spread of sulfide anions and the hazardous effect to both humans and other organisms, the development of selective and sensitive detection of sulfide has attracted increasing attentions.

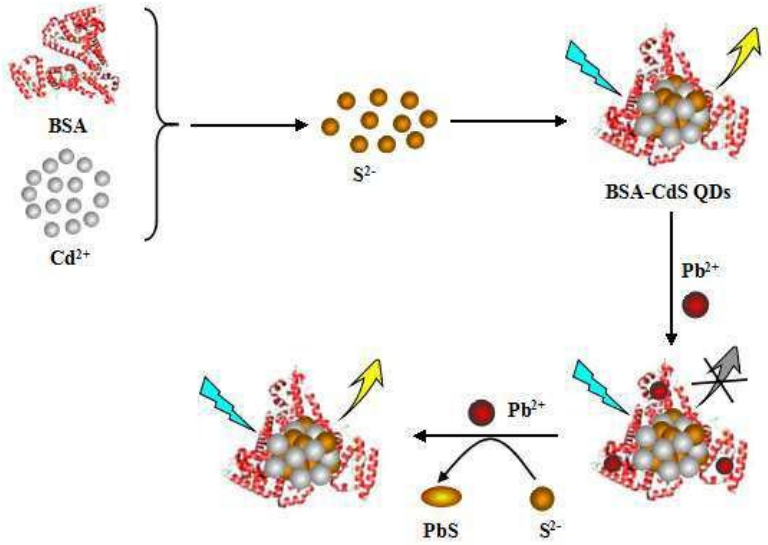
Up to date, many strategies have been proposed for the detection of sulfide anions, Whereas the most useful and effective method for sulfide anions detection are the fluorescence-based methods. Recently, several groups have made great progress in the development of fluorescence

probes for monitoring sulfide anions. These probes are mainly based on specific sulfide induced reactions, including quencher (such as copper(II)) removal,[8-10] azide reduction,[11-13] nitro reduction [14] and nucleophilic reaction [15,16] to achieve a fluorescent turn-on response. Zhang et al. designed and synthesized a highly luminescent Ru(II)–bipyridine complex. It could react with Cu^{2+} to form a hetero bimetallic Ru(II)–Cu(II) complex, the luminescence was strongly quenched through an excited-state electron transfer mechanism. In the presence of sulfide, due to the high affinity of S^{2-} to Cu^{2+}, stable CuS was formed and the luminescence of the Ru(II) complex was restored [8]. Ye et al. designed and synthesized a dinuclear ruthenium(II)–copper(II) complex, $[Ru(bpy)_2(phen\text{-}cyc)Cu](PF_6)_4$, with weakly luminescence, which could rapidly react with H_2S and give a strong red luminescence signal in aqueous media.[9] These luminescent probes could be used for the rapid and accurate detection of sulfide anions. However, the development of such chemical compounds usually requires a whole set of sophisticated organic reactions and purification. Probes bearing these functional group usually have the low solubility in aqueous solution which needs organic solvents for sulfide anions detection.

Semiconductor quantum dots (QDs) have generated marvelous interest in the fields of physics, chemistry and biology owing to their ideal optical properties in the past decade. As a class of fluorescence probe, QDs with variable surface capping ligands have been extensively used for cell labeling, tumor imaging and clinical diagnosis in biology and medicine.[17,18] They are usually used to detect cations such as Pb^{2+}, Cd^{2+} and Hg^{2+} via analyte-induced changes in photoluminescence in aqueous solution.[19] Recently, QDs have been applied to the detection of anions as well. Gore et al. designed a simple fluorescent probe for the direct detection of sulfide anions by virtue of the fluorescence quenching of MPA-capped CdS QDs.[20] Rajabi et al. reported a simple, fast precipitation method for preparing the ultra-small $Zn_{0.96}Mn_{0.04}S$ quantum dots in aqueous media, whose fluorescence could be effectively quenched by sulfide anions via the effective electron transfer from QDs to sulfide anions.[21] The QDs-based methodology are simple and quite straightforward and could realized a comparative low detection limit.

In this work, we presented a novel sensing method by using CdS QDs-based receptor for sulfide anions recognition. As shown in Scheme 1, the fluorescent CdS QDs could be generated in the presence of Cd^{2+}, S^{2-} and BSA. The BSA served as the capping molecule and was employed to render the CdS QDs stable against aggregation and water-soluble. As well-known, the

fluorescence properties of QDs had a close connection to the composition of surface capped layers. Abundant amino groups, 34 disulfide bond and 1 thiol existed on the BSA of QDs, thus, the surface of the BSA-CdS QDs could effectively bind pb^{2+} via forming Pb^{2+}/BSA-CdS complex, which could lead to the fluorescence quenching via a charge transfer process on the surface of the QDs. The addition of S^{2-} anions could turn on the fluorescence of BSA-CdS QDs, because S^{2-} could snatch the Pb^{2+} ions from the Pb^{2+}/BSA-CdS complex to form more stable PbS. Due to the relatively easy design and convenient handling, we developed a novel fluorescence probe for rapid and highly sensitive detection of sulfide.



Scheme 1 Schematic illustration of the BSA-CdS QDs-based sensing system for sulfide detection.

2. Experimental section

2.1 reagents

All reagents were of at least analytical grade. The water used in all experiments had a resistivity higher than 18 MΩ cm^{-1}. Cadmium (II) chloride ($CdCl_2$), sodium hydroxide (NaOH), Sodiumsulfide nonahydrate ($Na_2S•9H_2O$), trihydroxymethyl aminomethane (Tris) and hydrochloric acid were purchased from Beijing Chemical Works. Lead (II) and Bovine serum albumin were purchased from Sigma-Aldrich Corporation. The 0.1 mol/L Tris-HCl buffered

solution (pH 8.2) was used as the medium for detection process.

2.2 Apparatus

The fluorescence spectra were obtained by using a Shimadzu RF-5301 PC spectrofluorophotometer equipped with a xenon lamp using right-angle geometry. UV-vis absorption spectra were obtained by a Varian GBC Cintra 10e UV-vis spectrometer. In both experiments, a 1 cm path-length quartz cuvette was used. FT-IR spectra were recorded with a Bruker IFS66V FT-IR spectrometer equipped with a DGTS detector. All pH measurements were made with a PHS-3C pH meter. Transmission electron microscopy (TEM) experiments were performed on a Philips Tecnai F20 TEM operating at 200 KV acceleration voltage. The X-Ray powder Diffraction (XRD) patterns were obtained by a Empyrean XRD. Samples used for XRD measurements were solid powders prepared by drying the QD precipitate in vacuum.

2.3 Preparation of BSA-CdS QDs

BSA-CdS QDs were synthesized in aqueous solution. 300 μL 2.4 mmol/L BSA solution, 120 μL 50 mmol/L $CdCl_2$ solution and 0.1 mol/L Tris-HCl buffer (pH 8.2, 150 μL) were added into 2 mL calibrated test tube, and shaken thoroughly for 10 minutes. After that, 90 μL 30 mmol/L Na_2S solution was added into the test tube and diluted to 1500 μL with deionized water followed by the thoroughly shaking and equilibrated for 15 minutes. All the reaction conditions for the preparation of BSA-CdS QDs have been optimized. 50 μL BSA-CdS QDs was diluted to 1500 μL with deionized water. The fluorescence spectra were recorded from 405 nm to 650 nm with the excitation wavelength of 340 nm. The slit widths of excitation and emission were both 10 nm.

2.4 The quenching effect of Pb^{2+} on the BSA-CdS QDs

The BSA-CdS QDs solution (50 μL), 0.1mol/L Tris-HCl buffer (pH 8.2, 150μL), and different amount of Pb^{2+} was added into a 2.0 mL calibrated test tube. Then, the solution was diluted to 1500 μL with deionized water followed by the thoroughly shaking and equilibrated for 2 min until the solution was fully mixed. The fluorescence spectra were recorded from 405 nm to 650 nm with the excitation wavelength of 340 nm. The slit widths of excitation and emission were both 10

nm.

2.5 The detection of sulfide

15 μmol/L Pb^{2+} was added to a 2ml test tube containing 50 μL BSA-CdS QDs solution and 10 mmol pH 8.2 Tris-HCl buffer, and the mixture was incubated for 2 min. Different concentrations of sulfide were successively added into the calibrated test tube and diluted to the 1.5mL mark with deionized water followed by the thoroughly shaking. The other process was the same as that in the detection of Pb^{2+}. The fluorescence (FL) intensity of the maximum emission peak was used for the quantitative analysis of sulfide.

2.6 Disposal of lake water sample

The lake water samples were obtained from the Nanhu lake in Changchun. The lake water samples were filtered several times through qualitative filter paper before analysis and different concentrations of sulfide were added to prepare the spiked samples.

3. Results and Discussion

3.1 Spectra of the BSA-CdS QDs

TEM image in Fig. 1(A) revealed the shape of BSA-CdS QDs was nearly spherical with the average diameter of 6 nm. As shown in Fig. 1(B), there was an increased absorption below 300 nm and a shoulder around 279 nm that was the result of $1S_h$–$1S_e$ excitonic transition characteristic of CdS QDs.[22] The fluorescence emission spectra of the BSA-CdS QDs showed a fluorescent peak with maximum emission wavelength of 529 nm which arised from excitonic emission of CdS QDs.[23, 24] The results of XRD studies of the BSA-CdS QDs shown in Fig. S1, the (111), (220), and (311) planes are clearly distinguishable in the pattern. It is evident from the figure that the crystal structure of the BSA-CdS QDs is cubic. [25]

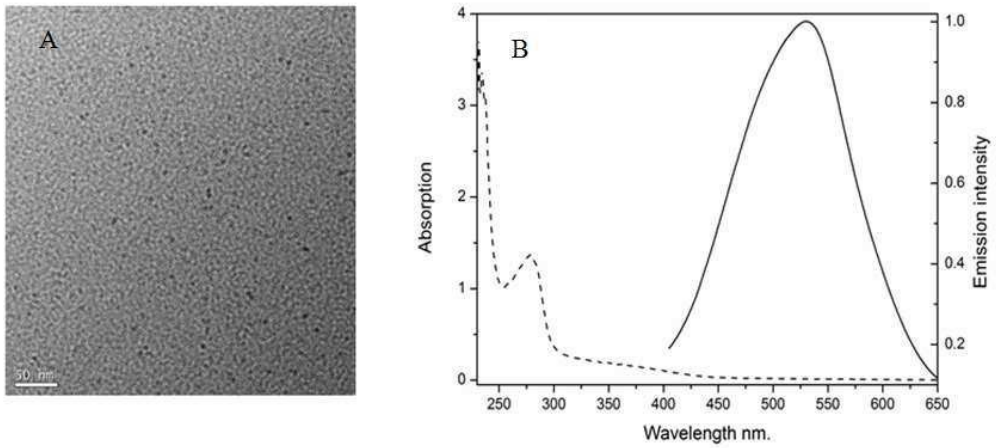


Fig. 1(A) TEM image of BSA-CdS QDs. **(B)** The UV-vis absorption (Dash line) and fluorescence emission spectra (Solid line) of BSA-CdS QDs.

The FT-IR spectra of the CdS crystals with and without BSA as stabilizers were compared to confirm the coordination of the BSA on the surface of the CdS QDs. As shown in the Figure S2 curve b, the majority of BSA functional groups could be clearly found through the amide I band (1657 cm^{-1}), amide II (1540 cm^{-1}) band and amide III (1400-1200 cm^{-1}) for –CONH group, which were the characteristic peak of BSA.[26,27] The disappearance of peaks around 2590–2550 cm^{-1}, which is actually corresponding to the S-H bond, supports the formation of Cd-S bonds on the QDs surface. In addition, peaks observed at 656 cm^{-1} indicates the presence of Cd-S bonds.[24] And these characteristic peaks were not observed in the FT-IR spectra of uncapped CdS crystals (Figure S2 curve a) which indicated the successful capping of BSA on the surface of the CdS QDs.

3.2 The optimization

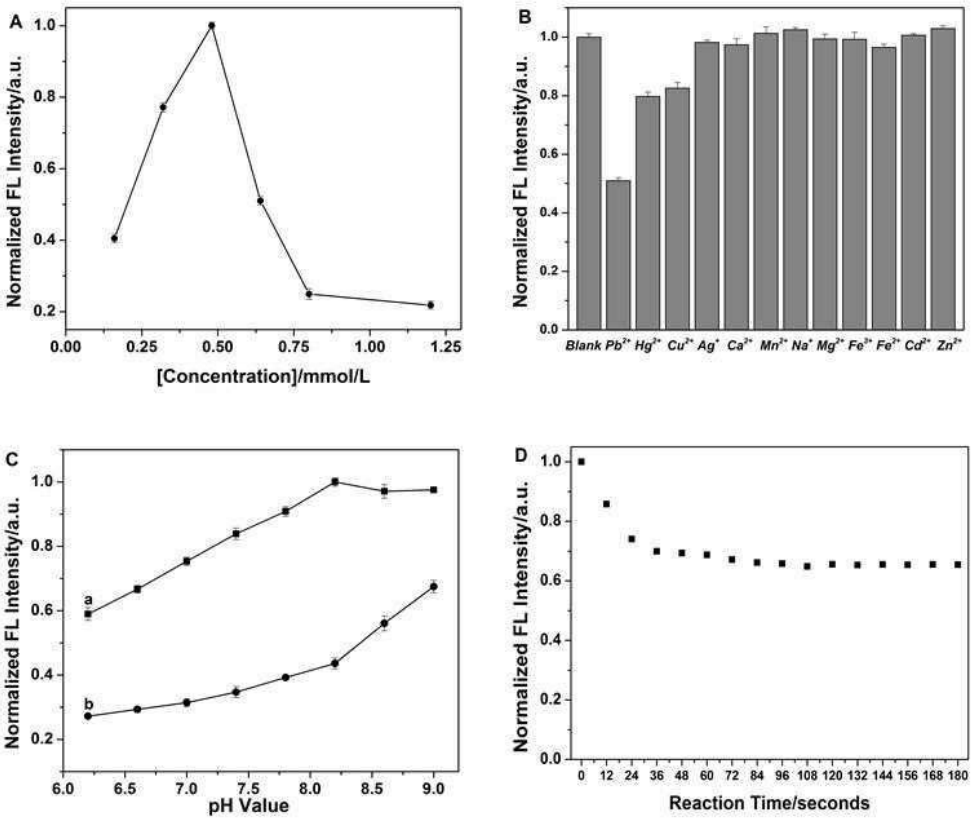


Fig. 2(A) The FL intensity of BSA-CdS QDs with different BSA concentrations (0.24, 0.36, 0.48, 0.64, 0.80, 1.20 mmol/L). **(B)** The quenching effect of 10 μmol/L Pb^{2+} or 50 μmol/L Hg^{2+}, Cu^{2+}, Ag^{+}, Ca^{2+}, Mn^{2+}, Na^{+}, Mg^{2+}, Fe^{3+}, Fe^{2+}, Cd^{2+} and Zn^{2+} on the fluorescence of BSA-CdS QDs. **(C)** Fluorescence intensity of BSA-CdS QDs assay system without Pb^{2+} (curve a) and with 10 μmol/L Pb^{2+} (curve b) in different pH environments (pH 6.2-9.0). **(D)** The quenching effect of Pb^{2+} on the fluorescence of BSA-CdS QDs at different incubation time.

Firstly, we studied the effect of the concentrations of BSA on the FL intensity of BSA-CdS QDs. As shown in Fig. 2(A), the FL intensity of BSA-CdS QDs increased dramatically with the increase of the concentration of BSA in the range from 0.24 to 0.48 mmol/L and decreased rapidly when the concentrations of BSA was higher than 0.48 mmol/L. The results indicated that the optimal concentration of BSA used for BSA-CdS QDs was 0.48 mmol/L.

To generate a sensitive and stable nanosensor with a low detection limit for sulfide, it is significant to choose the suitable material in the sensor fabrication process. So we investigated the quenching ability to the BSA-CdS QDs by several commonly mental ions including Pb^{2+}, Hg^{2+},

Cu^{2+}, Ag^{+}, Ca^{2+}, Mn^{2+}, Na^{+}, Mg^{2+}, Fe^{3+}, Fe^{2+}, Cd^{2+} and Zn^{2+} . The FL intensity of BSA-CdS QDs after addition of 10 μmol/L Pb^{2+} or 50 μmol/L other metal ions were shown in Fig. 2(B). The results demonstrated that Pb^{2+} could cause the biggest fluorescence quenching of the BSA-CdS QDs. Compared with Pb^{2+}, Hg^{2+} and Cu^{2+} showed a relatively low FL quenching ability. Though Cu^{2+} was always used for fabricating the sensor for sulfide, the Cu^{2+}-based sensor for S^{2-} recognition would be seriously interfered with the cyanide.[28, 29] Little change is observed when the BSA-CdS QDs was mixed with other metal ions (Ag^{+}, Ca^{2+}, Mn^{2+}, Na^{+}, Mg^{2+}, Fe^{3+}, Fe^{2+}, Cd^{2+} and Zn^{2+}) even with a higher concentration (50μmol/L) than Pb^{2+} (10μmol/L), indicating the approach offers excellent selectivity towards Pb^{2+} ions. Therefore, Pb^{2+} was selected to fabricate the sulfide sensor.

In this work, the effect of the solution pH on the fluorescence intensity of the BSA-CdS QDs and Pb^{2+}/BSA-CdS QDs was investigated. The BSA, the stabilizer of CdS QDs in this study, had a pI equal to 4.8. Therefore, BSA-CdS QDs was electronegative when the pH value higher than 4.8, which could enhance the electrostatic interaction between BSA and Pb^{2+}. As shown in Figure 2(C), it could be seen that the FL intensity of BSA-CdS QDs increased with the increase of the pH value in the range from 6.2 to 8.2 and kept a relatively stable when the pH value was higher than 8.2. The FL intensity of Pb^{2+}/BSA-CdS QDs increased slowly when the pH value increased from 6.2 to 9.0. The quenching ability of Pb^{2+} to BSA-CdS QDs reached the maximum value at pH 8.2. Therefore, pH value 8.2 was adopted in the further experiments.

The effect of incubation time on the fluorescence intensity of BSA-CdS QDs in the presence of 7.5 μmol/L Pb^{2+} was studied. The result in Fig. 2(D) showed that the quenching effect of Pb^{2+} on the fluorescence of BSA-CdS QDs was completed within 80 s and keep almost constant until 180 s. To ensure the completeness of fluorescence quenching of BSA-CdS QDs, we chose the 120s as the optimum incubation time.

3.3 The quenching effect of Pb^{2+} on the fluorescence of BSA-CdS QDs

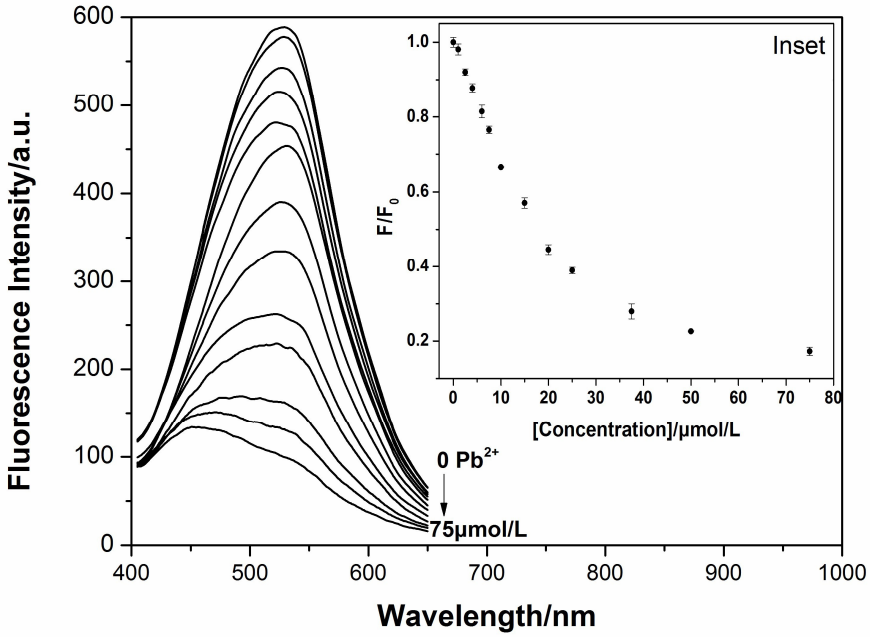


Fig. 3 The fluorescence spectra of BSA-CdS QDs in the presence of different concentrations of Pb^{2+}. The concentrations of Pb^{2+} is 0, 1, 2.5, 4, 6, 7.5, 10, 15, 20, 25, 37.5, 50 and 75 μmol/L, respectively. The inset showed the relationship between F/F_0 and the concentration of Pb^{2+}. F and F_0 were the fluorescence intensity of BSA-CdS QDs in the presence and absence of Pb^{2+}, respectively.

In this work, we studied the quenching effect of Pb^{2+} on the fluorescence of BSA-CdS QDs. As shown in Fig. 3, after the addition of Pb^{2+} to the BSA-CdS QDs system, the FL intensity of BSA-CdS QDs at 529 nm was gradually decreased with the increasing concentration of Pb^{2+}, which was due to a charge transfer process between Pb^{2+} and BSA-CdS QDs. Also, a blue shift was observed when the Pb^{2+} concentration was higher than 20 μmol/L, which was a consequence of the change of quantum confinement of the QDs.[30, 31] The Inset in Fig. 3 showed that the relative fluorescence intensity F/F_0 (F and F_0 were the fluorescence intensity of BSA-CdS QDs in the presence and absence of Pb^{2+}, respectively) and the concentration of Pb^{2+} exhibited a linear relationship in the range of 1 - 20μmol/L. We chose 15 μmol/L Pb^{2+} to fabricate the nanosensor for sulfide anions detection.

3.4 Fluorescence detection of sulfide anions

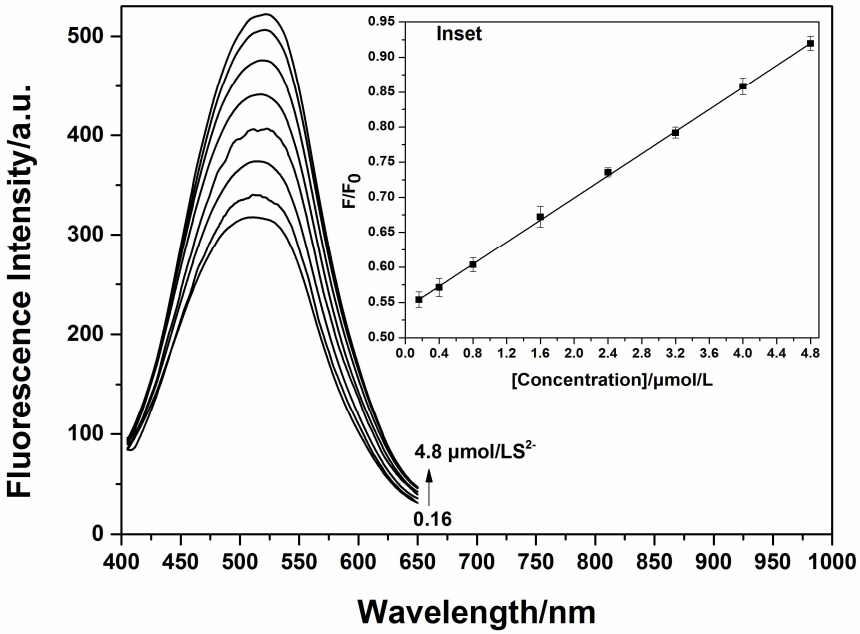


Fig. 4 The fluorescence spectra of BSA-CdS QDs/Pb^{2+} system in the presence of different concentrations of S^{2-}. The concentrations of S^{2-} is 0.16, 0.4, 0.8, 1.6, 2.4, 3.2, 4.0 and 4.8 μmol/L, respectively. The concentrations of Pb^{2+} was 15 μmol/L. The inset showed the relationship between F/F_0 and the concentration of S^{2-} (from 0.16 to 4.8 μmol/L). F_0 and F were the FL intensity of BSA-CdS QDs and Pb^{2+}/BSA-CdS QDs system after the addition of S^{2-}, respectively.

It is well-known that Pb^{2+} can coordinate with sulfide anions to form the stable species. As the stability constant of the PbS formed by S^{2-} and Pb^{2+} is larger than that of the complex of Pb^{2+} and BSA-CdS QDs, thus the pb^{2+}/BSA-CdS system could give some response to the target S^{2-} anions. S^{2-} anions can snatch the pb^{2+} from the BSA-CdS QDs to form more stable PbS and restore the fluorescence of BSA-CdS QDs to "turn on" state. Fig. 4 shows the evolution of fluorescence spectra of Pb^{2+}/BSA-CdS QDs system with increasing S^{2-} concentration under the optimum experimental conditions. It could be seen that the FL intensity of Pb^{2+}/BSA-CdS system obviously restored when S^{2-} concentration increased from 0 to 6.4 μmol/L. Furthermore, Inset in Fig. 4 showed that there was a good linear relationship between the relative fluorescence intensity ratio F/F_0 and the S^{2-} concentration in the range from 0.16 μmol/L to 4.8 μmol/L. The regression

equation is

$$F/F_0 = 0.54175+0.07906[S^{2-}], \mu mol/L$$

The corresponding regression coefficient (R^2) is 0.999, and the detection limit for S^{2-} is 0.05 μmol/L. Some analytical parameters in other methods for the detection of S^{2-} were listed in Table S1.[32-36] Compared with those reports about S^{2-} assay, our present method offered a lower detection limit. The result indicated that the proposed Pb^{2+}/BSA-CdS system was more sensitive for S^{2-} detection.

3.5 Interference study

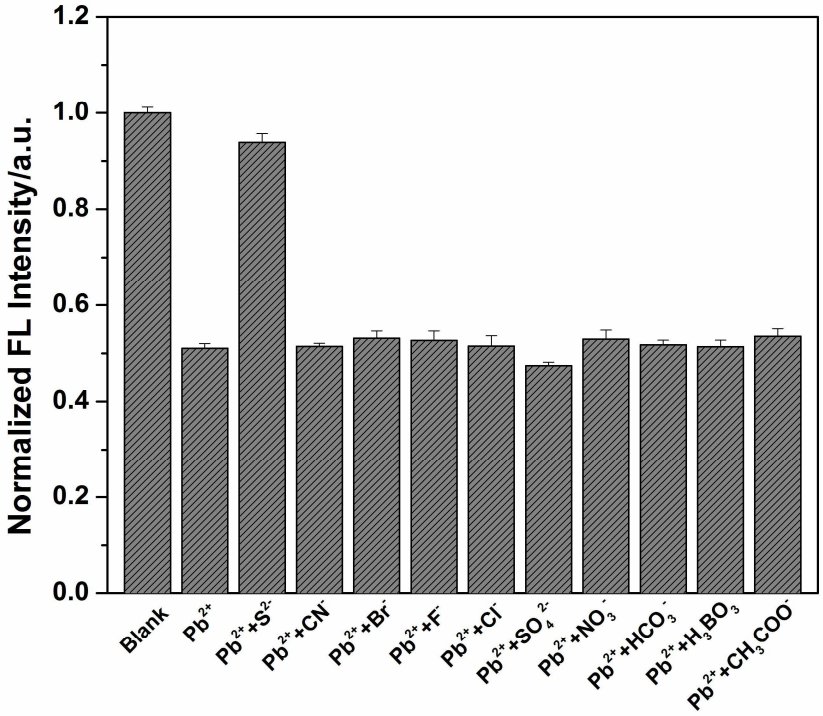


Fig. 5 Fluorescence restored behavior of 50μL BSA-CdS QDs in the presence of 15μmol/L Pb^{2+} and 5 μmol/L S^{2-} or 100 μmol/L potential coexisting anions. Bars: (1) BSA-CdS QDs only; (2) Pb^{2+}; (3) Pb^{2+}+S^{2-}; (4) Pb^{2+}+CN^-; (5) Pb^{2+}+Br^-; (6) Pb^{2+}+F^-; (7) Pb^{2+}+Cl^-; (8) Pb^{2+}+SO_4^{2-}; (9) Pb^{2+}+NO_3^-; (10) Pb^{2+}+HCO_3^-; (11) Pb^{2+}+H_3BO_3; (12) Pb^{2+}+CH_3COO^-. Reaction condition: 10 mmol/ L Tris-HCl buffer solution (pH 8.2) at 25℃.

Selectivity is a very important parameter to evaluate the performance of a new sensor, a highly

selective response to the target over other potentially competing species is necessary. Therefore, we further evaluated the selectivity of our nanosensor with various coexistence anions added. In order to investigate the influence of different coexisting anions on the fluorescence intensity of Pb^{2+}/BSA-CdS, a series of 100 μmol/L anions including CN^-, Br^-. F^-, Cl^-, NO_3^-, SO_4^{2-}, HCO_3^-, H_3BO_3 and CH_3COO^- were introduced to Pb^{2+}/BSA-CdS system. As shown in Fig. 5, the fluorescence of BSA-CdS QDs was quenched after the addition of Pb^{2+}. Only S^{2-} had a highly specific response to Pb^{2+}/BSA-CdS complex and the fluorescence of CdS QDs could be effectively restored. The other anions had little ability to recover the FL intensity of BSA-CdS QDs quenched by Pb^{2+} even with a 20 times higher concentration than that of sulfide. The results showed that this sulfide detection system could provide well ability in resisting interference.

3.6 Analytical applications

To further investigate the practical applications of this method, the detection of sulfide in lake water was carried out. The classical methylene blue (MB) colorimetric method, a standard method for hydrogen sulfide determination in naturalwater, was used as a contrast method to detect sulfide in lake water samples.[37, 38] The average recovery test was made by using the standard addition method, and the results were listed in Table S2. From Table S2, it could be seen that the results obtained by the proposed fluorescence method are in good agreement with those obtained by the conventional method. The RSD was lower than 3.7%, and the average recoveries of sulfide in the real samples was in the range of 100–104%. All the obtained results indicated that this method has potential in environmental applications for sulfide detection.

4. Conclusion

In summary, a novel nanosensor, Pb^{2+}/BSA-CdS complex, had been designed for the recognition and detection of sulfide. The fluorescent BSA-CdS QDs could be quenched by Pb^{2+} due to the charge transfer between BSA-CdS QDs and Pb^{2+}. Subsequent addition of S^{2-} to Pb^{2+}/BSA-CdS

solution lead to the fluorescence recovery of BSA-CdS QDs through forming the stable PbS compound. It constituted a "turn off-on" type fluorescence sensing system. Compared with the literatures about S^{2-} assay, our present method offered a fast and convenient analytical method by using CdS QDs. This method provides an alternative for the sensitive and selective detection of sulfide.

Acknowledgements

This work was financially supported by the National Natural Science Foundation of China (No. 21075050, No. 21275063) and the science and technology development project of Jilin province, China (No. 20110334).

References

1 X. F. Yang, L. Wang, H. Xu, M. Zhao, *Analytica Chimica Acta*, 2009, 1, 91-95.

2 C. Kar, G. Das, *Journal of Photochemistry and Photobiology a-Chemistry*, 2013, 251, 128-133.

3 X. Lou, H. Mu, R. Gong, E. Fu, J. Qin, Z. Li, *Analyst*, 2011, 4, 684-687.

4 L. Tang, X. Dai, M. Cai, J. Zhao, P. Zhou, Z. Huang, *Spectrochimica Acta Part a-Molecular and Biomolecular Spectroscopy*, 2014, 122, 656-660.

5 B. Sen, M. Mukherjee, S. Pal, K. Dhara, S. K. Mandal, A. R. Khuda-Bukhsh, P. Chattopadhyay, *Rsc Advances*, 2014, 29, 14919-14927.

6 H. Huang, Q. Li, J. Wang, Z. Li, X. F. Yu, P.K. Chu, *Plasmonics*, 2014, 1, 11-16.

7 F. Zheng, M. Wen, F. Zeng, S. Wu, *Sensors and Actuators B-Chemical*, 2013, 188, 1012-1018.

8 R. Zhang, X. Yu, Y. Yin, Z. Ye, G. Wang, J. Yuan, *Analytica Chimica Acta*, 2011, 691, 83-88.

9 Z. Ye, X. An, B. Song, W. Zhang, Z. Dai, J. Yuan, *Dalton Transactions*, 2014, 34, 13055-13060.

10 M. Li, Q. Liang, M. Zheng, C. Fang, S. Peng, M. Zhao, *Dalton Transactions*, 2013, 37, 13509-13515.

11 K. Wang, H. Peng, N. Ni, C. Dai, B. Wang, *Journal of Fluorescence*, 2014, 1, 1-5.

12 N. Adarsh, M. S. Krishnan, D, Ramaiah, *Analytical chemistry*, 2014, 18, 9335-9342.

13 B. Chen, P. Wang, Q. Jin, X. Tang, *Organic & Biomolecular Chemistry*, 2014, 30, 5629-5633.

14 Z. Wu, Y. Feng, B. Geng, J. Liu, X. Tang, *RSC Advances*, 2014, 57, 30398-30401.

15 J. Bae, J. Choi, T. J. Park, S. K. Chang, *Tetrahedron Letters*, 2014, 6, 1171-1174.

16 Q. Huang, X. F. Yang, H. Li, *Dyes and Pigments*, 2013, 3, 871-877.

17 M. A. Ali, S. Srivastava, M. K. Pandey, V. V. Agrawal, R. John, B. D. Malhotra, *Analytical chemistry*, 2014, 3, 1710-1718.

18 L. Saa, J. M. Mato, V. Pavlov, *Anal Chem*, 2012, 21, 8961-8965.

19 M. Vazquez-Gonzalez, C. Carrillo-Carrion, *Journal of biomedical optics*, 2014, 10, 101503-101503.

20 A. H. Gore, S. B. Vatre, P. V. Anbhule, S. H. Han, S. R. Patil, G. B. Kolekar, *Analyst*, 2013, 5, 1329-1333.

21 H. R. Rajabi, M. Shamsipur, A. A Khosravi, O. Khani, M. H. Yousefi, *Spectrochimica Acta Part a-Molecular and Biomolecular Spectroscopy*, 2013, 107, 256-262.

22 H. Matsumoto, T. Sakata, H. Mori, H. Yoneyama, *The Journal of Physical Chemistry*, 1996, 32, 13781-13785.

23 G. Garai-Ibabe, L. Saa, V. Pavlov, *Analytical chemistry*, 2013, 11, 5542-5546.

24 W. Tedsana, T. Tuntulani, W. Ngeontae, *Analytica Chimica Acta*, 2013, 783, 65-73.

25 S. S. Liji Sobhana, M. Vimala Devi, T. P. Sastry, A. Mandal, *J Nanopart Res*, 2011, 13 1747-1757.

26 S. Liu, F. Shi, L. Chen, X. Su, *Talanta*, 2013, 116, 870-875.

27 Y. Huang, Y. Luo, W. Zheng, T. Chen, *Acs Applied Materials & Interfaces*, 2014, 21, 19217-19218.

28 Y. Wang, H. Sun, L. Hou, Z. Shang, Z. Dong, W. Jin, *Analytical Methods*. 2013, 20, 5493-5500.

29 X. Lou, H. Mu, R. Gong, E. Fu, J. Qin, Z. Li, *Analyst* , 2011, 4, 684-687.

30 B. B. Campos, M. Algarra, B. Alonso, C. M. Casado,J. C. G. Esteves da Silva, *Analyst*, 2009, 12, 2447-2452.

31 L. Zhang, X. Lou, Y. Yu , J. Qin, Z. Li, *Macromolecules*, 2011, 13, 5186-5193.

32 W. Zhong, C. Zhang, Q. Gao, H. Li, *Microchimica Acta*, 2011, 176, 101-107.

33 J. Zhang, X. Xu, Y. Yuan, C. Yang, X. Yang, *Acs Applied Materials & Interfaces*, 2011, 8, 2928-2931.

34 B. H. Zhang, F. Y. Wu, Y. M. Wu, X. S. Zhan, *Journal of Fluorescence*, 2010, 1, 243-250.

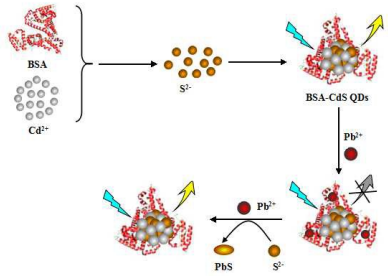
35 L. E. Santos-Figueroa, C. de la Torre, S. El Sayed, F. Sancenon, R. Martinez-Manez, A. M. Costero, S. Gil, M. Parra, *European Journal of Inorganic Chemistry*, 2014, 1, 41-45.

36 J. Liu, J. Chen, Z. Fang, L. Zeng, *Analyst* , 2012, 23, 5502-5505.

37 S. B. Xue, *Science and Technology Innovation Herald*, 2010, 31, 80-80.

38 J. F. da Silveira Petruci, A. A. Cardoso, *Microchemical Journa*l, 2013, 106, 368-372.

Table of Contents



Schematic illustration of the BSA-CdS QDs-based sensing system for sulfide detection