

Ligand-Capped CdTe Quantum Dots as a Fluorescent Nanosensor for Detection of Copper Ions in Environmental Water Sample

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Abstract In this work, as a novel fluorescent nano-sensor, a ligand-capped CdTe QDs (CdTe-L QDs) was designed for the detection and quantification of Cu²⁺ ions in environmental water samples. The synthesized QDs were characterized by transmission electron microscopy (TEM), thermo-gravimetric (TG) analysis, Fourier transform infrared (FTIR), UV–Vis spectrophotometry and fluorescence spectroscopy. Optical properties of the produced nanosensor were monitored by UV–Vis and fluorescence spectrophotometry. It was observed that fluorescence intensity of the produced nanosensor selectively quenched by adding Cu²⁺ ions in comparison to other metal ions tested. Using CdTe-L QDs, a rapid and facile analytical method was developed to determine Cu²⁺ ions in the concentration range of $5.16 \pm 0.07 \times 10^{-8}$ mol L⁻¹– $1.50 \pm 0.03 \times 10^{-5}$ mol L⁻¹ with a detection limit of $1.55 \pm 0.05 \times 10^{-8}$ mol L⁻¹. The nanosensor was successfully applied for the determination of Cu²⁺ ions in various water samples, and the results were compared with the standard method.

Keywords Quantum dots · Nano-sensor · Copper ions · Fluorescence · Heavy metal

Introduction

Quantum dots (QDs) are semiconductor nano-materials with remarkable optical properties, which are dramatically affected by their small size (2–12 nm), constituent materials, shape and surface chemistry [1–4]. Many investigations have been carried out regarding the importance of QDs in various fields including designing sensors [5–9]. Due to several advantages such as broad excitation spectra, narrow emission peak, and good photo-stability over organic dyes, QDs are excellent choices for designing fluorescent nanosensors [10–12].

Suitable surface modifications strategies have been utilized for designing QD-based nano-sensors. Various materials such as thioglycolic acid (TGA) [13], mercaptopropionic acid (MPA) [14] and polymeric materials [15] have been used for modification of the QDs surface [16]. In recent years, fluorescent nano-sensors have been extensively used for the detection of various types of analytes such as ions, molecules or even biomolecules [17–24].

Nowadays, due to the significance of heavy metals in human health, their detection is of great importance. Many chemical sensors have been reported for fast and inexpensive determination of these ions. Among various heavy metal ions, copper, although vital for human life, ranks second in toxicity after mercury and causes many serious diseases [25–27]. Hence, design and fabrication of novel sensors for detection of low levels of copper content in natural waters has specific significance. As an example, Yang et al. used phenol formaldehyde resin nanoparticles loaded with CdTe QDs for visual detection of Cu²⁺ ions [28]. They also used

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polyamine-functionalized carbon QDs as fluorescent probes for selective and sensitive detection of copper ions [29]. In addition, Jin et al. used hexadecyl trimethylammonium bromide (CTAB) modified CdSe/ZnS QDs as a fluorescent probe for the detection of Cu^{2+} ions [30].

In this work, based on new synthesis ligand capped CdTe QDs, a novel nano-sensor was prepared and characterized. The ligand was 4-((pyridin-2-yl)methyleneamino)-5-(1H-indol-3-yl)-4H-1,2,4-triazole-3-thiol (L), Fig. 1. Next, the applicability of the proposed L-capped CdTe QDs was studied as fluorescence probes for the monitoring of metal ions. It was found that the fluorescent nano-sensor is able to detect the copper ions selectively. When the mechanism of fluorescence quenching was investigated, parameters affecting the increasing ability for the detection of Cu^{2+} ions and the selectivity of the sensor towards other metal ions were optimized. In addition, the proposed nano-sensor was used to determine Cu^{2+} ions in real samples with satisfactory results.

Experimental

Materials

Thioglycolic acid (TGA, 98%), $\text{CdCl}_2 \cdot 5\text{H}_2\text{O}$ (99.99%), tellurium (Te) powder (99%) and sodium borohydride (NaBH_4 , 95%) were purchased from Sigma Aldrich. All other chemicals used were of analytical grade and were obtained from

Merck Co. Moreover, all solutions were prepared using double distilled water.

Instrumentation

The fluorescence studies were performed using a SCINCO's Fluorescence Spectrometer Fluoro Mate FS-2. The UV–Vis spectrophotometer Shimadzu (model, 1650 PC) was employed for UV–Vis spectra and absorbance measurements. FT-IR spectra were recorded by Bruker Tensor 27 FT-IR spectrometer (Germany). Characterizations of size and morphology of QDs were carried out using a Zeiss TEM at an acceleration voltage of 100 kV. Thermogravimetric (TG) analysis was carried out using a TA Instrument 2050 thermogravimetric device under N_2 atmosphere (25 mL min^{-1}) at a scan rate of $10 \text{ }^\circ\text{C/min}$. A Varian (model: 735-OES) inductively coupled plasma optical emission spectrometer (ICP-OES) was used for the determination of copper ions.

Synthesis of CdTe-TGA QDs

Here, 0.025 g of the precursor of Te and 0.025 g of NaBH_4 were dissolved in a flask containing 2.5 mL double distilled water with pure nitrogen gas for about 120 min under magnetic stirring. In the next step, 0.1 g of CdCl_2 was dissolved in another flask containing 80 mL double distilled water with pure nitrogen gas under magnetic stirring. 1.4 mmol of TGA was added in precursor of Cd and the pH of solution was adjusted to 8–9. Finally, the precursor of Te was transferred into a flask containing the precursor of Cd. Then, the resulting solution was refluxed at $100 \text{ }^\circ\text{C}$ for 1 h. CdTe-TGA QDs were synthesized according to previous experiences [31, 32].

Synthesis of the Ligand (L)

The procedure for the preparation of 4-((pyridin-2-yl)methyleneamino)-5-(1H-indol-3-yl)-4H-1,2,4-triazole-3-thiol (L) is as follow: A mixture of indole-1,2,3-triazole-3-thiol (0.01 mol), pyridine-2-carbaldehyde (0.01 mol,) and a catalytic amount of acetic acid was refluxed for 5 h in absolute ethanol (20 ml). Then, the solvent was evaporated to 5 mL, cooled to room temperature; and the colorless crystals of the product were filtered, washed with ethanol, and dried under reduced pressure.

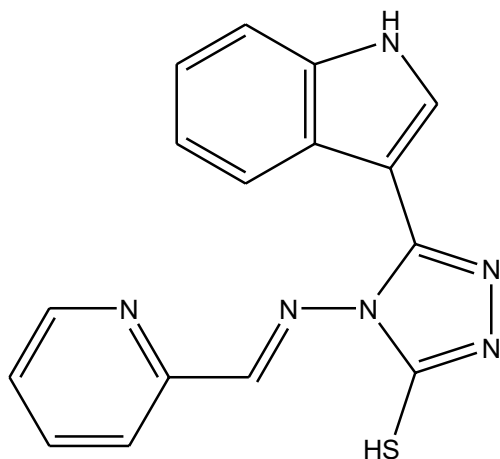


Fig. 1 Chemical structure of the synthesized ligand

Synthesis of CdTe-L QDs

CdTe-L QDs were obtained based on ligand exchange strategies from CdTe-TGA QDs and an organic ligand. First, 0.03 mmol of ligand was dissolved in 20 mL of acetonitrile and diluted with double distilled water to 40 mL. Then, 20 mL of synthesized CdTe-TGA QDs were added (2 mL min^{-1}) with a micropipette to the system dropwise. The resulted solution was kept for 4 days while it was sealed and stirring. Gradually, the color of the solution was changing from orange to a light yellow. The solution can be stable without any precipitation within 3 months. To explore the behavior of CdTe-L QDs, the interactions between CdTe-TGA QDs and ligand were investigated by TG analysis, FTIR, UV–Vis and fluorescence spectroscopy.

Measurements

Typical measurements were carried out as follows: the prepared CdTe-L QDs was diluted with double distilled water (1:4), and it was suspended into Tris-buffer solution (pH 6.5, 0.01 mol L^{-1}). The resulting solution (2 mL) was transferred into a $1 \text{ cm} \times 1 \text{ cm}$ fluorescent quartz cell and it was titrated with different metal ions. Various volumes of ion stock solutions ($1 \times 10^{-4} \text{ mol L}^{-1}$) were gradually added to the cell using a micropipette. The fluorescence spectra were recorded in less than 1 min after adding metal ions. To explore the behavior of CdTe-L QDs and the interactions between CdTe-TGA QDs and ligand, the fluorescence spectra were taken in two excitation wavelengths, separately. For

studying ligand behavior, excitation wavelength was selected 370 nm and emission spectra were recorded from 385 to 700 nm. Also, excitation wavelength was selected 390 nm and emission spectra were recorded from 405 to 700 nm for studying CdTe QDS behavior (ligand in this excitation wavelength (390 nm) does not have any emission).

Real Sample Measurements

The water samples were first filtered through Whatman filter paper. Then, 10 mL of the water samples were diluted by double distilled water to 100 mL, and the pHs of the solutions were adjusted to 6.5 using Tris-buffer (0.01 mol L^{-1}). A desired volume of CdTe-L QDs and double distilled water (2 mL) was transferred into the fluorescent quartz cell. Then, the solution was analyzed using the standard addition method, Cu^{2+} ions were added into these water samples and the resulting solutions were finally analyzed with the proposed methods, and the obtained results were compared with standard method (ICP-OES).

Results and Discussion

Optical Properties of the Nanosensor

The fluorescence spectra of the interactions between Ligand and CdTe-TGA QDs during different times at 25°C with excitation wavelength at 370 nm (Fig. 2a) and

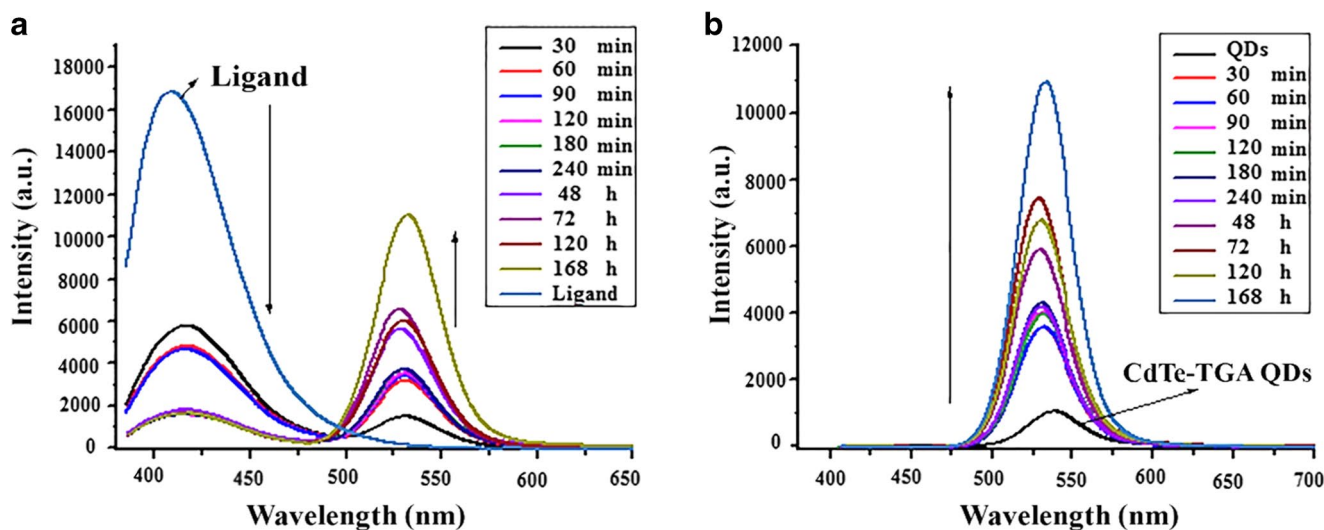


Fig. 2 The fluorescence spectra of pure ligand and its exchanging on the CdTe-TGA QDs surface during the synthesis time at room temperature (a) at λ_{ex} of the ligand (370 nm) (b) at λ_{ex} of QDs (390 nm)

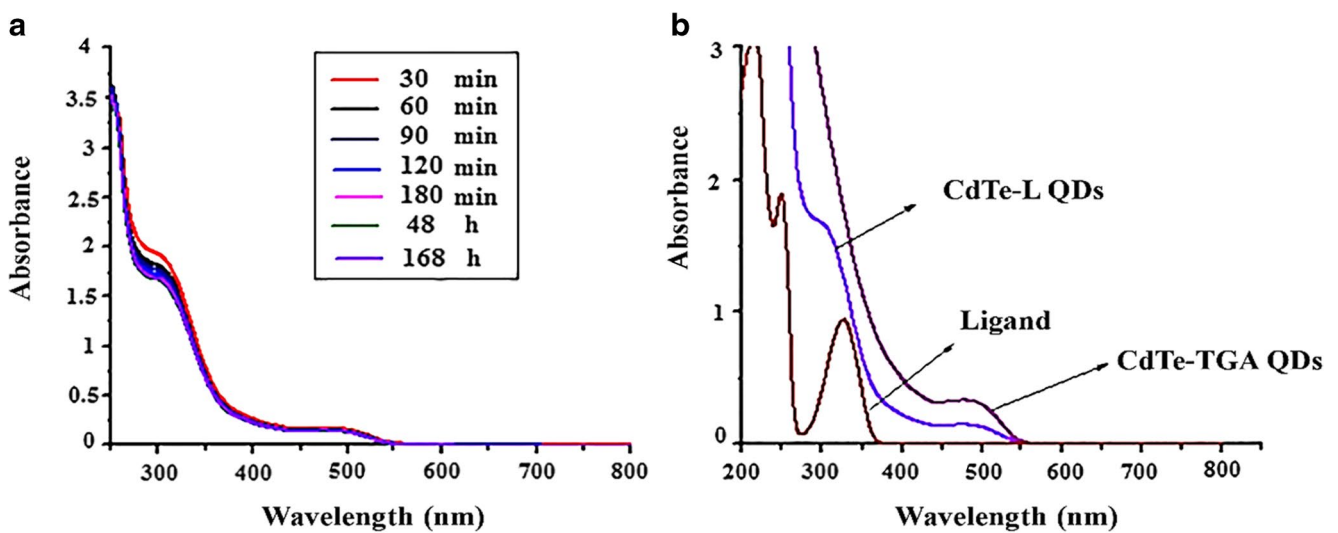
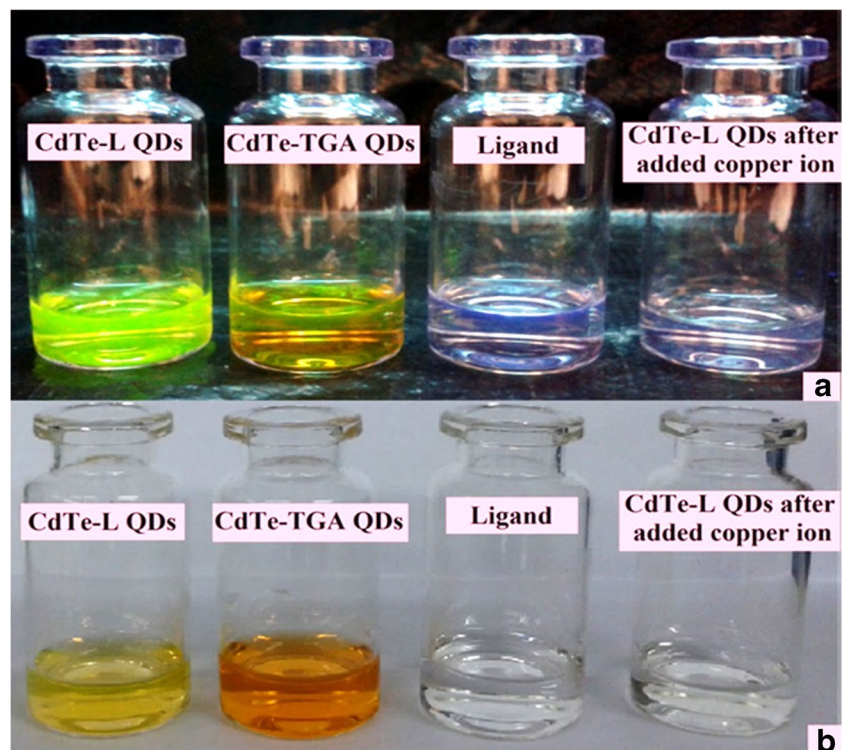


Fig. 3 **a** UV-Vis spectra of synthesized CdTe-L QDs during of time at room temperature; **b** UV-Vis spectra of the pure ligand, pure CdTe-TGA QDS and synthesized CdTe-L QDs

390 nm (Fig. 2b) are shown. An interesting observation is that the fluorescence intensity of CdTe QDs increases while the fluorescence intensity of ligand decreases by

increasing the time of interaction. Changes in fluorescence intensities might be due to the modification of surface QD because of replacing L with TGA molecules.

Fig. 4 Images of the ligand, CdTe-TGA QDs and CdTe-L QDs after addition of copper ion under **a** UV lamp (254 nm) and **b** visible light



This increasing of FL intensity after addition of L to the CdTe-TGA QDs, can be considered as a good indication for successful ligand exchange process.

This ligand exchange can also be demonstrated with a small decrease in particle size and a small blue shift in the band-edge absorption. During the time, a blue shift occurs in UV spectra of CdTe-ligand after ligand exchanging (Fig. 3a). Moreover, comparison of UV–Vis spectra of the pure ligand, pure CdTe-TGA QDs and CdTe-L QDs are shown in Fig. 3b. Another evidence for taking part in CdTe-L QDs exchange can be found in Fig. 4. Obviously, images in Fig. 4 show the ligand, CdTe-TGA QDs, and CdTe-L QDs under (a) UV lamp (254 nm) and (b) visible light. A change in color from orange (CdTe-TGA QDs) to light yellow (CdTe-L QDs) (Fig. 4) was observed.

Characteristics of the Nanosensor

The synthesized CdTe-L QDs TEM was shown in Fig. 5. The image shows that synthetic QDs were all spherical with a suitable morphology.

FT-IR spectra were used to verify the capping of the ligand on the surface of the CdTe QDs. FTIR spectra of the CdTe-TGA QDs, ligand and CdTe-L QDs are shown in Fig. 6. The FT-IR spectra of CdTe-TGA (Fig. 6a) showed a strong band at 3446 cm^{-1} assigned to stretching vibrations of hydroxyl group, and a weak but sharp band at 2550 cm^{-1} assigned to the stretching vibration of the thiol group. Moreover, the stretching vibrations of carboxyl group are found at 1646 and

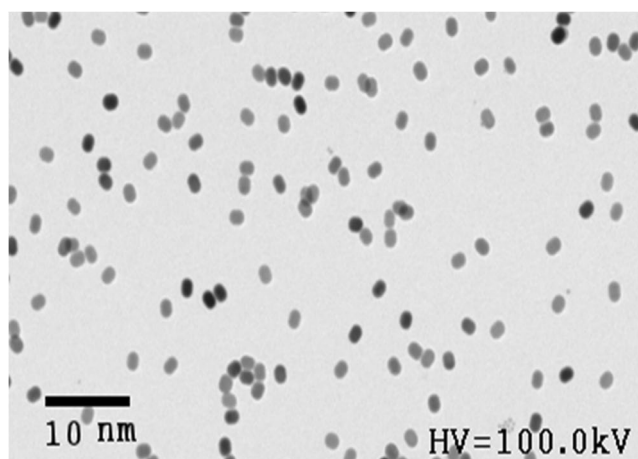


Fig. 5 TEM image of the CdTe-L QDs

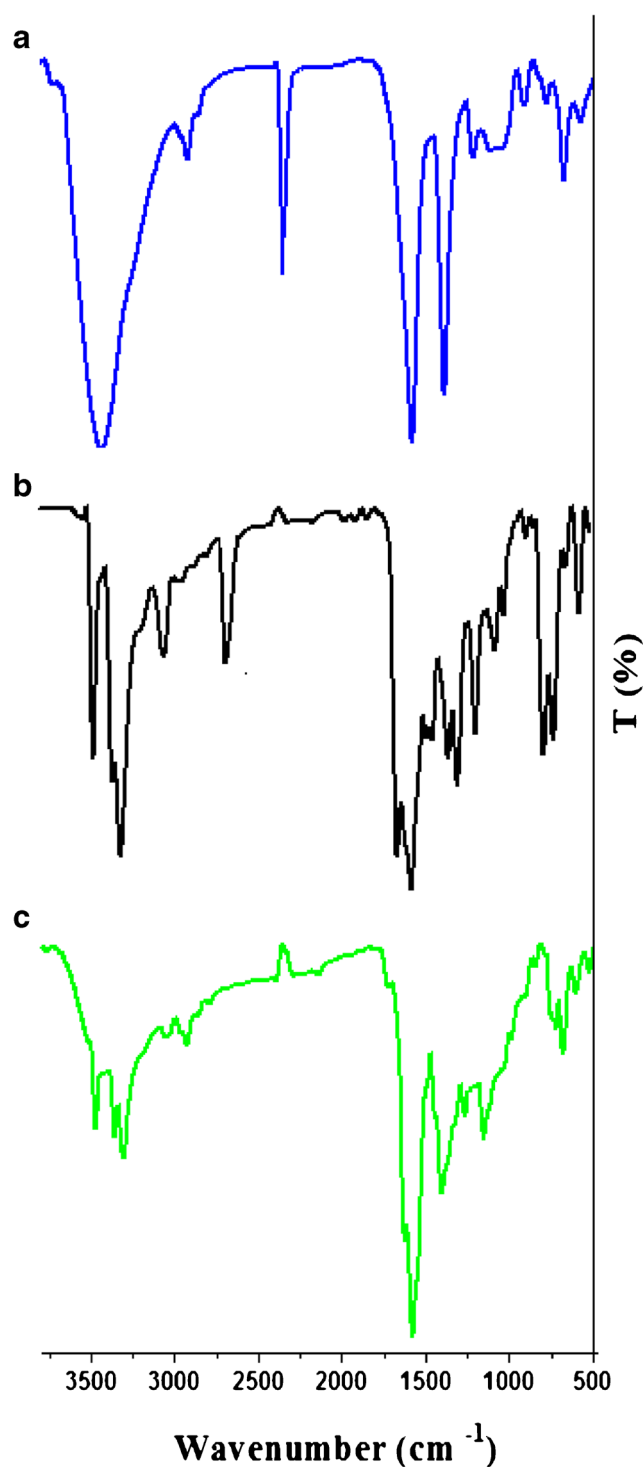


Fig. 6 FT-IR spectra of **a** CdTe-TGA QDs, **b** ligand and **c** CdTe-L QDs

1562 cm^{-1} . The FT-IR spectrum of the ligand (Fig. 6b) exhibited a strong peak at 3030 cm^{-1} corresponding to

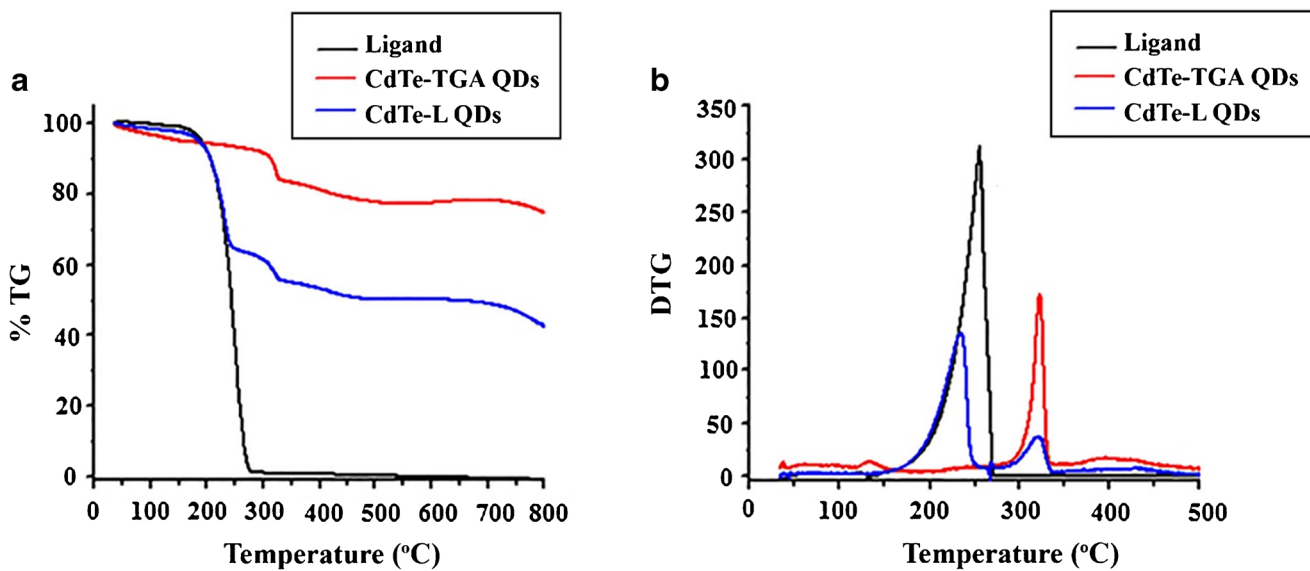


Fig. 7 a TG and b DTG curves of ligand, CdTe-TGA QDs and CdTe-L QDs

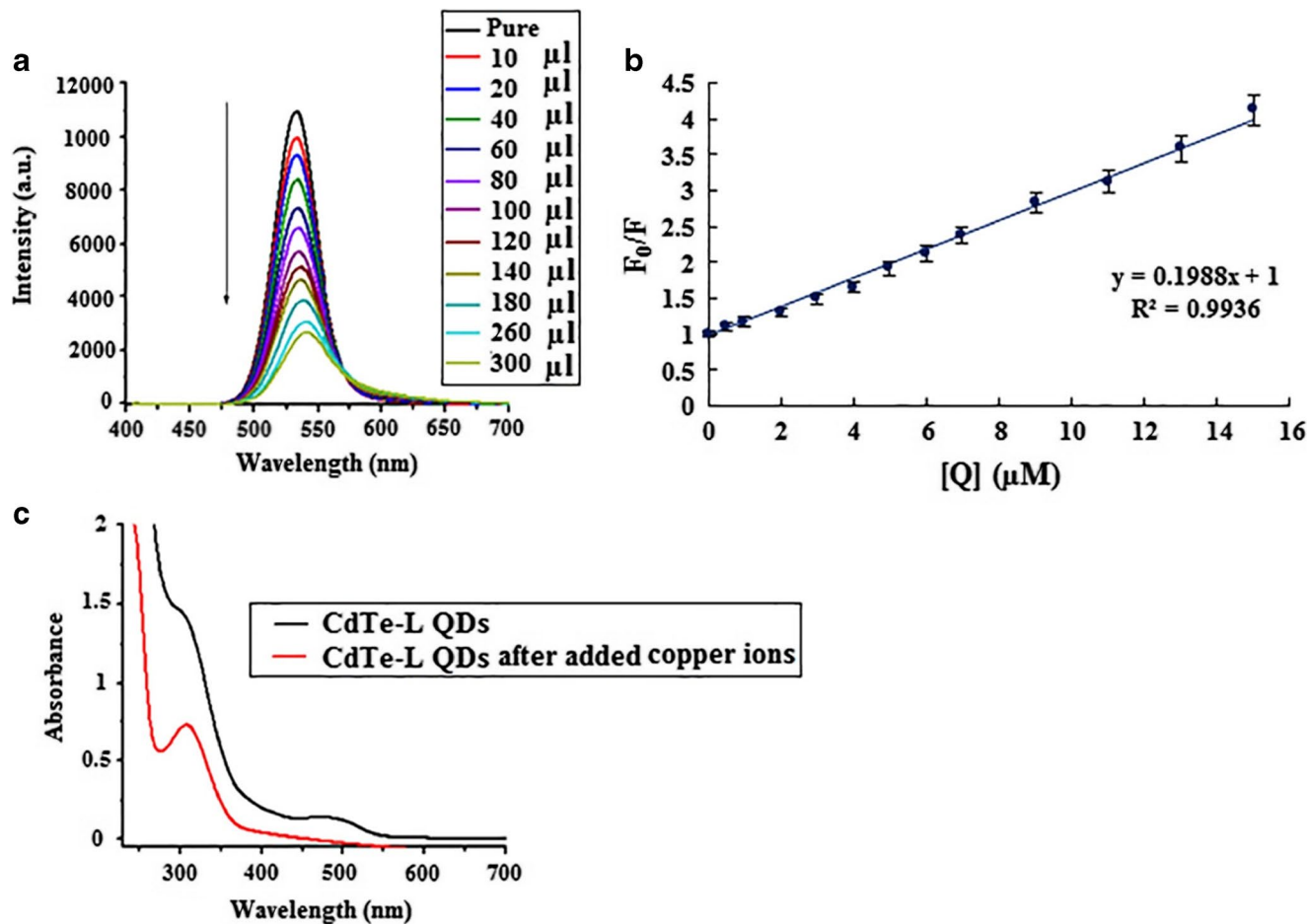


Fig. 8 a Fluorescence titration of Produced nanosensor solution in the presence of varying concentrations of Cu²⁺ ions, b Calibration curves of titration (Stern–Volmer plot) and UV–Vis spectra of synthesized CdTe-L QDs after addition of copper ions

Table 1 Comparison of this work with some previous similar reported probes for detect of copper ions

Fluorescent probes	LOD (M)	Reference
Cysteamine capped CdS QDs	1.5×10^{-6}	[33]
Glutathione-modified magnetic fluorescent $\text{Fe}_3\text{O}_4@\text{ZnS}$	0.2×10^{-6}	[34]
3,5-dichlorosalicylaldehyde and 2-(methylthio)aniline	0.20×10^{-6}	[35]
Carbon dots	0.047×10^{-6}	[36]
Ultrathin graphitic carbon nitride ($\text{g-C}_3\text{N}_4$) nanosheets	0.1×10^{-9}	[37]
Dual-emission fluorescent silica nanoparticle-based dye	10×10^{-9}	[38]
CdTe-L QDs	1.55×10^{-8}	This work

the stretching vibration of aromatic $-\text{CH}$ groups, and a weak band at 2580 cm^{-1} due to the S-H stretching vibration. The stretching vibrations of aromatic $-\text{NH}$ groups are located $3300\text{--}3500 \text{ cm}^{-1}$. In addition, the bands at 1580 and 1600 cm^{-1} correspond to aromatic ring chain vibrations of $-\text{CC}$ groups. The FT-IR spectra of the produced nanosensor (Fig. 6c) obviously showed characteristics of both CdTe-TGA QDs and ligand spectra. Figure 6c shows that the ligand exchange has occurred;

and Fig. 6c exhibits a spectrum similar to the CdTe-TGA QDs shown in Fig. 6a. It is important that there is a little shift in some absorption peaks of the FT-IR spectra of the produced nanosensor. This is due to the capping of the ligand on the surface of CdTe QDs.

The surface modification of CdTe QDs was also investigated by TG and DTG curves. As shown in Fig. 7, the TG and DTG curves showed that the maximum decomposition rate of the ligand, CdTe-L and CdTe-TGA QDs

Fig. 9 Selectivity of nanosensor toward Cu^{2+} ions **a** in absence of Cu^{2+} ions and **b** in presences of the same amount of Cu^{2+} ions

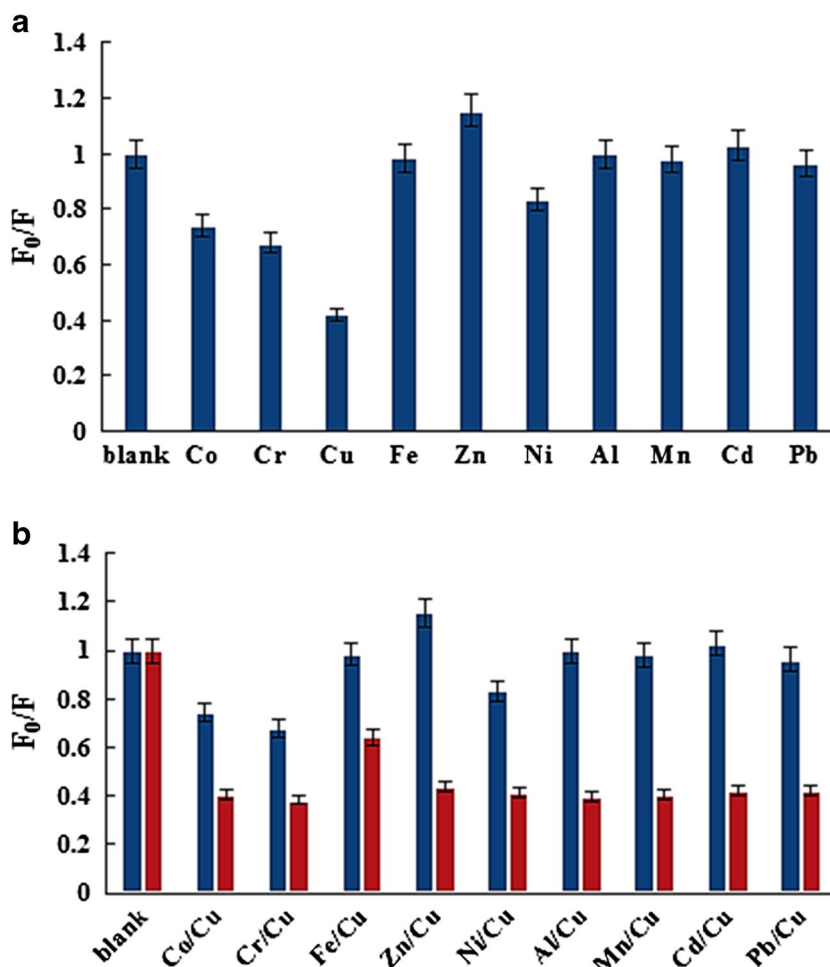
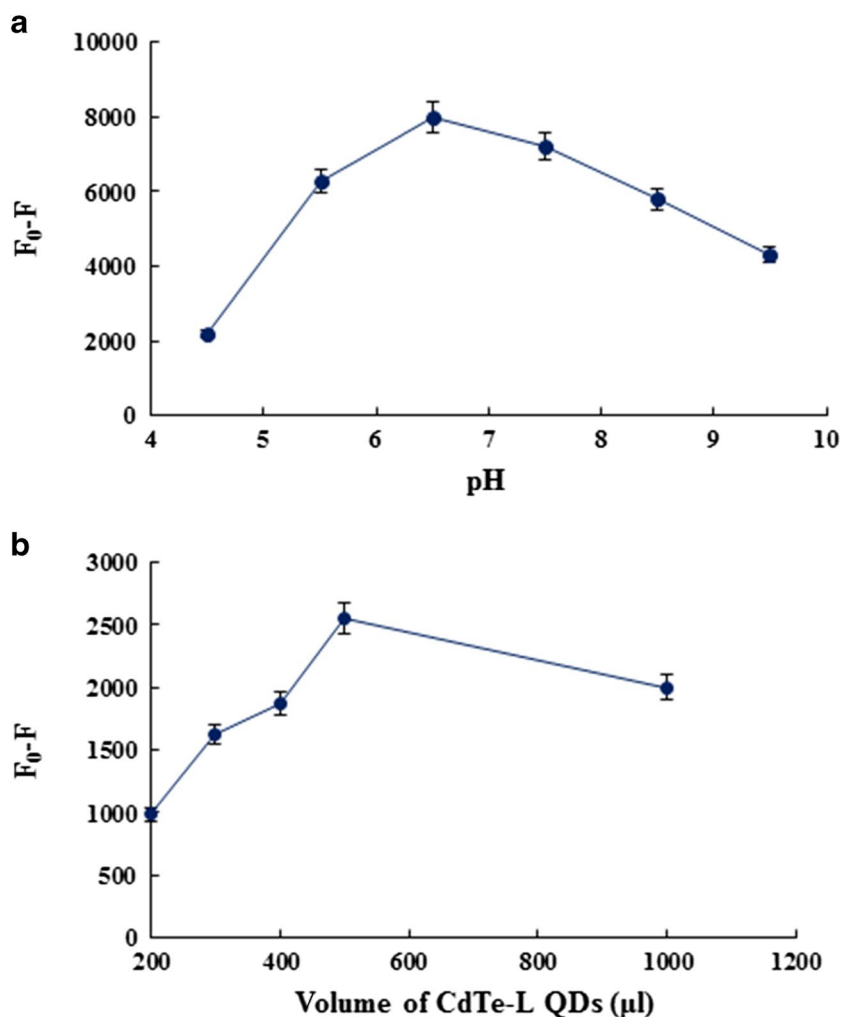


Fig. 10 Effect of **a** the pH and **b** volume of CdTe-L QDs on the fluorescence intensity of the nanosensor in the presence of same amount of Cu^{2+} ions



occurred at 255, 235 and 323 °C, respectively. The different thermal behavior of CdTe-L and CdTe-TGA QDs is a good indication of their dissimilar composition. It can be suggested that the thermal stability of CdTe-L QDs is decreased relative to CdTe-TGA QDs, which might be caused by the capping of ligand on the surface of QDs. In addition, the total weight loss of CdTe-L QDs at 450 °C was about 25% more than that of CdTe-TGA QDs.

Analytical Performance of the Nanosensor

Surface ligands can have important effects on fluorescence responses of QDs to metal ions. In fact, modification of QDs surfaces by suitable ligands leads to designing new fluorescent nano-sensors. As shown in Fig. 8a, the fluorescence intensity of CdTe-L QDs decreases with increasing concentration of Cu^{2+} ions. The quenching effect of Cu^{2+} ions on

fluorescence, the intensity of CdTe-L QDs was analyzed by the Stern–Volmer Eq. (1):

$$F_0/F = 1 + K_{sv}[Q] \quad (1)$$

Where F_0 and F are the fluorescence intensities of CdTe-L QDs at 540 nm in the absence and presence of a quencher (Cu^{2+} ion is the quencher in this study), respectively, K_{sv} is the quenching constant of the quencher, and $[Q]$ is the analyte (Cu^{2+} ion) concentration. The Stern–Volmer plot, shown in Fig. 8b, fits a good linear correlation ($R^2=0.9936$) over the concentration range of $5.16 \pm 0.07 \times 10^{-8} \text{ mol L}^{-1}$ – $1.50 \pm 0.03 \times 10^{-5} \text{ mol L}^{-1}$ from the formula. The detection limit is $1.55 \pm 0.05 \times 10^{-8} \text{ mol L}^{-1}$ (at a signal-to-noise ratio of 3). In Table 1, some previous reported works which used quantum dots for the detection of copper ions in water media have been compared. From Table 1, it can be seen that this work has a lower detection limit most of the compared probes. Furthermore, UV–Vis spectra of CdTe-L

QDs, after addition of optimum amount of Cu^{2+} ions, are shown in Fig. 8c.

Selectivity of the Proposed Nanosensor

Generally, selectivity is an important parameter in designing new chemical sensors. The selectivity of the proposed nano-sensor was evaluated by investigating the response in the presence of other metal ions. Therefore, to evaluate the selectivity of CdTe-L QDs for Cu^{2+} ions, the responses from other metal ions including Mn^{2+} , Zn^{2+} , Ni^{2+} , Pb^{2+} , Al^{3+} , Cr^{3+} , Cu^{2+} , Cd^{2+} , Co^{2+} and Fe^{3+} to the fluorescence spectrum of CdTe-L QDs were studied. The fluorescence emission of CdTe-L QDs was significantly decreased without any emission band shift by adding copper ions. As shown in Fig. 9, the influence of other ions on fluorescence intensity was very weak. The produced nano-sensor was rather selective towards copper ions, which makes it very attractive for the selective detection of Cu^{2+} ions. Moreover, fluorescence changes of a solution of the ligand ($10^{-5} \text{ mol L}^{-1}$) was studied while it was titrated by adding metal cations ($10^{-4} \text{ mol L}^{-1}$) separately. The emission of the ligand with excitation wavelength at 370 nm did not show any change by adding cations. Thus, the proposed nano-sensor only responds to copper ions rather than other cations.

Optimization of the Experimental Conditions

In order to obtain the maximum sensitivity for the quenching system, the effects of pH and the amount of produced nano-sensor solutions on the fluorescence quenching efficiency were investigated. The effect of pH on the fluorescence intensity of this system was studied to obtain an optimum pH for effective sensing Cu^{2+} ions. The fluorescence intensity was studied against pH in the range of 4.5 to 9.5 in order to obtain the optimum conditions to determine copper ions. The optimum fluorescence intensity was obtained in the pH range between 6.5 and 7.5 (Fig. 10a). At the acidic pH, increase in the concentration of H^+ is the result of the protonation of the heteroatoms group on the capped ligand; and at higher pH, the concentration of copper ion decreases due to precipitation of $\text{Cu}(\text{OH})_2$ [39]. The effect of the amount of produced nano-sensor solutions on the quenching efficiency was also investigated in the range of 200–1000 μL of stock solution. As shown in Fig. 10b, the optimal amount of CdTe-L QDs (500 μL) gives the highest sensitivity (i.e., the slope of calibration function) and the widest linear range of the calibration function. The quenching efficiency increased by increasing the produced nano-sensor volume up to 500 μL .

At a higher concentration, self-quenching or aggregation of CdTe-L QDs may occur.

Detection of Copper Ions in Environmental Water Samples

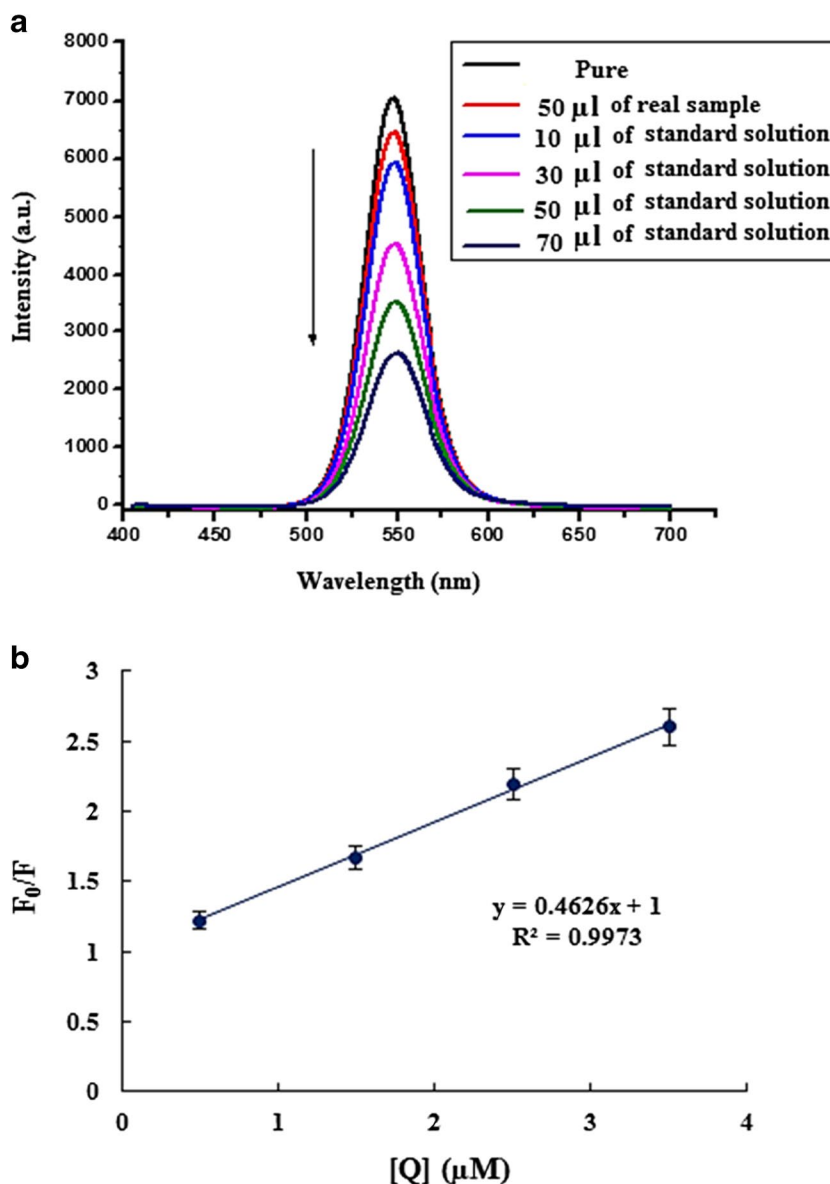
In order to evaluate the capability of the designed nano-sensor in real sample analysis, a standard addition method has been utilized to detect Cu^{2+} ions in various water samples (under optimal conditions). After analyzing the samples, the results were compared with the standard method (ICP-OES). The obtained results, summarized in Table 2, demonstrated that the proposed fluorescence nano-sensors are sensitive and dependable enough for practical detection of copper ions in water samples. Moreover, as shown in Fig. 11a, the fluorescence intensity of CdTe-L QDs is decreased with an increase in the concentration of Cu^{2+} ions (in one water sample). The Stern–Volmer plot, shown in Fig. 11b, fits a good linear correlation ($R^2 = 0.9973$).

Table 2 Results of Cu^{2+} ions determination in various water samples

Sample	V_x (μL)	V_s (μL)	aC_x (Cu) (mol L^{-1})
Tap water (Qazvin)	50	10	ND
		30	
		50	
		70	
Sea water (Khazar)	50	10	ND
		30	
		50	
		70	
Well water (Zibakenar)	50	10	$8.6 \pm 0.2 \times 10^{-5}$
		30	
		50	
		70	
Well water (Haftsangan)	50	10	$1.14 \pm 0.04 \times 10^{-4}$
		30	
		50	
		70	
Flume water	50	10	$1.12 \pm 0.03 \times 10^{-4}$
		30	
		50	
		70	
Wellhead water	50	10	$2.4 \pm 0.1 \times 10^{-5}$
		30	
		50	
		70	

^aThe results were compared with standard method (ICP-OES) with P-value (0.05), for 5 replicate measurements, the accuracy are less than 5%

Fig. 11 Copper content analysis of well water (Haftsangan) by the proposed nanosensor **a** The fluorescence quenching of the nanosensor solution by addition of various concentrations of standard solution of copper, **b** The related Stern–Volmer plot of the quenching



Conclusions

In this work, a novel fluorescent nano-sensor was introduced and successfully fabricated based on CdTe-L QDs for selective and sensitive detection of Cu^{2+} ions in aqueous solutions. CdTe-L QDs were characterized by fluorescence spectroscopy, UV–Vis spectrophotometry, FT-IR and TG analyses. FT-IR and TG analyses confirmed the presence of ligand around CdTe QDs. The size of CdTe-L QDs was estimated around 2 nm from TEM images. Moreover, CdTe-L QDs were directly applied to selective detection of Cu^{2+} ions in comparison to other cations. The fluorescence intensity of CdTe-L QDs was quenched when adding Cu^{2+} ions into the solution of nano-sensor. Under optimum conditions, the calibration plot was linear in the range between $5.16 \pm 0.07 \times 10^{-8} \text{ mol L}^{-1}$ – $1.50 \pm 0.03 \times 10^{-5}$

mol L^{-1} . The detection limit of produced nano-sensor was $1.55 \pm 0.05 \times 10^{-8} \text{ mol L}^{-1}$. Furthermore, the proposed nano-sensor was applied to determine Cu^{2+} ions in various water samples with satisfactory results.

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