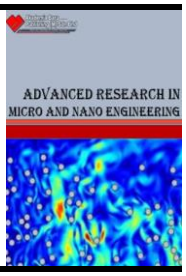
Penerbit Akademia Baru

Journal of Advanced Research in Micro and Nano Engineering

Journal homepage:
https://www.akademiabaru.com/submit/index.php/armne/index
ISSN: 2756-8210



Exploring Novel Approaches: Surface Functionalization of Metal Organic Semiconductor as Sensing Material for Volatile Organic Compounds Detection

Khairunnisa Waznah Baharin[1], Nurul Hazwani Aminuddin Rosli[1], Mohd Nurazzi Norizan[2], Mohd Afzanizam Mohd Rosli[3], Noor Aisyah Ahmad Shah[1], Safura Taufik[1], Nor Ain Azeany Mohd Nasir[1], Syed Mohd Shafiq Syed Ahmad[1], Norli Abdullah[1,*]

[1] Centre for Defence Foundation Studies, Universiti Pertahanan Nasional Malaysia, Kem Perdana Sungai Besi, 57000 Kuala Lumpur, Malaysia
[2] Bioresource Technology Division, School of Industrial Technology, Universiti Sains Malaysia, 11800 Penang, Malaysia
[3] Faculty of Technology and Mechanical Engineering, Universiti Teknikal Malaysia Melaka, Hang Tuah Jaya, 76100 Durian Tunggal, Melaka, Malaysia

ARTICLE INFO

Article history:
Received 10 May 2024
Received in revised form 15 June 2024
Accepted 23 July 2024
Available online 31 August 2024

Keywords:
Metal organic semiconductor; organic ligands; surface functionalization; sensors; volatile organic compounds

ABSTRACT

Detecting volatile organic compounds (VOCs) is imperative in healthcare, industrial safety, and environmental monitoring due to their potential harm to human health and the environment. Addressing the challenges in VOC detection, research has focused on creating sensors with rapid response and high selectivity, notably through surface functionalization of metal organic semiconductors. Metal organic semiconductors offer advantages over standard metal oxide semiconductors (MOS), demonstrating superior sensitivity and selectivity even at low temperatures and concentrations. Notably, conductive particle-polymer hybrids and conjugated polymers as metal organic semiconductors show promise for VOCs detection. This review comprehensively explores surface functionalization in metal organic semiconductors, covering principles, mechanisms governing gas sensing behavior and the pivotal role of surface functionalization in enhancing selectivity and performance. Additionally, various surface functionalization options, such as nanoparticles, nanostructures, and organic ligands, are discussed.

1. Introduction

Volatile organic compounds (VOCs) refer to a collection of organic chemicals that readily vaporize at room temperature and normal atmospheric pressure. They are categorized as volatile because of their high vapor pressure, allowing them to transition easily from solid or liquid states into the gas phase. VOCs encompass a broad spectrum of chemical compounds, including hydrocarbons, aldehydes, ketones, alcohols, ethers, aromatic compounds, halogenated compounds, and various others. These compounds primarily consist of carbon and hydrogen atoms, often combined with

* *Corresponding author.*
E-mail address: norli.abdullah@upnm.edu.my

https://doi.org/10.37934/armne.22.1.2642

other elements like oxygen, nitrogen, sulfur, or halogens. Some of the more familiar VOCs include benzene, formaldehyde and toluene.

VOCs can be found in the air indoors and outdoors [1]. VOCs are commonly found in various everyday products and materials, including solvents, paints, adhesives, cleaning agents, fuels, varnishes, cosmetics, building materials, and household products [2,3]. They can also be emitted from natural sources, such as vegetation, and from certain industrial processes [4]. Additionally, VOCs can be generated as byproducts of combustion and vehicle emissions [5]. Figure 1 represents various products of VOCs according to their sources.

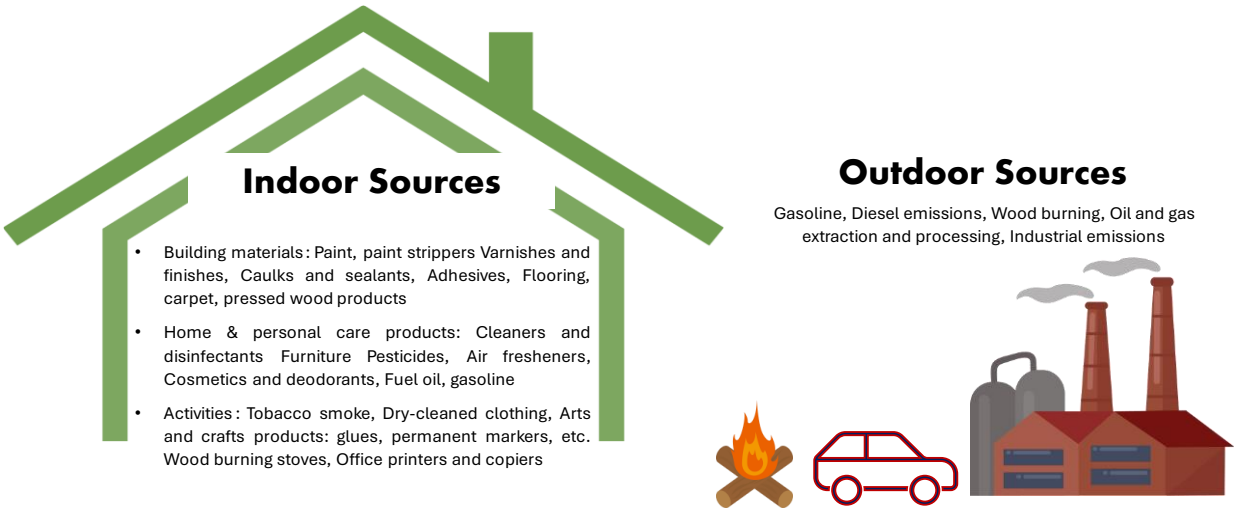


Fig. 1. Various products of VOCs according to their sources

While many VOCs are considered harmless, certain types can have detrimental effects on both human health and the environment. When exposed to high concentrations of specific VOCs over a short period, individuals may experience irritation of the eyes, nose, and throat, as well as symptoms like headaches, dizziness, and respiratory issues [6,7]. On the other hand, prolonged exposure to certain VOCs has been linked to more severe health consequences, such as liver and kidney damage, as well as central nervous system disorders [8,9]. Moreover, some VOCs are identified as potential carcinogens, posing a risk of cancer development. Table 1 represents the type of common volatile organic compounds, their source of emission and potential risk.

Detecting volatile organic compounds (VOCs) in the environment is essential to evaluate air quality, identify pollution sources and monitor the impact of human activities on the ecosystem. Various methods and technologies are employed for VOCs detection in environmental settings, including gas chromatography (GC), coupling gas chromatography with mass spectrometry (GC-MS), portable gas detectors, optical sensors, electronic noses, passive sampling methods involving the use of specialized sorbent materials and remote sensing techniques, such as differential optical absorption spectroscopy [10].

Portable gas detectors for VOCs detection often utilize various sensor technologies. Two commonly employed sensor types are MOS sensors and Photoionization Detectors (PID). Metal Oxide Semiconductor Sensors work by detecting changes in electrical resistance when exposed to VOCs. The resistance varies based on the concentration of VOCs in the air. These sensors are cost-effective and can detect a broad range of VOCs. Whereas, PID detectors operate by ionizing gas molecules in the presence of ultraviolet light. VOCs absorb the UV light and become ionized, producing a measurable current that corresponds to the VOC concentration. PID detectors are sensitive and provide real-time readings. These portable gas detectors are commonly used in industrial settings,

environmental monitoring, and occupational safety to identify and quantify the presence of VOCs in the air.

Table 1
Type of common volatile organic compounds, their source of emission and potential risk

Type of VOC	Source of emission	Effect	Reference
Benzene	tobacco smoke, vehicle emissions, industrial processes	headaches, dizziness, drowsiness and unconsciousness in humans	[11,12]
Formaldehyde	building materials and household products (plywood, glues, and adhesives)	severe respiratory tract and skin irritant and may cause dizziness or suffocation	[13]
Toluene	paint thinners, nail polish, adhesives, vehicle emissions	headaches, dizziness, and respiratory issues; long-term exposure may lead to liver, kidney, and nervous system damage	[14,15]
Ethylene Glycol	antifreeze, hydraulic brake fluids, and some paints.	dermal irritation, Nasal and or throat irritation	[16]
Acetone	nail polish remover, paints, and cleaning agents	irritation of the nose, throat, trachea, and lung	[17]
Chloroform	chlorinated water and used in the production of refrigerants and solvents.	May cause damage to organs (Liver, Kidney) through prolonged or repeated exposure. Harmful to aquatic life	[18]
Xylene	printing, rubber, and leather industries. It is also found in vehicle exhaust	irritate the eyes, nose, skin, and throat. Xylene can also cause headaches, dizziness, confusion, loss of muscle coordination, and in high doses, death	[19,20]
Methylene Chloride	paint strippers, adhesives, and aerosol sprays	mental confusion, lightheadedness, nausea, vomiting, and headache	[21]

Semiconductor metal oxide-based materials have garnered considerable interest for volatile organic compound (VOC) sensing, owing to their remarkable sensitivity, signal characteristics, ease of measurement and cost-effective fabrication [22,23]. MOS are extensively employed as sensing materials in gas sensors designed for VOCs detection. They exhibit high sensitivity, low cost, and compatibility with microfabrication techniques. MOS-based gas sensors typically operate by measuring the change in electrical conductivity of the semiconductor material when exposed to VOCs. Over time, significant advancements have been made to enhance the performance of MOS-based gas sensors for VOC detection. Researchers have focused on various aspects to improve the sensing capabilities of MOS-based gas sensors. These include material development, surface functionalization, nanostructuring and thin film techniques, sensor array and signal processing methods, as well as the development of low-power and portable devices (Figure 2). Through these efforts, the performance and applicability of MOS-based gas sensors for VOCs detection have been significantly enhanced. By continuously exploring and advancing these areas of research, scientists aim to further improve the sensitivity, selectivity, and overall performance of MOS-based gas sensors, paving the way for more efficient VOCs detection technologies.

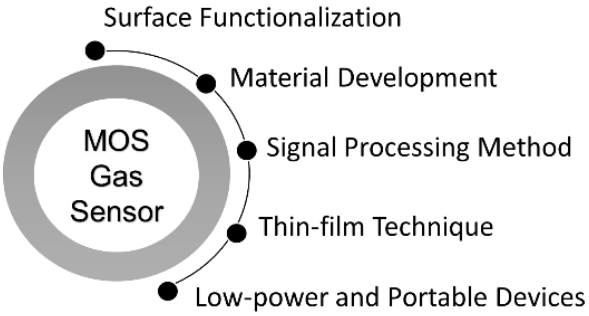


Fig. 2. Research on metal oxide semiconductor characteristics

Therefore, this review article is focused on the surface functionalization of MOS for the detection of VOCs. In recent years, researchers have made progress in developing surface-functionalized MOS materials for VOCs detection. Surface functionalization of MOS as sensing materials includes methods like doping with metals or non-metals, coating with organic molecules, and creating nanostructures. These techniques enhance sensitivity and selectivity by modifying surface properties, enabling better interaction with target analytes, and improving detection capabilities.

2. Metal Oxide Semiconductor

Metal oxide semiconductors are a unique class of materials that exhibit distinct electronic charge transport properties when compared to traditional covalent semiconductors. These semiconductors are composed of valence compounds characterized by strong ionic bonding. The conduction band minimum (CBM) and valence band maximum (VBM) of metal oxide semiconductors are primarily composed of the metal (M) ns orbital and oxygen (O) 2p orbital, respectively. The interaction between these metal and oxide orbitals leads to significant differences in charge carrier transport.

Generally, the M ns orbitals have high dispersion, while the O 2p orbital is localized, resulting in a smaller effective mass for electrons compared to holes. Metal oxide semiconductors possess wide band gaps, which can be tailored to achieve desired electrical properties. They also exhibit high stability, making them suitable for use in chemiresistive gas sensors. MOS can be categorized into two types: n-type MOS and p-type MOS. Due to the difference in charge carriers within the n and p type semiconductors, each type behaves differently when exposed to reducing or oxidising gases [24-26]. Figure 3 shows the schematic diagram of the sensing mechanism for n-type and p-type MOSs.

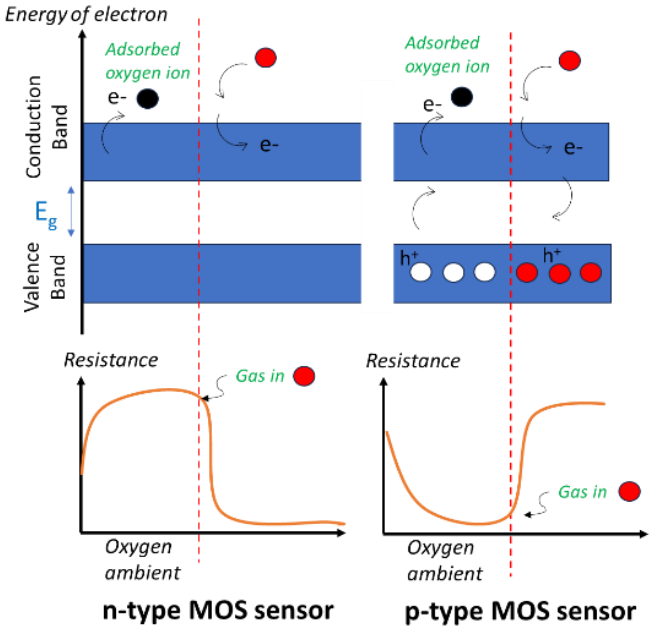


Fig. 3. Schematic diagram for sensing mechanism of n-type and p-type MOSs. Reproduced from [27]

Gas sensing research predominantly focuses on n-type semiconductors, although investigations into p-type semiconductors have also been conducted. The n-type oxides exhibit a decrease in resistance when exposed to reducing gases, making them compatible with measurement systems [28]. Due to their high sensitivity and rapid response time, n-type semiconducting materials have been predominantly utilized in MOS-based chemiresistors. Although the sensitivity of current p-type MOSs is lower than that of n-type MOSs, they offer several advantages in gas sensing applications. The p-type MOS demonstrate a unique oxygen adsorption property, enabling the design of high-performance gas sensors with fast recovery kinetics and independence from humidity [29,30]. Additionally, their conduction in the high-temperature range is less temperature-dependent compared to n-type MOSs. Several metal oxides, both p-type and n-type, such as SnO_2, WO_3, TiO_2, ZnO, Fe_2O_3, and Cr_3O_4, have been extensively studied as sensing materials due to their ease of synthesis and acceptable response to various VOCs, along with favorable response and recovery characteristics [31,32]. Figure 4 illustrates the progress in sensor research using MOS as sensing materials.

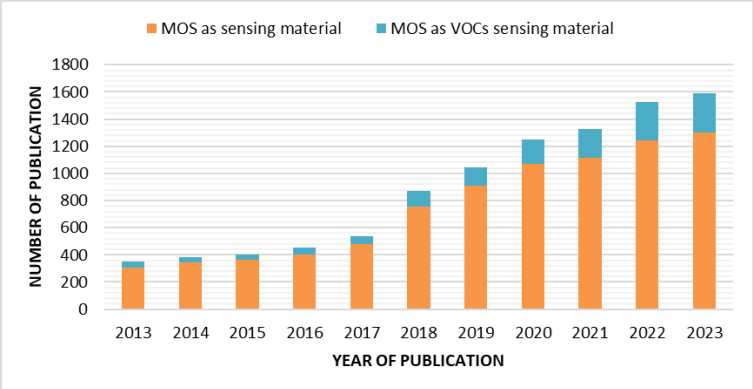


Fig. 4. Advancements in the research and development of metal oxide semiconductors (MOS) as sensing materials from 2013 to 2023. (Based on SCOPUS database from 2013 until 2023)

3. Type of MOS Functionalization

Functionalization methods provide possibilities to modify the surface properties of metal oxide semiconductors, enabling better interactions with target analytes and enhancing the performance of sensors. The selection of a functionalization technique depends on the specific needs of the sensor application and the desired alterations to the metal oxide semiconductor's surface. Various techniques can be employed to improve the selectivity, sensitivity, and stability of MOS-based VOCs gas sensors.

3.1 Metal Site Modification

Metal site modification in VOCs sensing materials involves introducing metal species onto the material's surface, influencing its catalytic activity and adsorption properties. This modification enhances sensitivity, selectivity, and response time, crucial for applications in environmental monitoring and industrial safety. As a way to increase the activity of catalysts or the sensitivity of sensors, functionalization of metal oxides by noble metals (gold (Au), platinum (Pt), silver (Ag), and palladium (Pd)) has been utilized extensively in previous work [33-36]. Tuning metal concentration allows for fine-tuning sensitivity, while synergistic effects from combining different metals contribute to superior performance. Careful modification ensures stability, reusability, and selective detection, making metal-modified sensing materials pivotal in advancing gas sensing technologies for diverse practical uses.

Postica *et al.,* proposed a potential method for developing gas sensor materials using Ag-ZnO nanocolumnar films to improve metal oxide surfaces by doping and noble nanoparticle functionalization. After doping the ZnO columnar films with Ag, the ethanol, acetone, n-butanol, 2-propanol, and methanol vapors' gas sensing characteristics were enhanced. It was discovered experimentally that surface functionalization with Ag with diameters between 6 and 12 nm improved the sensing characteristics of the Ag-doped ZnO columnar films towards VOC vapors, which is consistent with the computer models. Also, boosting the Ag amount had no discernible effect on the *p*-type behavior. Indicating at high dopant concentrations, the Ag atoms prefer to occupy the interstitial sites (Ag_i^*), where they produce neutral defects or separate at the grain borders. The electrical resistivity of the columnar Ag-doped ZnO film is decreased due to the significant amount of electron-rich dopant atoms present. Ag dopant atoms and Ag clusters have a synergistic impact on ZnO columnar films, which is shown to be very advantageous for the response to the detection of VOC vapors [37].

Zhou *et al.,* demonstrated Pt-SnO_2 nanoneedles through a facile hydrothermal process. From the FESEM analysis, 3.12 a.t% of Pt-SnO_2 nanomaterials indicate that synthesised material possesses long and thin needle-shaped morphologies grown in high density. The average length and diameters are ~5.5 ± 0.5µm and 150 ± 50 nm, respectively. The shape and aspect ratio of the SnO_2 nanomaterials is strongly influenced by the molar ratios of [Sn_4^+] and [OH^-] as well as by the pH of the growing fluid [38]. The creation of well-crystalline Pt-SnO_2 nanoneedles with a tetragonal rutile crystal phase was validated by morphological and structural characterizations [39].

Studies by Cho *et al.,* on the Au-doping process's modification of the MoS_2 have shown the effect of charge concentration toward VOC detection. Gold (Au) nanoparticles were incorporated into chemically exfoliated layers of MoS_2 using a simple solution-mixing technique. It was discovered that the n-doping effect of Au nanoparticles promoted the transport of electron charge from Au to MoS_2. MoS_2 can be tuned to sense hydrocarbon-based VOCs and compounds with oxygen functionalized attributable to the regulated n-doping effect. Eventually, early detection employing multichannel

sensing systems that have various sensitivities and can recognize patterns for target analytes will leverage this controlled chemical doping technique to tune the VOC-sensing capability of MoS_2 [40]. Figure 5 shows a schematic illustration of the controlled process of decorating Au onto MoS_2.

Au nanoparticle-modified porous TiO_2 (Au@TiO_2) nanospheres synthesized using a hydrothermal method followed by liquid reduction demonstrated high sensitivity to 100 ppm formaldehyde, acetone, ethanol, and isopropanol at 220 °C with response values of 45.2, 55, 29, and 50, respectively. The Au nanoparticles (~12 nm) were well anchored on porous TiO_2 nanospheres through epitaxial growth. The response/recovery times for 100 ppm acetone vapor were 12 s and 13 s. Work by Ren *et al.,* suggests that Au@TiO_2 nanospheres are promising for detecting toxic volatile vapors [41].

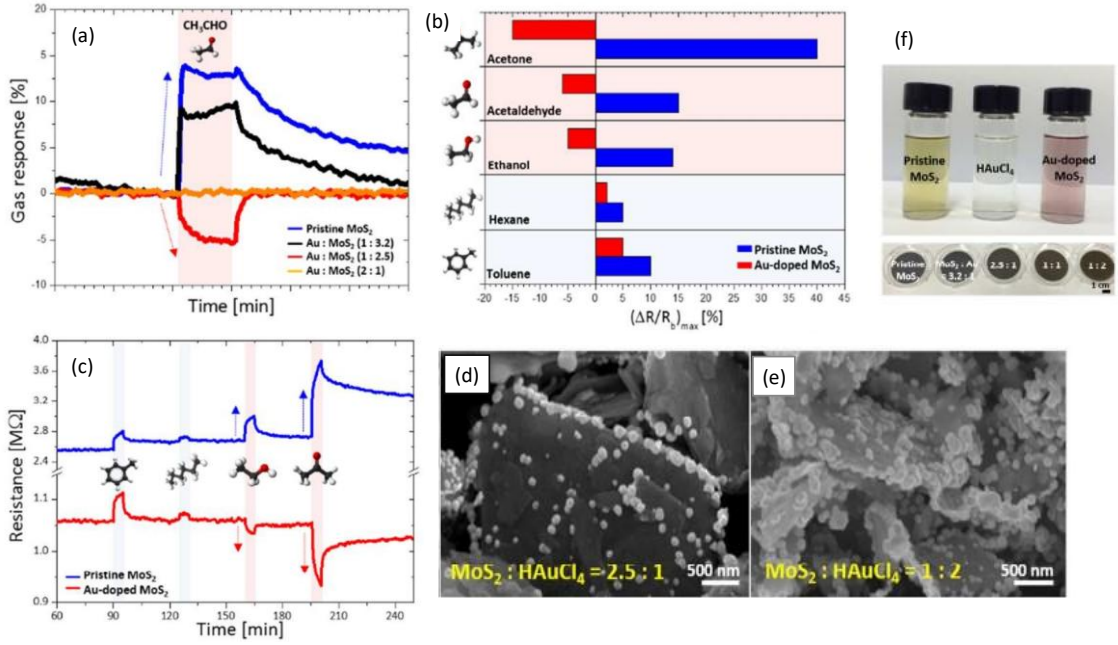


Fig. 5. (a) The fluctuation in resistance of the Au-doped MoS_2 sensor when exposed to acetaldehyde at a concentration of 1000 ppm; (b) Real-time changes in resistance; (c) The normalized response (ΔR/Rb) of both pristine MoS_2 and Au-doped MoS_2 sensors when exposed to different VOCs.; (d)-(e) SEM images Au-doped MoS_2 and (f) A photograph of pristine MoS_2 and Au-doped MoS_2 solutions and films. Reprinted (adapted) with permission from [40]Copyright 2017 American Chemical Society

Another work by Yang *et al.,* reported that under moderate circumstances, Au-WO_3 composite nanofibers (NFs) were electrospun to create a highly sensitive and selective gas-sensing material. The surface of the WO_3 nanofibers was then coated with uniformly sized Au nanoparticles (5–10 nm) to serve as catalysts and enhance the sensing response. The gas-sensing findings show the great responsiveness of the WO_3-Au composite NF sensor, especially the WO_3-Au-0.1M sensor, which has a response that is around ~60 times higher than the pure WO_3 sensors and much better selectivity towards n-butanol. The excellent catalytic activity of Au nanoparticles, which boosts the rate of an oxygen molecule to ion conversion, and the presence of multiple depletion layers at the surface of the WO_3-Au composite nanofibers, which results in a greater change in resistivity upon exposure to n-butanol, may be responsible for the enhanced response of the WO_3-Au composite nanofiber sensor towards n-butanol [42].

Huang *et al.,* explored the improvement of acetone-sensing capabilities to parts per billion (ppb) detection levels using Au/Pd-doped ZnO nanorods. The researchers successfully prepared ZnO nanorods doped with varying amounts of Au and Pd using a one-step microwave-assisted hydrothermal method. In particular, the sensor utilizing ZnO doped with 2.0 wt% Au demonstrates

superior response rates, rapid response and recovery features, optimal selectivity, a low operating temperature, and excellent long-term stability when exposed to acetone. Following the introduction of 2.0 wt% Au, the detection limit of the Au-doped ZnO sensor decreases to 5 ppb, while the response surges to 17 under 1 ppm acetone at 150℃, surpassing the ZnO sensor's responses by more than threefold. The excellent sensing capabilities can be ascribed to the substantial levels of chemically adsorbed oxygen generated by the extensive surface area of the porous ZnO nanorods doped with Au, along with the Au spillover mechanism [43].

3.2 Nanostructuring

The past ten years have seen a significant increase in interest in metal oxide semiconductors (MOS) due to their numerous uses in the monitoring of air quality, gas leaks, food safety, and medical diagnosis [44-47]. Scientific and technological significance has been given to nanostructured MOS of the p-type (nickel oxide (NiO), copper oxide (CuO), cobalt oxide (Co_3O_4)) and n-type (indium oxide (In_2O_3), zinc oxide (ZnO), tin oxide (SnO_2), titanium oxide (TiO_2), and tungsten trioxide (WO_3)), which are commonly employed to detect VOC chemicals such NO_x, CO, ozone, ethanol, etc [48-54].

Zhao *et al.,* introduced a novel method utilizing poly(ethylene oxide)-block-polystyrene (PEO-b-PS) as the template, SnO_2 nanocrystals (NCs) as tin supply, and titanium butoxide (TBOT) as the titania precursor to incorporate SnO_2 NCs into a 3D branching mesoporous TiO_2 framework. The nano size (3-5 nm), good dispersibility, and abundance of hydroxyl groups in SnO_2 NCs enable interaction with the PEO block. This interaction through hydrogen bonding, co-assembling with hydrolyzed TBOT to form a unique hierarchical branched mesoporous structure (SHMT). The resulting structure exhibits a three-dimensional flower-like morphology with mesoporous rutile TiO_2 branches, featuring regular cylindrical mesopores (≈ 9 nm). The SnO_2 NCs are evenly distributed within the mesoporous TiO_2 matrix, creating numerous n-n heterojunctions [55]. The sensor outputs exhibit an increase with the rise of operational temperature, reaching a peak at 350 °C. Whereas, a decrease in sensitivity at lower operational temperatures can be elucidated by the low activation energy required for the chemisorption of gas species on the surface. At higher temperatures, there is an increase of gas molecules desorbing from the surface, leading to a decrease in the response of the gas sensor as shown in Figure 6.

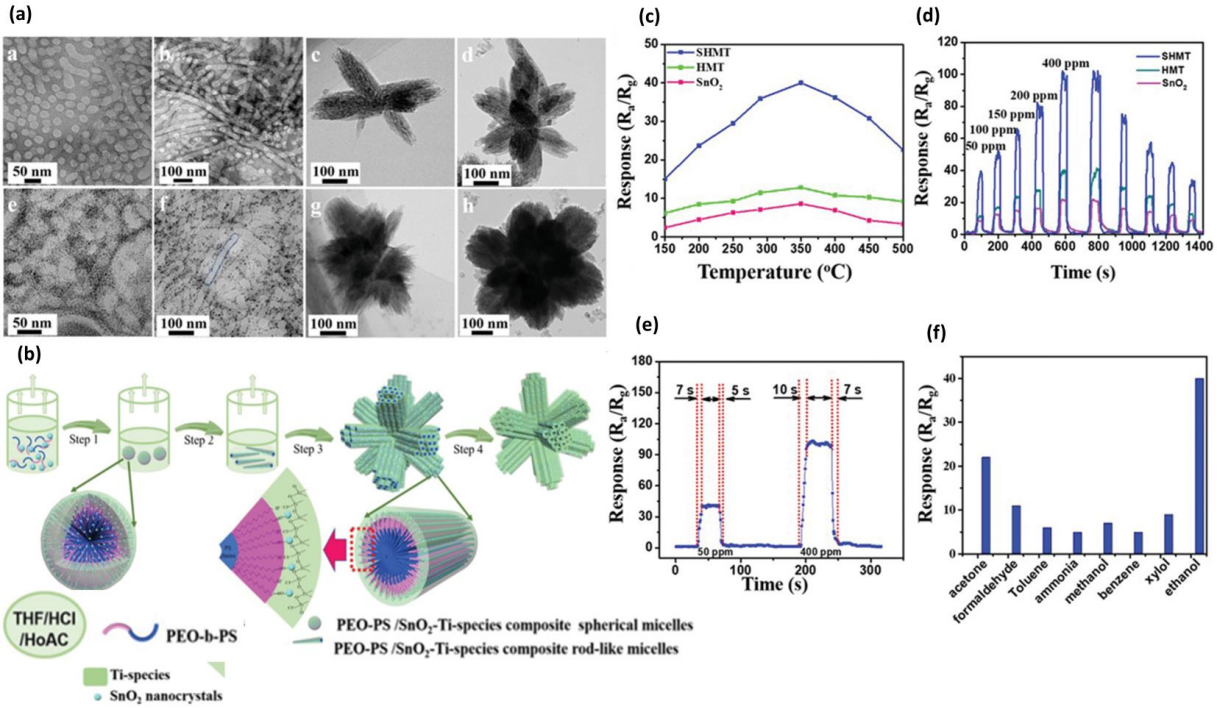


Fig. 6. (a) TEM images of the composites; (b) Illustration depicting the process of incorporating SnO_2 nanocrystals (NCs) into a 3D branched mesoporous TiO_2 framework, (c)-(d) Sensor responses to 50 ppm ethanol at different operating temperatures (150–500 °C); (e) Dynamic response-recovery curve; and (f) Sensor responses of SHMT to various gases at 50 ppm, evaluating selectivity. Reproduced from [55]

Hermawan *et al.,* reported a simple method for making spherical n-type SnO_2 uniformly decorated with p-type CuO nanoparticles for improving toluene gas detection. CuO-SnO_2 was produced utilizing a simple non-hydrolytic solvothermal that allowed for easy morphological control. The surface charge of the oxide was significantly influenced by the organic solvents used in the synthesis, which was advantageous for a consistent electrostatic self-decoration between positively charged p-type CuO and negatively charged n-type SnO_2. CuO was largely reduced to Cu metal under high concentrations of toluene exposure, damaging the p-n contact and creating a new metal-semiconductor contact, or "ohmic junction," which led to highly responsive and selective toluene gas at 400 ºC. Additionally, it was discovered that sensor resistance and responsiveness were affected by the quantity of particle decorating [56].

Zito *et al.,* synthesized a bicone-like ZnO structure using a rapid template-free microwave-assisted hydrothermal method. According to the results of the VOC-sensing experiments, the ZnO structure responded to butanone more strongly than it did to other VOCs like benzene, toluene, m-xylene, acetone, ethanol, acetaldehyde, and isopropanol. From the morphology analysis, the development of bicone-like ZnO structures indicates that each structure is made up of two cones (Figure 1(a)). The bicone structure has an average length of 1 µm and a diameter of ~400 nm (Figure 1(b)). Additionally, the ZnO-based sensor demonstrated improved butanone detecting performance at 400 °C, with a response of 29.4-100 ppm of butanone, high sensitivity to detect low butanone concentration (2 ppm), and a low detection limit of 0.41 ppm [57].

Fabrication of a room temperature resistive acetone gas sensor using MoS_2-CuO nanocomposite as a sensing layer was reported by Roy *et al.,* [58]. The sensor's responses for acetone gas concentrations of 10 ppm and 500 ppb, respectively, and a detection limit of 93 ppb were found to be 16.21 ± 0.32 and 4.35 ± 0.13. Acetone molecules absorb oxygen species from the CuO surface as they come into contact with it and give off electrons in the process. The charge concentration at the

junction is significantly increased. As a result, charges are reorganized, and the depletion zone in the CuO domain continues to grow, increasing the overall resistance through the CuO surfaces.

3.3 Polymer Coatings

The application of polymer coatings on MOS is a widely adopted strategy to enhance the sensing properties and selectivity of VOCs sensors. This technique involves the deposition of a thin layer of polymer onto the surface of the MOS. Various methods, such as spin-coating, dip-coating, spray-coating, or layer-by-layer deposition, can be employed to apply polymer coatings. The choice of an appropriate polymer depends on the specific target VOCs and their interaction with the metal oxide semiconductor. Recently, there has been considerable interest in utilizing nanomaterials based on conducting polymers (CPs) for constructing sensing devices that enable the swift and specific detection of various chemicals, gases, and vapors under ambient conditions. Among these, polythiophene and its derivatives stand out as extensively employed conducting polymers in gas sensing applications, showcasing high sensitivity to analytes [59-62].

Husain *et al.,* [63] successfully synthesized PTh and PTh/molybdenum oxide nanocomposites (PTh/MoO_3) using an in-situ chemical oxidative method (Figure 7). The materials' thermal stability, assessed through conductivity retention under isothermal and cyclic aging conditions, revealed that PTh/MoO_3 exhibited significantly higher conductivity retention compared to pristine PTh. At room temperature, PTh/MoO_3 demonstrated 18.22 times greater electrical conductivity than pristine PTh. Sensing experiments against ammonia, methanol, and acetone vapors at room temperature showed that the PTh/MoO_3 sensor outperformed the PTh sensor in terms of percent sensing response and reproducibility, with notable enhancements for all analytes.

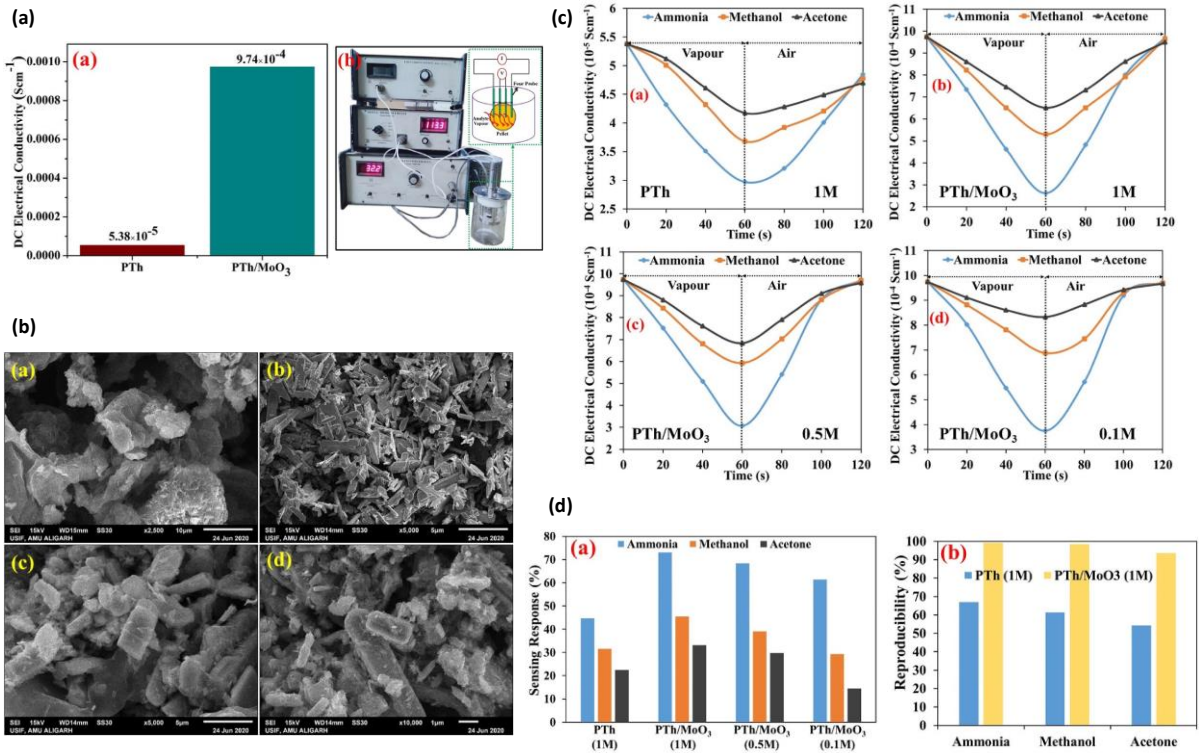


Fig. 7. (a) Conductivity and sensing experiments setup; (b) SEM images illustrate PTh, MoO_3 NPs, and PTh/MoO_3; (c) conductivity change of PTh and PTh/MoO_3-based sensor at 1 M, 0.5 M, in vapor and air; (d) sensing response and percent reproducibility of PTh and PTh/MoO_3 sensors for various analytes. Reproduced from [63]

In a recent publication, Khan *et al.,* [64]synthesised polymeric composite electrodes utilizing carbon nanotubes (CNTs) and copper oxide nanoparticles (CuO NPs) with the aim of detecting volatile organic compounds (VOCs). The CNTs underwent functionalization and opening through the reflux method, followed by impregnation with CuO NPs to form the CNTs/CuO nanocomposite. For the construction of the polymeric composite electrode, the CuO NPs-functionalized CNTs were dispersed in polyvinylidene difluoride (PVDF). The study also investigated the voltage response to various VOCs, including acetone, formaldehyde, ethanol, and spirit, using a multimeter setup. Over time, the voltage generated by each VOC displayed fluctuations, with distinct time intervals yielding the highest voltage for each compound. For example, the highest voltage was observed at 0.2 minutes for acetone, 6 minutes for formaldehyde, 0.1 minutes for ethanol, and 0.8 minutes for spirit.

Whereas Foronda *et al.,* [65] investigated the development of gas sensors utilizing a Polyaniline/Zinc oxide (PANI/ZnO) composite capable of detecting various VOCs such as ammonia, acetone, formaldehyde, methanol, and ethanol, as illustrated in Figure 8. The conductivity of these sensors was assessed at room temperature until saturation. PANI/ZnO composites with different additive ratios were drop-cast to form sensors, and their formability and mechanical behavior were examined. Exceptional selectivity for ammonia, with an average sensor response of 3496.67 mV across all sensors, was achieved using various matrix-additive ratios, surpassing the selectivity of Pure-PANI sensors limited to methanol and ethanol. The resistance patterns of PANI/ZnO revealed that formulations with fewer pores exhibited higher resistance. The inclusion of ZnO in the PANI matrix enhanced stability against methanol exposure. A radar plot was employed to illustrate distinctive sensor response patterns towards ammonia, acetone, formaldehyde, methanol, and ethanol.

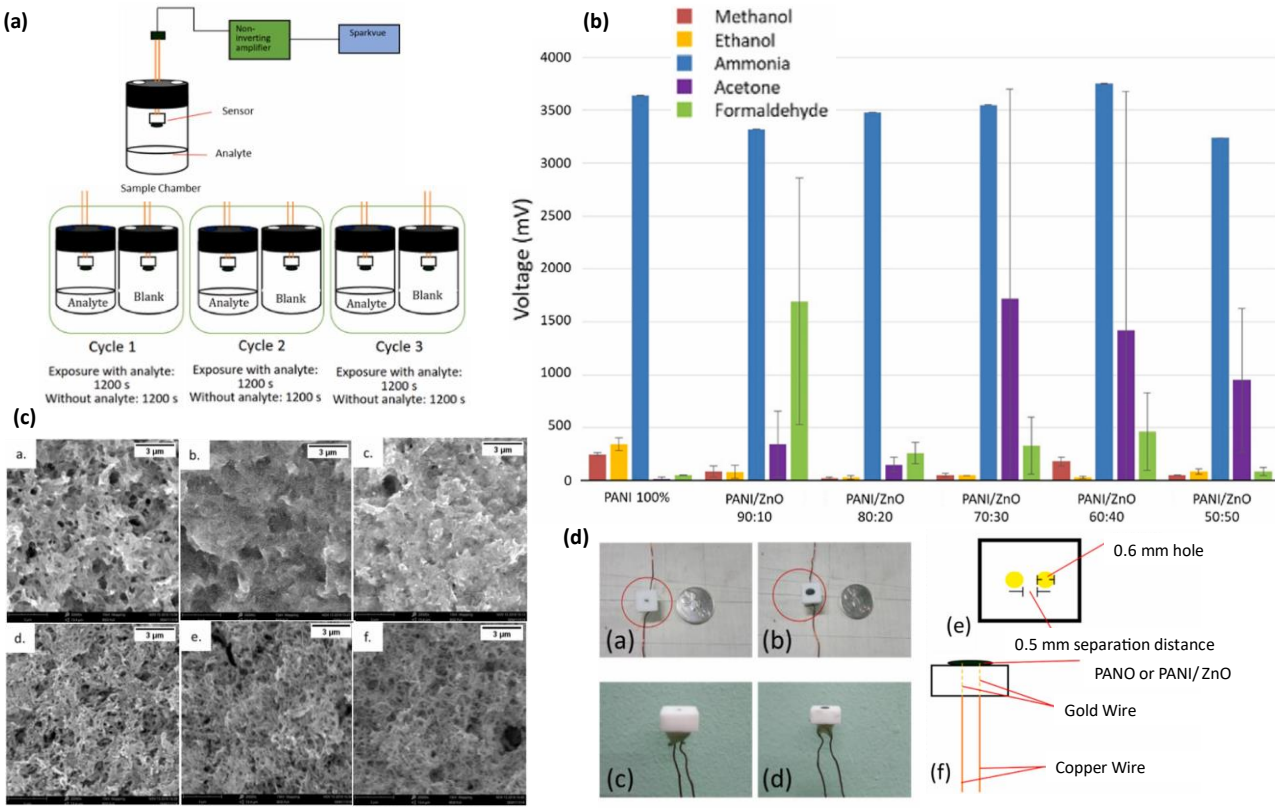


Fig. 8. Diagram of gas sensing set-up schematically and cycle run time (a); Average response of both PANI and PANI/ZnO sensors to all analytes (b); SEM images of PANI/ZnO (c); Schematic of the gas sensor substrate and reference sample (d); Reproduced from [65]

Farea *et al.,* [66]conducted a study utilizing polypyrrole/TiO_2 nanocomposites to develop a carbon monoxide (CO) gas sensor operating at room temperature. Gas sensors were created by depositing Ppy/TiO_2 nanocomposites onto interdigitated electrodes through drop-casting. The nanocomposites were synthesized using a chemical oxidation method. Compared to the pure Ppy sensor, the Ppy/TiO_2 sensor showed a substantial four-fold increase in sensitivity over a broad range of CO concentrations, spanning from 1 to 320 ppm. Moreover, the sensor exhibited a rapid response time of 36 seconds and a quick recovery time of 38 seconds. It demonstrated prolonged stability, excellent repeatability, and satisfactory reproducibility. These experimental findings clearly highlight the significant role of incorporating TiO_2 into the Ppy matrix in enhancing the gas sensor's overall performance.

3.4 Ligand Modification

Ligand conjugation with metal-organic semiconductors involves the attachment or bonding of ligand molecules to a metal-organic semiconductor material. This process can significantly influence the electronic and optical properties of the semiconductor, leading to tailored functionalities and improved performance in various applications [67]. The term "ligand" typically refers to molecules or ions that can bind to a central metal atom in coordination compounds.

Kim *et al.,* [68] (Figure 9) have successfully developed a tunable sensor for volatile organic compounds (VOCs) through thiolated ligand conjugation on MoS_2. They introduce a highly sensitive, stable, and cost-effective chemiresistor using MoS_2 bulk films, which can be functionalized by thiolated ligand conjugation through a straightforward solution mixing process. This process is followed by vacuum filtration to create sensing films from both primitive MoS_2 and 11-mercaptoundecanoic acid-conjugated MoS_2 (MUA-MoS_2) solutions. Both films exhibit remarkable sensitivity (detectable down to 1 ppm) and selectivity towards various VOC groups, including toluene, hexane, ethanol, propionaldehyde (propanal), and acetone. The MUA-MoS_2 film demonstrates a decrease in resistance (negative response) when exposed to oxygen-functionalized molecules (such as ethanol, propanal, and acetone), while other VOCs (toluene and hexane) induce a similar but diminished positive response compared to the primitive MoS_2 sensor.

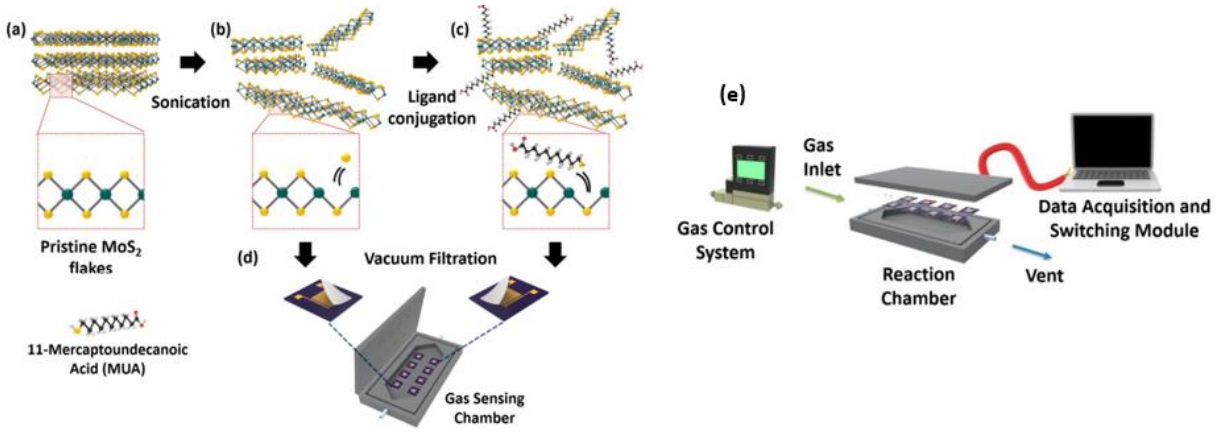


Fig. 9. The schematic depicts the preparation of MoS_2 chemiresistor. Reprinted with permission from reference [68]. Copyright 2014. American Chemical Society

Research conducted by S. Yuvaraj and colleagues [69] has demonstrated the suitability of hybrid nanostructures formed by functionalizing ZnO nanorods with macromolecules similar to porphyrin, specifically pyrene-based tetratopic ligands (PTL) terminated with four carboxyl (COOH) groups, for adsorbing volatile organic compounds (VOCs). The electrical resistance of ZnO-PTL is influenced by

the absorption of various VOCs, including ethanol, n-hexane, trimethylamine, and triethylamine. The response to these VOCs is significantly affected by illumination. To understand the interaction mechanism between PTL and VOCs, experimental studies have been complemented by first principles calculations. Both experimental and computational findings indicate that amines exhibit a higher affinity for binding to PTL compared to ethanol and n-hexane. The combined use of optical dyes and chemical ligands presents an innovative approach to designing chemical sensors.

4. Conclusion

In conclusion, the surface functionalization of metal-organic semiconductors offers promising avenues for enhancing the performance of resistive gas sensors, particularly in the detection of volatile organic compounds. Key strategies include metal site modification with noble metals such as Ag and Pt, nano-structuring, polymer coatings, and ligand modification. Metal site modification, as exemplified by Ag-doped ZnO columnar films and Pt-SnO_2 nano-needles, demonstrates improved sensing characteristics and electrical conductivity, highlighting the potential of noble metal functionalization in MOS-based sensors. Nano-structuring, involving the use of nano-structured MOS materials, enhances sensitivity to a wide range of VOCs. Methods such as incorporating SnO_2 nanocrystals into a 3D mesoporous TiO_2 framework and creating p-n junctions in CuO-SnO_2 nanomaterials contribute to improved gas sensing capabilities. Polymer coatings on MOS surfaces offer a versatile approach for tailoring sensor selectivity. Conducting polymers like polyaniline, polypyrrole, and polythiophene, when used as coatings, enables highly sensitive and selective detection of VOCs even at room temperature. Ligand modification, as demonstrated with thiolated ligand conjugation on MoS_2 and the use of pyrene-based tetratopic ligands on ZnO nanorods, presents a novel approach. These hybrid systems show high sensitivity and selectivity toward various VOCs, offering the potential for cost-effective and stable chemiresistors. In summary, the functionalization of metal-organic semiconductors through diverse techniques holds great promise for the development of advanced gas sensors capable of detecting and monitoring volatile organic compounds, addressing critical needs in indoor air quality, industrial safety, and healthcare applications. These strategies open doors to improved sensor performance, selectivity, and reliability, paving the way for enhanced environmental and safety monitoring.

Acknowledgement

The authors wish to thank the Centre for Research and Innovation Management, UPNM for funding this research under the Self-Fund grant scheme (Code Grant: SF0118-UPNM/SF/ST/2) and Post-doctoral grant scheme (Code Grant: UPNM/2023/ GPPP/SG/5).

References

[1] Zhou, Xihe, Xiang Zhou, Chengming Wang, and Handong Zhou. "Environmental and human health impacts of volatile organic compounds: A perspective review." *Chemosphere* 313 (2023): 137489. https://doi.org/10.1016/j.chemosphere.2022.137489

[2] Chiang, Wen-Chieh, Chao-Yu Chen, Ting-Chen Lee, Hui-Ling Lee, and Yu-Wen Lin. "Fast and simple screening for the simultaneous analysis of seven metabolites derived from five volatile organic compounds in human urine using on-line solid-phase extraction coupled with liquid chromatography-tandem mass spectrometry." *Talanta* 132 (2015): 469-478. https://doi.org/10.1016/j.talanta.2014.09.029

[3] Gao, Meiping, Wenwen Liu, Xiaoshuan An, Lei Nie, Zhenxia Du, Panjin Chen, and Xiaoyu Liu. "Emission factors and emission inventory of volatile organic compounds (VOCs) from hair products application in hair salons in Beijing through measurement." *Science of The Total Environment* 878 (2023): 162996. https://doi.org/10.1016/j.scitotenv.2023.162996

[4] Pan, Qi, Qing-Yu Liu, Jing Zheng, Yan-Hong Li, Song Xiang, Xiao-Jie Sun, and Xiao-Song He. "Volatile and semi-volatile organic compounds in landfill gas: Composition characteristics and health risks." *Environment International* 174 (2023): 107886. https://doi.org/10.1016/j.envint.2023.107886

[5] Tang, Jianyi, Yingjie Li, Xinling Li, Cheng Huang, Jiping Zhu, Qingyao Hu, Hongli Wang et al. "Intermediate volatile organic compounds emissions from vehicles under real world conditions." *Science of The Total Environment* 788 (2021): 147795. https://doi.org/10.1016/j.scitotenv.2021.147795

[6] Fang, Lin, Christina Norris, Karoline Johnson, Xiaoxing Cui, Jiaqi Sun, Yanbo Teng, Enze Tian et al. "Toxic volatile organic compounds in 20 homes in Shanghai: Concentrations, inhalation health risks, and the impacts of household air cleaning." *Building and environment* 157 (2019): 309-318. https://doi.org/10.1016/j.buildenv.2019.04.047

[7] Gałęzowska, Grażyna, Milena Chraniuk, and Lidia Wolska. "In vitro assays as a tool for determination of VOCs toxic effect on respiratory system: A critical review." *TrAC Trends in Analytical Chemistry* 77 (2016): 14-22. https://doi.org/10.1016/j.trac.2015.10.012

[8] Cakmak, Sabit, Robert E. Dales, Ling Liu, Lisa Marie Kauri, Christine L. Lemieux, Christopher Hebbern, and Jiping Zhu. "Residential exposure to volatile organic compounds and lung function: results from a population-based cross-sectional survey." *Environmental pollution* 194 (2014): 145-151. https://doi.org/10.1016/j.envpol.2014.07.020

[9] Wang, Juan, Christer Janson, Thorarinn Gislason, Maria Gunnbjörnsdottir, Rain Jogi, Hans Orru, and Dan Norbäck. "Volatile organic compounds (VOC) in homes associated with asthma and lung function among adults in Northern Europe." *Environmental Pollution* 321 (2023): 121103. https://doi.org/10.1016/j.envpol.2023.121103

[10] Vyas, Tanmay, Kamakshi Parsai, Isha Dhingra, and Abhijeet Joshi. "Nanosensors for detection of volatile organic compounds." In *Advances in Smart Nanomaterials and their Applications*, pp. 273-296. Elsevier, 2023. https://doi.org/10.1016/B978-0-323-99546-7.00006-9

[11] Salviano dos Santos, Vânia Paula, Andréa Medeiros Salgado, Alexandre Guedes Torres, and Karen Signori Pereira. "Benzene as a chemical hazard in processed foods." *International journal of food science* 2015, no. 1 (2015): 545640. https://doi.org/10.1155/2015/545640

[12] Di Fiore, Cristina, Pietro Pandolfi, Fabiana Carriera, Alessia Iannone, Gaetano Settimo, Vincenzo Mattei, and Pasquale Avino. "The presence of aromatic substances in incense: determining indoor air quality and its impact on human health." *Applied Sciences* 13, no. 12 (2023): 7344. https://doi.org/10.3390/app13127344

[13] Subasi, Nuriye Tuna. "Formaldehyde advantages and disadvantages: usage areas and harmful effects on human beings." *Biochemical Toxicology-Heavy Metals and Nanomaterials* 89299 (2020). https://doi.org/10.5772/intechopen.89299

[14] Kamani, Hossein, Marzieh Baniasadi, Hossein Abdipour, Leili Mohammadi, Shahla Rayegannakhost, Hossein Moein, and Ali Azari. "Health risk assessment of BTEX compounds (benzene, toluene, ethylbenzene and xylene) in different indoor air using Monte Carlo simulation in zahedan city, Iran." *Heliyon* 9, no. 9 (2023). https://doi.org/10.1016/j.heliyon.2023.e20294

[15] Filley, Christopher M., William Halliday, and B. K. Kleinschmidt-DeMasters. "The effects of toluene on the central nervous system." *Journal of Neuropathology & Experimental Neurology* 63, no. 1 (2004): 1-12. https://doi.org/10.1093/jnen/63.1.1

[16] Fowles, Jeff, Marcy Banton, Joanna Klapacz, and Hua Shen. "A toxicological review of the ethylene glycol series: Commonalities and differences in toxicity and modes of action." *Toxicology letters* 278 (2017): 66-83. https://doi.org/10.1016/j.toxlet.2017.06.009

[17] Li, Yu-Hua, Sheng-Hua Yang, Chung-Shin Yuan, Huazhen Shen, and Chung-Hsuang Hung. "Photocatalytic degradation of gaseous acetone by photocatalysts with visible light and their potential applications in painting." *Aerosol and Air Quality Research* 23, no. 3 (2023): 220358. https://doi.org/10.4209/aaqr.220358

[18] Williams, Amy Lavin, Christopher A. Bates, Nelson D. Pace, Megan J. Leonhard, Ellen T. Chang, and John M. DeSesso. "Impact of chloroform exposures on reproductive and developmental outcomes: A systematic review of the scientific literature." *Birth Defects Research* 110, no. 17 (2018): 1267-1313. https://doi.org/10.1002/bdr2.1382

[19] Niaz, Kamal, Haji Bahadar, Faheem Maqbool, and Mohammad Abdollahi. "A review of environmental and occupational exposure to xylene and its health concerns." *EXCLI journal* 14 (2015): 1167.

[20] Markić, Dragana Nešković, Ljiljana Stojanović Bjelić, Slađana Šiljak, Željko Jovičić, and Željka Cvijetić. "Health Risk Assesssment of Benzen, Toluene and Xylene at a Landfill." *QUALITY OF LIFE (BANJA LUKA)-APEIRON* 24, no. 1-2 (2023): 47-55. https://doi.org/10.7251/QOL2301047M

[21] Duan, Lizhe, Qinghang Yun, Gaoliang Jiang, Daoguang Teng, Guoli Zhou, and Yijun Cao. "A review of chloride ions removal from high chloride industrial wastewater: Sources, hazards, and mechanisms." *Journal of Environmental Management* 353 (2024): 120184. https://doi.org/10.1016/j.jenvman.2024.120184

[22] Tayebi, Noureddine, and Xing Su. "Sensitive and selective gas/VOC detection using MOS sensor array for wearable and mobile applications." In *2017 ISOCS/IEEE International Symposium on Olfaction and Electronic Nose (ISOEN)*, pp. 1-3. IEEE, 2017. https://doi.org/10.1109/ISOEN.2017.7968866

[23] Fois, Matteo, Timothy Cox, Norman Ratcliffe, and Ben de Lacy Costello. "Rare earth doped metal oxide sensor for the multimodal detection of volatile organic compounds (VOCs)." *Sensors and Actuators B: Chemical* 330 (2021): 129264. https://doi.org/10.1016/j.snb.2020.129264
[24] He, Haiping. "Metal oxide semiconductors and conductors." In *Solution Processed Metal Oxide Thin Films for Electronic Applications*, pp. 7-30. Elsevier, 2020. https://doi.org/10.1016/B978-0-12-814930-0.00002-5
[25] Albarakati, Alaa Jameel, and Ibrahim A. Matter. "N-type metal oxide semiconductor: Materials and their environmental applications." *Biointerface Research in Applied Chemistry* 13, no. 6 (2023): 519.
[26] Moumen, Abderrahim, Gayan CW Kumarage, and Elisabetta Comini. "P-type metal oxide semiconductor thin films: Synthesis and chemical sensor applications." *Sensors* 22, no. 4 (2022): 1359. https://doi.org/10.3390/s22041359
[27] Gautam, Yogendra K., Kavita Sharma, Shrestha Tyagi, Anit K. Ambedkar, Manika Chaudhary, and Beer Pal Singh. "Nanostructured metal oxide semiconductor-based sensors for greenhouse gas detection: Progress and challenges." *Royal Society open science* 8, no. 3 (2021): 201324. https://doi.org/10.1098/rsos.201324
[28] Akamatsu, Takafumi, Toshio Itoh, Noriya Izu, and Woosuck Shin. "NO and NO2 sensing properties of WO3 and Co3O4 based gas sensors." *Sensors* 13, no. 9 (2013): 12467-12481. ttps://doi.org/10.3390/s130912467
[29] Kim, Hyo-Joong, and Jong-Heun Lee. "Highly sensitive and selective gas sensors using p-type oxide semiconductors: Overview." *Sensors and Actuators B: Chemical* 192 (2014): 607-627. https://doi.org/10.1016/j.snb.2013.11.005
[30] Keiichi Kawakami, and Hiroaki Yanagida. " Effects of Water Vapor on the Electrical Conductivity of the Interface of Semiconductor Ceramic-Ceramic Contact." *窯業協會誌* 87, no. 1002 (1979): 112-115. https://doi.org/10.2109/jcersj1950.87.1002_112
[31] Sowmya, B., Athira John, and P. K. Panda. "A review on metal-oxide based pn and nn heterostructured nano-materials for gas sensing applications." *Sensors International* 2 (2021): 100085. https://doi.org/10.1016/j.sintl.2021.100085
[32] Betty, C. A., Sipra Choudhury, and Alpa Shah. "Nanostructured metal oxide semiconductors and composites for reliable trace gas sensing at room temperature." *Surfaces and Interfaces* 36 (2023): 102560. https://doi.org/10.1016/j.surfin.2022.102560
[33] Lee, Chul-Soon, Zhengfei Dai, Hua-Yao Li, Young-Moo Jo, Bo-Young Kim, Hyung-Gi Byun, Insung Hwang, and Jong-Heun Lee. "Highly discriminative and sensitive detection of volatile organic compounds for monitoring indoor air quality using pure and Au-loaded 2D In2O3 inverse opal thin films." *Sensors and Actuators B: Chemical* 273 (2018): 1-8. https://doi.org/10.1016/j.snb.2018.06.011
[34] Shinkai, Takeshi, Keigo Masumoto, Masaru Iwai, Yusuke Inomata, and Tetsuya Kida. "Study on Sensing Mechanism of Volatile Organic Compounds Using Pt-Loaded ZnO Nanocrystals." *Sensors* 22, no. 16 (2022): 6277. https://doi.org/10.3390/s22166277
[35] Kılıç, Alp, Onur Alev, Okan Özdemir, Leyla Çolakerol Arslan, Serkan Büyükköse, and Zafer Ziya Öztürk. "The effect of Ag loading on gas sensor properties of TiO2 nanorods." *Thin Solid Films* 726 (2021): 138662. https://doi.org/10.1016/j.tsf.2021.138662
[36] Öztürk, Sadullah, Arif Kösemen, Zühal Alpaslan Kösemen, Necmettin Kılınç, Zafer Ziya Öztürk, and Michele Penza. "Electrochemically growth of Pd doped ZnO nanorods on QCM for room temperature VOC sensors." *Sensors and Actuators B: Chemical* 222 (2016): 280-289. https://doi.org/10.1016/j.snb.2015.08.083
[37] Postica, Vasile, Alexander Vahl, David Santos-Carballal, Torben Dankwort, Lorenz Kienle, Mathias Hoppe, Abdelaziz Cadi-Essadek et al. "Tuning ZnO sensors reactivity toward volatile organic compounds via Ag doping and nanoparticle functionalization." *ACS applied materials & interfaces* 11, no. 34 (2019): 31452-31466. https://doi.org/10.1021/acsami.9b07275
[38] Lupan, Oleg, Lee Chow, Guangyu Chai, Alfons Schulte, S. Park, and H. Heinrich. "A rapid hydrothermal synthesis of rutile SnO2 nanowires." *Materials Science and Engineering: B* 157, no. 1-3 (2009): 101-104. https://doi.org/10.1016/j.mseb.2008.12.035
[39] Zhou, Qu, Lingna Xu, Ahmad Umar, Weigen Chen, and Rajesh Kumar. "Pt nanoparticles decorated SnO2 nanoneedles for efficient CO gas sensing applications." *Sensors and Actuators B: Chemical* 256 (2018): 656-664. https://doi.org/10.1016/j.snb.2017.09.206
[40] Cho, Soo-Yeon, Hyeong-Jun Koh, Hae-Wook Yoo, Jong-Seon Kim, and Hee-Tae Jung. "Tunable volatile-organic-compound sensor by using Au nanoparticle incorporation on MoS2." *Acs Sensors* 2, no. 1 (2017): 183-189. https://doi.org/10.1021/acssensors.6b00801
[41] Ren, Haibo, Huaipeng Weng, Jiarui Huang, Xiaojing Lu, and Sang Woo Joo. "Synthesis of Au nanoparticle-modified porous TiO2 nanospheres for detection of toxic volatile organic vapors." *Journal of Alloys and Compounds* 919 (2022): 165843. https://doi.org/10.1016/j.jallcom.2022.165843
[42] Yang, Xiaojiao, Vincent Salles, Yusuf Valentino Kaneti, Minsu Liu, Mathieu Maillard, Catherine Journet, Xuchuan Jiang, and Arnaud Brioude. "Fabrication of highly sensitive gas sensor based on Au functionalized WO3 composite

nanofibers by electrospinning." *Sensors and Actuators B: Chemical* 220 (2015): 1112-1119. https://doi.org/10.1016/j.snb.2015.05.121

[43] Huang, Jinyu, Jiaxi Zhou, Zhenhua Liu, Xuejin Li, Youfu Geng, Xiaoqing Tian, Yu Du, and Zhengfang Qian. "Enhanced acetone-sensing properties to ppb detection level using Au/Pd-doped ZnO nanorod." *Sensors and Actuators B: Chemical* 310 (2020): 127129. https://doi.org/10.1016/j.snb.2019.127129

[44] Yuan, Hongye, Nanxi Li, Weidong Fan, Hong Cai, and Dan Zhao. "Metal-organic framework based gas sensors." *Advanced Science* 9, no. 6 (2022): 2104374. https://doi.org/10.1002/advs.202104374

[45] Dadkhah, Mehran, and Jean-Marc Tulliani. "Green synthesis of metal oxides semiconductors for gas sensing applications." *Sensors* 22, no. 13 (2022): 4669. https://doi.org/10.3390/s22134669

[46] Eranna, G., B. C. Joshi, D. P. Runthala, and R. P. Gupta. "Oxide materials for development of integrated gas sensors—a comprehensive review." *Critical Reviews in Solid State and Materials Sciences* 29, no. 3-4 (2004): 111-188. https://doi.org/10.1080/10408430490888977

[47] Sharma, Swati, and Marc Madou. "A new approach to gas sensing with nanotechnology." *Philosophical Transactions of the Royal Society A: Mathematical, Physical and Engineering Sciences* 370, no. 1967 (2012): 2448-2473. https://doi.org/10.1098/rsta.2011.0506

[48] Chen, Hongjun, Renheng Bo, Aabhash Shrestha, Bobo Xin, Noushin Nasiri, Jin Zhou, Iolanda Di Bernardo et al. "NiO–ZnO nanoheterojunction networks for room-temperature volatile organic compounds sensing." *Advanced Optical Materials* 6, no. 22 (2018): 1800677. https://doi.org/10.1002/adom.201800677

[49] Deng, Shaojuan, Nan Chen, Dongyang Deng, Yuxiu Li, Xinxin Xing, and Yude Wang. "Meso-and macroporous coral-like Co3O4 for VOCs gas sensor." *Ceramics International* 41, no. 9 (2015): 11004-11012. https://doi.org/10.1016/j.ceramint.2015.05.045

[50] Xia, Shufeng, Huichao Zhu, Haitao Cai, Jiaqi Zhang, and Jun Yu. "Hydrothermally synthesized CuO based volatile organic compound gas sensor." *RSC Advances* 4, no. 101 (2014): 57975-57982. https://doi.org/10.1039/C4RA09083G

[51] Dong, Hongxing, Yang Liu, Guanghui Li, Xuewen Wang, Dan Xu, Zhanghai Chen, Ting Zhang, Jun Wang, and Long Zhang. "Hierarchically rosette-like In2O3 microspheres for volatile organic compounds gas sensors." *Sensors and Actuators B: Chemical* 178 (2013): 302-309. https://doi.org/10.1016/j.snb.2012.12.103

[52] Haddad, Kelsey, Ahmed Abokifa, Shalinee Kavadiya, Byeongdu Lee, Sriya Banerjee, Baranidharan Raman, Parag Banerjee, Cynthia Lo, John Fortner, and Pratim Biswas. "SnO2 nanostructured thin films for room-temperature gas sensing of volatile organic compounds." *ACS applied materials & interfaces* 10, no. 35 (2018): 29972-29981. https://doi.org/10.1021/acsami.8b08397

[53] Park, Jaebum, Jihoon Lee, Myung Sik Choi, and Jeung-Soo Huh. "Formaldehyde gas sensing characteristics of ZnO-TiO2 gas sensors." *Chemosensors* 11, no. 2 (2023): 140. https://doi.org/10.3390/chemosensors11020140

[54] Nayak, Arpan Kumar, Ruma Ghosh, Sumita Santra, Prasanta Kumar Guha, and Debabrata Pradhan. "Hierarchical nanostructured WO 3–SnO 2 for selective sensing of volatile organic compounds." *Nanoscale* 7, no. 29 (2015): 12460-12473. https://doi.org/10.1039/C5NR02571K

[55] Zhao, Tao, Pengpeng Qiu, Yuchi Fan, Jianping Yang, Wan Jiang, Lianjun Wang, Yonghui Deng, and Wei Luo. "Hierarchical branched mesoporous TiO2–SnO2 nanocomposites with well-defined n–n heterojunctions for highly efficient ethanol sensing." *Advanced Science* 6, no. 24 (2019): 1902008. https://doi.org/10.1002/advs.201902008

[56] Hermawan, Angga, Yusuke Asakura, Miki Inada, and Shu Yin. "A facile method for preparation of uniformly decorated-spherical SnO2 by CuO nanoparticles for highly responsive toluene detection at high temperature." *Journal of Materials Science & Technology* 51 (2020): 119-129. https://doi.org/10.1016/j.jmst.2020.02.041

[57] Zito, Cecilia A., Tarcísio M. Perfecto, Taís NT Oliveira, and Diogo P. Volanti. "Bicone-like ZnO structure as high-performance butanone sensor." *Materials Letters* 223 (2018): 142-145. https://doi.org/10.1016/j.matlet.2018.04.026

[58] Roy, Nirmal, Rupam Sinha, Harshal B. Nemade, and Tapas K. Mandal. "Synthesis of MoS2-CuO nanocomposite for room temperature acetone sensing application." *Journal of Alloys and Compounds* 910 (2022): 164891. https://doi.org/10.1016/j.jallcom.2022.164891

[59] Norizan, Mohd Nurazzi, Norli Abdullah, Siti Zulaikha Ngah Demon, Norhana Abdul Halim, Nurul Syahirah Nasuha Sa'aya, and Imran Syakir Mohamad. "Effect of reaction time on the structure and optical properties of P3HT/MWCNT-OH nanocomposites." *Polimery* 67, no. 5 (2022): 205-211. https://doi.org/10.14314/polimery.2022.5.3

[60] Nurazzi, N. Mohd, M. M. Harussani, S. Z. N. Demon, N. A. Halim, I. S. Mohamad, H. Bahruji, and N. Abdullah. "Research progress on polythiophene and its application as chemical sensor." *Zulfaqar Journal of Defence Science, Engineering & Technology* 5, no. 1 (2022).

[61] Wang, Shurong, Yanfei Kang, Liwei Wang, Hongxin Zhang, Yanshuang Wang, and Yao Wang. "Organic/inorganic hybrid sensors: A review." *Sensors and Actuators B: Chemical* 182 (2013): 467-481. https://doi.org/10.1016/j.snb.2013.03.042

[62] Pandey, Sadanand. "Highly sensitive and selective chemiresistor gas/vapor sensors based on polyaniline nanocomposite: A comprehensive review." *Journal of Science: Advanced Materials and Devices* 1, no. 4 (2016): 431-453. https://doi.org/10.1016/j.jsamd.2016.10.005

[63] Husain, Ahmad. "Electrical conductivity based ammonia, methanol and acetone vapour sensing studies on newly synthesized polythiophene/molybdenum oxide nanocomposite." *Journal of Science: Advanced Materials and Devices* 6, no. 4 (2021): 528-537. https://doi.org/10.1016/j.jsamd.2021.07.002

[64] Khan, Amir Ali, Ali Bahadar, Muhammad Hussain, Fida Ullah, Amir Ullah, and Sufian Rasheed. "Analytical evaluation of polymeric CNTs/CuO nanocomposite electrode for the room temperature detection of volatile organic compounds (VOCs)." *Results in Chemistry* 5 (2023): 100928. https://doi.org/10.1016/j.rechem.2023.100928

[65] Foronda, Juanito Raphael F., Lugas Gada Aryaswara, Gil Nonato C. Santos, Swathi NV Raghu, and Muhammad Akhsin Muflikhun. "Broad-class volatile organic compounds (VOCs) detection via polyaniline/zinc oxide (PANI/ZnO) composite materials as gas sensor application." *Heliyon* 9, no. 2 (2023). https://doi.org/10.1016/j.heliyon.2023.e13544

[66] Farea, Maamon A., Gita B. Bhanuse, Hamed Y. Mohammed, Mohammed O. Farea, Mohyeddine Sallam, Sumedh M. Shirsat, Meng-Lin Tsai, and Mahendra D. Shirsat. "Ultrahigh sensitive and selective room-temperature carbon monoxide gas sensor based on polypyrrole/titanium dioxide nanocomposite." *Journal of Alloys and Compounds* 917 (2022): 165397. https://doi.org/10.1016/j.jallcom.2022.165397

[67] Lima, Carlos FRAC, Ricardo JS Taveira, José CS Costa, Ana M. Fernandes, André Melo, Artur MS Silva, and Luís MNBF Santos. "Understanding M–ligand bonding and mer-/fac-isomerism in tris (8-hydroxyquinolinate) metallic complexes." *Physical Chemistry Chemical Physics* 18, no. 24 (2016): 16555-16565. https://doi.org/10.1039/C6CP02608G

[68] Kim, Jong-Seon, Hae-Wook Yoo, Hyung Ouk Choi, and Hee-Tae Jung. "Tunable volatile organic compounds sensor by using thiolated ligand conjugation on MoS2." *Nano letters* 14, no. 10 (2014): 5941-5947. https://doi.org/10.1021/nl502906a

[69] Sivalingam, Yuvaraj, Palani Elumalai, Surya VJ Yuvaraj, Gabriele Magna, Velappa J. Sowmya, Roberto Paolesse, Ki-Whan Chi, Yoshiyuki Kawazoe, and Corrado Di Natale. "Interaction of VOCs with pyrene tetratopic ligands layered on ZnO nanorods under visible light." *Journal of Photochemistry and Photobiology A: Chemistry* 324 (2016): 62-69. https://doi.org/10.1016/j.jphotochem.2016.02.023