Unique photoluminescence response of MoS$_2$ quantum dots over a wide range of As (III) in aqueous media

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Abstract

We report the solvothermal synthesis of MoS$_2$ based quantum dots (QDs) and the performance evaluation of bare QDs for the detection of aqueous As (III) oxidative state at room temperature and neutral pH over a vast range (0.1–1000 ppb). Concentration-dependent photoluminescence (PL) of the QDs enhances up to 50 ppb and then suppresses till 1000 ppb. It shows two distinctive slopes for enhancement and suppression. The enhancement is possibly due to the passivation of trap states or defects. The formation of tiny glassy As$_2$S$_3$ particles on the QD surface may be the possible reason for suppression. The pattern of optical absorption of QDs follows the similar patterns of PL. Still, it shows an enhanced absorbance in the near UV range below $\approx$300 nm, which increases with As (III) concentration up to 50 ppb and then decreases following the PL pattern. The MoS$_2$ QDs were characterized by using transmission electron microscopy, x-ray diffraction, UV–Vis, and PL spectroscopy. The enhancement and suppression results were excellently fitted with the modified Stern–Volmer equation. The detection of arsenic is possible using these linear fit equations as calibration curves.

Keywords: MoS$_2$, photoluminescence, arsenic, quantum dots

(Some figures may appear in colour only in the online journal)

1. Introduction

Heavy metals are a source of groundwater contamination all over the world. Among the heavy metals, arsenic (As) is considered to be one of the most toxic species and hazardous to human health [1]. The As (III) oxidative form is more dangerous, as it absorbs 50 times more and is less detectable than the As (V) oxidative form. The As (III) contamination is also known to be maximum at room temperature with pH $\sim$ neutral value [2]. Considering the adverse health effect, the World Health Organization suggested the permissible limit of arsenic in drinking water to 10 ppb [3]. The detection of such a lower concentration of arsenic in aqueous media is challenging. Instead of very costly, time- and resource-consuming, trained human resource-dependent analytical methods [4–6], it has become a genuine research challenge to develop accessible and cheap strategies that are quicker. The optical sensing method based on fluorescence techniques is one such focus area [7–9].

In recent years, two-dimensional (2D) transition metal dichalcogenides (TMDs) have received increasing attention for various applications [10]. Molybdenum disulfide (MoS$_2$) is one of such TMDs. The MoS$_2$ quantum dots (QDs) feature excellent mechanical and optoelectronic properties [11, 12]. The nanosized MoS$_2$ provides versatile chemical properties
and excellent dispersion in aqueous media [13, 14]. MoS$_2$ QDs also showed strong excitation-dependent fluorescence, mainly because of the quantum confinement effect [15]. The absorption and emission spectra and electrochemical redox potential changes with the particle size change comparable to that of excitons [16, 17]. Additionally, these types of QDs have surface states and trap levels. Surface recombination and trapping play significant roles in determining the luminescent properties of MoS$_2$ QDs [18].

The potential of MoS$_2$ as a material has been widely explored in various fields, including optoelectronics, energy storage, catalysis, biomedicine, and sensing applications [19–22]. Several modalities, such as field-effect transistors (FET), surface plasmon resonance, and photoluminescence (PL), have been considered for the development of a MoS$_2$ based sensor [23, 24]. Among them, optical detection methods are more attractive because of their operational simplicity and high sensitivity.

To impart the selectivity and sensitivity, which are important for practical applications, the QDs are functionalized with various strategies [25–27] while developing a QD-based sensor. Though the literature report shows standard fluorescence enhancement in MoS$_2$ QDs, these QDs were surface-functionalized or surface-passivated by some functional materials/molecules, such as glutathione, L-cysteine, TGA/cystamine/PDT, or gold nanoparticles [28–31]. Mostly, the enhancement of fluorescence was observed due to the interaction of detecting species with the functional materials/molecules used for surface functionalization and not solely due to the interaction between bare MoS$_2$ QDs and detecting species. To the best of our knowledge, there is only one report on label-free detection of Fe (III) using bare MoS$_2$ QDs, but a concentration-dependent quenching in fluorescence intensity was observed, and not an enhancement [32]. Several other fluorescence quenching results are also on records using functionalized MoS$_2$ QDs to detect hypochlorite disinfectant [33], nitro-explosives [34, 35], pesticide [36], metal ions such as Fe (III), Cr (VI), Cu (II), Au (III), Pb (II), and Hg (II) [29, 37–41].

While only a few credible works are present in the literature on arsenic detection using MoS$_2$ sheets [42–44], no reports were found on arsenic sensing using MoS$_2$ QDs. These facts encouraged to explore the usage of MoS$_2$ QDs for photo luminescence-based arsenic detection. Compared to MoS$_2$ nanosheets, zero-dimensional MoS$_2$ QDs provide a better defect-rich structure with plenteous active sites. MoS$_2$ QDs result from MoS$_2$ sheets due to the intra-plane S–Mo–S bonds cleaving. This situation creates a large surface area with more active sites, more edge atoms combined with high in-plane electron transport and leaving many unsaturated bonds at the surface of MoS$_2$ QDs [45]. The aqueous As (III) ions could thus interact with resulting unsaturated sulfur atoms of MoS$_2$ QDs, leading to feasible adsorption of As (III) ions onto the QD surface.

In this work, we synthesized water-dispersed MoS$_2$ QDs via solvothermal routes. The QDs were excited at a fixed wavelength of 360 nm, and the PL of excitons was studied over a vast range of As (III) concentrations varying from 0.1 ppb to 1000 ppb. The lowest point of aqueous arsenic concentration was determined to find the point at which this sensing is reasonable. The highest point of aqueous As (III) concentration was kept in the same order as the maximum level of aqueous As (III) concentration in groundwater [1]. The concentration-dependent PL’s experimental results showed an enhancement of PL of the MoS$_2$ QDs within the As (III) concentrations from 0.1 to 50 ppb, followed by a suppression up to 1000 ppb. We call the phenomenon as ‘suppression’ and not ‘quenching’, simply because the observed PL intensities beyond 50 ppb were still greater than PL of MoS$_2$ QDs with no As (III) interaction.

To the extent of our knowledge, this is the first report on ‘unique fluorescence enhancement’ with bare MoS$_2$ QDs and arsenic sensing using bare MoS$_2$ QDs. Also, the detection method of As (III) is directly based on the change in fluorescence of bare MoS$_2$ QDs without any functionalization, and the method is simple and straightforward.

2. Experimental methods

Molybdenum disulfide (MoS$_2$), sodium arsenite (NaAsO$_2$), N, N-dimethylformamide (DMF), poly-vinyl-pyrolidone [PVP/ (C$_6$H$_9$NO)] with molecular weight (MW) 58 000 and cetyl trimethyl ammonium bromide (CTAB) were procured from Alfa Aesar. Analytical grade chemicals were procured and used without purification. Deionized (DI) water from Milli-Q was used for the synthesis.

2.1. Preparation of MoS$_2$ QDs

Bulk MoS$_2$ with CTAB was first exfoliated to nanosheets by the solvent exfoliation method with slight modification, as reported by Coleman et al [10]. Typically, 1 g each of MoS$_2$ and CTAB was added to 100 ml of DMF and kept under sonication (Elmasonic S ultrasonic, Model S 60 H) for 10 h to exfoliate the MoS$_2$ powder. It was then centrifuged (REMI, Model RM-12C) at 4000 rpm for 15 min, and the supernatant was collected for further use.

MoS$_2$ QDs were synthesized by a solvothermal approach, as suggested by Xu et al with slight modifications [46]. Briefly, the supernatant of the MoS$_2$ sheets was refluxed at 180 °C for 8 h, followed by cooling at room temperature. It was then centrifuged at 5000 rpm for 30 min to separate the light-yellow colored (figure 6(c)(inset-i)) supernatant and collected as MoS$_2$ QDs.

2.2. Sensing of arsenic by MoS$_2$ QDs

A stock solution of 200 ppm Arsenic (III) was prepared by dissolving NaAsO$_2$ in DI water. Lower concentrations of arsenic and MoS$_2$ QDs were obtained by serial dilution using a buffer solution of pH 7. The resulting arsenic and MoS$_2$ QDs solutions were mixed in 1:3 ratios (As: MoS$_2$ QDs). Corresponding MoS$_2$ QDs solutions containing 0.1 to 1000 ppb As (III) were kept for 15 min before PL measurements. All the
3. Results and discussion

3.1. Verification of the formation of MoS₂ QDs

The formation of MoS₂ QDs was verified through structural and spectroscopic characterizations. The structural characteristics or morphology of the QDs was examined using a Talos Cryo transmission electron microscope (TEM) (Thermo Scientific). The spectra for UV–Vis absorbance, photoluminescence (PL), and Fourier transform infrared spectroscopy (FTIR) were obtained using a UV–Vis-NIR spectrophotometer (Shimadzu), RF-5301PC spectrofluorophotometer (Shimadzu), and Spectrum Two FTIR spectrometer (Perkin Elmer), respectively. The emission colors of the MoS₂ QDs were detected using a UV fluorescence analysis cabinet.

Figure 1 shows the UV–Vis spectra of the as-prepared MoS₂ nanosheets and QDs. MoS₂ nanosheets are known to show four distinct excitonic peaks, generally allocated as A (667 nm), B (608 nm), C (443 nm), and D (394 nm) excitons [22]. The first two peaks A and B are doublet peaks, the excitonic interband transition of 2D MoS₂ at the K point of the Brillouin zone, due to the spin orbit’s splitting transition [47, 48]. The other two peaks, C and D, originate from the interband evolution between occupied and unoccupied orbitals [49]. However, in MoS₂ QDs, all these peaks disappear, except for a peak near the UV region (λ < 300 nm), resembling the excitonic features of MoS₂ QDs [50, 51]. The broad absorption at 318 nm seen in MoS₂ QDs is due to the convolution of all the excitonic peaks [49], blue-shifted due to the quantum size effect [22].

The PL spectra of as-prepared MoS₂ nanosheets and QDs are shown in figure 1 as an inset. As MoS₂ nanosheets reduce to QDs, the weak red emission at 701 nm transforms into an intense blue emission at 459 nm due to the quantum confinement effect. The excitation wavelength was also shifted from 570 nm for MoS₂ nanosheets to 360 nm for MoS₂ QDs.

The bare MoS₂ QDs show strong photoluminescence. This effect results from the excitonic electron-hole recombination. The sulfur vacancies of unsaturated molybdenum ions contribute to the excess electrons in this process [30].

The crystallographic structure of the as-synthesized QDs was recorded using powder x-ray diffraction (XRD), as shown in figure 2. The observed diffraction peaks for MoS₂ QDs are at 2θ = 45.3, 39.91, and 49.34, corresponding to the (002), (103), and (105) planes, respectively, indicating the formation of mono- or few-layered MoS₂ QDs [52].

The TEM/HRTEM micrographs depicted in figure 3 represent the microstructures and morphologies of the as-synthesized MoS₂ QDs. The presence of almost spherical and well-dispersed QDs is evident in figure 3. A histogram was generated based on the information available from the observed 150 QDs and presented in figure 3. The average size of the QDs was ~4.5 nm. Figure 3(c) shows the HRTEM image of MoS₂ QDs. The corresponding d-spacing (0.23 nm) as indicated in the figure match with 103 planes of MoS₂ QDs [46].

The MoS₂ QD size determined by TEM is ~4.5 nm, while the corresponding size determined by Scherer equation is ~6.6 nm. Usually, TEM determines the particle size, whereas XRD determines the average crystallite size. As particles may be constituted by several crystallites, and therefore, usually the crystallite size determined by XRD is smaller than the particle size determined by TEM. However, all of our experiments were done using the QDs from the supernatant after centrifugation, that must be the lower limit of the particle size as determined by TEM. On the other hand, the crystallite size determined by the XRD technique needs larger amount of dry powder sample, which is collected after final ultrasonication and washing may contain bigger particles and that are usually precipitated during centrifugation.
Therefore, in this case, we are seeing a size difference determined by the two methods, although they are of the same order.

FTIR of the QDs was carried to study the surface chemical properties of the as-prepared MoS₂ QDs. Figure 4 shows the FT-IR spectrum of MoS₂ QDs. The peak at ∼494 cm⁻¹ is attributed to the stretching frequency of the Mo–S bond [35].

3.2. Spectral analysis of MoS₂ QDs and their interaction with arsenic

The optical properties of the QDs were investigated using UV–Vis absorbance and photoluminescence (PL) measurements in the presence and absence of As (III). Figure 5 depicts the TEM image of the MoS₂ after As (III) adsorption. Upon interaction with As (III), the QDs appeared to come closer to each other with respect to unexposed QDs (figure 5), but do not show complete agglomeration.

When the aqueous MoS₂ QDs were treated with standard As (III) solutions with varying concentrations from 0.1 to 50 ppb, an enhancement in absorbance was observed with the increase in arsenic concentration (figure 6(a)). However, the opposite phenomenon, a constant decrease in absorbance with increasing arsenic concentration was observed when the QDs were treated with solutions of 50 to 1000 ppb of As (III) (figure 6(b)).

The as-prepared QDs were luminescent (figure 6(c) (inset-ii)). The emission of MoS₂ QD was a blue emission with a peak located at 459 nm. The emissive blue color was...
also confirmed by irradiating MoS₂ QD under UV light (365 nm). As-prepared QDs also showed concentration-dependent PL spectra. Hence, these QDs can be employed as a PL probe to detect arsenic in aqueous media.

Figures 6(c) and (d) shows the PL spectra of the QDs incorporated with varying concentrations of As (III) from 0.1 to 50 ppb and 50 ppb to 1000 ppb, respectively, in solution. With increasing concentration, an enhancement in PL intensity up to 50 ppb and suppression beyond 50 ppb of As (III) concentration was observed when the QDs were excited with a constant laser operating at 360 nm. A minimal blue-shift during PL enhancement of MoS₂ QD, where the peak-shift from 459 nm to 451 nm (2.70 to 2.75 eV) was observed due to the variation in arsenic from 0 to 50 ppb. This slight spectral shift can be attributed to surface-state modifications of MoS₂ QDs when arsenic interacted with the QD surface. We observed no further change in the peak position for the concentration of 50–1000 ppb of arsenic. Instead, the PL intensity got suppressed beyond 50 ppb and the suppression remained centered at 451 nm. These trends of As (III) concentration-dependent PL measurements are similar to the previously recorded UV–Vis spectra under similar conditions.

Initially, the adsorption of As (III) happens at a low concentration on the surface of the MoS₂ QDs. The surface defects typically originate from the unsaturated sulfur (S²⁻) dangling bonds [53]. The factor contributing to PL enhancement is possibly surface passivation of trapping sites by eliminating those S²⁻ dangling bonds on the QD surface [54]. The luminescence of these QDs is very sensitive to their surface states, which may change due to physical or chemical interactions, leading to a change in radiative recombination efficiency. In the suppression case, various phenomena such as inner-filter effects, non-radiative recombination pathways, and electron transfer processes may be the reasons [55].

In our case, we initially see an enhancement of the photoluminescence of MoS₂ QDs in the presence of aqueous As (III), which is a rare phenomenon [56, 57]. At lower concentrations of arsenic, the initial adsorbed As (III) ions passivate the surface traps on the surface of MoS₂ QDs. Here, the effect of surface-defect passivation is dominant over the non-radiative recombination process, which might have occurred due to the unsaturated S²⁻ dangling bonds, and hence an enhancement in fluorescence was observed [58]. Passivation of trap states or defects may be the reason for such enhancement at relatively low concentrations of aqueous As (III). Since we observed PL enhancement till 50 ppb of As (III), we suppose that the surface defects of MoS₂ QDs got saturated on reaching this concentration.

However, when the concentration of aqueous As (III) is beyond a particular limit, which is 50 ppb in this case, the tiny glassy As₂S₃ particles may form on the MoS₂ QD surface. But, after the saturation of surface defects, the non-radiative pathway dominates over the saturated surface passivation. The extra As (III) ions may facilitate non-radiative recombination, resulting in suppressing the initial fluorescence enhancement due to the electron transfer from MoS₂ QDs to As (III) [53, 58]. The aqueous oxidative state of As (III) may interact with these As (III) rich sites and create a 3d¹⁰–3d¹⁰ metallophilic interaction leading to new energy-accepting levels on the As (III), which facilitates the Dexter energy transfer to As (III) and suppression of the initial enhancement [25, 59]. Thus, beyond 50 ppb, small As₂S₃ particles formed resulting in PL suppression due to non-radiative recombination and electron transfer processes. The schematic in figure 7 represents the photoluminescence response of the MoS₂ QDs in presence of various concentrations of As (III).

The Stern–Volmer equation is usually applied to fluorescence quenching measurements, but a modified equation derived from the original Stern–Volmer equation can be applied to fluorescence enhancement measurements. The trends of fluorescence were analyzed through the utilization of this modified Stern–Volmer equation [60], written as:

\[ \frac{F_0}{F - F_0} = \frac{1}{K_{SV}[C]} + 1, \]

where \( F_0 \) and \( F \) represent the PL intensities of MoS₂ QDs in the absence and presence of arsenic, respectively, [C] is the total arsenic concentration, and \( K_{SV} \) is the modified Stern–Volmer constant.

Although the fluorescence enhancement up to 50 ppb As (III) was followed by gradual suppression on further increase in As (III) concentration, we used the same equation to fit both enhancement and suppression trends. Figures 8(a) and (b) represents plots of concentration-dependent PL results in the form of a modified Stern–Volmer equation. The correlation coefficient (\( R^2 \)) values for both the enhancement (figure 8(a)) and suppression (figure 8(b)) trends are very close to 1, which proves that the data is well-fitted by the modified Stern–Volmer equation.

From figures 8(a) and (b) and supported by \( K_{SV} \) values from table 1, the change in relative PL intensity \( \frac{F_0}{(F - F_0)} \), corresponding to PL enhancement at 0.1–50 ppb arsenic
Figure 6. UV-Vis absorption spectra of MoS$_2$ QDs in the presence of varying concentrations of As (III) from (a) 0 to 50 ppb and (b) 50 to 1000 ppb. Photoluminescence spectra of MoS$_2$ QDs in the presence of varying concentrations of As (III) from (c) 0 to 50 ppb and (d) 50 to 1000 ppb. The inset (figure (c)) represent photographs of MoS$_2$ QDs (i) without UV irradiation and (ii) UV irradiation.

Figure 7. Schematic representation of photoluminescence response of the MoS$_2$ QDs in presence of various concentrations of As (III).
was four times greater than the same relative change produced due to suppression in PL with 50–1000 ppb arsenic (figure 8(b)). $K_{SV}$, which is the Modified Stern–Volmer constant of linear plots, its value for PL enhancement was 0.41. Simultaneously, it was a comparably smaller numerical value $-3.07 \times 10^{-3}$ with a minus sign mathematically denoting suppression for PL suppression.

We can calibrate the detected level of arsenic using these two trend lines and predict the arsenic concentration of test samples by choosing the right calibration curves, that is, figures 8(a) or (b), based on the information of the test samples’ PL measurements, with and without dilution.

We have graphically estimated, following the Benesi–Hildebrand method, the stoichiometry for the binding interaction of MoS$_2$ QDs with As(III) ions and corresponding values of association constants for PL enhancement and suppression trends based on the change in fluorescence intensity of QDs with metal ions [61]. We plotted separately $\frac{1}{F/F_0}$ versus $\frac{1}{C}$ for both the enhancement and suppression trends and checked the linearity.

The association constant $K_a$ was obtained by dividing each linear plot’s intercept by its slope. From figures 8(c) and (d), both the plots were perfectly linear with 99.9% linearity, suggesting that MoS$_2$ QDs followed 1:1 stoichiometry with As(III) ions during both the PL enhancement and PL suppression. The values of $K_a$ and $R^2$ are given in Table 1. Like $K_{SV}$, the $K_a$ value for PL enhancement was numerically more significant than that of PL suppression with a minus sign in latter again symbolizing suppression.

The limit of detection (LOD) of MoS$_2$ QDs towards As (III) was computed using the Stern–Volmer equation at lower concentration range (figure 8(a)) and a signal to noise ratio.

| Concentration of As (III) | Trend               | Modified Stern–Volmer | Benesi–Hildebrand |
|---------------------------|---------------------|------------------------|-------------------|
| 0.1–50 ppb                | PL Enhancement      | $K_{SV}$ (ppb$^{-1}$)  | $R^2$             |
|                           |                     | 0.41                   | 0.999             |
| 50–1000 ppb               | PL Suppression      | $-3.07 \times 10^{-3}$ | 0.999 $-0.027$    | 0.999 |

Figure 8. Modified Stern–Volmer plot within the concentration range of (a) 0.1 to 50 ppb ($R^2 = 0.999$), and (b) 50 to 1000 ppb ($R^2 = 0.999$). Benesi–Hildebrand plot within the concentration range of (c) 0.1 to 50 ppb ($R^2 = 0.999$), and (d) 50 to 1000 ppb ($R^2 = 0.999$).
The calculated LOD for As (III) was found to be 0.04 ppb. A comparison table of fluorescence-based detection of As (III) using various QDs is presented in Table 2. Results indicated that the As (III) detection capability of MoS2 QDs is superior than the reported one.

In summary, we have successfully demonstrated the synthesis of highly luminescent MoS2 QDs through a solvothermal route and their use as fluorescent probes. These QDs are extremely sensitive and easily detect aqueous As (III) in the test range of 0–1000 ppb range. The photoluminescence of these QDs was found to increase from 0.1 ppb to 50 ppb, and then gets suppressed till 1000 ppb. It was unique to observe arsenic concentration-dependent PL enhancement possibly due to the passivation of surface defects followed by ‘gradual suppression’ caused by small As2S3 particles through non-radiative recombination and electron transfer processes. Benesi–Hildebrand plots pointed 1:1 stoichiometry for MoS2 QD and As(III) interaction. Even after the addition of 950 ppb of arsenic though the PL intensity was suppressed, the PL enhancement with respect to arsenic-free MoS2 QD was still retained. The QDs can detect arsenic concentrations as low as 0.1 ppb, which is well below the WHO permissible limit of arsenic in drinking water. MoS2 QDs will prove to be a promising optical probe for detecting the presence of the As (III) oxidative state in water.

4. Conclusions

In summary, we have successfully demonstrated the synthesis of highly luminescent MoS2 QDs through a solvothermal route and their use as fluorescent probes. These QDs are extremely sensitive and easily detect aqueous As (III) in the test range of 0–1000 ppb range. The photoluminescence of these QDs was found to increase from 0.1 ppb to 50 ppb, and then gets suppressed till 1000 ppb. It was unique to observe arsenic concentration-dependent PL enhancement possibly due to the passivation of surface defects followed by ‘gradual suppression’ caused by small As2S3 particles through non-radiative recombination and electron transfer processes. Benesi–Hildebrand plots pointed 1:1 stoichiometry for MoS2 QD and As(III) interaction. Even after the addition of 950 ppb of arsenic though the PL intensity was suppressed, the PL enhancement with respect to arsenic-free MoS2 QD was still retained. The QDs can detect arsenic concentrations as low as 0.1 ppb, which is well below the WHO permissible limit of arsenic in drinking water. MoS2 QDs will prove to be a promising optical probe for detecting the presence of the As (III) oxidative state in water. The optical absorbance of these QDs was found to follow a similar pattern.
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Data availability statement

All data that support the findings of this study are included within the article (and any supplementary files).

CRediT authorship contribution statement

Anindya Datta and Tapan Sarkar conceived the experiments. Jamilur R Ansari and Md Farhan Naseh grew, characterized the materials and performed the PL measurements. Neelam Singh performed the UV–Vis measurements. All the authors discussed the data and wrote the manuscript together.

Competing financial interests

The authors declare no competing financial interests.

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