

Electronic Supplementary Information (ESI)

Direct detection of sulfide ions [S²⁻] in aqueous media based on fluorescence quenching of functionalized CdS QDs at trace levels: analytical applications to environmental analysis

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Experimental section

Equipments:

The absorption spectrum was acquired at room temperature on UV 3600 Shimadzu UV-VIS-NIR spectrophotometer with the use of 1.0 cm quartz cell. FL measurement of solutions were made with PC based Spectrofluorophotometer (JASCO Model FP-750, Japan) equipped with Xenon lamp source and 1.0 cm quartz cell. Both excitation and emission slits were fixed at 10 nm. The particle size distribution and zeta potential of CdS QDs in aqueous suspension was measured by dynamic light scattering with a Zetasizer Nano ZS (Malvern Instruments Ltd., UK). High-speed centrifuge model C-24 BL (REMI Instrument Ltd, Mumbai, India) was applied for centrifugation operation. The pH of solutions was measured with digital pH meter Model LI-120 (ELICO Hyderabad, India) with a combined glass electrode.

Reagents:

All chemical reagents were of analytical reagent grade and used as received without further purification. All aqueous solutions were prepared with doubly distilled water. Cadmium chloride ($\text{CdCl}_2 \cdot \text{H}_2\text{O}$) and Sodium sulfide ($\text{Na}_2\text{S} \cdot 3\text{H}_2\text{O}$) was purchased from S d fine-chem Ltd. (Mumbai, India). 3-Mercaptopropionic acid (MPA), Potassium dihydrogen orthophosphate dihydrate ($\text{KH}_2\text{PO}_4 \cdot 2\text{H}_2\text{O}$) and di-Potassium hydrogen orthophosphate (K_2HPO_4) for phosphate buffer preparation were procured from Spectrochem Chemicals (Mumbai, India). The standard stock solution of S^{2-} was prepared by dissolving sodium sulfide in water which was purchased from S d fine-chem Ltd. (Mumbai, India). The all coexisting anions were prepared by dissolving its corresponding salts in the doubly distilled water and stored at ambient temperature.

Synthesis of functionalized CdS QDs

Functionalized CdS QDs were synthesized via the procedures described by Winter et al. with some modifications.¹ Appropriate amounts of (CdCl₂.H₂O), Na₂S and MPA were first dissolved in doubly distilled water separately. The 10 mL of 0.1 mol L⁻¹ (CdCl₂.H₂O) solution was dropped into the 2.5 mL of 1.0 mol L⁻¹ MPA solution slowly with continuous stirring at room temperature. Then pH was adjusted by the drop wise addition of 0.10 mol L⁻¹ NaOH solution to raise the pH 6.0–7.0 with constant stirring. The solution was deaerated with N₂ for 30 min. Under vigorous stirring, 5.0 mL of 0.1 mol L⁻¹ Na₂S was dropped slowly in the flask, a clear yellowish suspension of CdS QDs were obtained. The solution turned yellow shortly after the Na₂S addition due to the CdS QDs formation. Similarly total four parallel sets as per above procedure was done. After stirring overnight (12h), resultant reaction mixture of all sets were centrifuged, washed with deionised water then with acetone and finally diluted to 100 mL with deionised water and stored at 4°C in dark for further use. The concentration of resultant CdS QDs was 0.02 mol L⁻¹ (calculated through the concentration of the S²⁻ added) and used for further measurements.

Characterization of functionalized CdS QDs

Firstly synthesized CdS QDs were characterized by the UV-Vis and FL spectra (Fig. 1a and 1b). It can be seen that the line widths of the FL spectra are narrow, which showed that as prepared CdS QDs were nearly monodisperse and homogenous. The particle size of the as prepared CdS QDs were calculated from absorption maximum of the UV-Vis spectra according to the calculation method specified in the literature.² The results showed that the particle diameters of the prepared CdS QDs were 2.29 nm and had concentration of 1.46 μM .

Dynamic light scattering (DLS) experiments was also carried out to measure particle size in the suspension. Fig. S1 shows the typical size and size distribution of synthesized CdS QDs measured by DLS. The average size of CdS QDs as determined by DLS is 11 nm and size distribution is found within the range of 8–14nm, which is considerably larger than estimated from absorption maximum of the UV-Vis spectra. This is because the DLS technique gives a mean hydrodynamic diameter of CdS QDs core surrounded by the organic and solvation layers and this hydrodynamic diameter is influenced by the viscosity and the concentration of the solution.³

To confirm the effectiveness of the capping, Zeta potential measurement was also performed for CdS QDs in order to characterize the surface charge of QDs as well as stability. The obtained Zeta potential of the QDs at alkaline pH (pH = 7.8) was found to be -18.2 mV. For small enough QDs, a high Zeta potential will confer stability i.e. the solution or dispersion will resist aggregation. When the potential is low attraction exceeds, repulsion and the dispersion will break and flocculate.⁴ Therefore colloids with high Zeta potential (negative or positive) are electrically stabilized while colloids with low zeta potentials tend to coagulate or flocculate.

Analysis of S²⁻ in environmental water samples

The applications of the proposed method were evaluated for determination of S²⁻ in the environmental water samples. Water samples in bulk are collected from different sources like as drinking water, tap water, lake and river available in local area. The sample collected was first filtered through filter paper (Whatmann No. 40) to remove suspended matter, impurities etc., then boiled for 5 min to remove dissolved gases. These samples spiked with standard S²⁻ at different concentration levels, and then sample was diluted within working linear range and analyzed with the method estimated by standard addition. Because an internal standard that corrects for plasma related effects could not be found, standard addition method is the best alternative to avoid interferences of the real sample matrix. Table S2 showed the quantification results of the S²⁻ in various water samples. The standard addition method was used for testing recovery. The recovery rate of the spiked samples ranged between 98.0% and 103%, indicating the determination procedure was free from interferences of the real sample matrix. These results demonstrate that the designed probe is applicable for S²⁻ ion detection in environmental water samples.

Figures:

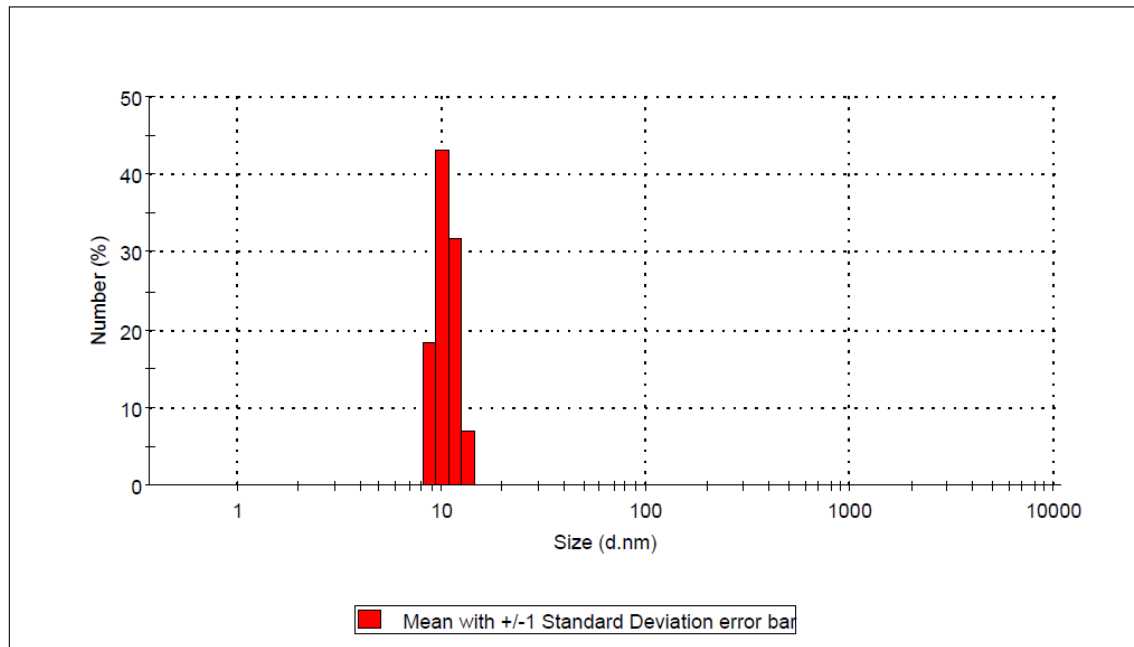


Figure S1: Particles size distribution measured by DLS of the CdS QDs colloidal solution ($0.0002 \text{ mol L}^{-1}$). Average size is 11 nm, 98% of the particles are between 8 to 14 nm (pH = 7.8).

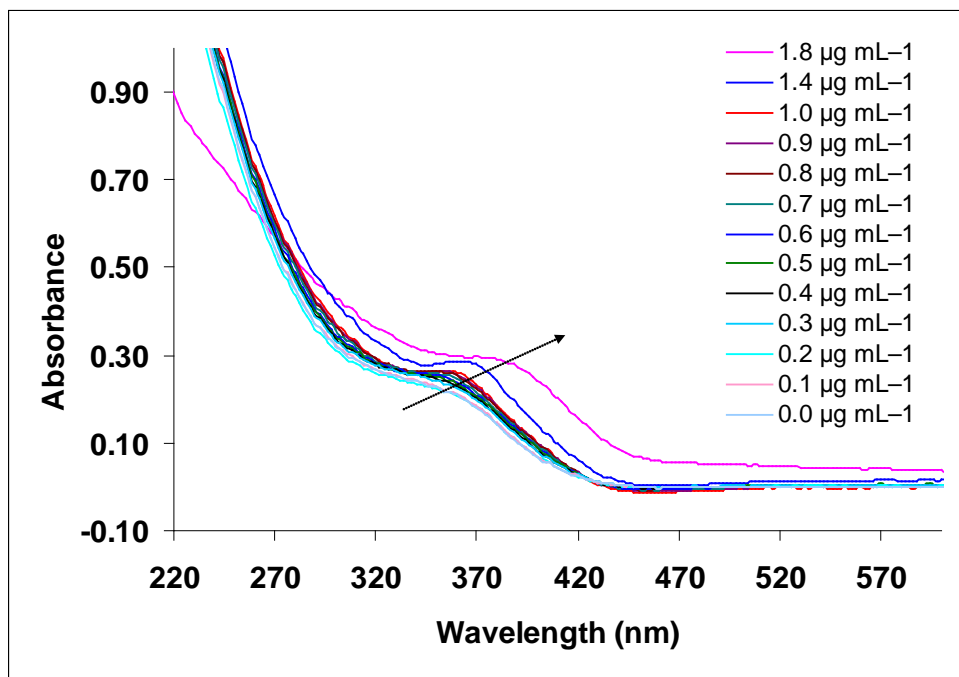


Figure S2: UV-Visible absorption spectra of only CdS QDs ($0.0002 \text{ mol L}^{-1}$) and after successive addition of S^{2-} from left to right (red shifted), 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9, 1.0, 1.4 and $1.8 \mu\text{g mL}^{-1}$ in to the CdS QDs ($0.0002 \text{ mol L}^{-1}$).

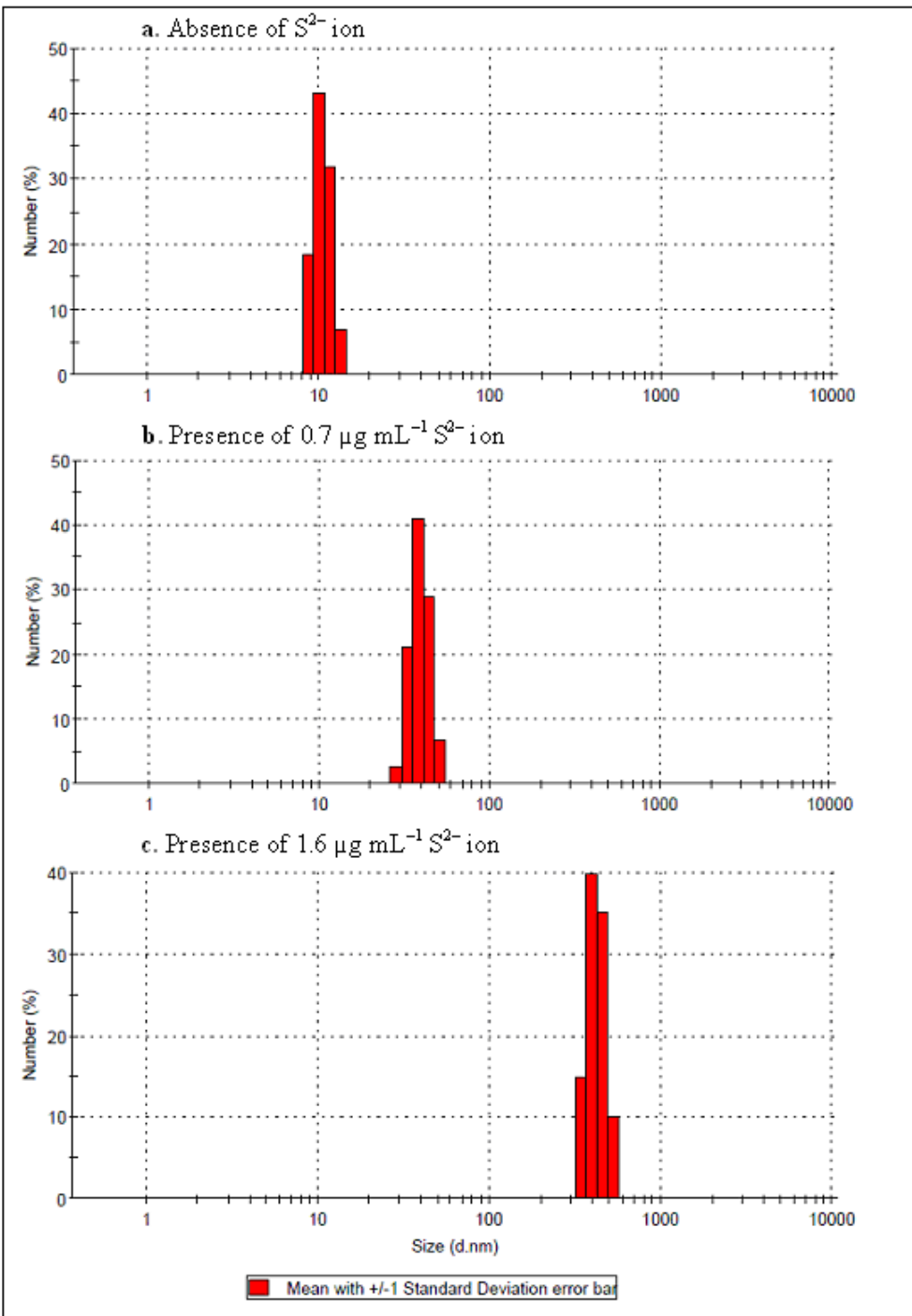


Figure S3: Demonstrating size distribution measured by DLS varies in response to the addition of S^{2-} concentrations in CdS QDs ($0.0002 \text{ mol L}^{-1}$); (a) in the absence of S^{2-} ions, (b) and (c) in the presence of 0.7 and $1.6 \mu\text{g mL}^{-1} S^{2-}$ respectively ($\text{pH} = 7.8$)

Table S1: Comparison of the linear range and detection limits of several nanomaterial based analytical methods for S²⁻ detection

Detection method	Linear range	Detection limit	References
ZnS:Mn Quantum Dots based fluorescent probe	2.5–38 μM	0.15 μM	[5]
ZnO/SiO ₂ nanocomposite based room-temperature phosphorescent sensor	4.88–10200 μM	1.64 μM	[6]
DNA-templated Gold/Silver nanoclusters as a fluorescent probe	0.5–2 μM	11 μM .	[7]
DNA templated copper nanoparticles as a fluorescent probes	2–20 μM	80 μM	[8]
Glutathione-modified gold nanoparticle as a colorimetric probe	5–15 μM	3 μM	[9]
MPA functionalized CdS QDs as a fluorescent probe	0.1–1.8 $\mu\text{g mL}^{-1}$ (3.1–56.3 μM)	0.21 $\mu\text{g mL}^{-1}$ 6.5 μM	This method

Table S2: Determination of S^{2-} in water samples from different water sources by standard-addition method (n=3)

Water samples studied*	Amount of S^{2-} standard added ($\mu\text{g. mL}^{-1}$)	of Total S^{2-} found** (n=3) ($\mu\text{g. mL}^{-1}$)	Recovery of S^{2-} added (%)	RSD (%)	Relative error (%)
Drinking Water (Dept. of Chemistry, SUK)	0.20	0.21	102.62	1.64	2.60
	0.40	0.42	103.73	1.16	3.74
	0.60	0.61	101.10	0.85	1.10
Tap Water (Dept. of Chemistry, SUK)	0.20	0.20	101.17	1.98	1.17
	0.40	0.41	102.88	0.83	2.88
	0.60	0.62	101.44	1.67	1.44
Lake Water (Rajaram Lake, Near SUK)	0.20	0.20	98.91	1.14	-1.09
	0.40	0.39	98.30	1.68	-1.70
	0.60	0.60	99.13	2.05	-0.87
Panchganga River (Kolhapur, MS, India)	0.20	0.20	98.97	3.10	-1.03
	0.40	0.41	101.33	1.26	1.33
	0.60	0.61	101.44	1.89	1.44

SUK = Shivaji University, Kolhapur

* Water samples were collected from different water sources in the campus.

** Average of three determinations

References

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