AN EXPERIMENTAL STUDY ON SURFACE MODIFIER ASSISTED EXFOLIATION OF MOLYBDENUM DISULPHIDE IN A MIXED SOLVENT

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ABSTRACT

Molybdenum disulphide (MoS₂) is a layered transitional metal dichalcogenide that exhibits unique properties when isolated into one or few layers. MoS₂ finds applications in electronics and optoelectronics, along with the ability to act as host materials to polymers. In this paper, we report the successful exfoliation and modification of MoS₂ with Lithium salt of 6 amino hexanoic acids (Li-AHA) in a mixed solvent of N-Methyl-2-Pyrrolidone (NMP) and deionized water. The X-ray diffraction studies showed reduction in size accompanied by increased strain, which indicates exfoliation. Photoluminescence was proved for the exfoliated sample using photoluminescence spectroscopy. The antimicrobial study results showed that the exfoliated MoS₂ had better zone of inhibition than pristine MoS₂.

Keywords: MoS₂, Exfoliation, Li-AHA, Photoluminescence, Antimicrobial

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INTRODUCTION

Layered substances are of fascinating interest in the field of research due to their unique crystallographic properties. There have been many reports that these layered materials, upon various treatments, can be isolated into single or few-layered substances.¹ These single-layered two dimensional (2D) materials show enhanced properties than that of their bulk counterpart.²⁻⁵ Among these 2D materials, molybdenum disulphide (MoS₂) is a prominent one, due to the various properties being exhibited by the material. The crystal structure of MoS₂ consists of layers of Mo stacked between two sulfide planes which are stacked and separated by van-der Waals forces. Due to thickness induced quantum confinement, a transition occurs from an indirect to direct bandgap, at the few to monolayer limit.⁶ Single layered MoS₂ possess unique physical as well as chemical properties and are potentially utilizable as hydrogen evolution catalysts.⁷⁻¹⁰ Also, there have been many studies reporting the efficiency of MoS₂ as components of electronics and optoelectronic devices.¹¹⁻¹⁶ It was suggested that single-layered MoS₂ can in some ways replace graphene, in applications where it requires thin and transparent semiconductors due to the non zero energy gap present in MoS₂.¹⁷ The size-dependent optical and electronic properties make MoS₂, one of the most researched transitional metal dichalcogenides (TMD)⁵⁰.

The various types of techniques for isolating layers of MoS₂ include, Scotch tape assisted micromechanical exfoliation¹⁸⁻¹⁹, intercalation assisted exfoliation²⁰⁻²¹, solution exfoliation²²⁻²³, physical vapor deposition²⁴⁻²⁵, hydrothermal synthesis²⁶, electrochemical synthesis²⁷, sulfurization of molybdenum oxides.²⁸ Among these different methods, liquid exfoliation method is a general simple technique with better exfoliation results.⁴⁹ Shen⁵³ et al. had reported that mechanical agitation using sonication method is sufficient to isolate monolayers, from their bulk counterpart. This method helps in forming stable dispersions. Dispersions of volumes typically in the range of hundreds of milliliters can be produced

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using the method of sonication.⁵⁴ Nanosheets or 2D materials produced using this method seems to have less basal plane defects.⁵⁵ O'Neill et.al⁵¹, had reported successful exfoliation of MoS₂ in N-methyl-2-pyrrolidone (NMP) in the absence of surfactants through the use of a carefully optimized solvent and prolonged aggressive mechanical agitation. The surface tension of NMP (40 mJ/m²) is similar to estimated surface energies of few-layered MoS₂ (46.5 mJ/m²).⁵² A systematic study of the stability of NMP during probe sonication demonstrates that NMP undergoes autoxidation that, in the presence of O₂ and H₂O, results in the formation of hydroperoxides.⁵⁰ These active species oxidize MoS₂ and facilitate exfoliation. Forsberg et.al⁵⁶ had reported the exfoliation of MoS₂ in water without any additives, but the dispersions were not much stable. The weak interlayer interaction and a large separation of 0.615 nm between MoS₂ layers enable the intercalation and easy diffusion of the Li-ions. Bindhu et al.³⁹ had reported the successful exfoliation of MoS₂ using Li-AHA in deionized water.

The present paperwork lay platform for the effective exfoliation of MoS₂ using a mixed solvent of NMP and water in the presence of Li-AHA. The results were compared with the samples exfoliated in solvents without the modifier. The samples were studied using X-ray Diffraction analysis (XRD), Fourier transforms Infrared Spectroscopy (FTIR) and Scanning Electron Microscope (SEM). The samples with better exfoliation were subjected to photoluminescence and antimicrobial properties to find out the biological attributes and applications of the material.

EXPERIMENTAL

Materials

The following materials are used in our experimental work:

Molybdenum Disulphide [HPLC, LR; MW: 160.06], 6-Aminohexanoic acid [Sigma Aldrich, Fluka Analytical, NT; MW: 131.17], Lithium Hydroxide (Monohydrate) [Molychem, GR; MW: 41.96] and N-Methyl-2-Pyrrolidone [RFCL, MW: 99.13].

Characterization

The crystal structure of the material was studied by X-Ray Diffraction (Philips X-Pert Pro.). The X-ray of wavelength ($\lambda=1.54 \text{ \AA}$) emanating from copper target filtered through nickel was used for our diffraction study. The XRD patterns were recorded with a step scan with step size of 0.05 between 5° and 80° (2 θ). The Fourier Transform Infrared Spectrum was recorded using (Thermo Electron Scientific). Photoluminescence property of the sample was studied using (JASCO Corp., FP-750, Rev. 1.00). The surface morphology of the sample was examined using FESEM, CARL Zeiss Germany, Model Ultra 55 FESEM with 1nm resolution, detector is INLENS.

Sample Preparation

2H-MoS₂ was used as received. 6-Aminohexanoic acid was neutralized using lithium hydroxide to obtain Li-AHA. 1:1 ratio was kept for MoS₂ and LiAHA.³⁹ One wt% of bulk MoS₂ was mixed up with N-methyl-2-pyrrolidone (NMP) and was stirred in a magnetic stirrer for 30 minutes. The required amount of LiAHA in distilled water was stirred in the magnetic stirrer for another 30 mins. The two solutions were mixed and were further sonicated using a probe sonicator for one hour 30 mins followed by centrifugation (3500 rpm) and then drying at 50°C for 18 hours. A similar procedure was followed for exfoliation in NMP and mixed solvent except that without the aid of LiAHA. The samples used for analysis were encoded as 2H-MoS₂(pristine MoS₂), N-MoS₂(MoS₂ in NMP), NH-MoS₂(MoS₂ in NMP and water) and Li-MoS₂(LiAHA assisted MoS₂ in NMP and water).

RESULTS AND DISCUSSION

The prepared samples were kept in a vial and the dispersion states were observed. The modified MoS₂ samples showed better dispersion states. The Li-MoS₂ solution exhibited a colour change from dark grey to light orange. This colour change can be attributed to better exfoliation that happened to the sample. The change in colour to orange shades could be due to the transfer of charge between acid molecules (AHA⁻) to the exfoliated MoS₂ nanosheets. The digital photographs of the samples taken are represented in Fig.-1.

Fig.-1: The Digital Photographs of Prepared MoS₂ Samples**X-ray Diffraction Analysis**

The X-ray diffraction (XRD) patterns of the prepared samples are presented in the Fig.-2. It is clear that there are peak shifts in the spectrum for treated samples when compared with the pristine 2H-MoS₂. The diffraction peaks located at $2\theta = 14^\circ$, 33° , 40° , 50° and 59° correspond to the planes of (002), (100), (103), (105) and (110), respectively, agreeing well with the hexagonal MoS₂ (JCPDS card no. 37-1492). The calculated structural parameters, from the XRD measurements are given in Table-1.

Fig.-2: XRD Spectra of (a). 2H-MoS₂ (b). N-MoS₂ (c).NH-MoS₂ (d) Li-MoS₂

Table-1: Structural Parameters of Samples Calculated from XRD Spectra

Sample	Average Crystallite Size	Dislocation Density	Lattice Strain
2H-MoS ₂	15.45(μ m)	4.189×10^{-3}	0.00187
N-MoS ₂	9.97(nm)	0.010	0.0294
NH-MoS ₂	9.69(nm)	0.0106	0.0307
Li-MoS ₂	8.14(nm)	0.0150	0.0362

It is clear from the table that the average crystallite size is lowest for Li -MoS₂. This reduction in crystallite size is a characteristic of exfoliated MoS₂.³⁰⁻³⁴ The decrease in crystallite size is in agreement with the fact that the layers are restacked to the turbostratic structure.³⁵ The broadness of the Bragg peaks in Fig.-2, for Li-MoS₂ was due to this reduction of crystallite size.³⁶ Similar results were observed by⁶¹ for graphite.

At reflection $2\theta = 14.5^\circ$, corresponding to (002) peak of 2H-MoS₂, the d spacing is calculated to be 6.15 Å and it matches with the reported value of 2H-MoS₂.³⁷ The increase in d-spacing from 6.15 Å for 2H-

MoS₂ to 6.318 Å⁰ for Li-MoS₂, which matches with theoretical interlayer spacing of LiMoS₂⁶⁰, indicates that the guest materials have been intercalated into the interlayer space of MoS₂.³⁸

It is noticed that the intensity of (002) diffraction peak of the Li-MoS₂ decreases as compared to the 2H-MoS₂ and it indicates the de-stacking of MoS₂ layers.³⁹ The decrease in (002) peak intensity suggests the reduction in thickness of bulk MoS₂ flakes.⁴⁰

Also in the Fig.-2d, for Li-MoS₂, a shift in the (002) peaks to lower angles is seen; and it indicates the lattice expansion along the c-axis for the introduction of crystal defects or strains owing to the curvature of the layers^[39]. This can be understood from the table.1; the lattice strain, as well as the dislocation density, is found to increase in the case of Li-MoS₂. Here the shift is marginal and hence it signifies the minimal lattice distortion which is also in accordance with the structural parameters calculated from the XRD spectrum. These results reflect that when sonicated, 2H-MoS₂ can overcome the van der Waal's forces that hold each layer and the layers get separated.

Fourier Transform Infrared Analysis

Fig.-3 shows the spectra of the samples. The FTIR peaks for 2H- MoS₂ is very narrow and very broad for monolayer or bilayer MoS₂⁴¹. Thus the broad peak is shown for the Li -MoS₂ at about 2100 cm⁻¹ can be referred to as an indication that some amount of exfoliation had happened. This broadened peaks, as well as the state of vibration, indicates the exfoliation of the sample and from the peak changes, it is clear that better exfoliation is shown for Li-MoS₂. Compared to 2H-MoS₂, Li-MoS₂ showed additional peaks at 2920 cm⁻¹ and 2847 cm⁻¹, which can be ascribed to CH₂ antisymmetric and symmetric stretching vibrations respectively.^{42,57-58,4} The peak at 1472 cm⁻¹ shows the presence of ammonium salt in the sample. These peaks shown for the Li-MoS₂ indicates the presence of amino hexanoic acid, which has been adsorbed to the surface of MoS₂, and better modification due to (AHA⁻) which can be observed from the increased peak intensity. The well resolved broad Mo = S and Mo-S-Mo peaks for Li-MoS₂ at 720 cm⁻¹ and 910 cm⁻¹ attributes to doubly bridged S²⁻ and ν (Mo=S) terminal S stretches respectively.⁴³ The peak at 1472 cm⁻¹ shows the presence of C-H bending mode in the sample.⁵⁹ The crystalline 2H- MoS₂ peak generally occurs at 365 cm⁻¹, but it was exhibited at ~ 430 cm⁻¹; this may be due to Mo-S-Mo peaks of highly crystalline MoS₂.⁴³

Fig.-3: FTIR Spectra of (a) 2H-MoS₂, (b) N-MoS₂, (c) NH-MoS₂, (d) Li-MoS₂

The weak peaks at about 460 cm⁻¹ are assigned to Mo-S vibration^[44], and that it is inferred with the results that better exfoliation was seen in Li -MoS₂.

Photoluminescence Spectrum of MoS₂

Photoluminescence (PL) is one of the major property that is being exhibited by MoS₂ when exfoliated^[19]. Strong photoluminescence occurs due to an indirect to direct bandgap transition in the d-electron system of MoS₂.⁴⁶ The PL spectrum of 2H-MoS₂ and that of Li-MoS₂, shown in Fig.-4 (a) and (b) indicates a strong peak intensity for Li-MoS₂, when compared with that of bulk material; which indicates an indirect bandgap in the bulk material.¹⁷ The peak at 468 nm in the 2H-MoS₂ is the characteristic peak of bulk MoS₂ indicating the presence of indirect bandgap. In Li assisted sample, a broad luminescence from ~ 550 nm to 650 nm is seen. The broad pronounced emission centered at 600 nm corresponds to the B1 direct excitonic transitions at K point of the Brillouin zone.^{29,46} The peak transition from 650 nm to 720 nm is related to the spin-orbit splitting in the valence band maximum. The emergence of this strong photoluminescence in the Li-MoS₂ indicates that luminescence quantum efficiency is much higher in multilayer MoS₂ than in bulk⁶, thereby confirming the better exfoliation of the sample. This photoluminescence property of MoS₂ when exfoliated can be made use in many applications such as p-type and n-type transistors⁴⁷, inkjet printing⁴⁸, as two-dimensional bandgap semiconductors.⁶

Fig.-4: Photoluminescence Spectrum of (a) 2H-MoS₂ (b) Li-MoS₂

SEM Analysis

The morphology of the 2H-MoS₂ and treated samples were studied using SEM analysis. The SEM images of the samples are shown in Fig.-5. The SEM images taken at 10,000x and 50,000x magnifications of the 2H-MoS₂ and treated MoS₂ samples are studied. The surface details of the samples can be estimated from these images. The multi-layers of pristine MoS₂ is clearly observed in the Fig.-5 (a) and (e). The SEM micrographs of treated MoS₂ show nanosheet structure with Li-MoS₂ exhibiting much thinner and well-dispersed layers. This is attributed to the effect of Li-AHA that effectively resulted in better exfoliation to the MoS₂ structure. From the des-stacked layer as seen in Fig.-5 (d) and (h), it is inferred that Li-AHA has a prominent functionalization effect on MoS₂ surfaces which can improve further interaction with guest materials.

Antimicrobial Studies

To realize the extent to which MoS₂ could be used in any biological applications, the antimicrobial study was conducted on Li-MoS₂ and 2H-MoS₂ for a comparison. The samples were studied in different organisms like *Bacillus cereus*, *Staphylococcus aureus*, *Escherichia coli*, and *Pseudomonas aeruginosa*. The figures are as, Fig.-6. Here zone of inhibition test is used to study antimicrobial activity. From the results, it is very clear that zone of inhibition is more for Li-MoS₂ than that of 2H-MoS₂. Inhibition zone for *Pseudomonas aeruginosa* is found to be the greatest and for the *staphylococcus aureus* the smallest. *Pseudomonas aeruginosa* is a gram-negative bacteria and a multidrug-resistant pathogen commonly known for its omnipresence, antibiotic resistance mechanisms. It is always associated with hospital-acquired infections such as ventilator-associated pneumonia and various sepsis syndromes. Treatment of *P. aeruginosa* infections can be difficult due to its natural resistance to antibiotics. *Bacillus*

cereus is a Gram-positive bacteria that can cause foodborne illness. These kinds of bacteria may grow when food is not properly cooked or kept in unhygienic atmosphere. Similar results were observed by.⁶³ From the zone inhibition test results, it is found that Li assisted MoS₂ has shown better zone of inhibition for these kinds of bacteria's, and could be used in biological applications.

Fig.-5: SEM Images of 2H-MoS₂ and Treated Samples

Fig.-6: Images Of Inhibition Zone Being Exhibited By Li assisted MoS₂ on : (a) *Escherichia coli*, (b) *Staphylococcus aureus*, (c) *Bacillus cereus*, (d) *Pseudomonas aeruginosa*.

Table-2: Zone of Inhibition being Exhibited by 2H-MoS₂ and Li -MoS₂

Name of Organisms	Zone of Inhibition (mm)	
	Pristine MoS ₂ (AB)	Li assisted MoS ₂ (MN)
<i>Bacillus cereus</i>	8	13
<i>Staphylococcus aureus</i>	-	8
<i>Escherichia coli</i>	-	9
<i>Pseudomonas aeruginosa</i>	13	18

CONCLUSION

The novel approach of treating MoS₂ with Li-AHA in a mixed solvent of NMP and deionized water showed better exfoliation results than that without the aid of modifier. The ultrasonication imposes mechanical agitations to the MoS₂ dispersion that has the potential to extract layers from the bulk form. In

the presence of Li-AHA, the Li^+ ions intercalate to the van der Waal spaces between the layers aiding further separation by increasing the interlayer spacing. Simultaneously, AHA^- ions get adsorbed to the MoS_2 surface imposing a partial negative charge to the surface. The repulsion between the individual sheets prevents the restacking of the sheets. Thus with the help of the modifier single and few-layered MoS_2 nanosheets can be synthesized. Further the solvent used, NMP, in the presence of O_2 and H_2O , auto oxidizes into hydroperoxides, which in turn oxidizes MoS_2 and facilitates exfoliation. Thus exfoliated MoS_2 nanosheets exhibited photoluminescence and antimicrobial activities. The photoluminescence emerges from the indirect to direct bandgap transition, when layers isolated from the bulk structure. Thus exfoliated MoS_2 can act as reinforcing filler materials due to the active sites imparted by AHA^- . This photoluminescence property can be made use in optoelectronic applications. The zone of inhibition test shows that the Li- MoS_2 exhibits zone of inhibition. The bacterial cells first come in contact with exfoliated MoS_2 owing to its high surface area. Once contacted, the sharp edges of MoS_2 causes membrane stress like cutters that would further disrupt and damages the cell membrane eventually resulting in cell death. Thus the antimicrobial activity coupled along with prepared Li- MoS_2 samples as a reinforcing⁶² additive to the suitable polymers is promising candidates for biomedical packaging.

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