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Hydrothermally synthesized 2H-MoS$_2$ under optimized conditions – A structure and morphology analysis

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Abstract

In this study, we obtained the optimized conditions to synthesize pure semiconducting 2H-MoS$_2$ nanomaterial, using a facile and scalable hydrothermal route under the variation of growth parameters such as reaction temperature, reaction time and sulfur precursors. The structural and phase identification of obtained MoS$_2$ powders was analysed using XRD and raman spectroscopy. The reproducible formation of pure 2H-MoS$_2$ phase is reported for the optimized reaction time of 22 h at a temperature of $200 \, ^\circ\text{C}$ using thiourea as sulfur source, with a high yield of 77.4%. FESEM analysis revealed nanoflower-like morphology of average diameter of 300–400 nm with identifiable petals of thickness $\sim 25$ nm for the formed 2H-MoS$_2$ under the optimized conditions. The crystallite size, strain and dislocation density were estimated theoretically using Williamson-Hall plots for the MoS$_2$ formed under the variation of growth temperatures. Tensile strain values were obtained for MoS$_2$ formed using thiourea, which correlated only with phase transitions from mixed 1T-MoS$_2$ to pure 2H-MoS$_2$. In contrast, only mixed 1T/2H-MoS$_2$ phase were obtained for MoS$_2$ powders using L-Cysteine, and correspondingly the strain values were extremely small, which may be due to no phase transition observed and presence of nanosheets without curved petal-like features. The results of this study provide optimized condition for the formation of semiconducting 2H-MoS$_2$ nanomaterial by a scalable route. This is useful for low-cost fabrication of flexible nanoelectronic devices such as non-volatile ReRAMs, supercapacitors and sensors based on 2H-MoS$_2$.

1. Introduction

Currently, 2D materials such as graphene, transition metal dichalcogenides (TMDCs), MXenes, boron nitride are much sought out nanomaterials for various applications in flexible nanoelectronic devices. Among transition metal dichalcogenides, MoS$_2$ is a widely researched material on account of its unique electronic, chemical, mechanical, optical, piezoelectric and antibacterial properties. Accordingly, it has been used for diverse applications such as non-volatile memory devices [1], light-emitting diodes (LEDs) [2], photodetectors [3, 4], sensors [5, 6], energy applications viz. batteries [7], supercapacitors [8], solar cells [9], hydrogen evolution reaction (HER) [10] as well as environmental remediation and photocatalysts for dye degradation [11, 12].

MoS$_2$ exists in three dominant polytypes viz. stable 2H hexagonal (semiconducting) phase, metastable 1T trigonal (metallic) and 3R rhombohedra (semiconducting) phase. The 2H-MoS$_2$ stable phase has interesting semiconducting properties with tunable bandgap of 1.3 to 1.9 eV [13], whereas 1T-MoS$_2$ metastable phase has more active sites and higher electrical conductivity [14, 15].

Both top-down and bottom-up approaches have been employed for the synthesis of MoS$_2$ viz. liquid exfoliation of bulk materials, mechanical exfoliation as well as chemical vapor deposition (CVD) and hydrothermal/solvothermal methods, respectively. Among the top-down approaches, mechanical exfoliation and liquid exfoliation are prevalently used for obtaining single-layer MoS$_2$ and multi-layer MoS$_2$, respectively.
Chemical Vapor Deposition technique has been used for growth of layer-dependent MoS2 for biosensing \cite{16, 17} and piezoelectric applications \cite{18}. Hydrothermal and solvothermal techniques are inexpensive and facile routes for large scale synthesis of MoS2.

Hydrothermal synthesis of MoS2 has been reported by several groups. Recently, there has been interest in studying low temperature hydrothermal synthesis of defect induced MoS2 nanosheets for HER catalytic applications \cite{19, 20}. Doped MoS2 viz. p-type, has been synthesized hydrothermally and its photo catalytic hydrogen production has been compared with intrinsic MoS2 \cite{21}. Study of hydrothermal synthesis of 1 T, 2H and mixed 1 T/2H phases of MoS2 under variation of different parameters like pH, reaction temperature, reaction time, surfactants and Mo/S ratio has been carried out by different groups \cite{22–24}. G H Jetani et al recently, reported formation of polycrystalline MoS2 with mixed 1 T/2H phase, under variation in pH of precursors, for photosensitivity experiments \cite{25}. Morphology change of MoS2 from nanosheets to nano flowers has also been reported under the variation of Mo source from sodium molybdate to molybdenum oxide \cite{26}. Controllable growth of MoS2 microstructures by the addition of surfactants like CTAB and PEG has been studied and formation of larger size and uniform nanosheet and nanoflower morphologies have been reported with increased concentration of surfactants \cite{27–29}. Study of the effect of various alcohols during hydrothermal synthesis of MoS2 was performed by X Leng et al, who reported MoS2 with diverse morphologies and properties as a function of the alcohols \cite{30}. The effects of reaction time, temperature and pH of the precursors viz. ammonium molybdate and thioacetamide were studied for the hydrothermal growth of MoS2 and mechanism proposed for the varying catalytic performance for 1 T, 2H and 1 T/2H mixed phase of MoS2 \cite{31}. Hence, in above works, variation of the growth parameters was performed and formation of different 1T-, 2H- and mixed 1 T/2H-MoS2 phases were reported towards different applications.

Few groups reported work towards optimization of 1 T dominant MoS2 phase. It has been proposed that an intercalation agent must be present, for the formation of 1 T dominant MoS2 phase, \cite{32}. Hydrazine hydrate intercalation of MoS2 over a period of 48 h has been carried out for optimized synthesis of stable 1T-MoS2 for high performance electrocatalytic applications \cite{33}. It has been shown that hydrothermal synthesis under high magnetic field also results in stable synthesis of 1T-MoS2 \cite{34}.

Our aim, in this work, was to synthesize and identify optimized condition for the formation of 2H-MoS2 phase using hydrothermal synthesis under the influence of variation of reaction temperature, reaction time and sulfur precursors using sodium molybdate dihydrate as Mo source. Structure and phase transition of different polymorphs of MoS2 samples obtained under varying growth parameters, was investigated systematically using XRD and raman spectroscopy. The morphology of the formed MoS2 nanostructures was examined using FESEM. Strain developed in the nanostructures was theoretically estimated using Williamson-Hall plots, under the variation of growth temperature and correlated with the phase transitions observed in MoS2. 2H-MoS2 semiconducting phase was reproducibly obtained at reaction time of 22 h and reaction temperature of 200 °C with a good yield. The identified optimized condition of synthesis of semiconducting 2H-MoS2 is useful for low-cost fabrication of MoS2 nanoelectronic devices.

\textbf{Figure 1.} Experimental process flow for the hydrothermal synthesis of MoS2.
2. Experimental

2.1. Materials and methods

MoS$_2$ synthesis was performed using hydrothermal route. Sodium molybdate dihydrate, thiourea and L-cysteine were procured from SRL Pvt. Ltd. Chennai and used as such without any purification. First, a dispersion of Mo precursor viz. 2.4195 g of Sodium Molybdate dihydrate (Na$_2$MoO$_4$.2H$_2$O, extrapure AR grade) was prepared in 20 ml of distilled water. To this dispersion, 3.0048 g of thiourea (CH$_4$N$_2$S, extrapure AR grade) was added and to obtain homogenous dispersion, the mixture was magnetically stirred for 10 min. The Mo to S ratio was kept fixed as 1:4 in all the experiments. Subsequently, the mixture was transferred to 100 ml Teflon coated stainless steel autoclave and kept for heating in a hot air oven at different temperatures (180 °C, 200 °C, and 220 °C) for two different reaction times (20 h and 22 h). The flowchart of the experimental part is depicted in figure 1. Afterwards, the autoclave vessel was cooled down to room temperature and the powders were kept for drying in an oven for 8 h at 80 °C. Similar procedure was repeated for the synthesis of MoS$_2$ with 4.895 g of L-cysteine (C$_3$H$_7$NO$_2$S, extrapure AR grade) as a sulfur precursor.

Figure 2. XRD of hydrothermally synthesized MoS$_2$, using thiourea as sulfur precursor for 20 h reaction time, at different reaction temperatures of (a) 180 °C, (b) 200 °C and (c) 220 °C.
MoS\textsubscript{2} synthesis was carried out using hydrothermal route and the phase evolution of 1\,T, mixed 1\,T-MoS\textsubscript{2}.

### 2.2. Characterizations

The crystal structure of as obtained samples was characterized by x-ray Diffraction (Bruker D8 Advance, Germany) using Cu-\(k\alpha\), radiation wavelength of 1.5406 Å. A Raman spectrum (solid state lasers, Horiba, 532 nm, 25 mW, France) was employed for the phase identification of the obtained powders. The morphology of the as synthesized powders was determined by field emission scanning electron microscopy (TESCAN-MIRA 3 LMH, Korea).

### 3. Results and discussion

MoS\textsubscript{2} synthesis was carried out using hydrothermal route and the phase evolution of 1\,T, mixed 1\,T/2H and pure 2H-MoS\textsubscript{2} phase was studied under the influence of varying reaction temperature, reaction time and sulfur precursors using XRD and Raman analysis. The morphology of the formed samples was examined using FESEM and the strain values were theoretically estimated using Williamson-Hall plots.

#### 3.1. Influence of variation of reaction temperature

Sodium molybdate dihydrate and thiourea were used as Mo and S precursors, respectively and the hydrothermal reactions were carried out for two different reaction times (20 and 22 h) at three different temperatures viz. 180 °C, 200 °C, and 220 °C, using DI water as a solvent. XRD plots are shown along with the standard JCPDS peaks for ease of comparison, as per practice [35]. Figure 2(a) shows the XRD plots of the sample powder obtained at 180 °C for 20 h, with peaks at 2\(\theta\) values of 11.28°, 18.40°, 31.61°, 33.84°, 47.5° and 56.59° corresponding to (002), (004), (100), (101), (105) and (110) planes of 1\,T/2H-MoS\textsubscript{2} suggesting the formation of mixed phase. The observed XRD values matched with standard JCPDS card no. 37-1492, which was used for indexing all the XRD spectra in this work. Presence of \(\alpha\)-MoO\textsubscript{3} is indicated by the peak appearing at 2\(\theta\) value of 28.31° relating to (021) plane. For an elevated temperature of 200 °C, several crystalline peaks are observed at 2\(\theta\) values of 12.84°, 27.28°, 30.06° and 51.18° corresponding to (020), (021), (130) and (170) planes of \(\alpha\)-MoO\textsubscript{3} (JCPDS card no. 05-0508), as shown in figure 2(b). It is known that orthorhombic \(\alpha\)-MoO\textsubscript{3} formation takes place around 200 °C, which is an intermediary product formed. Equation (1), below, depicts the intermediary \(\alpha\)-MoO\textsubscript{3} formation in the hydrothermal reaction of sodium molybdate dihydrate and thiourea.

\[
\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O} + 2\text{CH}_3\text{N}_2\text{S} + 4\text{H}_2\text{O} \rightarrow \text{Na}_2\text{MoO}_4 + 2\text{H}_2\text{O} + 2\text{NaOH} + 2\text{CO}_2 + 4\text{NH}_3 + 2\text{H}_2\text{S} \rightarrow \\
\text{MoS}_2 + 4\text{H}_2\text{O} + 4\text{NH}_3 + 2\text{NaCO}_3
\]

(1)

Alongside the \(\alpha\)-MoO\textsubscript{3} peaks, significantly sharp 1T-MoS\textsubscript{2} peaks corresponding to (002) and (004) planes are slightly shifted to higher 2\(\theta\) values of 11.39° and 18.60°. This may be on account of altered interlayer stacking in the metastable 1T-MoS\textsubscript{2}, upon increase in temperature, resulting in decrease in c-lattice parameter. Also, small intensity peaks corresponding to (100) and (110) planes of 2H-MoS\textsubscript{2} are seen in figure 2(b).

With increased reaction temperature of 220 °C for 20 h, further reaction of the intermediary MoO\textsubscript{3} takes place, leading to the formation of 2H-MoS\textsubscript{2}. This is reflected by the presence of several low intensity 2\(\theta\) peaks appearing at 13.32°, 32.04°, 33.84° and 56.34° corresponding to (002), (100), (101) and (110) planes of 2H-MoS\textsubscript{2}, as seen in figure 2(c).
The Raman spectrum, shown in figure 3, depicts the corresponding evolution of the phases of formed MoS₂. At lower reaction temperature of 180 °C, prominent A₁₈ out-of-plane and E₁₂₈ in-plane modes are seen, with A₁₈ transverse S-S vibrational mode to be stronger than E₁₂₈ longitudinal Mo-S mode. This clearly points to the development of 2H-MoS₂ phase. With increase in reaction temperature to 200 °C, dominant B₂₈ raman active mode along with J₁, J₂, J₃ and E₁₈ in-plane vibrational modes appear, confirming the α-MoO₃ phase formation along with 1T-MoS₂ phase. This is in accordance with the XRD shown in figure 2(b). At 220 °C, B₂₈ J₁, J₂, J₃ modes are significantly reduced and extremely weak A₁₈ and E₁₂₈ modes emerge, suggestive of an emerging 2H-MoS₂ phase.

Thus, as the reaction temperature is varied from 180 °C to 220 °C, we observe a transition in the phase from mixed 1T/2H-MoS₂ at 180 °C, to predominant MoO₃ and 1T-MoS₂ at 200 °C and the formation of an emerging 2H-MoS₂ phase at 220 °C.

3.2. Influence of variation of reaction time
With increased reaction time of 22 h, significant changes in the structure of the formed MoS₂, was observed.
At lower reaction temperature of 180 °C itself, the prolonged reaction leads to broad XRD peaks at 2θ values of 31.69°, 35.02° and 56.59° corresponding to (100), (101) and (110) planes of 2H-MoS2, along with small peaks at 11.27° and 28.36° corresponding to (002) 1T-MoS2 and (021) α-MoO3, respectively (see figure 4(a)). The longer reaction time promotes the growth of 2H-MoS2 as evidenced from XRD. For the reaction at elevated temperature of 200 °C, well-defined broad XRD peaks at 2θ values of 13.68°, 31.42°, and 56.59° are obtained corresponding to (002), (100) and (110) planes of hexagonal nanophase MoS2, as shown in figure 4(b).

Interestingly, under this condition, no XRD peaks due to 1T-MoS2 or α-MoO3 are observed. Thus, at 200 °C for 22 h, a pure 2H-MoS2 semiconducting phase is obtained, as per our objective. Hydrothermal reaction at these conditions was repeated several times, to ascertain the reproducibility of the formation of pure 2H-MoS2.

Subsequently, at slightly higher growth temperature of 220 °C, the prolonged reaction time, once again, shows the formation of metastable 1T-MoS2, as reflected by the presence of XRD peaks at 2θ values of 11.33° and 18.34°. This transformation of 2H-MoS2 phase at 220 °C to metastable 1T-MoS2 may be attributed to possible intercalation by water molecules at higher temperature, resulting in increased d-spacing along c-axis.

The raman spectra, shown in figure 5 confirms the phase transitions obtained for MoS2 in accordance with structure from the XRD data. Accordingly, weak A1g, E1g, J3 modes of 1T/2H-MoS2 and B2g modes of α-MoO3 appear at 180 °C. At 200 °C, dominant E1g in-plane and A1g out-of-plane modes are observed at 368.96 cm⁻¹ and 398.6 cm⁻¹, corresponding to pure 2H-MoS2 phase. Hence, both raman and XRD confirm the presence of pure 2H-MoS2 phase at 200 °C. At 220 °C, extremely low intensity A1g, E1g, J3 and E1g raman modes are observed.

Hence, with the chosen precursors of sodium molybdate dihydrate and thiourea for hydrothermal reaction of 22 h, at 200 °C, a pure 2H-MoS2 semiconducting phase is obtained, as per our objective. The yield percentage of synthesized MoS2 powders under different conditions is shown in table 1. In general, the yield percentage showed an increase with increase in the reaction temperature as well as reaction time for the majority of the hydrothermal reactions carried out (see table 1). However, the reaction carried out for 22 h at 200 °C gave the highest yield percentage of 77.4% for the well-formed pure 2H-MoS2 phase, as compared to 61.2% for a lower reaction time of 20 h. Therefore, the optimized condition to form pure semiconducting 2H-MoS2 phase using above precursors, is obtained for the reaction time of 22 h at 200 °C.
3.3. Effect of variation of sulfur sources

Further, the effect of change in sulfur source, as another parameter affecting the formation of MoS₂ was studied. When the sulfur source is changed to L-cysteine, a higher degree of crystalline XRD peaks are observed in the XRD plots of the samples under the reaction time of 20 and 22 h at different reaction temperatures.

For the case of 20 h reaction, at lower temperature of 180°C, small intensity XRD peaks at 11.38°, 30.95° and 40.73° related to 1T/2H-MoS₂ and at 13.08°, 24.96°, 28.41° and 54.78° related to α-MoO₃ are seen in figure 6(a), which may be ascribed to the nucleation of MoS₂ and intermediary MoO₃. The intermediary MoO₃ byproduct is, once again, formed during the reaction of sodium molybdate with L-cysteine, as given by equation (2) below,

\[
\text{Na}_2\text{MoO}_4 + 2\text{H}_2\text{O} + 2\text{C}_3\text{H}_7\text{NO}_2\text{S} + 6\text{H}_2\text{O} \rightarrow \text{MoO}_3 + 3\text{H}_2\text{O} + 2\text{NaOH} + 2\text{CH}_4 + 4\text{CO}_2 + 2\text{NH}_3 + 2\text{H}_2\text{S} + 2\text{H}_2
\]

\[
\text{MoS}_2 + 2\text{NaCO}_3 + 2\text{H}_2\text{O} + 2\text{NH}_3 + 4\text{CO}_2 + 10\text{H}_2
\]
intermediary MoO$_3$ nanorods along with few 1T corresponding to 2H-MoS$_2$ start to appear on account of intermediary
3.4. Morphology and strain studies
seen in like to nanophase. This is in corroboration with the broadening of XRD peaks with increase in temperature as
sheet-like structures with irregular shapes, are obtained at low reaction temperature of 180$^\circ$C. With the increase in temperature to 200$^\circ$C, more intermediary
MoO$_3$ rods and MoS$_2$ sheets. With further elevated temperature of 220$^\circ$C, once again leads to the formation of nano 1T
MoO$_3$ and clear E$_{1g}$, J$_3$, A$_{1g}$ modes obtained for this sample using thiourea fi approximately 25 nm.

Raman spectrum at 180$^\circ$C, reveals small B$_{2g}$, distinct J$_3$ and A$_{1g}$ modes indicating the formation of
orthorhombic phase of MoO$_3$ and 1T/2H phase of MoS$_2$, respectively. Dominant B$_{2g}$ and (B$_{1g}$, A$_{g}$) modes for
$\alpha$-MoO$_3$ and clear E$_{1g}$ and A$_{1g}$ modes of 2H-MoS$_2$ are visible at the enhanced reaction temperature of 200$^\circ$C. At
220$^\circ$C, the appearance of J$_3$, E$_{1g}$, E$_{2g}$ and A$_{1g}$ Raman modes show slight broadening, which can be attributed to
the formation of nano 1T/2H-MoS$_2$ phase, in confirmation with the XRD plots.

By extending the reaction time to 22 h, more intermediary $\alpha$-MoO$_3$ peaks along with distinct crystalline 1T/2H-MoS$_2$ peaks are obtained, at 180$^\circ$C and 200$^\circ$C, pointing to increased formation of intermediary $\alpha$-MoO$_3$ along with 1T/2H-MoS$_2$ crystallites (see figures S1(a) and S1(b)). Increasing reaction temperature to 220$^\circ$C, once again leads to the formation of nano 1T/2H-MoS$_2$ along with $\alpha$-MoO$_3$.

Raman spectra for corresponding samples obtained with variation in temperature is shown in figure 7. For the case of L-cysteine, FESEM images for the 20 h reaction sample are analysed. SEM micrograph, in figure 9, shows primarily nanosheets, which has also been previously reported by other groups [37]. MoS$_2$ sheet-like structures with irregular shapes, are obtained at low reaction temperature of 180$^\circ$C as seen in figure 9(a). The increase in reaction temperature to 200$^\circ$C, allows crystallization to result in well-formed intermediary MoO$_3$ nanorods along with few 1T/2H-MoS$_2$ nanosheets, as revealed clearly in SEM micrograph (see figure 9(b)). This is in corroboration with XRD and raman spectra for MoS$_2$ obtained using L-cysteine (see figures 6 and 7), where high intensity MoO$_3$ peaks are observed along with 1T/2H-MoS$_2$.

With the increase in temperature to 200$^\circ$C, several dominant crystalline peaks appear at 12.92$^\circ$, 23.18$^\circ$, 24.36$^\circ$, 28.08$^\circ$, 38.66$^\circ$ and 54.58$^\circ$ corresponding to (020), (110), (040), (021), (060) and (221) of $\alpha$-MoO$_3$ which tends to crystallize around 200$^\circ$C. Apart from $\alpha$-MoO$_3$ peaks, high intensity crystalline peaks at 11.50$^\circ$, 19.09$^\circ$, 32.15$^\circ$, 33.87$^\circ$, 48.82$^\circ$, 57.36$^\circ$ and 59.45$^\circ$ corresponding to (002), (004), (100), (101), (105), (110) and (008) of 1T/2H-MoS$_2$ are also obtained. This is suggestive of further growth of nucleated crystallites to form bulk-like MoO$_3$ rods and MoS$_2$ sheets. With further elevated temperature of 220$^\circ$C, slightly broad XRD peaks corresponding to 2H-MoS$_2$ start to appear on account of intermediary $\alpha$-MoO$_3$ undergoing reaction to form nano 1T/2H-MoS$_2$. The structure of the formed products as revealed by XRD is further confirmed by the raman spectrum shown in figure 7.

**Figure 7.** Raman spectra of hydrothermally synthesized MoS$_2$, using L-cysteine as sulfur precursor for 20 h reaction time, at different reaction temperatures of 180$^\circ$C, 200$^\circ$C and 220$^\circ$C.
peaks. Further, at elevated temperature of 220 °C, the intermediary MoO$_3$ grows to form nanosheet-like structure corresponding to 1 T/2H-MoS$_2$ phase (see figure 9(c)). The average lateral size of the nanosheets lies between 200–400 nm. The thickness of the nanosheets is approximately 40–50 nm (see figure 9). Hence,
in the case of L-cysteine as sulfur precursor, predominantly nanosheets formation takes place instead of nanoflowers, as compared with the case of thiourea.

We analyzed the crystallite size, strain and dislocation density only for the well-formed MoS$_2$ samples using thiourea at 22 h and L-cysteine at 20 h, as a function of variation in growth temperature. This choice was based
on the clear XRD and Raman spectra obtained for these samples, depicting the transition between mixed 1T/2H-MoS2 to pure 2H-MoS2 phase. The theoretical estimation of the crystallite size, strain and dislocation density was done using Williamson-Hall (W-H) equation, as given below,

\[
\beta \cos \theta = 0.9\lambda/D + 4 \varepsilon \sin \theta
\]  

where \(D\) is the crystalline size, \(\beta\) is the full width at half maximum of the peak intensity; \(\theta\) is the diffraction angle; \(\lambda\) is the wavelength (0.15406 nm); and \(\varepsilon\) is the crystalline strain. The calculated crystallite size was compared with the experimental values obtained from SEM micrographs and the theoretical strain values were correlated with the phase transitions observed from Raman spectra. Table 2 shows the calculated crystallite size, strain and dislocation density for the indicated synthesis conditions, in the case of thiourea as the precursor, considering 2θ values of dominant XRD peaks. Figure 10 shows the plots of \(\beta \cos \theta\) versus 4sin\(\theta\) for the dominant planes, obtained in the case of thiourea at reaction temperatures of 180°C, 200°C and 220°C, respectively for 22 h reaction. Linear fit of the data of these plots provides the values of \(R^2\), the strain (\(\varepsilon\)) from slope and crystallite size (D) from the y-intercept. The strain values obtained for the sample synthesized at reaction temperatures of 180°C, 200°C and 220°C were 0.02004, 0.02174 and 0.01405. It is observed that with increase in growth temperature, the strain does not follow a monotonic trend. At 180°C, the expanded interlayer spacing of 0.784 nm, along the (002) c-axis, observed in XRD figure 4(a), corresponds to an estimated strain value of 0.02004, which may be attributed to tensile strain along c-axis. The presence of \(E_2g\) and \(A_1g\) raman modes corresponding to mixed 1T/2H-MoS2 phase (see figure 5), at 180°C shows a transition to dominant \(E_2g\) and \(A_1g\) modes for pure 2H-MoS2 at 200°C and also (002) plane of 2H-MoS2 appears at \(2\theta\) values of 13.73° instead of 14.96°, suggesting interlayer expansion along c-axis. This is reflected by an increased strain value of 0.02174 (see table 2). It is known that small changes in the lattice structure in 2D materials may alter the lattice strains. Hence, strain-driven 2H to 1T transition have been observed in TMDCs [38, 39]. This strain value is higher than that of the bulk MoS2 strain \(\sim 0.019\), which may be on account of the formed nanophase-MoS2 [25]. At 220°C, the decreased strain value of 0.01405, once again alludes to phase transition from pure 2H-MoS2, to mixed 1T/2H-MoS2 phase. The decreased in the strain value, in this case, may be on the account of altered interlayer spacing due to intercalation of water molecules. Crystallite sizes of 14.11 nm, 44.72 nm and 20.38 nm are obtained using Williamson-Hall equation, as shown in table 2. Approximate average values of 16.03 nm, 10.50 nm and 26.34 nm for the petal thickness of MoS2 nanoflowers, were measured, from the obtained SEM micrographs (see figure 8), which are in reasonable agreement with the estimated values.

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| Synthesis conditions | hkl | 2θ(deg) | \(\beta \cos \theta\) (rad) | 4 sin \(\theta\) (deg) | D (nm) | \(\varepsilon\) | \(\varepsilon\) (nm\(^{-1}\)) |
|---------------------|-----|---------|-----------------|-----------------|------|-------------|------------------|
| 22 h, 180°C         | 002 | 11.27   | 0.00863         | 0.392           |      |             |                  |
|                     | 100 | 31.70   | 0.03666         | 1.092           |      |             |                  |
|                     | 101 | 35.02   | 0.00593         | 1.2             | 14.11| 0.02004     | 0.0050           |
|                     | 110 | 56.82   | 0.04188         | 1.9             |      |             |                  |
| 22 h, 200°C         | 002 | 13.73   | 0.01662         | 0.476           | 44.72| 0.02174     | 0.0005           |
|                     | 100 | 31.38   | 0.00403         | 1.08            |      |             |                  |
|                     | 110 | 56.59   | 0.04500         | 1.892           |      |             |                  |
| 22 h, 220°C         | 002 | 11.28   | 0.00364         | 0.392           | 20.38| 0.01405     | 0.0024           |
|                     | 100 | 31.97   | 0.00366         | 1.1             |      |             |                  |
|                     | 101 | 34.68   | 0.00558         | 1.192           |      |             |                  |
|                     | 110 | 57.43   | 0.02844         | 1.92            |      |             |                  |
For the case of L-cysteine as sulfur source, nanosheets and nanorod-like morphologies corresponding to MoS$_2$ and intermediary MoO$_3$ are seen in SEM micrograph in figure 9. Crystallite size, strain and dislocation density values for MoS$_2$ using L-cysteine, were also estimated from W-H plots, (see table S1). Extremely small strain values of $-0.0016$, $-0.0037$ and $0.002$ were obtained as a function of increase in growth temperatures for 20 h. Under this condition, a mixed 1 T/2H-MoS$_2$ phase was obtained at different temperatures, with morphologies changing from irregular crystallites to nanorods and nanosheets. The decreased strain values may result from absence of any curved petal-like features of the formed MoS$_2$ nanostructures.

4. Conclusion

In summary, a facile hydrothermal synthesis route was adopted to obtain pure, well-formed 2H-MoS$_2$ nanostructures by optimizing synthesis parameters such as reaction temperature, time and sulfur precursors. The optimized condition for forming pure semiconducting 2H-MoS$_2$ phase was obtained at 200 °C for 22 h reaction time using thiourea as sulfur precursor, as verified by the XRD and raman analysis. A number of trials were repeated at this condition to ascertain the reproducibility of the formed 2H-MoS$_2$ phase. The yield of the formed product was 77.4%, being much higher than at other reaction temperatures and time. In the case of L-cysteine as sulfur precursor, reaction at 20 and 22 h yielded mixed 1 T/2H-MoS$_2$ phases. MoS$_2$ nanoflower morphology with petal-like features were obtained with thiourea, while as for L-cysteine, nanosheets and intermediary nanorods were observed. The strain in the formed MoS$_2$ powders using thiourea, was estimated using W-H plots and the values of 0.02004, 0.02174 and 0.01405 for 22 h were obtained, with increase in reaction temperature. The changes in the tensile strain are related only to phase transitions from 1 T/2H-MoS$_2$ to 2H-MoS$_2$ on account of lattice structure changes. The strain values were extremely small and showed very little variation with reaction temperature for MoS$_2$ powders obtained using L-Cysteine, which may be due to non-changing 1 T/2H-MoS$_2$ phase and nanosheets without curved petal-like features. Hence, the results of this study can be used for low cost fabrication of various rigid and flexible nanoelectronic devices such as non-volatile ReRAM devices, strain sensors and bio-sensors using pure semiconducting 2H-MoS$_2$ obtained in a scalable manner.

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Data availability statement

All data that support the findings of this study are included within the article (and any supplementary files).

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