

Size Dependent Fluorescence Decay Dynamics of MoS₂ Nanoflakes

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Abstract

This study reports a profound method to prepare MoS₂, and the effect of ultraviolet light irradiation on its emission characteristics. The exfoliation of molybdenum di-sulfide (MoS₂) in a liquid phase has been achieved successfully via probe sonication for different time intervals followed by centrifugation method. Ultraviolet-visible (UV-vis) spectra of the obtained MoS₂ dispersions at different exfoliation times indicate that the concentration of MoS₂ nanosheets as well as MoS₂ quantum dots increased remarkably with increasing exfoliation time. We also note that the non-radiative recombination due to UV irradiation on MoS₂ results into the decrease of emission intensity.

Keywords: Fluorescence, nanosheets, Ultraviolet-visible (UV-vis) spectra, molybdenum di-sulfide, centrifugation

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INTRODUCTION

Transition metal dichalcogenide (TMD) materials with the chemical structure MX₂, such as MoS₂, MoSe₂, WS₂, TiS₂ etc., have attracted the scientific community because of their rich electronic and photonic properties [1-4]. These materials have profound impact in the fundamental science as well as in technological applications such as in sensors, phototransistors, photovoltaic, and integrated circuits etc. [5-8]. Among them, MoS₂ has received significant attention concerning its potential application in the optoelectronic devices because of the presence of a finite and direct energy gap in their low dimensional structures [9, 10]. Also, its optical and electronic properties are dependent on size [11]. Its band gap can be tuned from an indirect band gap (1.2 eV for bulk) to direct band gap (1.9 eV for monolayer) for decreasing thickness, which makes it applicable for various applications. The characteristic mechanical, electrical, thermal and optical properties of MoS₂, which are associated with their ultra-thin structures, usually do not exist in its bulk form [12, 13]. When MoS₂ becomes zero-dimensional quantum dots, it possesses strong quantum

confinement effect and the edge effect, which results in new physical properties [14]. It is made of 0.65 nm thick layers of Mo atoms sandwiched between two sulfide planes, which are stacked and separated by van der Waals forces [15]. This allows these layers to be easily cleaved along the basal plane using methods such as mechanical exfoliation, electrochemical method, liquid phase exfoliation using a sonicator etc. [16, 17]. Significant progress has been made in exfoliating MoS₂ directly from bulk MoS₂. The mechanical exfoliation is the easiest way to get thin MoS₂ layers, however it has some limitations, for example it provides uncontrolled and limited size flakes. On the other hand, liquid phase exfoliation method is considered to be simple, scalable and efficient technique to obtain thin MoS₂ layers [18]. The properties of MoS₂ nanosheets can be tuned using various methods including ion irradiation, laser and UV exposure [19-21]. There are some reports on the effect of UV light irradiation on materials, but its effect on the emission characteristics of MoS₂ has not been fully explored yet. As we know the UV irradiation on MoS₂ can generate electron hole pairs that can affect its properties, therefore,

exploring the photo-irradiation on the materials is essential not only for fundamental science, but also for industrial applications.

In this study, we investigated the effect of UV light on emission characteristics of MoS₂ nanosheets. After UV irradiation, there is a significant decrease of photoluminescence intensity. Our findings will bring new insights into simple and elegant preparation method of MoS₂ and UV effect on it.

EXPERIMENTAL SECTION

MoS₂ nanosheets have been prepared using a liquid phase exfoliation method [22]. In particular, Bulk MoS₂ powder (~2 μ m, Sigm-Aldrich) was mixed in N, N-di methyl formamide (DMF) with concentration 0.5 mg/ml. We have chosen DMF as a solvent because it has high surface energy. This mixture was probe sonicated for different durations (2, 4, 6, 8 and 10 h) at pulse 3 s on and 1 s off. The amplitude was kept at 30%. A transverse component of ultrasound waves can overcome the weak interlayer interaction between layered structure of bulk MoS₂ during the sonication process. After the sonication process, the solution was centrifuged at 4000 rpm and the supernatant was collected for further characterization. The solution was also centrifuged at different rpms like 4, 6, 8 and 10 k.

Characterization

The morphology of exfoliated MoS₂ was examined by Field emission scanning electron microscope (Ultra 55 FE-SEM Karl Zeiss). To analyze the optical properties of MoS₂, the exfoliated material was characterized by UV-visible spectrophotometer (Shimadzu UV-2450). A spectrofluorometer (Cary Eclipse, G9800 A) has been used at ambient conditions to obtain the emission spectra of exfoliated and UV irradiated MoS₂. WiTec model alpha-300 was employed to carry out the Raman spectroscopic characterization by excitation of a laser source with wavelength 532 nm and having an average power of 100 μ W.

RESULTS AND DISCUSSION

First, bulk MoS₂ was probe sonicated for only 2 h and centrifuged at 2000 rpm (Revolutions

per minute) to obtain MoS₂ nanosheets of different sizes and thicknesses. The formation of MoS₂ nanosheets and nanocrystals are shown in schematic diagram (Figure 1a).

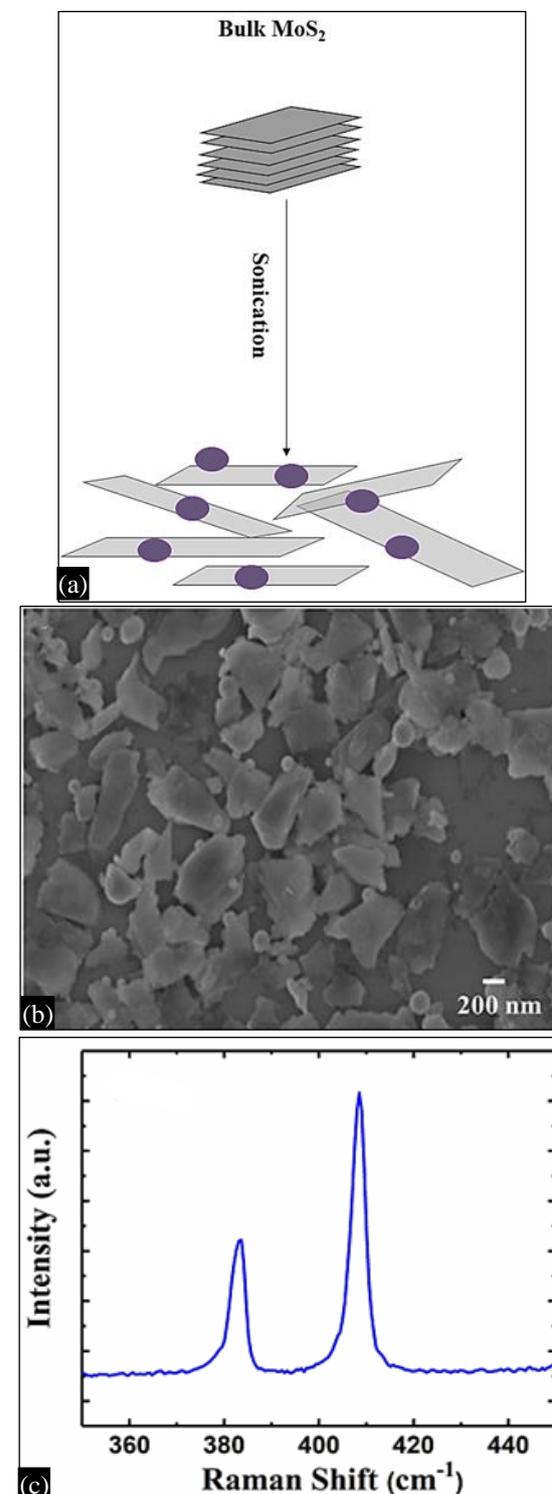


Fig. 1: (a) Schematic Diagram of Converting Bulk MoS₂ into Nanosheets; (b) SEM Image and (c) Raman Spectra of MoS₂.

SEM image of MoS₂ exfoliated for 2 h is shown in Figure 1b. The Raman spectra exhibit the main characteristic peaks of MoS₂ (Figure 1c). The in-plane mode (E_{2g}^1 mode) at 383 cm⁻¹ is because of the opposite vibration of two S atoms with respect to Mo atom whereas the out of plane mode (A_{1g} mode) at 408 cm⁻¹ arises due to the out of plane vibration of only S atom in opposite direction [23]. The difference between these two peaks is around 25 cm⁻¹ which confirms the formation of few layers of MoS₂.

The optical properties of MoS₂ before and after UV irradiation have been investigated by UV-vis absorption and photoluminescence spectroscopy. The sample exfoliated for 2 h using a probe sonicator, was further centrifuged at different rpms (2, 4, 6, 8 and 10 k) to collect MoS₂ nanosheets of different dimensions and thicknesses. The emission spectra have been obtained for the samples collected at various rpms of the centrifuge (Figure 2a). The decrease in the intensity of the emission peak with increase in rpm value of the centrifuge has been observed.

We have also observed the effect of sonication time on the photo-physical and photo-chemical properties of MoS₂. The increase in the sonication time provides additional solvodynamic forces, generated from increased temperature and pressure which causes the layers to breakdown into small nanosized crystals in the solution. The FL intensity decreases with the increase in the sonication time; as initially for 2 h of sonication, only MoS₂ nanosheets are present in the solution. The increase in the sonication time creates a greater number of small MoS₂ nanosheets. The quenching of PL intensity is associated with lattice distortion due to the creation of MoO₃. The blue shift of PL from the K point indicates the small lateral dimensions of MoS₂ owing to the quantum size effect. PL is due to direct excitonic band edge transition in case of thin MoS₂ 2d layers; whereas for nanocrystals, the PL emission is observed due to the quantum confinement effect below a critical size. Also, with the increase in the time-period of probe sonication, MoS₂ solution becomes darker, indicating its higher concentration in the

solution (Figure 3). The process of exfoliation can be explained by ultraviolet-visible (UV-Vis) spectroscopy. Quartz cell having 10 mm path length was used to record absorption spectra. It shows the features that can be assigned to the A and B excitons. These two excitons are generated due to the interlayer interaction and spin orbit splitting.

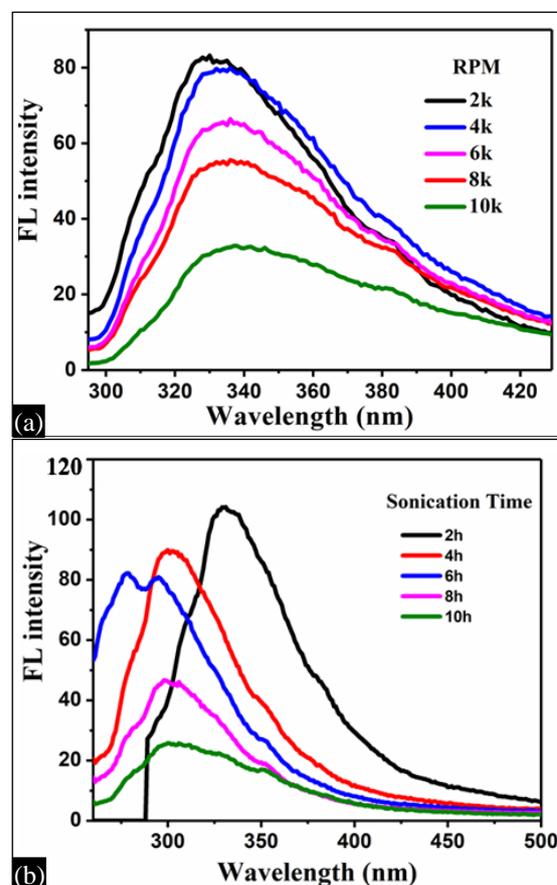


Fig. 2: (a) MoS₂ Exfoliated for 2 h and Centrifuged at rpm 2, 4, 6, 8 and 10 k; (b) The Emission Spectra of MoS₂ Exfoliated for 2, 4, 6, 8 and 10 h.



Fig. 3: MoS₂ Solutions Exfoliated for 2, 4, 6, 8 and 10 h.

The stress on the MoS₂ particles is placed by sono-physical energy through the low power sonication technique. This stress weakens the attraction between the MoS₂ layers created by the weak van der Waals force that clasp the MoS₂ sheets together. The dispersion of MoS₂ in DMF leads to the formation of sonopolymer, which sticks on to the MoS₂ layers. With the increasing sonication time, the formation of polymer bounded MoS₂ sheets as well as the distance between the MoS₂ layers increases. This leads to the formation of single to few layer MoS₂ sheets by simple sonication. The increase in the probe sonication time leads to the formation of quantum dots as well. The Figure 4 a shows the UV-vis absorption spectra of the MoS₂ dispersions in different exfoliation times. The absorbance of MoS₂ dispersions increases notably with the increasing sonication time. To determine the concentrations of suspension (c), Lambert-Beer's law has been used [24]. This law states that absorption is directly proportional to the quantity of absorbing materials.

$$A = \alpha \cdot L \cdot C$$

Here, A is the absorption, C is the concentration of the nanosheets which is defined as dispersed mass/dispersion volume, L (10 mm) is the optical path length and α is the absorption coefficient of suspension ($\epsilon = 7719 \text{ ml mg}^{-1} \text{ m}^{-1}$).

The concentration of MoS₂ in solvent against the exfoliation time plot is shown in the Figure 4b. The concentration of the synthesized MoS₂ sheets also increased remarkably with the increasing sonication time. The sonication of base MoS₂ material for 10 h yielded the maximum concentration. Further increasing the exfoliation time may increase the MoS₂ concentration but long-time sonication leaves structural defect which could disturb the electronic properties of MoS₂.

To extract the value of band gap, Tauc plot has been obtained corresponding to direct $((\alpha E)^2 \text{ vs. } E)$ and indirect $((\alpha E)^{1/2} \text{ vs. } E)$ band gaps. The following equation has been used to determine the optical band gap of MoS₂ [25].

$$\alpha h\nu = A(h\nu - E_g)^{1/2}$$

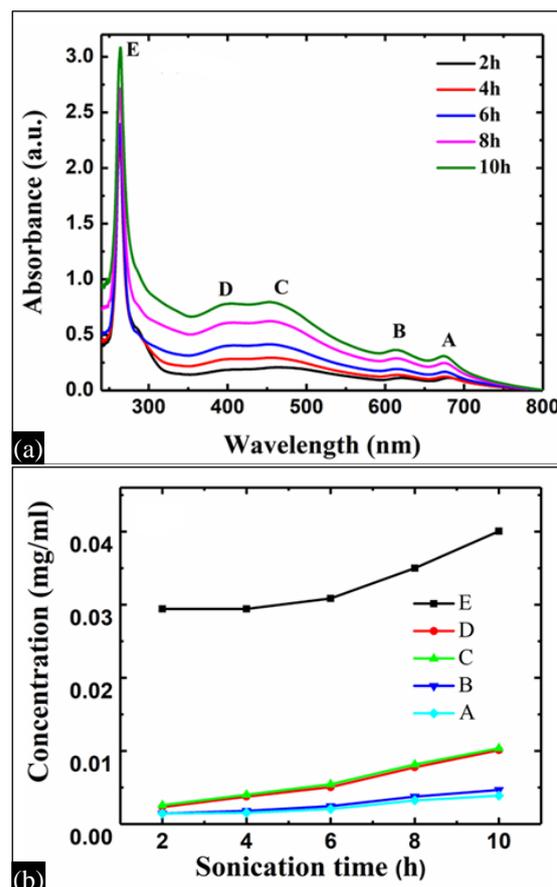


Fig. 4: (a) Absorption Spectra of MoS₂ Probe Sonicated for 2, 4, 6, 8 and 10 h; (b) Plot of MoS₂ Concentration vs. Sonication Time.

Here, α is the absorption coefficient, E_g is the optical band gap, A is the constant and $h\nu$ is the photon energy.

The relative intensity of the absorption peaks increases with the sonication time. Figure 4b shows the concentration of MoS₂ nanosheets as a function of sonication time. Five characteristic excitonic absorption bands (A, B, C, D and E) can be resolved from the absorption spectra of MoS₂ nano flakes. C and D bands are known as the direct excitonic transitions from the deep level in the valence to the conduction band at the M point of the Brillouin zone. The peak at 475 nm in the absorption of MoS₂ is attributed to the absorption of oxidized MoS₂. The A and B excitons are originated because of the direct excitonic electronic transition between the splitted valance bands and the minima of conductance band at the K point of the first Brillouin zone for MoS₂ nanosheets. The

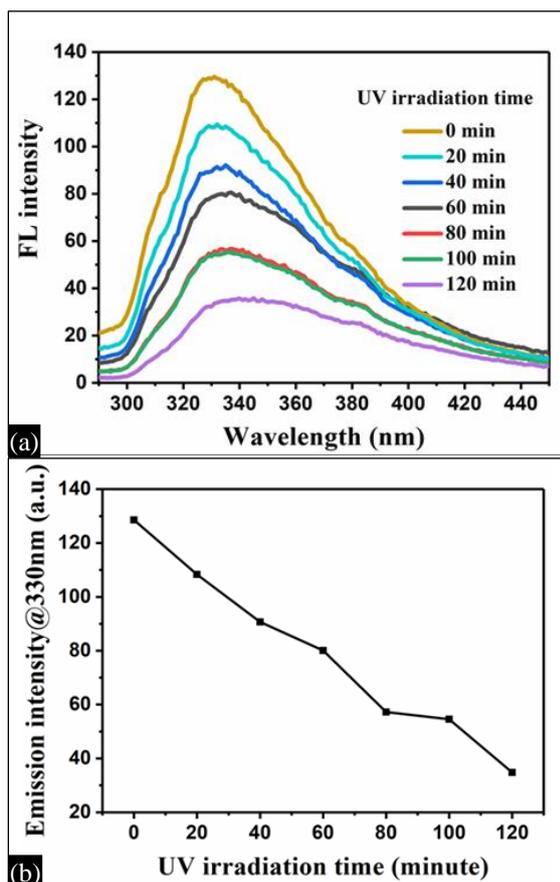


Fig. 5:(a) Fluorescence Spectra of MoS₂ Irradiated by UV Light for Different Time Periods;(b) The Emission Intensity at Wavelength 330 nm with Respect to the UV Irradiation Time.

broad peak around 450 nm corresponds to the transition in the K-point of the Brillouin zone. The peak below 300 appears due to the increased optical bandgap of small sized nanocrystals. As we are increasing the exfoliation time, The MoS₂ structure is becoming smaller. Absorption analysis reveals the existence of both few layers and nanocrystals in the exfoliated solution.

Now in order to get the details about the effect of UV exposure on PL, the emission spectra of MoS₂ was recorded for different time periods of UV irradiation (Figure 5a).

All our experiments have been carried out in the atmospheric environment, wherein O₂ and H₂O could dissolve easily. They can absorb photon and generate ozone, hydrogen radicals etc. When MoS₂ is irradiated by UV light, electron and hole pair is generated making it an

electron donor. As a consequence, it is attacked by the oxidants making it oxidized. The oxidation degree of MoS₂ is enhanced with increase of UV exposure time from 0 to 120 min, resulting in significant decrease of its PL intensity.

CONCLUSION

In summary, effective method is presented to prepare few layers of MoS₂ having different sizes as well as controlling their properties. We report the exfoliation of MoS₂ for different time periods using a probe sonication technique. The effect of UV light on emission characteristics of MoS₂ having different lateral size has also been probed. UV-vis spectroscopy shows the increased absorption with the increase in the sonication time. The change in photoluminescence of MoS₂ nanosheets arises due to its UV induced photochemical oxidation. These results could be beneficial for developing applications of MoS₂.

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