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NANOSENSORS BASED ON INDIVIDUAL HYBRID STRUCTURES AND THEIR APPLICATION IN GAS SENSING AT ROOM TEMPERATURE

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Abstract. Because the commercialization of nanosensors in the field of gas sensing is still in its infancy, many efforts have been made to develop efficient methods to increase their performances. A special attention was paid to the increase of the sensitivity and selectivity of the gas nanosensors based on individual micro - or nanostructures using different strategies. In this work, the recent results in the field of high-performance gas nanosensors obtained by the research group from Centre for Nanotechnology and Nanosensors, Technical University of Moldova in collaboration with Kiel University, Germany are highlighted and summarized. The quasi-uni-dimensional (1-D) and three-dimensional (3-D) individual hybrid structures based on zinc oxide were integrated into nanodevices using a focused ion beam/scanning electron microsc opy (FIB/SEM) instrument. The hybridization of the individual ZnO structures is shown to result in a considerable increase in gas response, as well as a change in selectivity to volatile organic compounds and ammonia. Particularly, an increase in hydrogen gas response (by about 2 times) was obtained by surface functionalization with $ZnAl_2O_4$ nanoparticles, while a change in selectivity to ethanol vapors and ammonia was obtained by surface functionalization with Fe_2O_3 nanoparticles or buckminster fullerenes (C_{60}) and carbon nanotubes (CNTs), respectively. The obtained results provide new avenues for the rational engineering of gas nanosensors by the use of hybrid nanomaterial systems with enhanced synergistic catalytic behavior and potential barrier manipulation.

Keywords: *hybrid materials, nanosensors, gas sensor, ZnO, room temperature.*

Introduction

The rapid progress of nanotechnologies by integration of bottom-up approaches has enabled a true revolution in the fabrication of high-performance devices based on individual structures of *n*-type and *p*-type metal oxides, such as ZnO, SnO_2, MoO_3, CuO, Fe_2O_3, TiO_2, etc. [1-7]. The opportunity of bottom-up approach compared to top-down ones is the possibility to fabricate complex devices based on individual 3-D structures such as ZnO tetrapods [8, 9]. For example, Sun *et al.* [10] designed a novel logic switch based on individual ZnO nanotetrapods, where the logic states depend on the direction of built-in potential induced by piezoelectricity and the source−drain current direction. Wang *et al.* [11] fabricated a force sensor with a sensitivity of 2.05 A/N based on an individual ZnO tetrapod using piezo-phototronic effect. In the field of gas sensing, the H_2 gas sensor was fabricated by Lupan *et al.* based on individual ZnO tetrapod [9], able to detect a concentration of H_2 gas down to 100 ppm at room temperature (RT). The excellent RT gas sensing properties of individual metal oxide structures are widely explained based on their high surface-to-volume ratio, which allows very sensitive transduction of the gas/surface interactions (adsorption or catalytic oxidation) into a change of the electrical conductivity [12]. Also, due to the diameter in nanometer range (radius is comparable with Debye length), the structures are practically fully depleted after surface redox processes, which makes such devices highly sensitive to surface reactions [12].

However, the pristine metal oxide micro- and nanostructures are known to have low selectivity to specific gases due to cross-sensitivity to other gases, as well as low stability in humid atmosphere [13]. Therefore, many methods have been elaborated for improvement/change in selectivity of metal oxides, including: (i) doping with transition metals, noble metals, rare earth metals, etc.; (ii) surface functionalization with different materials including noble metals (nanoparticles or thin layer), other metal oxides (*n*- or *p*-type), carbon based nanomaterials (nanotubes, graphene sheets, nanofibres, etc.), polymers, etc.; (iii) formation of composites/hybrid materials under different configurations such as compounds by simple mixing, core-shell, bi-layer or multi-layer structures; (iv) use of crystals with different sizes and morphologies in order to control the gas sensing activity as a result of different crystal planes; (v) use of molecular sieve membranes such as zeolites, polymers and metal-organic frameworks, etc. [1, 13-17]. The enumerated strategies are presented in form of diagram in Figure 1.

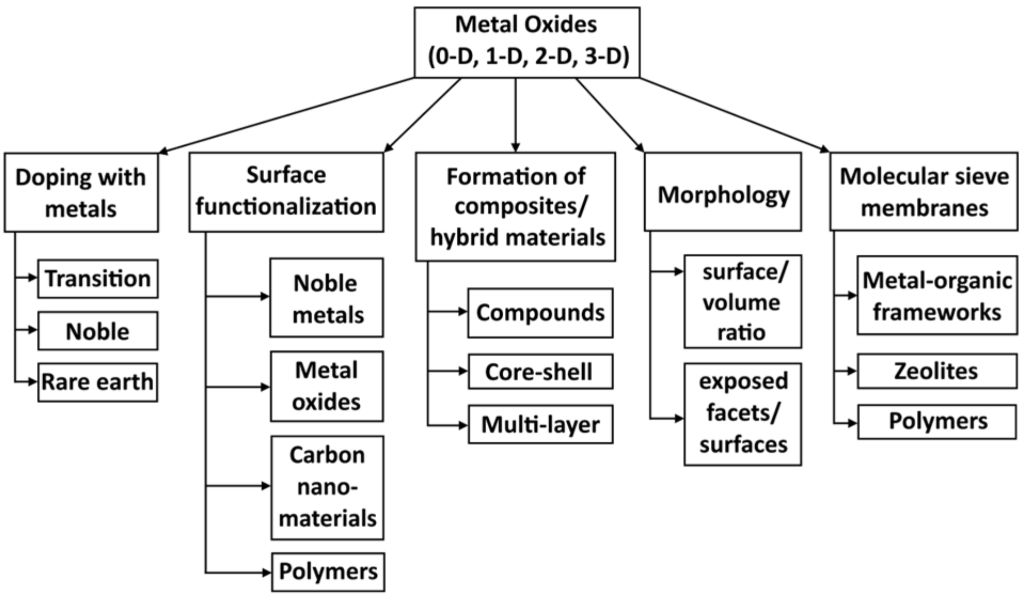

Figure 1. Summary in form of diagram of the elaborated methods for improvement/change in selectivity of metal oxides-based gas sensors.

Combination of different inorganic components could result in improved properties or performances [18]. Inorganic compounds, such as metal oxides have high chemical and thermal stability that allows their application under different operating conditions [18]. Moreover, they can be synthesized by different techniques in a large variety of morphologies, such as 0-D (nanodots), 1-D (nanowires, nanofibres, nanobelts, etc.), 2-D (nanosheets, multilayer structures, etc.) and 3-D (tetrapods, hierarchical structures, etc.) [18]. Therefore, hybrid materials have recently gained extensive interest in many fields and are promising candidates for use in selective gas sensing applications due to the combination of different mechanisms responsible for highly selective, fast and sensitive detection of gases, such as enhanced synergistic behavior, spill-over effect, potential barrier manipulations, etc. [17, 18]. However, there are only few reports in the literature on gas sensors based on individual hybrid micro- and nanostructures [19, 20], which serves as an additional motivation for research in this field.

Herein, the recent results in the field of high-performance gas nanosensors obtained by the research group from Centre for Nanotechnology and Nanosensors, Technical University of Moldova in collaboration with Kiel University, Germany are highlighted and summarized.

Hybrid structures based on semiconductor oxides

As it was discussed, the formation of hybrid material systems is an efficient method for the improvement of the sensing performances of gas sensors. With respect to metal oxides, as the principal component, different combinations with other materials can be used such as: (i) metals, (ii) other metal oxides and (iii) organic materials [17], etc.

In the case of combination with other metal oxides there is a high degree of freedom to modify the material properties. A complex summary on the given topic was made in a review paper by Miller and co-authors, which was recently published [17].

Because semiconductor oxides are of *p*- or *n*-type electrical conductivity, these materials can be combined in one of the following ways: (i) $n-n$; (ii) $n-p$ and (iii) $p-p$. Another classification can be obtained according to the type of formed structure (see Figure 2): (i) a simple mix between nanostructures (composite materials), which are noted using "−" (for example: SnO_2 − ZnO); (ii) core-shell structures, which are noted using "@" (for example: SnO_2@CuO); (iii) heterostructures with well-defined interface (multi-layer structures), which are noted using"/" (for example: CuO/ZnO); and (iv) combinations of the first three types of structures [17].

As a result, all the possibilities for improving the performance of the sensors can be summarized in a diagram like the one performed by Miller and the co-authors [17].

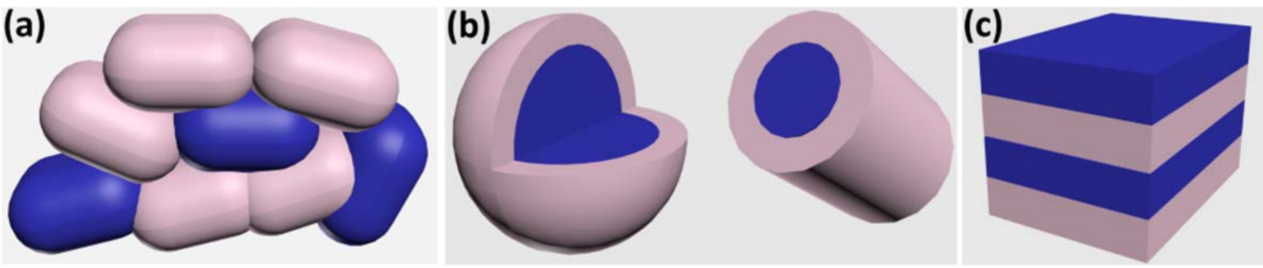

Figure 2. Schematic illustration of hybrid structures based on two different semiconductor oxides, highlighted by two different colors: (a) composite materials; (b) core-shell structures; (c) multilayer structures.

So, if to lead by the first principle (the combination by the type of electrical conductivity), it will be possible to control the depleted region of electrons, depending on the type of conductivity and the material output. In the case of the *n-p* type combination, a depletion region will be formed in the middle regardless of the type of materials [14, 16]. In the case of *n - n* or *p - p*, the depletion region may be enlarged or narrowed, depending on the work functions of the materials [14, 16, 17]. Choi *et al.* demonstrated the possibility to extend or narrow the hole accumulation layer in copper oxide nanowires by surface functionalization with Co_3O_4 (with lower work function of 4.5 eV) or NiO (with higher work function of 5.4 eV), respectively [21]. As a result, based on the functionalization with Co_3O_4 sensors that are more sensitive to oxidizing gases and less sensitive to reducing gases can be manufactured. A complementary situation is in the case of functionalization with NiO [21].

Another important issue are the catalytic properties of the added metal oxides which can lead to different synergistic effects, such as preferential absorptivity or different chemical reaction pathways [1, 17, 18, 22]. A clear definition of materials with synergistic effects was not reported, but it is widely explained as "… a material with properties superior to the sum of the properties of its components; a synergic material" [22, 23]. The major processes that affect the synergistic relationship between surface activity and conduction mechanisms of hybrid materials are adsorption/desorption reactions, geometric effect and the already mentioned modulation of the depletion region [22].

An interesting study about the catalytic properties of composite materials was performed by Jinkawa *et al.* [24]. In this study, SnO_2 was used as the backbone material and five different metal oxides (Cs_2O, La_2O_3, Sm_2O_3, MnO_2 and WO_3) were chosen as additives, covering a wide electronegativity range of metal cations. It was demonstrated that the addition of the basic metal oxides to SnO_2, such as La_2O_3, lead to the enhancement of catalytic activity not only for the dehydrogenation of ethanol gas to CH_3CHO but also for the consecutive oxidation of CH_3CHO to CO_2 [24]. Additionally, it was demonstrated that the addition of an acidic metal oxide, such as WO_3, enhanced only the dehydration reaction, showing even an adverse effect on the consecutive oxidation [24]. The results clearly demonstrate that the formation of hybrid composite structures is an highly efficient method to tune the catalytic properties of the formed composites and thus to control the gas sensing properties of metal oxides.

Individual 3-D hybrid microstructures – In search of high-performance room temperature gas sensors

In our studies, the nanodevices based on individual structures were fabricated using the method elaborated by Lupan *et al.* [2, 4 - 6, 9], which is based on the Focused Ion Beam/Scanning Electron Microscopy (FIB/SEM) techniques and the localized maskless deposition of metal or even insulator materials. This approach works similar to local chemical vapor deposition (LCVD) and the occurring reactions are comparable to, e.g., laser induced chemical vapor deposition (CVD) and micro stereolithography [2]. A schematic representation of the nanodevices fabrication is presented in Figure 3. For all devices a specially designed chip based on a SiO_2-coated Si substrate with deposited Au pads was used [4]. The chip configuration allows for the connection of 8 different individual structures between the Au pads by Pd deposition in FIB/SEM system (see Figure 3b-d). More information on the designed chip can be found in one of our previous work [4].

The release of the individual micro- and nanostructures from the initial substrate (for example nanowires from an array grown on different substrates or tetrapods from free-standing networks) is realized by sonication in ethanol followed by transfer to a SiO_2-coated Si substrate [6]. Using this method the following individual structures were successfully integrated into nanodevices: individual ZnO nanorods synthesized using an aqueous-based approach in a reactor for room temperature H_2 gas detection [2]; very thin CuO nanowires (10–100 nm in diameter) synthesized by thermal oxidation approach for highly sensitive room temperature ethanol vapors detection [6]; MoO_3 nanobelts for ethanol and methanol vapor detection [4]; very thin Fe_2O_3 nanowires (10 – 50 nm) synthesized by thermal oxidation for acetone vapor detection.

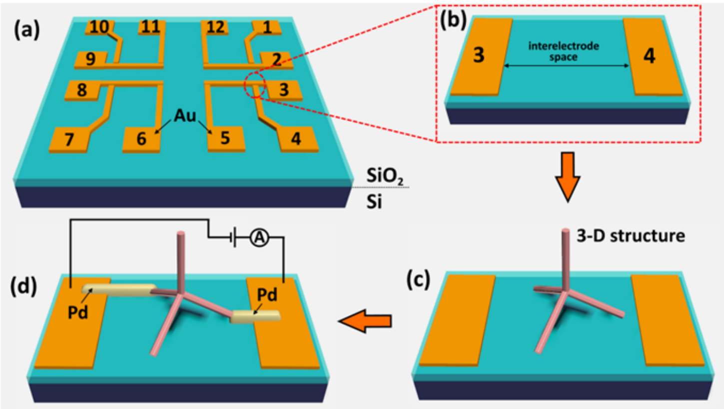

Figure 3. The schematic of nanodevices fabrication steps: (a) schematic illustration of the chip based on SiO_2-coated Si substrate with deposited Au pads for electrical connection, noted from 1 to 12; (b) zoomed view of the interelectrode space from (a); (c) deposition of individual 3-D structure for further interconnection to Au pads by deposition of Pd using FIB/SEM (d).

Moreover, it was demonstrated that the described method is suitable for successful integration of individual hybrid structures such as: Fe_2O_3 nanoparticle functionalized ZnO tetrapods (Fe_2O_3/ZnO) [25]; $ZnAl_2O_4$ nanoparticle functionalized ZnO microwires and tetrapods ($ZnAl_2O_4$/ZnO) [26]; Zn_2SnO_4 functionalized SnO_2 nanowires (Zn_2SnO_4/ZnO) [3]; carbon nanotubes (CNT)-functionalized ZnO tetrapods (CNT/ZnO) [27] as well as buckminsterfullerene (C_{60}) hybridized zinc oxide tetrapods [28]. Figure 4 shows the schematic diagram of gas sensors fabricated on individual 3-D hybrid structures based on ZnO for room temperature detection of different gases and vapors, which will be reviewed in this work. The experimental results show that the nanoparticles (Fe_2O_3, $ZnAl_2O_4$), CNT or C_{60} are firmly attached on the surface of the integrated individual structures after transfer on the SiO_2-coated Si substrate.

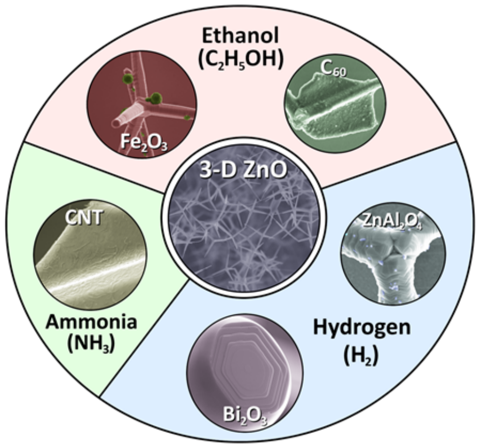

Figure 4. Schematic diagram of gas sensors fabricated on individual 3-D hybrid structures based on ZnO for room temperature detection of different gases and vapors.

The detection of ethanol in our daily life plays an important role for safety, as well as is a key element in breath alcohol analyzers for drivers, etc. [25, 29]. Ethanol is produced via alcoholic fermentation of glucose by gut bacteria and yeast and the acetone derives from oxidations of free fatty acids, influenced by glucose metabolism [30]. Furthermore, the detection of ethanol in human breath can be a good approximation of blood glucose profile during a glucose load [30]. Thus, it is very important to develop reliable, high performance and low-cost ethanol vapor detectors with high immunity to water vapor, which are presents in the breath. In our case highly selective ethanol vapor sensors were elaborated based on individual Fe_2O_3/ZnO and C_{60}/ZnO hybrid structures (see Figure 4). Fe_2O_3 was chosen due to its high stability under ambient conditions, high catalytic activity in the dehydrogenation reaction and its ring-opening reaction of hydrocarbon. Therefore, it can induce the higher selectivity to ethanol vapor of the ZnO microstructures. Alternatively, C_{60} can be utilized for such applications. C_{60} mainly exhibits *n*-type electrical conductivity and shows good response to volatile organic compounds (VOCs).

The Fe_2O_3-ZnO hybrid structures with high porosity were obtained by mixing in different weight ratios ZnO tetrapods (synthesized by a simple flame transport (FTS) approach) with Fe microparticles, followed by subsequent thermal annealing in air in a furnace at 1150 °C for 5 h [29]. The size of the synthesized tetrapods is in the range of 10 – 100 μm, while the diameter of the randomly distributed Fe_2O_3 nano- and microparticles on the surface is 0.1 – 5 μm [29]. The individual Fe_2O_3/ZnO hybrid structures (see Figure 5a), integrated into devices, showed excellent selectivity to ethanol vapor at room temperature [25]. Compared to individual ZnO tetrapod, the functionalized one showed an exceptional improvement in performance, i.e. improvement in UV response by about 80 times (on/off ratio of ~ 1400 to UV light with 15–20 mW/cm^2 and λ = 365 nm) and improvement in ethanol vapors response by about ~ 6 times (sensitivity of ~ 1%/ppm). The calculated sensitivity to all tested gases of the device is presented in Figure 5b, showing an excellent selectivity to ethanol vapor. The Buckminster fullerene (C60) based hybrid metal oxide materials (see Figure 5c) were synthesized using the same ZnO-T networks by drop-casting of water-based fullerene dispersions [28]. The gas sensing measurements of individual C_{60}/ZnO hybrid structures showed that a higher content of C_{60} on the surface of ZnO microstructures leads to an increase in ethanol response (~ 0.32%/ppm) at room temperature. The main mechanism of increased selectivity was explained on the basis of the interaction of VOCs with oxygen from the C_{60} layer, as well as charge transfer between C_{60} and gas molecules by weak ionic bonds at room temperature [28]. The calculated sensitivity to all tested gases of the device is presented in Figure 5d.

The improvement in H_2 gas response of individual ZnO structures was achieved by the formation of Bi_2O_3@ZnO shell-core structures and by surface functionalization with $ZnAl_2O_4$ nanoparticles [26, 31]. The monitoring/detection of H_2 gas is very important for semiconductor manufacturing processes, where it is used as reducing agent and carrier gas [32]. Also, the H_2 is an excellent source of clean energy [32]. Therefore, it's a crucial necessity for fast detection of H_2 gas leakage by gas sensors. Because H_2 gas is extremely flammable when mixed (even in small amounts) with ordinary air, it is very important to use the gas sensors operable at room temperature, which was the main goal of our investigations in the case of selective hydrogen gas sensors. The Bi_2O_3@ZnO hybrid structures were obtained by the same method as the Fe_2O_3-ZnO hybrid structures, i.e. using the FTS approach for synthesis of ZnO and by further mixing with Bi microparticles [31].

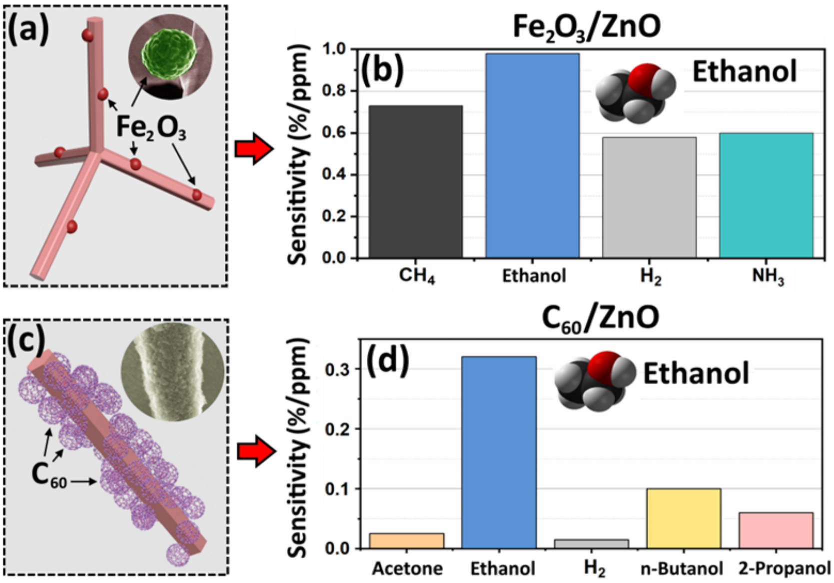

Figure 5. The schematic of hybrid structure and the room temperature sensitivity of individual hybrid structures to different gases: (a,b) Fe_2O_3/ZnO; (c,d) C_{60}/ZnO.

Bi_2O_3 is an important *p*-type semiconductor with four main crystallographic polymorphs denoted by α-, β-, γ -, and δ-Bi_2O_3 and regarding their unique optical and electrical properties they have not been investigated extensively as gas sensor materials, being additional motivation for our research [33]. The gas sensing measurements of individual Bi_2O_3@ZnO hybrid structures demonstrated excellent H_2 gas sensing properties, namely high sensitivity of ~ 70%/ppm at room temperature [31]. The selectivity compared to other gases was also tested, showing a negligible gas response (<1.5) to CH_4, ethanol and acetone. In order to check the influence of water vapor on the gas response, the measurements were performed at higher relative humidity of ~ 70%, showing a decrease in response by about 25% [31]. The lowest detection limit was found to be ~ 1 ppm.

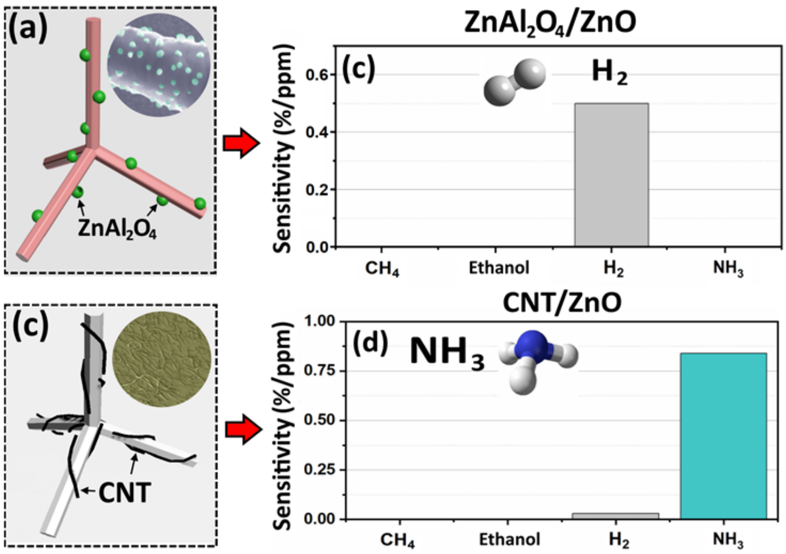

Figure 6. The schematic of hybrid structure and the room temperature sensitivity of individual hybrid structures to different gases: (a,b) $ZnAl_2O_4$/ZnO; (c,d) CNT/ZnO structure.

The formation reactions of oxide spinel compounds AB_2O_4-based on Zn are easily accessible by the calcination of ZnO [26, 29]. Due to its peculiar arrangement of its cations in the spinel structure, this can lead to a better mobility of the charge carriers. Therefore,

$ZnAl_2O_4$ structures hold great promise for a wide range of applications, including gas sensing [26, 29]. In our studies, the $ZnAl_2O_4$-ZnO hybrid networks were obtained using the method, described for Fe_2O_3-ZnO and Bi_2O_3-ZnO networks. In this case the ZnO networks were mixed with Al microparticles [29]. However, the SEM images showed the formation of randomly distributed microparticles with a rough surface which can form agglomerates with a diameter up to 10 μm, being comparable with arm diameter of ZnO tetrapods. Therefore, the successful integration of individual $ZnAl_2O_4$/ZnO hybrid structures was difficult to obtain. In order to avoid this issue, a simple method for the growth of small and homogenously distributed $ZnAl_2O_4$ crystals with a diameter of 50−100 nm on the surface of ZnO nano- and micro-structures using aluminum acetate basic hydrate was elaborated [26]. Based on the individual $ZnAl_2O_4$/ZnO microstructures (see Figure 6a) with different morphologies (microwires and microtetrapods) gas sensing devices were fabricated. The gas sensing measurements demonstrated that the functionalized structures showed higher gas response compared to the structures synthesized using FTS approach followed by further mixing with Al microparticles (ZnO:Al). For example, a $ZnAl_2O_4$/ZnO microwire with a diameter of ~ 400 nm and a $ZnAl_2O_4$/ZnO tetrapodal structures with a leg diameter of ~ 400 nm showed a H_2 gas sensitivity of ~ 0.19 %/ppm and ~ 0.5 %/ppm, respectively, at room temperature, compared to ~ 0.01 %/ppm obtained by employing a ZnO:Al microwire [26]. These results demonstrate the high efficiency of surface functionalization of individual ZnO microstructures for improvement of gas sensing properties. The room temperature sensitivities of $ZnAl_2O_4$/ZnO tetrapodal structure to H_2 gas and other tested gases are presented in Figure 6b, showing the high selectivity to H_2 gas, which was observed for all tested individual structures [26]. The improved H_2 gas sensing properties of functionalized samples were explained based on the good catalytic properties of $ZnAl_2O_4$, which can be also employed for synthesis, dehydrogenation, hydrogenation, dehydration, isomerization and combustion processes [26]. Another explanation was based on the higher oxygen coverage on the ZnO microstructure surface in air, especially in the areas around the $ZnAl_2O_4$ nanocrystals due to the specific structure of energy band diagram of $ZnAl_2O_4$/ZnO interface. Consequently, an electron flow from $ZnAl_2O_4$ nanocrystals to ZnO microstructures was induced, thus enhancing surface reactions of the gas absorption when the sensor was exposed to H_2 gas, i.e. to a higher gas response [1, 26, 29].

Another study was concentrated on the possibility to combine excellent room temperature gas sensing properties of carbon nanotubes, being ideal building nanoblocks for the construction of hybrid structures, and high sensitivity of ZnO tetrapodal networks [27]. Some reports demonstrated the excellent selectivity of carbon based nanomaterials to ammonia vapors at room temperature [27]. Therefore, the main idea of surface coating of ZnO tetrapodal structures with carbon nanotubes CNTs was to induce the high selectivity of individual ZnO microstructures to ammonia vapors at room temperature. The CNT-ZnO hybrid networks were obtained by the CNT (CarboByk 9810) infiltration of the ZnO templates, synthesized using a FTS approach [27]. The five devices based on individual CNT/ZnO microstructures (see Figure 6c) with different diameters and lengths of the arms were fabricated using the CNT-ZnO hybrid networks with 2.0 wt% of CNT. The individual structure with the smallest arm diameter (0.35 μm) demonstrated the highest sensitivity to ammonia vapors of ~ 0.8 %/ppm at room temperature. Figure 6d shows the sensitivity and to other gases, demonstrated the high selectivity to ammonia vapors. Because the gas-sensing mechanism of single tetrapod structures is mainly based on the modulation of conduction channels by surface reactions, the higher sensitivity of smaller microstructures can be explained by higher influence of surface reactions on the electron depletion region of ZnO [27, 34 - 38]:

$$\frac{I_{gas}}{I_{air}} \approx \left(\frac{D}{D - 2\Delta W} \right)^2 \qquad (1)$$

where *D* is the diameter of the tetrapod arm and ΔW is the change in the electron depletion region at the ZnO surface. The induced selectivity to ammonia vapors was explained based on efficient NH_3 molecules adsorption on the surface of CNT at room temperature with further electrons transfer to the underlying ZnO microstructure integrated in sensor, leading to a widening of the conduction channel [27, 34, 35, 38, 39]. All these results are summarized new fabrication strategy can underpin the future generation of advanced micro- and nano-materials for gas sensing applications and prevent gas levels that are hazardous to human health and could cause environmental damage too.

Conclusions

Based on the experimental data obtained and reported by Centre for Nanotechnology and Nanosensors, Technical University of Moldova, Republic of Moldova in collaboration with Functional Nanomaterials, Kiel University, Germany the following conclusions can be highlighted: (i) surface functionalization of individual ZnO microstructures with Fe_2O_3 nanoparticles with diameter of about 0.1 – 5 μm can lead to increase in room temperature gas response (by about one order in magnitude compared to ZnO:Fe) to ethanol vapors, as well as induce the high selectivity due to increased catalytic activity for dehydrogenation of ethanol molecules; (ii) the surface-to-volume ratio of C_{60} based film can be increased by its surface covering on ZnO microstructures. The individual microstructures of C_{60}/ZnO showed excellent gas sensing properties to VOCs vapors at room temperature; (iii) surface functionalization of individual ZnO microstructures with different morphologies (microwires or microtetrapods) with $ZnAl_2O_4$ nanoparticles with diameter of 50 –100 nm can lead to increasing in sensitivity to H_2 gas in operating temperature range from 20 to 150 °C; (iv) surface functionalization of ZnO microstructures with CNTs leads to change in selectivity to ammonia vapors, with possibility to operate at room temperature.

The research results demonstrate the importance of the synthesis of hybrid materials with unique properties based on semiconductor oxide structures and other metal oxides or carbon nanomaterials, to be applied for the selective and highly sensitive detection of different gases, such as hydrogen, ethanol, ammonia, etc. The developed strategy can be extended to other materials with promising sensory properties and represents an essential step in the field of new hybrid materials for high performance practical applications in automotive, environmental monitoring and medical diagnostics.

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