Functionalized Mn^{2+}-Doped Zinc Sulfide Quantum Dots as a Metal Ion Sensor for Industrial Wastes

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L-Cysteine-capped Mn^{2+}-doped ZnS quantum dots are prepared as a fluorescence probe for the detection of heavy metal contaminants, such as As$_2$O$_4{}^{2-}$, Cd^{2+}, CrO$_4{}^{2-}$, Ni^{2+}, Zn^{2+}, Ca^{2+}, Fe^{2+}, Cu^{2+}, Pb^{2+}, Co^{2+}, and Mn^{2+} ions. The results show that the L-cysteine-capped Mn^{2+}-doped ZnS quantum dots exhibit good sensitivity and selectivity for the detection of copper ions. The optimized concentration of L-cysteine-capped Mn^{2+}-doped ZnS quantum dots is determined as 2 mg/mL under pH 7.0 in phosphate buffer. The detection limit for this sensor system is 0.2 ppm with the linear range between 0.5 and 20 ppm. The effect of foreign ions such as Mn^{2+}, Fe^{2+}, Co^{2+}, and Ni^{2+} on the detection of Cu^{2+} solution is also evaluated. The results show that there is no significant difference in the measurements.

1. Introduction

Water wastes, including acid/base and heavy metals, usually cause serious pollution to the environment.[1,2] These contaminants are mainly from factories, agriculture, animal husbandry, and aquaculture. Among them, heavy metal wastes from the electroplating industry,[3] such as Cr, Cd, Ni, Zn, Hg, and Cu, are the major causes of water pollution. Currently, the most common metal ion pollutants are detected by instrumentation such as atomic absorption spectroscopy (AAS), voltammetry, inductively coupled plasma (ICP), potentiometry, and instrumental neutron activation analysis (INAA).[4] Most of these methods are sophisticated, expensive, and time-consuming.

Quantum dots (QDs), which are composed of the II-VI group such as CdSe, CdS, CdTe, and ZnS, have great application potential because of their novel size-dependent electronic and optical properties.[5,6] The advantages of QDs are their narrow, tunable spectrum[7,8] and stability against photobleaching[9–12] compared with organic dyes. QDs modified with different functional groups on the surface could form various QD conjugates, but also provide a new chemistry for application in materials and biomedical

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sciences.[13–18] QDs could be the fluorescent sensors for metal ions when the functional groups can bind selectively to a specific metal ion.[19,20] For instance, L-cysteine-capped CdSe/CdS QDs and 2-mercaptoacetic acid-capped QDs could be a fluorescent probe for copper(II),[18,21] mercaptoacetic acid-capped CdS QDs for mercury(II),[22] and thioglycolic acid-capped CdTe QDs for lead(II).[23] Therefore, functionalized QDs have been developed for metal ion sensors on the basis of the enhancement or quench effect on their fluorescence intensity.

However, there is a drawback that almost all the QDs above are toxic to the environment. ZnS QDs have the advantage of less toxicity than others.[24] In this study, L-cysteine-capped ZnS QDs are prepared and characterized, and then applied as a fluorescent sensor to detect the concentration of various metal ions. The optimized pH values and concentration of QDs are examined for the detection of various ions. The results show that L-cysteine-capped ZnS QDs exhibit good sensitivity and selectivity for the detection of copper ions. The detection limit of L-cysteine-capped ZnS QD solution (2 mg/mL) for Cu^{2+} is 0.2 ppm with the linear detection range between 0.5 and 20 ppm at pH 7. The results show a promising method of detecting the copper content in industrial waste, which is regulated at 3 ppm.

2.   Experiments

2.1   *Synthesis of L-cysteine-capped Mn^{2+}-doped ZnS QDs*
L-Cysteine-capped Mn^{2+}-doped ZnS QDs are prepared as described elsewhere.[25] 16 mmol L-cysteine and 64 mmol Tris are mixed and dissolved in 50 mL of water. 10 mL of zinc acetate acid solution (0.8 M containing 4 mM HCl) and 10 mL of manganese acetate solution (16 mM) are added dropwise into L-cysteine-Tris buffer solution. The L-cysteine-Zn solution is mixed with 20 mL of Na_2S solution (0.8 M) slowly. The reaction is maintained at 98 ºC for 24 h. The final solution is precipitated with 300 mL of ethanol and dried in vacuum.

2.2   *Measurement and instruments*
Absorption spectra are measured using UV/Vis spectroscopy U-3000 (Hitachi). Fluorescent spectra are measured using FP-6300 (Jasco). Powder X-ray diffraction (XRD) is performed using XRD-7000 (Shimadzu). The detection of quench effects is performed under room temperature using an ELISA reader (SpectraMax M2e, molecular devices). The excitation of L-cysteine-capped Mn^{2+}-doped ZnS QDs is 290 nm and the detection of the emission is at 590 nm. QDs and metal ion solutions were prepared in either phosphate buffer or Tris buffer solution. 200 μL of each solution is added into a 96-well plate for measurement.

3.   Results and Discussion

3.1   *Characterization of L-cysteine-capped Mn^{2+}-doped ZnS QDs*
Figure 1 shows the absorption and fluorescence spectra of L-cysteine-capped Mn^{2+}-doped ZnS QDs (The pure QD fluorescence is denoted as I0 in this study). They display an absorption edge near 290 nm with an emission maximum near 590 nm. The XRD
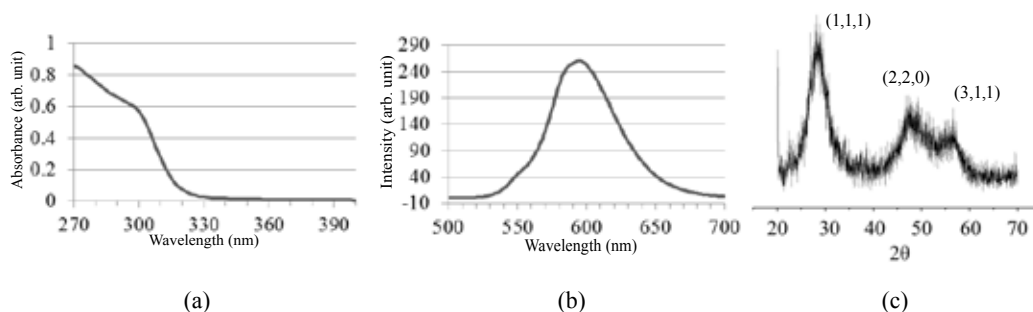
Fig. 1.   (a) Absorbance spectrum and (b) fluorescent spectrum of L-cysteine-capped Mn^{2+}-doped ZnS QDs. (c) XRD pattern for L-cysteine-capped Mn^{2+}-doped ZnS QDs.

patterns of the L-cysteine-capped Mn^{2+}-doped ZnS QDs have three characteristic peaks corresponding to the (1,1,1), (2,2,0), and (3,1,1) diffraction peaks of the cubic zinc blende phase. The average diameter for cysteine-capped Mn^{2+}-doped ZnS QD is about 5.1 nm as estimated using Scherrer's equation.

3.2   *Optimization of detection conditions*

Figure 2(a) shows the fluorescence intensity of L-cysteine-capped Mn^{2+}-doped ZnS QD solutions with different concentrations. The intensity is saturated when the concentration is over 5 mg/mL owing to their self-quenching effect. The effect of pH is revealed by the fact that the fluorescence intensity of the system is optimized at pH 7, as shown in Fig. 2(b). At pH 8, the fluorescence intensity is higher in the phosphate buffer solution than in the Tris buffer solution. Therefore, the optimum fluorescene probe system for detection is with 2 mg/mL L-cysteine-capped Mn^{2+}-doped ZnS QD at pH 7 in phosphate buffer solution.

3.3   *Effect of different metal ions on luminescence intensity*

The L-cysteine-capped Mn^{2+}-doped ZnS QD solution would have a different fluorescence quenching effect when it captures metal ions at different pHs, as shown in Fig. 3(a). The results show that the quenching effect of Cu^{2+} is significantly different from those of Co^{2+}, Mn^{2+}, and Pb^{2+} from pH 5 and 9 environments. It also shows that the fluorescence quenching effects are enhanced above pH 6, and the solubility of the L-cysteine-capped Mn^{2+}-doped ZnS QD is decreased at pH 5. We conclude that the detection would have the best selectivity for Cu^{2+} ion at pH 7-9.

Selectivity on different metal ions is determined by measuring the quenching ratio on the basis of the fluorescence intensity of the L-cysteine-capped Mn^{2+}-doped ZnS QD solution. Figure 3(b) demonstrates the quenching ratio of different metal ions. It shows that the detection by the L-cysteine-capped Mn^{2+}-doped ZnS QDs is more sensitive to Cu^{2+} than to other metal ions. The quenching ratio is substantial for Cu^{2+}, but much less for Pb^{2+}, Co^{2+}, and Mn^{2+}, and almost none for $As_2O_4^{2-}$, Cd^{2+}, CrO_4^{2-}, Ni^{2+}, Zn^{2+}, Ca^{2+}, and Fe^{2+}. It is concluded that detection by the L-cysteine-capped Mn^{2+}-doped ZnS QDs has a marked sensitivity and selectivity to Cu^{2+}.

(a)   (b)
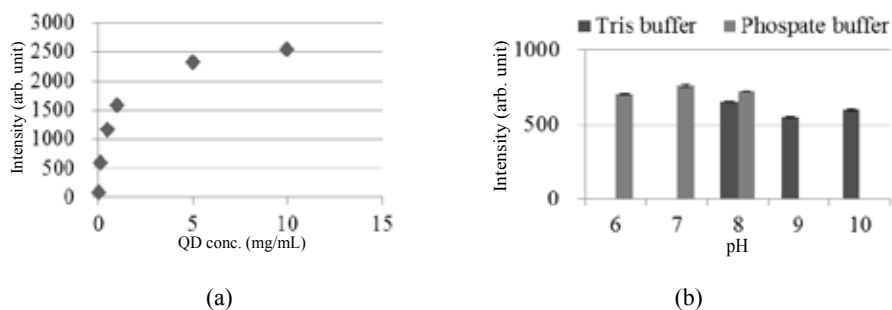
Fig. 2. (a) Fluorescence intensity of L-cysteine-capped Mn^{2+}-doped ZnS QD solutions with different concentrations. (b) Fluorescence intensity of L-cysteine-capped Mn^{2+}-doped ZnS QD

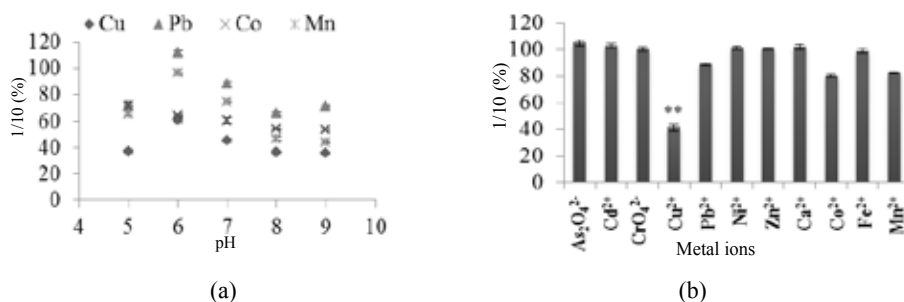(a)   (b)

Fig. 3. (a) Effects of pH and buffers on quenching effect. The concentration is 12 ppm for metal ions. (b) Effect of different cations on the fluorescence intensity of ZnS QDs.

Figure 4(a) shows the quenching ratio of various concentrations of Cu(II) solutions (0.1 to 4 ppm) vs. QD solutions (0.1 to 2 mg/mL). It shows that the linear range of sensing is between 0.5 to 1.5 ppm with the detection limit of 0.1 ppm when a 0.5 mg/mL L-cysteine-capped Mn^{2+}-doped ZnS QD solution is used. For experimental groups of L-cysteine-capped Mn^{2+}-doped ZnS QD solutions of 0.1 and 2 mg/mL, the detection limits are 0.05 and 0.20 ppm, respectively. The experiments are also extended to higher concentrations as shown in Fig. 4(b). We conclude that the L-cysteine-capped Mn^{2+}-doped ZnS QD solution of 0.1 mg/mL has better sensitivity and resolution but a small detection range. To detect a higher concentration of Cu(II), a higher concentration of L-cysteine-capped Mn^{2+}-doped ZnS QDs is required, which reduced the sensitivity of the quenching effect. The optimum fluorescence intensity is obtained at the L-cysteine-capped Mn^{2+}-doped ZnS QD concentration of 2 mg/mL and pH 7.0 in phosphate buffer. The detection limit for this sensor system is 0.2 ppm with the linear range between 0.5 and 20 ppm.

The L-cysteine-capped ZnS QD solution (2 mg/mL) is used for the detection of 12 ppm copper ion in the presence of foreign ions of various concentrations. The effect on the quenching ratio owing to various concentrations of foreign ions, Mn^{2+}, Fe^{2+}, Co^{2+}, and Ni^{2+}, is shown in Fig. 4(c). There is no significant difference in the quenching effect
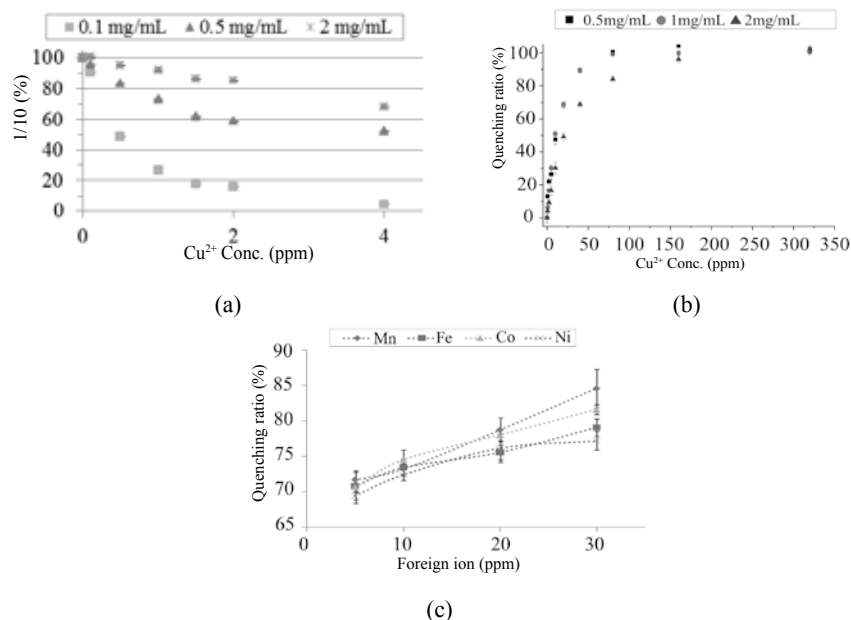
Fig. 4. (a) Effects of Cu(II) concentration vs. three concentrations of ZnS QDs. (b) Effects of Cu(II) concentration vs. three concentrations of ZnS QDs. (c) Foreign ion effect on Cu^{2+} detection by ZnS QDs.

even if the concentrations of the foreign ions are within 10 ppm, which is in agreement with the results shown in Fig. 4(c).

4.   Conclusions

Functionalized L-cysteine-capped Mn^{2+}-doped ZnS QDs have been developed as a novel fluorescence probe for the detection of metal ions based on the fluorescence quenching effect. The preparation of L-cysteine-capped Mn^{2+}-doped ZnS QDs is not only easy and inexpensive, but the application of this fluorescence probe is also very simple. The results show that L-cysteine-capped Mn^{2+}-doped ZnS QDs exhibit good sensitivity and selectivity for the detection of Cu^{2+} ions, which present a great potential for sensing Cu^{2+} ions in wastewater from the electroplating industry. In fact, the detection of Cu^{2+} ions might also be interfered with by the existence of Hg^{2+} ions. However, the concentration of Cu^{2+} is much larger than that of Hg^{2+} in the wastewater so that the interference in the detection can usually be ignored. The degree of interference could also be overcome by the selection of pH values and buffer solutions.

The detection limit represents the sensitivity of the sensor system, which depends on the concentration of the L-cysteine-capped Mn^{2+}-doped ZnS QD solutions used, since it is measured using the fluorescence quenching ratio. We conclude that a higher concentration of L-cysteine-capped Mn^{2+}-doped ZnS QD solution can have a wider linear range for the detection of metal ions but a lower sensitivity. On the other hand, a lower concentration of the L-cysteine-capped Mn^{2+}-doped ZnS QD solution can result in a

higher sensitivity but a narrower range. The optimum fluorescence intensity is obtained at the L-cysteine-capped Mn^{2+}-doped ZnS QD concentration of 2 mg/mL and pH 7.0 in phosphate buffer. The detection limit for this sensor system is 0.2 ppm with the linear range between 0.5 and 20 ppm. The results show a promising method of detecting the copper content in industrial waste, which is regulated at 3 ppm.

Acknowledgements

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