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Effect of Precursors' Concentration on Structural and Electronic Properties of Ammonium Ions (NH^{4+}) Intercalated 1T/2H Phase MoS_2

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In this study, we have prepared a mixed phase of 1T/2H-MoS_2 nanoflowers using a simple hydrothermal approach without loading any additional catalyst. The ammonium (NH^{4+}) ion intercalation has been induced to insert the 1T phase, with an increase in Mo precursor i.e., ammonium molybdate tetrahydrate concentration in an order of 1M, 1.4M, and 1.8M to obtain the mixed phase of 1T/2H-MoS_2. The synthesis confirmation and structural properties of mixed-phase has been investigated using X-ray diffraction (XRD), Raman spectroscopy, and X-ray photoelectron spectroscopy (XPS). The morphology of 1T/2H-MoS_2 clearly shows the reduction in grain size and an increase in active sites due to the change in morphology from the crumbled nanoflowers to the agglomerated tiny pin-like microstructures. XRD and Raman confirm the presence of mixed phase and it has been observed that crystallite size and the interplanar distance increase with the increase in NH4+ ions molar concentration (1-1.8 M). The mixed phase of 1T/2H-MoS_2 shows high absorbance in the visible region due to the presence of the metallic behaviour and a lowering in the bandgap (1.9 eV to 1.5 eV) is also clearly observed with the increase in concentration. From XPS, it has been concluded that the concentration of the 1T phase in the mixed 1T/2H-MoS_2 can be controlled by optimizing the concentration of the precursor during preparation such as with 1.8 M concentration, the developed 1T character is around 45.8 %. The mixed phase 1T/2H-MoS_2 is found to be a suitable candidate for gas sensing due to its improved interplanar spacing, adjustable bandgap, and enhanced active sites.

Keywords: Hydrothermal method, Optoelectronic properties, Pin-shaped microstructures, Tunable bandgap, X-ray Photoelectron Spectroscopy

1 Introduction

Transition metal dichalcogenides (TMDs) comprising a general formula MX_2, where M stands for a transition metal, such as Mo, W, Ti, and X belongs to a chalcogen atom, such as S, Se, and Te, are prepared using various methods with extensive diversity in electrical properties varying from semiconductors, metals to superconductors[1,2,3]. MoS_2, from the family of TMDs, is an extensively researched material because of the availability of direct bandgap in monolayers and good electron mobility of 60 $cm^2V^{-1}s^{-1}$ at 250 K and high current on/off ratio[4]. Based on the atomic arrangement of Mo/S atoms, MoS_2 can be found in two phases. The most prevalent and stable form of MoS_2 in the environment is the 2H phase. Both 1T and 2H phases show the arrangement such as each Mo atom is surrounded by six S atoms. A distinct difference between 2H-MoS_2 and 1T-MoS_2 is that 2H-MoS_2 is semiconducting in nature, whereas the latter is metallic[5]. Due to the metallic phase of 1T-MoS_2, it has gained huge attention in MoS_2-derived applications. Commonly, 1T-MoS_2 is produced by chemically exfoliating 2H-MoS_2 and intercalating it with alkali ions like Li^+, Na^+, and K^+. The resulting 1T-MoS_2 materials tend to be hydrophilic in nature[6]. The most common method of Li^+ intercalation involves the transfer of an electron from the reducing agent to MoS_2, which raises the electron density of Mo d-orbital. It leads to the 1T (metallic) phase transition by introducing instability in the 2H (semiconducting) phase. By improving the exposed active sites and the charge transfer characteristics of MoS_2 nanosheets, the catalytic activities of the 1T phase are enhanced[7]. As per reports, Li^+ intercalation of 2H-MoS_2 is one of the complicated methods to prepare 1T-MoS_2. Using the Na^+ ion intercalation, the best quality of nanosheets is obtained. By maintaining the growth kinetics, the hydrothermal process is the most used method to prepare 1T-MoS_2 nanosheets and their composites, specifically for electrocatalytic applications. For further improved electrocatalytic performance, reactions are optimized for 1T-MoS_2 nanosheets with morphologies in the form of tears,

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pinholes, and defects. 1T-MoS_2 finds promising uses in environmental monitoring, industrial and medical fields, etc. as an efficient sensor. For excellent sensitivity, a large surface area and chemical and thermal stability of the material are required. The effective surface-to-volume ratio, excellent electrical properties, and highly reactive active sites make MoS_2 a promising gas-sensing material[8]. For gas sensing, 1T or the mixed phase of 1T/2H-MoS_2 is preferable to pure 2H-MoS_2 due to its metallic properties. In 2H-MoS_2, the edge sites are excellent for adsorption and catalytic reactions whereas basal planes are catalytically inert. However, the basal planes of 1T-MoS_2 are rich in active sites compared to 2H-MoS_2, which is more desirable for improving the gas sensing performance and the sensitivity largely relies on the adsorption strength of gas molecules over the sensor's surface i.e. more active sites, more adsorption. For that reason, the phase exploitation between the 2H and 1T structure of MoS_2 is more necessary for the enhancement of gas sensing properties[9].

In the present work, encouraged by the alkali ion intercalation, we propose a novel and easy strategy for the synthesis of 1T/2H mixed phase of MoS_2 using the hydrothermal method with the addition of ammonium molybdate heptahydrate and thiourea for activating the ammonium ion (NH^{4+}) intercalation. Presence of more active sites, controlled electrical conductivity, and good optical properties, the as-prepared 1T/2H MoS_2 is expected to exhibit better gas sensing performances.

2 Materials and Methods

2.1 Chemicals

Ammonium Molybdate Tetrahydrate (AMT) $(NH_4)_6Mo_7O_{24}.4H_2O$, Thiourea $CS(NH_2)_2$, De-ionized (DI) water, and Ethanol. All the chemical are used as purchased without any further purification.

2.2 Synthesis procedure

A simple hydrothermal method was employed to synthesize a mixed 1T/2H-MoS_2 using 60 ml of ethanol/ DI water mixture with a 1:2 ratio as solvent by adding AMT as Mo precursor and thiourea as S precursor with 1:1 ratio by varying the molar concentration as 1, 1.4, and 1.8 M. To obtain a mixed solution, the used precursors were dissolved in 60 ml of DI/ethanol solvent and swirled at 600 rpm for 30 min. The entire solution was then put into a Teflon-lined autoclave and heated for 24 hours at 200 °C. The resulting slurry was rinsed four times with DI water and ethanol, and the precipitates were then put in the oven to dry at 100°C for 12 h and marked as MoS_2-1, MoS_2-1.4 & MoS_2-1.8 corresponding to their concentrations. Figure 1 illustrates the simplified representation of the synthesis of 1T/2H-MoS_2 using the hydrothermal method.

3 Results and Discussion

3.1 Structural and Morphological properties of prepared 1T/2H-MoS_2 with varying NH4+ concentration

The morphologies of MoS_2-1, 1.4 & 1.8 nanostructures were analysed. Figure 2 (a, b, & c) are SEM image representations clearly showing the nanoflowers morphology of MoS_2. From the SEM images, it has been observed that MoS_2-1 shows a structure of irregularly shaped bubbles with solid and thick surfaces (Fig. 2 (a)), which has been further converted into sharp and smaller microflower bubbles with sharp pin-shaped structure (Fig. 2(b)) and with an increase in concentration from 1 M to 1.4 M and later the crumbled microflowers seemed to be segregated into smaller sticks and agglomeration of the sticks was observed when concentration was raised from 1.4 M to 1.8 M (Fig. 2 (c)).

The XRD patterns of synthesized MoS_2 nanoflowers are shown in Fig. 3(a). MoS_2-1.8 exhibited three diffraction peaks at 13.8° (002), 32.6° (100), and 58.1° (110), whereas MoS_2-1.4 showed the diffraction peaks at 13.59° (002), 32.46° (100), and 57.64° (110), and MoS_2-1 registered the diffraction peaks at 14.03° (002), 33.12° (100), and 60.26° (110) as shown in Table 1. Some additional peaks around 11°, and 21° corresponding to (002) and (004) crystal planes appeared because of the partial intercalation of ammonium ions (NH^{4+}) increasing the interplanar spacing of MoS_2 and confirming the hybrid phase of 1T and 2H.

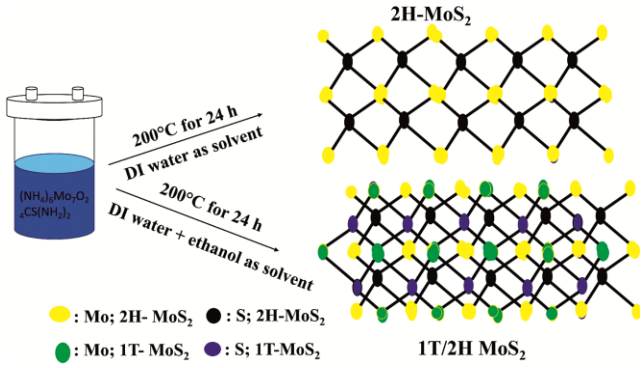

Fig. 1 — Schematic representation of the hydrothermal synthesis of 1T/2H-MoS_2 along with the corresponding atomic arrangements.

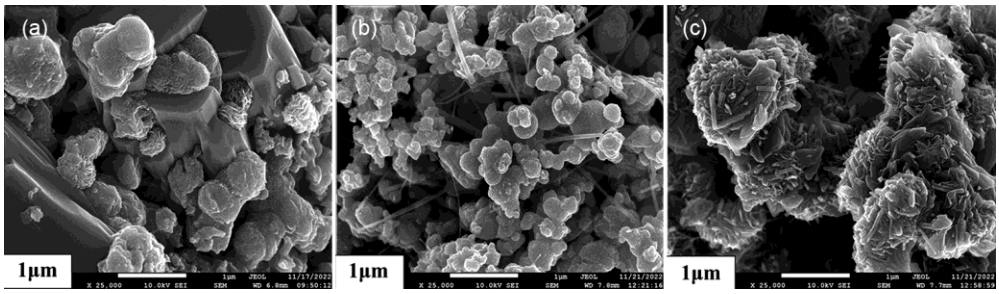

Fig. 2 — SEM images of (a) MoS2-1, (b) MoS2-1.4, & (c) MoS2-1.8.

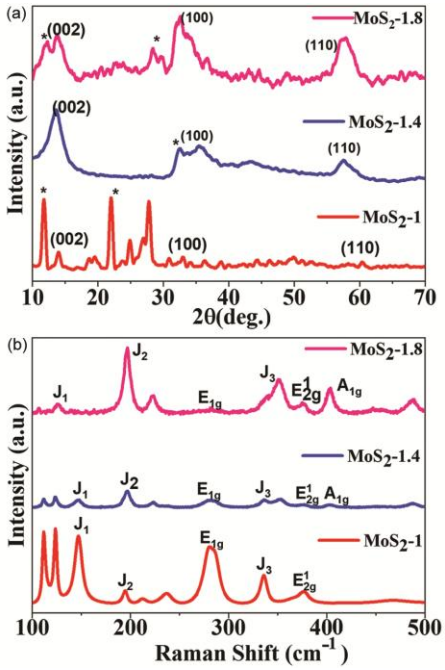

Fig. 3 — (a) X-ray Diffractograms, & (b) Raman Spectra of MoS_2-1, MoS_2-1.4, & MoS_2-1.8.

Figure 3(b) represents the Raman Spectra of the prepared MoS_2 nanoflowers with corresponding concentrations. As of the 2H-MoS_2, three peaks at 282.74 cm^{-1}, 376.29 cm^{-1}, and 404.03 cm^{-1} have been observed in MoS_2-1.8 corresponding to the E_{1g}, E_{2g}^1, and A_{1g} respectively, whereas for 1T, E_{1g} signifies the octahedral coordination of Mo, E_{2g}^1 represents the in-plane vibrations of two S atoms w.r.t. the Mo atoms in opposite direction, and A_{1g} is the out-of-plane vibration of S atoms in opposite directions[10]. The emergence of the peaks at 126.5 cm^{-1}, 196.7 cm^{-1}, and 351.9 cm^{-1} corresponding to J_1, J_2, and J_3 respectively demonstrated the formation of 1T-MoS_2. J_1 modes correspond to the zigzag chain's in-plane shearing mode relative to the other, J_2 to the shifts of S atom layers with respect to the Mo atoms, and J_3 to the stretching towards the out-of-plane component of one side of the zigzag chain relative to the other[8]. Herein,

Table 1 — Interplanar Spacing and crystallite size of the prepared MoS_2 samples with respect to the diffraction angle.

Sample	(002) 2θ (°)	Interplanar Spacing (nm)	Crystallite size (nm)
MoS_2-1.8	13.8°	0.65	0.13
MoS_2-1.4	13.59°	0.64	0.14
MoS_2-1	14.03°	0.63	0.19

MoS_2-1 does not exhibit the A_{1g} peak, whereas the intensity in MoS_2-1.4 is very low for the same, suggesting the dominance of basal planes in comparison to the edges in MoS_2-1.4[11]. Interestingly, MoS_2-1, 1.4 & 1.8 are seemed to exhibit 1T and 2H characteristic peaks resulting the higher J_1 and J_3 intensities in case of MoS_2-1.8 as compared to the others, suggesting that MoS_2-1.8 contains a good fraction of 1T.

3.2 Optical and Core level studies of prepared 1T/2H-MoS_2 with varying NH^{4+} concentration

To determine the effect of mixed-phase 1T and 2H-MoS_2 on the optical properties, UV-Vis measurements were performed and plotted in Fig. 4(a), the two peaks around 200-400 nm correspond to the strong optical absorption indicating a direct excitonic transition from the valence band to the conduction band. From Fig. 4(a), in the range 200-700 nm, weak light absorption has been noticed in MoS_2-1, which further decreased significantly after 350 nm.

On the other hand, for MoS_2-1.4 & MoS_2-1.8, a significant increase in the light absorption was noticed as compared to the MoS_2-1 and their light absorption remained high above 400 nm. Enhanced absorption was noticed in 1T/2H- MoS_2 nanostructures for 1.8M and 1.4M. The light absorption of 1T/2H-MoS_2 in the visible region has appeared almost twice that of the 2H phase dominant MoS_2. This has improved due to the increase in metallic (1T) character in 1T/2H MoS_2[12]. Further, the bandgap of 1T/2H-MoS2 has been calculated with all the performed concentrations using the tauc-plots and representations has been shown in Fig. 4(b-d)[8].

To determine the percentage of the 1T and 2H phases existing in the mixed 1T/2H-MoS_2, XPS analysis is important. The Mo 3d peaks were located at 228.8 eV and 231.4 eV which relate to the $Mo3d_{5/2}$ and $Mo3d_{3/2}$ respectively. The S 2p peaks were located between 161-163 eV which determines the S 2p state. The individual contributions of 1T & 2H in terms of percentage in the mixed form of MoS_2 with varied concentrations have been determined (Fig. 5(a-f)). The peaks in MoS_2-1 (Fig. 5(a)) are associated with the 1T phase of MoS_2, whereas the peaks in MoS_2-1 at 228.8 eV and 232.1 eV are related to the 2H phase of MoS_2[13].

The amount of the 1T and 2H nature present in mixed-phase MoS_2 are calculated from the deconvoluted peaks, determined by the area percentage occupied by the Mo peaks. According to the experimental results, the 1T character in MoS_2 developed to 27.9% (1 M), 36.3% (1.4 M), and 45.8% (1.8 M) when the precursor concentration ratio increased from 1 to 1.8 M, and subsequently the 2H ratio decreased. In addition, with the increase in concentrations, the intensity as well as the area percentage of the peak related to Mo^{6+} available around 236.2 eV also increased indicating the incomplete sulfurization of Mo precursor (Fig. 5 (e)).

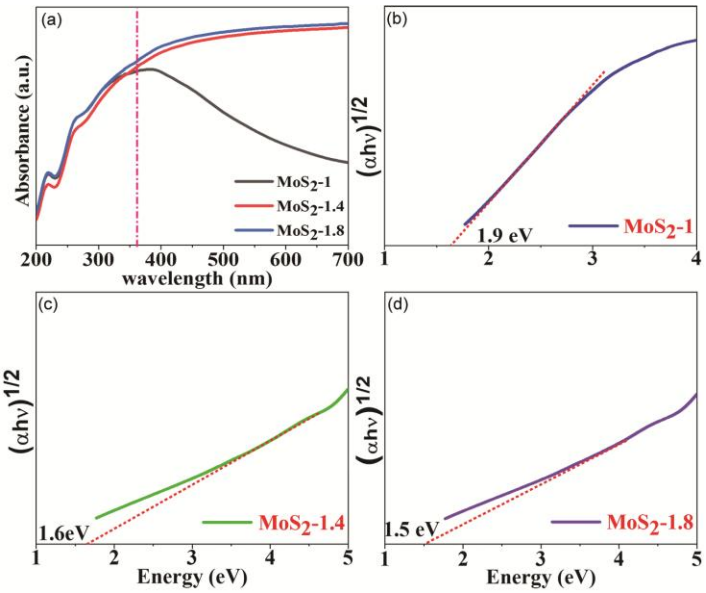

Fig. 4 — (a) UV-Vis Spectra and Tauc plots of (b) MoS_2-1, (b) MoS_2-1.4, & (c) MoS_2-1.8.

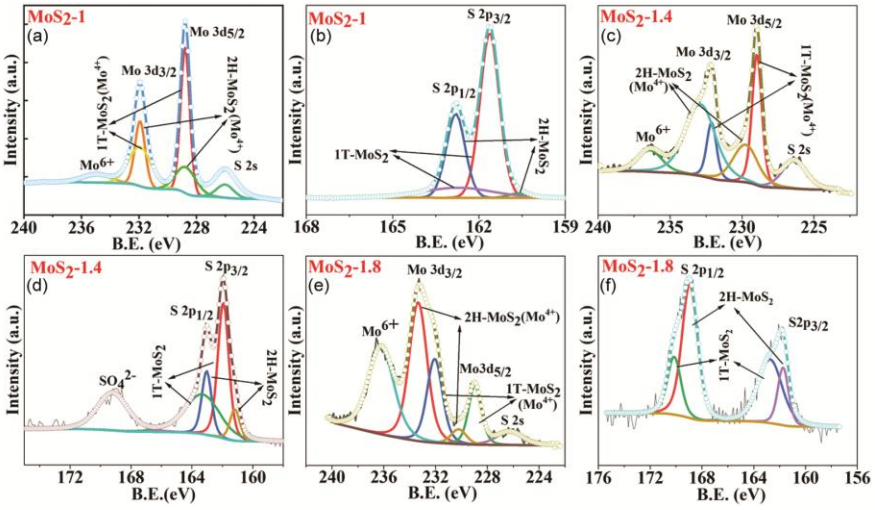

Fig. 5 — (a, c, e) XPS spectra of deconvolutedMo3d and S2p, (b, d, f) core levels differentiating 1T and 2H characters of MoS_2 for MoS_2-1, MoS_2-1.4, & MoS_2-1.8.

4 Conclusion

1T/2H-MoS_2 nanoflowers have been successfully prepared through the hydrothermal method at 200 ℃ with the Mo/S molar ratio 1, 1.4, and 1.8. MoS_2. The obtained MoS_2 indicates that the intercalation transpired with the increased concentration of NH^{4+} ions. The interplanar spacing between MoS_2 layers increases with an increase in concentration with the decrease in crystallite size and the crystallite size lies in the range of 0.13-0.19 nm. Intercalation induces the formation of 1T character of MoS_2 which has been validated by Raman, XPS, and UV-Vis spectroscopy. The presence of corresponding Raman modes (J_1, J_2, and J_3) have confirmed the existence of a mixed 1T/2H phase of MoS2. Further, the content percentage (1T/2H) has been obtained using Mo3d deconvoluted XPS spectra. Therefore, it is deduced that the mixed 1T/2H MoS_2 samples have been successfully prepared using the hydrothermal method, and the mixture of DI water with ethanol encouraged the synthesis of mixed 1T/2H-MoS_2 in hydrothermal conditions which are stable in nature. The microflower morphology has appeared to be turned into a pin-like structure by increasing the surface-to-volume ratio of individual grains along with more available active sites suggests that NH^{4+} intercalated 1T/2H-MoS_2 could be suitable for gas sensing.

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