Molybdenum Disulphide Nanoparticles Synthesis Using a Low Temperature Hydrothermal Method and Characterization

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Abstract. Molybdenum disulphide nanoparticles having crystallite size of 5.55nm, were synthesized by low temperature hydrothermal method. X-ray Photoelectron Spectroscopy (XPS) was employed to probe into the energy levels of the synthesized Molybdenum disulphide nanoparticle. Findings of XPS suggest the presence of Mo$^{6+}$, Mo$^{4+}$ and Mo$^{2+}$ oxidation states of Molybdenum 3d states. The Binding energy (BE) of sulphur was found to be 168.80 and 161.72 eV for S 2P$_{1/2}$ and S 2P$_{3/2}$ respectively, and the atomic percentage of Mo and S are in the ratio 1: 2.33, which patch up with the theoretical values.

Keywords: Molybdenum disulphide, Hydrothermal method, Oxidation state, XPS.

1. Introduction
The hydrothermal technique is one of the most important tools for advanced materials processing of mono-dispersed nanoparticles of various metal oxides and metal sulphides. Transition metal chalcogenides are now receiving researcher’s attention owing to its potential advantages in catalysis [1], lubricant applications [2], super capacitor, lithium ion [3] battery storage, photo detector [4], and other optoelectronic devices [5]. Transition metal oxides like MoO$_3$, WO$_3$ etc are chromogenic and can be implemented into solar cells in order to improve their efficiency [6]. Due to the easy tunability of band gap, with size and number of layers nanostructured MoS$_2$ finds applications in various optoelectronic devices.

Alike graphene, MoS$_2$ and WS$_2$ have enormously deferent properties in reduced layer numbers_limit than bulk materials [7]. MoS$_2$ having a controllable band gap with magnitude between 1.5–2.0 eV makes it superior over graphene of zero band gap. It follows a layered structure, where individual S-Mo-S layer (monolayer MoS$_2$) consists of one plane of Mo atoms sandwiched between two planes of S atoms [8]. Since Mo atoms reside between two S atoms, the localized direct bandgap states from Mo d orbitals are much less sensitive to out-of-plane interactions than the delocalized indirect bandgap states which include S p orbitals.

2. Experimental Details
The low cost, low temperature hydrothermal method enables synthesis of good quality crystals with desired composition owing to the precise control that can be established over composition and different reaction parameters during hydrothermal synthesis. Economic feasibility, relative simplicity in techniques involved and easily attainable temperature conditions are the key features of hydrothermal process which motivated us to prefer this method.

All reagents were of analytical grade and used without further purification. 1.21 gm of sodium molybdate (Na$_2$MoO$_4$.2H$_2$O), 0.14 gm of PEG 20,0000 and 1.56 gm of thiourea
(NH₂CSNH₂) were dissolved simultaneously in 30 ml of distilled water and the resulting solution was transferred into 100 ml Teflon jar and sealed in an autoclave kept in furnace at 200 °C for 11 hours and then cooled to room temperature naturally. The black precipitate obtained is centrifuged and washed several times in distilled water and ethanol then dried in air. Black powder was obtained after drying the sample 80 °C for about 8 hours.

Crystal structure and phase of sample were investigated through X-ray diffraction technique using Cu Kα₁ line of wavelength 1.5406Å using Bruker X-ray diffractometer with a step size of 0.02 and a scan rate of 3° per minute. Spectrum is recorded between the 20 values from 10 to 90°. Chemical purity and the composition of the materials were examined with the Energy Dispersive X-Ray Spectroscopy (EDS) techniques using Bruker electron microscope analyser. X-Ray Photoelectron Spectroscopy (XPS) were recorded using a multiprobe system having a Mg/Al X-Ray source and a hemispherical analyser operating in a Constant Analyser Energy (CAE) mode at Omicron nanotechnology.

3. Results and discussion

The obtained XRD and corresponding JCPDS spectra are shown in Figure 1 and the data tabulated in Table1. The peaks are compared with JCPDS card no 89-5112 and the rhombohedral phase of MoS₂ was confirmed. Different peaks at 20 values 13.69°, 32.85°, 35.61°, 42.30°, 57.54° correspond to hkl planes (003), (101), (012), (015), (110) respectively.

![Fig 1. XRD spectra of Rhombohedral MoS₂ along with its corresponding JCPDS peaks.](image1)

![Figure 2. Williamson-Hall plot of MoS₂.](image2)

The broadened peak of the XRD spectra signifies the smaller crystallite size of the sample and is calculated by exploiting Scherrer equation which gives a value 5.55nm. The modified Scherrer formula [9]

\[ \frac{\beta_{\text{total}} \cos \theta}{\lambda} = \frac{1}{L} + 4d \sin \theta \]

Table 1 Calculation of crystallite size

| 2θ(degrees) | Intensity | d value (Å) | hkl | FWHM | L(nm) |
|-------------|-----------|-------------|-----|------|-------|
| 13.69       | 999       | 6.12        | 003 | 1.72 | 04.65 |
| 32.85       | 226       | 2.71        | 101 | 0.82 | 10.14 |
| 35.61       | 207       | 2.62        | 012 | 1.97 | 04.23 |
| 42.30       | 286       | 2.19        | 015 | 2.05 | 14.17 |
| 57.55       | 126       | 1.58        | 110 | 1.98 | 14.57 |

Average crystallite size 5.55nm
is applied to the system to obtain a crystallite size which caters the presence of lattice strain experienced because of lattice defect. From W-H plot shown in Figure 2 it was found to be 4.53 nm with a compressive strain of 0.000749.

The energy Dispersive X-ray Spectroscopy (EDS) further confirmed the composition of the sample as molybdenum and sulphur. The graphical representation is shown in Figure 3.

![Figure 3. EDS Spectrum of MoS$_2$.](image)

In order to further understand the elemental identification and chemical state of the elements, X-ray photoelectron spectroscopy (XPS) measurements were carried out and Mo 3d, S 2s, and S 2p regions were analyzed [10]. The XPS recorded as such is shown in Figure 4(a), which indicates the presence of Mo, S and C atoms with the corresponding oxidation states. Elemental identification is done using the separation between the two peaks (for p, d and f states) and the peak area ratio of the XPS recordings. C 1s binding energy of carbon contamination occurs at 284 eV [11]. Multiplet splitting is prominent in atoms having unpaired d electrons. The broad and strong peak at Mo 3d$_{5/2}$ indicates the existence of more than one oxidation state for Mo.

![Figure 4. XPS Spectra of MoS$_2$.](image)
Figure 4. (a) XPS survey spectra of MoS\textsubscript{2} samples (b) Deconvoluted XPS spectra of MoS\textsubscript{2} Mo 3d states (c) Deconvoluted XPS spectra of MoS\textsubscript{2} S 2p states (d) XPS spectra of O 1S state.

The primary objective of studying the Mo 3d spectrum is to determine the relative percentages of different oxidation state present at the surface [12]. The deconvoluted spectra of Mo 3d are shown in Figure 4(b). Peaks assigned to Mo\textsuperscript{4+} 3d\textsubscript{5/2} (228.31 eV) and Mo\textsuperscript{4+} 3d\textsubscript{3/2} (232.19 eV), the expected values for Mo\textsuperscript{4+} in MoS\textsubscript{2}. It shows a small peak at around 234.57 eV, and 231 eV which corresponds to Mo\textsuperscript{6+} 3d\textsubscript{5/2}, Mo\textsuperscript{6+} 3d\textsubscript{3/2} respectively from Mo oxidation [13]. The corresponding S 2p peak consists of a doublet of S 2p\textsubscript{1/2} (168.80 eV) and S 2p\textsubscript{3/2} (161.72 eV), consistent with the S\textsuperscript{2−} type present in MoS\textsubscript{2}. S 2p\textsubscript{3/2} and S 2p\textsubscript{1/2} spin orbit doublet separated by 7.08 eV with intensity ratio 1:1.1. Mo 3d\textsubscript{5/2} and Mo 3d\textsubscript{3/2} are separated by 3.88 eV for Mo\textsuperscript{4+} oxidation state and 3.57 eV for Mo\textsuperscript{6+} oxidation states with intensity ratio 5:6.

Table 2 BE and % Area of peaks corresponding to different oxidation states

|     | BE in eV | FWHM | Area in % |
|-----|----------|------|-----------|
| Mo\textsuperscript{2+} 3d\textsubscript{5/2} | 225.25 | 2.05 | 02.47     |
| Mo\textsuperscript{4+} 3d\textsubscript{3/2} | 232.19 | 2.51 | 12.61     |
| Mo\textsuperscript{4+} 3d\textsubscript{5/2} | 228.31 | 1.48 | 10.38     |
| Mo\textsuperscript{6+} 3d\textsubscript{5/2} | 234.57 | 4.15 | 18.81     |
| Mo\textsuperscript{6+} 3d\textsubscript{3/2} | 231.00 | 1.00 | 04.58     |
| S\textsuperscript{2−} 2p\textsubscript{1/2} | 168.80 | 3.97 | 41.28     |
| S\textsuperscript{2−} 2p\textsubscript{3/2} | 161.72 | 2.50 | 09.86     |
| C 1s | 284.00   |      |           |
| O 1s | 531.80   |      |           |

The complete XPS analysis reports including different oxidation states, multiplet splitting and percentage area corresponding to BE is tabulated in table 2. This record confirms the fact that the addition of valence electron decreases binding energy. Trace amounts of MoO\textsubscript{3}/MoO\textsubscript{2} present in the sample may reduce Mo (VI) to Mo (V) species under X-ray bombardment. The atomic percentage calculated shows that Mo and S are in the ratio 1: 2.33 and it is in good agreement with the theoretical results. Also the percentage of Mo\textsuperscript{6+}/Mo\textsuperscript{4+} is found to be 1.02.

4. Conclusion

Molybdenum disulphide nanoparticles were prepared by hydrothermal method. The obtained sample is confirmed as 3R (Rhombohedral) structures with three repeating layers
of molybdenum and sulphur. The crystallite size of the material calculated as 5.55nm. The EDS spectrum confirmed the molybdenum and sulphur compositions for MoS$_2$. The XPS spectrum for the material suggests a binding energy of 232.19 eV and 228.31 eV for Mo 3d$_{3/2}$ and Mo 3d$_{5/2}$, of Mo$^{4+}$ state and 234.57 eV and 231 eV for corresponding Mo$^{6+}$ states. S$^{2-}$ states having binding energies 168.8 eV and 161.72 eV respectively, which reconcile with the theoretical values. The decrease in binding energy with the change of oxidation states is also studied.

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