Surfactant free synthesis and characterization of α-MoO₃ nanoplates: A feasibility study to remove methylene blue from aqueous medium

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Abstract. Orthorhombic α-MoO₃ nanoplates have been synthesized by surfactant free chemical method. The prepared samples were analysed by various characterization techniques viz. X-ray diffraction (XRD), Scanning electron microscopy (SEM), Energy dispersive analysis of X-ray (EDAX), Fourier transform infrared spectroscopy (FTIR), Raman spectroscopy and Diffused reflectance spectroscopy (DRS). The XRD profile revealed the orthorhombic phase of the prepared material and obtained structural parameter confirms the formation of α-MoO₃. EDAX depicts the prepared material’s compositional proportion and has no traces of the foreign elements as well. The topographic images of SEM indicate formation of nanoplate shaped MoO₃ having a thickness in range of 200 to 300 nm. FTIR and Raman, on the basis of vibrational behaviour of chemical bonds present in the material, confirm the formation of orthorhombic MoO₃. DRS study shows the band gap is about 2.95 eV. Further, the study of adsorption of methylene blue (MB) by synthesized MoO₃ shows its potential application in the waste water treatment.

1. Introduction
Molybdenum trioxide (MoO₃) occurs in varied crystal phases like monoclinic (β-MoO₃), hexagonal (h-MoO₃) and orthorhombic (α-MoO₃) [1]. Orthorhombic (α-MoO₃) is thermodynamically more stable in comparison to other phases and also possess unique layered structure. Each layer of it has octahedra MoO₆ as two sub-layers concorded with each other in (101) direction [2, 3]. Owing to this characteristic, it shows superior electrochemical, chemical, catalytic and electronic properties. As a result, α-MoO₃ had gained a significant importance in material world and have an various potential applications in the field of photo-catalysis [4], lithium ion batteries [5], electro-chromism [6], light emitting diodes [7], paints technology [8], as an antimicrobial agent [9] etc.

During the exploration of various synthesis routes for MoO₃, majority had preferred to employ non-vacuum or chemical methods to cut down the synthesis cost. While the complex methodology having consisting risky acids and sulphates pretended to a barricade towards the further deducing cost and high yield recipes as well [10-16]. Therefore, during the last couple of years researchers focused high throughput methodology by using simple techniques and harmless chemicals. In 2017, Haiyu Qin
et al.[17] synthesized α-MoO$_3$ by solid state chemical reaction using polyethylene glycol and oxalic acid. While Neeraj Kumar et al. in 2017, synthesized hexagonal phase MoO$_3$ by co-precipitation method using nitric acid in the synthesis process [18]. By thermo-chemical method involving nitric acid, nanorod morphology of MoO$_3$ was reported by Azad Kumar et al. (2017) [19]. Nano needles morphology was synthesized by Rathnasamy et al. using sodium dodecyl sulfate in the precursor solution by the simple co-precipitation method [20]. Ja In Gu et al. (2018) prepared MoO$_3$ by hydrothermal method using nitric acid based precursor [21]. Guru Prakash et al. (2018) synthesized alpha phase MoO$_3$ by solution combustion method using urea and acetic acid [22]. Saihuan He et al. (2019) [23] used nitric acid as a solvent for the synthesis of orthorhombic MoO$_3$ by hydrothermal technique. Xin Guan et al. (2020) used hydrochloric acid (HCL) in synthesizing MoO$_3$ by hydrothermal method to study adsorption enhanced visible light photocatalytic activity [24]. Looking towards these recent studies; the different forms of acids were used in aqueous or non-aqueous medium to prepare pure MoO$_3$. We prepared orthorhombic α-MoO$_3$ nanoplates by surfactant free chemical method consisting only Ammonium heptamolybdate tetrahydrate (AHMT) and distilled water. Prepared material analyzed by various characterization techniques. In addition to that we had studied its adsorption potential to remove methylene blue (MB) from the aqueous medium, as part of feasibility test for the waste water treatment application. For instance, no one report such type of the method and its study.

2. Material and Methods

2.1. Synthesis method

The Analytical Reagent grade AHMT was purchased from Merck and was used further without any purification. 4% W/V concentration solution was prepared by dissolving AHMT in distilled water with continuously stirring the solution at 60 °C on 700 RPM for 30 minutes, so that AHMT decompose into MoO$_3$, NH$_3$ and H$_2$O [12].

$$(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O} + \text{H}_2\text{O} = 7\text{MoO}_3 + 6\text{NH}_3 + 8\text{H}_2\text{O}$$

(1)

Then the solution was heated at 120 °C in order to evaporate the water from the solution and it results in a light green color powder left in the beaker. The left over powder was annealed at 400 °C in air. Annealed powder was then characterized by various sophisticated tools such as X-ray diffraction (XRD), Scanning electron microscopy (SEM), Energy dispersive analysis of X-ray (EDAX), Fourier transform infrared spectroscopy (FTIR), Raman spectroscopy and Diffused reflectance spectroscopy (DRS), to ensure the prepared material verification.

2.2. Adsorption measurement

The adsorption experiment was carried out in the dark environment at room temperature. Any form of external energy like heating, UV light exposure or stirring is not applied during the experiment, as these are the parameters may leads the increase adsorption rate. Annealed powder (i.e. MoO$_3$ ) was taken about 30 mg in 100 ml of solution of MB having concentration of 10 mg/L. Then after every 10 minute, 3 ml of solution was taken out for UV-Visible measurement. The 0.22 μm syringe filters was used for filtering MoO$_3$ particles during each UV-VIS measurement. Removal percentage of MB was calculated by following expression [25].

$$\text{Removal} (%) = \frac{C_i - C_f}{C_i} \times 100 \, (\%)$$

(2)

Where, $C_i$ is initial and $C_f$ is final concentration of MB.
3. Result and Discussion

3.1. Structure analysis

The structural properties of the prepared powder was investigated using Bruker make X-ray diffraction (XRD) having Cu Kα radiation of wavelength 1.54 Å. Figure 1 shows the XRD profile of the synthesized sample having major sharp peaks at 2θ values of 23.27°, 25.65° and 27.25°. The corresponding calculated d-spacing (3.80 Å, 3.47 Å, and 3.260 Å respectively) identified as (110), (040) and (021) planes using standard JCPDS card no. 05-0508 [8, 28]. That confirms, prepared material has the orthorhombic crystalline structure of MoO₃. Other minor peaks are also well matched with the standard JCPDS card. In addition to that, not a single peak was identified for other phases of MoO₃ viz. hexagonal and monoclinic [26-27].

![XRD pattern of α-MoO₃ sample annealed at 400 °C.](image)

The d-spacing for prepared sample was evaluated using the Bragg’s equation (3) [13],

\[ n\lambda = 2dsin\theta \] (3)

Where, \( n \) represents the diffraction order, \( \lambda \) represent X-ray wavelength, \( \theta \) represent angle of diffraction and \( d \) represents the interplanar distance of the parallel planes. Lattice parameters were evaluated using the following equation (4) [13].

\[ \frac{1}{d^2} = \frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2} \] (4)

The evaluated lattice parameters are \( a \), \( b \) and \( c \) is 0.3959 nm, 1.3852 nm and 0.3694 nm respectively, which are well matched with JCPDS card no. 05-0508. The average crystallize size (i.e. 23 nm) was calculated for (021) plane at \( 2\theta = 27.25° \) by using Debye- Scherer relation shown in equation (5) [13].

\[ D = \frac{0.9\lambda}{\beta\cos\theta} \] (5)

Where, \( \lambda \) is the wavelength of X-ray used, \( \theta \) is the position of major intense peak in degrees and \( \beta \) is the full width half maximum (FWHM) in radians.
The dislocation density and the micro strain were evaluated using below equation (6) & (7) [13] and were found 1.87 x 10^15 per m^2 and 0.0067 respectively.

$$\delta = \frac{1}{D^2}$$ (6)

$$\epsilon = \frac{\beta \cos \theta}{4}$$ (7)

3.2. Compositional Analysis
EDAX technique was utilized to measure the proportion of the elements present in the prepared sample. Molybdenum and oxygen contain in the sample was 25.5 % and 74.5 %, that match well with atomic percentage of its chemical formula and having the elemental ratio nearly equal to 3. Moreover, no other peak of any element was observed in the spectrum which represents the pure state of prepared MoO\textsubscript{3} sample.

3.3. Morphological Analysis
Scanning electron microscopy (SEM), make JEOL Japan was used to study the surface morphology and elemental composition of the prepared MoO\textsubscript{3} sample. Figure 3 shows the SEM images of prepared MoO\textsubscript{3} having the resolution of 2 μm and 0.5 μm. It clearly reveals the uniform plate like nanostructure of the prepared sample. The length of the sample ranges from 1 μm to 5 μm and the thickness ranges from 200 nm to 300 nm. The layered type structure of MoO\textsubscript{3} is been reported in the literature [8, 17, 26]. In which one layer is been overlaid on the other layer. Such type of plate like structure may have more slender sub plate intercalated inside. The elongation in one direction could be due to the thermal annealing effect at 400 °C. As seen from SEM images, these elongated stacked layers seem to be a loosely bounded to each other. If separated, that can be used in any nano-sized optoelectronic devices.

**Figure 2** Elemental composition spectra of α-MoO\textsubscript{3} sample.
3.4. FTIR Analysis
FTIR (Bruker make Alpha-T, FTIR) was used to assure the presence of different types chemical bonds and its basic behavior too. Figure 4 shows the FTIR spectrum of MoO$_3$ sample measured in the range of 4000-600 cm$^{-1}$. There were only two peaks in the spectrum, one at 993.3 cm$^{-1}$ and other at 862 cm$^{-1}$. A peak at higher frequency (i.e. at 993.3 cm$^{-1}$), mostly reported for the stretched bond of Mo=O, and it is the significance of layered orthorhombic nature of $\alpha$-MoO$_3$ [27, 28]. At the other end, lower frequency (i.e. 862 cm$^{-1}$) is generally assigned for Mo–O–Mo bond in which molybdenum is present in the +6 oxidation state [29]. Traces of N-H bond and water (H$_2$O) were not observed in the spectrum of sample.

3.5. Raman Analysis
Raman analysis was accomplished by Renishaw make Invia Raman microscope. In Raman spectra, there are three main regions indicating the significant structural modes of vibration such as, lattice modes (at below 200 cm$^{-1}$), deformation mode (200 - 400 cm$^{-1}$) and stretching mode (600 - 1000 cm$^{-1}$)
In the present study prepared sample shows (Figure 5) the intense peaks at 157.71 cm\(^{-1}\), 287.21 cm\(^{-1}\), 665.79 cm\(^{-1}\), 818.25 cm\(^{-1}\) and 995.35 cm\(^{-1}\). In the stretching mode we observed a three peaks; 995.35 cm\(^{-1}\), 818.25 cm\(^{-1}\) and 665.79 cm\(^{-1}\). These peaks correspond to stretching of the bonds Mo=O, Mo\(_2\) O and Mo\(_3\) O respectively [21, 30]. Hence, the peaks present in the stretching mode shows the sign of orthorhombic phase of MoO\(_3\). The remaining peaks in the spectra i.e. 157.71 cm\(^{-1}\) and 287.21 cm\(^{-1}\), are normally attribute to wagging modes of terminal oxygen [30].

![Raman spectra](image)

**Figure 5** Raman spectra, vibrational mode identification of \(\alpha\)-MoO\(_3\) sample.

### 3.6. Optical Properties

In the study of optical properties, diffuse reflectance measurement was performed by UV-Visible spectrophotometer (Shimadzu make UV3800, Japan) of synthesized MoO\(_3\) sample at room temperature. Figure 6(a) shows the diffuse reflectance spectrum in the wavelength range from 300 to 800 nm. The average reflectance intensity is about 55 % after 450 nm. In addition to this, a broad hump is clearly observed between 650 nm to 700 nm range, that may be due to inter-band transition in the structure arises because of defect bands. Due to the powder form of the synthesized sample, the Kubulka –Munk (K-M) function (equation 8) was used to calculate the band gap.

\[
\frac{(1-R_\infty)^2}{2R_\infty} = F(R) = \frac{K}{S}
\]

Where, \(F(R)\) represents the K-M function, \(k\) represents the absorption coefficient, \(S\) represents the scattering and \(R_\infty\) represents the reflectance at infinite thickness. The band gap of the prepared material is observed at 2.95 eV (Fig. 6(b)) that is well accordance with the reported values [26]. The band gap (2.95 eV) is also match with our visual color inspection of the powder i.e. light green color. The reduction of MoO\(_3\) leads to creates defect states, and that contributes to the light green color, also well explained in the literature [31, 32].
3.7. Adsorption Activity

The adsorption activity of synthesized α-MoO$_3$ nanoplates has been studied under dark condition. Consider the 100 ml solution of MB containing 30 mg MoO$_3$ is a dye solution. This dye solution undergoes for UV-VIS spectroscopy measurement to check the adsorption (i.e. removal) of MB. In the Figure 7 (a), MB curve (pure MB solution) shows the highest absorption of visible light. Then after every 10 minute of interval, dye solution undergoes for UV-VIS measurement. As the UV-VIS spectra shows, there is a continuous decrease of the absorption values as the time increase. After around 130 minutes the absorption is seems to be zero. That indicates the MB is completely adsorbed by the MoO$_3$. In other words, we can say that MoO$_3$ is capable to remove the MB of aqueous solution. Figure 7(b) shows the removal of MB (in percentage) from dye solution. It clearly shows that up to around 90 minutes the removal rate is increases about linearly. Then after is slow down and saturate around 130 minutes.

Figure 7 (a) Absorbance Vs. wavelength at every 10 minutes interval and (b) % Removal Vs. Time for removal of MB from dye solution.
4. Conclusion

Simplicity and easiness in synthesizing MoO$_3$ are the key features of this method. That leads to ecofriendly, economical and scalable synthesis of α-MoO$_3$ nanoplates without using any surfactant. The XRD confirms orthorhombic crystalline structure of α-MoO$_3$ with crystallize size of 23 nm. The stoichiometric composition of the MoO$_3$ was confirmed by EDAX. The SEM images reveal the formation of layered MoO$_3$ nanoplates. The thickness of the nanoplates ranges from 200 nm to 300 nm. FTIR peaks at 993 cm$^{-1}$ shows Mo=O stretching and 862 cm$^{-1}$ shows Mo=O–Mo vibration. Peaks at 665.79, 818.25 and 995.35 cm$^{-1}$ in the Raman spectrum confirms the orthorhombic phase of MoO$_3$. The sample shows the direct band gap of 2.95 eV. The synthesized α-MoO$_3$ nanoplates have removed almost 90% of methylene blue from the aqueous solution, and might be utilize in the waste water treatment purpose.

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