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Fluorescent sensing of sulfide ions based on papain-directed gold nanoclusters

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A sensitive and selective method has been developed for the determination of sulfide ions (S^{2-}) based on S^{2-} triggered fluorescence quenching of papain-directed Au nanoclusters. Under the optimized experimental conditions, the proposed method facilitated the determination of S^{2-} in the linear range 0.5–80.0 μM; the limit of detection was 0.38 μM at a signal-to-noise ratio of 3. In addition, the fluorescence intensity decreased selectively in response to S^{2-} relative to other ions. Based on multiple analyses, it is proposed that the fluorescence was quenched through the unique reactions between S^{2-} and the Au atoms/ions, and that the formation of Au_2S induced aggregation of the Au nanoclusters. The practicality of the proposed method for the determination of S^{2-} in natural water samples was verified. The results were in good agreement with those determined by the methylene blue colorimetric method. This new method may broaden the scope of techniques available for the determination of S^{2-}.

1. Introduction

Sulfide, a toxic pollutant, is of major environmental concern as it is produced as a waste product in many manufacturing and industrial processes.[1] Exposure to high levels of sulfide can result in irritation of the mucous membranes, and may lead to unconsciousness and respiratory paralysis.[2] Several techniques are available for the determination of sulfide, including colorimetry,[3–5] spectrometry,[6] electrochemistry,[7,8] chemiluminescence,[9,10] chromatography,[11,12] titration[13] and fluorimetry.[14–17] Fluorescence-based methods have a number of advantages, including high sensitivity and selectivity, easy operability, and low cost. However, the synthesis of fluorescent probes often involves time-consuming organic techniques or chemicals that are harmful to the environment, which strongly limits their practical applications. Therefore it would be useful to develop a facile and environmentally friendly method for the determination of sulfide.

The recent focus on metal nanoclusters with fluorescence properties is driven by their unique attributes, including their outstanding optical characteristics, their convenient preparation, and their non-toxicity. In addition to their use in cell labelling,[18,19] metal nanoclusters have also opened up a promising avenue for the development of fluorescent probes for the determination of various analytes. Metal nanoclusters have been used for the determination of metal ions,[20–26] anions,[27,28] biomolecules,[29–32] and other organic molecules.[33–35] Au nanoclusters (AuNCs) have been studied extensively; fluorescent protein-directed AuNCs are particularly interesting. Because of their simple synthesis, biocompatibility and optical stability over a wide pH range,[36] AuNCs are anticipated to have applications as nanosensors in chemistry, the life sciences and environmental analyses.

Despite much research into methods of monitoring the bisulfide ion (HS^-) or hydrogen sulfide (H_2S) based on the fluorescence of metal nanoclusters, the application of metal nanoclusters to the fluorescent sensing of the sulfide ion (S^{2-}) in aqueous solution remains limited. To the best of our knowledge, highly sensitive and selective methods for the determination of S^{2-} in aqueous media have only been developed using Ag NCs,[37] AuNCs,[38,39] Au/Ag NCs[40,41] and Cu nanoparticles.[42] There is therefore still scope for the development of simple and effective metal nanocluster probes for the determination of S^{2-}.

Inspired by the specific interactions between S^{2-} and Au atoms/ions, we present here a new method for sensing S^{2-} based on the ability of S^{2-} to quench the fluorescence of papain-directed AuNCs[43] (Scheme 1). The experimental results demonstrated the sensitive, concentration-dependent response of the prepared AuNCs to S^{2-} and the good selectivity for S^{2-} compared with other ions. This method was also demonstrated to be appropriate for the determination of S^{2-} in real environmental samples.

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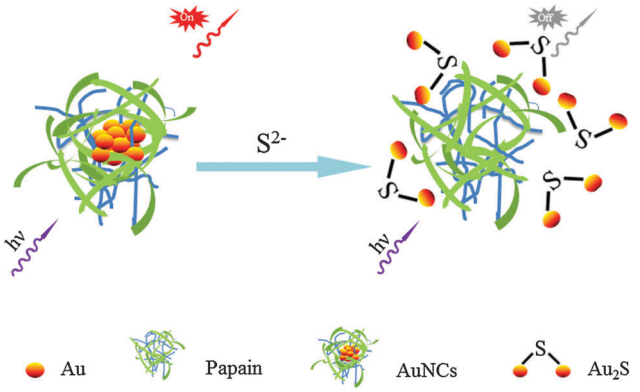

Scheme 1 Schematic illustration of the quenching of the AuNCs induced by S^{2-}.

2. Experimental

2.1. Chemicals and instrumentation

Papain was obtained from Solarbio Co. Ltd (Beijing, China). Chloroauric acid ($HAuCl_4 \cdot 3H_2O$) was purchased from Beijing Chemical Factory (Beijing, China). Na_2CO_3, Na_2SO_4, $NaNO_2$ and other common chemicals were obtained from Sinopharm Chemical Reagent Co. Ltd (Shanghai, China). All the chemicals used in this work were of analytical-reagent grade and were obtained from commercial sources and used directly without additional purification. Deionized water ($\geq$18.2 MΩ) prepared using a Millipore water system was used throughout the experiments. All glassware was thoroughly cleaned with freshly prepared 3 : 1 HCl/HNO_3 (*aqua regia*) and rinsed thoroughly with Mill-Q water prior to use.

All the fluorescence spectra were measured and recorded with a PerkinElmer LS-55 spectrofluorimeter. The high-resolution transmission electron microscopy (HRTEM) images were recorded on a JEOL JEM-3010 transmission electron microscope (Beijing, China). The size distribution of the particles was measured with a Zetasizer 3000Hs laser particle analyser. Absorption spectra were collected on a UV-2250 UV-visible spectrophotometer (Shimadzu, Japan). Fourier transform infrared (FTIR) spectra were recorded using an FTIR spectrophotometer (WQF-410, Beijing, China).

2.2. Synthesis of AuNCs

Papain-directed AuNCs were synthesized according to a previously published method with some modifications.[43] Briefly, 0.5 mL of 2.5 mM $HAuCl_4$ and 0.5 mL of 35 mg mL^{-1} papain were mixed sequentially. The sample mixture was incubated at 37 °C for 5 min. Then 100 μL of 1 M NaOH solution was introduced and the sample solution was further incubated at 37 °C for 6 h. The papain-directed AuNCs were obtained when the colour of the solution changed to brown. The final solution was stored at 4 °C before use.

2.3. Fluorescent determination of S^{2-}

A typical procedure for the determination of S^{2-} was conducted as follows. S^{2-} solutions of different concentrations were obtained by serial dilution of the stock solution. A 100 μL volume of the as-prepared solution of AuNCs was mixed with 100 μL of buffer solution (pH 9). Then 200 μL of S^{2-} solutions of various concentrations were added. After mixing for about 5 min, deionized water was added to bring the final volume to 1 mL and the solution was incubated at 55 °C for 35 min. Finally, the solution was cooled to room temperature for measurement of the fluorescence spectra.

To evaluate the fluorescence selectivity of the papain-directed AuNCs to S^{2-}, various metal ions and other anions were used in the selectivity experiments: Ca^{2+}, Mg^{2+}, K^+, Ba^{2+}, NO_3^-, PO_4^{3-}, SO_4^{2-}, CO_3^{2-}, HCO_3^-, Ac^-, NO_2^-, I^-, Cl^- and Br^- were tested and the responses recorded and analysed.

2.4. Determination of S^{2-} in samples of natural water

Samples of natural water were used to evaluate the feasibility of this method. Samples of river and pond water were separately taken from the Xiang River and Taozi Lake and tap water was collected from the laboratory. All the water samples were filtered through a 0.45 μm Micropore membrane and centrifuged for 10 min at 10 000 rpm before analysis. To determine the feasibility of this method, we also used methylene blue to determine the concentrations of S^{2-} in the samples of natural water.

3. Results and discussion

AuNCs with a red fluorescence emission were synthesized by mixing papain and $HAuCl_4$. As a result of the very low solubility product (K_{sp}) of Au_2S, the obtained AuNCs were used as a probe to determine S^{2-} in aqueous solution.

3.1. Fluorescence response of AuNCs to S^{2-}

The effect of S^{2-} on the fluorescence emission was monitored (Fig. 1). When the AuNCs were excited at 470 nm, the maximum emission peak was observed at 650 nm (curve a). The spectral profile was consistent with that reported previously.[43] When the AuNCs were combined with a 500 μM solution of S^{2-}, the red fluorescence of the AuNCs became very weak and the fluorescent intensity was significantly quenched (curve b).

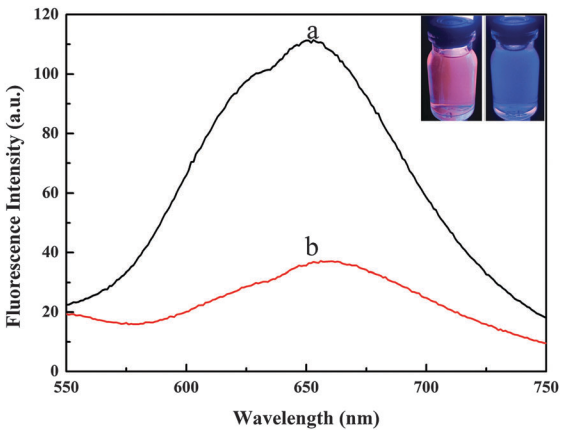

Fig. 1 Fluorescence emission spectra of (a) AuNCs and (b) AuNCs + 500 μM S^{2-} (pH 9, 55 °C, 35 min). Inset: Photographs of the AuNCs in the absence (left) and presence (right) of 500 μM S^{2-} under UV irradiation.

In addition, the colour of the solution changed from red to undetectable under UV irradiation in the presence of S^{2-} (Fig. 1, inset). Hence the papain-directed AuNCs were shown to respond to S^{2-} within a certain concentration range.

3.2. Optimization of the sensing method

The fluorescence response was affected by some key factors, *e.g.* the pH of the reaction solution, the reaction temperature and time. Thus to obtain a better response towards S^{2-}, these parameters were optimized.

3.2.1. pH of the reaction solution. The effect of pH on the reaction of the AuNCs with S^{2-} was evaluated by varying the pH to determine the optimum value. In view of the fact that the AuNCs precipitated in the pH range 3–6,[43] the experiments were carried out by adjusting the pH from 6 to 12. Fig. 2a shows the fluorescence response of the AuNCs in reaction media at various pH values after the addition of S^{2-}. The decrease in fluorescence ($F_0 - F$) gradually became larger below pH 9 and then decreased at pH values above 9 (F and F_0 denote the fluorescence intensity at 650 nm with and without S^{2-}, respectively); the maximum quenching efficiency was obtained when the pH of the solution was 9. The reason for these observations may be related to the isoelectric point of papain (pI = 8.75). S^{2-} does not exist as H_2S in alkaline media, promoting the reaction between S^{2-} and the AuNCs. Therefore pH 9 was chosen as the most suitable pH and was used in further experiments.

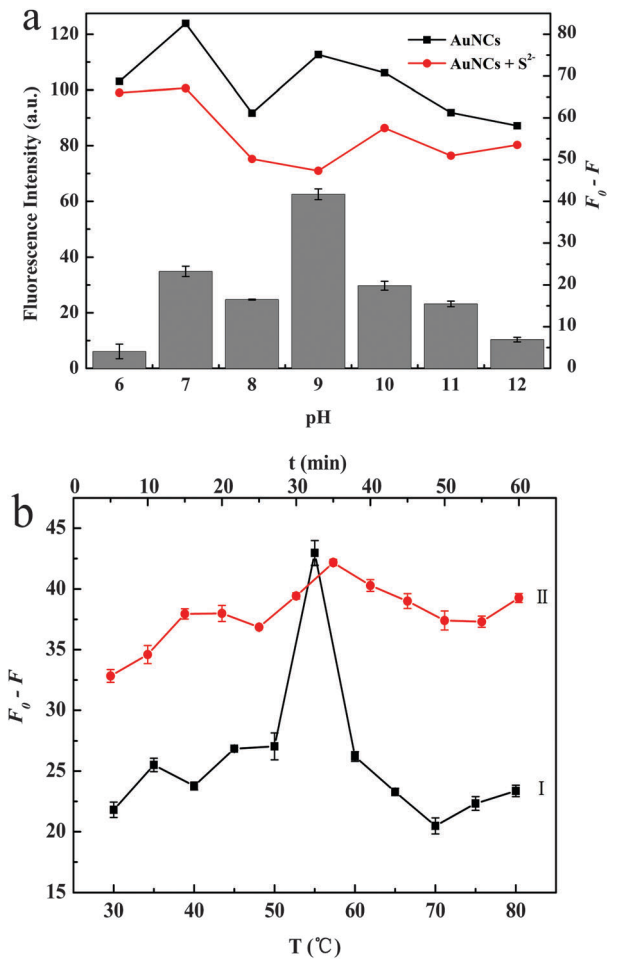

Fig. 2 (a) Effect of pH on the decrease in fluorescence ($F_0 - F$) of the AuNCs (100 μL AuNCs, 50 μM S^{2-}, 55 °C, 35 min). (b) Effect of the incubation temperature on the decrease in fluorescence ($F_0 - F$) of the AuNCs (100 μL AuNCs, 50 μM S^{2-}, pH 9) at (line I) different temperatures for 35 min and (line II) at 55 °C for different times. All data were collected at 650 nm.

3.2.2 Reaction temperature and time. To evaluate the influence of the reaction temperature and time on the detection response, the reaction temperature was varied from 30 to 80 °C in 5 °C increments and the reaction time was varied from 5 to 60 min in 5 min increments for the reaction with 50 μM S^{2-}. Fig. 2b shows that the value of ($F_0 - F$) for the AuNCs initially increased with increasing reaction temperature and the highest value was obtained at 55 °C; this was followed by a decrease in ($F_0 - F$) as the temperature was increased further (line I). With increasing temperature, the number of collisions between the AuNCs and S^{2-} is also increased. However, when the temperature is >55 °C, papain may be degraded and the structure of the AuNCs changes; therefore there were fewer reactions between the AuNCs and S^{2-}. The ($F_0 - F$) value for the AuNCs reached a maximum at a reaction time of 35 min when the reaction temperature was 55 °C (Fig. 2b, line II). Therefore subsequent experiments were carried out at 55 °C for 35 min.

3.3. Sensitivity of the sensing method

The sensitivity of the quantitative determination of S^{2-} was evaluated under the optimum experimental conditions by monitoring the change in the fluorescence of the AuNCs with the addition of various concentrations of S^{2-}. When different concentrations of S^{2-} (0.5, 1.0, 5.0, 10.0, 20.0, 50.0, 80.0, 100.0, 150.0 and 200.0 μM) were added to the solution of AuNCs, the fluorescence emission of the AuNCs varied (Fig. 3a). To quantify the relationship between the fluorescence intensity of the AuNCs and the concentration of S^{2-}, the change in the fluorescence of the AuNCs at 650 nm with increasing concentrations of S^{2-} was evaluated (Fig. 3b). The relationship between the value of ($F_0 - F$) for the AuNCs and the concentration of S^{2-} was linear in the range 0.5–80.0 μM (Fig. 3b, inset) and was described by the linear regression equation ($F_0 - F$) = 0.750c + 0.363, with a correlation coefficient of 0.995, where c was the concentration of S^{2-}. The limit of detection was estimated to be 0.38 μM ($3\sigma/k$, where σ is the standard deviation for the blank solution, n = 10 and k is the slope of the calibration graph). This is much lower than the maximum concentration (15 μM) of S^{2-} permitted in drinking water by the World Health Organization. A red shift in the maximum fluorescence peak was observed with increasing concentrations of S^{2-}. We speculated that the red shift may be caused by the formation of metal complexes or changed polarity in the local environment of the AuNCs.

Comparisons with some other methods for the determination of S^{2-} are shown in Table 1; the present method had a satisfactory sensitivity without the need for sophisticated instruments or time-consuming procedures. Compared with other metal

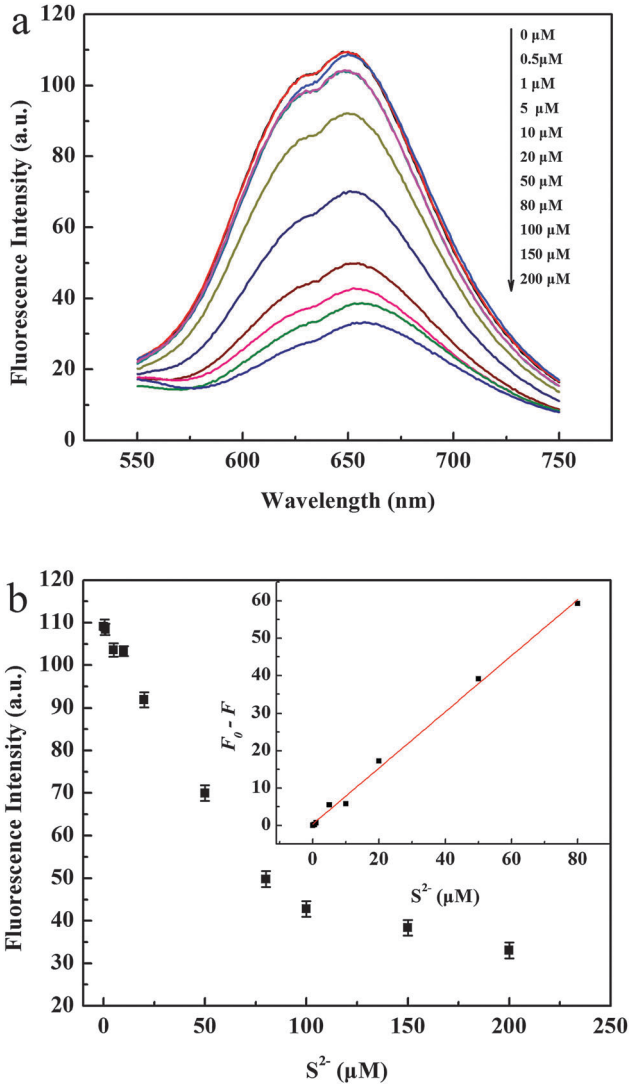

Fig. 3 (a) Fluorescence emission spectra of the AuNCs in the presence of different concentrations of S^{2-}. (b) Change in fluorescent intensity with the concentration of S^{2-} (λ_{max} = 650 nm). Inset: Calibration graph for the fluorescent probe.

Table 1 Comparison of sensitivities of this method with other methods for the determination of S^{2-}

Method	Linear range (μM)	Limit of detection (μM)	Ref.
Colorimetry	1.0–10.0	0.30	4
Spectrometry	0.16–781.25	0.16 and 0.19	6
Electrochemistry	1.09–16.3	0.30	7
Fluorescence	0.10–30.0	0.029	38
This method	0.5–80.0	0.38	—

nanoclusters used for the quantitative determination of S^{2-}, the synthesized AuNCs have some excellent advantages. This sensing method has a wider detection range than BSA-stabilized gold nanoclusters.[38] In addition, the papain-directed nanoclusters do not require expensive reagents (such as DNA[40,42]) and complex preparation procedures.[37,39,41] The AuNCs could be used as an economic and simple fluorescent sensing system for S^{2-}, although the detection limit needs to be improved. Overall, the fluorescence method could be used for the determination of S^{2-} in the concentration range 0.5–80.0 μM.

3.4. Selectivity of the fluorescent method

Along with the requirement for sensitivity, high selectivity is also an essential feature for probes used in practical applications. To further examine the selectivity of this method for the fluorescence-based determination of S^{2-}, the fluorescence response in the presence of various environmentally relevant metal ions and anions was evaluated under the optimized conditions. Because Ag^{+}, Ni^{2+}, Fe^{3+}, Al^{3+}, Hg^{2+}, Cu^{2+}, Cr^{3+} and Pb^{2+} can form a precipitate with S^{2-} in water, interference from these ions could be neglected. Other metal ions (Ca^{2+}, Mg^{2+}, K^{+} and Ba^{2+}) in the form of salts were used as controls in the selectivity study. The anions used for the evaluation of the selectivity of this method included NO_3^{-}, PO_4^{3-}, SO_4^{2-}, CO_3^{2-}, HCO_3^{-}, Ac^{-}, NO_2^{-}, I^{-}, Cl^{-} and Br^{-}. The fluorescence response towards S^{2-} was evaluated in the presence of all these species. Fig. 4 shows that only S^{2-} induced a decrease in the fluorescence intensity at 650 nm; equivalent concentrations of the other ions did not cause an obvious change in fluorescence. The proposed sensing method was therefore highly specific to S^{2-}. Only a small variation in the fluorescence intensity was observed in the absence of S^{2-}, but in the presence of coexisting ions. In contrast, the changes in the fluorescence intensity of the AuNCs showed a striking decrease after adding S^{2-} to the solutions containing other cations/anions, which suggested that the interference from the above-mentioned ions could be neglected. Moreover, the interference from $S_2O_3^{2-}$ and SO_3^{2-} could be eliminated by adding $Na_2S_2O_8$ to the sensing system.[38] Thus the papain-directed AuNCs showed excellent selectivity towards S^{2-} over other ions, illustrating that the fluorescence method was highly suitable for the analysis of environmental samples.

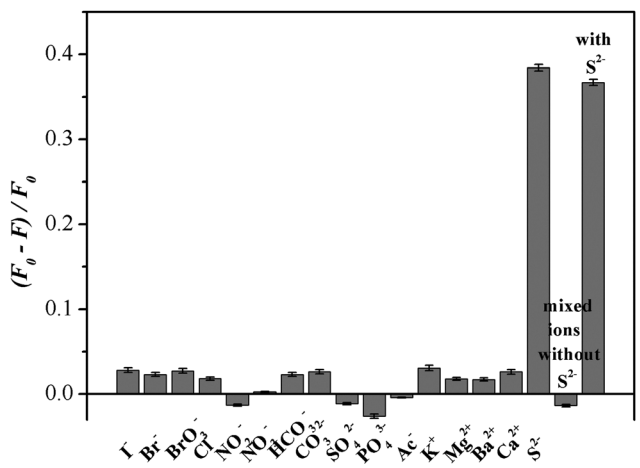

Fig. 4 Relative emission intensity $[(F_0 - F)/F_0]$ of the AuNCs after the addition of various ions at a concentration of 50 μM. All data were collected at 650 nm.

3.5. Mechanism of the proposed fluorescence-based method

A plausible explanation for the mechanism of the sulfide-induced fluorescence quenching of the AuNCs relied on the formation of the Au_2S species. Because the solubility product (K_{sp}) of Au_2S is only 1.58×10^{-73} M^2, when S^{2-} ions are added to the solution of AuNCs, the S^{2-} may react with the Au atoms/ions at the surface of the nanoclusters to form an Au_2S precipitate while neutralizing the surface charge of the AuNCs, leading to aggregation of the AuNCs.

This postulate was verified using HRTEM, UV-visible absorption spectrometry and FTIR measurements. Fig. 5a shows that the shape of the synthesized AuNCs was almost spherical and no aggregation was apparent in the absence of S^{2-}. The majority of these AuNCs were about 3 nm in size (Fig. 5a, inset). After the addition of S^{2-} (200 μM), the size of the AuNCs increased dramatically and the particle size distribution became irregular, suggesting aggregation (Fig. 5b). Therefore, along with the increase in the size of the particles, the fluorescence of the AuNCs was quenched. The observed aggregation of the AuNCs supports the hypothesized mechanism of fluorescence quenching.

To further confirm that the observed aggregations were generated by the formation of Au_2S, not Au nanoparticles, the UV-visible spectrum of papain-directed AuNCs was measured before and after the addition of S^{2-} (Fig. 6). In the presence of 500 μM S^{2-}, the absorption spectrum of the AuNCs showed a slight change and no characteristic surface plasmon band of large Au nanoparticles was seen, confirming the formation of Au_2S.

To verify that the change in fluorescence was not caused by reaction between the S^{2-} and papain, FTIR spectrometry was used to monitor the changes in the structure of papain. Fig. 7 shows (a) the FTIR spectrum of papain and the spectra of AuNCs in (b) the absence and (c) the presence of S^{2-}. Compared with native papain, a shift in the amide I band from higher to lower wavenumbers in the region 1600–1700 cm^{-1} (the C=C stretching vibration band moved from 1651.07 to 1592.46 cm^{-1}) was apparent for the papain–AuNC conjugates; the $-CH_2$ bending vibrations at 1455.44 cm^{-1} also moved to 1414.59 cm^{-1}. The data suggested a change in the structure of papain, which was consistent with a previous study.[43] However, the addition of S^{2-}did not cause the spectral profile of the papain–AuNC conjugates to return to that of native papain. The position and intensity of the absorption peak were basically the same as those observed for the papain-directed AuNCs, indicating that there was no interaction between the amino acid residues in papain and S^{2-}. Therefore the decrease in the fluorescence intensity caused by S^{2-} was not derived from interactions between the added S^{2-} and papain.

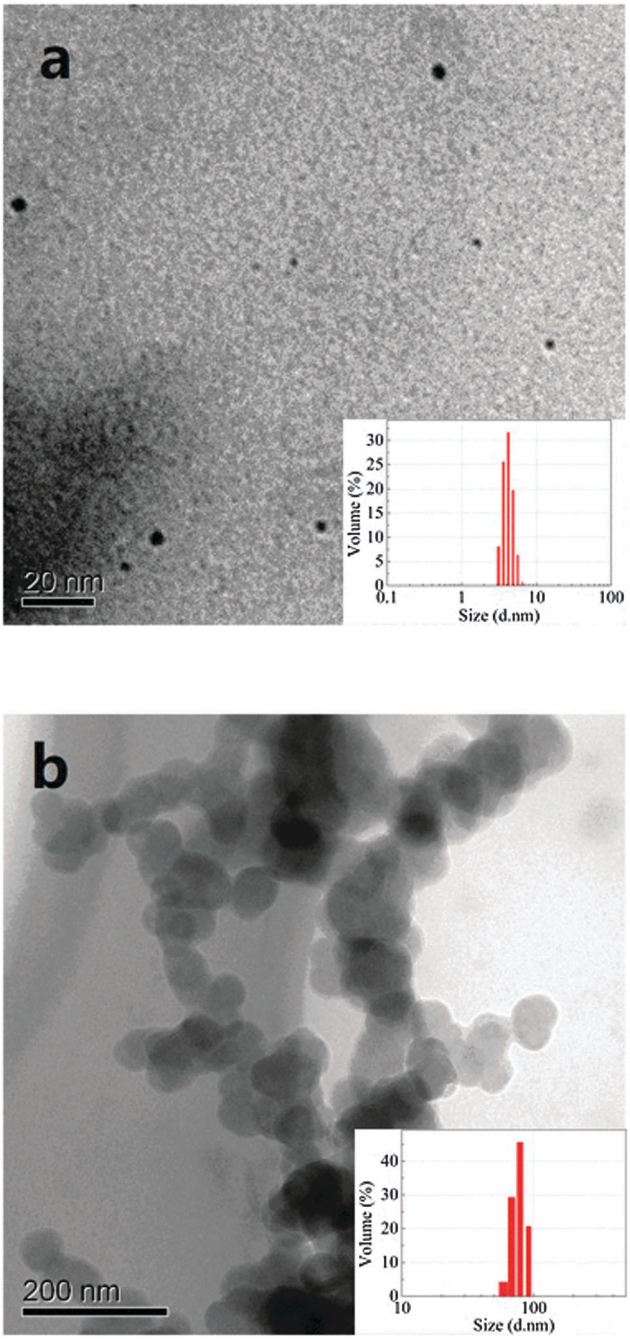

Fig. 5 HRTEM images of the AuNCs in (a) the absence and (b) the presence of 200 μM S^{2-}. Inset: Size histogram of different sizes of AuNCs.

3.6. Application to samples of natural water

Determination of the solubility of the fluorescence probes in water and their stability in high ionic strength environments are basic requirements for exploring the potential application of these probes.[44] Because the structure of the AuNCs used in this study was directed by papain and the biomolecules had a natural solubility in water, we could neglect this factor. However, the stability of the fluorescence probe in high ionic strength media required investigation. NaCl was selected to evaluate the effect of ionic strength on the fluorescence response. Fig. 8 shows that the intensity of the fluorescence of the papain-directed AuNCs remained almost constant despite changes in the concentration of the high-salt media. Even when the concentration of NaCl was increased to 1 M, only a 3% variation in the fluorescence intensity was observed. The results indicated that the fluorescence probe was highly stable under high ionic strength conditions and thus may be applied to the determination of S^{2-} in samples of natural water.

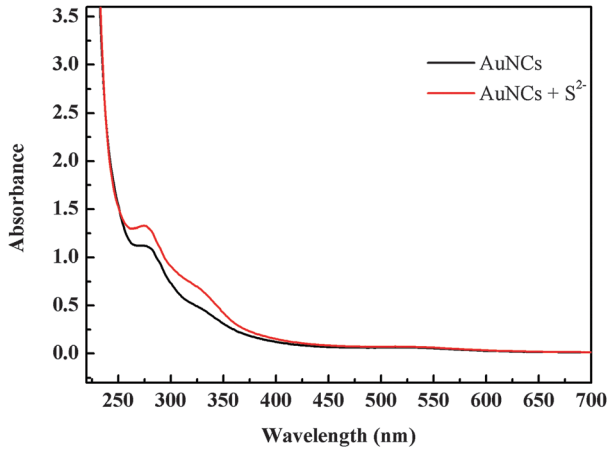

Fig. 6 UV-visible absorption spectra of the fluorescent AuNCs in the presence of 500 μM S^{2-}.

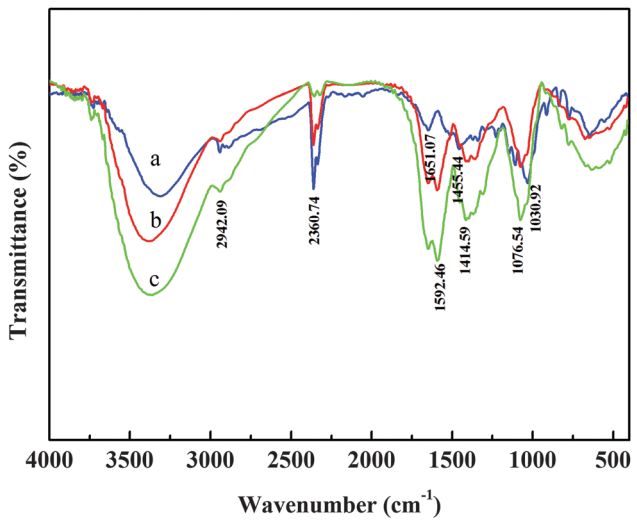

Fig. 7 FTIR spectra of (a) papain, (b) AuNCs and (c) AuNCs + 200 μM S^{2-}.

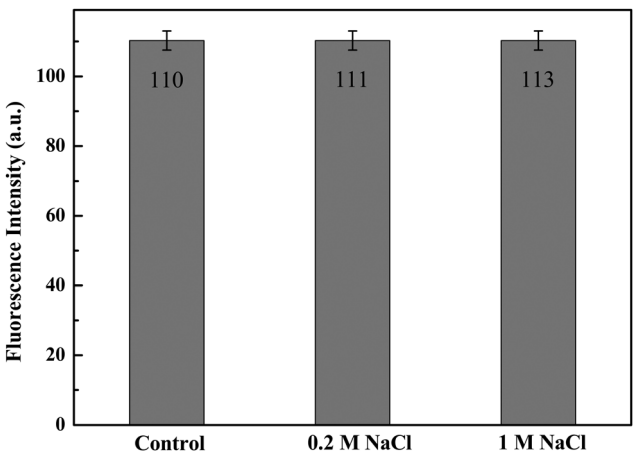

Fig. 8 Fluorescence intensity of the AuNCs at different concentrations of NaCl.

Table 2 Determination of S^{2-} in natural water samples

		Colorimetric method			Fluorescent method		
Sample	S^{2-} added (μM)	Mean S^{2-} [a] (μM)	RSD [b] (%)	Recovery (%)	Mean S^2 (μM)	RSD (%)	Recovery (%)
River water	20.00	19.43	4.11	97.15	20.58	4.41	102.90
Pond water	20.00	19.84	1.08	99.20	19.57	2.38	97.85
Tap water	20.00	19.00	2.59	95.00	20.16	1.47	100.80

[a] Mean of three determinations. [b] Relative standard deviation.

The concentration of S^{2-} in several environmental water samples (tap, river and pond water) was determined in triplicate using the optimum conditions (pH 9, 55 °C, 35 min); S^{2-} was not detected in any of the samples. However, after spiking the water samples with 20 μM S^{2-}, a significant decrease in the fluorescence intensity was observed. Table 2 summarizes the experimental results. The recovery of S^{2-} was between 97.85 and 102.90% and the results showed good agreement with the values determined by the conventional methylene blue colorimetric method. Hence the results obtained for the samples were satisfactory and indicated that the proposed fluorescence method was reliable for monitoring environmental samples.

4. Conclusions

A new fluorescence method has been successfully developed for the sensitive and selective determination of sulfide ions using papain-directed AuNCs as a fluorescence probe. The detection mechanism is based on the ability of sulfide ions to quench the fluorescence of AuNCs *via* the specific interaction between the sulfide ions and Au atoms/ions. Compared with previously reported methods, this method is low cost and does not require sophisticated instrumentation. This method has many advantages, including high sensitivity, a wide detection range and a low detection limit. In addition, the method is adequate for the determination of sulfide ions in complex natural water samples.

Acknowledgements

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