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Low power continuous-wave nonlinear optical effects in MoS_2 nanosheets synthesized by simple bath ultrasonication

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ABSTRACT

Here, we have unveiled low power continuous-wave nonlinear optical properties of a few layer (4-12L) Molybdenum disulfide (MoS_2) dispersion in *N*, *N*-dimethylformamide (DMF) by using spatial self-phase modulation technique. The effective third-order nonlinear susceptibility of the monolayer has been estimated to be as high as ~10^{-8} esu. Also a low power technique of syntheses of stable and a few-layer (4-12L) MoS_2 dispersion in DMF has been demonstrated here by utilizing ultrasonication bath treatment combined with the natural gravitation sedimentation effect starting from the bulk MoS_2 powder. The synthesized samples are exhibiting interesting linear optical absorption and photoluminescence (PL) after exfoliation to a few layer nanosheets (NSs) and the exciton binding energies have been determined from PL emission data in association with 2D hydrogenic Bohr-exciton model. The specific capacitances (C_{sp}) of the electrode prepared with MoS_2 NSs have been measured by electrochemical measurement and the highest value of C_{sp} is 382 Fg^{-1} for 4L sample. The reported intensity driven change of C_{sp} in the presence of light emitted from light emitting diodes of various colours is unprecedented. The demonstrated technique can be scaled up for large scale and easy synthesis of other 2D materials having applications in optoelectronics and energy devices.

1. Introduction

There is a renaissance in the studies of atomically thin two-dimensional (2D) layered materials of transition metal dichalcogenides (TMDs), having unique properties for applications in flexible and transparent optoelectronics [1], sensors [2], nonlinear optical (NLO) devices, laser and sustainable energy [3]. Among TMDs, molybdenum disulphide (MoS_2) has been found to be a useful material for developing photonic switching devices due to its high current on/off ratio, mobility [1,4] and quantum confinement effects in the atomic levels [4–6]. MoS_2 and its nanocomposites have been found to be as promising materials for photocatalytic and hydrogen generation experiments [7–10]. It has been shown that MoS_2 nanocomposites exhibit enhanced photocatalytic activity in compared to those of pure MoS_2 and commercial TiO_2 (P25) under visible-light irradiation [7,8]. Recently, it has been reported that MoS_2 and graphitic carbon nitride nanocomposites showed an enhanced photocatalytic activity [9]. MoS_2, when exfoliated to monolayer, exhibits direct bandgap nature with a finite bandgap unlike graphene having zero bandgap. Monolayer MoS_2 can be used in light emitting devices [1] due to opening of its energy gaps and transformation from indirect to direct bandgap nature [11]. Thus a lot of research interest has been shown by various researchers for the fabrication of monolayer MoS_2 nanosheets (NSs) by mechanical exfoliation [12,13]. Recently, ultrasonication treatment, being simple and having ease of mass production, has been tried for syntheses of 2D layered materials in different organic solvents [12–15].

Another groundbreaking discovery of laser in 1960 has led to several innovations in determining properties of materials as well as in development of new nanomaterials [16,17] and when nanomaterials are exposed to laser light it might induce several NLO effects, such as multiphoton absorption, nonlinear refraction (NLR) etc. [18–20]. The interesting NLO properties of 2D materials of graphene, hBN, MoS_2, $MoSe_2$ [21–23] etc. have been reported earlier by using the well-known *Z*-scan and spatial self-phase modulation (SSPM) techniques with pulsed as well as continuous wave (CW) laser irradiations [24,25]. SSPM of laser light has recently been used to prove nonlocal electron coherence in MoS_2 NSs by using pulsed fs and CW lasers [24,25] and achieved NLR value of ~10^{-5} esu at 700 nm (fs) and ~10^{-4} esu at 532 nm (CW)

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laser excitations [24,25].

Li et al. [25] have proposed that the vertical alignment of MoS_2 NSs along the polarization axis of incident laser light is responsible for showing high order nonlinearity in MoS_2 NSs. There are several experimental and theoretical methods, such as Stark effect, semi-empirical computational method, density functional theory, and ab-initio quantum mechanical calculations for the determination of polarizability of different nanomaterials [26–29]. Among them, DC Stark effect is one of the easiest method to find out the polarizability of the nanomaterials [30]. Klein et al. [31] have reported the electric field dependent DC Stark effect of mono and a few layer MoS_2 NSs and extracted the values of mean DC exciton dipole moment (μ) and hyperpolarizability (α). Their reported values of μ and of α are 1.35 D and $(0.58 \pm 0.25) \times 10^{-8}$ DmV^{-1}, respectively [31]. Yin et al. [10] have reported synthesis of MoS_2/CdS nanosheets-on-nanorod heterostructure which exhibits a much enhanced H_2 evolution rate of 49.80 mmol g^{-1} h^{-1}. Wu et al. [32] have synthesized MoS_2 ultrathin NSs by Li exfoliation technique and demonstrated their electrochemical performances with maximum C_{sp} of the electrode is 270 Fg^{-1} at a scan rate of 10 mVs^{-1}.

Fabrication of MoS_2 NSs have been demonstrated, so far, by using very high power (>100 W) probe sonicator over a long time and in harsh environments [12,15]. However, in this work we have utilized the low power bath ultrasonication technique to exfoliate a few-layer (4-12L) MoS_2 NSs by using a sonicator of 17 W power only and also it has been shown by a calculation that it is sufficient to exfoliate the van der Waal's (VdW) interaction energy between the two planes. The synthesized materials have been characterized by using Transmission electron microscopy (TEM), Atomic force microscopy (AFM) and Raman spectroscopy techniques and it has been shown that it consists of a few-layer of MoS_2 NSs. In the UV–Vis absorption and PL emission characteristics, the excitonic absorption peaks (A, B, C, D) are found to be present in the dispersion of MoS_2 NSs (S3) which consisting mostly with four-layers of MoS_2 NS. The position of excitonic absorption peaks has been found to vary due to the enhancement of the direct transition from deep valence band (VB) to the conduction band (CB) as it is exfoliated from bulk to a few layers. The 2D excitonic binding energy (E_b) for 12L, 5L and 4L samples are calculated to be 427, 533, and 587 meV, respectively from PL emission spectra by using 2D hydrogenic exciton model which are less than the values as obtained from UV–Vis absorption spectra and somewhat lower than the theoretical value of monolayer MoS_2 NS. A low power CW He-Ne laser has been used in this work and demonstrated the NLO properties of synthesized materials. The experimental data have been simulated by standard SSPM theory and highest NLR value has been unambiguously determined to be 1.24×10^{-5} cm^2/W. The third order nonlinear susceptibility of the monolayer ($\chi^{(3)}_{mono}$) is extracted to be ~10^{-8} esu, which is comparable to that of monolayer MoS_2. Such high order nonlinearity has been obtained due to polarization formed within MoS_2 NSs. In addition, we have studied the electrochemical performance of the electrodes made with a few-layer MoS_2 NSs and quadri-layer NSs exhibit specific capacitance (C_{sp}) of 382 Fg^{-1}. We have reported here the light emitting diode (LED) driven change of C_{sp} and the origin of light-driven change of capacitance has been provided.

2. Experiment

2.1. Materials and reagents

All the chemical reagents are used as-received without any further purification. Bulk MoS_2 powder is purchased from Loba Chemie (CAS: 1317-33-5). *N*, *N* Dimethylformamide (DMF) is purchased from Sigma Aldrich and used it as received.

2.2. Synthesis of molybdenum disulfide nanosheets (MoS_2 NSs)

In this typical synthesis, 240 mg of bulk MoS_2 powder is mixed with 30 ml of DMF in a flat bottomed beaker (Borosil, 100 ml) and the mixture is then sonicated in a bath ultrasonicator (Oscar Ultrasonic, Model: FP-108-15-1) for 2 h. A schematic of the whole synthesis process is shown in Fig. S1. The water in the bath sonicator is changed frequently in order to avoid the heating of water. With the aim of achieving exfoliated i.e. thinner NSs of MoS_2, the mixture is now divided into three parts. All the parts are kept in undisturbed condition at room temperature. Part-I is collected by a micropipette in a vial and centrifuged at 5000 rpm for 5 min on the same day. Then, the centrifuged solution is collected carefully by a micropipette in a separate glass bottle, and named as S1. On the next day decanted part of the stock samples (i.e., Part-II) is centrifuged at 5000 rpm for 5 min and collected in glass bottles, named as S2. The same process is repeated for the last part (i.e., Part-III) of the sample on the next to next day and named the collected sample as S3. The colour of the S1, S2, and S3 are appeared to be light gray to light green. Basically, during centrifugation, the larger MoS_2 flakes got settled down and the exfoliated MoS_2 sheets dispersed in the liquid and as we kept the Part-II and Part-III in undisturbed condition, because of gravitation sedimentation larger particles are settled down. So there is a large possibility to obtain light particles, and it is found that S2 and S3 are consisting with mostly 5L and 4L MoS_2 NSs.

2.3. Characterizations

The formation of quadri and penta-layer MoS_2 NSs is confirmed by Transmission electron microscopy (TEM) (JEOL JAM 2100) and Atomic force microscopy (AFM) (Veeco-diCP-II, Model: AP0100). Micro-Raman studies are performed using an ISA Lab Raman system equipped with a 532 nm laser with a 50× objective, giving a spot size about 1 μm with a spectral resolution better than 2 cm^{-1}. Raman spectra and AFM experiments are performed on a thin film. To prepare thin film, the suspension of S1, S2, and S3 are spin coated on a pre-cleaned glass substrate and then heated to 80 °C for 2 h. The optical absorption spectra of the as-prepared MoS_2 NSs dispersed in DMF is recorded using a UV–Vis spectrophotometer (Hitachi, U-3010). During the stability test, the samples are put in three separate desiccators to protect dust, moister, and thermal evaporation. The PL emission spectra of the MoS_2 NSs dispersed in DMF are recorded at room temperature using a spectrofluorometer (Perkin Elmer LS-55) equipped with a pulsed Xenon discharge lamp as a source of excitation. The nonlinear refractive index is measured by using a continuous wave (CW) He-Ne laser and in a home built spatial self-phase modulation (SSPM) experimental set up. The dipole moment and the hyperpolarizability of the samples are determined by DC excitonic Stark effect experiment (details of experimental methods are available in the supplementary information) and by monitoring the change in 'A' excitonic absorption peak position with the application of the DC electric field across the quartz cuvette containing the MoS_2 NSs dispersion in DMF. The absorption characteristics have been monitored in a commercially available UV–Vis absorption spectrophotometer as discussed earlier. Electrochemical measurement that is cyclic voltammetry (CV) is done in a Potentiostat (Models: K-Lyte-1.0, Kanopy Techno Solution Pvt. Ltd).

3. Results and discussion

3.1. TEM, AFM analyses and UV–Vis absorbance spectra

The MoS_2 NSs are synthesized by ultrasonication process by