Self-induced Raman mode splitting on few layer MoS_2 developed by Scooping after Ultrasonication on dilute HCl

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Abstract

Molybdenum disulfide (MoS_2) nanostructures are finding applications in various optoelectronic devices. MoS_2 is having layered geometry in its bulk form. It is possible to extract single and few layers of MoS_2 which exhibit wonderful optoelectronic properties. In this work MoS_2 nanostructures were grown through cost effective exfoliation method using liquid solvent medium. Using the exfoliated MoS_2 nanostructures in liquid phase MoS_2 few layers were grown by dip coating method. The structural properties of these few layers were analyzed by UV-Vis- NIR absorption spectroscopy, X- ray diffraction and Raman scattering spectroscopy. Raman spectroscopy is a very useful tool to identify even a single molecule and gives information about the number of monolayer in the sample. Interesting results such as peak splitting of important vibrational modes are observed in some of the samples.

Keywords: photoluminescence emission, Raman spectral analysis, SILAR, direct exfoliation, scooping ultrasonication, fabrication methods

Introduction

Atomically thin MoS_2 layers is a promising material in various optoelectronic applications[1-3]. Monolayer MoS_2 has direct band gap of 1.8 eV and shows profound photoluminescence emission (PL) [4-6]. Raman peak shifts and peak splitting of E_{2g}^1 and A_g^1 modes are reported due to strain, doping and defects [7-9]. Studies show peak splitting of phonon mode E2g1 due to external applied strain of

0.8% or more or due to self induced strain [10-11]. Peak shift in phonon mode A_g^1 is the indication of defect or doping [12-13]. Peak splitting in mode A_g^1 is reported as a result of adsorbance of O_2, H_2O or p type doping [14-15]. Raman spectral analysis is a very useful tool to estimate the number of layers in the sample. A Raman peak separation of 18-19 per cm indicates presence of monolayers, 20-25 per cm bi to few layers and separation above 26 per cm indicates bulk samples [16]. PL measurement is a tool to confirm monolayer MoS_2. Even then if there is the formation of negative charge trapping via trion formation PL emission will be submissive [17]. Strain and defects in the sample also affects the PL emission [18-19].

In our study we developed MoS_2 bulk and few layers on micro glass substrates by chemical dip, SILAR and direct exfoliation method after subjecting to thorough ultrasonication in suitable liquid solvents. Samples were dried naturally and annealed for 2 hrs at 2000 C and were characterized by UV-Vis-NiR spectroscopy, micro Raman analysis with an excitation laser wavelength 532 nm and XRD (for bulk samples). We observe characteristic Raman peak shift from 19.2 per cm to 27 per cm for various samples. For samples with peak separation 19.2 cm and 20.1 cm characteristic peaks of MoS_2 in Raman spectra found to undergo splitting.

Experimental:

Commercially procured MoS_2 bulk powder was used to exfoliate few layer nanostructure of MoS_2.

Chemical Dip:

0.1 g and 0.6 g of MoS_2 powder was dispersed separately into 100 ml acetone, isopropanol alcohol, Conc. HNO_3, Conc. HCL and aquaregia by magnetical strirring for 2 hrs each at room temperature and 70^0C. The stirred solution was dip coated to well cleaned glass substrates with dip duration 5 min, ex dip duration 10 sec, inward dip speed 1000 mm/s, outward dip speed 700 mm/s, dip length 75 mm and number of cycles 100. The samples were naturally dried and annealed at 200^0C for 2 hrs

Successive Ionic Layer Absorption Reaction (SILAR) Method:

0.1 g and 0.6 g MoS_2 powder dispersed separately into 100 ml Conc. HCl, Conc.HNO_3, aquaregia by magnetic stirring for 2 hrs each and used as cationic precursor. 0.6 g of Na_2S flakes were dissolved in 100 ml deionized water by stirring 5 min and is used as anionic precursor. Deionized water was used for rinsing. Samples were prepared on glass substrates with dip duration 40 S, ex dip 5 S, dip in speed 3000 mm/s, dip out speed 1000 mm/s, dip length 75 mm by alternate dipping

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into cationic and anionic solutions as per SILAR technique. The samples were naturally dried and annealed at 200^{0}C for 2 hrs.

Direct exfoliation or scooping after Ultrasonication:

0.1g MoS_2 powder was dispersed separately into 50 ml solution of 30 ml deionized water and 20 ml acetone, and 50 ml solution of 30 ml deionized water and 20 ml Conc. HCl. The dispersion was ultrasonicated for 2 hrs with normal bath heating. After ultrasonication the dispersion was left undisturbed for 2 hrs. MoS_2 films floated on the top of the liquid were carefully transferred to pre-cleaned glass substrates. The process was repeated three times with same prepared dispersion and described here as exfoliation/scooping 1, 2 & 3. The samples were naturally dried and annealed at 200^{0}C for 2 hrs. As Raman peak separation was reduced to 20.235 per cm and observed peak splitting in the sample (MU_3T) for third exfoliation in dil. HCl, the experiment was repeated with dil. HCl up to five exfoliations with two lesser concentrations of MoS_2 (0.05 g, 0.02 g). The samples were naturally dried and annealed at 200^{0}C for 2 hrs.

Results and Discussions:

The samples were subjected to Raman scattering with an excitation laser wavelength of 532 nm with an integration time of 30 s to confirm the formation of MoS_2 few layers. Figure 1 shows the Raman spectra of samples prepared by dip coating of MoS_2 dispersion in acetone and IPA respectively in the case of naturally dried and annealed samples. Sample M7 and M7A indicate the MoS_2 few layers prepared from MoS_2 exfoliated using acetone. Raman scattering result confirms that the characteristic Raman peaks A_{1g} and E^1_{2g} of MoS_2 are seen and these peaks show separation of 25.73 cm^{-1} (M7) for the naturally dried sample and a separation of 26.79 cm^{-1} (M7A) in the case of annealed sample. A separation of this range shows the presence of few layer deposition of MoS_2. M9 and M9A are samples prepared from MoS_2 dispersion on IPA. The peak separations were found to be 25.74 cm^{-1} (M9) and 27.86 cm^{-1}(M9A) [16].

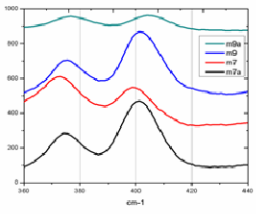

Figure 1: Raman spectra of MoS_2 nanostructures prepared by dip coating of MoS_2 dispersion in acetone and IPA respectively for naturally dried and annealed samples.

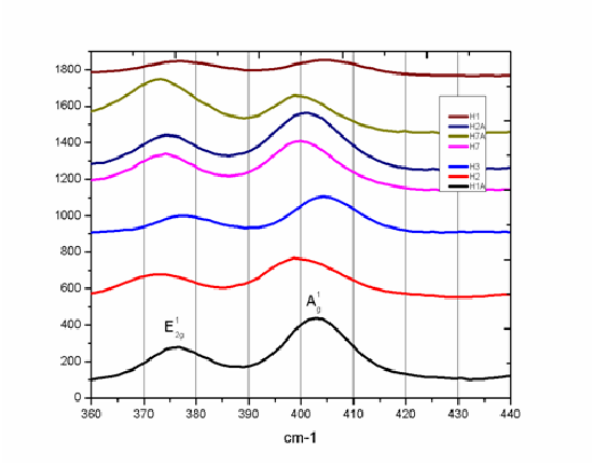

Figure 2: Raman spectra of samples developed by dip coating with dispersion of MoS_2 in Conc. HNO_3, Aqua regia and Conc. HCl.

Raman spectra of samples developed by dip coating method using precursor dispersion of MoS_2 in Conc.HNO_3(H1, H1A), Aquaregia (H_2, H_2A), room temperature Conc. HCl (H_3, H_3A) and hot Conc. HCl (H7) are shown in figure 2. Peak separation of characteristic peaks of naturally dried and annealed samples were found to be 26.87 cm^{-1}(H1), 27.46 cm^{-1}(H_1A), 26.65 cm^{-1}(H_2), 26.44 cm^{-1}(H_2A), 27 cm^{-1}(H_3), 25.65 cm^{-1}(H7), 26.21(H7A) [16]. The peaks and peak separation confirm formation of MoS_2 few layers.

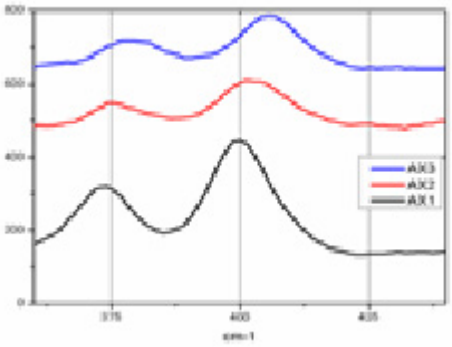

Figure 3: Raman spectra of MoS_2 few layers developed by SILAR method.

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As per figure 3, the characteristic peak separation were found to be 27.29 (AX1 – precursors Conc.HNO_3 and Na_2S), 26.12 (AX2- precursors Aquaregia and Na_2S) and 27.45(AX3- precursors conc. HCl and Na_2S) [16]. In this method too the sample shows stacking of one layer upon another irrespective of which precursor is used and whether the sample is as deposited at normal temperature or annealed at 200^0C as seen in other fabrication methods elaborated here.

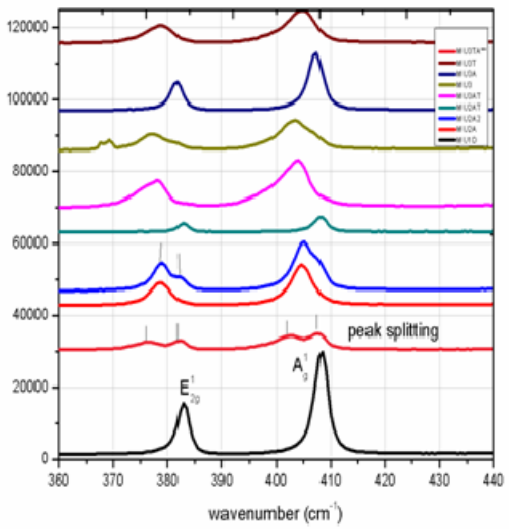

Figure 4: Raman spectra of directly exfoliated samples fabricated by scooping after ultrasonication of precursor dispersion in acetone and Conc. HCl dilued with deionized water.

Figure 4 show Raman spectra of directly exfoliated samples fabricated by scooping after ultrasonication of precursor MoS_2 (1 g) dispersion in acetone and Conc. HCl dilued with deionized water. Characteristic peak separations are 25.58 (MU1D- MoS_2 dispersion in DI water), 26.12(MU2A- MoS_2 disperion in acetone mixed DI water, naturally dried), 26.12 (MU2A2- MoS_2 dispersion in acetone mixed DI water, annealed at 200^0C for 2hrs), 25.03 (MU2AT- MoS_2 dispersion in acetone mixed DI water exfoliated second time, naturally dried), 26.12 (MU3AT- MoS2 dispersion in dil. HCl exfoliated for second time), 26.12 (MU3- MoS_2 dispersion in dil. HCl, naturally dried), 25.58 (MU3A- MoS_2 dispersion in dil.HCl annealed), 25.58 (MU3T- MoS_2 dispersion in dil. HCl- exfoliation 3, naturally dried), 20.1(MU3TA- MoS_2 dispersion in dil.HCl–exfoliated third time-annealed)

[16]. Both the characteristic peaks split in sample MU3TA. Symptoms of strain are shown by sample MU_2A_2. The results of peak deformation have been reported by [12-17]. The peak splitting is also an interesting result which led the experiment further to be performed in acidic medium with different concentrations of MoS_2 and exfoliation from the same precursor for five times with continuous ultrasonication in between each exfoliation.

Figure 5 shows Raman spectra of directly exfoliated samples in acidic medium. 0.05 g of MoS_2 in 50 ml dil. HCl was ultrasonicated for 2 hrs and allowed to settle for 2 hrs. This process was repeated five times to check whether monolayer samples of MoS_2 can be procured by this method. Peak separations are 24.6 (201-naturally dried), 24.9(201A-annealed), 25.7 (202 - naturally dried), 24.8 (202A - annealed), 25.4 (203 - naturally dried), 26.8 (203A-annealed), 19.2 (204-naturally dried), 24.9(204A-annealed), 25.4(205-naturally dried) and 25.1(205A-annealed). Both characteristic peaks were splitted in sample 204 [16].

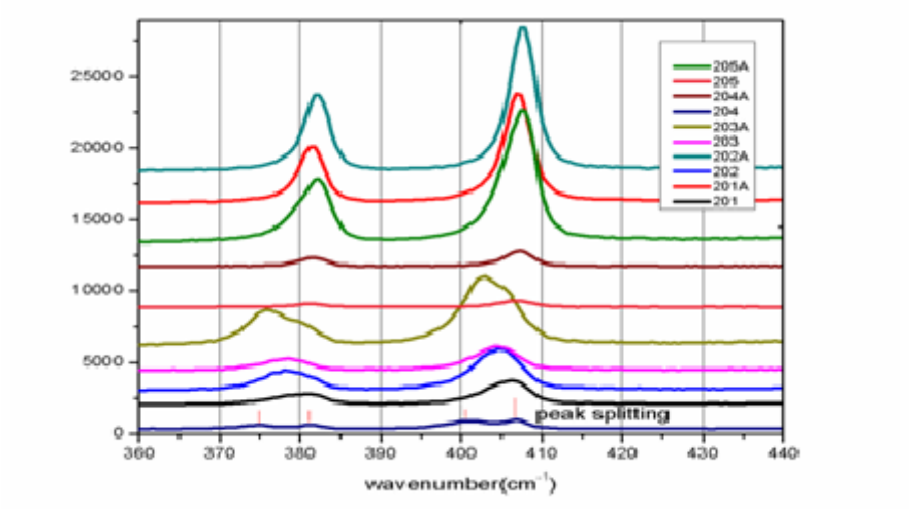

Figure 5: Raman spectra of MoS_2 samples which were exfoliated for five times after ultrasonication in acidic precursor prepared with 0.05 g of MoS_2 bulk powder.

Figure 6 shows Raman spectra of MoS_2 samples which were exfoliated for five times after ultrasonication in acidic precursor. 0.02 g of MoS_2 was dispersed in 50 ml dil. HCl. This dispersion was ultrasonicated for 2 hrs and allowed to settle for 2 hrs. The process was repeated five times to get thinner samples with the expectation that performing scooping experiment after ultrasonication with lighter concentra-

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tion of precursor may yield monolayer. No characteristic peak splitting observed was observed in this experiment. Peak separations were noted as 25.9 (501-naturally dried), 25.7(501A-annealed), 25.1(502-naturally dried), 24.1(502A-annealed), 25(503-naturally dried), 24.7(503A-annealed), 25(504-naturally dried), 24.1(504A-annealed), 25(505-naturally dried) and 26.8(505A-annealed).

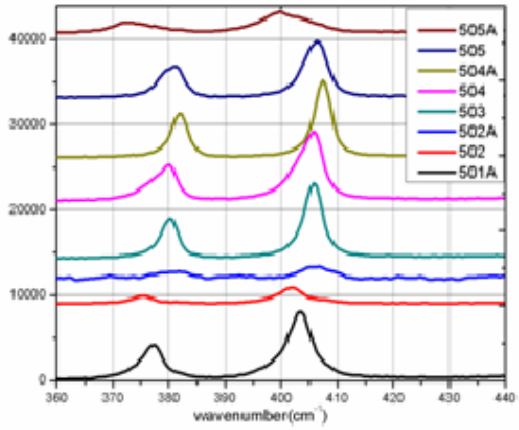

Figure 6: Raman spectra of MoS_2 samples which were exfoliated for five times after ultrasonication in acidic precursor prepared with 0.02 g of MoS_2 bulk powder.

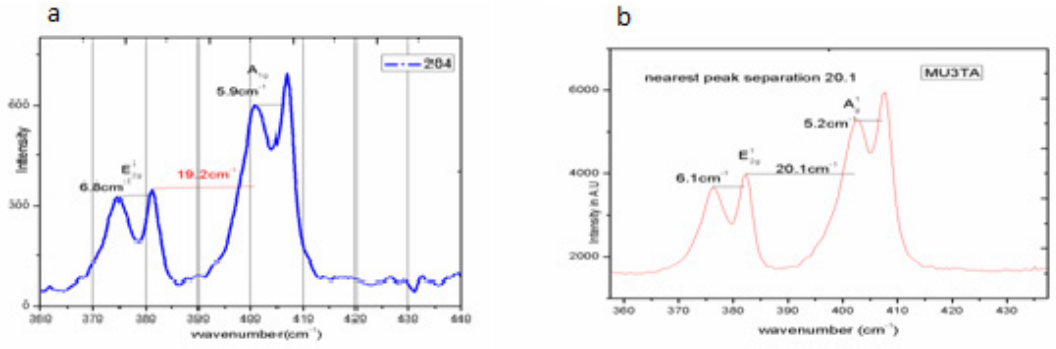

Figure 7: Peak splitting of characteristic vibration modes of specific exfoliated MoS_2 few layers from dispersion after ultrasonication of MoS_2 powder (0.5 g and 1 g) in dil. HCl.

Figure 7 demonstrate the random peak splitting observed in samples 204 and MU3TA. Sample 204 (0.05 g of MoS_2 – naturally dried) represents the exfoliated sample with lesser precursor concentration than that of sample MU3TA (1 g MoS_2 - annealed). But lowering the concentration is not giving any explicit information about formation of monolayer or about peak splitting. The peak splitting observed too were found to be random and can't be explained based on the concentration, or whether the sample is naturally dried or annealed. But the result is quite interesting which can give information about strain, defects or formation of trions in the sample.

Raman spectral analysis shows that the samples developed by various above said methods were exhibiting both the characteristic peaks of MoS_2. The peak separation of each sample was calculated so as to understand the thickness of the samples. The peak separation lies in the range 19.2 cm^{-1} to 27.6 cm^{-1}. Peak separation of 19.2cm^{-1} and 20.1cm^{-1} indicate the presence of mono and bi layers but this is in samples with peak splitting. The split or shift in E^1_{2g} may be due to self-induced strain developed in the sample due to weak van der Waals forces or due to substrate influence, and the split in peak A_{1g} may be due to adsorption of H_2O or O_2, or defect sites due to monosulphur vacancy. As the ultrasonication was done on dil.HCl, the peak splitting of A_{1g} may be caused by the influence of the ultrasonicating medium. We haven't observed peak splitting in the case of ultrasonication in acetone mixed DI water or in the case of chemical dip or SILAR developed samples. Detailed study is to be done to find the reason for splitting of A_{1g} peak.

Conclusion:

MoS_2 few layers were developed from bulk precursor powder through various cost effective methods like chemical dip, SILAR and direct exfoliation after ultrasonication in various liquid solvent medium. Raman analysis shows that the samples are few layers to bulk in nature. Two samples showed peak separation of 19.2 and 20.1 respectively indicating mono and bilayers. Peak splitting was observed in both the characteristic peaks of MoS_2 in this case. Peak separation for other samples falls in range 24 to 27 per cm. The split in characteristic peak E^1_{2g} may be due to self induced strain developed within the sample during the process of fabrication. Peak splitting in A_{1g} may be due to adsorption of H_2O, O_2, mono sulfur vacancy or influence of ultrasonicating medium.

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