

Introduction

1.1 Chemical Sensors

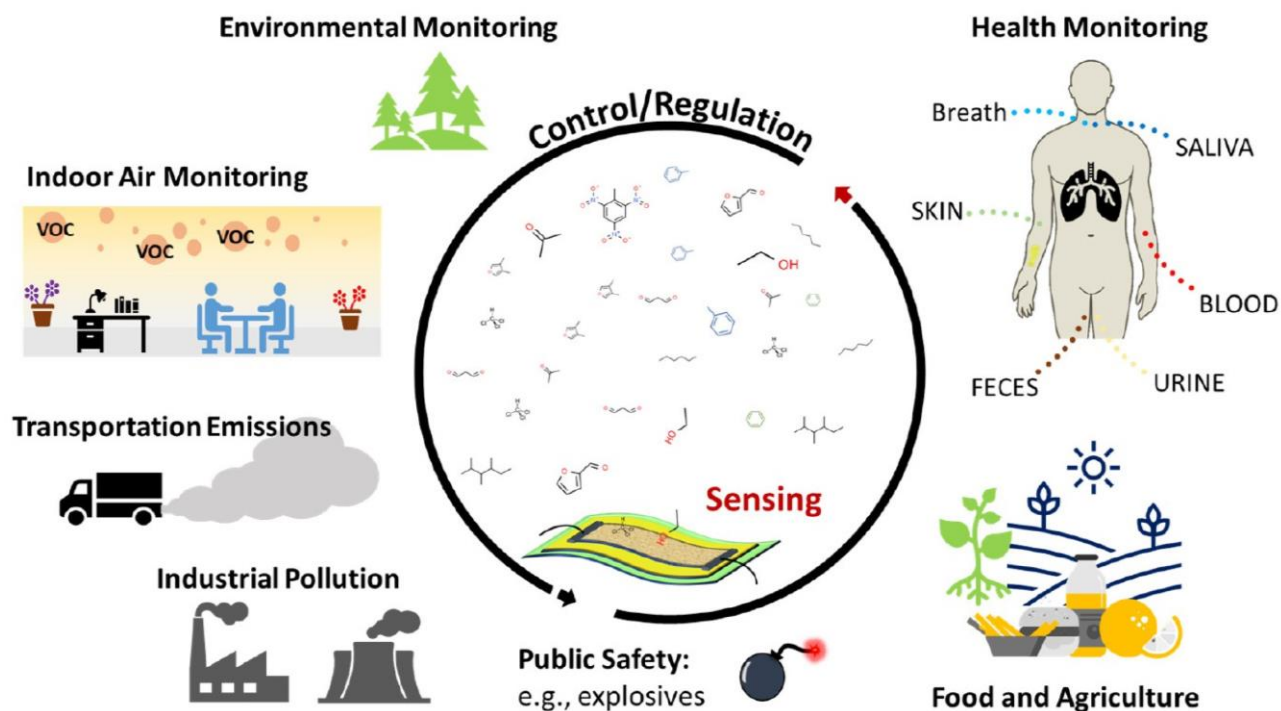


Figure 1.1: Application of Gases and Volatile Organic Compounds Sensors. Figure adapted from reference [Khatib *et al.*, 2021].

Rapid industrialisation is required for the growth and development of civilization. Nonetheless, factories emit flammable and poisonous gases/volatile organic compounds (VOCs), which is a big problem. In addition, vehicles emit highly harmful NO_x , SO_x , and CO_x pollutants, which have direct effects on the environment and human health. The paint and polymer industries utilise highly toxic volatile organic chemicals such as xylene, which have a direct impact on the health of workers and are a source of residential pollution. In contrast, gases and volatile organic compounds in exhaled breath and other biofluids can serve as biomarkers for the early detection of disease [Khatib *et al.*, 2021].

Currently, mass spectrometry (MS) with gas chromatography is employed for the trace identification of gases and volatile organic compounds (VOCs). In addition to being cumbersome, expensive, energy-intensive, and time-consuming, these techniques also have the considerable disadvantage of being immobile, which hinders their deployment on-site. These challenges are addressed by sensing technology, which demonstrates an effective gas/VOCs sensing technique. Consequently, sensing technology is required for the monitoring and control of gases/VOCs in numerous domains, such as environmental monitoring, food and agriculture, health monitoring, and public safety (Figure 1.1). However, the low reactivity and low concentrations of the vast majority of gases and volatile organic compounds make it difficult to design sensors.

Based on the interactions of gases/VOCs with the sensing material, the sensors are built

particularly for a particular purpose. There are two methods of detection: selective detection and cross-reactive detection. The selective sensing method focuses on detecting well-defined and specific volatile organic compounds (VOCs) in the presence of interfering gaseous species utilising receptors that are carefully developed and extremely selective. In the cross-reactive method, each sensor in an array responds to all (or a substantial subset) of the VOCs present in the desired combination of compounds, often known as "electronic nose" or "artificial nose." Due to the limited number of gases/VOCs in the tested system, the selective sensing approach is optimal for environmental monitoring, including indoor air quality, transportation emission, industrial pollution, and public safety monitoring, whereas the cross-reactive sensing approach is more suitable for food and health monitoring applications involving complex mixtures of gases and VOCs.

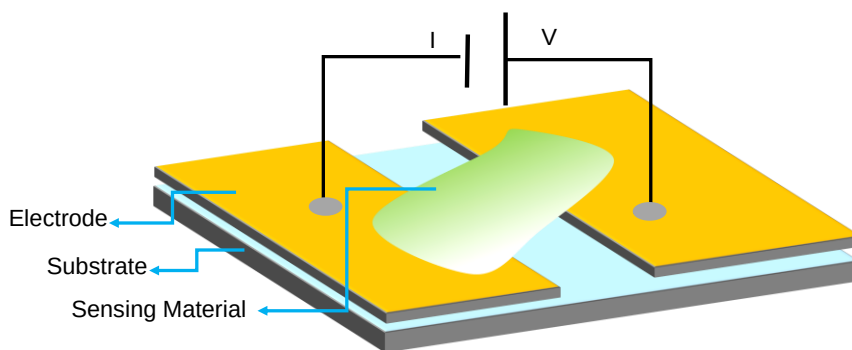


Figure 1.2: The typical design of a chemiresistive sensor.

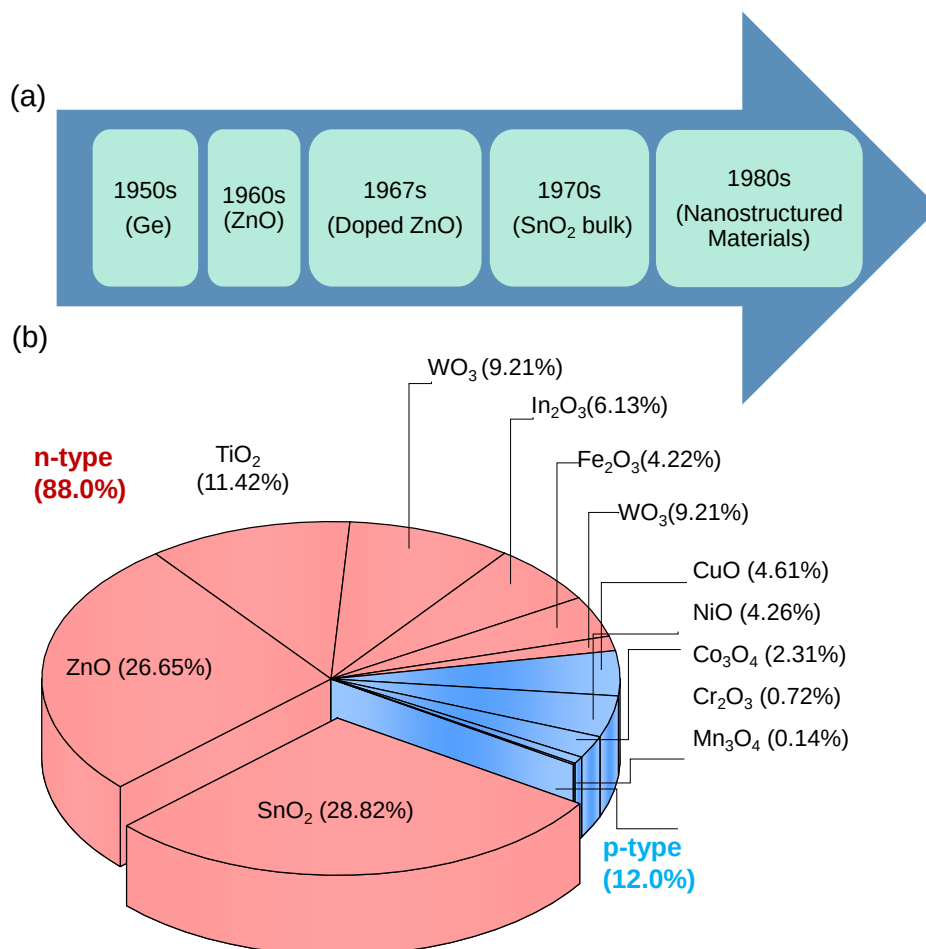


Figure 1.3: (a) Brief timeline on evolution of gas sensing materials and (b) Studies on n- and p-type oxide semiconductor gas sensors (internet search of Web of Science on 22 May 2023). Figure 1b adapted from reference [Masuda, 2022a].

A sensor is an electronic device that converts an external physical or chemical change (temperature, pressure, humidity, gases, and volatile organic compounds) into a readable signal (electrical, gravimetric, and optical). The performance of the sensor is dependent on basically two factors: device architecture and sensing material.

Among numerous transduction sensing systems such as electrical, gravimetric, optical, and optical interferometry, electrical are the best because to their high sensitivity, ease of use, low cost, and portability. The output signal of electrically transduced sensors is an electrical signal. Literature uses a variety of electrical transduced sensing device architectures, ranging from chemiresistive to field effect transistor, electrochemical to capacitive, depending on the type of electrical signal. The chemiresistive sensors stand out due to their simplicity, affordability, and portability. Figure 1.2 depicts the conventional design of a chemiresistive sensor. Sensing material, electrode material, and substrate are the primary components of a chemiresistive sensor. Although all three dimensions of a sensing device are crucial, the selection of a new sensing material has become increasingly significant over time.

As illustrated in Figure 1.3, significant emphasis has been placed on the development of novel sensing materials for gases/VOCs sensing devices. The phenomena of sensing are first detected in Bell's laboratory in the United States, beginning with the detection of a change in the resistance of Ge semiconducting material in response to a change in the oxygen concentration of the surrounding environment [Neri, 2015]. In the 1960s, further ZnO semiconducting materials demonstrated a response to various gases. In 1967, the issue of ZnO material's low sensitivity was resolved by doping it with noble metal. Using SnO₂ as a bulk material, Japanese scientists create the first commercial gas sensor in the 1970s [Neri, 2015]. The sensor showed a positive response to ethanol, but only at exceptionally high temperatures. Around this time, Feynman delivered his famous lecture "There is plenty of room at the bottom," and scientists grasped the significance of nanoscience and attempted to increase sensor performance by employing various synthetic processes and characterisation tools. Over the few decades there are varieties of material explored in literature for e.g., metal oxides, polymers, 2D materials for the sensing. SMO-based chemiresistive gas sensors are an important class of sensors primarily because they are rugged, cost-effective, and handy (Figure 1.3b). Among them SnO₂ because of their high chemical stability and thermal stability helps in the enhancement of sensor's performance [Masuda, 2022a].

1.2 Sensing Mechanism

The sensing mechanism is fundamentally driven by two phenomena: the reception, which includes the recognition of external stimuli by the sensing material, and the transduction involves transformation of these stimulus changes into a readable output. Reception phenomenon is determined by the surface structure of the sensing material, whereas transduction phenomena is a mix of the bulk structure and device design of the sensing material. The variables influencing the phenomenon are discussed in detail below.

1.2.1 Reception mechanism (Interactions between gases/VOCs with sensing material)

In the first stage, chemiresistive sensors detect a change in the physical property caused by the interaction between the analyte and the sensing material. Depending on the enthalpy of the reaction, the phenomena can be classified as chemisorption or physisorption when the sensing gas/VOCs adsorb on the surface of the sensing material (Figure 1.4)[Askim et al., 2013].

Physisorption between the gas/VOCs and the sensing material, including van der Waals forces, hydrogen bonding, coordination, and π - π interactions may lead to a reversible or partially reversible response.

Chemisorption, that occurs from the reactivity of a sensing material with the gas/VOCs, can provide high selectivity and sensitivity, and frequently results in an irreversible response.

In essence, the specific kind of interaction is controlled by the chemical structure of the gas/VOCs and the sensing material, which combined are the main determinant of the sensitivity, selectivity, and reversibility of sensing devices [Meng et al., 2019].

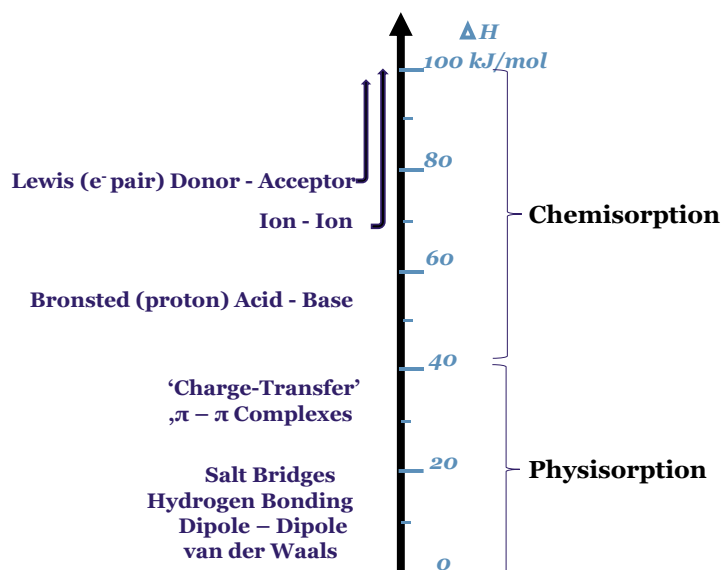


Figure 1.4: Spectrum of intermolecular interactions that can be used to probe VOC signals presented as absolute values of ΔH . Figure adapted from reference [Askim et al., 2013].

1.2.2 Transduction Mechanisms (Conversion of interaction to readable output)

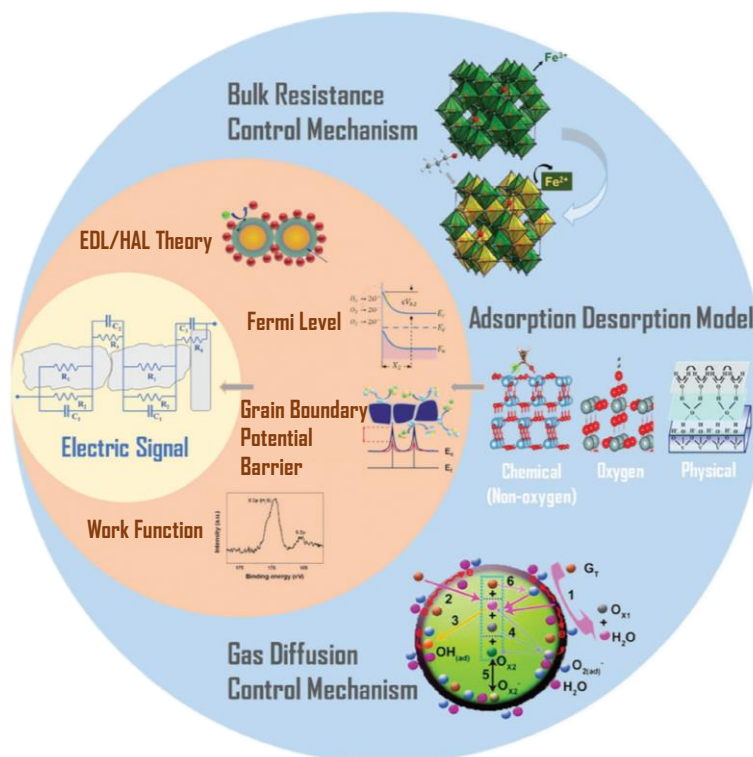


Figure 1.5: Various plausible sensing mechanisms during the gas-analyte interaction. Figure adapted from reference [Ji et al., 2019].

In addition, for chemiresistive sensing to be completed, the analyte-material interaction must generate a change in one or more physical properties, such as conductivity, work function,

and/or permittivity, which are often realised by the fundamental gas sensing mechanisms [Meng et al., 2019]. Mechanisms clarify why a gas can alter the electrical characteristics of a sensor. The extensively employed gas sensing mechanisms may be categorized into two groups (Figure 1.5)[Ji et al., 2019].

One category includes techniques such as Fermi level control theory, grain boundary barrier control theory, and EDL/HAL theory that explain the changes in electrical characteristics from a somewhat microscopic perspective. These aspects are more theoretical, because changes in electrical characteristics are always followed by changes in physical properties, such as energy bands and work functions, in any application.

The other category of theory is somewhat macroscopic and focuses mostly on the interaction between solids and gases. This type of theory includes the adsorption/desorption model, the bulk resistance control mechanism, and the gas diffusion control mechanism. Based on real physical events, these theories enable improved understanding of the process of gas sensing reactions using contemporary material analysis tools. These latter models may also be used to explain some of the physics concepts outlined in the earlier theory, such as why bands move and bend and why the grain boundary barrier varies.

Further, simulation-based theoretical studies (DFT for example) for the better understanding of different sensing mechanisms to develop much improved sensor compositions with precise tunability in properties should be stressed upon.

1.3 Major parameters influencing sensing performance

Particle size, particle morphology, porosity, doping by noble metals and aliovalent ions, effect of crystal phases and selectively exposed highly reactive crystalline planes, humidity, operating temperature, oxide heterojunction and homojunction, etc., are the most influential factors on sensor performance (Figure 1.6) [Das et al., 2022]. By selecting the right operating temperature, heteroatom doping, exposing high energy crystal faces preferentially, adding a catalytic overlayer, etc., the selectivity may be altered. Similarly, response and recovery may be accelerated by boosting charge transport inside the sensor, and stability can be enhanced by high temperature processing, doping, etc. Excellent sensing performance is exhibited by materials with features such as tiny particle size, high carrier density, adsorbed oxygen, oxygen defects, surface area, and pore volume.

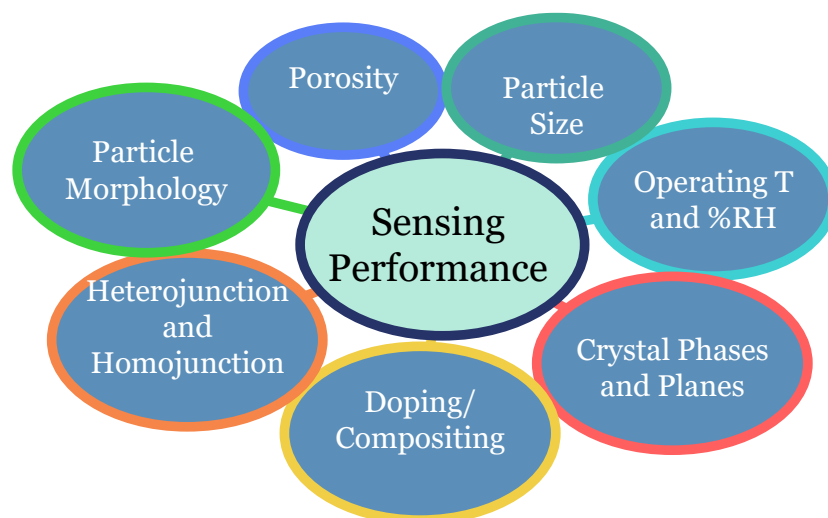


Figure 1.6: Characteristics of sensing material.

The changes in the nature of adsorbed background gases, reducing test gases/VOCs, and oxidising test gases/VOCs as a function of temperature are a crucial factor affecting the sensing

performance. As the temperature, pressure, and concentration of the gas/VOCs increase, these interactions can increase to a certain limit however high operating temperature increases cost, degrades the material, and affects the sensor's stability.

1.4 Literature Survey

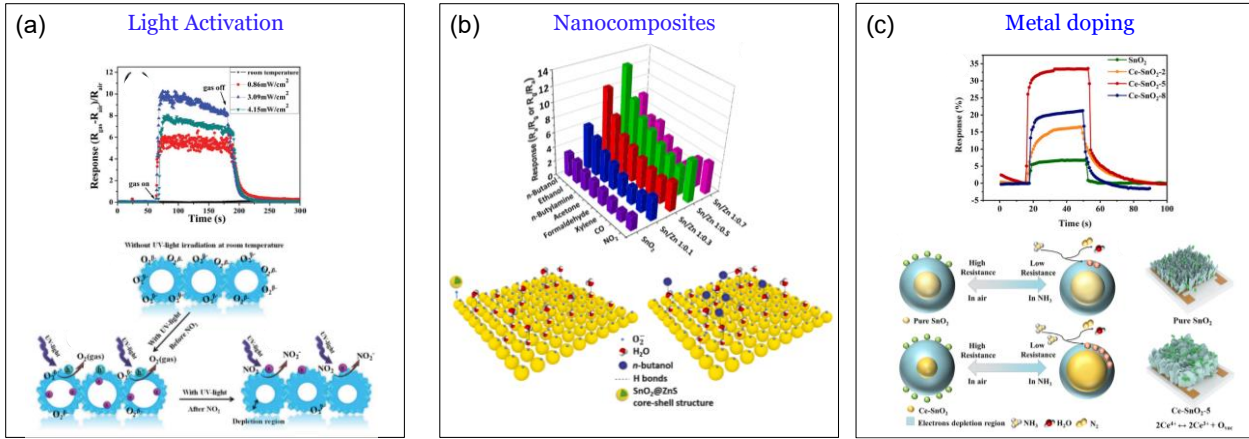


Figure 1.7: Sensing characteristics at low operating temperature of (a) Ultraviolet Light Based on SnO₂ Monolayer Array Film, (b) SnO₂@ZnS core-shell hollow spheres and (c) single petal-like Ce-doped SnO₂. Figures in a-c are adapted from [Liu et al., 2019], [He et al., 2023a] and [Yuan et al., 2023a] respectively.

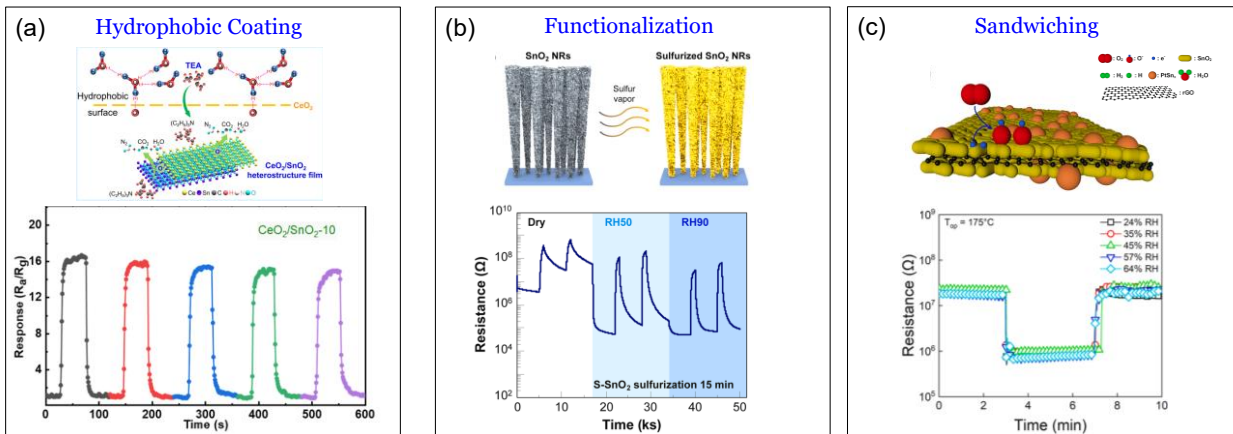


Figure 1.8: Humidity tolerant characteristics of (a) CeO₂/SnO₂ Heterostructure Films, (b) SnS₂/SnO₂ Nanorod Heterostructure and (c) sandwich-structured PtSn_x-rGO-SnO₂ nanocomposites. Figures in a-c are adapted from [Zhu et al., 2022], [Suh et al., 2022] and [Li et al., 2022a] respectively.

For many real-time gas monitoring applications, high-precision gas/VOC sensors operating at room temperature are desirable due to their low energy consumption, cost-effectiveness, and device miniaturization/flexibility. Semiconducting metal oxide is the subject of the majority of research on sensing materials, which play a vital role in the performance of gas sensors. In literature, different methodologies have been utilized to lower the operating temperature in metal oxide-based sensors. Visible light, ultraviolet light, infrared light, and even infrared light all affect the response of the RT sensors. Liu et al. used UV-light activation on SnO₂ array film to enhance room temperature sensitivity toward NO₂ gas (Figure 1.7a). In addition, heterojunctions are typically generated at the interfaces of different metal oxides, which can significantly accelerate the electron transmission between distinct particles, hence increasing the sensor's response speed. For example, He et al. fabricated the gas sensor based on plate-like SnO₂@ZnS core-shell hollow spheres, which exhibited the highest sensing response (~12.6) and

ultrafast response/recovery times (70/92 s) towards 100 ppm n-butanol at RT (Figure 1.7b). Doping metal ions into metal oxides can also enhance the number of active sites and defects on the surface of nanocrystals, hence boosting the amount of oxygen species and the number of gas molecules adsorbed to the sensor's surface. For example, Yuan et. al. fabricated a sensor based on a Ce-doped SnO₂ nanostructure exhibiting a high response towards ammonia with LOD of 780 ppt with fast response and recovery time of 4.4 s/12.8s than those of the pure SnO₂ (Figure 1.7c).

Even though great progress has been made in the development of new metal oxides for gas sensing at RT, there are still several obstacles and hurdles to achieve high response, quick response/recovery speed, high selectivity, and long-term stability. The endurance and long-term stability of sensors for application in variable environmental circumstances, such as varying humidity levels, which might severely affect the sensing characteristics of many RT gas sensors, is one of the most serious issues. There are different methodologies adopted for inducing humidity-tolerant behavior in literature. For example, Zhu et al. explored the coating of a hydrophobic CeO₂ thin layer over SnO₂ nanostructures to make it humidity tolerant (Figure 1.8a). Further, Suh et al. utilized the functionalization approach and formed a SnS₂/SnO₂ structure for the humidity-tolerant NH₃ sensor at RT (Figure 1.8b). Then method of sandwiching the sensing layer is developed by Li et al. for the humidity-tolerant detection of NO₂ at RT (Figure 1.8c). However, all the adopted approaches degrade the sensing performance at RT drastically.

Thus, developing room temperature operable gas/VOC sensors in dynamic humidity conditions is required. So, the literature survey of the most important gases/VOC sensors (nitrogen dioxide, xylene, ammonia, and triethylamine) operable at room temperature for environmental and healthcare monitoring are discussed in detail sections below.

1.4.1 Room temperature nitrogen dioxide sensors

Continuous indoor air quality monitoring and early disease diagnosis have never been more vital than in the current pandemic era [Giovannini et al., 2021; Mamun & Yuce, 2020]. NO₂, the most common toxic gas, induces various respiratory diseases even for short-term exposure at a low concentration of 5 ppm [Q. Li et al., 2022; Z. Zhang et al., 2018]. Various sensing strategies based on chemiresistive, optical, and electrochemical responses are explored for NO₂ sensing [Cai et al., 2022; Hofman et al., 2022; Shah et al., 2022]. Nevertheless, chemiresistive sensors, due to their low cost and portability, stand out by far [Majhi et al., 2021; Mane et al., 2017]. Also, chemiresistive NO₂ sensors with a good detection limit can be used for the early diagnosis of asthma through an exhaled breath [Z. Zhang et al., 2015].

SnO₂, a wide bandgap (3.6 eV) n-type semiconductor as chemiresistive sensing material, demonstrates good sensitivity and stability [Kang et al., 2022a]. However, SnO₂-based sensors suffer from the significant drawback of low gas diffusion sites due to agglomeration and high operating temperature [Bahuguna et al., 2020; Xiao et al., 2016]. To tackle these issues, incorporating conducting additives such as graphene in SnO₂ is a well-explored approach in the literature [Lee et al., 2015; Modak & Jagtap, 2022; Thomas et al., 2020; Wu et al., 2019; L. Zhang et al., 2019]. Reduced graphene oxide (rGO) acts as a dispersive and conductive support system for anchoring SnO₂ nanoparticles, and SnO₂ prevents aggregation and re-stacking of rGO sheets due to π - π interaction and reduces the base resistance providing an alternative conducting pathway [B. Zhang et al., 2018]. Thus, intrinsic catalytic properties of SnO₂ and good electrical conductivity of rGO form a suitable nanocomposite/nanohybrid material for NO₂ sensing [Yi Cheng et al., 2015]. However, the synergistic effect of SnO₂-rGO nanocomposite/ nanohybrid on NO₂ gas sensing gets influenced by choice of synthesis method to a large extent. A brief literature survey of SnO₂-rGO nanocomposites material for NO₂ sensing is shown in Table 1.1.

Table 1.1: Literature comparison of SnO₂ and graphene-based nanocomposites for chemiresistive NO₂ sensing.

Sensing Material	Synthetic Technique	LOD (ppb)	Response (a, b, c) {concentration, ppm}	Temp (°C)	Response/Recovery time (s)	Chemisorption (Nanohybrid)		References
						Sn-O-C	Sn-C	
3D SnO ₂ -rGO	Hydrothermal	2000	11.2 ^a {110}	55	NA/ 373	NA	NA	[L. Li et al., 2015]
SnO ₂ -rGO	Hydrothermal	NA	696 ^b {1}	75	660/ 360	NA	NA	[Xiao et al., 2016]
SnO ₂ {221}-graphene	Hydrothermal	NA	18.3 ^a {5}	RT	130/1800	NA	NA	[L. Zhang et al., 2019]
SnO ₂ -rGO	Mixing and electrospinning	NA	95 ^b {1}	200	NA/NA	NA	NA	[Lee et al., 2015]
SnO ₂ -rGO	Electrostatic force directed assembly	1000	2.9 ^b {100}	RT	NA/NA	NA	NA	[Mao et al., 2012]
SnO ₂ -rGO	Solvothermal	NA	247.8 ^b {10}	200	39/15	NA	NA	[Gui et al., 2017]
SnO ₂ -rGO	Hydrothermal	NA	65.5 ^a {5}	RT	12/ 17	NA	NA	[Z. Wang et al., 2018]
SnO ₂ -RGOH	Hydrothermal	2.8	32.1 ^c {5}	RT	177/ 260	NA	NA	[Wu et al., 2020]
SnO ₂ -graphene	Mixing and Microwave Heating	NA	24.66 ^b {1}	150	175/ 148	NA	NA	[Kim et al., 2017]
3D Graphene aerogel-SnO ₂	Hydrothermal	NA	6.5 ^c {50}	RT	190/ 224	NA	NA	[Liu et al., 2014]
SnO ₂ -rGO film	Direct Mixing	15.7	15 ^a {1}	60	NA/NA	NA	NA	[Zhu et al., 2017]
SnO ₂ -rGO	Hydrothermal	NA	69.78 ^b {5}	50	135/ 200	NA	NA	[H. Zhang et al., 2014]

1.4.2 Room temperature xylene sensors

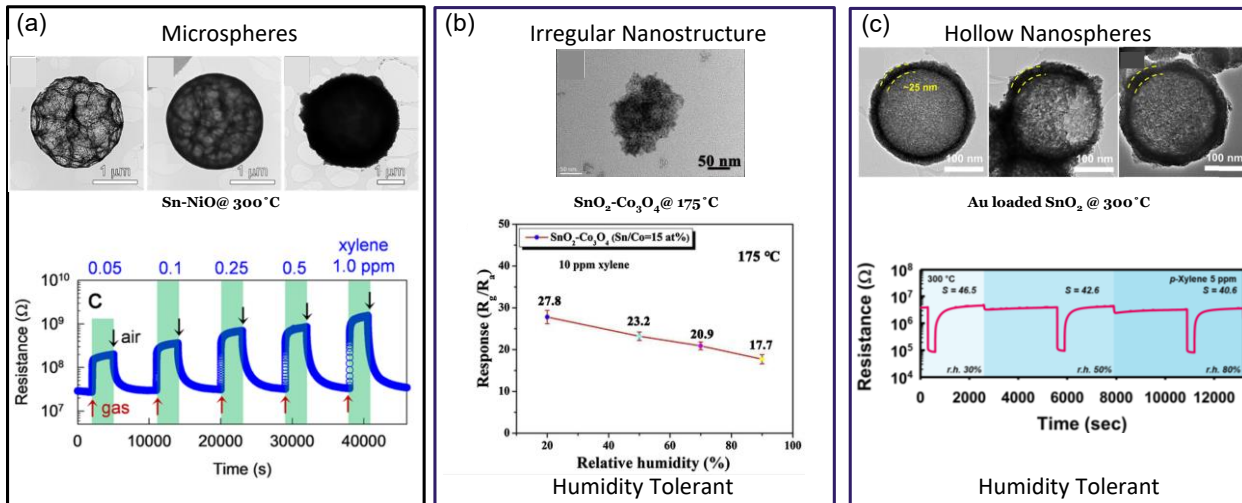


Figure 1.9: Xylene sensing characteristics of (a) Sn-NiO microspheres, (b) Sn-NiO irregular nanostructure and (c) Au loaded SnO₂ hollow nanospheres. Figures in a-c are adapted from [Kim et al., 2018a], [Guo et al., 2020b], and [Park et al., 2020] respectively.

Xylene is considered one of the most harmful carcinogens by the International Agency for Cancer Research (IACR); that introduces toxicity to the environment and directly affects human health [Gallego et al., 2009].

Xylene, one of the components of cigarette smoke, happens to be one of the major contributors to indoor pollution [Alonso et al., 2010]. Long-term exposure to xylene >14 ppm may lead to headaches, irritation to the respiratory organ, and acute mental problems [Raton, 2004]. Further, xylene vapors (10-100 ppb) from breath and urine act as a potential biomarker for non-invasive detection of lung[Jia et al., 2019][Gregis et al., 2018] and prostate cancer [Jiménez-Pacheco et al., 2018], respectively. Thus, the detection and measurement of xylene are important in developing a highly selective and sensitive sensor. The resistive xylene sensors based on metal oxides suffer a major drawback of high operating temperatures. Various nanostructured materials such as NiO[Gao et al., 2017b][Kim et al., 2018a][Kim et al., 2016a], SnO₂ [Park et al., 2020], V₂O₅ [Vijayakumar et al., 2017], TiO₂ [Kang et al., 2020], MoO₃ [Cho et al., 2019], ZnO [Woo et al., 2014], NiCo₂O₄ [Du et al., 2020][Gao et al., 2019a], Co₃O₄ [Morsy et al., 2020][Guo et al., 2020b], WO₃ [Li et al., 2017a][Lv et al., 2019] [Gao et al., 2019b], CoCr₂O₄ [Lee et al., 2019] have been reported in the literature (Figure 1.9).

For example, Kim *et al.* synthesized Sn-doped NiO microspheres showing a response of 65.4 at 300 °C for 1 ppm of xylene [Kim et al., 2018a]. Guo *et al.* fabricated a xylene vapor sensor using an SnO₂-Co₃O₄ nanocomposite forming an irregular nanostructure, shows a response of 100 at an operating temperature of 175 °C at 100 ppm concentration [Guo et al., 2020b]. Park *et al.* performed the morphological tuning of SnO₂ and configurational tuning using Au catalyst for a highly selective xylene sensor operable at 300 °C with the best response of 771.3 in 0% RH, which decreased drastically in the presence of 30% RH to 45.6 for 5 ppm of xylene [Park et al., 2020]. Lv *et al.*, using Au-doped hierarchical WO₃ hollow microspheres, fabricated a xylene sensor with a response of 8.5 towards 10 ppm xylene at 340 °C [Lv et al., 2019]. Woo et al. prepared branched Ni-doped ZnO NWs with excellent xylene sensing properties towards 5 ppm with a response of 42.4 at 400 °C [Woo et al., 2015]. Qu *et al.* developed a robust xylene sensor using mixed Ni-Co oxide microspheres, showing a response of 11.5 at 255 °C [Qu et al., 2018]. A detailed literature table comprising xylene sensors fabricated using different materials, dopants, morphology, and functionalization strategies is tabulated in Table 1.2. It can be observed that even though there are significant reports on resistive xylene sensors, a major trade-off between the low operating temperature and response of the sensor remains, with a minimal/negligible response at room temperature towards xylene vapors.

Table 1.2: Comparison of xylene sensing performance of different sensing materials.

S.No.	Sensing Material	LOD (ppb)	Conc. (ppm)	Response (a, b, c)	Temp. (°C) & RH (%)	Humidity Effect	Response time (s)/ Recovery time (s)	Selectivity (R _{Xylene} /R _{Ethanol})	Stability (days)	Ref.
1	Au@SnO ₂ hollow spheres nanoreactors	10	5	771.3 ^a 45.6 ^a	300 & 0 300 & 30	30-80% less change in response compared to 0-30 % RH drastic change	172 & N.A.	5.4	30	[Park et al., 2020]
2	Fe-doped α-MoO ₃ nanoarrays	356	100	28.5 ^a	340	20-30% change slight change in response	2/23	N.A.	30	[Cho et al., 2019]
3	NiCo ₂ O ₄ hierarchical tubular nanostructures	1000	100	9.2 ^a	220	N.A.	20/9	N.A.	30	[Du et al., 2020]
4	Nb-doped NiO nanosheets	2	100	335.1 ^a	370	N.A.	63/66	7.1	N.A.	[Qiu et al., 2020]
5	SnO ₂ -Co ₃ O ₄ microstructure	50	100	101.9 ^a	175	20-90% slight change in response	204/ 367	12.4	50	[Guo et al., 2020a]

6	Peptide-Hydrogel-Based Composite Material	5000	50	95 ^b	R.T.	N.A.	0.6 / 0.54	p-xylene> m-xylene> o-xylene	120	[Singha et al., 2019]
7	Sn-doped NiO multiroom spheres microreactor	3.4	1	65.4 ^a	300	N.A.	280 / N.A.	N.A.	28	[Kim et al., 2018a]
8	NiO/ NiWO ₄ Composite Yolk-Shell Spheres with Nanoscale NiO Outer Layer	22.7	5	343.5 ^a	350-450	N.A.	225/ N.A.	10.5	N.A.	[Kim et al., 2017c]
9	Sn doped NiO	300	100	20.2 ^a	225 & 50	(15%-100% RH) response decreased	298 & 223	12	20	[Gao et al., 2017a]
10	V ₂ O ₅ Nanofibers	N.A.	100	27 ^a	R.T.	N.A.	80/ 50	N.A.	30	[Vijayakumar et al., 2017]
11	NiO/ NiMoO ₄ nanocomposite	20	5	101.5 ^a	375	N.A.	N.A.	N.A.	14	[Kim et al., 2016a]
12	Au-loaded WO ₃ ·H ₂ O nanocube	200	5	26.5 ^a	255	N.A.	1/ 2.5	N.A.	N.A.	[Li et al., 2017a]
13	Au-decorated hierarchical ZnO porous rose-like architecture	1000	20	76.47 ^a	206	N.A.	2/ 24	N.A.	30	[Lee et al., 2018]
14	Pt-doped CoCr ₂ O ₄ hollow spheres	19	5	558.8 ^a	275	Response increased on 80% RH	300/ 600	87.8	N.A.	[Lee et al., 2019]
15	Au-Loaded WO ₃ Hollow Microspheres	300	10	8.5 ^a	340	N.A.	10/ 5 (20 ppb)	N.A.	45	[Lv et al., 2019]
16	Hollow WO ₃ -NiO nanoflowers	50	50	354.7 ^a	300	Response decreased on increasing humidity	51/ 57	10.3	15	[Gao et al., 2019b]
17	NiO/ NiCr ₂ O ₄ nanoparticle	50	100	66.2 ^a	225	Response decreased at 90%RH	1217/ 591	11.8	30	[Gao et al., 2019a]
18	Co ₃ O ₄ / GF	500	20	36.3 ^b	R.T.	N.A.	160/ 235	N.A.	N.A.	[Morsy et al., 2020]
19	NiGa ₂ O ₄ -NiO heterostructures	500	100	16.3 ^a	230	N.A.	N.A.	N.A.	N.A.	[Chen et al., 2019]
20	ZnO Nanoparticles	N.A.	50	4.4 ^a	300	N.A.	8/ 13 at 100 ppm	N.A.	20	[Cao et al., 2008]
21	Mesoporous α-Fe ₂ O ₃ nanostructures	N.A.	100	6.45 ^a	340	N.A.	1/ 13	N.A.	30	[Li et al., 2014]
22	Ni doped branched ZnO nanowires (NWs)	40	5	42.44 ^a	400	N.A.	N.A.	2.5	N.A.	[Woo et al., 2015]
23	W-doped NiO nanotubes	N.A.	200	8.74 ^a	375	N.A.	178/ 152	N.A.	30	[Feng et al., 2015]
24	Cr ₂ O ₃ / ZnCr ₂ O ₄ nanocomposite	N.A.	5	69.2 ^a	275	Slight effect of humidity	N.A.	26.7	N.A.	[Kim et al., 2016b]
25	Pd-doped WO ₃ ·H ₂ O	100	10	21 ^a	230	N.A.	1/ 2.5	N.A.	N.A.	[Li et al., 2017b]
26	Sn-doped NiO	300	100	20.2 ^a	225 & 50	N.A.	298/ 223	12	20	[Gao et al., 2017b]
27	Porous coral-like NiCo ₂ O ₄ nanospheres	232	100	16.4 ^a	260 & 40	N.A.	26/ 27	N.A.	N.A.	[Zhang et al., 2018b]
28	Cr-doped WO ₃ Nanoflowers	5000	100	35.04 ^a	255 & 30	From 30 to 95% RH response decreased ~9%	1/2	N.A.	30	[Li et al., 2018a]

29	Sn ²⁺ -doped NiO	500	200	25.2 ^a	250 & 50	20, 50, 70 and 90 responses decreased	79/ 98 (at 0.5 ppm)	14	15	[Gao et al., 2018]
30	MOFs Derived NiFe ₂ O ₄ Fusiformis	10000	500	31.52 ^a	300	N.A.	50.1/ 40.3	N.A.	30	[Zhang et al., 2019b]
31	Au-Loaded Hierarchical MoO ₃ Hollow Spheres	500	100	22.1 ^a	250	N.A.	2/ N.A.	N.A.	180	[Sui et al., 2017]
32	Mixed Ni-Co oxides	97	5	11.5 ^a	255	Humidity resistant 11 to 95% RH	6/ 9	2.69	30	[Qu et al., 2018]
33	Co-doped branched ZnO nanowires	N.A.	5	19.55 ^a	400	N.A.	N.A./1268	2.3	N.A.	[Woo et al., 2014]
34	Core-in-hollow-shell structured Cr–NiO micro/nanospheres	1000	5	20.9 ^a	220	N.A.	N.A.	N.A.	N.A.	[Cao et al., 2014]
35	α-MoO ₃ / α-Fe ₂ O ₃ nanostructure composites	N.A.	5	4.79 ^a	206	N.A.	87/ 190	N.A.	N.A.	[Jiang et al., 2015]
36	Pompon-like Co ₃ O ₄ and Cr-doped Co ₃ O ₄ hierarchical nanostructures	1150	5	6.38 ^a	139 & 43	N.A.	15-30/ 10-30	4.26	N.A.	[Li et al., 2016b]
37	WO ₃ decorated TiO ₂	1000	1	12.37 ^a	160	N.A.	410/ 2563 (10 ppm)	N.A.	28	[Chen et al., 2016]
38	C-Doped WO ₃		50	75 ^a	320	N.A.	N.A.	N.A.	N.A.	[Deng et al., 2012]
39	Cr ₂ O ₃ @ZnO Hetero-junction Hierarchical Nanostructures	2 μL/L	5 μL/L	4 ^a	280 & 26	N.A.	4/ 9	N.A.	30	[Qin et al., 2018]
40	Nano CeO ₂ film	N.A.	100	1.7 ^a	30	N.A.	224/ 13	N.A.	N.A.	[Subbiah et al., 2018]
41	V ₂ O ₅	N.A.	100	27.9 ^a	27	N.A.	113/ 43	N.A.	N.A.	[Vijayakumar et al., 2015]

1.4.3 Room temperature ammonia sensors

Rapid growth and advancements in chemical industrialization, the agriculture sector, and Internet of Things (IoT) applications demands the continuous environmental monitoring to control the release of harmful gases [Jorgenson et al., 2007; Tang et al., 2020; Yousefi et al., 2021; Zhang et al., 2016]. Among various volatile amines, ammonia (NH₃) is most primarily produced by agricultural and industrial activities such as fertilizers worldwide at a large scale [Kwak et al., 2019; Timmer et al., 2005]. Ammonia is also generated by human metabolic activity, regardless of industrial and explosive leakage. NH₃ is present in breath, the so-called breath marker for disturbed urea balance caused by kidney disease and stomach infections. The concentration of NH₃ in the exhaled breath of healthy persons is about 0.4–1.8 ppm, while that in end-stage renal disease patients is around 0.8–14.7 ppm [Li et al., 2018b; Wu et al., 2023]. Hence, disease state monitoring and environmental exposure assessment applications demand highly sensitive, faster, and more selective NH₃ sensors that can operate under various environmental conditions. SMO-based sensors have attracted tremendous attention in gas sensing because of their excellent sensitivity, simple configuration, low cost, straightforward preparation process, and ability to achieve real-time measurement [Lee et al., 2020]. SnO₂ is one of the most suitable candidates in the metal-oxide family and has received significant attention because of its low cost, simple synthesis, and novel physical and chemical properties [Kim et al., 2020]. Furthermore, SnO₂ has a wide bandgap of 3.6 eV with a tetragonal lattice, resulting in superior gas-sensing characteristics such as high sensitivity and long-term stability, giving this material a competitive advantage in the gas sensor field when compared to other SMO materials [Masuda, 2022b; Nascimento et al., 2022].

However, the SnO₂ based chemiresistive sensors majorly suffers from high operating temperature and low sensitivity towards ammonia [Bulemo et al., 2017; Choi et al., 2019b; Li et

al., 2016a; Suematsu et al., 2020; Yang et al., 2018; Zhao et al., 2020].

Table 1.3: Sensing performance of recently reported ammonia sensors:

Sensing Material	Temp (°C)	Conc ⁿ (ppm)	Response (a, b, c)	T _{res.} (s)	T _{rev} (s)	LOD (ppb)	RH (%)	Reference
g-C ₃ N ₄ @WO ₃	25	10	19.1 ^b	35	9	108	30	[Zou et al., 2022]
Ppy/f-MWCNT	25	100	26.6 ^a	16	110	5000	30	[Lawaniya et al., 2022]
SiMW	25	100	50 ^a	200	>500	200	30	[Le et al., 2022]
MoS ₂ @5keV	25	200	340 ^a	30	47.9	NA	50	[Rajbhar et al., 2023]
Ti ₃ C ₂ T _x /SnS ₂	18	10	42.9 ^a	161	80	10	26	[He et al., 2023b]
WS ₂ /W ₁₈ O ₄₉	25	5	25 ^a	73	189	50	18	[Manoharan et al., 2023]
Bi ₂ Se ₃ /Bi ₂ O ₃	25	180	8.5 ^b	134.5	23.5	5000	20	[Das et al., 2023]
WS ₂ /MoO ₃	25	3	31.58 ^a	57	226	200	30	[Ou et al., 2022]

Table 1.4: Literature survey of chemiresistive gas sensors fabricated using SnO₂ nanosheets.

Sensing gas/VOC	Temp (°C)	Response (a, b, c) (conc. ppm)	T _{res.} (s)	T _{rev} (s)	LOD (ppm)	RH (%)	Ref.
H ₂	300	7.5 ^b (500)	6	12	NA	NA	[Choi et al., 2019a]
CH ₄	300	1.3 ^b (500)	18	28	NA	NA	
HCHO	120	57 ^b (100)	1.1	1.5	NA	NA	[Wang et al., 2019]
Ethylene glycol	220	395 ^b (400)	65	72	1.37	NA	[Wan et al., 2018]
Acetic acid	340	672 ^b (500)	11	6	NA	NA	[Wang et al., 2015]
CO	300	60 ^b (100)	8	15	NA	30%	[Zeng et al., 2013]
Ethanol	165	50.1 ^b (50)	29	136	NA	NA	[Zhang et al., 2013]
Ethanol	275	33 ^b (100)	11	125	NA	NA	[Sun et al., 2013a]
Ethanol	300	39.6 ^b (6)	1	9	NA	NA	[Lou et al., 2012]
Ethanol	250	73.3 ^b (100)	NA	NA	NA	NA	[Sun et al., 2011a]
CO	300	-(100)	1	3	NA		
Ethanol	275	56.2 ^b (100)	NA	NA	NA	NA	[Sun et al., 2011b]
Ethanol	350	48.37 ^b (100)	8	NA	NA	NA	[Xu et al., 2010]

^a ΔR/R_a (%) or ΔG/G_a (%) or ΔI/I_a (%),

^b R_a/R_g or G_a/G_g or I_a/I_g,

^c ΔR/R_a or ΔG/G

a or $\Delta I/I_a$

NA: Not Available

$R_a/I_a/G_a$: resistance/current/conductance of material in presence of air

$R_g/I_g/G_g$: resistance/current/conductance of material in presence of gas

Consequently, for tuning the selectivity towards ammonia and lowering down the operating temperature of SnO₂ based sensors, doping and heterostructures of SnO₂ nanomaterial is well explored in literature, but existing sensors still suffers from major drawback of low response, high limit of detection and deteriorating effect of humidity at room temperature [Kang et al., 2022b; Kim et al., 2019b; Majhi et al., 2021]. For example, Boomashri et al. constructed a sensor based on Sb-doped SnO₂ thin films that demonstrated a 138% response to 250 ppm ammonia at ambient temperature [Boomashri et al., 2023]. Yuan et al. fabricated a Ce-doped SnO₂-based sensor that demonstrated a 33.62 % response ($\Delta R/R_0$) to 0.03 ppm ammonia with an LOD of 780 ppt at ambient temperature and 60% relative humidity [Yuan et al., 2023b]. Xu et al., for instance, constructed an ammonia sensor based on SnO₂-SnS₂ hybrids that is operative at ambient temperature and displayed a response (I_g/I_a)=2 towards 100 ppm at 30% RH [Xu et al., 2015]. Singh et. al., developed an ammonia sensor employing MoS₂/SnO₂ composite, which demonstrated a response ($\Delta R/R_0$) = 53% towards 50 ppm ammonia in the humidity range of 40-90% RH at room temperature [Singh et al., 2021]. Table 1.3 shows the recently reported ammonia sensors using various nanomaterials. Further, the morphology-controlled synthesis of the SnO₂ nanomaterial with high specific surface area and interface sites is found to have significant effect on the improvement of gas sensing performance but no selectivity towards ammonia is achieved till now as shown in Table 1.4 [Gouveia et al., 2023].

1.4.4 Low temperature triethylamine sensors

There have been many serious efforts to reduce the operating temperature by modifying the oxide's surface and making hybrid nanomaterials [Xu et al., 2020], doping [Xu et al., 2015], faceted or 1-D growth [Haddad et al., 2018], and hetero-structuring and complementing sensor with UV illumination [Chen et al., 2015; Sharma et al., 2018; Yang et al., 2019]. In this manner, the chemical and physical characteristics of the oxide may be altered, hence increasing gas diffusion on the surface, thereby reducing response time and operating temperature. SnO₂ hybrids with CNTs [Yan et al., 2019], graphene oxide [Salehi et al., 2014], GaN [Bajpai et al., 2012], ZnO core-shell nanostructure [Kalidoss et al., 2019], and metal dopants Pt [Poloju et al., 2017], Au [Moon et al., 2019] [Quan et al., 2020], Pd [Moon et al., 2019], Ni [Tan et al., 2011], and their oxides) have demonstrated improved VOC sensing capability in comparison to pure SnO₂. Fluorination of the surface of metal oxide (5-10 nm) can speed up the reaction process and reduce the operating temperature of sensors by enhancing surface electric conductivity and charge density [Sysoev et al., 2017]. Table 1.5 presents a brief literature review of fluorinated materials utilised for VOC sensing applications. Other than fluorocarbons, there are just two studies on fluorinated-SnO₂ for NO₂ and LPG gas detection [Kemnitz et al., 1998; Wang et al., 2013a].

Table 1.5: Literature survey of the fluorinated materials used for sensing applications.

Material	Fluorinating Precursor	Synthesis method	Conc (ppm)	LOD (ppm)	Temp (°C)	Analyte	Ref.
Fluorinated MOF	(AlF ₅ (OH ₂)) ²⁻ (NbOF ₅) ²⁻	Chemical synthesis	25	NA	RT	SO ₂	[Tchalala et al., 2019]

Fluorinated graphene ink	FG powder dispersed in IPA	Sonication	20%- 70% (RH)	NA	RT	Humidity	[Hajian et al., 2019]
Fluorinated graphene	SF ₆	Gas phase fluorination	--	NA	RT	Photo-detector (UV, visible and NIR)	[Xu et al., 2019]
Fluorinated graphene	SF ₆	Gas phase fluorination	2	NA	RT	NH ₃ , CO	[Zhang et al., 2016a]
Fluorinated graphene	Graphite Fluoride,	Hummers method	2	NA	400	NH ₃	[Kang et al., 2018]
F-SnO ₂	NH ₄ F	Dip coating	25 % LEL	NA	300	LPG	[Chaisitsak, 2011]
SnO ₂ and fluorine modified graphene	F ₂ gas	thermal fluorination of SnO ₂ modified graphene	50	NA	400	NO	[Kim et al., 2019]
F- SnO ₂	NH ₄ F	Hydrothermal	33	NA	RT	NO ₂	[Wang et al., 2013a]
Fluoro-graphene	Fluorinated graphite polymer	Solution Processing	1 pM	0.4pM	RT	NH ₃	[Tadi et al., 2016]

1.5 Objectives and Scope of the Thesis

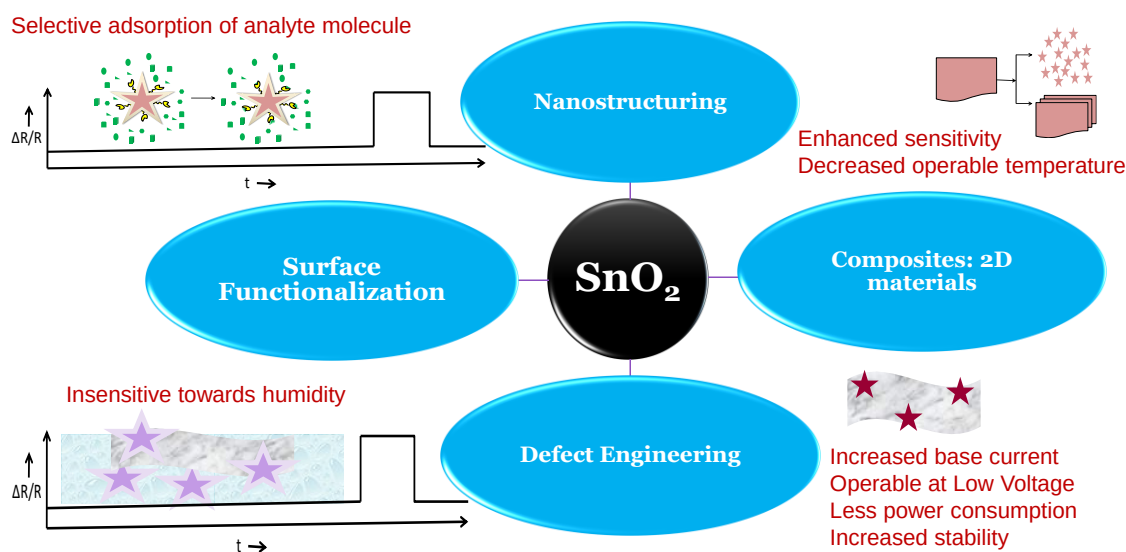


Figure 1.10: Schematic depiction of objectives and scope of this thesis work.

SnO₂ nanomaterials have gained tremendous attention in chemical sensors, but the high-temperature operation and humidity intolerance behavior increases the cost with compromised stability of existing chemiresistive sensors. Therefore, the overall objective of the thesis work is focused on tuning the SnO₂ nanomaterials for the room temperature and humidity tolerant sensing of toxic gases and volatile organic compounds (Figure 1.10). The specific objectives include:

1. To optimize the solution processable synthesis and processing of SnO₂-rGO nanocomposites, Sn-SnO₂ nanocomposites, SnO₂ nanosheets and F-SnO₂ films for sensing applications.
2. To perform the detailed structural, chemical, morphological and surface characterisation of synthesized nanomaterials.
3. To optimize fabrication of chemiresistive sensor and test the performance toward different

gas/VOC at room temperature and fluctuating humidity for the identification of response, selectivity and sensitivity.

4. To test the long-term stability, repeatability, reproducibility.
5. To establish the structure-property relationship between the sensing material and the sensing gas/VOC by proposing well suited sensing mechanisms.

This research will focus on the synthesis of SnO₂ nanomaterials and characterization of morphological, structural, physical, chemical, optical, and electrochemical changes in the properties of their surface functionalities, nano structuring, nano compositing, and defect engineering for effective sensing performance at room temperature and in variable humidity.

The scope of each research chapter (3-6) of the thesis work is as follows:

1. The SnO₂-rGO nanohybrid sensor's performance needs to be optimized so that synergistic functional properties of rGO and SnO₂ can be exploited. So, in our work, SnO₂-rGO is synthesized at optimized conditions by the solvothermal method, and the componential combination approach is adopted for establishing an excellent active sensing material for chemiresistive sensing of NO₂ gas.
2. The roles of expensive noble Pt, Pd, and Au catalyst-loaded metal oxides are well studied in the literature to enhance the interaction of metal oxide-based gas sensors with xylene, Sn metal-loaded SnO₂ is an unexplored system for gas/VOC sensing. In our work, Sn metal in the Sn-SnO₂ nanocomposite acts as an efficient nanocatalyst for chemiresistive VOC sensing for selective detection of xylene at room temperature. The synergy of the nanosphere-type morphology and the nanocatalytic behavior of metallic Sn in the Sn-SnO₂ nanocomposite are realized, resulting in reliable xylene sensing.
3. In the process of detecting ammonia, ammonia molecules face huge interference from polar water molecules which degrades the sensing performance of existing materials for environment and health monitoring of ammonia. So, this study advances a new methodology to handle these difficulties by synthesizing porous SnO₂ nanosheets via a pH-controlled, single-step solvothermal process. The investigation characterizes and optimizes the structural, morphological, and surface features of the SnO₂ nanosheets, resulting in better sensing performance. The sensors produced from these SnO₂ nanosheets demonstrate an exceptional sensitivity towards ammonia and have the capacity to work proficiently in moist conditions at room temperature.
4. Surface fluorination of metal oxide can accelerate the reaction process and decrease the operating temperature. However, a clear understanding of the fluorination mechanism and its influence on the band structure is still missing in the literature. So, an in-depth study is carried out to understand the fluorination process. Further prepared F-SnO₂ films improved the electrochemical stability of pre-deposited metal mesh electrodes by keeping them intact. The fluorination of SnO₂, further optimized to restrict to low percentages (<1%), produced excellent responses for VOCs and humidity resistant nature even at moderate temperatures while keeping the sensing element transparent.

1.6 Conclusions

The introductory chapter of the thesis presented the basics of SnO₂ nanomaterials and their specific importance in the field of gas sensing devices. Further, the modification of nanomaterials via nanocomposites, nano structuring and doping is discussed for the tailoring of properties for the specific gas or VOCs. Role of nanocomposites, nano structuring, and doping for inorganic metal oxides is summarized with its application in vast field of interest. In the upcoming chapters, the synthesis and application of SnO₂ nanomaterials for sensing applications is elaborated.

