Promising Nature of MoO₃ Nanostructures in Gas Sensing Applications – A Review

Jaya Bharti, Arshali Sasi, C. Sasi Kumar

Abstract— Molybdenum trioxide (MoO₃) is a transition metal oxide with a wide band gap. It is an n-type semiconductor material with an oxygen deficiency. MoO₃ used as a sensing element for many of the reducing and oxidizing gases and proved to be a promising candidate for the same. Many literatures are available in this context; out of which some are explained in this article. This discussion covers the gas sensing response of different type of nanostructures of molybdenum trioxide and selectivity of particular structure toward the gas being sensed. It also includes the graphical representation of the variation of sensitivity/sensor response with the concentration of test gas. Lastly conclusions have been made on the basis of the discussion given in the following sections.

Index Terms— Sensing mechanism, Gas sensing response of Molybdenum trioxide, MoO₃ Nanostructures

I. INTRODUCTION

The metal oxide based sensor is an interactive material which interacts with the environment and generates a response and convert it into the quantifiable or interpretable term. Metal oxide like Cr₂O₃, ZnO, SnO₂, NiO, SrO, WO₃, TiO₂, Nb₂O₅, CeO₂ and MoO₃ based semiconductor sensors are suitable for sensing reducing and oxidizing gases. These materials as sensing element were first identified by Taguchi (Figaro) in 1968. The application of gas sensors found in many fields such as environmental monitoring, public securities, domestic pollution control, automobile exhaust/emission control applications, air conditioning system in airplanes, spacecraft and houses, sensor networks etc. In early years of gas sensing field bulk or thick films were employed as sensing material but at present many research have been done which includes the use of nanostructured metal oxide based gas sensors because nanostructures have large surface to volume ratio hence it shows better control on the gas sensing properties. [1]

Among all metal oxides only transition metal oxide materials with d⁰ and d¹⁰ electronic configuration found reliable for gas sensing applications. Metal oxide nanostructures react in the form of films and work on the principle of solid state gas sensor in which resistance/conductance will change on exposure of test gases. [2] Among all metal oxide gas sensors the transition metal oxide nanostructures are more popular due to their versatile properties. Transition metal oxide sensor worked on the principle of conduct metric sensor in which either conductance or resistance varies when target gas is passed over the sensing element. The conductance/resistance of the semiconducting oxide based sensor depends upon oxygen vacancy, the interstitial ions and chemisorbed oxygen. The gases to be sensed cause a change in the oxygen balance to vary the resistance/conductance value. [3] In the temperature range of 100°C-500°C the oxygen chemisorbed on the surface of metal oxide in molecular form (O₂⁻) below 200°C and atomic form (O) at higher temperatures. [4] The oxygen anions O₂⁻, O and O²⁺ are stable below 100°C, between 100°C-300°C and above 300°C respectively. [5] The variation in the resistance or conductance value is depend upon the type of gas being sensed i.e. when reducing gas is passed over the sensing material the resistance of the material will decrease (conductance will increase) as the reducing gas helped to liberate free electrons in contrast when oxidizing gases passes over the material the resistance of the material will increase (conductance will decrease) due to the fact that oxidizing gas takes up free electrons.

II. GAS SENSING MECHANISM AND RESPONSE OF MOO₃ NANOSTRUCTURE

Since MoO₃ is an n-type semiconductor material so the majority charge carriers are electrons. [1] MoO₃ nanostructures are highly selective for the gas sensing application because of its interesting electrical and structural properties. MoO₃ is polymorphous in nature and commonly it has three structures i.e. thermodynamically stable orthorhombic α-MoO₃ phase, metastable monoclinic β-MoO₃ and hexagonal h-MoO₃. Out of these three phases α-MoO₃ phase is of great interest due to its anisotropic characteristics and unusual chemistry of multiple valance states in which highly asymmetrical MoO₆ octahedra are interconnected with their edges along [001] direction and interlinked with the edges along [001] and [100]. This type of structure results in the double layer planer structure. [6][7] Due to its polymorphous nature the particular phase of MoO₃ is strongly dependent on the synthesis method and growth conditions. [8] The sensing mechanism of the MoO₃ involves lattice oxygen rather than chemisorbed oxygen. In terms of Kroger-Vink notation the reaction of oxygen with MoO₃ sensor in case of reducing gas can be written as [3]:

\[ O_2 \rightarrow V_{O}^{2+} + O^{-}_{2} \]  \hspace{1cm} (1)

For reducing gas the equation will be:

\[ R + O^{-}_{2} \rightarrow RO + 2e^{-} \]  \hspace{1cm} (2)

For reducing gas the equation will be:

\[ \text{Oxidizing gas} + O_{(ads)}^{2+} + 2e^{-} \rightarrow \text{Oxidizing gas}_{(ads)}^{2+} + O_{2}^{2-}_{(ads)} \]  \hspace{1cm} (3)

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III. GAS SENSING MECHANISM AND SENSITIVITY/SENSOR RESPONSE OF MoO$_3$ TOWARDS REDUCING GASES

Sensitivity towards H$_2$—

Hydrogen is found to be one of the potential sources of future energy needs. It is very beneficial to store and obtain energy from H$_2$ for manufacturing house hold and industrial applications. Therefore numerous research studies are been carried out in production storage and sensing of hydrogen. Being smallest of all elements available and colorless, odorless nature of hydrogen renders complexity in sensing performance of molybdenum trioxide sensors which operates at low operating temperature with high temperature. Semiconducting metal oxide based devices which operates at low operating temperature with high sensitivity are most reliable choice for sensing H$_2$ gas. Gas sensing performance of molybdenum trioxide sensors depends upon the change in the oxygen balance of the oxide layer which leads to a variation in its conductance or resistance. When MoO$_3$ exposed to H$_2$ gas it transform Mo$^{6+}$ to lower oxidation states Mo$^{5+}$ and Mo$^{4+}$. These changes lead to a visible color change of metal oxide well below the flammability limit. According to M.B. Rahmani et al. the following reaction may take place:

\[
\text{H}_2(\text{gas}) \rightarrow \text{H}_2(\text{ads}) \quad (4)
\]

\[
\text{H}_2(\text{gas}) + O^-_{\text{surface}} \rightarrow \text{H}_2O + e^- \quad (5)
\]

Where H$_2$(gas) - H$_2$(ads) and O$^-$ (surface) and represents H$_2$ in gas phase chemisorbed H$_2$ and surface oxygen ions.

When the conductive Au/Pd layer deposited on the MoO$_3$ thin film it will help to dissociate the H$_2$ molecules in the form of electron and H$^+$ ion. When these H$^+$ ions transferred to the MoO$_3$ layer and get absorbed; it will mainly reacts with the lattice corner sharing oxygen by forming theoretical H$_2$O groups and H$_x$MoO$_3$$_x$ structures. This process repeats itself for remaining H$^+$ ion and subsequent layers of MoO$_3$. At higher temperatures the H$_2$O molecules ultimately formed and escape from their respective positions leaving behind the oxygen vacancies which leads to the formation of MoO$_{3-x}$ as per the reaction given below:

\[
\text{MoO}_3 + x\text{H}^+ + xe^- \leftrightarrow \text{H}_x\text{MoO}_3 \quad (6)
\]

\[
2\text{H}_x\text{MoO}_3 \leftrightarrow x\text{H}_2 0 + 2\text{MoO}_3-x/2 \quad (7)
\]

On the other hand in the recovery period when the reduced film exposed to the air which contains oxygen; the film reverts back to its oxidized condition. Other results by different authors with the operating temperature and concentration of test gas are given in Table 1. This reaction can be described as given below:

\[
(x/4)O_2 + \text{MoO}_3-x/2 \leftrightarrow \text{MoO}_3 \quad (8)
\]

Table 1

<table>
<thead>
<tr>
<th>Sensitivity of MoO$_3$ towards H$_2$</th>
<th>Sensitivity %</th>
</tr>
</thead>
<tbody>
<tr>
<td>350°C - Lamellar thin films</td>
<td>30</td>
</tr>
<tr>
<td>225°C - Platelet structure</td>
<td>25</td>
</tr>
<tr>
<td>50°C - Nanoflakes</td>
<td>15</td>
</tr>
</tbody>
</table>

There are some reports are available for H$_2$ sensing In 2004 S.S. Sunu investigated the gas sensing properties of MoO$_3$ along with the electrical properties. The target gases used were NH$_3$, H$_2$ and LPG. In this work the concentration used was from 500ppm H$_2$ down to 50ppm. The sensitivity of 500ppm H$_2$ at 623K and 673K were 23% and 42.5%. Sensitivity towards 50ppm H$_2$ was 14% at 623K but less than 5% for lower concentrations. Other works related to H$_2$ gas sensing were reported in 2009 and 2013 by M.B. Rahmani and Manal M.Y.A. Alsaiw respectively. M.B. Rahmani et al. studied the gas sensing properties of thermally evaporated lamellar MoO$_3$ and the sensor response were measured with respect to the varying concentration of H$_2$ at 225°C. Maximum sensor response achieved was 24% for 1% H$_2$. In 2013 Manal M.Y.A. Alsaiw et al. synthesize two-dimensional α-MoO$_3$ nanoflakes by liquid based organic solvent assisted grinding and sonication method and the suspension was deposited on two types of substrates i.e. Glass and Si; to compare and investigated the gas sensing response of the resultant product towards H$_2$ gas. The response factor value
or sensitivity and sensor response is more for MoO$_3$ deposited on Si substrate (MoO$_3$/Si) it is maximum ~89% (SR=9) at 50°C and decreases with temperature and attains a minimum value ~6 % (SR=1) at 300°C. For MoO$_3$/Glass the maximum and minimum value of sensitivity and sensor response were ~58% (SR=2.3) at 200°C and ~15% (SR=1.2) at 300°C respectively. All measurement and test were carried out for 1% H$_2$. [8]

### Sensitivity towards CO

The intrinsic sensing performance of MoO$_3$ to CO arises from the nonstoichiometry of the MoO$_3$ nanorods and its defect structure present in the material in the form of Mo$^{5+}$ ions. [5][10]. The defect equilibrium of oxygen vacancy can be written in terms of Kroger–Vink notation:

$$O_3 \rightarrow V_{O_3}^2+ + O_3^{2+} \quad (9)$$

Where, $O_3$, $V_{O_3}^2+$ and $O_3^{2+}$ are lattice oxygen, oxygen vacancy in the lattice and interstitial oxygen respectively. [3][10]

When MoO$_3$ sensor exposed to CO gas it gets oxidized and electrons are liberated to the conduction band which results in the decrease of sensor resistance. [5]

$$CO_{(gas)} \rightarrow CO_{(ads)} \quad (10)$$

Depending upon the operating temperature of the sensor the sensing mechanism can be explained by following reactions: [11][12]

$$CO_{(ads)} + O^-_{(ads)} \rightarrow CO_2 \rightarrow CO_{2(gas)} + e^- \quad (11)$$
$$CO_{(ads)} + O_{2(ads)} \rightarrow CO_2 \rightarrow CO_{2(gas)} + O^- \quad (12)$$
$$CO_{(ads)} + O_{2(ads)} \rightarrow CO_{2(gas)} + 2e^- \quad (13)$$

All of these reactions are for the case when interstitial oxygen reacts with the CO gas but when adsorbed gas reacts with lattice oxygen the reaction will be as follows:

$$CO_{(ads)} + O_3 \rightarrow CO_{2(gas)} + V_{O_3}^{2+} + 2e^- \quad (14)$$

From above explained mechanism when the adsorbed CO from equation a reacts with the sensor material it is clear from equation b-d that the concentration of equilibrium interstitial oxygen will decreases and according to equation e the concentration of oxygen vacancy will increase. Both the conditions will result in an increase in conductance or decrease in resistance of the sensor material due to the liberation of free electrons. [10]

<table>
<thead>
<tr>
<th>Table 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>S</td>
</tr>
<tr>
<td>N</td>
</tr>
<tr>
<td>1</td>
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<tr>
<td>2</td>
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<tr>
<td>3</td>
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<tr>
<td>4</td>
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<tr>
<td>5</td>
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<tr>
<td>6</td>
</tr>
</tbody>
</table>

![Sensitivity of MoO$_3$ nanostructures towards CO](image)

In this context work have been reported by E. Comini in 2000 according to which RF sputtered thin films of α-MoO$_3$ are sensitive towards CO is 45% at 300°C; the CO concentration was 30ppm. [11] Later in 2002 K. Galatsis reported a work which include synthesis of MoO$_3$ thin film by Sol gel synthesis and tested as CO sensing material. As earlier the operating temperature was 300°C and they achieved the sensitivity of MoO$_3$ thin films for much lower concentration of CO i.e. 10ppm. The sensor response was found to be 1.05. [13] In 2005 E. Comini again worked on the same but the synthesis technique adopted this time was different by which they were successfully achieved a lower operating temperature for CO sensing. For MoO$_3$ nanorods synthesized by Infrared irradiation heating the operating temperature was 200°C and sensitivity towards 100ppm of CO was 160 % . [14] In 2007 ARNAB GANGULY investigated the gas sensitivity of sol-gel synthesized MoO$_3$ nanoparticles which were in the range of 10-100nm which was confirmed by Scanning electron microscopy(SEM) . Instead of giving a particular value of the sensitivity of MoO$_3$ nanoparticles they gave an estimate of the comparative sensitivities towards NO$_2$, NO and CO and found that the...
sensitivity is maximum for NO₂ and least for CO. The heater voltage was kept at 7.5V. In 2012 a paper regarding the gas sensing performance of MoO₃ nanorods was given by Shouli Bai. In their work MoO₃ nanorods were synthesized by Probe Ultrasonic synthesis and the working temperature used was 290°C and for 40ppm of NO₂ the sensitivity was 102.9. In 2014 Shouli Bai again investigated the gas sensing performance to improve the sensitivity of sensor material to detect the presence of CO attributable to 10ppm. The operating temperature used was 292°C and they attain the sensor response higher than the previous work i.e. 375. Sensitivity towards NH₃

When MoO₃ nanostructures exposed to NH₃, the ammonia molecules interact with the adsorbed oxygen and release electrons to the material which will decrease the resistance of the sensing material as per the equation:

\[
\text{NH}_3(gas) \leftrightarrow \text{NH}_3(ads)
\]

(15)

\[
2\text{NH}_3(ads) + 3/2\text{O}_2(ads) \leftrightarrow \text{N}_2 + 3\text{H}_2\text{O} + 3e^-
\]

(16)

Ammonia being a reducing gas, the resistance of the MoO₃ film decreases on passage of ammonia and the resistance drop is proportional to the concentration of ammonia. S.S. Sunu in 2004 reported the gas sensing properties of MoO₃, the target gas used was NH₃. In their work the MoO₃ synthesized by prolonged heating of Ammonium hepta molybdate tetra hydrate for 30 hr at 673K. The resultant product was confirmed to be MoO₃ by XRD analysis and structure was Platelet type structure confirmed by SEM. According to their study MoO₃ can be used as sensor material for sensing ammonia down to 25ppm and sensitivity achieved was 20% at around 350°C. The simple template directed hydrothermal synthesis to develop MoO₃ nanorods was employed by Antonella M. Taurino in 2006. The research also incorporated the gas sensing performance of MoO₃ nanorods towards NH₃ and some other gases. The working temperature selected was comparatively higher for (420°C) thicker film than the (370°C) thinner one. When the film thickness was around 50 µm the Sensitivity was 93% for 10ppm of NH₃. G.E. Buono-Core in 2013 synthesized MoO₃ thin films by Photo-chemical metal-organic deposition process and the precursor used was molybdenum dixo tropolonate and evaluated its sensitivity towards ammonia gas. The sensitivity of the material was 55±2.75 for 50ppm NH₃ and operating temperature was 350°C. Sensitivity of MoO₃ nanostructures at room temperature (RT) have been reported recently in 2015 by S. YANG according to which MoO₃ nanosheets synthesized by Physical vapour deposition are sensitive to NH₃ gas at RT; but the concentration they chose was very high up to the range of 1000ppm and the sensor response was 11.7.

Sensitivity towards H₂S

When H₂S gas passed over the surface of MoO₃ sensing

<table>
<thead>
<tr>
<th>Material</th>
<th>Morphology</th>
<th>Synthesis Technique</th>
<th>Detect ed concentration</th>
<th>Sensitivity/ Sensor response</th>
<th>Operating temperature</th>
</tr>
</thead>
<tbody>
<tr>
<td>MoO₃ Powder</td>
<td>Orthorhombic</td>
<td>Platelet structure of (NH₄)₆MoO₃₇·4H₂O</td>
<td>Proton heating</td>
<td>25ppm</td>
<td>S=20% (623K) (350°C)</td>
</tr>
<tr>
<td>2</td>
<td>MoO₃ Nanorods ds (t = 150 µm)</td>
<td>Hydrothermal synthesis</td>
<td>1000pp</td>
<td>S=537 %</td>
<td>420°C</td>
</tr>
<tr>
<td>3</td>
<td>α-MoO₃ Thin Films (avg. particle size ~300nm)</td>
<td>Photocatalytic Deposition</td>
<td>500pp</td>
<td>S=55±2.75</td>
<td>350°C</td>
</tr>
</tbody>
</table>

Table 3

Figure 3

Table 3

<table>
<thead>
<tr>
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<td>350°C</td>
</tr>
</tbody>
</table>
element it reacts with the oxygen ion to form H₂O and SO₂ by releasing electrons back to the conduction band hence increasing the conductance or decreasing the resistance of the sensor. The equation can be written as:

\[
H_2S_{\text{ads}} + 3O^\cdot_{\text{ads}} \rightarrow H_2O + SO_2 + 3e^- \quad (17)
\]

On removal of H₂S gas there is a decrease in conductance of the material and reaction can be written as \[^{19}\]

\[
R + O^\cdot_2 \rightarrow RO + 2e^- \quad (18)
\]

\[
\text{Table 4}
\]

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</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>α-MoO₃</td>
<td>Nanoparticles ~100nm</td>
<td>Solvo thermal method</td>
<td>20ppm H₂S</td>
<td>S=370°C</td>
<td>375°C</td>
<td>[20]</td>
</tr>
<tr>
<td>2</td>
<td>MoO₃</td>
<td>Thin Film</td>
<td>Spray pyrolysis</td>
<td>400ppm H₂S</td>
<td>S=12.7°C</td>
<td>350°C</td>
<td>[19]</td>
</tr>
</tbody>
</table>

**Figure 4**

Sensor Response of MoO₃ towards H₂S

Gas sensitivity of MoO₃ nonmaterial towards H₂S investigated and studied by many authors but very few reports are available in this perspective. The gas sensing response of MoO₃ towards H₂S was reported by two researchers Won-Sik Kim and D. V. Ahire in 2009 and 2012 respectively. Won-Sik Kim studied the gas sensing properties of MoO₃ Nanoparticles ~100nm.Nanoparticles of MoO₃ were synthesized by Solvo thermal method and tested for its sensitivity towards H₂S. Results revealed that MoO₃ Nanoparticles proved to be a promising candidate and highly selective for H₂S gas sensing with a very high response of 370 for 20ppm H₂S at 375°C. \[^{20}\] D. V. Ahire et al. developed MoO₃ thin films by spray pyrolysis method and found these films suitable for H₂S gas sensing in the operating temperature range of 200°C-350°C and observed that the response was maximum at 350°C ~12.72 and minimum at 200°C ~1.06. The concentration of H₂S used was 400ppm. \[^{19}\]

**Sensitivity towards VOC**

The sensing mechanism in case of VOC is complex. In all VOC ethanol is much popular in the sensing field and mechanism of sensing can be explained by assuming the transformation of ethanol to aldehyde Firstly the O-H bonds of adsorbed ethanol molecules heterolytically dissociate to create ethoxide group and hydrogen the reaction can be written as given below :\[^{14}\]

\[
C_2H_5OH_{(\text{gas})} \rightarrow C_2H_5OH_{(ads)} \quad (19)
\]

\[
C_2H_5OH_{(ads)} \rightarrow C_2H_5O_{(ads)} + H^+_{(ads)} \quad (20)
\]

Hence the H atom bind with a nearby lattice O anions to form the hydrogen molybdenum bronze (HₓMoO₃) simultaneously the oxygen of ethoxide group establish an ionic bond with the unsaturated metal site. This process can be explained by following reactions \[^{21}\] \[^{22}\]:

\[
C_2H_5OH_{(ads)} + H^+_{(ads)} + -O - Mo - O - Mo \rightarrow C_2H_5O_{(ads)} - Mo - O - Mo - OH \quad (21)
\]

After this reaction the dehydrogenization of ethoxide group took place and it donates the proton to the cation. It is basically due to the reducible cationic nature of Molybdenum

\[
C_2H_5O_{(ads)} - Mo - O - Mo - OH \rightarrow CH₃CHO + H - Mo - O - Mo - OH \quad (22)
\]

The adsorbed hydroxyl group converted in to H₂O when desorbed from the surface and leaving behind surface oxygen vacancy and partially reduced metal. To finish acetaldehyde oxidized and form H₂O and CO₂.The concerned equation for this is described below \[^{21}\]:

\[
C_2H_5OH + O^\cdot_2 \rightarrow CH₃CHO + H₂O + V_{O}^{3+} + 2e^- \quad (23)
\]

Some literature illustrating the sensitivity of MoO₃ sensor and its variation with concentration of test gas and temperature are given in the Table 5:

**Table 5**

<table>
<thead>
<tr>
<th></th>
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<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>MoO₃</td>
<td>Thin films</td>
<td>Sol-gel</td>
<td>100ppm Ethanol</td>
<td>S=6.7</td>
<td>300°C</td>
<td>[13]</td>
</tr>
<tr>
<td>2</td>
<td>Orthorhombic Powder</td>
<td>Prolonged heating</td>
<td>LPG</td>
<td>500ppm</td>
<td>S=42</td>
<td>673 K</td>
<td>[9]</td>
</tr>
</tbody>
</table>
MoO₃ are shows potential application in the area of sensing for some volatile organic compound like ethanol, methanol and CH₄. Some reports are available in this regard reveals that MoO₃ based sensor are more frequently used for ethanol sensing. **K. Galatsis in 2002** observed the gas sensing response of MoO₃ thin film and found that sensor response was 6.7 for 100ppm at 300°C but MoO₃-WO₃ thin films were more suitable for ethanol than the un-doped one. MoO₃-WO₃ the sensor response was increased upto 10 for same temperature and concentration of target gas. [13] Work done in 2004 by S.S. Sunu also in included the gas sensitivity of MoO₃ towards LPG and the evaluated sensitivity was 42.5% for 500ppm at 673K. [9] In 2005 E. Comini reported that the gas sensing response of MoO₃ nanorods synthesized by infrared irradiation heating and found that the sensitivity towards methanol is lower than CO for the same temperature and concentration. [14] After that in 2006 S. Barazzouk reported the gas sensing performance of MoO₃-based sensor the results discovered are attributed to sensor response of 10 for 500ppm CH₄ at comparatively operating temperature of 500°C. [3] **Shouli Bai in 2012** was successful in achieving a good sensor response for comparatively lower concentration of CH₄ ~40ppm the calculated value was 14.8 at 290°C. [5] Later in 2012 and 2013 D. V. Ahire and Longqiang Wang respectively worked in this direction for ethanol sensing of MoO₃ nanostructures. D. V. Ahire et al. used spray pyrolysis method to synthesis thin film of molybdenum oxide ad found that these thin films are sensitive towards ethanol at comparatively low temperature 200°C and the sensor response was 11.1 for 400ppm ethanol. [19] In contrast Longqiang Wang reported a work in which the comparison of the gas sensing properties of as purchased MoO₃ nano powder and Crystalline/amorphous-Core/shell MoO₃ (C/A-C/S MoO₃) were compared. The results revealed that the sensor response for the C/A-C/S MoO₃ composite was approximately 10 times higher than that of raw MoO₃ nano-powders. The sensor response for raw MoO₃ was 4.5 and for C/A-C/S MoO₃ composite this value was 56. The temperature and concentration of target gas which was ethanol were 180°C and 500ppm respectively. [21] In 2015 Li-li Sui reported the synthesis of three dimensional flower like hierarchical structure of α-MoO₃ by solvo thermal route without using any template of surfactant and used these structure for sensing triethylamine(TEA) down to 0.5 ppm. The sensor response at 250°C for 100ppm of TEA was found to be 416. [23]

### IV. GAS SENSING MECHANISM AND SENSITIVITY/SENSOR RESPONSE OF MOO₃ TOWARDS OXIDIZING GASES

#### Sensitivity towards O₂

<table>
<thead>
<tr>
<th>Material</th>
<th>Morphology</th>
<th>Synthesis Method</th>
<th>Detected Concentration</th>
<th>Sensitivity</th>
<th>Operating Temperature</th>
</tr>
</thead>
<tbody>
<tr>
<td>N₂O</td>
<td>Thin films</td>
<td>Sol-gel</td>
<td>100ppm O₂</td>
<td>S=39</td>
<td>370°C</td>
</tr>
</tbody>
</table>

Very few reports are available regarding the sensing properties or MoO₃ towards O₂ out of which only one report is provided with experimental results for analysis purpose. **K. Galatsis in 2002** observed the gas sensing response of MoO₃ thin films and its binary oxides with WO₃ and TiO₂ synthesized by Sol-gel process. Sensor response for 1000ppm of O₂ was 39 at 370°C. [13]

#### Sensitivity towards NO and NO₂

NO₂ gases are very hazardous for the environment and are of great interest in the field of sensing technology. Interaction of oxidizing gas like NO, and its compound with MoO₃ based sensor element directly takes place on the oxide surface. During this process NO₂ molecules consumed conduction electrons which results in the oxygen concentration decrease at the surface of oxide hence increasing the depletion region

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**Figure 4**

Sensitivity of MoO₃ Nanostructures towards VOC

<table>
<thead>
<tr>
<th>Sensor Response</th>
<th>Concentration of test gas in ppm</th>
</tr>
</thead>
<tbody>
<tr>
<td>16</td>
<td>0</td>
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</table>

**Table 6**

<table>
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<tr>
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<th>Detected Concentration</th>
<th>Sensitivity</th>
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<td>100ppm O₂</td>
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at the surface.\[^{[4],[5]}\] As discussed above the NO\(_2\) molecules have high electron affinity it capture electrons from conduction band of MoO\(_3\) to form the adsorbed NO\(_2\) and this reaction can be explained as per the equation given by Shouli Bai et al. in 2012 as:

\[
\text{NO}_2(\text{gas}) \rightarrow \text{NO}_2(\text{ads}) \tag{24}
\]

\[
\text{NO}_2(\text{ads}) + e^- \rightarrow \text{NO}_2(\text{ads})^- \tag{25}
\]

Overall reaction for the sensing mechanism can be written as \[^{[4],[5]}\],

\[
\text{NO}_2(\text{gas}) + \text{O}^-_{\text{(ads)}} + 2e^- \rightarrow \text{NO}_2(\text{ads})^- + \text{O}^2_{\text{(ads)}} \tag{26}
\]

<table>
<thead>
<tr>
<th>S. No</th>
<th>Material</th>
<th>Morphology</th>
<th>Synthesis technique</th>
<th>Detected concentration / target gas</th>
<th>Sensitivity / SR</th>
<th>Operating temperature</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Orthorhombic MoO(_3) Powder</td>
<td>Particle size 0.5 - 2 (\mu)m</td>
<td>Powder purchased MoO(_3) Powder</td>
<td>NO: 250ppm, NO(_2): 100ppm</td>
<td>S= 80, 750%</td>
<td>200°C</td>
<td>[3]</td>
</tr>
<tr>
<td>2</td>
<td>MoO(_3) Nanorods ((t=150\mu\text{m}))</td>
<td>Hydrothermal synthesis</td>
<td>NO(_2): 2ppm</td>
<td>S=28%</td>
<td>320°C</td>
<td>[16]</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>MoO(_3) Nanoparticles 10-100 nm</td>
<td>Sol-gel synthesis</td>
<td>NO(_2): 500ppm</td>
<td>S=N</td>
<td>Heating</td>
<td>[12]</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>(\alpha)-MoO(_3) Lamellar films (a width of 150 (\mu)m and 50 (\mu)m)</td>
<td>Thermal evaporation</td>
<td>NO(_2): 10ppm</td>
<td>SR=118%</td>
<td>225°C</td>
<td>[4]</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>(\alpha)-MoO(_3) Nanorods 50 (\mu)m</td>
<td>Ultrasonic synthesis</td>
<td>NO(_2): 40ppm</td>
<td>S=10, 290°C</td>
<td>0.5-2 (\mu)m</td>
<td>[5]</td>
<td></td>
</tr>
</tbody>
</table>

Table 7

For NO gas the operating temperature is \(\approx 200°C\) which was identified by S. Barazzouk in 2006; the sensor response for 250ppm of NO was calculated to be 80. In the same work S. Barazzouk et al. reported the sensor response of MoO\(_3\) powder for 100ppm NO\(_2\) was more than or NO i.e. 750 at same operating temperature i.e. 200°C. \[^{[3]}\] According to the work reported by Antonella M. Taurino in April 2006 sensitivity of MoO\(_3\) Nanorods (Film thickness 150 \(\mu\)m and 50 \(\mu\)m) which was synthesized by hydrothermal method was found to be 28% and 26% for 2ppm and 1ppm NO\(_2\) respectively. This report also reveals the act that the sensitivity of sensor was improved and operating temperature was decreased when we trim down the film thickness.\[^{[14]}\] In 2007 ARNAB GANGULY investigated the gas sensitivity of sol-gel synthesized MoO\(_3\) nanoparticles. Instead of giving a particular numerical value of the sensitivity of nanoparticles they gave an estimate of the comparative sensitivities of MoO\(_3\) nanoparticles towards NO\(_2\), NO and CO and found that the sensitivity is maximum for NO\(_2\) least for CO and the sensitivity for NO lies between these two when they used 500ppm of each gas for detection.\[^{[12]}\] In 2010 a work was presented by M.B. Rahmani according to which lamellar thin films of \(\alpha\)-MoO\(_3\) which were developed by Thermal evaporation can detect the 10ppm of NO\(_2\) gas at much lower than others i.e. at 225°C and the sensor response was 118%. \[^{[4]}\] Gas sensing performance of nanorods of MoO\(_3\) was given by Shouli Bai in 2012. In their work MoO\(_3\) nanorods were synthesized by Probe Ultrasonic synthesis the working temperature was 290°C and for 40ppm of NO\(_2\) sensitivity was found to be 102.9.\[^{[8]}\]

V.
VI. VARIATION IN SENSITIVITY /SENSOR RESPONSE FOR 100PPM OF DIFFERENT GASES AT DIFFERENT TEMPERATURE

<table>
<thead>
<tr>
<th>Nanorods</th>
<th>CO</th>
<th>200°C</th>
<th>2.8</th>
<th>1000ppm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Thin film</td>
<td>Ethanol</td>
<td>300°C</td>
<td>6.7</td>
<td>1000ppm</td>
</tr>
<tr>
<td>Nanorods (Film thickness 150µm)</td>
<td>NH₃</td>
<td>420°C</td>
<td>6.37</td>
<td>1000ppm</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Temperature</th>
<th>Sensitivity/SR Vs. Temperature</th>
</tr>
</thead>
<tbody>
<tr>
<td>200°C</td>
<td>CO</td>
</tr>
<tr>
<td>300°C</td>
<td>Ethanol</td>
</tr>
<tr>
<td>420°C</td>
<td>NH₃</td>
</tr>
</tbody>
</table>


VII. CONCLUSION

On the basis of above discussion following conclusions can be derived –

- The optimum temperature range to sense CO gas by any of the nanostructure of MoO₃ is approximately 200°C-300°C. The sensitivity/sensor response is more and operating temperature is less when the morphology of MoO₃ is in the form of Nanorods.
- The optimum working temperature of MoO₃ nanostructures hen the target gas is ammonia NH₃ is in the range of 350°C-420°C. For different concentration of NH₃ the sensitivity is different. The sensor response/sensitivity increases with the concentration of target gas within the given temperature range. Sensor response/sensitivity is also vary with the morphology of MoO₃; same as for CO gas the sensor response/sensitivity of MoO₃ nanostructures toward NH₃ is more for Nanorods than other structures.
- For NO $T_{operating}$ is ≤200°C or above but for NO2 this range lies between 200°C-320°C. Another conclusion that can be made is that MoO₃ nanostructures as more selective to NO than NO2. The lamellar thin films and nanorods of MoO₃ are best suited for low operating temperatures and more sensitivity of NO2.
- The operating temperature for O₂ sensing is approximately 370°C. For H₂ sensing 2D nanostructures of MoO₃ is more suitable i.e. lamellar thin films and nanoflakes and operating temperature is of order of 200°C and 225°C respectively. On contrast for H₂S gas; nanoparticles are more preferable but for H₂S the operating temperature more than H₂ i.e. 375°C but sensor response is comparatively high.

- Among all VOCs ethanol gas was of great interest in sensing field. MoO₃ sensors are more selective to ethanol sensing it can sense from 100ppm upto 500ppm ethanol and the operating temperature range is 180°C-300°C depending upon the structure used. The sensor response is highest for ethanol when the composite of C/A/C/S MoO₃ was used. The working temperature for CH₄ sensing can be as high as 500°C and sensor response can lie in the range of 10-15. Nonorods are suitable for LPG and can achieve the sensitivity upto 42.5% for 500ppm at 350°C. The reducing gas like CH₄ helps to liberate free electrons and reduce the resistivity of the sensor material on the other hand the oxidizing gases like NO₂ adopt the free electrons which lead to an increase in the resistivity of the sensor.

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