Preparation and Characterization of Few Layered MoS_2 Nano Flakes

M.S. Gopika, B. Bindhu

Abstract--- Two dimensional layered materials have become a prominent area of current research and development due to the significant properties exhibited by them. Exploiting graphene's layered structure have led to the property enhancement and thereby making it a good candidate for potential applications. MoS2 (Molybdenum disulphide), a transition metal dichalcogenide possess exceptional electrical, thermal and mechanical properties which can be well exploited on exfoliation. The present work report the exfoliation of pristine MoS2. The layers of pristine MoS2 are held together by weak van der Waals interaction, which is disturbed by the addition of a suitable modifier facilitating the exfoliation process. The modifier treated MoS2 is elucidated by powder X-ray diffraction, Photoluminesence and Raman spectroscopy.

Keywords--- CTAB, Exfoliation, MoS2, Ultrasonication.

I. INTRODUCTION

Two dimensional transition metal dichalcogenides (TMD) has attained considerable attention in the research field owing to their exceptional properties analogous to that of graphene. MoS_2 is one among the TMDs which exhibits property enhancement on exfoliation from bulk form to monolayers [1]. It finds application in sensing, energy storage and catalysis. [2] But proper exfoliation techniques are needed for facilitating the use of material to suitable applications. MoS_2 consists of strong covalent bonds within the layers and weak van-der-waals interaction between the layers. It is composed of S-Mo-S sandwich layers, where the middle molybdenum atom is coordinated by six S-atoms by strong bonds in a single 2D layer of MoS_2[3].

Inclusion of MoS_2 as a filler in to the polymer matrix brings out polymer composites with excellent properties. In order for better property enhancement the dispersion of the filler must be optimized. Also the compatibility of the filler with the matrix is also to be considered to a large extent . Because these factors paves way for better interfacial interaction between the filler and the polymer matrix , thereby promoting significant property enhancement in the composite [3]. The compatibility of the filler and the matrix can be effectively improved through suitable modification of the filler using chemical surfactants. In the case of MoS_2 the layered structure is initially exfoliated before incorporating into the polymer matrix, since the property enhancement is well achieved in exfoliated form of MoS_2 [2]. Different types of exfoliation techniques for better dispersion of MoS_2 are performed like ultrasonication [2], covalent functionalization [4], addition of surfactants [5] and shear mixing [6]. Exfoliated MoS_2 without any surface modification tends to restack due to the weak van der Waals interaction between the individual sheets, through which the homogeneous dispersion of the filler is disrupted and thereby retarding the property enhancement of the composite [7]. This situation bring about the need for modification of the MoS_2 sheets using advisable non-covalent functionalization techniques.

In this work we report the liquid phase exfoliation and modification of MoS_2 using the CTAB modifier and the property enhancement is analysed using powder X-ray diffraction, Photoluminesence and Raman spectroscopy.

II. EXPERIMENTAL

A. Materials

Molybdenum disulphide (MoS_2) (99% purity), Molecular weight 160.06g/mol is purchased from LOBA Chemie. Cetyl trimethyl ammonium bromide (CTAB) (98% purity), Molecular weight 364.45g/mol and N, N-Dimethylformamide (DMF) (98% purity) were obtained from Sigma Aldrich.

B. Exfoliation of MoS_2

Exfoliation of MoS_2 is done through the ultrasonication process. A known amount of MoS_2 is added in the solvent DMF and is mechanically stirred for about 30 min. The stirred solution is ultrasonicated with a bath sonicator for 8 hrs. Ultrasonication destructs the van der Waals force between the layers of MoS_2 thereby converting the bulk MoS_2 into nanoflakes. The solution is then centrifuged at 4000rpm for 10 min and the product obtained is then dried in vacuum at 60^{o}C.

C. Modification of MoS_2

A colloidal suspension of exfoliated MoS_2 and DMF was prepared. Cetyl trimethyl ammonium bromide (CTAB) was dissolved in 100mL distilled water and the solution is added into the colloidal suspension under stirring at 60^{o}C for 8hrs. The solution is then centrifuged at 4500 rpm for 8 min, washed with hot water thrice for the removal of Bromine. The product is then dried in vacuum at 60^{o}C for 24hrs.

D. Characterization

The powder X-ray diffraction analysis of the samples were carried out using XPERT-PRO X-ray diffractometer with Cu K_α radiation (λ=1.5406A^o) operating at 30 mA and 40 kV. Photouminescence (PL) spectra of the pristine, exfoliated and modified MoS_2 were obtained from the spectroflurometer with a 450w high pressure Xenon lamp at room temperature. The input excitation wavelength of the source is 532nm.

Revised Manuscript Received July 10, 2019.

M.S. Gopika, Department of Physics, Noorul Islam Centre for Higher Education, Kumaracoil, Tamil Nadu, India.

B. Bindhu, Department of Physics, Noorul Islam Centre for Higher Education, Kumaracoil, Tamil Nadu, India. (e-mail: bindhu.krishna80@gmail.com)

Raman spectroscopic analysis of the samples is carried out using HR 800 micro-Raman, HORIBA Jobin Yovon, France at the scanning range of 250 to 500 cm with a laser source of excitation wavelength 514 nm.

III. RESULTS AND DISCUSSIONS

A. X-Ray Diffraction Analysis

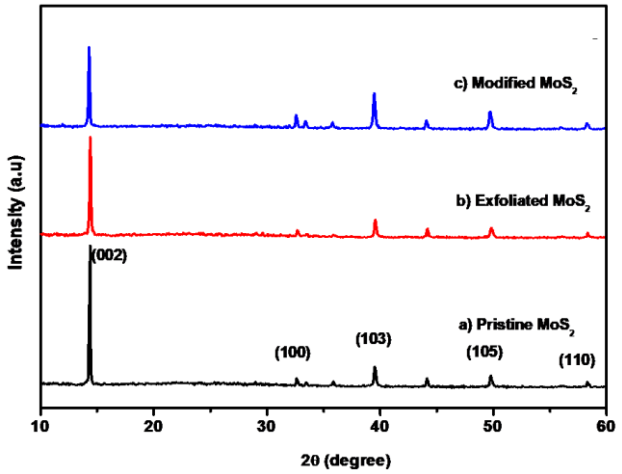

Fig. 1: X-ray diffraction patterns of pristine, exfoliated and modified MoS_2

The diffraction peaks in Fig 1 located at 2θ values 14^o, 33^o, 40^o, 50^o and 59^o correspond to the (002), (100), (103), (105) and (110) planes respectively of the Hexoganal phase of the MoS_2. The XRD pattern of the sample matches well with the reported data of Hexagonal MoS_2 (JCPDS card file No.37-1492). There is no significant shift in the 2θ value for exfoliated MoS_2 and modified MoS_2. But the intensity of the characteristic peaks (002) of MoS_2 is seems decreased to a certain extent, where as the remaining peak intensities (100), (103),(105) and (110) are increased.[8], [9] The particle size was calculated using Scherrer formula,

$$D = \frac{0.9\lambda}{\beta cos\theta}$$

Where, λ is the wave length of the X-ray ($1.5406A^o$), β is the full width of the peak at half its maximum intensity in radian, θ is the Bragg's diffraction angle and D is the average crystallite size. The crystallite sizes obtained for the Pristine MoS_2, Exfoliated MoS_2 and Modified MoS_2) are given in Table 1. Crystallite size of the MoS_2 particle decreases and the variation in peak intensity of the (002) lattice plane after exfoliation, indicates the successful exfoliation of bulk MoS_2 to MoS_2 nanoflakes.

Table 1: Crystallite size of the samples

Sample	Crystallite Size (nm)
Pristine MoS_2	13.01
Exfoliated MoS_2	10.59
Modified MoS_2	9.62

Table 1 clearly shows that the size of the MoS_2 particle has decreased for the exfoliated and modified samples. This result of decrease in intensity for (002) peak justify that exfoliation has occurred for the DMF treated MoS_2 and CTAB modified MoS_2 which means the interlayer separation has been increased.

B. Photoluminescence

The emission spectrum from the Photoluminescsnce studies is shown in Fig 2. The luminescene peak of untreated MoS_2 occured at 639.94nm Fig 2a. For the exfoliated and modified samples the peak got red shift Fig 2b and 2c. Red shift of the peak is an indication of exfoliation.

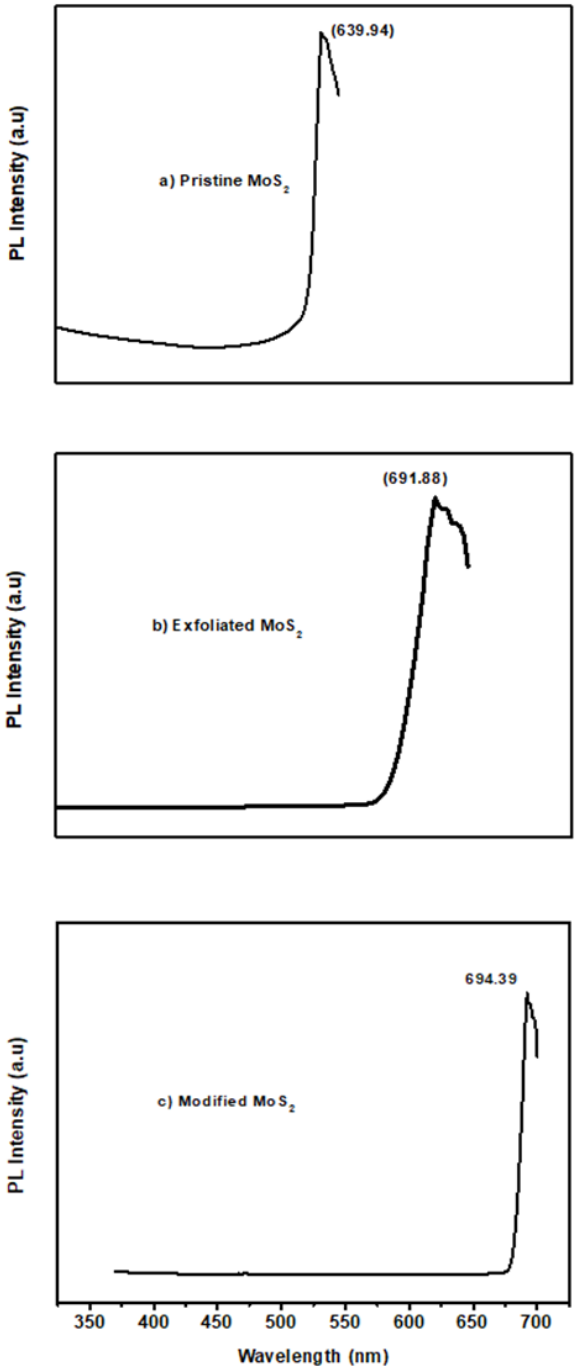

Fig. 2: Photoluminescence of pristine, exfoliated and modified MoS_2

C. Raman Spectroscopy

The Raman spectrum of the pristine MoS_2 and exfoliated MoS_2 samples as shown in Fig 3. Raman spectrum was used to confirm the formation of few layer MoS_2 nanosheets.

The single layer MoS_2 exhibits strong band at 384 & 400 cm^{-1}, which are associated with the in-plane vibrational (E^1_{2g}) and the out of plane vibrational (A_1g) modes respectively. [8] As the formation of monolayer increases, a red shift of the (E^1_{2g}) band and a blue shift of the (A_{1g}) bands would be observed. Results indicate that the (E^1_{2g}) and A_{1g} bands for the pristine and MoS_2 nanosheets are located at 373 and 376 cm^{-1}, and 399 and 397.20 cm^{-1}, respectively. The energy difference between two Raman peaks (Δ) can be used to identify the number of MoS_2 layers. It can be seen that the Δ value obtained for the two samples is about 26 and about 21.2 cm^{-1}, respectively, indicating the existence of the two to three layered MoS_2 nanosheets after sonicating pristine MoS_2 powders in DMF.[10] And also the decreasing Δ value signifies the successful exfoliation of MoS_2 layers.[12], [13]

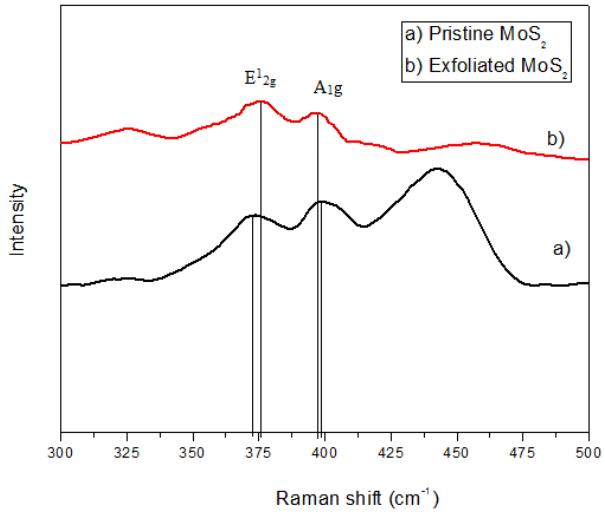

Fig. 3: Raman Spectra of pristine MoS_2 and exfoliated MoS_2

IV. CONCLUSIONS

Bulk MoS_2 is successfully exfoliated using liquid phase method and modified using CTAB. Through proper surface modification, MoS_2 can be used as a very good filler in polymer composite for property enhancement because of it better compatibility and dispersion in the polymer matrix. The samples were analysed using the XRD, Photoluminescence and Raman spectroscopy. From the XRD analysis it is clear that there is a notable decrease n the particle size of the material on processing and the reduction in the intensity of the peak shows the exfoliation of the MoS_2 sheets. In the PL analysis the red shift of the peaks of exfoliated and modified MoS_2 samples supports the formation of MoS_2 single layers. The Raman spectroscopic analysis also shows the formation of MoS_2 nanoflakes.

REFERENCES

1. Liu K et al, "Growth of large area and highly crystalline MoS_2 thin layers on insulating substrates", Nano Letters 12 (2012) 1538-1544.
2. Coleman J N et al, "Two-dimensional nanosheets produced by liquid exfoliation of layered materials", Science 331 (2011) 568-571.
3. Bindhu B, Sharu BK, Gopika MS, Praseetha PK and Veluraja K, "Molybdenum disulfide nanoflakes through Li-AHA assisted exfoliation in an aqueous medium", RSC Advances 6 (2016) 22026–22033.
4. Sham ML and Kim JK, " Surface functionalities of multi-wall carbon nanotubes after UV/Ozone and TETA treatments", Carbon N Y 44 (2006) 768–777.
5. Afanasiev P, Xia G-F, Berhault G, Jouguet B and Lacroix M, "Surfactant-Assisted Synthesis of Highly Dispersed Molybdenum Sulfide", Chem Mater 11(1999) 3216–3219.
6. Lozano K and Barrera E V, "Nanofiber-reinforced thermoplastic composites. I. Thermoanalytical and mechanical analyses", Journal of Applied Polymer Science 79 (2000) 125–133.
7. Zhou K, Liu J, Wen P, Hu Y and Gui Z, " A noncovalent functionalization approach to improve the dispersibility and properties of polymer/MoS_2composites", Applied Surface Science 316 (2014) 237–244.
8. Ye L, Xu H, Zhang D and Chen S, "Synthesis of bilayer MoS_2 nanosheets by a facile hydrothermal method and their methyl orange adsorption capacity", Materials Research Bulletin 55 (2014) 221–228.
9. Afanasiev P, "Synthetic approaches to Molybdenum sulphide materials," Comptes Rendus Chimie 11 (2008) 159–182.
10. Gao, D et al, "Ferromagnetism in freestanding MoS_2 nanosheets", Nanoscale Research Letters, 8 (2013) 129.
11. Ma L et al, " Cationic surfactant-assisted hydrothermal synthesis of few-layer molybdenum disulfide/graphene composites: Microstructure and electrochemical lithium storage", Journal of Power Sources 264 (2014) 262–271.
12. Kibsgaard J, Chen Z, Reinecke B N, and Jaramillo T F, "Engineering the surface structure of MoS_2 to preferentially expose active edge sites for electro catalysis", Nature Materials 11 (2012) 963–969.