Metal Oxide Nanostructures for Sensor Applications

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Abstract

Human health, environmental protection and safety are just a few examples of current humankind main concerns, that drive the scientific community to develop sensors able to precisely monitor and alert to possible harms in real time. Over the years, semiconductor metal oxide-based materials have been largely employed as sensors dedicated to several applications, being particularly interesting at the nanometer scale, since it is largely known that smaller crystallite size enhances sensor's performance. Moreover, these materials are highly appealing as they can be produced by low-cost wet-chemical synthesis routes and are in general nontoxic, earth abundant and low-cost. This manuscript extensively reviews the recent developments of nanostructured semiconductor metal oxide sensors ranging from gas to humidity sensors, including ultraviolet (UV) sensors and biosensors. Zinc oxide (ZnO), titanium dioxide (TiO_2), tungsten trioxide (WO_3), copper oxide (CuO and Cu_2O), tin oxide (SnO and SnO_2), and vanadium oxide (VO_2, V_2O_5)-based sensors either as nanoparticles or as continuous films/layers are described. Their sensing properties are correlated to size, shape, presence of defects, doping elements, amongst other relevant parameters. Different techniques and methods of fabricating these materials are addressed. The review is concluded with novel approaches for functionalization and future perspectives for sensor developments.

Keywords: semiconductor metal oxides; low-cost materials; nanostructures; sensors; sensing properties.

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1. Introduction

1.1 Metal oxide nanomaterials

Nanotechnology is compromised as a group of novel technologies capable of designing, producing, characterizing and controlling structures, materials, devices and systems at the nanometer scale, i.e. less than 100 nanometres. This term is very transversal, being used across many fields, such as chemistry, medicine, biology, physics, materials science, environment, engineering, amongst others. The structures or materials at the nanometer scale can be classified as: 0D (zero dimension) if all three spatial dimensions are in the nanometric range, *i.e.* nanoparticles or clusters; 1D (one dimension) if two dimensions are in the nanometric range, like nanotubes, nanorods and nanowires; or 2D (two dimensions) if only one spatial dimension is nanometric, such as in thin films or nanosheets. 3D (three dimensional) materials implies that the 0D, 1D and 2D elements are in close contact forming interfaces, for example compact polycrystals with nanosized grains or 3D porous nanostructures (Figure 1) [1].

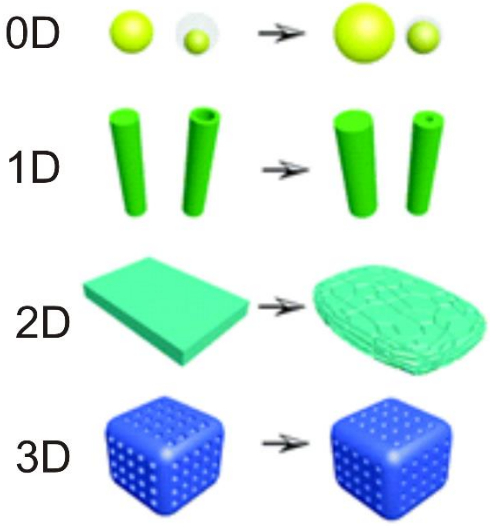


Figure 1. Scheme of the types of nanostructured materials based on their dimensions: 0D, 1D, 2D and 3D [1]. Reproduced with permission of *Royal Society of Chemistry* (2018).

Nanosized materials possess unique and enhanced chemical, physical and mechanical properties when compared to their bulk counterparts due to their high specific surface area and surface-to-volume ratio [2-4]. Generally, the high surface-to-volume ratio of nanomaterials increases as nanoparticle size decreases [5]. Moreover, the size reduction of materials gives rise to quantum confinement phenomena, which modify their intrinsic properties with respect to their corresponding bulk materials [6]. Nanomaterials can occur in several morphologies ranging from nanorods, nanowires, nanowhiskers, nanoflakes, nanocubes, nanopillars, nanospheres, and others [3, 7, 8]. Carbon-based, metal, ceramic, polymeric and metal oxide nanoparticles are well-known classes of nanoparticles [3]. The latter are largely investigated since these are earth abundant, environmentally benign, low cost and, in some cases, chemically stable with suitable electrical and optical characteristics [9-16]. Moreover, these materials display exceptional properties that include mechanical stress tolerance, high optical transparency, high carrier mobilities, wide band gap, high dielectric constant, superconductivity, amongst others [16, 17]. Metal oxides are ionic compounds composed by positive metallic and negative oxygen ions [16], and can exhibit metallic, semiconductor or insulator characteristics [18]. In metal oxides, although the s-shells of positive metallic ions are always fully filled by electrons, their d-shells may not be completely filled [19]. Semiconductor metal oxides can either be classified as *n*-type, in which electrons are the majority charge carriers, or *p*-type, in which the majority charge carriers are holes.

Metal oxide electronic, physical and chemical properties can be engineered by modifying their size, structure, composition, stoichiometry and by doping [4, 20]. Nevertheless, the electronic structure range of these materials is extensive, being divided into two main categories, i.e. transition and non-transition metal oxides, where the latter englobes the pre- and post-transition metal oxides. Transition metal oxides are known to have small energy difference between a cation d^n and either a d^{n+1} or d^{n-1} configuration, which allows a fast transformation between the different forms, however with unstable structures. Metal oxides with d^0 and d^{10} electronic configurations are characterized as materials with stable properties. The d^0 configuration is found in transition-metal oxides such as, TiO_2, V_2O_5 and WO_3, whereas d^{10} configuration is found in post-transition-metal oxides, as ZnO or SnO_2. Regarding the pre-transition-metal oxides, these are expected to be inert in several applications, since these have large band gaps, electrons and holes are hardly formed [21]. In general, nanoparticles of metal oxides have high density of corner or edge surface sites [22].

Over the years, semiconductor metal oxides have been extensively studied for applications ranging from solar cells [23-26], passing through their integration in electrochromic devices [27-30], lithium-ion batteries [31-33], photocatalyst agents [9, 10, 14, 34-38] and as sensors [39-42]. The interest on the latter application with semiconductor metal oxides has been reported half a century ago and has been increasing along the years due to their practical applications in everyday life, as well as in environmental protection, bio detection, to name just a few. Nowadays, semiconductor metal oxide nanostructures are widely chosen to be integrated in sensors due to their exceptional intrinsic properties associated to their high surface-to-volume ratios, high surface reaction activity, high catalytic efficiency, strong adsorption ability, and electron and phonon confinements [43]. Gas sensors are amongst the most common sensing devices, in which semiconducting metal oxides are frequently used as gas-sensing materials [44]. Another type of sensor where metal oxides are largely present are humidity sensors, which normally determine the amount of water vapor present in a gas that can be a mixture, such as air, or a pure gas, such as nitrogen or argon [45]. UV photosensors/photodetectors are also frequently used in terms of sun/UV exposure, as well in environmental safety, flame detection, among others [46]. And finally, biosensors that are designed to have a fast response, be low-cost and portable in both clinical and non-clinical applications [47].

1.2 Sensors for different applications

Detection systems for monitoring air and water quality using semiconductor metal oxides are of great interest to improve the selectivity and sensitivity of current sensing devices, and at the same time allowing simultaneous measurements of numerous parameters with real-time response [48]. In the literature, application of metal oxides in gas sensors is vast, with several studies reporting the advantages of integrating these materials in such devices, as well as their gas sensing performance in respect to the size properties [21, 44, 49-52].

The gas sensing technology is largely spread in different industrial fields, but also in domestic environments, some examples are the automotive industry, for indoor air quality control, greenhouse gas monitoring, among others [52]. The most important parameters of gas sensor devices are their sensitivity, operating temperature, selectivity, long-term stability, energy consumption, reversibility, low humidity dependence and finally production cost [44, 52]. Thus, for these devices to be commercially viable, they must be stable during operation, with a uniform and reproducible signal for a prolonged period of time, despite being able to precisely detect a specific gas even in mixtures of different gases. Moreover, the precise control of metal oxide electronic and structural properties, including grain size distribution, local doping, grain boundaries and surface states is mandatory to obtain optimized performance of such devices [53].

Liu *et al.* [52] has classified gas sensors based on their sensing methods in two groups: (a) methods based on variation of electrical properties and (b) methods based on variation of other properties. Semiconductor metal oxide gas sensing relies on the variation of electrical properties [49]. Gas sensors based on ZnO, TiO_2, SnO/SnO_2, WO_3, CuO/Cu_2O, and V_2O_5 are commonly used to detect combustible, reducing, and oxidizing gases [41, 52, 54-59], and sensing is mainly based on the resistance change responses to the target gases [52]. SnO_2 followed by WO_3 (Figure 2 (a)) are the most commonly used semiconducting metal oxides in commercial gas sensors [60]. In general, reducing gases, such as H_2S, NH_3, CO, H_2, SO_2, CH_4, and HCHO cause an increase of conductivity in *n*-type semiconductors and a decrease in *p*-type semiconductors, while the opposite effect is observed for oxidizing gases (NO, N_2O, NO_2, CO_2, O_3 and Cl_2) [61, 62].

Humidity sensors have been receiving a lot of attention in industrial, medical and even in domestic environments for human comfort. For example, these devices are employed in microelectronic and automobile industries, but also in the pharmaceutical field, food processing, humidity control in hospitals and houses, among other applications [45]. The humidity sensor performance is directly related to the properties of the sensing material including porosity, surface area, pore size distribution and morphology [63]. In similarity to the gas sensors, these devices are expected to have constant response, high sensitivity, fast response time, negligible hysteresis, chemical and physical stability, wide operating humidity range and low cost [64].

There are several humidity evaluation terms, nevertheless the most accepted are absolute and relative humidity (RH), where the latter is normally described. Per million by weight (PPM_w) or volume (PPM_v) and dew/frost point (D/F PT) are subclasses of absolute humidity [45, 65]. Generally, RH is temperature dependent, and can be described by Equation 1 [65]:

$$RH = \frac{P_V}{P_S} \text{x } 100 \qquad (1)$$

where P_V is the actual partial pressure of water vapor present in a gas and P_S is the saturated vapor pressure of the gasat a given temperature. Nowadays, RH sensors are largely commercialized and can be categorized into three classes, *i.e.* ceramic-based sensors, organic polymer-based sensors, and organic/inorganic hybrid sensors (polymer/ceramic). Ceramic-based sensors can be designed using either semiconducting or dielectric metal oxide materials. Moreover, these sensors are divided into two groups in accordance to their sensing mechanisms, *i.e.* impedance (resistive) or capacitive categories, in which the former uses the conductance, and the latter, the capacitance properties of the sensing layer. Impedance-based sensors are subdivided into ionic-conduction and electronic-conduction. The *p-n* heterojunction humidity sensors are also included in ceramic-based sensors [65]. Different approaches have also been suggested, in which an integrated solution having a humidity sensor chip that contains humidity sensors of capacitive type is shown on Figure 2 (b) [66].

Another kind of devices that have recently drawn growing attention are UV sensors/photodetectors, which are interesting for everyday life in terms of sun/UV irradiation exposure, but also for environmental safety, medicine, military defence, flame detection, environmental sensors, space exploration, among others [67, 68]. UV photodetectors detect light in the ultraviolet wavelength ranging from 100 nm to 400 nm.

A high-performance photodetector must have high sensitivity and spectral selectivity, as well as a fast and linear response speed, together with high light transmission and improved chemical and physical stability [69, 70]. The most important parameters of photodetectors are sensitivity, responsivity and external quantum efficiency (EQE) [69]. These parameters are normally used to categorize the UV sensor performance. UV photodetector sensitivity is given by Equation (2) [69], while the responsivity is estimated according to the Equation (3) [13, 71]. The external quantum efficiency, which is defined as the number of electrons detected per light photon, [69, 72] can be obtained by Equation (4).

$$S = \frac{\Delta I}{I_{dark}} \text{ x } 100 \qquad (2)$$

$$R = \frac{\Delta I}{P_{UV}} \qquad (3)$$

$$EQE = \frac{hc}{e\lambda} . \frac{I_{ph} - I_{dark}}{P_{UV}} \qquad (4)$$

where ΔI is the difference between the photocurrent and the dark current, I_{dark} is the dark current, and P_{UV} is the UV light power, h is Planck's constant, c is the speed of light in vacuum, e is the electron charge, and λ is the exciting wavelength. Several photodetectors types have been reported, including photoconductors, metal-semiconductor-metal (MSM) photodetectors, Schottky photodiodes and *p-n* junction photodiodes. A photoconductor is composed by a semiconductor material with two ohmic contacts, forming a radiation-sensitive resistor. MSM photodiodes are based on two back-to-back Schottky diodes and using an interdigitated electrode configuration on top of the active layer. Schottky diodes consist of a metal layer that contacts a semiconductor material, and the metal/semiconductor junctions exhibit rectifying behaviour. *p-n* junction photodiodes are based on a heterojunction of a *p-* and *n-* type materials, without the requirement of a reverse bias and displaying improved noise performance [73]. The *p-i-n* has an intrinsic layer and provides additional sensitivity and performance over that of the basic *p-n* junction photodiode due to the reveres bias operation. Nevertheless, innovative approaches to extract the best photodetector performance, more recently with nanostructured metal oxides, are under constant development (Figure 2 (c)).

Metal oxide nanostructures are also widely present in biosensors. A biosensor is described as a sensing device that combines a transducer for signal detection with a biologically sensitive and selective component, *i.e.* bioreceptor (antibody, enzyme, receptor protein, nucleic acid, whole cell or tissue section). Typically enzymes are used as bio component, and they are large protein molecules that act as a catalyst in chemical reactions, remaining unchanged during the process [74]. Upon interaction of a target molecule with the bio component, a signal is generated and detected by the transducer (Figure 2 (d) [75]). It is possible to occur optical or electrical signals [76]. This signal is proportional to the concentration of the component. The target molecules/analytes can be proteins, DNA, glucose, cholesterol, toxins, hormones, bacteria, among others [77]. These devices are considered a powerful analytical tool in medical diagnostics with the fast and precise detection of diseases, virus , food quality and safety, fermentation industry, in metabolic engineering and other areas [47, 78]. The device is expected to be highly accurate, homogeneous and reproducible, despite having optimized response time, high stability, sensitivity, specificity, selectivity (low interference) and bioactivity [76, 79].

There are many types of biosensors, in which these are mainly classified according to bioreceptors and transducers. The most common are immunosensors, calorimetric, DNA, enzyme-based, tissue-based, optical, thermal, optical, piezoelectric and electrochemical biosensors, in which the latter is subdivided in conductimetric, amperometric and potentiometric sensors [74, 78]. The most successful commercial biosensor is the amperometric glucose biosensor, with which diabetic patients are able to periodically monitor blood glucose levels [74]. Nevertheless, the full integration of metal oxides nanostructures in biosensors still raises questions regarding the maintenance of their bioactivity for extended periods of time and their toxicity.

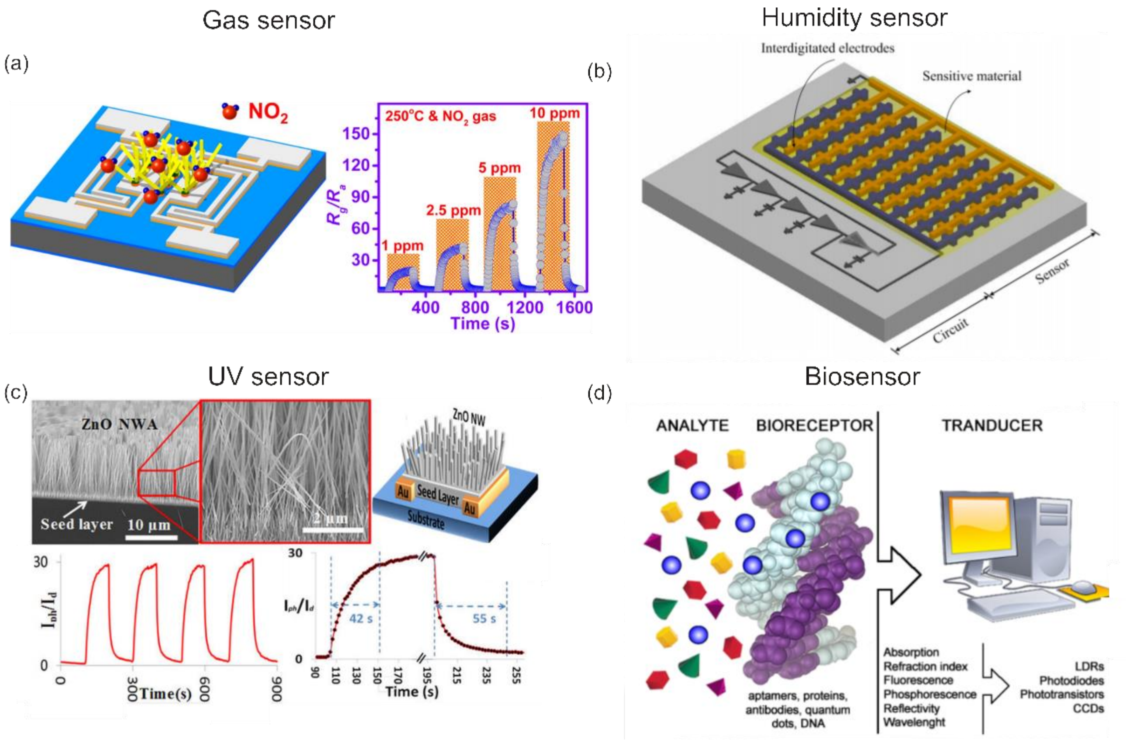


Figure 2. (a) Gas sensor and its respectively gas sensing characteristics for NO_2 [80], (b) integrated humidity sensor [66], (c) photoresponse characteristics of a UV photodetector [81] and (d) biosensor detection process [75]. Reproduced with permission of *Elsevier* [80], *MDPI* [66], *Springer Nature* [81], and *Intech* (2018) [75].

1.3 Sensing mechanisms

The mechanisms responsible for gas, humidity and UV responses have similar concepts. Despite being a controversial topic, the mostly accepted mechanism for these sensors is resultant of a change in electrical conductivity or resistivity of the semiconductor metal oxide materials [82, 83]. In the case of gas sensors, the gas sensing is resultant of a shift on equilibrium of the surface chemisorbed oxygen reaction due to the presence of a target gas, creating extrinsic surface acceptor states that immobilize conduction band electrons from the near-surface region of an *n*-type semiconductor material. For *p*-type semiconductor materials, the chemisorption of oxygen leads to an accumulation surface layer which alters their conductance [44, 61]. Under ambient conditions, the oxygen molecules are adsorbed on surface of the *n*-type semiconductor materials and can capture inner free electrons from of these materials. The negative charge trapped in these oxygen species causes a depletion layer near the surface, which results in the reduction of the conduction layer $[O_{2(g)} + e^- \rightarrow O_2^-{}_{(ads)}]$ [71, 82]. When the sensor is exposed to reducing or oxidizing gases, this will affect the density of charge carriers (*n*-type electrons or *p*-type holes) in the near-surface region of each grain. Reducing gas molecules will remove surface-bound oxygen atoms, releasing immobilised electrons, whereas oxidising gases immobilise conduction-band electrons from the near-surface region by creating additional surface-acceptor states. Thus, the gas molecules will result in the decrease or increase of the depletion layer thickness by changing the surface-state density, which in consequence leads to a change in the materials' conductance [44].

In summary, upon interaction with oxidizing gases, the gas species will act as acceptors, which will lead to a resistance increase for *n*-type semiconductor metal oxides. When the oxidizing gases are adsorbed on *n*-type material surface, it will gain electrons from the adsorbed oxygen, which will increase the depletion region, and thus decrease its conductivity [39]. The opposite behaviour is observed for *p*-type metal oxide materials. Figure 3 (a) shows the negative surface charge causing the upward band bending of conduction (E_C) and valence (E_v) bands, the electron depleted region (space-charge layer), the average thickness, *i.e.* the depth of band bending region (q.Vs), and the effective surface potential barrier (eV). The depth and height (eV) of the band bending depend on the overall surface charge present (amount and type of adsorbed oxygen). In Figure 3 (b), it is represented the grain boundary structures and corresponding band models showing the electron conduction mechanism. In polycrystalline sensing materials, the electronic conductivity occurs through the percolation paths along grain-to-grain contacts depending on the value of potential barrier (eV) or Schottky barrier of the surrounding grains. Upon gas exposure, the Schottky barrier between two grains is lowered facilitating the electronic conduction in sensing layers through different grains via grain to grain percolation path [84].

In fact, the gas adsorption on the surface and the change in the resistance of metal oxide semiconductors are quite complex processes. It has been accepted that the sensor resistance is a function of the gas partial pressure, following a power-law response, in which the power-law exponent is specific to the gas and temperature used [85-87]. Several studies have extensively discussed the processes, including when using metal oxide nanostructures. In the case of metal oxide nanowires, the conductivity for *n*- and *p*-type materials, Equations 6 and 7, respectively, can be described as [88, 89]:

$$G_n = \frac{\sigma_d}{\ell}\pi\left(\frac{D}{2} - L_{D_n}\right)^2 = N_d q \mu_n \frac{\pi(D-2L_{D_n})^2}{4\ell} \qquad (6)$$

$$G_p = \frac{\sigma_a}{\ell}\pi\left(\left(\frac{D}{2}\right)^2 - \left(\frac{D}{2} - L_{D_p}\right)^2\right) = N_a q \mu_p \frac{\pi(D L_{D_p} - L^2{}_{D_p})}{\ell} \qquad (7)$$

where $\sigma = q\mu N$ is the conductivity of the nanowire; D is its diameter; ℓ is the length; N is the carrier concentration; μ is the carrier mobility; q is the carrier charge; and L_{Dn} and L_{Dp} are the thicknesses of the depletion and accumulation layers, respectively.

The gas-sensing response for *n*-type (Equation 8, (S_{OX}^{n})) and *p*-type (Equation 9, (S_{OX}^{p})) semiconducting metal oxide to an oxidizing gas can be defined as [62]:

$$S_{OX}^{n} = \frac{R_{og}}{R_a} \qquad (8)$$

$$S_{OX}^{p} = \frac{R_a}{R_{og}} \qquad (9)$$

where R_{og} and R_a are the sensor electrical resistances measured with an oxidizing gas and pure dry air, respectively.

In the case of reducing gases, the gas species act as donors, *i.e.* electrons will be injected into *n*-type material surface, reducing the depletion region and releasing the band bending, and this will lead to a resistance decrease in the case of *n*-type materials and increase for *p*-type materials [39, 61]. The gas-sensing response for *n*-type (Equation 10, (S_{rd}^{n})) and *p*-type (Equation 11, (S_{rd}^{p})) semiconducting metal oxide to a reducing gas is normally represented as [62]:

$$S_{rd}^{n} = \frac{R_a}{R_{rg}} \tag{10}$$

$$S_{rd}^{p} = \frac{R_{rg}}{R_a} \tag{11}$$

where R_{rg} and R_{a} are the sensor electrical resistances measured with an reducing gas and pure dry air, respectively.

Mechanisms of water vapor adsorption on metal oxide surfaces have been well studied [45, 90, 91], and it is known that most metal oxides have adsorbed hydroxyl groups on their surface which influences the surface phenomena, including the response of a sensor to the detected gas [92]. In general, water molecules can be adsorbed by an acid-base type dissociative chemisorption followed by hydrogen bonded physisorption, however some oxides can also chemisorb water vapor through redox reactions involving electron transfer to the metal oxide [63, 92]. Moreover, water molecules have been reported to increase the conductivity of *n*-type semiconductor metal oxides and to decrease the conductivity of *p*-type semiconductor metal oxides, in which this effect was related to the donation of electrons from the chemically adsorbed water molecules to the oxide surface [67, 91].

The mechanism of all the ceramic humidity sensors, of ionic and electronic conduction (resistive) types and capacitive, depends on the superficial water vapour adsorption, which is based on chemical and physical adsorptions and capillary condensation processes. Resistivity-type humidity sensors measure the electrical resistance in response to humidity. Most of the available humidity sensors utilize the ionic type humidity-sensing mechanism. In ionic sensing devices, when the ceramic surfaces adsorb water, their electrical properties change, and by increasing the humidity, the conductivity increases and thus the dielectric constant increases [65, 93]. On the other hand, capacitive-type humidity sensor mechanism relies on electrical permittivity that is sensitive to humidity variation, and the electrical response is linked to water adsorption-desorption processes on the exposed surface of the sensing material [94].

The UV sensing process occurs when the semiconductor metal oxide with oxygen molecules adsorbed on its surface and without any UV irradiation, can capture free electrons present in the *n*-type semiconductor and form a low conductivity depletion layer in the near-surface region. When exposed to UV irradiation at a photon energy above the materials' band gap, electron-hole pairs are photogenerated [$hv \rightarrow e^- + h^+$], and the holes migrate to the surface along the potential slope. This potential slope is produced by band bending and discharge of negatively charged adsorbed oxygen ions through surface electron-hole recombination, leading to oxygen photo desorption [95] [$h^+ + O_2^-{}_{(ads)} \rightarrow O_{2(g)}$] (Figures 3 (c) and (d)). This hole-trapping mechanism through oxygen adsorption and desorption enhances the high density of trap states due to the dangling bonds at the surface and thus enhances the photoresponse [96]. The stability and performance of UV sensors are highly influenced by the surrounding environment. Several studies reported that the photodetection of metal oxide nanostructured sensors is strongly dependent on the ambient gas conditions, with significant differences regarding measurements in air, vacuum or inert gases [97-99].

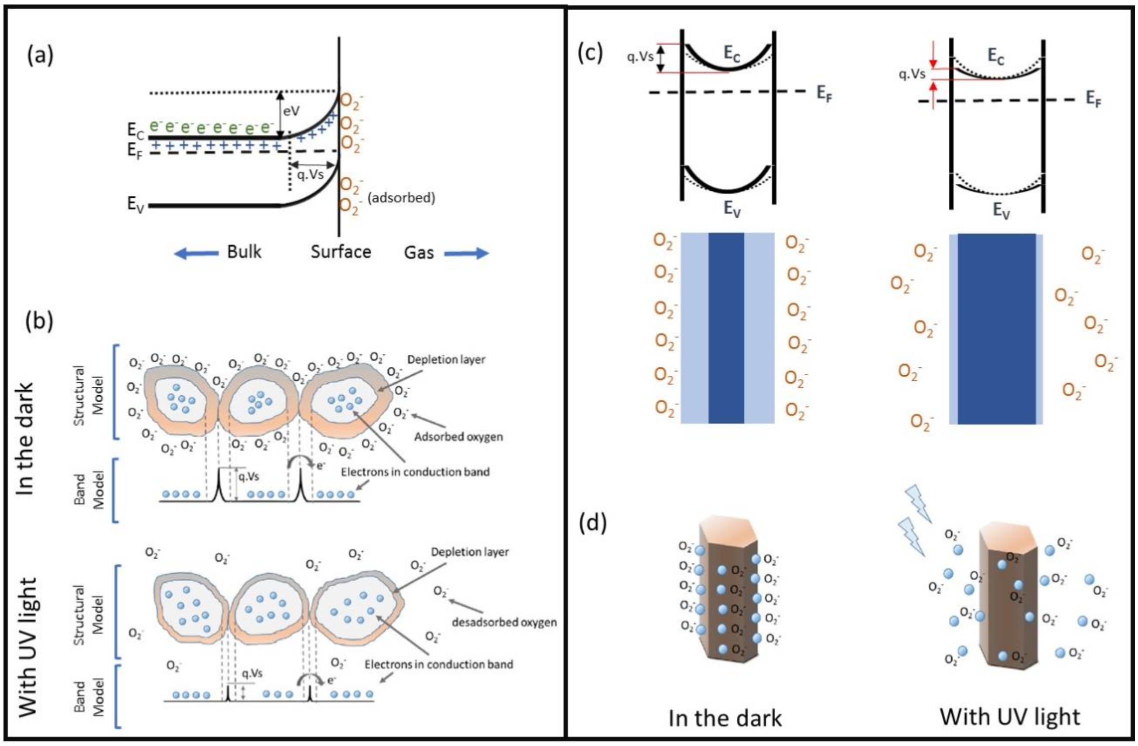


Figure 3. (a) Scheme of the band bending in a wide band gap semiconductor after chemisorption of charged species on surface sites (E_C and E_V are the conduction and valence band energies in the grain bulk, respectively, E_F is the Fermi level, e^- is the conducting electrons and $^+$ the donor positions [49, 85]. (b) Schemes of the structural and band models of a *n*-type semiconductor, and (c) and (b) dark and UV irradiation processes [71, 88]. Reproduced with permission *MDPI* [71], and *Elsevier* [49], [85] and [88] (2018).

Regarding biosensors, as previously described, the devices combine a biological element with a transducer to detect specific target analytes and thus produce quantifiable and processable signals [47, 77, 100]. Generally, the measurement of electrical properties in biological systems is from electrochemical nature, in which the bioelectrochemical element will act as the main transduction element. Moreover, for electrochemical detection, enzymes are mostly used, due to their specific binding capabilities and biocatalytic activity. Antibodies, antibody fragments or antigens are usually used in immunosensor to monitor binding events in bioelectrochemical reactions [100]. These electrochemical detection techniques can generate a measurable current (*amperometric*), a measurable potential or charge accumulation (*potentiometric*), or change in the medium conductive properties between electrodes (*conductometric*), but also measurements as function of impedance, both resistance and reactance (*impedimetric)*, and using transistor technology (*field-effect*) to measure current as a result of a potentiometric effect at a gate electrode [100].

Recently, metal oxide materials have been integrated in novel biosensing devices, since they exhibit enhanced electron-transfer kinetics and strong adsorption capability. These properties guarantee appropriate microenvironments for the immobilization of bio molecules and result in enhanced electron transfer and improved biosensing characteristics. The biosensing process involving metal oxide materials relies on the biomolecules binding to these materials via physical adsorption or chemical binding. Physical adsorption of a biomolecule depends on several parameters such as surface morphology, reaction medium and net surface charge, especially when it arises due to weak interactions, such as van der Waals, electrostatic and physisorption. Nevertheless, short-range forces including charge, steric, depletion and solvent interactions can also affect the biointerface. An effective biointerface with metal oxide materials guarantees an enhanced electron transfer rate and assists the biomolecule to maintain a stable biological activity [47]. It has also been reported that adding metal oxides to unlike surfaces can increase the adhesion of negatively-charged bacteria due to their positive charge and hydrophobicity, this is of particular importance for producing high performance biosensing devices [101].

This review will address the two main types of nanostructured semiconducting metal oxide sensors including *n*-type, *i.e.* zinc oxide, titanium dioxide, tungsten oxide, tin dioxide, and vanadium oxides, but also materials displaying *p*-type characteristics, *i.e.* copper oxides and tin monoxide. Their sensing properties, production techniques and methods will be discussed from an application-oriented perspective. An overview on different sensors such as gas, humidity, UV and biosensors having these nanomaterials integrated will also be presented.

2. Semiconductor metal oxide nanostructures

Semiconductor metal oxides have been largely employed in electronics and opto-electronics with their incorporation on transistors, circuits, or panel displays, and more recently on printed and paper electronics [102-104]. Nevertheless, the sensing technology has evolved over the last years and continues to grow to guarantee human well-being, quality and safety from food to air, but also for environmental protection. ZnO, TiO_2, WO_3, CuO/Cu_2O, SnO/SnO_2 and VO_2/V_2O_5 are examples of such materials and have been integrated in several kinds of sensors, *e.g.* gas, humidity, UV and biological sensors. These materials can adopt the most distinct structures at the nanoscale, ranging from nanowires to nanospheres or nanosheets, which will directly influence their performance in the final sensing applications.

2.1 Zinc oxide

Zinc oxide has been extensively studied since 1935 due to its integration in several applications with special interest in ZnO-based electronic and optoelectronic devices. ZnO is an *n*-type semiconductor with a wide band gap of 3.2-3.4 eV and a large exciton binding energy of 60 meV at room temperature [105]. At room temperature and pressure, ZnO crystallizes in the hexagonal *wurtzite* structure in which each anion is surrounded by four cations at the corner of a tetrahedron [105]. Other structures may appear like "*zinc blend*" (the term is originated from compounds like ZnS that can present cubic or hexagonal phases) and "*rocksalt*" (with a cubic phase) but, under ambient conditions they are not thermodynamically stable phases. Hexagonal ZnO *wurtzite* structure has a unit cell with lattice constants $a = 0.3296$ nm and $c = 0.52065$ nm [106] and ratio $c/a = 1.602$, corresponding to *P6₃mc* space group [105, 107]. This ZnO space group is characterized by presenting two interconnecting sublattices of Zn^{2+} and O^{2-} ions in which each zinc ion is surrounded by a tetrahedral of four oxygen ions [105]. The zinc and oxygen ions are arranged alternatively along the *c*-axis and exhibit positive and negative polar plane rich in Zn^{2+} and O^{2-}, respectively. This Zn^{2+} and O^{2-} tetrahedral coordination is the origin of a polar symmetry along the hexagonal axis [105, 108]. This asymmetry along the *c*-axis is responsible by an anisotropic growth of 1D ZnO crystallites. The most common and stable ZnO crystal exhibit a *wurtzite* structure with four face terminations – the polar Zn terminated (0001) and O terminated $(000\bar{1})$ facets, and the non-polar $(10\bar{1}0)$ facets, containing equal number of Zn and O atoms [14, 105, 108-110]. Figure 4, shows a schematic representation of the ZnO hexagonal *wurtzite* structure facets and an atomic model of the polar and non-polar facets.

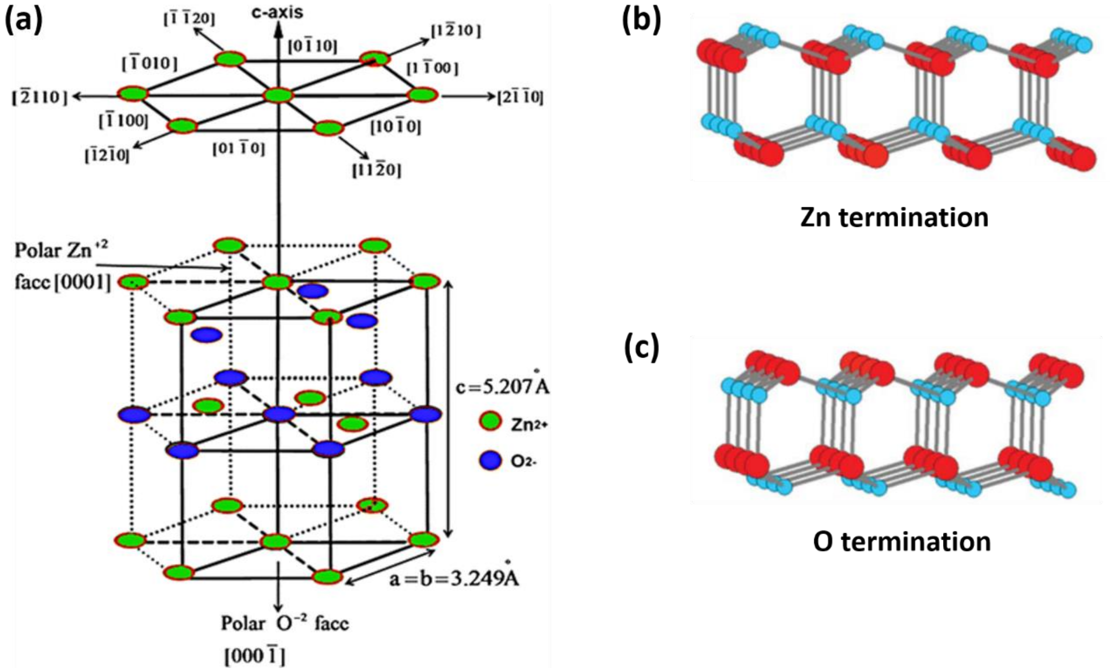


Figure 4. (a) Schematic of the unit cell of the ZnO hexagonal wurtzite structure and the correspondent ionic position of Zn^{2+} and O^{2-} [107]; (b) and (c) Side view of ZnO *wurtzite* facets with (0001) Zn and $(000\bar{1})$ O termination, respectively [111]. Reproduced with permission of *Springer Nature* [107] and the *Royal Society of Chemistry* (2018) [111].

It is well known that polar facets possess different chemical and physical properties from non-polar facets, and that O terminated polar facets also present a slightly different electronic structure [105]. These characteristics are responsible for the vast properties presented by ZnO such as piezoelectricity and spontaneous polarization, being a key factor in crystal growth and in defect generation [105].

When used in gas sensing or in other applications, it has been found that the polar Zn terminated (0001) facets are more active than polar O terminated $(000\bar{1})$ and the non-polar $(10\bar{1}0)$ facets due to the abundance of OH^- that adheres to low-coordinated Zn sites, forming highly active ·OH radicals [111, 112].

The growth of different ZnO nanostructures has been reported by several authors in the past few years. Different synthesis methods can be employed to produce ZnO nanostructures, such as chemical bath deposition, electrospinning, electrodeposition, laser assisted flow deposition (LAFD) and also hydrothermal/solvothermal synthesis, either by conventional or by microwave assisted heating [13, 14, 113-123]. Depending on the synthesis method, precursors used and their concentration, solution pH or even the solvents selected, zinc oxide may present different nanostructures ranging from nanorods, nanofibers, nanoneedles, nanowires, nanoplates, nanostars, tetrapods to nanoflowers [14, 108, 113, 124-127], as shown in Figure 5.

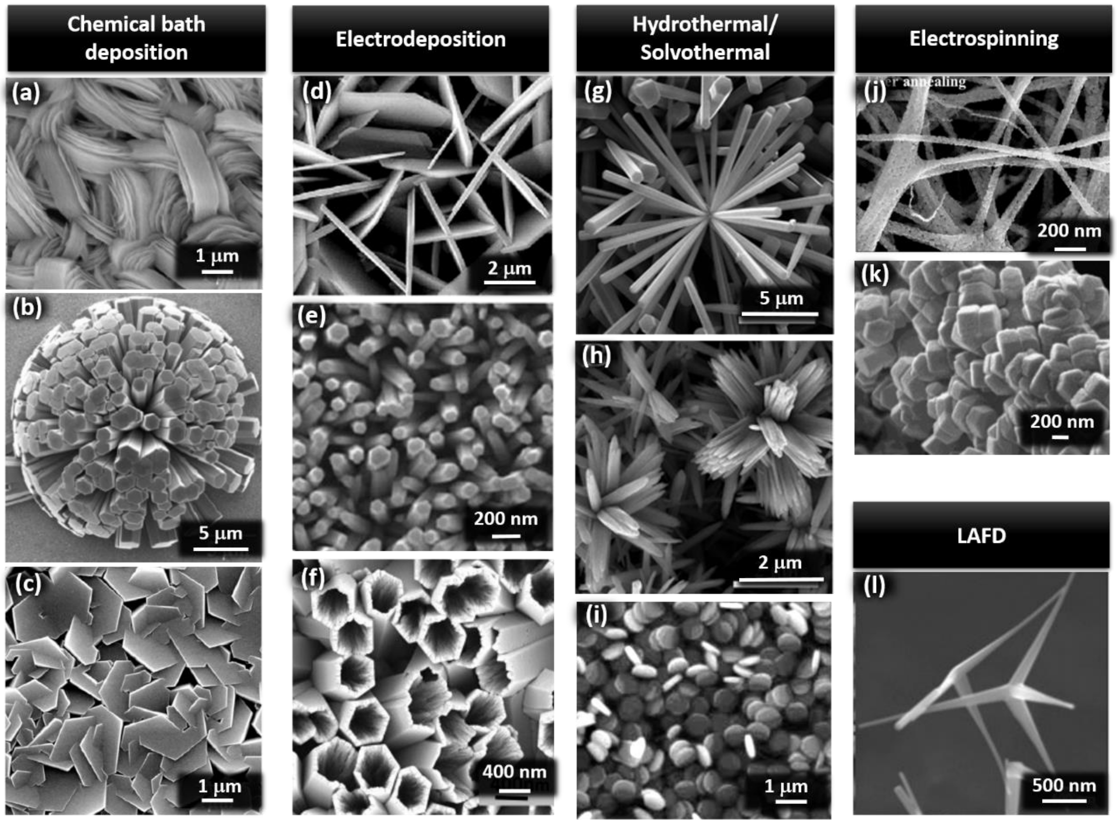


Figure 5. Different ZnO morphologies produced by different synthesis techniques: (a), (b) and (c) chemical bath deposition [113]; (d), (e) and (f) electrodeposition [123, 128, 129]; (g), (h) and (i) hydrothermal/solvothermal synthesis [112, 130]; (j) and (k) electrospinning [116, 117] and (l) laser assisted flow deposition [121]. Reproduced with permission of *Elsevier* [112, 113, 116-118, 121, 123, 128, 129] and *Royal Society of Chemistry* (2018) [130].

Zinc oxide is an inexpensive and earth abundant material, nontoxic and chemically stable, which makes it suitable to be used in several applications, such as field effect transistors [131-134], solar cells [121, 135-137], piezoelectric generators [138-140], photocatalysis [14, 141, 142], as a platform for SERS applications [143, 144] and in sensors [13, 71, 122, 145].

Metal oxides semiconductors are commonly used as gas sensors in environmental monitoring and in industrial applications allowing the production of low cost and small devices [146]. ZnO is capable to detect a great variety of different gases, such as CO_2, H_2S, NO_2, NO, NH_3, C_3H_8 and CH_4 [146-150]. The detection of carbon dioxide is of vital importance for human life. The use of inexpensive and highly sensitive miniaturized sensors are of great interest for environmental control of indoor air quality and pollution (considering the impact of CO_2 emissions on the global warming) [147].

The most recent studies are focused on devices miniaturization allied to increased sensitivity. So, many authors are studying the influence of ZnO morphology on gas detection since just by changing its shape it is possible to enhance sensor performance, opening new ways to produce more selective gas sensors [150]. Gupta *et al.* [146] studied the sensitivity of different ZnO nanostructures, nanowires, nanobelts and tetrapods in the detection of H_2S and NO. Gupta found that sensors based on ZnO nanobelts were more sensitive to NO gas, and that ZnO tetrapods were more sensitive in detecting H_2S gas while ZnO nanowires had no response in detecting NO, H_2S, NH_3, CO and CH_4. The high sensitivity of nanobelts to these gases may be due to their low thickness (< 20 nm) when compared to the nanowire's diameter (≈ 100 nm), thus presenting a larger surface to volume ratio. It was found that the response mechanism to detect H_2S arises from changes in the grain boundary resistance, while for the detection of NO it arises from changes in the grain boundary and intragrain resistances [146].

Jonca *et al.* [150] studied the use of cloudy-like, isotropic and nanorods ZnO nanostructures for detection of CO, NH_3 and C_3H_8 gases. The ZnO nanorods nanostructures presented higher sensitivity to the detection of this type of gases.

Nitrogen oxide gases like NO and NO_2 are environmentally harmful gases formed during the combustion in automotive and factories and are frequently associated to greenhouse gas effect [149]. NO_2 is a very strong oxidizing gas, so the reaction takes place directly with the ZnO surface and not with the oxygen chemisorbed at the surface. NO_2 molecules will then consume conduction electrons, increasing the depletion region at the surface, thus reducing ZnO conductivity [151]. Several authors have studied the use of different ZnO nanostructures for detection of NO and NO_2 gases. Sadek *et al.* [151] used ZnO nanobelts to detect NO_2 gas with concentration as low as 0.51 ppm. Cho *et al.* [152] used ZnO nanorods and was able to detect NO_2 gas concentrations of 1 ppm. Figure 6 shows several gas sensors produced with nanostructured ZnO sensitive layers.

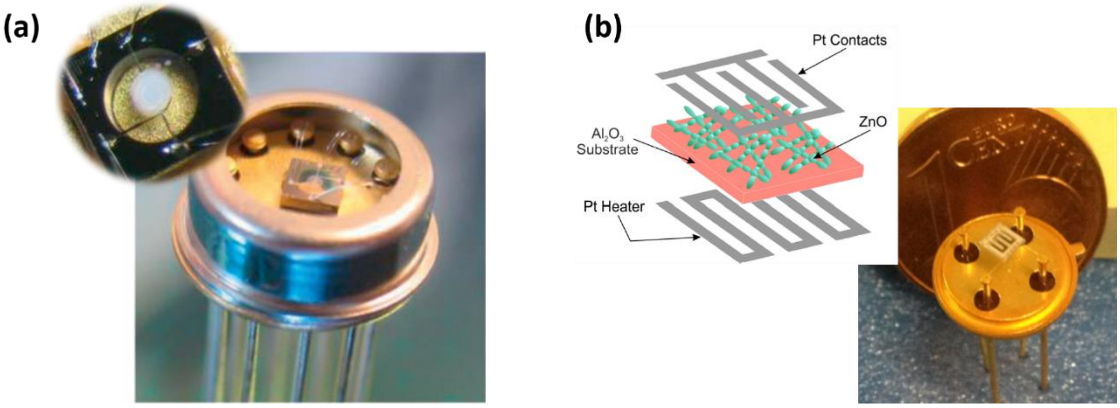


Figure 6. (a) Miniaturized gas sensor with a ZnO sensitive layer for the detection of CO, NH_3 and C_3H_8 gases [150]; (b) Schematic and digital image of a ZnO based sensor for the detection of NO_2, H_2 and CH_4 gases [153]. Reproduced with permission of *Elsevier* (2018) [150] and [153].

Another way to improve ZnO gas sensor performance is by doping the semiconductor metal oxide with other materials. Dilonardo *et al.* [154] doped ZnO nanostructures with Au nanoparticles and was able to detect NO_2 gas at 0.2 ppm concentration , presenting a total recovery time of 30 seconds after removing the gas. Moreover, Li *et al.* [155] used ZnO/NiO nanoheterojunction with porous morphology to detect ethanol. Li was able to detect 100 ppm of ethanol at 200 °C. By using a heterojunction the sensing mechanism may be a result of two factors. ZnO is a *n*-type semiconductor and in the presence of ethanol interaction with O^{2-}, O^- at the crystal surface will occur, leading to an increase of conductivity. On the other hand, NiO is a *p*-type semiconductor as such, the reductive ethanol molecules will react with oxygen ions adsorbed at the NiO surface and release electrons that will recombine with holes in *p*-type NiO, leading to a decrease in holes concentration and, consequently to a resistance increase [155]. Ethanol molecules may also combine with holes in NiO nanostructures and produce intermediates CH_3CHO molecules which will react with the absorbed oxygen, resulting in increased sensitivity ethanol for this type of heterojunction [155]. Moreover, it has been reported that in the heterostructure sensor, electrons will be transferred from *n*-type ZnO to *p*-type NiO, while holes are transferred in the opposite way until the system reaches equilibrium at the Fermi level. This will lead to the formation of the hole depletion layer and increase the amount of chemisorbed oxygen species. The increase of such species allows more surface chemisorbed oxygen species to participate in the oxidation-reduction reactions at the sensing material's surface and thus impose an enhanced change in sensor resistance [155, 156].

The control of humidity levels is of great importance in some environments, such as in clean rooms, food management, medical area and chemical substances storage [157]. When using ZnO nanostructures, it is expected that the impedance of the sensor increases with the increase of adsorbed water at the sensor's surface and that sensors present low hysteresis, high sensitivity with a short recovery time. Some researchers have studied the use of ZnO nanostructures in humidity sensing applications.

Ghanem *et al.* [157] produced a humidity ZnO sensor that presented a resistivity variation in the presence of humidity changing between 15-95 %, with hysteresis error of 2 % at 100 °C. Also, Herrán *et al.*[158] used ZnO nanoparticles to monitor humidity at room temperature. With a response time of 5 seconds, Herrán was able to measure humidity in the range of 0 to 80 %.

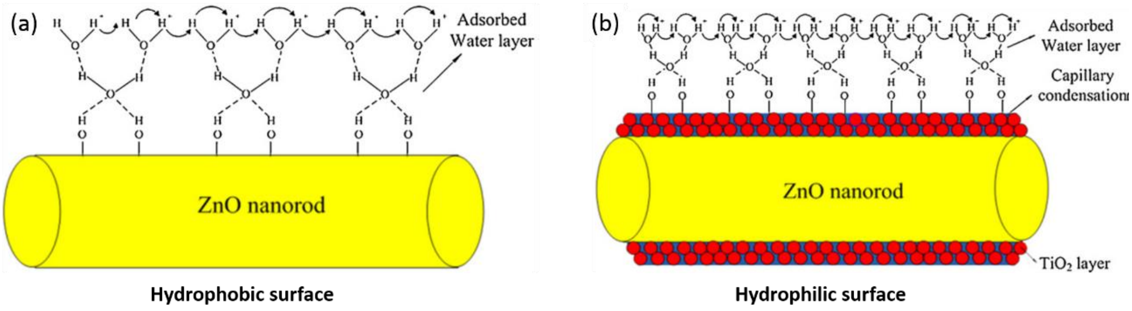
Also, in the case of humidity sensors, it is possible to improve sensor properties by synthesizing a composite nanostructured material. Sin *et al.* [159] produced humidity sensors based on ZnO/SnO_2 cubic structures. The advantages of using a composite sensor are higher thermal stability and increased electron mobility. When using a ZnO/SiO_2

cubic structure, Sin was able to obtain sensitivity of 22.5 at 90 RH%, a much higher value when compared to the sensitive values of 7.5 and 2.3, obtained with only ZnO or SnO_2, respectively [159]. The same ZnO/SiO_2 composite was used by Qing *et al.* [160]. The mesoporous ZnO/SiO_2 produced by Qing presented a high surface area, with uniform structured pores that enhanced water vapour adsorption at the surface, enhancing sensitivity. The produced sensor presented improved humidity sensing in a range of 11 to 95 RH%, with a response time of 50 seconds and maximum humidity hysteresis of 2 % [160].

Leilei *et al.* [161] have reported the use of a ZnO/TiO_2 composite for humidity detection . The main disadvantage of using ZnO in humidity sensors is the fact that this semiconductor material can be very hydrophobic, which difficults sensitivity improvement . On the other hand, TiO_2 is a hydrophilic material due to the observed dissociative adsorption of water at Ti^{3+} defects sites. Nevertheless, the use of this material may bring some disadvantages, such as high resistance, pronounced hysteresis and short long-time stability [161-163]. So, the use of a ZnO/TiO_2 composite as complementary materials will favour the enhancement of humidity sensor properties. The ZnO/TiO_2 nanorods composite produced by Leilei *et al.* [161] presented a considerable sensitivity enhancement when compared with single ZnO or TiO_2 sensors, with an enhancement of 31 and 1380, respectively. The use of a TiO_2 coating will enhance the water adsorption at the sensor's surface, due to the rough surface of TiO_2 and its remarkable hydrophilicity. Moreover, with the increase of humidity, capillary condensation will occur in the pores with smaller radius than the Kelvin critical radius (TiO_2 surface and ZnO/TiO_2 interface). The formation of these pores is due to the nanoscale grain boundaries of the TiO_2 shell. The introduction of this shell leads to the adsorption of more water molecules by increasing the hydrophilicity of the surface area and by inducing capillary condensation.

The phenomenon will contribute to the polarization of adsorbed water molecules and induce accelerated capacitance response [161].

Figure 7, shows the adsorption model proposed by Leilei *et al.* [161].



Hydrophobic surface

Hydrophilic surface

Figure 7. Humidity adsorption models for (a) ZnO nanorods; (b) ZnO/TiO_2 composite nanorods [161]. Reproduced with permission of *Elsevier* (2018).

The UV photoresponse of ZnO material was first observed by Mollow in the 1950s [164]. Since then, zinc oxide has been one of the most studied metal oxide material used in UV sensor applications. Initially, researchers had focused their attention on the development of ZnO thin films-based sensors however these films presented some intrinsic drawbacks, such as a slow response time and recovery speed. So in the past decade, many authors have reported the use of ZnO nanostructures (like nanorods, nanostars and tetrapods) with the aim of increasing the photoresponse by increasing the sensor surface area [114, 165-170]. Due to the fact that ZnO photoresponse is related to adsorption and desorption of chemisorbed oxygen from (0001) polar facets, the use of 1D nanostructures presents some advantages due to its large surface to volume ratio, allowing increase of the sensor's photoresponse and/or reduction of the active area (very important for devices miniaturization) [164, 166].

Many are the factors that can influence the sensitivity of a ZnO UV sensor including substrate, ZnO particles morphology or even sensor configuration. Alenezi *et al.* [81] developed a series of flexible sensors with different configurations that presented distinct values of photocurrent response. With a bridging nanosizing configuration, Alenezi *et al.* [81] were able to improve sensitivity, with an ultrafast response time (90 ms) and also a fast recovery time (210 ms). Pimentel *et. al.* reported a set of studies demonstrating the production of ZnO UV sensors constructed on rigid or flexibles substrates (glass or PET/PEN) and also on cellulosic based substrates [13, 71, 122]. Figure 8 shows ZnO UV sensors produced on cellulosic based substrates and glass.

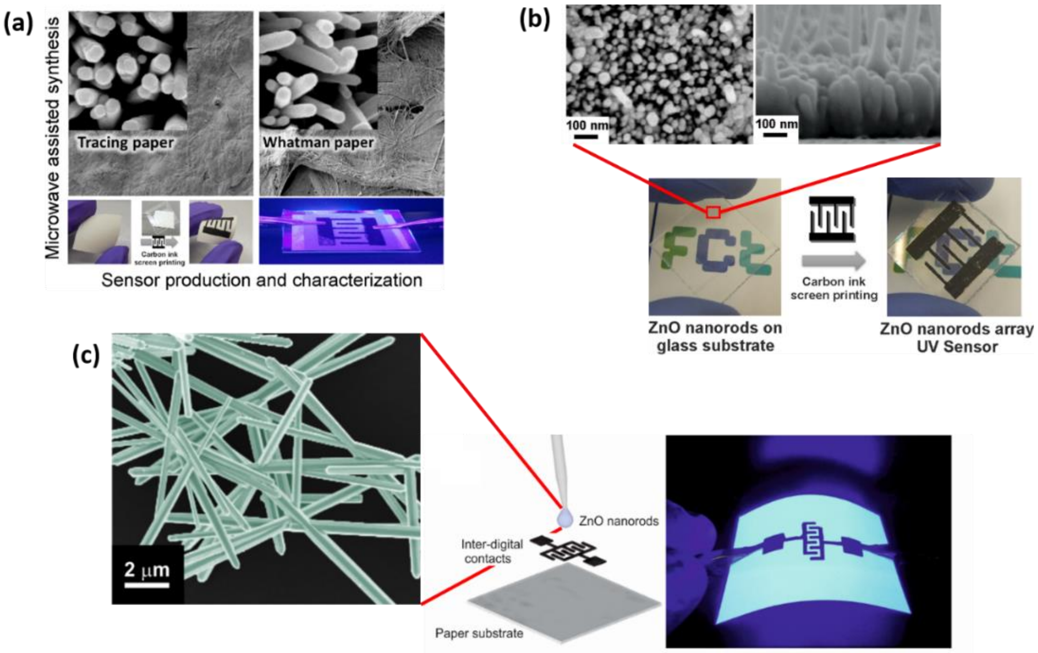


Figure 8. (a) ZnO UV sensor produced on tracing and Whatman paper [13]; (b) Transparent UV sensor produced on glass substrate [71]; (c) UV sensor produced with ZnO nanowires on top of graphite electrodes, screen printed on paper substrate [122]. Reproduced with permission of *MDPI* [13] and [71], and *ACS publications "Copyright (2018) American Chemical Society"* [122].

A disadvantage of using ZnO nanostructures in UV sensing is the low photocurrent value, mainly due the small size of individual nanowires. Some different methodologies are being employed by researches in order to enhance the photoresponse of ZnO UV sensors. Bai *et al.* [171] showed the difference in using ZnO nanowires aligned horizontally along the substrate or using the same nanowires placed vertically against the substrate. By a transfer process, it was possible to transfer the vertically oriented nanowires into a well aligned horizontal orientation and this way increasing the photoresponse current from 1.8 μA to 12.22 mA, with an on/off current ratios of 82000 [171].

One of the most important characteristics that are being studied by scientific community is sensor miniaturization. Portable and small photodetectors have a wide range of applications, such as the monitoring of UV dosage for skin cancer prevention, optical communications and also in astronomy [172]. Nasiri *et al.* [172] produced small ZnO photodetectors with excellent selectivity and milliampere photocurrents. A spray flame synthesis technique was used (see Figure 9 (a)), producing ZnO nanoparticles with a diameter of ≈ 19 nm. The high sensitivity of this sensor is mainly due to the highly pure crystal surface and the very small particle size that originated ultra-porous ZnO nanoparticle film, presenting increased photocurrent from 260 μA to 1.2 mA [172].

Another very interesting concept for UV sensor application is presented by Park *et al.* [164]. Park was able to produce a wireless UV sensor platform based on ZnO nanorods where real-time collected signals are sent to a smartphone through Bluetooth connection, with responsivity as high as 0.55 A W^{-1}, response time of 3.1 s and recovery time of 1.25 s. Figure 9 (b) shows a photograph of the photocurrent measurement by a smartphone.

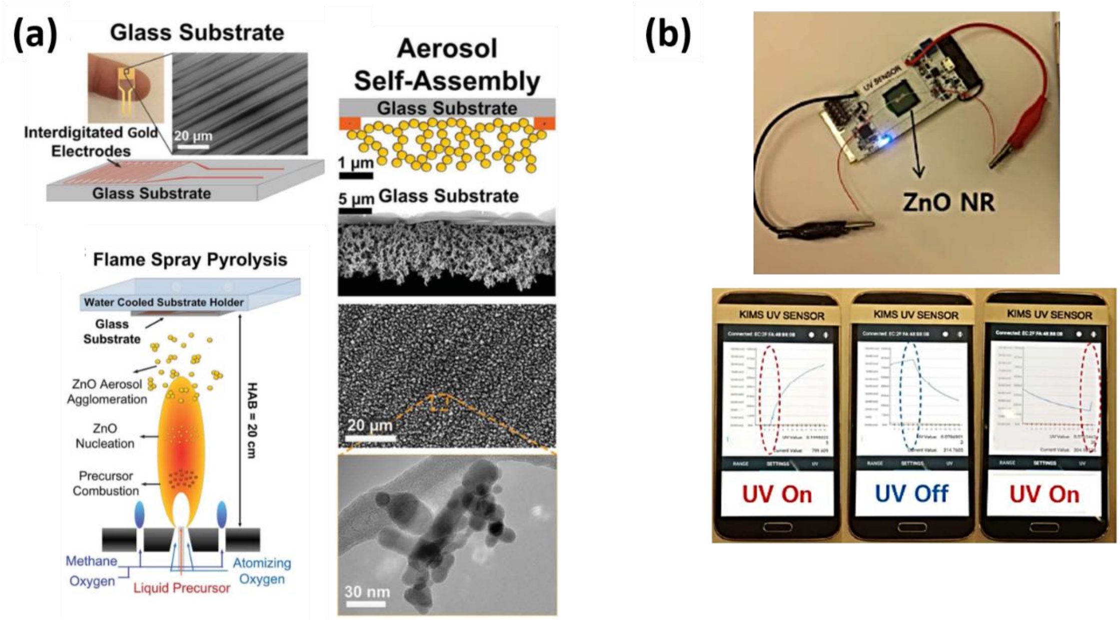


Figure 9. (a) Schematic of a ZnO photodetector production by flame spray pyrolysis [172]; (b) Photographic image of a ZnO UV sensor Bluetooth-connected to a smartphone [164], where it is visible the photocurrent variation under on/off cycles of UV radiation. Reproduced with permission of *John Wiley and Sons* [172] and *Royal Society of Chemistry* (2018) [164].

The most recent approach in ZnO UV sensors is the use of graphene as conductive layer to improve their performance [173-175]. The advantage of using graphene relies on its superior conductivity (that prevents recombination of electron-hole pairs in the ZnO/graphene composite) and transmittance (over 97.7 % for a single layer graphene, which maximizes UV-light absorption), allowing a reduction in response and recovery time, and increasing the photocurrent gain [174]. Duan *et al.* [174] was able to produce a ZnO UV sensor with responsivity of 0.039 A W^{-1}, extremely short response and decay time of 37 μs and 330 μs, respectively.

Zinc oxide is a biocompatible material, with high isoelectric point ($IEP_{ZnO} \approx 9.5$), high surface activity and electron communication feature [176, 177]. For these reasons, ZnO can be functionalized with a wide range of biological materials with low IEP values, through electrostatic interaction, such as enzymes (like glucose oxidase and cholesterol oxidase), antibodies or even DNA [176, 178, 179]. Several reports have demonstrated the application of ZnO as biosensors, *i.e.* in DNA immobilization [180], in glucose level detection [176, 177, 181], for cardiac biomarker detection [179, 182, 183] and also for cancer diagnostic [178, 184, 185].

Probably the application of ZnO for glucose detection is one of the most studied biosensors. For glucose levels detection , ZnO biosensors are produced by immobilization of glucose oxidase enzyme onto ZnO nanostructures [176]. The high IEP_{ZnO} value will promote the formation of zinc oxide/ glucose oxidase complexes during functionalization (glucose oxidase are negatively charged molecules, that will be readily attracted and immobilized onto positively charged zinc oxide).

The detection of glucose by the functionalized electrodes can be described by the following electrochemical reactions: glucose oxidase enzyme oxidizes glucose and as a result δ-gluconolactone and H_2O_2 are produced [181]. Finally, with the oxygen consumption and H_2O_2 oxidation, it is possible to evaluate the amperometric response of the biosensor [176, 181]. The use of ZnO nanostructures, with high surface-to-volume, in glucose biosensors, will provide a large specific surface area for glucose oxidase adsorption.

Gallay *et al.* [176] was able to produce a ZnO nanowire-based glucose sensor capable of detecting very low glucose concentrations of about 9 μM. Wahab *et al.* [181] used ZnO nanorods for the detection of glucose with concentration ranging from 1 μM to 10 mM. Wang *et al.* [177] synthesized ZnO nanocombs, forming a highly porous structure, that were then immobilized with glucose oxidase, showing a detection limit of 0.02 mM.

One of the most key areas of investigation is the development of rapid systems for the diagnostic of cancer. Researchers have found that some biomolecules like DNA molecules, human serum albumin and angiotensin II molecules can be effectively immobilized just by modifying the ZnO nanostructures surface [184]. Viter *et al.* [178] have demonstrated that by using photoluminescence properties of ZnO nanorods, it was possible to develop a cancer cell recognition system. By immobilization of SSEA-4 antibodies on ZnO nanorods that were then deposited on the cell probe, it was possible to record photoluminescence spectra that increased when compared with the signal of control samples. Moreover, it was possible to observe that the intensity was correlated with the extent of malignancy in target cell population [178]. Another method for the detection of cancer cells was presented by Rui *et al.* [185]. By adsorbing Cytochrome *c* (Cyt.c) onto ZnO surface, this latter study used ZnO nanosheets to detect H_2O_2 from living cancer cells. Cyt.*c* was found to promote direct electron transfer at the electrode surface [186].

For cardiovascular disease diagnosis, it was possible to develop a sensor that may detect specific concentration ranges of biomarkers that are associated with those diseases. The presence of cardiac troponin (cTnT and cTnI biomarkers) in blood circulation is an indicative of cardiovascular disease [179, 182]. Shanmugam *et al.* [182] developed a flexible and disposable electrochemical sensor capable of detecting very low concentrations of target analyte cTnT with only 20 μL of solution. The limit of detection was identified at 0.1 ng L^{-1}. Tan *et al.* [183] produced a biosensor based on ZnO nanoparticles that was capable of converting the biological interaction of cTnI into an electrical signal. This study also detected the cTnI biomarker in a concentration range of 1 ng mL^{-1} to 10 µg mL^{-1}, withdetection limit of 2.191 ng ml^{-1} and sensitivity of 15.8 nA $(g/mL)^{-1}$.

2.2 Titanium dioxide

TiO_2 is a *n*-type semiconductor usually appearing in an amorphous state or as three crystalline phases: the tetragonal phases, anatase and rutile, and an orthorhombic phase, brookite [187]. Rutile is the most stable phase, in which both anatase and brookite are metastable, transforming to rutile when heated [188]. It has been reported that phase transformation of the amorphous state to anatase occurs from 300 to 500 °C, and further transformation to rutile occurs at 600-1000 °C [103, 189].

Rutile and anatase tetragonal structures contain six and twelve atoms per unit cell, respectively. For both phases, each Ti atom is coordinated to six O atoms and each O atom is coordinated to three Ti atoms. The TiO_6 octahedron is slightly distorted, with two Ti-O bonds somewhat greater than the other four, having some of the O-Ti-O bond angles distorted from 90 º (greater distortion in anatase than rutile). The structures of rutile and anatase crystals consist of chains of TiO_6 octahedra, sharing four edges in anatase and two in rutile. In the case of brookite, it has distorted TiO_6 octahedra sharing three edges. Moreover, brookite has eight formula units in the orthorhombic cell, in which the interatomic distances and O-Ti-O bond angles are similar to those of rutile and anatase, nevertheless it has six different Ti-O bonds [190, 191]. Rutile, anatase and brookite unit cells are presented in Figure 10.

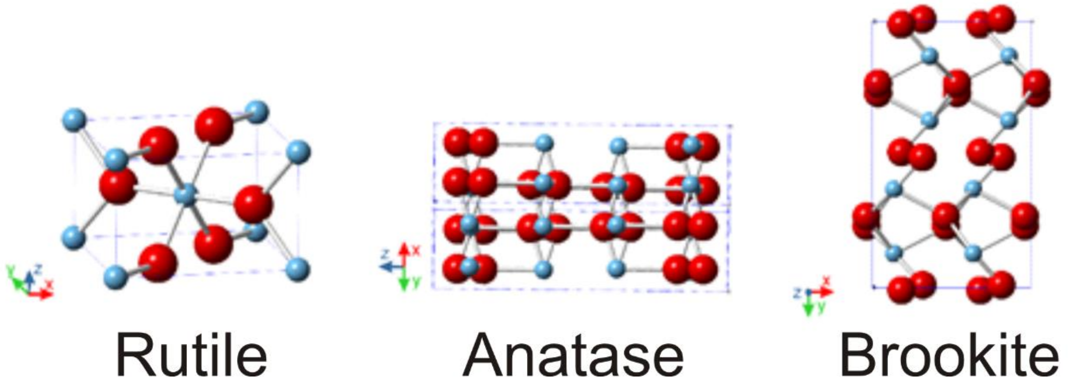


Figure 10. Unit cells of TiO_2 rutile, anatase and brookite [192]. Reproduced with permission of *Intech*.

TiO_2 is a wide energy band gap material, typically displaying optical band gaps of 3.0 and 3.2 eV for rutile and anatase, respectively [193], and varying from 3.13 to 3.40 eV [188, 193] for brookite. Nevertheless, its optical bang gap for nanostructured materials can be engineered by adding structural defects or doping with non-metal and metal elements also to narrow its band gap [194-196]. TiO_2 has a high refractive index (2.71 for rutile, 2.53 for anatase and 2.64 for brookite [191]), high dielectric constant (TiO_2 thin films ranging from 40 to 86 [197, 198]) and high resistivity extending to 10^8 Ω.cm [199]. The lattice parameters for rutile ($P4_2/mnm$) are a= 0.4594 nm and c= 0.2958 nm, while anatase ($I4_1/amd$) has lattice parameters of a= 0.3785 nm and c= 0.9515 nm, and brookite ($Pbca$) has lattice parameters of a= 0.9184 nm, b= 0.5447 nm, and c= 0.5145 nm [191, 200].

Several techniques have been reported to produce TiO_2 nanostructures or thin films including sol-gel method [201], wet-chemical techniques [202, 203], thermal evaporation [204], sputtering [205], electrodeposition [206], hydrothermal and solvothermal synthesis [207-210], microwave irradiation [10, 192], amongst others. Various and distinct structures have been reported for TiO_2 nanomaterials, especially as nanoparticles, including nanowires, nanorods, nanotubes, nanobelts, nanowhiskers, nanospheres and others [10, 203, 211-213].

TiO_2 is known to be an inexpensive material, earth abundant, chemically stable, non-toxic, biocompatible, and environmentally friendly [203, 214], which makes it prone to be applied in numerous fields, including solar cells [25, 215, 216], self-cleaning [217, 218], photocatalysis [9, 10, 192], H_2 production [219], CO_2 reduction [220, 221], sensors [222-224], among others. Anatase is the preferred phase for solar cell integration since it has high electron mobility, low dielectric constant and lower density [225, 226]. TiO_2 has been widely investigated for photocatalytic H_2 evolution, photoelectrochemical water splitting, reduction of CO_2 to hydrocarbons, and pollutant degradation for many years. In terms of photocatalytic activity, anatase is expected to exhibit an indirect band gap that is smaller than its direct band gap. Rutile presents a direct band gap or an indirect band gap that is comparable to the direct one. It is known that semiconductors with indirect band gap generally exhibit longer charge carrier life times and thus longer electron-hole pair life would facilitate charge carriers participation in surface reactions [227]. Nevertheless, it has been reported that the mixture of both phases displayed higher photocatalytic activity than pure phases [228]. In the case of brookite, this material is the least investigated TiO_2 polymorph, however it has been reported to display higher photocatalytic activity than anatase or rutile [229].

In terms of sensors, and as previously mentioned, a high-quality sensor is expected to have greater sensitivity, high detection limit, response/recovery time and stability and longer life cycles. These parameters are related to characteristics of the sensing material, such as grain size and microstructure, which directly influence the sensor’s sensitivity [199]. In this sense, nanostructured materials have been extensively used in sensors over the years, including nanostructured TiO_2 materials that have enhanced chemical stability allowing low temperature operation. This materials has inert characteristics, and is resistance to harsh atmospheric conditions, despite being low-cost in terms of production and compatible with wet-chemical synthesis routes [230].

TiO_2 has been widely used as photoactive layer of gas sensors, where TiO_2-based gas sensors are typically chemiresistive, having the working principle of typical *n*-type semiconductor gas sensor materials based on its conductance change mechanism due to adsorption/desorption process of oxidizing and reducing gases [231].

Liu *et.al.* [232] reported the hydrothermal synthesis of TiO_2 nanocrystals with various percentages of exposed {001} facets displaying *p*-type and *n*-type sensing responses towards ethanol (Figure 11 (a)). In another study, TiO_2 nanowire sensors revealed excellent selectivity and high sensitivity down to 100 ppm NO_2 at room temperature with response and recovery times of 10 s and 19 s, respectively. Furthermore, the nanowires displayed good repeatability and selectivity against various interfering gases such as NH_3, H_2, and CH_4 [233]. TiO_2 nanostructured films composed of different morphologies, nanoparticles and nanotubes were synthesized by hydrothermal method and it has been shown that sensing films composed of nanotubes demonstrated a high sensor response to toluene [234].

It is also known that well-ordered porous metal oxide structures are highly efficient for improving gas sensing, in which this porosity increases surface area of the material, enhancing its interaction with the gaseous species [231]. TiO_2 spongy layers with double-scale porosity at the meso and nano-scale have been reported and exhibited sensitivity of 44 ppm to ethanol at 250 °C. Moreover, response of the material was demonstrated to be independent of ambient humidity with a response time as low as ∼10 s [235].

Another approach that has been widely used is doping with small metal clusters. Doping will have a significant effect for the metal oxides which are dominated by defect chemistry (via oxygen vacancies). Oxygen vacancies are considered important reactive agents for several adsorbates, in such a way that surface reactions are influenced by this type of point defect [49]. Ruiz *et al.* [236] reported the effect of doping TiO_2 with chromium, in which it has been observed that the addition of Cr retarded the anatase-to-rutile TiO_2 transformation, moreover these materials revealed to be sensitive to 1000 ppm CO, but also to NO_2. In another study, it has been described TiO_2 sol-gel films doped with gold nanoparticles used as both optical and conductometric sensors for the detection of CO and H_2 [237]. The combination of different oxides has also been reported to surpass limitations of each metal oxide material. Carney *et al.* [238] produced TiO_2-SnO_2

nanofiber-structured films that were tested for sensing H_2. This combination allowed to increase TiO_2 gas sensitivity and supress SnO_2 sensors limitations that utilize low-temperature chemisorption (under 400 °C) of gases on the surface. Above 400 °C, SnO_2 exhibits poor sensing performance, while TiO_2 is stable at higher temperatures.

In terms of humidity sensors, TiO_2 is known to have superior humidity sensitivity with the preferably hydrophilic property resulting from the surface defects, *i.e.* the Ti^{3+} defect sites or oxygen vacancies sites, that can adsorb water molecules in the atmosphere [239]. Nevertheless, reported TiO_2-based humidity sensors usually display limited sensitivity resultant of low surface/volume ratio, high resistance or poor charge transfer process of single phased TiO_2 material. Thus, several approaches have been designed to overcome these limitations. Ultrathin 2D TiO_2 nanosheets with high specific surface area and surface oxygen vacancy defects have been reported as having ultrahigh humidity sensing performance. These nanostructured sensors revealed significant impedance variation from RH 11% to 95%, short response time (3 s) and recovery time (50 s), as well as small hysteresis ~ 4.6% (Figure 11 (b)) [239]. Lin *et al.* [240] reported a humidity sensor based on graphene/TiO_2 that at 12-90 %relative humidity , exhibited a sensing response ($S = 151$) and humidity hysteresis value of < 0.39 %. In another study, flexible sensors based on TiO_2 and conducting polymers have been described. These humidity sensors demonstrated hysteresis (range of 30–90 % RH) of 2 % RH, with response time of 30 s, and recovery time of 45 s [241]. Doping TiO_2 was also considered for producing enhanced humidity sensors. Zare *et al.* [242] reported the effect of doping TiO_2 with silver in terms of humidity sensitivity, while Buvailo *et al.* [243] showed TiO_2-based nanomaterial doped with LiCl to produce conducting thin film sensors. The latter sensors were measured in the RH range of 5-95 % and revealed 0.75 and 1 s for sensor response and recovery time, respectively.

Recently, TiO_2 has been considered as a good alternative for the most common used UV sensors, *i.e.* silicon-based sensors [244], as TiO_2 is highly photoactive and stable under UV irradiation due to its band gap [67, 245, 246]. Highly oriented rutile TiO_2 nanorod arrays were synthesized by hydrothermal method and tested as UV sensors achieving a photocurrent of 12.87 $\mu A\ cm^{-2}$ under 365 nm UV light exposure [224]. In another study, anodic TiO_2 anatase nanotube arrays were tested as UV sensors showing high responsivity of 13 $A\ W^{-1}$ under λ = 312 nm and fast response with rise time and decay time of 0.5 and 0.7 s, respectively [247]. Epitaxial TiO_2 thin films were fabricated on $LaAlO_3$ single crystal substrates by RF magnetron sputtering, and the sensor exhibited a maximum photoresponse of 3.63 $A\ W^{-1}$ at 310 nm and ultrahigh response speed (~90 ns) [248]. Nano-branched TiO_2 arrays were integrated on self-powered UV sensors. The photosensitivity increased from 0.03 to 0.22 $A\ W^{-1}$ exhibiting excellent spectral selectivity and fast response (0.05 s decay time) [249].

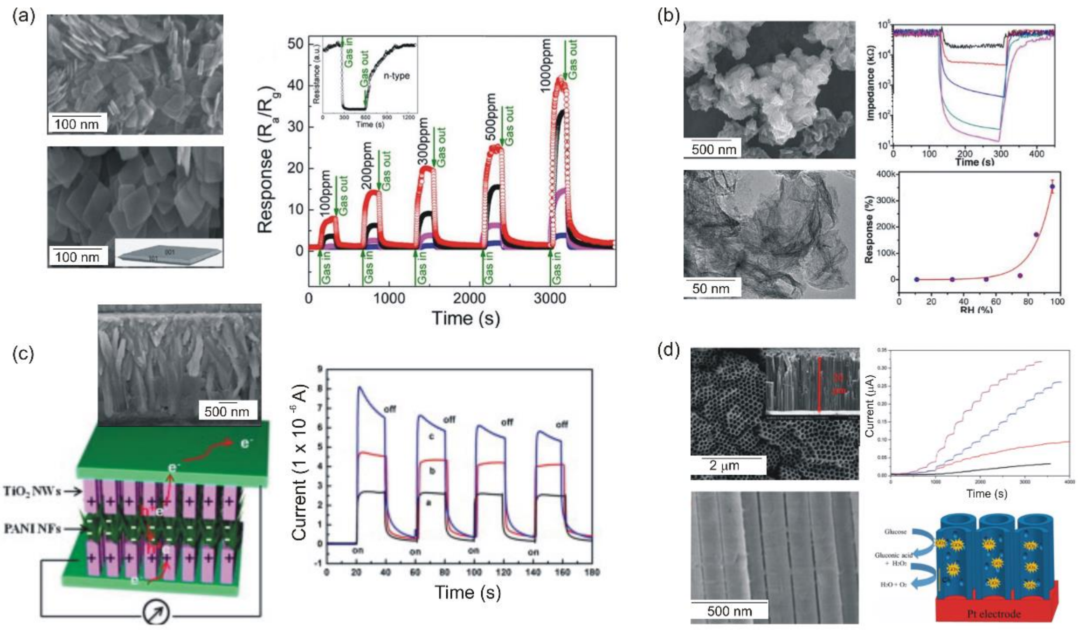


Figure 11. (a) SEM images of TiO_2 nanosheets together with the response and recovery curves of the sensors as a function of ethanol concentration [232]. (b) SEM and TEM images of TiO_2 nanosheets for humidity sensors together with the transient responding dynamics of the impedance of TiO_2 nanosheets-based sensor and calibration curve [239]. (c) SEM images of TiO_2 nanowires/PANI/TiO_2 nanowires heterostructured arrays to be used as UV photodetectors together with the time responses of photocurrents under UV light [250]. (d) SEM and schematic diagram of glucose detection on mesoporous GO/TiO_2 nanotubes. The graph showed the current responses with successive injections of glucose [251]. Reproduced with permission of *Elsevier,* [232], [239] and [250], and *Royal Society of Chemistry* (2018) [251].

D. Nunes *et al.* [246] reported the microwave synthesis TiO_2 nanostructured films grown on bacterial nanocellulose (BNC), tracing paper and polyester film substrates to produce flexible and disposable UV sensors (Figure 12). The UV devices showed responsivities of 0.33 $\mu A\ W^{-1}$, 0.16 $\mu A\ W^{-1}$ and 0.07 $\mu A\ W^{-1}$ for TiO_2 films grown on BNC, tracing paper and polyester substrates, respectively. The structural characteristics of the TiO_2 films and substrates were correlated to differences in the UV photodetection.

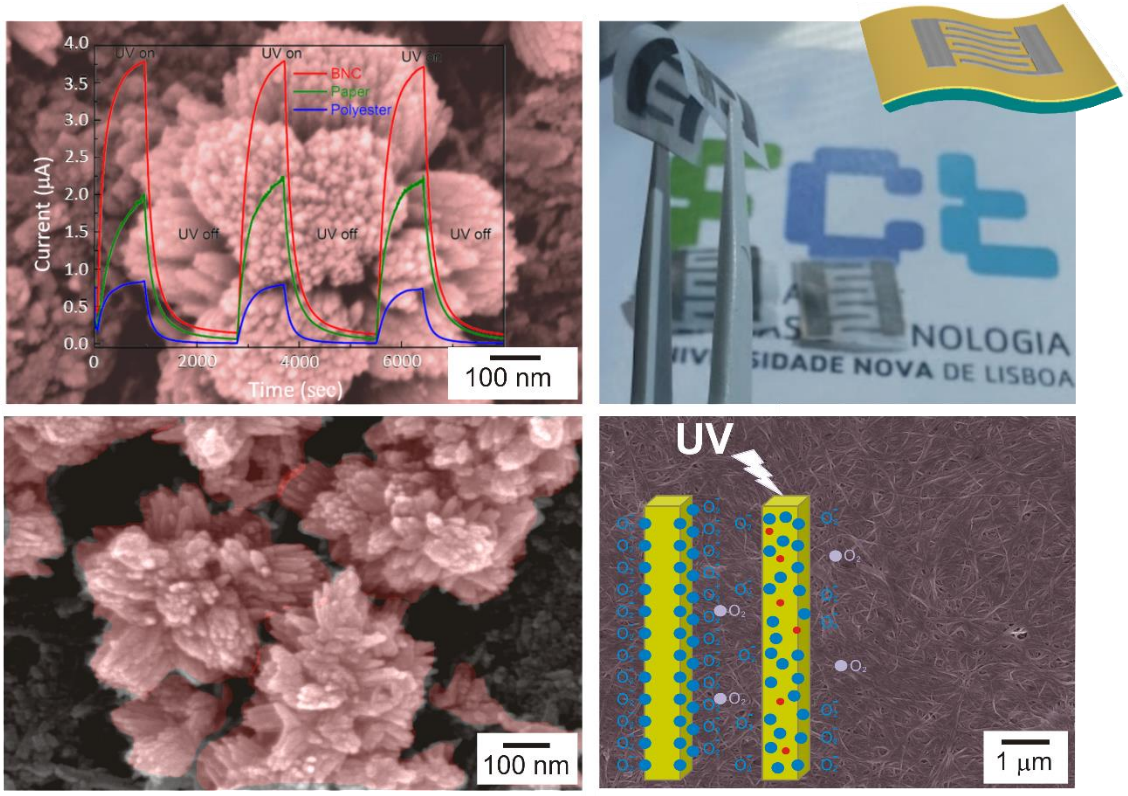


Figure 12. TiO_2 nanostructured films composed by nanorod flower-like structures to be integrated as the photoactive layer of flexible UV sensors. The films were grown on tracing paper, bacterial nanocellulose and polyester substrates. The cycling behaviour of the photodetectors at 10 V and under a 360 nm UV source were investigated. The schematic diagrams of dark and UV irradiation processes are presented. Images reproduced with permission of *Springer Nature* (2018) [246].

Another solution proposed to reduce electron-hole recombination is production of metal-doped TiO_2 materials. It has been reported that Au nanoparticles deposited on TiO_2 nanotubes showed good wavelength selectivity with high photocurrent as compared to pure TiO_2 devices [252]. The addition of other oxides has also been addressed, for example in the case of SnO_2, it possesses high electron mobility, suggesting a faster diffusion transport of photon-induced electrons to TiO_2 [253]. Chen *et al.* [253] reported SnO_2-TiO_2 nanomace arrays exhibited responsivity of 0. 145 A W^{-1} at 365 nm, rising time of 0.037 s, and decay time of 0.015 s. Zu *et al.* [250] reported a self-powered UV photodetector based on heterostructured arrays of TiO_2 nanowires/polyaniline nanoflowers/TiO_2 nanowires (Figure 11 (c)). The heterostructure revealed improved sensing performance when compared to bare TiO_2 nanowires.

Metal oxides sensing applications, including in biosensors, is growing fast in recent years. In the case of biosensors, these devices are a rapidly expanding field in analytical chemistry, with an estimated 60 % annual growth rate [254]. This impulse is coming from health-care industry, food quality and safety, but also from environmental monitoring. When comes to using TiO_2 in biosensors, several studies have focused on producing 1D nanostructures forming continuous arrays [223, 251, 255, 256]. The use of TiO_2 nanotube/nanorod arrays is related to large internal surface area, negative surface charge and high refractive index of these arrays allowing incorporation of biomolecules and high analyte sensitivity [223, 255]. Mun *et al.* [223] reported the production of TiO_2 nanotube arrays for label-free optical interferometric biosensing using a protein A capture probe and an immunoglobulin analyte [223]. Mesoporous TiO_2 nanotube arrays had immobilized glucose oxidase (GO) to produce a biosensor for amperometric detection of glucose. The amperometric response of glucose on the GO/TiO_2 electrode was reported to be proportional to glucose concentration in the range from 0.1 to 6 mM with a sensitivity of 0.954 $\mu A\ mM^{-1}\ cm^{-2}$ (Figure 11 (d)) [251]. Hu *et al.* [255] produced carbon-doped TiO_2 nanotube arrays for simultaneous detection of 5-hydroxytryptamine and ascorbic acid, which can also be readily regenerated photocatalytically to recover its high selectivity and sensitivity. Gao *et al.* [256] reported a graphene/TiO_2 nanorods/chitosan nanocomposite modified carbon ionic liquid electrode to produce an electrochemical DNA biosensor for detection of the transgenic soybean sequence of MON89788. The target ssDNA sequence was detected in the range from 1.0×10^{-12} to 1.0×10^{-6} mol L^{-1} with detection limit of 7.21×10^{-13} mol L^{-1}.

In another approach, TiO_2 nanoparticles were used to produce a nanocomposite with graphene oxide nanosheets. The amperometric response of the glucose biosensor fabricated by the TiO_2-graphene composite was linear against a concentration of glucose ranging from 0 to 8 mM at -0.6 V. The highest sensitivity was shown at 6.2 μA mM^{-1} cm^{-2}, and the glucose biosensor based on the TiO_2-graphene composite showed higher catalytic performance for glucose redox than a pure TiO_2 and graphene biosensor [257]. Another study demonstrated the enzyme immobilization by amperometric biosensors with TiO_2 nanoparticles to detect phenol compounds [258].

2.3 Tungsten trioxide

Tungsten trioxide is one of the most investigated transition metal oxide materials exhibiting a wide variety of novel properties. WO_3 is a *n*-type semiconductor material with a wide energy band gap varying from 2.6 to 3.25 eV [29, 259]. WO_3 can present different crystallographic phases, such as cubic, hexagonal, monoclinic, triclinic, tetragonal and orthorhombic [260-264]. The cubic WO_3 is hardly obtained experimentally, but oxygen vacancies in the WO_3 lattice are capable of increasing the cell symmetry from monoclinic via tetragonal to cubic phase [265].

The most studied WO_3 phases are the monoclinic ($P2_{1/n}$), orthorhombic (*Pbcn*) and hexagonal (*P*6/*mmm*). The monoclinic phase lattice parameter was reported to be a= 0.7301 nm, b= 0.7539 nm, and c= 0.7689 nm [266] and consists of WO_6 octahedral connected by corner sharing of oxygen atoms, connected in the *a*-, *b*- and *c*- directions; the orthorhombic phase with lattice parameters of a= 0.7333 nm, b= 0.7573 nm, and c= 0.7740 nm [267] is based on two octahedral, $WO_5(H_2O)$ (with two oxygen atoms forming W=O and W-OH_2 bonds) and WO_6 with W-O bonds sharing the same bond length; the hexagonal phase with cell parameters a= 0.7298 nm and c= 0.7798 nm [268] consists of WO_6 octahedral structures sharing equatorial oxygen atoms, forming trigonal and hexagonal tunnels [261, 264]. Both monoclinic and hexagonal phases consist of WO_6 octahedral, but with different arrangements. Figure 13shows SEM images of the different morphologies and WO_3 crystallographic phases.

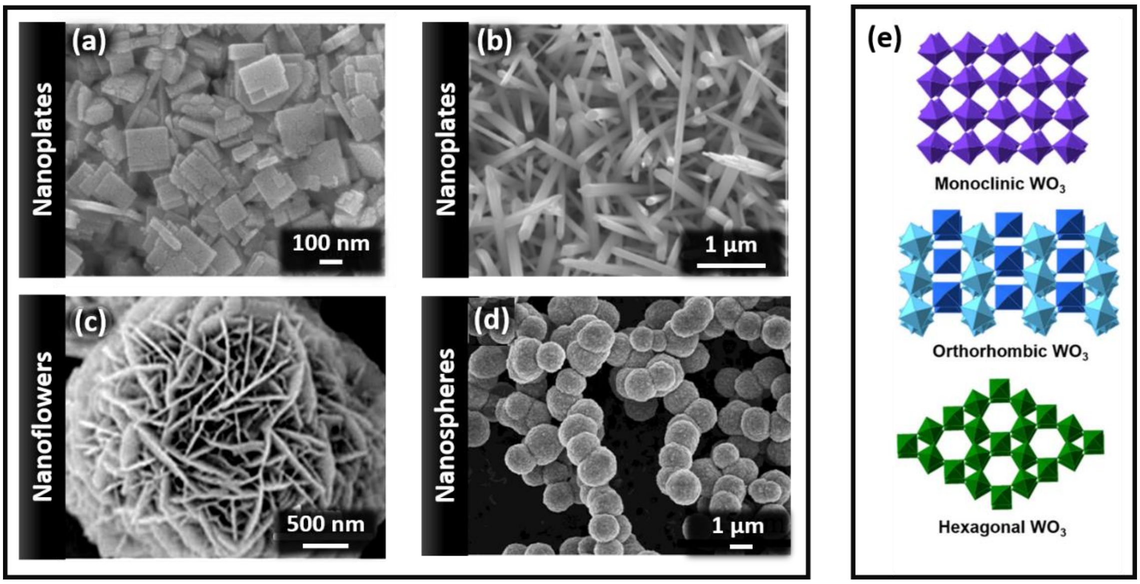


Figure 13. SEM images of WO_3 (a) nanoplates produced by microwave hydrothermal method [269]; (b) nanowires produced by thermal evaporation [270]; (c) nanoflowers produced by hydrothermal method [271]; (d) microspheres produced by hydrothermal method [272]. (e) Crystallographic structures of different WO_3 phases [262]. Reproduced with permission of *Hindawi* [269], *Elsevier* [270], [271], and [272], and *Springer Nature* (2018) [262].

Many researchers have concentrated their studies on novel and more efficient synthesis techniques for producing WO_3 nanostructures, such as conventional and microwave hydrothermal/solvothermal syntheses [273-275], electrodeposition [276], chemical bath deposition [277], chemical vapour deposition [278] and electrospinning [279, 280]. By using these different synthesis techniques, tungsten trioxide may grow with different morphologies like nanoplates [269, 281, 282], nanowires [270, 283, 284], nanorods [285, 286], nanoflowers [271, 287] and hollow nanospheres [272, 288].

Due to its thermochromic properties, WO_3 is mostly used in intelligent electrochromic windows, surfaces for energy-efficient architectures and flat-panel displays [289-295]. Moreover, this material is widely used in solar photocatalysis [273, 296, 297], but it has also been demonstrated that this semiconductor material exhibits enhanced chemical sensing properties and is used in several sensing applications [298-301].

WO_3 has been largely employed in gas sensors with remarkable gas sensing properties for the detection of NO_2 [302-304]. In Ref. [303], it has been shown the NO_2 response of lamellar-nanostructured WO_3 particles. The gas sensor exhibited high sensor response (S = 150-280) to dilute NO_2 (50-1000 ppb) in air at 200 °C. Sensitive porous WO_3 nano-crystalline based NO_2 sensor has been reported in [304]. The sensor showed high sensitivity to low NO_2 concentration in the range from 50 to 550 ppb with relatively fast response time (∼ 3 min) and recovery time (∼ 1 min). A three-dimensional hierarchical WO_3 nanostructure with nanosheet-assembled morphology has been used in gas sensors. The sensor response to 40 ppb NO_2 was reported to be 2.4. It has also been reported that this sensor has good selectivity to NO_2, as the signal was higher for this gas when compared to other oxidizing gases (Cl_2) or reducing gases (CO, H_2S, NH_3, acetone and ethanol) [305]. An *et al.* [306] reported WO_3 nanotube sensors with responses of 144-677% in NO_2 concentration range of 1-5 ppm at 300 °C.

Lin *et al.* [57] reported WO_3 hollow-sphere gas sensors with satisfactory sensitivity to alcohol, acetone, CS_2, NH_3, and H_2S. With increasing gas concentration, sensitivity of the sensors sharply increased. The sensors were more sensitive to alcohol and acetone than to other organics. Another work showed a WO_3 nanowire-like structure for high sensitivity NH_3 gas sensor. The NH_3 gas-sensing properties of these nanowires were measured, showing maximum response of 9.7-1500 ppm at 250 °C with response and recovery times of 7 and 8 s, respectively [307]. WO_3 nanostructures synthesized by hydrothermal method were reported in Ref. [308]. The responses for the sensors increased significantly with the increase of the acetone gas concentration. One of the sensors demonstrated increased sensitivity from 4.1 to 15.8 when the concentration of acetone was changed from 10 ppm to 400 ppm. The sensing selectivity was also explored by comparing the response to acetone, ethanol, formaldehyde and ammonia gases with various concentrations.

The use of WO_3 in the form of films for gas sensing was also investigated. Oriented WO_3 nanoflakes array films were tested as gas sensors in Ref. [298]. The WO_3 thin film sensor exhibited responses of 2.8-9.8%, 12.8-68.9% and 26.2%-85% respectively, to 0.1-10 ppm of H_2S concentration at various operating temperature such as 100 °C, 200 °C and 300 °C, respectively. The WO_3 thin film sensor showed a high response to H_2S that increased with H_2S gas concentration. Sulfur dioxide gas sensors based on WO_3 screen printed thick films composed of nanopowders were demonstrated in [309]. The sensors exhibited responses to 1-10 ppm SO_2 at 200-300 ºC, which has been shown to be strongly dependent on WO_3 morphology. Nanoparticle WO_3 films were used as gas sensors for ethanol and H_2S. The working temperature of the sensor was between 150 and 250 °C and it was possible to detect 200 ppb of ethanol and 20 ppb of H_2S [310].

Different approaches have been designed to efficiently enhance the gas sensing characteristics of WO_3, including doping with noble elements, other metal oxides (forming of *p-n* heterojunction) or carbon-based materials. Au nanoparticle modified WO_3 nanorods were tested as H_2 sensors, exhibiting larger response to H_2, *i.e.* 50 ppm and recovery time lower than 10 s [311]. In another study, Pt nanoparticles were functionalized on WO_3 hybrid nanorods to be used as gas sensor. The gas sensing to varied concentrations (1, 5, 20, 100 and 200 ppm) of ethanol and methanol at 220 °C were demonstrated, with better performance than pure WO_3 [312]. In Ref. [313], Cr-doped WO_3 nanofibers were reported to have high response towards 100 ppm xylene and long term stability. Ag doped WO_3-based powder sensors for detection of NO gas in air were reported in Ref. [314], demonstrating a sensitivity of 38.3 at 250 ºC. This value was compared to the sensor without Ag doping. 3D hierarchical monoclinic-type structural Sb-doped WO_3 gas sensing material was described in Ref. [315]. The results of gas sensor measurements indicated that the 3D material has superior sensitivity (S = 122) and high selectivity to ppm-level NO_2 at 30 °C. It has been demonstrated that abundant structural defects derived from Sb doping modification, reduced band gap, and 3D hierarchical microstructure played a key role on the NO_2 gas sensing performance.

Ref. [316], reports CuO/WO_3 heterostructured nanocubes that were used to sense H_2S gas in a concentration as low as 50 ppb. By combining these with electric modulation, the sensors simultaneously exhibited fast recovery and ultrahigh sensitivity for detecting H_2S gas at low temperature. Nanocrystalline TiO_2:WO_3-based hydrogen sensors were reported in Ref. [317]. The sensitivity to H_2 was observed to be 0.91 and 0.94 at 200 ºC depending on the amount of Pd doping, with a response time of 1 min. Kumar *et al.* [318] reported a sensor based on the Pd/WO_3-ZnO nanocomposite showing remarkably improved H_2 sensing performance, good stability and excellent selectivity when compared to that of pure WO_3 and ZnO, at a relatively lower operating temperature (200 ºC) and with a low detection range of 10-1000 ppm. The Pd/WO_3-ZnO composite sensor exhibited a stable response over 20 cycles towards 100 ppm of H_2 at 200 ºC. The response and recovery time achieved were 16 s and 62 s, respectively, towards 100 ppm H_2 at 200 ºC. Shouli *et al.* [319] reported WO_3-SnO_2 nanocomposites to act as NO_2 sensors. The sensor exhibited the highest response for 186 to 200 ppm of NO_2 at operating temperature of 200 °C, with an increased response when Zn or MgO were added (responses of 251 and 418, respectively).

Zhang *et al.* [279] produced pure WO_3 and graphene oxide-WO_3 composite nanofibers to be applied as gas sensors. The graphene oxide-WO_3 composite nanofibers displayed the highest response of 35.9-100 ppm acetone at 375 °C, which is 4.3 times higher than that of pristine WO_3 nanofibers. Good selectivity and stability to acetone were also demonstrated for the composite nanofibers (Figure 14 (a)). WO_3 nanorods/graphene nanocomposites to act as NO_2 sensors were described in [320], and their gas sensing performance was compared to pure WO_3 nanorods. The response of WO_3 nanorods/graphene to 25 ppb, 100 ppb, 500 ppb and 1 ppm NO_2 were 13, 25, 40 and 61, respectively, while those of WO_3 nanorods were 2.6, 3.3, 5 and 5.3, respectively. In Ref. [321], Pd-WO_3/reduced graphene oxide (rGO) hierarchical nanostructures were used as efficient hydrogen gas sensors. These materials were sensitive to 20 ppm of hydrogen gas at room temperature, and the best operating temperature in terms of sensitivity (10^2) was 100 ºC with responses of < 1 min.

The relation between humidity and gas sensing was also explored. In Ref. [322], the effect of relative humidity on NO_2 sensitivity of a SnO_2/WO_3 heterojunction gas sensor was investigated. The sensor showed high sensitivity and a pseudo-linear response to NO_2 in the range 0-5 ppm in dry air. Response to variations in relative humidity was reported to be small at RH levels below 40%, with the sensor becoming saturated at higher values of RH. Strong interference effects were observed, with sensitivity to NO_2 decreasing rapidly as the RH of the atmosphere increased. Hybrid sensors were developed from Fe-doped WO_3 film and reduced graphene oxide top layer. The sensors were tested towards different concentrations of NO_2 and relative humidity at different temperatures ranging from 25 °C to 100 °C, showing fast dynamics to humidity when compared to NO_2. A response time of 6.7, 6.6 and 4.9 min and 6.54, 5.9 and 5.47 min to 10 % RH and 50 % RH, respectively at temperatures of 25, 50 and 100 °C were obtained [323].

The humidity-sensing process is generally based on the adsorption of water molecules and structure defects play a key role in this process. WO_3 is an interesting alternative as a humidity sensing material since it has a variety of nonstoichiometric defects and oxygen vacancies [324]. Several approaches have been developed to increase WO_3 humidity sensitivity. In Ref. [325], the effect of Ni doping was studied, in which the humidity sensing properties of pure WO_3 were significantly improved by Ni dopant. This was justified with the high surface area and smaller band gap energy of Ni-WO_3. The sensitivity was improved with the increase in relative humidity. A Li/K co-doped 3D ordered material (3DOM) WO_3 humidity sensor was presented in Ref. [324] (Figure 14 (b)). The sensor response and recovery times were 15 and 10 s, respectively, with the maximum hysteresis of 3 % RH for 11 to 95 % RH, indicating good sensor reliability. The enhanced humidity sensing behaviour was attributed to structural defects, adsorbed oxygen and the coeffect of Li/K. Moreover, to access the interaction of this material with other gaseous species that might be present in ambient air, its gas sensing performance was evaluated.

Several other studies reported the humidity sensing of WO_3 materials and when in association with other materials. In Ref. [326], the photoelectric responses of nanocrystalline WO_3 film to humidity under UV light irradiation were investigated in humidity range of 20-80 % RH at room temperature. Dong *et al.* [327] reported a WO_3 film deposited on silicon nanoporous pillar arrays to be used in capacitive humidity sensors. With relative humidity changing from 11 % to 95 % sensitivity over 16000 % at an optimal measuring frequency of 1000 Hz, has been reported. The response and recovery times were determined to be ∼104 and ∼ 94 s, respectively, with maximum humidity hysteresis ∼ 5.3 % at 65 % RH. Patil *et al.* [328] reported on the humidity sensing properties of poly(2, 5-dimethoxyaniline)/WO_3 composites. The sensor demonstrated to change linearly over an humidity range of 23-84 % with maximum percentage response factor of ~651 at 87 % RH, as well as quick response (humidification, 27 s and desiccation, 136 s) and narrow hysteresis (~5 %). In another study, WO_3-ZnO nanocomposites were produced and their humidity sensitivity tested. It has been shown that when % RH increases, there is a decrease in the resistance for the humidity range from 15 % to 95 %. The sensor showed a maximum sensitivity of 16.42 M Ω/% RH and narrow hysteresis (1.09 %) [329].

WO_3 has also the potential to be integrated in UV photodetectors/sensors since it has an indirect large energy band gap (3.3 eV). Lately, WO_3 nanostructures have been used to overcome limitations reported for WO_3-based UV sensors, such as slow response times (> 1 min) [330]. WO_3 nanosheets were used as high-performance UV photodetectors/sensors, showing excellent optoelectronic performance with high sensitivity (293 A W^{-1}), fast response speed (40 ms), high on/off ratios (2000) and high external quantum efficiency (997 %) [331]. Li *et al.* [332] reported WO_3 nanowires synthesized on carbon papers to be used as UV photodetectors/sensors (Figure 14 (c). These WO_3 hierarchical sensors demonstrated response and decay times of about 3 s and 20 s, respectively. In another study, hexagonal WO_3 nanowires were also tested as UV photodetectors. An increase of more than two orders of magnitude in conductance was obtained under UV illumination at 312 nm with a photoconductivity gain of 4.6×10^3 [333]. In Ref. [334], WO_3 nanobelts were produced via electrospinning for application as UV photodetectors. The sensor's photocurrent increased to ~ 12 nA and then rapidly decreased to its initial value (12 pA) once the light is turned off, suggesting high sensitivity of the photodetector with photo-dark current ratio up to 1000. A responsivity and external quantum efficiency up to 2.6×10^5 A W^{-1} and 8.1×10^7 %, respectively, have also been demonstrated. Shao *et al.* [335] reported 3D WO_3 nanoshale structured materials synthesized using hydrothermal synthesis. The UV photodetector fabricated with 3D WO_3 nanoshale showed good photoresponsivity (5.1 A W^{-1}), which was attributed to the internal gain introduced by surface oxygen adsorption–desorption process, as well as high surface to volume ratio of the 3D nanoshale structure. In Ref. [330], an ultraviolet photodetector was fabricated from WO_3 nanodiscs and reduced graphene oxide composite material. A maximum photoresponsivity of 6.4 A W^{-1} at 347 nm was observed under 20 V bias. The rise time (as measured from 10 % to 90 %) and fall time (from 90 % to 10 %) of the photodetector were reported to be 13 and 16 ms, respectively.

UV photodetectors/sensors with WO_3 in the form of films were also explored. Cook *et al.* [336] reported WO_3 films produced by inkjet printing to be used as UV photodetectors. Large on/off ratio of 3538 and high responsivity up to 2.70 A W^{-1} at 5 V bias (0.54 A W^{-1} V^{-1}) were obtained. In another study, a monolayer WO_3-based UV-A photodetector was reported. The sensor has demonstrated fast response time of less than 40 μs and photoresponsivity reaching ∼0.329 A W^{-1}. Long-term stability exceeding more than 200 cycles without any visible degradation was also showed [337].

In terms of biosensors, the remarkable properties of WO_3 that include reversible change of conductivity, high sensitivity, selectivity and biocompatibility, make this material suitable for integration in biosensors [338]. Deng *et al.* [339] reported direct electron transfer of cytochrome *c* at WO_3 nanostructures. A combination of direct electrochemistry of cytochrome *c* at the nanostructured WO_3 surface and enzymatic catalytic activity of cytochrome *c* towards H_2O_2 resulted in a third-generation H_2O_2 biosensor with high selectivity. The biosensor demonstrated a wide linear detection range from 3×10^{-7} to 3×10^{-4} M, low-detection limit (2.4×10^{-7} M) and short response time of 5 s. Liu *et al.* [340] reported WO_3 nanowires with high length-diameter ratio that were used to immobilize hemoglobin to fabricate a mediator-free nitrite biosensor. The biosensors displayed superior performance for detection of nitrite with a wide linear range of 1 to 4200 μM, as well as an extremely low detection limit of 0.28 μM (Figure 14 (d)). Anithaa *et al*. [341] reported WO$_3$ nanoparticles with monoclinic (γ) and orthorhombic (β) structures synthesized by simple microwave irradiation to be applied for mediator-free dopamine detection. The γ-WO$_3$ modified glassy carbon electrode exhibited a linear response over a wide concentration range of 0.1 μmol L^{-1}-600 μmol L^{-1} of dopamine with lowest detection limit of 24 nmol L^{-1}. The dopamine sensor showed excellent anti-interference ability against electroactive species and metal ions with good stability and reproducibility. In Ref. [342], polyethylene glycol assisted WO$_3$ nanoparticles were used for L-dopa bio-sensing applications. The detection limit to L-dopa was demonstrated to be 120 nM.

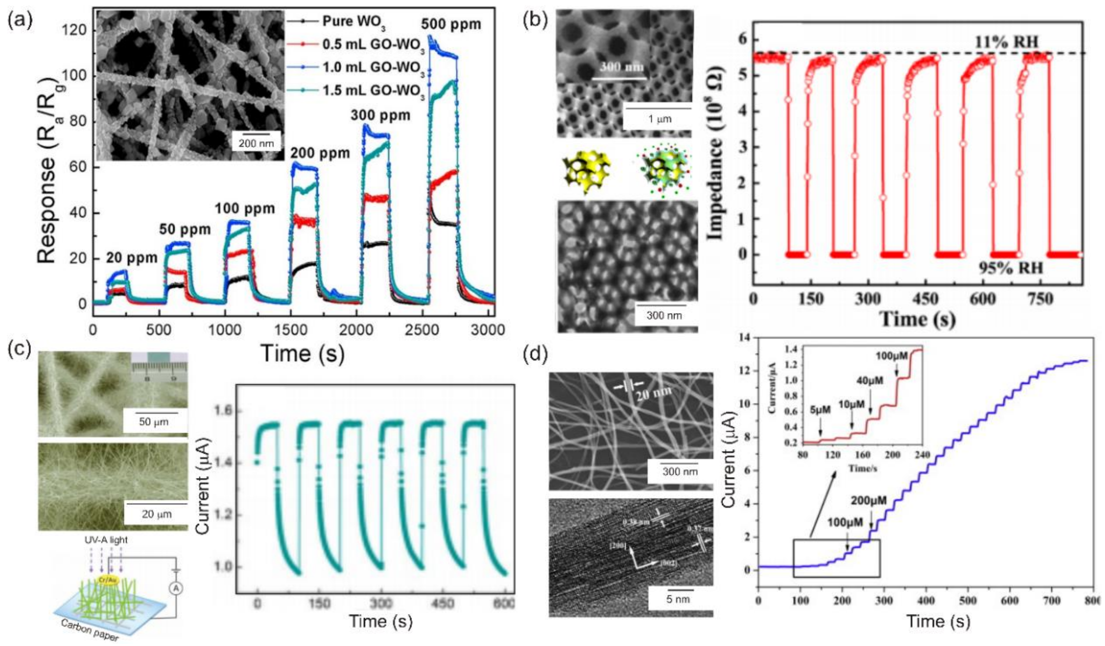


Figure 14. (a) Graphene oxide-WO$_3$ composite nanofibers and dynamic gas sensing curves of the sensors as a function of acetone concentration [279], (b) SEM and TEM image of a Li/K co-doped 3D ordered material to be used as WO$_3$ humidity sensor [324] and realtime impedance under different RH. (c) SEM images of WO$_3$ nanowires and the scheme of the UV photodetector with its corresponding light switching ‘‘ON’’ and ‘‘OFF’’ curve [332]. (c) SEM and TEM images of WO$_3$ nanowires and the graph shows the current–time response of the Nafion/hemoglobin/WO$_3$ nanowires/glassy carbon electrode [340]. Reproduced with permission of *Elsevier* [279] and [340], *ACS publications “Copyright (2018) American Chemical Society”* [324], and *Royal Society of Chemistry* (2018) [332].

In Ref. [343], bovine hemoglobin was electrostatically immobilized on WO_3 nanoparticles, multiwalled carbon nanotubes were added and this was applied to modify a carbon paste electrode. The fabricated biosensor showed suitable electrocatalytical properties in the simultaneous determination of levodopa (L-DOPA), folic acid, and uric acid. Santos *et al.* [338] reported the synthesis of WO_3 nanoparticles by hydrothermal method with different structures (Figure 15) to be used as nitrite biosensors. In this study, c*c*NiR was chosen as model enzyme due to its high catalytic activity towards nitrite reduction, and c*c*NiR modified (c*c*NiR/WO_3/ITO) electrodes were produced. The biosensors demonstrated sensitivities of 2143 mA M^{-1} cm^{-2}.

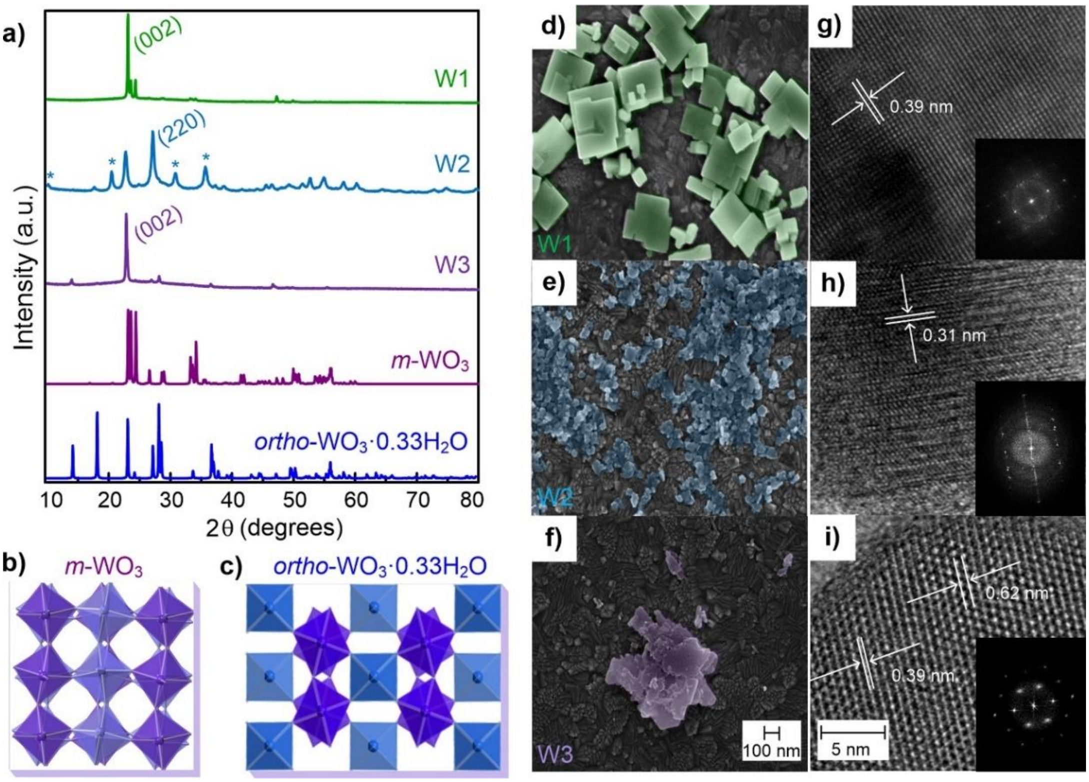


Figure 15. (a) to (i) XRD, SEM and TEM measurements of hydrothermally synthesized WO_3 powders to be used as nitrite biosensor [338]. Reproduced with permission of *Elsevier* (2018).

Marques *et al.* [262] reported WO_3 nanoparticles synthesized by microwave assisted hydrothermal synthesis which were used to impregnate non-treated regular office paper substrates. This allowed the production of a paper-based colorimetric sensor (Figure 16 (a)) able to detect electrochemically active bacteria in different growing stages by electrochromic reaction. A colorimetric relation between the growing stage of bacteria and WO_3 nanoparticles concentration was presented with RGB analyses (Figure 16 (b)).

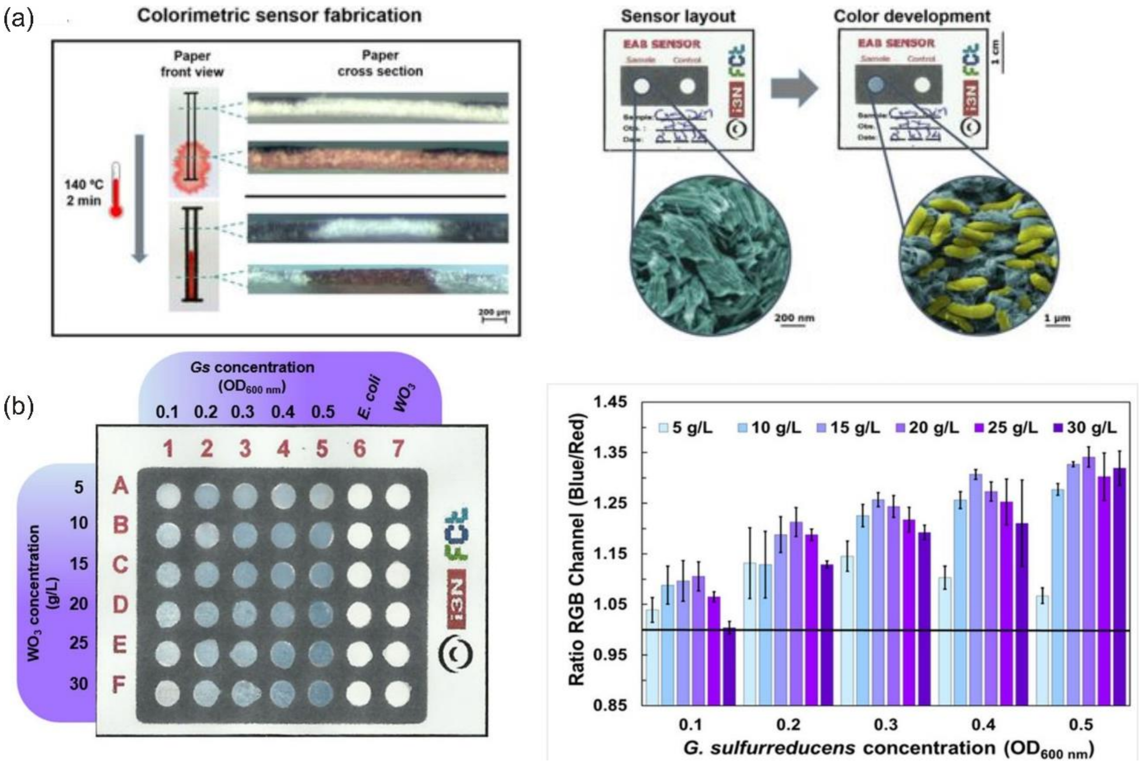


Figure 16. (a) Scheme of the colorimetric sensor fabrication with the hydrophobic barriers formation together with the photograph of paper-based sensor photograph of the Colorimetric assays of h-WO_3 nanoparticles at different concentrations, and (b) RGB analyses of *h*-WO*3* nanoparticles at 15 g/L in contact with *Geobacter sulfurreducens* cells, with the negative control *E. coli* and a blank test [262]. Reproduced with permission of *Springer Nature* (2018).

Righettoni *et al.* [344] reported Si:WO_3 sensors for highly selective detection of acetone for easy diagnosis of diabetes by breath analysis. The biosensor was able to detect low acetone concentrations (down to 20 ppb) with high signal-to-noise ratio in ideal (dry air) and realistic (up to 90 % RH) conditions. At 90 % RH, healthy humans (≤ 900 ppb acetone) and diabetes patients (≥ 1800 ppb) could be distinguished by a gap of 40 % in sensor response. In Ref. [345], 3D graphene network and WO_3 nanowire composites were demonstrated to produce a multifunctional colorimetric and electrochemical biosensing platform. The peroxidase-like activity of composite was investigated to colorimetrically detect H_2O_2. Moreover, the produced biosensor showed an ultrahigh sensitivity of 1.306 mA mM^{-1} cm^{-2} to dopamine and linear range up to 150 μM, as well as low detection limit (238 nM) and response time (4 s). Li *et al.* [346] reported WO_3-TiO_2 hybrid films prepared on ITO electrodes for multi-functionalized biosensors. Electrochemical oxidation and reduction of of norepinephrine and riboflavin (Vitamin B2) was demonstrated. In another study, an universal photoelectrochemical sensing platform was fabricated based on the composition of protoporphyrin IX, WO_3 and reduced graphene oxide on ITO electrode for detecting cysteine in aqueous solution. The biosensor for detection of cysteine showed linear range of 0.1 to 100 μM and the detection limit was 25 nM [347]. Santos *et al.* [348] reported WO_3 nanoparticle-based conformable pH sensors compatible with wearable biomedical devices, since pH is a vital physiological parameter that can be used for disease diagnosis and treatment as well as in monitoring other biological processes. These sensors showed sensitivity of -56.7 ± 1.3 mV/pH in a wide pH range of 9 to 5.

2.4 Copper oxides

Copper oxides are abundant materials, eco-friendly, non-toxic and are compatible with wet-chemical synthesis routes that originate low-cost devices [11, 349, 350]. The most common copper oxides are copper(I) oxide or cuprous oxide (Cu_2O), reddish material, and copper(II) oxide or cupric oxide (CuO), black material. Both copper oxides are *p*-type semiconductors displaying a bulk direct band gap from 2-2.17 eV in the case of Cu_2O [351, 352] and a narrow bandgap of 1.2 eV (bulk) for CuO, that is controversial regarding being direct or indirect [353, 354]. The *p*-type character of both oxides is usually attributed to the presence of negatively charged Cu vacancies [355-357]. Cu_2O possesses high carrier mobility of about 100 cm^2 $V^{-1}s^{-1}$ at room temperature and long carrier diffusion length ranging up to several micrometers [358]. Upon photoexcitation, the excitons of Cu_2O are found to be long-lived (10 µs) [351].

Cu_2O crystallizes as in a cubic structure with space group *Pn3m* (224) and lattice parameter of 0.42696 nm [350]. Its unit cell contains six atoms, in which four copper atoms are positioned in a face-centred cubic lattice and the two oxygen atoms forming a body-centred cubic sublattice a face-centered cubic (fcc) sublattice. The oxygen atoms occupy tetrahedral interstitial positions in respect to the copper sublattice, in a way that oxygen is tetrahedrally coordinated by copper, while copper is linearly coordinated by two adjacent oxygens [350, 359]. CuO has a complex monoclinic tenorite crystallographic structure, and it belongs to the *C*2/*c* (15) space group with lattice parameters a= 0.46833 nm, b= 0.34208 and c=0.51294 nm [360, 361]. Each Cu is coordinated to four coplanar O at the corners of a nearly rectangular parallelogram (CuO_4-plaquettes) [362]. The oxygen is coordinated to four Cu at the corners of a distorted tetrahedron. The six nearest O to each Cu complete a strongly distorted octahedron. The CuO_4 parallelograms form ribbons along [110] direction altering to [010] direction. Each ribbon is linked to adjacent chains of other groups by sharing corners [360, 361]. The structure can be considered as being based on two types of zig-zag Cu-O chains running along the [101] and the $[10\bar{1}]$ directions [363]. Both copper oxides unit cells are represented in Figure 17.

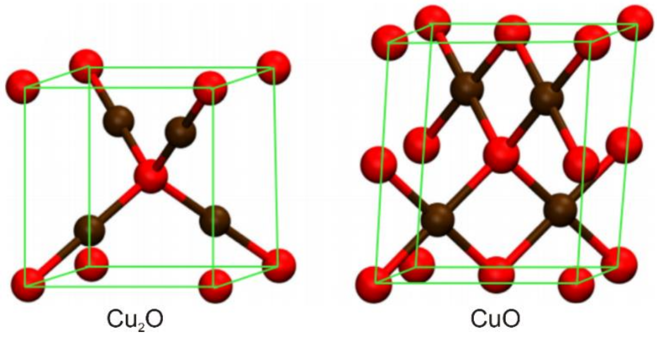


Figure 17. Unit cells of cuprous oxide Cu_2O and cupric oxide CuO [364]. Reproduced with permission of *Elsevier* (2018).

The thermal oxidation of metallic copper into both Cu_2O and CuO has been largely reported [11, 349, 365-371], as copper displays high oxygen affinity [372]. The oxide phase formation starting from copper by thermal oxidation can be described as follows: $Cu \rightarrow Cu + Cu_2O \rightarrow Cu_2O \rightarrow Cu_2O + CuO \rightarrow CuO$. Cu_2O oxidation occurs at temperatures as low as 100 °C [372]. In contrary, CuO formation is slow and is considered a product of Cu_2O oxidation (CuO starts at 300 ºC [373]). Its formation is possible above a certain critical thickness of a Cu_2O layer on the metal surface, thus Cu_2O serves as precursor to CuO [372]. The reactions involved can be summarized as follows [366]:

$$4Cu + O_2 \rightarrow 2Cu_2O \qquad (12)$$

$$2Cu_2O + O_2 \rightarrow 4CuO \qquad (13)$$

Thermal oxidation of copper, is an attractive technique due to its simplicity, high-quality and low-cost, nevertheless it is a time consuming route [374]. Besides thermal oxidation, several other techniques have been used to produce copper oxides, including hydrothermal synthesis [367, 375], microwave irradiation [376] and microwave oxidation [11], sol-gel method [377, 378], spray pyrolysis [25, 379], electrodeposition [380, 381], sputtering [382, 383], among others.

Several structures at the nano/micrometer scales have been reported for both Cu_2O and CuO materials, such as nanowires [384-386], nanorods [387, 388], nanobelts [389, 390], nanowhiskers [391, 392], nanocubes [55, 393, 394], octahedral nanostructures [395, 396], nanospheres [349, 397-400], hierarchical nanostructures [401], and others (Figure 18).

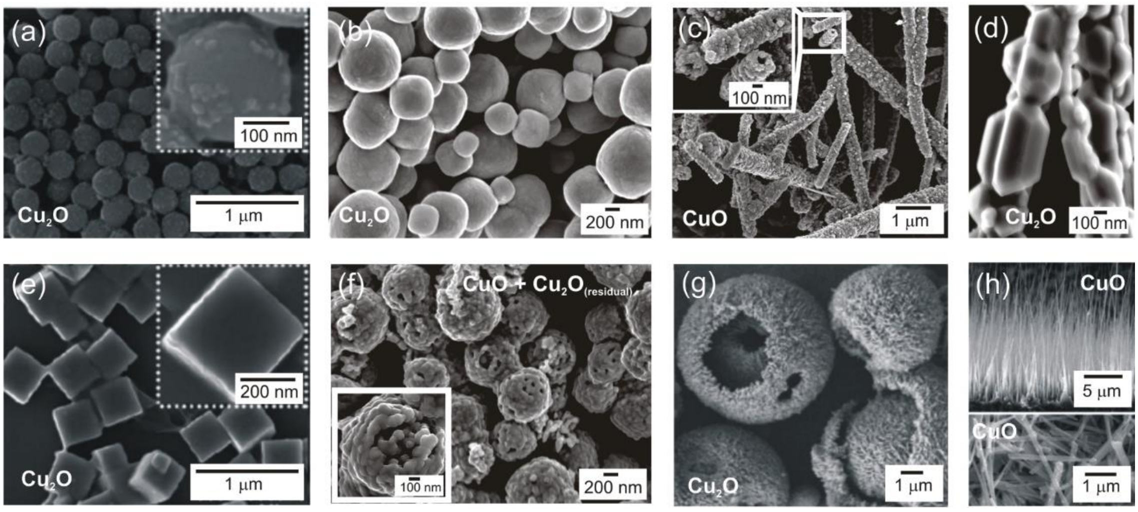


Figure 18. SEM images of Cu_2O spheres in (a) [55] and (b) [349], (c) CuO nanotubes, (d) Cu_2O nanowires [11], (e) Cu_2O nanocubes, (f) CuO nanospheres [349], (g) hierarchical hollow Cu_2O microspheres [401] (h) CuO nanowires [386]. Reproduced with permission of *Royal Society of Chemistry* [55] and [11], *Materials Research Society* [349], *John Wiley and Sons* [401], and *Elsevier* (2018) [386].

Cu_2O and CuO have been proposed for several applications over the years, including photocatalysis [402, 403], solar cells [404, 405], electrodes in lithium ion batteries [406, 407], thin-film transistors [368], sensors [375, 408, 409], among others. With emphasis to the latter application, integration of both materials in sensors has been extensively investigated over the years, due to their intrinsic *p*-type properties [410]. The application of Cu_2O in gas sensors is much less studied than for CuO [55]. Cu_2O nanowires were tested as gas sensors towards H_2, showing a response of 33.3 % and recovery time of ~10 min [411]. Tang *et al.* [412] reported on the gas sensing performance of Cu_2O nanocages towards gasoline. In another study, sensitivity of hierarchical Cu_2O microspheres toward 100 ppm ethanol was estimated to be 8.2, which is much higher than the value of 1.5 measured for solid Cu_2O microspheres [401]. The gas sensitivity of Cu_2O nanocubes and nanospheres were tested for ethanol vapor, with clear sensitivity differences regarding particle size and morphology [55]. Sensors based on Cu_2O films have also been reported, demonstrating high sensitivity, fast response time, and fast recovery time for methane gas at an operation temperature as low as 180 °C. At a 2.5 %

CH_4 concentration, the films demonstrated sensitivity around 70 %. The fast and high response of Cu_2O sensor for methane was justified by the increase of resistance in intrinsic *p*-type Cu_2O in the presence of methane gas [413].

CuO nanostructures have been integrated in gas sensors for detection of a variety of reducing as well as oxidizing gases including acetone, ethanol, propanol, H_2S, CO, O_3, NO_x, methanol, formaldehyde, H_2, toluene and ammonia [414]. Kim *et al.* [386] reported CuO nanowire gas sensors for air quality control in automotive cabin, showing a resistance decrease upon exposure to 30–100 ppm NO_2, and increase upon contact with $\leq$ 5 ppm NO_2. Yang *et al.* [415] reported on the synthesis of CuO 3D flower- and 2D branching sheet-like CuO nanostructures exhibiting an enhanced gas response to the five gases. At 1000 ppm, the CuO flower sensor demonstrated responses to ethyl-acetate (4.6), ethanol (4.0), acetone (3.8), xylene (3.6) and toluene (2.8). The sheet-like structures resulted in lower responses. The gas-sensing mechanism of *p*-type CuO semiconductor was explained by the change in resistance caused by the adsorption/desorption and reactions of gas molecules at the semiconductor surface. In another study, CuO nanoparticles were used for ethanol sensing showing fast response and recovery times below 10 s and responses greater than 2.3 at 100 ppm of ethanol at 200 °C (Figure 19 (a)) [416]. Flower-like CuO nanostructures with porous nanosheets demonstrated good H_2S gas sensing performance with maximum responses between 2.10 and 2.15 for five consecutive sensing cycles at 1 ppm, showing good reproducibility. The flower-like CuO nanostructured sensor was exposed to other types of gases (NO_2, H_2, CO, C_2H_5OH and NH_3) and for 100 ppm of NH_3, the sensor showed a response sensitivity of 1.42 [417]. CuO nanowires were integrated as ethanol gas sensors, showing responses of 1.06, 1.11, 1.14, 1.18, 1.24, and 1.27 for ethanol gas concentration of 25, 50, 100, 200, 500, and 1000 ppm, respectively [418]. CuO wormlike structures were also tested as gas sensors towards ethanol [419].

When it comes to gas sensors with films, Choi *et al.* [420] reported on the direct printing synthesis of CuO hollow spheres to form a film. This film based on CuO hollow spheres exhibited a high, stable response of ∼2 to H_2S, while for C_2H_5OH, the response was ∼3, which was 2 times higher than that (∼1.5) of CuO powder. CuO thin films were also reported for gas sensing applications. The gas sensitivity was demonstrated to increase up to 5.1 in the presence of CO_2 gas at 160 °C, while in the presence of N_2 gas, it reached only 1.43 even at 200 °C [421].

It has also been reported combinations of metal oxide materials to obtain a *p*-/*n*-heterojunction. In Ref. [422], flower-like *p*-CuO/*n*-ZnO nanorods heterojunction was produced showing response of 98.8to 100 ppm ethanol, which was 2.5 times that of ZnO material, with response and recovery time of 7 s and 9 s, respectively. Good selectivity and long-term stability were also reported with response to low concentration of ethanol (1 ppm) of 9.68 using the flower-like *p*-CuO/*n*-ZnO heterojunction nanorods. In another study, sensors based on ZnO/CuO nanostructures were tested as gas sensors and had investigated their H_2S-sensing properties, with sensor response of 2.7, and response time within 37 s [423]. CuO-MnO_2 nanocomposites were also reported, with response time of 120 s and recovery within 600 s [424]. Sensors based on mixtures of Cu_2O and CuO has also been reported. Meng *et al.* [425] showed Cu_2O/CuO sub-microsphere based sensors with responses up to 2.1–50 ppb of H_2S gas at 95 °C, with recovery time of about 76 s. Zhou *et al.* [426] reported porous Cu_2O/CuO cubes with enhanced gas sensing properties. For acetone concentrations of 50, 100, 200, 400, 500 ppm, the obtained responses were 3.0, 4.4, 6.5, 9.0 and 9.9, respectively. Cu_2O and

CuO were also mixed with metal nanoparticles, forming a hierarchical hollow nanostructure that was applied for CO sensing [427].

The mixture of copper oxides to carbon-based materials has also been addressed. In Ref. [428], CuO-reduced graphene oxide sandwiched nanostructure was investigated to determine its hydrogen sensing characteristics. In another study, reduced graphene oxide conjugated Cu_2O nanowire mesocrystals demonstrated higher sensitivity toward NO_2 at room temperature, surpassing the performance of Cu_2O nanowires networks and rGO sheets. This composite showed sensitivity of 67.8 % at 2 ppm and calculated limits of detection of 82 ppb [429].

Humidity-sensing studies of *p*-type semiconducting materials are scarce. Hsueh *et al.* [430] reported on the fabrication of humidity sensors by growing CuO nanowires on glass substrates. These sensors demonstrated that resistance of the CuO nanowires increased with the increase of relative humidity (52-90 %) due to the *p*-type nature of CuO. In another study, nanostructured Cu_2O porous films were exposed to humidity. The increase of resistance with increasing RH values is a characteristic response of *p*-type metal oxides, in which holes are the majority charge carriers. Up to 48 %RH , the linear increase of response percentage has been reported. The average response and recovery time evaluated for low RH were 151±6 and 145±18 s, respectively, with a maximum rate of 4.38±0.16%/RH [431]. Wang *et al.* [432] reported on CuO nanowire humidity sensors, that show steady state currents of about 2.44, 2.32, 2.23, and 2.15 μAwhen measured with 20, 40, 60, and 80 % relative humidity, respectively.

A blend of Cu_2O nanopowder and poly-N-epoxypropylcarbazole was also tested as humidity sensor, with an abrupt decrease of resistance at 30 % RH [433]. In another study, the electronic conduction and capacitance of an Au/CuO/Cu_2O/Cu sandwich structure was investigated and revealed to be dependent on humidity [434]. Yuan *et al.* [435]

reported highly sensitive humidity sensors based on CuO inorganic-organic hybrid nanowires. Ref. [436] showed an urchinlike CuO modified by rGO composite that was integrated in humidity sensors revealing much higher impedance than pure CuO (Figure 19 (b)). The mixture of metal oxides was also investigated, in which moisture sensing of Cu_2O doped ZnO nanocomposites was reported by Pandey *et al.* [437], with the response and recovery time of this material shown to be 76 and 296 s, respectively.

Copper oxides based UV/near-UV sensors have also been reported, but in this case composing a heterojunction to enhance their performance due to an additional charge separation effect [438]. Wang and Cho [438] reported *p*-CuO nanowire/*n*-ZnO nanosheet heterojunctions and its application for near-ultraviolet light detection. Under different illumination conditions, the photocurrent detection limit was around 16.8 mW mm^{-2}. Hong *et al.* [439] demonstrated n-silicon nanowire arrays with a layer of CuO nanoflakes to be applied as photodetectors/sensors highly sensitive to visible and near-infrared light irradiation. The photocurrent obtained for this device was 0.96 μA at 0.48 W cm^{-2} for a 405 nm laser, 4.41 μA at 5 W cm^{-2} for a 532 nm laser and 4.92 μA at 5.5 W cm^{-2} for a 1064 nm laser (Figure 19 (c)). In another study, CuO nanowires were used to produce a *p*-CuO/*n*-ZnO heterojunction nanostructured photodetector/UV sensor. The responsivity was reported to be 0.040 A W^{-1} for 350 nm and an applied bias of 1 V and for a 2 V bias it increased to 0.123 A W^{-1} [440]. Ok *et al.* [441] demonstrated UV photodetectors/sensors based on *p*-Cu_2O thin film and *n*-ZnO nanowires for formation of a *p–n* heterojunction. These named all-oxide UV devices resulted in a responsivity of ~ 50 A W^{-1} at 360 nm.

Several studies reported the integration of copper oxides in biosensors [442-446]. Liu *et al.* [442] reported a sensor for the detection of glucose and hydrogen peroxide based on Cu_2O nanocubes wrapped by graphene nanosheets. A linear response over glucose concentration range of 0.3 to 3.3 mM was reported, with a detection limit of 3.3 μM, high selectivity and short response time (< 9 s). The enzymeless sensor also exhibited good response toward H_2O_2, with the linear response ranging from 0.3 to 7.8 mM at −0.4 V and detection limit of 20.8 μM. Cu_2O shuriken-like nanostructures produced by hydrothermal synthesis were tested as nonenzymatic glucose biosensors. The glucose sensors exhibited wide linear detection range (from 0.01 μM to 11.0 mM), ultra-low detection limit (0.035 μM) and high sensitivity (0.933 mA mM^{-1} cm^{-2}) [444]. In another study, carbon quantum dots/octahedral Cu_2O nanocomposites were tested as non-enzymatic glucose and hydrogen peroxide amperometric sensors. Amperometric sensing of glucose was realized with linear response range from 0.02 to 4.3 mM and showed a detection limit of 8.4 μM. The nonenzymatic sensor revealed an electrocatalytic reduction of H_2O_2 with linear response range from 5 μM to 5.3 mM and detection limit of 2.8 μM [447]. Ref. [446] showed leaf-like CuO nanoparticles for detecting glucose. This sensor exhibited high sensitivity (246 mA mM^{-1} cm^{-2}), short response time (within 5 s), linear dynamic range of 1.0 to 170 mM and low limit of detection (0.91 mM). In Ref. [448], CuO nanotube arrays were used as biosensors for glucose detection showing sensitivity of 1.89 mA mM^{-1} cm^{-2} and linear range from 5 μM to 3.0 mM.

Copper oxides were also tested as biosensors in film form. Inkjet-printed CuO nanoparticles to produce films were integrated in nonenzymatic glucose biosensors. The sensors showed high and reproducible sensitivity of 2762.5 μAm M^{-1} cm^{-2} with wide linear-detecting range of 0.05−18.45 mM and detection limit of ~0.5 μM [449]. A nonenzymatic glucose biosensor based on printed CuO nanoparticles film was also demonstrated in [450]. The biosensor showed linear response toward glucose in the range of 0.1 to 6.5 mM at a lower detection limit of 0.5 μM glucose. CuO thin film based uric acid biosensor has been reported to have good linearity over a wide uric acid concentration range of 0.05 mM to 1.0 mM with enhanced response of 2.7 mA mM^{-1} and long shelf life (> 14 weeks) [445].

Two metal oxides were also employed in biosensors. In Ref. [451], a ZnO–CuO composite matrix based biosensor was demonstrated for detection of total cholesterol, for which sensitivity was reported to be 680 μA mM^{-1} cm^{-2} and 760 μA mM^{-1} cm^{-2} towards free cholesterol and total cholesterol respectively with response time of 5 s, with long shelf life. Vertically-aligned ZnO nanorods decorated with CuO were produced and integrated in high-performance nonenzymatic glucose sensors. The fabricated electrodes exhibited high sensitivity (2961.7 μA mM^{-1} cm^{-2}), linear range up to 8.45 mM, low limit of detection (0.40 μM) and short response time < 2 s (Figure 19 (d)) [443].

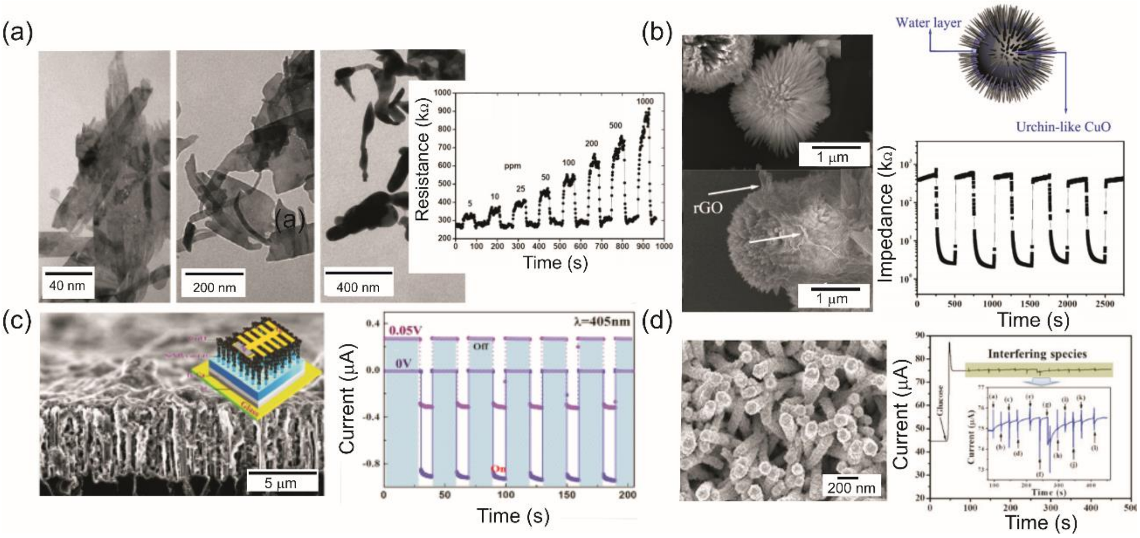


Figure 19. (a) TEM images of CuO nanoparticles for ethanol gas sensing [416], (b) SEM images of CuO/rGO composites for humidity sensors [436]. (c) *p–n* Heterojunctions of CuO/Si Nanowire Array to be used as photodectors/UV sensors [439]. (d) CuO modified ZnO nanorods to produce highly efficient non-enzymatic glucose sensors [443]. The graphs represent the sensors' response, resistance, current and impedance variations. Reproduced with permission of *ACS publications "Copyright (2019) American Chemical Society"* [416], *"Copyright (2018) American Chemical Society"* [436] and [439], and *Springer Nature* (2018) [443].

2.5 Tin oxide

There are two well-known tin oxide compounds, *i.e.* tin (IV) oxide or stannic oxide (SnO_2) and tin (II) monoxide or stannous oxide (SnO). SnO_2 is a *n*-type semiconductor, with a wide energy band gap ($E_g \sim 3.6$ eV for bulk at room temperature). SnO_2 has a tetragonal structure ($a = b = 0.4737$ nm and $c = 0.3186$ nm), similar to the rutile structure [452, 453] with space group $P4_2/mnm$ (136) [454]. SnO is a *p*-type semiconductor with a direct band gap of 2.5-3.0 eV and an indirect band gap of 0.5-0.7 eV [455-458]. The origin of *p*-type conductivity of SnO is mainly attributed to Sn vacancies and O interstitials [355]. Moreover, the native *p*-type character of SnO has been reported to result in more effective hole transport path and higher hole mobility due to the closer position of Sn-5s and O-2p components [458, 459]**.** SnO also has tetragonal structure ($a=b= 0.37986$ nm, $c= 0.48408$ nm) with space group $P4/nmm$ (129) [460].

The SnO_2 unit cell consists of two metal atoms and four oxygen atoms. Each Sn atom is placed at the center of six O atoms, nearly forming the corners of a regular octahedron. Oxygen atoms are surrounded by three Sn atoms that approximate the corners of an equilateral triangle [461]. In the case of SnO, this material has a layered structure with Sn-O-Sn layered pyramids, where oxygen atoms are tetrahedrally bonded to tin atoms. The Sn atoms are situated at the apex of regular square-based pyramids that are based on O atoms [355]. The unit cells of tetragonal SnO_2 and SnO are represented in Figure 20.

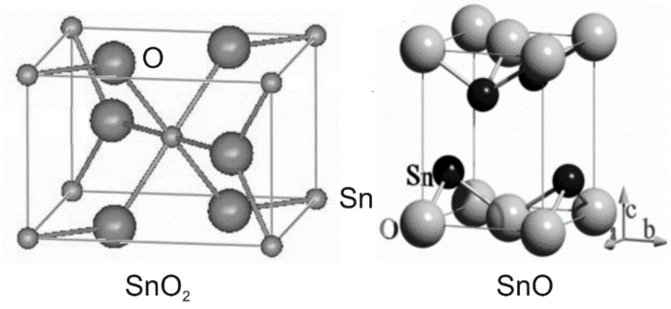


Figure 20. Unit cells of both SnO_2 [462] and SnO [463]. Reproduced with permission of *MDPI* [462] and *APS Physics* (2018) [463].

SnO is formed at the initial stage of Sn oxidation and it is a metastable phase that converts to SnO_2 even in the absence of oxygen if exposed to a certain temperature. The specific temperature to convert SnO to SnO_2 is unclear, varying from 250 to 600 ºC and depends on several factors, such as deposition method, initial oxygen concentration, annealing temperature and humidity [464]. Nevertheless, it is accepted that SnO is unstable above 270 °C in comparison with SnO_2, which makes it frequently known as precursor or intermediate phase in the production of SnO_2 nanostructures [457].

Several techniques have been reported to yield SnO and SnO_2 nanostructures and thin films, including hydrothermal synthesis [465-467], microwave irradiation [468, 469], precipitation method [470, 471], sol-gel technique [472-474], rf magnetron sputtering [475, 476], spray pyrolysis [477, 478], among others. SnO_2-doped material plays an important role as transparent conductive oxide material with remarkable electrical and optical properties in the form of thin films [453]. Antimony, indium and fluorine are examples of doping elements. The electrical properties of the SnO_2 films are critically depend upon its oxygen stoichiometry [477]. When passing to nanostructures, several nano- and microstructures have been reported for both SnO and SnO_2, such as nanoparticles [479, 480], nanorods [468, 481], nanobelts [482, 483], nanowhiskers [484, 485], nanowires [486-488], nanoflowers [489, 490], spheres [491, 492], among others.

Both SnO and SnO_2 have been used in numerous applications, such as thin film transistors [475], anodes for Li-ion batteries [493-495], water splitting for production of hydrogen [496], photocatalysis [497, 498] and sensors. In the latter application, SnO_2 has been extensively applied, with emphasis on gas sensing. In fact, SnO_2 is one of the most used materials as gas sensors [499]. Several SnO_2 nanostructures have been investigated for the detection of different gases, such as ethanol, H_2, O_2, CO, NO, NO_2 and NH_3 at moderate temperature, due to its fast-response speed, high exciton binding energy, high chemical stability, prominent selectivity, and low cost [500-503]. In Ref. [503], it has been shown ethanol gas sensors based on nanosheets-assembled SnO_2 hollow spheres showing responses from 2.4 to 23.5 for 10–500 ppm ethanol, and at the ppb level, showed a response of 1.1 toward 500 ppb of ethanol. The sensor response time was about 5 s (Figures 21 (a) and (b)). SnO_2 nanoparticles were also produced using the hydrothermal synthesis with conventional oven (Figure 21 (c)). Huang *et al.* [504] reported porous flower-like SnO_2 nanostructures for gas sensors (Figure 21 (d)). The sensor responses to 100 ppm ethanol and n-butanol were 42.6 and 77.2, respectively, at a working temperature of 240 °C. In addition, these sensors also exhibited a good response to methanol, 2-propanol, and acetone. Ref. [497] demonstrated hierarchical SnO_2 based ultrathin nanosheets that were tested as gas sensors for ethanol, ammonia, benzene, acetone, toluene, methanol and diethyl ether. The sensor sensitivity to 5 ppm ethanol is around 5.13 which increases to 183.8 for 500 ppm ethanol. The response and recovery time of hierarchical nanostructures to 100 ppm of ethanol were 1 and 2 s, respectively. The responses of this sensor to eight gases were also compared and the largest response was observed only for ethanol with a value of up to 44.7, implying good selectivity of the sensor for ethanol (Figure 21 (e)). In another study, square-shaped SnO_2 nanowires forming a sphere-like superstructure were tested as gas sensors. These sensors showed sensitivity of 5.5 for acetone concentration as low as 20 ppm, and the response and recovery times were 7 and 10 s, respectively [505]. SnO_2 nanorod sensors were also reported in Ref. [506] exhibiting sensitivity of 31.4 for 300 ppm of ethanol with both response and recovery time around 1 s. Liu *et al.* [507] reported tubular SnO_2 nanomembranes fabricated by rolled-up technology. The sensor exhibited a highly stable response to acetone detection at 20 ppm. Kuang *et al.* [508] reported hierarchical SnO_2 nanostructures composed of numerous one-dimensional nanorods and tested as gas sensors. The responses of sensors with six different ethanol concentrations (5, 10, 25, 50, 75 and 100 ppm) were 7, 13, 32, 44, 59 and 72, respectively (Figure 21 (f)).

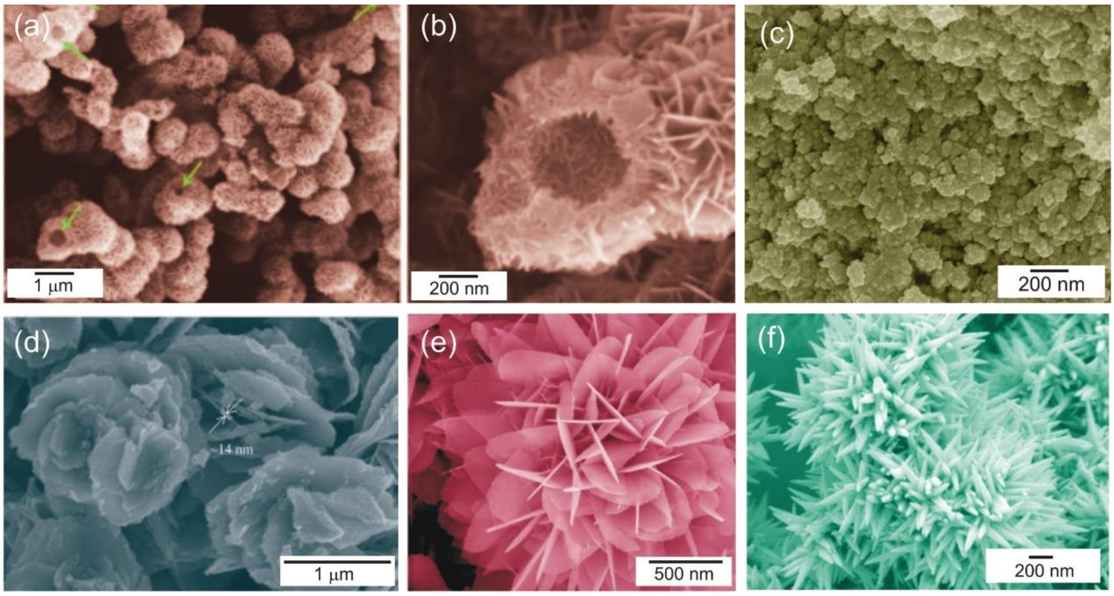


Figure 21. SEM images of (a-b) nanosheets-assembled SnO_2 hollow spheres for ethanol gas sensor [503], (c) SnO_2 nanoparticles produced at CENIMAT using hydrothermal synthesis, (d) porous flower-shaped SnO_2 nanostructures [504], (e) hierarchical SnO_2 based ultrathin nanosheets [497], and (f) hierarchical SnO_2 nanostructures made of superfine nanorods [508]. Reproduced with permission of *Elsevier* [503], [504] and [508] and *ACS publications "Copyright (2018) American Chemical Society"* [497],

Choi *et al.* [509] reported a SnO_2 nanowire-based gas sensor for detecting NO_2. The sensitivity was determined to be 18 and 180 when NO_2 concentration was 0.5 and 5 ppm, respectively (at 200 ºC). Suman *et al.* [510] reported a sensor based on SnO micro-disks, showing a response of ~13 to 100 ppb of NO_2, and selectivity against potential interferent gases such as H_2, CO and CH_4 was also demonstrated. In another study, SnO, SnO_2 and Sn_3O_4 nanobelts had their efficiency as gas sensors compared. SnO and Sn_3O_4 exhibited higher sensitivity and selectivity relative to potential interferent gases (H_2, CO and CH_4) than SnO_2 nanobelts (Figure 22 (a)) [511].

Doping elements, such as, Ag, Au, Pd, Pt, and other metal oxides are used to enhance the sensing properties, such as, sensitivity, response time and reproducibility for a specific gas [502]. Kolmakov *et al.* [486] reported the sensing ability toward oxygen and hydrogen of individual SnO_2 nanowires and nanobelts before and after functionalization with Pd catalyst particles. Sb-doped SnO_2 nanowires were tested as gas sensors and resulted in sensitivity of 1.76 upon exposure to 10 ppm ethanol and recovery time of about 5 s [512]. Reduced graphene oxide was also explored with tin oxides for gas sensors. Wei *et al.* [513] reported the gas-sensing of a silver-decorated tin oxide/reduced graphene oxide ($Ag/SnO_2/rGO$) composite with a sensitivity to 400 ppm ethanol of 95.3 at optimum operating temperature (280 °C). The SnO_2/rGO sensor was also tested demonstrating a lower sensitivity of 55.3. A hierarchical SnO_2/rGO nanostructure was described in Ref. [514], with sensitivity of 78 to 10 ppm H_2S at 100 °C and response time of 7 s. NH_3 gas sensors based on Pd, SnO_2 and rGO ternary nanocomposite was demonstrated in Ref. [515], with response and recovery time of 7 and 50 min, respectively, at NH_3 testing concentration of 100 ppm.

The combination of different metal oxides has also been widely addressed in gas sensing. Core-shell WO_3-SnO_2 nanofibers have been synthesized via a coaxial electrospinning approach. The sensors exhibited good response to ethanol (5.09 at 10 ppm) and short response/recovery time (18.5 s and 282 s) [516]. A sensor based on ZnO/SnO_2 composites with a hollow nanostructure was reported in Ref. [517]. The sensitivity to 30 ppm ethanol was shown to be 34.8, which was about seven times higher than the sensor based on pristine SnO_2 hollow spheres (the response was 5.1). The sensor exhibited response to ppb-level ethanol and response time was 1 s. In another study, gas sensors fabricated from SnO_2-SnO nanocomposite with *p-n* heterojunctions exhibited an enhanced sensing performance for NO_2 gas detection, with limit of detection and sensitivity of 0.1 ppm and 0.26 ppm^{-1}, respectively [518]. Another *p-n* heterojunction was demonstrated with CuO–SnO_2 gas sensors for CO gas [519]. A sensor based on a hierarchical CoO/SnO_2 heterojunction demonstrated response up to 145 when exposed to 100 ppm ethanol gas. This sensor was demonstrated to be effectively higher when compared to SnO_2 only sensors (13.5 for SnO_2) [520]. Gas sensors based on SnO_2-decorated NiO nanostructures demonstrated excellent sensitivity and selectivity towards toluene, with response of 66.2-100 ppm, which was 50 times higher than that of pure NiO nanospheres (1.3-100 ppm). Additionally, the sensor had surpassingly low detection limit (ppb-level), showing response of 1.2-10 ppb toluene [521].

Similarly to copper oxides, integration of *p*-type materials, *i.e.* SnO, in humidity sensors is diminished. However, as observed for gas sensors, there are several studies demonstrating the use of SnO_2 in such sensors. Parthibavarman *et al.* [522] reported humidity sensors based on SnO_2 nanoparticles produced under microwave irradiation. This sensor showed fast response time (32 s) and recovery time (25 s) with relative humidity range of 5-95% in air at room temperature. Kuang *et al.* [92] reported the production of SnO_2 humidity nanodevice using a single SnO_2 nanowire as the sensing unit. The response time and recovery time of this sensor was 120-170 and 20-60 s, respectively. Ordered SnO_2 nanostructures were used as humidity sensors, showing a response and recovery time of 32 s and 42 s for 11-96 % RH, respectively. The hysteresis for the SnO_2 nanostructured sensor was < 5 % [523]. SnO_2 and Li^+-doped SnO_2 porous nanofibers were fabricated via electrospinning and tested as humidity sensors. The doped materials demonstrated better performance than the SnO_2 nanofiber-based sensor, in which an ultrafast response and recovery time within 1 s has been reported for the doped-sensor at a relative humidity level of 85 % [524]. Another study described humidity sensors based on ion-doped SnO_2 nanofibers (KCl) developed by screen-printing. It has been shown that impedance of the sensor decreased by more than five orders of magnitude with increasing relative humidity from 11 % to 95 %, with response and recovery time of 5 and 6 s, respectively [525].

Several studies also demonstrated humidity sensors based on different metal oxides. In Ref. [526], SnO_2/ZnO heterojunction nanostructured films demonstrated remarkable humidity-sensing performance exhibiting sensitivity of 90.56 to humidity. Nanostructured TiO_2–SnO_2 thin films produced by sol–gel process showed over three orders change in the resistance during relative humidity variation from 20 to 90 % [527]. Hybrid nanomaterials have also been described. Zhang *et al.* [528] reported a MoS_2/SnO_2 hybrid film sensor with ultrafast response/recovery behaviours. Three distinct nanocomposites based on SnO_2-CuO, SnO_2-Fe_2O_3 and SnO_2-SbO_2 and their humidity sensing performance were described in Ref. [529]. It has been shown that when relative humidity increases, the resistance of the nanomaterials decreases. of Amongst all other composites, SnO_2-SbO_2 showed maximum sensitivity for humidity (12 MΩ/%RH). Humidity sensors based on reduced graphene oxide and tin oxide (rGO-SnO_2) nanocomposites were also reported [530]. These sensors demonstrated stability over 30 days at 95 % RH (Figure 22 (b)).

As SnO_2 is wide bandgap material with consequent transparency in the visible spectral region, it has been reported for UV sensing. Huang *et al.* [72] reported single-crystalline SnO_2 nanobelt with amorphous embedded Sn nanodots , to produce an individual nanobelt-based UV photodetector/sensor. The responsivity value of the nanobelt photodetector excited by 300 nm-light was 56 A W^{-1}. This sensor also demonstrated high external quantum efficiency (EQE) ($\sim 2.3 \times 10^4$), fast response time (less than 0.3 s) and high on/off current ratio ($\sim 2.75 \times 10^3$). The photoresponse of SnO_2 nanobelts has been investigated under UV light in Ref. [531], and shown that the source–drain current increased to ~ 80 µA in air and up to ~ 900 µA in vacuum, demonstrating SnO_2 nanobelts potentialities as UV sensors. SnO_2 nanowires were tested as UV photodetectors in [532], with the photoelectric current exhibiting rapid photo-response as an UV lamp was switched on and off. In another study, photodetectors based on thin SnO_2 nanowires have been reported. These exhibited excellent light selectivity and stability and high EQE value of 1.32×10^7 [533]. SnO_2 hollow nanospheres have been used as an active material to fabricate UV photodetectors. The UV sensor exhibited peak UV responsivity of 2680 A W^{-1} and high external quantum efficiency of 9.8×10^5 % [534]. Lu *et al.* [535] reported ultrahigh gain in photodetectors based on single SnO_2 nanowires with ferromagnetic Ni electrodes.

SnO_2 has been also combined with other metal oxides to produce UV photodetectors/sensors. Xie *et al.* [536] reported UV photodetectors based on CuO/SnO_2 *p-n* nanoscale heterojunctions. The responsivity for the single SnO_2 nanodevice was 1.9 A W^{-1} while for the *p-n* heterojunction it was 10.3 A W^{-1}. The wavelength-dependent photocurrent-to-dark current ratio was estimated to be ∼592 for the CuO/SnO_2 photodetector at 290 nm. $ZnO-SnO_2$ nanowire arrays were synthesized by a near-field electrospinning method for flexible ultraviolet photodetectors application. These sensors exhibited excellent photoresponse properties to 300 nm ultraviolet light illumination including high I_{on}/I_{off} ratios (up to 10^3), good stability and reproducibility [537]. Another work described fully transparent photodetectors produced from electrospun $ZnO-SnO_2$ heterojunction nanofibers. This photodetector exhibited excellent operating characteristics, including high UV-sensitivity and photo-dark current ratio, and fast response speed [538]. TiO_2/SnO_2 branched heterojunction nanostructures with TiO_2 branches on electrospun SnO_2 nanofiber were developed for self-powered UV photodetector. Under UV irradiation, the self-powered UV photodetector exhibited responsivity of 0.6 A W^{-1}, high on/off ratio of 4550, rise time of 0.03 s and decay time of

0.01 s [539]. SnO_2 nanosheet films with branched TiO_2 nanoneedles on SnO_2 nanosheets, forming a heterojunction core–shell structure have been used to integrate UV photodetectors/sensors. These UV photodetectors showed responsivity of 0.6 A W^{-1}, high on/off ratio (440,563%), fast response for rise time 0.02 s and decay time 0.004 s [540]. A self-powered UV photodetector based on TiO_2 coated SnO_2 mesoporous spheres has been described in Ref. [541]. Under UV irradiation, this sensor displayed high on/off ratio of 11519, fast rise time of 0.007 s and decay time of 0.006 s.

Tin oxides are also largely present in biosensors. In Ref. [542], SnO_2 nanorod arrays have been tested as H_2O_2 biosensors. This sensor demonstrated sensitivity of 379 μA mM^{-1} cm^{-2}, low detection limit (0.2 μM) and high selectivity with apparent Michaelis–Menten constant estimated to be as small as 33.9 μM. Nanostructured SnO_2 thin films were presented as glucose sensors. These sensors exhibited higher response, fast rise time 8 s and suitable recovery time 53 s upon working at room temperature with a glucose concentration between 50-200 mg L^{-1} [543].

As mentioned previously, tin oxides have been doped or combined with other elements or metal oxide materials, including for biosensing. A mediator-free horseradish peroxidase-based H_2O_2 biosensor was constructed with Sb-doped SnO_2 nanowires as immobilization matrix for enzymes. The sensor showed sensitivity of 100 mA M^{-1} cm^{-2}, and detection limit of 0.8 μM at a signal-to-noise ratio of 3. The Michaelis–Menten constant was calculated to be 0.76 mM and the sensor demonstrated long-term stability [544]. Hydrogen peroxide biosensors based on Ni doped SnO_2 nanoparticles has been reported [545]. A horseradish peroxidase/Ni-SnO_2 nanocomposite has been studied exhibiting a linearity range from 1.0×10^{-7} to 3.0×10^{-4} M with detection limit of 43 nM. The apparent Michaelis–Menten constant of horseradish peroxidase on the nano-Ni–SnO_2 was estimated as 0.221 mM. Cr-doped SnO_2 nanoparticles based biosensors for selective determination of riboflavin in pharmaceuticals has been described in [546]. This sensor responded linearly to riboflavin over a concentration range of 0.2×10^{-6} to 1.0×10^{-4} M with detection limit of 107 nM. Shen *et al.* [547] reported the synthesis of Au-SnO_2 hybrid nanospheres with enhanced photoelectrochemical biosensing performance. The biosensor displayed suitable analytical performance for detection of cysteine with a broad linear range (from 0.4 mM to 12 mM) and low detection limit (0.1 mM). In Ref. [548], ZnO/SnO_2 heterostructured nanomaterials were explored to build a biosensing platform for detecting H_2O_2 by immobilizing hemoglobin with chitosan. The biosensor sensitivity was 52.8 mA cm^{-2} M^{-1}, with linear range from 2.0×10^{-6} to 3.7×10^{-4} M. The detection limit of H_2O_2 was 4.6×10^{-7} M when signal-to-noise ratio was 3.

The incorporation of carbon-based materials in tin oxides for biosensing has also been investigated. Zhu *et al.* [549] reported graphene/SnO_2 composite nanosheets loaded with noble metal nanoparticles to be applied as biosensors for nonenzymatic glucose detection. The amperometric response has been shown to be linear for glucose concentrations ranging from 2 to 20 mM with sensitivity of 20.3 μA mM^{-1}. Multiwalled carbon nanotubes-SnO_2-Au composite was tested as glucose biosensor by absorbing glucose oxidase on the hybrid material. The glucose biosensor demonstrated linear range from 4.0 to 24.0 mM, high stability with its voltammetric response remaining stable after 50 cycles [550]. A sensitive amperometric acetylcholinesterase biosensor, based on SnO_2 nanoparticles, carboxylic graphene and nafion for the detection of methyl parathion and carbofuran has been developed in Ref. [551]. The biosensor showed favourable affinity to acetylthiocholine chloride with an apparent Michaelis-Menten constant of 131μM, detecting methyl parathion in a linear range from 10^{-13} to 10^{-10} M and from 10^{-10} to 10^{-8} M. This device detected carbofuran in a linear range from 10^{-12} to 10^{-10} M and from 10^{-10} to 10^{-8} M. The detection limits of methyl parathion and carbofuran were 5×10^{-14} M and

5×10^{-13} M, respectively. Another study demonstrated amperometric acetylcholinesterase biosensors based on a nanocomposite of multi-walled carbon nanotubes, SnO_2 nanoparticles and chitosan. These biosensors exhibited a wide linear range from 0.05 to 1.0×10^5 μg/L with detection limit for chlorpyrifos of 0.05 μg/L. Based on the inhibition of pesticides, using chlorpyrifos as model pesticide, the biosensor exhibited a wide range, low detection limit, good reproducibility, and high stability. Using cabbages, lettuces, leeks and pakchois, acceptable recovery of 98.7–105.2 % was reported [552]. In Ref. [553], a carboxylated multiwalled carbon nanotubes–SnO_2 nanoparticles–graphene–chitosan composite was demonstrated as an amperometric biosensor (Figure 22 (d)). Lysine oxidase enzyme was immobilized covalently on the surface of the composite. The biosensor exhibited wide linear range (9.9×10^{-7} M–1.6×10^{-4} M), low detection limit (1.5×10^{-7} M), high sensitivity (55.20 μA mM^{-1} cm^{-2}) and fast amperometric response (< 25 s).

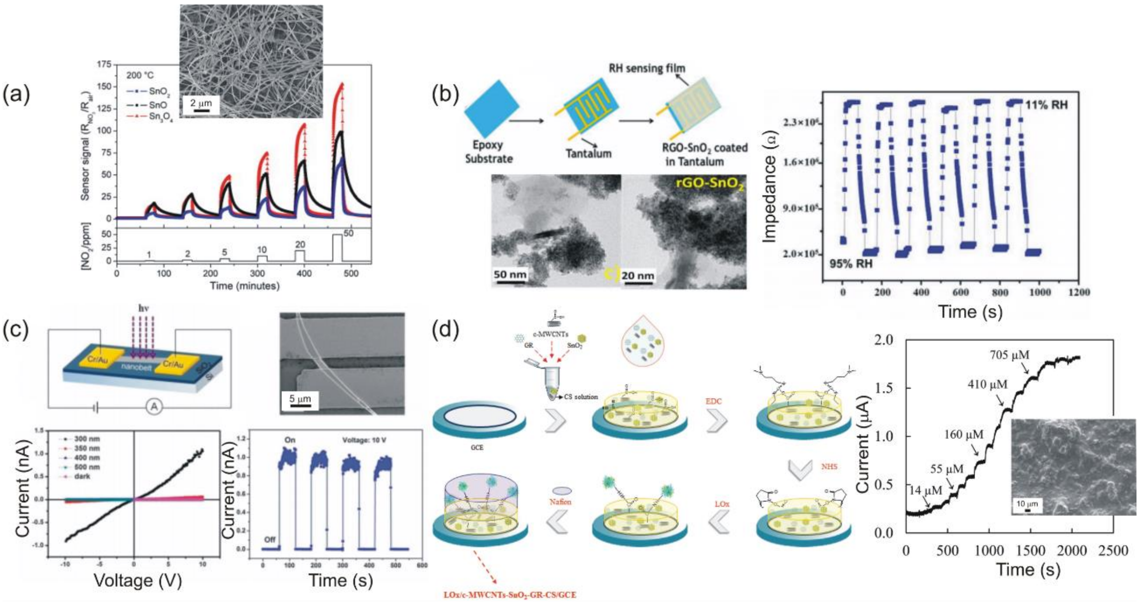


Figure 22. (a) SEM image of SnO_2 nanobelts. The graph showed the sensitivities of the gas sensor under exposure to NO_2, with concentrations ranging from 1 to 50 ppm of NO_2 [511]. (b) Schematic diagram of the rGO-SnO_2 humidity sensor [530], and the nanocomposite morphology. The graph shows the long-term stability of the rGO-SnO_2 sensor after being exposed to 95 % RH for 30 days. (c) Schematic illustration of a Sn-embedded SnO_2 nanobelt photodetector, and corresponding SEM image. The *I-V* curves of the photodetector exposed to light with different wavelengths and under dark conditions, with the time-dependent response of the photodetector [72]. (d) Production scheme of the carboxylated multiwalled carbon nanotubes–SnO_2 nanoparticles–graphene–chitosan composite biosensor together with its current-time response to successive addition of L-lysine into a stirred solution of 0.025 M [553]. Reproduced with permission of *MDPI* [530], *Royal Society of Chemistry* [72], and *Elsevier* (2018) [511] and [553].

2.6 Vanadium oxide

Vanadium oxide is a 3d transition metal compound which may display different valence states, ranging from +II to +V, and form a variety of oxides such as V_2O_5 (orthorhombic phase), V_2O_3 (rhombohedra phase), V_3O_7 (monoclinic phase), V_4O_9 (orthorhombic phase), V_6O_{13} (monoclinic phase) and also VO_2 [554-557].

The allotropic phases of VO_2 systems may include VO_2(R) (tetragonal/rutile phase, $P4_2/mnm$), VO_2(M) (monoclinic phase, $P2_1/c$), VO_2(B) (monoclinic phase, $C2/m$) and VO_2 (A) (tetragonal phase, $P4_2/ncm$) [558-561], however the most stable is VO_2(R) phase. Crystal structure of these four VO_2 polymorphs, is based on bcc oxygen lattice, with a somewhat regular oxygen octahedra, and vanadium in octahedral sites . In VO_2(R) and VO_2(M), the oxygen octahedra is aligned along two perpendicular directions, while for VO_2(B) and VO_2 (A) the oxygen octahedra is aligned along just one direction [559]. Despite having the same chemical formula, the crystalline and electronic structures are very distinct, exhibiting different electrical and optical properties [560, 562]. On table 1, the crystallographic parameters of the different vanadium oxide phases are shown.

Table 1. Space group and lattice parameter of the different vanadium oxide phases [563-568].

Crystallographic phase	**Space group**	**Lattice parameter (Å)**		
		A	*B*	*c*
VO_2 Monoclinic	$P2_1/c$	5.753	4.753	5.383
VO_2 Monoclinic	$C2/m$	12.03	3.693	6.42
VO_2 Tetragonal	$P4_2/ncm$	8.440	8.440	7.680
VO_2 Tetragonal/Rutile	$P4_2/mnm$	4.554	4.554	2.856
V_2O_3 Rhombohedral	D3*d*	4.9517	14.005	2.8283
V_2O_5 Orthorhombic	P*mmn*	11.510	3.563	4.369
V_3O_7 Monoclinic	C2/*c*	18.626	3.622	13.719
V_4O_9 Orthorhombic	C*mcm*	10.356	8.174	16.559
V_6O_{13} Monoclinic	C*m*	11.900	3.680	10.200

VO_2(A) and VO_2(B) are thermodynamically metastable phases that present a layered structure similar to V_2O_5 [569]. VO_2 (A) was reported as an intermediate phase in the transformation $VO_2(B) \rightarrow VO_2(R)$ [569]. Moreover, when heated to temperatures around 68 °C, the VO_2(M) phase presents a Mott metal-insulator transition that is characterized by a change in crystal structure from semiconductor phase ($P2_1/c$) to metallic phase VO_2(R) ($P4_2/mnm$) [558, 569]. Figure 23 shows a schematic representation of the unit cell of each oxidation phases of vanadium oxides.

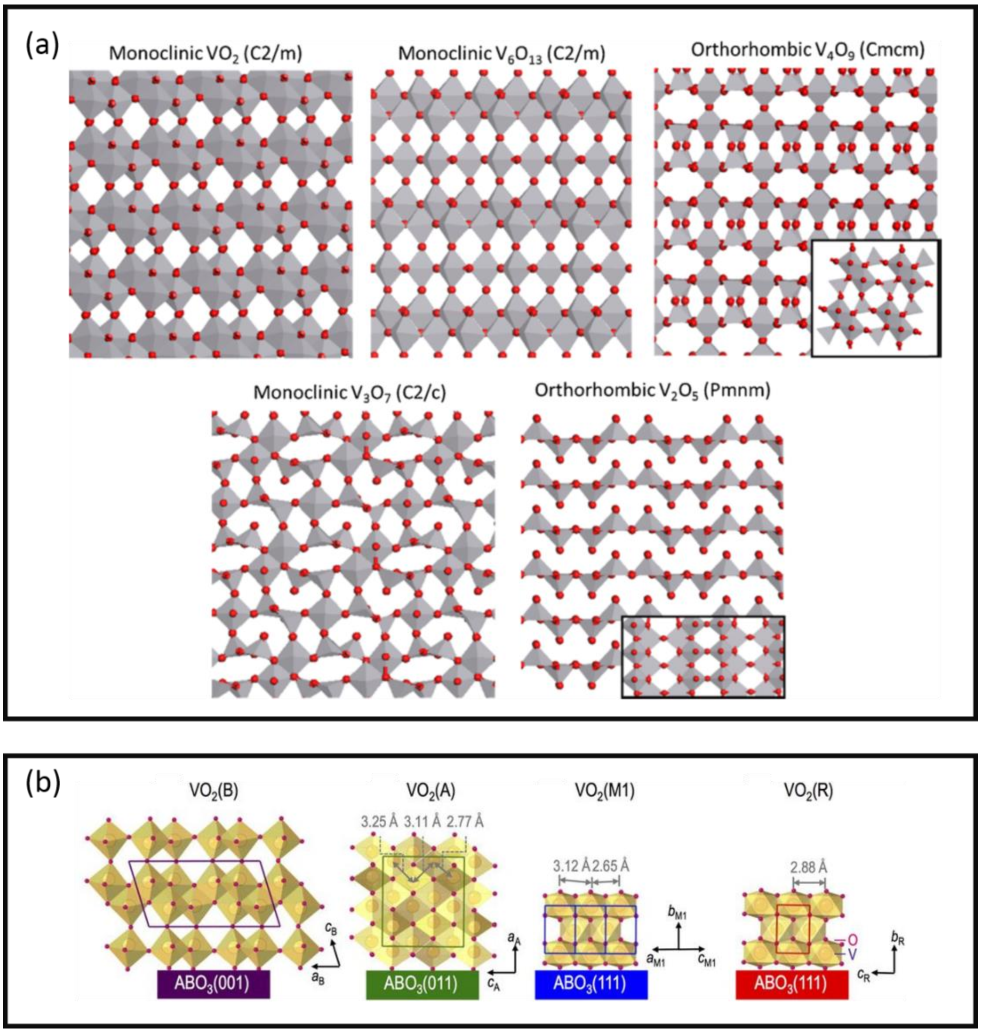


Figure 23. Schematic representation of (a) the *a*-axis of the lattice of V***n***O$_{2n+1}$ for *n* = 2, 3, 4 and 6 [556] and (b) VO$_2$(B), VO$_2$(A), VO$_2$(M) and VO$_2$(R) phases [560]. Reproduced with permission of *John Wiley and Sons* [556] and *Springer Nature* (2018) [560].

Due to their electronic and structural properties this class of oxides can be used in a vast number of applications, from catalysis [570], environmental pollution control optoelectronics [571, 572], in smart thermochromic and electrochromic windows [556, 573, 574], optical switches [575, 576] and in energy storage [577, 578]. In terms of sensing applications, reports have shown that the most used phases are VO$_2$(R) and V$_2$O$_5$, due to their metal to insulator transition at relatively low temperature that may alter resistivity by three orders of magnitude [560].

Different nanostructures can be synthesized via hydrothermal/solvothermal method [571, 572, 579], chemical bath [555], chemical vapor deposition [580], thermal evaporation [570], electrodeposition [578, 581, 582] and electrospinning [583]. With these production methods, it is possible to obtain different vanadium oxide morphologies, such as spheres [572], nanotubes [584, 585], nanorods [571], nanobelts [579], nanowires [570]. On Figure 24, it is possible to observe some of the vanadium oxide nanostructures reported.

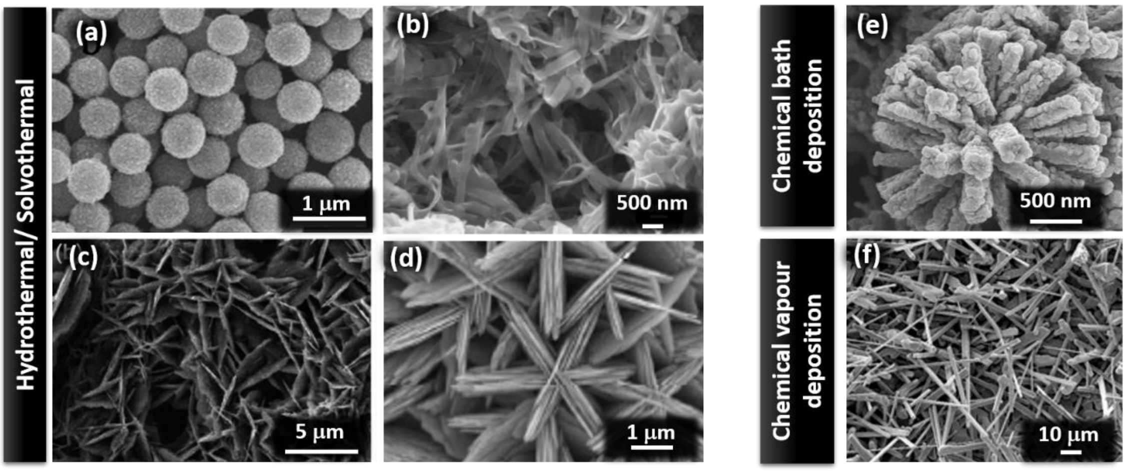


Figure 24. (a) V_2O_5 hollow spheres [572]; (b) V_2O_5 nanobelts [579]; (c) $VO_2(M)$ nanoflowers [558]; (d) VO_2 carambola shaped nanostructure on graphene [586], reproduced with permission of Royal Society of Chemistry (2018); (e) V_2O_5 urchin-like structures [555], and (f) VO_2 nanorods [580]. Reproduced with permission of *Royal Society of Chemistry* [572] and [586], *Wiley and Sons* [579] and [558]; *Springer Nature* [555] and *Elsevier* (2018) [580].

Gas sensors based on nanostructured vanadium pentoxide, V_2O_5, are the most used for detection of combustible gases [572, 579]. Wu *et al.* [572] synthesized V_2O_5 hollow spheres and suggested that by using this type of nanostructures, gas sensing properties would by greatly improved due to their high ratio of volume to surface area. When V_2O_5 nanostructures are exposed to reducing gases, V^{5+} species are partially reduced to V^{4+}, originating formation of oxygen vacancies thus increasing conductivity of the sensor (this phenomena can be optically observed due to a material colour change from yellow to dark blue) [572, 584]. Wu was able to detect trimethylamine (one of the toxic gases released by the decomposition of fish and other seafood) with detection limit of 10 ppb, response of 1.283 and maximum recovery time of 150 s at a working temperature of 370 °C [572]. Griogorieva *et al.* [571] produced V_2O_5 nanorods that showed stable response to trimethylamine (detecting 10 ppm with sensor response of 1 to 3 %), but weak response to carbon monoxide (only 0.3 % at 180 °C), with short response time of 32 s. For the detection of ethanol, Liu *et al.* [579] used V_2O_5 nanobelts synthesized via hydrothermal method. These sensors were tested in a temperature range between 150 and 400 °C, with an increasing concentration from 10 to 100 ppm of ethanol. The lowest detection limit was about 5 ppm, with response and recovery time of 30 to 50 s [579]. Also, Liu *et al.* [555] used V_2O_5 urchin-like structures and nanorods not only for detection of acetone, but also of isopropanol and ammonia, with detection range of 10 to 1000 ppm and recovery time of 200 to 500 s.

Another interesting approach was presented by Liang *et al.* [580] that investigated sensing properties of VO_2 decorated with gold nanoparticles to NO_2 gas. It was found that VO_2 nanowires decorated with the smallest Au nanoparticles exhibit sensitivity to NO_2 of 0.5 to 5 ppm. Liang attributed this response enhancement to a “spillover effect” and to changes in the depletion layer caused by the presence of Au nanoparticles [580]. The small particle size and high number of particles accelerate dissociation and adsorption of oxygen at VO_2 surface and thus improve the sensor response from 1.14 to 3.22. This report also showed that VO_2 decorated with Au was also sensitive to acetone, ethanol, isopropanol and NH_3, with response of 1.04, 1.08, 1.12 and 1.05, respectively [580].

Vanadium oxide nanostructures have been widely used in the detection of toxic and flammable gases, however the high working temperature necessary to achieve good sensitivity, still remains a major challenge. Schneider *et al.* [587] developed nanostructured V_2O_5 films for detection of hydrogen, methane and propane, with a good response (0.2) in the presence of 5 to 300 ppm of gas at 200 ºC (Figure 25 (a)).

Some authors have reported the use of vanadium oxide as humidity sensor. Yin *et al.* [558] reported on the hydrothermal synthesis of VO_2(B) nanoflowers and their heat-transformation into VO_2(M), as well as their humidity sensing characteristics. Both sensors presented fast response and recovery time, with good stability and reproducibility. It was found that VO_2(M) nanostructures were more sensitive at high RH while VO_2(B) nanostructures presented higher sensitivity at low RH values [558].

In semiconductor nanomaterials, oxygen vacancies and oxygen ions adsorbed at the surface are active sites, thus water vapour is ionized to OH^- and H^+ [558, 588]. Subsequently, another H_2O molecule is adsorbed to the H^+ bond between two neighbouring OH^- groups. In the presence of high humidity levels, H_2O layers are formed at VO_2(M) surface that may be dissociated into H_3O^+. This will cause the depletion layer to decrease, promoting an increase in surface conductivity. In metallic VO_2(B) phase, with a lower resistance, the dominant charge carriers are electrons, e^-. For high humidity values and due to the polarity of H_2O molecules, some of these e^- are electrostatically attached to positively charged H^+ forming hydrogen bonds [26]. The density of free electrons at VO_2(B) surface decreases, increasing materials' resistance with humidity increase [558].

To improve the sensors' response to RH variation , some authors have reported on the use of some additive or the formation of hybrid composites, such as VO_2 – carbon nanotubes composites [589]. Doping with other semiconductor materials induces additional atomic defects modifying sensing properties [583]. Araújo *et al.* [583] doped TiO_2/WO_3 composites with different percentages of V_2O_5 that demonstrated a change in impedance of an order of magnitude when detecting RH ranging from 40 to 100 %.

Moreover, Evans *et al.* [589] produced humidity sensors based on VO_2 – carbon nanotubes composites. These nanocomposites presented high response to water vapour, with sensitivity between 2.7 and 3.6, when increasing the RH to 50 %. Devices resistance was reduced by incorporation of carbon nanotubes, CNTs, suggesting that these significantly contribute to the increased composites' conductivity [589] (Figure 25 (b)).

The use of vanadium oxides in UV sensing is not common, nevertheless some reports show that this semiconductor presents a good responsivity to UV radiation. Zhai *et. al.* [590] reported on the photoconductive of centimeter-long V_2O_5 nanowires produced by hydrothermal method. These nanowires presented responsivity of ∼482 A W^{-1} and EQE ∼132800% at 450 nm and 1.0 V. Wu *et al.* [591] demonstrated responsivity of a single microwire to UV radiation. Photoconductor made of a single nano/microwire can yield much higher sensitivity and responsivity than the bulk material. The VO_2 microwire photodetector presented responsivity of 7069 A W^{-1} and response time of ≈ 126 ms (Figure 25 (c)).

One interesting approach is using the V_2O_5 nanostructures as photochromic UV detectors. Miyazaki *et al.* [592] produced a V_2O_5 based composite that exhibit photochromic properties when irradiated with UV light. These showed multichromism, changing from yellow to green and to pale blue with good reversible photochromic properties when placed in the dark. Miyazaki assumed that UV irradiation is responsible for V_2O_5 reducing from +5 to +4 states and associated colour change. Optical band gap increased with UV irradiation due to increase in carrier concentration (Figure 25 (d)).

Other studies reported doping of vanadium oxides with other metal oxides to increase responsivity, response and recovery time of UV sensors. Vanadium oxide doping exhibited an enhancement in luminescence and in photo-sensing properties. These properties arise from formation of defect states within the bandgap, which traps and de-traps electrons. Srivastava *et al.* [593] reported substitution of some vanadium atoms in ZnO, which lead to an increase in UV sensitivity and responsivity, which was attributed to trapping and de-trapping of electrons at V^{4+} and V^{5+}-related defect states. Whereas the V^{5+} state is empty, the V^{4+} state has an extra available electron that when illuminated by UV irradiation will move to the conduction band and increase photocurrent. This study also showed that sensor responsivity increased for 1.76 % of vanadium content to 120 µA W^{-1} when compared to undoped material (4 µA).

The use of vanadium oxide semiconductor in biosensing applications is rather rare. Nevertheless, being a biocompatibility material, V_2O_5 have attracted much attention for the fabrication of bio-electrodes, due to their high catalytic properties and also to their high electron transfer [594]. Suresh *et al.* [595] doped V_2O_5 with Ni for determination of dopamine (an electroactive neurotransmitter vital in the central nervous system) at nanomolar level. The doped nanoparticles showed a good response to dopamine in concentrations ranging from 6.6 to 96.4 µM, with sensitivity of 132 nA μM^{-1} and limit of detection of 28 nM. Suresh suggested that Ni-$V^{5+}{}_2O_5$ causes oxidation of dopamine and is then electrochemically reduced to Ni-$V^{4+}{}_2O_5$. and after donation of an electron to the carbon electrode is regenerated to Ni-$V^{5+}{}_2O_5$.

Most of existing reports are related with the use of V_2O_5 nanocomposites. Yang *et al.* [596] produced an electrochemiluminescence (ECL) aptasensor for the detection of mucin 1 (a biomarker associated to breast and pancreatic cancer) using V_2O_5 nanospheres as peroxidade mimics. V_2O_5 was synthesized and added to ABEI (*N*-(4-aminobuthyl)-*N*-(ethylisoluminol)), functionalized with silver nanoparticles, thus forming a nanocomposite that was applied to the sensor electrode. The produced sensors' signal increased by about 2.7 times. Yang suggested that V_2O_5 nanospheres are responsible for loading a large number of luminuphores with an enhanced ECL signal. This approach displayed detection range of 10 fg mL^{-1} to 10 ng mL^{-1}, with a limit of detection down to 3.33 fg mL^{-1} [596].

Other composites using V_2O_5 nanostructures and carbon nanotubes were reported. These nanocomposites were used to improve sensing properties. Xiaobing *et al*. [597] reported the development of carbon nanotubes/V_2O_5/chitosan nanocomposite for detection of ciprofloxacin (an antibiotic widely used in health and agricultural industries, which the residues may cause skin infections and respiratory infections). This sensor combines the biocompatibility of V_2O_5, the efficient electron transfer of carbon nanotubes and the effective fil-forming strength presented by chitosan. Moreover, it presented good selectivity and low limit of ciprofloxacin detection (0.5 ng mL^{-1}) on milk, with a recovery rate of 94.5-97.87% (Figure 25 (e)) [597].

Sun *et al.* [598] also used this nanocomposite (nanotubes/V_2O_5/chitosan) for fabrication of electrodes for immobilization of single-stranded DNA. The experiments performed by Sun suggested that the synergistic effect of V_2O_5/Carbon nanotubes leads to increased amount of single-stranded DNA being adsorbed onto the electrode's surface, thus increasing the electrochemical response. The biosensor produced by Sun *et al.* was able to detect concentrations in the range of 1.0×10^{-11} to 1.0×10^{-6} mol L^{-1}, with detection limit of 1.76×10^{-12} mol L^{-1}.

Another biosensor based on these types of nanocomposites electrodes was reported by Alagappan *et al.* [594] for detection of methylglyoxal, which is responsible for complications in diabetic patients. This bioelectrode was able to measure concentrations of methyglyxal in par-boiled rice ranging from 0.1 to 100 µM, with sensitivity of 1130.86 µA cm^{-2}, limit of detection of 2 nM and response time <18 s. Vanadium oxide has an isoelectric point of 3 which allows electrostatic attraction of the glutathione cofactor, that has a high isoelectric point (5.93). In the absence of methyglyxal, glutathione will oxidize to hemithioacetal at -2.74 mV, while in the presence of 0.1 µM of methyglyxal the the required potential is -32.29 mV [594].

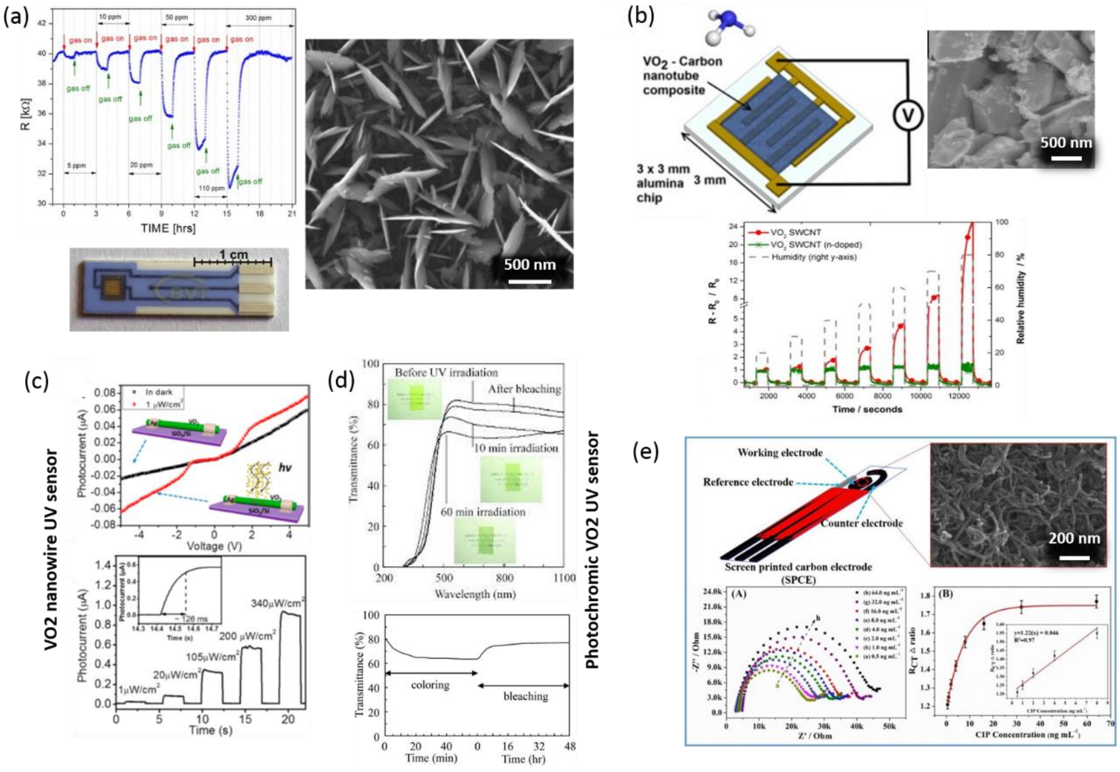


Figure 25. (a) V_2O_5 nanostructured film for hydrogen gas sensing application [587]; (b) VO_2-carbon nanotube composite for humidity sensor [589]; (c) VO_2 microwire UV photodetectors and the correspondent photocurrent at 4 V under different UV illumination intensities (the inset show the response time) [591]; (d) UV-VIS spectra of the V_2O_5 nanostructured photodetector when irradiated with UV light and their time dependence of the transmittance when coloring and bleaching [592]; (e) Schematic, SEM image and Nyquist plots of the carbon nanotube/V_2O_5 electrodes used in biosensing application [597]. Reproduced with permission of *Elsevier* (2018) [587], [589] and [597]; *ACS publishing "Copyright (2018) American Chemical Society"* [591]; and *Royal Society of Chemistry* (2018) [592].

3. Overview of the metal oxide sensors performance

This section describes the comparison between all the different metal oxides discussed above, organized by sensor device type. Table 2 summarizes different metal oxide nanostructures employed as gas sensors. Metal oxides have been largely integrated in gas sensors over the years and several types of gases, including NO_2, H_2 to C_2H_5OH and NH_3, have been evaluated at different concentrations. The temperature at which sensing experiments are carried out, is also imperative. As can be seen from Table 2, the used temperatures are widely diverse and even if some sensors work at room temperature (RT), which enables low cost devices and improves long-term stability, most of the nanostructures investigated show working/operating temperatures from 200 to 500 ºC. This range of temperatures is too high from a practical use point-of-view and leads to energy waste and emissions increase, which enhances danger of explosion when dealing with flammable gases.

In terms of metal oxides used, ZnO and TiO_2 are largely employed as gas sensors due to their high chemical stability, simple and cost effective production, easy surface oxygen adsorption, amongst others factors [233, 599]. Nevertheless, operation temperatures of both sensors are still high which limits their integration in real-time gas monitoring devices. The response/recovery times, especially for ZnO nanostructures, need deeper investigation for reaching fast responses, which may include surface modification, additive doping or light activation. WO_3 is considered a promising material for gas sensors having extensive application for environment and safety monitoring. WO_3 is an abundant material and can be synthesized by low-cost wet-chemical routes. However, in terms of gas sensing, this material has a drawback of intersecting sensitivity, which limits distinction of two gases in a mixture [600]. Nevertheless, sensitivity of WO_3 to several gases has been tested and in some cases low detection limits (in the order of ppb) were achieved, especially for NO_2 (Table 2). The operation temperature is also lower (< 300 ºC for the presented nanostructured sensors) when compared to ZnO and TiO_2, presenting fast response/recovery times.

Copper oxide-based gas sensors have been reported over the years, especially to form *p-n-* heterojunctions. Copper oxides have *p*-type characters, besides being eco-friendly, non-toxic and compatible with wet-chemical synthesis routes. However, Cu_2O phase is unstable and easily converts to CuO. This thermal instability can influence the gas sensors behaviour, especially since Cu_2O demonstrates gas sensing activity at ∼200 °C [400]. From Table 2, it is possible to observe that the operation temperature of copper oxide-based nanostructured devices is also lower than 300 ºC and that the response/recovery times are expressively different depending on the nanostructure or composite/mixture used. SnO is also thermally unstable and converts to SnO_2 when heated, which limits its utilization as gas sensors. On the other hand, SnO_2 is widely used in gas sensors [499] for detection of different gases, like ethanol, H_2, O_2, CO, NO, NO_2 and NH_3, due to its fast-response speed, high chemical stability, selectivity and low cost. Moreover, the presented nanostructured sensors work at temperatures < 300 ºC, with low detection limits (ppm) and fast response/recovery times. Vanadium oxides have recently been considered for gas sensing. V_2O_5 has been reported for combustible gases detection due to its good chemical and thermal stability. Nevertheless, the operation temperature, response/recovery times and detection limits of these sensors vary expressively depending on nanostructure used and vanadium oxide phase.

Table 2. Summary of overall performance of nanostructured metal oxides-based gas sensors.

Metal oxide nanostructure	**Gas**	**Temperature (º C)**	**Detection limit**	**Response time (s)**	**Recovery time (s)**	**RH %**	**Ref.**
ZnO nanowires, nanobelts and tetrapodes	H_2S and NO	RT	200 ppb H_2S 1 ppm NO	-	-	-	[146]
ZnO cloudy-like nanoparticles, isotropic nanoparticles	CO, C_3H_8, and NH_3	340, 400, and 500	100 ppm CO 100 ppm C_3H_8 19 ppm NH_3	-	-	50	[150]
ZnO nanobelts	NO_2	300 – 350	0.51 ppm	-	-	-	[151]
ZnO nanorods	NO_2	300 – 450	1 ppm	180	-	-	[152]
Au-doped ZnO nanostructures	NO_2	300 and 550	0.5 ppm	450	587_300 ºC 1020_550 ºC	-	[154]
ZnO nanorod arrays with NiO nanosheets Nanoheterojunctions	C_2H_5OH	200	100 ppm	55	70	-	[155]
TiO_2 nanowires	NO_2	RT	100 ppm	10	19	-	[233]
TiO_2 spongy layers	C_2H_5OH	350	44 ppm	10	-	40	[235]
Cr-doped TiO_2 films	CO NO_2	500	1000 ppm CO, 2 ppm NO_2	-	-	30 and 50 for NO_2	[236]
Au-doped TiO_2 films	CO H_2	300	5 ppm CO 8.5 ppm H_2	15 CO 480 H_2	10 CO 9.6 H_2	dry	[237]
TiO_2-SnO_2 nanostructures	H_2	400	-	60-120	300-420	-	[238]
Lamellar-nanostructured WO_3 particles	NO_2	200	50-1000 ppb	-	-	-	[303]
Porous WO_3 nanocrystalline	NO_2	300	50- 550 ppb	180	60	-	[304]
Three-dimensional hierarchical WO_3 nanostructures	NO_2	120_800 ppm	40-800 ppb	120_800 ppm	41_800 ppm	-	[305]
WO_3 nanotubes	NO_2	300	1-5 ppm	15-40	70-100	-	[306]
WO_3 nanowire-like structures	NH_3	250	9.7-1500 ppm	7	8	-	[307]
Pt-WO_3 hybrid nanorods	C_2H_5OH and CH_3OH	220	1, 5, 20, 100 and 200 ppm	9	-	-	[312]
Pd-WO_3/reduced graphene oxide Hierarchical nanostructures	H_2	100	20 ppm	60	-	-	[321]
Cu_2O nanowires	H_2	200	1000 ppm	-	600	dry	[411]
CuO 3D flower-nanostructures	C_2H_5OH	260	10-1000 ppm	5	15	-	[415]
CuO flower-like nanostructures	H_2S	RT	100 ppb - 20 ppm	240-480	900-3300	dry	[417]
CuO/ZnO nanorod heterojunction	C_2H_5OH	300	1 ppm	7	9	-	[422]
CuO-MnO_2 nanocomposite	NH_3	-	100 ppm	120	600	-	[424]
Cu_2O/CuO sub-microspheres	H_2S	95	50 ppb	-	76	-	[425]
Porous Cu_2O/CuO cubes	C_3H_6O	150	500 ppm	1	25	-	[426]

Nanosheets-assembled SnO_2 hollow spheres	C_2H_5OH	350	500 ppb	-	5	-	[503]
Porous SnO_2 nanoflowers	C_2H_5OH	240	100 ppm	2	15	dry	[504]
Hierarchical SnO_2 based ultrathin nanosheets	C_2H_5OH	-	100 ppm	1	2	-	[497]
Square-shaped SnO_2 nanowires	C_3H_6O	290	20 ppm	7	10	-	[505]
SnO disk-like structures	NO_2	200	100 ppb	-	-	-	[510]
Sb-doped SnO_2 nanowires	C_2H_5OH	300	10 ppm	1	5	-	[512]
Hierarchical SnO_2/rGO nanostructure	H_2S	100	10 ppm	7	-	-	[514]
WO_3-SnO_2 nanofibers	C_2H_5OH	-	10 ppm	18.5	282	-	[516]
SnO_2-decorated NiO nanostructures	C_7H_8	250	1.2-10 ppb	-	-	15-90//10 ppm	[521]
V_2O_5 hollow spheres	Trimethylamine	370	10 ppb	-	150	-	[572]
V_2O_5 nanorods	Trimethylamine	175	10 ppm	32	330	-	[571]
V_2O_5 nanobelts	C_2H_5OH	200	5 ppm	30	50	-	[579]
V_2O_5 urchin-like and rod structures	C_3H_6O	150	10 - 1000 ppm	-	200 and 500	30	[555]
VO_2 decorated with gold nanoparticles	NO_2	25-100	0.5 - 5 ppm	-	-	-	[580]
Nanostructured V_2O_5 film	H_2, CH_4, and C_3H_8	200	5 - 300 ppm	-	-	-	[587]

Nanostructured metal oxides-based humidity sensors that can detect humidity changes in a vast range of values, between 0 and 100% RH, have been reported for all the discussed metal oxide materials (see Table 3). ZnO presents a good detection range, however it has the disadvantage of being hydrophobic, which limits sensitivity improvement. On the other hand, TiO_2 often presents superior humidity sensitivity due to its hydrophilic properties, which arise from surface defects. This material presents fast response times but longer recovery times. Moreover, the use of TiO_2 may lead to low long-term stability. WO_3 is also an interesting alternative for humidity sensors due to its high sensitivity, which is generally attributed to structural defects. The use of copper, tin and vanadium oxides as a humidity sensor is not so common, nevertheless they all present fast response and recovery time and good long-term stability.

Table 3. Summary of overall performance of nanostructured metal oxides-based humidity sensors.

Metal oxide nanostructure	**Detection range (%RH)**	**Response time (s)**	**Recovery time (s)**	**Hysteresis (%)**	**Ref.**
ZnO	15 - 95	7	14	1.8	[157]
ZnO nanoparticles	0 - 80	5	-	8.6	[158]
ZnO/SnO_2	11 - 95	50	100	2	[160]
ZnO/TiO_2	11 - 95	774.9	19.7	-	[161]
TiO_2 nanosheets	11 - 95	3	50	4.6	[239]
TiO_2/graphene	12 - 90	121	68 – 128	<0.39	[240]
TiO_2/conducting polymer	30 - 90	30	45	2	[241]
TiO_2:LiCl	5 - 95	0.75	1	-	[243]
WO_3:Li:K	1 - 95	15	10	3	[324]
WO_3 on nanoporous silicon	11 - 95	104	94	5.3	[327]
WO_3/Poly(2,5-dimethoxyaniline)	23 - 84	27	136	5	[328]
WO_3: ZnO	15 - 95	65	360	1.09	[329]
CuO nanowires	52 - 90	-	-	-	[430]
Cu_2O porous film	Up to 58	151	145	4.38	[431]
CuO:ZnO	10 - 90	76	296	2.30	[437]
SnO_2 nanoparticles	5 - 95	32	25	-	[522]
SnO_2 ordered nanostructures	5 - 96	32	42	< 5	[523]
SnO_2 nanofiber	Up to 85	1	1	-	[524]
Ion doped SnO_2 nanofiber	11 - 95	5	6	-	[525]
VO_2	Up to 92 %	5 – 8	2 – 3	7	[558]
$TiO_2/WO_3/V_2O_5$	40 - 100	-	-	-	[583]

Table 4 shows that ZnO, WO_3 and SnO_2 are largely employed as UV sensors/photodetectors, while other metal oxides, such as CuO/Cu_2O, are used to produce *p*- *n*- heterojunctions. On the other hand, the use of TiO_2 and vanadium oxides in such devices is not widespread, nevertheless some studies have reported their behaviour as photoactive layers for UV sensors. The photocurrents, I_{on}/I_{off}, responsivity and response/recovery times vary expressively for each sensor, largely depending on the metal oxide and even nanostructure used. Moreover, sensor behaviour is widely influenced by substrate, UV lamp and the environment where the measurements are carried out. Nevertheless, comparing metal oxides, it can be seen that ZnO shows the highest values of photocurrent and I_{on}/I_{off}, and for that reason it is largely investigated for UV sensor applications. ZnO 1D nanostructures are especially interesting due to large surface to volume ratio, which increases the photoresponse. WO_3 and SnO_2 also display acceptable I_{on}/I_{off} values, which make them interesting to be integrated in UV sensors. Moreover, the presented WO_3 nanostructures revealed fast response/recovery times. Vanadium oxides and TiO_2, on the other hand, show lower photocurrent and I_{on}/I_{off}.

Table 4. Summary of overall performance of nanostructured metal oxides-based UV photodetectors.

Metal oxide nanostructure	**Photocurrent**	**Dark current**	**On/off ratio (I_{on}/I_{off})**	**R ($A\ W^{-1}$)**	**Response time (s)**	**Recovery time (s)**	**Ref.**
ZnO nanowire	12.22 mA (rigid substrate) 14.1 mA (flexible substrate) (3 V)	-	8.2×10^3 1.2×10^4	-	-	-	[171]
ZnO nanorod arrays (glass substrate)	5 mA (5 V)	90 µA	55	4×10^{-4}	60	-	[71]
ZnO nanorod arrays (cellulose substrate)	10.36 µA (10 V)	0.76 µA	13.63	1.19×10^{-6}			[13]
ZnO ultraporous nanoparticle networks	1.2 mA (5 V)	3.61 nA	3.4×10^5	-	~250	~150	[172]
ZnO nanorods	-	-	1.09×10^4	55.5	3.1	1.25	[164]
TiO_2 nanorod arrays	249.68 µA (2.5 V)	-	-	13	-	-	[247]
TiO_2 nanorod flower-like structure (cellulose substrate)	3.78 µA (10 V)	0.15 µA	25.2	$3.3\ 10^{-7}$	-	-	[246]
WO_3 nanosheets	2.5×10^{-5} A	-	2×10^3	293	0.04	~0.08	[331]
WO_3 nanowires	0.1 nA (1 V)	17.2 nA	172	-	~70	~140	[333]
WO_3 nanobelts	12 nA (5 V)	12 Pa	1×10^3	2.6×10^5	-	-	[334]
3D WO_3 nanoshale	4.5 µA (20 V)	-	-	5.1	6.3	0.5	[335]
WO_3 nanodiscs/rGO	~1.1 µA (20 V)	-	-	6.4	0.013	0.016	[330]
CuO/Si nanowire array heterojunction	0.96 µA (0 V)	-	-	3.89×10^{-4}	6×10^{-5}	8×10^{-5}	[439]
CuO nanowire/ZnO branched nanowires heterojuntion	~1.7 mA (1 V)	~0.7 mA	2.43	0.123	-	-	[440]
Cu_2O film/ZnO nanowire	~0.5 µA (2 V)	-	-	~50	-	-	[441]
SnO_2 nanowire	2.1 µA (1 V)	19.4 nA	108	-	-	-	[533]

SnO_2 nanowire arrays	130 µA (12 V)	77 μA	1.69	-	-	-	[532]
SnO_2 hollow nanospheres	0.01 A	-	-	2680	38	137	[534]
SnO_2 nanobelts-Sn nanodots	1.1 nA (10 V)	4×10^{-4} nA	2.75×10^{3}	56	<0.3	<0.3	[72]
CuO/SnO_2 *p-n* nanoscale heterojunctions	-	-	-	10.3	-	-	[536]
TiO_2 branches on electrospun SnO_2 nanofibers	-	-	4550	0.6	0.03	0.01	[539]
V_2O_5 centimeter-long nanowires	25.8 nA (1 V)	12.5 nA	2.06	~482	-	-	[590]
VO_2 microwire	-	-	-	7069	0.126	-	[591]

By analysing Table 5, it is possible to observe that ZnO and WO_3 nanostructures are largely employed in biosensing applications. On the other hand, vanadium oxides are mostly combined with other nanostructures, such as graphene or carbon nanotubes, to form composites, and thus enhance their sensitivity. Zinc oxide is mostly used for detection of glucose, as its high IEP promotes glucose oxidase adhesion. Copper oxides are also highly investigated for glucose detection, presenting high sensitivities and low detection limits. WO_3 nanostructured biosensors can detect very low concentrations of analyte and presents high sensitivity to different analytes. Also, WO_3 presents chromogenic properties, which enable its use in colorimetric sensors thus allowing production of low-cost disposable biosensors, using cellulose as substrate. Although TiO_2 can be used in biosensing applications, the sensitivity presented by this type of nanostructures is very low, showing a very low detection limit. SnO_2 nanostructures are used in biosensing when doped or combined with other elements, presenting high sensitivity and low detection limit.

Table 5. Summary of overall performance of nanostructured metal oxides-based biosensors.

Metal oxide nanostructures	Analyte	Analyte concentration	Detection limit	Sensitivity	Ref.
ZnO nanowires	Glucose	0.03 to 1.52 mM	9 µM	17 µA/ cm^2mM	[176]
ZnO nanocombs	Glucose	0.02 to 4.5 mM	0,02 mM	15.33 µA/cm^2mM	[177]
ZnO nanorods	SSEA-4 antibodies	2 mM	Optical detection	-	[178]
ZnO nanosheetes	Cytochrome *c*	1 to 1000 µM	0.1 µM	-	[185]
ZnO	cTnT	1 to 100 ng/mL	0.1 ng/L	-	[182]
ZnO nanoparticles	cTnI	1 ng/mL – 10 µg/mL	2.191 ng/mL	15.8 nA(g/mL)$^{-1}$	[183]
TiO_2 nanotubes arrays	immunoglobulin	115 mg/mL	14 ng/mL		[223]
TiO_2 nanotubes	Glucose oxidase	0.1 – 6 mM	-	0.954 µA/cm^2mM	[251]
Carbon-doped TiO_2 nanotubes arrays	5-hydroxytryptamine and ascorbic acid	5 to 150 µM	4.1 × 10^{-8} M	-	[255]
graphene/TiO_2 nano rods/chitosan	Transgenic soybean sequence of MON89788	1.0×10^{-12} to 1.0×10^{-6} mol L^{-1}	7.21 × 10^{-13} mol/L	-	[256]
Graphene nanosheets/TiO_2	Glucose oxidase	0 to 8 mM	-	6.2 µA/cm^2 mM	[257]
TiO_2 nanoparticles	Laccase	0.075 to 150 µM	0.75 µM	2.6 µA/cm^2µM	[258]
WO_3 nanoparticles	*cc*NiR	5 to 50 µM	5 µM	2143 mA/cm^2mM	[338]
WO_3 nanoparticles	cytochrome	3 × 10^{-7} to 3 × 10^{-4} M	2.4 × 10^{-7} M	63.51 mA/cm^2M	[339]
WO_3 nanowires	hemoglobin	1 to 4200 µM	0.28 µM	-	[340]
WO_3 nanoparticles	dopamine	0.1 to 600 µM	24 nM	-	[341]
WO_3 nanoparticles	L-dopa	0.1 to 1 µM	120 nM	-	[342]
WO_3 nanoparticles/carbon nanotubes	hemoglobin	60 to 1280 µM	0.07 µM	-	[343]
WO_3 nanoparticles	Geobacter Sulfurreducens cells	15 g/L	Optical detection		[262]
Graphene/WO_3	peroxidase	150 µM	238 nM	1.306 mA/cm^2mM	[345]
WO_3-reduced graphene	cysteine	0.1 to 100 µM	25 nM	-	[347]
Cu_2O nanocubes/graphene nanosheets	glucose	0.3 to 3.3 mM	3.3 µM	-	[442]
Cu_2O shuriken-like nanostructures	glucose	0.01 µM to 11.0 mM	0.035 µM	0.933 mA/cm^2mM	[444]
Cu_2O/carbon quantum dots	glucose	0.02 to 4.3 mM	8.4 µM	-	[447]
CuO	glucose	1.0 to 170 mM	0.91 mM	246 mA/cm^2mM	[446]
CuO nanotubes	glucose	5 µM to 3.0 mM	0.1 µM	1.89 mA/cm^2mM	[448]
CuO nanoparticles	glucose	0.05−18.45 mM	~0.5 µM	2762.5 µA/cm^2mM	[449]
CuO nanoparticles	glucose	0.1 to 6.5 mM	0.5 µM	2419.8 µA/cm^2mM	[450]

CuO nanoparticles	Uric acid	0.05 mM to 1.0 mM	0.14 mM	2.7 mA/cm^2 mM	[445]
ZnO – CuO	cholosterol	0.12 to 12.93 mM	-	680 µA/cm^2 mM	[451]
ZnO – CuO	glucose	up to 8.45 mM	0.40 µM	2961.7 µA/cm^{2}mM	[443]
SnO_2 nanorods	H_2O_2	50 to 200 mg/L	0.2 µM	379 µA/cm^{2}mM	[542]
SnO_2:Sb nanowires	H_2O_2	-	0.8 µM	100 mA/cm^{2}M	[544]
ZnO/SnO_2 heterostructured	H_2O_2	2.0×10^{-6} to 3.7×10^{-4} M	0.46 µM	52.8 mA/cm^{2}M	[548]
Graphene/SnO2 nanosheets	Glucose	2 to 20 mM	-	20.3 µA/cm^{2}mM	[549]
Carbon nanotubes/SnO_2/graphene/chitosan	Lysine oxidase enzyme	0.99 to 160 µM	0.15 µM	55.20 µA/cm^{2}mM	[553]
V_2O_5:Ni	dopamine	6.6 to 96.4 µM	28 nM	132 nA/cm^{2}µM	[595]
V_2O_5 fuctionalized with Ag	Mucin1	10 fg/mL to 10 ng/mL	3.33 fg/mL	-	[596]
Chitosan/V_2O_5/carbon nanotubes	DNA	1.0×10^{-11} to 1.0×10^{-6} M	1.76×10^{-12} M	-	[598]
Chitosan/V_2O_5/carbon nanotubes	methyglyxal	0.1 to 100 µM	2 nM	1130.86 µA/cm^{2}M	[594]

4. Field-effect transistor structures for sensing applications

4.1. Advantages and challenges of sensing with (oxide nanostructure) field-effect transistors

While the oxide nanostructures exposed in the previous sections enable by themselves remarkable sensing performance, potential for miniaturization, parallel sensing, faster response time, improved selectivity and sensitivity and seamless integration with electronic manufacturing processes can be greatly enhanced when sensing is based on field-effect transistors (FETs) [601, 602]. In fact, and considering that oxide nanostructures can be grown on or transferred to FETs at low temperatures, the FET sensing approach seems to be perfectly tailored for the so-called system-on-foil concepts, combining the advantages of both “More Moore” (small size, high speed) and “More than Moore” (multifunctional) paths [603].

The great advantage of nanostructures compared to thin films of bulk materials for sensing was already extensively demonstrated throughout this review paper and naturally these advantages are also extended to FET structures. Nanowires have been the selected nanostructure for most of the FET sensors reported so far. From a device point of view, two main reasons can be pointed out for this: first, they enable the confinement of charge transport essentially along one direction of the nanostructure, assuring improved electrical properties [604]; second, due to their 1D shape nanowires are easier to integrate between two electrodes (source and drain) [603].

Fabrication of FET sensors involves more processing steps than conventional conductometric sensors, requiring integration of an extra terminal (gate), electrically insulated from the oxide semiconductor nanostructure by a gate dielectric. As in conventional nanowire FETs, different device structures can be conceived for FET sensors, such as back-gate, top-gate, horizontal or vertical surrounding-gate [605]. The back-gate nanowire FET, depicted in Figure 26, is the most widely explored FET structure for sensing. While it potentiates an inefficient gate control of the drain-to-source current (I_{DS}) across the nanowire due to non-uniform electrostatic contact of a nanowire with a planar dielectric, this structure has at least two great advantages for sensing applications: first, its straightforward fabrication. In fact, considering the simpler approach, the FET sensors can be fabricated by drop-casting a solution containing dispersed nanostructures in a solvent on a highly-doped Si substrate (gate) having a thermally grown SiO_2 layer. Then, source-drain electrodes can be defined on the edges of a single nanowire following a pick-and-place approach, *e.g.*, using photolithography and e-beam evaporation; second, a back-gate configuration enables the nanowire surface to be readily exposed to the surrounding ambient, which is crucial to explore most of the sensing mechanisms.

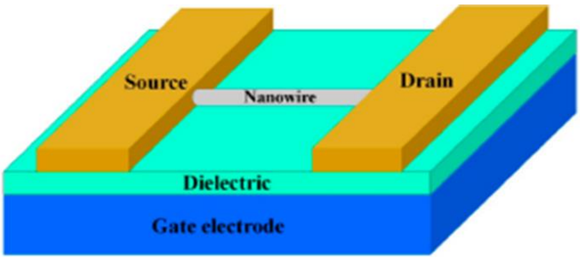


Figure 26. Schematic cross section of a back-gate nanowire FET. Reproduced with permission of *MDPI* (2018) [602].

This last argument brings a very interesting comparison to nanowire FETs used for electronic applications, which is particularly relevant when considering oxide nanostructures as the heart of these sensors: while on "electronic FETs" intense research has been carried out to block the interaction between oxide nanostructure surface and the surrounding environment, as it is well known that this can greatly affect device performance [606], in sensing FETs the nanowire's surface is intentionally left to interact with the ambient. Nevertheless, one should naturally understand that for both types of nanowire FETs the control of existing surface defect states by routes as doping, annealing or ozone treatments is a crucial requirement to establish stable and reliable platforms to work with [607, 608].

Many successful attempts to use FETs sensors based on oxide nanostructures have been reported during the last decades. While a detailed review on this topic would constitute an extensive document on its own and is thus out of the scope of the present review article, oxide nanostructure-based FETs are too relevant to be left out of any comprehensive review on oxide sensors. As such the next subsection presents major considerations on what has been perhaps the most active research area regarding sensing with oxide nanowire FETs: gas sensors. The reason for narrowing the discussion to a single type of sensors is that most of the concepts exposed can be the eadily applied to other types, where sensing also relies on interactions at the oxide nanostructure surface, given that those interactions will eventually affect carrier concentration which is one key aspect governing the properties measured on a FET. Based on this concept, significantly improved sensing performance when FET structures are used have been shown for humidity, UV and biosensors [92, 609, 610].

4.2. Gas sensing with oxide nanowire field-effect transistors

FETs for gas sensing have been studied for more than four decades. Back in 1975, Lundstrom *et al.* demonstrated hydrogen sensing on a Si-based metal oxide semiconductor FET (MOSFET), demonstrating that the threshold voltage (V_T) of the device was a function of hydrogen partial pressure [611]. At this point it is worth noticing that MOSFET gas sensors reported by many other researchers since this initial report work under a different principle compared to the oxide nanowire-based FET sensors under discussion in this section. While MOSFET gas sensors rely on catalytic interaction between a metal gate and gas molecules, which results in a measurable change of I_{DS} within the Si channel of a conventional MOSFET, oxide nanowire-based FET sensors rely on the direct interaction between the oxide semiconductor and the gas. This interaction (adsorption or desorption of gas molecules) leads to multiple measurable changes on device characteristics, such as I_{DS}, V_T, mobility (μ) and subthreshold swing (S) [602, 612, 613]. These effects are a consequence of variation of the carrier concentration within the nanowire as the gas-nanowire interactions occur. Considering an *n*-type oxide nanowire (*e.g.*, SnO_2, ZnO, In_2O_3), oxidizing and reducing gas environments will result in decreased and increased carrier concentration, respectively. While this is also seen on two-terminal oxide nanowire-based conductometric gas sensors, the gate-to-source voltage (V_{GS}) in FET gas sensors can significantly enhance these effects, *i.e.*, taking the device to operate with a specific V_{GS} can result in very large sensor sensitivity. This arises as a consequence of the free carrier concentration modulation by V_{GS}, which in turn affects the rate and extent of oxidation/reduction reactions taking place at the oxide nanowire surface [614, 615]. By operating the FET sensor at its subthreshold regime these effects are maximized, given that channel carriers are substantially depleted and thus, conductance changes caused by gas adsorption become much more significant [612].

The effect of V_{GS} on the carrier concentration also brings another advantage to FET-based gas sensors, which is the ability to operate at considerably lower temperatures than conductometric gas sensors: the latter are typically operated at 200-500 °C to decrease response and recovery times, given that gas adsorption/desorption are thermally-activated processes. As these response/recovery times are carrier concentration dependent, FET-based gas sensors can even operate at room temperature, as demonstrated with several *n*-type oxide semiconductor nanowires [612]. For instance, while the reported limits of NO_2 detection for individual In_2O_3 nanowire resistor sensors are $\approx$ 500 ppb at an operating temperature of 400 °C, In_2O_3 nanowire FET sensors exhibit limits of detection of 20 ppb at room temperature [615, 616], which is even lower than the 53 ppb required for monitoring of air quality standards [613, 615]. This brings significant advantages, such as low power consumption, longer device lifetime and reduced explosion hazards [612, 614].

Despite the proven advantage of V_{GS} control for sensing performance, other methods have also been used to enhance nanowire FET gas sensors. The most striking examples are nanoparticle decoration of the nanowire, local heating and light irradiation.

Pd, Pt, Ag, Au, ZnO and NiO nanoparticles have been used to modify the surface of oxide nanowires, resulting in improved sensitivity of FET sensors [617]. Two examples are shown in the figure below, one for NiO-functionalized SnO_2 nanowires used for CO detection [618] and another for Pd-coated SnO_2 nanowires used for H_2 detection [619]. The proposed mechanisms for these significant improvements are based on the created heterojunctions or Schottky barrier-type junctions (nanowire-nanoparticle), resulting in the formation of depletion regions or even purely chemical catalytic effect when considering nanoparticles of noble metals [612].

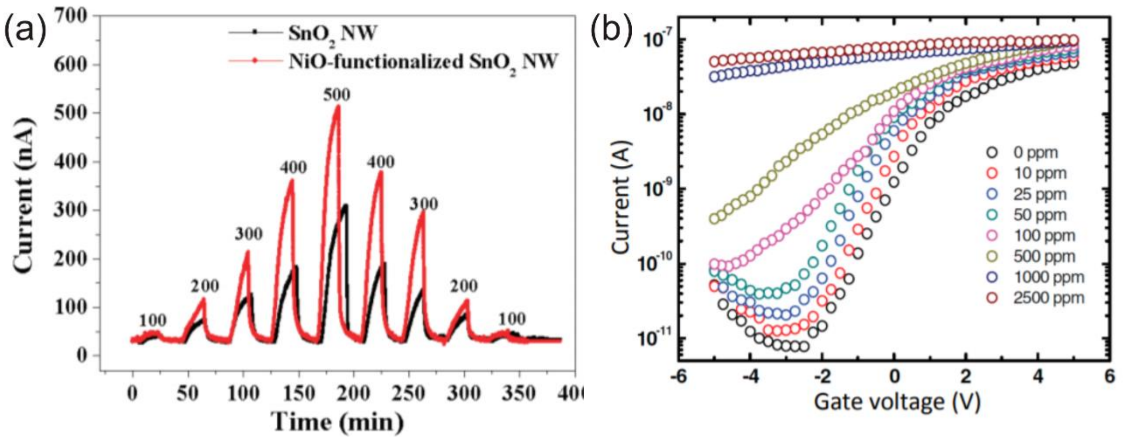


Figure 27. Enhancements on FET gas sensor sensitivity by functionalization of SnO_2 nanowires: (a) response curve for pure and NiO-functionalized SnO_2 nanowire-based sensor to CO, for a concentration of detected gas between 100 and 500 ppm, and operation temperature of 250 °C; (b) transfer characteristics of Pd-functionalized SnO_2 nanowire channel under different H_2 partial pressures, for operation temperature of 100 °C. Reproduced with permission of *ACS publishing* "Copyright (2018) American Chemical Society" [618] and *Wiley* [619].

A good example on how gas selectivity can be enhanced using the combined effect of V_{GS} and local heating was given by Dattoli *et al.* [620] with SnO_2 nanowire FET sensors and volatile organic compound analytes. By treating temperature- and gate-dependent analyte response variations as an identifying "fingerprint", an average recognition rate of 98 % was achieved using a statistical pattern recognition procedure. This value dropped to 76.7 % for measurements with gate in the grounded state.

The effect of light irradiation can also be quite relevant to achieve faster FET gas sensors. For instance, this was demonstrated already in 2002 for SnO_2 nanobelt FETs, by illumination with UV light with energy near the SnO_2 bandgap. Law *et al.* [621] concluded that the UV-generated carriers accelerated desorption velocity of NO_2 on the device . Similar effects were reported when using In_2O_3 nanowires [615].

An extensive list of oxide nanowire FET sensors based on SnO_2, ZnO, In_2O_3, Ga_2O_3 or Fe_2O_3 using the advantages of FET structures for sensing mentioned above have been demonstrated for detection of several gas molecules, such as NO_2, NH_3, CO, H_2, H_2S, CH_4 and O_2. In some cases, limits of detection in ppb range and response/recovery times of few seconds, were possible to achieve thus enabling real-time monitoring,. Detailed reviews on this can be found for instance in [612, 614, 622].

A last note should be considered regarding the feasibility of bringing these oxide nanowire FET sensors to large-scale manufacturing. The pick-and-place methodology used to prepare most of the nano-FET structures reported in literature is indeed a serious limitation, requiring selection of a single wire for deposition/patterning of source-drain electrodes. A process enabling direct growth of oxide semiconductor nanowires with controlled density on a receiver substrate, without requiring any transfer methods, would surely be desirable to overcome this limitation. A good example on how to achieve this was reported by Zhang *et al.* [615]. The authors used Si/SiO_2 substrates with tuned catalytic particle density to grow In_2O_3 nanowires by laser ablation. With this a network with multiple wires was obtained, which could then be contacted using standard photolithography and metal deposition, as shown in the figure below. Besides the simplified fabrication process and compatibility with large-scale manufacturing, these multiwire gas sensors also offer improved sensitivity to NO_2 and selectivity between NO_2 and NH_3 than single wire devices (Figures 28c and d). Selectivity reached 5 ppb, as compared to 20 ppb of single wire FETs, which was tentatively attributed to the formation of nanowire/nanowire junctions within the network, with associated depletion layers. Regarding selectively, it was associated with the possibility of having conductance changes in opposite directions upon exposure to NH_3 owing to a specific doping level distribution within the network.

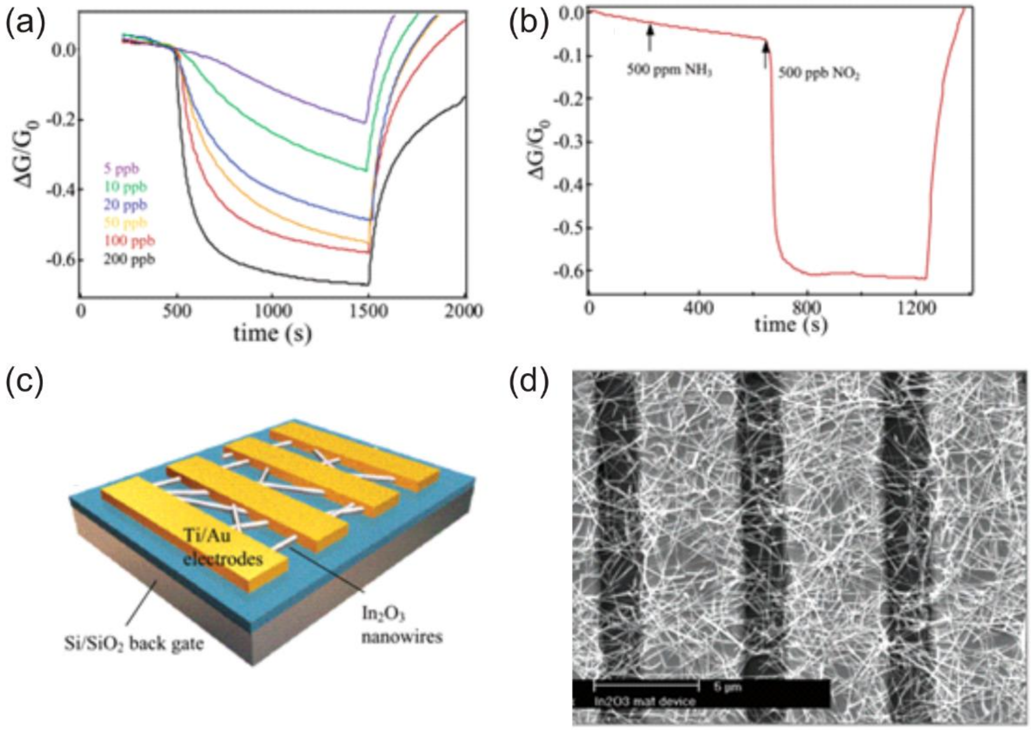


Figure 28. Multiwire In_2O_3 FET gas sensor: (a) schematic of device structure; (b) top-view scanning electron microscope image of the device; (c) sensing cycles corresponding to NO_2 concentrations between 5 and 200 ppb; (d) selective sensing to NH_3 and NO_2. Reproduced with permission of *ACS publishing “Copyright (2018) American Chemical Society”* [615].

Nonetheless, for integration in low-temperature and even flexible substrates, reliable transfer or direct growth methods of oxide nanowires that are compatible with the low thermal budgets need to be implemented. This is still one of the major bottlenecks inhibiting advances of flexible oxide nanoelectronics [603].

5. Conclusions and future perspectives

This review presented and summarized the latest advances in sensing technologies, focusing in four types of sensors, *i.e.* gas, humidity, UV and biosensors. This work was centered in semiconductor metal oxides at the nanoscale, which potentiates sensors performance due to nanomaterials intrinsic properties such as, high surface-to-volume ratios and high surface reaction activity. The selected metal oxides have in common the fact that these are earth abundant, low-cost, nontoxic and compatible with wet-chemical synthesis routes. The sensing mechanisms of the presented sensors and the general properties of the selected metal oxides have been discussed in detail. It has been demonstrated that distinct nanostructures, such as nanowires, nanotubes, core-shell nanostructures, nanosheets, nanofibers, nanocubes, nanospheres, amongst others, are the path for novel and enhanced sensor materials. The main limitations of the current sensors have been addressed, and several approaches to increase materials' sensitivity and general sensor behaviour have been discussed, which included the effect of doping and combination with other metal oxides to produce nanocomposites or carbon-based materials. A last section on FET-based sensing showed that the extra gate electrode of these structures compared to two-terminal sensors enables significant improvements on sensor performance, namely on sensitivity, selectivity and response/recovery time. However, large scale manufacturing of oxide nanostructure FET sensors on flexible substrates still requires major advances on reliable routes to obtain controlled density of high-quality networks of nanostructures on those substrates.

In terms of future perspectives, the scientific community has been focused on the development of innovative synthesis strategies capable of specifically tuning the metal oxide structures at the nanoscale, as well as their intrinsic properties. For example, this could be observed in the evolution of UV sensors with single 1D nanostructures that originated high performance devices. These nanostructures are expected to diminish defect density and thus facilitate transport of carriers in the nanostructures, which enables high external quantum efficiency and fast response time.

Miniaturization of sensors maintaining or increasing sensor sensitivity and selectivity is also one of the major concerns of researchers nowadays, as well the production of flexible and low-priced systems. The use of inexpensive, lightweight, abundant, recyclable, and environmentally friendly substrates, such as polymer and paper-based materials, is a reliable way to produce the next generation sensing devices expected to be highly adaptable, disposable, eco-friendly, sustainable and recyclable smart products. Moreover, these substrates allow large-scale production of devices and can be easily associated to printing methods.

In the near future, it is expected flexible sensing devices capable of being incorporated into opto-electronic smart devices such as solar cells, in a way that all these technologies can emerge into a broad range of low-cost and disposable consumer products to our everyday life. The flexibility and conformability of this new generation of sensors will allow them to become part of the Internet of Things (IoT) revolution, providing well-being, satisfaction and comfort to the final users.

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