Historical perspective

Recent progress and perspectives of gas sensors based on vertically oriented ZnO nanomaterials

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ABSTRACT

Vertically oriented zinc oxide (ZnO) nanomaterials, such as nanorods (NRs), nanowires (NWs), nanotubes (NTs), nanoneedles (NNs), and nanosheets (NSs), are highly ordered architectures that provide remarkable properties for sensors. Furthermore, these nanostructures have fascinating features, including high surface-area-to-volume ratios, high charge carrier concentrations, and many surface-active sites. These features make vertically oriented ZnO nanomaterials exciting candidates for gas sensor fabrication. The development of efficient methods for the production of vertically oriented nanomaterial electrode surfaces has resulted in improved stability, high reproducibility, and gas sensing performance. Moving beyond conventional fabrication processes that include binders and nanomaterial deposition steps has been crucial, as the materials from these processes suffer from poor stability, low reproducibility, and marginal sensing performance. In this feature article, we comprehensively describe vertically oriented ZnO nanomaterials for gas sensing applications. The uses of such nanomaterials for gas sensor fabrication are discussed in the context of ease of growth, stability on an electrode surface, growth reproducibility, and enhancements in device efficiency as a result of their unique and advantageous features. In addition, we summarize applications of gas sensors for a variety of toxic and volatile organic compound (VOC) gases, and we discuss future directions of the vertically oriented ZnO nanomaterials.

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1. Introduction

Rapid advancements in nano-science and technology have paved the way to develop novel nanostructured materials for many potential device applications [1–4]. The properties of nanostructured materials are unique because they generally diverge from those of bulk materials when critical dimensions are on the nanometer (nm) scale (1–100 nm) [5]. To utilize these nanomaterials, attention has been paid to tailoring their properties and constructing novel multifunctional nanostructures. Among different potential nanomaterial applications, their utility in gas sensors has been particularly attractive to meet ongoing needs for improved performance [5–9].

For decades, metal oxide semiconductors (MOSs) have dominated commercial gas sensing. MOS nanomaterials exhibit many attractive features, such as high chemical and thermal stability, high surface area, tunable electronic states, quantum confinement, high electron mobility, and excellent catalytic properties [5,6]. Various types of MOS nanomaterials have been explored for gas sensing applications. Examples include nanostructured variants of tin oxide (SnO₂), indium oxide (In₂O₃), zinc oxide (ZnO), tungsten trioxide (WO₃), cuprous oxide (Cu₂O), cobalt oxide (Co₃O₄), nickel oxide (NiO), and titanium oxide (TiO₂) [10–17]. Among these, ZnO stands out as a promising and widely investigated nanomaterial for sensing applications: ZnO nanomaterials possess high thermal and chemical stability, high mobility of conduction electrons, and diverse sensing properties that can include the detection of biomolecules, chemicals, and gases [18]. Importantly, this development has been assisted by the fact that nanostructures and morphologies of ZnO can be prepared on a large scale using simple wet chemical routes at relatively low temperatures compared to typical metal oxide syntheses [19–21].

The sensing performance of gas sensors depends on the nanomaterial morphology, surface-to-volume ratios, crystallinity, electronic properties, and the deposition method used in device fabrication [22–25]. Two steps (i.e. synthesis of the desired nanomaterials and assembly of the nanomaterials on the electrode surface) are needed for sensor device fabrication. Most sensors utilize pre-synthesized nanomaterials during the fabrication process, wherein nanomaterials are mixed with the binders or solvents to prepare pastes/slurries. These pastes/slurries are then deposited on the electrode surface by drop casting, spin coating, or screen-printing [10–18,25]. A downside of this approach is that it can result in an inhomogeneous or dense film, poor stability, and limited electrical contact on the electrode. Moreover, binders can block the catalytically active sites, which reduced the sensing performance and leads to poor reproducibility and stability [26]. Therefore, direct integration of nanomaterials on electrode surfaces is beneficial as it promotes high stability, adhesion, and improved electrical contact between the sensing materials and sensor electrode chips [27].

In this feature article, we detail recent progress in vertically oriented ZnO nanomaterial based gas sensors. We discuss direct integration on the electrode surfaces of such nanomaterials, including nanorods (NRs), nanowires (NWs), nanotubes (NTs), nanoneedles (NNs), and nanosheets (NSs), and then we summarize and compare their sensing performance. Finally, we discuss the advantages, challenges, and future

directions for the development of high-performance gas sensors using functionalized vertically oriented ZnO nanomaterials.

2. Gas sensing properties of ZnO nanomaterials

2.1. Gas sensing mechanism and properties of MOS gas sensors

2.1.1. Basic principle of MOS gas sensors

The fundamental and typical gas sensing mechanism of conductometric MOS gas sensors is based on the change of resistance induced due to the chemical interactions between the adsorbed oxygen ions and exposed target gas molecules on the surface of MOS gas sensors [28,29]. However, the gas sensing mechanism also changes depending upon the types of MOSs (n-type MOSs and p-type MOSs) and gaseous analytes. For example, in the case of an n-type MOS gas sensor with electrons (e[−]) as majority carriers, the resistance decreases for reducing gases (donor) and increases for oxidizing gases (acceptor). Similarly, for a p-type MOS gas sensor with holes as majority charge carriers, the gas sensing mechanism is opposite to it. In general, from the air atmosphere, oxygen molecules (O₂) with high electronegativity and lone pairs of electrons are chemisorbed onto the surface of an n-type MOS film [29]. Since O₂ molecules are oxidizing gases and act as acceptors of electrons, they are ionized into different oxygen species (O₂[−], 2O[−], O^{2−}) by trapping electrons from the conduction band of the n-type MOS. It should be noted that the formation of different types of chemisorbed oxygen ionic species such as O₂[−], O[−], and O^{2−} are strongly dependent upon the operation temperature of the gas sensor [30]. An electron depletion layer or charge space region emerges on the surface of the n-type MOS, and a potential barrier is created due to the decrease in electron density (Fig. 1a) [23]. Therefore, the electron conduction of the MOS decreases, thus resulting in an increase in resistance. This is also called the baseline resistance in air. The depth of the depletion layer from the surface of an MOS sensor is defined as the Debye length (L_D) and usually measures a few nanometers (nm) [31].

The calculation of the Debye length of an MOS gas sensor is expressed as follows [32]:

$$L_D = \left(\frac{\epsilon k T}{q^2 n_d} \right)^{1/2} \quad (1)$$

where ϵ , k , T , q , and n_c are the static dielectric constant, Boltzmann's constant, absolute temperature, electrical charge of the carrier, and carrier concentration, respectively. In contrast, the width of depletion or accumulation layer is calculated as follows [32]:

$$x = 2L_D \left(\frac{q V_s}{k T} \right)^{1/2} \quad (2)$$

where V_s is the potential barrier height [32]. When reducing gases (CO, H₂, NH₃, H₂S, C₂H₅OH, etc.) are exposed to the MOS gas sensor, the gas molecules are adsorbed on the MOS surface and then react with chemisorbed oxygen ions, thereby releasing electrons back into the electron depletion layer (the schematic diagram in Fig. 1 shows the gas sensing mechanism for an n-type MOS with reducing gas). This results in a decrease in the electron depletion layer's thickness and

Fig. 1. Schematic illustration of the gas sensing mechanism of (a) an n-type MOS sensor, and (b) a p-type MOS sensor during air and reducing gas conditions, Reproduced from the Ref. [23] with permission, Copyright 2019, Royal Society of Chemistry.

potential barrier (as shown in Fig. 1a), which eventually decreases the resistance of the MOS gas sensor. In contrast, with oxidizing gases (NO_2 , NO , O_3 , etc.), the results are inversed: namely, the electron depletion layer and potential barrier grow, which increases the resistance of the MOS gas sensor. However, the p-type MOS behaves completely contrarily to the n-type MOS (Fig. 1b). Since our review is focused on n-type ZnO based nanostructures, the discussion is limited to n-type MOSs only. The MOS nanomaterials used as gas sensing materials are generally crystalline or polycrystalline in nature, which are interconnected with different grains having grain boundaries. According to Yamazoe et al. [33], the gas sensing behavior of a sensor is governed by three key functions: the receptor function, transducer function, and utility factor. The receptor function includes the ability of metal oxide sensing materials to recognize the oxygen molecules and target analytes in the surrounding atmosphere, and the interaction between them. However, this function will be greatly changed if the metal oxide is modified with other impurities or new constituents. On the other hand, the transducer function entails the transformation of the surface interaction phenomenon (charge carrier mobility and change of resistance) into an electrical signal (i.e., sensor response). The depletion layer formed due to the chemisorbed oxygen ion species results in a double Schottky barrier between adjacent grains (as shown in Fig. 2), which hinders the carrier mobility inside the grain. However, the potential barrier is modulated in the presence of target gases, resulting in a decrease in resistance due to the electrons' mobility from one grain to another grain. Finally the last function, utility factor, concerns the effect of response behavior in a porous sensing body during the diffusion and chemical reaction of target gas molecules inside the pores. Thus, the receptor function deals with intraparticle issues, the transducer

function with interparticle issues, and the utility factor with gas accessibility issues [34]. The sensing properties of MOS gas sensors depend upon various factors, such as structural features, dopants, modification of MOS with foreign materials, noble metals, morphology, working temperature, etc., which will be further detailed later. Furthermore, the gas sensing performance of these sensors can be evaluated using a few important parameters, such as response or sensitivity (S), selectivity, response/recovery time, operation temperature, stability, etc. [24]. Accordingly, for an n-type MOS gas sensor, the response values are expressed as R_a/R_g , $(R_a - R_g)/R_g$, and $(R_a - R_g/R_g) \times 100\%$ (where R_a and R_g are the resistance of sensors in air and the target gas, respectively). However, for the oxidizing gases, R_a and R_g need to be reversed. The time needed to reach 90% of the resistance change during exposure to the target gas is defined as the response time (T_{resp}), and the time needed to recover 90% of the resistance after extraction of the target gas is defined as recovery time (T_{recv}) [23].

2.1.2. Mechanism for enhancement of gas sensing properties

Recently, a great variety of novel synthetic processes have been employed to produce interesting MOS based nanostructures for gas sensing applications. Considerable attention has been paid to improving their sensing properties, such as sensitivity, selectivity, reproducibility, reduced working temperature, etc. To this end, various strategies have been undertaken and investigated. The sensing performance of MOS based gas sensors is affected by various parameters, such as morphology, grain size, porosity, decoration of noble metals, construction of p-n junctions, working temperature, etc. This section discusses the effect of the above factors on the sensing properties and their mechanisms.

Fig. 2. Receptor function, transducer function and utility factor as well as the physicochemical or the material properties involved for semiconductor gas sensors, Reproduced from Ref. [34] with permission, Copy right 2017, Elsevier.

2.1.2.1. Effect of noble metal modification. In gas sensing applications, noble metal catalysts such as Au, Pt, Ag, and Pd have been widely studied for the decoration onto MOS gas sensor surfaces to enhance their sensing properties, such as sensitivity, selectivity, response/recovery, and reduced working temperature. Two sensitization effects, called electronic sensitization and chemical sensitization, are mainly responsible for the enhanced sensing behavior of gas sensors [32]. The chemical sensitization effect is also known as the spillover effect in many of the sensors. In this effect, metal nanoparticles, which are excellent catalysts, can dissociate molecular oxygen into oxygen species by quickly adsorbing on MOS surfaces and then spilling over on them. As a result, more oxygen ionic species are adsorbed on the sensor surface. Furthermore, the target gas molecules can be directly adsorbed onto the active sites of these noble metal catalysts and then migrate onto the MOS surface to react with already existing chemisorbed oxygen ions. Thus, this effect eventually leads to a faster adsorption of oxygen and target gas molecules, thereby increasing the sensing performance. Fig. 3a shows the chemical sensitization process of an n-type MOS. Occurring simultaneously with the chemical sensitization effect, the electronic sensitization effect also greatly enhances the sensing performance. In this effect, when a noble metal catalyst has electronic contact with an MOS sensor, the charge transfer occurs from the MOS sensor to the noble metal catalyst due to the difference in their work functions. As a result, the electrons accumulate in the noble metal catalyst, resulting in a charge depletion layer on the MOS sensor surface. This process eventually yields a “Schottky potential barrier,” which is characterized by a band bending in the MOS sensor. This whole process increases the baseline resistance of the gas sensor. After the target gas reacts with adsorbed oxygen ions on the sensor surface, the released electrons lead to the decrease in sensor resistance and hence the potential barrier height. The height and depth of the potential barrier at the surface depend on the charge carrier concentration, which in turn directly depends on the amount and type of adsorbed oxygen ions [35]. Fig. 3b

shows the mechanism of the electronic sensitization effect along with the band bending and charge transfer process [36]. Fig. 3c and d show the baseline resistance changes that occur before and after noble metal loading [37].

2.1.2.2. Effect of P–N heterojunction. Researchers around the world have tried many approaches to enhance gas sensors' performance, because single-component MOS gas sensors are not able to satisfy all practical demands. One of these approaches is to design heterojunction nanostructures by combining n-type MOSs with p-type MOSs or vice versa to form a p–n junction heterostructure. The enhanced sensing properties of p–n junction heterostructures are generally attributed to the synergistic effect of the heterointerface between p- and n-type MOSs. In a typical p–n junction nanostructure, the electrons from the conduction band of n-type MOSs will be transferred to the lower energy valence band of p-type MOSs at their interface to equalize the Fermi level energy. This process results in a “band bending” at the heterointerface of p- and n-type MOSs, which further extends the width of the electron depletion layer [23], as shown in Fig. 4a. This process increases the baseline resistance in air (R_a) of the sensor, making it more sensitive for gas sensing reactions, which results in high sensing performance. In addition, the selectivity of the gas sensor can also be controlled when one of the components shows high catalytic activity toward a specific target gas. For instance, the decoration of n-type MoS_2 nanoparticles on p-type CuO nanorods to design $CuO-MoS_2$ p–n heterojunction nanostructures significantly enhances the selectivity to H_2S (Fig. 4b) [38]. This can be attributed to the transformation of a resistive $CuO-MoS_2$ p–n junction into a highly conducting $CuS-MoS_2$ metal p–n junction nanostructure upon exposure to H_2S , as well as the combination of the synergistic effect of a binary nanostructure and the modulation of the charge transfer at the heterointerface (Fig. 4c).

Fig. 3. (a) Schematic diagram of chemical sensitization process of MOS (SnO₂) sensor deposited with Pd nanoparticle (Reproduced from Ref. [32] with permission, Copyright 2019, Elsevier), (b) depicts the electronic sensitization mechanism of Au catalyst showing energy band diagrams of both ZnO and Au/ZnO nanostars before and after CO exposure (Reproduced from Ref. [36] with permission, Copyright 2017, Elsevier), and (c and d) Schematic diagrams of the baseline resistance changes before and after Au noble metal loading on WO₃·H₂O sensor. Reprinted with permission from Ref. [37], Copyright 2017, Elsevier.

2.1.2.3. Effect of microstructure and surface morphology

2.1.2.3.1. Effect of grain size, porosity, crystallinity, and size of gas molecules. It is known that MOS based sensing materials are composed of aggregate particles with many grains that are interconnected with their neighbors by grain boundaries. The sizes of these grains play an important role in changing the sensitivity of MOS gas sensors. This is because on the surface of grains, adsorbed oxygen molecules in the form of oxygen ionic species extract electrons from the conduction band and trap them near surface, which induces band bending and a charge depletion layer [39]. Xu et al. proposed a relation between the particle size (D) and the width of the depletion layer (L_d) through a semi-quantitative model (Fig. 5) [40]. According to this model, if $D \gg 2L_d$, the electronic conductivity of sensing nanomaterials is determined by Schottky barrier heights at grain boundaries, which are independent of the individual grain size. Hence, with decreasing grain size, the surface area increases, leading to high sensitivity. If $D \geq 2L_d$, the depletion layers around the grains create narrow conduction channels. In this case, the conductivity depends on the barriers at the grain boundary and the cross-sectional area of the channels. When $D < 2L_d$, the depletion layer is larger than the grain, and therefore inter-grain barriers for charge transport are insignificant. As a consequence, the gas sensitivity increases for materials with small particle sizes. The gas sensing reactions also occur due to the typical gas-solid interaction. Hence, the sensing properties of a gas sensor are dependent on the pore size and porosity of sensing materials [40]. In addition, this porosity affects the surface area and diffusion rate of gases, which eventually alter the sensing response because porous bodies facilitate gas diffusion inside the sensing films and obtain higher sensing properties. There are different kinds of porous materials: microporous (<2 nm), macroporous

(~50 nm), and mesoporous (2 to 50 nm). In gas sensing, large pores are beneficial for diffusion of gas molecules but induce low surface area, while smaller pore size provides higher surface area but limits the target gas diffusion and mass transport within the sensing layer. Hence, mesoporous materials with appropriate pore sizes and surface area are ideal candidates for gas sensing applications. According to Sakai et al., the gas diffusion dynamics in the response of gas sensors is defined by the following equation [41]:

$$Dk = \frac{4r}{3} \left[\frac{2RT}{\pi M} \right]^{1/2} \quad (3)$$

In addition, the crystallinity of sensing materials also affects gas sensing properties. For example, Xu et al. proposed a relationship between crystallinity (polycrystalline and single crystalline) and porosity, and the gas sensing performance of In₂O₃ nanostructures [42]. In their study, the In₂O₃ nanostructures with a single-crystalline structure and larger pore size showed enhanced sensing performance (Fig. 6b). Such single-crystalline nanostructures are beneficial for charge carrier transportation through the semiconductor matrix during the gas sensing process. Furthermore, larger pores provide more active sites for adsorption of oxygen molecules and target gas, enhancing the gas sensing performance [43]. On the other hand, In₂O₃ nanostructures with small pores (Fig. 6a) possess many potential barriers between the adjacent particles and grain boundaries due to the formation of depletion layers; this hinders the mobility of electrons, resulting in a decrease in the sensor performance. In contrast, a single-crystalline In₂O₃ nanostructure with the absence of grain boundary can decrease the potential barrier in the sensing film (Fig. 6b) and enhance conductivity.

In addition to pore size and crystallinity of materials, the molecular size of gas analytes is important for the adsorption of gas molecules and gas sensing reactions, especially for selectivity. The gas sensing properties can be regulated depending on the pore size of sensing materials and the molecular size of target gases. For example, Tian et al. [44] established the relationship between the pore size of metal organic frameworks (MOFs), a molecular sieving material coated with ZnO nanorods, and the molecular kinetic diameter of different test gases, as shown in Fig. 7. They prepared MOFs such as ZIF-8 with a nominal pore diameter of 3.4 Å. In Fig. 7c, it can be seen that the molecular size of formaldehyde is smaller than the rest of the VOCs, which allows the passing of the ZIF-8 to be detected. Therefore, the selectivity to formaldehyde is higher than that to other gases (Fig. 7d). It can hence be concluded that the selectivity of a gas sensor can be tuned by regulating the pore size of the sensing body, which depends on the kinetic molecular diameter of the gas molecules.

2.1.2.4. Effect of different morphologies. Morphology controlled synthesis of nanostructures into various shapes and sizes is one of many approaches to enhance the sensing performance of gas sensors. Hence, preparing MOS nanostructures with precisely controlled morphologies is important. In view of this, significant research progress has been made in producing different morphologies of nanostructures for the development of high-performance gas sensors. Here, we explain the typical gas sensing mechanisms of MOS nanostructures with different sizes and morphologies, such as nanoparticles, nanorods, and nanowires, to further review materials related to these structures. Shankar et al. [45] proposed the gas sensing mechanism of ZnO nanostructures with two different morphologies, namely nanoparticles and nanowires, toward ethanol, as shown in Fig. 8. Fig. 8a shows that the ZnO nanoparticles contain numerous potential barriers in grain boundaries due to the formation of the space charge region at their intergranular contacts. As a result, the percolation path is broadened, which hinders the transport of charge carriers, increasing the potential barrier height (Fig. 8a) and the resistance of the sensor during the gas sensing reaction. On the other hand, in the case of ZnO nanowire structures, the intergranular contact resistance is reduced due to the unidirectional percolation path (UPP), which decreases the potential barrier height and thus the sensor resistance [32]. Rai et al. [46] investigated the effects of different morphologies of ZnO, such as nanoparticles and nanorods, on sensing properties, and they compared their sensing mechanism with regard to morphology and interelectrode gaps. The authors proposed that the number of grains present between interelectrode gaps affects the sensing performance (response) (Fig. 8). Since grain boundaries are regarded as highly resistive barriers, the overall resistance of ZnO nanoparticles increases during NO₂ sensing. The response to NO₂ is measured by R_g/R_a ; the higher the R_a value, the lower the response to NO₂ will be. Furthermore, Tamaki et al. proposed a relationship between number of grains and resistance, in which the sensor resistance is directly related to the number of grains between two electrodes, as follows [47–49]:

$$R_a = 2R_a(i) + (N-1)R_a(gb) = (2R_a(i) - R_a(gb)) + R_a(gb)N \quad (4)$$

where $R_a(i)$ and $R_a(gb)$ are the resistance at the interface and at the grain boundary in the air, respectively, and N is the number of grains present in the electrode gap.

2.1.2.4.1. Effect of crystal planes. It is known that in MOS gas sensors, the sensing reactions result from the adsorption and desorption of oxygen molecules and from the target gas occurring on the sensor's surfaces. Hence, the gas sensing characteristics of an MOS gas sensor are strongly dependent on the nature of its crystal facets exposed to the gas molecules [50]. Different crystallographic facets have different atomic terminated features, which show different gas sensing properties [51]. In this regard, during the synthesis of nanostructures, the growth condition is a crucial factor in controlling morphologies and exposing facets. The effect of crystal planes on the gas sensing properties

of MOS gas sensors have been reported by various authors. ZnO, a promising n-type MOS, has been studied in many fields, including the field of gas sensors. The most stable crystal structure of ZnO in ambient conditions is wurtzite with a hexagonal structure, which is tetrahedrally coordinated with zinc and oxygen atoms stacked alternatively along the c -axis [52]. ZnO has two different crystal surfaces: polar (Zn terminated (0001) plane and O terminated (000-1) plane) and nonpolar (mix terminated (100)). Of the two, the polar crystal facets (0001) have high surface energy and a high crystal growth rate shows different properties than polar facets. Many studies have investigated ZnO as a gas sensor with high-energy crystal facets exposed. For example, Han et al. [53] examined three types of ZnO nanostructures, flakes, columns, and pyramids, by hydrothermal routes. The dominant surfaces of ZnO flakes, columns, and pyramids are (0001), {100}, and {101} facets, respectively (as shown in Fig. 9a-i). The ethanol gas sensing properties of these gas sensors reveal that the responses (R_a/R_g) of ZnO flakes, columns, and pyramids are in the order of 75.7, 31.5, and 9.3, respectively, at 350 °C (Fig. 9j). In addition, many other reports on the effect of crystal facets have been published and are helpful to understand their influence in gas sensing performance [54–57]. The surface atomic structures of wurtzite ZnO with different crystal facets, shown in Fig. 9h-k, play a crucial role in gas sensing and adsorption of oxygen species. Due to the unsaturated oxygen coordination of the Zn terminated (0001) plane, it shows a strong chemisorption process. In contrast, in the case of O terminated (000) and {101} planes, the absorption of oxygen is weak because the terminated O²⁻ ions are less prone to further absorbing any oxygen species. Hence, it can be concluded that the gas sensing activity of the ZnO crystal facets is in the order of (0001) > {10-10} > {10-11} and (000-1), respectively [53].

2.1.2.5. Effect of working temperature. It is known that the gas sensing reaction occurs at the gas-solid interface, which affects the receptor function of sensors. The operating temperature strongly influences the receptor function and thus determines the sensing performance. It should be noted that the formation of different types of chemisorbed oxygen ionic species, such as O₂⁻, O⁻, and O²⁻, are strongly dependent upon the operation temperature of a gas sensor, as shown in the following equations [35,40,45,52,58]:

Usually, MOS based gas sensors are heated at elevated temperatures (between 100 °C to 400 °C) to observe the gas sensing performance. As shown in Fig. 10a, the appearance of a volcano shaped (rise-maximum-decline) tendency is due to the temperature-dependent reaction between the chemisorbed oxygen and target gas. A sensitivity below the optimum working temperature value can be expected, because the target gases do not have enough thermal energy to react with the adsorbed oxygen species [59]. The response slowly increases with a rise in temperature up to the optimum temperature, which can be expected to the fact that the thermal energy obtained is high enough to overcome the activation energy barrier to the sensing reaction. However, when the operating temperature is further increased, the response of the sensor gradually decreases, which may be due to the difficult adsorption of both oxygen and target gas molecules on the sensor surface at high temperatures. Hence, in general, an optimum operating temperature is considered to obtain a high response. The relative humidity (RH) has a greater influence on the semiconducting gas sensor. In high humidity conditions, the water molecules disturb the gas sensing performance. For example, recently, Zhang et al. [60] investigated a spinel type

Fig. 4. (a) Schematic illustrations of the energy band structures at heterojunction interfaces of a p-n junction (Reproduced from Ref. [23] with permission, Copyright 2019, Royal Society of Chemistry, (b) schematic illustration of H₂S sensing mechanism of CuO-MoS₂ p-n heterojunction, and (c) schematic illustration of the energy band diagram of p-n junction CuO-MoS₂ sensor (b-c, Reproduced from Ref. [38] with permission, Copyright 2019, Elsevier).

oxide (NiFe₂O₄) for acetone gas sensors. They tested the response of the prepared NiFe₂O₄ sensor to 100 ppm acetone in different RH conditions (25 to 98%) at an operating temperature of 250 °C. Their results showed that the response as well as the baseline resistances almost linearly decreased with the increasing RH, which can be explained by the fact that water molecules slowly occupied the reaction zone of the sensing material surface (Fig. 10b-c). On the other hand, when the operating temperature was reduced to room temperature (RT), the adsorbed oxygen ions on the surface of the MOS sensor were mainly O₂⁻ ions. At RT operation, the RH effect also had a strong influence on the sensor performance [61,62]. In wet atmosphere, H₂O molecules compete for the surface reaction sites with oxygen molecules and in turn limit oxygen adsorption. The number of oxygen species decreases as the RH level increases, causing a decline of the baseline resistance in ambient atmosphere with a lower sensor response [62].

3. Detection of different toxic, VOC, and combustible gases

The rapid industrialization and increase in the number of automobiles have led to severe pollution in indoor and outdoor

environments due to the release of toxic and hazardous gases, and volatile organic compounds (VOCs). VOCs are organic chemicals with high vapor pressure and a low boiling point, which makes them volatile in nature [63]. Common pollutants of VOCs include acetone, ethanol, benzene, formaldehyde, methanol, benzene, xylene, toluene, and n-butanol, among others. Common examples of toxic gases are CO, H₂S, NH₃, NO₂, SO₂, trimethylamine, etc. In addition, hydrogen (H₂) gas is regarded as an explosive gas when it is mixed with air. These gases are dangerous to the environment, health, and safety. Therefore, the development of high-performance gas sensors is important for the early detection of these life-threatening gases. Due to the adverse effects of these gases on human health and society, several environmental safety and health agencies have set guidelines regarding the exposure limit for human beings, such as the Occupational Safety and Health Association (OSHA), the National Institute of Occupational Safety and Health (NIOSH), and the American Conference of Governmental Industrial Hygienists (ACGIH). Table 1 lists a few VOC, toxic, and combustible gases with their properties, exposure limits, and harmful effects [64–84].

Fig. 5. Schematic illustration of the model depicting the relationship between particle diameter and charge depletion layer on the gas sensitivity (Reproduced from Ref. [40] with permission, Copyright 2012, MDPI AG, Basel, Switzerland).

4. Synthesis of vertically oriented ZnO nanostructures

Different morphologies of nanomaterials possess different advantageous attributes in terms of surface-active sites, surface area, and electronic properties, which facilitate gas diffusion, absorption, and sensing reactions [85]. Vertically oriented nanostructures in particular are currently garnering attention for the fabrication of different sensing devices [86–94]. The utilization of vertically and directly grown nanostructures on the supporting electrode/substrate avoids the use of conductive binders (used to fix nanomaterials on the electrode surface) and higher annealing temperatures. Furthermore, these nanostructures offer an excellent surface area for biomolecule immobilizations (i.e. enzymes) and surface modification with metal/metal oxides [95]. Considering the excellent properties of vertically oriented nanomaterials, ZnO has attracted increased interest due to its easy and tunable growth capabilities. One of the most favorable aspects of vertically oriented ZnO nanostructures is the high reproducibility of the desired nanostructure's morphology, which leads to reproducible sending device fabrication [95].

The most common methods for growing vertically oriented ZnO nanostructures are the thermal evaporation, hydrothermal, electrochemical, and electrodeposition methods [96–100]. These are all time dependent, which is beneficial for growing similar nanomaterials in different experiments. In comparison with the high temperature based thermal evaporation method, the hydrothermal method provides better control over ZnO nanostructure morphology because it utilizes a seeded surface and low growth temperature. Umar et al. [101] and Djurišić et al. [102] recently summarized the growth methods of vertically oriented ZnO nanostructures. In the present review article, we evaluate vertically

Fig. 6. Schematic illustration of sensing mechanism and the potential energy barriers in the In_2O_3 nanoplates sensor with smaller pore size (a) and larger pore size (b) (Reproduced with permission from the Ref [42], Copyright 2019, Elsevier).

Fig. 7. (a) TEM image of typical synthesized ZnO@ZIF-8 nanorods arrays, (b) their aperture sizes, (c) table showing the comparison of different test gases kinetic molecular diameters with ZIF-8 pore size, and (d) Formaldehyde selectivity of ZnO@ZIF-8 nanorods sensor in presence of other interfering gases. Reproduced from the Ref. [44] with permission, copyright 2016, American Chemical Society.

oriented ZnO nanostructures with different morphologies, such as NWs, NRs, NTs, NNs, and NSs (Scheme 1), in gas sensing applications.

5. Gas sensing applications of vertically oriented ZnO nanomaterials

5.1. ZnO NW based gas sensors

NWs offer the advantage of a high surface area and other exciting properties [22]. In ZnO NW based gas sensors, gases can diffuse rapidly and effectively through the porous network, allowing a large surface area to participate in the gas sensing reactions [103]. Methods such as direct growth of vertical, horizontal, and bridging NWs have been explored for the production of NW functional gas sensing electrodes [103–105]. Among these methods, vertically oriented NWs are most often used for gas sensing applications as a result of the ease of their formation. Vertically oriented NWs can yield highly stable pathways for rapid electron transport, which enhances sensitivity to achieve ultra-low detection limits [103]. As a result of the outstanding properties of vertically oriented ZnO NWs, several studies have explored their responses to reducing and oxidizing gases. Table 2 details the comparative sensing performance of vertically oriented ZnO NW based gas sensors for toxic and VOC gases, including hydrogen sulfide (H_2S), ethanol, hydrogen (H_2), nitrogen dioxide (NO_2), CO, ammonia (NH_3), and acetone. Specific highlights of these results are discussed in the following subsections.

5.1.1. H_2S sensors

Reliable detection of ppb–ppm levels of hazardous H_2S is required for practical applications of this class of gas sensor. Chen et al. reported ultra-sensitive ppb levels of H_2S detection with a vertically oriented ZnO NW based gas sensor, and they studied its nano size effect on gas sensing properties [106]. The dendritic (tree-branched) ZnO 20 nm diameter NWs responded to 5 ppb H_2S , representing a performance

enhancement compared to the 50–70 nm diameter ZnO NW based device. The nano size effect also appeared to provide for high selectivity, and 500 ppb H_2S was detected with high sensitivity compared to other interfering gases. Approaches for further enhancing the sensing performance of only vertically oriented ZnO NW based gas sensing devices include the surface functionalization of ZnO NWs with noble metal catalysts, doping, and surface coating with metal oxides. A gas sensor with sluggish or incomplete recovery has limited use in practical applications. Hence, the design of high-performance H_2S sensors with high sensitivity and selectivity and simultaneously good reversibility remains a challenge. Woo et al. reported that molybdenum (Mo) doped vertically oriented ZnO NW networks are highly sensitive and selective with reversible H_2S gas sensors [107]. They found the diameters of the pure ZnO NWs to be in the range of 50–80 nm, whereas the length was in the order of a few micrometers (Fig. 11b). The ZnO NWs were doped with Mo using MoS_2 coating by a successive ion layer adsorption and reaction (SILAR) method, followed by heat treatment at 600 °C (as shown in Fig. 11a–b). The experimental evidence showed that the Mo^{6+} was doped to the lattice of ZnO. Furthermore, Woo et al. investigated the effect of Mo doping on the sensing properties and found that the designed Mo doped ZnO NW sensor showed a high selectivity to H_2S and high response, with a 14.11-fold change in resistance at 5 ppm at an operating temperature of 300 °C and a lower cross-response to other interfering gases (Fig. 11d–e). The pure ZnO NW sensor showed long recovery (10 min of purging H_2S) for 5 ppm of H_2S at 300 °C. In contrast, the Mo doped ZnO NW sensor exhibited complete recovery in H_2S free ambient atmosphere, which is likely due to the stability of the Mo based NW surface. The high selectivity of the Mo doped ZnO NW sensor to H_2S was attributed to the strong chemical affinity of MoO_3 to H_2S and the regenerative adsorption/desorption of the MoO_3 surface [107].

The above discussion showed that in spite of using the doping method and reducing the diameter of pure ZnO NWs to nanoscale, the temperature still remains high for the gas response to H_2S . Recently,

Fig. 8. (a–b) Schematic illustration of gas sensing mechanism of ZnO nanoparticles and nanowires toward ethanol vapor depicting the potential barrier modulation with respect to morphology. (Reproduced from Ref. [45] with permission, Copyright 2017, American Chemical Society), (c–d) TEM images of ZnO nanorods and nanoparticles, respectively, and (e) the schematic illustration of the conduction of current in ZnO nanorods and nanoparticles containing grain boundaries (Reproduced from the Ref. [46] with permission, Copyright 2014, American Chemical Society).

the construction of p–n heterojunctions has emerged as an efficient approach to enhance the sensing properties of pure ZnO NW gas sensors in terms of operating temperature and selectivity. Ashwini et al. [108] demonstrated the preparation of an inorganic–organic combination to develop a p–n junction as a gas sensor. Initially, the ZnO NWs were grown on a biaxially oriented polyethylene terephthalate (BOPET) flexible substrate using a facile hydrothermal process with ZnO nanoparticles as seeds. The p-type Co Phthalocyanine was coated with different thicknesses (5–25 nm) on the ZnO NWs using a conventional thermal evaporation technique. Choosing BOPET as the substrate is advantageous due to its flexibility, cost effectiveness, and lightweight properties. Moreover, the polar ester groups in the PET chains facilitate the strong adhesion with the ZnO surface's polar facets due to dipolar

attraction. In Ashwini et al.'s study, the ZnO NWs consisted of two polar surfaces, Zn^{2+} terminated (0001) and O^{2-} terminated (000 $\bar{1}$), which were tetrahedrally coordinated with Zn^{2+} and O^{2-} ions planes, resulting in a normal dipole moment and spontaneous polarization along the c-axis of ZnO NWs. The ZnO NW–cobalt (Co) Phthalocyanine p–n heterojunctions provided fast responding and highly sensitive ambient temperature H_2S gas sensors. The 25 nm thick Co Phthalocyanine (p-type) coating on the ZnO NWs resulted in fast response/recovery times and a high response (268%) to 5 ppm H_2S at ambient temperatures. The sensor showed a p-type gas sensing behavior due to its high thickness of p-type CoPc coating on ZnO NWs. The enhanced sensitivity of this p–n heterojunction based gas sensor was attributed to the direct interaction of H_2S with the Co centers (due to the lower availability of

Fig. 9. TEM and HRTEM image of ZnO flakes (a–c), column (b–e), and pyramids (c–f), corresponding ethanol responses of three gas sensors (g), atomic stacking model of wurtzite ZnO showing different crystal facets (h) and (i–k). Schematic presentation of the three morphologies models for (i–k). Reproduced with permission from Ref [53], Copyright 2009, American Chemical Society.

oxygen species), which increased the depletion layer width and blocked the hole conduction channels. It can be concluded that the ZnO-CoPc p-n heterojunction sensor is a promising candidate for H_2S gas sensing applications due to its RT sensitivity, fast response/recovery, and high stability.

Ramgir et al. further enhanced the response and selectivity to H_2S at RT by employing Au nanoparticle functionalization on vertically oriented ZnO NWs [109]. The vertically oriented ZnO NWs were grown on a Si (100)/ SiO_2 (100 nm) substrate using a facile hydrothermal method followed by optimized Au deposition (0–5.7%) by RF sputtering. The ZnO NWs had a diameter in the range of 50–250 nm, while their length varied from 1 to 2 μm . The surface morphology of the synthesized ZnO NWs contained a quasi-hexagonal end with a polar plane [0001] oriented along the c-axis. The modification of Au nanoparticles on the ZnO NWs did not change any surface morphology. However, the modification of ZnO NWs with 1.2 atom% Au provided a 16-fold increase in the gas sensor response to 5 ppm H_2S as compared to pure ZnO NWs. In a metal-semiconductor (n-type) junction based sensor, a Schottky junction barrier is formed when the work function (Φ) of the metal (M) is larger than the electron affinity (χ) of the semiconductor. The barrier (B) height thus formed is given as:

$$\Phi_B = \Phi_M - \chi \quad (9)$$

The work function of Au metal is 5.1 eV and the electron affinity of ZnO is ~ 2.08 eV; hence, the Schottky junction barrier will result at the Au-ZnO interface. A plausible reason for the enhanced sensor response of Au-ZnO NW gas sensors is the dual role of Au: first, in the formation of nano-Schottky type barrier junction barriers at the ZnO-Au interface, and second, in the catalytic dissociation of molecular oxygen by Au

nanoparticles, which increases the resistance and thus the response. The increased response kinetics are facilitated by the reaction of H_2S with a large number of oxygen species (O_2 at RT) provided by the catalytic dissociation of Au metal, and the large number of active sites due to the high surface-to-volume ratio of ZnO NWs. In conclusion, noble metal functionalization on ZnO NW based sensors is believed to be an effective approach for highly sensitive and selective H_2S gas sensing.

5.1.2. Ethanol sensors

Noble metal loading on ZnO NWs has proven effective to enhance ethanol gas sensing properties [110,111]. For example, high-sensitivity Pd-ZnO NW based devices were effective for detecting 500 ppm ethanol at 230 °C [111]. Shi et al. proposed a novel ZnO NW joint (NWs clumped together at the top) structure with high sensitivity and fast response/recovery values of 19 to 28 s at 275 °C for ethanol gas sensing [112]. The enhanced ethanol sensing performance is the result of oxygen afforded by the high surface area and large length-to-diameter ratio of ZnO NWs, and the modulation of electronic barriers at the multi-junction joints in ZnO NWs.

Na et al. designed a p-n heterojunction nanostructure of Co_3O_4 deposited on ZnO NWs for selective detection of ethanol and NO_2 [113]. They grew ZnO NWs on Al_2O_3 substrates using a vapor-liquid-solid (VLS) method, and then deposited lenticular nano scale p-type Co_3O_4 islands using the thermal evaporation technique. Initially, at an operating temperature of 200 °C, the response of the Co_3O_4 -ZnO NW based sensor was slightly improved as compared to bare ZnO NWs. However, when the operating temperature was increased to 400 °C, the Co_3O_4 -ZnO NW based sensor showed high selectivity to 100 ppm ethanol, with a response of 22 and minimal cross sensitivity. Both ZnO NW and Co_3O_4 -ZnO NW sensors showed the n-type gas sensing properties.

This indicates that the electrical conduction in the Co_3O_4 -ZnO NW sensor is dominated by the n-type ZnO NW configuration. However, compared to the H_2S discussed in the previous section, which is detectable even at RT by vertically oriented ZnO NW based sensors, the highest response to ethanol by the current Co_3O_4 -ZnO NW sensor at a high temperature (400 °C) needs further explanation. The sensing reaction of ethanol and oxygen species is written as follows:

Prior to the oxidation of ethanol to CO_2 and H_2O as products, it undergoes two intermediate decomposition reactions, shown in the equations below. The complete oxidation of ethanol on the ZnO NWs' surface may occur at an elevated temperature because of this the pure and Co_3O_4 -ZnO NW sensors show low responses at 200 °C. However, by increasing the temperature up to 400 °C, the Co_3O_4 loaded ZnO NW sensor shows the highest response. This can be explained by the acidic-basic properties of the used metal oxide catalyst. For example, ethanol gas can be either dehydrogenated at the basic oxide surfaces or dehydrated on an acidic oxide surface at a high temperature. The reactions are as follows [114]:

The enhancement of $\text{C}_2\text{H}_5\text{OH}$ at 400 °C in the present study is taken into account by the catalytic effect of Co_3O_4 for the total conversion of ethanol to CO_2 and H_2O at the favorable temperature of Co_3O_4 (~380 °C) [115]. The extension of the electron depletion layer due to the p-n junction of the Co_3O_4 -ZnO NW sensor is another possible reason for the enhanced response. However, the gas responses are completely dependent on different sensor configurations.

Other p-type oxides, such as NiO [116], manganese oxide (Mn_3O_4) [117], and chromium oxide (Cr_2O_3) [118], have also been used to modify vertically oriented ZnO NW surfaces. NiO functionalized ZnO NWs display enhanced sensing sensitivity and selectivity to ethanol. Na et al. reported that NiO modified ZnO NW based gas sensors had high selectivity and high sensitivity of 29.04 to 5 ppm of ethanol at 450 °C, as compared to pure ZnO NWs (3.65) [116]. As discussed in the literature [114], the enhanced response to and selective detection of ethanol by the deposition of basic oxides (NiO) onto ZnO NWs can be explained by the dissociation of $\text{C}_2\text{H}_5\text{OH}$ into more reactive products (CH_3CHO and H_2). In another study, Kwak et al. examined the effect of Mg doping on urchin-like ZnO NW networks for ethanol gas sensing, and they obtained a high response of 343 to 5 ppm ethanol at 350 °C [119]. They demonstrated that the urchin-like morphology of Mg doped ZnO NW networks played a crucial role in increasing the gas response due to the large number of NW-NW contacts. In addition, the high selectivity to ethanol of Mg doped ZnO NW sensors is attributed to the acidic-basic properties of Mg. Since Mg is a basic element, the dehydrogenation reaction $\text{CH}_3\text{CHO}(\text{g}) + \text{H}_2(\text{g})$, which shows higher reactivity with negative oxygen species, is mostly favored. The high response is explained by the effective near-surface electron depletion layer and the numerous NW-NW contacts [116]. The studies reviewed above imply that the high ethanol sensing properties of ZnO NW based sensors are due to changes in the acidic-basic properties of the sensing materials, especially the addition of basic oxide additives to the sensing materials.

5.1.3. H_2 sensors

ZnO NW networks show high sensitivity and faster response to many target gases when compared to other NW configurations as a result of their high surface area and many NW-NW junctions [120]. However, bare ZnO NW networks often suffer from limited H_2 selectivity in the presence of other interfering gases. Different strategies have been employed to address this issue. One method is to use a porous metal

Fig. 10. (a) The relation between response and operation temperature of Au@ZnO and ZnO NPs sensors. Reproduced from the Ref. [58] with permission, Copyright 2019, American Chemical Society; (b) effect of responses, and (c) baseline resistance with different relative humidity for NiFe_2O_4 sensor to 100 ppm acetone at 250 °C (Reproduced with permission from Ref. [60], Copyright 2019, Elsevier).

organic framework (MOF) as a membrane filter over ZnO NWRs to improve selectivity to H_2 gas [121]. In this case, the MOF acts as a molecular sieve and selectively absorbs target gas molecules as a function of their kinetic diameters.

Drobek et al. proposed MOF encapsulated ZnO NWs for high-selectivity H_2 gas sensors with negligible response to other interfering gases such as benzene and toluene [122]. They further showed a high-selectivity H_2 gas sensor fabricated using a SIM-1 nanomembrane coated ZnO NWs [123]. SIM-1 stands for substituted imidazole material-1, which is isostructural with zeolite imidazole frameworks (ZIF-8) and has pore apertures <0.34 nm and cage sizes of ~0.8 nm. The authors grew vertically oriented ZnO NWs on Au/Pt/Ti patterned interdigitated electrodes (PIEs) and coated the ZIF based materials using a solvothermal treatment method (Fig. 12a-e). When compared to pristine ZnO NW based sensors, the ZnO/SIM-1 NW based sensors were remarkably selective to H_2 at 300 °C and showed negligible responses to other interfering gases, such as acetone, methane, toluene, ethanol, and benzene (Fig. 12f). The excellent selectivity to H_2 of ZnO/SIM-1 NW sensors is attributed to the small pore apertures that can accommodate H_2 transfer but block larger molecules. The current molecular sieving membrane (SIM-1) coated ZnO NW gas sensors are a promising tool for H_2 detection, and they can be used in many fields, both domestic and in industries. The current approach is highly flexible because the synthesis method can be applied to prepare different gases with different MOs and MOFs to tune the selectivity to a specific gas [123].

Table 1

List of VOC, toxic, and combustible gases with their physical properties, uses, threshold limit values (TLVs), and immediately dangerous to life or health (IDLH) health effects.

Gas	Properties/use	TLV*	IDLH	Health effect	Ref.
H ₂ S	Colorless, poisonous gas, flammable, rotten egg smell/ paper, oil, gas and waste treatment industries, chemical industries	10 ppm OSHA and ACGIH	100 ppm (NIOSH)	Known as chemical asphyxiation, death due to react with hemoglobin reducing the oxygen flow in blood, quickly paralyzes the olfactory system	[64–66]
CO	Colorless, odorless, tasteless, non-irritating/–	50 ppm (OSHA) and 35 ppm (NIOSH)	1200 ppm (NIOSH)	Fatal death due to the bind of hemoglobin and reduction oxygen transportation, headache, Nausea, dizziness, collapse, loss of consciousness	[67,68]
NO ₂	Pungent odor, not flammable,	3 ppm (ACGIH)	20 ppm (NIOSH)	Photochemical smog, produce ozone, irritating to eyes, lung damage	[69,70]
NH ₃	Colorless, strong and sharp smell, corrosive and hazardous/ precursor to food and fertilizer, drug synthesis, laboratory use as alkaline	25 ppm (ACGIH)	300 ppm (NIOSH)	Irritant, corrosive and hazardous to skin, eyes, respiratory tract of humans	[71]
Trimethylamine (TMA)	Highly flammable, colorless, fishy odor,	10 ppm (ACGIH)	—	Irritate to eyes, skin, nose, throat	[72,73]
Ethanol	Colorless, volatile (BP: 78.3 °C), inflammable, alcoholic smell, low toxicity	1000 ppm	3300 ppm (NIOSH)	Irritation of eyes, Headache, drowsiness, difficulty in breathing	[74]
Acetone	Colorless liquid, pungent odor/ used to dissolve plastics, pharmaceuticals, laboratories as reagent, solvent	750 ppm (ACGIH)	25,00 ppm (NIOSH)	Fatigue, nausea, dizziness, narcosis, muscle weakness, dryness in mouth, harmful to nerve system	[75]
Formaldehyde	Colorless, flammable/ as industrial fungicide, germicide and disinfectant, production of urea, phenolic resins	20 ppm (NIOSH)	20 ppm (OSHA) and 100 ppm (NIOSH)	Human carcinogen (nasopharyngeal cancer) pulmonary damage and leukemia at 6 ppm)	[76,77]
n-butanol	Colorless liquid, flammable, slightly toxic, vinous odor/ used as solvent in industry, ingredient for perfumes and flavor, extraction of oils, cosmetic nail products, drugs	100 ppm (NIOSH)	8000 ppm (NIOSH)	Dizziness, headache somnolence, dermatitis, lacrimation, photophobia, blurred vision	[78]
Toluene	Colorless liquid, aromatic odor/used in production of paints, nail polish, lacquers, adhesives, rubber, leather tanning	100 ppm (NIOSH)	500 ppm (NIOSH)	Allergenic, central nervous system depression, dizziness, headache, fatigue, irritation of eyes, and skin, unconsciousness	[79]
Methanol	Colorless, flammable, high toxicity, mild odor/ automotive fuel, preparation of dyes, color, drugs, perfumes,	200 ppm (ACGIH)	6000 ppm (NIOSH)	Nausea, abdominal pain, dizziness, headache, blurred vision, eye irritation, drowsiness	[80]
Benzene	Colorless, highly flammable, strong aroma, chronic toxicity	1 ppm (OSHA)	500 ppm (NIOSH)	Carcinogenic effect (leukemia), narcotic effect due to inhalation, fatal death (2%, 5–10 min exposure)	[81,82]
Xylene	Colorless, flammable liquid, sweet odor/ petroleum and wood processing industry	100 ppm (ACGIH)	900 ppm (NIOSH)	Irritate to eyes, nose, skin and throat, headache, dizziness, confusion, loss of muscle coordination, fatal death in high dose	[83]
H ₂	Colorless, tasteless, highly flammable, low minimum ignition energy (0.017 mJ), nontoxic, explosive/ used as fuel in vehicles, metal smelting, glassmaking, petroleum extraction	NA	NA	Pure form is a chemical asphyxiant, dizziness, nausea, vomiting, stinging of the nose and throat, headaches and drowsiness	[84]

* TLV is defined as the maximum concentration of a chemical permitted during a working day of 8 h for repeated exposure without producing adverse health effects.

Scheme 1. Different vertically oriented ZnO nanowires (NWs), nanorods (NRs), nanotubes (NTs), nanoneedles (NNs) and nanosheets (NSs) for gas sensing applications.

To reduce the operating temperatures of gas sensing devices, Lupan et al. investigated a Pd functionalized ZnO NW based gas sensor to detect H₂ gas [104]. This device displayed a high response of 13,100 (I_g/I_a) to 100 ppm H₂ at RT in 30% relative humidity (RH). The sensitivity and selectivity were attributed to the known reactivity of the Pd NPs with hydrogen. Lupan et al. also investigated the doping of ZnO NWs with Ag [124] and Cd [125] as alternative approaches to H₂ sensing at ambient temperatures. It can be concluded that noble metal deposition, especially Pd nanoparticle deposition, would be an effective approach for the highly sensitive and selective detection of H₂ at RT.

5.1.4. NO₂ sensors

ZnO NWs have also been utilized for NO₂ sensing applications [126–128]. Ahn et al. proposed the synthesis of bridged vertically oriented ZnO NWs on a SiO₂/Si/Ti/Pt substrate for NO₂ sensing [129]. They obtained fast response/recovery properties of a NO₂ sensor at 225 °C via oxygen vacancies and the formation of barriers at the NW network junction points [120]. To grow ZnO NWs, a seed layer is needed. However, this layer can potentially cause a parallel circuit (leakage current) that can compromise the sensor response. Nguyen et al. grew ZnO NWs on a dendritic Au catalyst without using a seed layer [130]. The NW-NW junctions were formed on the device and the reduced current leakage provided for enhanced sensing responses.

To further improve the sensing properties of sensors for NO₂, Chen et al. designed novel core-shell ZnGa₂O₄/ZnO NWs vertically grown on

Table 2
Comparisons of gas sensing properties of vertically oriented ZnO NW based gas sensor.

Electrodes/Substrates	Materials	Synthesis method	Target gas	Concentration (ppm)	Temp. (°C)	Sensitivity (S) [R_a/R_g or $*(R_a-R_g/R_a) \times 100$]	Response (s)/Recovery time (s)	Ref.
Au/SiO ₂ /Pt/Si ₃ N ₄ /Si	ZnO NWs	Hydrothermal	H ₂ S	0.005	300	0.81	–	[106]
Al ₂ O ₃ /Au	Mo-ZnO NRs	Carbothermal reduction & successive ionic layer adsorption (SILAR)	H ₂ S	5	300	14.11	–	[107]
Biaxial oriented polyethylene terephthalate (BOPET)	n-ZnO NWs-p-CoPc	Hydrothermal	H ₂ S	10	RT	268%*	26/–	[108]
SiO ₂ /Si	Au-ZnO NWs	Hydrothermal	H ₂ S	5	RT	79	40/15	[109]
Al ₂ O ₃	Au-ZnO NWs	Thermal oxidation	Ethanol	1000	300	478	–	[110]
ZnO:Ga/SiO ₂ /Si	Pd-ZnO NWs	Carbothermal reduction	Ethanol	500	230	61.5%*	–	[111]
Patterned Cu/ Pt/Cr	ZnO NWs	Hydrothermal	Ethanol	100	275	99.1	19/28	[112]
Al ₂ O ₃ /Au	Co ₃ O ₄ -ZnO NWs	Thermal evaporation	Ethanol	100	400	22	–	[113]
Si	ZnO NWs	Thermal evaporation	Ethanol	100	400	58.17	–	[115]
Al ₂ O ₃	NiO-ZnO NWs	Thermal evaporation	Ethanol	5	450	26.15	–	[116]
Al ₂ O ₃	Mg-ZnO NWs	Thermal evaporation	Ethanol	5	350	343	–	[119]
Si/SiO ₂ /Ti/Pt/Au	ZnO-ZIF-8 NWs	Thermal evaporation & Solvothermal	H ₂	50	300	1.44	–	[122]
Si/SiO ₂ /Ti/Pt/Au	ZnO-SIM-1 NWs	Thermal evaporation & Solvothermal	H ₂	50	300	2.5	–	[123]
Au/SiO ₂ /Pt/Si ₃ N ₄ /Si	Pd-ZnO NWs	Electrodeposition	H ₂	100	RT	13,100	–	[104]
FTO	Ag-ZnO NWs	Electrochemical deposition	H ₂	100	RT	50	22/11	[124]
FTO	Cd-ZnO NWs	Electrochemical deposition	H ₂	100	RT	274%*	14/11	[125]
Al ₂ O ₃ /Au	ZnO NWs	Thermal evaporation	NO ₂	100	250	6	–	[126]
Si/SiO ₂ /C NWs	ZnO NWs	Hydrothermal	NO ₂	0.5	200	140	–	[127]
SiO ₂ /Si/Ti/Pt	ZnO NWs	Carbothermal reduction	NO ₂	0.5	225	14	24/12	[129]
Si/SiO ₂ /Cr-Pt/Au	ZnO NWs	Carbothermal reduction	NO ₂	1	300	51%*	15/20	[130]
ZnO: Ga/SiO ₂ /Si	ZnGa ₂ O ₄ /ZnO core-shell NWs	Reactive evaporation	NO ₂	10	250	10,24	90/120	[131]
Pt/Au/Al ₂ O ₃	ZnO NWs	Hydrothermal	NO ₂	5	250	3.3	25/21	[132]
p-Si/SiO ₂ /Au	ZnO NWs	Thermal evaporation	NO ₂	10	300	2,37,263%*	570/180	[133]
Si/graphene	ZnO NWs	Thermal evaporation	NO ₂	10	200	27	200/330	[135]
Si/SiO ₂ /Ti/Pt/Au	NWs/graphene							
Glass	Pd-ZnO NWs	Thermal evaporation	CO	0.1	20	1.02	210/–	[136]
Al ₂ O ₃	ZnO NWs	Hydrothermal	CO	200	250	93%*	1/0.002	[137]
Al ₂ O ₃	ZnO-ZIF-CoZn NWs	Solvothermal	Acetone	100	260	27	43/60	[138]
ZnO:Ga/SiO ₂ /Si	Pt-ZnO NWs	Thermal evaporation + UV irradiation	NH ₃	1000	300	36%*	–	[139]
Al ₂ O ₃	Co-ZnO NWs	Thermal evaporation	Xylene	5	400	19	–	[140]

* $(R_a-R_g/R_a) \times 100$.

electrode chips. These NWs displayed a fast response (90 s) and recovery (120 s) with good repeatability and linearity at ambient temperatures [131]. Chen et al. utilized hydrothermally grown vertically oriented ZnO NWs for sensitive and selective detection of NO₂ in the presence of different interfering gases [132]. The structure of nanomaterials influences the sensing properties. Therefore, Park et al. designed and compared typical (normal) ZnO NWs with nanograined networked ZnO NWs [133]. The normal ZnO NWs were synthesized on Au coated substrates, whereas the nanograined ZnO NWs were synthesized from ZnSe NWs. The fabricated nanograined ZnO NW based sensor showed a greatly enhanced response (237,263%) to 10 ppm NO₂ at 300 °C compared to the normal ZnO NWs (6.5%). The improved sensitivity of the sensor was the result of the high surface area and high number of junctions from the crossed NWs.

Vertically oriented ZnO NWs have been utilized to prepare heterojunction structures (n-n and p-n) with other p- and n-type metal oxides to enhance sensing performance. Park et al. designed n-n ZnO-ZnO and p-n CuO-ZnO NW junctions for NO₂ sensing [134]. The air-bridge structures with heterojunctions showed higher sensitivity with the n-n junction based nanostructured device than with the p-n junctions. Recently, Khai et al. generated catalyst-free, vertically oriented, high-density ZnO NW arrays on graphene/Si substrates for sensor formation (Fig. 13a-d) [135]. These ZnO NW/graphene nanostructures exhibited a high sensitivity to NO₂ at 200 °C with a long response/recovery time. The sensing performance of the ZnO NW/graphene based sensor was attributed to different factors, including oxygen vacancies in the lattice of ZnO NW arrays, large specific surface areas, and the formation of p-n heterojunctions between the ZnO NW (n-type) and graphene (p-type) (Fig. 13e-f). Moreover, the

graphene buffer layer played a crucial role in the vertical growth of ZnO NWs.

5.1.5. Other gas sensors

Recently, Choi et al. demonstrated the utility of a Pd nanodot functionalized ZnO NW based CO sensor [136]. The prepared sensor was highly sensitive to CO (0.1 ppm) at RT (20 °C) with a high response of 1.02 relative to other gases (i.e., benzene and NO₂). Ghosh et al. reported an ultra-fast and reversible gas sensor based on ZnO NW arrays [137]. The sensor response was fast (1 s) with ultra-fast recovery time (2 ms) to 200 ppm CO when tested at an operating temperature of 250 °C. Such sensors possess benefits for practical applications wherein real-time CO monitoring is needed. Yao et al. designed an acetone gas sensor using a core@shell structured ZnO NW-ZIF array [138]. Selectivity and sensitivity to acetone were improved as a result of the selectivity from the ZIF (sieve membrane). In this scheme, different sizes of ZnO NWs (50–100 nm) were grown on a ZnO seeded sapphire substrate, followed by coating with a hydrophobic and catalytic ZIF-CoZn (ZIF-CoZn). The ZIF-CoZn was isostructural with ZIF-8 or ZIF-67, and thin films with different thicknesses (5–15 nm) were investigated (Fig. 14a-b). The results revealed that thin (5 nm) ZnO-ZIF-CoZn NW arrays showed the highest response to 100 ppm acetone at 260 °C (Fig. 14c-f).

Chang et al. demonstrated NH₃ sensing based on Pt NPs deposited on ZnO NWs [139]. They obtained a response of 36% to 1000 ppm NH₃ using a Pt-ZnO NW based gas sensor at 300 °C. The performance of the sensor was attributed to the catalytic activity of the Pt NPs. Woo et al. prepared branched ZnO NWs doped with Co for highly sensitive and selective xylene detection [140]. As shown in Fig. 15a, the ZnO NWs were first grown on an Al₂O₃ substrate using a thermal

Fig. 11. (a) Schematic diagram of preparation method of Mo modified ZnO NWs grown on alumina substrate, (b–c) SEM images ZnO NW and Mo doped ZnO NWs network sensors, (d) selectivity test plot of Mo modified ZnO NWs at 300 °C in presence of different gases including H₂S, and (e) response vs different concentrations of H₂S at 300 °C. Reproduced from Ref. [107] with permission, Copyright 2014, Royal Society of Chemistry.

evaporation technique. The as-grown ZnO NWs were then transformed to CoO NWs by a cation exchange reaction after thermal evaporation of CoCl₂ at 700 °C. The final branched Co doped ZnO NWs were grown from the CoO NWs, with the Co centers acting as catalysts for this process. The prepared Co doped ZnO NW gas sensor showed a high response (19) and selectivity to 5 ppm xylene at 400 °C with negligible cross responses (Fig. 15b–d).

5.2. ZnO NR based gas sensors

The gas sensing properties of a nanomaterial depend on its surface area and porosity relating to gas adsorption/diffusion, the sensing reaction, and the charge transfer phenomenon occurring at its surface [5,6]. Therefore, while designing a nanomaterial, the common goal is to obtain an optimum surface area. In contrast to ZnO NWs, ZnO NRs have the advantage of a low synthesis temperature while still maintaining excellent properties (i.e., high surface area, good charge carrier mobilities, and highly active surface sites for easy gas adsorption) [141]. However, the aspect ratios (width/length) of ZnO NWs are higher than those of ZnO NRs. Nevertheless, vertically oriented ZnO NRs have several

advantages in gas sensing applications. In the following subsections, we discuss their gas sensing performance, which is also summarized in Table 3.

5.2.1. H₂S sensors

Significant effort has been focused on ZnO nanostructure based sensors for H₂S. However, issues such as poor gas response/recovery, high working temperatures, and gas sensing stability still remain [142,143]. Hosseini et al. reported a RT operated H₂S sensor based on vertically oriented ZnO NRs with flower structures and a length of 1.9 μm and a diameter of 300–500 nm [144]. The vapor phase transport (VPT) method was used to synthesize these NRs, which were grown along the c-axis in (0002) crystal planes perpendicular to the substrate. Interestingly, the vertically aligned ZnO NR based sensor displayed a higher response ($R_s = 581$) to 5 ppm H₂S at 26 °C than at 250 °C ($R_s = 3.7$). The sensor showed a high selectivity to H₂S gas among many interfering gases, such as CO, CH₄, methanol, ethanol, acetone, and H₂. However, the response and recovery times of this sensor were 320 s and 3592 s, respectively for 1 ppm of H₂S, which are very long. On the other hand, the sensor showed good stability even after 5 months of storage in air. The high selectivity of this ZnO NR based H₂S sensor was attributed to the strong affinity of ZnO to H₂S even at RT compared to other gases, and the smaller bond dissociation energy of H-SH (381 kJ/mol) compared to other interfering gases [85]. On the ZnO sensing surface, the H₂S gas molecules reacted not only with oxygen species (O₂⁻) but also with the ZnO sensor directly, and decomposed to form zinc sulfide (ZnS). The sensing reaction of ZnO to H₂S is explained by the following reactions [4,144]:

In addition, the enhanced response of the sensor was further explained by the porous network structures of flower-like nanostructures, oxygen vacancies, and potential barrier modulation on ZnO surfaces.

To further enhance the response, selectivity, and working temperature, Hosseini et al. reported ZnO NRs with flower-like bundles grown directly on SiO₂/Si substrate without any catalyst layer using the VPT method. Later, a Au nanoparticle layer with a nominal thickness of 6 nm was deposited on the ZnO NR surface by a sputtering process, which showed a significantly enhanced response to H₂S when tested at RT (Fig. 16a) [145]. Au nanoparticles are often decorated on the sensor surface due to their chemical and electrical sensitization mechanism. The Au-ZnO NR sensor showed high selectivity to 6 ppm H₂S and an excellent response (1270) compared to the bare ZnO sensor (Fig. 16b–c). The stability and reproducibility of the Au-ZnO NR sensor were tested after 30 days, and showed 2.5% variation in response. Fig. 16d shows a schematic representation of the gas sensing mechanism of Au-ZnO NR based gas sensors. The high selectivity to H₂S as compared to other interfering gases can be attributed to the lower bond energy of H₂S than other tested gases, which can possibly be broken at RT [144]. Since Au nanoparticles have a strong chemical affinity to sulfur compounds, there must be a strong chemical interaction between Au and H₂S. Furthermore, ZnO is decomposed with the spontaneous reaction of H₂S to form ZnS, increasing the sensing response [146]. Here, Au nanoparticle sensitization not only introduces extra active sites but also provides a high surface area (Fig. 16d), which leads to more adsorbed oxygen species [144]. Due to the chemical sensitization effect of Au nanoparticles, oxygen molecules and H₂S molecules are easily dissociated followed by spill over on the ZnO surface for further sensing reaction. In addition, Schottky barriers at the interface of Au and ZnO NRs increase the width of

Fig. 12. (a–b) Schematic representation of synthesis procedure of ZnO NWs and SIM-1 coated ZnO NWs (SIM-1/ZnO NWs), (c–d) FESEM images of ZnO and SIM-1/ZnO NWs, (e) H₂ selectivity test of pure ZnO NWs and SIM-1/ZnO NWs sensors in presence of different gases tested at 300 °C, and (f) kinetic diameter of various gases w.r.t pore aperture of SIM-1 MOFs. Reproduced from Ref. [123] with permission, Copyright 2018, Elsevier.

the depletion layer and hence resistance. Thus, the enhanced responses of this sensor are attributed to nano-Schottky junctions at the Au and ZnO interfaces (electronic sensitization), spillover effects (chemical sensitization) from the catalytic activity of Au, more surface-active sites from oxygen vacancies, and the Au catalyst facilitating H₂S adsorption and surface reactions.

Qi et al. reported the growth of vertically oriented ZnO NRs on flat ceramic substrates for improved H₂S sensor fabrication [147]. They

passivated ZnO NRs with an additional layer of ZnS to enhance sensor response and stability. The passivated ZnO-ZnS core-shell structure showed a high response of 13 to 10 ppm H₂S with high selectivity at RT. In another study, Qi et al. further improved the sensing performance in ZnO-SiO₂ NR structures [148]. The ZnO-SiO₂ NR based sensors displayed a high response of 116 and high selectivity to 10 ppm H₂S at RT. The SiO₂ layer on the ZnO NRs also improved the recovery time of the sensor, with the ability to detect at ppb levels of H₂S. In summary,

due to the combined effects of electronic and chemical sensitization, noble metal nanoparticles are a good choice to modify MOS surfaces to improve the sensing performance at RT in terms of sensitivity, selectivity, and response/recovery speed. In addition to the excellent role of noble metal additives, their homogeneous distributions with optimized sizes are important in the enhancement of sensor response.

5.2.2. Ethanol sensors

Efforts have been made to integrate gas sensors on flexible substrates to reduce fabrication cost and bring a new dimension to the metal oxide sensor market. Ahn et al. grew vertically oriented ZnO

NRs on a flexible plastic substrate for ethanol vapor sensing [149]. They focused on polyimide (Kapton™) substrate and achieved a response of 3.11 to 100 ppm ethanol with a long response/recovery (4 min/5.3 min) at an operating temperature of 300 °C. It is important to note that although this polymer is known for its high thermal stability, persistent heating to such a temperature will cause degradation. Furthermore, the vertically oriented ZnO NRs grown on polyimide substrates failed to achieve high sensing performance. Yi et al. took advantage of the fact that ZnO NWs and NRs can be readily grown on stainless-steel foils for gas sensing applications [150]. Specifically, they coated ZnO NRs with graphene (ZnO NR graphene) to form

Fig. 13. (a–d) FE-SEM images of vertically grown ZnO NWs on graphene/Si substrate, (e) schematic of an energy band diagram of ZnO NWs and graphene before and after contact, and (f) gas sensing mechanism of ZnO NWs/graphene hetero-nanostructure sensor in air and NO_2 gas. Reproduced from Ref. [135] with permission, Copyright 2018, Elsevier.

hybrid structures, which improved ethanol sensitivity (90 for 50 ppm) at 300 °C.

As mentioned earlier, MOFs have attracted attention in gas sensing as a result of their high surface area, tunable pore size, and molecular sieving properties. Zhou et al. reported a core-shell structure of ZnO@MOF NR arrays [151] using two ZIFs with different pore sizes (i.e., ~3.4 Å for ZIF-8 and ~4.8 Å for ZIF-71). They analyzed the sensor performance as a function of the pore size of ZIFs and the size of gas molecules (Fig. 17). The ZnO-ZIF-71 based sensor showed a high response and selectivity to ethanol compared to interfering gases. The selectivity was attributed to the molecular size of ethanol (4.53 Å) and its match to the pore size of ZIF-71 (4.8 Å). In the case of ZIF-8 (~3.4 Å), the sensor responses for ethanol, acetone, and benzene gases impeded. It can be concluded from the above discussion that by varying the pore size of ZIFs, the selectivity of gas sensors can be controlled.

5.2.3. H_2 sensors

Simple, fast, and cost-effective fabrication processes to synthesize vertically oriented ZnO NR arrays on substrates are preferred. Lee et al. efficiently grew ZnO NR arrays on a Pt-electrode alumina substrate for H_2 sensing [152]. The highest response of the ZnO NR gas sensor was found to be 24.8% for 500 ppm H_2 at 250 °C. Among different noble metals, Pd is commonly used to surface modify ZnO NRs for H_2 sensing [153–155]. However, the Pd NPs' size and density of coverage greatly affects the gas sensing properties. Chang et al. proposed a H_2 sensor based on Pd-ZnO NR arrays [153] with higher responses of 1106 to 500 ppm H_2 at 260 °C. The sensing performance of this Pd-ZnO NR sensor was due to the oxygen spillover (chemical effects) and Pd^{2+}/PdO redox properties (electronic effects). Similarly, Jiao et al. investigated ZnO NRs functionalized with Pd NPs prepared by a sputtering method [154]. The Pd was oxidized to form PdO-ZnO NRs at high calcination temperatures. Devices produced from thin Pd layers (4 nm) displayed

Fig. 14. (a) Synthesis procedure of ZnO@ZIF-CoZn gas sensors on Al_2O_3 substrate, (b) detection strategy on core-sheath NW arrays, (c) response-recovery curves to acetone at 260 °C, (d) effect of humidity on sensitivity by varying different RH (0–90%), (e) response vs operating temperature plot of all the gas sensors tested from 200 to 400 °C for 10 ppm acetone, and (f) response-recovery curve of all the sensors for 100 ppm acetone at 260 °C. Reproduced from Ref. [138] with permission, Copyright 2016, MDPI AG, Basel, Switzerland.

Fig. 15. (a) Schematic diagram ZnO NWs and Co doped ZnO NWs growth, (b–c) response vs temperatures relationship of pure ZnO NWs and co-doped ZnO NWs sensors, and (d) selectivity test of co-doped ZnO NWs for 5 ppm of different gases tested at 400 °C. Reproduced from Ref. [140] with permission, Copyright 2014, American Chemical Society.

a high sensing response to 1000 ppm H₂ at 350 °C. However, at higher temperatures and thicknesses of Pd layers, drastically changed sensor responses were observed.

Kim et al. proposed Pd functionalized ZnO NR based devices for H₂ sensing [155]. They compared ZnO NRs' surface coated with amorphous Pd layers to those with crystalline Pd NPs. The sensing response of amorphous Pd/ZnO NR devices was remarkably high (12,400% at 2% H₂) when compared to those functionalized with crystalline Pd NPs. This performance was attributed to the complete covering of ZnO NRs with an amorphous Pd layer and the large interfaces between Pd and ZnO. In addition, the amorphous Pd layer coating prevented surface contamination over ZnO NRs, and these sensors maintained their initial sensing performance for >5 months.

ZnO crystals with nonpolar {100} facets show the highest adsorption of H₂. Vallejos et al. reported a highly sensitive H₂ sensor based on aerosol-assisted vertically oriented ZnO NRs [156]. In this study, the grown ZnO NRs were highly crystalline with structures dominated by {100} surface facets. The sensors were tested for several gases at various temperatures between RT and 350 °C. A high response was obtained to 100 ppm H₂ at 350 °C with a fast response time of 35 s and low cross sensitivity to other interfering gases, such as ethanol, CO, acetone, NO₂, and toluene. Rashid et al. demonstrated an RT-operable flexible H₂ sensor

based on the Pd-decorated ZnO NRs grown on a polyimide (PI) tape [157]. The results showed that the Pd NPs with 8 nm size displayed good responses (91%) to 1000 ppm H₂ at RT. Notably, the H₂ sensing performance was unaffected even when the sensor was bent to a 90° angle.

5.2.4. NO₂ sensors

Nguyen et al. examined a NO₂ sensor using vertically oriented ZnO NR based chips [158]. The sensor was highly selective with a sensitivity of 6 for 10 ppm NO₂ at 450 °C. However, this high operating temperature is not suitable for practical applications. Efforts have therefore been made to reduce the temperature and improve the sensing performance [159–163]. One approach includes designing n-n and p-n heterojunction nanostructures with two metal oxides. For instance, Sun et al. designed an n-n heterojunction nanostructure between CaO and ZnO NRs for NO₂ sensing [159]. The enhanced performance indicated a synergetic benefit from combining these materials. In another study, Oh et al. reported high-performance NO₂ gas sensors based on ZnO NRs grown using an ultrasonic irradiation method [160]. The sensor was highly sensitive to 10 ppb NO₂ at 250 °C with fast response/recovery time.

Zou et al. demonstrated ZnO NR/TiO₂ NP heterostructures for enhanced NO₂ sensing [161]. The optimal working temperature of the

Table 3

Comparisons of gas sensing properties of vertically oriented ZnO NR based gas sensor.

Electrodes/Substrates	Materials	Synthesis method	Target gas	Concentration (ppm)	Temp. (°C)	Sensitivity (S) [R_a/R_g or $^*(R_a-R_g/R_a) \times 100$]	Response (s)/Recovery time (s)	Ref.
SiO ₂ /Si	ZnO NRs	Vapor phase	H ₂ S	5	25	581	–	[143]
SiO ₂ /Si	Au-ZnO NRs	Vapor phase	H ₂ S	3	25	375	–	[145]
Flat ceramic	ZnO NRs-ZnS	Hydrothermal	H ₂ S	10	RT	13	–	[147]
Flat ceramic	ZnO NRs-SiO ₂	Hydrothermal	H ₂ S	10	RT	116	–	[148]
Interdigital flexible plastic	ZnO NRs	Hydrothermal	Ethanol	100	300	3.11	240/318	[149]
Stainless steel foils	ZnO NRs-graphene/metal	Hydrothermal	Ethanol	50	300	90	–	[150]
Interdigital alumina plate	ZnO-ZIF-71 NRs	Hydrothermal	Ethanol	50	250	325%*	–	[151]
Al ₂ O ₃ /Pt ceramic	ZnO NRs	Sonochemical	H ₂	500	250	24.8%*	147/379	[152]
Si/SiO ₂ /Pt/Cr	Pd-ZnO NRs	Hydrothermal	H ₂	500	120	60.7	14/–	[153]
Glass	Pd-ZnO NRs	Hydrothermal	H ₂	500	350	3.6	–	[154]
SiO ₂ /Si	Amorphous Pd-ZnO NRs	Hydrothermal	H ₂	20,000	RT	12,400%*	227/95	[155]
Si/PI/flexible polyester	Pd/ZnO NRs	Hydrothermal	H ₂	1000	RT	91%*	–	[157]
Glass/Pt/Cr	ZnO NRs	Hydrothermal	NO ₂	10	450	6	–	[158]
Si/Au	n-CaO-ZnO NRs	Thermal evaporation	NO ₂	200	300	141.66	–	[159]
Al ₂ O ₃ /Pt	ZnO NRs	Ultra-sonic irradiation	NO ₂	0.01	250	37%*	270/240	[160]
Glass	ZnO NRs/TiO ₂ NPs	Hydrothermal	NO ₂	50	180	350	–	[161]
Glass/Pt	ZnO NRs	Hydrothermal	NO ₂	5	100	333	–	[162]
Glass	ZnO NRs	Hydrothermal	NO ₂	100	150	113.32	–	[163]
Si/Si	ZnO NRs/porous Si NWs	Hydrothermal	NO ₂	50	RT	35	–	[164]
Glass	ZnO NRs	Hydrothermal	LPG	500	350	60%*	100/70	[165]
Glass	Pd-ZnO NRs	Hydrothermal	LPG	2600	225	60%*	80/60	[166]
Al ₂ O ₃ /Au	Au-ZnO NRs	Hydrothermal	Triethylamine (TEA)	50	40	4	1.3/85	[167]
Al ₂ O ₃ /Au	Au-ZnO/SnO ₂ core-shell NRs	Hydrothermal	TEA	50	40	12.4	1.2/75	[168]

* $(R_a-R_g/R_a) \times 100$. **Fig. 16.** (a) SEM image of Au decorated-ZnO NRs, (b) response transient of the Au decorated-ZnO NRs and bare ZnO NRs sensors to 3 ppm H₂S at RT, (c) responses of the Au/ZnO nanorod-based sensor and pure ZnO nanorod-based sensor to different gases. Reproduced from the Ref. [145] with permission, Copyright 2015, Elsevier.

Fig. 17. (a) The mechanism of using the difference between the pore sizes of ZIF-8 and ZIF-71 and the gas molecular sizes to select gases passing the ZIFs membrane of ZnO@ZIF NRAs, (b) Gas sensing response of ZnO NRAs, ZnO@ZIF-8 NRAs and ZnO@ZIF-71 NRAs sensors to 50 ppm of different gases at 250 °C. Reproduced from the Ref. [151] with permission, copyright ©2018, Elsevier publisher.

ZnO NR/TiO₂ sensor was 180 °C, whereas the highest response value of 350 was obtained at 10% concentrations of TiO₂. The active sites were assumed to be created by the attachment of TiO₂ NPs onto ZnO NRs. Chang et al. grew ZnO NRs on an inkjet-printed seed layer for NO₂ sensing [162]. Longer ZnO NRs showed a higher response of ~355% to 5 ppm NO₂ at 100 °C. Using a similar approach, a low temperature based NO₂ sensor was proposed by Jagadale et al. [163]. To further reduce the working temperature, Liao et al. recently reported ZnO NR/porous silicon NW (ZnO/p-Si NWs) hybrid nanostructures for highly sensitive NO₂ sensing at RT [164].

5.2.5. Other gas sensors

Guray et al. examined the liquid petroleum gas (LPG) sensing performance of different aspect ratio ZnO NRs that were vertically oriented [165]. Raising the aspect ratio to 40 (ZnO₄₀) increased the surface area, the number of electron donors related to oxygen vacancies, and the sensory responses. Furthermore, a high response to 2000 ppm LPG with ZnO₄₀ NRs was measured at 350 °C. To reduce the operating temperature and enhance the sensing performance, Lokhande et al. prepared LPG sensors based on Pd-sensitized ZnO NRs grown on glass substrates [166]. These Pd-ZnO NRs showed a 60% improved sensing performance for 2600 ppm LPG compared to bare ZnO NRs at ~225 °C. In another study, Ju et al. proposed a trimethylamine (TEA) sensor based on Au-ZnO NRs coated with SnO₂ to form a Au-ZnO-SnO₂ core-shell NR structure [167]. The ZnO NRs were grown vertically on an Al₂O₃ substrate using a seed mediated hydrothermal method followed by SnO₂ shell deposition by pulsed laser deposition (PLD); then, Au NPs were deposited by a DC sputtering process (Fig. 18a-c). The Au-ZnO-SnO₂ NR based gas sensor displayed a high (12.4) and fast (1.2 s) response to 50 ppm TEA at a low temperature (40 °C) (Fig. 18d-e).

The enhanced sensing performance to TEA was attributed to the depletion layer formation (Schottky contacts) at the Au/SnO₂ interface and n-n SnO₂/ZnO heterojunction. Chung et al. reported a flexible acetylene sensor based on Ag-ZnO NRs grown on a flexible substrate [168]. The sensor showed a high response of 27.2 with fast response and recovery (62 s and 39 s) to 1000 ppm acetylene measured at 200 °C with a negligible drop in performance at a 90° bending angle. All in all, the large effective surface area, the ordered arrays of ZnO NRs, and small grain size are suggested to enhance sensing performance. Furthermore, the high catalytic activity of Ag to selectively absorb and activate acetylene contributes heavily to the improved selectivity.

5.2.6. Other vertically oriented ZnO nanomaterial based gas sensors

Many other novel vertically oriented ZnO nanomaterials have been explored as potential candidates in gas sensing applications, such as nanotubes (NTs), nanoneedles (NNs), and nanosheets (NSs) (Table 4). Among these nanostructures, NTs offer several advantages, including charge carrier transport and their length, low grain size, and high surface area from a combination of inner and outer surfaces of their tubular morphology [169,170]. Acharyya et al. synthesized hexagonal vertically oriented ZnO NTs for ethanol gas sensing at RT [169]. The ZnO hexagonal NT arrays were grown on a fluorine doped tin oxide (FTO) glass substrate with a combination of electro deposition and selective electrochemical etching methods (Fig. 19a-b). These ZnO NT based gas sensors showed the highest response to ethanol among other gases investigated. A 65% response to 700 ppm ethanol at RT was obtained for ZnO NTs. The enhanced gas sensing performance for ethanol was explained by the formation of the depletion layer and the modulation of barriers (Fig. 19c-d). In another study, Maithy et al. examined the effect of ZnO NT surface modification with Pd and reduced graphene oxide (rGO) on gas sensing performance [170]. The results revealed that Pd modified ZnO NT based gas sensors had a high response (55.7% for 100 ppm) to methanol, whereas the r-GO-ZnO NTs offered high sensitivity to ethanol (67% for 100 ppm) at RT. Recently, Gonzalez-Chavarri et al. reported a ZnO NN based NO₂ sensor [171]. This gas sensor showed a high response of 6 and the highest selectivity to 5 ppm NO₂ with little interference from benzene and formaldehyde at 195 °C. The same authors also investigated the influence of humidity and found that even at 80% relative humidity (RH), the response of the sensor to 0.5 ppm NO₂ was around 350%, which was much higher than for the other two gases.

When compared to the other vertically oriented ZnO nanomaterials, vertically oriented ZnO NSs offer the interesting features of superior charge carrier transport, high aspect ratios, and controllable thickness, which combine to facilitate high sensing performance [171,172]. Ju et al. demonstrated the direct growth of ZnO NSs for ethanol sensing [172]. They grew three types of ZnO NSs with varying hydrothermal reaction times for ethanol sensing experiments (Fig. 20a-c). The sensor responses to 100 ppm ethanol were evaluated at different operating temperatures (200–450 °C), and the highest response of 38.4 was obtained for ZnO NSs-8 h at an optimum operating temperature of 400 °C (Fig. 20d-e). The gas sensor based on ZnO NSs-8 h showed a higher response than those based on the others analytes (Fig. 20f). The enhanced ethanol response compared favorably to the other interfering gases evaluated and was attributed to the faster absorption of smaller ethanol molecules on ZnO NSs' surface and the high electron donating effect of this gas (Fig. 20g). Recently, Cao et al. proposed an ethanol sensor based on Al doped ZnO NSs and investigated the effect of metal diffusion on gas sensing [173]. The ZnO NS based sensors displayed a higher response to 100 ppm ethanol vapor than the ZnO NR based sensors at an optimum operating temperature of 370 °C with fast response/recovery times of 1.6/1.8 s. Furthermore, the ZnO NS based sensors showed high selectivity to ethanol gas at 370 °C. The stability of these sensors was investigated over one month and it was found

Fig. 18. (a) Fabrication of core-shell structure of Au-loaded SnO_2/ZnO NRs, (b) SEM image of sensor device, (c) sensor fixed on an electric bracket, (f) response transient of all three gas sensors such as ZnO NRs, SnO_2/ZnO NRs and Au/ SnO_2/ZnO NRs tested at 40 °C for 50 ppm TEA, and (g) temperature dependent response behavior of Au/ SnO_2/ZnO NRs sensor tested from 40 to 280 °C. Reproduced from Ref. [167] with permission, Copyright 2015, American Chemical Society.

that their response was nearly constant. The excellent ethanol sensing performance of ZnO NSs was explained by their smaller thickness resulting in a wider depletion layer, high charge transfer from the inner to the outer surface and vice versa, a greater number of electron-generating sites caused by Al doping, an increased number of oxygen defects, and a greater barrier modulation. Compared to the conventional two-step process of sensor fabrication, direct growth of vertically oriented ZnO NSs on substrates has great potential in gas sensing. The gas sensing properties of

these nanostructures have not been explored in detail, and this should be considered an emerging approach. Zhao et al. [174] prepared ZnO nanodisk (ND) based gas sensors directly on Au comb-shaped SiO_2/Si substrate using a thermal evaporation method from a mixture of ZnCl_2 and InCl_3 at 450 °C. For comparison, another sensing material, ZnO nanorod arrays, was deposited on the substrate by annealing ZnCl_2 at 450 °C. The electron microscopy results showed that ZnO NDs and ZnO NRs were exposed mainly in polar (0001) and nonpolar {010} planes, respectively.

Table 4

Comparisons of gas sensing properties of other vertically oriented ZnO nanomaterial-based gas sensor.

Electrodes/Substrates	Materials	Synthesis method	Target gas	Concentration (ppm)	Temp. (°C)	Sensitivity (S) [R_a/R_g or $^*(R_g-R_g/R_a) \times 100$]	Response (s)/Recovery time (s)	Ref.
FTO	ZnO NTs	Electrodeposition	Ethanol	700	27	65%*	271.8/91.8	[169]
FTO	ZnO NTs/Pd	Electrodeposition	Ethanol	100	27	48.17%*	43.4/111.5	[170]
FTO	ZnO NTs/rGO	Electrodeposition	Ethanol	100	27	67.01%*	41.1/98.3	[170]
$\text{Al}_2\text{O}_3/\text{Pt}$ interdigital	ZnO NNs	Hydrothermal	NO_2	5	195	6	–	[171]
$\text{Al}_2\text{O}_3/\text{Au}/\text{Pt}$	ZnO NSs	Hydrothermal	Ethanol	100	400	40	8/17	[172]
$\text{Al}/\text{Al}_2\text{O}_3/\text{Pt}$	Al-ZnO NSs	Hydrothermal	Ethanol	100	370	90.2	1.6/1.8	[173]
SiO_2/Si	ZnO NDs	Thermal evaporation	Trimethylamine	200	300	60	NA	[174]

* $(R_g-R_g/R_a) \times 100$.

Fig. 19. (a) Schematic of ZnO NTs sensor device on FTO substrate, (b) FESEM images of ZnO NTs, (c) schematic showing adsorption of water molecule on ZnO NT surface, and (d) schematic showing potential barrier modulation of ZnO NTs in air and target gas conditions. Reproduced from Ref. [169] with permission, Copyright 2016, Elsevier.

The Brunauer-Emmett-Teller (BET) surface area results showed that ZnO NDs had a smaller surface area ($13.70 \text{ m}^2/\text{g}$) than the ZnO NRs ($16.11 \text{ m}^2/\text{g}$). Furthermore, the sensor based on ZnO NDs exhibited better gas sensing performance for Triethylamine (TMA) as compared to ZnO NRs at 300°C in spite of its lower surface area. The enhanced gas sensing properties of ZnO NDs was mainly attributed to the ZnO polar (0001) plane's high activity in absorbing oxygen ionic species. Hence, it was concluded that ZnO as a gas sensing material with exposed polar (0001) facet showed improved sensing performance for many target gases. This better gas sensing performance was explained by the smaller thickness, high surface area, wide depletion layers, and fast gas molecule adsorption over the entire surface of vertically oriented ZnO nanodisk structures. The synthesis of vertically oriented ZnO nanostructures is simple, but the gas sensing performance of bare ZnO nanostructures is limited. Hence, hybridization/decoration of ZnO nanostructures with other metal or metal oxide becomes essential for enhancing gas sensing performance.

6. Conclusions and future perspectives

In this paper, we have reviewed recent research on vertically oriented ZnO nanomaterials for gas sensing applications. There are currently many challenges in the development of nanomaterial based sensing devices to detect toxic and VOC gases, such as H_2S , ethanol,

H_2 , NO_2 , CO, NH_3 , xylene, TEA, and acetone. Different approaches are available to synthesize sensing materials, and their direct integration onto the sensor electrodes have offered important performance enhancements in gas sensing applications. However, the higher operating temperatures complicate practical applications. Growing nanomaterials directly onto the sensor chips streamlines sensor fabrication (Scheme 2). Furthermore, it avoids the use of binders/polymers to fix nanomaterials onto electrodes, integrates stable nanomaterials onto the electrode surfaces, and produces high surface areas. Despite the general progress in nanomaterials, however, few can be directly grown on substrates/electrodes. Importantly, ZnO stands out as enabling the engineering of nanoscale vertically oriented structures on electrode surfaces.

As a result of the aforementioned advantages, we have concentrated our discussion on directly grown vertically oriented ZnO nanomaterials on electrode surfaces that are currently used to fabricate a variety of gas sensors. These nanomaterials provide high carrier mobilities with high surface area, which are essential for ppb level sensing performance. The surface functionalization of vertically oriented ZnO nanomaterials with specific metal catalysts, dopants, and other metal oxides is a convincing approach for improving sensing response, selectivity, and response/recovery time. Extensive use of ZnO nanomaterial reveals that the oxygen vacancy defects play a major role in enhanced sensing. Nanowires offer better surface area than nanorods, nanotubes, and nanosheets due to their high aspect ratio, thus resulting in the better

Fig. 20. FESEM images of ZnO NSs with different hydrothermal reaction times (a) 3 h, (b) 8 h, and (c) 12 h; relationship between temperature and responses of three types of ZnO NSs sensors (d), sensor response at different ethanol concentrations at 400 °C (e), selectivity test of sensors tested at 400 °C in the presence of different analytes (f), and gas sensing mechanism over ZnO NSs in air and ethanol atmospheres. Reproduced from Ref. [172] with permission, Copyright 2014, Elsevier.

Scheme 2. Progress in nanomaterials-based gas sensor device fabrication.

sensing performance of nanowire based gas sensors (Tables 2–4). In addition, nanowires are an excellent choice for their surface modification with other metals or metal oxides to enhance their gas sensing properties.

Despite the extensive use of ZnO nanomaterials for gas sensing, their selectivity and high operating temperature remain questionable, and vertically aligned ZnO nanomaterial based sensors are yet to be commercialized. Recently, MOF and ZIF as molecular sieve membranes have shown promise in improving selectivity due to their controllable pore aperture and excellent porosity. The molecular sized pores in these membranes block larger gas molecules from interacting with the active sensing materials. However, more studies are necessary to clearly understand these processes and select optimal MOFs for the selective diffusion/blocking of gases. The sensitivity of gas sensors depends upon several factors, such as depletion layer formation due to Schottky junctions, oxygen adsorption,

heterojunction formation, and charge transfer/reactions between analyte gases and sensing materials. The functionalization of ZnO nanomaterial with noble metal catalysts or metal oxides is one of the better approaches to enhance sensitivity by lowering the operating temperature. The noble metal/metal oxide NPs' dispersion, size, and density greatly affect sensing performance. Therefore, controlled deposition of noble metals/metal oxides on the ZnO surface with optimized nanosized dimensions is necessary.

An improved low-temperature growth approach for vertically oriented ZnO nanomaterials on flexible substrates is important for cost effectiveness and applications requiring new form factors. The use of bimetallic NPs (nano-alloys) to modify ZnO nanomaterials' surface can potentially provide superior catalytic properties. Therefore, there are many opportunities for vertically oriented ZnO nanomaterial surface modification for improved gas sensing properties. The ease of using vertically oriented ZnO nanomaterials on electrode surfaces in different architectures makes them the ideal choice for further modification/functionalization investigations targeting a wide range of applications.

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