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Colorimetric and fluorescent dual-mode strategy for sensitive detection of sulfide: Target-induced horseradish peroxidase deactivation

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ABSTRACT

Environmental pollution caused by sulfide compounds has become a major problem for public health. Hence, accurate detection of sulfide anions (S^{2-}) level is valuable and vital for environmental monitoring and protection. Here, we report a new colorimetric/fluorescent dual-mode sensor for the determination of S^{2-} based on the inhibition of enzyme activity and the unique optical properties of produced 2,3-diaminophenazine (DAP), thus making the analytical results more convincing. In this strategy, horseradish peroxidase (HRP) enzyme is used for catalyzing the H_2O_2-mediated oxidation of o-phenylenediamine (OPD) to produce DAP, and the color changed to bright yellow and produced orange yellow fluorescence. But the presence of S^{2-} could cause the deactivation of HRP, which decreased the amount of DAP and consequently resulted in a substantial SPR band fading and an evident fluorescence quenching simultaneously. The mechanism of S^{2-} sensor was examined by combining the UV–vis absorption spectra, fluorescence spectra and electrospray ionization mass spectrometry analysis. Under optimal conditions, the colorimetric and fluorescent linear responses of the proposed method exhibited a wide linear range from 2.5 nM–7.5 μM with ultralow detection limits of 1.2 nM and 0.9 nM, respectively. Some potential interferents (such as F^-, Cl^-, Br^-, I^-, SO_4^{2-}, SO_3^{2-}, SCN^-, $H_2PO_4^-$, HPO_4^{2-}, Ac^-, NO_3^-, CO_3^{2-}) in real samples showed no interference. Moreover, the proposed method offered advantages of simple, low-cost instruments and rapid assay without the utilization of nanomaterials and has been successfully applied to determine S^{2-} content in lake water samples with satisfying recoveries over 97.6 %. More importantly, the present S^{2-} sensor not only afforded a new optical sensing pattern for bioanalysis and environment monitoring, but also extends the application field of HRP-catalyzed OPD–H_2O_2 system.

Keywords: Dual-mode strategy; sulfide; horseradish peroxidase deactivation; o-phenylenediamine; hydrogen peroxide;

1. Introduction

Sulfide anions (S^{2-}) are one of the widespread toxic anion pollutants which come from diverse sources including nature and human activities [1]. The application of sulfur-containing chemicals in many industrial processes and immobilization of sulfur-containing minerals by bacteria are responsible for the presence of S^{2-} in wastewater efuents and natural waters, respectively [2]. As a toxic pollutant, S^{2-} is of great concern for the environment, and the concentration of S^{2-} is regarded as an important environmental index for spring, surface and waste water [3]. Physiologically, S^{2-} combines with protons to form HS^- or H_2S and chronic exposure to protonated sulfide anions would pose a great threat to human, such as diabetes, Down's syndrome, Alzheimer's disease and liver cirrhosis [4-7]. Hence, monitoring the level of S^{2-} by using simple and low-cost assays is of great importance in biological and environmental fields.

Many traditional analytical methods, such as ion chromatography [8], capillary electrophoresis [9], inductively coupled plasma atomic emission spectroscopy [10] and electrochemical assays [11,12] have been established for the detection of S^{2-}. Unfortunately, these methods usually require high costs, time-consuming, complicated pretreatment processes and specific experts to run the systems, which limit their wide application. Compared with these methods, optical methods have drawn much attention because of low cost, high sensitivity and rapidity, and even can be easily monitored by naked eyes. In recent years, various colorimetric/fluorescent probes including Au@Ag core-shell nanoparticles NPs (Au@Ag NPs) [13], 3,3′,5,5′-tetramethylbenzidine (TMB) [14], L–DOPA stabilized AgNPs [15], 4-nitrophenol (4-NP) [16], carbon dots (CDs) [17], yeast extract-stabilized Cu nanoclusters (Cu NCs) [18], Ce(III) ions functionalized silver nanoclusters (Ce(III)/AgNCs complex) [19], sulfanilic acid and glutathione functionalized graphene quantum dots (SSGQDs) [3] have been developed, which provide an effective sensing platform for the detection of S^{2-}. For example, Deng and co-workers reported a convenient colorimetric method for the determination of S^{2-} based on the target-induced shielding against the peroxidase-like activity of GNPs [20]. Barati et al. established two novel metal-ion-mediated fluorescent probes based on CDs for the indirect detection of S^{2-} [21]. Despite the importance of above optical sensors, their use still shows drawbacks. On the one hand, most

of the sensors suffered from the disadvantages of high cost, time-consuming and complex preparation or modification of nanomaterials, which strongly limits their commercial applications in many fields. On the other hand, compared with multi-signal sensing techniques, single mode-based assays offered only one kind of output signal, thus lacking attractive diversity and improved accuracy [22]. Considering these, developing a new dual-mode sensing platform with simplicity, sensitivity and efficiency for the detection of S^{2-} was still highly desired.

O-phenylenediamine (OPD) could be oxidized by hydrogen peroxide (H_2O_2) to obtain 2,3-diaminophenazine (DAP) [23-25]. DAP is bright yellow colored and exhibits an orange yellow fluorescence under the irradiation of ultraviolet light. Thus, DAP is a kind of promising chromophore and organic fluorophore. The chromogenic response has already been utilized to develop a series of assays for relevant reactants in the previous literatures [26-29]. However, to the best of our knowledge, no literature reported about the target-induced horseradish peroxidase deactivation for dual-mode sensing of S^{2-}.

In the study, we developed a new, convenient and dual-mode sensor with both colorimetric and fluorometric readout for detecting S^{2-} by using OPD as the substrate. Previous reports have shown that H_2O_2 could oxidize OPD via the catalysis of horseradish peroxidase (HRP) to produce DAP, showing a bright yellow color as well as an orange yellow fluorescence when irradiated by ultraviolet light [25]. More interestingly, the dual-mode response of the OPD/ H_2O_2/HRP sensing system can be inhibited by introducing the S^{2-}, revealing the deactivation of HRP by S^{2-}. Based on the above facts, a rapid and sensitive method for S^{2-} detection was established and successfully applied to analyze S^{2-} in lake water samples. This is the first method in which OPD/H_2O_2/HRP system has been used for the dual-mode sensing of S^{2-}.

2. Experimental

2.1. Reagent and chemicals

All chemicals were of analytical grade and used without further purification. O-phenylenediamine (OPD) and 2,3-diaminophenazine (DAP) were purchased from Tianjin Zhiyuan Chemical Reagent Co., Ltd. (Tianjin, China). Horseradish peroxidase (HRP, 300

units/mg) was obtained from Aladdin Biochemical Technology Co., Ltd. (Shanghai, China). Sodium sulfide ($Na_2S·9H_2O$, 98%), hydrogen peroxide (30 wt% H_2O_2), sodium acetate (NaAc), acetic acid (HAc), potassium iodide (KI), sodium nitrate ($NaNO_3$), sodium hydroxide (NaOH) and sodium carbonate (Na_2CO_3) were achieved from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). Sodium fluoride (NaF), sodium chloride (NaCl), sodium bromide (NaBr), sodium sulphate (Na_2SO_4), sodium sulfite (Na_2SO_3), potassium thiocyanate (KSCN), Disodium hydrogen phosphate (Na_2HPO_4), sodium dihydrogen phosphate (NaH_2PO_4) acquired from Nanjing Nanshi Chemical Reagent Co., Ltd. (Nanjing, China). Ultrapure water (18.2 M cm^{-1}) prepared by a Millipore system (Millipore, USA) was used throughout the whole experiments.

2.2. Instruments.

UV–visible absorption spectra were recorded using an Agilent 8453 UV–vis spectrometer (Agilent, USA). Fluorescence measurements were performed on a Shimadzu RF-5301 PC fluorescence spectrophotometer. Electrospray ionization mass spectrometry (ESI-MS) was carried out on a Finnigan LCQ ion trap mass spectrometer (Waters MS Technologies, Manchester, UK). The pH value of buffer was adjusted by titrating with HAc and controlled by a PHS-3C pH meter (Leici, Shanghai).

2.3. Procedure for dual-mode sensing assay

A typical dual-mode sensing assay for S^{2-} was carried out as follows. Firstly, 50 μL of 0.15 μg mL^{-1} HRP and 100 μL of S^{2-} standard solution with various concentrations were mixed in 1500 μL of HAc/NaAc buffer (50 mM, pH 6.0). Secondly, 200 μL of 0.2 mM OPD solution and 100 μL of 5 mM H_2O_2 were successively added to each of the mixture solutions, which were shaken and equilibrated at incubation temperature of 20 °C for 15 min. Finally, NaOH (50 μL, 0.5 M) was added to the mixture solutions to end the enzymatic reaction. Such solutions were transferred separately into 1 cm quartz cuvette and directly monitored by UV–vis spectrometer and fluorescence spectrophotometer, respectively. The ΔA_{417nm} signal ($\Delta A = A_0–A$, where A_0 and A are the absorbance at 417 nm in the absence and presence of S^{2-}) and fluorescence quenching efficiency ($Effq = (F_0–F)/F_0$, where F_0 and F are the fluorescence intensity at 560 nm in the absence and presence of S^{2-}) were used as a

criterion to appraise the performance of colorimetric and fluorescent sensor, respectively.

2.4. Specificity of the sensor

Selectivity is another key parameter in sensing assay. To evaluate the selectivity of dual-mode sensor for detecting S^{2-}, several potential interfering substances (F^-, Cl^-, Br^-, I^-, SO_4^{2-}, SO_3^{2-}, SCN^-, $H_2PO_4^-$, HPO_4^{2-}, Ac^-, NO_3^-, CO_3^{2-}) coexisting in real water samples were selected and pre-mixed with 100 μL of 25 μM S^{2-}. Afterwards, they were separately added to the HRP-catalyzed OPD–H_2O_2 sensing system. All experiments were carried out under the optimized conditions.

2.5. Analysis of S^{2-} in real samples

For real samples analysis, lake water samples were collected from Chaohu Lake (Hefei, China), and the analysis was conducted after the sample collection. Firstly, the water samples were filtered with 0.22 μm Millipore filter to remove the insoluble components. Then, a series of spiked samples was prepared by adding standard solutions containing various concentrations of S^{2-} in water samples. Following that, the resulting solutions were added into the OPD/ H_2O_2/HRP sensing system as mentioned. Finally, content of S^{2-} in lake water samples was calculated according to linear equation obtained from a standard solution of S^{2-}.

3. Results and Discussion

3.1. Design and principle of the sensing system

The working principle of the designed dual-mode method for sensing the S^{2-} is schematically shown in Scheme 1. Previous report has shown that OPD as a substrate could be oxidized by H_2O_2 via the catalysis of HRP to form DAP, exhibiting a bright yellow color as well as an orange yellow fluorescence when irradiated by ultraviolet light [25]. However, the introduction of S^{2-} can cause the deactivation of HRP and, hence, further affects the amount of DAP produced, which is accompanied by a substantial SPR band fading and an evident fluorescence quenching simultaneously. Thus, a new dual-mode sensor for the detection of S^{2-} was established by coupling three reactions, which can be expressed by the following equations:

$$OPD + H_2O_2 \xrightarrow{\text{activated HRP}} DAP \quad (1)$$

$$S^{2-} + \text{activated HRP} \longrightarrow \text{deactivated HRP} \quad (2)$$

$$OPD + H_2O_2 \xrightarrow{\text{deactivated HRP}} DAP \quad (3)$$

To demonstrate the proposed sensing mechanism, several control tests were implemented under the different conditions by using visual color readout, UV–vis absorption and fluorescence spectrophotometer. As indicated from Fig. 1A and B, the control groups (pure OPD and OPD/H_2O_2) always remained colorless and exhibited negligible fluorescence at incubation temperature of 20 °C for 15 min (curve a, b). In contrast, as a result of adding HRP into the OPD/H_2O_2 solution, an obvious absorption peak at 417 nm and corresponding fluorescence emission peak at 560 nm were observed ((curve c), which is consistent with the results that of pure DAP aqueous solution (Fig.S1). Furthermore, the molecular ion peak at 211.1 (m/z, $[M+H]^+$) ascribed to DAP can be obviously observed in the mass spectrometry (Fig. S2). These results indicated HRP essentially catalyzes the oxidative reaction of OPD/H_2O_2 system to form DAP. However, the introduction of S^{2-} into the OPD/H_2O_2/HRP system resulted in a substantial SPR band fading and an evident fluorescence quenching simultaneously (curve d), indicating the presence of S^{2-} can cause the deactivation of HRP which affects the amount of DAP produced. Meanwhile, the corresponding color/fluorescence change of different test solutions were shown in Fig. 1C and D, which provide a convenient and instrument-free mean for the readout of S^{2-} sensing.

3.2. Optimization of detection conditions

Based on HRP manufacturer suggestion (https:// www.aladdin-e.com), the sensing system should be better carried out at an effective working pH of 6.0 and an effective incubation temperature of 20 °C. Under these conditions, other possible experimental parameters including HRP concentration, incubation time, OPD concentration, H_2O_2 concentration and ending agent were investigated in detail. ΔF was used as a criterion to optimize the detection conditions and defined as F_0–F, where F_0 and F are the fluorescence of sensing system in the absence and presence of 1.25 μM S^{2-}, respectively.

The concentration of HRP has great influence on the performance of the proposed assay,

which has been optimized first. Fig. 2A shows that ΔF increased with the increment of HRP concentration up to 3.75 ng/mL, above which it decreased. So, 3.75 ng/mL of HRP was selected for the following study. Different incubation time ranging from 3 min to 21 min was investigated to study its effect on the ΔF. The result shows that the highest ΔF is obtained at 15 min, and then the ΔF decreases with the increase of incubation time (Fig. 2B), which has been chosen as the optimal time for the following study. The effect of the concentration of OPD and H_2O_2 on the ΔF was displayed in Fig. 2C and D, respectively. It can be obviously seen that the concentration of OPD and H_2O_2 being too high or too low is not suitable for S^{2-} detection. The experiments show that the highest ΔF is obtained when the OPD concentration is 20 μM and the H_2O_2 concentration is 0.25 mM. Therefore, 20 μM of OPD and 0.25 mM of H_2O_2 were used for the dual-mode assay. Fig. S3A and B indicate the fluorescence spectrum of OPD/H_2O_2/HRP/S^{2-} system with adding 12.5 mM of NaOH is more stable than that in the absence of NaOH. Thus, 12.5 mM of NaOH in this study was used to end the enzymatic reaction.

3.3. Linearity and detection limit

Under the optimal conditions employed here, the sensitivity and dynamic measurement range of colorimetric and fluorescent dual-mode sensor for detecting S^{2-} was evaluated. Fig. 3A depicts the UV–vis absorption spectra of the OPD/H_2O_2/HRP sensing system with different concentrations of S^{2-} ranging from 0 to 7.5 μM. It is clearly observed that the absorption intensity decreased gradually with increasing S^{2-} concentration, which was attributed to the deactivation of HRP by S^{2-}. Fig. 3B shows a typical S^{2-} concentration–response curve, and the ΔA_{417nm} increased linearly with the logarithm of the concentration of S^{2-} ranging from 2.5 nM to 7.5 μM ($Y_1 = 0.1071$ Log (C) + 0.2805, $R^2 = 0.9931$) (inset of Fig. 3B). Likewise, the fluorescence spectrum of S^{2-}-treated OPD/H_2O_2/HRP system with different concentrations from 0 to 7.5 μM was also observed, as shown in Fig. 3C. Fig. 3D shows a typical S^{2-} concentration–response curve, and a satisfying linear relationship between the $(F_0\text{-}F)/F_0$ signal and the logarithm of S^{2-} concentrations in the range from 2.5 nM to 7.5 μM, $Y_2 = 0.2959$ Log (C) + 0.7488, was shown in the inset of Fig. 3D. Meanwhile, the photographs of OPD/H_2O_2/HRP system with different concentrations of S^{2-} under

ambient light and a 365 nm UV lamp were taken. A dramatic color change from bright yellow to pale yellow and an obvious fluorescence intensity transformed from strong to weak can be observed (Fig. 3E). On the basis of dual-mode signal response, the S^{2-} level could be simply visualized by the naked eye and further quantified by UV-vis or fluorescence spectra. The detection limits of colorimetric and fluorescent sensor were calculated by a signal-to-noise ratio of 3 ($3\sigma/B$). Here, σ represents the standard deviation of blank measurements, and B means the slope of linear equation. Thus, the colorimetric and fluorescent sensor can be used to detect S^{2-} with a detection limit of 1.2 and 0.9 nM, respectively. A comparison of characteristics between the proposed method and other S^{2-} sensors reported elsewhere was summarized in Table 1 [20, 30-36]. The detection limit and linear range of S^{2-} in this work were comparable or even better than those of reported sensors. In addition, the repeatability of the dual-mode biosensor was also evaluated by five repeated measurements of 1.25 uM of S^{2-} under optimal experiment conditions, and the relative standard deviation (RSD) was 1.0 % and 1.2 %, demonstrating the reliability of the proposed method (Fig. S4).

3.4. Selectivity

Selectivity is another key parameter in sensing assay. To evaluate the selectivity of the dual-mode sensor for detecting S^{2-}, several potential interfering compounds coexisting in real sample, including F^-, Cl^-, Br^-, I^-, SO_4^{2-}, SO_3^{2-}, SCN^-, $H_2PO_4^-$, HPO_4^{2-}, Ac^-, NO_3^-, CO_3^{2-} were examined. As shown in Fig. 4A, the ΔA_{417nm} and the $(F_0\text{-}F)/F_0$ signal in the presence of S^{2-} with single other ions were almost similar to those in the presence of S^{2-} without interfering substances. Moreover, the color/fluorescence changes of different tested solutions in Fig. 4B and C were in good accordance with the above corresponding ΔA_{417nm} and $(F_0\text{-}F)/F_0$ signal, respectively. These results demonstrate that only target S^{2-} could result in the deactivation of HRP, and the potential interfering substances had no evident effect on the absorbance/fluorescence intensity and the color of tested solutions.

3.5. Real sample assay

To test the feasibility of the developed sensor for practical application, we applied it to determine the concentration of S^{2-} in lake water samples. The recovery experiments with

adding different concentrations (100, 300 and 500 nM) of S^{2-} standard solutions were carried out and the results are shown in Fig. 5. According to above linear equation, the average concentration of S^{2-} in lake water samples (1 and 2) were calculated to be 108.4±3.6, 297.5±10.8, 514.8±16.1, 101.5±4.1, 292.9±9.7, 510.1±18.2 nM as well as 103.8±4.4, 306.1±11.5, 509.7±18.7, 99.3±4.3, 302.1±12.5, 508.2±17.9 nM by colorimetric and fluorometric measurements, respectively. The recoveries of known amount of S^{2-} in lake water samples were between 97.6% and 108.4% with the RSD ranging from 3.1% to 4.3%. These results reveal that the proposed sensor was of high accurate and could be applied for rapid detection of S^{2-} in real samples in a simple way.

4. Conclusions

In summary, we constructed a label-free and reliable colorimetric and fluorescent dual-mode sensor for the quantitative detection of S^{2-} based on the OPD/H_2O_2/HRP system. In the study, OPD could oxidized by H_2O_2 via the catalysis of HRP to produce DAP, while the introduction of S^{2-} induced the deactivation of HRP, which decreased the amount of DAP and consequently resulted in a substantial SPR band fading and an evident fluorescence quenching simultaneously. Under the optimal conditions, the dual-mode sensor has a good dynamic range and a relatively low detection limit of 1.2 nM and 0.9 nM by colorimetric and fluorometric measurements, respectively. More importantly, this method is successfully applied to the detection of S^{2-} in lake water samples with high simplicity, feasibility and reproducibility, illustrating its great potential in biological and environmental fields. Compared with the previously reported method [37], the present sensing platform has several extraordinary features as following: (1) the developed method does not require complicated synthetic procedures and specific modification approach, making it more convenient and easy operations; (2) The sensing assay can present colorimetric and fluorescent dual-readout signal, making the experimental results more convincing.

Conflicts of interest

There are no conflicts of interest to declare.

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Figure captions

Scheme 1. (A) Schematic illustration of the dual-mode sensor for the detection of S^{2-} based on target-induced deactivation of horseradish peroxidase. (B) Photographs and UV−vis absorption/fluorescence spectra in the presence (1) and absence (2) of S^{2-}.

Fig. 1. (A) Absorbance and (B) fluorescence emission spectra of (a) OPD, (b) OPD + H_2O_2, (c) OPD + H_2O_2 + HRP, and (d) OPD + H_2O + HRP + S^{2-} in 50 mM HAc/NaAc buffer at pH 6.0. The corresponding photographs under (C) visible light and (D) 365 nm UV light. The final concentrations of the OPD, HRP, H_2O_2 and S^{2-}, are 20 μM, 3.75 ng/mL, 0.25 mM and 1.25 μM respectively.

Fig. 2. Optimization of the reaction conditions for the detection of S^{2-}. Plots of fluorescence intensity in the absence and presence of S^{2-} and plots of ΔF signal versus the (A) HRP concentrations (1.25–6.25 ng/mL), (B) reaction time (from 3 to 21 min), (C) OPD concentrations (5–37.5 μM) and (D) H_2O_2 (0.05–0.5 mM). The final concentrations of the OPD, HRP, H_2O_2 and S^{2-}, are 20 μM, 3.75 ng/mL, 0.25 mM and 1.25 μM, respectively.

Fig. 3. (A) UV-vis absorption spectra of the OPD/H_2O_2/HRP sensing system upon addition of various concentrations of S^{2-} (from 0 to 7.5 μM). (B) A dose–response curve between S^{2-} concentration and the ΔA_{417nm} signal under optimum conditions (inset: linear calibration plot versus the logarithm of S^{2-} concentrations). (C) Typical fluorescence emission spectra of the OPD/H_2O_2/HRP sensing system in the presence of varying S^{2-} concentrations (from 0 to 7.5 μM). (D) A dose–response curve between S^{2-} concentration and the $(F_0\text{-}F)/F_0$ signal under optimum conditions (inset: linear calibration plot versus the logarithm of S^{2-} concentrations). (E) Photographs of the tested solutions under (1) ambient light and (2) 365 nm UV lamp. Error bars represent the standard deviations (n = 3).

Fig. 4. (A) Selectivity of the dual-mode sensing system toward various potential interfering substances. (B) Photographs (ambient light and UV light) of the solutions from 1 to 14 represent (1) control, (2) S^{2-} + F^-, (3) S^{2-} + Cl^-, (4) S^{2-} + Br^-, (5) S^{2-} + I^-, (6) S^{2-} + SO_4^{2-}, (7) S^{2-} + SO_3^{2-}, (8) S^{2-} + SCN^-, (9) S^{2-} + $H_2PO_4^-$, (10) S^{2-} + HPO_4^{2-}, (11) S^{2-} +Ac^-, (12) S^{2-} + NO_3^-,

(13) S^{2-} + CO_3^{2-} and (14) S^{2-}, correspondingly. The concentration of other potential interfering substances and S^{2-} was 1.25 μM.

Fig. 5. Dual-mode detection of the content of S^{2-} for the lake water samples spiked with different concentrations (100, 300 and 500 nM) of S^{2-} standard solutions. The error bars represent the standard deviation (n=3).

Table 1 Comparison of different sensors for S^{2-} detection.

System	Signal output	Linear range (μM)	LOD (nM)	References
iodide/Cu@Au nanoparticle	Colorimetry	0 – 10	300	[30]
ABTS–Au (III) system	Colorimetry	0.5 – 15	280	[31]
β-FeOOH) nanorods/TMB/H_2O_2	Colorimetry	5 – 30	2190	[32]
bare Au nanoparticles	Colorimetry	0.5 – 10	80	[20]
Cyclen-capped FPNs[a]–Cu^{2+} complex	Fluorescence	0 – 80	2100	[33]
CDs/PEI/NB[b]/Cu^{2+}	Fluorescence	0.1 – 8.0	60	[34]
MTT[c]-AuNDs	Fluorescence	0.87 – 16	2	[35]
DNA-Au/Ag NCs	Fluorescence	0 – 9	0.83	[36]
OPD/H_2O_2/HRP	Colorimetry/fluorescence	0.0025 – 7.5	1.2/0.9	this work

[a] fluorescent polymeric nanoparticles

[b] polyethyleneimine and Nile Blue

[g] 6-mercapto-striazolo(4,3-b)-s-tetrazine

Declaration of competing interests

☒ The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

☐The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

Credit Author Statement

Jie Bao conceived the project and prepared writing-original draft. Mass spectrometry experiment was done by Shu-Xin Xu. Lihua Zhao and Guoyu Peng collected and processed the water samples included in this study. Haifeng Lu contributed to review, editing and funding acquisition.

Graphical abstract

Highlights

- A new and label-free colorimetric and fluorescent dual-mode sensor was designed to detect S^{2-}.
- The sensing mechanism is designed by target-induced horseradish peroxidase deactivation.
- The detection limits of S^{2-} are as low as 1.2 nM and 0.9 nM by colorimetric and fluorometric method, respectively.
- The proposed method is successfully applied to the detection of S^{2-} in real samples.