MAA encapsulated MoS_2 Quantum Dots as a fluorescent probe for the sensing of flavonoid

Shivani Bharti, Kedar Singh*

School of Physical Sciences, Jawaharlal Nehru University, New Delhi, 110067

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Corresponding Author: kedar@mail.jnu.ac.in

Abstract: Transition metal dichalcogenide (TMDs) quantum dots (QDs) have attracted widespread attention among scientific community as fluorescent nanomaterial. Among TMDs, MoS_2 has received particular interest due to its novel and intriguing optical properties. In this work hydrothermal method is used to prepare aqueous soluble MoS_2 QDs using Molybdenyl acetylacetonate and thiourea as Mo and S precursors, respectively. The solubility of unfunctionalized MoS_2 is poor in water and organic solvent, therefore thioglycolic acid is used as surfactant for surface functionalization and to enhance the aqueous solubility & stability. These functionalized QDs have been synthesized at pH 11 using hydrothermal method and explored their structural and optical properties. The as synthesized QDs are characterized using TEM, XRD, FTIR, UV-Vis and PL spectroscopy. The morphological shape of as prepared QDs is spherical with size 4-6.5 nm. The MAA encapsulated MoS_2 QDs are further explored as fluorescent probe for the sensitive sensing of flavonoid Quercetin.

Keywords: Colloidal, fluorescent, transition metal dichalcogenides, flavonoid

Introduction: Szent-Gyorgyi are the first to isolate and identify bioflavonoids[1]. Bioflavonoids are the important class of bioactive molecules with effective antimicrobial, anti-inflammatory, antibacterial, antitumor and anticancer properties[2, 3]. Anthocyanidins, flavans, flavonols, anthoxanthins, and flavanones are the five subclasses of bioflavonoids. Quercetin is one of the flavonols mainly found in leafy vegetables, herbs, vegetables, seeds, red wine and fruits. The chemical structure of Quercetin consists of catechol ring and hydroxyl (-OH) groups at position 3′,4′, 3, 5 and 7 which makes it a potential material for numerous biomedical applications like anti-blood platelet, anti-carcinogenic, radical scavenger, expanding blood vessels because of antioxidant properties[4]. As Quercetin is an important antioxidant which plays important role for treating numerous diseases and also present in the daily diet of human. In spite of the high dietary intake of Quercetin, only 0.4-1% is excreted in urine[5]. Thus, it is necessary to develop a sensitive and selective probe for the sensing of Quercetin in biological samples and pharmaceutical drugs.

The luminescent properties of metallic nanostructures, Quantum dots (QDs) and organic fluorescent dyes are used to detect analytes in the fluorescence-based methods. The unique properties of QDs like high quantum yield, broad absorption spectrum, good extinction coefficient, narrow and tunable emission spectra have fascinated researcher's interest worldwide. QDs possess excellent optical properties and have been widely utilized for the detection of toxic molecules, ions, small molecules, and biomacromolecules[6–8]. MoS_2 QDs have attracted more interest because of their high solubility in an aqueous medium and the presence of large number of active edge atoms. The synthesis of MoS_2 QDs has been explored by using several methods including liquid exfoliation, lithium intercalation and hydrothermal[9]. The tunable emission

properties of MoS_2 QDs makes them a potential material for sensing applications. MoS_2 nanostructure owing to their unique structures, high stabilities, low toxicity and high surface to volume ratio make them extremely attractive in the field of biosensing[10, 11]. There is still a critical need for the development of facile and widely accessible synthesis methods for the preparation of fluorescent MoS_2 QDs for biological applications. Ideally, these methods should synthesize small size, low polydisperse and colloidal nanoparticles with stability in a broad range of pH and various ionic buffers. For biological applications, there should be different functional groups available on the surface of nanostructure for surface modification with biomolecules such as peptides, proteins or drugs[12]. Most importantly the synthesized nanostructure should be stable and do not agglomerate in biological media i.e., intracellular environment and demonstrate an improved quantum yield.

In this manuscript, we have synthesized functionalized water soluble MoS_2 QDs using hydrothermal approach. Mercaptoacetic acid (MAA) encapsulated MoS_2 QDs were further utilized for the sensitive and selective sensing of Quercetin. The optical properties of synthesized MAA capped MoS_2 QDs have been explored using UV-Visible spectroscopy, and Photoluminescence (PL) spectroscopy. The structural and morphological characteristics have been studied using X-Ray diffraction (XRD), Transmission electron microscopy (TEM) and Fourier Transform Infrared spectroscopy (FT-IR), and. The sensing of Quercetin has been done based on the variation in the emission signal of MAA encapsulated MoS_2 QDs.

2. Experimental Section

2.1. Chemicals and reagents: The chemicals and reagents utilized in all the investigations are of analytical grade and have been used without any further purification. Mercaptoacetic acid [$HSCH_2CO_2H$], and Molybdenyl acetylacetonate [$MoO_2(acac)_2$] were procured from Sigma Aldrich. Thiourea [CH_4N_2S] and Sodium hydroxide [NaOH]were purchased from Fisher Scientific. BOROSIL glassware is used for all the synthesis procedure. For the cleaning of the glassware chromic acid was used, followed by rinsing with DI water, ethanol, and acetone step by step and dried before using.

Synthesis of MoS2 nanostructures: The current methodology utilizes hydrothermal method to synthesize MAA encapsulated MoS_2QDs. Thiourea and Molybdenyl acetylacetonate are used as precursors for S and Mo, respectively. Mercaptoacetic acid (MAA) is used as surfactant and for the functionalization of nanostructures. Firstly, 3.5 mM of Molybdenum acetyloacetonate is dissolved in 60 ml DI followed by the addition of 96 µl of MAA. The above solution is stirred for 20 minutes at 100 ℃. After cooling down the solution for some time the pH was set to 11 using 1 M NaOH solution. To the above prepared solution, add 15 mM of thiourea. After 15 minutes of magnetic stirring, the solution was transferred to 100 ml Teflon tube and sealed. The temperature of the stainless-steel autoclave was maintained at 220 ℃ for 24 hours. The supernatant containing QDs were collected after centrifugation.

2.3. Characterizations: Electronic absorption spectra were recorded using U-3900 Spectrophotometer-LABINDIA and emission spectra using F-4700 FL Spectrophotometer-LABINDIA. De-Ionized water was used as solvent to record the absorption and emission characteristics of the samples. Structural measurement of as prepared sample was done using a TEM; JOEL 2100F, high resolution transmission electron microscope (200 kV) (TEM). For TEM measurements, 5-10 µL QDs sample was drop casted over carbon support film of a 300 mesh Cu grid and let the sample dry for some time. Fourier transform infrared (FTIR) spectrum was recorded with FTIR spectrometer (Shimadzu 8400, Japan) utilizing KBr pellets in the range from 4000 cm^{-1}– 400 cm^{-1}. XRD was recorded using Rigaku mini-Flex 600, Japan, 1.54 A°. The sample was dried at 50℃ and then

XRD spectra was recorded. Zeta potential was measured using Malvern.

3. Results and Discussion: MoS_2 QDs are synthesized by one pot hydrothermal method using Molybdenyl acetyacetonate, Thiourea and MAA. In the synthesis process MAA and Thiourea could work as reducing agent due to the existence of various functional groups and as a source of S precursor, respectively. MAA will also work as a surface encapsulation agent and provide carboxyl groups over MoS_2 QDs surface which enhances the aqueous stability and solubility of synthesized QDs. Figure 1 (a) shows the TEM micrograph of MAA encapsulated MoS_2 QDs. The micrograph shows that the particles do not show any agglomeration and are well dispersed in aqueous media. The obtained size ranges from 4 nm – 6.5 nm with spherical morphology. The XRD pattern shown in Figure 2 (b) shows no obvious diffraction peaks, which may be due to their very small size. These small size QDs hardly have layer-layer interaction between each other. Bulk MoS_2 shows a diffraction peak at $2\Theta = 14.4°$ corresponding to the (002) plane[13]. However, its absence in the MoS_2 QDs XRD spectra reveals the lack of interlayer action in synthesized QDs. Figure 2 (c) depicts the FT-IR spectrum of MAA encapsulated MoS_2 QDs. The presence of surface passivated groups over MoS_2 QDs surface is confirmed by FT-IR spectra. The characteristic peak at 3452 cm^{-1} illustrates the O-H bond of the adsorbed H_2O[14]. The characteristic band at 1635 cm^{-1} is due to the stretching of C=O bond present in the stabilizing agent MAA. A sharp peak corresponding to the stretching of S–H group of MAA lies in the region 2550 cm^{-1} – 2670 cm^{-1}. However, the absence of S–H in the MAA encapsulated MoS_2 QDs indicates the binding of the S atom of S-H group of the MAA to the Mo atoms lying on the surface of MoS_2 QDs. In the fingerprint region, the absorption band at 463 cm^{-1} arises due the stretching of Mo-S bond[15].

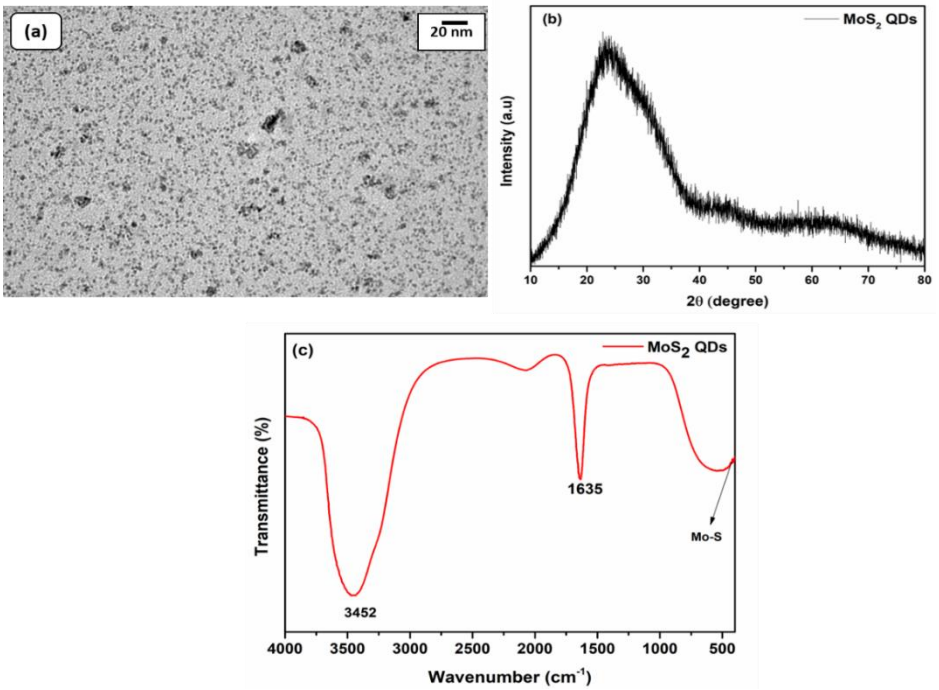

Figure 1: (a) TEM micrograph of MAA encapsulated MoS2 QDs, (b) XRD spectrum of MoS2 QDs and (c) FT-IR spectrum of MoS2 QDs.

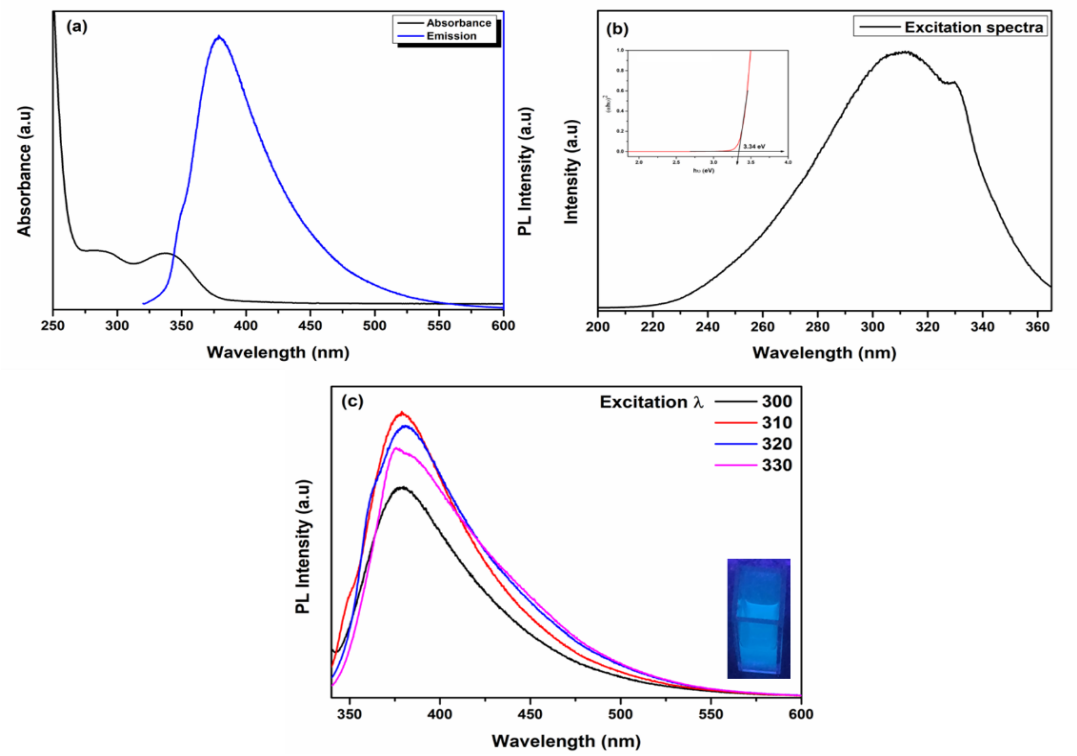

Figure 2: (a) Absorption and emission spectra (b) excitation spectra (inset shows the tauc plot) and (c) excitation dependent emission spectra of MAA capped MoS2 QDs.

The optical characteristics of MAA encapsulated MoS_2 QDs are explored using UV-Visible and PL spectroscopy. Figure 2 (a) illustrates the absorption and emission spectra of prepared MoS_2 QDs. It has been reported that low dimensional or MoS_2 QDs show strong blue shift in the absorption peak when the dimension of the nanostructure reduced to less than 50 nm because of the quantum confinement effect [16]. The shoulder absorption peak observed at 340 nm can be ascribed to the direct transitions from the deep valence band to the conduction band in MoS_2 QDs. The absence of peaks in the higher wavelength region i.e. 600 nm–700 nm shows the absence of 2D MoS_2 with large lateral dimensions[17]. Also because of the strong quantum confinement effect the band gap of the QDs is enhanced, which is calculated using Tauc's relation[18]. Using Tauc's relation a graph is plotted between $(\alpha h\nu)^2$i.e. square of the absorption energy and E as shown in inset in Figure 2(b). By extrapolating the tangent, the obtained bandgap is 3.34 eV which is much larger than monolayer MoS_2i.e. 1.9 eV and bulk $MoS_2$with band gap 1.2 eV[19].

The excitation spectrum of MAA capped MoS_2 QDs (Figure 2(b)) illustrates an intense peak at ~310nm. Also, the emission spectrum shows a strong emission peak at 380 nm when excited at 310 nm. PL investigation is commonly used to explore the transition properties, carrier migration, and trapping properties. The higher emission intensity reveals the higher recombination rate of e-h pairs[20]. Also, the as synthesized MAA capped MoS_2 QDs show bright blue color when seen using UV lamp with 365 nm wavelength light, while they reflect light greenish color when observed with daylight. When as synthesized QDs are excited with different excitation wavelengths (300 nm- 330 nm) as shown in Figure 2(c), the emission spectra show a slight shift in the emission peak of ~ 2-3 nm. This excitation dependent emission spectrum is due to the polydisperse nature of the QDs[21]. Zeta potential was measured to know

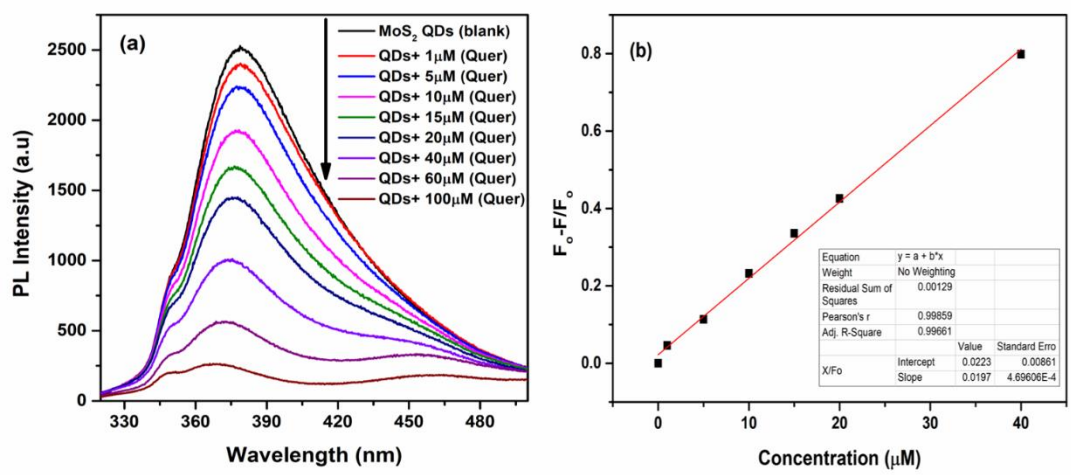

Figure 3: (a) PL spectra (λexc= 310 nm) of MAA encapsulated MoS2 QDs in the presence of variable concentration of Quercetin (0-100 μM) and (b) Plot showing the relative fluorescence intensity (Fo-F/Fo) vs the concentration of analyte Quercetin.

the colloidal stability of MAA capped MoS_2 QDs in aqueous media. Zeta potential was found to be -31.2 mV. The results suggest that synthesized QDs are highly stable in aqueous media.

Sensing of Quercetin: To explore the luminescence properties of QDs towards the detection of Quercetin, we have done the fluorescence titration experiment. For sensing experiment, we have diluted 100 μL QDs in 3 mL solvent and then different concentration of Quercetin (1μM-100μM) are added to it. All the samples are incubated for 10 minutes so that MoS_2 QDs-Quercetin complex can completely react with an effective reduction in emission intensity. The excitation wavelength for all the samples is set to be 310 nm. From the emission spectra, it has been observed that there is quenching in the PL of QDs after adding Quercetin. The Quenching of QDs i.e., reduction in the emission intensity as the concentration of Quercetin increases from 1μM - 100μM. The fluorescence quenching efficiency is analyzed using Stern-Volmer equation[22]:

$$\frac{F_o - F}{F_o} = K_{S-V}[Q] + 1$$

Where Fo and F are the emission intensities of QDs in the absence and presence of Quercetin respectively. [Q] is the molar concentration of Quercetin and $K_{S\text{-}V}$ is the quenching constant.

The quenching of emission of QDs may result from the strong complex formation between MoS_2 QDs and Quercetin. The formed complex Quercetin-MoS_2QDs might prevent the non-radiative electron to hole transfer and enhances the release of decreasing recombinant fluorescence, resulting in reduction of concentration of fluorescent molecule. It was observed that PL quenching was linear when the concentration of quencher was low i.e. till 40μM, while the linearity disrupts when concentration increases from 60- 100 μM. Notably when the concentration of Quercetin reaches to 100 μM, the emission intensity of the MoS_2 QDs quenches almost completely. The sensitivity of the fluorescent probe calculated using the slope from Figure 3(b) is $1.97 \times 10^4 M^{-1}$, which is good for sensing quercetin.

4. Conclusions: In the present manuscript water soluble MAA capped MoS_2 QDs are synthesized using one pot hydrothermal method. The prepared QDs shows high intensity PL emission at 380 nm with excitation wavelength 310 nm. The as prepared MoS_2 QDs shows the excitation dependent PL spectra because of the polydispersity of the synthesized QDs. FTIR confirms the functionalization of MoS_2 QDs

with mecrcaptoacetic acid successfully. The as prepared MAA encapsulated QDs exhibit spherical morphology with size 4-6.5 nm with intense blue emission. The high negative zeta potential confirms the colloidal stability of QDs in aqueous media. The fluorescence results and stability of synthesized MAA encapsulated MoS_2 QDs show that they can be further utilized as fluorescent tag for biomedical applications. We have utilized MoS_2 QDs as fluorophore for the sensitive sensing of Quercetin in aqueous medium with sensitivity of $1.97 \times 10^4 M^{-1}$.

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