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Upconversion and downconversion photoluminescence and optical limiting in colloidal MoS_2 nanostructures prepared by ultrasonication

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ABSTRACT

Nano structures of MoS_2 are trending up as a smart optoelectronic material nowadays. Photoluminescence, linear and non-linear optical properties of highly crystalline MoS_2 quantum dot (QD)-nano flake (NF) colloidal dispersion in de-ionized water prepared by cost effective mechanical grinding assisted bath ultrasonication and centrifugation is reported in this article. Particle size, which varies with the sonication time and centrifuging speed, is confirmed by TEM and dynamic light scattering (DLS) analysis. The absorbance spectra show characteristic A, B, C and D excitonic transitions of NFs and high energy E peaks of QDs. MoS_2 QD-NF dispersion exhibits appreciable photon upconversion and down conversion photoluminescence (PL) that are applicable to solar cells. The photoluminescence emission red shifts with red shift in excitation wavelength. Time correlated fluorescence decay measurement estimates the life time and it varies with the particle size. Raman spectra of spin coated MoS_2 dispersion confirm the hexagonal structure and formation of few layered MoS_2 in-plane (E^1_{2g}) and out-of-plane (A_{1g}) vibrational modes. Selective area diffraction patterns confirm the crystallinity and hexagonal nature of the grown nanostructures. Non-linear optical studies of the samples exhibit reverse saturable absorption (RSA) which is applicable to optical limiting devices.

1. Introduction

Nanostructures of transition metal dichalcogenides (TMDC - MoS_2, WSe_2, WS_2 etc.) are widely being studied in the field of nano photonics and optoelectronics due to its extraordinary optical and electronic properties of these materials [1]. Optical limiting [2], mode-locking [3], upconversion [4], field effect transistors [5], sensors [6], solar cells [7], hydrogen evolution reaction (HER) systems [8], cancer treatment [9] and memory applications [10] are some of the regimes where TMDC are being explored. MoS_2 is a layered material with an indirect bandgap of 1.2 eV in the bulk [11] and a direct bandgap of 1.9 eV in monolayers [12]. Nanostructures of MoS_2 are generally prepared by various expensive methods such as chemical vapor deposition (CVD) [13], pulsed laser ablation [14] etc. Liquid exfoliation method is a cost effective method for preparing MoS_2 colloidal dispersions [15]. Grinding assisted ultrasonication is a good liquid exfoliation method to exfoliate very thin layers of MoS_2 from bulk [16–18]. Sonication followed by centrifuging is reported for fabrication of MoS_2 QDs [19]. The minimum size of the QDs and NFs that can be produced in the MoS_2 colloidal dispersion varies with the sonication parameters such as sonication power and duration, centrifuging parameters such as rpm and duration, presence of surfactants, nature of the solvent etc. [20,21].

The onset of quantum confinement effect (QCE) in very small nanostructures can be explicitly identified from the absorption and photoluminescence (PL) spectra [22,23]. The absorbance peaks generally show blue shift as a consequence of QCE [24]. Size tuned and excitation dependent PL emission ranging from violet to red has been reported by various research groups using photoluminescence measurement techniques [25,26]. Time resolved photoluminescence measurement is an efficient tool to study the life time of excited state [27,28]. MoS_2 QDs exhibits photon upconversion and down conversion [19], a property which finds promising application in solar cells along with semiconductors having bandgap in visible range to explore the IR and UV range of solar spectrum effectively [11]. Non-linear properties of MoS_2 monolayers are used in ultrafast optical pulse detection and as a direct probe for analyzing the structural and electronic properties of monolayers [29]. Non-linear optical studies by z-scan method is very basic for checking the nature of transmittance with change in the input light

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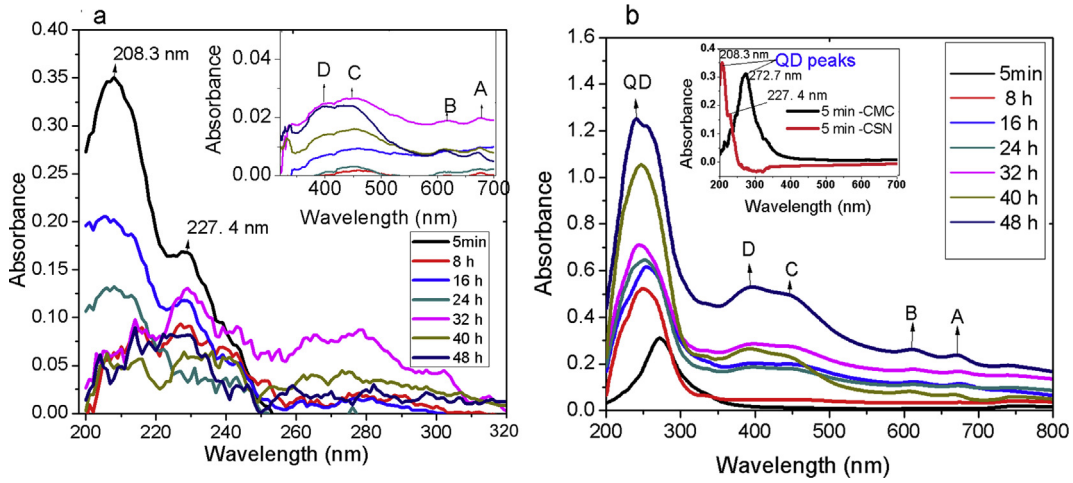

Fig. 1. Absorbance spectra of a) CSN MoS_2 – inset shows A, B, C, D excitonic peaks of NF MoS_2 b) CMC MoS_2 QD-NF – inset shows the QD peaks of 5 min CSN and 5 min CMC.

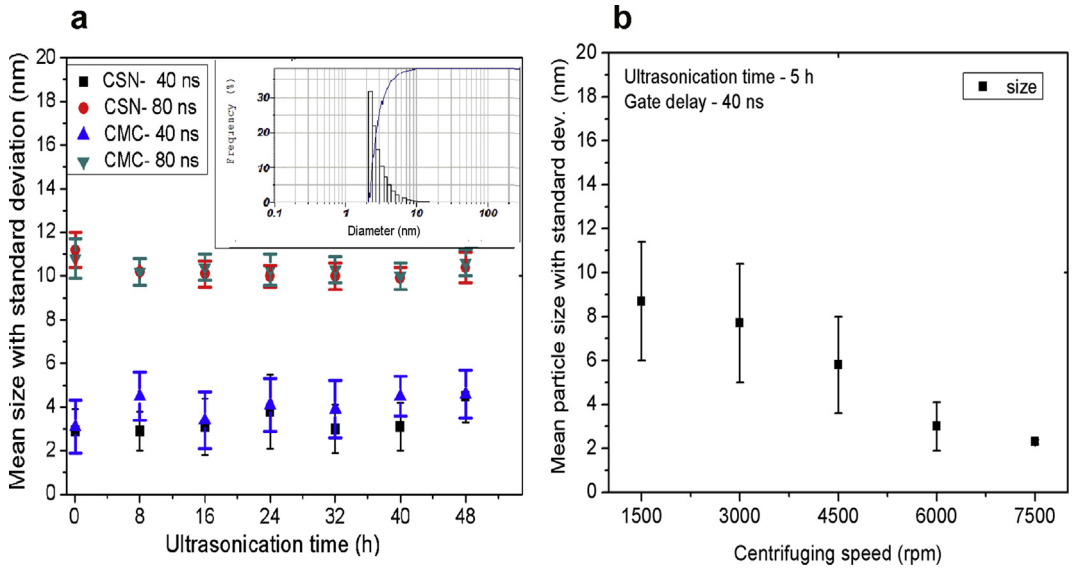

Fig. 2. a) Mean particle size with standard deviation of MoS_2 (CSN & CMC) colloid analyzed by DLS method for different ultrasonication time and gate delay times of 40 and 80 ns. Inset shows the particles size distribution of 5 min sonicated CMC MoS_2 b) Mean particle size with standard deviation with change in centrifuging speed.

intensity. Reverse saturable absorption of MoS_2 finds application in optical limiters as it blocks transmittance with increase in laser intensity [30].

Focus on few layered MoS_2 nanostructures with both upconversion and downconversion PL, and non-linear optical properties are not widely studied. In this paper upconvertion and downconversion PL, time-correlated PL life time and RSA behavior of MoS_2 nanostructures prepared by the cost effective ultrasonication method is reported.

2. Experimental

Commercially available MoS_2 powder was ground mechanically in an agate mortar for 3 h. 0.1 g of the ground MoS_2 powder was dispersed in 50 ml of de-ionized (DI) water. The dispersion was then subjected to bath ultrasonication for 5 min and, 8, 16, 24, 32 and 48 h. The supernatant of the dispersion (sample code CSN) was collected and dispersed into 5 ml DI water in each case. Samples were also collected from middle portion of the 50 ml dispersion (sample code CMC). All the samples were then subjected to centrifugation for 15 min at 8000 rpm. To study the effect of centrifuging speed, sonication time was fixed as 5 h, and centrifuging speed was varied as 1500 (sample code - C1), 3000 (C2), 4500 (C3), 6000 (C4) and 7500 (C5) rpm. Few layered thin films were prepared on glass substrates by spin coating (1000 rpm for 6 min, annealed for 10 min at 130 °C) and are used for structural characterization by Raman spectroscopy.

Absorption measurements were done using Jasco V–570 UV/VIS/NIR Spectrophotometer. Particle size, zeta potential and electrophoretic mobility measurement were done using dynamic light scattering (DLS) technique (Horiba, Nano Particle Analyzer SZ–100). TEM images were taken to confirm the particle size measurement. Upconversion and downconversion PL measurements were carried out using Cary Eclipse Varian Fluorescence Spectrophotometer. Time resolved photoluminescence decay of MoS_2 colloidal dispersions were measured using Delta Pro Fluorescence Lifetime System (Horiba). Spin coated samples were characterized by Raman spectroscopic analysis (Jobin Yvon Lab RAM HR Spectrophotometer with Ar ion laser, 514.5 nm). Non-linear optical properties of the MoS_2 nanostructures were studied by Z scan technique (Nd-YAG laser, 532 nm, 10 Hz).