Promising Nature of MoO_3 Nanostructures in Gas Sensing Applications – A Review

Jaya Bharti, Arshali Sasi, C. Sasi Kumar

Abstract— Molybdenum trioxide (MoO_3) is a transition metal oxide with a wide band gap. It is an n-type semiconductor material with an oxygen deficiency. MoO_3 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, MoO_3 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 Cr_2O_3, ZnO, SnO_2, NiO, SrO, WO_3 ,TiO_2 ,Nb_2O_3 ,CeO_2 and MoO_3 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 d^0 and d^{10} 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 sensors 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 (O_2^-) below 200°C and atomic form (O^-) at higher temperatures. [4].The oxygen anions O_2^- , O^- and O^{2-} 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 on contrast when oxidizing gas 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.

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II. GAS SENSING MECHANISM AND RESPONSE OF MOO3 NANOSTRUCTURE

Since MoO_3 is an n-type semiconductor material so the majority charge carriers are electrons. [1] MoO_3 nanostructures are highly selective for the gas sensing application because of its interesting electrical and structural properties. MoO_3 is polymorphous in nature and commonly it has three structures i.e. thermodynamically stable orthorhombic α-MoO_3 phase, metastable monoclinic β-MoO_3 and hexagonal h-MoO_3. 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 MoO_6 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 MoO_3 is strongly dependent on the synthesis method and growth conditions. [5] The sensing mechanism of the MoO_3 involves lattice oxygen rather than chemisorbed oxygen. In terms of Kroger-Vink notation the reaction of oxygen with MoO_3 sensor in case of reducing gas can be written as [3]:

$$O_O \rightarrow V_O^{2+} + O_i^{2-} \quad (1)$$

For reducing gas the equation will be:

$$R + O_i^{2-} \rightarrow RO + 2e^- \quad (2)$$

For reducing gas the equation will be:

$$\text{Oxidizing gas} + O_{(ads)}^- + 2e^- \rightarrow \text{Oxidizing gas}_{(ads)}{}^- + O_{(ads)}^{2-} \quad (3)$$

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III. GAS SENSING MECHANISM AND SENSITIVITY/SENSOR RESPONSE OF MOO3 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 and measuring. Since H_2 is highly flammable gas it requires intense caution in presence of oxygen and at elevated temperature. Semiconducting metal oxide based devices which operates at low operating temperature with high sensitivity are most reliable choice for sensing H_2 gas. [8] 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. [4]. According to M.B. Rahmani et al. the following reaction may take place:

$$H_{2(gas)} \rightarrow H_{2(ads)} \quad (4)$$

$$H_{2(gas)} + O^-_{(surface)} \rightarrow H_2O + e^- \quad (5)$$

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_2O groups and H_xMoO_3 structures [8]. This process repeats itself for remaining H^+ ion and subsequent layers of MoO_3 .At higher temperatures the H_2O 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:

$$MoO_3 + xH^+ + xe^- \leftrightarrow H_xMoO_3 \quad (6)$$

$$2H_xMoO_3 \leftrightarrow xH_2O + 2MoO_{3-x/2} \quad (7)$$

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: [8]

$$(x/4)O_2 + MoO_{3-x/2} \leftrightarrow MoO_3 \quad (8)$$

Table 1

S. No	Material	Morphology	Synthesis Technique	Detected concentration	Sensitivity/ Sens	Operating temp	Ref.
1	Orthorhombic MoO_3 Powder	Platelet type structure	Prolonged heating of ammonium hptamolybdate tetrahydrate	50ppm H_2	S= 14%	623 K (350 °C)	[9]
2	α-MoO_3	Lamellar thin films (avg. w. and l. of 5 and 50µm)	Thermal evaporation	1% H_2	S= 24%	225° C	[4]
3	α-MoO_3	Nanoflakes	Solvent Assisted grinding and sonication method	1% H_2	MoO_3/Glass S.R. =2.3 MoO_3/Si S.R. =9	200° C 50°C	[8]

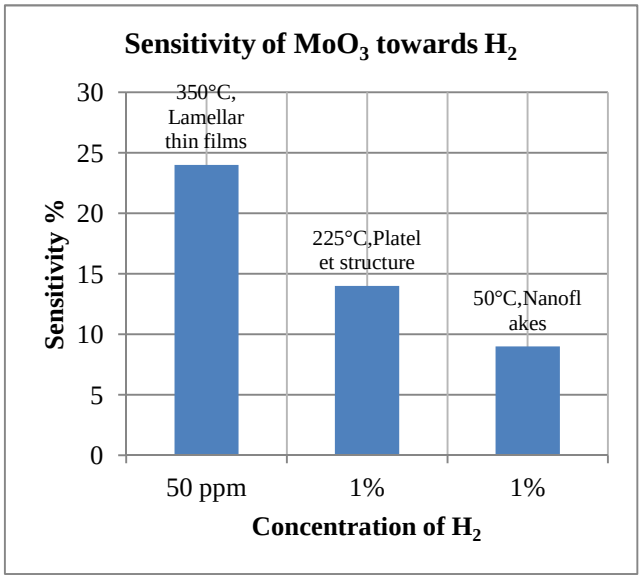

Figure 1

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. [9] Other works related to H_2 gas sensing were reported in **2009 and 2013 by M.B. Rahmani and Manal M.Y.A. Alsaif 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. [4] **Manal M.Y.A. Alsaif 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

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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**:

$$O_O \rightarrow V_O^{2+} + O_i^{2-} \quad (9)$$

Where, O_O, V_O^{2+} and O_i^{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 librated 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]

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

Or

$$CO_{(ads)} + O_{2(ads)}{}^- \rightarrow CO_3^- \rightarrow CO_{2(gas)} + O^- \quad (12)$$

Or

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

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:

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

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 2

S. No	Material	Morphology	Synthesis technique	Detected concentration	Sensitivity/ Sensor response	Operating temperature	Ref.
1	α-MoO_3	Thin films	RF sputtering	30 ppm	S=45%	300°C	[11]
2	MoO_3	Thin films	Sol-gel	10 ppm	S=1.05	300°C	[13]
3	MoO_3	Nano rods	Infrared irradiation	100 ppm	S=160 %	200°C	[14]
4	MoO_3	Nano particles 10-100nm	Sol-gel citration	500 ppm	S=NO_2 >NO> CO	Heater Voltage 7.5V	[12]
5	α-MoO_3	Nano rods	Ultrasonic synthesis	40 ppm	S= 21.7	290°C	[5]
6	α-MoO_3	Nano rods	Hydrothermal synthesis	10 ppm	S=37.5	292°C	[10]

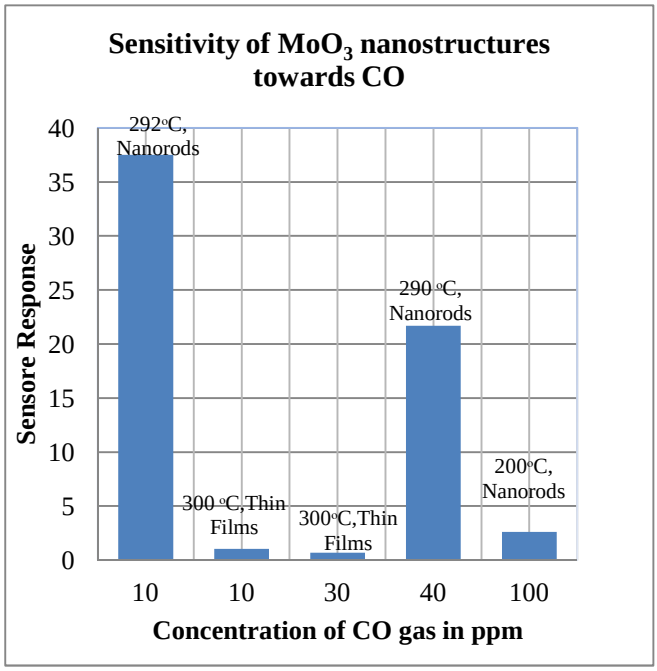

Figure 2

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 MoO3 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 MoO3 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

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sensitivity is maximum for NO_2 and least for CO. The heater voltage was kept at 7.5V. [12] In **2012** a paper regarding the gas sensing performance of MoO_3 nanorods was given by **Shouli Bai**. In their work MoO_3 nanorods were synthesized by Probe Ultrasonic synthesis and the working temperature used was 290°C and for 40ppm of NO_2 the sensitivity was 102.9. [5] 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. 37.5. [10]

Sensitivity towards NH_3

When MoO_3 nanostructures exposed to NH_3, 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 [15]:

$$NH_{3(gas)} \leftrightarrow NH_{3(ads)} \quad (15)$$

$$2NH_{3(ads)} + 3/2O^-_{2(ads)} \leftrightarrow N_2 + 3H_2O + 3e^- \quad (16)$$

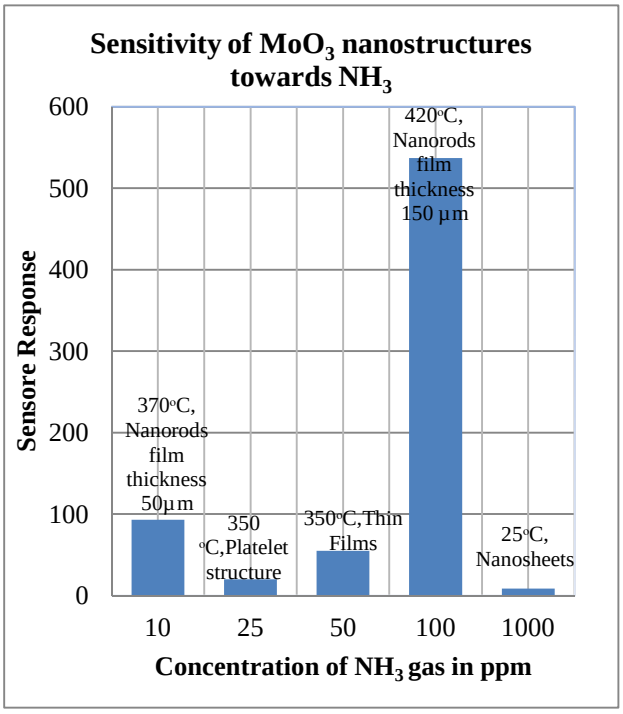

Figure 3

Table 3

S. No	Material	Morphology	Synthesis Technique	Detected concentration	Sensitivity/ Sensor response	Operating temperature	Ref.
1	Orthorhombic MoO_3 Powder	Platelet type structure	Prolonged heating of $(NH_4)_6.Mo_7O_{24}.4H_2O$	25ppm	S= 20%	623K (350°C)	[9]
2	MoO_3	Nanorods (t = 150µm)	Hydrothermal synthesis	100ppm	S=537 %	420°C	[16]
		Nanorods (t = 50µm)		10ppm	S=93%	370°C	
3	α-MoO_3	Thin Films (avg. particle size ~300nm)	Photo-chemical metal-organic deposition (PMOD)	50ppm	S=55± 2.75	350°C	[17]
4	Micro / nano α-MoO_3	α-MoO_3 Microbelts	Physical Vapour Deposition	1000ppm	S=3.5	RT	[15]
		Branched α-MoO_3 Microbelts		1000ppm	S=10	RT	
		α-MoO_3 nanosheets		1000ppm	S=11.7	RT	

Ammonia being a reducing gas, the resistance of the MoO_3 film decreases on passage of ammonia and the resistance drop is proportional to the concentration of ammonia.[18] **S.S. Sunu** in **2004** reported the gas sensing properties of MoO_3; the target gas used was NH_3 .In their work the MoO_3 synthesized by prolonged heating of Ammonium hepta molybdate tetra hydrate for 30 hr at 673K.The resultant product was confirmed to be MoO_3 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. [9] The simple template directed hydrothermal synthesis to develop MoO_3 nanorods was employed by **Antonella M. Taurino in 2006** .The research also incorporated the gas sensing performance of MoO_3 nanorods towards NH_3 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 NH_3. [16] G.E. **Buono-Core in 2013** synthesized MoO3 thin films by Photo-chemical metal-organic deposition process and the precursor used was molybdenum dioxo 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. [17]Sensitivity of MoO_3 nanostructures at room temperature (RT) have been reported recently in **2015 by S. YANG** according to which MoO_3 nanosheets synthesized by Physical vapour deposition are sensitive to NH_3 gas at RT ; but the concentration they chose was very high upto the range of 1000ppm and the sensor response was 11.7. [15]

Sensitivity towards H_2S –

When H_2S gas passed over the surface of MoO_3 sensing

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element it reacts with the oxygen ion to form H_2O and SO_2 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:

$$H_2S_{ads} + 3O^-_{ads} \rightarrow H_2O + SO_2 + 3e^- \quad (17)$$

On removal of H_2S gas there is a decrease in conductance of the material and reaction can be written as [19]:

$$R + O_i^{2-} \rightarrow RO + 2e^- \quad (18)$$

Table 4

S. No	Material	Morphology	Synthesis technique	Detected concentration and target gas	Sensitivity/ Sensor response	Operating temperature	Ref.
1	α-MoO_3	Nanoparticles ~100nm	Solvo thermal Method	20ppm H_2S	S=370	375° C	[20]
2	MoO_3	Thin Film	Spray pyrolysis	400ppm H_2S	S=12.72	350° C	[19]

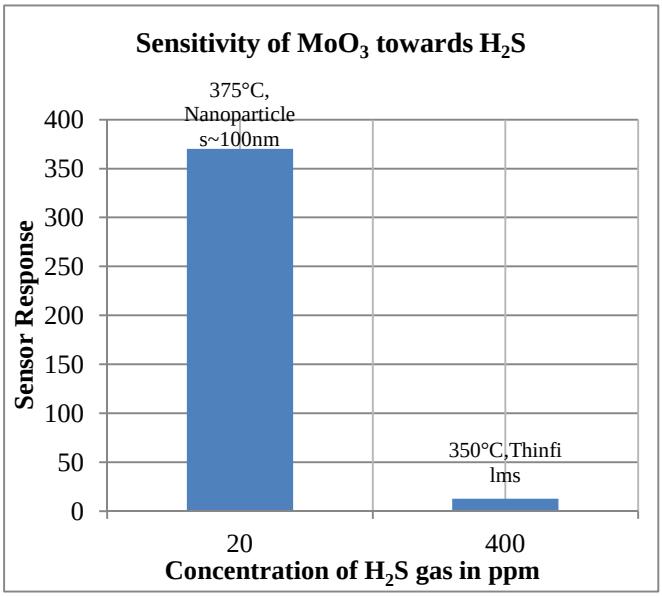

Figure. 4

Gas sensitivity of MoO_3 nonmaterial towards H_2S investigated and studied by many authors but very few reports are available in this perspective. The gas sensing response of MoO_3 towards H_2S 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 MoO_3 Nanoparticles ~100nm.Nanoparticles of MoO_3 were synthesized by Solvo thermal method and tested for its sensitivity towards H_2S. Results revealed that MoO_3 Nanoparticles proved to be a promising candidate and highly selective for H_2S gas sensing with a very high response of 370 for 20ppm H_2S at 375°C. [20] **D. V. Ahire et al.** developed MoO_3 thin films by spray pyrolysis method and found these films suitable for H_2S 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 H_2S 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 cab be written as given below :[14]

$$C_2H_5OH_{(gas)} \rightarrow C_2H_5OH_{(ads)} \quad (19)$$

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

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

$$C_2H_5O_{(ads)} - Mo - O - Mo - OH \rightarrow CH_3CHO + H - Mo - O - Mo - OH \quad (22)$$

The adsorbed hydroxyl group converted in to H_2O when desorbed from the surface and leaving behind surface oxygen vacancy and partially reduced metal. To finish acetaldehyde oxidized and form H_2O and CO_2The concerned equation for this is described below [21]:

$$C_2H_5OH + O_i^{2-} \rightarrow CH_3CHO + H_2O + V_O^{2+} + 2e^- \quad (23)$$

Some literature illustrating the sensitivity of MoO_3 sensor and its variation with concentration of test gas and temperature are given in the Table 5:

Table 5

S. No	Material	Morphology	Synthesis technique	Detected concentration / target gas	Sensitivity / SR	Operating temperature	Ref.
1	MoO_3 Thin films		Sol-gel	100ppm Ethanol	S= 6.7	300° C	[13]
2	Orthorhombic MoO_3 Powder	Platelet type structure	Prolonged heating of $(NH_4)_6Mo_7O_{24}.4H_2O$	500ppm LPG	S=42.5%	673 K (350 °C)	[9]

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3	MoO_3	Nanorods	Infrared irradiation Heating	100ppm CH_3OH	$S_{methanol} < S_{CO}$	200° C	[14]
4	Orthorhombic MoO_3 Powder	Particle size 0.5 -2 µm	Purchased MoO_3 Powder	500ppm CH_4	S=10	500° C	[3]
5	α-MoO_3	Nanorods	Ultrasonic synthesis	40ppm CH_4	S=14.8	290° C	[5]
6	MoO_3	Thin Film	Spray pyrolysis	400ppm Ethanol	S=11.1	200° C	[19]
7	Raw MoO_3 and C/A-C/S MoO_3 composite	α-MoO_3	Purchased MoO_3 Powder	500ppm Ethanol	SR=4.5	180° C	[21]
		C/A-C/S MoO_3 composite	Controlled dehydration routs	500ppm Ethanol	SR=56	180° C	
8	flower-like α-MoO_3	hierarchical structure	Solvothermal rout without surfactant	100ppm of TEA	SR=416	250° C	[23]

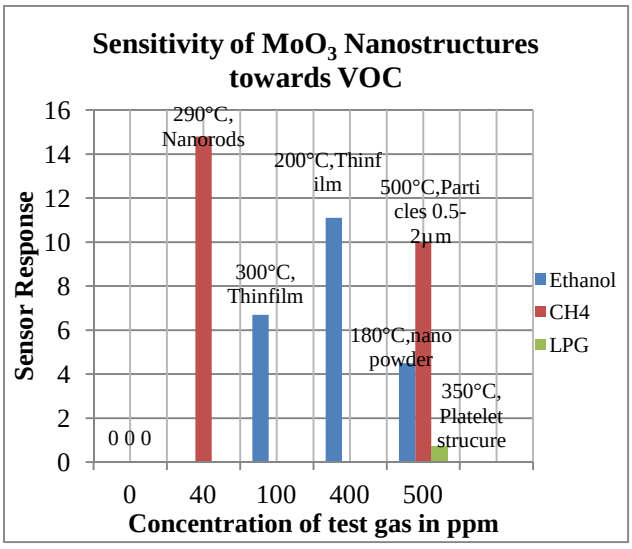

Figure 4

MoO_3 are shows potential application in the area of sensing for some volatile organic compound like ethanol, methanol and CH_4. Some reports are available in this regard reveals that MoO_3 based sensor are more frequently used for ethanol sensing. **K. Galatsis in 2002** observed the gas sensing response of MoO_3 thin film and found that sensor response was 6.7 for 100ppm at 300°C but MoO_3-WO_3 thin films were more suitable for ethanol sensing than the un-doped one. MoO_3-WO_3 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 MoO_3 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 MoO_3 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 o MoO_3-based sensor the results discovered are attributed to sensor response of 10 for 500ppm CH_4 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 CH_4 ~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 MoO_3 nanotructures. **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 senor 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 MoO_3 **(**C/A-C/S MoO_3**)** were compared. The results revealed that the sensor response for the C/A-C/S MoO_3 composite was approximately 10 times higher than that of raw MoO3 nano-powders. The sensor response for raw MoO_3 was 4.5 and for C/A-C/S MoO_3 composite this value was 56 .The temperature and concentration of target gas which was ethanol were 180°C and 500pm respectively.[21]In 2015 Li-li Sui reported the synthesis of three dimensional flower like hierarchical structure of α-MoO_3 by solvo thermal rout 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 O_2

Table 6

S. No	Material	Morphology	Synthesis technique	Detected concentration and target gas	Sensitivity/ Sensor response	Operating temperature	Ref.
1	MoO_3	Thin films	Sol-gel	1000ppm O_2	S=39	370° C	[13]

Very few reports are available regarding the sensing properties or MoO_3 towards O_2 out of which only one report is provided with experimental results for analysis purpose. **K. Galatsis in 2002** observed the gas sensing response of MoO_3 thin films and its binary oxides with WO_3 and TiO_2 synthesized by Sol-gel process. Sensor response for 1000ppm of O_2 was 39 at 370°C. [13]

Sensitivity towards NO and NO_2

NO_x gases are very hazardous for the environment and are of great interest in the field of sensing technology. Interaction of oxidizing gas like NO_x and its compound with MoO_3 based sensor element directly takes place on the oxide surface. During this process NO_2 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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at the surface. [4],[5] As discussed above the NO_2 molecules has 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:

$$NO_{2(gas)} \rightarrow NO_{2(ads)} \quad (24)$$

$$NO_{2(ads)} + e^- \rightarrow NO_{2(ads)}{}^- \quad (25)$$

Overall reaction for the sensing mechanism can be written as [4], [5]:

$$NO_{2(gas)} + O^-_{(ads)} + 2e^- \rightarrow NO_{2(ads)}{}^- + O^{2-}_{(ads)} \quad (26)$$

Table 7

S. No	Material	Morphology	Synthesis technique	Detected concentration / target gas	Sensitivity / SR	Operating temperature	Ref.
1	Orthorhombic MoO_3 Powder	Particle size 0.5-2 µm	Purchased MoO_3 Powder	250ppm NO	S= 80	200°C	[3]
				100ppm NO_2	S= 750	200°C	
2	MoO_3	Nanorods (*t*= 150µm)	Hydrothermal synthesis	2ppm NO_2	S=28 %	320°C	[16]
		Nanorods (*t*= 50µm)		1ppm NO_2	S=26 %	240°C	
3	MoO_3	Nanoparticles 10-100 nm	Sol-gel citration	500ppm NO and NO2	S=NO_2> NO	Heater Voltage 7.5V	[12]
4	α-MoO_3	Lamellar thin films(avg. *w* and *l* 5 and 50µm)	Thermal evaporation	10ppm NO_2	SR= 118 %	225°C	[4]
5	α-MoO_3	Nanorods	Ultrasonic synthesis	40ppm NO_2	S=10 2.9	290°C	[5]

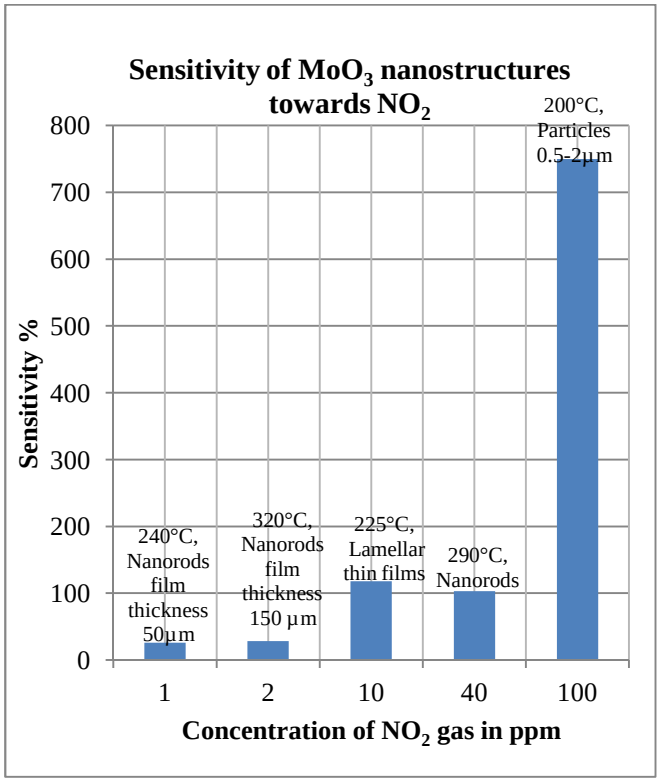

Figure 5

For NO gas the operating temperature is ≈ 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 150µm and 50µm) 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.[16] 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 and 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 α-MoO_3 which were developed by Thermal evaporation can detect the 10ppm of NO_2 gas at much lower temperature 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. [5]

V.

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

Table 8

Nanorods	**CO**	**200°C**	**2.6**	**100ppm**
Thin film	**Ethanol**	**300°C**	**6.7**	**100ppm**
Nanorods (Film thickness 150µm)	**NH3**	**420°C**	**6.37**	**100ppm**

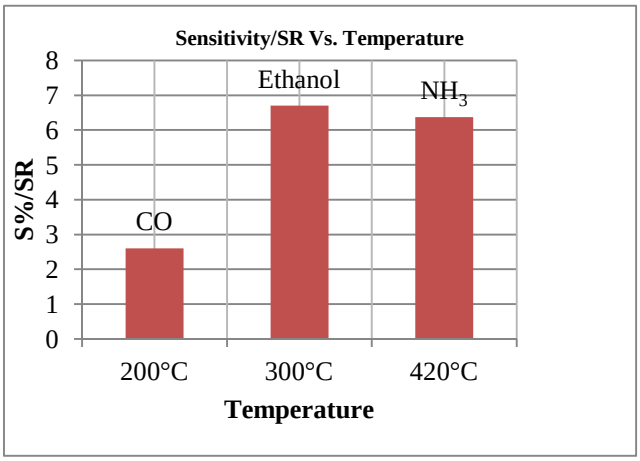

Figure 6

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 MoO_3 is approximately 200°C-300°C. The sensitivity/ sensor response is more and operating temperature is less when the morphology of MoO_3 is in the form of Nanorods.
- The optimum working temperature of MoO_3 nanostructures hen the target gas is ammonia NH_3 is in the range of 350°C-420°C. For different concentration of NH_3 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 MoO_3; same as for CO gas the sensor response /sensitivity of MoO_3 nanostructures toward NH3 is more for Nanorods than other structures.
- For NO $T_{operating}$ is ≈200°C or above but for NO_2 this range lies between 200°C-320°C .Another conclusion that can be made is that MoO_3 nanostructures as more selective to NO_2 than NO. The lamellar thin films and nanorods of MoO_3 are best suited for low operating temperatures and more sensitivity of NO_2.
- The operating temperature for O_2 sensing is approximately 370°C. For H_2 sensing 2D nanostructures of MoO_3 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 H_2S gas; nanoparticles are more preferable but for H_2S the operating temperature more than H_2 i.e. 375°C but sensor response is comparatively high.
- Among all VOCs ethanol gas was of great interest in sensing field. MoO_3 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 MoO_3 was used. The working temperature for CH_4 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 CH_4 helps to liberate free electrons and reduce the resistivity of the sensor material on the other hand the oxidizing gases like NO_x adopt the free electrons which lead to an increase in the resistivity of the sensor.

REFERENCES

1. R. John Bosco Balaguru, Mimic of a Gas sensor, Metal Oxide Gas Sensing Mechanism, Factors Influencing the Sensor Performance and Role of nanomaterials based gas sensors, NPTEL – Electrical & Electronics Engineering – Semiconductor Nanodevices.
2. Yu-Feng Sun 2012, Metal Oxide Nanostructures and Their Gas Sensing Properties: A Review, Sensors 2012.
3. S. Barazzouk 2006, MoO_3-based sensor for NO, NO_2 and CH_4 detection., Sensors and Actuators B 119 (2006) 691–694
4. M.B. Rahmani, November 2009, Gas sensing properties of thermally evaporated lamellar MoO_3, Sensors and Actuators B 145 (2010)
5. Shouli Bai, 2012 , Ultrasonic synthesis of MoO_3 nanorods and their gas sensing properties., Sensors and Actuators B 174 (2012) 51– 58
6. Rao M.C.2013, Review Paper - Structural Stoichiometry and Phase Transitions of MoO_3 Thin Films for Solid State Microbatteries, Research Journal of Recent Sciences , Vol. 2(4), 67-73, April (2013)
7. H. Bhavani Naga Prasanna 2014, Structural, Morphological, Optical & Infrared properties of nanocrystalline MoO_3 thin films, International Journal of ChemTech Research Vol.6, No.3, pp 1988-1990, May-June 2014
8. Manal M.Y.A. Alsaif , November 2013, Two dimensional α-MoO_3 nanoflakes obtained using solvent-assisted grinding and sonication method: Application for H_2 gas sensing., Sensors and Actuators B 192 (2014) 196– 204
9. S.S. Sunu, Electrical conductivity and gas sensing properties of MoO_3, Sensors and Actuators B 101 (2004) 161–174
10. Shouli Bai, 2014, Intrinsic characteristic and mechanism in enhancing H_2S sensing of Cd-doped -MoO_3 nanobelts. Sensors and Actuators B 204 (2014) 754–762
11. E. Comini 2000, Carbon monoxide response of molybdenum oxide thin films deposited by different techniques, Sensors and Actuators B 68 2000. 168–174
12. Arnab Ganguly, March 2007, Synthesis, characterization and gas sensitivity of MoO_3 nanoparticles., Bulletin of Material Science, Vol. 30, No. 2, April 2007, pp. 183–185
13. K. Galatsis , 2002, Comparison of single and binary oxide MoO_3,TiO_2 and WO_3 Sol- gel gas sensors , Sensors and Actuators B 83, 2001
14. Elisabeth Comini , December 2005 ,Metal oxide nano-crystals for gas sensing, Review, Analytica Chimica Acta 568 (2006) 28–40
15. S. YANG, September 2014, Controlled Synthesis of Micro/Nano MoO_3 by Physical Vapor Deposition and Its Gas Sensing Properties to NH_3 Gas at Room Temperature. Ferroelectrics, 477: 112–120, 2015
16. Antonella M. Taurino, ,2006 , Synthesis, electrical characterization, and gas sensing properties of molybdenum oxide nanorods ., Applied Physics Letter 88, 152111 (2006)
17. G.E. Buono-Core, Synthesis and characterization of thin molybdenum oxide films prepared from molybdenum dioxo tropolonate precursors by photochemical metal-organic deposition (PMOD) and its evaluation as ammonia gas sensors., Journal of Non-Crystalline Solids 387 (2014) 21–27
18. A.K. Prasad 2003, Comparison of sol–gel and ion beam deposited MoO_3 thin film gas sensors for selective ammonia detection, Sensors and Actuators B 93 (2003) 25–30
19. D. V. Ahire , Sep. 2012, Preparation of MoO_3 Thin Films by Spray Pyrolysis and Its Gas Sensing Performance ., International Journal On Smart Sensing And Intelligent Systems, Vol. 5, No. 3, September 2012
20. Won-Sik Kim , Gas sensing properties of MoO_3 nanoparticles

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synthesized by solvo-thermal method., Journal of Nanoparticles Research (2010) 12:1889–189
21. Longqiang Wang,, December 2013, Synthesis of Crystalline/Amorphous Core/Shell MoO_3 Composites through a Controlled Dehydration Route and Their Enhanced Ethanol Sensing Properties., Crystal Growth & Design
22. E. Comini 2003, Response to ethanol of thin films based on Mo and Ti oxides deposited by sputtering, Sensors and Actuators B 93 (2003) 409–415
23. Li-li Sui, November 2014, Construction of three-dimensional flower-like -MoO_3 with hierarchical structure for highly selective triethylamine sensor., Sensors and Actuators B 208 (2015) 406–414

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