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Review of Recent Advances of ZnO Nanowires Based Sensors Devices

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Abstract This paper presents the recent advances of ZnO Nanowires Based Sensors Devices. ZnO, an *n*-type, direct metal oxide semiconductor with a broad band gap, is projected to be the next generation functional nanomaterial for a wide range of sensing applications. Due to their exceptional optoelectronic, physicochemical, and electrical properties, such as low dielectric constant, abundant Zn-O bonds, high luminous transmittance, good physicochemical stability, enormous excitation binding energy, non-toxicity, biocompatibility, large surface area to volume ratio, and others, ZnO and its composites have opened a new era in the fabrication of sensors. The uses of ZnO nanostructures in the fields of environmental monitoring, biomedicine, and optical sensing are outlined in this thorough overview. To gain a better understanding of the function of ZnO in each of these sensors, fundamental sensing mechanisms of ZnO based sensors are explored. Limitations of the current methodologies and the forecast for the future have also been discussed.

Keywords: *Zinc Oxide (ZnO), Nanostructured, Doping, Nanostructure, LEDs, Nanowires, UV, Sensors, Nanoparticles (NPs)*

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1. Introduction

ZnO is an *n*-type semiconductor material, falls in group II-VI [1]. Like other semiconductors, ZnO has dual properties of both conductors and insulators [1]. Its electrical properties are controllable via doping processes [1]. ZnO has a wide band gap of 3.37 eV compared to 1.1 eV in silicon [1]. ZnO has other interesting properties such as high exciton binding energy, thermal stability, environmental compatibility, high mechanical and optical gain, and radiation hardness [2]. These properties made ZnO a leading material for several electronic and optoelectronic devices [1]. The high binding energy permits the fabrication of ZnO based photo-electronic devices possessing high optical efficiency, while the wide band gap eases the application of ZnO thin films for short wavelength optoelectronic devices [3].

In recent years, many researchers have reported on devices based on ZnO nanostructured nanowires because of their high specific surface area, low cost, and ease of manufacturing [1]. Due to the mentioned properties and others, ZnO is selected in several applications in the development of high-performance semiconductor devices [1].

Due to the mentioned properties and others, ZnO is selected in several applications in the development of high-performance semiconductor devices [1]. The ZnO crystalline structure exists as wurtzite and zinc blende as shown in Figure 1, which led it as a perfect polar symmetry along the hexagonal axis, which is responsible for the physical and chemical properties, including piezoelectricity and spontaneous polarization [4].

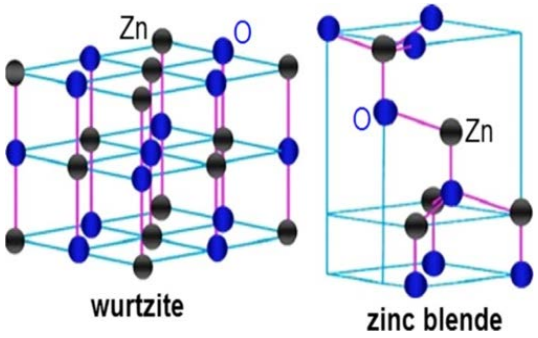


Figure 1. ZnO structures [1,4]

2. ZnO Doping

It is important while discussing ZnO based devices to highlight some guidelines of the doping processes of ZnO nanowires enabling the designer to be aware of the doping limitations [1]. The doping processes of ZnO nanowires were investigated and reported by Nahhas [1]. The doping

of ZnO nanowires improves their electrical and optical properties [1]. ZnO nanowires can be doped with Al, Ga, Sb, Ag, Cu, As, and Mo [5]. The intrinsic ZnO is *n*-type due to oxygen vacancies and thus, doping it with *p*-type dopants has proven to be extremely difficult [6]. However, that work has shown that *p*-type impurities can potentially reduce the charge leakage and electron screening effect [7]. Among the *p*-type dopants, Lithium (Li) is an excellent candidate because it can take off centered positions by replacing Zn atoms in the Wurtzite structure [8]. The *p*-type doping is considered one of the biggest issues in the development of ZnO based p-n junction devices [9]. GaN is one of the materials that can be used to bypass this issue without sacrificing the advantages of a ZnO material [10]. GaN is a wide band gap semiconductor with a very similar lattice constant as ZnO and where *p*-type doping can be reliably achieved with Mg doping, in place of *p*-ZnO. In many applications, the *p*-type doping of ZnO is desired such as p-n heterojunction structure [11]. There are several reports on ZnO-based heterojunctions with *p*-type semiconductors such as Si, AlGaN, and GaN [12].

3. ZnO Nanostructures

ZnO is semiconductor wide band gap material with a band gap energy of 3.10 eV to 3.37 eV at room temperature and a large excitonic binding energy of 60 MeV [1,13]. ZnO is a polar semiconductor with two crystallographic planes with opposite polarity and different surface relaxation energies [13]. The crystal structures formed by ZnO are wurtzite, zinc-blende, and rock salt which are suitable for nanostructures [14].

The synthesis of ZnO nanostructures has been an active field for the last fifteen years because of their wide applications as biosensors, transducers, and catalysts. In recent years, semiconducting nanostructures have been the focus of considerable research due to their unique properties that can be exploited in various functional nano-devices especially for intracellular sensors [15]. Nano-device functionality has been demonstrated with these nanostructure materials in the form of electric field-effect switching [16], single electron transistors [17], biological and chemical sensing [18], and luminescence [19] for one dimensional semiconducting nanostructure [19]. Due to the small dimensions of nanowires and nanorods combined with a very large contact surface and strong binding with biological and chemical reagents, nanowires and nanorods will have important applications for intracellular environment [20]. A literature survey reveals that ZnO nanorods show *n*-type semiconducting property and their electrical transport is highly dependent on the adsorption and desorption nature of chemical species [21].

4. ZnO Nanostructure Growth and Characterization

The chemical growth technique is one of the methods used for the ZnO nanostructures fabrication. Equal molar concentrations of two solutions, zinc nitrate hexahydrate and hexamethylenetetramine are used for the growth of the ZnO nanowires and nanorods on the glass tip [22]. The structural morphology and the size distribution of the ZnO nanowires and nanorods were investigated by Field Emission Scanning Electron Microscope (FESEM) at different magnifications [22]. The ZnO nanowires and nanorods cover a small part of the silver-coated glass tip varying from 3 mm and down to 10 µm [22]. The nanostructure has a rodlike shape with a hexagonal cross section and primarily aligned along the perpendicular direction [23]. The nanorods are uniform in size with a diameter of 100-120 nm and a length of 900-1000 nm [23].

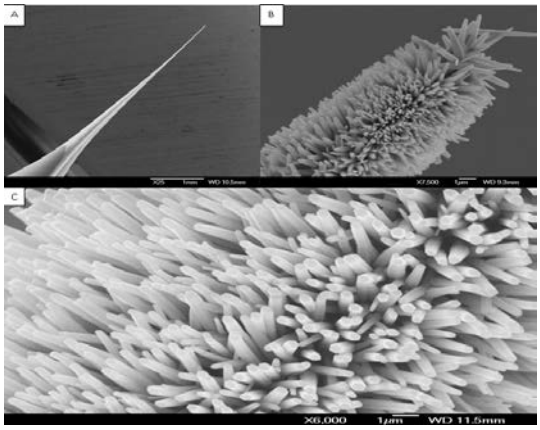


Figure 2. FESEM images at different magnifications of the Ag-coated glass tip without (a) and with (b,c) grown ZnO nanorods [22,23]

5. ZnO Nanostructure-Based Intracellular Measurements

5.1. Intracellular Calcium Ion Measurements

Table 1. Summary of ZnO nanostructure-based intracellular metal ion-selective biosensors (PVC: Poly Vinyl Chloride; BGC: Borosilicate Glass Capillary)

Ref	[24]	[5]	[25]	[18]	[17]	[26]
Enzyme/Electrode	PVC/Ag wire	PVC/BGC	PVC/Ag wire	PVC/IBGC	PVC/BGC	PVC/BGC
Immobilization Mode	Physical adsorption	Physical adsorption	Physical adsorption	Physical adsorption	Physical adsorption	Physical adsorption
ZnO Synthesis	ACG	ACG	ACG	ACG	ACG	ACG
ZnO Morphology	Nanowires	Nanorods	Nanorods	Nanorods	Nanorods	Nanorods
Response Time(s)	<1 min	fast	20 s	fast	fast	fast
Ion-Selection	Ca^{2+}	Ca^{2+}	Ca^{2+}	Na^{+}	Mg^{2+}	K^{+}
Sensitivity (mV/decade)	26.4	29.67	113.92	72	26.1	41.47
Linear Response Range	1 µM-0.1 M	100 nM-10 mM	1 µM-1 mM	0.5 mM-100 mM	500 nM-100 mM	25 µM-125 mM
Interfering Ions	No tested	No tested	Na^{+}, Mg^{2+}, K^{+}	Ca^{2+}, K^{+}, Mg^{2+},	Ca^{2+}, Na^{+}, K^{+}	No tested

Metal ions play dominant roles in medical physics, especially for cell morphology, so it is important to detect the metal ion concentration and changes in concentration of specific ions for cell biology [24]. The most prominent ions are Ca^{2+}, Mg^{2+}, K+, Na+, Fe^{2+}, Cu^{2+}, Zn^{2+}, etc. Every ion has its own chemistry and fundamental biology with different physical and chemical characteristics [25]. All the metal ions play important roles in biological systems [26]. Every metal ion has its own importance in living systems by acting as cofactors in enzymes, as osmotic regulators, as current carriers and consequently as factors in information processing and as integrator and stabilizers of proteins and lipids [27]. Recently, nanostructured ZnO based ion-selective sensors were fabricated by effective, simple techniques for measuring specific ion concentrations in intracellular as well as extracellular environments [28]. Calcium ions play important roles in regulating enzyme activity, neuronal activity, muscle contraction, vesicle exocytosis, cell development and death [27]. Clinical situations in which the in vivo monitoring of Ca^{2+} is of interest include, for example, organ-transplantations, hemodialysis, or exchange transfusion, during which rapid change in the concentration of the ionized calcium may occur [27]. Therefore, it is important to know its concentration in different types of extra- and intracellular compartments [27]. Such applications have made Ca^{2+} one of the most interesting elements to sense. Other industrial applications are Ca^{2+} ion measurements in boiler water, soils, and fertilizers [28].

5.2. Intracellular Sodium and Potassium Ion Measurements

While the intracellular concentration of Na is usually low in such environments, and the role of intracellular Na is not fully understood, the intracellular concentration of K was relatively higher compared to that of Na [29]. Potassium (K) is the main intracellular ion in the body and its levels are essential for normal homeostasis [30]. It is contained primarily within the intracellular fluid compartment, with only about 2% of total body potassium present in the extracellular fluid [31]. In that work, preliminary intracellular detection of most essential metal ions, and glucose, was performed in oocytes and adipocyte cells [31]. The aim of that work was to characterize ZnO nanorods and present their application as an intracellular selective ion sensor [32]. That sensor was based on ZnO nanorods grown on borosilicate glass capillaries that can penetrate the cell membrane [33]. The electrochemical potential difference response of ZnO nano discs to changes in the Na electrolyte solution was measured with a range from 0.5 mM to 100 mM [34].

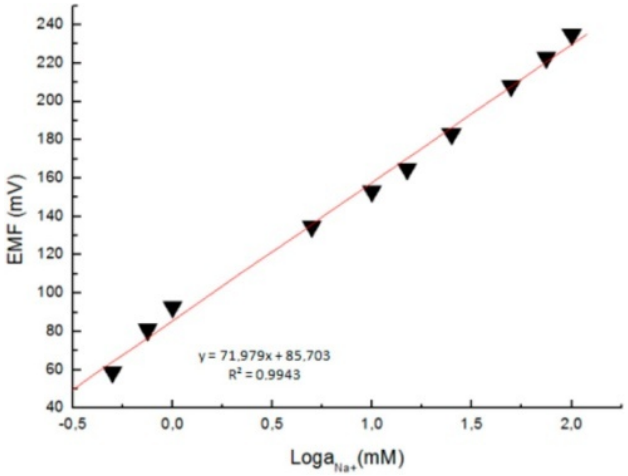
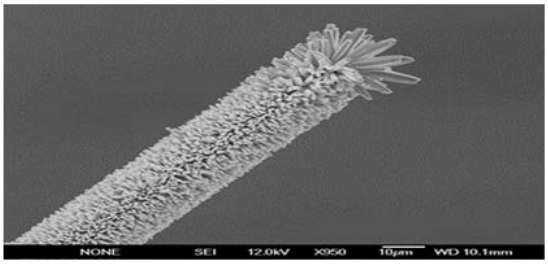
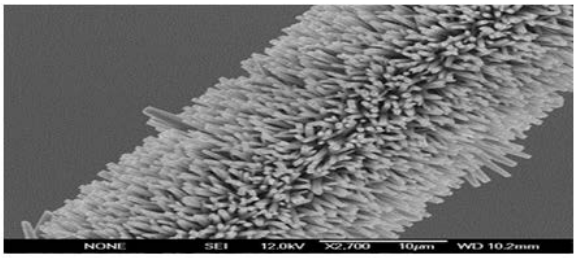


Figure 3. Calibration curve of electrochemical potential difference between the Na^+-selective ZnO nanorod and the Ag/AgCl reference microelectrodes *vs.* the Na^+ concentration [34]

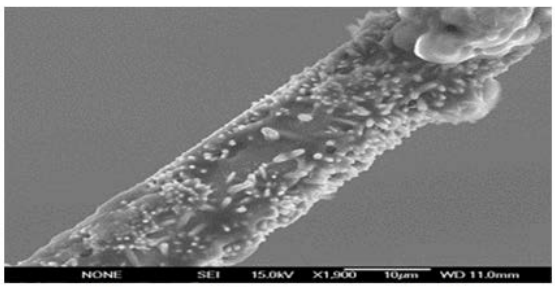
All the microelectrodes were investigated pre- and post-experimentally with scanning electron microscopy to make sure that the nanorods on the K^+ K^+ selective microelectrodes were not dissolved as shown in Figure 4.



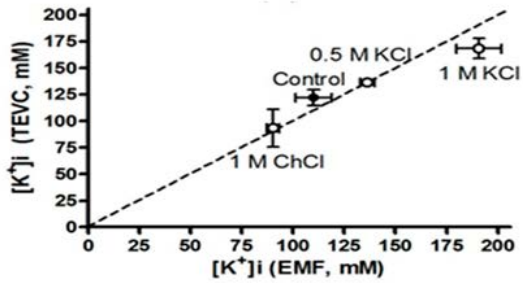
a. FESEM images of the K^+-selective microelectrode before [34].



b. FESEM images of the K^+-selective microelectrode before [34]



c. FESEM images of the K^+-selective microelectrode after [34]



d. Data points are expressed as mean values for control oocytes and oocytes injected with 50 nL of indicated test solution [34]

Figure 4. Intracellular K^+ concentrations in Kv channel-expressing Xenopusoocytes measured with electrophysiological and K+-selective microelectrode methods [34]

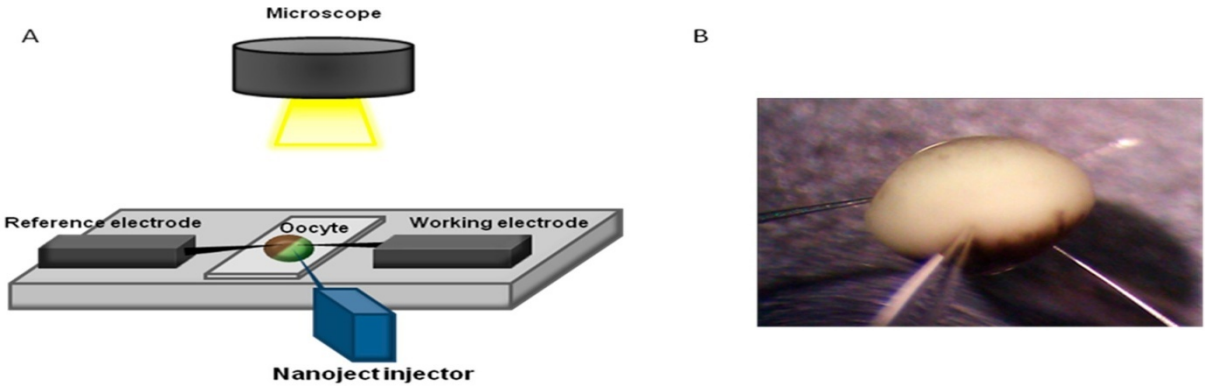


Figure 5. Experimental setup for simultaneous test solution injection and potentiometric measurements, (A) Schematic illustration of the setup and (B) Photography of Xenopus oocyte penetrated by the reference electrode (left), measurement electrode (right), and injector (middle) [34]

The sensor showed a good performance in sensitivity, stability, selectivity, reproducibility for Na^+ detection and small interference from other ions [35]. Furthermore, the sensor is easy to fabricate and easy to insert in large cells [35]. The measured intracellular Na^+ and K^+ concentrations in single human adipocytes and frog oocytes were consistent with values found in the literature [36]. Potentiometric measurements were done in parallel with electrophysiological measurements to verify the accuracy of the detected concentrations [37]. The experimental setup for injection and detection of K^+ is shown in Figure 5 [37].

6. ZnO Structures for Chemiresistive Gas Sensing

As mentioned before, ZnO has been employed to design chemiresistors, in which changes of electrical resistance occur when gas molecules react onto their surface [38]. Specifically, oxygen molecules adsorbed on the surface of the ZnO can ionize in oxygen species (O^{-2}, O^-, O^{2-}) [39], capturing electrons from the conduction band, leading to formation of the depletion layer and, thus, increasing the resistance of the sensor [38]. When reducing gases, such as ethanol, approach the ZnO surface, oxygen species will interact with these gas molecules and release electrons trapped back into the conduction band, causing the resistance of the sensor to decrease [40,41,42]. During exposure to oxidizing gases as SO_2, which act as an electron acceptor, the resistance of the sensor increases [40,43]. In this way, gas detection is achieved by varying the resistance of the sensor [38]. Currently, according to that study, efforts are devoted to developing micro-chemists using zero dimensions (0D) using zero dimensional (0D), one dimensional (1D), two dimensional (2D) and three dimensional (3D) nanostructures [40]. Table 1 presents a compilation of some of the most relevant works reporting ZnO sensors based on different morphologies. Besides, a few of them were selected to be presented and discussed in more detail in the next subsections [40,43].

6.1. ZnO Nanoparticles and Quantum Dots

ZnO nanoparticles and quantum dots exhibit 0D morphology and high surface area-to-volume ratio, which is key to increase the sensor's figure of merit [44]. The techniques employed for developing nanoparticles and quantum dots (QDs) with controlled size and shape include spray pyrolysis [43], hydrothermal method [45,46,47], sol gel wet chemical method and others [48,49,50]. It is very important to control the growth rate and the nucleation process to achieve nanoparticles and QDs with suitable properties for sensing applications, and usually chemical processes are the preferred over other methods as reported by Niarchos et al. [48,49,50].

Synthetize ZnO nanoparticles further applied as humidity sensor by spreading the nanoparticles onto electrodes (paper) surface and annealing at 100°C to bind the material as a film [54]. Nanoparticles coalescence resulted in better long-term stability proving to be an alternative material to improve paper-based devices stability over humidity [54].

ZnO nanoparticles morphology can be designed to improve sensitivity and selectivity, where the surface reactivity is dependent on the metal oxide crystalline faces facing out [55,56,57]. In this direction, Ryzhikov et al. [58] prepared ZnO nanoparticles with different morphologies (nanorods, isotropic, and cloud-like) by organometallic route and tested them as gas sensor for CO, C_3H_8, and NH_3. ZnO nanoparticle morphology showed significant influence on sensors response and selectivity for reducing gases [58]. Nanorods showed the highest response to C_3H_8 and CO, whereas, for NH_3 detection no effect of morphology could be observed [58]. The authors highlighted that the ZnO nanoparticles control was made without drastic changes on the synthetic route and that the sensor response and selectivity could be related to basal and lateral crystalline faces presence and percentage, justifying the nanorod higher sensitivity to propane [58]. Another strategy highly explored to improve nanostructured ZnO performance as gas sensor is the doping process of ZnO. For instance, Jaballah et al. [59] prepared sensing devices based on ZnO nanoparticles and ZnO nanoparticles doped with Mg as shown in Figure 6a. The Mg-ZnO (M_3ZO) platform showed a response 200 % higher than pristine ZnO nanoparticles for 5 ppm of ethanol at 250 °C, the best operating temperature as shown in Figure (6a).

The proposed sensing mechanism explores the idea of ethanol acting as a reducing gas by interaction with oxygen species absorbed at the oxide surface as shown in Figure 6a [59]. Once the gas is adsorbed, oxygen species release the trapped electrons from the depletion layer to the oxide bulk decreasing its electrical resistance as shown

in Figure 6a. The authors estimated that by doping ZnO with Mg^{2+}, the adsorption of oxygen species during the material synthesis is favored since the dopant will act as donor [59]. Once the gas sensing is dependent on these oxygen species, higher concentration of oxygen species led to improved sensing response to ethanol [59].

Metal oxide quantum dots have also demonstrated promising sensing performance, indicating that very small particles (2-10 nm) with charge carriers confined in all three spatial dimensions can boost electrical properties of semiconductors, offering insights to the new era of gas sensors [44,60]. Specifically, ZnO QDs have also been successfully applied in chemiresistive sensors, being one of the three most explored metal oxide quantum dots along with SnO_2 and TiO_2 [44]. In this direction, ZnO QDs with different grain sizes can be obtained by wet chemical method with different reaction times as a parameter able to modulate sensors response to gas analytes such as demonstrated by Hu et al. [50]. In this case, the sensors demonstrated direct correlation between signal response and crystal grain size when applied to H_2S sensing. This correlation could be corroborated by mathematical calculation method [50].

Comparing ZnO QDs with ZnO nanoparticles it is possible to observe the better performance of ZnO QDs as shown in Figure 6b [50]. Both ZnO nanoparticles and ZnO QDs sensing is based on the same mechanism, the depletion theory [50]. Nevertheless, ZnO QDs presents higher resistance once the band gap is larger thanks to quantum confinement effect and higher amount of oxygen vacancies as shown in Figure 6b [59]. Therefore, ZnO QDs and their greater number of surface-sensing active sites for isoprene adsorption leads to increased sensing response [50].

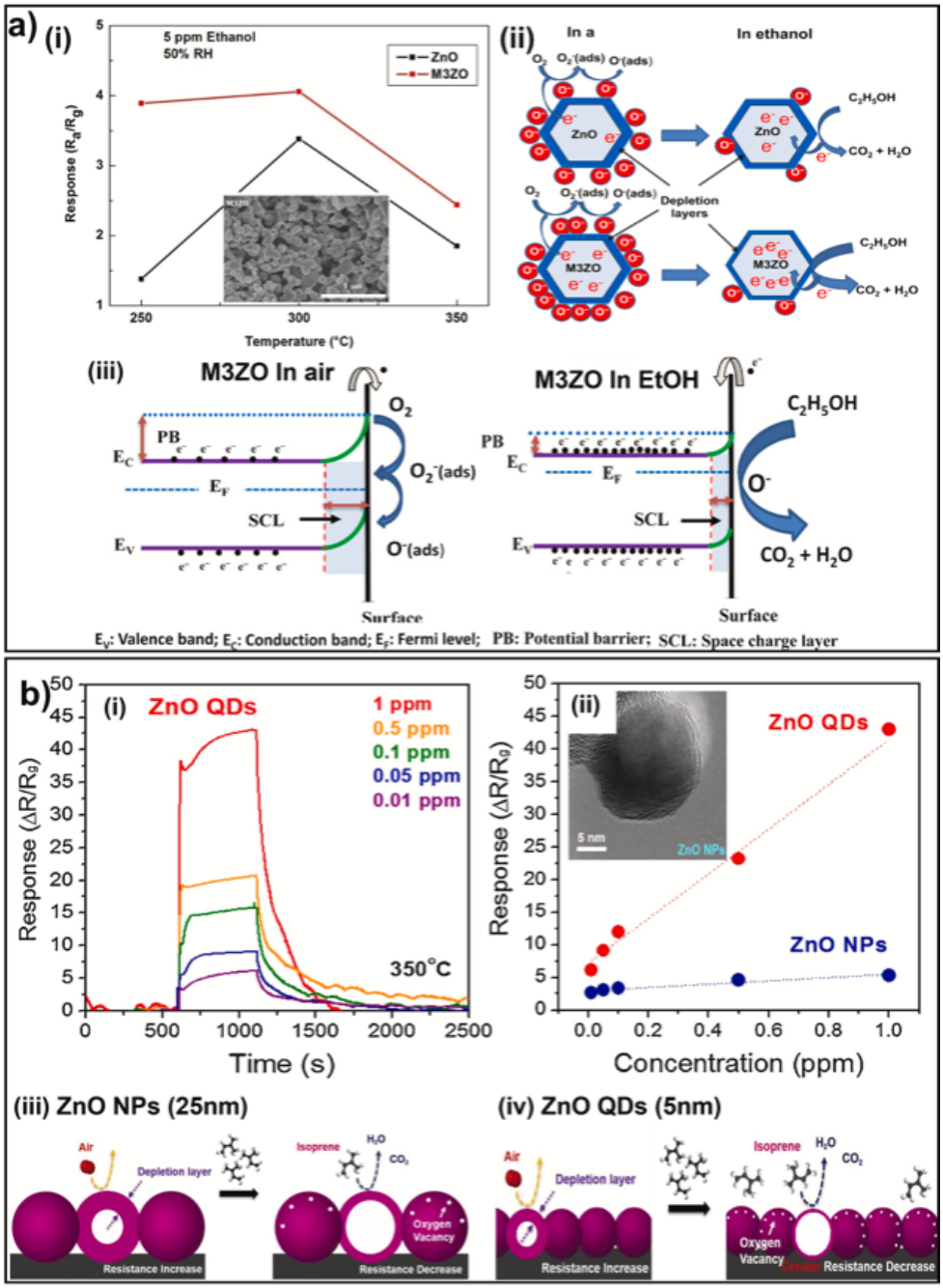


Figure 6. (a) ZnO nanoparticles doped with Mg (b) dynamic response curves of ZnO QDs at 350°C as a function of isoprene concentration [51,52]

In another example, researchers synthesized ZnO QDs with 2.53 nm of diameter and showed a high selective response towards H_2 when compared to the other six (interferents) volatiles [49]. In this case, ZnO QDs sensitivity and selectivity could be addressed to the reaction of H_2 molecules with oxygen species absorbed onto the sensor surface, and then with ZnO creating acceptor surface states and releasing electrons to ZnO QDs bulk [49]. Moreover, QDs have been largely exploited in combination with other compounds as sensing layer. In a recent study, Sun et al. [48] prepared a mixed platform using ZnO QDs and SnO_2 hollow nano- spheres, which hybrid platform showed a better sensing performance towards formaldehyde than the sensors based on the pristine of ZnO QDs and pristine SnO_2 [48]. The improvement was attributed by the authors as a heterojunction formation resulting from the distinct materials combination [48]. More examples of hybrid material obtained with ZnO QDs are discussed in further sections [48].

6.2. 1D ZnO Nanostructures

One-dimensional ZnO nanostructures are versatile materials employed in supercapacitors [61], photocatalytic degradation [62] and batteries [63]. Additionally, these structures have also been applied in gas sensors [64] in varied morphologies, such as nanotubes [64].

The judicious choice of the production method and associated parameters can be an excellent way to improve the material performance towards sensing applications [67]. For example, when ZnO nanowires are prepared by electrospinning and calcined at different temperatures, the resulting material might present different performance over gas detection based on the junction formation for each treatment temperature. The temperature optimization can be an ally on the sensing performance improvement [67], as well as the optimization of all synthesis parameters might direct influence the sensor performance. Post treatment of ZnO nanostructures is also a strategy for properties modulation and improvement of sensing properties [67]. Researchers have explored low-temperature plasma treatment of electro spun ZnO nanofibers aiming to increase nanofibers surface area and porosity for better gas sensing performance [68].

This proposition could be corroborated by DTF calculations and adsorption energy variation according with ZnO nanofibers surface treatment. Such evidence indicates the direct influence of plasma treatment on electrons movement and electrical resistance after exposure to the gas analyte. Thus, the improvement of 1D sensor properties of ZnO has been increasingly expanded beyond the conventionally found structures [68]. Aside from the high surface area and great amount of available active sites, ZnO 1D nanostructures sensing mechanism benefits from improved charge carriers' mobility thanks to a continuous conducting channel formed along the 1D preferential axes. With that in mind, it would be very important future contributions comparing the length of 1D nanostructures based on the same material with its sensing performance [68]. Besides solid and porous ZnO 1D nanostructures, hollow ZnO nanofibers have also been extensively explored in gas sensors and although it is a 1D morphology, the most recent classification indicates its 3D character, evidenced by the internal exposed surface available for gas adsorption [68].

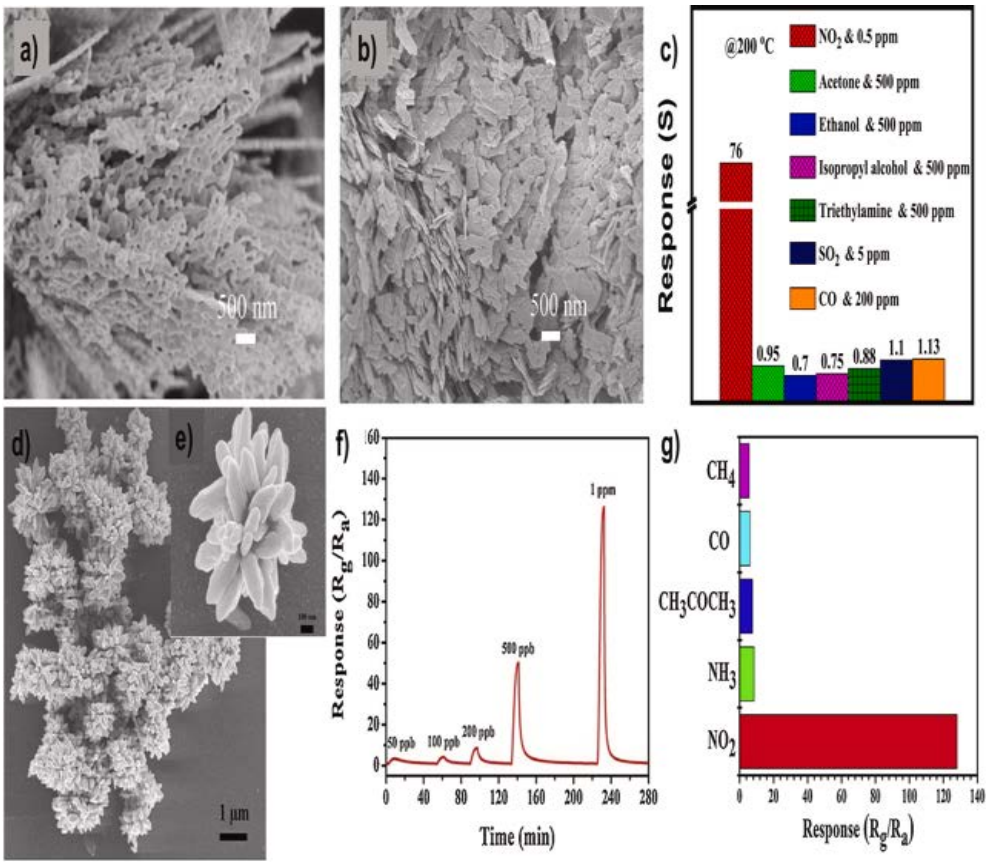


Figure 7. Scanning electron microscopy of ZnO [51,52,53]

6.3. 2D ZnO Nanostructures

The development of 2D materials composed of a single or a few atomic layers has been shown to be a promising strategy for optoelectronic devices [69]. Graphene, for example is a 2D material that has aroused enormous scientific interest owing to their appealing mechanical, electrical and optical properties [69] combined to high porous volume for gas diffusion [70]. All these features have driven the development of sensor devices that show high sensitivity to toxic gases with fast response. Two common ZnO 2D nanostructures normally employed as sensors are nanosheets [51,71,72,73] and nanoplates. To compare different 2D morphologies in sensors application, Duy et al. [51]. The prepared platforms based on ZnO nanosheets as shown in Figure 7a and nanoplates as shown in Figure 7b exposed to low concentrations of NO_2 [51]. By modulating the hydrothermal synthesis parameters, materials with different morphologies and related sensing behaviors could be achieved. The nanoplates were characterized to have a 15 nm thickness, which is almost 10 times smaller than 3D ZnO (100 nm). Besides lower thickness, 2D ZnO is also highlighted by the increased surface area, and both together contribute for a high response (S = 76 for 0.5 ppm of NO_2) and selectivity towards NO_2 against acetone, ethanol, isopropyl alcohol, triethylamine, SO_2 and CO as shown in Figure 7c [51]. Furthermore, the authors reported a calculated limit of detection of 3 ppt towards NO_2 [51].

6.4. 3D ZnO Nanostructures

The 3D ZnO nanostructures have advanced morphologies that can be employed for developing chemiresistive sensors with interesting properties [74,75], although some limitations may occur owing to the difficult to control the synthesis parameters and limited production rate [76]. ZnO nanoflowers, for instance, have been successfully employed in chemiresistive sensors by distinct research groups through different methods [77,78,79]. ZnO nanoflowers have been prepared by Song et al. as shown in Figure 7 (d,e) by a hydrothermal method with an average diameter of 0.9-1 nm.

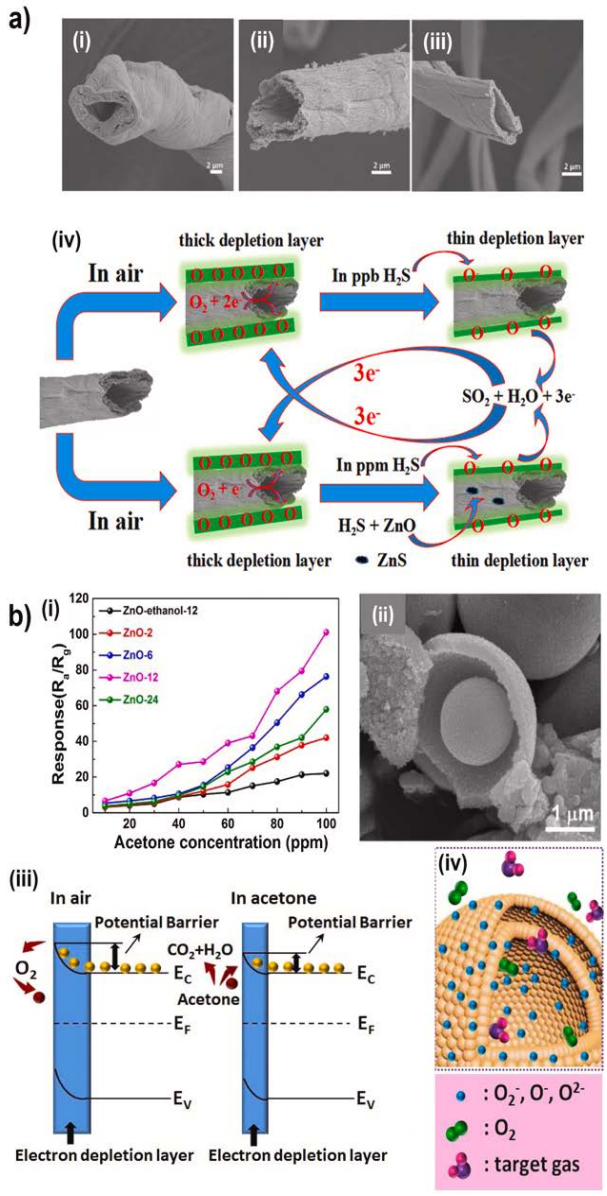


Figure 8. (a) SEM images of hollow ZnO nanotubes obtained at (i) 500°C, (ii) 600 °C and (iii) 700 °C [65,66]

The pure ZnO nanoflowers sensing performance towards NO_2 monitoring as shown in Figure 7f was attributed to the formation of an Schottky barrier between the ZnO film and Au electrodes yielding to a detection limit of 50 ppb and high selectivity for NO_2 as shown in Figure 7 (g) [53]. 3D ZnO nanostructures are usually composed of hollow spheres and nanofibers. Usually, multiple steps reactions and methods are necessary to achieve hollow nanostructures which is time consuming and costly [82]. Therefore, the development of straightforward and effective one-step synthetic to produce hollow nanostructures is still challenging. Both hollow ZnO nanofibers/nanotubes/nanoneedles and spheres have been explored for gas sensing and their properties studied to better understand its influence on the final sensing performance [82]. Some reports defend the electron-hole pair segregation, where electrons are located on the external surface while most holes are located on the internal surface [83,84]. Sensor response time has been related to wall thickness of hollow ZnO nanotubes, indicating that response time can be greatly decreased by reducing the wall thickness [85]. Besides, sensor response can be improved by enhancing the number of shell structures in hollow ZnO nanospheres [86]. Moreover, hollow ZnO nanostructures are advancing on the pathway of large-scale production as demonstrated by Na et al. [65]. The authors achieved hollow ZnO nanotubes as sensor device for H_2S detection with outstanding figures of merit such as surface area of 31 m^2g^{-1}, response time of 29 s and sensor response of 85% for 10 ppm of H_2S for optimized synthesis temperature as shown in Figure 8a [66]. For hollow ZnO structures, it has been demonstrated that double-shelled can operate on gas sensing detection with a response time of 1 second upon exposure to 100 ppm of acetone along with low limit of detection, low temperature of operation and high selectivity as shown in Figure 8b [66]. The sensing mechanism for hollow spheres consider the depletion theory in which oxygen species are adsorbed onto double-shelled ZnO hollow microsphere surfaces capturing electrons from ZnO conduction band and releasing them when in contact with the target gas as shown in Figure 8b [66]. Besides, the interspace between the shells is advantageous to gas diffusion as well as double shells offering large active sites ensuring the gas access from different direction and resulting in high response as shown in Figure 8b [66].

7. Conclusions

In this review, the most recent advancements in ZnO-based chemiresistive gas sensors over the previous ten years were examined. ZnO has drawn a lot of attention due to its remarkable capabilities for sensing a wide range of analytes, including alcohols, ethers, ammonia, and CO. The synthesis of hierarchical and functional ZnO structures, which have been extensively investigated for sensing applications, has been made possible by the invention and improvement of synthesis techniques, as detailed throughout this study. Production of ZnO based (organic and hybrid) composites with regulated morphology, shape, and surface has received a lot of attention to improve sensing performance in terms of sensitivity, selectivity, responsiveness, and recovery time, as well as long-term stability. Particularly, it has been shown that heterojunctions made from dissimilar materials in nanocomposites can be useful.

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