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2	A ZnS quantum dot based super selective fluorescent chemosensor
3	for soluble ppb-level total arsenic [As(III) + As(V)] in aqueous media:
4	Direct assay utilizing aggregation-enhance emission (AEE) for
5	analytical application †
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70 **1. Reagents and Chemicals**

All the chemicals procured are commercially available and used as received without any purification. Zinc acetate dehydrate (Zn (OOCCH₃)₂.2H₂O), sodium (meta)arsenite (NaAsO₂), disodium hydrogen arsenate heptahydrate (Na₂-HAsO₄.7H₂O), thiosalicyclic acid (TSA), ethylenediaminetetraacetic acid disodium salt dehydrate (C₁₀H₁₄N₂Na₂O₈.2H₂O), sodium dihydrogen phosphate (NaH₂PO₄.H₂O) and sodium hydrogen phosphate (Na₂HPO₄) were purchased from Sigma-Aldrich. Sodium hydroxide was purchased from Merck, India. Deionized double distilled water was used throughout the experiment for preparing solutions.

78 **2. Instrumentation**

79 The pH of solutions is measured with Eutech-510 ion pH-meter, which was pre-80 calibrated with standard pH buffer tablets (pH 7). The UV-vis absorption spectra are recorded 81 with a Shimadzu UV-2450 spectrophotometer in the 1 cm-path length cuvette against the solvent 82 reference in the range 200-800 nm. The steady-state fluorescence was recorded with a Jobin-83 Yvon-Spex Fluorolog-3 spectrofluorimeter. The time-resolved photoluminescence lifetime 84 decays were collected by using a time-correlated single photon counting (TCSPC) picosecond 85 spectrophotometer (LifeSpec-II, Edinburgh Instruments, U.K.). Samples were excited with a 86 pulsed diode (EPLED-295, pulse width 67.9 ps) centered at 295 nm and emission signals were 87 collected at magic angle 54.7° using a photomultiplier tube (H10720-01 Photosensor module from 88 Hamamatsu). The laser repetition rate was kept at 5 MHz, and the excitation peak power was \sim 70 89 mW. The Instrument Response Function (IRF) is ~ 270 ps. The data were analyzed by using F900 90 Software from Edinburgh Instruments. Fourier transform infrared spectroscopic (FTIR) 91 measurements are performed with a Perkin-Elmer FTIR spectrophotometer RX1 in range 300-92 4000 cm⁻¹ using KBr pellets. The morphology of the ZnS QD was also monitored by atomic force 93 microscopy (AFM), Agilent Technologies, Model 5500. Field Emission Scanning Electron 94 Microscopy (FESEM) images were taken with FEI NOVA NANOSEM 450 instrument having an 95 operating voltage of 5 kV. 20 µL of liquid sample was drop-casted on glass grids for FESEM

96 analysis. High-Resolution Transmission electron microscopy (HR-TEM) images are taken using 97 the JEOL Model JEM-2010 electron microscope with an operating voltage of 200 kV. 20 µL of 98 dilute liquid samples were drop-casted on carbon-coated copper grids (Allied Scientific Products, 99 India) for HRTEM analysis. Selected Area Electron Diffraction (SAED) pattern was also 100 obtained from HR-TEM analysis. Energy Dispersive X-ray (EDX) microanalysis was performed 101 using both HRTEM and FESEM instrument for compositional analysis. Dynamic Light 102 Scattering (DLS) measurements were carried out using Malvern Nano ZS instrument employing a 103 4mW He-Ne laser (wavelength (λ) of 632.8 nm) and an Avalanche Photo Diode (APD) detector 104 to get the hydrodynamic radius (R_h) of the particle. A cuvette of 1 cm path length was used for 105 DLS measurements. X-ray diffraction (XRD) pattern of the sample is collected using Bruker D8 106 Diffractometer unit with nickel-filtered Cu K_a line ($\lambda = 1.54$ Å) in the 2 θ range of 5°-80° at a 107 scanning rate of 5.0° min⁻¹. The XRD data is analyzed using JCPDS software.

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3. Preparation of TSA-capped ZnS QD

109 Synthesis of water-soluble ZnS QD was carried out using TSA as capping agent as well 110 as the source of sulfur. For the preparation of the sample, the optimum molar ratio of TSA: Zn:: 111 4: 1 was taken. The pH of the solution was adjusted to ~9.0 by using 1 (M) NaOH and again 112 stirred for some time to ensure proper mixing. Then the mixture was refluxed by hydrothermal 113 method for 5 hours at 80-90 °C. The scheme for the formation of TSA- capped ZnS QD are 114 described as follows (**see Scheme 1**).



120 Scheme S1. The formation process of the TSA-capped ZnS QD.

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4. Characterization of TSA-capped ZnS QD

- **4.1. UV-Vis absorbance spectra**
- 126 The room temperature optical absorption spectra of TSA-ZnS QD were shown in **Figure**
- **S1**. The as-prepared aqueous solution of TSA-capped ZnS QD was colorless.



Figure S1. UV-Vis absorption spectra of TSA-capped ZnS QD at pH 7.4 buffer.

4.2. Photoluminescence (PL) emission spectra

Photoluminescence (PL) spectra of TSA capped ZnS QD is carried out at room temperature at excitation wavelength of 295 nm at pH 7.4 buffer medium (shown in Figure S2). The emission maximum is found to be at 420 nm. The origin of emission spectra is due to the sulfur vacancy in ZnS host.¹ The ultraviolet blue emission peak corresponds to an excitonic emission that could be associated to the radiative recombination of the hole in the valence band and electron in the conduction band.² Fluorescence measurements were performed from 315 to 570 nm, keeping excitation slit at 3 nm and emission slit at 2 nm with excitation at 295 nm.



- 182 subsequent attachment with the QD surface which indicates the formation of ZnS QD. The peak 183 for C=O also shifts from 1679 cm⁻¹ to 1649 cm⁻¹ (curve B). The peaks at 645 cm⁻¹ are 184 characteristic of Zn-S vibration and also characteristic of cubic ZnS which are in good agreement 185 with reported results in the references.³
- 187 **Table S1.** Tentative vibrational assignments of TSA-capped ZnS QD.
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Functional Groups	TSA only	TSA-ZnS QD
O-H Stretching	3500 and 3011 cm ⁻¹	3432 cm ⁻¹
C=O Stretching	1679 cm ⁻¹	1649 cm ⁻¹
S-H stretching	2697 and 2519 cm ⁻¹	Disappeared
C-H bending and O-H bending	1409 cm ⁻¹	1396 cm ⁻¹
Zn-S stretching	-	645 cm ⁻¹

190 4.4. X-ray diffraction (XRD) pattern of the sensor



203 Powder XRD pattern of TSA-capped ZnS QD was shown in **Figure S4**. The three 204 primary characteristic peaks at 2θ values of 28.1, 47.8 and 57.1 have been assigned to the 205 diffraction from the (111), (220), and (311) planes, respectively, matching the cubic zinc blende

crystal structure phase (JCPDS No. 05-0566).⁴ The broadness of the diffraction peaks illustrates
 the nanocrystalline nature of the samples.⁵

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4.5. Transmission electron microscopy (TEM) studies

209 Transmission electron microscopy (TEM) has been used to characterize the TSA-capped 210 Zn QD in aqueous solution. Particle size and morphology of the TSA-ZnS QD were resolved by 211 transmission electron microscopy (TEM) as shown in Figure S5. According to the TEM results 212 the QD were nearly monodisperse with spherical shape. The existence of spherical clusters of the 213 average diameter of about ~16.1 \pm 0.5 nm was observed in Figure S5A (TEM image). High-214 resolution transmission electron microscopy (HRTEM) image (Figure S5B) of TSA-ZnS QD showed clear lattice fringes with an interplanar spacing of 0.28 Å. The selected area electron 215 216 diffraction (SAED) pattern (Figure S5C) showed clear lattice fringes and crystalline nature of 217 ZnS QD.





Figure S5. (A) TEM image (B) HRTEM image (lattice fringes) and (C) SAED pattern of TSA-



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233 4.6. Dynamic light scattering (DLS) of TSA-capped ZnS QD



The hydrodynamic particle size distribution of the TSA-ZnS QD was measured by using dynamic light scattering (DLS) technique. The mean hydrodynamic particle size of TSA-ZnS QD was estimated to be 22.3 ± 0.2 nm (see Figure S6). The average hydrodynamic particle size of TSA-ZnS QD by using DLS method is little higher than that of TEM measurement due to solvent effects.

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248 4.7. Energy dispersive spectroscopy (EDX) of TSA-capped ZnS QD

The EDX analysis (see Figure 7 and Table S2) clearly showed that the presence of elements such as Zn and S indicating that the ZnS QD is composed of zinc and sulfide element only.



262 **Table S2.** EDX pattern of TSA-capped ZnS QD.

Ele	ement	Weight (%)	Atomic (%)
Zn K		34.93	20.84
S K	6	65.07	79.16
Total	1	100.00	100.00

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264 4.8. Elemental area mapping pattern of TSA capped ZnS QD



Figure S8. Elemental area mapping pattern of TSA capped ZnS QD.

272 **4.9.** Photoluminescence lifetime decay of TSA-capped ZnS QD

To monitor the lifetime of TSA-capped ZnS QD, we further carried out time-correlated single photon counting (TCSPC) study (see Figure S9). The average fluorescence lifetime (τ_{av}) of TSA-capped ZnS QD was estimated to be 2.24 ns at λ_{em} = 420 nm during excitation with 295 nm

276 pulsed LED source. The lifetime parameters are shown in **Table S3**.

277 TSA-ZnS QDs $\lambda_{exc} = 295 \text{ nm}$ 278 IRF $\lambda_{ems} = 420 \text{ nm}$ $\tau_{avg} = 2.24 \text{ ns}$ 279 Log (counts) 1000 280 281 100 282 283 10 284 30 40 10 20 50 285 Time (ns)

Figure S9. Photoluminescence lifetime decay of TSA-ZnS QD at pH 7.4. The sample was excited using a 295 nm pulsed LED source and the decay was monitored at 420 nm.



Table S3. Fluorescence lifetime parameters of TSA-capped ZnS QD.

keeping excitation slit at 3 nm and emission slit at 2 nm with excitation at 295 nm.

emission studies was 1 cm. Fluorescence measurements were performed from 315 to 570 nm,

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317 **6.** Calculation of limit of detection (LOD)

To validate this method, the limit of detection (LOD) was obtained by drawing the calibration curve (**see Figure 3** in the main manuscript) in the very low concentration region. The limit of detection (LOD) is estimated by the eqn. $(1)^{6,7}$

321 Limit of detection (LOD) = $\frac{3\sigma}{K}$ (1)

322 Where, σ is the standard deviation of the intercept of the blank (QD-only) obtained from 323 a plot of PL intensity vs. [QD-only], and K is the slope obtained from the linear part of the plot of 324 PL intensity of QD vs. [Arsenic]. Some details on how to calculate the detection limit are shown 325 below: firstly, standard deviation (σ) of the instruments for this fluorimetric method was obtained 326 from statistical analysis of the blank sample. The linear fitting equation at low As(III) 327 concentrations was y = 264617 + 6192 x (R²=0.99336), so the slope (K) is 6192. Similarly, the 328 linear fitting equation at low As(V) concentrations was $y = 264686 + 1626 \times (R^2=0.9916)$, so the slope (*K*) is 1626. Using 3σ /slope rule,⁷ the limit of detection was estimated to be 0.79 ± 0.01 ppb 329 330 for As(III) and 2.79 ± 0.02 ppb for As(V) using the as-prepared TSA-ZnS QD. The LOD values 331 for both of As(III) and As(V) are remarkably lower than that of MCL reported value as well as 332 other reported values in literature (see Table S4). That means, we can easily detect arsenic (As) 333 even below ~3 ppb in aqueous medium using the PL method.

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System	Method	LOD value	Reference
Fluorescent-based	Colorimetrically and	54.91 nM (ca. 4.12	Anal. Chem. 2014, 86,
probe	Fluorimetrically via	ppb) for arsenite ion	11357-11361 ⁹
	PL turn-on method		
Magnetic iron oxide	Fluorimetrically via	300 nM for As(III)	Chem. Commun.,
nanoparticles	PL turn-on method	ion	2014 , 50, 8568-8570 ¹⁰
Di-oxime based	Colorimetrically and	0.23 µM for As(III)	Analyst, 2015, 140,
fluorescent probe	Fluorimetrically via	ion and 1.32 μ M for	2979–298311
	PL turn-on method	As(V) ion	
ZnO QD	PL turn-off method	27.0 ppb for As(III)	Anal. Methods, 2016,
		ion	8, 445-452 ¹²
TSA-capped ZnS	PL turn-on method	0.79 ± 0.01 ppb for	Our present work
QD		As(III) and 2.79 \pm	
		0.02 ppb for As(V)	

Table S4. List of other reported limit of detection (LOD) values for arsenic.

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7. Selectivity study or Competitive study

345 The selective sensing of the analyte is an important criterion for a successful sensor. 346 Therefore, we have also carried out studies with various common coexisting metal cations, such 347 as Ca(II), Al(III), Fe(III), Co(II), La(III), Mn(II), Pb(II), Cu(II), Hg(II), and Na(I) and as well as anions, such as Cl⁻, F⁻, CN⁻, OAc⁻, NO³⁻, H₂PO₄⁻, HPO₄²⁻, PO₄³⁻ and S²⁻ under similar 348 349 experimental conditions that have been used for the determination of both arsenic [As(III) and As(V)] in the dispersion of TSA-ZnS QD. In order to check the selectivity of the sensor (QD) 350 351 towards arsenic detection, we carried out fluorescence experiments with our sensor (QD) and 250 352 ppb of different ions (cations and anions included). It is important to note that the detection of 353 arsenic (As) was not perturbed by any other coexisting ions. Our fluorescence spectroscopic 354 measurements (see Fig. 4) show that the aqueous solution of our sensor is extremely specific 355 toward arsenic [both As(III) and As(V)] in the presence of other ions in the water medium.

As shown in **Fig. 4A-B**, only the addition of arsenic led to drastic photoluminescence intensity change (PL enhancement) of the TSA-ZnS QD, and no significant changes of PL intensity were observed upon addition of other ions mentioned. These also indicate that only arsenic (As) has strong interaction with TSA-ZnS QD, resulting in the enhancement of PL intensity of QD.

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362 8. pH dependence study

363 For biological applications, the appropriate pH condition for a successful probe is of 364 utmost importance. In the absence and presence of arsenic, the PL intensities of our sensor (TSA-365 ZnS QD) were estimated at different pH values using phosphate buffer (10 mM). Moreover, this 366 chemosensors (in the absence of As) exhibited stable fluorescence emission in the pH range of 367 6-11, making it well applicable for physiological pH conditions (pH, ~ 7.4) (see Figure S11). 368 This study clearly showed that the PL intensity of QD is almost independent over the pH range 369 6–11 (Figure S11 and Figure S12). This result demonstrated that our sensors were very much useful in an environmental system for chemical detection of toxic soluble arsenic. 370



Figure S11. pH dependent PL study of the TSA-capped ZnS QD in the absence of arsenic (As) at
different pH in 10 mM phosphate buffer at 25° C.



Figure S12. pH dependent PL study of the TSA-capped ZnS QD in the presence of arsenic (As)
at different pH in 10 mM phosphate buffer at 25^o C.

It was clearly observed that the fluoresce intensity of our sensor (QD) in the presence of arsenic was hardly affected between pH 6 and 10 in 10 mM phosphate buffer medium, indicating that this pH range is suitable for fluorescence studies for the recognition of As (**see Figure S12**). In the present work, a pH of ~7.4 buffer (10 mM) solution was chosen throughout the sensing experiments for physiological purpose. Unless otherwise mentioned, the following experiments were done in the optimized conditions.

- 400 9. Plausible PL turn-on mechanism
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9.1. Time resolve fluorescence lifetime study

The mechanism of binding of the arsenic species to the TSA-ZnS QD has been substantiated by different methods such as Fourier transform infrared (FTIR) spectroscopy, zeta potential measurements, dynamic light scattering technique (DLS) and fluorescence lifetime (TCSPC) studies. The arsenic (As) assisted 'turn-on' behavior of TSA-capped ZnS QD is demonstrated from the fluorescence lifetime decay (TCSPC) experiment (see Figure S13). As shown in Figure S13, the data were well fitted with biexponential equation (see eqn. 1) and the

average fluorescence lifetime was given in Table S5. The average lifetime of TSA-capped ZnS QD is 2.24 ns, whereas in the presence of 250 ppb As (III), the fluorescence lifetime is found to be 2.28 ns (see Table S5). The lifetime result clearly indicates that there is ground-state interaction between TSA-ZnS QD and As(III).6

 $\tau_{av} = a_1 \tau_1 + a_2 \tau_2$(1)







Figure S13. Fluorescence lifetime decay of TSA-ZnS QD in the presence of 250 ppb arsenic (As)

Time (ns)

 $\lambda_{\text{ems}} = 420 \text{ nm}$

- at λ_{em} = 420 nm and λ_{ex} = 295 nm (pH 7.4 buffer).
- **Table S5.** Fluorescence lifetime (λ_{exc} =295 nm) decay parameters of TSA-ZnS QD at 420 nm in

the presence of arsenic, at pH 7.4 and T = 298 K.

System	7 ₁ (ns)	α_1	$ au_2$ (ns)	α2	$ au_{av}(\mathbf{ns})$	χ^2
TSA-ZnS QD only	0.79	0.79	7.70	0.21	2.24	1.08
TSA-ZnS QD + 250 ppb arsenic	0.82	0.77	7.27	0.23	2.30	1.09

430 9.2. Fourier Transform Infrared Spectroscopic Study

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432 Figure S14 represents the FTIR spectra of free TSA capping, TSA-capped ZnS QD and 433 TSA-capped ZnS QD with arsenic. Pure TSA (curve A) shows the IR band of O-H str (3500 and 434 3011 cm⁻¹), C=O str (1679 cm⁻¹), S-H str (2697 and 2519 cm⁻¹) and C-H/O-H bending (1409 cm⁻¹) 435 ¹). In the TSA-capped ZnS QD, the absence of characterictic –SH band is attributed to the 436 cleavage of S-H bond and its subsequent attachment with the QD surface which indicates the formation of ZnS QD. The peaks around 645 cm⁻¹ are characteristic of Zn-S vibration and also 437 438 characteristic of cubic ZnS which are in good agreement with reported results in references.³ The 439 peak for C=O also shifts to 1649 cm^{-1} from 1679 cm^{-1} (curve **B**).

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Figure S14. FT-IR spectra of (A) Free TSA only, (B) TSA-capped ZnS QD and (C) TSA capped
ZnS QD in the presence of 250 ppb arsenic (As(III)).

In the presence of 250 ppb arsenic, the carboxylic oxygen of TSA in TSA-capped ZnS quantum dots become engaged in coordination with the arsenic. Both O-H and C=O stretching frequencies were decreased upon addition of As (250 ppb) and a new band is appeared at 838 cm⁻¹ (see curve C) due to symmetric stretching frequency of As-O.^{7, 8} The important IR bands are listed in **Table S6**.

456 Table S6. Tentative vibrational assignments of TSA-ZnS QD in the presence of arsenic (As).457

Functional Groups	TSA only	TSA-ZnS QD	TSA-ZnS QD + 250
			ppb arsenic (As)
O-H Stretching	3500 and 3011 cm ⁻¹	3432 cm ⁻¹	3472 cm ⁻¹
C=O Stretching	1679 cm ⁻¹	1649 cm ⁻¹	1635 cm ⁻¹
S-H stretching	2697 and 2519 cm ⁻¹	Disappeared	Disappeared
C-H bending and O-H	1409 cm ⁻¹	1396 cm ⁻¹	-
bending			
Zn-S stretching	-	645 cm ⁻¹	-
As-O stretching	-	-	838 cm ⁻¹

9.3. Schematic representation of mechanism

The mechanism of TSA-capped ZnS QD with arsenic ions is presented in Scheme S2. In our synthesized TSA-capped ZnS QD, the sulfur atom of the thiol group remains attached to the surface of the ZnS QD and the negatively charged carboxyl group (at higher pH) is accessible for selective coordination with arsenic ion (As-O bond formed which is supported by FTIR data). We propose that As(III) can coordinate with three TSA-capped ZnS QD (as shown in Scheme S2) followed by aggregation, resulting in an increase in PL intensity. As shown in the Scheme S2, three TSA-capped ZnS QD can be attached to the trivalent arsenic, which in turn leads to the agglomeration of the QD and enhancement of PL (due to AEE).



485 Scheme S2. Schematic representation showing the mechanism of As(III) with TSA-capped ZnS
486 QD through As-O linkage.

488 9.4. Dynamic light scattering (DLS) study

We further studied of dynamic light scattering (DLS) measurements of TSA-ZnS QD in the presence of a different concentration of As(III). The hydrodynamic particle diameter of our chemosensor was gradually increasing with the increasing concentration of As(III) from 2 ppb to 250 ppb (see Figure S15 and Table S7). We also plot normalized intensity as a function of hydrodynamic diameter (see inset, Figure S15). The results clearly indicate aggregation which enhanced the PL intensity.

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509 Figure S15. Dynamic light scattering (DLS) data fitted with Gaussian function for TSA-capped
510 ZnS QD in the absence and presence of different concentration (0 to 250 ppb range only) of

511 As(III) at pH 7.4. Inset shows DLS data with line connection plot.

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513 **Table S7.** Hydrodynamic particle diameter of TSA-ZnS QD in the absence and presence of

Diameter (nm)

 22.3 ± 0.2

 $\frac{50.8 \pm 0.1}{68.6 \pm 0.2}$

 78.8 ± 0.3

 91.3 ± 0.4

 105.7 ± 0.2

 164.2 ± 0.4

 190.1 ± 0.5

514 different concentrations (2 ppb to 250 ppb) of As(III), as obtained from DLS.

Sample

QD + 0 ppb As(III)

QD + 2 ppb As(III)

QD + 10 ppb As(III)

QD + 20 ppb As(III)

QD + 30 ppb As(III)

QD + 50 ppb As(III)

QD + 100 ppb As(III)

QD + 250 ppb As(III)

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521	We also measure the hydrodynamic particle diameter (from DLS) of the sensor in the
522	presence of $As(V)$ and the particle size increases but here the tendency of increase is less
523	compared to As(III) (see Figure S16 and Table S8).

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536 Figure S16. Dynamic light scattering (DLS) data of TSA-capped ZnS QD in the presence of 10

- 537 ppb and 250 ppb As(V) at pH 7.4.
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539 **Table S8.** Hydrodynamic particle diameter of TSA-ZnS QD in the absence and presence of

540 different concentrations (10 ppb and 250 ppb) of As(V), as obtained from DLS.

Sample	Diameter (nm)
QD + 0 ppb As(V)	22.3 ± 0.2
QD + 10 ppb As(V)	48.7 ± 0.3
QD + 250 ppb As(V)	93.3 ± 0.5

542 9.5. Zeta potential measurements

We also measured the zeta potential of TSA-capped ZnS QD in the presence of As(III) or As(V) analytes (see **Figure S17**). In the present experiment, free TSA-capped ZnS QD possess a zeta potential of about -32.6 mV. Upon addition of a particular concentration of As(III) (250 ppb), the zeta potential of the sensor changes to -15.5 mV. But in the addition of As(V) analyte (250 ppb), the zeta potential of the QD changes to -21.3 mV. This results also indicate that more aggregation is obvious in the presence of As(III) than with As(V) and hence more PL enhancement results with As(III).



559 Figure S17. Zeta potential plot of TSA-capped ZnS QD in the presence of As(III) and As(V)

560 at pH 7.4.

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562 9.6. Transmittance electron microscopic (TEM) images

We have also measured the size of TSA capped ZnS QD by using TEM techniques in the presence of a different concentration of arsenic (As) from 2 ppb to 250 ppb. When As(III) was added to TSA-ZnS QD, the average particle size was increased substantially (from 14.5 nm to 120 nm) suggesting the formation of aggregates (**see Figure S18A-F and Table S9**). This result also supports the aggregation-enhanced emission (AEE) in our chemosensor in the presence of arsenic (As) ions.



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Figure S18A-F. TEM images of TSA-ZnS QD in the absence and presence of different
concentrations of As(III), entire concentration range: (A) 0 ppb, (B) 2 ppb, (C) 10 ppb, (D) 50
ppb, (E) 100 ppb and (F) 250 ppb of As(III).

574 Table S9. Particle diameter of TSA-ZnS QD in the absence and presence of different
575 concentration (2 ppb to 100 ppb) of As(III) by using TEM study.

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Sample	Diameter (nm)
QD + 0 ppb As(III)	16.1 ± 0.5
QD + 2 ppb As(III)	34.8 ± 0.2
QD + 10 ppb As(III)	53.8 ± 0.1
QD + 50 ppb As(III)	67.1 ± 0.4
QD + 100 ppb As(III)	84.5 ± 0.3
QD + 250 ppb As(III)	107.8 ± 0.3

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We also measure the particle size (from TEM) of the sensor in the presence of As(V), the particle size is found to increase but the tendency of increase is lesser compared to As(III) (see

580 Figure S19 and Table S10).



Figure S19. TEM images of TSA-ZnS QD in the absence and presence of (A) 0 ppb and (A) 10

 $589 \qquad \text{ppb and (B) } 250 \text{ ppb } \text{As(V)}.$

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591 Table S10. Particle diameter of TSA-ZnS QD in the absence and presence of a different592 concentration of As(V) by using TEM study.

Sample	Diameter (nm)
QD + 0 ppb As(V)	16.1 ± 0.5
QD + 10 ppb As(V)	30.6 ± 0.3
QD + 250 ppb As(V)	77.3 ± 0.4

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595 **10. Real water-sample analysis**

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10. Ital water-sample allaly

597 To ensure the validity of this fluorimetric method in real sample analysis, the proposed 598 method has been applied for total arsenic determination in both the pond water and tap water 599 samples from within the campus. The pond water and tap water samples were first filtered to 600 avoid any particulate suspension by Whatman 42 filter paper and then all the samples (both tap 601 and pond water) were treated with disodium salt of ethylenediaminetetraacetic acid (Na₂EDTA) 602 for complexation with other metal cations [especially Fe(III) ion] but it does not form complexes 603 with arsenite and arsenate. The pH of all the solutions was adjusted to ~7.4 by using sodium 604 phosphate buffer. Then, we spiked the real water samples (both tap and pond water) with various 605 concentrations of arsenic [As(III), As(V) and mixture of As(III) + As(V) (1:1 ratio)] 606 (concentration range: 0, 5, 30, 50 and 100 ppb) and assessed the feasibility of our proposed nano-607 sensor (TSA-ZnS QD). The complete summarized results are shown in **Table S11-13.** From the 608 tabular data, we observe that our developed chemosensor (TSA-capped ZnS QD) is highly 609 specific and has got high sensitivity toward arsenic (As) in the real water samples also. The 610 results show good recovery rate, which indicates that the proposed method could also work in 611 environmental water samples. The negligibly small value of RSD (below 3.00%) indicates that 612 the proposed method gives accurate results.

613

614 Table S11. Recovery analysis of spiked As(III) with one representative Pond water and Tap615 water samples from campus.

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Sample types	Spiked As(III)	Total As(III)	Mean recovery	RSD (%) ^b
	(ppb)	found (ppb) ^a (Mean ± SD)	(%) of As(III)	
Tap water	0	0	-	-
Tap water	5	4.94 ± 0.05	99.8	1.01
Tap water	30	29.5 ± 0.4	99.7	1.35
Tap water	50	49.0 ± 0.8	99.6	1.63
Tap water	100	99.5 ± 1.8	101.3	1.81
Pond water	0	0	-	-
Pond water	5	4.92 ± 0.06	99.6	1.22
Pond water	30	29.2 ± 0.4	98.7	1.37
Pond water	50	49.2 ± 0.9	100.2	1.83
Pond water	100	99.3 ± 2.6	101.9	2.62

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⁶18 ^aMean of three determination and ^bRelative standard deviation from three determinations

- **Table S12.** Recovery analysis of spiked As(V) with one representative Pond water and Tap water622 samples from campus.

Sample types	Spiked As(V)	Total As(V)	Mean recovery	RSD (%) ^b
	(ppb)	found (ppb) ^a (Mean ± SD)	(%) of As(V)	
Tap water	0	0	-	-
Tap water	5	4.93 ± 0.05	99.6	1.01
Tap water	30	29.4 ± 0.4	99.3	1.36
Tap water	50	48.7 ± 0.9	99.2	1.85
Tap water	100	99.2 ± 1.9	101.1	1.92
Pond water	0	0	-	-
Pond water	5	4.88 ± 0.05	98.6	1.02
Pond water	30	28.8 ± 0.5	97.6	1.74
Pond water	50	49.6 ± 1.2	101.6	2.42
Pond water	100	99.8 ± 2.8	102.6	2.81

⁶²⁵ ^aMean of three determination and ^bRelative standard deviation from three determinations

Table S13. Recovery analysis of a spiked mixture of As(III) and As(V) [1:1 ratio] with one
representative Pond water and Tap water samples from the campus.

Sample types	Spiked mixture of As(III) and As(V) (ppb)	Total arsenic [As(III)+As(V)] found (ppb) ^a (Mean ± SD)	Mean recovery (%) of total arsenic	RSD (%) ^b
			[As(III)+As(V)]	
Tap water	0	0	-	-
Tap water	5	4.92 ± 0.05	99.4	1.02
Tap water	30	29.2 ± 0.4	98.6	1.37
Tap water	50	48.6 ± 0.9	99.0	1.85
Tap water	100	99.6 ± 1.9	101.5	1.91
Pond water	0	0	-	-
Pond water	5	4.90 ± 0.05	99.0	1.02
Pond water	30	29.0 ± 0.6	98.7	2.06
Pond water	50	49.2 ± 1.2	100.8	2.44
Pond water	100	99.3 ± 2.7	102.0	2.72

641 ^aMean of three determination and ^bRelative standard deviation from three determinations

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