Chemically Grown MoO$_3$ Nanorods for Antibacterial Activity Study

Neha Desai, Sawanta Mali, Vijay Kondalkar, Rahul Mane, Chang Hong and Popatrao Bhosale*

1Materials Research Laboratory, Department of Chemistry, Shivaji University, Kolhapur, India
2School of Applied Chemical Engineering, Chonnam National University, Gwangju, South Korea

Abstract

In the present investigation, sea urchin like morphology of h-MoO$_3$ nanorods are successfully synthesized by chemical bath deposition (CBD) technique. The thermal stability, structural details, morphology and compositional analysis of MoO$_3$ was done using thermogravimetry (TGA), X-ray diffraction (XRD), scanning electron microscopy (SEM), high resolution transmission electron microscopy (HR-TEM), selected area electron diffraction (SAED) and X-ray photoelectron spectroscopy (XPS) techniques respectively. The thermal analysis reveals presence of sharp exothermic peak at 409°C indicating irreversible phase transition. X-ray diffraction pattern showed hexagonal to orthorhombic phase transition after annealing at 450°C. As synthesized h-MoO$_3$ shows well oriented hexagonal rods with sea urchin like architecture while that of annealed MoO$_3$ sample revealed 2D layer by layer growth. The SAED pattern confirms single crystalline nature of as synthesized h-MoO$_3$ and polycrystalline nature of annealed α-MoO$_3$. While XPS study of both confirms Mo$^{6+}$ and O$^{2-}$ oxidation states of elements. Furthermore, characteristic antibacterial properties of h-MoO$_3$ and α-MoO$_3$ against gram positive Bacillus megaterium, Streptococcus aureus and gram negative Escherichia coli is noted.

Keywords: MoO$_3$; CBD; Hexagonal rods; XPS; HR-TEM

Introduction

The transition metal oxides (TMOs) are attracting a great deal of attention in the field of material science due to its variety of crystal phases and properties. The nano crystalline TMOs such as TiO$_2$, WO$_3$, MoO$_3$ and ZnO are the most widely studied by various researchers all over the world [1-8]. Among the TMOs, molybdenum trioxide (MoO$_3$) exhibits better intercalation chemistry with unique chemical, electrochemical, electronic and catalytic properties. The MoO$_3$ exhibits variety of crystal phases such as orthorhombic (α-MoO$_3$), monoclinic (β-MoO$_3$) and hexagonal (h-MoO$_3$) [9,10], out of these orthorhombic MoO$_3$ phase possess a unique 2 dimensional (2D) layered structure in which each layer is consists of two sub layers stacked along (010) direction [11]. The h-MoO$_3$ is constructed by the zig-zag chains of [MoO$_3$] octahedral which are interlinked together through cis position giving a one dimensional tunnel structure [12]. The tunnel structure facilitates electron-hole pair separation under irradiation and enhances the photochromic performance. As a result of this, MoO$_3$ have potential applications in dye-sensitized solar cell, solar cells, supercapacitors, batteries [16,17], light emitting diodes etc. [18]. Besides MoO$_3$ show polymorphism, therefore can be synthesized in different morphologies such as nanofibers [19], nanorods [20], nanobelts [21], nanowires [22] for various applications.

Recently, in addition to photo electrochemical properties, TMOs nanoparticles have been investigated for their antimicrobial activity due to their extra stability and non toxic nature. Antibacterial agents are very important in the textile industries, water disinfection, medicine and food packing. Number of organic substances shows the antibacterial activity but most of them are toxic in nature. Hence in the recent years there is growing demand for metal oxide nanoparticles as antibacterial agent due to their high stability and non toxic nature [23-25]. Recently Zollfrank et al. reported that antimicrobial activity of transition metal acid MoO$_3$ is related to their surface acidity involving the intermediate formation of molybdic acid [26]. The toxicity of MoO$_3$ towards pathogenic bacteria has been studied by K. Krishnamoorthy et al. [27]. As per this report prepared MoO$_3$ nanoparticles exhibit good antibacterial activity against 4 tested bacterial species E. coli, S. Typhimurium, B. Subtilis, E. Faeckels.

In this view we are reporting synthesis of nanocrystalline h-MoO$_3$ using a simple and low cost chemical bath deposition technique studies on its phase transition and characteristic antibacterial properties exhibited towards gram positive and gram negative bacteria.

Experimental

Materials

All the precursor chemicals used for the synthesis were of AR (Analytical reagent) grade and directly purchased. The ammonium heptamolybdate tetrahydrate (AHM) (NH$_4$)$_6$Mo$_7$O$_24$.4H$_2$O (Merck, 99%) and concentrated nitric acid HNO$_3$ (Merck) were used for the synthesis of MoO$_3$.

Method

The nanocrystalline MoO$_3$ was synthesized by chemical bath deposition technique. Various experimental runs were carried out for concentrations such as 0.025 M, 0.05 M and 0.075 M solutions of AHM in order to optimize the preparative parameter. For 0.025 M and 0.075 M AHM concentration, a sluggish and bulky precipitate was obtained. While for 0.05M, white coloured crystalline precipitate was obtained. In a typical synthesis, 15 mL of 0.05 M AHM solution was taken in a typical reaction. The temperature of reaction bath was increased slowly up to 50°C. To this 5 mL of conc. HNO$_3$ was added drop wise with
constant stirring to obtain a clear solution. This clear solution was then stirred for 15 min thereafter the temperature of reaction bath was maintained to 70°C, at this temperature formation of initial seed nuclei can be observed by naked eye. The reaction bath was maintained at 70°C for 30 minutes to obtain the white coloured precipitate of h-MoO3. Finally, the precipitate of h-MoO3 was filtered off with deionized water and then dried in constant temperature oven at 110°C for an hour.

**Characterization of h-MoO3**

The thermal analysis was carried out upto 1000°C in nitrogen atmosphere using TGA-DSC model (SDT Q600 V20.9 Build 20) at a scanning rate of 10°C/min. The phase identification of synthesized sample was performed by X- ray diffractometer ( Brucker AXS, D2 model ) at a scanning rate of 0.2° per min in the range of 20° to 80° with Cu (Kα target at 1.54 Å). The surface morphology was examined by field emission scanning electron microscopy (FE-SEM) (Hitachi S 4700) and scanning electron microscopy (SEM) (JEOL-JSM-6360A) equipped with energy dispersive X-ray analyser (EDS). Transmission electron microscopy (TEM), high resolution transmission electron microscopy (HRTEM) and selected area electron diffraction (SAED) were performed with a transmission electron microscope (TECNAL F20 Philips). The surface area analysis was carried out in nitrogen atmosphere. An X-ray photoelectron study to confirm oxidation state of molybdenum and oxygen in both the phases of MoO3 was carried out using XPS (VG multilab 2000- Thermoscientific, USA, k-alpha) with a multi channel detector. For the SEM analysis of S. Aureus, aliquots of 1mL of controls and cells exposed to α-MoO3. After drying the samples overnight at room temperature specimens were further sputter coated with gold. SEM images were then acquired by Field emission scanning electron microscope.

**Antibacterial activity**

The antibacterial activity of MoO3 was evaluated against gram positive bacteria like Bacillus megaterium, Streptococcus aureus and gram negative bacteria Escherchia coli by using cup plate method [28]. The cups were prepared in the nutrient agar medium with the help of sterilized cork borer and it was seeded with the 18 h old broth culture of each organism. The solution of each test compound was made in hot distilled water at different concentration such as 10⁻¹, 10⁻² and 10⁻³ mg/ml and added to the cups. After inoculation of test samples of MoO3, the Petri plates were incubated at 37°C for 48 h. The zone of inhibition was recorded in mm after 48 h. Ciprofloxacin was used as a standard control to represent zone of inhibition.

**Results and Discussions**

**Growth and reaction mechanism**

The properties of the nanomaterial are largely dependent on their growth mechanism. For the synthesis of h-MoO3 all the preparative parameters such as concentration of precursors, temperature, time, choice of precursors were optimized at initial stages to get desired morphology. The (NH₄)₆Mo₇O₂₄•4H₂O (AHM) and conc. HNO₃ acts as reaction partner for the formation of MoO3. The formation of MoO3 can be understand as per the following reaction mechanism [29].

\[
(NH_4)_6Mo_7O_{24} \cdot 4H_2O (aq.) + 6HNO_3 \rightarrow 7MoO_3 + 6NH_4^+ + 6H_2O
\]

As per the above reaction mechanism, dissociation of AHM takes place to produce 6NH₄⁺ and MoO₃⁻⁶ ion. In the next step concentrated nitric acid ionizes to H⁺ and NO₃⁻ ions. The ionisation of AHM released NH₄⁺ and NO₃⁻ ions combine together to form NH₄NO₃. Finally solid MoO3 get separated as microcrystallites in acidic medium.

As the formation of MoO3 follows the principle of Ostwald ripening law [30]. The growth mechanism for the formation of MoO3 is graphically represented in the Figure 1.

According to the Ostwald ripening phenomena initially there is formation of seed nucleus. Once these seed nucleus attain critical size they act as nucleation centres and favours growth of hexagonal rods. The smaller crystallites are kinetically stable while the larger crystallites are thermodynamically stable. The kinetically stable smaller crystallite sacrifices itself to form thermodynamically stable larger crystallites in accordance with Ostwald ripening phenomenon. Hence at 70°C when the growth of multinucleation centre was completed resulting in the formation of larger crystallites. Further these larger crystallites attain directional growth to form 1D hexagonal rod. So in the present investigation, hexagonal rods assembled themselves to form sea urchin like architecture.

**Thermal analysis**

TGA-DSC analysis was performed in order to understand the thermal behaviour of MoO3. Figure 2 shows TGA curve in the temperature range of 25°C to 1000°C for h-MoO3.

Below 500°C, three weight losses were observed. The first weight loss equivalent to 5.375% in temperature range of 50°C -150°C was due to the desorption of physically adsorbed water molecules at the surface of h-MoO3 sample. The next weight loss observed at 350°C.
corresponds to the loss of ammonia and other nitrates. The sharp exothermic peak at 409°C indicates the irreversible phase transition from hexagonal to orthorhombic MoO$_3$. We observe no weight loss in 450-700°C temperature range. It indicates the formation of thermodynamically stable α-MoO$_3$. Therefore according to the TGA-DSC analysis it is clear that the h-MoO$_3$ is a metastable phase while α-MoO$_3$ is a thermodynamically stable phase [31].

**Structural analysis**

The phase identification of MoO$_3$ sample was carried out by using XRD. Figure 3a shows diffraction pattern of as synthesized MoO$_3$ sample.

The XRD pattern of as synthesized MoO$_3$ was well indexed with JCPDS Card No.21-0569 [32]. We observe no secondary diffraction peaks due to impurities or other phases indicating presence of single, hexagonal phase of MoO$_3$. The lattice parameters ‘a’ and ‘c’ of as synthesized h-MoO$_3$ were determined from the standard equation no.1.

$$\frac{1}{d^2} = \frac{4}{3} \left( \frac{h^2 + hk + k^2}{a^2} \right) + \frac{1^2}{c^2}$$  \hspace{1cm} (1)

The calculated values of lattice parameters were a = 10.48 Å and c = 14.91 Å which are in good agreement with standard values. The crystallite size was calculated by using the Debye-Scherrer equation,

$$D = \frac{0.9\lambda}{\beta \cos \theta}$$  \hspace{1cm} (2)

The crystallite size calculated from the most intense (210) peak at 2θ = 25.88 was 36.63 nm. The ‘as synthesized’ h-MoO$_3$ was annealed at 450°C for 4 hours. The annealing changes colour of the sample from whitish to grey. Figure 3b shows diffraction pattern obtained for annealed MoO$_3$ sample. The sharp intense diffraction peaks in the XRD pattern of the annealed MoO$_3$ sample were well matched with JCPDS Card No.05-0508 [33]. Furthermore, due to absence of impurities no secondary diffraction peaks were observed. This confirmed the formation of single phase and crystalline orthorhombic molybdenum trioxide. The calculated values of lattice parameters were a = 3.961, b = 13.87 Å and c = 3.69 Å using Equation no.3,

$$\frac{1}{d^2} = \frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2}$$  \hspace{1cm} (3)

The crystallite size calculated from the (021) planes (2θ = 25.79) using Debye-Scherrer equation is found to be 66. An increase in the crystallite size was observed from XRD pattern as a result of annealing.

**Figure 3:** (a) XRD pattern of as synthesized sample. (b) XRD pattern of annealed sample.

**Morphological analysis**

The surface morphology of both h-MoO$_3$ and α-MoO$_3$ was characterized by SEM and FESEM analysis. Figure 4a and 4b clearly indicates presence of 1D hexagonal rods. These rods are well oriented and assembled to form a ‘sea urchin’ like architecture. The sea urchin like structure has average diameter of about 3 micron. The sea urchin like structure is believed to be due to nucleation, growth and attachment mode. The MoO$_3$ exhibits 3 polymorphic forms α-MoO$_3$, β-MoO$_3$ and h-MoO$_3$. Among all these polymorphic forms h-MoO$_3$ exhibits superior physical and chemical properties over the other. Further growth of well oriented hexagonal rods can occur to give 2D structure. After annealing at 450°C 1D hexagonal nanorods gets converted into 2D plate like structure for α-MoO$_3$ as observed from Figure 4c and 4d.

To give more emphasis on morphological features of MoO$_3$, FESEM images are shown in Figure 5. From Figure 5a and 5b of h-MoO$_3$ it is observed that 1D rods are monodispersed having average length of about 1 micron. The individual rods are polygon crystals with hexagonal cross section and well developed facets without any impurity [34]. Figure 5c and 5d indicates 2D plate like structure of α-MoO$_3$. The α-MoO$_3$ has tendency to undergo layer by layer deposition [35]. The plate like structure shows presence of thinner sub plates intercalated...
within it. Thus MoO$_3$ exhibits good intercalation chemistry and form a basis for good morphology.

In order to determine detail crystal structure and to gain more insight into the morphological aspects of as synthesized h-MoO$_3$ and annealed α-MoO$_3$ HRTEM analysis was carried as shown in Figure 6. Figure 6a displays TEM image of h-MoO$_3$. It clearly indicates presence of single nanorod having a length of about 1 micrometer. This image is well consistent with FESEM results. The Figure 6b shows selected area electron diffraction (SAED) pattern of h-MoO$_3$. The bright dotted SAED pattern confirms single crystalline nature of h-MoO$_3$ [36].

Furthermore Figure 6c shows TEM image for α-MoO$_3$. It reveals presence of nanoplate like structure having number of sub plates intercalated within it. This plate like structure has a average diameter of about 100 nm. This result well matches with morphological study. Figure 6d shows SAED pattern of α-MoO$_3$. The distinct bright rings pattern indicates polycrystalline nature of α-MoO$_3$ [37].

**Surface area analysis**

The BET surface area and pore volume were evaluated by using nitrogen adsorption and desorption isotherm. The BET data of both as synthesized h-MoO$_3$ and annealed α-MoO$_3$ is presented in the table. From BET analysis, it can be observed that both surface area and pore volume was decreased after annealing. As a result of annealing smaller crystallites assembled to form larger crystallites [38,39]. Moreover XRD study reveals that crystallite size also increases from 36 to 63 nm after annealing. Therefore increase in the crystallite size results in decrease in surface area (Table 1).

**Compositional analysis**

The quantitative analysis of both as synthesized and annealed MoO$_3$ was carried out by using EDS technique. Figure 7 shows a typical EDS spectrum of h-MoO$_3$ and α-MoO$_3$. The prominent peaks observed at 2.4 keV and 0.52 keV confirming the presence of Mo$^{3+}$ and O$^{2-}$ elements respectively. The inset table shows expected and observed atomic percentage of molybdenum and oxygen. The observed atomic percentage of Mo$^{3+}$ and O$^{2-}$ are in good agreement with theoretical atomic percentage of respective elements.

The X-ray photoelectron spectroscopy was used to determine the chemical bonding and surface composition of h-MoO$_3$ and α-MoO$_3$ the samples. The XPS survey spectrum of MoO$_3$ was shown in the Figure 8a. The survey spectrum shows peaks for Mo, O and C. The C 1S peak at 284.6 eV is used as reference. The binding energies of all other elements were calibrated using C 1S peak. The Mo 3d core level spectrum of as synthesized h-MoO$_3$ shows doublets at 235.12 eV and 232.05 eV from Figure 8b [40] which is attributed to B.E. of the 3d$^3$ and 3d$^5$ orbital electrons of Mo$^{6+}$. The energy difference between them is 3.07 eV which is for h- MoO$_3$. The O1s core level spectrum of h-MoO$_3$ exhibit binding energy at 529.91 eV which is due to presence of lattice oxygen in MoO$_3$ as shown in Figure 8c. The Mo3d core level spectrum of annealed α-MoO$_3$ shows spin orbit doublet at 236.24 eV and 233.07 eV for Mo3d$_{3/2}$ and Mo3d$_{5/2}$ respectively confirming +6 oxidation state of molybdenum as shown in Figure 8d [41,42]. The energy difference

| Sample  | SBET(m$^2$/g) | VTotal (mL/g) |
|---------|--------------|--------------|
| h-MoO$_3$ | 3.58         | 0.0063       |
| α-MoO$_3$ | 6.16         | 0.0095       |

**Table 1: Surface area and pore volume of h-MoO$_3$ and α-MoO$_3$**
The presence of inhibition zone revealed the biocidal activity of MoO₃ nanoparticles. From this result, we conclude that both the phases of MoO₃ are reactive against gram positive bacteria like Bacillus megaterium, Streptococcus aureus and gram negative bacteria Escherchia coli respectively. The standard drug used for reference was ciprofloxacin. The zone of inhibition in mm observed for various bacterial strains are shown in Table 2.

The antibacterial activity study

Cup plate method [28] was used to conduct antibacterial activity against gram positive bacteria like Bacillus megaterium, Streptococcus aureus and gram negative bacteria Escherchia coli respectively. The standard drug used for reference was ciprofloxacin. The zone of inhibition in mm observed for various bacterial strains are shown in Table 2.

In our case there is an interaction between MoO₃ nanoparticles and bacterial strains. The bactericidal effect of the metal nanoparticle has been attributed to their small size and high surface to volume ratio. As per the literature survey the antibacterial activity of metal oxide nanoparticles is due to membrane or oxidative stress mechanism. If there is a direct interaction between the nanomaterials and bacterial species then membrane stress mechanism occurs. The cell death may occur due to excess level of oxygen species after exposure to nanomaterials following the oxidative stress mechanism. However, the antibacterial activity of MoO₃ is related to the release of hydroxinium ion according to the following reaction [26].

\[ \text{MoO}_3 + \text{H}_2\text{O} \rightarrow \text{H}_3\text{MoO}_4 \]

\[ \text{H}_3\text{MoO}_4 + 2\text{H}_2\text{O} \rightarrow 2\text{H}_2\text{O} + \text{MoO}_4^{2-} \]

Initially the molybdenum trioxide reacts with the water to form molybdic acid. This molybdic acid comes in contact with the water to release the hydroxinium ion. These hydroxinium ions again transformed into the molybdic acid at equilibrium. According to this reaction mechanism MoO₃ should be in contact with water for antibacterial activity (Figure 10).

To further confirm the antimicrobial activity of MoO₃ nanoparticles SEM images were taken to determine the changes in the cell morphology of S. Aureus. The Figure 10a shows normal circular shaped cells with intact cell membrane. On the other hand Figure 10b shows the cells are shrunk and deformed after exposure to MoO₃ nanoparticles. This fact indicates the cell damage of bacteria [46,47] thus confirming the antibacterial activity of MoO₃ nanoparticles. All these discussion suggest that studying the direct surface interaction between the metal oxide nanoparticles and bacterial species leading to the cell death. All these aspects are really important for further investigations. The designing of nanomaterials with multiple mechanisms of antibacterial action provides a new paradigm in the fight against resistant bacterial species.

Conclusions

In the proposed research work, we have successfully synthesized hexagonal MoO₃ via chemical bath deposition method. MoO₃
exhibited phase transformation from hexagonal to orthorhombic after annealing. XRD study confirms hexagonal and orthorhombic phase for as synthesized and annealed sample respectively. The as synthesized MoO₃ shows well oriented hexagonal rods assembled together to form sea urchin like architecture. This morphology reveals better intercalation chemistry and anisotropic growth mechanism. After annealing, the one dimensional hexagonal nanorods were transformed into two Dimensional plates like structures. Hence herein, we are reporting one 1D as well as 2D morphology for MoO₃. The XPS analysis of both samples concludes Mo with (+6) oxidation state and oxygen with (-2) oxidation state. HRTEM images confirms highly crystalline nature of sample. Both the phases of MoO₃ exhibit good antibacterial activity against two bacterial species Streptococcus aureus and Bacillus megaterium whereas α-MoO₃ exhibits good antibacterial activity against gram negative E. coli. The phenomenon of nanointerface is also important in order to study the antibacterial activity of nanocrystalline MoO₃. Thus antibacterial activity of MoO₃ is an innovative approach for the destruction of micro-organisms in hospitals and public places.

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