

# GAS SENSORS BASED ON METAL OXIDE NANOPARTICLES AND THEIR APPLICATION FOR ENVIRONMENTALLY HAZARDOUS GASES DETECTION – A MINI-REVIEW

Justyna Jońca\*, Izabela Sówka

Department of Environment Protection Engineering, Faculty of Environmental Engineering,  
Wrocław University of Science and Technology, Wrocław, Poland

\* Correspondence: justyna.jonca@pwr.edu.pl

## Abstract

Hazardous gases have adverse effects on living organisms and the environment. They can be classified into two categories, i.e. toxic gases (e.g. H<sub>2</sub>S, SO<sub>2</sub>, CO, NO<sub>2</sub>, NO and NH<sub>3</sub>) and greenhouse gases (e.g. N<sub>2</sub>O, CH<sub>4</sub> and CO<sub>2</sub>). Moreover, their presence in confined areas may lead to fire accidents, cause serious health problems or even death. Therefore, monitoring of these substances with gas sensors allows assessing the quality of the atmosphere, helps avoiding accidents and saves lives. Metal oxide semiconductor gas sensors (MOS) are one of the most popular choices for these applications owing to their numerous advantages, i.e. high sensitivity, long lifetime and short response time. However, these devices have their limitations as well. They exhibit baseline drift, sensor poisoning and poor selectivity. Although much has been done in order to deal with those problems, the improvement of MOS sensors continues to attract researchers' attention.

The strict control of gas sensing materials preparation is one of the approaches that helps to improve MOS sensors performance. Nanomaterials have been found to be more suitable candidates for gas detection than materials designed at microscale. Moreover, it was found that the regular and ordered morphology of metal oxide nanostructures, their loading with noble metals, or the formation of heterojunctions can exert additional influence on the properties of these nanostructures and improve their gas sensing performance, which will be described in the following sections of this paper. Following a discussion of the operation principle of MOS sensors, a comprehensive review of the synthesis and application of metal oxide nanoparticles in the construction of the MOS sensors dedicated for environmentally hazardous gases is presented. The paper discusses also present issues and future research directions concerning application of nanotechnology for gas sensing.

**Keywords:** metal nanoparticles, metal oxide nanoparticles, heterojunction, gas sensors, hazardous gases

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## 1. Introduction

Growing urbanization and industrialization are inseparably connected with emission of hazardous gases into the atmosphere. The release of chemical pollutants such as  $\text{NO}_x$ ,  $\text{NH}_3$ ,  $\text{CH}_4$ ,  $\text{H}_2\text{S}$ ,  $\text{SO}_x$ ,  $\text{CO}$  and  $\text{CO}_2$  from industry emission, automobile exhaust and household waste has a negative impact on the environment and on human health (e.g. acid rain, global warming, sick house syndrome, depletion of ozone layer) (Table 1). Therefore, it is important to assure proper verification of air pollution levels via monitoring of key toxic and greenhouse gases (Wetchakun et al., 2011; Keswani, Akselrod, Anenberg, 2022). Appropriate air quality standards have been established in many countries and multiple air pollutant measurements methods have been adopted. The standard analytical techniques such as optical spectroscopy and gas chromatography-mass spectrometry are time-consuming, expensive and cannot be used in real-time or in the field conditions (Jońca et al., 2022b). For this reason, in recent years, considerable interest has arisen in miniaturized sensor technologies. The calculated worldwide value of sensor market is \$190 billion till 2021 and it is expected to reach up to 1 trillion by 2025 (Manisalidis et al., 2020).

Indeed, the use of miniaturized gas sensors plays an important role in preventing fire, explosion accidents, environment monitoring, detection of hazardous gases, transportation, space missions, defense, etc. (Wetchakun et al., 2011; Keswani, Akselrod, Anenberg, 2022; Jońca et al., 2022b). Owing to their small size and low weight, miniaturized sensors can be easily installed on monitoring stations and autonomous platforms giving the possibility for continuous, real-time, *in situ* measurements of pollutants with high spatial and temporal resolution (Jońca et al., 2022b). Moreover, miniaturized sensors can be incorporated on portable devices and serve as early warning systems in case of unexpected gas leaks in confined areas, which otherwise may cause health problems or even death. Metal oxide semiconductor gas sensors (MOS) are one of the most popular choices for these applications. Although these sensors are available on the market, their improvement in terms of selectivity, sensitivity, stability still remains an important issue (Jońca et al., 2022b). Their performance depends, among others, on the sensitive layer chemical composition, porosity and microstructure/nanostructure. Nanomaterials exhibit excellent physical, chemical, electrical and catalytic properties for which they are good candidates for the development of gas sensors (Wetchakun et al., 2011; Jońca et al., 2022a; Dhall et al., 2021). Indeed, with nanotechnology advancement, it is possible to prepare a wide variety of metal oxide nanomaterials with well-known morphology and physicochemical properties. Moreover these nanomaterials can be mixed together (formation of heterojunctions) and further loaded with noble metals in order to achieve precise targeting, thus increasing the selectivity of prepared sensors (Yang et al., 2021; Liu et al., 2016).

**Table 1.** Characteristics of common hazardous gases. Prepared on the basis of Keswani et al.

Gas	Properties	Sources	Toxicity or environmental impacts
NO <sub>2</sub>	<ul style="list-style-type: none"> <li>- Reddish-brown gas with an irritating odor</li> <li>- Forms gaseous nitric acid and toxic organic nitrates</li> </ul>	<ul style="list-style-type: none"> <li>- Produced by all combustion in air, transportation sector and industrial processes</li> </ul>	<ul style="list-style-type: none"> <li>- Irritating the lungs, lowers resistance to respiratory infection</li> <li>- When transformed to nitric acid it can corrode metals, degrade rubber and damage tree and crops</li> </ul>
NO	<ul style="list-style-type: none"> <li>- Nonflammable but corrosive gas with high chemical activity</li> </ul>	<ul style="list-style-type: none"> <li>- Produced by all combustion in air</li> </ul>	<ul style="list-style-type: none"> <li>- Irritating to eyes and respiratory system</li> <li>- Severe symptoms may appear within several hours after exposition (breathing problems, irregular respiration pulmonary edema, death)</li> </ul>
N <sub>2</sub> O	<ul style="list-style-type: none"> <li>- Colorless gas with a sweet odor</li> </ul>	<ul style="list-style-type: none"> <li>- Produced from nitrogen based fertilizers and released naturally from oceans</li> </ul>	<ul style="list-style-type: none"> <li>- Greenhouse gas</li> </ul>
H <sub>2</sub> S	<ul style="list-style-type: none"> <li>- Colorless, toxic, flammable gas with characteristic odor of rotten eggs</li> </ul>	<ul style="list-style-type: none"> <li>- Produced during several industrial activities</li> <li>- Produced naturally by humans, animals and bacterial breakdown of organic matter or wastes</li> </ul>	<ul style="list-style-type: none"> <li>- Irritating to respiratory system</li> </ul>
CO	<ul style="list-style-type: none"> <li>- Colorless, odorless, and non-irritating gas</li> </ul>	<ul style="list-style-type: none"> <li>- Produced during incomplete burning of any substance that contains carbon</li> </ul>	<ul style="list-style-type: none"> <li>- Prevents oxygen from being absorbed into the bloodstream.</li> </ul>
NH <sub>3</sub>	<ul style="list-style-type: none"> <li>- Colorless gas with a pungent odor</li> </ul>	<ul style="list-style-type: none"> <li>- Produced by the decomposition of animal manures</li> </ul>	<ul style="list-style-type: none"> <li>- Irritating to eyes</li> </ul>
CH <sub>4</sub>	<ul style="list-style-type: none"> <li>- Colorless and odorless gas</li> <li>- Combustible gas</li> </ul>	<ul style="list-style-type: none"> <li>- Produced by an aerobic digestion of organic material</li> </ul>	<ul style="list-style-type: none"> <li>- Greenhouse gas</li> <li>- When trapped can reach dangerously explosive levels</li> </ul>
SO <sub>2</sub>	<ul style="list-style-type: none"> <li>- Colorless gas with sharp smell that easily forms sulfuric acid, sulfurous acid and sulfate particles</li> </ul>	<ul style="list-style-type: none"> <li>- Produced by industrial processes</li> <li>- May be released during fuel combustion</li> </ul>	<ul style="list-style-type: none"> <li>- Irritates the nose and throat</li> <li>- May cause shortness of breath</li> </ul>
CO <sub>2</sub>	<ul style="list-style-type: none"> <li>- Colorless and odorless gas</li> </ul>	<ul style="list-style-type: none"> <li>- Main product of combustion</li> </ul>	<ul style="list-style-type: none"> <li>- Greenhouse gas</li> <li>- Can create an oxygen deficiency and asphyxiation or suffocation</li> </ul>

Source: (Keswani, Akseirod, Anenberg, 2022)

The purpose of this work is to give an overview of gas sensors based on metal oxide nanoparticles. Therefore, the operating principle of MOS sensors is briefly presented in Section 2 and different nanoparticle synthesis methods are discussed in Section 3. Different ways to apply nanotechnology for gas sensing improvement are described in Section 4. This section discusses: the influence of nanoparticles morphology and dimensionality (Subsection 4.1), the effect of heterojunctions (Subsection 4.2) and the impact of metal oxide nanoparticles loading with noble metals on gas sensing properties (Subsection 4.3). Several examples of application of discussed solutions to detection of chosen hazardous gases are provided within the Section 5. Conclusions, current issues and future trends are provided in Section 6.

## 2. Semi-conductive gas sensors

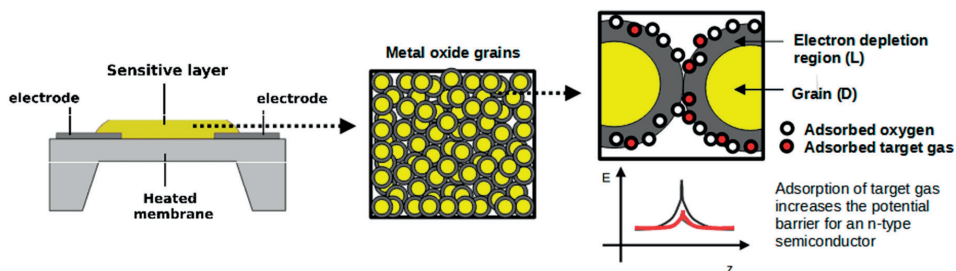
The detection principle of a MOS sensors can be described as an interfacial gas-solid interaction (receptor function), followed by the conversion of this interaction into an electrical signal caused by a change of the resistance of the sensor material (transducer function) (Ji, Zeng, Li, 2019).

In the literature, there are two mechanisms of the receptor function, i.e. the mechanism of ionosorption and the mechanism of oxygen vacancies (Gurlo, Riedel, 2007). In the ionosorption mechanism, the chemisorption of various oxygen species on the MOS surface is considered to be the basis of the detection mechanism. In the oxygen vacancy mechanism, on the other hand, changes in the electrical properties of the MOS are induced by an oxidation/reduction reaction on its surface. In both cases, the parameters of the sensors depend on the physical and chemical interactions between the gas molecules and the sensitive layer (i.e. operating temperature of the sensor), the physical (e.g. grain size, porosity) and chemical (e.g. surface modification with noble metal nanoparticles) properties of the layer itself, as well as on environmental factors such as temperature and humidity.

Oxygen species ( $O_2^-$ ,  $O^-$ ,  $O^{2-}$ ,  $O_2$ ) play an important role in the working mechanism of MOS sensors (Barsan, Schweizer-Berberich, Göpel, 1999; Ruhland, Becker, Müller, 1998; Fine et al., 2010). The operating temperature of the sensor determines what forms of oxygen exist on the surface of a sensitive material. At lower temperatures,  $O_2^-$  ions predominate, while at higher temperatures the  $O^{2-}$  form prevails. As a result, chemical reactions on the surface of the sensitive material will proceed differently at different operating temperatures of the sensor (Korotcenkov et al., 2004). In addition, it has been proven that at temperatures below 180°C, the kinetics of the redox reaction at the oxide surface is very slow, becoming a limiting factor for the gas detection mechanism. At higher temperatures, surface reactions are characterized by better kinetics, and thus cease to be a factor determining the rate of gas detection. At temperatures above 260°C, the diffusion rate of the analyzed molecules in the sensitive material becomes the limiting factor for gas

detection, indicating that the grain morphology, material surface to volume ratio and its porosity may dominate gas detection processes (Wang et al., 2015).

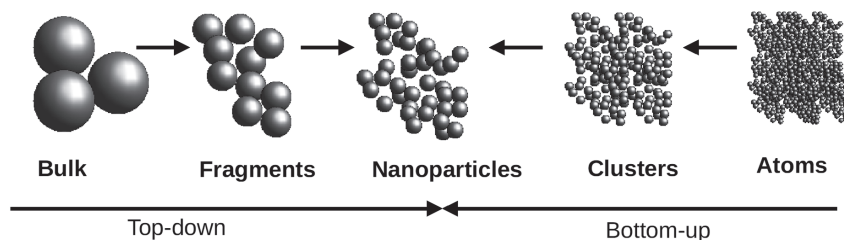
The adsorbed oxygen species modifies the charge distribution on the surface of the semiconductor, and more precisely extracts electrons from its conduction band, generating areas depleted in negative charges. Therefore, potential barriers are formed in the entire material at the grain boundary, which affect the flow of charge carriers in the sensitive layer (Ruhland, Becker, Müller, 1998). Depending on the type of sensitive material (i.e. whether it is an n-type or p-type semiconductor) and the gas nature (whether it is oxidizing or reducing), the absolute change in electrical resistance of a material can vary by several orders of magnitude. While the oxidizing gas robs the surface of the sensitive material of electrons, the opposite is true for the reducing gas. For example, the injection of oxidative gas (e.g.  $\text{NO}_2$ ) decreases the number of charge carriers in the n-type semiconductor, thus increasing the resistance of the sensitive material (Figure 1) (Fine et al., 2010).



**Figure 1.** Principle of MOS sensors functioning based on n-type semiconductor towards oxidative gas

### 3. Nanomaterials preparation methods

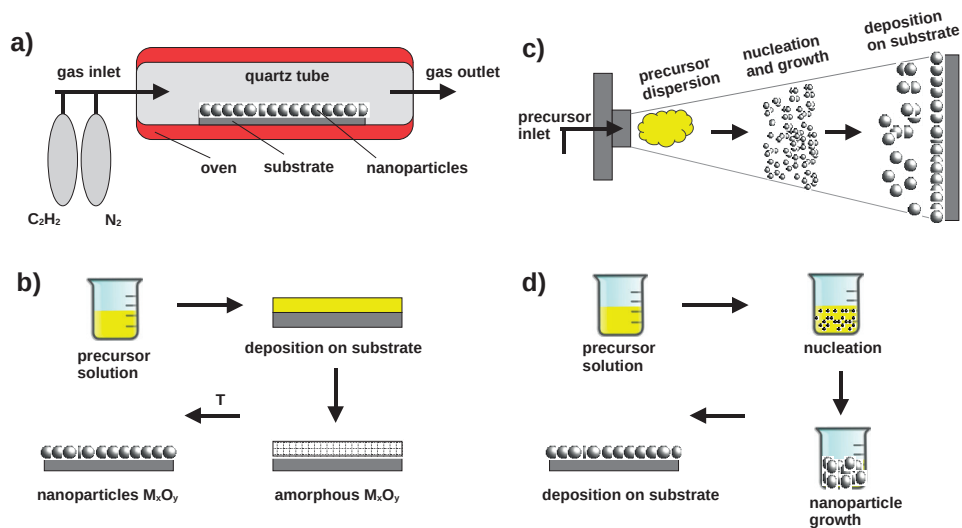
The MOS sensors performance can be optimized by designing sensitive layers at the nanoscale. Over the years, a whole range of methods for the synthesis of nanoparticles have been developed, which can be broadly divided into top-down and bottom-up methods (Figure 2).



**Figure 2.** Schematic representation of top-down and bottom-up approaches used for the nanoparticle preparation

Top-down methods consist in the physical fragmentation of larger batches of material. These methods include electroplithography and photolithography, ion or plasma etching and milling. Top-down processes are associated with high production efficiency, but control over product morphology is limited. In addition, these techniques require the use of complex and expensive equipment (Abid et al., 2022). In bottom-up methods, nanomaterials are created atom by atom. Atoms join together to give rise to crystallographic planes or atomic clusters that can further grow into larger particles and material structures. Depending on the phase in which these processes take place, we can distinguish:

– Vapour-phase techniques (Figure 3a), where precursor molecules in gaseous form are deposited on a substrate, forming building blocks that, when “fed” with successive portions of precursor, grow to the desired size. These techniques include ion or magnetron sputtering, laser ablation and chemical vapour deposition (CVD). Typically, high purity materials are obtained, and depending on the reaction conditions, both polycrystalline and amorphous materials can be produced. Vapour-phase techniques, however, require expensive equipment, and the morphology of the obtained nanostructures cannot be fully controlled (Manawi et al., 2018).



**Figure 3.** A diagram illustrating the bottom-up techniques in the gas phase (a), in the liquid phase (b), aerosols-based techniques (c) and colloid-based techniques (d)

– Liquid-phase techniques (Figure 3b), in which precursor molecules dispersed in liquid solvents are deposited on the substrate, where – as a result of chemical reactions – the process of nanostructures forming begins. These techniques include the method of atomic layer deposition or electrodeposition. These processes can be

easily scaled up to industrial applications, with relatively small financial outlays. In these techniques, it is much easier to control the temperature and heat dissipation, which provides better control of the morphology of the resulting nanoparticles (compared to gas phase techniques) (Weintraub et al., 2010).

- Aerosol-based techniques (Figure 3c), where nanoparticles are synthesized, processed and transported in the gas phase, usually at atmospheric pressure. Aerosol nanoparticles can be neutral or charged depending on the synthesis process, and can consequently be mechanically or electrostatically collected on the substrate. Aerosol-based techniques typically yield spherical nanoparticles or their agglomerates of high purity and well-defined structure (or porosity). These methods are also environmentally friendly because they do not generate post-reaction waste (Zhang et al., 2021).

- Colloid-based techniques (Figure 3d), where the entire process of nanostructure formation takes place in solvents, in the so-called colloidal systems. These systems are stabilized by various types of surfactants, which gives full control over the size and shape of the resulting nanoparticles. These techniques include precipitation, hydrothermal and sol-gel methods. The main disadvantages of this approach include difficulties in scaling the process to industrial applications and the production of environmentally harmful post-reaction waste (Kolahalam et al., 2019).

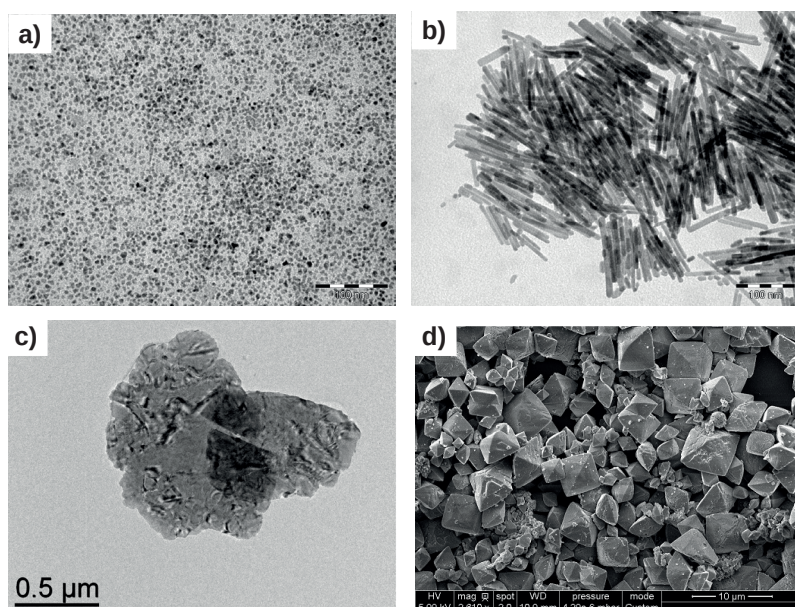
## **4. Different ways of improving gas sensing properties of MOS sensors using nanotechnology**

### **4.1. Control of the morphology and dimensionality of the nanostructures**

Depending on the number of dimensions in nanoscale, nanostructures can be divided in three groups: zero-dimensional structures (0 D), one-dimensional structures (1D), two-dimensional structures (2D). Moreover, composite structures made up of one or more low-dimensional structures are also known as three-dimensional structures (3D structure) (Kolahalam et al., 2019). The classification of nanostructures according to the type of dimensionality and the corresponding exemplary morphology is presented in Table 2. Transmission Electron Microscopy and Scanning Electron Microscopy images of chosen metal oxide nanoparticles are presented on Figure 4.

**Table 2.** Classification of nanostructures according to the type of dimensionality and typical morphology

Type	Characteristics	Example morphology
Structure 0D	Three dimensions in nanoscale	Nanoparticles, nanodots
Structure 1D	Two dimensions in nanoscale	Nanotubes, nanorods, nanofibres
Structure 2D	One dimension in nanoscale	Nanosheets, nanodiscs, superlattices
Structure 3D	composed of one or more types of materials with lower dimensions	hierarchical nanoflowers, nanospheres, octahedral structures



**Figure 4.** Transmission Electron Microscopy (a, b, c) or Scanning Electron Microscopy (d) images of chosen metal oxide nanostructures: (a) ZnO nanoparticles (0D), (b) ZnO nanorods (1D), (c)  $\text{WO}_3$  nanodiscs (2D), (d)  $\text{SnO}_2$  hierarchical octahedra (3D)

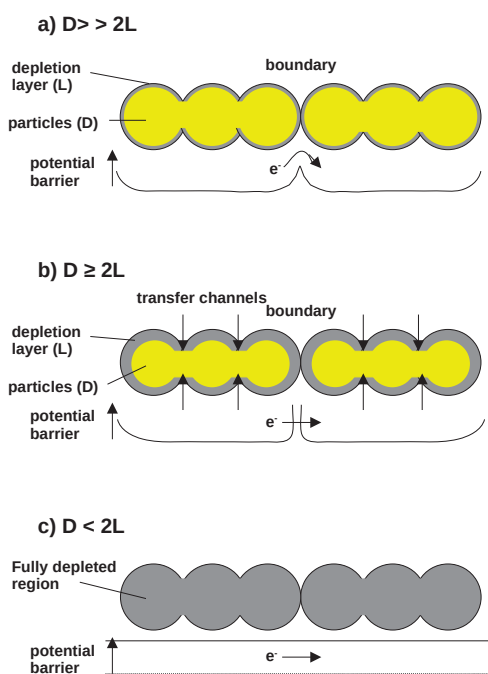
#### 4.1.1. The effect of size

The reduction in grain size to the nanoscale is one of the most effective strategies for the enhancement of the gas-sensing properties. Grains within the sensitive layer form larger aggregates that are connected to each other by the grain boundaries. With respect to the relationships between the grain size ( $D$ ) and the width of the electron depletion layer ( $L$ ), three gas sensing mechanisms can be considered (i.e. boundary control, neck control and grain control) (Figure 5) (Sun et al., 2012):

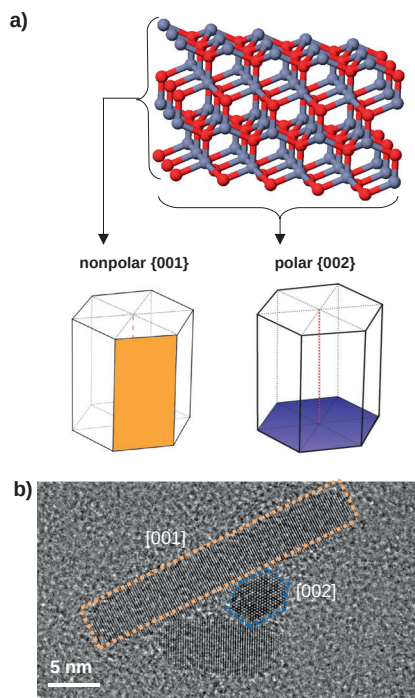
- 1) When  $D \gg 2L$ , most of the grains interior is unaffected by surface interactions with the gaseous mixture. The conductivity of the sensor is assured by the grain boundary barriers, as shown in Figure 5a. In this case the sensitivity of the sensor is independent of the grain size.



- 2) When  $D \geq 2L$ , the depletion layer around each neck forms a transfer channel, as depicted in Figure 5b. The conductivity of the sensors depends on both mentioned channels and the grain boundary barriers. In this case, the sensitivity of the sensing material becomes dependent of the grain size and increases with the reduction of the grain size.
- 3) When  $D < 2L$ , the depletion layer extends throughout the whole grains and the transfer channels between the grains are mislaid (Figure 5c). This leads to dramatic decrease in conductivity of the sensing material. Because there are no significant barriers for charge transport, the energy bands are nearly flat throughout the grains. The sensitivity is controlled entirely by the grains (Weintraub et al., 2010). The grain size effect was investigated by many research teams (Section 5, Table 3). For example, Du et al. (2012), prepared NiO nanoparticles with diameters ranging from 11,5 to 31,5 nm. Nanoparticles with the smallest diameter turned out to be the most sensitive and selective towards  $H_2S$ .



**Figure 5.** Schematic model of the effect of the crystallite size on the sensitivity of semiconductor metal oxide gas sensors: (a)  $D \gg 2L$ ; (b)  $D \geq 2L$ ; (c)  $D < 2L$



**Figure 6.** Schematic representation of atoms arrangement within the ZnO {002} and {100} (a) facets and HRTEM images of ZnO nanoparticles (b)

#### 4.1.2. The effect of shape

The influence of nanoparticle shape on the gas sensing performance of metal oxides has drawn much attention (Section 5, Table 3). After an initial period of nucleation and incubation, nano objects with well-defined, crystallographic facets are formed. For example, the ZnO nanostructures tend to maximize the areas of the polar {002} and nonpolar {001} facets because of their lower energy (Figure 6). These individual facets are characterized by different properties and thus exhibit different interactions with the target gas depending on its nature. Under controlled growth conditions it is possible to design nanoparticles with exposed preferential facets and thus to master adsorption selectivity of the sensitive layer (Vallejos et al., 2016). For example, Ryzhikov et al., (2015) investigated gas sensing properties of ZnO anisotropic nanoparticles, isotropic nanoparticles and cloudy-like aggregates. The nanoparticles were created using a one-pot organometallic approach, which can be classified as colloid technique (see above). The mechanism of growth and stabilization of ZnO particles have been described earlier (Kahn et al., 2005). Sensors prepared with the anisotropic nanoparticles showed the highest response to both CO and C<sub>3</sub>H<sub>8</sub>, whereas sensors based on cloudy-like structures exhibited the weakest response to C<sub>3</sub>H<sub>8</sub>. No effect of the ZnO morphology has been evidenced for NH<sub>3</sub> gas. The mechanism beneath this phenomenon was studied theoretically, among others, by Jiang et al. (2022). The authors concluded that the adsorption selectivity of individual ZnO facets towards chosen gases is attributed to a joint effort of electronic structure matching and geometric matching: the former allows specific gas/slab interactions, the latter decides the strength of the interactions. These results emphasize the influence of the reactivity of individual ZnO crystallographic faces and the nature of the target gas on the parameters of the sensor.

#### 4.1.3. The effect of dimensionality

The dimensionality of nanostructures can also have a significant impact on the response of the sensors. It is systematically reported that 3D hierarchical nanostructures exhibit superior gas sensing performance as compared to nano-objects with lower dimensions (Section 5, Table 3). For example, Jońca et al. (2016) prepared SnO<sub>2</sub> nanoparticles (0D structure) and hierarchical octahedron-like structures (3D structure) built of these nanoparticles. When exposed to low concentrations of CO (i.e. 0.25–20 ppm), the hierarchical structures showed greater sensitivity than SnO<sub>2</sub> nanoparticles, but had a lower upper limit of detection (i.e. 100 ppm vs. 500 ppm). These enhanced gas sensing properties towards low CO concentrations were explained by large porosity of the octahedra that was assured at three different levels: “i) the erratic layer of micron-sized grains generates a primary porosity, ii) the multi-walled structure allows the gas to diffuse inside each octahedra between their walls and iii) the walls of the octahedra are made porous by the self-assembly process, which generates defects.” In such a case, both

inner and outer walls of the microstructure are accessible to gaseous molecules. Therefore, the entire octahedra are spontaneously converted into a highly conducting state when exposed to CO molecules (Jońca et al., 2016).

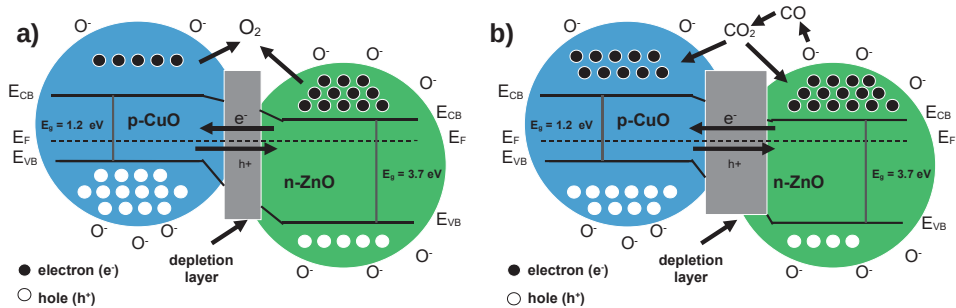
## 4.2. Preparation of metal oxide heterojunctions

Heterojunction refers to the area at the contact boundary between two semiconductors with different band gap widths. Due to the different chemical and physical parameters of both materials (i.e. band structure, dielectric constant, lattice constant, electron affinity), the phenomenon of mismatch at the interface gives heterojunctions new properties that have been used, among others, in the construction of sensors. As mentioned above, semiconductors can be divided into two types, i.e. p-type (concentration of electron holes > concentration of free electrons, e.g. CuO, NiO, Fe<sub>2</sub>O<sub>3</sub>) and n-type (concentration of free electrons > concentration of electron holes, e.g. ZnO, WO<sub>3</sub>, SnO<sub>2</sub>). Depending on what types of semiconductors will be connected, three types of heterojunctions are distinguished, i.e. n-n, p-p and p-n (or n-p).

### 4.2.1. p-n (or n-p) heterojunction

The gas sensing properties of the p-n heterojunction have been explored by many research groups for the detection of NO<sub>2</sub>, CO<sub>2</sub>, H<sub>2</sub>S, NH<sub>3</sub>, etc. (Section 5, Table 3). These sensors exhibited higher sensitivity, better selectivity and shorter response/recovery times than the devices based on single oxides. For example, Jońca et al. (submitted) have prepared and explored gas sensing properties of CuO-ZnO p-n heterojunction showing that at appropriate mass ratio of CuO to ZnO nanoparticles it is possible to detect selectively CO in the presence of C<sub>3</sub>H<sub>8</sub> and NH<sub>3</sub>. The gas sensing mechanism of p-type semiconductors combined with n-type semiconductors can be described as follows. When the CuO connects with the ZnO, an internal self-built electrical field at the interface is formed via charge carriers diffusion due to their different work functions, electron affinities and band gaps. In the electrical field, the electrons move from ZnO to CuO, whereas the holes flow in the opposite direction until the Fermi level (EF) is achieved (Figure 7a). This process leads to the creation of a potential barrier at the heterojunctions as the band bending and a wide depletion layer appears at the interface. When the system is exposed to the reducing gas, its molecules react with pre-adsorbed oxygen species and the electrons are injected back to the interfaces of the CuO and ZnO. The electrons return to the conduction band (CB) of the CuO and recombine with the holes in the valence band (VB). This process reduces the hole concentration in the CuO hole accumulation layer and increases the resistance of CuO. Additionally, the electrons injected to the ZnO CB increase the electron concentration in the ZnO layer (Yang et al., 2021). These electrons transfer from ZnO to CuO until a new equilibrium is obtained (Figure 7b). This process further

reduces the hole quantity in the VB of the CuO, which greatly increases the resistance of the CuO. This results in a significant improvement in the response of the CuO/ZnO gas sensor.



**Figure 7.** The band diagram of the ZnO/CuO heterojunction (a) in the air (RH 50%); (b) in the CO. Reprinted with permission (Kahn et al., 2005)

#### 4.2.2. p-p and n-n heterojunction

Band bending can also occur in n-n and p-p heterojunctions. For example, the n-n type heterojunction effect was studied by Zeng et al. (2019) who has shown that the  $\text{SnO}_2\text{-Sn}_3\text{O}_4$  heterostructure offers better gas sensing performance towards  $\text{NO}_2$  than a pure  $\text{SnO}_2$  sensor. The gas sensing mechanism of combined n-n semiconductors can be described as follows. Due to the different work function of  $\text{Sn}_3\text{O}_4$  (3.9 eV) and  $\text{SnO}_2$  (4.9 eV), the electrons will flow from  $\text{Sn}_3\text{O}_4$  to  $\text{SnO}_2$  until the Fermi level ( $E_F$ ) is achieved. An electron accumulation layer and an electron depletion layer is formed at the interface on the side of  $\text{SnO}_2$  and  $\text{Sn}_3\text{O}_4$ , respectively. When the system is exposed to  $\text{NO}_2$ , the electrons trapped in the accumulation layer tend to react with this oxidizing gas since it provides more active sites for the adsorption of target molecules than any other parts of the heterostructure. A good deal of electrons are drawn out in this process, decreasing the accumulation layer and leading to sharp increase of sensor resistance.

The p-p type heterojunction was investigated, for example NiO-CuO, by Wang et al. (2015). After the junction has formed at the interface between these semiconductors, a hole depletion layer and a hole accumulation layer will be created at the interface on the side of NiO and CuO, respectively. The adsorbed oxygen ions inject holes into the hole depletion layer, leading to a thinner width of the depletion layer and lower resistance than pure NiO. When the heterojunction is exposed to a reducing gas, i.e.  $\text{H}_2\text{S}$ , the reaction between  $\text{H}_2\text{S}$  molecules and the adsorbed oxygen ions will inject electrons to the sensitive layer that will combine with the holes from the accumulation layer and increase the measured resistance.

### 4.3. Decoration with noble metal nanoparticles

Numerous studies have shown that decorating metal oxide surfaces with noble metal nanoparticles (i.e. Au, Ag, Ru, Rh, Pd, Os, Ir and Pt) can improve the sensitivity, selectivity and response/recovery time of gas sensors (Section 5, Table 3). The decoration of ZnO, a typical n-type semiconductor, will be used as an example to explain the mechanism behind the improvement of the mentioned sensor parameters. Two mechanisms may illustrate the role of metal in the gas sensing mechanism described in Section 2:

- 1) Oxygen molecules tend to adsorb on noble metal nanoparticles. When exposed to the target gas, these excess oxygen molecules are “captured” by zinc oxide, which increases the number of active sites involved in detection (Nakate et al., 2016);
- 2) Since the work function of the noble metal is much higher than that of zinc oxide, the formation of a metal-semiconductor junction will cause a certain amount of electrons to flow from the surface of the metal oxide towards the metal nanoparticles. At the interface between the metal and the semiconductor, the so-called Schottky barrier is formed and equilibrium is reached (i.e. the same amount of electrons flow from the semiconductor to the metal as from the metal to the semiconductor). Adsorption of CO on the metal surface will disturb this balance, causing an increase in the flow of electrons towards the semiconductor, and consequently a decrease in its resistance (Choi et al., 2019).

The type of precious metal used to decorate the semiconductor obviously has a huge impact on the properties of the sensor. In the work of Esfandiari et al. (2012) it has been shown that TiO<sub>2</sub> nanoparticles decorated with Pd and Pt show better detection efficiency than pure TiO<sub>2</sub>, but it was in the case of Pd that the highest sensitivity and the shortest response time was obtained. Interesting results were achieved also by Kim et al. (2015) who tested the detection efficiency of four sensitive layers, including pure WO<sub>3</sub>, Au/WO<sub>3</sub>, Pd/WO<sub>3</sub> and AuPd/WO<sub>3</sub>. WO<sub>3</sub> nanorods after decoration with precious metals showed greater sensitivity to acetone, especially in the case of AuPd/WO<sub>3</sub>. While the response time has also improved with the sensitive layers containing precious metals, the recovery time has unfortunately deteriorated. This is probably due to the excessive size of the metal nanoparticles and/or the excessive coverage of the WO<sub>3</sub> nanorods.

Indeed, the concentration of precious metal nanoparticles deposited on the surface of the semiconductors can also affect the performance of the sensor. Arunkumar et al. (2017) prepared a highly selective and sensitive CO sensor by decorating hierarchical ZnO structures (3D structure) with gold nanoparticles. The work examined sensitive materials with different gold content in the sensitive layer (i.e. from 1% to 4% by weight). It turned out that as the concentration of Au nanoparticles increased from 1% to 3% by weight, the sensitivity of the sensor to the target gas increased. However, further increasing the concentration of gold (up

to 4% by weight) caused the sensitivity of the sensor to drop drastically. Increasing the concentration of noble metal nanoparticles to a certain level is accompanied by the phenomenon of their agglomeration, which in turn reduces the number of active sites and negatively affects gas diffusion in the sensitive layer.

## 5. Applications of nanotechnology solution for environmentally hazardous gases detection with MOS sensors

Examples of applications of different nanotechnology strategies for environmentally hazardous gases detection are presented in Table 3. Multiple research groups investigated the effect of morphology and dimensionality, the effect of heterojunctions and the effect of noble metal loading on gas sensing properties of metal oxide based gas sensors showing that these approaches led to the development of sensitive layers with extraordinary properties that can in the future replace gas sensing devices available today on the market.

**Table 3.** Application of different nanotechnology strategies for environmentally hazardous gases detection

Nanostructure	Target gas	Main outcome of the work	Ref
<b>The effect of morphology and dimensionality</b>			
NiO nanoparticles (0D) with different diameters	H <sub>2</sub> S	Nanoparticles with the smallest diameter obtained (i.e. 11.5 nm) turned out to be the most sensitive and selective to H <sub>2</sub> S	(Sun et al., 2012)
Isotropic and anisotropic ZnO nanoparticles (0D)	CO and NH <sub>3</sub>	Anisotropic nanoparticles exhibited higher sensitivity towards CO (and propane) but no effect of morphology was noticed for the NH <sub>3</sub> gas	(Ryzhikov et al., 2015)
WO <sub>3</sub> nanoparticles (0D), nanorods (1D), nanosheets (2D) and hierarchical nanoflowers (3D)	NH <sub>3</sub> and CH <sub>4</sub>	From among all investigated nanostructures, the 3D hierarchical nanoflowers-based gas sensor offers the best sensitivity and fastest response time	(An et al., 2020)
SnO <sub>2</sub> nanoparticles (0D) and octahedra (3D)	CO	Hierarchical structures showed greater sensitivity in the low range of CO concentrations (i.e. 0.25 - 20 ppm) than nanoparticle based sensors	(Jońca et al., 2016)
ZnO nanowires and nanoparticles	N <sub>2</sub> O	The nanowires are more effective gas sensing materials with an order of magnitude higher sensitivity values compared to the ZnO nanoparticles	(Deb et al., 2007)
<b>The effect of heterojunctions</b>			
CuO-NiO core-shell microspheres	H <sub>2</sub> S	The core-shell microspheres sensor exhibited enhanced H <sub>2</sub> S sensing properties as compared with bare CuO microspheres	(Wang et al., 2015)

Nanostructure	Target gas	Main outcome of the work	Ref
SnO <sub>2</sub> -Sn <sub>3</sub> O <sub>4</sub> hierarchical spheres	NO <sub>2</sub>	The sensitivity towards NO <sub>2</sub> was improved as compared to pure SnO <sub>2</sub> and Sn <sub>3</sub> O <sub>4</sub> sensors	(Zeng et al., 2019)
ZnO-CuO nanorods	CO <sub>2</sub>	Sensor is not sensitive to environmental gases such as CO, NO <sub>2</sub> and H <sub>2</sub> S.	(Deb et al., 2007)
WO <sub>3</sub> @SnO <sub>2</sub> core-shell nanosheets	NH <sub>3</sub>	The highest sensitivity to NH <sub>3</sub> was achieved with the shell thickness of 20 nm	(Yuan et al., 2020)
ZnO nanoparticles mixed with CuO nanoparticles	CO	At appropriate ratio of CuO and ZnO in the sensitive layer it is possible to detect selectively CO in the presence of ammonia and propane	(Jońca)
ZnO nanowires decorated with α-Fe <sub>2</sub> O <sub>3</sub> nanoparticles	CO	The sensitivity and selectivity towards CO was improved as compared to bare ZnO nanowires	(Lee et al., 2019)
NiO-ZnO nanodisks	SO <sub>2</sub>	High sensitivity towards SO <sub>2</sub> with short response time and good stability (30 days) was achieved with the NiO-ZnO nanodiscs-based sensor	(Zhou et al., 2019)
<b>The effect of noble metal loading</b>			
Au loaded ZnO nanoparticles	CO	The Au/ZnO sensor containing 3% mass. gold showed the best CO detection performance	(Arunkumar et al., 2017)
Au loaded ZnO nanorods	NO <sub>2</sub> and NH <sub>3</sub>	The sensor showed selectivity to NH <sub>3</sub> in dark and selectivity to NO <sub>2</sub> in visible-light.	(Wang et al., 2020)
Pd loaded ZnO nanoparticles	NH <sub>3</sub>	Pd loaded ZnO nanoparticles allow sensitive and quite selective detection of NH <sub>3</sub> in presence of H <sub>2</sub> S, CO, CH <sub>4</sub> and NO <sub>2</sub>	(Mhlongo et al., 2019)
Pt or Au loaded WO <sub>3</sub> nanoparticles	SO <sub>2</sub>	The lowest detection limit and the highest selectivity were achieved with Pt/WO <sub>3</sub> (1% Pt mass) allowing detection of SO <sub>2</sub> in the presence of, among others, NO <sub>2</sub> and NH <sub>3</sub>	(Liu et al., 2021)
Ag loaded ZnO hierarchical microspheres	CO and CH <sub>4</sub>	The Ag/ZnO nanostructure exhibit superior gas sensing performance than bare hierarchical ZnO microspheres. Moreover, the sensor exhibits temperature-modulated dual selectivity detection for CO at 130°C and CH <sub>4</sub> at 200°C	(Wang et al., 2021)
Ag, Au or Pt loaded TiO <sub>2</sub> nanoparticles	NO	The highest sensitivity towards NO was achieved with Au/TiO <sub>2</sub> nanostructure. Interestingly, loading with Pt has a negative impact on NO sensing performance, whereas the Au addition has no impact on it	(Karmaoui et al., 2017)
Pt loaded SnO <sub>2</sub> hierarchical nanoflowers	CH <sub>4</sub>	The Pt-doped SnO <sub>2</sub> nanoflowers significantly improve the sensitivity and reduce optimal operating temperature as compared to undoped SnO <sub>2</sub>	(Xue et al., 2019)

## 6. Conclusions and future trends

This mini-review presents several solutions to improve the efficiency of gas detection using sensors based on semiconductor metal oxides designed at the nanoscale, i.e. control of the morphology of nanostructures, formation of heterojunctions and decoration of metal oxide nanoparticles with noble metals (e.g. Pt, Pd, Au). In general, the morphology of nanostructure significantly influences the gas detection performance and can even be considered as the basis for the design of MOS sensors. The preparation of heterojunctions is relatively simple and gives unlimited possibilities to create new combinations and consequently new gas sensors. In order to further improve the properties of sensitive layers noble metal nanoparticles can be combined with the ordered structure and morphology of metal oxide nanoparticles.

While many approaches have been proposed, there is still much work to be done. Unfortunately, in most works, although high sensitivity, satisfactory selectivity or short response/recovery time are achieved thanks to the different nanotechnology approaches, the problem of sensor stability is ignored or the presented results refer to short observations (e.g. 1 month). One of the reasons for the occurrence of signal drift over time is the nanoparticle aggregation at high temperatures. This process changes properties of the sensitive layer and as an effect the parameters of the sensor over time. The agglomeration can be prevented by using low-temperature synthesis techniques and by lowering the operating temperature of the sensor. That is why researches focus today on the design of sensors that could operate at low temperatures (Cui et al., 2013; Zeng et al., 2019; Li et al., 2019). Higher stability can also be achieved with 1D nanomaterials (nanorods, nanofibers, etc.), which generally have a higher degree of crystallinity and larger flat surfaces than spherical nanoparticles (Arafat et al., 2012).

The repeatability of sensor fabrication is not often described in the literature either, but is essential if these devices are to be commercialized in the future. Manufacturing methods should allow precise control of thickness of the sensitive layer and the size of nanoparticles. This seems especially important in the case, for example, of core-shell type nanoparticles. The Debye length of core-shell nanoparticles should be of the same order as the thickness of the shell itself. Therefore, if the thickness of the coating is a few nanometers higher than the Debye length, the sensor response may be much lower than expected. The highest degree of control of the synthesis of core-shell systems is provided by deposition plasma (e.g. sputtering, PLD and ALD) (Vander et al., 2009). However, much cheaper methods such as spin-coating and dip-coating may be good enough for some applications.

Increasingly, gas sensors are constructed with the use of platforms developed in MEMS technology (i.e. microelectromechanical system), with which not all techniques for the preparation of sensitive layers are compatible (Vander et al.,



2009). For example, the popular screen-printing method is very difficult to apply with MEMS systems in which the deposition region is smaller than  $100\text{ mm} \times 100\text{ mm}$ . Metal oxide nanoparticles can be precisely deposited in the form of thin layers by ink jet printing. However, agglomerates of nanoparticles larger than  $5\text{ }\mu\text{m}$  may block the print head. Other methods such as CVD or PLD are also interesting solution provided that proper masking techniques are used to protect adjacent sensor elements.

To sum up, in the coming years, research should be conducted not only to develop new sensitive layers, but also to ensure that these sensors show a stable response over time to the target gas, as well as to deliver technologies for effective and reproducible deposition of nanoparticles on the MEMS devices.

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## CZUJNIKI NA BAZIE NANOCZĄSTEK TLENKÓW METALI I ICH ZASTOSOWANIE W DETEKcji GAZÓW NIEBEZPIECZNYCH DLA ŚRODOWISKA

### Abstrakt

Niebezpieczne gazy mają niekorzystny wpływ na organizmy żywe i środowisko. Zaliczamy do nich gazy toksyczne (np.  $H_2S$ ,  $SO_2$ ,  $CO$ ,  $NO_2$ ,  $NO$  i  $NH_3$ ), gazy cieplarniane (np.  $N_2O$ ,  $CH_4$  i  $CO_2$ ). Co więcej, ich obecność w zamkniętych pomieszczeniach może doprowadzić do pożarów, spowodować poważne problemy zdrowotne, a nawet doprowadzić do śmierci. Monitorowanie tych substancji za pomocą czujników gazowych może pomóc uniknąć wypadków i uratować życie. Półprzewodnikowe czujniki gazowe na bazie tlenków metalu (MOS) są jednymi z najpopularniejszych w tych zastosowaniach ze względu na swoje liczne zalety, takie jak wysoka czułość, długa żywotność i krótki czas odpowiedzi. Urządzenia te mają również swoje ograniczenia, tj. wykazują dryft odpowiedzi w czasie, mogą ulec dezaktywacji i charakteryzują się słabą selektywnością, dlatego nadal prowadzone są badania nad poprawą parametrów czujników MOS.

Ścisła kontrola procesu przygotowania materiałów czułych jest jedną z metod pozwalających na poprawę wydajności czujników MOS. Stwierdzono, że nanomateriały są bardziej odpowiednie do wykrywania gazów niż ich odpowiedniki zaprojektowane w mikroskali. Stwierdzono również, że regularna i uporządkowana morfologia nanostruktur tlenków metali, pokrywanie ich nanocząstkami metali szlachetnych lub tworzenie heterozłączy może poprawiać skuteczność wykrywania gazów. W przedstawionej pracy dokonano przeglądu metod syntezy i zastosowania nanocząstek tlenków metali w konstrukcji czujników gazów niebezpiecznych dla środowiska. W artykule omówiono również aktualne problemy i przyszłe kierunki badań nad zastosowaniem nanotechnologii do detekcji gazów.

**Słowa kluczowe:** nanocząstki metali, nanocząstki tlenków metali, heterozłącze, czujniki gazu, gazy niebezpieczne

