

# $\alpha$ -MoO<sub>3</sub> Nanopowder: A Transition Metal Nano-Oxide and its Photo-Chromic Properties: An Overview

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**Abstract**—In Photochromism, there are effectively two changes occurs simultaneously, firstly a chemical change arises when the molecule is exposed to UV light that enables conjugation to take place in the molecule and secondly a structural change also occurs to enable the overlap of orbitals. As an n-type semiconductor, molybdenum-trioxide (MoO<sub>3</sub>) has been implemented in photochromism (PC), electrochromism, catalysis etc. One of the most important parameters that could affect the mechanism of photochromism is the concentration of oxygen vacancies in the material. MoO<sub>3-x</sub> increased the oxygen vacancies after solar light irradiation. The LSPR resonance wavelengths of most plasmonic semiconductors are conventionally located in the long-wavelength range of the near-infrared (NIR) and even the middle-infrared (MIR). Photo chromic MoO<sub>3</sub> based smart films can reversibly modulate solar heat by transition between transparent and colored states in response to varying solar radiation conditions. Generally, without solar irradiation, the wide band gap MoO<sub>3</sub> (E<sub>g</sub> was reported between 2.9~3.2eV) is highly transparent to the solar light. Upon solar ultraviolet (UV) irradiation, it will transform into an absorbing blue colored state, which can shield solar light and shines bright as a smart “curtain”.

## 1. INTRODUCTION

Among these chromogenic materials, photo chromic materials are those for which the optical properties can be changed upon electromagnetic radiation. The word Photochromism is derived from the Greek words ‘phos’ (light) and ‘chroma’ (colour), and it therefore implies the generation of colour under the influence of light.[1] Molybdenum trioxide (MoO<sub>3</sub>) belongs to a class of TMOs known for their chromogenic properties and show reversible change in optical spectra when exposed to an electric field (electrochromism), UV irradiation (photochromism), or heat (thermochromism). Molybdenum<sup>VI</sup> trioxide (MoO<sub>3</sub>) is an interesting wide band gap n-type TMO since it may form several allotropes with oxygen vacancies. The optical and electronic properties of MoO<sub>3</sub> depend on oxygen vacancy concentration and can therefore be modified by varying it [2]. The photo chromic response of MoO<sub>3</sub> thin film was extended from ultraviolet (UV) light to visible light

after the cathodic polarization pre-treatment.[3]. For wide-band gap semiconductors, the free carrier concentration can be tuned by either adjusting the doping concentration or optimizing the synthesis parameters, which shows a higher advantage than metal nanocrystals where the LSPR properties were largely limited due to the fixed carrier density. MoO<sub>3-x</sub> (0.125<x<1) with higher oxygen vacancy concentration shows quasi-metallic behavior, while MoO<sub>3-x</sub>(0<x<0.125), such as Mo<sub>9</sub>O<sub>26</sub> and Mo<sub>8</sub>O<sub>23</sub> are n-doped semiconductor.[4]. MoO<sub>3-x</sub> increased the oxygen vacancies after solar light irradiation and this absorption band was ascribed to the plasmonic resonance of the quasi-metallic 2D flakes.[5].

## 2. STRUCTURE OF A-MOO3 NANOPARTICLES:

MoO<sub>3</sub>'s intrinsic layered nature readily accommodates large quantities of positive ions, resulting in potential band-gap manipulations. [6]. Additionally, the layered structure also offers superior charge transfer. On this basis, amorphous MoO<sub>3</sub> with a partly layered structure shows better photochromic properties than those crystalline ones, due to more defective sites available for charge transfer. [7]. The formation of +4 and +6 oxidation states of molybdenum in molybdenum oxide with required phase and the novel characteristic properties differing from their bulk counterpart mainly depends on the method of synthesis.[8]. Considerable research effort has concentrated on synthesizing MoO<sub>3</sub> nanostructures with specific morphologies, sizes, crystal structures, and dopant using various synthesis techniques including sol-gel, combustion, hydrothermal synthesis, chemical vapor deposition and pulsed laser ablation. [9-11]. Considerably MoO<sub>3</sub> have an orthorhombic lattice structure with JCPDS card number 05-0508. The sharp diffraction peaks of MoO<sub>3</sub> at (020), (110), (040), (021) and (060) indicates a highly crystalline orthorhombic structure ( $\alpha$ -Phase). The intensity of the diffraction peak of planes is very strong as shown below, indicating a crystal orientation along (001). XRD spectra of

MoO<sub>3</sub> powders of M1 and M2, respectively, found to be 18 nm and 50 nm.[8]. The  $\alpha$ -MoO<sub>3</sub> nanofibers have an orthorhombic lattice system of the space group *Pbnm* with lattice parameters: *a* = 3.9621 Å, *b* = 13.8570 Å and *c* = 3.6960 Å (JCPDS: 76–1003 *a* = 3.9628 Å, *b* = 13.855 Å and *c* = 3.6964 Å). Interestingly, no peaks of any other phases or impurities were detected, indicating high purity of the  $\alpha$ -MoO<sub>3</sub> nanofibers.[12]. Fig. 1 shows the XRD pattern of MoO<sub>3</sub>. [12]. One layer of corner sharing MoO<sub>6</sub> octahedral, and two MoO<sub>3</sub> monolayers, which have the structure of one of the slabs oriented perpendicular to the *b*-axis of  $\alpha$ -MoO<sub>3</sub>. The  $\alpha$ -MoO<sub>3</sub> can be regarded as rows of MoO<sub>6</sub> octahedral which are perpendicular to the long *b*-axis.[13]. Fig. 2 shows the crystal view of  $\alpha$ -MoO<sub>3</sub> structure.[13].

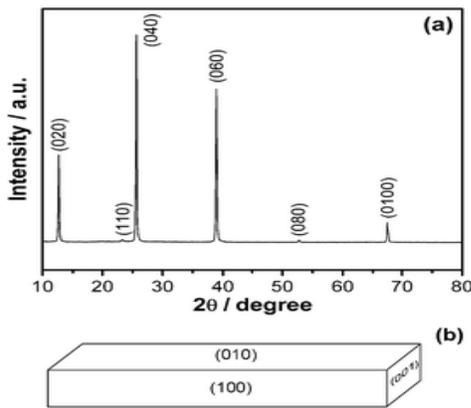


Fig. 1: Image is to copyright to *Cryst Eng Comm* 927933,2011.Ref[12].

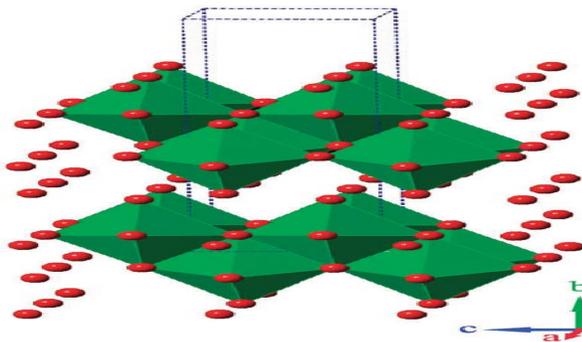


Fig. 2: Image is to copyright to *Chem., Commun.*, 2011, 47, 10305–10307. Ref[13]

### 3. MECHANISM OF PHOTOCROMIC ACTIVITY:

The absorption edge for MoO<sub>3</sub> films rises at ~ 400 nm. The strong absorption below 400 nm is an intrinsic property of the material and originates from inter-band (valence band to conduction band) and exciton transitions. The shape of the optical absorption band is Gaussian, which indicates the existence of localized centers. The growth of an asymmetric absorption band after coloration is associated with the

existence of many discrete bands.[14][15]. It is well known that molybdenum oxide forms substoichiometric oxides (MoO<sub>3-x</sub>) upon evaporation in vacuum or in a reducing atmosphere resulting in the formation of principal defects (i.e. oxygen vacancies) in the oxide. There may also be other defects associated with impurities, for which the valence states are lower than Mo<sup>6+</sup>. [14]. This concept occurs in color center model. The color center concept, i.e., absorption due to the localized states, makes it meaningful to represent the characteristic absorption feature in colored films by using Smakula's equation,

$$N_s f_s \approx 0.87 \times 10^7 n (n^2 + 2) 2 a P d \Omega / 2 \dots (1)$$

where *N<sub>s</sub>* is the number of color centers per cm<sup>2</sup>, *f<sub>s</sub>* an oscillator strength, *n* the refractive index of the uncolored material, *a<sub>p</sub>* the absorption coefficient (cm<sup>-1</sup>) at peak potential (*E<sub>p</sub>*), *d* the film thickness,  $\Omega/2$  the full width at half maximum (FWHM, in eV) of a Gaussian-type absorption band.[14][16]. According to Mie theory for nanospheres, the electromagnetic resonance energy is dependent on the nanospheres' size (*a*) and shape ( $\chi$ ).

As the size of nanospheres decreases, the resonance wavelength decreases. That is the absorption peaks shift to lower energy with an enlarged size. For nanorods, it obeys the Gans theory, the aspect ratio of the length and diameter (*R=A/B*) affects the peak shift and the rod contains two absorption peaks.[17]. A hydrogenated MoO<sub>3</sub> film appears blue due to the intervalence-charge transfer from the newly formed Mo<sup>5+</sup> to adjacent Mo<sup>6+</sup> upon optical excitation. The controversy remains, whether the optical properties are sufficiently described by the intervalence charge transfer theory between Mo<sup>5+</sup> and Mo<sup>6+</sup> ions, or by polaron absorption (small-polaron theory, which nonetheless relies on the formation of Mo<sup>5+</sup> states.[18].

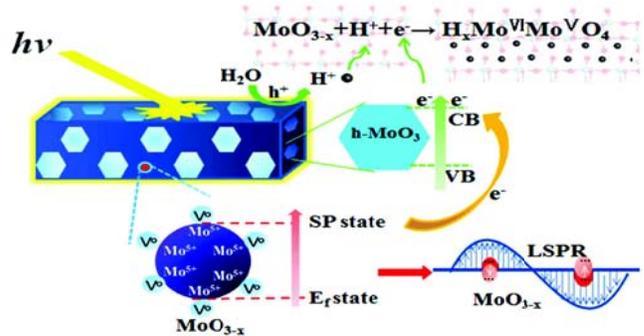


Fig. 3: Image is to copyright to *Li et. al. Nanoscale*, vol. 9, no. 24, pp. 8298–8304, 2017.Ref no [17].

A schematic representation of photochromic activity of MoO<sub>3</sub> & release of excitons are shown in fig.3 and fig.4 respectively.

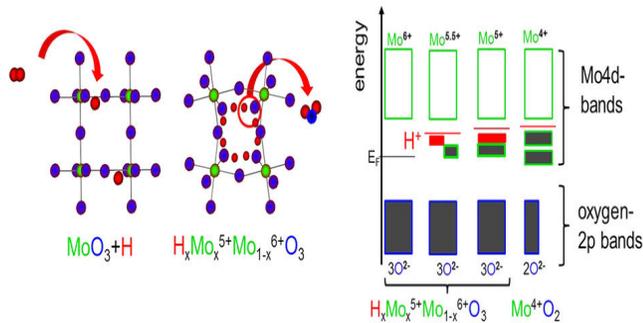


Fig. 4: Image is to copyright to A. Borgschulte *et. al. Sci. Rep.*, vol. 7, no. September 2016, pp. 1–9, 2017. Ref no [18].

#### 4. ENHANCEMENT OF PC PROPERTIES:

To realize the purpose of improving the photochromism of  $\text{MoO}_3$ , promoting the charge transfer rapidly and reversibly is the basic requirement. Combining  $\text{MoO}_3$  with suitable organic components is one promising way to achieve photochromic reversibility, since an efficient bridge through which the charges, specifically the electrons and/or protons, can reversibly transfer between the inorganic and organic moieties, can be constructed.[19]. A number of methods have been proposed such as modification of noble metals like Au and Pt through accelerating the separation of electron-hole pairs[20], combining with other metal oxides like  $\text{WO}_3$  through Mo to W transition,[21] and so on. Combining  $\text{MoO}_3$  with suitable organic components is one promising way to achieve photochromic reversibility, since an efficient bridge through which the charges, specifically the electrons and or protons, can reversibly transfer between the inorganic and organic moieties, can be constructed.[19]. R.Wang et al. reported better photo chromic efficiency of  $\text{MoO}_3$  by producing  $\text{MoO}_3$ -butylamine inorganic-organic nanocomposites.[22] Another way to achieve enhanced PC activity of  $\text{MoO}_3$  is to tune it with other inorganic oxide as a core shell structures. In comparison with pure  $\text{MoO}_3$  and other reported  $\text{MoO}_3$  samples, TM-x exhibited much better photochromic properties so far, ascribing to its unique heterostructure ( $\text{TiO}_2@/\text{MoO}_3$  Core shell structure)[23].

#### 5. CONCLUSION

In this review article, the recent progress in the field of Photochromism of  $\text{MoO}_3$  nanooxide, its structure and its mechanism have been discussed. This Transition metal oxide have a significant feature of PC efficiency which it can be use in a board area of applications as in area display, smart window, optical storage media, optical processing, and chemical sensors and so on. Further researches might be directed to achieve the colouration - decolouration mechanism with less of the time.

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