This is an Accepted Manuscript, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this Accepted Manuscript with the edited and formatted Advance Article as soon as it is available.

You can find more information about Accepted Manuscripts in the Information for Authors.

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal’s standard Terms & Conditions and the Ethical guidelines still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this Accepted Manuscript or any consequences arising from the use of any information it contains.
Advances in designs and mechanisms of MoO₃ nanostructures for gas sensors: A holistic review

Ritu Malik¹, Nirav Joshi², Vijay K. Tomer*¹,*

The rapid expansion and development of industrial sectors and corridors have posed a significant threat to the world today owing to the deteriorating air quality resulting from the release of harmful and toxic gases into the atmosphere. To combat and tackle down air pollution, reliable and precise sub-ppm detection of these gases is highly desirable for human safety and the environment. For a gas sensor to perform at its level best, the choice of nanomaterials is a critical factor that can significantly impact the robustness, stability, cost-effectiveness, sensitivity and selectivity of the sensing device. Molybdenum trioxide (MoO₃), as an n-type semiconducting metal oxide, has been rated as the research hotspot material in recent years for its utility in a wide range of important technological applications. Thanks to the advancement of synthesis techniques which has made it possible to explore numerous novel nanostructures and integrate them into smart gas sensing devices. In this quest, this review is an effort to highlight various nanostructures of MoO₃ and the influence of these morphologies on its gas sensing performance. A detailed morphological overview of pristine MoO₃ nanomaterials ranging from one-dimensional (1-D) to three-dimensional (3-D) nanostructure formation followed by preparation of different heterostructures including MoO₃/metal oxides (p-type and n-type), MoO₃/noble metal decoration, and MoO₃/2D materials in the thematic domain of gas sensing has been presented. Finally, a future outlook on the further progress of the MoO₃ gas sensors based on the current scenario is also suggested.

Introduction

The recent advancement in technology and its rapid adaptation by society has indeed marked an unparalleled impression on the quality of our lives. Nevertheless, the increasing usage of energized devices and various other components to sustain the routine lifestyle has undoubtedly dented our mother earth with the increased emissions of toxic and greenhouse gases and spilling of hazardous chemicals/substances into the atmosphere. As a consequence, last two decades have witnessed a surprising upsurge in the environmental monitoring technologies along with the routine industrialization. One important aspect to mitigate environmental pollution is monitoring toxic and hazardous gases, where the search for faster, more sensitive, and low power consumption gas sensors is never-ending. As an example, an efficient and quick detection of the harmful gases as a result of accidental of at petrochemical plants/ sewage plants/mines could not only save money but also many important lives. With the assistance of a distributed network of gas sensors, a single sensor in such a network should accurately identify gases present in a complex mixture, be sensitive enough to detect harmful gases at the lower concentrations, function at low power consumption, and be cheap enough to provide high spatial resolution across a wide range of sensors. Yet, the commercially available gas sensors are not mature with respect to some of these characteristics. In particular, the selectivity between NH₃, NOₓ, and CO for room temperature operation is still a matter of concern for commercially available gas sensors, especially in the low ppm range. Besides, most of the existing gas sensors work at temperatures tens or hundreds of degrees above room temperature and require a huge amount of power for their functioning. So far, a variety of gas sensors including acoustic, electrochemical, optical, and resistance sensors have been developed based on their working principle; however, metal oxide (MOx) based resistive gas sensors have enjoyed the privilege over other materials for their high sensitivity, easy fabrication, lightweight, low fabrication cost, and simple detection method.

Molybdenum trioxide (MoO₃), is one of the intriguing wide band gap n-type semiconductor with three unique polymorphous crystalline forms: orthorhombic α-MoO₃ (thermodynamically stable phase), monoclinic β-MoO₃ (low temperature metastable phase), and hexagonal h-MoO₃ phases. MoO₃ has several merits like unique layered structure, tunable band gap, high electron mobility, low cost-phase-controlled synthesis, non-toxic and excellent electrochemical property which prompts increasing interest in this fascinating material. In particular, the α-MoO₃ has excited the research community with its layered anisotropic structure wherein the layers are parallel to the (010) crystal plane. Every layer is composed of two further sublayers which are formed by corner-sharing MoO₆ octahedra along the [001] and [100] directions. The two sublayers then bind together with van der Waals forces by sharing the edges of the octahedra along the [001] direction to form MoO₆ octahedra layers. These layers then alternately stack along the [010] direction to form an α-MoO₃ structure. This unique layered structure of α-MoO₃ has increases content of pentavalent Mo⁵⁺ ions, which possesses strong affinity to oxygen. Since gas sensors function by the reaction between oxygen and adsorbed analyte gas molecules, the presence of Mo⁵⁺ increases the adsorption effect, thus resulting in enhancing the gas sensor response. In recent times, the MoO₃ based gas...
ARTICLE

One dimensional (1-D) MoO₃ nanostructures for gas sensor:

In recent years, the development of 1-D MoO₃ nanostructures with a high S/V ratio has received tremendous attention due to their speedy charge transfer throughout one spatial dimension in the range of 1–100 nm. The 1-D nanostructure materials consist of a networked structure which reduces the agglomeration while simultaneously facilitating the diffusion of the analyte gas molecules on the material surface. Ultralong 1-D structures are known for providing a direct transport path for electrons to propagate along the axis, which greatly enhances the gas sensing performance. Moreover, the gas sensors made of these 1-D nanostructures offer ultra-sensitivity, fast response, higher stability, low-temperature operations, and less power consumptions. Till date, variety of 1-D nanostructures including nanobelts, nanorods, nanowires, and microrods have been utilized in gas sensors and the following section summarizes about these nanostructures with their gas sensing performance and mechanism. An overview of gas sensors based on 1-D MoO₃ nanostructures is listed in Table 1.

MoO₃ Nanobelts (NBs):

Nanobelts of MoO₃ are one of the most prominent 1-D morphologies that have attracted huge attention owing to their single crystalline nature and large aspect ratio. It is due to their faceting nature which makes the NBs suitable candidates for probing size and dimensionality dependent physical or chemical phenomena. Yang et al. prepared the NBs of Zn doped MoO₃ using the hydrothermal (HT) method and demonstrated the ethanol sensing performance. The group prepared the nanocomposites in various Mo/Zn ratios, and the FESEM images in Figure 1a–f reveal that increase in the Zn ionic content in the layered MoO₃ causes an increase in the spaces between its layers to accommodate more Zn ions, thereby broadening the width of the MoO₃ nanobelts. The operating temperature (OT) dependent response towards 1000 ppm ethanol gas in Figure 1h reveals that the Zn doping in MoO₃ not only causes a depreciation in the OT by 100 °C but also enhances the response by at least 15 times than the pure MoO₃ NBs. Besides, the response (Tₜₐₚ) and recovery (Tᵣₑᵣ) transients to different concentrations of ethanol at the OT of 240 °C in Figure 1i display good reversibility along with a selective response to the ethanol gas was also observed among the other tested gases in Figure 1j. The improved gas sensing performance was accredited to the increased ethanol concentration, the enhanced dehydrogenation progress at a lower temperature, diminishing probability of ethoxy recombination, and the narrowed band gap owing to the Zn doping.

To further promote the sensing properties and selectivity improvement, combination of two metal oxides could be an ideal method. For example, Wang and his group combined MoO₃ NBs with RuO₂ nanoparticles by a simple soaking method and demonstrated that the prepared MoO₃@RuO₂ nanocomposites had superior sensing characteristics. The NBs (diameter ~ 0.8 μm)
The morphology was confirmed in the FESEM results as displayed in Figure 1(k,l), however, no apparent change in the morphology and dimension of the MoO$_3$ NBs was observed on account of addition of RuO$_2$ nanoparticles (Figure 1(m,n)). Due to the n-type behavior of pristine MoO$_3$ NBs and MoO$_3$@RuO$_2$ nanocomposites, it was quite evident that pristine MoO$_3$ NBs demonstrated an impressive sensing performance (Figure 1o) while the electronic movement greatly impacted the resistance of nanocomposite. While evaluating the sensing response for Triethylamine (TEA) gas, the results in Figure 1p illustrated that an OT dependent response of 9.22 and 71.43 was observed at 260 °C and 300 °C for MoO$_3$ NBs and MoO$_3$@RuO$_2$ nanocomposites. The transient response curve in Figure 1q not only illustrated a fast response and recovery (2 s and 10 s) behavior for the prepared nanocomposites but also displayed the benefit of functionalization of pristine MoO$_3$ NBs with RuO$_2$ nanoparticles in enhancing the sensing properties. Additionally, the histogram results in Figure 1r also confirmed the good selective response of the MoO$_3$@RuO$_2$ nanocomposites for TEA gas. The TEA sensing mechanism in Figure 1s illustrated that the existence of highly catalytic RuO$_2$ NPs significantly increases the resistance of nanocomposites in air. Also, the O$_2$ molecules in air tend to get absorbed to generate oxide ions while and a great mass of electron are trapped onto the oxygen. These electrons flow from MoO$_3$ to RuO$_2$ to generate a potential barrier at their interface which gets reduced in the TEA atmosphere, thus causing a 5 times response for MoO$_3$@RuO$_2$ nanocomposites than pure MoO$_3$ NBs.

Xylene is one of the toxic and colorless VOC whose over exposure results in cardiovascular and kidney problems. To detect the xylene, the formation of n-n heterostructures is one of the novel approach, following which the group of Gu et al. had detected xylene gas by preparing an n-n type heterostructure comprising of Fe$_2$O$_3$ NPs and MoO$_3$ NBs by a two-step HT method. The morphological analysis results in Figure 2a, and 2b shows that the MoO$_3$ NBs are ~200-300 nm in width while ~2-3 nm in length, and also the nanobelt structure of MoO$_3$ was retained even after uniformly doping of Fe$_2$O$_3$ NPs (Figure 2c and 2d). The sensor response to the xylene gas at different OTs in Figure 2e displayed that although the pure MoO$_3$ detected xylene gas at a lower temperature than the Fe$_2$O$_3$/MoO$_3$ NBs, yet the former exhibited a lower maximum response than the nanocomposite. The selectivity results in Figure 2f reveals that the response to the xylene gas was the highest for Fe$_2$O$_3$/MoO$_3$ NBs, and ~250% improvement in the sensitivity was observed than pure MoO$_3$ NBs. The research group attributed the superior sensing performance to the unique n-type heterojunction between MoO$_3$ NBs and Fe$_2$O$_3$ nanospheres. Another example was reported by Wang and co-workers on very known p-n heterostructures because of their effective charge separation, long-life of charge carrier to make them more favorable to achieve high sensor response and selective sensing towards target analytes. They utilized a simple dipping-annaeling process and developed p-n heterojunctions of CoMoO$_3$ and MoO$_3$. The MoO$_3$ NBs were smooth, having 100 nm thickness, 100-300 nm width, and a few micrometers length (Figure 2g), while the rough surface of CoMoO$_3$/MoO$_3$ nanocomposites in Figure 2h illustrated the successful growth of the CoMoO$_3$ NPs on the MoO$_3$ NBs. The TEM results in Figure 2i and 2j further confirmed the uniform dispersion of CoMoO$_3$ nanoparticles (20-50 nm diameter) on the surface of MoO$_3$ NBs. The sensing results towards triethylamine (TMA) gas in Figure 2k reveals that the CoMoO$_3$/MoO$_3$ nanocomposites-based sensors show better sensing performance while causing a reduction of 60 °C in the optimum temperature as compared to the pristine MoO$_3$ NBs. The sensing response as the function of TMA concentration in Figure 2l reveals the stronger response (4-fold) of the nanocomposite to 200 ppm TMA then the pure MoO$_3$, while the dynamic responses in Figure 2m were seen to be perfectly repeatable and reproducible during 3 cycles of switch ‘on’ and ‘off’ measurement. It was concluded that the formation of potential barrier between the CoMoO$_3$ (p-type) and the MoO$_3$ (n-type), the stronger oxygen adsorption of CoMoO$_3$, and the formation of crystallographic defects all together resulted in superior sensing performance.

Noble metal NPs such as Ag, Au, Pt, and Pd, with their outstanding catalytic effect, have been known to improve the sensing attributes of the MoO$_3$ NBs. For instance, Zhang et al. have prepared catalytic Au NPs doped MoO$_3$ NBs via hydrothermal method and displayed superior sensing performance to TMA gas. The MoO$_3$ NBs were 100-300 nm wide and 10-20 µm (Figure 3(a,b)), while the FESEM image in Figure 3c revealed that several Au NPs were stick on the surface of the NBs. In addition, the HRTEM image in Figure 3d displayed the non-continuous distribution of Au NPs (diameter ~10-20 nm) on the MoO$_3$ NBs surface, which confirms the high crystallinity of the MoO$_3$ NBs and Au NPs. The sensing response of the prepared materials towards TMA gas demonstrated an increase-maximum-decay (IMD) type of pattern with the increase in the OT (Figure 3e). The OT has a considerable impact on the sensing performance of the material owing to the thermal energy of the analyte gas molecule for clearing the energy barrier of the surface reaction and later converting the adsorbed oxygen for further attracting the electrons from the semiconductor. The dynamic response-recovery curves in Figure 3f displayed a fast response (T$_{rec}$~7s) and recovery (T$_{rec}$~10s) time for Au@MoO$_3$ NBs to 10 ppm TMA gas. Besides, the as-prepared materials also demonstrated the highest response to the TMA gas (Figure 3g). Overall, the improved sensing performance was accredited to the catalytic Au NPs, which with the help of reactive oxygen species, improves the electrons exchange process between Au NPs and MoO$_3$.

In the last couple of decades, the detection of VOC present in the indoor environment has received much attention. The VOCs are produced as a result of gaseous emission from commonly uses household products such as nail pains, wall paints, furniture, and cleansers and causes both short- and long-term effects on the person’s health. Formaldehyde (HCHO) is one of the VOCs found in many daily usage products, such as carpets, wood, and other plastic products, widely used in every household. There have been several ways to enhance the selectivity of a sensor for a specific VOC and have remained a great topic of interest among researchers. For example, Gu and coworkers had prepared MoO$_3$ NBs using a facile HT method and surface-decorated with Pt NPs to illustrate superior
sensing response towards HCHO gas. The SEM image in Figure 3h reveals the width of pristine MoO₃ NBs to be ~200-400 nm with very minute thickness (inset). The other SEM images (Figure 3i-m) further displayed the increasing presence of Pt NPs with its loading amount on the MoO₃ NBs. The TEM images in Figure 3n and 3o for M-Pt3 (Pt-loading amount = 0.61%) not only confirms the presence of the highly crystalline MoO₃ NBS but also revealed the occurrence of small Pt NPs on the surface of the MoO₃ NBs. The response results in Figure 3p expose the poor performance of pure MoO₃ NPs while with the appropriate Pt% decorated MoO₃ (M-Pt3), NBS cause an improved sensing response to the formaldehyde gas. An outstanding selectivity to formaldehyde gas among the other interfering gases was illustrated in Figure 3q. The M-Pt3 sensor shows no response to ethanol, while a negligible response of 0.1% to acetone was observed. The sensing mechanism in Figure 3r reveals that the astounding sensing performance was due to the presence of the highly catalytic Pt NPs, which reduces the adsorption activation energy of HCHO on the surface of MoO₃ and also assists in forming of spillover region around the Pt NPs on the surface of MoO₃ NBs. Overall, according to the research reported by Xu et al., the oxygen species tends to preferable adsorb on Mo⁵⁺ causing an increase in the intensity of chemisorbed oxygen on the surface of NBs, thus enhancing the gas sensing response. In addition, the higher specific surface area of NBs provides more absorption sites and contributes positively in the gas sensor response.

MoO₃ Nanoribbons (NRBs):

Similar to the nanobelts, the nanoribbons (NRBs) morphology has been quite a popular 1-D material with oxide nanostructures offers spontaneous electron transfer and ensures that the diffusion of the gas molecule results in improving the sensor response along with optimizing the response/recovery times of the gas sensor. The group of Yang et al. demonstrated a one-step HT method for uniformly loading the orthorhombic MoO₃ NRbs on the exfoliated graphene oxide (GO) supporting layers (Figure 4i-1). The SEM image in Figure 4i-2 revealed that the as-synthesized products were composed of large amounts of NRbs (length ~10 μm) loaded on the graphene nanosheets while MoO₃ NRbs were also clearly located on either side of the graphene nanosheet in Figure 4i-3. The hydrogen sensing responses in Figure 4f displayed the nil response of pure graphene nanosheets despite the fact that a little addition of graphene in MoO₃ NRbs enhances the response and reduces the Teoff/Tr rec time considerably. The selectivity results for the GO/MoO₃ NRbs in Figure 4h further attest to the fact that the sensor responded perfectly to the H₂ gas. Such a high response was credited to the formation of innumerable MoO₃/graphene heterojunctions (Figure 4i) and also the high surface area of the nanocomposite as a result of adding the graphene networks, which not only loosened the structure but also enhances the conductivity of the sensor.

The group of Yang et al. have prepared Fe-doped orthorhombic MoO₃ (α-MoO₃) nanoribbons and demonstrated superior H₂ sensing performance. The first-principles Density functional theory (DFT) calculations was used to calculate the adsorption of O₂ and H₂ molecules on the surface of Fe/MoO₃ (Scheme 3). It was observed that the oxygen was adsorbed in parallel to the surface of the Fe/MoO₃ in three modes, i.e., along the x-axis (mode O-1) with adsorption energy being -0.539 eV; y-axis (mode O-2) with adsorption energy of -0.461 eV and perpendicular to the plane of the Fe-doped MoO₃ (mode O-3) with adsorption energy being -0.673 eV. The results in Scheme 3a indicated that the oxygen atoms numbered 1 was - 0.09 e, and numbered 2 was -0.06 e in the adsorbed oxygen molecule. This causes the transfer of -0.15 e from the Fe-MoO₃ to the adsorbed oxygen molecule. These theoretical results further confirmed the capturing of the electrons from the adsorbed oxygen on the surface of Fe/MoO₃.

In most cases, metal oxide-based gas sensors operated at high temperatures (100-200 °C), which hinders the monitoring of the gas composition in the explosive species environment since high temperatures could trigger an explosion. In this way, RT sensors are more favorable due to low power consumption, simplified manufacturing processes, and reduced operating costs. Yang et al. utilized a simple HT method to prepare MoO₃ NRbs and demonstrated superior hydrogen sensing performance. A ribbon-like morphology was observed in the SEM image (Figure 4j) for pure MoO₃ with an average thickness, width, and length of ~90 nm, 270 nm, and 20 μm, respectively, however, the sample calcined in hydrogen gas atmosphere at 300 °C (Figure 4k) demonstrated a depreciated size in all dimensions as compared to the pristine MoO₃ NRbs. The room temperature response transients to H₂ gas in Figure.
4l revealed a typically n-type sensing performance and a fast response/recovery speed. Besides, histogram results in Figure 4m further indicated an excellent selectivity of the MoO$_3$ NRs sensors to the H$_2$ gas. It was also revealed that the sample annealed in the hydrogen atmosphere was ~2.5 responsive to the H$_2$ gas compared to the pristine MoO$_3$. The reason being the higher concentrations of Mo$^{4+}$ and chemisorbed oxygen ions in MoO$_3$ treated at 300 °C (Figure 4n) under hydrogen atmosphere, which resulted in triggering the redox reactions due to increased collision between H$_2$ and O$_2$.

MoO$_3$ Nanorods (NRs):

Owing to the obvious advantages offered by the multi-component heterostructures, which included tunable chemical composition and synergistic properties, Yuan et al. $^{74}$ had prepared 1D α-MoO$_3$ NRs by using a facile HT method and used them as backbone for growing porous NiC$_2$O$_4$ nanosheets (Figure 5a) via chemical deposition (CBD) method. The FESEM results in Figure 5b-1 and 5b-2 for α-MoO$_3$ NRs reveal its clean surface with uniform length (20 μm) and width (200 nm). A cluster of porous NiC$_2$O$_4$ nanosheets coated on the surface of 1D α-MoO$_3$ NRs (Figure 5b-3) further indicated a porous and complex surface of the NiC$_2$O$_4$/α-MoO$_3$ composite. The gas sensing results in Figure 5c displayed the nil response of pure 1D α-MoO$_3$ NRs and NiC$_2$O$_4$ towards ethanol, while the NiC$_2$O$_4$/α-MoO$_3$ composite indicated a p-type semiconductor behavior. Furthermore, NiC$_2$O$_4$/α-MoO$_3$ composite showed good repeatability and excellent stability without any deviation in response upon alternate purging of fresh air and 1 ppm ethanol vapor (Figure 5d). The cross-responses to different gases in Figure 5e also revealed the highest response of the NiC$_2$O$_4$/α-MoO$_3$ composite to the ethanol gas. The research group attributed the superior response to the unique heterostructure between α-MoO$_3$ and NiC$_2$O$_4$, which owing to their different acid-base and reductive-oxidative properties promote the adsorption and oxidation of ethanol.

As stated earlier, the surface doping of SMOx with noble metals is also considered a brilliant approach owing to their higher catalytic activity $^{129-134}$. In particular, Ag NPs being comparatively cheaper and higher catalytic performance, have been extensively explored in promoting the sensing performance in oxide-based sensors. Considering this, the research group of Tian et al. $^{75}$ have successfully demonstrated the decoration of Ag NPs on the surfaces of α-MoO$_3$ NRs. The morphological results in Figure 5f-1 displays the presence of α-MoO$_3$ NRs with smoother surfaces having lengths and diameters of about 10 μm and 200-300 nm, respectively. The Ag NPs of ~20 nm size were clearly observed in the Ag-MoO$_3$ sample (Figure 5f-2), which was further confirmed in the TEM results in Figure 5g-1 and 5g-2. The sensing response results in Figure 5h unveiled the utility of Ag decoration on pure α-MoO$_3$ for enhancing the response towards TEA gas. The effect of temperature on the dynamic transient response curves (Figure 5i) pointed out the incomplete recovery of response to its baseline due to the slower desorption of the gases. The cross-response results in Figure 5j confirm the excellent selectivity of the sensor towards the TEA gas among a variety of other tested gases due to the interaction between basic nature of TEA gas and acidic MoO$_3$ surface. Besides, the electronic and chemical sensitization of Ag NPs was also accounted as major factor in realizing the high response of the Ag/α-MoO$_3$ NRs.

TEA is, as we know, one of the toxic, volatile, and explosive gases used in the fish processing industry $^{4,21}$. It is, therefore utmost important to design superiorly responsive gas sensors for real-time detection of TEA at low OT. For example, Yang and coworkers $^{97}$ utilized a facile hydrothermal method for preparing α-MoO$_3$ NRs (Figure 6a) for detecting TEA gas at low operating temperatures. The α-MoO$_3$ NRs with clean and smooth surfaces and having a length of 10 mm and diameters ranging around 200-300 nm were observed in Figure 6b1-b3. The sensing results for TEA gas in Figure 6c reveals that the MoO$_3$ with NRs-type morphology possess a higher response than the particles based MoO$_3$ at an identical OT. The histograms revealing the response-recovery time in Figure 6d confirmed that a high concentration of TEA causes the $T_{rr}$ to be less than 10 s with longer recovery times and vice-versa. The cross-response results of the sensor for determining its discrimination ability in Figure 6e revealed that the sensor distinguishably detects the TEA gas among other tested gases under the identical tested condition. It was concluded that the high TEA response was not only a result of attractive forces between acidic and basic nature of MoO$_3$ surfaces and TEA molecules, respectively but also resulting from the highly active lattice oxygen, and fast adsorption/desorption kinetics from the sensor surface.

As discussed earlier, heterostructure formation plays a key role on the interface to enhance sensing performance $^{21,135,136}$. Therefore, designing 1D-MoO$_3$ heterostructures with appropriate counterparts is of great importance in order to achieve excellent TEA sensing performance. So, it was further revealed by Bai et al. $^{108}$ that α-MoO$_3$ can dissociate the C-N bond present in the TEA at the desired temperature. They synthesized n-n heterojunction of α-MoO$_3$/BiVO$_4$ via metal-organic decomposition method (Figure 6f) and displayed improved sensitivity towards TEA gas. The SEM and TEM results in Figure 6g-1 and 6g-2 clearly showed the development of BiVO$_4$/MoO$_3$ composite as nanorods and also the growth of BiVO$_4$ nanoparticles on MoO$_3$ nanorods. The response curves in Figure 6h showed an IMD trend for all the materials, however, the response of BiVO$_4$/MoO$_3$ composite was much better than others, however, the longer $T_{rr}$ for BiVO$_4$/MoO$_3$ composite was due to the strong binding of the TEA molecules on the surface of α-MoO$_3$ which ultimately resulted in poor desorption rate (Figure 6i). In the end, the excellent selectivity results in Figure 6j pointed to the fact that TEA, due to its lower C-N bond energy, gets oxidized very easily. It was finally concluded that n-n heterostructured MoO$_3$/BiVO$_4$ composite was primarily responsible for the increased sensor response.

MoO$_3$ Nanofibers (NFbs):

Recently, wet chemical approaches and electrospinning methods have increasingly become popular for the preparation of SMOx NFs that allow the creation of nanostructures with multiple...
configurations and morphological features. In line with this, Guo et al. 78 have prepared SnO$_2$ doped MoO$_3$ NFs (diameter~100 nm) by using a wet-chemical method for the detection of carbon monoxide (CO) gas by screen printing the NFs on alumina substrates (Figure 7a). The response transients in Figure 7b reveals the good reversible behavior of the SnO$_2$/MoO$_3$ under alternative purging of CO and N$_2$ gases. The concentration-based sensing results in Figure 7c displayed an increasing response with the increment in the CO concentration. Besides, the SnO$_2$/MoO$_3$ with NFs morphology exhibited ~2-folds response to 300 ppm CO than the pristine α-MoO$_3$ NBs. The selectivity histograms in Figure 7d revealed that the nanocomposite sensor showed a better response to the CO gas owing to its fine nanofiber diameter and high S/V and. The inset SEM image shows that the SnO$_2$/MoO$_3$ nanocomposite exhibit diversely oriented fibers with diameter and length ranging from 20-100 nm and of 2–8 μm, respectively. It was later concluded that the SnO$_2$ doping assisted in enhanced sensing performances at low OTs while the unique NFs morphology of SnO$_2$/MoO$_3$ nanocomposite and the acidic nature of the doped NFs improves the sensitivity of the SnO$_2$ doped MoO$_3$ NFs.

In another work, the group of Mondal et al. 114 had tailored highly crystalline and ultra-long MoO$_3$ NFs by applying temperature pulsing method during HT growth. The SEM image in Figure 7e demonstrated the presence of highly crystalline ultra-long nanofibers having several tens of micrometer of length and width in the range of 200–300 nm. The sensing results in Figure 7f confirmed that the MoO$_3$ with NFs morphology (M5 – M8) possesses better response at lower operating temperature than the MoO$_3$ with NBs structure (M1 – M4) to the ethanol gas. Owing to the high surface area and more surface defects in MoO$_3$ NFs, a high selectivity (Figure 7g) to the ethanol gas was observed among other tested VOCs. In last, it was concluded that the large surface area and presence of surface defects were the prime reasons for the improved sensing performance of the MoO$_3$ NFs.

MoO$_3$ Nanowires (NWs): Metal Oxide nanostructures as nanowires offer a great alternative for low-concentration sensing performance, and their conventional processing enables integration with electronic devices for very large-scale production. Luo et al. 87 had utilized the HT method to prepare ultra-long α-MoO$_3$ NWs based flexible nanowire paper (size ~ 200 mm x 300 mm) on a hydrophobic substrate. The NWs (Figure 8a) demonstrated high crystallinity, good dispersion, long length (~1 mm), uniform diameter (~300 nm), and good sensitivity towards the H$_2$ gas. The results in Figure 8b reveals the increasing response of the sensor (prototype of H$_2$ sensor in inset) with temperature from 230–260 °C. The response/ recovery transient curve in Figure 8c accounts for a fast $T_{on}$ and $T_{off}$ and matches well with the commercial grade sensors for the detection of H$_2$ leakage. Besides, the α-MoO$_3$ NWs paper sensor was found to have excellent repeatability (Figure 8d) wherein the sensitivity, $T_{on}$, and $T_{off}$ are nearly unchanged even after seven repeated cycles. The sensor perfectly detected lower concentration of H$_2$ gas (below 1.5%), however, the $T_{on}$ and $T_{off}$ were increased at these lower concentrations (Figure 8e). The high H$_2$ sensing response was attributed to the high specific surface and porous structures of NWs paper, which eases the absorption of O$_2$ molecules on the sensor surface.

MoO$_3$ Microrods (MRds): Similar to nanorods, the morphology of Microrods (MRds) provides a more surface-volume ratio to achieve rapid adsorption-desorption results in high sensitivity at low concentrations. The group of Liu et al. 88 utilized a facile hydrothermal route to prepare hexagonal MoO$_3$ from peroxomolybdate solution in the presence of NH$_4$Cl. The SEM image in Figure 8f confirmed a rod-like morphology for h-MoO$_3$ MRds with the length and diameter ranging from 12–25 μm and 1.0–3.5 μm, respectively. The selectivity of the h-MoO$_3$ MRds in Figure 8g demonstrated the excellent response to the ethanol gas among a variety of other tested gases. The sensing results in Figure 8h divulge that the h-MoO$_3$ MRds sensor possesses a detection limit of 5 ppm to ethanol and its increases with the concentration of ethanol gas.

Two-dimensional (2-D) MoO$_3$ nanostructures for gas sensor

The 2-D materials increasingly become popular for their sheet-like structures, nanoscale thickness, and high S/V ratio 4,14,20,134,137-139. As a 2-D carbon nanosheet, the graphene, since its discovery, has exhibited important physico-chemical properties, e.g., which make it a hotpot material in many technological important applications, including solar photovoltaics, energy materials, and medicine, and so ignited a quest in discovering other materials that are analogous to graphene in terms of structure and properties. 5,13,14,20,140,141. The research efforts have progressed with a great pace, and a variety of inorganic graphene analogues having layered structures have been developed, which includes oxides (TiO$_2$, SnO$_2$, WO$_3$, MoO$_3$, etc.), chalcogenides (MoSe$_2$, WS$_2$, WSe$_2$, etc.), and a few perovskite-like crystals have been acknowledged for sensing applications. 3,142,143. The 2-D materials are strong adsorbents to organic molecules, and at high temperatures, they tend to partially lose oxygen to become oxygen-deficient and so are considered as the most suitable candidates in VOCs sensing 144. Among the various 2-D nanostructures of MoO$_3$, the nanosheets 64,80,81,145, nanoflakes 146-148, nanoplates 79,149,150, nanolamella 151, nanopaper 152, thin film 153-156, microsheet 157 and microplanks 158 morphology of MoO$_3$ have recently received great research interest in gas sensing applications as they can be used in designing nanodevices with desired crystal orientation due to their anisotropic structures. An overview of gas sensors based on 2-D MoO$_3$ nanostructures is listed in Table 2.

MoO$_3$ Nanosheets (NSs): The 2-D layered MoO$_3$ with a sheet-like structure has emerged as a model oxide material for its excellent sensing properties to a range of VOCs. The group of Liu et al. 40 exfoliate bulk α-MoO$_3$ into single and few-layer NSs by using grinding and sonication methods (Figure 9a-1) and observed an enhanced sensing feature for 2D-MoO$_3$ NSs.
as compared to its bulk powder counterpart. The sensor structure and the equivalent circuit model for sensor testing are demonstrated in Figure 9a-2. The MoO_3 NSs with dimensions in the range of 10–100 nm were recorded in the TEM images (Figure 9b-1), whereas the HRTEM image in Figure 9b-2 shows the multi-layer edges near the periphery of these NSs unveiling its 2-D structure. The operating temperature response (Figure 9c) of the bulk MoO_3 and MoO_3 NSs obtained from different sonication solvents towards 100 ppm alcohol vapor reveal the higher response of MoO_3 with NSs morphology. Similar results were also observed in Figure 9d wherein the MoO_3 NSs exhibited faster response and recovery speed than bulk MoO_3. The histogram representing the cross-sensitivity of the MoO_3 NSs in Figure 9e clearly shown that the sensor possesses a better response to the alcohol among other VOCs. This increased sensing performance of MoO_3 NSs is attributed to its layered structure, offering enhanced surface area and more reactive sites. Contrary to using the exfoliation strategy from single-crystal MoO_3, the Wang and coworkers 44 used a facile hydrothermal technique to prepare MoS_2 NSs and calcine them at different temperatures to obtain MoO_3 NSs with varied thickness. The SEM micrograph in Figure 9f revealed the formation of NSs with uniform and smooth surfaces. The sensing results in Figure 9g presented that the MoO_3 NSs detect the xylene gas at higher OT than the MoS_2 NSs, while the MoO_3 calcined at 400 °C (MoO_3 NSs-4) shows the maximum response among the various MoO_3 NSs structures calcined at different OTs. The response/recovery performance of MoO_3 NSs-4 studied in Figure 9h toward 10 ppm xylene showed quicker T_on and T_off for the sensor. Further, the cross-sensitivity results of the sensor in Figure 9i demonstrated its excellent selectivity towards the xylene gas among a variety of other interfering gases. It was finally concluded that the excellent sensitivity was mainly due to the larger SSA causing increased adsorption of oxygen and the intrinsic porous structure, which results in the abundant surface defects.

Another poisonous and colorless VOC, i.e., TMA, drawn significant attention because initially, the smell looks pungent, but it could rapidly paralyze the olfactory system and cause unawareness, headache. The group of Shen and coworkers 44 detected TMA by developing porous α-MoO_3 ultrathin NSs using a one-step solvothermal (ST) route followed by calcination. The main process of the synthesis procedure and the NSs (size between 500 and 800 nm) obtained at different calcination temperatures are presented in Figure 10a. The OT based response of α-MoO_3 NSs to 50 ppm TMA in Figure 10b depicts an IMD trend for all the materials, yet the NSs obtained at 400 °C calcination temperature shown the highest response among others. The cross-sensitivity results (Figure 10c) of the α-MoO_3-400 to different gases revealed that the response to TMA gas was way higher than to the other test gases. In addition, the sensor displayed minute fluctuation to the TMA gas (Figure 10d) over the course of 3 months, indicating its great stability and reproducibility. This high response was accredited to the porous and ultrathin configuration of α-MoO_3-400, which provides numerous active sites for the adsorption of TMA molecules faster on the sensor surface. The adsorption energies for TMA and O_2 on α-MoO_3 NSs were estimated to be −2.16 and −0.5 eV by DFT calculations. The results in Scheme 4a1 and 4b1 displayed the energetically favorable adsorption positions of TMA on α-MoO_3, and the α-MoO_3 containing O-vacancy (Ov-α-MoO_3) are Mo atom and O-vacancy, respectively. Due to the steric hindrance, the TMA is primarily physically adsorbed on two oxygen atoms and forms a bridge-like structure (O-TMA-O) in TMA-O-α-MoO_3. The adsorption energies of TMA on α-MoO_3 and Ov-α-MoO_3 are −2.16 and −0.25 eV, respectively. The density of states (DOS) results in Scheme 4b1 and 4b2 indicated that on introducing the oxygen vacancy, the Fermi level enters the conduction band, thus causing in lowering the band gap of TMA-O-α-MoO_3 than that of TMA-α-MoO_3. Since the smaller band gap is more favorable to the electron transfer, the TMA states appear in the conduction band near the Fermi level, indicating that the interaction between TMA and Ov-α-MoO_3 is enhanced.

Surface modification with the noble metal is a known practice in the sensing field. Essentially, noble metal NPs can facilitate the adsorption of oxygen molecules and accelerate the transfer of electrons to metal oxide surfaces 34. For instance, the research group of Yan et al. 146 used a chemical reduction method for depositing Au NPs onto the MoO_3 surface to prepare Au-loaded MoO_3 NSs. The TEM image in Figure 10e displayed the average distribution of Au NPs of size 10-15 nm on the surface of MoO_3 NSs. The temperature-dependent response curves towards ethanol in Figure 10f exhibited an ‘increase–maximum–decrease’ tendency, whereas the Au@MoO_3 NSs possess ~12 times better response than the pristine MoO_3. Same behavior was illustrated in Figure 10g, wherein the Au@MoO_3 NSs show the highest response to the ethanol gas, among others. This high sensing response was accredited to the presence of highly catalytic Au NPs, which assists in enhancing the gas diffusion on the sensor surface.

MoO_3 Nanoflakes (NFks):
Compared to 1D architectures, 2D nanoflakes can provide more efficient electron transport and better mechanical stability due to fewer grain boundaries. In addition, nano-flakes allow surface reactivity and selectivity to be tuned through crystal facet engineering. Tang et al. 146 had developed MoO_3 NFks coupled reduced graphene oxide (MoO_3-rGO) composites for detecting the ethanol gas. The preparation process in Figure 11a revealed that the ultrathin MoO_3-GO were prepared first via HT method, which upon calcination under optimum temperature leads to the formation of MoO_3-rGO NFks. The SEM micrograph of MoO_3-rGO in Figure 11b-1 presented the NFks kind of morphology having a diameter in the range from nanometer to micrometer, while the TEM image in Figure 11b-2 confirms the even distribution of NFks having a diameter 190 nm. These unique 2D NFks of MoO_3-rGO assisted in a high sensitive response towards ethanol gas. The OT dependent response in Figure 11c indicated high sensitivity of the MoO_3-rGO sensor against the pure MoO_3 due to the slightly large SSA of MoO_3-rGO than MoO_3. Besides, the cross-sensitivity results in Figure 11d presented the excellent sensitivity and selectivity of the MoO_3-rGO sensor to the ethanol gas, which was attributed to the high volume of MoO_3 in the nanocomposite as compared to the pristine MoO_3. In addition, the presence of GO substrates in MoO_3-rGO offers large

This journal is © The Royal Society of Chemistry 20xx J. Name., 2013, 00, 1-3 | 7
surface accessibility and fast carrier transport, which facilitated the gas analyte adsorption/diffusion and transport across the sensor surface, while the defects or edge areas in the GO also majorly contributed to the adsorption of the gas molecules.

Considering the potential of the heterostructured nanocomposites consisting of two or more types of metal oxides due to their individual synergetic effect in enhancing the sensing response, the group of Gao and coworkers prepared porous MoO$_3$/SnO$_2$ NFks using graphene sheets (G) as sacrificial templates (Figure 11e) and revealed the excellent sensing performance towards H$_2$S which is a poisonous, corrosive and flammable gas. The TEM micrographs of MoO$_3$/SnO$_2$ NFks in Figure 11f demonstrated the presence of the agglomerated structure with porous SnO$_2$ NFks (diameter ~ 8–12 nm). The results in Figure 11g presented that the MoO$_3$/SnO$_2$ NFks demonstrated better sensing properties (~5 times response) than the pure SnO$_2$ and that too at lower working temperature. The cross-sensitivity results in Figure 11h further attests to the superior sensing response of the MoO$_3$/SnO$_2$ NFks to the H$_2$S gas as compared to the pure SnO$_2$ based sensor. The superior sensing response of the MoO$_3$/SnO$_2$ NFs was credited to the presence of large surface area, and n–n heterojunctions which favors the faster gas diffusion thus resulting in improving the H$_2$S sensing performance. In another work, the group of Comini et al. utilized an evaporation-condensation method to prepare Au-loaded MoO$_3$ NFks for detection of H$_2$S gas. Due to the smaller dimension and better separation, a large number of H$_2$S molecules became absorbed on the surface of Au-MoO$_3$ NFks, ultimately resulting in enhanced sensing performance. The TEM micrographs in the inset of Figure 11i revealed the clear presence of homogenized Au NPs (diameter ~ 10–12 nm) on the surface of the MoO$_3$ NFks. The RT dependent response of pure MoO$_3$/SnO$_2$ NFks (Figure 11i-1) and Au-MoO$_3$/SnO$_2$ NFks (Figure 11i-2) indicated the increased response of the MoO$_3$ NFks with Au functionalization. The results further revealed a 10 times better response for Au-MoO$_3$ sensor than pure MoO$_3$ NF while the optimum OT gets reduced from 450 °C to 400 °C. The dynamic response/recovery transients in Figure 11j depict the excellent reversible response, which, when exposed to reducing gas, increases and restored to the initial values on account of exposing to the natural air. From the results, it was concluded that the Au-MoO$_3$ NFks owing to its enhanced surface area and formation of Schottky barriers at the interface between Au and MoO$_3$, promotes gaseous oxygen dissociation, which ultimately resulted in enhancing the sensor response to the H$_2$S gas.

MoO$_3$ Nanoplates (NPts):

Nanoplates have been actively used as sensing elements in sensing devices, and these nanoplates are mainly synthesized via wet chemical approaches such as hydrothermal or solvothermal due to their simple operation, low cost, and controlled morphology. The group of Chen and coworkers had developed α-MoO$_3$ NPts using molybdate-based inorganic-organic hybrids and demonstrated superior sensing performance to the ethanol gas. The TEM image in Figure 12a displayed several overlapping quadrilateral plates (average length ~ 1–2 μm). The sensitivity of the α-MoO$_3$ NPts as a function of the concentrations in Figure 12b presented the highest response of the sensor to the ethanol vapors among other tested reagent vapors. The response of the α-MoO$_3$ NPts sensor to the OT in Figure 12c shows that the OT causes no apparent influence on the response in the low concentration range, whereas, in the higher concentration region, the α-MoO$_3$ NPts shows better sensitivity at lower temperatures.

In addition, UV light illumination is one of the alternative ways to improve recovery speed. On illuminating the sensor with the UV light, the adsorbed oxygen ions on the surface are removed, thus providing a clean surface with more fresh interaction sites that are readily available for interaction with the target gas. Using this method, the group of Kalanur et al. prepared a H$_2$ sensor by depositing Pd NPs on hydrothermally synthesized MoO$_3$ NPts. The SEM images in Figure 12d–1 for pure MoO$_3$ NPts revealed their length, width, and thicknesses to be in the range of 1–4 μm, 100–150 nm, and 10–20 nm, respectively. Also, the NPts-type morphology of MoO$_3$ was found to remain unchanged after Pd deposition and UV exposure (Figure 12d–2). The TEM image (Figure 12e) further supported the SEM results wherein the Pd NPts (diameter ~5–20 nm) were clearly deposited on the smooth surface of MoO$_3$. The RT I–V characteristics of the sensor in the open air (Figure 12f) displayed that the current level increased with the H$_2$ concentration. The studied mechanism in Figure 12g indicated the chemochromic effect as a result of the structural changes from H$_2$ gas. This indicated the co-occurrence of oxygen vacancies and water molecules in the MoO$_3$ crystal. Due to the spillover effect, the Pd NPs dissociate the adsorbed H$_2$ molecules into H$_2$ atoms, which are transferred onto MoO$_3$ NPts and assisted in generating oxygen vacancies.

Air quality issues caused by exhaust gases from rapid industrialization have become a serious problem worldwide in recent years. Particularly nitrogen dioxide (NO$_2$), which causes photochemical smog and acid rain, is one of the toxic gases emitted during combustion in the industry. The high risk of respiratory and lung disease will increase when exposed to this gas. Therefore, a reliable NO$_2$ sensor for air quality monitoring is needed, and in this regard, the group of Felix and coworkers utilized a facile polymeric solution method to prepare rectangular α-MoO$_3$ NPts and demonstrated good NO$_2$ sensing performance. The SEM image in Figure 12h illustrated a well-faceted rectangular NPts morphology of the α-MoO$_3$ samples prepared at 400 °C for 1h as a function of the number of layers deposition. The transient response curves in Figure 12i revealed that the resistance for NO$_2$ increased while an opposite behavior was observed for the H$_2$ gas. Also, the sensor was able to exhibit a highly reversible response down to the sub-ppm values for both gases. The response results as a function of the OT and the NO$_2$ concentration in Figure 12j revealed an increase-maximum-decrease kind of pattern for all the tested concentration ranges. The results indicate that the unique synthesis method assisted in the growth of 2-D MoO$_3$ NPts on crystalline substrates thus eliminating the requirement of any transfer process and leading to the development of high-performance gas sensor.

MoO$_3$ Nanolamella (NLm):
Various VOCs are extremely volatile and harmful to people even at low concentrations, and formaldehyde (HCHO) is one of them, which has recently become a major indoor pollutant. Overexposure to this VOC can cause throat irritation, eye irritation, and even cytotoxic effects. The group of Shen and coworkers\textsuperscript{151} have utilized a ST method to developed Ni-doped α-MoO$_3$ NLM and demonstrated a promising formaldehyde gas sensor. The SEM image in Figure 13b revealed that the response followed an IMD pattern. Besides, the optimized Ni/α-MoO$_3$ NLM indicated a ~4 folds response as compared to the pristine MoO$_3$ under the identical testing conditions, thus revealing the benefits of doping Ni NPs in MoO$_3$. The dynamic response characteristics of sensors to increasing formaldehyde concentration Figure 13c represented a fast response/recovery of the Ni/α-MoO$_3$ NLM at all concentration values (detection limit ~3 ppm). The selectivity results in Figure 13d further attest to the high response of the Ni/α-MoO$_3$ NLM to the formaldehyde, among other tested gases. The improved formaldehyde sensing performance of Ni/α-MoO$_3$ NLM was the result of formation of the p-n junction and the increase of concentration of oxygen vacancies.

**MoO$_3$ Nanopaper (NPr):**

Working in the direction of ‘one stone two birds’, Lee and coworkers\textsuperscript{152} designed a free-standing, flexible, semitransparent ultrathin MoO$_3$ NPr sensor (Figure 13e) from the MoO$_3$ NPs for the detection of TMA and H$_2$S. Due to the presence of Lewis-acid sites, the MoO$_3$ exhibited a high sensitivity to both TMA and H$_2$S. The SEM images in Figure 13f-1 to 13f-4 confirmed the formation of uniform MoO$_3$ NPr, which consists of highly interconnected MoO$_3$ NPs coated on the electrodes. The MoO$_3$ NPs with a width of 200-400 nm and length of 100-200 µm could bridge two electrodes over the gap (100 µm). The OT dependent MoO$_3$-NPr sensor in Figure 13g depicted maximum responses to TMA and H$_2$S at 325 and 250 °C, respectively. The selectivity of the MoO$_3$-NPr sensor at 325 °C in Figure 13h revealed a good selectivity towards TMA, whereas the dynamic sensing curves of the MoO$_3$-NPr sensor in Figure 13i revealed that the sensor could detect both H$_2$S (25 ppb) and TMA (4.26 ppb) gas at a very low concentration which is much better than the detection results of human nose. It was concluded that the high chemical affinity of MoO$_3$ to the H$_2$S analytes was the reason for its sensitive, selective, and reversible detection at 250 °C, whereas the acid–base interaction between acidic MoO$_3$ and basic TMA was responsible for its detection at 325 °C.

**MoO$_3$ Thin Films (TFm):**

The thin-film (TFm) morphology is one of the extensively explored 2-D structures of oxide materials for gas sensing applications. For MoO$_3$, numerous techniques, including spray pyrolysis, sol-gel, sputtering, pulsed laser deposition, chemical vapor deposition, thermal evaporation, and electrochemical deposition, have been taken into practice for the deposition of MoO$_3$ films.\textsuperscript{65,67,68,71} The research group of Pandeeswari et al.\textsuperscript{13} have utilized the spray pyrolysis technique to develop α-MoO$_3$ films for detection of TMA vapors in mixed environment at low OT. The FESEM image in Figure 14a clearly presented a film surface morphology for α-MoO$_3$ TFm consisting of rectangular crystallites with an average width of 62 nm and length of 450 nm. The response of the film for different TMA concentrations in Figure 14b indicated an increase in the response up to 50 ppm, over which the response became saturated (curve a), which could be due to the limited number of oxygen-adsorption sites. With the increase in the TMA concentration, more electrons were freed-up, which decreases the electrical resistance (curve b). The transient response/recovery curves in Figure 14c revealed an instantaneous change in the resistance, while for a given concentration of TMA, the $T_{res}$ was greater than the $T_{rec}$. The selectivity results of the α-MoO$_3$ TFm sensor in a mixed-vapor environment (Figure 14d) revealed very little variation in the resistance to the TMA gas, thus revealing a good selectivity towards TMA.

In order to further enhance the sensor response compared to the above-mentioned gas sensors, it is essential to adjust the morphology, modify the surface or combine other oxide and 2-D materials. The group of Mane et al.\textsuperscript{14} prepared MoO$_3$/V$_2$O$_5$ TFm using the chemical spray pyrolysis (CSP) deposition method (Figure 14e) for the detection of NO$_2$ gas. The variation in response of MoO$_3$/V$_2$O$_5$ TFm towards NO$_2$ at different OT in Figure 14f presented an IMD pattern, while the maximum response was observed at 200 °C. The dynamic response curves of MoO$_3$/V$_2$O$_5$ TFm in Figure 14g revealed that both $T_{res}$ and $T_{rec}$ decreases with an increase in OT whereas, the larger $T_{rec}$ at lower OT was ascribed to more prominently adsorbed O$_2$ species on the sensor surface. The gas response results in Figure 14h show that the response of gases for MoO$_3$/V$_2$O$_5$ TFm varied in the pattern of CO $<$ CO$_2$ $<$ H$_2$S $<$ NH$_3$ $<$ SO$_2$ $<$ NO$_2$. The higher gas response of 80% for NO$_2$ gas could be due to the unpaired e$^-$ in nitrogen which forms the bond with the oxygen present on the surface and subsequently promotes the chemisorption.

Flexible and wearable gas sensors using flexible substrate have been an active area of research to overcome the problem of operating temperature. In addition, most of the sensors fabricated so far have been based on the deposition of sensing layers on mechanically rigid substrates such as alumina, glass, quartz, or Silicon. In addition, the precise detection of humidity in the indoor climate has also emerged as a research hotspot in recent times\textsuperscript{136,140,162,164} and so the group of Ma and coworkers\textsuperscript{14} prepared α-MoO$_3$ TFm by a simple solution method and prepared a transparent humidity sensor which consisted of laser-etched Fluorine-doped tin oxide (FTO) electrode onto which the annealed α-MoO$_3$ thin film was coated (Figure 14i). The SEM image in Figure 14j revealed that the FTO substrate has an important influence on the film formation process as the morphologies of the film on the channels and FTO electrodes are not exactly the same. Figure 14k represented the excellent transmittance of the prepared sensing device derived from the thin α-MoO$_3$ film and transparent FTO substrate, which are particularly helpful in achieving superior response to humidity under ambient conditions (Figure 14i). The dynamic current–time curve in the presence of NO$_2$ sensor was presented in Figure 14l.
Figure 14m revealed the superfast $T_{\text{res}}$ and $T_{\text{rec}}$ of the humidity sensor. In addition, the sensor possesses good anti-interference ability as its selectivity to moisture was way higher than other test gases (Figure 14n) under similar testing conditions.

MoO$_3$ Microsheets (MSh):

Due to the high degree of anisotropy and chemical functionality of 2D microsheets have attracter researchers to develop reliable and robust gas sensors. Jiang et al. 157 had developed MoO$_3$ MSh by thermally oxidizing the MoO$_2$ nanospheres, which were prepared by a HT method. The FESEM micrographs of MoO$_3$ MSh in Figure 15a depicted the formation of homogeneous MSh with the length and thickness of a single MSh about 2-3 μm and 150 nm, respectively. The OT dependent response of the MoO$_3$ MSh in Figure 15b indicated an IMD pattern with a maximum at 275 °C. Additionally, the cross-sensitivity of the prepared sensor to the TEA among a variety of interfering gases in Figure 15c revealed that the MoO$_3$ MSh response to the TEA was highest when compared to the precursor MoO$_2$ and commercial MoO$_3$ material. The stability results of the MoO$_3$ MSh sensor during a 5-month exposure to TEA gas (Figure 15d) indicated a nil deviation in the baseline resistance (in the air), thus demonstrated an excellent repeatability of the sensor. Besides, the sensor response and recovery time measured during this period remained highly stable. The high content of O$_2$ vacancy on the MoO$_3$ surface and its chemical reaction with the TEA gas molecules were identified as the prime reasons for the excellent sensing performance of the sensor.

MoO$_3$ Micro-planks (MPks):

Lamellar structures such as Micro-planks have recently received a lot of attention due to their large domain structures made up of abundantly assembled nanosheets. MoO$_3$ has a tendency to form a lamellar structure in order to achieve high sensing properties. Halwar et al. 158 put forth a screen printing method for the production of MoO$_3$ MPk and CuO doped MoO$_3$ MPk for CO detection. The FESEM image in Figure 15e illustrated the wooden plank-like structure of the agglomerated MoO$_3$ particles having thickness, width, and length in the range of 1-1.8 μm, ~7.32 μm, and 31.13 μm, respectively. Besides, the surface of the MPk was uniform with very clear boundaries and a few gaps. The results in Figure 15f indicated that the resistance decreases with an increase in the OT, thus revealing its n-type behavior. The CO sensing results in Figure 15g presented that the prepared materials have good sensitivity towards CO gas, and the response was highest among other test gases while the transient curves in Figure 15h demonstrated an increase in the sensor response with increasing CO concentration and the sensor also demonstrated a quick $T_{\text{res}}$ and $T_{\text{rec}}$ to the CO gas. Later it was concluded that the superior sensing performance was due to the collective effects of the thermal energy, excess oxygen species, and catalytic property of copper dopants.

Three-dimensional (3-D) MoO$_3$ nanostructures for gas sensor:

Among various morphological structures, 3-D hierarchical nanostructures (HNS) are assembled from 0-D (nanoparticles), 1-D (nanowires, nanorods, nanotubes, etc.), and 2-D (nanosheets) materials have become increasingly popular among researchers for various applications 165-168. In particular, these 3-D HNS owing to their large SSA and minimized interparticle agglomerations, provides an easier gas molecule diffusion and faster charge propagation on the material’s surface, thus resulting in high sensitivity and a faster response sensing speed 169. Till now, a variety of 3-D MoO$_3$ nanostructures, including nano/micro-flower 83,84,166-168,70, hierarchical 53,73,130-135, nanorays 177-179, hollows spheroids 180,181, core-shell 182-184, microcage 185, nanopompon 186, and microbox 187 have been designed and used in the gas sensing applications (Table 3).

MoO$_3$ Nanoflower (NFLs):

As discussed above, 3-D hierarchical nanostructures such as nanoflowers are generally constructed by low-dimensional construction units that are an effective way to enhance the sensing properties. The group of Sui et al. 81 utilized a surfactant-free ST route to prepare 3-D α-MoO$_3$ NFLs (diameters ~3–5 μm) consisting of microrods with diameters ranging between 150–200 nm and grown radially from the center of the NFLs. The SEM images (Figure 16a-1) illustrate the flower-like coral morphology (average diameters ~150–200 nm and lengths ~2–3 μm) seemingly grown from the MoO$_3$ flower center. The same results were further confirmed by the TEM image in Figure 16a-2. The sensing results in Figure 16b indicated that depression in α-MoO$_3$ NFLs sensor response with increasing OT from 250 to 370 °C was observed for the TEA gas. Additionally, superior response and high selectivity were further confirmed from the cross-sensitivity results in Figure 16c. The transient response result for the sensor in Figure 16d illustrated a fast recovery and response of the sensor to the TEA gas. The exciting sensing performance is the result of the high electronic conduction of the n-type MoO$_3$ and less agglomerated 3-D hierarchically assembled structures of MoO$_3$ NFLs which provide more active sites for the adsorption of TEA molecules.

In addition, the availability of different precursors also allows different nanostructures to be synthesized using a single-step or double-step HT procedure. For example, flower-like morphology exhibits numerous edge sites which interact strongly with gas analytes due to their high catalytic reactivity and thus provides a high sensing response 188. Liu et al. 84 utilized the sodium citrate, and PEG assisted HT method to prepare hierarchical MoO$_3$ NFLs (Figure 16e) for ethanol gas sensing. The SEM image in Figure 16e displayed the hierarchical and rose-like NFLs architectures composed of densely packed thin porous Ss (thickness ~15–18 nm) arranged in a multilayered stacking structure. The OT dependent response of MoO$_3$ NFLs to ethanol in Figure 16f presented a response in the IMD pattern with the maximum response at 300 °C. Besides, the response depicts no sign of saturation with the gas concentration increasing from 100 to 700 ppm in Figure 16g. The voltage of the sensor under different OT revealed the highest voltage from 40 to 80 °C (Figure 16h) whereas the voltage sharply increases when
ethanol gas is purged in the chamber while it returns to its original state when the ethanol gas is out of the measurement chamber. The repetitive response results in Figure 16d demonstrated no significant change in the sensor response while delivering a fast $T_{on}$ and $T_{rec}$ for the sensor. The excellent response to ethanol was accredited to the high SSA and high S/V ratio of MoO$_3$ NFLs, which assisted in improving the reaction sites for gas analytes.

The group of Wang et al. $^{170}$ had experimentally carried and theoretically verified (with DFT) the detection of CO using Zn-doped MoO$_3$ hierarchical microflowers using the density of states (Scheme 5). As can be seen, a significant amount of deformation of Zn-MoO$_3$ surface was observed on account of adsorption of CO, and a charge transfer value of 0.451 e was obtained, thus indicating strong chemisorption. The electron transfer during the adsorption process was verified from the distinct continuous region in Scheme 5b, which is related to the formation of new chemical bonds. A shifting to the lower energy after adsorption was observed in DOS curves which indicated the chemical action in this system. Finally, the introduction of Zn atom promoted the adsorption ability of MoO$_3$ (010), which backs to the experimental results stating the superior gas-sensing performance of Zn-MoO$_3$ samples to CO.

MoO$_3$ Hierarchical Nanostructures (HNS):
Hierarchical nanostructures are perceived as one of the most promising materials and have been widely used in gas sensors due to nanoporous structures with less agglomerated architectures. The group of Li et al. $^{171}$ presented a hexadecyl trimethyl ammonium bromide (CTAB) assisted HT synthesis of $\alpha$-MoO$_3$ HNS NBs, which self-assembled into bundles and aggregate into bird’s nest-like shape HNS and demonstrated superior ethanol sensing performance. The SEM and TEM images in Figure 17a-1 and Figure 17a-2 respectively displayed the presence of a bird’s nest-like HNS with perfectly aligned nano- or micro-porous structures. The length of the single NB is about 250–500 nm, which was wider than that of the monodispersed NBs, and this could be due to the side-sharing assembly of two NBs with the help of CTAB. The OT dependent response of the MoO$_3$ NBs and MoO$_3$ HNS in Figure 17b revealed the ~2.3 folds higher response of MoO$_3$ HNS than its counterpart at 340 °C, while its response was always higher than MoO$_3$ NBs at all the temperature values. The transient response curves in Figure 17c demonstrated the good repeatability of the sensor response to its ground state, although the response/recovery kinetic property of MoO$_3$ HNS was much better than the MoO$_3$ NBs. The superior sensing performance was accredited to the nanoporous geometry, which owing to its minimized stacking configuration, provide abundant sites for chemical reaction as well as effective diffusion channels for gases.

In another work, the research group of Sui and coworkers $^{172}$ prepared a 3-D flower-like $\alpha$-MoO$_3$ HNS from 1-D single-crystalline NBs via a one-step template free ST method and achieved fast detection of TEA at 170 °C. The growth process of $\alpha$-MoO$_3$ HNS, as depicted in Figure 17d, revealed the formation of flower-like nanostructures from precursor nanoparticles and nanobelts. The mechanism of formation was further supported by TEM images in Figures 17e-1 to 17e-4. The SEM image in Figure 17e-5 displayed the presence of numerous NBs (thickness $\sim$20–30 nm) with interconnected sharp tips and rough rims, which are radially assembled into flower-like shapes. The temperature-dependent response in Figure 17f indicated a decrease in the responses of the sensors to TEA gas with an increase in the OT 170 to 290 °C. The response of the sensor as a function of TEA concentrations in Figure 17g presented that the MoO$_3$ HNS possesses the highest response among other MoO$_3$ nanostructures. The cross-sensitivity results in Figure 17h revealed that an excellent response was observed towards the TEA gas. The research group had ascribed the superior sensing performance to the following reasons: (1) the fast oxidation of TEA gas, (2) superior electronic conduction of MoO$_3$, (3) 3-D hierarchically assembled structures, and (4) large SSA and pore volume of the $\alpha$-MoO$_3$ HNS.

As one of the important VOC, ethanol has always demanded for a reliable and robust sensor for it has been in demand in breath analysis, food industries, and the biomedical field. Several approaches have been used to improve the sensing performance of metal oxide-based ethanol sensors. The group of Xia et al. $^{173}$ utilized the facile HT method to prepare 3-D porous $\alpha$-MoO$_3$ sponges with 1-D NRs as building blocks. The schematic in Figure 18a illustrated the formation of porous sponges wherein some NRs randomly grown on the lateral surface of other NRs evolving into a branch which is well crisscrossed to form porous sponges. The SEM image in Figure 18b indicated that the monodispersed NRs (length of 100-200 nm) assembled into porous, spongy-like hierarchical structure with abundant interconnected hollow spaces. The gas-sensing performance in Figure 18c revealed that the 3-D porous $\alpha$-MoO$_3$ sponges possesses ~2 times response than monodispersed MoO$_3$ nanorods in all the concentration range. Figure 18d further indicated that both the sensors possess similar response-recovery dynamics. It was later concluded that the improved sensing performance was not only due to the interconnected porous structures but also due to the significant fraction of the atoms participating in ethanol gas-sensing reaction.

Similarly, the group of Li and coworkers $^{77}$ used the CTAB and polyvinyl pyrrolidone (PVP) to respectively prepare NFs and NSs assembled MoO$_3$ HNS under HT conditions (Figure 18e). SEM images of the NFs assembled MoO$_3$ HNS in Figure 18f-1 and 18f-2 clearly demonstrated the presence of a large number of NFs having sizes 20–25 μm and are assembled around an invisible center. For the NSs assembled MoO$_3$ HNS in Figures 18g-1 and 18g-2, smooth NSs (thickness $\sim$ 20–30 nm) were arbitrarily arranged on the surface of the sphere while numerous NSs were found to cut across each other. The OT dependent response in Figure 18h revealed the better ethanol sensing performance of NS-MoO$_3$ HNS than that of NF-MoO$_3$ HNS. Same was the case with the response/recovery results in Figure 18i. It was later concluded at the high response of NS-MoO$_3$ HNS was due to its higher SSA and the scattered intersection of various NSs on the spherical surface, which causes the formation of semi-closed spaces on the surface of the NS-MoO$_3$ HNS.

MoO$_3$ Nanoarrays (NARs):

This journal is © The Royal Society of Chemistry 20xx

J. Name., 2013, 00, 1-3 | 11
From the perspective of human health, most VOCs are toxic and hazardous, and xylene is one of the carcinogenic gas from BTX (benzene, toluene, and xylene) group. To detect the xylene gas, the group of Qin et al. utilized a two-step solid-state chemical reaction route to prepare Y-doped α-MoO$_3$ NARs composed of nanorods (NRs). The SEM image in Figure 19a displayed the presence of orderly self-assembly NARs having a diameter of about 30 nm. The cross-sensitivity results in Figure 19b revealed that the Y/α-MoO$_3$ NARs have a better selective response than that of the pristine α-MoO$_3$ to all the gases, however, the highest response was observed for the xylene gas. The transient response curves in Figure 19c revealed a very fast response time of the sensors, whereas the long-term stability of the sensors for 30 days in Figure 19d displayed that the response value decreases with time. It was concluded that the defects induced in α-MoO$_3$ NARs after the Y-doping allow larger contact area between α-MoO$_3$ and xylene molecules. Besides, the Y dopants along with increasing the electron donor defects and oxygen vacancies assisted in accelerating the mobility of oxygen ions, thus resulting better response to the xylene gas.

Similarly, Qin and coworkers utilized a solid-state chemical reaction route and prepared α-MoO$_3$ 2-D nanoplates (thickness ∼50 nm) and developed self-assembled orderly NARs (inset of Figure 19e). The OT dependent response to xylene in Figure 19e indicated that the sensor based on S2 (NARs) exhibited better sensing performance than the sensor based on S1 (NPs) but a higher OT due to the close array structure of S2. The transient response in Figure 19f indicated a fast response/recovery time for both the sensor, wherein the response time was close to 1s toward the xylene gas. The stability results in Figure 19g revealed that the response was highest on the 5th day, which observed a sharp drop on the 10th day and stabilized on the 20th day. Besides, the cross-sensitivity results in Figure 19h demonstrated the highest response to the xylene gas. This excellent sensing performance was attributed to the relatively larger SSA and preferentially exposure of the active crystal face.

To further enhance the sensor performance compared to pristine α-MoO$_3$, Qin and his group used a facile solid-state chemical reaction method to develop Fe-doped α-MoO$_3$ (Figure 19i). The orderly array structure self-assembled by NPs was observed in the SEM images in Figure 19j. The OT dependent response to xylene gas in Figure 19k displayed an IMD pattern, whereas the Fe-loaded samples determine better response at a relatively lower temperature than that of pristine MoO$_3$. The response-recovery transients in figure 19l demonstrated a fast response time for all the Fe-doped α-MoO$_3$ materials because the presence of Fe ions generates more oxygen vacancies on the surface of the sensor, which is not a case with pure MoO$_3$. The cross-sensitivity results in Figure 19m revealed that the Fe-doped α-MoO$_3$ NARs displayed the highest response to the xylene gas due to the presence of the benzene ring-like structure, which provides a greater number of electrons for reacting with the oxygen species absorbed on the surface of the sensor. It was concluded that the excellent sensing features of Fe-doped MoO$_3$ NARs arise from its larger SSA, which generates more reactive sites and thus resulting in an enhanced sensing response to xylene gas.

MoO$_3$ Hollow Spheres (HSp): 3-D nanostructures, such as hollow spheres and mesoporous structures, have frequently been used for gas sensing applications. There are plethora of synthetic routes used to design these nanostructures, but the solvothermal approach has paid much more attention due to an easy and cost-effective approach to controlled morphology. Sui et al. have utilized a combination of template-free ST method and calcination process to synthesize monodisperse, hierarchical α-MoO$_3$ HSp of average diameters ∼400-600 nm (Figure 20a). The OT dependent sensing performance towards xylene in Figure 20b displayed an IMD pattern with the maximum response at 250 °C, which was 40 °C less as compared to pure α-MoO$_3$ (290 °C). The cross-sensitivity results in Figure 20c indicated poor selectivity for the pure α-MoO$_3$, whereas the optimized Au/α-MoO$_3$ HSp demonstrated maximum sensitivity to the xylene gas, among others. Besides, the sensor displayed poor sensing performance to gases including ethanol, hydrogen, ammonia, acetone, formaldehyde, and chlorobenzene (Figure 20d). The reason for the improved sensing performance could be due to the Au NPs, which on coordinating with the aromatic rings of xylene, dissociate them faster as compared to the other test gases. Using a similar ST strategy, Zhang and coworkers first time reported the MoO$_3$/Bi$_2$MoO$_6$ hollow microsphere for detecting the TMA gas. The SEM and TEM image in Figure 20e displayed the presence of a hollow microsphere (diameter ∼1.2 μm) whose surface was found to be smooth with some pores observed on it. The temperature-dependent response to TMA in Figure 20f revealed a depression in the sensor response as the OT increases from 170 to 330 °C. The real-time gas response results to TMA at 170 °C in Figure 20g presented an increase in response with the increase of TMA concentration, and an excellent linear relationship to the TMA was also observed. The cross-sensitivity results in Figure 20h unveiled the excellent response to the TMA gas, which could be ascribed to the unique HSp morphology, which provides an excellent surface for the TMA molecules’ diffusion and reaction and the synergistic effect from heterojunction between MoO$_3$ and Bi$_2$MoO$_6$.

MoO$_3$ Core-shell (CSh): In recent times, researchers have proposed highly effective and advanced sensors based on porous core-shell (CSh) structures with higher selectivity and stability. Lee et al. have utilized HT method to prepare MoO$_3$ core and the atomic layer deposition (ALD) method to deposit ZnO shell and prepare MoO$_3$–ZnO CSh nanorod sensors (Figure 21a). The SEM image in Figure 21b-1 depicted a typical rod-like morphology with diameter and length being ∼100 nm and ∼1000 nm, respectively, whereas the TEM image in Figure 21b-2 revealed that the NR consists of a central core (diameter ∼120 nm) which is surrounded by a shell (thickness ∼30 nm). The OT dependent sensing performance in Figure 21c indicated that the MoO$_3$–ZnO CSh sensor shows a better response than the pristine MoO$_3$ at all temperature ranges. The cross-sensitivity results in
Figure 21d revealed that the MoO$_3$–ZnO CSh sensor showed good selectivity to ethanol, among others. The long-term stability results in Figure 21e showed that the MoO$_3$–ZnO CSh sensor response is highly stable and repeatable.

Similarly, in another work, the Xu and coworkers $^{183}$ anchored NiO porous NSs on α-MoO$_3$ NBS using a simple method and developed α-MoO$_3$@NiO CSh P-N heterostructured nanocomposite (Figure 21f). The SEM images in Figure 21g revealed the structure of α-MoO$_3$, which was composed of 10 NBS with a uniform size distribution. This structure of NBS was well maintained in α-MoO$_3$@NiO CSh, however, the surface becomes more coarser than pristine α-MoO$_3$ NBS, which could be due to the successful growth of NiO NSs on its surface in the process of forming the CSh structure. The sensing results in Figure 21h exhibited an IMD kind of volcano-shaped pattern to the acetone gas, wherein the optimized α-MoO$_3$@NiO CSh nanocomposite sensor demonstrated the highest response at its optimal OT due to the highest amount of heterogeneous interfacial bonds. Besides, the response to the acetone gas was also the highest (Figure 21i) among other interferring test gases. The high sensing performance of the α-MoO$_3$@NiO CSh was attributed to its larger SSA to toxic analyte sensing. This review imprints the recent progress and developments made in this area.

MoO$_3$ Microcage (MCg):

One of the metal oxide nanostructures, such as the microcage, is known for its peculiar high-surface architectures conducive to adequate oxygen adsorption and ability to interact with target gas species on the surface. The group of Zhu et al. $^{180}$ utilized a facile template-free HT method to prepare hollow MoO$_3$ microcage as a result of the inside-out Ostwald-ripening and the acidic etching (Figure 22a). The SEM image in Figure 22b-1 displayed the solid MoO$_3$ polyhedrons with a diameter in the range of 1.5–4 μm, while the SEM image of MoO$_3$ MCg in Figure 22b-2 presented a well-shaped hollow cage structure having a smooth surface and a diameter of around 1–1.5 μm. The open holes were also observed on the cage surface, which exposes hollow interior space. The OT dependent sensing performance to the ethanol in Figure 22c displays an IMD pattern, wherein the hollow cages-based sensor demonstrated a better response than the solid polyhedron to the ethanol gas. The response transients of both MoO$_3$-based sensors to ethanol in Figure 22d indicated good repeatability as no change in responses after four reversible cycles was observed for both sensors. It was concluded that the gas adsorption and diffusion were highly facilitated in the hollow MoO$_3$ cages, which provided a larger number of surface-active sites for enhancing the ethanol response.

MoO$_3$ Nano-pompon (NPMn):

Xylene is one of the major VOCs commonly used in the paint industry, and its overexposure may cause skin irritation, hearing and memory loss and may pose a risk of neuroathesia syndrome. The accurate detection of this toxic analyte is therefore essential to ensure a healthy and clean working environment. Jiang et al. $^{186}$ used a facile ST method to develop Ni-doped MoO$_3$ NPMn and demonstrated superior xylene sensing properties. The SEM image in Figure 22e unveiled the presence of rough pommom with a diameter of 200–300 nm, while the inset (TEM image) unveiled the presence of 2-D NSs assembling into the pommom. The OT dependent sensing response in Figure 22f indicated an IMD pattern wherein the peak performance was observed at 250 °C. Besides, The Ni/MoO$_3$ NPMn displayed a better sensing response than the pristine MoO$_3$ at every temperature range. The transient response curves in Figure 22g revealed a very fast $T_{90}$ for the optimized Ni/MoO$_3$ NPMn towards xylene gas due to the increase in number of reactive sites by Ni doping. The cross-sensitivity results in Figure 22h revealed that the Ni/MoO$_3$ NPMn demonstrated a better response to every gas (highest for xylene) than the pristine MoO$_3$ under similar testing conditions. It was concluded that the high SSA obtained and finely-tuned crystallite size after Ni-doping induced changes in oxygen composition and were responsible for the improved xylene sensing performance.

MoO$_3$ Microboxes (MBx):

Other metal oxide nanostructures, such as microboxes, are known for their hierarchical and hollow structures to enhance high sensitivity due to their accessible surface to adsorbed oxygen species and more active sites. Furthermore, their high surface-to-volume ratio mass transfer accessibility could help to achieve rapid response/recovery to target gas. The group of Zhang et al. $^{187}$ used HT method to prepare hierarchical MoO$_3$ MBx from MnCO$_3$ microcubes (MCBs) as the templates. Figure 22i revealed the formation of MoO$_3$ MBx wherein firstly, the nanocomposite of uniform MnCO$_3$ MCBs and MoS$_2$ NSs was prepared by a NT method to form MoS$_2$@MnCO$_3$ CSh MCBs, following which the MnCO$_3$ MCBs templates were removed by HCl washing to obtain the hierarchical Mo$_3$ S$_2$ MCBs, which were calcined at high temperatures to prepare hierarchical MoO$_3$ MBx. The SEM image in Figure 22j revealed the presence of regular MCBs of size about 2–3 μm along with some small openings on its surface, which indicated the hierarchical and hollow MCB structure of MoO$_3$ samples. The OT dependent sensing response in Figure 22k indicated an IMD pattern with maximum response to the ethanol gas at 260 °C. The reproductibility of the sensor to ethanol gas tested in the 3 cycles (Figure 22l) represented no change in the sensing performance along with a fast $T_{90}$ of the sensor. The cross-sensitivity results in Figure 22m and selectivity coefficients in Figure 22n indicated that under identical testing conditions, the sensor responded excellently to the ethanol, which was a result of the hierarchical and hollow structure of MoO$_3$ MBx.

Conclusion and Future scope:

This review imprints the recent progress and developments made in the thematic domain of gas sensing for various MoO$_3$ nanostructures. Herein, we have summarized the different morphologies and structures of MoO$_3$, each with a peculiar sensing performance towards a particular target gas. Various top-down and bottom-up approaches to fabricate the MoO$_3$ nanostructures with different sizes and shapes have been discussed in detail. This comprehensive review concluded to the very fact that those...
morphologies of MoO$_3$ which possess a high surface-to-volume ratio, e.g., nanotubes, nanoflowers, hierarchical nanostructures, core-shell, and microspheres, have been able to attract wide attention among researchers as these morphologies allow for the easy penetration of gas molecules in their porous structure thus resulting in high sensor response. The sensing performance of these nanostructures has been reviewed to detect various hazardous and flammable gases and organic vapors such as ammonia, nitrogen dioxide, hydrogen sulfide, chloride, carbon monoxide, and ethanol formaldehyde, acetone, methanol, etc. Generally, the MoO$_3$-based gas sensors show high sensitivity and lower detection limit; however, their selectivity and operation temperature are major concerns. Some strategies are used to overcome the problem, like surface modification using noble metal NPs or doping/modification with other material and light illumination, but they do not entirely fulfill the requirement for the usage of MoO$_3$ in commercial applications. Following are the key conclusions with the MoO$_3$-based gas sensors to improve their sensing performance:

a) The response could be enhanced by using porous and hollow structures, as it can provide fast adsorption-desorption, diffusion, and transmission of gas molecules to achieve high sensor response at low concentration.

b) Surface modification using noble metal or doping of metal ions could increase the number of reaction sites on the surface results in more oxygen vacancies to interact with target gas and enhance the selectivity.

c) Formation of heterostructures or composites with other oxides or 2-D materials can form abundant oxygen vacancies and creates a more active site for the interaction. This can control the Fermi level and transfer the electrons from a higher energy level to a lower energy level, leading to increased response value and fast response.

d) Light illumination/irradiation could help to achieve high sensor response and fast $T_{on}$/$T_{off}$ at RT by generating photo-induced electron-hole pairs on the MoO$_3$ surface with the chemisorption process.

Although there has been extraordinary progress in designing gas sensors using novel nanostructures, there are still many challenges and problems towards achieving high sensing performance, reproducible synthesis process, high selectivity, miniaturization of the sensor, power consumption/operation temperature. This is very important because the mass-scale production of sensor devices requires a reliable and reproducible process. One of the key challenges is the durability of the sensor at RT since humidity is the main interference for a room temperature sensor. So, from a practical point of view, it is important to investigate the sensing performance under different humid conditions to establish the relationship between the sensing properties and environmental conditions. Another key challenge is selectivity or the interference of gases, which can often hinder sensing performance. There have been few reports on gas sensors detecting the specific gas, but not all the gases, and sometimes detection of specific gas out of a mixture of gases is a major concern. In the case of resistive-based sensors, it is hard to discriminate the gases which can give similar resistive change/response. To enhance the selectivity and remove undesirable confounders, a diffusion filter layer can be made with microporous materials (e.g., zeolite and metal-organic frameworks, active carbon, and polymers (e.g., Nafion65) $^{189}$. In this case, only the filtered molecule can reach the surface of the sensing material. Güntner et al. $^{190}$ demonstrated superior selective sensing towards formaldehyde by using zeolite membranes. With a zeolite Mobile-Five (MFI)/Al$_2$O$_3$ membrane, the Pd-doped SnO$_2$ sensor displayed astounding selectivity (>100) for formaldehyde (down to 30 ppb) at 90% relative humidity.

Lastly, the important aspect to consider is OT in the case of MoO$_3$-based gas sensors. Undoubtedly, temperature plays a vital role in SMOx-based gas sensors to achieve fast response/recovery speed and high sensitivity. At low temperatures, the reaction rate on the metal oxide surface is sluggish, resulting in poor sensor response. By increasing the temperature, the thermal energy given is high enough to overcome the activation energy barrier for the surface reaction; thus, the reaction rate increases and the sensor displays an increasing response to the target gas. However, in order to achieve a high sensor response, we need to compromise the power consumption. To solve this issue, the idea of a low-powered or self-powered microheater has been proposed with advanced MEMS technology to achieve the best possible sensing performance with less power consumption. In addition, an in-depth study of the gas sensing mechanism of MoO$_3$ nanostructures and metal oxides is still needed. Several models and hypotheses on the metal oxide-based gas sensing system are described by the researchers, but there is no such mechanism model that works for an extensive range of gas molecules. Additional analysis may be needed by some advanced tools such as DFT or first principle study.

In conclusion, the key motive of this review was not only to summarize state-of-art but also to inspire the readers and excite curiosity, driving them to further investigate MoO$_3$ based gas sensors. Future directions for understanding more about MoO$_3$-based nanostructures, their sensing mechanism, and future applications have been discussed.

Conflicts of interest
There are no conflicts to declare.

Acknowledgements
This work was carried out with financial assistance from the Brazilian funding agencies: São Paulo Research Foundation-FAPESP (2014/23546-1).
A. T. Güntner, S. Abegg, K. Wegner and S. E. Pratsinis, Sensors Actuators, B Chem., 2018, 257, 916–923.

J. Li, L. Wang, H. Liu, J. Zhao, X. Li, H. Wei and Y. Han, J. Alloys Compd., 2017, 694, 939–945.

J. Li, H. Liu, H. Fu, L. Xu, H. Jin, X. Zhang, L. Wang and K. Yu, J. Alloys Compd., 2019, 788, 248–256.

Y. Mo, Z. Tan, L. Sun, Y. Lu and X. Liu, J. Alloys Compd., 2020, 812, 152166.

X. Li, D. Jiang, Y. Fan, N. Zhang, C. Liu, S. Adimi, J. Zhou, S. Wen and S. Ruan, Inorg. Chem. Front., 2020, 7, 1704–1712.

D. Jiang, W. Wei, F. Li, Y. Li, C. Liu, D. Sun, C. Feng and S. Ruan, RSC Adv., 2015, 5, 39442–39448.

Z. Li, W. Wang, Z. Zhao, X. Liu and P. Song, RSC Adv., 2017, 7, 28366–28372. DOI: 10.1039/D1MA00374G

H. Fu, Z. Wu, X. Yang, P. He, X. An, S. Xiong and D. Han, Appl. Surf. Sci., 2021, 542, 148721.

S. Zhang, P. Song, J. Zhang, Z. Li, Z. Yang and Q. Wang, RSC Adv., 2016, 6, 50423–50430.
| Class     | Material      | Synthesis Method                        | Gas            | Conc. (ppm) | Operating temp (°C) | Response | Resp./Reco. time (s/s) | Ref  |
|-----------|---------------|----------------------------------------|----------------|-------------|---------------------|----------|------------------------|------|
| Nanobelt  | MoO$_3$/Fe$_2$(MoO$_4$)$_3$ | Hydrothermal | Toluene | 50           | 250 | 5.3 | <10/<30 | 101 |
|          | MoO$_3$/ZnO    | Hydrothermal | Ethanol  | 100          | 250 | 19 | 2.5/3.5 | 102 |
|          | MoO$_3$        | Hydrothermal | Ethanol  | 800          | 300 | 174 | 42^*/4^* | 103 |
|          | Zn/MoO$_3$     | Hydrothermal | Xylene  | 100          | 206 | 7.99 | 32/264 | 104 |
|          | MoO$_3$/Fe$_2$O$_3$ | Hydrothermal | Xylene  | 100          | 206 | 6.9 | 87/190 | 105 |
|          | Ce/MoO$_3$     | Hydrothermal | TMA     | 100          | 240 | 17.4 | <10/<20 | 106 |
|          | MoO$_3$        | Chemical spray pyrolysis | NO$_3$ | 100          | 200 | 68%(%)  | 15/150 | 107 |
|          | Fe/MoO$_3$     | Hydrothermal | Xylene  | 100          | 206 | 6.1  | 20/75  | 108 |
|          | Au/MoO$_3$     | Hydrothermal | 1-butyl amine | 100     | 240 | 300 | 23/388 | 109 |
|          | In$_2$O$_3$/MoO$_3$ | Hydrothermal + Chemical synthesis | TMA     | 10          | 260 | 31.69 | 6/9 | 110 |
|          | Zn-MoO$_3$     | Hydrothermal | Ethanol  | 1000        | 240 | 321 | 15/121 (100 ppm) | 111 |
|          | RuO$_2$/MoO$_3$ | Chemical synthesis | TEA | 100          | 260 | 12.8 | 7/10 | 112 |
|          | Fe$_2$O$_3$/MoO$_3$ | 2-step hydrothermal | Xylene | 100 | 233.5 | 22.48 | 4/102 | 113 |
|          | CoMoO$_3$/MoO$_3$ | Hydrothermal + dipping-annealing process | TEA | 100 | 220 | 104.8 | <10/<10 | 114 |
|          | Au/MoO$_3$     | Hydrothermal + Chemical synthesis | TMA     | 50          | 280 | 70 | 6/9 | 115 |
|          | Pt/MoO$_3$     | Hydrothermal + Chemical reduction | Formaldehyde | 200 | RT | 39.3 | 17.8/10.5 (100 ppm) | 116 |
|          | W/MoO$_3$      | Hydrothermal | TMA     | 50          | 200 | 13.8 | 6/11 | 117 |
|          | Pd/MoO$_3$     | Spray pyrolysis + chemical dip | NO$_3$ | 100 | 200 | 95.2%(%) | 74/297 | 118 |
|          | Cd/MoO$_3$     | Hydrothermal | H$_2$ | 100          | 140 | 378.5 | 23/45 (50 ppm) | 119 |
|          | MoO$_3$        | Hydrothermal | TMA     | 50          | 240 | 582 | 15/50 (1 ppm) | 120 |
| Nanoribbon| MoO$_3$        | Hydrothermal | H$_2$ | 100          | 200 | 14.1 | 21/75 | 121 |
|          | MoO$_3$/Graphene | Hydrothermal | H$_2$ | 1000        | RT | 20.5 | 10/30 | 122 |
|          | MoO$_3$        | Hydrothermal | H$_2$ | 1000        | RT | 17.3 | 10.9/30.4 | 123 |
|          | MoO$_3$        | Hydrothermal | H$_2$ | 100          | RT | 3.2^* | 3/16 | 124 |
|          | MoO$_3$        | Hydrothermal | NH$_3$ | 25          | 450 | 60 | 21/216.9 (5 ppm) | 125 |
| Nanorod   | NiO$_2$:O$_x$/MoO$_3$ | Hydrothermal + Chemical deposition | Ethanol | 1 | 350 | 20 | N.G. | 126 |
|          | Ag-MoO$_3$     | Hydrothermal + Chemical reduction | TEA | 100         | 200 | 408.6 | 3/107 | 127 |
|          | MoO$_3$        | Hydrothermal | TEA    | 100         | 300 | 101.74 | 4/88 | 128 |
|          | MoO$_3$/BiVO$_4$ | Hydrothermal + metal organic deposition | TEA | 100         | 125 | 1.86 | 15/110 | 129 |
|          | MoO$_3$/GO     | Solvothermal + annealing | NH$_3$ | 100         | 200 | 15.3 | 5/84 | 130 |
|          | MoO$_3$        | Hydrothermal | NO$_3$ | 100         | 110 | 84 | 20/45 | 131 |
|          | h-MoO$_3$      | Chemical bath technique | NH$_3$ | 50          | 200 | 67 | 183/202 | 132 |
|          | p-Si/MoO$_3$   | Hydrothermal + physical vapor deposition | CO$_2$ | 100         | 250 | 12.08 | 8/15 | 133 |
|          | rGO/MoO$_3$    | Hydrothermal + in-situ microwave | H$_2$ | 40          | 110 | 44.7 | 109/36 | 134 |
| Nanofiber | SnO$_2$/MoO$_3$ | Hydrothermal + wet chemical | CO | 300         | 300 | 2.4 | 1430/1524 | 135 |
|          | MoO$_3$        | Hydrothermal | Ethanol | 100         | 180 | 300 | 45/138 | 136 |
| Nanowire  | MoO$_3$        | Hydrothermal | H$_2$ | 1.5(%)       | 260 | 0.85 | 28/42 (500 ppm) | 137 |
| Microrod  | MoO$_3$        | Hydrothermal | Ethanol | 500         | 332 | 8.24 | N.G. | 138 |
|          | MoO$_3$        | Probe sonication | TMA | 1000         | 200 | 2533 | 8/9 (1 ppm) | 139 |
|          | h-MoO$_3$      | Microwave assisted hydrothermal | Acetone | 10          | 200 | 1.48 | 60/500 | 140 |

**Table 1**: A detailed overview of gas sensing performance using 1-D MoO$_3$ based gas sensors.
| Class          | Material     | Synthesis route/ morphology                          | Gas     | Conc. (ppm) | Operating temp. (°C) | Response | Resp. /Reco. time (s/s) | Ref |
|---------------|--------------|------------------------------------------------------|---------|-------------|----------------------|----------|-------------------------|-----|
| Nanosheet     | MoO₃         | Grinding + Sonication                                | Alcohol | 100         | 300                  | 33       | 21/10                   | 46  |
|               | MoO₃         | Hydrothermal + calcination                           | Xylene  | 10          | 400                  | 9.1      | 7.1/6.8                 | 41  |
|               | MoO₃         | Solvothermal + annealing                             | TMA     | 50          | 133                  | 51.47    | 12/200                  | 44  |
|               | Au/MoO₃      | Hydrothermal + calcination + Chemical reduction      | Ethanol | 200         | 280                  | 169      | 22/5                    | 46  |
| Nanoflake     | MoO₃/rGO     | Hydrothermal + calcination                           | Ethanol | 100         | 310                  | 53       | 6/54                    | 46  |
|               | MoO₃/SnO₂    | Chemical synthesis                                  | H₂S     | 10          | 115                  | 43.5     | 22/10                   | 47  |
|               | Au/MoO₃      | Thermal evaporation + sputtering                     | H₂S     | 15          | 400                  | 260      | 60/480                  | 48  |
| Nanoplate     | MoO₃         | Chemical synthesis                                  | Ethanol | 800         | 300                  | 58       | 10*/40*                 | 49  |
|               | MoO₃         | Polymeric solution method                            | NO₂     | 100         | 250                  | 47.9     | N.G.                    | 50  |
| Nano lamella  | Ni/MoO₃      | Solvothermal                                         | Formaldehyde | 100      | 255                  | 41       | 4/12                    | 51  |
| Thin film     | MoO₃/V₂O₅    | Chemical spray pyrolysis                             | NO₂     | 100         | 200                  | 80(%)    | 118/1182                | 54  |
|               | MoO₃         | Hydrothermal                                         | Ethanol | 100         | 260                  | 23(%)    | 111/66                  | 55  |
| Microsheet    | MoO₃         | Hydrothermal + Thermal oxidation                     | TEA     | 100         | 275                  | 27.1     | 3/50                    | 57  |
| Micro plank   | MoO₃         | Chemical synthesis                                  | CO      | 100         | 150                  | 74.87    | 80/110                  | 58  |

Table 2: A detailed overview of gas sensing performance using 2-D MoO₃ based gas sensors.
Table 3: A detailed overview of gas sensing performance using 3-D MoO₃ based gas sensors.
Scheme 1: Schematic of the illustration of various morphologies of MoO$_3$ based gas sensor
Scheme 2: Yearly publication demonstrating increasing interest in MoO$_3$ based gas sensor in the last three decades. (Source: ISI Web of Science database and search criteria ‘MoO$_3$ + gas sensor’).
Figure 1: (a-f) FESEM images of pure MoO$_3$ NBs and ZM-1–ZM-5; (g) the average thicknesses of pure MoO$_3$ NBs and Zn doped MoO$_3$ NBs; (h) Gas sensing responses of sensors based on pure MoO$_3$ NBs and Zn doped MoO$_3$ NBs to 1000 ppm ethanol at different OT; (i) Response and recovery curves of sensors based on pure MoO$_3$ NBs and ZM-3 to different concentrations of ethanol at the OT of 240 °C; (j) Cross-sensitivity to various gases at different temperatures; Reproduced with permission from Ref 103, Copyright 2017 Elsevier. (k, l) FESEM images of pure MoO$_3$ NBs; (m, n) FESEM images of RuO$_2$/MoO$_3$ NBs; (o) Schematic diagram of possible gas sensing mechanisms of RuO$_2$/MoO$_3$ NBs; (p) Response to 10 ppm TEA gas versus OT; (q) Response transient to 10 ppm TEA at 300 °C; (r) Responses of pristine and RuO$_2$/MoO$_3$ NBs gas sensors to different gases (10 ppm) at 300 °C. Reproduced with permission from Ref 60, Copyright 2019 Elsevier.
Figure 2: (a,b) SEM and TEM image of pure MoO$_3$ NBs; (c,d) SEM and TEM image of Fe$_2$O$_3$/MoO$_3$ NBs; (e) OT dependent response of sensors to 100 ppm xylene; (f) Response of sensors to 100 ppm various gases at their optimum OT. Reproduced with permission from Ref 104, Copyright 2019 Elsevier. (g) FESEM image of pure MoO$_3$ NBs; (h) FESEM image of CoMoO$_4$/MoO$_3$ nanocomposites; (i,j) Low and high-magnification TEM images of CoMoO$_4$/MoO$_3$ nanocomposites; (k) Response of sensors to 10 ppm of TMA at different OT; (l) Response and recovery curves toward different concentrations of TMA; (m) Response and recovery curves of sensor based on CoMoO$_4$/MoO$_3$ nanocomposites to 5 ppm TMA after 3 cycles of gas in and off at 220 °C. Reproduced with permission from Ref 105, Copyright 2018 Elsevier.
Figure 3: (a,b) FESEM images of pure MoO$_3$ NBs, (c) FESEM image Au@MoO$_3$ nanocomposites; (d) TEM images of Au@MoO$_3$ nanocomposites; (e) Response curves of the sensors to 10 ppm trimethylamine gas at different OT; (f) Response and recovery time curves of the sensors based on Au@MoO$_3$ NBs to 10 ppm TMA at different OT; (g) Response values of the Au@MoO$_3$ nanocomposites sensor towards 10 ppm different gases at the working temperature of 280 °C. Reproduced with permission from Ref $^{72}$, Copyright 2016 Elsevier. (h) The SEM images of the pristine nanowires, the inset picture is a low-magnified SEM image; (i-m) SEM images of Pt/MoO$_3$ NBs; (n,o) TEM images of Pt-decorated MoO$_3$ NBs; (p) The dynamic sensor response of pristine and Pt/MoO$_3$ NBs towards HCHO gas of 200 ppm at 27 °C; (q) Sensor response to different gas with concentration of 200 ppm; (r) The schematic diagram for HCHO sensing behavior of Pt/MoO$_3$ NBs in air and in HCHO containing atmosphere. Reproduced with permission from Ref $^{73}$, Copyright 2019 Elsevier.
Figure 4: (a) SEM images of as-prepared samples synthesized at different OT; (b) Schematic diagram of the H₂ sensing mechanism of MoO₃ NRbs; (c) Dynamic response of different MoO₃ sensors toward 500 ppm of H₂; (d) Schematic illustration of the fabrication process of sensor; (e) Sensitivity, response time, and recovery time of different MoO₃ sensors; (f) Relation among the sensitivity (S), Mo content and O_{chem} content of the MoO₃ NRbs. Reproduced with permission from Ref 100, Copyright 2015 American Chemical Society. (f-1) TEM image and schematic diagram of graphene oxide used as the hydrothermal precursor; (f-2) SEM image of the MoO₃ NRbs/graphene nanocomposite; (f-3) HRTEM images of individual MoO₃ NRbs; (g) The RT response curves of the MoO₃ NRbs/graphene to 500 ppm H₂ in air; (h) Selectivity to 1000 ppm H₂ of M/G-1.5 against other gases with the same concentration; (i) Schematic diagram of pure MoO₃ NRbs and MoO₃ NRbs/graphene under air and H₂ containing atmospheres. Reproduced with permission from Ref 106, Copyright 2017 Elsevier. (j) SEM images of the original MoO₃; (k) SEM image of MoO₃ treated at 400 °C; (l) The dynamic response curves towards 750 ppm H₂ gas at 25 °C; (m) The selectivity of S-H3 to different gases with concentrations of 1000 ppm; (n) The schematic diagram of the H₂ sensing mechanism of the sensor based on MoO₃ NRbs both in air and in H₂ atmosphere. Reproduced with permission from Ref 56, Copyright 2019 Elsevier.
Scheme 3: The optimized structure (a) and the electronic density difference (b) of the adsorption of two H2 on the Fe-doped MoO3 with one pre-adsorbed oxygen ions. The red, blue and white ball represents the O, Mo and H atoms. Reproduced with permission from Ref. 123, Copyright 2021, Elsevier.
Figure 5: (a) Schematic illustration of synthesis of NiCo$_2$O$_4$/α-MoO$_3$ nanocomposite; (b-1, b-2) SEM image of pristine α-MoO$_3$; (b-3) Magnified SEM image of NiCo$_2$O$_4$/α-MoO$_3$ composites; (c) Dynamical response transients to different concentrations of ethanol; (d) Long-term stability of NiCo$_2$O$_4$/α-MoO$_3$ nanocomposites towards 1 ppm ethanol at 350 °C; (e) Selectivity towards 1 ppm interfering gases at 350 °C. Reproduced with permission from Ref 74, Copyright 2019 Elsevier. FESEM images of the pure α-MoO$_3$ NRs (f-1) and AgNPs-decorated α-MoO$_3$ nanorods (f-2); (g) TEM images of the 2%Ag-MoO$_3$; (h) Sensing response towards 100 ppm of TEA at varied OT; (i) Sensing transients of the 2%Ag-MoO$_3$ sensor towards 100 ppm of TEA; (j) Cross-response of 2%Ag-MoO$_3$ at 200 °C. Reproduced with permission from Ref 75, Copyright 2019 Elsevier.
Figure 6: (a) Schematic illustration for preparation of two MoO₃ products and sensing measurement of actual sensors; (b) FESEM images of the MoO₃ NRs; (c) Sensor responses to 100 ppm TEA vapor as a function of OT from 100 to 350 °C; (d) Response and recovery times of the sensor at various concentrations of TEA gas; (e) Sensor responses of the MoO₃ NRs to various gases with an identical concentration (100 ppm) at 300 °C. Reproduced with permission from Ref 97, Copyright 2019 Elsevier. (f) Schematic diagram of α-MoO₃/BiVO₄ composite synthesis process; (g) SEM and TEM image of 16Mo/Bi composite; (h) Responses at different OT to 20 ppm TEA; (i) Response-recovery time to 20 ppm TEA; (j) Response to 20 ppm different gases at 125 °C. Reproduced from Ref 108 with permission from the Centre National de la Recherche Scientifique (CNRS) and The Royal Society of Chemistry.
Figure 7: (a) Schematic illustration of the growth mechanism of SnO$_2$ doped MoO$_3$ NFbs; (b) Response–recovery curves of SnO$_2$ doped MoO$_3$ NFbs at 300 °C; (c) Responses as a function of CO concentration at 300 °C; (d) Selectivity of pristine α-MoO$_3$ NBs (red) and SnO$_2$/MoO$_3$ NFbs (blue) towards various gases of 300 ppm at 300 °C, (inset) high-magnification SEM micrographs of SnO$_2$/MoO$_3$ NFbs. Reproduced with permission from Ref 76, Copyright 2017 Elsevier. (e) SEM image of M4 grown at constant temperature; (f) Response of M1-M8 devices in exposure to 100 ppm ethanol at different OTs; (g) Selectivity study towards 200 ppm of different VOCs. Reproduced with permission from Ref 114, Copyright 2019 Elsevier.
Figure 8: (a) SEM and TEM image of as-synthesized α-MoO$_3$ NWs; (b) The sensitivities of different sensors to 1.5% H$_2$; (c) Response-recovery of the sensor to 1.5% H$_2$; (d) Repeatability to 1.5% H$_2$; (e) Dynamic response resistances of the flexible NWs paper for different H$_2$ concentration (100 ppm - 1.5%). Reproduced with permission from Ref 82, Copyright 2017 Elsevier. (f) Typical SEM image of h-MoO$_3$ MRds; (g) The selectivity of the h-MoO$_3$ MRds gas sensor to 500 ppm gases at the OT of 332 °C and 380 °C; (h) Sensitivity of sensors based on h-MoO$_3$ MRds to the exposure of different concentration of ethanol at different OTs. Reproduced with permission from Ref 98, Copyright 2015 Elsevier.
Figure 9: (a-1) Three-step liquid exfoliation process; (a-2) schematic illustration of the fabricated sensor and image of the operating principle; (b) TEM image showing the layered nature of the MoO$_3$ NSs; (c) The results of the sensor response using bulk MoO$_3$ and MoO$_3$ NSs toward 100 ppm alcohol vapor at different OTs; (d) Transient sensor response toward 100 ppm alcohol vapor at different temperatures, (inset) response and recovery curves at its optimum OT; (e) responses of sensors made of MoO$_3$ NSs toward 100 ppm VOCs. Reproduced with permission from Ref 80, Copyright 2016 Royal Society of Chemistry. (f) SEM images of MoO$_3$ NSs-400 samples; (g) Sensor responses at varied OTs towards 10 ppm xylene; (h) Response/recovery curve of the MoO$_3$ NSs sensor towards 10 ppm xylene at 300 °C; (i) Responses of MoO$_3$ NSs sensor to 10 ppm different gases at 300 °C. Reproduced with permission from Ref 81, Copyright 2020 Elsevier.
Figure 10: (a) Schematic Diagram for the Preparation of α-MoO$_3$ along with the SEM images of different materials; (b) Responses versus the OT to 50 ppm TMA gas; (c) Responses versus 50 ppm of various gases at 133 °C; (d) Responses of α-MoO$_3$-400 sensor to 10 ppm TMA at 133 °C for 90 days. Reproduced with permission from Ref 64, Copyright 2019 American Chemical Society. (e) TEM images of Au@MoO$_3$ nanocomposites samples, (f) Response to 200 ppm ethanol at different OTs; (g) Gas responses to 200 ppm test gases at 280 °C. Reproduced with permission from Ref 145, Copyright 2016 Elsevier.
Scheme 4: Structures (top view) of TMA-α-MoO$_3$ (a1) and TMA-Ov-α-MoO$_3$ (b1). The density of states of TMA-MoO$_3$ (a2) and TMA-Ov-MoO$_3$ (b2). Reproduced with permission from Ref 64, Copyright 2019 American Chemical Society.
Figure 11: (a) Schematic diagram of the preparation of MoO$_2$-rGO; (b) SEM and TEM images of the MoO$_2$-rGO; (c) Response to 100 ppm of ethanol under different OTs; (d) Response of sensors towards different VOCs. Reproduced with permission from Ref 146, Copyright 2019 Elsevier. (e) Illustration for the Preparation Process of MoO$_2$/SnO$_2$ NFs; (f) SEM images of MoSn-S2; (g) Sensor responses to 10 ppm of H$_2$S concentration; (h) response to 10 ppm of various test gases. Reproduced with permission from Ref 147, Copyright 2019 American Chemical Society. (i) Response towards various gases at different OTs. (Left) Pure MoO$_2$ NF and (Right) Au-MoO$_2$ NFks, (inset) SEM image of Au-MoO$_2$ NFks; (j) Dynamic response of Au-MoO$_3$ toward H$_2$ (100, 250, 500 ppm), Acetone (25, 50, 100 ppm) and Ethanol (10, 25, 50 ppm) at 450 °C. RH = 40% at 20 °C, with an applied voltage equal to 1 V. Reproduced with permission from Ref 148, Copyright 2018 Elsevier.
Figure 12: (a) TEM image of α-MoO₃ NPs; (b) The sensitivities of the α-MoO₃ NPs sensors as a function of the concentrations of different reagent vapors; (c) The sensitivity changes of the α-MoO₃ NPs sensors at various OTs under ethanol vapor with a concentration range of 5–800 ppm. Reproduced with permission from Ref 149, Copyright 2011 Royal Society of Chemistry. (d-1) SEM images of MoO₃; (d-2) SEM image of MoO₃-Pd nanocomposite. The insets show corresponding low-resolution images; (e) HRTEM image of MoO₃-Pd nanocomposite; (f) Current-voltage characteristics of the MoO₃-Pd nanocomposite in presence of different concentration of H₂ gas at RT; (g) Proposed mechanism of interaction of H₂ gas with MoO₃-Pd nanocomposite. Reproduced with permission from Ref 79, Copyright 2017 Elsevier. (h) SEM image of the as-grown MoO₃ nanostructures prepared on silicon substrates at 400 °C for 1 hour with 3-layer depositions; (i) Transient gas sensing response as function of the NO₂ concentration at 250 °C for the layered α-MoO₃ nanoplates, (Inset) Transient H₂ sensing response as a function of the concentration at 250 °C; (j) Sensor signal as a function of the OT at different NO₂ concentrations. Reproduced with permission from Ref 150, Copyright 2020 Royal Society of Chemistry.
Figure 13: (a) SEM images 5 mol% Ni-doped α-MoO$_3$; (b) Response vs optimum OT of the sensors to formaldehyde gas at a concentration of 100 ppm; (c) Gas-sensing transients to 5–100 ppm formaldehyde operated at optimal OT; (d) Comparison in the response of the sensor to 100 ppm different test gases at 255 °C. Reproduced with permission from Ref 151, Copyright 2017 Elsevier. (e) Schematic figure of the MoO$_3$-NPr gas sensor; (f) SEM images of the MoO$_3$-NPr gas sensor; (g) Responses of the MoO$_3$-NPr sensor to 5 ppm TMA and H$_2$S with respect to the OT; (h) Selectivity of the MoO$_3$-NPr sensor at 325 °C; (i) Response–recovery curves of the MoO$_3$-nanopaper sensor to different H$_2$S concentrations at 250 °C and 325 °C; (insets) the response of the sensor to various gas concentrations. Reproduced with permission from Ref 152, Copyright 2017 Royal Society of Chemistry.
Figure 14: (a) SEM micrograph of spray deposited $\alpha$-MoO$_3$ TFm with a thickness of 520 nm; (b) Response of $\alpha$-MoO$_3$ film for different TMA concentrations with error bars; (c) Transient response of $\alpha$-MoO$_3$ film for different TMA concentrations; (d) Transient TMA sensing response of $\alpha$-MoO$_3$ film in mixed amine environment. Reproduced with permission from Ref 153, Copyright 2014 Elsevier. (e) The technological flow for the MoO$_3$-V$_2$O$_5$ gas sensor device fabrication; (f) The variation in response of ($\text{MoO}_3$)$_{0.4}$($\text{V}_2\text{O}_5$)$_{0.6}$TFm at different OTs; (g) The transient response curves of typical ($\text{MoO}_3$)$_{0.4}$(V$_2$O$_5$)$_{0.6}$TFm; (h) The gas response and selectivity coefficient study of typical ($\text{MoO}_3$)$_{0.4}$(V$_2$O$_5$)$_{0.6}$TFm operating at OT of 200 °C for 100 ppm concentration of various gases. Reproduced with permission from Ref 154, Copyright 2018 Elsevier. (i) Schematic device structure of the transparent humidity sensor; (j) SEM images of the $\alpha$-MoO$_3$ TFm on the surface of channel and FTO electrode; (k) photograph of the transparent device; (l) Schematic diagram of humidity sensing mechanism for the $\alpha$-MoO$_3$ TFm; (m) Dynamic response/recovery curve for one cycle; (n) Sensitivity of the device to different analytes. Reproduced with permission from Ref 156, Copyright 2020 Royal Society of Chemistry.
Figure 15: (a) Typical FESEM image of the MoO$_3$ MSh; (b) Responses of the sensors to 100 ppm TEA in the OT range of 200-325 °C; (c) Responses of the sensors to different gases at 275 °C; (d) Dynamic response of MoO$_3$ MSh-based sensors at 275 °C during 5 months exposure to 100 ppm TEA. Reproduced with permission from Ref 157, Copyright 2018 Royal Society of Chemistry. (e) SEM micrographs of Cu9; (f) Variation of resistance versus temperature for different samples; (g) Sensitivity versus temperature for different gases at varied OT; (h) sensitivity versus time for various CO gas concentration in ppm. Reproduced with permission from Ref 158, Copyright 2019 IOP Publishing.
Figure 16: (a) Typical SEM and TEM images of α-MoO$_3$ flower-like HNS; (b) The responses of α-MoO$_3$ thick-film sensor versus the OT to 100 ppm TEA gas; (c) The responses of α-MoO$_3$ thick-film sensor to 100 ppm gases at different OTs; (d) The transient response–recovery characteristics of α-MoO$_3$ sensor with different concentrations of TEA gas at the OT of 250 °C. Reproduced with permission from Ref 83, Copyright 2015 Elsevier. (e) Schematic illustration of the possible formation process for the MoO$_3$ NFL architectures and SEM image of aggregated state of NFLs; (f) Gas response to ethanol (400 ppm) at a series of OT; (g) Gas response to varied ethanol concentration at OT of 300 °C; (h) Gas response and recovery curves of the sensors; (i) Repeat response-recovery characteristics of the sensors. Reproduced with permission from Ref 84, Copyright 2016 Springer.
Scheme 5: (a) The structure, (b) deformation charge density, (c) HOMO, (d) LUMO, (e) DOS and (f) PDOS of CO-adsorbed MoO3 (010) adsorption system. Reproduced with permission from Ref 170, Copyright 2020 Elsevier.
Figure 17: (a) SEM and TEM images of nest-like MoO$_3$; (b) response vs temperature towards 200 ppm ethanol; (c) ethanol concentration vs. response property at 340 °C, Blue line symbol for nest-like MoO$_3$ and red for monodispersed MoO$_3$ NBs. Reproduced with permission from Ref 171, Copyright 2015 Elsevier. (d) Schematic of formation process of the α-MoO$_3$ NFLs; (e-1 to e-4) TEM micrographs of the intermediate products collected at different reaction stages; (e-5) SEM images of α-MoO$_3$ product prepared for 8 h; (f) The response vs OT to 10 ppm TEA gas; (g) The response vs varied TEA concentration; (h) The response versus 10 ppm various gases, Reproduced with permission from Ref 172, Copyright 2015 Royal Society of Chemistry.
Figure 18: (a) Schematic illustration of the evolution process of porous $\alpha$-MoO$_3$ sponges; (b) SEM images of porous $\alpha$-MoO$_3$ sponges; (c) Responses to ethanol with different concentration at 250 °C, (inset) response versus operating temperature of the two sensors exposed to 100 ppm methanol; (d) Dynamic ethanol sensing transient towards 100 ppm ethanol at 250 °C. Reproduced with permission from Ref 173, Copyright 2016 Elsevier. (e) Schematic diagram of the possible formation mechanism for the NFbs-assembled and the NSs-assembled hierarchical MoO$_3$ structures; (f) SEM images of the NFbs-assembled hierarchical MoO$_3$ structures; (g) SEM images of the NSs-assembled hierarchical MoO$_3$ structures; (h) The gas response to 400 ppm ethanol at different OTs; (i) Response-recovery characteristics of sensors at 300 °C to 400 ppm ethanol. Reproduced with permission from Ref 77, Copyright 2019 Elsevier.
Figure 19: (a) The SEM image of 1% Y-doped sample; (b) The response curve of samples to 100 ppm different gases at the OT of 370 °C; (c) The response/recovery curve of samples for 100 ppm xylene at 370 °C; (d) the stability of samples for 100 ppm xylene at 370 °C. Reproduced with permission from Ref 177, Copyright 2017 Elsevier. (e) The response to 100 ppm gas at the different OTs, (Inset) The SEM images of samples S2; (f) The dynamic response curves to 100 ppm xylene at 370 °C; (g) the stability of the samples to 100 ppm xylene at 370 °C; (h) The response of sample S2 to 100 ppm gas at the different OTs. Reproduced with permission from Ref 178, Copyright 2017 Elsevier. (i) A schematic representation for the synthesis of Fe-doped MoO$_3$ NARs; (j) SEM images of MoFe$\_3$; (k) The response curves of samples to 100 ppm xylene at the different OTs; (l) The response and recovery curves for 100 ppm xylene at 340 °C; (m) The response of samples to 100 ppm different gases at 340 °C. Reproduced with permission from Ref 179, Copyright 2020 Elsevier.
Figure 20: (a) The SEM images of a single sphere obtained by calcination; (b) The responses vs the OT to 100 ppm toluene gas; (c) The responses vs. 100 ppm various gases at their relative optimized OTs; (d) The responses of 2.04Au/α-MoO₃ sensor versus 100 ppm gases. Reproduced with permission from Ref 180, Copyright 2017 American Chemical Society. (e) SEM and TEM images of the calcined MoO₃/Bi₂Mo₃O₁₂ spheres; (f) Responses of the sensors toward 50 ppm of TMA at different OTs; (g) The gas response-recovery characteristics of the MoO₃/Bi₂Mo₃O₁₂ sensor to varied concentrations of TMA measured at 170 °C; (h) The responses of the MoO₃/Bi₂Mo₃O₁₂ sensor toward 100 ppm of various gases. Reproduced with permission from Ref 181, Copyright 2019 American Chemical Society.
Figure 21: (a) Schematic representation of synthesis of MoO$_3$-ZnO CSh; (b) SEM and TEM image of MoO$_3$-ZnO CSh NRs; (c) Response of the prepared materials to 200 ppm of ethanol at different OTs; (d) Selectivity of the pristine MoO$_3$ and MoO$_3$-ZnO CSh NR sensor at 350 °C; (e) Long-term stability of MoO$_3$-ZnO CSh NR sensor at 350 °C. Reproduced with permission from Ref 182, Copyright 2018 Elsevier. (f) Schematic illustration of synthesis of α-MoO$_3$@NiO composites; (g) SEM images of as-prepared materials; (h) Response vs OT for 100 ppm acetone gas; (i) Selectivity towards 100 ppm various gases at their optimal OTs. Reproduced with permission from Ref 183, Copyright 2019 Royal Society of Chemistry.
Figure 22: (a) Growth mechanism of hollow \( \text{MoO}_3 \) cage; (b-1) SEM images of solid \( \text{MoO}_3 \) polyhedrons; (b-2) SEM images of hollow \( \text{MoO}_3 \) MCg; (c) The gas response vs OT for 200 ppm ethanol gas; (d) The gas response of the tow sensors towards different gas concentrations at 350 °C. Reproduced with permission from Ref 185, Copyright 2019 Elsevier. (e) FESEM images of S-5% NPMn, (inset) TEM image of S-5%; (f) Responses vs OTs to 100 ppm xylene gas; (g) Response and recovery curves of S-0 and S-5% sensors; (h) Responses to 100 ppm different test gases (X: xylene, E: ethanol, M: methanol, A: acetone, F: formaldehyde, H: hydrogen sulfide, T: toluene, B: benzene) at 250 °C. Reproduced with permission from Ref 186, Copyright 2019 Elsevier. (i) Schematic illustration of the formation process of hierarchical \( \text{MoO}_3 \) MBx; (j) FESEM image of hierarchical \( \text{MoO}_3 \) MBx; (k) Response of sensor based on hierarchical \( \text{MoO}_3 \) MBx to 100 ppm of ethanol at different OTs; (l) Response/recovery curves of sensors to 100 ppm ethanol at 260 °C; (m) Gas response of hierarchical \( \text{MoO}_3 \) MBx to 100 ppm test gases at 260 °C; (n) selectivity to ethanol (S_{ethanol} and S_{gas}, gas responses to ethanol and other gases, respectively). Reproduced with permission from Ref 187, Copyright 2017 Elsevier.