International Journal of Materials Science ISSN 0973-4589 Volume 12, Number 1 (2017)

One step and facile hydrothermal synthesis of hexagonal molybdenum trioxide nanorods and its photo response

Himanshu Mishra
Department of Physics, Institute of Science,
Banaras Hindu University,
Varanasi, Uttar Pradesh, India.

Anchal Srivastava*
Department of Physics, Institute of Science,
Banaras Hindu University,
Varanasi, Uttar Pradesh, India.

*Corresponding author
Email: anchalbhu@gmail.com

Abstract
Present study reports the one pot facile synthesis of metastable hexagonal phase of molybdenum trioxide (h-MoO_3) using ammonium heptamolybdate (AHM) as starting material and HNO_3 as reducing agent. The synthesized nanostructures are nanorods in shape having length ~ 50 µm and diameter ~ 200 nm. The samples have been characterized by using X-ray diffractometer (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM) and Raman spectroscopy. The photoresponse of micrometer thick *h*-MoO_3 film on glass substrate also have been studied. It was found that the amount of photocurrent increases with increase in the frequency of the incident radiation.

Keywords: MoO_3, nanorods, photocurrent.

Introduction

Since last few decades, nanostructures have gained much attention in the field of energy, electronics, optical and sensing applications [1, 2]. Various transition metal oxides have been extensively studied in this regards [3, 4]. Among various transition metal oxides molybdenum oxide (MoO_3) is one of the most studied materials. As we know, MoO_3 exists in three different phases, orthorhombic (α-MoO_3), hexagonal (*h*-MoO_3) and monoclinic (*β*-MoO_3). Among these three, α-MoO_3 is the most studied as it is thermodynamically stable phase and exhibits a unique layered structure which permits it to be cleaved easily along their basal planes [5-7]. *h*-MoO_3 is a metastable phase whose basic building unit is a distorted MoO_6 octahedron to form layered structure through corner-sharing mode. Two adjacent layers of *h*-MoO_3 are joined together with weak Vander Waals forces [6]. Sometimes metastable phases provide much novel and enhanced results in comparison to their thermodynamically stable structures but their synthesis is usually difficult. Till date, several methods for the synthesis of *h*-MoO_3 have been reported [8-10]. But there are very few reports about its photoresponsivity. So, a facile and fast synthesis route and its photoresponsivity need further investigation.

Present study focuses the one pot, facile and fast synthesis of *h*-MoO_3 using hydrothermal method. A micrometer thick film of *h*-MoO_3 have been prepared onto a glass substrate using nebulizer coating method and photoresponse of the *h*-MoO_3 film have been studied.

Methods

Ammonium heptamolybdate ($(NH_4)_6Mo_7O_{24}$, AHM) and nitric acid (HNO_3) have procured from Hi-Media, India. All the chemicals were of analytical grade and used without any further purifications. Throughout the experiment de-ionized (DI) water has been used for the solution preparation. Ethanol has been used for the dispersion of *h*-MoO_3 for thin film deposition.

In a typical hydrothermal synthesis route of *h*-MoO_3, 4.8 g of AHM is dissolved in 68.8 ml of DI and stirred for 10 min. at 40^{O}C to make a transparent solution. After that 11.2 ml of HNO_3 has been added to this transparent solution and again stirred for 10 min. at 40^{O}C. After that the solution is transferred into a stainless steel lined Teflon autoclave having capacity 100 ml and put for the hydrothermal reaction for 8 hrs. at 180^{O}C (figure 1). After the completion of the reaction the light white precipitate has been filtered and washed thrice with DI and ethanol. The filtered and washed precipitate has been dried for 8 hrs. at 60^{O}C. Finally the dried sample has been crushed into tiny powder form.

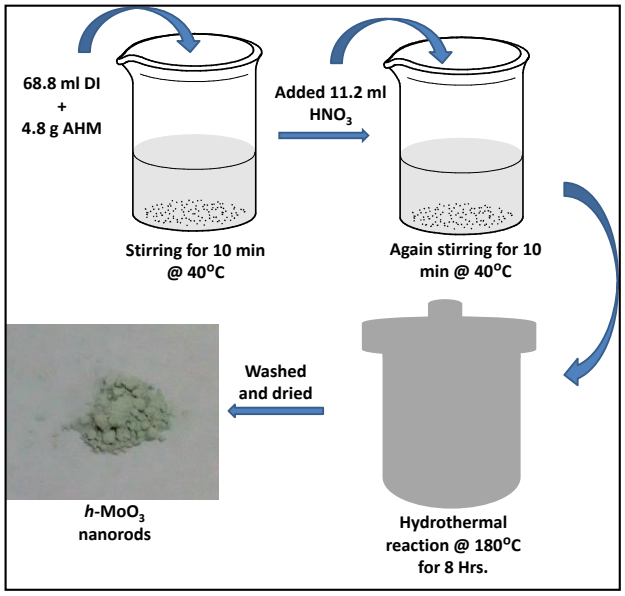

Figure 1: Schematic showing the hydrothermal synthesis of *h*-MoO_3 nanorods.

Results

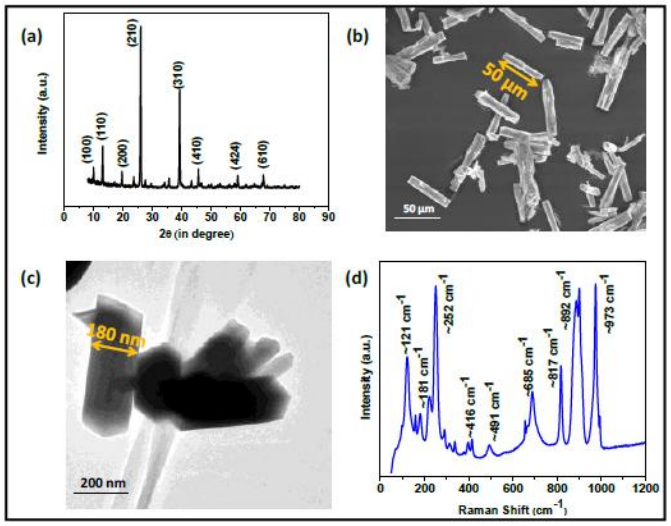

Figure 2: X-ray diffraction graph (a), SEM image (b), TEM image (c) and Raman spectra (d) of *h*-MoO_3**.**

h-MoO_3 nanorods have been synthesized using facile and fast hydrothermal route. The synthesized samples have been characterized by using X-ray diffractometer (XRD, PANanalytical X'Pert Pro, Germany) to confirm the phase of the synthesized sample. To understand its morphology and structure scanning electron microscopy (SEM, Zeiss, Germany) and transmission electron microscopy (TEM, FEI Technai G^2, USA) have been performed. To find the different vibrational and rotational modes of the *h*-MoO_3 Raman spectra (inVia confocal Raman microscope, USA) of the sample has been recorded in the range of 0 cm^{-1} to 1200 cm^{-1}. The XRD graph, SEM and TEM image and Raman spectra of the sample have been shown in the figure 2. A micron thickness thin film of the *h*-MoO_3 has been deposited onto glass substrate and its photoresponse study has been done under different frequencies of incident radiation. The photoresponse of the nebulizer coated *h*-MoO_3 thin film onto a glass substrate has been shown in the figure 3 (a). Figure 3 (b) shows the enlarged view of the yellow encircled region.

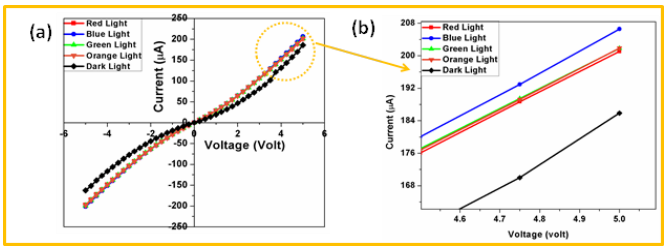

Figure 3: (a) Photocurrent versus applied voltage graph at a constant intensity of incident light of different frequencies and (b) enlarged view of the encircled region.

Discussion

Figure 2 (a) shows the XRD graph of *h*-MoO_3 nanorods. All the XRD peaks have been indexed successfully for the hexagonal phase of MoO_3 (JCPDS Card no. = 21-0569). Peaks at 25.97°, 39.23° and 13.07° corresponds to the (210), (310) and (110) planes of the *h*-MoO_3. Large intensity and narrow FWHM of the XRD peaks show that the synthesized nanorods possess high crystallinity. SEM image (figure 3 (b)) of *h*-MoO_3 shows that *h*-MoO_3 nanostructures are nanorods. The size of the nanorods is found to be ~50 µm. TEM image of the *h*-MoO_3 nanorods is shown in figure 3 (c). From TEM image the diameter of the nanorods are found to be ~180 nm. Aspect ratio is defined as the ratio of the length to the diameter of the nanorods. In our case, for *h*-MoO_3 nanorods, the aspect ratio is ~ 278 which is quite large. Raman spectra of *h*-MoO_3 nanorods have been shown in figure 3 (d). All the Raman peaks (in cm^{-1}) are listed in the following Table 1 and has been compared with the other reports present in the literature.

Table 1:

Hans Joachim et.al. [11]	Pan et.al. [12]	Atuchin et.al. [13]	Silveria et.al. [14]	Vargas-Consuelos et.al. [15]	Present Work
973	980	978	982	985	975
900	916	912	923	922	902
690	901	901	903	901	885
492	887	880	885	884	819
414	690	691	695	694	685
396	489	492	493	494	665
316	412	398	415	417	494
253	395	319	397	401	417
222	312	250	318	318	395
180	250	219	249	254	338
148	217	176	220	222	315
	173	134	171		294
	134	121			249
					219
					181
					159
					121

h-MoO_3 nanorods have been crushed into fine powder and dispersed into ethanol (1 mg/ 10 ml) by ultrasonication

process. The glass substrate was heated up to 80^{O}C using hotplate and a micron thickness film was deposited using nebulizer. Aluminum metal has been used for making contacts on the film. Photo current was recorded for different biasing voltages at a constant illumination intensity of incident light. Four different lasers (orange, green, red and blue) of same power have been used as the incident light sources. Figure 3 (a) shows the photocurrent graph under different biasing voltages for dark, orange, green, blue and red color light sources. It was found that for small input voltage the amount of photocurrent is also very small. But by increasing the biasing voltage, beyond 2 V there is a large change in the photocurrent. The variation of the photocurrent is found to be different for all the different colors. For dark current it is minimum and for blue color it is maximum. It was found that the photocurrent increases up to 200 µA for the biasing voltage of 5.0 V. This is shown more clearly in the figure 3 (b) which is the enlarged view of yellow encircled region. This enhancement in the photocurrent could be understood by using following:

As we know that the MoO_3 is a large band gap semiconductor material, so there will be very small number of electrons in the conduction band. As a beam of light is made incident on it, there is a possibility that some of the electrons will jump from the valence band to the conduction band. As

$$E = h\nu \qquad \ldots\ldots. (1)$$

Where,

E = energy of the incident light,

h = Planck's constant

ν = frequency of the incident light.

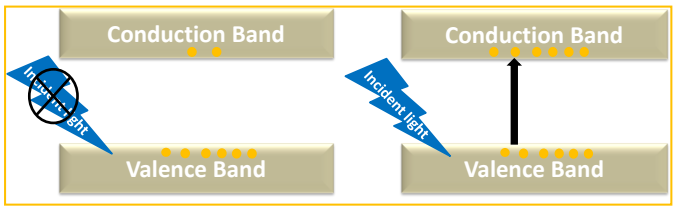

Figure 4: Schematic showing the process in case of absence of light and in presence of light.

So, a light radiation with high frequency will possess larger energy, hence blue color will have more energy than the red, orange and green color. In this way in presence of blue color the number of electrons jumping from valence band to conduction band will be maximum. As we know material having large number of electrons in conduction band will show maximum conduction. Hence, there will be maximum increment in current in presence of blue color. However, in case of other colors the density of electrons jumping from valence band to the conduction band is less and shows a small change in the photocurrent.

Conclusion

In summary, we have synthesized *h*-MoO_3 nanorods using one pot facile and fast hydrothermal route. The synthesized samples were in pure form and shows high crystallinity as found from the XRD graph. SEM and TEM characterization shows that the nanorods are of ~50 µm in length and ~180 nm in diameter. The micro-thickness thin film of *h*-MoO_3 deposited onto glass substrate shows a large enhancement in photocurrent in presence of blue radiation. This shows that this material will show a better photoresponse for the higher frequencies radiations and may become a strong candidate for the development of UV light sensors.

References

[1] Shipway AN, Katz E, Willner I, "Nanoparticle arrays on surfaces for electronic, optical, and sensor applications", *ChemPhysChem*.;1(1), 18-52, 2000.

[2] Jain PK, Huang X, El-Sayed IH, El-Sayed MA "Noble metals on the nanoscale: optical and photothermal properties and some applications in imaging, sensing, biology, and medicine", *Accounts of chemical research*, 41(12), 1578-86, 2008.

[3] Meyer J, Hamwi S, Kröger M, Kowalsky W, Riedl T, Kahn A "Transition metal oxides for organic electronics: energetics, device physics and applications", *Advanced Materials*, 24(40), 5408-27, 2012.

[4] Korotcenkov G, "Metal oxides for solid-state gas sensors: What determines our choice?", *Materials Science and Engineering: B*, 139(1), 1-23, 2007.

[5] Li W, Cheng F, Tao Z, Chen J, "Vapor-transportation preparation and reversible lithium intercalation/deintercalation of α-MoO_3 microrods", *The Journal of Physical Chemistry B*, 110(1), 119-24, 2006.

[6] Bullard JW, Smith RL, "Structural evolution of the MoO_3 (010) surface during lithium intercalation", *Solid State Ionics*, 160(3), 335-49, 2003.

[7] Chen JS, Cheah YL, Madhavi S, Lou XW, "Fast synthesis of α-MoO_3 nanorods with controlled aspect ratios and their enhanced lithium storage capabilities", *The Journal of Physical Chemistry C*, 114(18), 8675-8, 2010.

[8] Bai S, Chen S, Chen L, Zhang K, Luo R, Li D, et al. "Ultrasonic synthesis of MoO_3 nanorods and their gas sensing properties", *Sensors and Actuators B: Chemical*, 174, 51-8, 2012.

[9] Chithambararaj A, Bose AC, "Hydrothermal synthesis of hexagonal and orthorhombic MoO_3 nanoparticles", *Journal of Alloys and Compounds*, 509(31), 8105-10, 2011.

[10] Pan W, Tian R, Jin H, Guo Y, Zhang L, Wu X, et al. "Structure, optical, and catalytic properties of novel hexagonal metastable *h*-MoO_3 nano-and microrods synthesized with modified liquid-phase processes", *Chemistry of Materials*, 22(22), 6202-8, 2010.

[11] Song J, Wang X, Ni X, Zheng H, Zhang Z, Ji M, et al., "Preparation of hexagonal-MoO_3 and electrochemical properties of lithium intercalation into the oxide", *Materials research bulletin*, 40(10), 1751-6, 2005.

[12] Chithambararaj A, Bose AC, "Investigation on structural, thermal, optical and sensing properties of meta-stable hexagonal MoO_3 nanocrystals of one dimensional structure", *Beilstein journal of nanotechnology*, 2(1), 585-92, 2011.

[13] Song J, Ni X, Gao L, Zheng H, "Synthesis of metastable *h*-MoO_3 by simple chemical precipitation", *Materials Chemistry and Physics*, 102(2), 245-8, 2007.

[14] Song J, Ni X, Zhang D, Zheng H, "Fabrication and photoluminescence properties of hexagonal MoO_3 rods", *Solid State Sciences*, 8(10), 1164-7, 2006.

[15] Vargas-Consuelos C, Camacho-López M, "A facile method to prepare hexagonal molybdenum trioxide

microrods", *Superficies y vacío*, 27(4), 123-5, 2014.

Acknowlwdgement: HM is thankful to the Raman Lab, Department of Physics, BHU, Varanasi, India for provding the Raman facility. HM is thankful to Dr. Vyom Parashar for SEM characterizations. AS is thankful to DST, India and CAS Department of Physics, Insitute of Science, BHU for providing financial assistance.