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Copper nanoparticles: A new colorimetric probe for quick, naked-eye detection of sulfide ions in water samples

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ABSTRACT

This study introduces a new method for the visual and spectrophotometric detection of chemical species using copper nanoparticles (Cu NPs). A simple method for the synthesis of Cu NPs for rapid colorimetric visual detection of sulfide ions (S^{2-}) in water samples is described. The Cu NPs sensor detects sensitive and selective color change in the presence of micromolar levels of S^{2-} that can be observed with the naked eye and monitored using a UV–vis spectrophotometer. The color change quantitatively correlates with the concentration of S^{2-} from 12.5×10^{-6} M to 50.0×10^{-6} M. Samples of tap water and river water were spiked and analyzed using the proposed system. The results showed that the sensor exhibited excellent detection for S^{2-} in the water samples. A main advantage of the new method is that it provides good selectivity for detecting S^{2-} without the need for complex readout equipment. The proposed method has a high potential for rapid environmental monitoring of sulfide ions.

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1. Introduction

Nanoscience is the exploration of materials by fabricating nanometer scale materials with novel and improved properties that can affect all areas of physical and chemical science. Nanomaterials show unique properties. One important nanomaterial is metal nanoparticles [1,2]. Noble metal nanoparticles (NPs) are of interest for their physico-chemical properties and potential applications in fields such as catalysis, electronics, plasmonics, and biotechnology. These nanoparticles, gold, silver and copper have drawn attention for their promising properties. As the dimensions of the particles dispersed in liquid media decrease to nanometer size, a strong UV–vis band appears that does not exist on the bulk metal spectrum.

The properties of these nanoparticles give rise to increased localized surface plasmon resonance (LSPR) absorption and can be used in the development of analytical methods such as optical sensing. Surface plasmon resonance (SPR) results from surface electromagnetic waves that propagate in a direction parallel to the metal–dielectric interface. LSPR mode is responsible for the peaks observed in the absorption spectra of metallic nanoparticles. An extinction band appears when the incident photon frequency is resonant with the collective excitation of the conduction electrons. At resonant frequency, the incident light is absorbed by the nanostructure and some of these photons will be scattered at the same frequency in all directions [3,4].

For gold, silver, and copper nanoparticles over a range of 10–60 nm, the SPR peaks are positioned at about 520 nm, 400 nm, and 570 nm, respectively. When dispersed in aqueous media, the nanoparticles are responsible for the purple (gold), yellow (silver) and red (copper) color of the colloid solutions [5–8]. The SPR properties of gold and silver nanostructures have been useful for a variety of applications. Nanoparticles with well-controlled sizes have recently been used as suitable probes in colorimetric determinations [9–16].

Preparation of plasmonic nanostructures has been limited to the use of gold and silver nanoparticles. Cu is less expensive than Au and Ag, but displays a localized plasmon band in the visible part of the spectrum. Unfortunately, the preparation and application of copper nanostructures has not received as much attention as that of Ag and Au nanoparticles. The major difficulty in the use of Cu-based plasmonic nanostructures is their tendency to oxidize after preparation [17–19]. In this study, simple and efficient methods previously reported by Wu and Chen [7] and Sun [8] were used to synthesize Cu NPs. The experiments showed that the synthesized Cu NPs were relatively stable in aqueous solution and can be used as a colorimetric probe.

The drinking water for the province of Khuzestan in southwest Iran is mainly supplied by the Karun River. The quality of the river water has deteriorated in the past few years because of pollution loads from cities in Khuzestan and surrounding regions. The toxicity of S^{2-} in its liberated hydrogen sulfide form (H_2S) is

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well-known [20,21]; it is commonly found in natural water and wastewater samples and is an important pollution index for water. Sulfide detection is essential to environmental protection, biological research and other fields.

Determination of the presence of small amounts of sulfide requires sensitive methods. Various methods have been used for the determination of S^{2-} concentrations, including classical [22], optical, [13,16,23–26] electrochemical [20,21,27–29] and electrophoresis [30]. Some techniques, such as chromatography, have complex processes that require expensive apparatus and maintenance costs or are unsuitable for online analysis. Titrimetry is the only technique suitable for macro-analysis. Colorimetric methods have garnered attention because they can be easily monitored with the naked eye without special instrumentation.

No reports have been found on the spectrophotometric detection of chemical species using Cu NPs. The proposed method is a selective and sensitive colorimetric assay method for S^{2-} using Cu NPs LSPR. The results of this study demonstrate that the proposed optical sensor can be applied to determine micromolar concentrations of S^{2-} in water samples in just a few minutes. Moreover, this colorimetric probe is faster for online analysis of S^{2-} than other methods.

2. Experimental

2.1. Materials and reagents

All chemicals were of analytical reagent grade purity. Stock solutions of sulfide ions were prepared daily at a concentration of 100 mg L^{-1} by appropriate dissolution of $Na_2S \cdot 9H_2O$ (98%; Sigma Aldrich) salt in basic medium (0.1 mol L^{-1} NaOH). They were stored in a tightly capped bottle. The solution remained stable for a few days if stored in a refrigerator.

The solutions were alkaline because of the NaOH supply and volatile H_2S exhaust into the gas atmosphere was negligible. The stock solution was standardized using the common iodimetric titration method. Hydrazine hydrate (80%), cetyltrimethylammonium bromide (CTAB), NaOH and copper (II) nitrate were purchased from Merck (Darmstadt, Germany) and phosphoric acid (84–85%) from Fluka (Buchs, Switzerland). All solutions were prepared with doubly distilled water and all experiments were performed at ambient temperature (25 ± 2 °C).

2.2. Apparatus

Spectrophotometric measurements were carried out using a Cintra 101 spectrophotometer (GBC Scientific Equipment, Australia) with a 1 cm polymeric cell. A pH meter (model 632 Metrohm, Herisau, Switzerland) and a transmission electron microscope (TEM; 906E, LEO, Germany) were employed.

2.3. Synthesis of Cu nanoparticles

The current procedure for synthesis is a modified version of methods developed by Wu and Chen [7] and Sun [8] for Cu nanoparticles. The synthesis of Cu NPs was achieved in a capped bottle (200 mL) by mixing 4 mL of 0.1 mol L^{-1} solution of Cu^{2+}, 5 mL of 1% CTAB solution as a stabilizing agent, and 5 mL NaOH (0.005 mol L^{-1}) to increase the pH of the solution. The mixture was stirred at 80 °C for 5 min. Then 2 mL of hydrazine hydrate (99.9%) was added and the reaction solution was vigorously stirred at 80 °C for 45 min.

At this stage, the reduction of copper ions to metallic copper could proceed. After addition of hydrazine hydrate solution, the solution changed from colorless to red within 20 min, which indicated the formation of Cu NPs. The resulting product was then cooled to room temperature and used for the next determinations.

In most synthesis protocols, N_2 gas is passed to avoid the oxidation of Cu NPs [7,8]. In the present method, this was not necessary. The reduction of copper ions by hydrazine has some advantages. Nitrogen evolution occurred slowly, which maintains homogeneity of the reaction solution and also produces an inert atmosphere. Furthermore, hydrazine can increase the pH of the solution. The overall reaction is represented as

$$Cu^{2+} + 2OH^- \rightarrow Cu(OH)_{2(S)}$$

$$Cu(OH)_{2(S)} + 2OH^- \rightarrow [Cu(OH)_4]^{2-}_{(aq)}$$

$$4[Cu(OH)4]^{2-}_{(aq)} + N_2H_4 \rightarrow 2Cu_2O_{(s)}\ (\text{yellow}) + N_{2(g)} + 8OH^- + 6H_2O$$

$$2Cu_2O + N_2H_4 \rightarrow 4Cu^0\ (\text{red}) + N_{2(gas)} + 2H_2O\ (\text{pH} \sim 10 \text{ at } 80\ ^\circ\text{C})$$

The colloidal dispersion of the metal exhibits absorption bands in the ultra-violet visible region at about 570 nm. It has been reported that Cu NPs less than 100 nm in size typically exhibit a surface plasmon peak at around 570 nm [7,8,31,32]. Previous research has shown that the Cu NPs does not change in inert atmosphere. In the presence of oxygen dissolved in the aqueous solution, the Cu NPs concentration and the intensity of the LSPR peak gradually decreased as a result of oxidation [7,31]. In the present study, however, absorption intensity remained unchanged for a few days after formation and no precipitation and oxidation occurred. This indicates that the Cu NPs were very stable in aqueous solution in the presence of CTAB and extra hydrazine in a capped bottle.

2.4. Procedure

To evaluate the optical characteristics of the Cu NPs solution as a LSPR-based sulfide sensor, 2 mL prepared Cu NPs solution was added to 5 mL volumetric flasks with 1 mL NaOH (0.005 mol L^{-1}) solution to adjust pH and different concentrations of sulfide ions. After the addition of the analyte, the solution was mixed slowly and a portion was transferred within 5–6 min into a 1 cm spectrophotometric cell to record absorbance. Absorbance was measured at 570 nm, which is λ_{max} of the Cu NPs SPR peak at room temperature against a blank

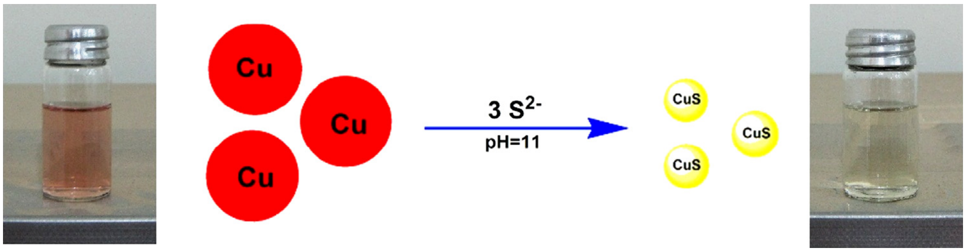

Fig. 1. Schematic illustration for the colorimetric sensing of S^{2-}based on etching of Cu NPs. [Condition of 10 mL: Cu NPs solution = 2 mL, $[OH^-] = 5 \times 10^{-4}$ mol L^{-1}, $[S^{2-}] = 30 \times 10^{-6}$ mol L^{-1}, and reaction time: 5–6 min]. (For interpretation of the references to color in this figure, the reader is referred to the web version of this article.)

reagent. ΔA (SPR) was used as the analytical signal. Note that the order of addition of the reagents is very important. A schematic of the reaction mechanism is shown in Fig. 1

3. Results and discussion

The strong interaction between Cu^{2+} and Cu^{+} cations with S^{2-} anions (pKsp (CuS)=35.2 and pKsp (Cu_2S)=47.6) [33] led to the current investigation of the interaction between Cu NPs and sulfide ions, to serve as a sensor for the presence of S^{2-} in aqueous media.

Typically, the colloidal solution of Cu NPs is red because of its SPR absorption band. In the present study, the formation and stability of Cu NPs in aqueous solution were confirmed using UV–vis spectral analysis. Synthesized Cu NPs were stable in ambient air after 20 min of exposure to air, but, upon the addition of the S^{2-}solution to a colloidal solution of Cu NPs, the color of the solution diminished and turned yellow in about 2–4 min (etching time). These observations are shown in Fig. 1.

Fig. 2 shows the UV–vis spectra for the Cu NPs in the presence and absence of sulfide ions. The intensity of the SPR band decreased as the amount of S^{2-} increased, indicating a considerable decrease in the concentration of the Cu NPs. This phenomenon is caused by the interaction of Cu NPs with S^{2-} and the formation of colloidal precipitation of CuS or Cu_2S. Copper cations and sulfide anions have a high affinity for reacting with each other. The solubility product constant (pKsp) of CuS and Cu_2S are 35.2 and 47.6, respectively. The pKsp of the anions with Cu^{2+} are: 12 (I^-), 8.3 (Br^-), 6.7 (Cl^-), 19.32 (OH^-), 13.4 (SCN^-), and 7.64 ($C_2O_4{}^{2-}$). The pKsp of heavy-metal ions and S^{2-} are Al^{3+} (6.7), 22.5 (β-Zn^{2+}), 24.9 (β-Ni^{2+}), 18.1 (Fe^{2+}), and 27.5(pb^{2+}) [33]. The stability constant of Cu^{2+} and S^{2-} is 2 to 3 orders of magnitude greater than that of other metal ions. It is reasonable to conclude that CuS and Cu_2S compounds form in the Cu NPs system upon the addition of sulfide ions, resulting in absorption quenching of the Cu NPs at 570 nm. The new Cu NPs based strategy for sulfide sensing was developed on the basis of these results.

3.1. TEM analysis

The TEM image for a typical sample resultant of Cu NPs show completely discrete particles with a mean diameter of about 50 nm (Fig. 3). TEM measurements indicated that the addition of Cu NPs to the sulfide ion solution decreased the amount and size of Cu NPs from the interaction (etching) between Cu NPs and S^{2-}.

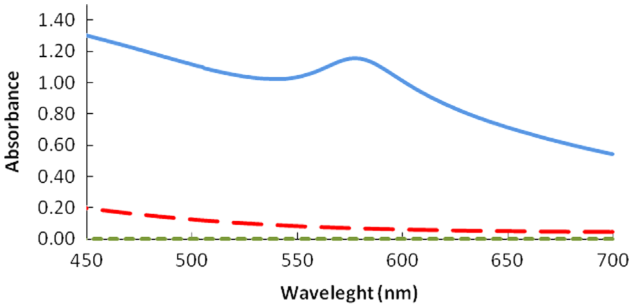

Fig. 2. UV–vis absorption spectra of Cu NPs (—), Cu NPs+S^{2-} (——) and blank (———) solutions. [Condition of 10 mL: Cu NPs solution=2 mL, [OH^-]= 5×10^{-4} mol L^{-1}, [S^{2-}]=30×10^{-6} mol L^{-1}, and reaction time: 5–6 min].

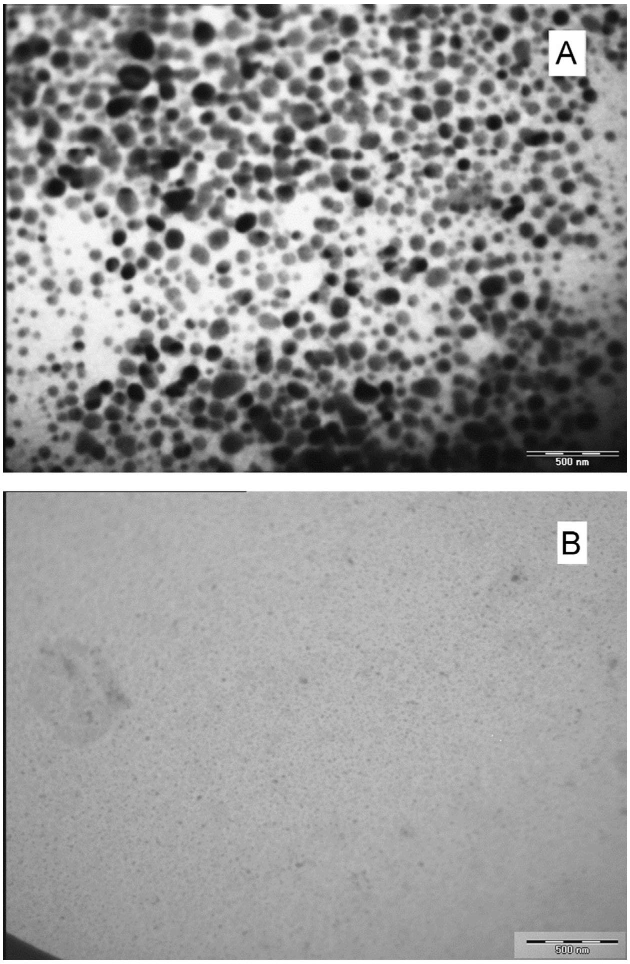

Fig. 3. TEM images of Cu NPs in the absence (A) and presence (B) of sulfide ion.

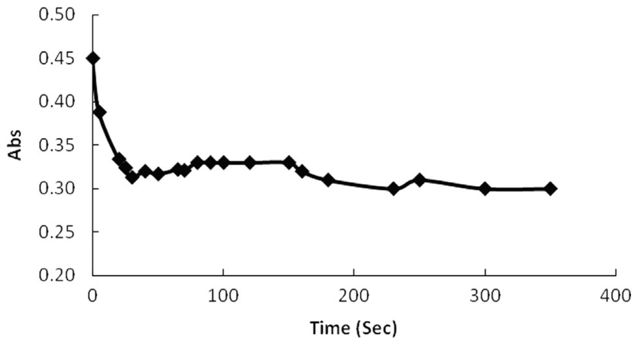

Fig. 4. The changes of the absorbance at 570 nm with time. [Condition of 10 mL: Cu NPs solution=2 mL, [OH^-]=5×10^{-4} mol L^{-1}, [S^{-2}]=30×10^{-6} mol L^{-1}, and reaction time: 5–6 min].

3.2. Optimization of the sensing system

The stability of Cu NPs in ambient air for more than 20 min is an important parameter. Prior to the application of the proposed sensor for the detection of S^{2-}, the effect of other influencing factors was also investigated.

3.3. Effect of time (etching time)

Fig. 4 shows the changes in absorbance at 570 nm over time during the first few minutes after initiation of the reaction. It is evident that absorbance reached a minimum after about 5 min

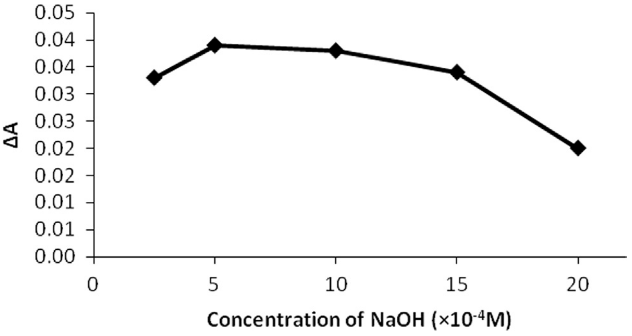

Fig. 5. Dependence of the surface plasmon intensity on the concentration of NaOH. [Condition of 10 mL: Cu NPs solution=2 mL, $[OH^-]=5\times10^{-4}$ mol L^{-1}, $[S^{2-}]=30\times10^{-6}$ mol L^{-1}, and reaction time: 5–6 min].

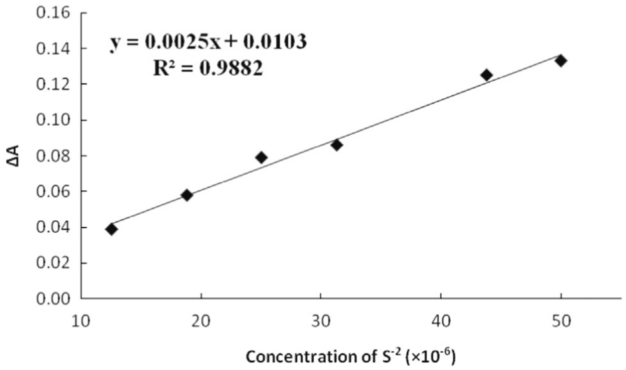

Fig. 6. Calibration curve of the relationship between the LSPR intensities and the S^{2-} concentration (n=6). [Condition of 10 mL: 2 mL Cu NPs solution, $[S^{2-}]$=(12.5, 18.8, 25, 31, 43, 50) × 10^{-6} mol L^{-1}, $[OH^-]=5\times10^{-4}$ mol L^{-1}; and reaction time: 5–6 min, n=3].

Table 1
Determination of S^{2-} in the presence of various species [condition of 10 mL: 2 mL Cu NPs solution, $[OH^-]=5\times10^{-4}$ mol L^{-1}; reaction time: 5–6 min, appropriate volume of S^{2-} standard solution].

Interfering species[a]	Tolerated ratio $[C_{species}]/[C_{S2-}]$
Cl^-, Na^+, Ca^{2+}, Cl^-, I^-, K^+, PO_4^{3-}, F^-	500
CO_3^{2-}	300
Mg^{2+}	200
SO_4^{2-}, NH_4^+	100
Zn^{2+}	40
Co^{2+}, Fe^{3+}	1

[a] All cations were prepared from nitrate salts and anions were prepared from sodium and/or potassium salts.

and remained nearly constant afterwards, indicating that the etching reaction was completed within 5 min. All the absorbance measurements were performed within 5–6 min from the addition of the Cu NPs solution.

3.4. *Effect of pH of solution*

The influence of pH on the reaction of S^{2-} was expected since sulfide ions are the conjugate base of a weak acid, H_2S ($pKa_1=7.04$, $pKa_2=14$), and may exist in three forms (S^{2-}, HS^-, and H_2S) in aqueous solution. S^{2-} is able to effectively etch Cu NPs, nevertheless, the relative concentrations of these forms are highly dependent on the pH value of the solution. The relative concentration of S^{2-} at high pH was greater than that at low pH value. Nearly all forms were converted to S^{2-}, so the influence of the pH of the solution was critical for the sensitive detection of S^{2-}. Fig. 5 shows the effect of NaOH concentration on Cu NPs LSPR peak intensity. As seen, absorbance increased up to a known concentration of NaOH and then decreased, probably from precipitate formation or aggregation. A concentration of 5×10^{-4} M was selected as optimum for NaOH.

3.5. *Analytical performance*

Under the optimal conditions, the ΔA (SPR) were monitored upon the addition of increasing concentrations of S^{2-} over 5–6 min. The method showed good linearity over the calibration range 12.5×10^{-6}–50.0×10^{-6} mol L^{-1} (Fig. 6). The correlation of determination (r^2) was 0.9882. The limit of detection (LOD=8.1×10^{-6} mol L^{-1}) was calculated as LOD=$X_b\pm3S_b$, where S_b is the standard deviation of the blank signals and X_b is the average of blank signals [34]. The relative standard deviation for the determination of 15×10^{-6} mol L^{-1} of S^{2-} was 4.14% (n=6).

Table 2
Determination of S^{-2} in spiked water samples [condition of 10 mL: 2 mL Cu NPs solution, $[OH^-]=5\times10^{-4}$ mol L^{-1}; reaction time: 5–6 min, n=3].

Water sample*	**Add** ($\times10^{-6}$ mol L^{-1})	**Found** ($\times10^{-6}$ mol L^{-1})	**Recovery (%)**
Tap water (Ahvaz, Iran)			
	18.7	20.3	97.1
	31.2	30.3	108.5
Karon river water (Ahvaz-Iran)	18.7	17.1	91.4
	31.2	29.1	93.3

* 5 mL of water samples was spiked.

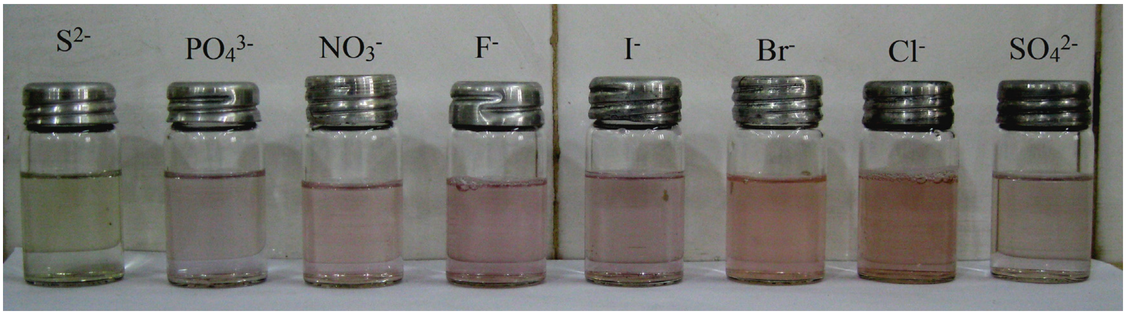

Fig. 7. Photographic images of the colorimetric response of Cu NPs to various anions. [Condition of 10 mL: 2 mL Cu NPs solution, $[OH^-]=5\times10^{-4}$ mol`L^{-1}; minutes, $[S^{2-}]=30\times10^{-6}$ mol L^{-1}, other anions are 500 fold of S^{2-} concentration, reaction time: 5–6 min]. (For interpretation of the references to color in this figure, the reader is referred to the web version of this article.)

Table 3
Comparison purposed method with some of methods reported in the literature for determination of S^{2-}.

Analytical technique	Sample matrix	LDR[a] ($\times 10^{-6}$ mol L^{-1})	LOD[b] ($\times 10^{-6}$ mol L^{-1})	Ref.
Iodimetry	Waste water	3–930	Unknown	[19]
Spectrophotometric	Spiked river water sample	10–10000	24	[13]
Spectrophotometric	Spiked hot-spring water sample	10–600	Unknown	[25]
Electrochemical method (carbon paste electrode)	Wastewater sample	0.15–2.5	0.05	[20]
Electrochemical method (modified glassy carbon)	River water sample	1.25–112.5	0.3	[21]
Electrochemical method (potentiometric sensor)	Wastewater sample	0.6–100	0.38	[27]
Electrochemical method (modified Au electrode)	Mountain stream water	0.5–12.7	0.3	[29]
This method	River and tap water samples	12–50	8.1	This work

[a] Linear dynamic range (LDR).
[b] Limit of detection (LOD).

3.6. *Interference study*

The selectivity of Cu NPs for sulfide ion detection in presence of Na^+, K^+, Ca^{2+}, Mg^{2+}, Fe^{3+}, Zn^{2+}, Al^{3+}, $SO_4{}^{2-}$, F^-, Cl^-, $NO_3{}^-$, Br^-, I^-, and $PO_4{}^{3-}$ was investigated. A fixed amount of S^{2-} (1 mg L^{-1}) was used with different amounts of foreign species and the recommended procedure was followed to study the effect of the species on the determination of the sulfide ions. The results are given in Table 1; an error of 10% in concentration was considered acceptable.

Remarkably, no color change in the solutions were observed in less than 6 min for the common anions $SO_4{}^{2-}$, F^-, Cl^-, $NO_3{}^-$, Br^-, I^-, and $PO_4{}^{3-}$ even at a 500-fold higher concentrations than that of S^{2-} (Fig. 7). This selectivity can be visualized with the naked eye. As seen, the color of the solution did not change in the presence of the individually tested anions, except for the sulfide ions (yellow).

3.7. *Analysis of spiked water samples*

The proposed method was applied to determine trace levels of sulfide ions in two water samples. Sulfide ions were not detected in either sample. To further evaluate the sensing system, 5 mL each of tap water (without pretreatment) and Karun River water (after pretreatment) were spiked and determined using the proposed method. The experimental results are shown in Table 2. The recovery of sulfide concentration was between 90% and 110% (low recovery may be due to the loss of S^{2-} from oxidation or volatilization during analysis). The analytical results of the samples were satisfactory and demonstrated that the proposed method can provide low level detection of S^{2-} in a few minutes. A comparison between the proposed method and other analytical methods is summarized in Table 3.

4. Conclusions

A sensitive, highly selective colorimetric method for determining S^{2-} using Cu NPs is presented. It was possible to determine the concentration of S^{2-} by the naked eye and a UV–vis spectrophotometer. The proposed method is: (1) is highly selective; (2) requires only 5–6 min to detect S^{2-} ions in aqueous solutions; and (3) does not require specialized equipment, making it very attractive for online detection. Although sulfide ions cannot be determined quantitively in concentrations lower than linear calibration range, the presence of sulfide ions in micromolar levels and below of the linear calibration range can be detected by naked eye. It is hoped that this method will be exploited as an effective means of detecting S^{2-} for environmental monitoring based on nanosensors. The proposed method is simpler and faster than a variety of methods recently reported methods to determine the presence of sulfide ions.

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