

Graphene quantum dots combined with copper(II) ions as a fluorescent probe for turn-on detection of sulfide ions

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Abstract A fluorescent probe for the sensitive and selective determination of sulfide ions is presented. It is based on the use of graphene quantum dots (GQDs) which emit strong and stable blue fluorescence even at high ionic strength. Copper(II) ions cause aggregation of the GQDs and thereby quench fluorescence. The GQDs-Cu(II) aggregates can be dissociated by adding sulfide ions, and this results in fluorescence turn on. The change of fluorescence intensity is proportional to the concentration of sulfide ions. Under optimal conditions, the increase in fluorescence intensity on addition of sulfide ions is linearly related ($r^2=0.9943$) to the concentration of sulfide ions in the range from 0.20 to 20 μM , and the limit of detection is 0.10 μM (at 3 σ /s). The fluorescent probe is highly selective for sulfide ions over some potentially interfering ions. The method was successfully applied to the determination of sulfide ions in real water samples and gave recoveries between 103.0 and 113.0 %.

Keywords Graphene quantum dots · Copper(II) ions · Fluorescent probe · Sulfide ions · Quenching · Fluorescence recovery

Introduction

Graphene, a one-atom thick and two-dimensional honeycomb lattice of sp^2 hybridized carbon atoms, has achieved great interest within the scientific research in recent years. Graphene is a promising step for future nanodevices because of its properties, such as large surface area, good electronic transportation, superior mechanical flexibility, energy-storage media, and environmental friendly nature [1–5]. A new kind of zero-dimensional fluorescent material called graphene quantum dots (GQDs) is obtained when the graphene sheet is smaller than 100 nm [6]. As a new kind of luminescent carbon nanomaterial, GQDs have a superior chemical inertness, higher surface area, and larger diameter compared with conventional QDs and carbon dots [7]. Due to the pronounced quantum confinement and edge effects, GQDs possess high photoluminescence, slow hot-carrier relaxation, and useful in the construction of nanoscale optical and electronic devices [8, 9]. Importantly, the carboxylic acid moieties at the edge impart GQDs with excellent water solubility, which eases the function with various organic, polymeric, inorganic or biological species [10]. In addition, the low toxicity and good biocompatibility of GQDs have been reported [11, 12]. These distinct advantages make GQDs have a great promising material to replace the commonly used semiconductor nanocrystals for a number of optical biosensing and bioimaging related applications [13–15].

The concentration of sulfide ions is an important environmental index, because sulfide ions have a lethal property at high concentrations [16]. Moreover, sulfide ions can irritate mucous membranes and even have an extreme action on the

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nerve system, which cause unconsciousness and respiratory paralysis [17]. In addition, sulfide ions levels are related to various diseases, such as Alzheimer's disease [18], Down's syndrome [19], and liver cirrhosis [20]. Therefore, developing a rapid and sensitive method for monitoring sulfide ions is highly important to ensure human health safety. Great progress has been made regarding sulfide ions detect devices in the past several years, such as chromatography [21], titration [22], extraction [23], fluorimetry [24], spectrophotometry [25], and an electrochemical method [26]. Considering practicality and convenience, fluorimetry method is acceptable. Thus, many fluorescent probes have been reported recently for the detection of sulfide ions.

Sulfide ions can react with copper ions to form stable CuS species, which has a low-solubility product constant ($K_{\text{sp}} = 6.3 \times 10^{-36}$). With this property, we designed a GQDs- Cu^{2+} system that acts as an effective fluorescent probe for sulfide ions detection in water. The oxygen-containing groups on the GQDs surface can interact with Cu^{2+} ions, leading to fluorescence quenching of the GQDs [27]. When sulfide ions were added to the assay solution, a turn on fluorescence signal was detected. The change of fluorescence intensity was proportional to the concentration of sulfide ions. Thus, the on-off-on switching in the fluorescence of GQDs was expected to provide a quantitative determination of sulfide ions in water samples.

Experimental

Reagents

$\text{Hg}(\text{NO}_3)_2$, AgNO_3 , $\text{Cd}(\text{NO}_3)_2$, $\text{Mn}(\text{NO}_3)_2$, FeCl_3 , BaCl_2 , AlCl_3 , MgCl_2 , ZnCl_2 , CaCl_2 , KCl , NH_4Cl , Na_2S , CuCl_2 , NaF , NaCl , NaBr , NaI , NaClO , CH_3COONa , NaNO_2 , NaNO_3 , Na_2CO_3 , Na_2HPO_4 , Na_2SO_4 , Na_2SO_3 , $\text{Na}_2\text{S}_2\text{O}_3$, NaSCN , NaOH , H_3BO_3 , and $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$ were obtained from Sinopharm Chemical Reagent (Shanghai, China) (<http://www.sinoreagent.com/>). H_2SO_4 and HNO_3 were purchased from Yantai Shuangshuang Chemical Co., Ltd (Yantai, China) (<http://shuang-pla.51pla.com/>). Graphene oxide (GO) was purchased from SXFNANO Materials Tech Co., Ltd (Nanjing, China) (<http://graphene.cn.china.cn/>). All other chemical agents used were of analytical grade and used without further purification.

Synthesis of graphene quantum dots

GQDs were synthesized according to previously described methods [27]. In summary, GO (5 mg) reacted with concentrated H_2SO_4 (30 mL) and HNO_3 (10 mL) for 5 h under ultrasonic conditions using the ultrasonic cleaner. To obtain a solid product, the suspension was diluted with distilled water

(250 mL) and centrifuged for 15 min ($10464.48 \times g$). The solid product was redispersed in distilled water (50 mL), and the pH was adjusted to 12 with NaOH. The suspension was moved into a poly(tetrafluoroethylene) (Teflon)-lined autoclave (100 mL) and heated at 180°C for 10 h. After cooling at room temperature, the black suspension was filtered through a $0.22 \mu\text{m}$ microporous membrane to obtain a pellucid filtered solution. The filtrated solution was dialyzed using the dialysis bag (8000–14000 Da) for 24 h. Consequently, blue fluorescent GQDs were achieved.

Characterization

Fourier transform infrared (FT-IR) spectra were recorded using an FT-IR spectrophotometer (Nicolet 5700, Thermo Electron Corporation, MA, USA) at resolution of 4 cm^{-1} in the range of $600\text{--}4000 \text{ cm}^{-1}$. UV-vis absorption spectra were recorded on a Thermo Scientific NanoDrop 2000/2000C spectrophotometer (USA) using a 1 cm path length quartz cell. Zeta potential and size distribution were measured using a Malvern Zeta/sizer Nano-ZS90 (ZEN3590). Transmission electron microscopy (TEM) analyses were performed on a JEM-1230 electron microscope (Japan) operating at 100 KV. The TEM samples were prepared by drying a droplet of GQDs solution on a Cu grid. Fluorescence intensity was recorded on the luminescence spectrometer (Perkin-Elmer LS-55, Perkin-Elmer Instruments, UK). Raman spectra were collected using INVIA spectrophotometer (Renishaw, UK) with the excitation wavelength at 514 nm.

Procedure for detecting sulfide ions

GQDs ($20 \mu\text{L}$, $80 \mu\text{g mL}^{-1}$), CuCl_2 ($10 \mu\text{L}$, 1 mM) were mixed with boron boric acid buffer (40 mM, pH 7.0, $960 \mu\text{L}$) and incubated for 1 min to obtained the GQDs- Cu^{2+} system. Different concentrations of sulfide ions ($10 \mu\text{L}$) were added into the GQDs- Cu^{2+} system and incubated for 1 min. The fluorescent intensity of the resulting solution was recorded from 380 to 600 nm through excitation with 320 nm light. The spectral bandwidths were set as 5 nm. The procedure of sulfide ions detection was conducted at room temperature.

Selectivity and interference of probe

Sulfide ions ($10 \mu\text{L}$, $20 \mu\text{M}$) and these potentially interfering ions (SCN^- , $\text{S}_2\text{O}_3^{2-}$, SO_3^{2-} , SO_4^{2-} , PO_4^{3-} , CO_3^{2-} , NO_3^- , NO_2^- , AC^- , ClO^- , I^- , Br^- , Cl^- , and F^-) ($10 \mu\text{L}$, $200 \mu\text{M}$) were added into the GQDs- Cu^{2+} system, respectively, and then the fluorescence spectra were detected for investigation the selectivity of probe. For interference experiment, sulfide ions ($10 \mu\text{L}$, $20 \mu\text{M}$) were added into the GQDs- Cu^{2+} -anion system, and the fluorescence spectra were detected.

Analysis of sulfide ions in water samples

Drinking water and tap water samples were obtained from a local water supply system, and were filtered through a 0.22 μm membrane. Water samples were spiked with known concentrations of sodium sulfide solutions following the standard addition method. The spiked samples were then added into the GQDs- Cu^{2+} system, and the fluorescence spectra were detected.

Results and discussion

Characterization of graphene quantum dots

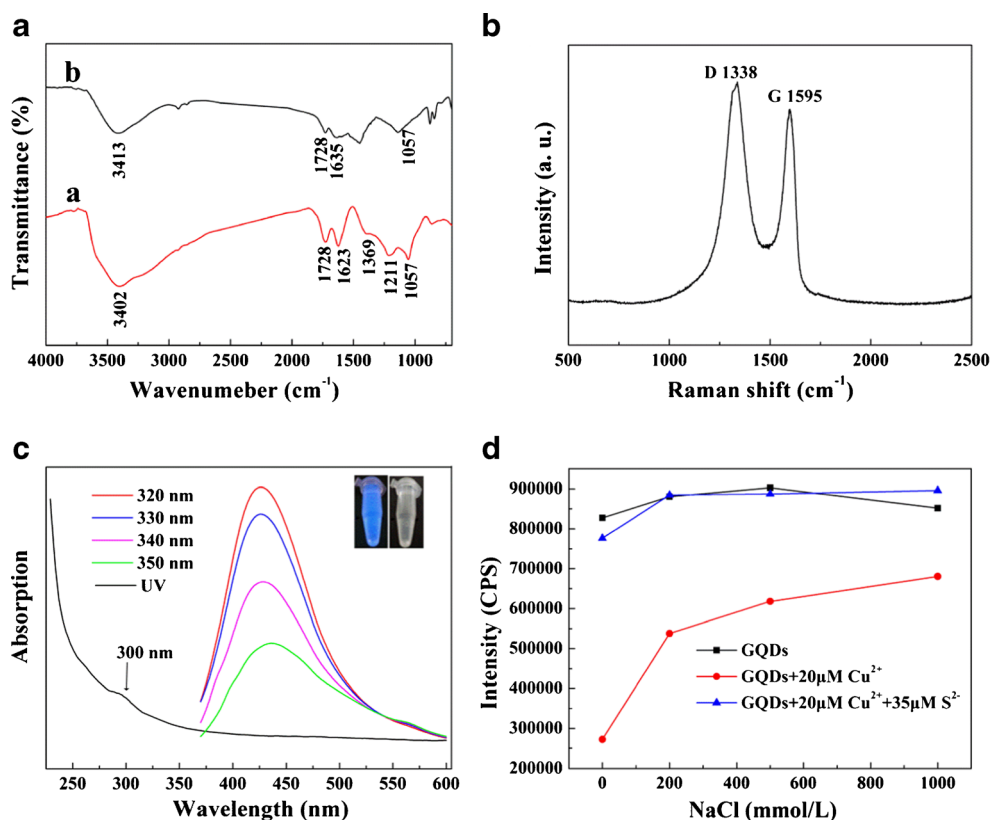
The structure of GQDs and GO were characterized via FT-IR, and the results are shown in Fig. 1a. Compared with the spectrum of GO, the band of carboxyl (1728 cm^{-1}) and hydroxyl groups (3413 cm^{-1}) of GQDs dramatically decreased, and the epoxy groups ($1369\text{--}1057\text{ cm}^{-1}$) almost disappeared. These results suggest that a few oxygen-containing functional groups were destroyed during the reaction, and the GO were changed into small photoluminescent species [28]. The Raman spectroscopy of the GQDs (Fig. 1b) shows the partially

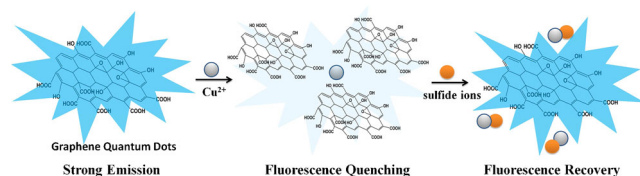
disordered crystal structure of GQDs that the scattering at the edges caused [29].

The UV-vis absorption spectrum and fluorescence emission spectra of GQDs are shown in Fig. 1c. The GQDs solution has a broad absorption with a weak shoulder at approximately 300 nm. These results are consistent with those from a previous report [27]. The fluorescence spectrum of the GQDs has a strong peak at 427 nm when the excitation was 320 nm. Similar to most fluorescent carbon-based nanomaterials, GQDs possessed the property of excitation-dependent fluorescence behavior. As shown in Fig. 1c, the fluorescence spectrum peaks of the GQDs shift from 427 to 436 nm with the excitation wavelength increasing from 320 to 350 nm. This excitation-dependent fluorescence behavior may result from the optical selection of differently sized GQDs and surface defects of GQDs [30]. As shown in the inset, the GQDs exhibit an intense blue fluorescence color under irradiation with 365 nm UV light.

To determine the stability of GQDs under a highly ionic strength environment, the fluorescence of GQDs was measured in a solution of 40 mM boron boric acid buffer (pH 7.0) containing different concentrations of NaCl. Figure 1d shows that GQDs have stable fluorescence even under high ionic strength conditions and the quenching effect of Cu^{2+} was weakened with the increasing concentration of

Fig. 1 **a** FT-IR spectra of GO (a) and GQDs (b). **b** Raman spectrum of GQDs. **c** UV/Vis absorption and PL spectra of GQDs at different excitation wavelengths (Inset: photographs of an aqueous solution of the GQDs under 365 nm UV light and visible light). **d** The influence of NaCl concentration (0, 200, 400, 600, 800, 1000 mM) on GQDs and the probe fluorescence





Scheme 1 Schematic illustration of the preparation processes of sulfide ions detection based on GQDs- Cu^{2+} systems

NaCl. This finding suggests that GQDs have a great potential for sensing applications under complicated conditions.

Detection principle for sulfide ions

As shown in Scheme 1, GQDs with many oxygen-containing groups act as the electron donors. Cu^{2+} ions can easily combine with the oxygen-containing groups, which functions as the bridge for the resulting in GQDs aggregation. Consequently, the fluorescence of GQDs was quenched through energy or electron transfer process from the GQDs to Cu^{2+} ions. Sulfide ions then had a higher affinity for the electron donors atoms in Cu^{2+} ions than oxygen-containing groups, leading to the dissociation of the GQDs aggregation and the fluorescence was turn on. At that time, the intensity enhancement of the GQDs was directly related to the amount of sulfide ions added to the GQDs aggregation solution. Thus, the on-off-on switching in

the fluorescence of GQDs was expected to provide a quantitative determination of sulfide ions in water samples.

To confirm this principle, transmission electron microscopy (TEM), size distribution and Zeta potential were performed. Figure 2 shows the morphology and size distribution of GQDs, GQDs aggregates, and GQDs- Cu^{2+} system with sulfide ions. Figure 2a shows that the GQDs were monodispersed in pure water with an average diameter of 20.22 nm (Fig. 2d). The GQDs aggregated when Cu^{2+} ions were added (Fig. 2b), and the average diameter increased to 483.02 nm (Fig. 2e). However, the GQDs aggregates are redispersed and the average diameter decreased to 28.53 nm when sulfide ions were added (Fig. 2c and f). The zeta potentials of GQDs, GQDs aggregates, and GQDs- Cu^{2+} system with sulfide ions were -33.80 , -13.20 , and -34.10 mV, respectively. These results confirmed that Cu^{2+} can make the GQDs aggregate and the Cu^{2+} induced GQDs aggregation can be destroyed after introducing sulfide ions.

Optimization of experimental conditions

To obtain the best detecting conditions, potential effects of relevant experimental parameters, including the pH, quenching effect of different metal ions, and concentrations of Cu^{2+} were evaluated.

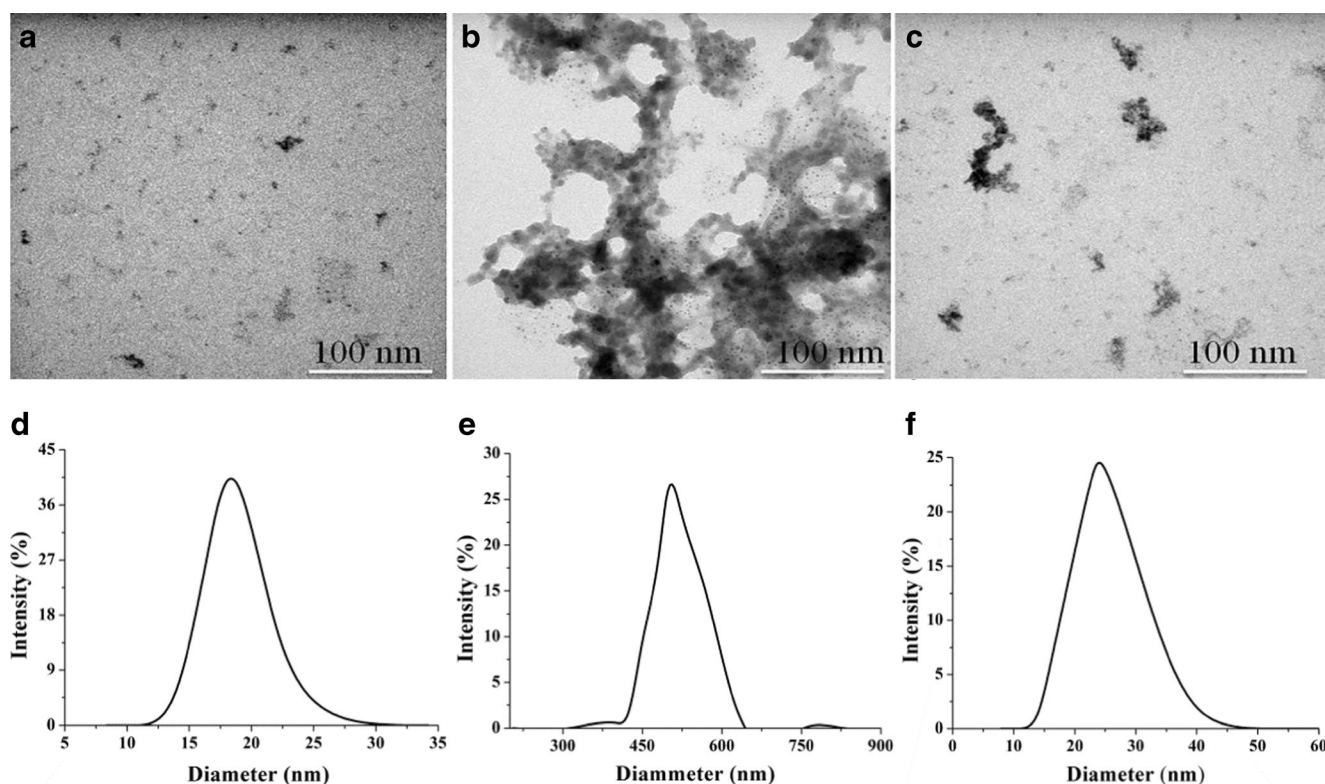


Fig. 2 TEM images: GQDs dispersed in pure water (a), GQDs with addition of $20\ \mu\text{M}$ Cu^{2+} ions (b), and GQDs with addition of $20\ \mu\text{M}$ Cu^{2+} ions and $30\ \mu\text{M}$ sulfide ions (c). Size measurements: GQDs

dispersed in pure water (d), GQDs with addition of $20\ \mu\text{M}$ Cu^{2+} ions (e), and GQDs with addition of $20\ \mu\text{M}$ Cu^{2+} ions and $30\ \mu\text{M}$ sulfide ions (f)

Fig. 3 **a** Fluorescence quenching of the GQDs with addition of Cu^{2+} ions (10 μM) in different pH buffer solutions. **b** Fluorescence quenching of the GQDs with addition of different ions (all ions were at 20 μM). F and F_0 are the fluorescence intensity of the GQDs in the presence and absence of different cations, respectively. **c** Fluorescence quenching of the GQDs with addition of different concentrations of Cu^{2+} ions in buffer solution (pH 7.0, 40 mM). The Cu^{2+} ions concentrations are 0, 1, 4, 7, 10, 20, 40, 80 and 200 μM , respectively. (Inset: fluorescence intensity change at 430 nm as addition with Cu^{2+} ions from 0 to 200 μM). F and F_0 are the fluorescence intensity of the GQDs in the presence and absence of Cu^{2+} ions, respectively

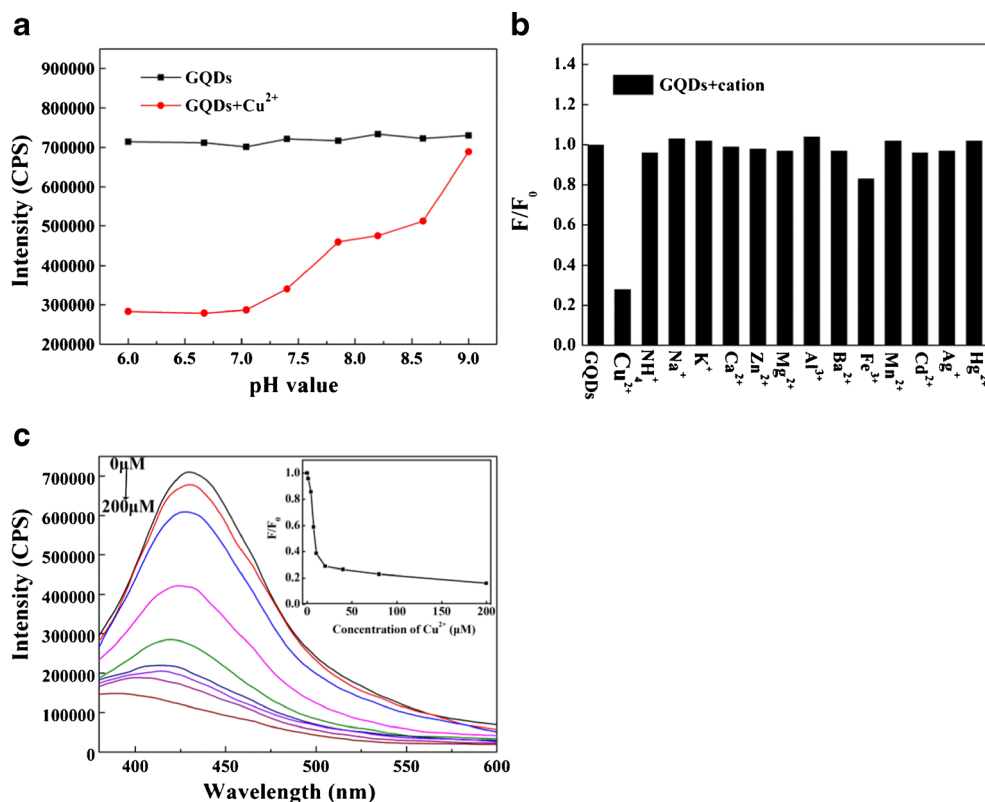


Figure 3a shows that this fluorescence probe is pH-dependent. This result can be ascribed to two reasons. First, the carboxylate groups on the surface of GQDs would be deprotonated in a basic solution, leading to electrostatic repulsion between the GQDs, and preventing the formation of GQDs- Cu^{2+} aggregates. Second, Cu^{2+} reacted with OH^- and formed $\text{Cu}(\text{OH})_2$ at alkaline conditions, and prevented the coordination of Cu^{2+} ions to the oxygen-containing groups of GQDs. Thus, Cu^{2+} ions cannot quench the fluorescent

intensity of GQDs at alkaline conditions. Therefore, the pH 7.0 buffer solution is chosen to obtain high sensitivity and wide linear range.

The quenching effect of different cations, including Cu^{2+} , NH_4^+ , Na^+ , K^+ , Ca^{2+} , Zn^{2+} , Mg^{2+} , Al^{3+} , Ba^{2+} , Fe^{3+} , Mn^{2+} , Cd^{2+} , Ag^+ , and Hg^{2+} were investigated. Cu^{2+} ions have the highest quenching ability for the fluorescence of the GQDs, and Fe^{3+} ions have a slight quenching effect (Fig. 3b). Meanwhile, other ions show little quenching of fluorescence of the

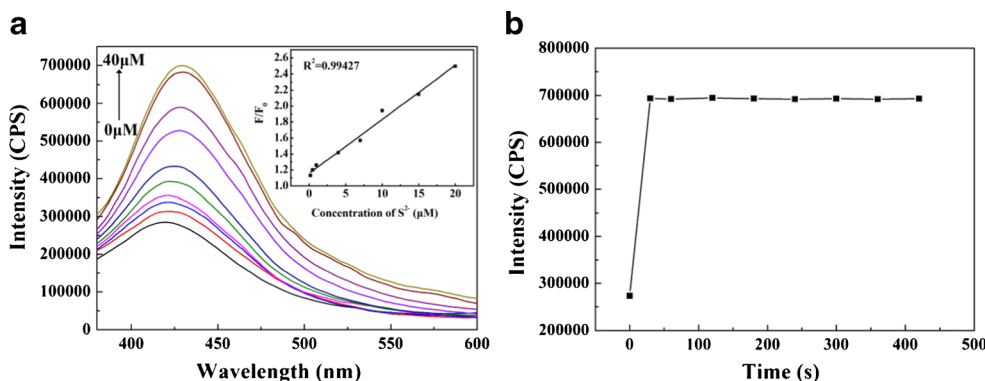


Fig. 4 **a** Fluorescence intensity recovery of GQDs- Cu^{2+} systems with addition of different concentrations of sulfide ions in buffer solution (pH 7.0, 40 mM). The concentrations of sulfide ions are 0, 0.20, 0.50, 1, 4, 7, 10, 15, 20, and 40 μM , respectively. (Inset: Stern-Volmer plot of F/F_0 recovery at 430 nm of GQDs- Cu^{2+} systems with addition of sulfide

ions from 0.20 to 20 μM). F and F_0 are the fluorescence intensity of the GQDs- Cu^{2+} systems in the presence and absence of sulfide ions, respectively. **b** Time-dependent fluorescence intensity recovery of GQDs- Cu^{2+} systems with addition of sulfide ions (sulfide ions were at 20 μM) in buffer solution (pH 7.0, 40 mM)

Table 1 Comparison of optical methods reported in the literature for determination of sulfide ions

Analytical technique	Sample matrix	LDR ¹ (μM)	LOD ² (μM)	Reference
Colorimetric probe ^a	River and tap water	12.00–50.00	8.10	[31]
Colorimetric probe ^b	River water	20–100.00	10.00	[32]
Fluorescent probe ^c	Tap and river water	1.35–10.00	1.35	[33]
Fluorescent probe ^d	Tap and Ground water	1.20–26.00	0.33	[24]
Fluorescent probe ^e	Running water	5.00–35.00	0.15	[34]
Fluorescent probe ^f	Environmental water	3.10–56.30	6.50	[35]
This method	Tap water and drinking water	0.20–20.00	0.10	This work

^a Copper nanoparticles^b Gold nanorods (GNRs) nonaggregation-based colorimetric probe^c Benzimidazole-based fluorescent chemosensor^d Zinc sulfide quantum dots doped with manganese^e Dinitrobenzenesulfonate ester coupled with poly(ethylene glycol)^f Functionalized CdS quantum dots¹ Linear dynamic range² Limit of detection

GQDs. The selectivity quenching may be ascribed to the fact that Cu^{2+} ions have a strong affinity toward the oxygen-containing groups on the GQDs surface than other metal ions [27]. Therefore, Cu^{2+} ions were selected as the optimal quenching ion.

The effect of the Cu^{2+} concentration on fluorescence intensity of GQDs is shown in Fig. 3c. The results indicated that the fluorescence intensity of GQDs gradually decreased as the Cu^{2+} ions concentration increased. The results also indicated that the F/F_0 value rapidly decreased from 100 to 62.50 % with increasing Cu^{2+} ions concentration from 0 to 10 μM, and then tended to slowly decrease. Thus, 10 μM Cu^{2+} ions were used in the following experiments.

Quantitative determination of sulfide ions

At optimized conditions, the fluorescence intensity recovery efficiency of GQDs- Cu^{2+} systems in the presence of sulfide ions with different concentrations were recorded. The fluorescence intensity of GQDs- Cu^{2+} systems gradually recovered through adding sulfide ions with concentrations ranging from 0.20 to 40 μM (Fig. 4a). The inset image indicates that a good linear relationship exists, which ranges from 0.20 to 20 μM with a high correlation coefficient ($r^2=0.9943$). The linear regression equation and detection limit (3 σ/s) for sulfide ions were $F/F_0=0.06763x+1.15668$ and 0.10 μM, respectively. In addition, the fluorescence intensity recovery of the GQDs- Cu^{2+} systems with sulfide ions was completed within 30 s (Fig. 4b). Moreover, the detection limits are low enough to detect common levels of sulfide ions in water. The detection limits and linear ranges for sulfide ions in this method were compared with other previously reported optical probes, and

the results are listed in Table 1. Our method was significantly more sensitive than previous optical probes.

Selectivity and interference of this probe

The selectivity and interference of this probe were investigated as shown in Fig. 5. Sulfide ions can significantly restore the fluorescence intensity of the GQDs- Cu^{2+} systems but no clear enhancement is observed with potentially interfering ions. The results indicated that GQDs- Cu^{2+} system based fluorescence sensing is highly selective for sulfide ions. The possible interference of these potentially interfering ions was also

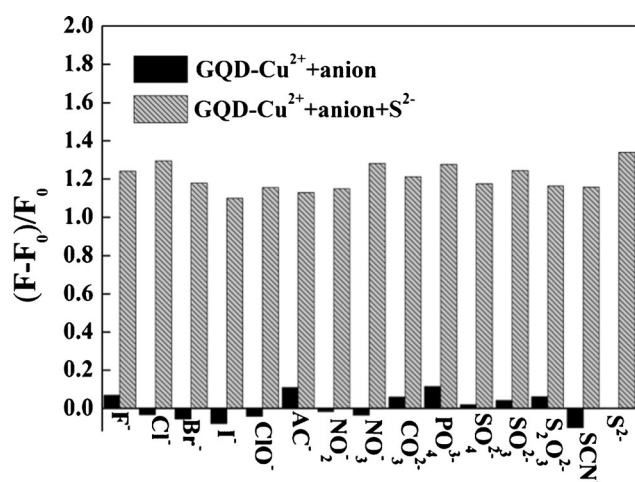


Fig. 5 Selectivity and interference of GQDs- Cu^{2+} systems in buffer solution (pH 7.0, 40 mM) towards other anions. The concentrations of sulfide ions and each of the other anions are 20 and 200 μM, respectively. F and F_0 stand for the fluorescence intensity of the GQDs- Cu^{2+} systems in the presence and absence of other anions, respectively

Table 2 Determination results of sulfide ions in water samples by using GQDs-Cu²⁺ based fluorometric sensors ^a

Samples	Added sulfide ions (μM)	Measured sulfide ions (μM)	Recovery (%)	RSD (%)
Tap water	1.00	1.13	113.00	2.34
	7.00	7.40	105.70	1.79
	15.00	15.50	103.30	1.45
Drink water	1.00	1.11	110.00	2.38
	7.00	7.33	104.71	1.21
	15.00	15.45	103.00	0.74

^a The standard deviation was obtained by three measurements

evaluated. The results showed that these potentially interfering ions only have a small effect on the fluorescence intensity of GQDs-Cu²⁺-sulfide systems. These good properties imply that the proposed method can be applied for the detection of sulfide ions in water samples.

Detection of sulfide ions in water samples

This probe was investigated to detect sulfide ions in water samples. The results are shown in Table 2. The recovery of spiked sulfide ions ranged from 103.00 to 113.00 %. The relative standard deviation (RSD) was lower than 2.50 %. The results indicated that the probe is applicable for quantifying sulfide ions in water samples.

Conclusions

We demonstrated a GQDs-Cu²⁺ system for the detection of sulfide ions in water samples with rapid, sensitivity and selectivity. This method is achieved based on the fact that Cu²⁺ can quench fluorescence intensity of GQDs, and the addition of sulfide ions can make it recovers. This method has several advantages: (1) The detection method has a wide linearity from 0.20 to 20 μM with a sensitive detection limit of 0.10 μM (3 σ/s). (2) The detection method is highly selective for sulfide ions, and these potentially interfering ions only have a small interference on the fluorescence intensity. (3) This probe is rapid with a response time of less than 30 s. (4) The GQDs is an environment friendly material and has stable fluorescence intensity even with high ionic strength. (5) This probe is simple in design and has been successfully applied to detect sulfide ions in tap water and drink water. We envision that this method was promising applications for further applications.

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