Metal oxide nanowire chemical sensors: innovation and quality of life

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Metal oxides are emerging as important active materials for applications such as sensors. Recent advances in the preparation of metal oxide materials offer unique possibilities for their integration into devices with new capabilities, for example, wearable/flexible devices, smart textiles for well-being and health monitoring in everyday life, or with innovative sensing architectures such as work function, surface ionization, magnetic, self-heating, and Schottky-based devices. This review presents the author's opinion on innovations and challenges in the field of metal oxide nanowire chemical sensors.

Introduction

Nanotechnology and nanoscience are increasingly attracting attention and investments all over the world. Available literature as well as the Internet does not offer a unique definition for nanotechnology. Nanotechnology operates at the first level of atom and molecule organization, which forms the core and starting point for definition of materials' fundamental and functional properties. Nanotechnology is essential to acquire knowledge of the matter, and nanoscale phenomena hold the promise for fundamentally new applications and to build a first step toward industrial prototyping and commercialization. For this reason, control (at this scale level) is essential to create new, broad and revolutionary technologies and platforms for every area of interest, such as industry, biomedicine, environmental engineering, safety and security, food and water resources quality control, and energy conversion.

In particular, sensors have (and would have) an increasing impact on many aspects of our life: chemical sensors are indeed a required interface to acquire chemical information out of our surroundings in real time. This information may provide control systems with feedback on an incredibly large number of chemical processes: detection of toxic analytes and explosives, alarming systems for gas appliances, security systems to protect workers from chemical hazards, outdoor monitoring, food chain control, health, and wealth monitoring. Moreover, chemical sensors may be spread out and used in networks, to monitor chemical information as a function of location and time, giving a distribution map of harmful and toxic chemicals over large areas during the day. The quality of atmospheric air, such as indoor air, may be monitored and correlated to chronic diseases, for example, getting insights on how to increase health and wealth.

In fact, in Italy (the author's country), the concepts of spirit, mind, body, and wellness accompany everyone's everyday life and have a great meaning. Over the years, this concept has gained more and more value and, at present, it refers not only to the absence of diseases but also to a general condition where spirit, mind, and body, including psychological, mental, and physical health, are considered as a whole.

Unfortunately, in order to be used in real applications, chemical sensors should fulfill stringent requirements depending on the specific purpose and operation conditions (sensing performances in terms of sensitivity, selectivity and response kinetics, and reliability (drift and stability)). These requirements are strictly correlated to the active materials used and that is why materials design is the starting point for the development of new sensors and new gas sensor technologies. Therefore, the impact of material design in the research and development of chemical sensors is fundamental.

On account of these reasons and applications, gas sensor technology is becoming essential in various aspects of our everyday life. Still, advancements in nanotechnology are effectively needed to improve the sustainability of our society and quality of life. This short review article reports the author's personal opinions about

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the key advances that have been made and what is yet to be done in this field.

Chemical sensors

Conductometric chemical sensors based on metal oxide semiconductors have been known since 1954–1962, when the effects of reaction of metal oxides with the surrounding atmosphere were discovered [1–3] and the first commercial gas sensor was developed [4]. Since then these sensors attracted the attention of researchers working on sensors, because of low cost of fabrication, simple preparation and operation, and large number of potential detections and applications together with the possible device miniaturization. The improvement of their sensitivity, selectivity, stability, and speed (i.e. response and recovery rates) remains a challenge. The interaction between gas molecules and active oxide takes place at its surface; therefore, the atoms of the surface are crucial in chemical sensing performances. Nanowires in particular present a high surface-to-volume ratio that provides a way to enhance the effects of surface phenomena (that are at the base of chemical sensing mechanism); moreover, they may be single crystalline and have well-defined crystal orientations, leading to controlled reactions and increased stability. Response dynamics should be faster compared to their polycrystalline counterpart because there is no need for gas diffusion preliminary to surface reaction. Finally, some of the interesting effects that can be exploited in chemical sensing (such as self-heating) exist only for the nanowire morphology.

Innovation is always the key to open new frontiers and boost the scientific and technological progress. Concerning chemical sensors, there are different ways to bring innovations: designing sensors using new transduction mechanism, sensors for the detection of new chemicals, improving the sensitivity of a known active material or lowering the detection limit for a chemical species, developing room-temperature chemical sensors, improving compatibility with large-scale production systems, portability, and wearability. Most of the chemical sensors reported in literature have been designed based on empirical expertise rather than basic knowledge of materials. On the contrary, fundamental studies are crucial to understand gas-sensing mechanism and select the key factors that influence their performances in order to have a secure ground to boost concrete innovations.

Metal oxides have been integrated into functional devices since long time: tin, titanium, tungsten, and zinc oxides have been extensively investigated, especially for chemical sensing, due to their better thermal, chemical, and mechanical stability compared to organic materials. The key features that an ideal sensor should have include operation at room temperature, no need of filters, heating systems or radiation to ease response or recovery dynamics, low detection limits, high sensitivity and selectivity, high reproducibility, fast response and recovery, and low cost. This would be an ideal sensor of course, but some of these features cannot be discarded, if we are looking for a real device.

Recently, flexible/wearable sensors (Fig. 1) have attracted a lot of attention especially due to their potential impacts on the preparation of portable–wearable systems for health and wealth monitoring throughout our entire life. The use of nanomaterials (semiconducting nanowires, metal oxide nanowires, and carbon-based nanomaterials) with high surface-to-volume ratio can allow the achievement of improved sensing performances.
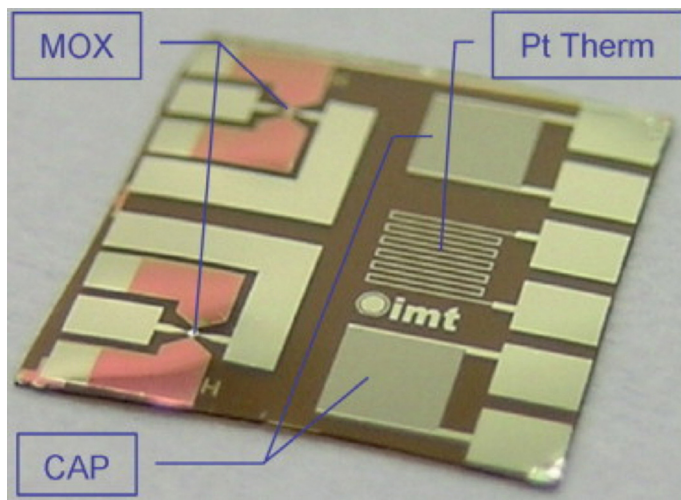

FIGURE 1

Microscope photograph of the multi-sensor platform. Reprinted with permission from Ref [11]. Copyright (2009) by the Elsevier.

Researchers are making efforts to incorporate different sensors into our daily life, using common substrates such as plastic, textile, and paper. The preparation of oxide-based sensors on these transducers is mandatory to develop sensor networks of light, hand-held, portable, consumer devices.

A number of approaches have been reported for the preparation of these devices, with most of them using post-growth integration procedures (see reviews [5,6]). Here we will just briefly discuss some aspects relevant for flexible/wearable chemical sensors. The direct preparation on flexible/wearable substrate has the advantages of easier fabrication processes and low cost. However, the growth of high-quality oxide nanowires on flexible substrates has been difficult primarily due to its thermal requirements to avoid substrate damage. In the case of wearable/flexible substrates, the deposition temperature must be well below the plastic–glass transition or thermal degradation temperature of the substrate. Furthermore, when dealing with solution phase methods there may be restriction on the precursors and solvents. On the other hand, dry or wet techniques may be used to transfer the as-deposited high-quality oxide nanowires from the host substrates to plastic ones.

One of the first methods proposed was the superlattice nanowire pattern transfer (SNAP) [7] approach in 2007 concerning the integration of silicon nanowires into biological and chemical sensors on plastic. Later, other technologies were also reported for the assembly of metal oxide nanowires. The most used methods, and compatible with large-scale production, are contact or roll printing [8], the Langmuir–Blodgett technique [9], and dielectrophoresis [10]. Dielectrophoretic assembly allows a precise positioning with the use of electromagnetic fields between metal contacts, which is in principle compatible with flexible substrates provided the solution does not damage the substrate, and metal contacts are necessary to induce alignments.

Flexible sensors

Most of the studies about flexible/wearable metal oxide sensors do not concern metal oxide nanowires. Indeed, these works still deserve attention because, thanks to the easier integration, research efforts were often devoted to other key issues essential for

the validation of the final device, such as the long-term stability of the entire device and the effects of repeated bending stress. The lack of sensor stability over long-term operations or bending influence on sensing performances, for example, can prevent commercialization of sensors. Courbat et al. [11,12] have studied, for several months, the continuous operation of metal oxide polycrystalline gas sensors on polyimide hotplates and found out that comparable or even better results may be expected from nanowire-based devices. Kinkeldei et al. [13] have shown the integration of gas sensor arrays into textile using carbon black and polymers, and they were able to eliminate the influence of bending on sensors.

The integration of ZnO nanorods by thermolysis-assisted chemical solution on polyimide sensing transducers was reported in 2010 [14]. Ethanol sensing performances were studied in the concentration range of 10–100 ppm and as a function of the operating temperature (100–300°C). The response increased as both concentration and operating temperature increased, as expected. The response toward 100 ppm of ethanol at an operating temperature of 300°C was 3.11, while response and recovery times were 3–5 min. Ahn et al. demonstrated that the integration into flexible transducers did not worsen the sensing capabilities of metal oxide nanowires, which were comparable to the ones reported in literature, and this is an important achievement.

In 2012, another important result was presented: the direct growth of zinc oxide nanowires on carbon fiber that allowed mechanical flexibility [15]. The growth included two steps: the electrodeposition of zinc on carbon microfiber followed by a thermal oxidation to achieve the oxide nanowires. The carbon microfibers had a diameter of 10 μm, zinc oxide nanostructures covered uniformly the entire fabric, and the nanowires were single crystals. Gas measurements were performed in a nitrogen background introducing traces of oxygen and hydrogen at different operating temperatures up to 320°C. Figure 2 shows the best responses toward oxygen obtained at 280°C ($\sim$10–500 ppm). Response and recovery times were fast (few seconds) for both hydrogen and oxygen, while the power consumption was lower than 0.6 μW.

Different hydrogen flexible sensors have been reported, mainly based on metal [16] or carbon active materials [17–19] using high temperatures to grow nanotubes or graphene and dry transfer printing to transfer the nanostructures on plastic. Lim et al. prepared a hydrogen sensor with Pd nanotubes using ZnO nanowires as templates [16]. However, the polycrystalline nature of palladium nanostructures makes the sensor much more sensitive to bending stress and its flexible design causes changes in the electrical resistance due to formation of cracks between the Pd grains. However, single-crystalline nanowires are much more resistant to bending stress because of their flexibility. Rashid et al. [20] reported the development of a flexible hydrogen sensor prepared on polyimide substrates. A zinc oxide thin film prepared by sol–gel technology was used as seed layer for the nanorods' growth using the hydrothermal method. The oxide nanostructures were catalyzed with palladium nanoparticles deposited by sputtering. The functional tests were performed at room temperature in an open space where a constant flow of hydrogen diluted in nitrogen was delivered closed to the sensor surface. Mechanical flexibility, robustness, and repeatability were investigated. The overall resistance increased with bending for the strain between the polyimide and zinc oxide nanorods. As the palladium nanoparticles start to cover the nanorods, the response decreases. The most important result is that bending the device did not significantly affect the sensing performance, except from small differences between the responses, the response time increased <2%. This is an essential feature for a possible use in real sensing devices. Figure 3 shows the real-time responses at various concentrations. The slight increase in the response was attributed to a higher surface reactivity during bending that activated the adsorption of gas molecules.

In addition, a reliability test was performed cycling through bending and relaxation of the flexible sensor 10^6 times. Surprisingly, no significant degradation of the sensing performances was observed until 10^5 cycles. This confirms the possible use of such chemical sensors in real applications. As 10^6 cycles are reached, there is a slight degradation mainly attributed to the loss of adhesion of ZnO on polyimide substrate (Fig. 4). Although these studies are not commonly performed, they are essential: it is not realistic to propose a practical use of these sensors without these investigations.

Recently, nonconventional substrates have been used, such as graphene sheets. Hydrothermal technique has been used to
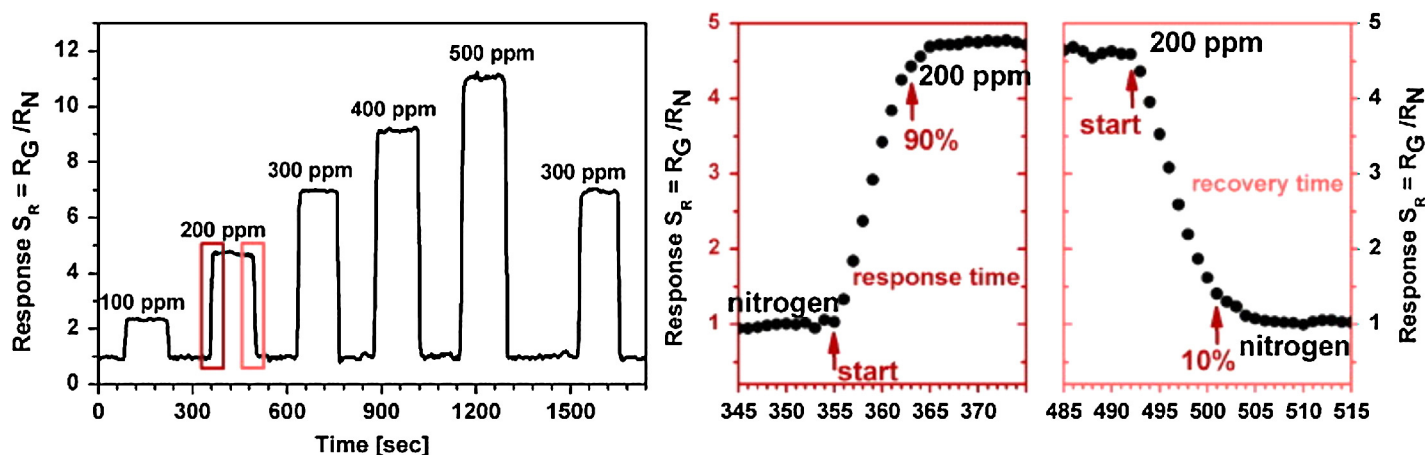

FIGURE 2

(a) Response transient of the ZnO-μC sensor under exposure to different O_2 concentrations (0–600 ppm of O_2 in pure nitrogen) at 280°C, (b) response time, and (c) recovery time. Reprinted with permission from Ref [15]. Copyright (2012) by the Elsevier.
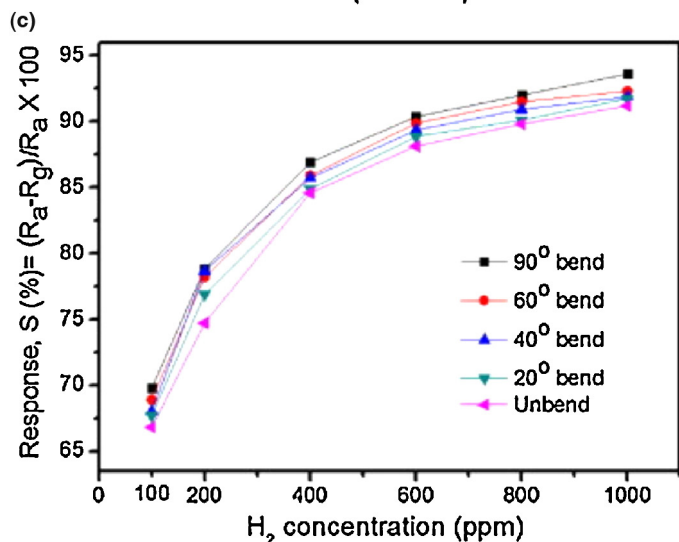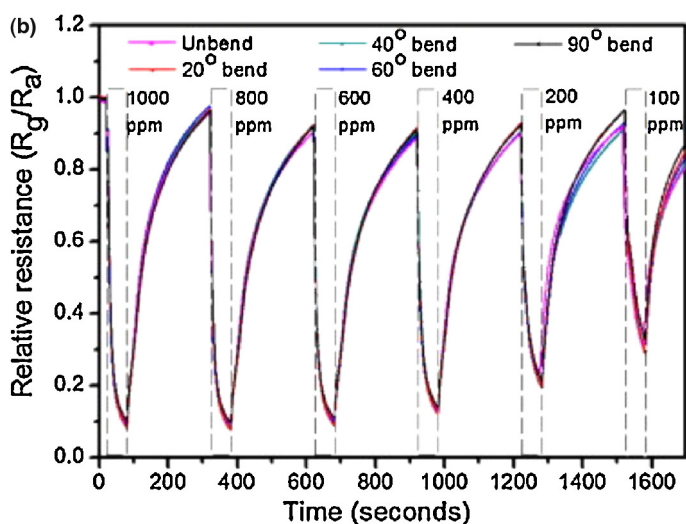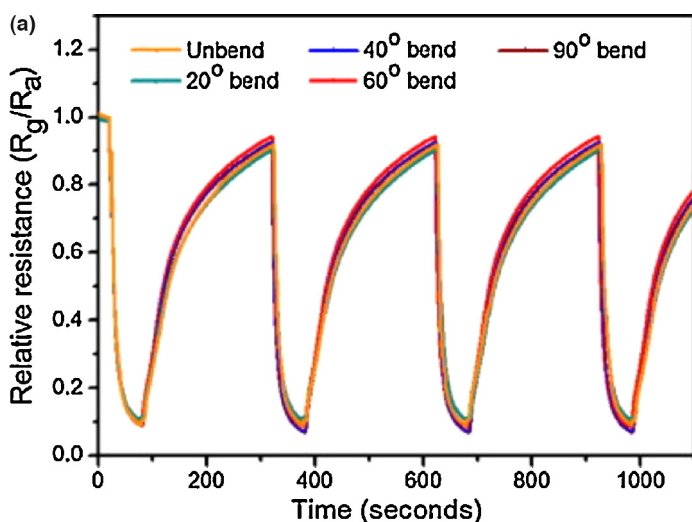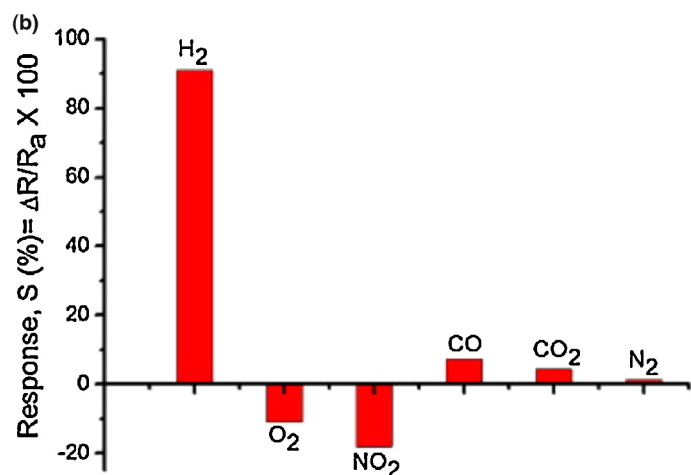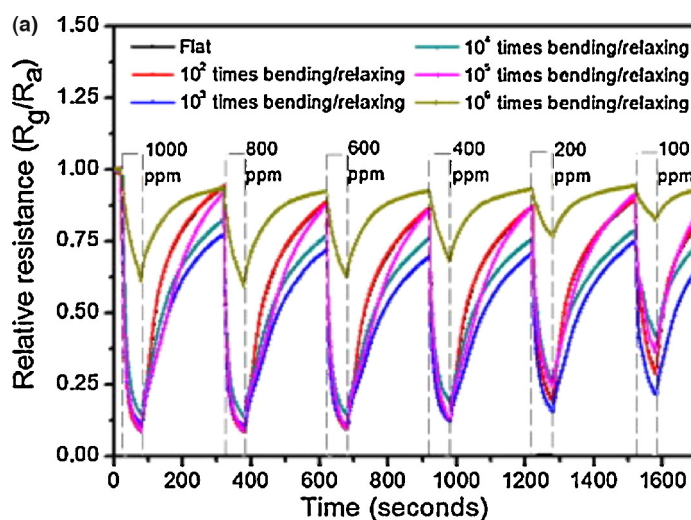
FIGURE 4

(a) The reliability test of the flexible sensor and (b) selectivity of sensors with various gases (15 s Pd sample). Reprinted with permission from Ref [20]. Copyright (2013) by the Elsevier.

FIGURE 3

Performance of the flexible sensor for various bending angles (0°, 20°, 40°, 60°, 90°) for 15 s Pd loading, (a) repeatability at 1000 ppm, and (b) and (c) sensor response at various concentrations. Reprinted with permission from Ref [20]. Copyright (2013) by the Elsevier [20].

prepare zinc oxide nanorods on one or both sides of flexible, reduced graphene sheets (rGss), forming sandwich heterostructures of ZnO/G/ZnO or two-layered heterostructures of ZnO/G. The morphology of the nanostructures was a result of the seed solution concentration. These structures showed field emission and gas-sensing properties but, for these measurements, materials were deposited on rigid transducers. Acetone, formaldehyde, hydrogen sulfide, nitrogen dioxide, ammonia, and hydrogen were tested with maximum concentrations of 50 ppm at a working temperature of 260°C. The combination of zinc oxide nanostructures with graphene resulted in a higher response toward all the species tested, especially to ethanol. Another advantage is the very fast response and recovery time reported (10 s) [21]; however, a way to use these unconventional substrates as sensing transducers to gain a real innovation for chemical sensors is still found wanting.

An interesting use of graphene was presented by Yi et al. [22]. Vertically aligned ZnO oxide nanorods were deposited on a metal foil and graphene was used as the top conductive electrode as reported in Fig. 5. This hybrid architecture was able to accommodate the bending deformation without mechanical or electrical
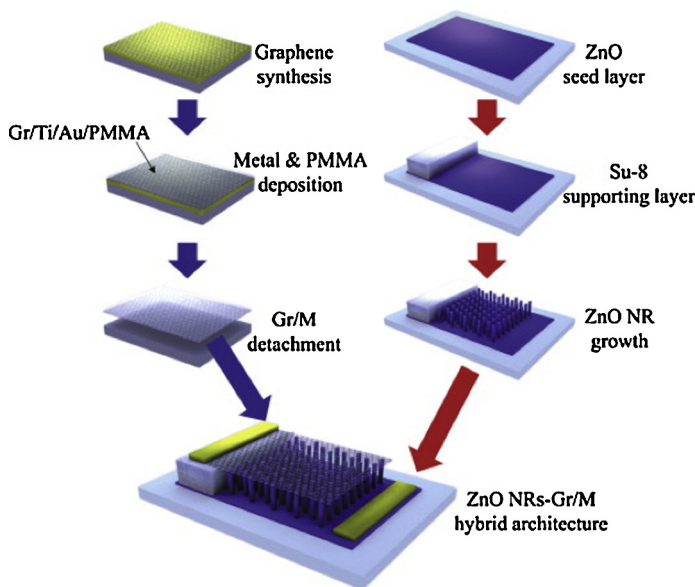
FIGURE 5

Schematic illustration of the key steps for fabricating the ZnO NRs–Gr/M hybrid architectures. Reprinted with permission from Ref [22]. Copyright (2011) by the Elsevier.

failure up to 100 times with bending radius below 0.8 cm. The prepared gas sensor showed a response to ethanol up to 10 ppm at an operating temperature of 300°C.

These works report on the use of hybrid structures to enhance the gas-sensing performances. These complex configurations may add or increase new or existing challenges. The more critical are thermal and electrical stabilities over long-term operation (stability is one of the biggest advantages of using inorganic materials, in particular oxides, instead of organic materials), together with reproducibility, an essential feature for commercial sensing devices in a large-scale production. Therefore, dealing with these hybrid structures, great attention must be paid to measure all these characteristics and not only the individual sensing performances.

Smart textiles

Smart textile is a key tool to monitor health during our entire life, which is currently becoming popular and can be used also for energy harvesting from environment or human body [23–25]. Smart textiles research has been ongoing for the past 20 years and, yet, few commercial products are on the market. Compared to flexible-plastic chemical sensors, smart textile ones have more constraints: they have to resist to the abrasive weaving process and are exposed to environmental contamination, need to sustain repeated bending stress while being gas permeable, resist to washing treatments, work with low power, and have a wearing comfort.

ZnO nanowire arrays were grown on Kevlar fiber and used as ultraviolet sensors with fast response and good repeatability, even when bended [26]. Lim et al. have integrated ZnO nanorods into a multifunctional wearable sensor working at room temperature [27]. A zinc oxide seed layer was deposited by sputtering on the fabric and ZnO nanorods were grown by hydrothermal technique at 90°C. The obtained sensor was tested toward hydrogen and UV exposure; 500 ppm of hydrogen produced a response of 1.4 with response and recovery times in the order of minutes. Furthermore,

the robustness toward stress and washing was investigated. Repeated stretching, twisting, and sonication in water were performed showing a relative small variation in the electrical properties before and after each cycle. This UV and hydrogen sensor on fabric showed promising performances [27]. Moreover, as suggested by the authors, the use of ZnO nanogenerators (proposed by Wang et al. [28]) may be incorporated into the device to achieve a self-powered wearable sensor. The research on metal oxide integration into smart textile is still at the nascent stage, although it seems promising to the author.

Toward zero power sensors

Unfortunately, power consumption is the real problem for the integration of metal oxides into flexible and/or wearable sensors, as these materials normally need to operate at relatively high temperatures (100–500°C). Strategies to reduce the working temperature are necessary to achieve flexible sensors.

Room-temperature sensing

Room-temperature sensing has been proposed for selected gases mainly on rigid substrates. Nitrogen oxide interaction with metal oxides at room temperature is one of the most studied areas. Fan et al. [29] reported the possibility to monitor NO_2 presence at room temperature with ZnO field-effect transistors on silicon. Due to the slow interaction dynamics, the response time was relatively slow, and electro-desorption was used to achieve the complete recovery of the conductance values after the gas interaction applying high voltages to the gate. The electric field-assisted absorption/desorption may increase selectivity and sensitivity even with flexible field-effect transistor chemical sensors. Room-temperature carbon monoxide sensing was achieved also with nanowire/carbon nanotube composite materials, with a response of 1–50 ppm [30].

Recently, non-stoichiometric tungsten oxide has been proposed for room-temperature chemical sensors. Its good performance was attributed to the large amounts of oxygen vacancies that can serve as the adsorption site and facilitate the chemisorption of oxygen at low temperatures. Zhao et al. [31] reported interesting results for room-temperature sensing performances of ammonia of $W_{18}O_{49}$ nanowire networks, even at a sub-ppm level, compared to WO_3 nanowires, which exhibited sensitivity to ammonia only at high temperatures [32].

Possible strategies to lower the working temperature are surface modification, functionalization, doping/addition, fabrication of heterostructures, or illumination with UV light. These options have been recently extensively reviewed by Zhang et al. [33]. However, there are not enough studies to substantiate the reliability of these room-temperature sensors. Moreover, the influence of humidity at room temperature may be detrimental and, in environmental applications, problems due to water condensation on the metal oxide surface may occur. Therefore, the real exploitation of these chemical sensors for real functioning devices is not that close and there are still challenges to face to reach room-temperature sensors commercialisation.

Self-heating

Self-heating is a strategy that may allow good sensing performances on flexible/wearable substrates keeping low substrate temperatures, without the need of a heater in the transducer. This

strategy has been proposed for chemical gas sensor development on rigid substrates [34]. It exploits the peculiarities of a nanowire of being single crystalline with no grain boundaries. Recently, it was proven also with parallel networks of nanowires/nanotubes [35]. Although single nanowire sensors have not yet reached large-scale production, aligned nanowire sensors may be easily integrated into flexible devices using nanocombing [36] or dielectrophoresis [35] techniques. Due to the power dissipated by the Joule effect induced by the bias current applied in conductometric measurements, nanowires heat up to relatively high temperatures and can eventually melt. This self-heating process of nanowires can be used to achieve desired sensor performances without the use of external heaters. The tiny mass of the nanowire allows the achievement of working temperatures in the range of 100–400°C, needed for chemical sensing, with few tens of microwatts for a single nanowire device. The integration of this type of sensor with low power electronics with continuous and pulsed self-heating of nanowires has been demonstrated with power consumption in the microwatt range [37,35]. Additionally, in the case of aligned parallel nanowires, the presence of a large amount of nanowires between the electrodes has two advantages: (1) it reduces the risk of damaging the sensor due to failure/burning of a nanowire and (2) the conductivity range of this multiple nanowire sensors allows much easier and cheaper electronics for its operation. In the case of carbon nanofibers, the self-heating methodology has been proven with a power consumption below 1 mW and without the need for external alignment processes, thus simplifying even more the sensor fabrication [38].

New sensing architectures

New nanoscale effects may allow or suggest new transduction principles for chemical sensors. Using different transduction principles or innovative transducers compared to the conventional ones is always a significant milestone for sensors in general and in particular for chemical ones.

Schottky-contact nanosensors

Recently, Schottky contact-based sensors have been proposed in contrast with the conventional Ohmic contact sensors, since they have promising characteristics, such as enhanced sensitivity and improved response kinetics. Tuning the Schottky barrier height, a response of 4 orders of magnitude higher than the one obtained using an Ohmic-contacted device was achieved in the detection of 400 ppm CO at 275°C [39], due to the chemisorbed surface gases and the amplification role played by the nanowire to Schottky barrier effect. Schottky-contact devices open new approaches to the development of extremely sensitive sensors with fast response time. Sensitivity, response signals, and the recovery time of these sensors depend on the changes of the barrier that, in turn, is modified through the adsorption of gas molecules.

This significant enhancement can be attributed to the tunability of the Schottky barrier height at the metal–semiconductor contact, which can be further increased or decreased by the strain-induced piezoelectric potential.

Piezotronic effect consists in a change in the carrier dynamics at the metal–semiconductor junction interface due to piezoelectric polarization. Piezotronic effect exists in wurtzite/zinc blend materials and it has been proposed to gate the carrier transport properties of the semiconductors [40,41] as well as to control the Schottky barrier height formed at the metal–semiconductor junction [42].

The piezotronic effect [43] has been combined with the Schottky contact to develop a room-temperature sensing device. ZnO micro/nanosensors for the detection of hydrogen and nitrogen dioxide at room temperature have been recently presented [44]. The strain induced by piezoelectric polarization charges is essential to modify the band structure of the contact, introducing a gating effect on the transport through the metal–semiconductor junction. The charge carrier transport across the metal–semiconductor junction is modulated, and this improves the response even at room temperature. Figure 6 shows the scanning electron microscopy (SEM) image of the grown nanowires, the schematic illustration of the experimental setup for this measurement, and the response toward hydrogen and nitrogen dioxide at room temperature. When there is a strain, sensing performances are greatly improved. Moreover, the piezotronic effect may also be used to shift the Schottky barrier height at the contacts to tune the conductivity to its optimal response range. Nevertheless, for this architecture, the realization of real functioning chemical sensor prototype is still challenging and reliability studies are still lacking.

FET chemical sensors

In conductometric sensors, the measured signal is the current flowing among the network or in the single nanowire or nanoparticle layer, with the indissoluble effect of grain boundaries and contacts. The electrical potential change caused by the gas interacting with the oxide surface may be directly used as a transduced signal. Work function readout sensors were introduced more than 20 years ago [45]. After the first pioneering work in 1994, Siemens and Micronas developed a flip-chip variant of the device allowing a precise mounting and using low processing temperatures in this suspended gate FET structure. The advantages include room-temperature operation, possibility of multiple readout channels on a single chip, and possibility to use many types of active materials. Unfortunately, there are no reports on the integration of metal oxide nanowires in this architecture, but studies on work function change of metal oxide nanowires show good results for room-temperature sensing [46], and they suggest possible implementation of nanowires in SGFET sensors.

Moreover, another interesting architecture was presented [47]: a hybrid chemical gas sensor, based on the 'one key to one lock' configuration, which can be used for the selective detection of a specific reducing gas among the complex ambient background. The concept is based on three principles: good electron mobility as well as chemical and thermal stability of metal oxide nanowires; suppression of the nonspecific sensitivity of metal oxides in deep enhancement-mode field-effect transistors (E-mode FETs); and enhancement of selectivity and sensitivity by functionalization with metal nanoparticles. Different sensing elements specific for a single target were integrated into a single platform. Enhancement-mode (E-mode) Mg-doped In_2O_3 nanowire FET arrays with different metal nanoparticles (Au, Ag, and Pt) were operated and tested at room temperature and demonstrated their ability to distinguish among three reducing gases (CO, C_2H_5OH, and H_2) (Fig. 7). Furthermore, sensors also exhibit high sensitivity, low power, and fast response, which are important for practical applications.
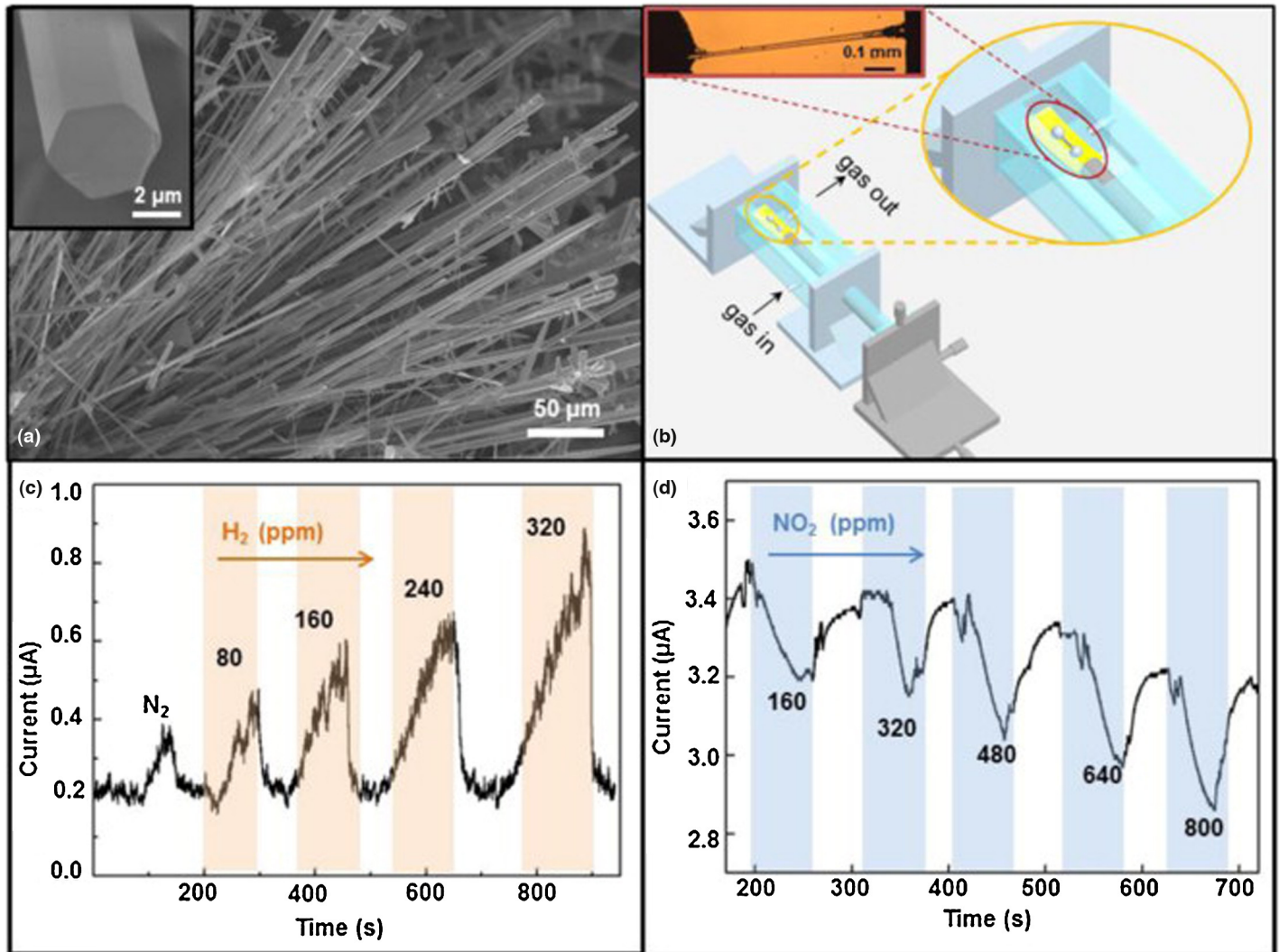
FIGURE 6

(a) Scanning electron microscopy (SEM) images of the as-grown ZnO NWs. (b) Schematic illustration of the experimental setups. Inset: the optical image of an as-fabricated gas sensor device. (c) Current response of a Pd-functionalized H_2 sensor to different hydrogen concentrations. (d) Current response of a NO_2 sensor to different NO_2 concentrations. Reprinted with permission from Ref [44]. Copyright (2015) by the Elsevier.
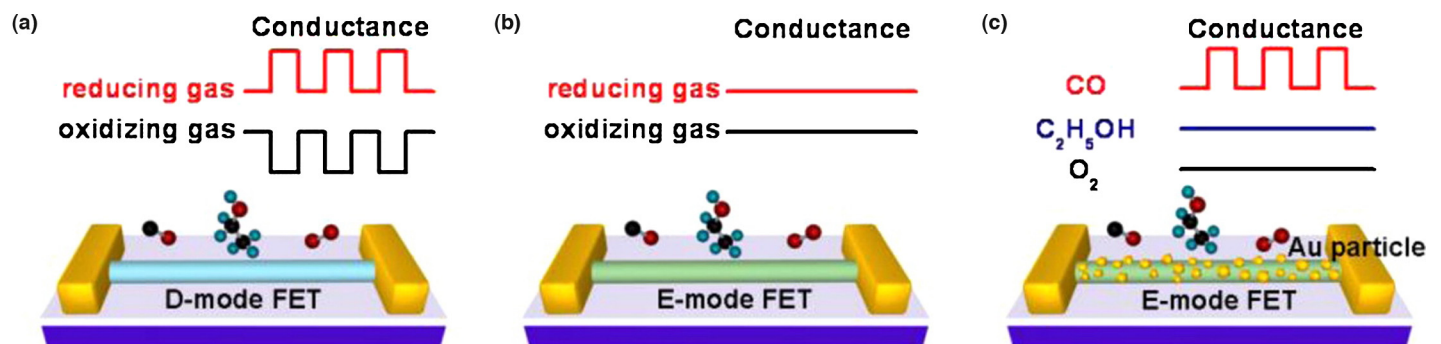

FIGURE 7

Illustration of the design concept 'one lock to one key' sensor configuration. (a) Conventional D-mode FETs for the detection of both reducing and oxidizing gases. (b) Deep E-mode FETs with very large positive threshold voltage yield no response to any target gas. (c) Combing the deep E-mode FETs as a sensing platform, metal nanoparticles are decorated onto the nanowire channel surface to introduce the gas-specific selectivity and sensitivity to the particular target gas to achieve the ideal 'one lock to one key' configuration, exhibiting the unique single target gas-specific response. Reprinted with permission from [47]. Copyright (2013) by the American Chemical Society.

This approach may facilitate the achievement of nanowire-based highly selective and sensitive chemical sensors, but reliability studies are still lacking.

Surface ionization sensors

The surface ionization transduction principle in chemical sensors was presented in 2009 [48] for metal oxide nanowires. It consists in the absorption of chemical species at the metal oxide surface with transfer of electronic charge, when the adsorbed species are extracted and collected by an electrode positioned close to its surface. Surface ionization presents low sensitivity to air consti-tuents and common air contaminants such as N_2, O_2, H_2O, NO, NO_2, and O_3. Moreover, it can be easily combined with conducto-metric sensor transduction readout, thanks to their similar architecture, combining their advantages and intrinsic comple-mentarities to maximize the sensing performances. Results on ZnO nanowires and flat films were compared confirming that the ionization efficiencies are maximized by layers with textured surfaces and surface morphology roughness in the nanometer range allowing detection limits into the ppb concentration range. Recently, on chip fabrication of surface ionization gas sensors was proven [49]. Microelectromechanical systems with integrated hea-ters were designed to measure surface ionization gas signals. The ion emitter was the interdigital electrode on top of the dielectric membranes, while the current readout was a flat-plate counter electrode, positioned at a short distance above the oxide layer. The responses were orders of magnitude higher compared to the ones reported for thin film and similar to the ones of parallel nanowire devices due to the sharp edges of the photolithographic interdi-gital geometry. This device may be produced on a large scale, even if there are still technological challenges to overcome, such as the positioning of the top electrode.

Magnetic gas sensors

Another completely new transduction principle is the exploitation of magnetic instead of electrical properties modifications due to surface–gas interaction in the active material. Metal oxides cover all the different aspects of materials properties, from insulator to superconductors, and also magnetic properties. Some of these magnetic oxides have already been studied for conventional chemical sensing [50–52]; however, just few studies report the change in magnetic properties due to the gas–surface interaction [53]. Nevertheless, because the variation of magnetic properties is more pronounced at lower temperatures compared to conducto-metric variations, magnetic transduction may have several advan-tages for the development of chemical sensors. The scarce literature data on these effects can be ascribed to the difficulties of combining magnetic and gas-sensing technologies in cost-ef-fective ways to measure the weak variations induced in the mag-netic properties. Recently, Matatagui et al. [54] reported the combination of a magnetostatic surface wave oscillator with a layer of magnetic oxide nanoparticles in what they called a *mag-nonic gas sensor*. The perturbation of the magnetic properties of the magnetic oxide layer induces a frequency shift in the magneto-static surface wave oscillator that can be registered in the presence of different gases. Relatively low concentrations of different VOCs were detected with low response time and good reproducibility, paving the way for a completely new ground for research and

experimentations. The use of magnetic properties in chemical sensors is at an early stage and that is the reason it is so promising and challenging. Nevertheless, the combination of magnetic and conductometric transduction seems a synergic way to increase the sensing performances also in terms of selectivity.

Challenges

Nanowire sensors are not yet commercially available for chemical sensor applications, to the best of the author's knowledge. This can be ascribed to several challenging issues that are yet to be completely understood and investigated. The remarkable perfor-mance obtained with nanowire devices is normally obtained on single prototypes and optimized using a trial-and-error approach. Reproducibility, reliability, and stability of sensing devices have been hardly investigated, with the influence on the performances of electrical contacts and their design being rarely studied. Selec-tivity is another critically important issue for the commercializa-tion that is normally not fully addressed. Researchers normally focus their effort on increasing sensitivity and decreasing response kinetics or detection limits. Despite the research efforts in chemi-cal sensors, in the last years several issues still remain unresolved and some of them are far from being resolved. For example, selectivity is intrinsically limited by the working principle of conductometric chemical sensors, so, in order to fulfill specific requirements, alternative sensing mechanisms must be explored or data post processing must be extensively used. Moreover, even if sensitivity may be greatly improved, researchers must keep in mind that when we are dealing with complex or hybrid structures, stability may be reduced. It is important to study sensors as a whole, not just the sensing material.

Conclusions and perspectives

Nanotechnology still holds the promise to increase efficiency of industries in bringing profoundly new applications, but to achieve this specific goal, synergic and coordinated investigations involv-ing researchers from different disciplines, such as material science, engineering, physics, and chemistry (as well as even market devel-opers) are necessary.

Chemical sensor technology is an indispensable tool to create new lifestyles that are compatible with a sustainable society. To boost further advancement, it is crucial to cover all the aspects of the analysis, prior to a possible commercialization. The study of the sensing system in its entirety (not just the active material functional properties) has pivotal importance and it is still chal-lenging, similar to carrying out 'real' tests as close as possible to field tests to confirm the feasibility and clearly demonstrate the potentiality of chemical sensors, and the synergic combination of functional and fundamental characterizations using 'operando' studies [55].

Nanoscale materials and fabrication technologies allow new sensing architectures possibilities that can also improve the fun-damental understanding of the chemical sensing mechanism. In the last years, many advances have been made: scientific discov-eries have produced technological innovations such as flexible and wearable sensors, room-temperature sensors, and new sensing mechanisms or architectures (work function, surface ionization, magnetic, self heating, and Schottky-based devices). These inno-vations would have an impact also on new relevant areas such

as food and agriculture, welfare and nanomedicine, producing significant changes in our lifestyle. Nanotechnology expectations may be overestimated for a short term, but in the long term there will be great implications on healthcare, productivity, and environment. Metal oxide in particular is still the most promising class of sensing materials in the author's opinion, thanks to easy fabrication methods and chemical stability. Metal oxides were the first to be commercialized in the form of thick films for conductometric chemical sensors and they will be part of the future in chemical sensors in different forms.

Finally yet importantly, real progress and advancement largely depend on the challenging spirit of every successful researcher that leads to new ideas and innovations improving the overall quality of life.

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References

[1] G. Heiland, et al. Zeit. Phys. 138 (1954) 459.
[2] A. Bielanski, et al. Nature 179 (1957) 668.
[3] T. Seiyama, et al. Anal. Chem. 34 (1962) 1502.
[4] N. Taguchi, U.S. Patent 3,631,436 (1971).
[5] X. Liu, et al. ACS Nano 6 (2012) 1888, http://dx.doi.org/10.1021/nn204848r.
[6] M. Liu, et al. Nano–Micro Lett. 4 (2012) 142.
[7] M.C. McAlpine, et al. Nat. Mater. 6 (2007) 379, http://dx.doi.org/10.1038/nmat1891.
[8] Z. Fan, et al. Adv. Mater. 21 (2009) 3730, http://dx.doi.org/10.1002/adma.200900860.
[9] J. Park, et al. Nanotechnology 19 (2008) 395303, http://dx.doi.org/10.1088/0957-4484/19/39/395303.
[10] S. Raychaudhuri, et al. Nano Lett. 9 (2009) 2260, http://dx.doi.org/10.1021/nl900423g.
[11] J. Courbat, et al. Proc. Chem. 1 (2009) 597, http://dx.doi.org/10.1016/j.proche.2009.07.149.
[12] A. Oprea, et al. Sens. Actuators B: Chem. 171-172 (2012) 190, http://dx.doi.org/10.1016/j.snb.2012.02.095.
[13] T. Kinkeldei, et al. Sens. Actuators B 174 (2012) 81.
[14] H. Ahn, et al. Electrochem. Solid-State Lett. 13 (2010) J125, http://dx.doi.org/10.1149/1.3479692.
[15] M. Tonezzer, et al. Physica E 44 (2012) 1098, http://dx.doi.org/10.1016/j.physe.2010.11.029.
[16] M.A. Lim, et al. ACS Nano 6 (2011) 598, http://dx.doi.org/10.1021/nn204009m.
[17] Y. Sun, et al. Appl. Phys. Lett. 90 (2007) 213107.
[18] Y. Sun, et al. Adv. Mater. 19 (2007) 2818.
[19] Y. Sun, et al. J. Phys. Chem. C 112 (2008) 1250, http://dx.doi.org/10.1021/jp076965n.
[20] T.-R. Rashid, et al. Sens. Actuators B: Chem. 185 (2013) 777, http://dx.doi.org/10.1016/j.snb.2013.01.015].
[21] R. Zou, et al. J. Mater. Chem. A 1 (2013) 8445, http://dx.doi.org/10.1039/c3ta11490b.
[22] J. Yi, J.M. Lee, W.I. Park, Sens. Actuators B: Chem. 155 (2011) 264, http://dx.doi.org/10.1016/j.snb.2010.12.033.
[23] Y. Qin, et al. Nature 451 (2008), http://dx.doi.org/10.1038/nmat1891, U809–U805.
[24] W.X. Guo, et al. J. Am. Chem. Soc. 134 (2012) 4437, http://dx.doi.org/10.1021/ja2120585.
[25] M. Stoppa, et al. Sensors 14 (2014) 11957, http://dx.doi.org/10.3390/s140711957.
[26] J.M. Liu, et al. ACS Appl. Mater. Interfaces 3 (2011) 4197, http://dx.doi.org/10.1021/am200797f.
[27] Z.H. Lim, et al. Sens. Actuators B: Chem. 151 (2010) 121, http://dx.doi.org/10.1016/j.snb.2010.09.037.
[28] Y. Qin, et al. Nature 451 (2008) 809, http://dx.doi.org/10.1038/nature06601.
[29] Z. Fan, et al. Appl. Phys. Lett. 86 (2005) 123510.
[30] A. Yang, et al. Appl. Phys. Lett. 91 (2007) 133110, http://dx.doi.org/10.1063/1.2783479.
[31] Y. Zhao, et al. Sens. Actuators B 137 (2009) 27.
[32] G. Neri, et al. Sens. Lett. 6 (2008) 590.
[33] J. Zhang, et al. Adv. Mater. (2015), http://dx.doi.org/10.1002/adma.201503825.
[34] J.D. Prades, et al. Sens. Actuators B: Chem. 144 (2010) 1, http://dx.doi.org/10.1016/j.snb.2009.09.040.
[35] J. Guilera, et al. Sens. Actuators B: Chem. 221 (2015) 104.
[36] J.Y.H. Yao, et al. Nat. Nanotechnol. 8 (2013) 329, http://dx.doi.org/10.1038/nnano.2013.55.
[37] J.D. Prades, et al. Appl. Phys. Lett. 93 (12) (2008) 123110–123113.
[38] O. Monereo, et al. Sens. Actuators B: Chem. 211 (2015) 489.
[39] Z.L. Wang, Abs. Pap. Am. Chem. Soc. 235 (2008).
[40] L. Chen, et al. Nano Energy (2014), http://dx.doi.org/10.1016/j.nanoen.2014.11.039.
[41] G. Bai, et al. Adv. Opt. Mater. (2014), http://dx.doi.org/10.1002/adom.201400375.
[42] P.H. Yeh, et al. Adv. Mater. 21 (2009) 4975.
[43] Z.L. Wang, Nano Today 5 (2010) 540.
[44] R. Zhou, et al. Nano Energy 12 (2015) 588.
[45] B. Flietner, et al. Sens. Actuators B 22 (1994) 109–113.
[46] N.S. Ramgir, et al. Sens. Actuators B: Chem. 186 (2013) 718.
[47] X. Zou, Nano Lett. 13 (2013) 3287.
[48] A. Hackner, et al. IEEE Sens. J. 9 (2009) 1727.
[49] B. Bouxin, Sens. Actuators B: Chem. 182 (2013) 25.
[50] E.R. Kumar, et al. Sens. Actuators B 191 (2014) 186.
[51] N. Rezlescu, et al. Sens. Actuators B 114 (2006) 427.
[52] S. Wang, et al. RSC Adv. 4 (2014) 57967–57974.
[53] P. Alex, et al. Nanotechnology 18 (2007) 165502.
[54] D. Matatagui, et al. Nanoscale 7 (2015) 9607, http://dx.doi.org/10.1039/C5NR01499A.
[55] N. Barsan, et al. Sens. Actuators B 121 (2007) 18.