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Application of Functionalized ZnSe Nanoparticles to Determinate Heavy Metal Ions

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Abstract In this paper, ZnSe nanoparticles, which were modified with mercaptoacetic acid (MAA), worked as novel fluorescence sensors for the quantitative determination of copper(II) and nickel(II). Under the optimal conditions, the fluorescence intensities of functionalized ZnSe nanoparticles were quenched by the addtion of copper(II) or nickel(II) ions, there were linear relationships between the relative fluorescence intensity ($logF_0/F$) and the concentration in the range of 140–2,000 μg/L for copper(II) (R=0.9973) and 30–1,000 μg/L for nickel(II) (R=0.9992), the limits of detection were 50 μg/L and 5 μg/L, respectively.

Keywords Spectrofluorimetric detection · ZnSe nanoparticles · Copper(II) · Nickel(II)

Introduction

Heavy metal ions are matter of pollution in marine, lake and groundwater as well as in industrial and even treated effluents, they are also major hazards to the soil-plant system [1, 2]. Meanwhile, they cause serious problems for human health and ecology [3, 4]. Copper is one of the heavy metal ions and the essential elements for many living organisms [5], but it is also toxic at high concentration levels and causes liver damage in infants and some functional handicaps [6]. Nickel is widely used in modern industry, its overexposure in human beings can provoke serious effects including lung, cardiovascular and kidney diseases [7-9]. So the determination of heavy metal ions in the environment and biological samples is of tremendous interest and importance.

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Many methods and techniques have been developed for the determination of heavy metal ions. Including atomic absorption spectrometry (AAS) [10, 11], inductively coupled plasma optical emission spectrometry/mass spectrometry (ICP-OES/MS) [12, 13], electrochemical analysis [14], neutron activation analysis (NAA) [15], X-ray fluorescence spectrometry (XRF) [16] and so on. These methods are widely used, but they require sophisticated and expensive instrument, the procedure used in these methods are requiring long executing times. Compared with these methods, the fluorescence spectroscopy method is used more and more popular by the virtue of simple, fast and high effective.

Some organic fluorescent dyes were popular during the past decades, though some problems existed with them, including narrow excitation bands and broad emission spectra [17]. In recent years, the semiconductor nanoparticles have developed rapidly, which are composed of atoms from groups II–VI or III–V elements in the periodic table, with physical dimensions ranging from 1 to 100 nm [18]. As a result of quantum confinement effect, the semiconductor nanoparticles have unique optical properties [19, 20], they display broad excitation spectra, narrow symmetric and tunable emission spectra, which make them conquer the limits of organic fluorescent dyes. Now they are more and more used as fluorescence probes for detecting biological materials and metal ions.

In this paper, ZnSe nanoparticles were synthesized by hydrothermal synthesis method, they were investigated by transmission electron microscopy (TEM) and X-ray diffraction (XRD), the results showed the shape of these ZnSe nanparticles is regular, monodisperse, and the average diameter is about 40 nm. In order to be water-soluble, these nanoparticles were modified with mercaptoacetic acid (MAA). Under the optimum conditions, the fluorescence intensities of functionalized ZnSe nanoparticles were quenched by copper(II) or nickel(II), respectively. The two analytes were distinguished and determined according to the different fluorescent emission wavelengths. And the extent of the fluorescence intensity quenchment was proportional to the concentration of the analytes. The use of ZnSe nanoparticles as fluorescence probes leads to a particularly sensitive and quantitative assay for detecting copper(II) and nickel(II).

Experiments

The preparation of nano-ZnSe fluorescence probe

The synthetic procedure of ZnSe nanoparticles was as follows: In a typical procedure, the mixture of 0.7129 g Zn powder (99.95%) and 0.2914 g Se powder (99.95%) was put into a Teflon lined autoclave with 30 mL capacity, and then 20 mL 3 mol/L NaOH solution was added into the autoclave. The autoclave was sealed, maintained at 180°C for 24 h, and cooled to room temperature naturally. At last, the brilliant yellow product of ZnSe solid powder was collected by filtration, washed with distilled water and ethanol, and then dried at 78°C in vacuum.

Under vigorous stirring, the ZnSe nanoparticles reacted with the mercaptoacetic acid (MAA) in the circumstances of buffer solution of phosphate (PBS, pH=7) for 3 h. And then the colloidal solution was sealed lightproofly for one night. Then the functionalized nanoparticles solution was taken into a 500 ml brown jar and was stored in buffer solution at room temperature. The obtained solution was ready for the following experiment.

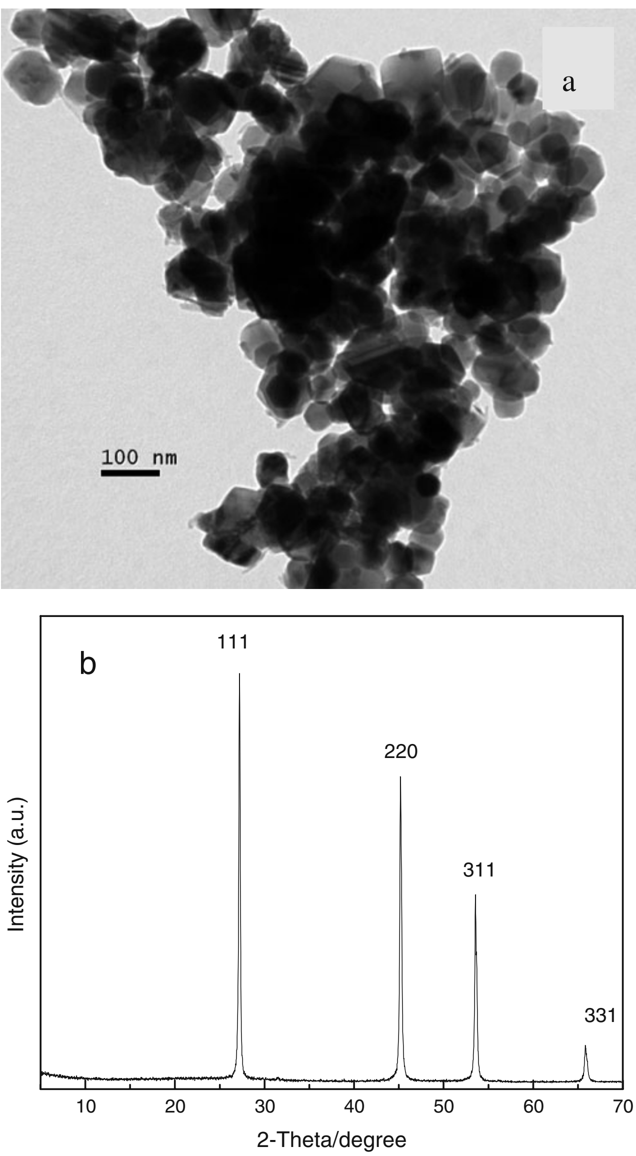

Fig. 1 **a** the TEM image of ZnSe nanoparticles. **b** the XRD of ZnSe nanoparticles

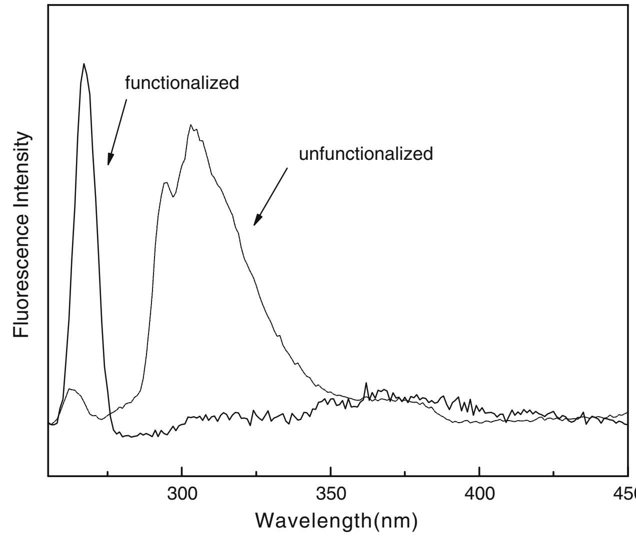

Fig. 2 Fluorescence spectra of pure ZnSe nanoparticles and functionalized ZnSe nanoparticles

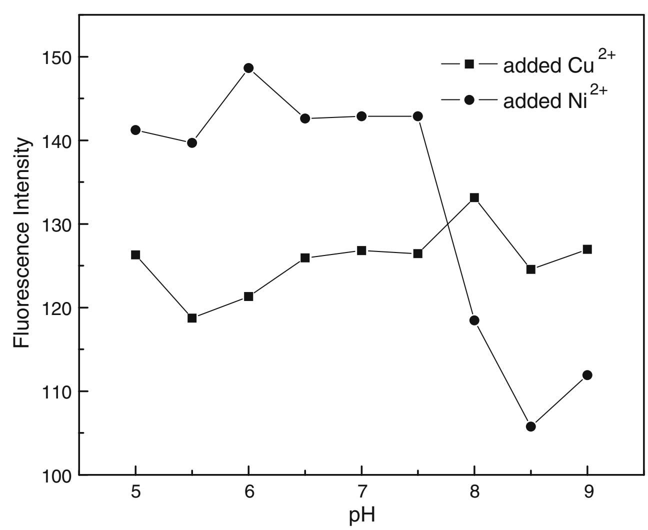

Fig. 3 Effect of pH on the fluorescence intensity of ZnSe–MAA system at presence of Cu^{2+} or Ni^{2+}

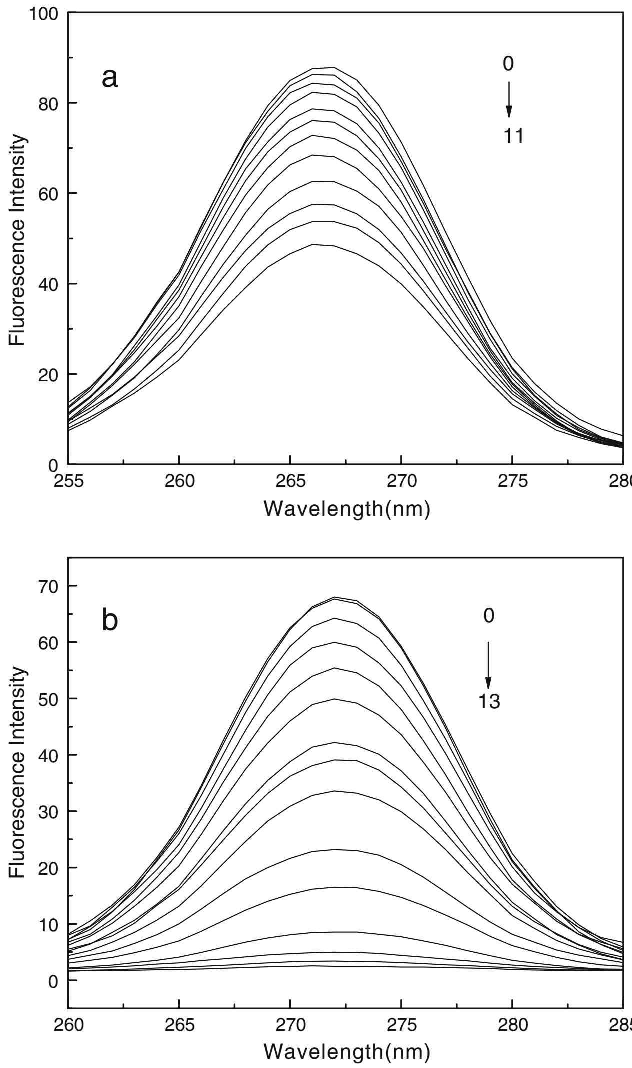

Fig. 4 **a** Fluorescence emission spectra of nano-ZnSe-Cu^{2+} complex (in the presence of different concentrations of Cu^{2+}) obtained in PBS buffer solution pH=5.5 after exciting it at 242 nm. Cu^{2+} (concentration of 0.01 g/L) volume(ml) was (from top to bottom) 0.0, 0.35, 0.40, 0.50, 0.75, 1.00, 1.50, 2.00, 2.50, 3.50, 4.00, 4.50, 5.00). **b** Fluorescence emission spectra of nano-ZnSe-Ni^{2+} complex (in the presence of different concentrations of Ni^{2+}) obtained in PBS buffer solution at pH=8.5 after exciting it at 244 nm. Ni^{2+}(concentration of 0.01 g/L) volume(ml) was (from top to bottom) 0.0, 0.075, 0.10, 0.15, 0.20, 0.25, 0.35, 0.4, 0.5, 0.75, 1.00, 1.50, 2.0, 2.5)

Determination of copper(II) and nickel(II) with functionalized nano-ZnSe fluorescence probe

The functionalized nanoparticles solution was used to detect copper(II) or nickel(II) with the following procedure: 19 mL functionalized nanoparticles solution and a series of known volumes copper(II) or nickel(II) standard solution were added into a series of dry 25 mL brown calibrated flaskes, the solution were diluted to volume with double distilled water, and then the fluorescence emission intensity were measured at 266 and 272 nm for copper(II) and nickel(II), respectively.

Results and discussion

Characterization of ZnSe nanoparticles

The morphology of ZnSe nanoparticles investigated by transmission electron microscopy (TEM) was shown in Fig. 1a. The typical TEM image of ZnSe nanoparticles showed that the shape of these ZnSe nanparticles was regular, monodisperse, and the average diameter was about 40 nm. The XRD pattern (Fig. 1b) revealed that the ZnSe nanoparticles were crystal of cubic sphalerite structure, which was consistent with the JCPDS card number 37–1,463.

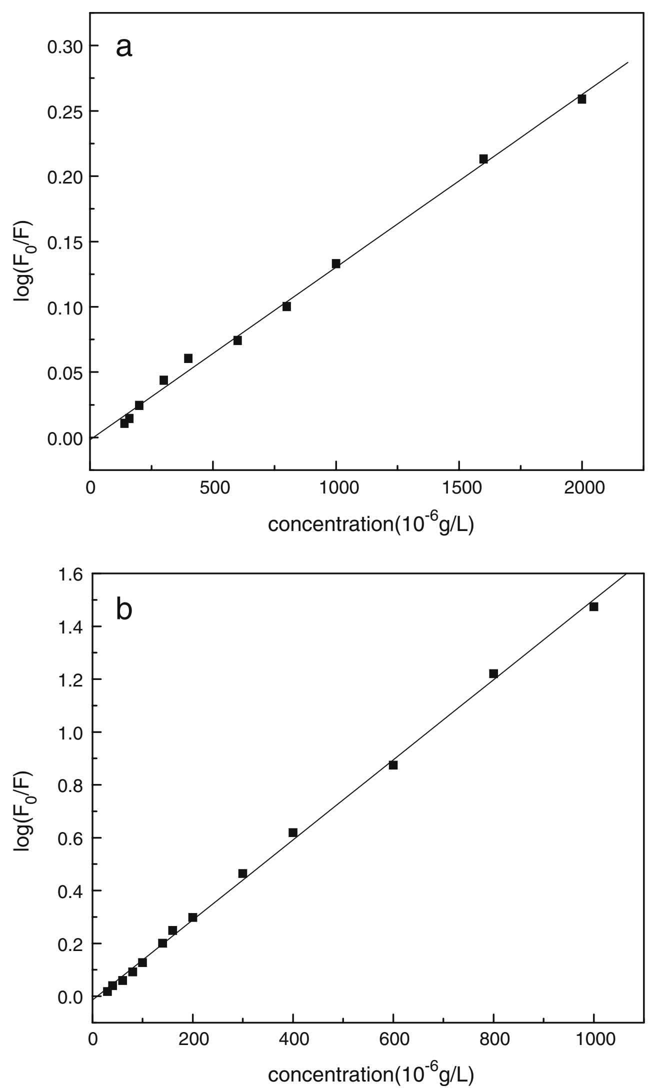

Fig. 5 **a** the straight line equation was found between the relative fluorescence intensity and the concentration of Cu^{2+} in the range of 140–2,000 μg/L. **b** the straight line equation was found between the relative fluorescence intensity and the concentration of Ni^{2+} in the range of 30–1,000 μg/L

Table 1 Test of the interference ions on the fluorescence intensity of functionalized ZnSe nanoparticles at presence of Cu^{2+} and Ni^{2+}

Coexisting substance	Coexisting concentration (10^{-4}g/L)	Change fluorescence intensity at presence of Cu^{2+}%	Change fluorescence intensity at presence of Ni^{2+}%
K^{+}	250	−1.9	−1.2
Na^{+}	250	−2.0	−1.3
Fe^{3+}	50	−2.5	−1.8
Cd^{2+}	50	+4.7	+3.2
Ca^{2+}	250	−1.5	+1.5
Co^{2+}	50	+2.3	−1.3
Mg^{2+}	250	−1.5	−2.0
Zn^{2+}	200	+2.1	+1.6
Al^{3+}	100	+5.0	+3.8
Pb^{2+}	250	−4.3	−4.0
SO_4^{2-}	100	+2.7	+1.0
I^{-}	100	+3.2	+2.5
Cl^{-}	150	+1.8	+2.3
NO_3^{-}	100	+2.2	+3.0

Fluorescence spectra of unfunctionalized ZnSe and functionalized ZnSe nanoparticles

The fluorescence spectrum of unfunctionalized ZnSe nanoparticles and functionalized ZnSe nanoparticles were shown in Fig. 2. It can be seen that the fluorescence of unfunctionalized ZnSe nanoparticles in the range from 290 to 340 nm were completely quenched, at the same time, the peak at 258 nm shifted to 263 nm was dramatically enhanced in intensity after modified with mercaptoacetic acid. Also we can see that the fluorescence spectra of functionalized ZnSe nanoparticles with a peak at 263 nm were narrower and more symmetric. It can be explained that the fluorescence spectra of unfunctionalized ZnSe nanoparticles with a peak at 306 nm was an emission wavelength from extrinsic fluorescence band, and the fluorescence spectra of functionalized ZnSe with a peak at 263 nm was an intrinsic nanocrystal fluorescence.

Factors affecting the determination

The fluorescence emission spectra of many matters are sensitive to their surrounding environment. As shown in Fig. 3 the pH of the solution has a great effect on the fluorescence intensities of the system. It can be seen that the fluorescence intensities of functionalized ZnSe nanoparticles were dramatically quenched at presence of Cu^{2+} at pH=5.5, and greatly quenched at presence of Ni^{2+} at pH=8.5. So the optimal pH of detecting Cu^{2+} and Ni^{2+} were 5.5 and 8.5. To obtain good detecting results, 0.1 mol/L phosphate buffer solution (PBS) was chosen for the further experiments.

At the same time, the reacting time of functionalized ZnSe nanoparticles and Cu^{2+} (or Ni^{2+}) was investigated, through the investigation, the optimal reacting time was 30 min, and then the quenching fluorescence spectra is stable.

Table 2 Results of the analysis of synthetic samples (Cu^{2+})(n=3, P=95%)

Number	Amount (10^{-6}g/L)	Addition of Cu(10^{-6}g/L)	Average recovery%	RSD%
1	400	100	99	1.4
2	500	100	103	3.3
3	700	100	95	2.3

Analytical performance of functionalized ZnSe nanoparticles and the mechanism of reaction

The fluorescence emission spectra of functionalized ZnSe nanoparticles reacting with copper(II) and nickel(II) were recorded in 0.1 mol/L phosphate buffer solution(PBS) at pH=5.5 and pH=8.5, respectively. The results were shown in Fig. 4. The fluorescence intensities were significantly quenched by the additions of Cu^{2+} or Ni^{2+}. These quenching effectes were found to be concentration dependence, so these systems can be used for the development of sensitive and selective method for detecting Cu^{2+} and Ni^{2+} ions.

The quenching effects of Cu^{2+} or Ni^{2+} ions on the fluorescence emission spectra of functionalized ZnSe nanoparticles could be used to develop a new method for the determination of Cu^{2+} or Ni^{2+} ions. In investigation, it was found that the plots of F_0/F versus the concentration of Cu^{2+} or Ni^{2+} ions did not fit conventional linear Stern–Volmer equation. It indicated that both dynamic and static quenching seem to act together, here suggesting a more complex quenching model-the modified Stern–Volmer equation [21-24]. It was shown below, has been proposed for the mechanisms of this system where both static and dynamic quenching act together.

$$\log(F_0/F) = K_{sv}[Q] + C \quad (1)$$

Table 3 Results of the analysis of synthetic samples (Ni^{2+})(n=3, P=95%)

Number	Amount (10^{-6}g/ml)	Addition of Ni (10^{-6}g/ml)	Average recovery%	RSD%
1	160	40	104	1.1
2	200	40	104	1.9
3	300	40	103	2.6

where F_0 and F are the luminescence intensities of functionalized ZnSe nanparticles at absence of Cu^{2+} or Ni^{2+} ions and at presence of Cu^{2+} or Ni^{2+} ions, [Q] is the concentrations of Cu^{2+} or Ni^{2+} ions, and C is constant. In this paper, Ksv was 1.322×10^{-4} for Cu^{2+} and 1.51×10^{-3} for Ni^{2+}, C was −0.00181 for Cu^{2+} and −0.0141 for Ni^{2+}. The calibration plots of log(F_0/F) versus [Q] showed good linear relationships for the concentration of copper(II) in the range from 140 to 2,000 μg/L and for the concentration of nickel(II) in the range of 30–1,000 μg/L (Fig. 5), the correlation coefficient(R) was 0.9973 for copper(II) and 0.9992 for nickel(II). The limits of detection were 50 μg/L for Cu^{2+} and 5 μg/L for Ni^{2+}, respectively.

Interference study

Various coexisting ions have the potential to quench or enhance the fluorescence intensity of functionalized ZnSe nanoparticles. Under the conditions of the recommended assay, Effects of different coexisting ions on the fluorescence intensities of functionalized ZnSe nanoparticles at presence of Cu^{2+} and Ni^{2+} were investigated, respectively. The results showed in Table 1, it can be seen that: the tolerance limits of Zn^{2+}, K^+, Na^+, Mg^{2+}, Ca^{2+} were more than 10^{-2} g/L, and other coexisting ions such as Cd^{2+}, Co^{2+}, Fe^{3+} aslo did not interfere with the determination of Cu^{2+} at 10^{-4} g/L and Ni^{2+} at 10^{-5} g/L level. Consequently, this method is suitable for the analysis of Cu^{2+} and Ni^{2+}.

Analytical applications

In order to test the possibility of practical application, a systematic study of a sequence of detection systems in the determination of copper(II) and nickel(II) was carried out. Which was based on the tolerance to foreign coexisting substances presented in Table 1. The results were shown in Tables 2 and 3. From Tables 2 and 3, it can be seen that the average recovery of Cu^{2+}(Ni^{2+}) was between 99 and 105%. Moreover, the relative standard deviation (R.S.D.) was lower than 4%, which was showing a good precision of this method and met the requirement of microanalysis. Therefore, the developed fluorescence method is applicable to the determination of Cu^{2+}(or Ni^{2+}).

Conclusions

In this paper, ZnSe nanoparticles have been successfully synthesized by hydrothermal synthesis method, and the mercaptoacetic acid was modified on the surface of ZnSe nanoparticles, which made ZnSe nanoparticles water-soluble and biocompatible. Under the optimal conditions, the fluorescence intensities of functionalized ZnSe nanoparticles were quenched at presence of copper(II) or nickel (II). Based on this, they can be used as fluorescence probes in the determination of the concentration of copper(II) or nickel(II). The use of composite nanoparticles as fluorescence probe leads to a particularly inexpensive, simple, and sensitive assay. Future studies of the mechanism in this field will open up the way to the application.

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