Probing into crystallography and morphology properties of MoS$_2$ nanoflowers synthesized via temperature dependent hydrothermal method

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Abstract

This paper reports the formation of flower-like hierarchical molybdenum disulfide (MoS$_2$) nanoparticles following a simple one-step hydrothermal process with varying temperatures (200 °C and 220 °C). The as-synthesized particles were examined crystallographically by X-ray diffraction (XRD) method which revealed the formation of hexagonal MoS$_2$ (2H-MoS$_2$) and that the crystallite size of the particles increased with increasing hydrothermal temperature. Surface morphological characteristics of the particles were investigated by a field emission scanning electron microscope (FESEM) and interesting details were revealed such as the rounded 3D flower-like microstructure of the MoS$_2$ particles and the petals of the flowers were composed of platelets built up by stacked-up MoS$_2$ nanosheets. With the increase in hydrothermal temperature, the interlayer spacing of stacked layers of intense (002) plane is slightly decreased although the crystallinity of the material is improved. Both diameter and thickness of the nanoflowers and the nanoplatelets increased twice with increasing the temperatures. A visual crystallographic perspective was presented through simulation of 3D wireframe unit cell associated with the individual lattice planes as observed in the XRD pattern of the samples. In addition, a plausible growth mechanism is proposed for the formation of the obtained MoS$_2$ nanoflowers on the basis of experimental observations and analysis.

1. Introduction

Both the preparation and property studies of novel two-dimensional (2D) and/or three-dimensional (3D) nanostructured materials based on metal chalcogenides such as metal–oxides, -sulfides, -selenides, -nitrides with controlled morphology have attracted enormous interest that has steadily grown worldwide because of their exotic properties that are important for various innovative applications [1–12]. In recent years, intensive research has been devoted to producing high-quality 2D and 3D metal sulfide (CoS$_2$, FeS$_2$, MoS$_2$, NiS$_2$, SnS$_2$ and WS$_2$) nanostuctures of various morphologies e.g. nanoparticles, nanoflowers, nanosheets, nanospheres and nanolamellar morphology [2, 6, 13–18]. Among the widely known metal sulfides, molybdenum disulfide (MoS$_2$) is a naturally occurring, well-defined two-dimensional (2D) layered material that has been reported to be an excellent material capable of various

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applications owing to its exceptional structural, morphological, optical, thermal, electrical, mechanical, electrochemical, electronic and many other physicochemical properties [6, 15–20]. Due to its layered morphology and tunable direct bandgap, nanostructured MoS2 has found potential as anode materials in lithium/sodium storage [16, 21, 22], as a catalyst in electrocatalytic reactions [2, 14, 18, 23, 24], in electronics [17, 20, 25], photocatalysis [26, 27], enzymatic reactions [28], antibacterial [29], sensing [27], and photoelectrochemistry [30] etc. Most if not all of these above-mentioned applications depend, to a large extent, on the surface-morphological characteristics of the particles which would dictate essential properties like specific surface area, crystallinity, ability to engage defects etc.

Various hierarchical MoS2 nanomaterials with different morphologies including 2D tubes-, plates-, ribbons-, sheets-like morphology, and 3D particles-, flakes-, porous-, flowers-like morphology have been obtained via a variety of synthesis procedures; both chemical and/or physical [1, 2, 13, 14, 16–19, 21, 24, 31–35]. MoS2 flower-like nanostructures have recently gained wide traction due to their unique structural characteristics [16, 21, 24, 27, 36].

The synthesis method usually plays a crucial role in obtaining the desired morphology and related physicochemical characteristics which would be suitable for specific industrial and engineering applications [23, 25]. Zhao et al summarized the diverse synthetic approaches, phase, and electronic band structures of metastable MoS2 [15]. For the synthesis of flower-like MoS2 morphology, hydrothermal has usually been the method of choice [16–18, 21, 24, 36]. Hu et al synthesized MoS2 nanoflowers by a hydrothermal method followed by freeze-drying [16]. Lu et al used a simple hydrothermal method via altering reaction temperatures to produce MoS2 nanoflowers consisting of nanosheets to be explored as high-performance lithium-ion battery anodes [21]. Wang et al prepared amorphous MoS2 nanoflowers via hydrothermal synthetic routes and discussed their performance in hydrogen evolution reaction (HER) [24]. Zhang et al managed to synthesize synthesized 3D flower-like MoS2 microspheres via a simple hydrothermal approach [36].

Usually, the petals forming the nanoflowers are 2D entities that arrange to form hierarchical three-dimensional (3D) morphologies. Thus, these hierarchical flower-like nanostructures can combine the advantages of 2D morphology along with the relatively higher dimensional 3D morphology. MoS2 2D layers generally consist of a hexagonal layer of Mo atoms sandwiched between two layers of sulfur where the interlayer interaction is dominated by van der Waal’s forces [1]. Usually, proper tuning of properties can and does play a critical role in various applications of MoS2. For example, exfoliation of MoS2 layers or limiting the bulk MoS2 to a few layers tend to transform the indirect band-gap of MoS2 to a direct one making them excellent semiconductor materials suitable for optoelectronic and nanoelectronics [6]. Tuning the morphology to adjust the ratio of edge sites with that of the surface sites also has important ramifications for these types of 2D layered materials in catalytic applications [2, 18, 37]. Thus, it is critical to evaluate the optimized conditions for maximizing the physicochemical characteristics required for specific application purposes. Detailed investigations into the synthesis parameters and their effects leading to the structural modifications are paramount.

In this work, we have synthesized flower-like MoS2 via a simple hydrothermal method. We followed a previously reported synthesis template [28] and chose two different synthesis temperatures (200 °C and 220 °C) to observe its effects on various properties. These temperatures were picked due to previous literature suggesting the formation of well-defined flower-like MoS2 around these regions. Higher temperatures were not chosen due to the practical limitations of the Teflon pots used during the hydrothermal treatment. The as-synthesized MoS2 particles were crystallographically investigated by XRD and Raman spectroscopy and the effects of varying temperatures on grain size, crystallinity, etc. were evaluated. These properties hold particular importance for the effectiveness of the particles in electrocatalysis, sensing, or optoelectronics [37, 38]. We have generated 3D visualization of the crystal structures of the particles by applying theVESTA (visualization for electronic and structural analysis) software. Structural visualizations are important for creating databases and for initializing structures for various theoretical calculations. We have essentially studied the effect of temperature on various structural parameters; which would be useful for condition based-structure simulation. Effect on morphology and change in interlayer spacings were investigated by electron microscopic techniques. Again the change in spacings strongly influences its applicability in batteries due to enhanced capacity of metal insertion within the layers, and also in HER due to the electron hopping mechanism for layered materials [21, 37]. Effects on optical properties such as the bandgap of the particles were investigated by UV−vis spectroscopy. The nature and value of the bandgap both have important repercussions for MoS2 being utilized as a semiconductor [25]. Overall, various facets of this paper discuss the effect of temperature variation on different properties of MoS2 hierarchical flower-like particles, that dictate its performance in important applications.

2. Experimental details

2.1. Materials

Ammonium molybdate tetrahydrate (NH₄)₂MoO₄.4H₂O) with purity of 81–83% (MoO₃ basis) was purchased from Sigma-Aldrich Co. Ltd. Thiourea (CH₄N₂S) with purity of 99.9% (dried basis) was purchased

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from Merck Life Science Pvt. Ltd. Absolute ethanol (C₂H₅OH) with purity of 99.9% was purchased from Changshu Hongsheng Fine Chemical Co. Ltd. All the materials used for the synthesis of MoS₂ hierarchical nanostructures were of Analytical Reagent (AR) grade and were used directly without any further purification. Millipore water (18 MΩ cm⁻¹) was used throughout for the preparation of different solutions and further purification process.

2.2. Synthesis of MoS₂ nanoflowers

MoS₂ nanoflowers were fabricated by via a simple one-step hydrothermal method with varying temperatures using (NH₄)₆Mo₇O₂₄·4H₂O and CH₄N₂S as starting materials. The hydrothermal synthetic methodology was performed with an optimized molar ratio 1:30 of Mo to S source materials. In a typical synthesis procedure, 0.028 M (NH₄)₆Mo₇O₂₄·4H₂O and 0.84 M CH₄N₂S were dissolved in 36 ml of Millipore water under constant stirring at room temperature to produce a transparent homogeneous solution. The above solution was stirred at 900 rpm for 1 h following which it was transferred to a 100 ml Teflon-lined stainless steel autoclave and sealed. The hydrothermal reaction was carried out in a hot air oven at two different temperatures of 200 and 220 °C for 6 h. The autoclave was then naturally cooled down to the room temperature. The resultant black precipitate was filtered out and washed several times with Millipore water and absolute ethanol repeatedly. Finally, the sample was collected and dried at 60 °C for 24 h. The different temperatures used in the synthesis process allowed us to observe the influence of synthesis temperature on the crystallographic and morphological properties of MoS₂.

2.3. Characterization of synthesized MoS₂ nanoflowers

The crystallographic characteristics of the as-synthesized samples were examined using powder XRD method (PAN analytical X’pert pro, Netherlands) with monochromatized Cu-Kα₁ radiation (λ = 1.54060 Å), scanned between 2θ range of 5° to 80°. Raman spectra of the samples were re-record on a confocal micro-Raman system UniRam with an excitation source of 532 nm laser (15 mW power). The surface morphology of the samples was observed by a FESEM (Tescan Maia3). The structural model depicting a 3D crystallographic representation was achieved using the VESTA theoretical tool. The absorption spectra of the samples were investigated by a Double Beam UV–vis Spectrophotometer (Motra’s UV Plus).

3. Results and discussion

3.1. Crystallographic identification

The basic crystallographic informations such as the crystal structure, crystallite size and purity of the as synthesized materials was evaluated by the XRD patterns. Figures 1(a)–(b) shows the XRD patterns and plots of (βcosθ)/λ versus (sinθ)/λ of the as prepared MoS₂ products. Figure 1(a) demonstrates the XRD pattern of the samples synthesized at 200 °C (lower segment) and 220 °C (upper segment). The identified peak positions at 13.55, 32.58 and 57.14° in the lower segment (200 °C); and 14.00, 33.28 and 58.83° in the upper segment (220 °C) and their relative intensities were in agreement respectively with the (002), (100) and (110) crystal planes of the hexagonal 2H-MoS₂ (standard JCPDS card no. 37–1492; space group P6₃/mmc, No. 194) [2,6,16,22] with unit cell parameters of a = b = 3.16 Å and c = 12.29 Å; α = β = 90°; γ = 120°. No peaks corresponding to any impurity and other phases of any material were observed indicating high purity and good
crystallinity of synthesized materials. The % yield obtained for the MoS$_2$ sample synthesized at 200 °C was determined to be 89.53% and for the MoS$_2$ sample synthesized at 220 °C it was 91.10%. The details of the calculation were provided in the supporting information (SI) (available online at stacks.iop.org/NANO/3/035001/mmedia). It was interesting to observe that the intensity of diffraction peaks became stronger and sharper with the increase of synthesis temperature suggesting improvement in crystallinity and increment of crystallite sizes. In XRD plots, the width of XRD peaks is considerably broadened at lower synthesis temperature, indicating small size of crystallites. The broadening is observed at 200 °C due to the smaller-sized nanocrystallites.

The strong intense (002) diffraction peak reveals that the material has a large number of crystal planes oriented in that particular direction and corresponds to the stacking of single layers of MoS$_2$ 2D nanosheets [24, 31]. All the diffraction peaks shifted to a slightly higher angle with increasing synthesis temperature indicating lowered interplanar spacing (d-spacing). This phenomenon of decreased d-spacing with increasing synthesis temperature has also been previously observed [21, 39, 40]. We suggest the increased crystallite size of the particles to be the reason behind that. An increasing particle/crystallite size would increase the van-der waal’s interaction between the layers and thus would bring them closer. Moreover, the ratio of d-spacing between the (100) and (110) lattice planes was estimated to be ~1.72, which is very close to $\sqrt{3}$:1, further authenticating the hexagonal structure of MoS$_2$ [41]. The estimated crystallite sizes from the Scherrer’s relation [10] using the full width at half maxima (FWHM) values of the diffraction peaks obtained via their Gaussian fitting were within the range of 3–10 nm. Also, the dominant (002) peak observed in the XRD pattern of the 200 °C sample is relatively broad compared to the (002) peak observed in the XRD pattern observed of the 220 °C sample, which could also be attributed to the larger crystallite size of the former.

Figure 1(b) demonstrates the size-strain plot of ($\cos \theta$)/$\lambda$ versus (sin$\theta$)/$\lambda$ of the MoS$_2$ samples synthesized at 200 °C (lower segment) and 220 °C (upper segment). Generally, stress and strain almost always exist in the nanostructured materials (nanomaterials). Most of the cases, these stresses are residual stresses introduced into the system during the adopted synthesis process of nanomaterials. The positive value of strain indicates the tensile strain, whereas the negative value corresponds to the compressive strain of nanomaterials. Table 1 shows the summary of identified peak positions, relative intensities, corresponding lattice planes and calculated crystallite sizes using the FWHM obtained from the XRD patterns. In the present study, compressive strain was observed in both samples. Less compressive strain observed in the high temperature (220 °C) sample would indicate lesser deformation when compared to the low temperature (200 °C) sample against applied stress. Thus from a mechanical strength related application viewpoint the MoS$_2$ (220) would be more suitable. Moreover, the average crystallite size ($D_{ave}$) was also observed using Williamson–Hall method and its value was found to be ~3.32 nm and ~7.38 nm for the samples synthesized at 200 °C and 220 °C, respectively. The reason behind the larger crystallite size in the higher temperature sample can be understood by considering the phenomena of grain growth in the metallurgical processes where, with increasing temperature, the grain boundaries are removed and different crystallite zones are merged to form a larger crystallite [10].

The anisotropic properties including specific heat, tensile strength, dielectric strength, and electric as well as magnetic permeability of polycrystalline materials are related to the orientation distribution function of crystallites and its average value provides the orientation factor. The orientation factor signifies the process of orienting or the state of being oriented. The position or positioning in relation to the points of the compass or other specific directions is known as the orientation factor of any given state. The orientation factor is represented as $O_{hkl}$, where hkl is the orientation of planes, also known as the miller indices. For defining $O_{hkl}$ mathematically, it requires the values of $I_{ld}$ and $I_{exp}$ and a summation of their ratio, where $I_{ld}$ is assigned to the standard value of intensity and $I_{exp}$ is the experimental value of the intensity. Mathematically, it is expressed by equation (1):

$$O_{hkl}(\%) = \frac{I_{exp}/I_{ld}}{\sum(I_{exp}/I_{ld})} \times 100$$

(1)

Further insights into the phase formation of the MoS$_2$ particles can be obtained by examining their lattice vibrations (phonons), and Raman spectroscopy was performed for this purpose. Raman spectra of the MoS$_2$ samples synthesized at two different temperatures are put up in figure 2. Both the samples contained three distinct Raman peaks at 147, 194, and 237 cm$^{-1}$, which can be attributed to the presence of elemental sulfur [22]. One intense peak was observed at 281 cm$^{-1}$ ($E_{1g}$ in-plane symmetric stretching of terminal atoms), characteristic of hexagonal MoS$_2$ [19, 24]. The other two peaks appearing at 374 and 413 cm$^{-1}$ reveal first-order Raman vibration modes $E_{2g}$ (in-plane opposite vibrations of Mo/S atoms) and $A_{1g}$ (out-of-plane of S atoms), respectively, within the S-Mo-S layer of hexagonal MoS$_2$ [24, 26, 32]. The Raman peak at 464 cm$^{-1}$ is assigned to
Table 1. A summary of identified peak position (2θ value) and relative intensity with crystallite size for MoS2 nanoflowers.

| Synthesis temperature | 200°C | 220°C |
|-----------------------|-------|-------|
| Synthesis temperature | 13.55 | 14.00 |
| 2θ (degree)           | 32.58 | 33.28 |
| Intensity (a. u.)     | 193.56| 1088.45|
| Interplaner spacing (d nm) | 0.653 | 0.632 |
| Lattice plane (h k l) | (0 0 2) | (0 0 2) |
| FWHM (/degree)        | 2.61 | 1.11 |
| Crystallite size (D nm) | 3.03 | 7.13 |
| Average crystallite size (Dav) | 3.32 nm | 7.38 nm |
| Strain value (type)   | −0.0705 (compressive) | −0.0133 (compressive) |
| Lattice plane (h k l) | (1 0 0) | (1 0 0) |
| FWHM (/degree)        | 0.81 | 1.02 |
| Crystallite size (D nm) | 10.11 | 8.04 |
| Average crystallite size (Dav) | 7.39 | 9.60 |
| Strain value (type)   | 3.32 nm | 7.38 nm |
| Lattice plane (h k l) | (1 1 0) | (1 1 0) |
| FWHM (/degree)        | 1.21 | 0.94 |
| Crystallite size (D nm) | 7.39 | 9.60 |
| Average crystallite size (Dav) | 7.39 | 9.60 |
| Strain value (type)   | −0.0705 (compressive) | −0.0133 (compressive) |
the secondary phonon mode (longitudinal acoustic mode at M point; LA(M)) [24]. With the increasing hydrothermal temperature, the intensity of all Raman peaks becomes sharper and more intense, revealing enhancement of crystalline quality and reduction of structural defect states, which is in accordance with the results obtained from XRD [21, 24]. The relatively larger FWHM values and weaker intensity of the $E_{1g}$ peak can be attributed to the phonon confinement and also indicates that the crystal structures include substantial defect sites [19, 21, 24]. Moreover, the intensity of $E_{2g}$ peak is higher than that of $A_{1g}$, indicating that the synthesized MoS$_2$ samples have strong in-plane opposite vibrations, which suggests that the edges of MoS$_2$ nano-flowers are highly exposed [26, 32]. The schematic illustrations of different Raman phonon modes are depicted in figure 2(b) elucidating the displacement of Mo and S atoms in diverse vibrating modes.

### 3.2. Morphology analysis

The surface morphology of the particles was examined by FESEM and a flower-like round hierarchical morphology was quite evident across both sets of particles corresponding to different synthesis temperatures. Figures 3(a)–(b) elucidates the low and high magnification FESEM images of MoS$_2$ nanoflowers synthesized at 200 °C. From the low magnification FESEM image (figure 3(a)), it is clearly visible that the MoS$_2$ sample is composed of highly dense and uniform agglomerated 3D flower-like hierarchical structures. The dimension of these structures on average is closer to 500 (±10) nm in diameter. The high magnification FESEM image (2b), reveals that the MoS$_2$ nanoflowers consist of ultrathin nanoplatelets of about 15 (±3) nm in thickness (the thickness of individual platelets is marked by yellow arrows and marked as symbol B). These nanoplatelets show a tendency for agglomeration to form 3D flower-like morphology (denoted by blue encircled area A). In these nanoflowers, some platelets randomly situate in the center of the overall flower whereas some platelets intersect with each other. Figures 3(c)–(d) displays the low and high magnification FESEM images of MoS$_2$ hierarchical nanostructures obtained at 220 °C. Figure 3(c) provides the low-magnification FESEM image portraying 3D flower-like hierarchical MoS$_2$ nanoparticles with high uniformity. The estimated sizes of these MoS$_2$ flower-like
structures were apparently in the range of \( \sim 500–700 \) (\( \pm 15 \)) nm on average. It is obvious that the morphology of the flower-like grains is uniform in each region (as represented by the blue dotted circles and marked with symbol A in figure 3(c)). Figure 3(d) elucidates the high magnification FESEM image revealing that the MoS\(_2\) nanoflowers are made up of numerous stacked 2D nanosheets (nanoplatelets) having diameters in the range of 150–180 (\( \pm 5 \)) nm (as indicated by the blue arrows in the blue dotted rectangle marked by ‘C’ in figure 3(d)). The thickness of the platelets was in the range of 30–35 nm (the thickness of an individual nanoplatelet is marked by yellow arrows and indicated as symbol B in figure 3(d)). These nanoplatelets were attached to each other to produce the 3D flower-like hierarchical nanostructure of MoS\(_2\) crystals. The morphology of the particles in all their regions is uniform (as represented by blue dotted circles). The average thickness of the platelets and the overall size of the MoS\(_2\) flowers increase with increasing synthesis temperature as was evident from figure 3, signifying enhanced growth post nucleation and improved morphological quality. Moreover, the surface morphology of the hierarchical nanostructures reported in this article resembles to the typical nanoflower morphology reported previously for the hydrothermal synthesis of MoS\(_2\) [18, 19, 21, 24, 32]. The rounded flower-like morphology assembled by nanoplatelets of MoS\(_2\) hierarchical nanostructures suggesting more effective sensing performances for easy distribution of interacting surfaces.

3.3. Crystallography visualization perspective

Figure 4 displays the 3D wireframe structure model with individual crystal planes, as observed in the XRD pattern of hierarchical MoS\(_2\) nanostructures. From figure 4(a), it can be observed that the crystallographic sites for Mo and S atoms are in the hexagonal unit cell of MoS\(_2\) crystal structure. Moreover, each Mo atom is attached to four S atoms (two S1 and two S2 atoms) and each S atom is shared by two Mo atoms, leading to the formation of hexagonal MoS\(_2\) structure. In a hexagonal MoS\(_2\) crystal structure, each Mo atom is trigonally primitively coordinated with the nearby S atoms. The simulated interatomic distances of Mo and S atoms in MoS\(_2\) structure
obtained by employing the VESTA theoretical tool are provided in table 3. The observed crystal planes in XRD pattern, (002), (100), and (110) are displayed in figures 4(b), (c) and (d), respectively.

### 3.4. Growth mechanism of MoS2 nanoflowers
Based on the crystallographic and morphological analysis, the plausible growth mechanism of MoS2 nanoflowers consisting of stacked 2D nanosheets (nanoplatelets) is proposed as illustrated schematically in figure 5. In this synthesis process, the growth mechanism consists of three stages; (i) rapid nucleation, (ii) oriented aggregation and (iii) self-assembly. Firstly, water containing (NH₄)₆Mo₇O₂₄·4H₂O and CH₄N₂S as respectively Mo⁴⁺ and S²⁻ sources collide elastically with each other at room temperature and form a transparent homogeneous solution. The synthesis of MoS2 nanoflowers is carried out at the temperatures of 200/220 °C, which lies between the boiling point and critical temperature of water. In hydrothermal treatment, the hydrolysis of CH₄N₂S to H₂S gas begins to create high pressure leading to the formation of MoS2 nuclei which grow into S-Mo-S layers. Subsequently, the growth of nanosheets takes place during oriented aggregation of primary nuclei due to high stress. These nanosheets act as core to initiate the formation of nanoflowers through self-assembly process. The driving force behind the peculiar hierarchical disposition may be any one of the factors including van der Waals forces, ionic interactions, hydrogen bonds, hydrophobic interactions, and synergistic parameters. Furthermore, as the hydrothermal temperature is increased, the nucleation process becomes more dominant resulting in favor of increasing sizes, and the quality of crystals of MoS2 nanoflowers, as observed in the crystallography and morphology analysis.

### 3.5. Optical properties
It is well known that an optical transition (absorption and/or emission) occurs when a photon is absorbed or emitted by the defect states [42, 43]. Therefore, in order to correlate the optical properties with crystallography and morphology analysis of MoS2, UV–vis spectroscopy was carried out using an aqueous dispersion of the MoS2 particles. Figure 6(a) depicts UV–vis absorption spectra of MoS2 samples synthesized at two different temperatures. Both MoS2 samples reveal broad absorption within 300 to 700 nm. The obtained UV–vis
absorption spectra elucidate three excitons; exciton A at 400 nm (3.1 eV), exciton B at 547 nm (2.26 eV), and exciton C at 570 nm (2.17 eV) (as indicated by blue dotted lines in figure 6(a)), due to the electronic transitions at energy levels indicating the adsorption sites are different [43–45]. Excitonic peaks observed at lower wavelength and higher wavelength regions signify the indirect to direct band transition at the edge of the Brillouin zone and quantum confinement phenomenon, respectively [10, 28]. The corresponding optical band gaps (E_g) are evaluated from UV–vis spectra by using the Tauc equation (2);

\[
(\alpha h\nu)^n = A(h\nu - E_g)
\]  

(2)

Where \( \alpha \) is the absorption coefficient obtained using Beer–Lambert law, \( h\nu \) is the energy of the incident photon, \( n \) is 2 or \( \frac{1}{2} \) for direct or indirect bandgap transition and A is characteristic of material with constant value [10, 42].

Figure 6(b) displays the intercept on the abscissa of the plot of \( (\alpha h\nu)^2 \) against photon energy \( h\nu \) revealing the bandgap energy of the samples. The corresponding bandgap for the MoS_2 sample synthesized at 200 °C was calculated to be 1.96 eV and it was 1.81 eV for the MoS_2 sample at 220 °C. The obtained result agreed well with the reported band gap values for MoS_2 hierarchical nanostructures ranging between 1.58–2.32 eV [27, 29, 30]. The higher band gap value of MoS_2 sample synthesized at a lower temperature could be assigned to the small crystallite size and particle size of its nanoparticles which could be resulting in a quantum confinement effect [10, 46]. No obvious linear relation was established for \( n = \frac{1}{2} \) demonstrating the absence of any indirect band gap in the MoS_2 samples.

Figure 5. Schematic illustration for the plausible growth mechanism of 3D MoS_2 hierarchical nanoflowers assembled by stacked 2D nanosheets synthesized via hydrothermal method with varying temperatures.

Figure 6. (a) UV–vis absorption spectra and (b) Tauc plots for assessing optical band gap of MoS_2 nanoflowers synthesized via hydrothermal method at two different temperatures (200 °C, 220 °C) for 6 h.
4. Conclusions

In summary, 3D MoS$_2$ hierarchical nanoflowers consisting of stacked 2D nanoplatelets were successfully synthesized by a facile hydrothermal method at two different temperatures, using (NH$_4$)$_6$Mo$_7$O$_{24}$·4H$_2$O and CH$_3$N$_2$S as starting materials. A significant change is reflected in crystallography and morphology characteristics of nanostructures with varying the synthesis temperature. The XRD patterns revealed that the synthesized MoS$_2$ hierarchical nanoflowers are well crystallized and both crystallinity and crystallite sizes enhance with increasing temperature. FESEM micrographs revealed that both of the as-synthesized materials possessed uniform hierarchical rounded 3D flower-like morphology composed of nanoplatelets which were basically stacked ultrathin 2D nanosheets. Increasing the hydrothermal temperature increases the thickness of the platelets by almost twice. Visualization of the corresponding crystal structures via 3D wireframe structure model associated with different lattice planes has been carried out from a crystallographic perspective. The bandgap of the material as a semiconductor. A plausible growth mechanism has been proposed, which is correlated with experimental observations and analysis. We believe that the findings in this paper will have a considerable impact while analyzing its fabrication condition-based properties which would be critical in different range of applications.

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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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