Materials Engineering Strategies to Control Metal Oxides Nanowires Sensing Properties

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Metal oxides (MOXs), in the form of nanowires, have proved to be an excellent active sensing layer of chemoresistive sensors due to their unique physical/chemical properties such as single crystallinity, exceptional electrical properties, and so on. Indeed, MOXs nanowires-based gas sensors show fast dynamic response with excellent reproducibility, stability, and reactivity toward various gas analytes. However, their limited selectivity and high operation temperature that lead to high power consumption are still major issues that need to be addressed. To improve these characteristics, researchers nowadays are working in the direction of modifying nanowires with different strategies. These strategies include nanowires heterostructures, decoration with particles (metals and metal oxides), core–shell structures, and surface functionalization with self-assembled monolayers and modification with graphene (pristine and oxidized). By employing these strategies, nanowires sensing performances, especially their selectivity, sensitivity, and response, can immensely enhance. Hence, in this review article, the above-mentioned strategies to improve the sensing performance of MOXs nanowires are reviewed. Attention is paid to underlying sensing mechanisms and improved sensing characteristics. In addition, MOXs gas sensing mechanism, working principle of conductometric gas sensors, and different synthesis techniques, used to modify nanowires, are also briefly discussed.

1. Introduction

Whenever someone talks about materials in the gas sensor field, immediately metal oxides (MOXs) come to the mind. The reasons behind their great success in the gas sensor field are their exceptional physics/chemical properties, ease of synthesis in various forms (thin/thick films, nanostructures, etc.), low-cost, and reversible reactions with gas analytes. Besides gas sensors, MOXs were also used for many other applications such as transistors, solar cells, batteries, superconductivity, and so on. In particular, nanostructured MOXs were found to be highly efficient as active layers of sensors due to their high surface-to-volume ratio, high crystallinity, and excellent stoichiometry. Over the years, many MOXs such as zinc oxide (ZnO), nickel oxide (NiO), tin oxide (SnO₂), etc. were synthesized in different nanostructured forms (nanotubes, nanorods, nanobelts, etc.) and successfully explored as an active sensing layer for the detection of various gas analytes. However, in the last few years, MOXs in nanowires (NWs) morphology were gaining great attention due to their well-defined crystal orientation, single crystallinity, excellent electrical properties, and faster response dynamics as gas diffusion prior to surface reactions is not required.[1]

Besides their success, MOXs nanowires still suffer from selectivity and high temperature operation issues. To further improve their performances and overcome these obstacles, nowadays researchers are working on the modification of nanowires via different strategies. These strategies include nanowires heterostructures, quasi-1D core–shell structures, particle decoration, surface functionalization with self-assembled monolayers (SAMs), modification with graphene and MOX@MOF core–sheath structures. Nanowires based heterostructures may synergistically combine the properties of two different materials in a single sensing platform at nanoscale level.[2] While, core–shell structures offer high surface area, lower rate of charge recombination, and full depletion regions, which are desirable properties to increase the sensing performance.[3] Moreover, nanowires functionalized with SAM molecules enhance the surface-specific interaction with gas analytes due to the presence of SAM functional groups; hence, improves the sensor selectivity.[4,5]

In this review article, the above-mentioned strategies to improve the sensing performance of MOXs nanowires based chemoresistive sensors have been reviewed. In particular, attention has been paid to summarize the gas sensing mechanism suggested by the authors along with improvement in the sensor response, detection limits and working temperatures. The last decade’s works have been reviewed in this review article. Moreover, the working principle of conductometric gas sensors, gas sensing mechanism, and synthesis techniques were briefly discussed.
2. Metal Oxide Nanowires Based Conductometric Gas Sensor

The use of metal oxides (MOXs) nanowires for gas sensing application was started in early 2000, when Kolmakov et al. have synthesized the SnO$_2$ nanowires by using porous anodic alumina templates. The conductometric gas sensors based on these nanowires were finally used for the detection of CO and O$_2$. Subsequently, until now immense progress has been achieved in this direction. Indeed, MOXs based conductometric or chemoresistive gas sensors were immensely used over the years for the detection of various gas analytes due to their simple operation, ease of fabrication and low cost. The working principle of these devices depends upon the change in conductance/resistance that occurs due to the interaction between the active sensing layer and the gas analyte. The nature of interaction depends on the type of active layer (p-type or n-type semiconductor) and the nature of gas molecules (oxidizing or reducing). For example, when n-type MOXs interact with reducing gas such as acetone, the increase in conductance is observed due to the donation of electrons from gas analyte to metal oxide. While their interaction with an oxidizing gas such as NO$_2$ results in a decrease in conductance due to electrons capturing from the semiconducting layer. Vice versa is true for p-type MOXs. Furthermore, conductometric gas sensing device possesses three main components: active sensing layer, electrodes, and heating element. An active sensing layer can be in different forms such as thin film, nanowires, and so on. While the heating element is used to operate the sensor at different temperatures and the highest response at a given temperature for specific gas is regarded as the optimal working temperature of the sensor.

Moreover, the performance of MOXs nanowires-based gas sensors is immensely depend upon the adsorbed oxygen ions on their surface. In particular, when MOXs operated at elevated temperatures in air, oxygen molecules adsorb on the MOX surface in form of ions and capture electrons from MOX. The type of these ions depends on the temperature, e.g., in the temperature ranging from 100 to 300 °C these adsorbed ions are in the form of O$^-$, while at temperature >300 °C, O$^{2-}$ ions are observed. Furthermore, this capturing of electrons results into the formation of core–shell structures as shown in Figure 1. Specifically, the adsorption of oxygen ions causes the formation of an electron depletion layer (EDL) as a shell around the semiconducting core of n-type MOXs. While, in p-type metal oxides hole accumulation layer (HAL) as a shell is formed around the insulating core. Hence, when n-type MOXs exposed to reducing gas such as carbon monoxide (CO), it donates electrons to the MOX, which results in an increase in conductance of the sensor and vice versa when it reacts with oxidizing gases.

The reaction between CO molecules and adsorbed oxygen ions on n-type MOXs is expressed as follows

$$\text{CO}_{(\text{gas})} \rightarrow \text{CO}_{(\text{ads})}$$  \hspace{1cm} (1)

$$\text{CO}_{(\text{ads})} + \text{O}^{2-}_{(\text{ads})} \rightarrow \text{CO}_2(\text{gas}) + e^-$$  \hspace{1cm} (2)

This reaction causes a change in the density of adsorbed oxygen ions. For detail about charge carrier transport, sensing mechanism, and structure of conductometric sensing devices, readers can refer to the review article by Kaur et al..

Furthermore, when considering complex structures like nano-heterostructures of NWs, SAM-functionalized NWs, etc. many other factors, apart from the interaction between the adsorbed oxygen ions and MOX, also play crucial roles. For example, in heterostructure-based sensors, the junction between two nanostructured materials changes the charge carrier transport and also enhances the overall surface area for reaction with gas molecules. On the other hand, in SAM-modified nanowires, the interaction between the gas analyte and SAM molecules enhances the sensor response along with selectivity. Hence, these types of additional parameters must

![Figure 1](image-url). Schematic of formation of electronic core–shell structures in a) n-type and b) p-type metal oxide semiconductors. Reproduced with permission. Copyright 2020, American Chemical Society.
be considered when describing the gas sensing mechanism of engineered nanowires structures.

3. Synthesis of Tailored MOXs Nanowires Structures for Gas Sensing

Over the years, different techniques were employed to synthesize the MOXs nanowires. The most common techniques are template-assisted electrochemical synthesis,\(^\text{11}\) hydrothermal growth,\(^\text{12}\) vapor–liquid–solid mechanism (VLS),\(^\text{7}\) and thermal oxidation.\(^\text{13}\) Readers can refer to the review article by Kaur et al.\(^\text{1}\) for a detailed introduction of some of these growth techniques. However, to tailor these nanowires, sometimes similar or combinations of different techniques were employed.\(^\text{2,3}\) For example, in order to synthesize branched-like heterostructures of NiO and ZnO, vapor phase mechanisms were employed.\(^\text{9}\) The SEM images of branched-like NiO/ZnO heterostructures were shown in Figure 2. Furthermore, the selected area electron diffraction study (SAED) reveals the epitaxial growth of ZnO nanowires along (101)-planes on the strongly oriented NiO nanowires along (200) crystallographic planes.

While, Xue et al.\(^\text{14}\) have synthesized ZnO branched p-Cu\(_x\)O@n-ZnO heterostructures by different techniques. First, to grow p-Cu\(_x\)O@n-ZnO heterostructure, solution processing for Cu\(_x\)O nanowires and ALD for ZnO coating was used. Finally, on the heterostructure ZnO nanowires branched were grown using hydrothermal method. The TEM images of these grown heterostructures are presented in Figure 3.

On the other hand, fabrication core/shell (C/S) nanostructure can also be done by using different and same techniques.\(^\text{1,8}\) However, it has been found from the literature that ALD is widely employed to grow the shell on nanowires as it offers thickness control at an atomic level.\(^\text{3,15–17}\) In this regard, Park et al.\(^\text{15}\) have synthesized SnO\(_2\)-core/ZnO–shell via two methods. First of all, SnO\(_2\) nanowires based core was deposited by thermal evaporation, which is followed by growth of ZnO shell with ALD. The detailed structural investigation reveals that both core and shell are single crystalline (see Figure 4).

While, highly crystalline ZnO–SnO\(_2\) core–shell nanowires were grown by continuous two-step vapor growth method at different growth temperatures for core and shell.\(^\text{8}\) Furthermore, Raza et al. have employed two different techniques, i.e., vapor phase growth for SnO\(_2\)-core and ALD for NiO shell. Nanostructural investigations confirm that the SnO\(_2\) nanowires were single crystalline in nature, while NiO shell was found to be polycrystalline. The TEM images of these grown core–shell structures were shown in Figure 5.

Furthermore, to decorate nanowires with metal or MOXs particles, different techniques such as DC sputtering,\(^\text{18}\)
spin-coating,[19] drop-casting,[20] and solution-processable tech-
niques[21,22] were reported in the literature. In one such work, NiO-decorated SnO$_2$ nanowires were synthesized via thermal evaporation (nanowires) and DC sputtering (NiO).[18] Figure 6 shows SEM, TEM, and XRD spectra of these decorated nanowires. Indeed, NiO nanoparticles were found to possess hexagonal structure.

Other important strategies, used to enhance the sensing performance of MOXs nanowires, are functionalization with SAMs and graphene (pristine and oxidized). To functionalize MOXs generally, organosilanes based SAMs such as (3-aminopropyl)trimethoxysilane were employed.[4] Indeed, for their attachment on MOX surface, hydroxyl (–OH) groups are required, these can be generated via different processes such as piranha solution treatment, oxygen plasma, etc.[5] Generally, the dip method was used for SAM formation of MOXs surface. In this method, –OH groups containing MOXs nanowires were dipped inside the SAM solution for a prolonged duration of time. The reaction involved the formation of polysiloxane which is attached to the silanol groups (–SiOH) that are present on the surface via Si–O–Si bonds. Figure 7 showed the formation of organosilane on the silicon surface.[5] Depending on the type of silanes, different functional groups such as amine, epoxy, and so on can be generated on MOXs nanowires surface and can be explored for sensing applications.

Furthermore, the incorporation of graphene, graphene oxide (GO), and reduced graphene oxide (rGO) with MOXs nanowires is another way to improve the sensing performance. Rafiee et al.[23] have fabricated graphene/ZnO nanowires for detection of low acetone concentration. First of all, the dispersed solution of graphene in deionized water was spin-coated onto the substrate and then the deposition of solution-processed ZnO nanowires was performed on the graphene layer. The SEM imaged along with EDX mapping of graphene/ZnO nanowires structure is shown in Figure 8. In this work, ZnO nanowires were found to have hexagonal structure.

To conclude, all above-mentioned strategies were found to significantly affect the sensing performances of MOXs nanowire. In the following sections, we will review the achieved results in terms of gas sensing.

4. Different Strategies to Modify MOXs Nanowires Surface

In this section, we will review breakthrough reports published in the last decade on modified metal oxide nanowires for gas sensing applications. Attention has been paid to the modification strategies, gas sensing mechanism, and improved sensing characteristics.

4.1. MOX–MOX Heterostructures

Building an interface between two different metal oxide nanostructures is one of the innovative ways to improve their gas sensing properties. Heterostructures in different nanostructure forms provide unique properties such as efficient charge carrier transport, large reaction surface, and superior gas sensing performance. However, constructing these heterostructures using 1D-nanostructures such as nanowires is a challenging task, but it opens new ways to improve the electronic properties of the materials at the nanoscale level. This novel idea brings two
Figure 5. Bright-field transmission electron microscopy (TEM) images of pristine SnO$_2$: a) an overview and b) isolated nanowire along with the corresponding SAED patterns as an inset. BF-TEM images for the SnO$_2$/NiO-X C–S nanowires: c) an overview of the SnO$_2$/NiO-200 C–S nanowires, isolated nanowire from the samples, d) SnO$_2$/NiO-50, e,f) SnO$_2$/NiO-100, and g) SnO$_2$/NiO-200. h) Corresponding SAED pattern of the isolated SnO$_2$/NiO-200 nanowire (g). i) HAADF-STEM image for the SnO$_2$/NiO-200 samples, j–l) HRTEM images for the SnO$_2$/NiO-200 sample and the magnified view of the lattice fringes. m) HAADF-STEM image for the SnO$_2$/NiO-100 nanostructures, and corresponding images for EDX elemental mapping. Reproduced with permission.[3] Copyright 2020, American Chemical Society.
different nanostructured metal oxides into one single sensing platform through the formation of heterojunction. With junction formation, the Fermi levels of dissimilar metal oxides come to an equilibrium, resulting in charge transfer and depletion region formation at the interface. These factors act as the main foundation to alter the sensor performances.

It has been seen that the improvement in sensing performances of heterostructures occurs due to many different reasons, i.e., i) enhancement of surface area, ii) band bending due to Fermi level equilibrium, iii) charge carrier separation, iv) synergistic reactions, v) catalytic effects, etc. However, conclusive studies to explain a detailed mechanism are still lacking. But we cannot deny the fact that the presence of secondary material on a host nanowire changes the sensing parameters drastically. Therefore, it is highly interesting to study these heterostructures to further understand the underlying sensing mechanisms. There are different types of nanowires based heterostructures reported in the literature such as branched, core/shell, nanoparticle decorated as shown in Figure 9. In the following subsections, all these heterostructures and their sensing will be reviewed.

4.1.1. Branched Heterostructures

Branched heterostructures are one of the most novel forms of nanostructures used for gas sensing applications. In this category of heterostructures, both the metal oxides are grown in the form of 1D nanowires. The growth of these heterostructures can be performed by using one technique by two-step method [2,9,24] or by using two different fabrication techniques [14,25] for each metal oxides. In this case, it is very crucial to control the size and crystal structure of the nanowires, as it is directly related to their sensing properties. In this context, Khoang et al. [26] have reported a study on designing n–n type heterostructures of SnO2/ZnO for ethanol sensing. Authors found that, by controlling the secondary material (ZnO) growth, the sensing of heterostructures can greatly be affected. The sensors optimal working temperature was found to be 400 °C, with a response of 16.2 toward 500 ppm of ethanol. The enhancement in the sensing performance was mainly related to two factors (shown in Figure 10). First, the charge transfer between two materials

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**Figure 6.** Morphology characterizations of bare SnO2 NWs and NiO-decorated SnO2 NWs sensors: a) 12 sensors fabricated on a alumina substrate, b) SEM image of the as-grown SnO2 NWs, c-e) TEM images of the bare SnO2 NWs and NiO nanoparticles-decorated SnO2 NWs, d-f) HRTEM image of bare SnO2 NWs and nanoparticles-decorated SnO2 NWs, g,h) XRD patterns of bare SnO2 NWs and NiO nanoparticles decorated SnO2. Reproduced with permission.[18] Copyright 2012, AIP Publishing.

**Figure 7.** Stepwise formation of organosilane on a silicon substrate. Reproduced with permission.[5] Copyright 2020, Royal Society of Chemistry.
creating a depletion region, which helps to generate more oxygen ions on the surface of heterostructures that in turn increases the reactivity toward ethanol gas molecules. Second, due to percolation network of nanowires, built potential barriers at junctions between NWs modulates the charge transfer between two electrodes. This has major effect when the surface reacts to ethanol molecules with oxygen ion at junctions resulting in lowering the potential barrier and increasing the charge transfer throughout the nanowire network. Due to these two phenomena the sensing response of the heterostructures increases compared to pure SnO$_2$ nanowires. Similarly many other studies on n–n type heterojunction based on ZnO/TiO$_2$, TiO$_2$/V$_2$O$_5$, etc. have been found in literature. [27–30]

Further, p–n type branched heterostructures were also significantly explored to improve the sensing performance of pristine nanowires. [9,14,31,32] It has been observed that p-type metal oxides have been more commonly used to improve the performance of n-type metal oxides. In an interesting work, the gas sensing performance of SnO$_2$ nanowires toward NO$_2$ has been improved by depositing TeO$_2$ nanowires on the top. [31] It has been found that the change in performance of nanowires is mainly attributed to the formation of p–n junction due to the difference of work function between two materials. This changes the overall resistance of the heterostructures in comparison to the pristine nanowires, leading to a high response toward NO$_2$. On the other hand, using n-type metal oxides as a secondary material to change the performance of p-type metal oxide has been rarely observed. However, in recent years researchers starts working in this direction. In one such work, ZnO has been used to enhance the gas sensing response of NiO [9] and CuO [14] nanowires for acetone detection. Interestingly, the electrical behavior of host nanowires (NiO, CuO) changes after the deposition of ZnO NWs (from p-type to n-type shown in Figure 11) on p-type nanowires.

The major reason behind this change is that the ZnO covers the whole surface of NiO nanowires before starting to grow in the form of nanowires. In addition, the formation of p–n junction due to the difference of Fermi levels equilibrium leads to create a depletion region at the junction. This results in an increase in the overall resistance of the heterostructure sensing system which in turn improves the sensing performance.

Furthermore, recently Kaur et al. [2] have published a highly distinguished report on the fabrication of novel branched-like heterostructures consisting in NiO/NiWO$_4$/WO$_3$ (p–p–n) for gas sensing application. [2] NiO nanowires were used as a backbone to grown WO$_3$ nanowires on top of them. During the growth process of secondary material (WO$_3$), the reaction between NiO and WO$_3$ leads to the formation of intermediate NiWO$_4$ seed prior to the growth of WO$_3$ nanowire. Due to this reaction, besides the formation of the simple p–n heterostructure, a more complex heterostructure, i.e., NiO/NiWO$_4$/WO$_3$ (p–p–n junction) were formed. These heterostructures devices were tested toward several different oxidizing and reducing gas analytes. In particular, sensors show higher response toward NO$_2$ and acetone at 300 and 400 °C, respectively, in comparison to both the pristine metal oxide nanowires. The superior performances of these heterostructures were mainly based on the control of charge carrier transport through two interfaces (NiO/ NiWO$_4$ (p–p) and NiWO$_4$/WO$_3$ (p–n) junction) as shown in Figure 12. Specifically, the presence of a large number of free electrons in the conduction band of WO$_3$ at 300 °C attracts electron-loving NO$_2$ gas. By contrast, due to thermal excitation at higher temperature (400 °C), significant electron–hole recombination occurs, broadening the HAL in p-type materials (NiO, NiWO$_4$). Therefore, the heterostructures show more selective behavior toward electron donating gas such as acetone.

Furthermore, there have been no reports found in the last decade on p–p type metal oxide branched-like heterojunction. All the reports based on metal oxide-based branched heterostructures have been summarized in Table 1.

### 4.1.2. Core/Shell Heterostructures

C/S heterostructures are another most widely used nanostructure form to enhance the sensing properties of pristine metal oxide nanowires. This method is an excellent way to increase the interface area between two materials. The major factor that
influences the sensing performance of pure nanowires is the thickness of the shell deposited on the core nanowire and the interjunction synergy between them. By playing with the thickness of the shell, the interaction between shell and gas molecules can be directly affected changing the sensing properties.

Using SnO$_2$ and ZnO is one of the most common combinations that has been employed to fabricate core/shell heterostructures for gas sensing application.$^{[8,15,35]}$ As these two metal oxides have been highly exploited separately in this field, it is interesting to see how they performed when put together into one sensing platform. In this context Hwang et al.$^{[8]}$ reported a study on using SnO$_2$ as a shell to improve the sensing performance of bare ZnO nanowires. Among several gas analytes, these C/S structures showed the best response toward NO$_2$ at low temperature (200 °C) and toward ethanol at higher temperature (400 °C) in comparison to pristine ZnO nanowires (see Figure 13). The improvement in sensing behavior was mainly related to the thin shell layer of SnO$_2$ on top of ZnO nanowires. The thickness of SnO$_2$ layer was ≈15–20 nm, which was considered to be fully depleted on the formation of a junction between these materials. Due to this, the resistance of the C/S structures increases almost seven times more than the ZnO nanowires. Thus, this effect significantly increases the response of the sensor when interacting with the gas analyte. A similar theory has been presented also in the case when ZnO was used as a shell to improve the sensing of SnO$_2$ nanowire core.$^{[15]}$

On the other hand, p-type MOXs such as NiO, CuO are also used to enhance the sensing performance of n-type MOX nanowires. In a recent report, the effect of thickness of NiO shell layer grown by ALD on top of SnO$_2$ nanowire core for hydrogen detection was investigated.$^{[3]}$ It has been observed that the NiO shell has a huge effect to modulate the sensing response as shown in Figure 14. The shell thickness varies from 2 to 8.2 nm and it reduces the overall electrical conductance of the sensors drastically. The main reasons behind the change in the sensing performance were found to be a) the formation of hole accumulation layer within the NiO shell, and b) modulation of barrier height at the NiO/SnO$_2$ interface. In addition to these, the thickness of the NiO shell layer also played an important role in determining the sensor response. Indeed, the best response was found when the shell thickness was 4.2 nm. This value is very similar to the thickness of the hole accumulation layer, which is directly related to the Debye length. By continuing to increase the shell thickness, the response of the sensors starts to decrease because the shell is no longer depleted. Similarly, in a recent report published by Hamid et al.$^{[36]}$ SiO$_2$ shell was used to enhance the hydrogen response of SnO$_2$ nanowires. Different factors were involved for the higher and selective response of these C/S heterostructures. First, due to the higher surface area of heterostructures, second the width of the electron-depletion layer increases further due to

![Figure 10. The schematic illustration of the gas sensing mechanism of a) the bare SnO$_2$ nanowires and b) the SnO$_2$/ZnO hierarchical nanostructures gas sensors. Reproduced with permission.$^{[26]}$ Copyright 2012, Elsevier.](image-url1)

![Figure 11. a) Dynamic response of NiO/ZnO heterostructure sensing device. b) Dynamic response of NiO sensing device toward reducing gases (ethanol black color; 5–5–20–50 ppm at 400 °C; acetone, red color; 10–10–30–100 ppm at 400 °C) measured at a relative humidity of 50% at 20 °C. c) Proposed energy band structure diagram for p-NiO/n-ZnO heterojunctions. Reproduced with permission.$^{[9]}$ Copyright 2018, Elsevier.](image-url2)
a strong core–shell coupling shown in Figure 15. However, the selective behavior toward hydrogen was mainly attributed to the masking effect of SiO₂ shell that helps hydrogen to diffuse easily the SnO₂ NWs surface in comparison to other gases.

Furthermore, most commonly p-type metal oxides were used to improve the sensing characteristics of n-type materials. In an interesting report by Kim et al.[16] ZnO shell was deposited by the ALD technique on the core of CuO in order to enhance its sensing performance toward C₆H₆. Different shell thickness from 5 and 110 nm has been used to modulate the sensing response. Similar to previous works, the sensing improvement was related to the formation of a junction between two materials and on the formation of an electron depletion layer within the ZnO shell layer as shown in Figure 16. Due to the p–n junction at the interface, there is a transfer of electrons and holes between two MOXs that leads to the formation of a depletion layer. Additionally, when oxygen molecules get adsorbed at the surface of ZnO, they extract the electrons and create an EDL layer near the surface. When the thickness of ZnO layer is lower than the ZnO Debye length, complete depletion of shell occurred. All these effects modulate the overall resistance of the heterostructure sensor system in comparison to the pristine nanowire sensors. Hence, when a reducing gas interacts with the surface of these C/S heterostructures, it releases the electron back into the conductance band significantly enhancing the sensing performance of the sensor.

Additional, a summary of some other interesting reports on C/S heterostructure based sensors have been presented in Table 2. All these tabulated reports present similar gas sensing mechanisms.

4.1.3. MOX Nanoparticle Decoration
Besides fabricating heterostructures and core–shell structures of nanowires, decoration of nanowires with other
MOXs nanoparticles is also an interesting strategy to alter their sensing properties. In this strategy, MOXs nanoparticles prepared by a certain method are deposited on the top of host nanowires. It has been found that these types of additives play an extremely important role to tune the sensing properties of nanowires via controlling the donor density, enlargement of EDL by the creation of p–n junction, catalytic promotion of reaction between the gas analyte and sensing layer and selective detection of a specific gas analyte by manipulating the acid–base properties.[43–46] Having said that, the parameters like amount of loading, incorporation of particles into the lattice of the host material, their configuration and phase determine the sensing properties of the final modified sensor.[43]

In 2012, Na et al.[43] have decorated the ZnO nanowires network with NiO for volatile organic compound detection. Interestingly, as compared to bare ZnO nanowires and Ni-doped ZnO nanowires, NiO decorated ones showed superior performance toward C₂H₅OH and HCHO. The reason behind their superior performance was found to be the formation of the p–n junction that causes the increase in sensor resistance due to the extension of EDL near the surface.

### Table 1. Sensing performance of different Branched heterostructures.

| Materials | Gas tested concentration | Response | Working temperature [°C] | Detection limit | Response (T<sub>res</sub>) and recovery (T<sub>rev</sub>) time | Reference |
|-----------|--------------------------|----------|---------------------------|----------------|-----------------------------------------------------------|-----------|
| ZnO/SnO₂  | Ethanol/25 ppm            | 3        | 400                        | N/A            | N/A                                                       | [26]      |
| In₂O₃/SnO₂| CO/200 ppm               | 1.9      | 300                        | N/A            | T<sub>res</sub> = 135 s, T<sub>rev</sub> = 610 s          | [33]      |
| ZnO/TiO₂  | Ethanol/500 ppm           | 50.6     | 320                        | N/A            | T<sub>res</sub> = 5 s, T<sub>rev</sub> = 10 s             | [27]      |
| TiO₂/V₂O₅ | Ethanol/1000 ppm          | 32.1     | 350                        | N/A            | T<sub>res</sub> = 6 s, T<sub>rev</sub> = 7 s              | [28]      |
| TiO₂/Ag₁₋₃V₂O₅ | Ethanol/100 ppm | 31.8 | 350 | N/A | T<sub>res</sub> = 7 s, T<sub>rev</sub> = 8 s | [29] |
| Fe₂O₃/TiO₂ | Trimethylamine (TMA)/30 ppm | 13.9 | 250 | N/A | T<sub>res</sub> = 0.5 s, T<sub>rev</sub> = 1.5 s | [25] |
| VO₂/ZnO   | Acetone/200 ppm           | 5.01     | RT                         | N/A            | T<sub>res</sub> = 8 s, T<sub>rev</sub> = 21 s             | [30]      |
| NiO/ZnO   | Acetone/100 ppm           | 10       | 400                        | 0.08 ppm       | N/A                                                       | [9]       |
| NiO/ZnO   | Ethanol/50 ppm            | 6.7      | 400                        | 0.06 ppm       | N/A                                                       | [9]       |
| TeO₂/SnO₂ | NO₂/10 ppm               | 10.25    | 100                        | N/A            | T<sub>res</sub> = 250 s, T<sub>rev</sub> = 1000 s         | [31]      |
| SnO₂/ZnO/Au | NO₂/10 ppm              | 11.2     | 300                        | 28.9022 ppb    | T<sub>res</sub> = 118 s, T<sub>rev</sub> = 197 s         | [34]      |
| ZnO/Cu₂O  | Acetone/50 ppm            | 6.38     | 250                        | N/A            | T<sub>res</sub> = 62 s, T<sub>rev</sub> = 90 s           | [14]      |
| SnO₂/Bi₂O₃/Pt | NO₂/1 ppm               | 27.75    | 50                         | N/A            | N/A                                                       | [32]      |
| NiO/NiWO₄/WO₃ | Acetone/30 ppm        | 48.3     | 400                        | 0.7 ppm        | N/A                                                       | [2]       |
| NiO/NiWO₄/WO₃ | NO₂/5 ppm               | 169.4    | 300                        | 57 ppb         | N/A                                                       | [2]       |

Figure 13. a) Gas responses (R<sub>g</sub>/R<sub>a</sub> or R<sub>a</sub>/R<sub>g</sub>) in air and R<sub>y</sub>: resistance in gas to 10 ppm NO₂ and 200 ppm of CO, C₃H₈, CH₄, H₂, and C₂H₅OH at 200 and 300 °C (R<sub>y</sub>/R<sub>a</sub> for NO₂ and R<sub>a</sub>/R<sub>y</sub> for other reducing gases). b) Gas responses (R<sub>y</sub>/R<sub>a</sub> or R<sub>a</sub>/R<sub>y</sub>) to 10 ppm NO₂ and 200 ppm of CO, C₃H₈, CH₄, H₂, and C₂H₅OH at 400 °C (R<sub>y</sub>/R<sub>a</sub> for NO₂ and R<sub>a</sub>/R<sub>y</sub> for other reducing gases). Reproduced with permission.[8] Copyright 2010, Elsevier.
ZnO nanowires sensors showed excellent response with enhanced selectivity toward C2H5OH and HCHO. In Figure 17, the responses of all three sensing devices were shown. In another excellent work, a huge amount of enhancement in the SnO2 nanowires sensor was observed after the decoration with NiO nanoparticles toward H2S gas (see Figure 18).18 This enhancement in sensor response was attributed to the enlargement of EDL due to the formation of the p–n junction and continuous formation of n–p–n–p junctions between NiO particles and SnO2 nanowires that results into the blockage of electron percolation in the SnO2 NWs network. Furthermore, instead of using NiO, SnO2 nanowires were functionalized with CuO particles for H2S detection.47 Similar to the work on NiO decorated SnO2 nanowire, the formation of p–n heterojunctions and linkage were found to be the major reason behind the improvement in sensing response toward H2S.

Furthermore, Kwak et al.48 have decorated SnO2 nanowires with chromium oxide (Cr2O3) particles for gas sensing mechanism. The modified sensors showed improved response toward trimethylamine (TMA) and again the formation of the p–n junction, which leads to an increase in EDL, was found to be the main reason behind this enhancement. While, iron oxide (Fe2O3) nanoparticles decorated indium oxide (In2O3) nanowires showed excellent performance toward acetone.49 The detailed investigation reveals that the improved sensing response toward acetone was due to both electronic (variation in interfacial potential barrier and EDL width) and chemical (creation of active adsorptions sites for gas molecules by Fe2O3 nanoparticles on In2O3 nanowires surface) phenomenon (see Figure 19).

To enhance SnO2 nanowires sensor response toward NO2, Ko et al.50 have synthesized islands of vanadium oxide (V2O5) on their surface with the ALD technique. Up to 50 cycle of V2O5, the sensor response was found to increase and creation of depletion layer between these two materials was the main reason behind the enhanced response. Recently, Han et al.51 have decorated the CuO nanowires with ZnO nanoparticles and it turns out to be improved the sensor response toward NO2. It has been observed that after the decoration with ZnO nanoparticles, modulation of HAL of CuO nanowires occurs which enhances the sensor response. Figure 20 depicts the schematic of the effects caused by the CuO/ZnO heterojunction.

In Table 3, few reports are presented on MOXs decorated nanowires. The underlying sensing mechanisms are similar to those discussed above.
4.2. Metal Particle Decoration

Up to now, a significant amount of research has been done on decoration with noble metal nanoparticles to promote the sensitization of metal oxide nanowires surface to enhance their gas sensing properties. Different deposition techniques have been used to decorate metal particles on nanowires surface. Table 4 summarizes the reports on metal nanoparticle decorated nanowire-based gas sensors. It can be clearly seen that noble metals such as Au, Pt, Pd, and Ag have been extensively used to improve the sensing performance of pure MOX nanowires.

In 1991, Yamazoe et al.[71] have described the effect of adding noble metals to a semiconductor sensor can be categorized into two ways “chemical sensitization” or “electronic sensitization” (see Figure 21). According to the author, the enhancement mechanism significantly depends on the type of metal catalyst used and change in the work function of metal oxide (like in the case of Ag and Pd, but not for Pd). During the chemical sensitization, a spill-over effect occurs which is a well-known catalytic effect produced by the metal nanoparticles. In this case, the decorated metal particles enhance the sensor sensitivity by increasing adsorption sites at the surface. While, during the electronic sensitization the increase in sensing response is directly related to the interaction between the metal particle and surface of metal oxide at the interface. This effect is commonly observed in the case of Ag and Pd as they form stable oxide (AgO, PdO) in reaction with air. This, in turn, leads to the creation of an electron-depletion region, which directly effects the work function of the active metal oxide sensor. These phenomena have been widely employed by the researchers in last decade to improve the sensor response, sensitivity, and recovery time.

In a report published by Katoch et al.[66] on the functionalization of ZnO nanowires using Pt nanoparticles that not only enhanced the sensor response toward NO2 gas but also lower their working temperature from 200 to 300 to 100 °C. This improvement in the sensing behavior was attributed to the catalytic properties of Pt, which help to produce more active sites at the surface for adsorption and dissociation of NO2. A similar effect has been presented in other reports.[58,65] Furthermore, Trung et al.[61] report the improvement of SnO2 nanowires response by the addition of Pd nanoparticles for CO detection. The addition of Pd nanoparticles increases the response of the SnO2 and also improves the recovery time. Author attributes this change due to the spill-over generated by Pd, as it acts as...
catalyst to increase the rate of dissociation of oxygen molecules, which leads to more active sites on the surface. Addition to this due to the difference of work function between SnO2 (4.5 eV) and Pd (5.5 eV) the electrons start to flow from SnO2 to Pd creating a Schottky barrier at the interface (shown in Figure 22). This effects the overall resistance of the nanostructured sensors and the interaction with incoming CO molecules due to the presence of higher number of oxygen ions to react. The interaction between CO molecules and oxygen ions leads to the release of electrons back to the barrier, which causes the further reduction of sensor resistance.

Furthermore, gold (Au) is another extensively used metal to improve the sensing behavior of MOX-based gas sensors. [4,6,22] Recently, Zeb et al.[70] used bimetal (Au–Pd) to modify the surface of WO3 nanowires for the detection of n-butanol. Due to the presence of bimetal, the change in sensing behavior is mainly dominated by the highly induced electronic sensitization (see Figure 23). Both the metal particles extract electrons from the metal oxide surface creating a thick depletion layer that increases the resistance of the sensor in air. As n-butanol has low bonding energy, long hydrocarbon chains react to the sensor surface much easily. The author also points out that the small size and high crystalline metal particles provide a higher surface area that in turn increases active oxygen molecules making the sensor more sensitive. Thus, the decoration of MOXs nanowires with metal particles is an excellent strategy to improve the sensor performance.

4.3. Surface Functionalization of Metal Oxide Nanowires

SAMs functionalized surfaces are getting considerable attention in electronics devices such as sensors due to their unique structure that allows immobilization of biomolecules[5] as we all enhancement of the surface specific interaction with the gas molecules. [6] SAMs are 2D ordered molecular arrangements that spontaneously form on the surface of a variety of substrates such as gold, metal oxides.[5] One of the most important advantages of SAMs process is that it does not require any costly instrument. For example, in the dip method only vial, organic solvent, SAM molecules and maybe low temperature heating system are required to perform the SAM functionalization process.[5] SAMs possess three main parts, i.e., a head-group, which binds with the surface under concern; backbone is an aromatic oligomer or aliphatic chain responsible for molecular ordering; and endgroup that defines the functional-ity of the SAM, surface energy, topography and can further be used for various purposes, i.e., immobilization of biomolecules, patterning, detection of gas analytes, etc. In Figure 24, the structure of SAM is presented.

In an interesting work, organic–inorganic hybrid bases gas sensor was proposed based on SnO2 nanowires (inorganic part) and N-[3-(trimethoxysilyl)propyl]ethylenediamine1 (en-APTAS, organic part) for the selective, rapid, and low concentration detection of NO2.[72] The sensing performance of this hybrid gas sensors is shown in Figure 25. Clearly, among all tested gas analytes, the highest response was observed for NO2. The theoretical investigations reveal that the selectivity of hybrid sensors is due to the suitable alignment of the gas–SAM frontier molecular orbitals with respect to the SAM–nanowires Fermi level that favors the charge-carrier transfer.

Recently Singh et al.[4] have functionalized VLS grown ZnO nanowires with two different SAM molecules, namely, (3-aminopropyl)trimethoxysilane (APMTS) and 3-glycidoxypropyltrimethoxysilane (GLYMO) for selective acetone detection. The gas sensing mechanism was described based on the formation

| Materials                  | Gas tested concentration | Response | Working temperature [°C] | Detection limit | Response (Tres) and recovery (Trrev) time | Reference |
|----------------------------|--------------------------|----------|--------------------------|-----------------|------------------------------------------|-----------|
| SnO2/ZnO                   | NO2/0.5 ppm              | 8.3      | 200                      | 15 ppb          | Tres = 15.8 s                             | [8]       |
|                            | Ethanol/200 ppm          | 280      | 400                      | N/A             | Trrev = 5 s                              |           |
| α-Fe2O3/ZnO                | Ethanol/100 ppm          | 17.8     | 280                      | N/A             | N/A                                      | [37]      |
| SnO2/ZnO                   | NO2/5 ppm                | 6.19     | 25/under UV              | N/A             | N/A                                      | [15]      |
| SnO2/ZnO                   | Ethanol/20 ppm           | 32.9     | 400                      | N/A             | N/A                                      | [35]      |
| SnO2/ZnO                   | C6H6/10 ppm              | 30       | 300                      | N/A             | N/A                                      | [38]      |
| SnO2/Pt                   | C6H6/10 ppm              | 13       | 300                      | N/A             | Tres = 60 s                             | [39]      |
| SnO2/Pt                   | C6H5/0.1 ppm             | 279      | 300                      | N/A             | N/A                                      | [40]      |
| CuO/ZnO                   | C6H5/1 ppm               | 6        | 300                      | N/A             | N/A                                      | [16]      |
| W18O49/TiO2               | NO2/5 ppm                | 36.5     | RT                       | N/A             | Tres = 5 s                              | [41]      |
| TiO2/SnO2                 | Acetone/100 ppm          | 13.7     | 280                      | N/A             | Tres = 2 s                              | [42]      |
| SnO2/NiO                  | H2/200 ppm              | 78       | 500                      | 0.9 ppm         | Tres = 2 min                             | [3]       |
| ZnO/SnO2                  | CO, C6H6, C5H6/10 ppm    | 42–48    | 300                      | N/A             | Tres = 2 min                             | [17]      |
| SnO2/SiO2                 | H2/200 ppm              | 93       | 500                      | 0.1 ppm         | N/A                                      | [36]      |
of core–shell structure due to oxygen chemisorption and interaction of acetone molecules with APTMS monolayer amine (−NH₂) groups (see Figure 26). Specifically, GLYMO enhances the EDL, which in turn increases the electronic exchange between ZnO nanowires and acetone. While in the case of APTMS, not only the width of EDL increases, but the interaction of acetone with −NH₂ results into the enhancement of response, selectivity and detection limits.

4.4. Modification of Metal Oxide Nanowires with Graphene (Pristine and Oxidized)

Another material that needs no introduction and is recently been employed to enhance the sensing performance of MOXs nanowires is graphene in pristine and oxidized form (GO and rGO). Graphene consists of a single 2D layer of sp²-hybridized carbon atoms and possessed many favorable properties such as high charge carrier mobility, high mechanical stiffness, and extremely large surface area (2630 m² g⁻¹) that can be explored in the gas sensing field. While, GO is oxidized graphene and possesses functional groups like hydroxyl (−OH), carboxylic (−COOH), etc. whose interactions with gas molecules can be explored. Lastly, rGO is obtained after the reduction of GO and exhibits a large number of defects and dangling bonds; hence, offers better sensing performance. By merging the properties of these materials with MOXs nanowires, an ultrasensitive gas sensor can be developed.

To achieve higher sensitivity toward H₂S, cuprous oxide nanowires/nanoparticles were decorated on the top of GO nanosheets. The blend was prepared by mixing GO solution and copper acetate aqueous solution (Cu(Ac)₂) with further addition...
Figure 18. Transient responses of a) bare SnO$_2$ NWs sensor and b) NiO-decorated SnO$_2$ NWs sensor to c) H$_2$S at 300, 350, and 400 °C responses, d) response times, and e) recovery times of bare SnO$_2$ NWs sensor and NiO-decorated SnO$_2$ NWs sensors as a function of operating temperature. Reproduced with permission.[18] Copyright 2012, AIP Publishing.

Figure 19. a) Schematic diagrams showing the depletion layer and potential barrier forming in a pristine In$_2$O$_3$ nanowire (above) and Fe$_2$O$_3$-functionalized In$_2$O$_3$ nanowire (below) upon exposure to air and acetone gas. b) Energy band diagrams of the In$_2$O$_3$–Fe$_2$O$_3$ system in vacuum, air and acetone gas. The energy bandgaps, $E_g$ of In$_2$O$_3$ and Fe$_2$O$_3$ are 3.6 and 2.2 eV, respectively. The electron affinities, $X_c$ of In$_2$O$_3$ and Fe$_2$O$_3$ are 3.5 and 4.7 eV, respectively. Debye length of In$_2$O$_3$ is $\approx$ 25 nm. $W_{D(P)}$ and $W_{D(F)}$ denote the depletion layer widths of the pristine and Fe$_2$O$_3$-functionalized In$_2$O$_3$ nanowire. $W_{C(P)}$ and $W_{C(F)}$ denote the conduction path widths of the pristine and Fe$_2$O$_3$-functionalized In$_2$O$_3$ nanowire. Reproduced with permission.[49] Copyright 2015, Elsevier.
Figure 20. Schematic view of the effects caused by the CuO/ZnO heterojunction. a) Diagram of the p-CuO and n-ZnO heterojunction band. b) Reaction of a CuO NWs to NO2 gas. c) Reaction of a CuO NWs with ZnO heterojunction to NO2 gas. Reproduced with permission.[51] Copyright 2015, MDPI.

Table 3. Sensing performance of different MOX particle decorated heterostructures.

| Materials       | Gas tested concentration | Response | Working temperature (°C) | Detection limit | Response (T_{res}) and recovery (T_{rev}) time | Reference |
|-----------------|--------------------------|----------|--------------------------|----------------|--------------------------------------------|-----------|
| NiO/ZnO         | Ethanol/5 ppm            | 29.04    | 450                      | 0.017 ppm      | N/A                                        | [43]      |
| NiO/SnO2        | H2S/10 ppm               | 1372     | 300                      | N/A            | T_{res} = 6 s                              | [18]      |
| CuO/SnO2        | H2S/5 ppm                | 15       | 300                      | N/A            | T_{res} = 6 s, T_{rev} = 8 s               | [47]      |
| CuO/SnO2        | H2S/10 ppm               | 26.3     | 250                      | N/A            | T_{res} = 2.5 min, T_{rev} = 99 min        | [52]      |
| CuO/WO3         | H2S/100 ppm              | 3.75     | 300                      | N/A            | N/A                                        | [53]      |
| Co2O3/SnO2      | H2/10 ppm                | 40       | 300                      | N/A            | T_{res} = 3 s, T_{rev} = 6 s               | [54]      |
| Co2O3/SnO2      | TMA/5 ppm                | 9.87     | 450                      | 1.5 ppb        | T_{res} = 7 s, T_{rev} = 412 s             | [48]      |
| Fe2O3/In2O3     | Acetone/500 ppm          | 9.6      | 200                      | N/A            | T_{res} = 40 s, T_{rev} = 80 s             | [49]      |
| Fe2O3/WO3       | Toluene/100 ppm          | 8        | 200                      | N/A            | T_{res} = 150 s, T_{rev} = 10 s            | [55]      |
| CuO/In2O3       | H2S/5 ppm                | 9170     | 25                       | 400 ppb        | T_{res} = 4 s, T_{rev} = 140 s             | [56]      |
| Co2O3/WO3       | H2/2000 ppm              | 6        | 200                      | N/A            | T_{res} = 40 s, T_{rev} = 50 s             | [19]      |
| V2O5/SnO2       | NO2/5 ppm                | 69       | 250                      | 139 ppm        | N/A                                        | [50]      |
| SnO2/ZnO        | NO2/1 ppm                | ≈45      | 150                      | N/A            | N/A                                        | [57]      |
| SnO2/ZnO        | Ethanol/100 ppm          | 14       | 250                      | N/A            | N/A                                        | [57]      |
| ZnO/CuO         | NO2/100 ppm              | 4.1      | 250                      | N/A            | T_{res} = 25 s, T_{rev} = 150 s            | [51]      |
of NaOH under magnetic stirring. Afterward, the solution was transferred to an autoclave for hydrothermal reaction. The sensor exhibits 20% response toward 1 ppm of H2S at 40 °C with excellent recovery, long-term stability, and selectivity. To explain the sensing mechanism, the author proposed two aspects that were responsible for the increase in sensor resistance upon exposure with H2S gas. The first one is the interaction of H2S with adsorbed oxygen ions (O2−) (donation of electrons to sensing layer), which results into the depletion of the hole accumulation region, hence an increase in resistance of the sensor. While, the second one is the formation of metallic CuS due to the interaction of H2S gas with Cu2O, which further increases the sensor resistance.

Recently, a low-concentration ethanol sensor was developed by the combination of graphene and ZnO nanowires. [23] In this work, ZnO nanowires were hydrothermally grown on graphene nanosheets, which were previously deposited on the interdigitated electrode containing glass substrate. The graphene/ZnO nanowires sensor exhibits a two times higher response as compared to pristine ZnO nanowires at 200 °C.

The sensing performances of these devices are shown in Figure 27. It has been observed that the formation of heterojunction between ZnO nanowires and graphene nanosheets, which results into the formation of potential barriers, plays an extremely important role in defining the sensor response toward ethanol. Figure 28a,b represents the band structure of ZnO nanowires and graphene before and after junction formation in the air. When this heterostructure is exposed to ethanol vapors, it donates electrons to the ZnO NWs, which remarkably decreases the potential

Table 4. Sensing performance of different metal particle decorated heterostructures.

| Materials          | Gas tested concentration | Response | Working temperature [°C] | Detection limit | Response (Tres) and recovery ( Trev) time | Reference |
|--------------------|--------------------------|----------|---------------------------|-----------------|------------------------------------------|-----------|
| Pt/In2O3 NWs       | O2/100 ppm               | 2        | 50                        | N/A             | Tres = 100 s Trev = 120 s                 | [58]      |
| Pt/ZnO NWs         | Ethanol/50 ppm           | 32.6     | 265                       | N/A             | N/A                                      | [21]      |
| Ag/SnO2 NWs        | Ethanol/100 ppm          | 228.1    | 450                       | N/A             | Tres = >0.5 s Trev = >100 s               | [22]      |
| Au/SnO2 NWs        | NO2/0.1 ppm              | 3        | 200                       | N/A             | Tres = 35 s Trev = N/A                    | [10]      |
| Au/ZnO NWs         | Toluene/100 ppm          | 8.6      | 340                       | 30 ppm          | Tres = 36 s Trev = 45 s Trev = 64 s Trev = 43 s | [59]      |
|                    | Benzene/100 ppm          | 6.4      |                           | N/A             |                                          |           |
| Au/ZnO NWs         | Ethanol/50 ppm           | 7        | 325                       | N/A             | Tres = 5 s Trev = 20 s                    | [60]      |
| Pd/WO3 NWs         | H2/1000 ppm              | 3        | 300                       | N/A             | Tres = 1.26 min Trev = 41.52 min         | [20]      |
| Pd/SnO2 NWs        | CO/1 ppm                 | 1.8      | 400                       | N/A             | Tres = 10 s Trev = 60 s                  | [61]      |
| Au/ZnO NWs         | Ethanol/100 ppm          | 33.6     | 380                       | N/A             | Tres = 3 s Trev = 1 s                    | [62]      |
| Pd/TiO2 NWs        | Isopropanol/1000 ppm     | 27.5     | 200                       | N/A             | N/A                                      | [63]      |
| Pd/ZnO NWs         | Acetone/500 ppm          | 153.8    | 300                       | N/A             | Tres = 6 s Trev = 14 s                   | [64]      |
| Au/ZnO NWs         | Acetone/500 ppm          | 68.3     | 300                       | N/A             | Tres = 3 s Trev = 29 s                   | [64]      |
| Pt/TiO2 NWs        | NO2/100 ppm              | 5.7%     | 300                       | N/A             | Tres = 3 min Trev = 3 min                | [65]      |
| Pt/ZnO NWs         | NO2/0.1 ppm              | 1.08     | 100                       | N/A             | Tres = 160 s Trev = 121 s               | [66]      |
| Au/WO3 NWs         | H2S/10 ppm               | 80       | 350                       | N/A             | Tres = 30 s Trev = 200 s                 | [67]      |
| Pt/SnO2 NWs        | Toluene/1 ppm            | 40       | 300                       | N/A             | Tres = >450 s Trev = >400 s             | [68]      |
| Au/VO2 NWs         | NO2/5 ppm                | 3.22     | 25                        | N/A             | N/A                                      | [69]      |
| Pd/VO2 NWs         | n-Butanol/100 ppm        | 69       | 200                       | N/A             | Tres = 8 s Trev = 16 s                  | [70]      |
| Au–Pd/VO2 NWs      | n-Butanol/100 ppm        | 93       | 200                       | 1 ppm           | Tres = 4 s Trev = 12 s                  | [70]      |
barriers (see Figure 28c). Due to this decrease in potential barrier width, excess electrons move toward the graphene side and lower the majority of holes carriers in graphene nanosheets (hence increasing the resistance of graphene nanosheets). Hence, the whole system, i.e., heterostructure of ZnO nanowires and graphene nanosheets works as a p-type sensing layer.

4.5. MOF-Coated Nanowires (MOX@MOF Core–Sheath Structure)

Another interesting strategy that was recently put forward to improve the sensing performance of nanowires is their coating with metal organic frameworks (MOFs) thin films, i.e., MOX@MOF core–sheath structure.[76] MOFs are crystalline porous materials that can be prepared by combining metal ions or clusters with organic ligands.[77] In particular, these materials possess interesting properties like tunable porosity, large surface area, sites for functionalization, etc. that can be useful for designing highly efficient sensors.[77] For example, hierarchical ZnCo$_2$O$_4$ microflower-based sensors exhibit high response toward acetone due to their high specific surface area, small particle size, and high porosity.[76] Hence, improvement in sensing performance of MOX nanowires can be expected by their coating with MOFs thin films. Yao et al.[76] were the first one who reported the ZnO@ZIF-CoZn core–sheath nanowire arrays for VOCs sensing. In this work, ZnO nanowires core was prepared by hydrothermal method and their coating was done with MOF sheath comprising zeolitic imidazolate framework-CoZn (ZIF-CoZn). The schematic representation of ZnO@ZIF-CoZn core–sheath based sensing fabrication is shown in Figure 29. Interestingly, ZnO@ZIF-CoZn core–sheath nanowires exhibit a 20-times higher response toward acetone as compared to bare ZnO nanowires at 260 °C. This enhancement was ascribed to the excellent catalytic properties of Co$^{2+}$ in ZIF-CoZn in the temperature range of 200–300 °C. Indeed, these Co$^{2+}$ ions help to generate the active oxygen species by dissociating the oxygen molecule from the air. Finally, these active oxygen species promote the catalytic oxidation of acetone gas. Not only the response but the selectivity of ZnO nanowires toward acetone were also improved by controlling the gas transport in MO/MOF interface.[79] In particular, ZIF-8-DMBIM (DMBIM = 5,6-dimethylbenzimidazole)-based MOF thin film was coated to n-ZnO nanowires array and explored for the detection of acetone and benzene series chemicals (see Figure 30). Indeed, ZIF-8-DMBIM promotes the selective penetration of acetone molecules due to its smaller aperture, hence improves the selectivity of nanowires.

In a similar work, ZnO nanowires grown using catalyst-assisted vapor phase growth were encapsulated with ZIF-8
MOF to realized ZnO@ZIF-8 structure. The ZnO@ZIF-8 sensors showed high selectivity toward H₂ as it easily diffuses through the MOF membrane due to its smaller kinetic diameter (2.89 Å) as compared to other gases.

Hence, this interesting strategy has the potential to design high performance sensing devices not only for the detection of acetone and hydrogen but also other important gas analytes such as environmental pollutants.

5. Conclusion

In summary, we have reviewed the last decade progress in the field of different strategies used to improve the metal oxides nanowires sensing performance. These strategies include nanowires heterostructures, 1D core–shell structures, MOX@MOF core–sheath structures, particle decoration, surface functionalization with SAMs, and modification with graphene. It has been observed that sensor characteristics such as selectivity, optimal working temperature, response, and detection limits were improved after the nanowires modification. For example, after the decoration of ZnO nanowires with Pt particles, a lower optimal working temperature was observed as compared to bare ZnO nanowires along with a response enhancement. While, after the surface functionalization of ZnO nanowires with APTMS monolayer, sensor response, selectivity, and detection limit were improved toward acetone due to the interactions between acetone molecules and amino group of APTMS. These types of functional entities such as carboxylic, epoxy, hydroxyl, etc. also exist on the surface of oxidized graphene, but their interactions between analytes after modification of nanowires is still not explored. This can be due to the limited knowledge of molecular interactions of functional molecular groups of oxidized graphene with analytes. We believe these strategies (surface functionalization with SAMs and medication with oxidized graphene) may be extremely helpful to fabricate ultrasensitive sensing device. However, this is only possible if fundamental chemist/physicist work alongside researcher working in the field of chemical sensors. Moreover, it was also seen that regardless of recent progress in nanotechnology still n-type MOXs are mainly employed for modification as compared to p-type ones. Due to this, our knowledge about the whole picture of underlying sensing mechanism is still limited. Having said that the following sensing mechanisms were generally considered to explain the change in sensing properties after modification via different strategies.

1) MOX-MOX heterostructures (branch-like, core–shell, and MOX particle decoration: The main reason behind the improvement was found to be the formation of depletion region due to the difference in work function of two materials that lead to charge separation and band bending phenomena. Moreover, surface area enhancement after the modification also affects the sensing performance.

2) Decoration with metal particles: Both chemical and electronic sensitization were found to be the main reasons of improvement in sensor performances. In chemical sensitization, decorated metal particles increase the adsorption sites
on nanowires surface via spill-over effect. While, in electronic sensitization effect, the direct interactions between metal particles and nanowires due to the difference in work functions leads to the improvement in sensing performances.

3) Surface functionalization with SAMs: The enhancement in the width EDL of nanowires and interactions between SAMs terminal groups and analyte molecules leads to the improvement in sensing performances.

4) Modification with Graphene (pristine and oxidized: The formation of heterojunction between nanowires and graphene layer plays an extremely important role in the sensing performances improvement.

Figure 26. Gas sensing mechanism of bare and SAM (10 × 10⁻³ m APTMS and GLYMO) functionalized ZnO NWs for acetone detection. Reproduced with permission.[4] Copyright 2020, Wiley-VCH.
Figure 27. a, b) Dynamic resistance curves of ZnO NWs and Gr/ZnO NWs to different concentrations of ethanol at their optimum working temperature. c) Calibration curves of different sensors to ethanol gas at the optimum working temperature, and d) selectivity test of ZnO NWs and Gr/ZnO NWs gas sensors at their optimum working temperature. (All tests were done at the sensor’s optimum working temperature.) Reproduced with permission. [23] Copyright 2021, Elsevier.

Figure 28. Band structure of ZnO and graphene a) before and b) after contact in ambient air and c) in ethanol vapor. Reproduced with permission. [23] Copyright 2021, Elsevier.
5) MOX@MOF core–sheath structure: Catalytic reactivity of metal ions toward oxygen molecules and control of analyte diffusion through the MOF layer plays an extremely important role in enhancing the sensing performance of nanowires. Clearly, after the modification of nanowires their sensing performances were greatly improved. These modified nanowires sensor can be used to develop an array of sensors (electronic nose). The arrays of sensor can then be used for advanced
applications such as environmental monitoring, indoor monitoring, food quality control, and many others. However, to explain change in sensing performances, the general MOXs sensing mechanism, more suitable for thin films, were still employed. Indeed, the sensing mechanism specifically for nanowires can also be deeply understood and this can be helpful for driving further improvements in the sensing performances.

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This article was amended on April 7, 2022 to adjust two columns in Table 1: Response and Working Temperature.

Conflict of Interest

The authors declare no conflict of interest.

Keywords

gas sensors, graphene, heterostructures, metal oxides, nanowires, self-assembled monolayers, sensing mechanism

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