A simple colorimetric method based on “on–off–on” mode for detection of H₂S and Hg²⁺ in water

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Abstract
It is of great significance to develop efficient platforms for the detection of hypertoxic Hg²⁺ and H₂S. Colorimetric have received much attention for the detection of H₂S and Hg²⁺ in the last decades. In this work, an “on–off–on” mode colorimetric method based on MnO₂/multi-wall carbon nanotubes (MnO₂/MWCNTs) composite was constructed. MnO₂/MWCNTs composite can oxidize TMB directly to form blue product (ox TMB) with a good simulated oxidase activity. In the presence of H₂S, it can decompose the MnO₂/MWCNTs composite causing the absorbance of the chromogenic system to decrease. When Hg²⁺ is introduced, the formation of Hg–S bond between Hg²⁺ and H₂S inhibited the decomposition ability of H₂S toward MnO₂ composite, thus resulting in a color change from colorless to blue. Based on this phenomenon, the proposed “on–off–on” colorimetric sensor can be used for detection of H₂S (off) and Hg²⁺ (on). Under optimized experimental conditions, this sensor showed a satisfactory linear relationship of H₂S and Hg²⁺ with pleasant repeatability, acceptable method accuracy and stability. More importantly, the proposed colorimetric sensor has been successfully applied to the detection of H₂S and Hg²⁺ in real samples, which not only provides a simple and cost-effective method to detect H₂S and Hg²⁺ but also hopefully makes a certain contribution to environmental protection.

Keywords Colorimetric · “On–off–on” mode · Detection of H₂S · Detection of Hg²⁺
physical and chemical, it is difficult to detect both species using the same method [25]. Therefore, it is meaningful to construct a fast, sensitive and simple detection method for detection of H$_2$S and Hg$^{2+}$ in water.

Currently, a more intelligent output signal mode named the “on–off–on” switch strategy has attracted extensive attention due to the merits of wide detection range, high sensitivity, flexible design and strong anti-interference ability [26, 27]. Definitely, the “on–off–on” mode includes three steps. The initial “turn-on” state with a strong signal is the first step. The “turn-off” state provoked by introduction of a quencher probe is the second step. The “switch-on” state, which can be restored when the target was introduced to expend the quencher probe, is called the third step. Thus, this “on–off–on” mode endows the sensor with not only high sensitivity and low background signal, but also superior specific recognition ability [28]. However, the current “on–off–on” mode mostly relies on traditional fluorescent probes, and the synthesis process of fluorescent probes is often difficult and time-consuming [29]. Therefore, a simple, fast and sensitive method will be helpful to further promote the use of “on–off–on” mode in practical application. It is also well known that sulfide anion exhibits stable inherent affinity for metal ions such as zinc ($K_{sp}$ for ZnS = 2 × 10$^{-25}$), copper ($K_{sp}$ for CuS = 6 × 10$^{-36}$) and mercury ($K_{sp}$ for HgS = 2 × 10$^{-53}$) [24]. So, based on this property, H$_2$S can be used as an intermediate for the detection of heavy metal ions. Because of the strong intrinsic affinity of sulfide anion for mercury ($K_{sp}$ for HgS = 2 × 10$^{-53}$) [24], the detection of mercury ions can be realized using the principle that H$_2$S and Hg$^{2+}$ react to generate HgS (Hg$^{2+}$ + H$_2$S = HgS + 2H$^+$). Recently, colorimetric sensors have attracted a lot of attention and have been regarded as hopeful for recognizing pollutants in practical samples due to the advantages of low consumption, rapid output, high sensitivity, naked-eye sensing and suitable for real-time field analysis [30–32]. Based on this, we constructed a simple colorimetric platform for detection of H$_2$S and Hg$^{2+}$ for the first time in an “on–off–on” mode. Briefly, on account of the good oxidase-like of MnO$_2$/MWCNTs, TMB was oxidized directly to blue product ox TMB in the absence of oxidant (“signal-on” state). When the H$_2$S is presented, the oxidase activity of MnO$_2$/MWCNTs composite is greatly weakened due to the competitive reactions of H$_2$S and TMB with MnO$_2$/MWCNTs (“off” mode). Based on the color of TMB and the change of the absorbance at 652 nm, the colorimetric detection of H$_2$S can be realized by the reaction system of MnO$_2$/MWCNTs composite and TMB. But, when Hg$^{2+}$ is introduced into the reaction system, Hg$^{2+}$ can react with H$_2$S to generate HgS, resulting in the reduction of H$_2$S in the system, so the mimic oxidase activity of MnO$_2$/MWCNTs composite was retained and the absorbance of the ox TMB increased with the concentration of Hg$^{2+}$ (“switch-on” state). Therefore, based on the reaction between MnO$_2$ and TMB, H$_2$S and MnO$_2$, H$_2$S and Hg$^{2+}$, the detection of H$_2$S or Hg$^{2+}$ in water can be realized through the “on–off–on” of the reaction system signal.

**Experimental**

**Chemicals and materials**

All reagents used were of analytical reagent grade. Carboxylic Multi-walled Carbon Nanotubes (MWCNTs, > 95%) and Manganese (II) sulfate (MnO$_2$S, anhydrous) were obtained from Macklin Biochemical Co., Ltd. (Shanghai, China). Potassium permanganate (KMnO$_4$, > 99.8%) was purchased from Chuandong Chemical Co., Ltd. (Chongqing, China). Sodium sulfide nonahydrate (Na$_2$S·9H$_2$O, 98.0%) was obtained from Xilong Scientific Co., Ltd. 4,3,3,5,5-tetramethylbenzidine (TMB) was obtained from Yuanye Biotechnology Co., Ltd. (Shanghai, China). Dimethyl sulfoxide (DMSO, AR), Acetic acid glacial (AR, > 99.5%), Sodium acetate (AR, > 99%), Sodium phosphate dibasic (Na$_2$HPO$_4$, 99.0%) and sodium dihydrogen phosphate (NaH$_2$PO$_4$) were purchased from Tianjin cameo chemical reagent (Tianjin, China). Citric acid (AR, > 99.5%) and trisodium citrate dehydrate (AR, > 99%) was purchased from Youpu reagent Co., Ltd (Tianjin, China). Mercury chloride (HgCl$_2$, > 99.5%) was purchased from Silver Lake Chemical Co., Ltd. (Guizhou, China). Tris(hydroxymethyl) aminomethane (Tris, ultra-pure grade) was purchased from Solarbio Co., Ltd. The experimental water was all ultra-pure water, which was from tap water purified by a Water Milli-Q system (Merck KGaA, Germany).

**Equipments**

X-ray diffraction (XRD) analysis was performed on a Shimadzu XRD-6000 diffractometer (Shimadzu, Shimadzu, Japan). Scanning electron microscope (SEM) characterization was completed on HITACHI SU5000 (Hitachi, Japan). The characterization of elements was carried out by the X-ray Photon spectroscopy (XPS, Thermo, SCIENTIFIC ESCALAB Xi+, USA) and pH was monitored by pHST-310 Ohaus pH meter (USA). The UV–Vis absorption spectra were tested on a UV-5500PC UV–Visible spectrophotometer (Metash, Shanghai, China). The FT-IR characteristic measurement was carried out by L1600400 Spectrum Two infra-red spectrometer (PerkinElmer, Llantrisant, UK). Raman spectra were acquired by a micro-Raman spectrometer (Thermo, Dxr 2Xi, USA) equipped with 785 nm wavelength excitation lasers.
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Synthesis of MnO$_2$/MWCNTs

The synthesis process of MnO$_2$/MWCNTs was based on Gong’s methods and modified slightly [33]. Like the reported method, the acid-treated MWCNTs (0.0216 g) were added into 33.3 mL (0.095 M) KMnO$_4$ solution and stirred for 48 h in order to facilitate MnO$_4^-$ to adsorb on the wall of MWCNTs. After that, 33.3 mL MnSO$_4$ (0.085 M) solution was added drop by drop and stirred strongly, then the obtained reaction mixture was sonicated for 15 min. Finally, the suspension was centrifugated, washed several times with distilled water until the purple color disappears, and dried at 60 °C. The dark brown product was ground finely and stored at 4 °C for later use.

Colorimetric detection of H$_2$S and Hg$^{2+}$

The principles of detection of H$_2$S and Hg$^{2+}$ are illustrated in Scheme 1. MnO$_2$ nano-materials are an efficient biomimetic oxidase and have been used in catalysis and sensor fields broadly because of the merits of high activity, low cost, strong stability, abundant availability and environmental friendliness [34–37]. Excitingly, we found that the intrinsic oxidase activity of MnO$_2$ doped with MWCNTs can be significantly enhanced. Because of the excellent oxidase activity of MnO$_2$/MWCNTs, it can oxidize TMB solution into ox TMB (“on” Mode). In the presence of H$_2$S, MnO$_2$ reacts with H$_2$S to form Mn$^{2+}$ ions, which weakens the mimic enzyme activity of MnO$_2$. It can effectively inhibit the generation of ox TMB, so the color of reaction system changes from dark to light (“off” Mode). However, when Hg$^{2+}$ ions are introduced into the reaction system, Hg$^{2+}$ can react with H$_2$S to form HgS, so that the mimic oxidase activity of MnO$_2$/MWCNTs composite was retained and TMB is oxidized by ox TMB (“on” Mode).

The detection of H$_2$S was carried out in a 1.5 mL centrifugal tube, which containing 700 μL of the 0.6 M NaAC–HAC (pH = 4.5) buffer solution, 6 μL MnO$_2$/MWCNTs composite (0.5 mg/mL) and 140 μL different concentrations of Na$_2$S solution (100 μM, 80 μM, 60 μM, 40 μM, 20 μM 1 μM). After incubating at room temperature for 1 h, 100 μL TMB (6 mM) was added for 3 min. Finally, the absorption spectra recorded by a UV–Vis multiscan spectrometer.

Similar to the detection method for H$_2$S, different concentrations of Hg$^{2+}$ (10 and 100 µM) were added to the reaction system. Briefly, 700 μL NaAC–HAC (0.6 M) solution, 140 μL Hg$^{2+}$ and 140 μL Na$_2$S solution (100 μM) were added into the tube and reacted for 10 min to generate HgS and the formation of H$_2$S in the reaction system is reduced. Afterwards, 6 μL MnO$_2$/MWCNTs composite was added quickly and incubated at room temperature for 50 min. The last, TMB (100 μL) was added to react for 3 min and the absorption spectra were collected like the above detection of H$_2$S.

Results and discussion

Characterization of materials

To ensure the success of the experiment, it was necessary to confirm whether the MnO$_2$/MWCNTs composite was synthesized successfully. Primarily, the morphology of MWCNTs and MnO$_2$/MWCNTs was characterized by SEM (Fig. 1A, B). From Fig. 1A, we can see that MWCNTs show the long tubular features. And we dimly saw that MWCNTs were completely wrapped by the synthesized MnO$_2$ (Fig. 1B). XPS was used to analyze the quantitative elemental of the MnO$_2$/MWCNTs composite. In the survey spectrum of MnO$_2$/MWCNTs composite (Fig. 1C), all the elements of manganese (Mn 2p, Mn 2s), oxygen (O 1s peak) and carbon (C 1 s peak) in the composite can be observed. In the XPS spectrum of MnO$_2$/MWCNTs composite (Fig. 1C), the energy separation of Mn 2p$_{3/2}$ and Mn 2p$_{1/2}$ was 11.8 eV, indicating that Mn$^{4+}$ formed predominantly in the MnO$_2$ [38]. The O 1s spectra (Fig. 1E) could be separated...
into three distinct peaks, the O 1s peak at 529.6 eV is due to the lattice oxygen ions bound to Mn, and the peaks at 531.0 eV and 532.4 eV are relevant to oxygen atoms in the surface hydroxyl groups and adsorbed water, respectively [39]. XPS data for high-resolution C1s peaks were also analyzed (Fig. 1F), the main styles of carbon species in MnO2/MWCNTs composite including C–C/C–H (284.8 eV), C–O (284 eV) and C=O (286 eV) were observed, which were assigned to the nanotubes [40].

We also used XRD to study the crystalline phases of MWCNTs and MnO2/MWCNTs composite. As interpreted in Fig. 2A, the diffraction peaks at 2θ values of 26° and 42° in the XRD spectra for the MWCNTs were consistent with literature reports [34]. In the XRD patterns of the synthesized MnO2/MWCNTs composite, the distinct diffraction peaks at 2θ values of 12°, 24°, 37°, and 65° were related to the MnO2, consistent with literature reports [41]. The Raman spectroscopy equipped with 785 nm wavelength excitation lasers was used for characterizing the structures of the MnO2/MWCNTs composite, as demonstrated in Fig. 2B. The D band at 1344.0 cm⁻¹ is attributed to the disorder or the defect of MWCNTs-COOH, the G band at 1579.2 cm⁻¹ was fixed with the transformation of sp² aromatic carbon into sp³ carbon, the existence of a G band and D band strongly confirmed the existence of the MWCNTs [41, 42]. What is more, the characteristic band of the symmetric stretching vibration of ν₂ (Mn–O) in the MnO₂ groups centered at 640 cm⁻¹ was also detected, which strongly proves the successful synthesis of MnO₂/MWCNTs composite [41]. The oxygen-containing groups of MnO₂/MWCNTs composite were analyzed by FT-IR spectroscopy. In the FT-IR spectra of MWCNTs (Fig. 2C), the characteristic peaks at 3428.98 cm⁻¹ was related with the stretching vibrations of hydroxyl group (O–H), the characteristic peaks at 1748.02 cm⁻¹, 1630.26 cm⁻¹, 1567.5 cm⁻¹ and 1042.04 cm⁻¹ were, belong to C=O of carboxyl group, C=C bonds, the conjugated –C=C– bonds of aromatic ring and the asymmetrical stretching vibrations of C–O–C, respectively. For the FT-IR spectra of MnO₂, the stretching vibrations of Mn–O can be found at 518.75 cm⁻¹. And the characteristic peaks of MnO₂ and MWCNTs can be found in the FT-IR spectra of MnO₂/MWCNTs composite, which showing that MnO₂/MWCNTs composite was combined triumphantly [38]. Besides, we also used the UV–Vis absorption spectra to research the formation of MnO₂/MWCNTs composite. As depicted in Fig. 2D, a wide UV–Vis absorption band ranging from 300 to 600 nm of MnO₂ can be observed [43], while carbon nanotubes dispersion has no observable peak in visible range. The above results strongly demonstrate the successful synthesis of MnO₂/MWCNTs composite.
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Feasibility of the designed colorimetric method

It is important to evaluate the oxidase-mimicking activity of the prepared MnO$_2$/MWCNTs composite, which can directly affect the signal response of TMB. Primarily, the oxidation activities of MWCNTs, MnO$_2$ and MnO$_2$/MWCNTs composite at the same concentration (2.0 mg/mL) were investigated. As depicted in Fig. 3A, MnO$_2$/MWCNTs composite revealed a high oxidase activity compared with other components, such as MWCNTs, MnO$_2$, Mn$^{2+}$. Moreover, except for MnO$_2$ and MnO$_2$/MWCNTs composite, other components basically have no absorption peak at 652 nm, which further proves the irreplaceability of the composite. To further prove the oxidase activity of the synthesized MnO$_2$/MWCNTs composite, we also studied the effect of the addition of hydrogen peroxide (H$_2$O$_2$) on the experimental results. As revealed in Fig. 3B, the introduction of H$_2$O$_2$ weakened the oxidase activity of MnO$_2$/MWCNTs. This may be due to the reduction of MnO$_2$ to Mn$^{2+}$ by H$_2$O$_2$ [44]. Furthermore, we also initially explored the feasibility of the proposed

Fig. 2 A XRD pattern of MWCNTs and MnO$_2$/MWCNTs composite. B Raman spectra of MnO$_2$/MWCNTs composite with 785 nm laser excitations. C FT-IR spectra of MWCNTs, MnO$_2$ and MnO$_2$/MWCNTs. D UV–vis absorption spectra of MWCNTs, MnO$_2$ and MnO$_2$/MWCNTs.

Fig. 3 A UV–Vis spectra responses of different materials react with TMB at the same concentration (2.0 mg/mL). B UV–Vis absorption spectra of different materials (2.0 mg/mL) reacted with TMB with or without H$_2$O$_2$. C UV–Vis absorption spectra of the addition of H$_2$S and Hg$^{2+}$ at different concentrations (the concentration of MnO$_2$/MWCNTs composite is 0.5 mg/mL).
colorimetric strategy for detecting H$_2$S and Hg$^{2+}$. As shown in Fig. 3C, with different concentrations of H$_2$S were added (1 µM, 100 µM) the color and absorption peak at 652 nm of ox TMB also decreased with the H$_2$S induced decomposition effect. However, it is interesting that when Hg$^{2+}$ was introduced, the absorbance values of ox TMB at 652 nm can increase with the increase of Hg$^{2+}$ concentration. These results strongly prove the possibility of using the colorimetric sensor for H$_2$S and Hg$^{2+}$ detection. In addition, we also studied the oxidase activity of the synthesized MnO$_2$/MWCNTs using a color-producing reaction. The presence of MnO$_2$/MWCNTs can oxidize the substrate TMB to form blue ox TMB. We also calculated the value of $K_m$ (2.86 mM) and $V_{max}$ (5.13 × 10$^{-8}$ Ms$^{-1}$) for MnO$_2$/MWCNTs according to Michaelis–Menten kinetics ($v = V_{max}[S]/(K_m + [S])$, where [S] is the concentration of substrate, $v$ is the initial velocity, $K_m$ is the Michaelis–Menten constant, and $V_{max}$ is the maximal reaction velocity. We also compared this composite with other oxidase mimics (Fig. S1 and Table S1), and ultimately found that MnO$_2$/MWCNTs exhibits good oxidase activity (the detailed calculation process is presented in the Supplementary information).

**Optimization of experimental parameters**

To acquire the best performance of the colorimetric method, the important experimental conditions were optimized, such as the amount of MnO$_2$/MWCNTs composite, buffer type, pH of NaAC–HAC buffer, reaction time between the MnO$_2$/MWCNTs composite and H$_2$S, reaction time between H$_2$S and Hg$^{2+}$, the reaction time between the TMB substrate and MnO$_2$/MWCNTs composite, etc. First, as indicated in Fig. S2A, the optical absorption behavior of ox TMB as a function of the concentration of MnO$_2$/MWCNTs composite, when the concentrations of MnO$_2$/MWCNTs composite were increased, the color of the reaction solutions gradually deepened and the absorbance at 652 nm of the solutions increased. As seen from Fig. S2B, we investigated the effect of MnO$_2$/MWCNTs on TMB oxidation in several commonly used buffer solutions, such as NaAC–HAC buffer (0.6 M, pH = 4.5), Phosphate buffer solution (NaH$_2$PO$_4$–Na$_2$HPO$_4$, 0.2 M, pH = 4.5), Tris–HCl buffer (Tris–HCl, 0.05 M, pH = 4.5), Citric acid–Sodium citrate buffer (CA–CANa, 0.1 M, pH = 4.5), Citric acid–Sodium hydroxide–Hydrochloric acid buffer (CA–NaOH–HCl, pH = 4.5), Sodium phosphate dibasic–Citric acid buffer (Na$_2$HPO$_4$–CA, pH = 4.5). It is obvious from the results that the NaAc buffer has the best response effect, so the NaAc buffer is selected as the reaction buffer solution. The oxidation effect of MnO$_2$/MWCNTs composite and the signal response of the reaction system can be affected by the pH value of buffer. Therefore, the influence of NaAC–HAC buffer with different pH values was investigated, as described in Fig. S2C, the absorbance value reached the maximum when the buffer pH was 4.5, which showed that pH 4.5 was used for H$_2$S and Hg$^{2+}$ detection in this system.

Because the H$_2$S can decompose MnO$_2$ in acidic conditions, the reaction time of H$_2$S and composite would affect the signal response of the system. So, we optimized the reaction time of H$_2$S and MnO$_2$/MWCNTs composite. As exhibited in Fig. S3A, with the increase of reaction time of H$_2$S and MnO$_2$/MWCNTs composite, the response signal was basically stable after 1 h. When the system was used for Hg$^{2+}$ detection, the reaction time of H$_2$S and MnO$_2$/MWCNTs composite would become stable after 50 min of reaction (Fig. S3B). Of course, the reaction time of H$_2$S and Hg$^{2+}$ to generate HgS was also studied, as performed in Fig. S3C, when the reaction reaches 10 min, the absorbance of the system reaches the maximum. In addition, we also explored the reaction time of MnO$_2$/MWCNTs composite to oxidize TMB. As shown in Fig. S3D, when MnO$_2$/MWCNTs composite reacted with TMB, after 3 min of reaction, the absorbance value of ox TMB tend to be steady. Consequently, we selected 3 min as the reaction time between the TMB substrate and MnO$_2$/MWCNTs composite. Besides, we studied the characteristic absorption peak of MnO$_2$/MWCNTs composite at 300–600 nm in different concentrations of H$_2$S to further demonstrate that H$_2$S can resolve MnO$_2$ in acidic conditions. As showed in Fig. S4, with the concentration of H$_2$S increasing, due to the decomposition of MnO$_2$ by H$_2$S, the characteristic absorption of MnO$_2$/MWCNTs composites also decreased gradually. This result further verifies that H$_2$S can decompose MnO$_2$ into Mn$^{2+}$.

**Analytical performance of colorimetric detection of H$_2$S and Hg$^{2+}$ ions**

To assess the sensing performance of MnO$_2$/MWCNTs for colorimetric detection of H$_2$S and Hg$^{2+}$, various concentrations of H$_2$S and Hg$^{2+}$ under the optimized conditions were measured. As shown in Fig. 4A, the absorbance value progressively decreased upon the increasing H$_2$S concentration, which was consistent with the result of color change in Fig. 4B (inset). Moreover, it can be obtained from Fig. 4B that the absorbance values exhibited a negative correlation with the H$_2$S concentration (1–100 µM). And the linear regression equation was $Y = 0.712 − 0.007X$, $R^2 = 0.998$, the limit of detection (LOD) was 0.96 µM. For Hg$^{2+}$ detection, due to the strong affinity between H$_2$S and Hg$^{2+}$, we selected the H$_2$S concentration (100 µM) with the best inhibitory effect to minimize the absorbance value of the reaction system. When Hg$^{2+}$ ions (10–100 µM) was added, we found that the absorbance intensity of ox TMB was turned on again. And the absorbance value change at 652 nm was in a good linear relationship with the concentration of Hg$^{2+}$ (Fig. 2C, D). The linear equation was $Y = 0.007X − 0.004$. 

$$V = V_{max}[S]/(K_m + [S])$$

Here, $V$ is the initial velocity, $V_{max}$ is the maximum reaction velocity, $K_m$ is the Michaelis–Menten constant, and $[S]$ is the concentration of substrate.
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Fig. 4 A UV–Vis spectra responses of ox TMB with different concentrations of \( \text{H}_2\text{S} \) in NaAc–HAC buffer at 25 °C. B Linear curve in the range of \( \text{H}_2\text{S} \) from 1 to 100 μM. Inset: corresponding visual color. C UV–Vis absorption spectra of ox TMB with different concentrations of \( \text{Hg}^{2+} \) in NaAc–HAC buffer at 25 °C. D Linear curve in the range of \( \text{Hg}^{2+} \) from 10 to 100 μM. Inset: plot of correlation concentrations and corresponding visual color. Experimental conditions were the same as the optimized results. The error bars represented the standard deviations based on three independent measurements.

(\( R^2 = 0.993 \)) with a LOD for \( \text{Hg}^{2+} \) of 1.84 μM. In addition, to further demonstrate the practical application ability of this method, we also compared the built approach to other existing approaches for \( \text{H}_2\text{S} \) and \( \text{Hg}^{2+} \) detection (Table S2). The data in this table show that the linear concentration range and detection limit of \( \text{Hg}^{2+} \) determination at the proposed strategy were similar to those methods. These results further proved the application ability of this method in actual sample detection.

Selectivity, reproducibility and stability of the colorimetric method

To evaluate the selectivity of the constructed colorimetric method to \( \text{H}_2\text{S} \) and \( \text{Hg}^{2+} \), several common ions in water were researched under the same conditions. As observed from Fig. 5A, it can be clearly observed that only \( \text{H}_2\text{S} \) can significantly inhibit signal generation. Conversely, other ions could hardly lead to a visible decrease in the signal even their concentration is ten times higher than that of \( \text{H}_2\text{S} \) (80 μM). Although glutathione (GSH) also causes decreased signaling, it will not cause much disruption because GSH is not common in aquatic samples. Beyond that, we also investigated the selectivity of this method for \( \text{Hg}^{2+} \) detection. Potential interference from other metal ions was investigated by evaluating the response of the sensor to 60 μM Cu\(^{2+}\), Ag\(^{+}\), Cd\(^{2+}\) and 600 μM K\(^+\), Mg\(^{2+}\), Ca\(^{2+}\), Fe\(^{3+}\), Mn\(^{2+}\) and Zn\(^{2+}\). As performed in Fig. 5B, it was worth noting that compared with other interfering ions mercury ions can cause a significant signal response. This result may be related to the formation of extremely insoluble sulfide (HgS, \( K_{sp} = 2 \times 10^{-53} \)) by the reaction of \( \text{Hg}^{2+} \) and \( \text{H}_2\text{S} \). And we also assessed the reproducibility of the proposed method, as presented in Fig. 5C, D intra-batch and inter-batch experiments were used to verify the repeatability of the constructed method. The same batch of synthetic MnO\(_2/\)MWCNTs composite was used to test \( \text{Hg}^{2+} \) ions with three different concentrations (40 μM, 60 μM, 80 μM). The results showed that the RSD between the three groups of parallel experiments is less than 3.50%. Three batches of materials synthesized at different times were used to detect \( \text{Hg}^{2+} \) ions with three different concentrations (40 μM, 60 μM, 80 μM). As shown in Fig. 5D, the RSD values of the results were less than 3.98%. What is more, five independent measurements of 80 μM \( \text{Hg}^{2+} \) were performed in Fig. 5E, and the RSD values of the results were 1.90%, indicating that the method has good reproducibility. Furthermore, we also explore the stability of the synthesized MnO\(_2/\)MWCNTs composite with the reason that it played a very important role in the process of sample detection. The stability of the composite was tested every 5 days for up to 30 days, as shown in Fig. 5F, the signal response is still the same as the initial values and the RSD values of 7 tests is less than 4.14%. This result strongly proves that the composite has excellent stability and also
indicates the potential of the MnO₂/MWCNTs composite for long-term application.

**Detection of H₂S and Hg²⁺ real samples**

To further value the potential application and feasibility of the “on–off–on” colorimetric sensor, we examined H₂S and Hg²⁺ in actual samples, we took the tap water and lake water and (obtained from Yue Lake on the campus of Guizhou University) to prepare H₂S (40 μM, 60 μM, 80 μM) and Hg²⁺ (40 μM, 60 μM, 80 μM) solution to perform experiment. We used a 0.22 μm membrane to remove the impurities in the lake water samples, and tap water is not treated in any way. As revealed in Fig. S5A and B, the detection results of lake water and tap water are in good agreement. As shown in Table 1, we check the recovery and precision of the proposed method. The results in the table showed that the obtained recovery rates were satisfactory and the recovery rates of H₂S in tap water and lake water were 108.08–104.5% and 101.77–108.56%, respectively. And the recovery values of Hg²⁺ in tap water and lake water were 95.82–109.51% and 99.48–106.34%, respectively. In order to further explore the application of this method in more complex samples, we also detected H₂S in orange juice samples. The treatment process is shown in supporting information, and the results are shown in Table S3. These results indicated that the constructed “on–off–on” colorimetric pattern has good detection ability for H₂S and Hg²⁺, which supplied a likely strategy for quick, simple and effectively detection of H₂S and Hg²⁺ in water.

**Conclusions**

In this work, we proposed a low-cost, rapid and convenient method for colorimetric detection of H₂S and Hg²⁺ based on a signal “on–off–on” mode. Based on “on–off–on” color and spectral change with H₂S and Hg²⁺, the constructed “on–off–on” colorimetric pattern can be used for the detection of H₂S or Hg²⁺ by the decomposition of MnO₂/MWCNTs composite by H₂S and the principle of the formation of extremely insoluble sulfide (HgS) between H₂S and Hg²⁺. Moreover, during the signal generation process, the proposed tactics do not require any reiterant separation and extraction process, which simplifies the process of producing a signal that requires multiple reactions in an experiment. Therefore, the introduction of other interfering substances during the experiment can be avoided, and further improve
the accuracy of the detection results. What is more, the proposed “on–off–on” mode sensor has acceptable results for H₂S and Hg²⁺ detection in actual samples, which further prove the application ability of the proposed method in actual sample testing. In brief, in this work we not only constructed a convenient and efficient colorimetric detection platform, which can be used to detect H₂S and Hg²⁺ in water, expanding its application prospect in environmental, food analysis and biological, but also supplying ideas for the exploited of new-type and high-performance artificial enzyme simulation based on nano-materials.

Supplementary Information  The online version contains supplementary material available at https://doi.org/10.1007/s44211-022-00171-x.

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