

Semiconductor Gas Sensors Made from Metal Oxides Functionalized with Carbon Nanotubes

Vladimir AROUTIOUNIAN

Yerevan State University, 1 A. Manoukian St., Yerevan, 0025, Republic of Armenia
Tel.: 374 60 710315, fax: 374 60 710355
E-mail: kisahar@ysu.am

Received: 15 October 2018 / Accepted: 30 November 2018 / Published: 31 December 2018

Abstract: Properties of semiconductor gas sensors made from metal oxide functionalized with carbon nanotubes are analyzed. An information about methods of manufacture of such nanomaterial and measurement setup are reported. It is shown that the decoration of such metal oxide sensors allow to detect H_2 , H_2S , CH_4 , CO , O_3 , C_6H_6 , NH_3 , NO_2 , C_2H_5OH , acetone and methanol.

Hydrogen peroxide vapor SnO_2 -MWCNTs sensors are investigated. Results of study of the propylene glycol, methylformamide and formaldehyde SnO_2 -MWCNTs nanosensors are reported.

Keywords: Nanomaterial, Multiwall carbon nanotube, Metal oxide, Functionalization, Gas sensor, Sensitivity, Gas, Hydrogen peroxide, Propylene glycol, Methylformamide, Formaldehyde.

1. Introduction

Some thin or thick films of metal oxides show a fast response to varying gas atmospheres. Semiconductor gas sensors made from n-type semiconductor metal oxides, proposed in 1962 [1], have been widely used now for detection of different gases. The information about commercial products made of tin dioxide can be found in www.figarosensor.com, www.honeywell.com, www.sinkera.com etc. Such sensors are mainly based on a change in its resistivity R after the gas exposure. Their advantages are rather high response (sensitivity), simple design, low cost. But they need in high pre-heating of work body, i.e. high consumption of energy. The lack of selectivity and long-term stability often limit their applications. The range of the operating temperatures of commercial SnO_2 sensors spans from 200 to 500 °C. For example, the sensor for O_3 gas is the most effective at 350 °C [2-3]. Many SnO_2 -based sensors detecting organic compounds and

hazardous gases (e.g., CO and NO) operate at temperatures up to 400 °C [4]. Existing platinum wire sensors need also in its pre-heating above 400 °C and have very high cost.

We think that the main problem today - develop new semiconductor gas sensors working at or nearby room temperature of work body and use of metal oxides functionalized (decorated) with carbon nanotubes. In addition, today's sensors should be cheap, have small sizes for some applications, its easy include into microelectronic integral circuits. We shortly report below results of our investigations of metal oxide carried out with the aim to decrease the temperature of their work body.

Note that different gas, smoke, and ion-selective sensors were developed at Yerevan State University. Gas sensors were made from Bi_2O_3 , SnO_2 , ZnO , TiO_2 , In_2O_3 , Ga_2O_3 , Fe_2O_3 , $NaBiTi_2O_6$, $LaAlO_3$ - $CaTiO_3$, $Bi_2V_4O_{11}$ thin films and ceramic materials as well as porous silicon [5-8]. Our Bi_2O_3 smoke detectors are competitive with photoelectric (optical) and ionization

detectors of smoke, which currently can be widely used in fire-alarm systems [9-10]. Independent testing of our adsorptive type smoke detectors in the USA confirmed it. We also investigated simple and mixed metal oxide photo-electrodes for photo-electrochemical conversion of solar energy [11].

We will report below results obtained by other authors also.

2. Metal Oxide Hydrogen Sensor

Let shortly report our results of development of metal oxide hydrogen sensors. Many types of H_2 sensors are known (see, for example, review-papers [5, 7-8, 12-13]). One of the main objectives for researches at YSU was to decrease the metal oxide particles size which increases the effective surface area for gas adsorption. The nanosized particles, porosity of the films, and the large surface/ volume ratio ensure high sensitivity. At certain critical nano-crystallite size, the sensitivity of the gas sensor increases sharply when the nano-crystallite size becomes comparable with the double space-charge layer thickness of the semiconductors.

There are different methods for getting nanoparticles with required sizes. The sol-gel techniques are among these methods. The sol-gel process has many advantages with respect to other processes. Among them, low processing temperatures and possibilities of chemically tailoring the starting solutions can lead to manufacture of new compositions and better control of the final microstructure as well as high specific area of the sensing layer. Our efforts were mainly focused on improving the nanocrystalline SnO_2 processing technique [14-15].

Results of our R&D works are presented in [12-13]. We studied the response of sensors to detect the presence of H_2 in air at various temperatures of pre-heating of work body (25-300 °C). The maximal response is registered in the 80-130 °C range of operating temperatures. At the same time, rather high sensitivity to H_2 gas at room temperatures was observed.

The measurements were carried out at different concentrations of H_2 and carbon monoxide (CO) in the air to check selectivity of sensors (Fig. 1).

Our hydrogen leakage sensor is shown in Fig. 2. Most part of it contain batteries for pre-heating of work body of the sensor. A decrease in operating temperature leads to a decrease in the size of the sensor due to a necessity smaller quantity of batteries. Comparison of heater power consumption shown that, in particular, it is 5 and more times lower for our sensor, but the sensitivity to hydrogen is much higher. Data of Figaro TGS 2442, 2611, 3870 and 821 sensors, as well as our sol-gel and porous silicon sensors developed at YSU, are presented in Fig. 3.

Other reviews of hydrocarbon, NO_x and carbon monoxide gases metal oxide sensors were published in [3, 14-16].

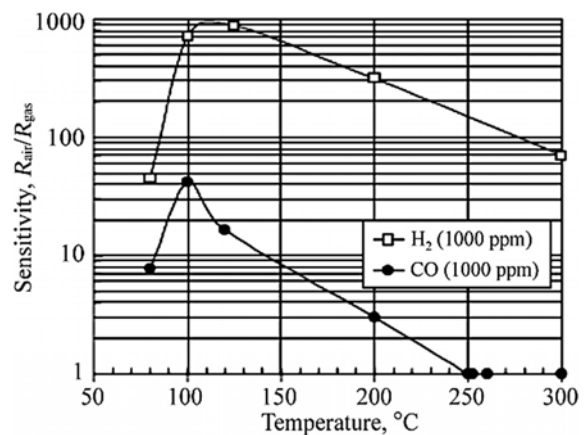


Fig. 1. Response to the 1000-ppm concentration of H_2 or CO gases versus sensor operating temperature [5].



Fig. 2. Hydrogen leakage sensor.

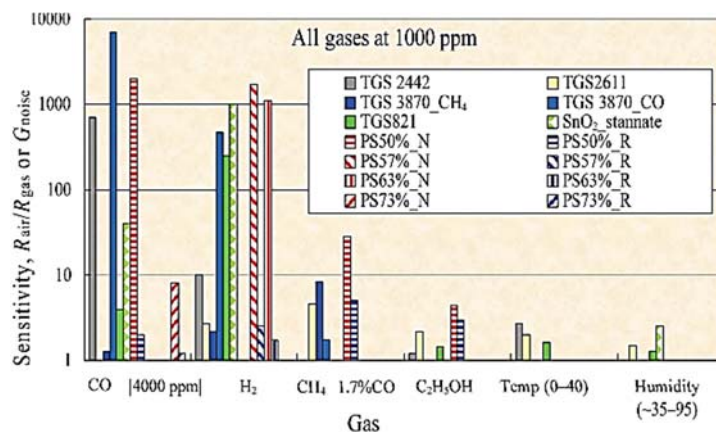


Fig. 3. Sensitivity of different sensors to gases [4].

Several studies [16-20] have been focused on the doping of the SnO₂ matrix in order to increase the sensitivity of sensors. Introduction of transitional metal cations into an oxide matrix leads to an increase in surface states, active sites and free carriers, which is important for applications. For example, the addition of Nb into TiO₂ enhanced the response to CO as it induces the formation of new electronic states due to its donor-type behavior. Doping of tin dioxide with vanadium leads to higher response towards SO₂ gas, because of their redox activity for SO₂ oxidation to SO₃. Doping with CuO, MoO₃ and Fe₂O₃ leads to lowering of pre-heating temperature of the work body and increasing in gas response. Vanadium cations serve as reducible catalytic centers to promote oxidation reactions and enhance O₂ consumption [20]. It is known also that dispersed V–O-support structure adsorbs CO gas at ambient temperature.

3. Carbon Nanotubes

Carbon nanotubes (CNTs) are graphene sheets of covalently bonded carbon molecules rolled into hollow cylinders. There are two main types of CNTs: single-walled nanotubes, which have a single carbon layer with a diameter of ~1–5 nm, and multi-walled nanotubes (MWCNTs), which have multiple layers of carbon (with an interlayer spacing of 0.34 nm) concentrically nested together. Multi-walled carbon nanotubes (MWCNTs) have outer diameters as small as 5.5 nm and inner diameters as small as 2.3 nm. CNTs show many interesting effects and properties, which are marked, in particular, in the first publication in the field of S. Iijima [21], books of P. Harris [22], M. Endo, *et al.* [23] as well as many reviews and papers. Many modern synthesis methods (arc discharge, laser ablation or chemical vapor deposition etc.) leading to enhanced production of CNTs are discussed in the literature.

CNTs demonstrated unique mix of electrical, optical, thermal and mechanical properties. The potential of applications of CNTs is shown in a wide range of science and technology: nanoelectronics, sensors, displays, hydrogen storage, batteries etc. (see, for examples review-papers [24-28]).

4. Preparation of Nanomaterial and Measurement Setup

MWCNT membranes, which were used for the preparation of nanocrystalline MWCNTs/SnO₂ powder, were kindly provided by our colleagues from the University of Szeged, Hungary. Membranes were prepared by the decomposition of acetylene (CVD method) using a Fe, Co/CaCO₃ catalyst [29-30]. The hydrothermal method of the manufacture of the nanocomposite is presented in details in articles [31-33]. The surface of MWCNTs/SnO₂ thick films was ruthenate by dipping samples into the 0.01 M RuOHCl₃ aqueous solution. Reasons for the choice of

ruthenium as a catalyst were reported in [31-35]. Gas sensors reported made of such a nanomaterial.

The morphologies of prepared SnO₂/MWCNT nanocomposite powders were studied by scanning electron microscopy using Hitachi S-4700 Type II FE-SEM equipped with a cold field emission gun, SEM-EDX and an X-ray diffraction method using the Rigaku Miniflex II diffractometer (single range: 2- D10–80, utilizing characteristic X-ray (CuK) radiation). Results of these investigations were presented in detail in [31-32].

We used the setup developed in [33] for measurements of parameters of gas sensors.

5. Metal Oxide Gas Sensors Decorated with Carbon Nanotubes

There is strong demand of cheap, high-sensitive and selective gas sensors involves domestic safety, homeland security, quality control, environmental monitoring et al. The development of gas nanosensors and sensor arrays made from CNTs has attracted intensive research interest in last years because of their potential for the selective and rapid detection of various gaseous species by novel nanostructures integrated in miniature and low-power consuming electronics. When electron-withdrawing molecules (e.g. NO₂, O₂) or electron-donating molecules (e.g. NH₃) interact with the *p*-type semiconducting CNTs, they will change the density of holes in the nanotube, which changes the conductance of CNTs. This creates the basis for applications of CNTs as chemical gas sensors [8].

As is shown in [26-27, 36], seems, the use of pristine CNT as sensors does not usually promising.

Special interest is attended to investigation of possibilities of manufacture of different metal oxide composites functionalized (decorated) with CNTs. MWCNTs are mostly used for the functionalization of metal oxide gas sensitive materials as MWCNTs have a huge specific surface area and a nanoscale structure, which exposes a large number of sites at which the gases can react. Detection of various gases can be realized at different temperatures of pre-heating of nanosensor, which open possibilities to make selective sensing. Electrical conductivity of CNTs is much higher in comparison with the conductivity of metal oxides, that can open possibilities to increase the sensitivity of sensors. The CNTs lead mostly to reducing in the resistance of the sensing materials. The metal oxide nanoparticles mainly control the sensing properties. Since metal oxide film has mainly *n*-type of conductivity and MWCNTs have *p*-type, there are two different depletion regions in these hybrid films. Note that the first depletion region is located at the metal oxide surface and the second one is located in the interface between the metal oxide nanoparticles and MWCNTs. The adsorption of gas molecules changes both the thickness of depletion layers at the surface of SnO₂ nanoparticles and at the *p*-MWCNTs/*n*-SnO₂ heterojunctions. The appearance

of nanochannels and formation of heterojunctions lead to an enhanced sensitivity of such a hybridized gas sensor as the change in barrier height or in the conductivity of the metal oxide sensitive layer may modulate the depletion layer at the p - n junction. Latter may cause the improvement in the performance of the gas sensor at low operating temperature. For example, when the MWCNTs/SnO₂ composites are exposed to the NH₃ gas, NH₃ molecules may interact with the MWCNTs by replacing the pre-adsorbed oxygen, resulting in oxidation of NH₃ gas at the surface and removing the oxygen accordingly. Therefore, the potential barrier of the heterojunction formed by MWCNTs and SnO₂ can be modulated and the conductivity of the composite material during the exposure to the NH₃ gas can be changed.

We mentioned above that MWCNT membranes prepared at Yerevan State and Szeged (Hungary) Universities were mainly used for the manufacture of the nanocomposite SnO₂/MWCNT thin film gas sensors by the sol-gel method (see, for example, [14]). Note also that the surface modification of the CNTs/metal oxide hybrid gas sensors with noble metals (Pt, Pd, Au, Ru, Rh) promotes an improvement of the gas sensors sensitivity and selectivity because of these metals or its oxides are the catalysts for chemical reactions taking place on the surface [37, 38]. As usual, the response (sensitivity) to gases of the MWCNT/SnO₂/Pd sensors was determined as the ratio of the sensor resistance in the air (R_{air}) to the sensor resistance in the presence of the pollutant after reaching a steady state (R_{gas}). The increase in the electrons concentration in the conduction band of the n -type semiconductor oxide leads to the reduction of its resistance in the case of the detection of reducing gases.

It is known also that Ru is a sensitizer for SnO₂ and allows thus enhance the sensor response and selectivity to hydrocarbons. Ruthenium stimulates an increase in the rate of oxidation and other surface reactions, involving adsorption of oxygen from the air on the surface of structure which causes an increase in the depletion layer of semiconductor near-surface region and hence leads to the enhancement of the sensor response. Our investigations have shown that high response appears only after sensibilization of the MWCNT/SnO₂ tablets in 0.01 and 0.03 M Ru(OH)Cl₃ water solution. Sensors made from the MWCNT/SnO₂/Pd tablets sensitized with 0.03 M Ru(OH)Cl₃ solution during 20 min demonstrated their high response to hydrogen and isobutane already at 120 °C (Fig. 4).

Vapors of isobutane gas are hazardous to the human health and used in the cooling plant as well as a fuel. Note that we did not detect isobutane by our sensors made of pure SnO₂ and pure CNTs. So, we have here sin-energetic effect. Sensor response to the 5000 ppm isobutane for our sensors made of the nanocomposite MWCNT/SnO₂/Pd sensitized with the 0.01 M (a) and 0.03 M (b) Ru(OH)Cl₃ solution [89] was registered at operating temperature 100–350 °C. The resistance of the sensor decreased 10 times during

~10 and ~30 s after the injection of isobutane and hydrogen, respectively. The dependence of the response on the concentration of isobutane is almost linear for the WCNT/SnO₂/Pd sensors (see the inset in Fig. 5).

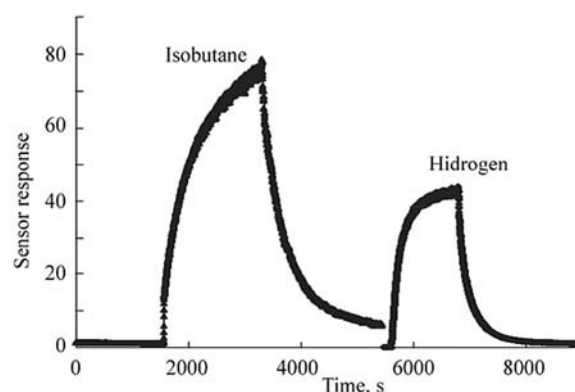


Fig. 4. Sensor response to the 500 ppm hydrogen and isobutane for the sensor made of the nanocomposite MWCNT/SnO₂/Pd sensitized with the 0.03 M Ru(OH)Cl₃ solution at 120 °C [39].

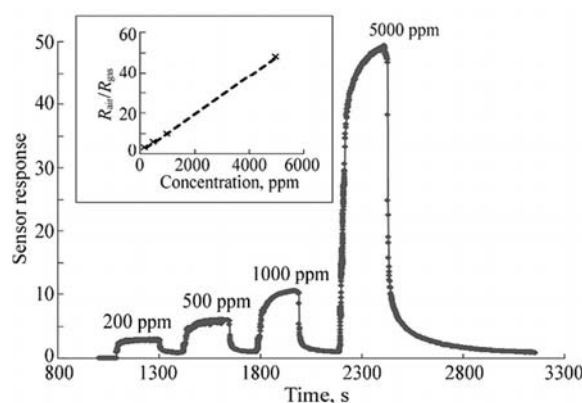


Fig. 5. Sensor response to different concentration of isobutane of the MWCNT/SnO₂/Pd sensors sensitized in the 0.01 M Ru(OH)Cl₃ solution.

We manufactured also the thick film MWCNT/SnO₂ powder nanocomposite using the sol-gel preparation technique (obtaining samples with MWCNTs/ SnO₂ ratio 1:50) as well as the hydrothermal synthesis (samples with MWCNTs/ SnO₂ ratio 1:4 and 1:8). They have good response to isobutane at temperatures higher than 200 °C. The sensitization of films in the 0.01 M Ru(OH)Cl₃ solution leads to better response at 250 °C. Prepared sensors were sensitive to isobutene already at its concentration of 50-200 ppm. Maximal response reached about 50 at the 5000 ppm concentration. The increase in operating temperature up to 250 °C leads to sharp decrease in both response and recovery times down to 1–2 and 10 seconds, respectively. With the following increase in operating temperature (≥ 300 °C), adsorbed oxygen desorbs increasingly

from the surface. As a result, the response to isobutane is sharply decreased.

A set of samples made without any catalysts has relatively high response to methanol and ethanol vapors. But sensors made from MWCNT/ SnO₂ nanocomposites with Ru catalyst shown an improvement in sensitivity and selectivity to alcohol vapors. Sharp rise in response to methanol and ethanol vapors up to 10³ and higher was detected. At that, the cross-sensitivity to other gases decreases. The response to methanol and ethanol vapors is maximal at the operating temperature of 200 °C and decreases exponentially with temperature rise up to 300 °C.

The surface-ruthenate nanocomposite containing large amount of SnO₂ (1:50) nanocrystallites shows high response both to methanol and ethanol vapors.

Gas sensors can be made from SnO₂-coated CNTs, SnO₂-filled CNTs and SnO₂-doped CNTs [40-49].

Using mixed SnO₂ nanoparticles with 1 wt% CNTs (100:1) sensing materials, gas sensors were fabricated on micro-platforms made of thin SiNx membrane [48]. Such sensors were characterized to NO₂, NH₃ and xylene gases, respectively, as a function of operating temperature from 180°C to 380°C. 220°C was the optimal temperature to have the best sensitivities. Nanosensors have good selectivity at power operation below 30 mW, at the same time the selectivity of the NO₂ gas was better than it for the NH₃ and xylene gases. The measured highest sensitivities for the NO₂, NH₃, and xylene at 220 °C were 1.06 at 1.2 ppm, 0.19 at 60 ppm and 0.15 at 3.6 ppm, respectively, were also observed.

Thick-film ruthenate SnO₂/MWCNTs VOCs were prepared using three methods: hydrothermal synthesis, sol-gel technique and their combined process. It was shown that the optimal conditions for applications as acetone, toluene, ethanol and methanol vapors sensors in view of high response and selectivity relative to each other depend on choice of material synthesis method, mass ratio of the nanocomposite components and selected operating temperature (see Fig. 6) [32].

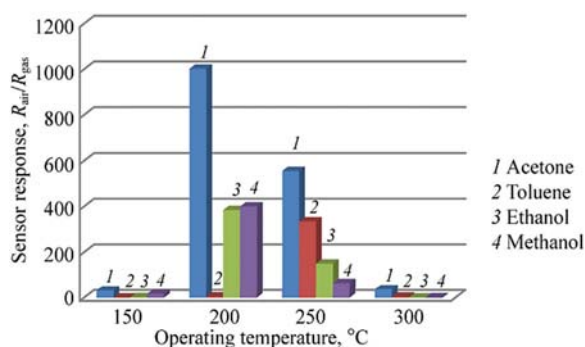


Fig. 6. Response of samples to VOCs vs operating temperature [32].

With increase in operating temperature, the response to acetone vapor rises up to 360.4 value at 250 °C while the selectivity remains sufficiently high. The largest response to acetone vapors is fixed for the

set of samples with 1:200 mass ratio of the components to 1000 ppm acetone vapors exposure at 250 °C operating temperature (Fig. 6). Response and recovery times of these sensors are about 22 s and 27 s, respectively.

MWCNTs/ SnO₂ sensor structures having the mass ratio of the components 1:4 and 1:24 exhibit selective sensitivity to acetone and toluene vapors at 150 °C operating temperature, respectively. The samples with a mass ratio of 1:200 were selective and sensitive to vapors of acetone at operating temperatures 200–250 °C. The high sensitivity to vapors of methanol and ethanol was detected in structures made by various methods with the mass ratios of 1:8, 1:24, 1:50 and 1:66 at the operating temperature 200 °C [32].

Thin film ethanol sensors made from α -Fe₂O₃/MWCNTs (25:1 weight ratio) were manufactured by the electron beam deposition method [49]. The response of manufactured sensors was investigated at different temperatures of the sensor work body and concentration of gas vapors (Fig. 7). Best response of prepared sensors to ethanol vapors was detected already at work body temperature of 150 °C.

Dependence of sensor response to acetone vapors concentration is linear from 100 ppm up to 2000 ppm (Fig. 8). Morphology of α -Fe₂O₃/MWCNTs nanocomposite powder is shown in [50].

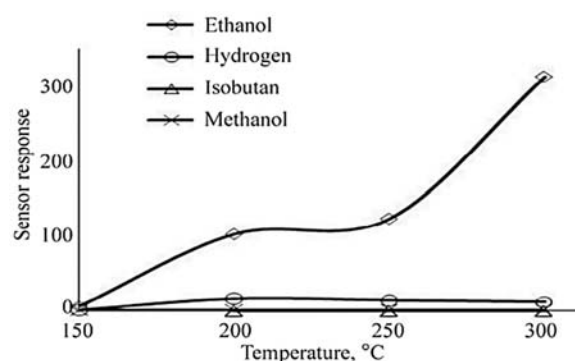


Fig. 7. Response of the α -Fe₂O₃/MWCNTs sensors at different operating temperatures. The gas concentration was 5000 ppm [49].

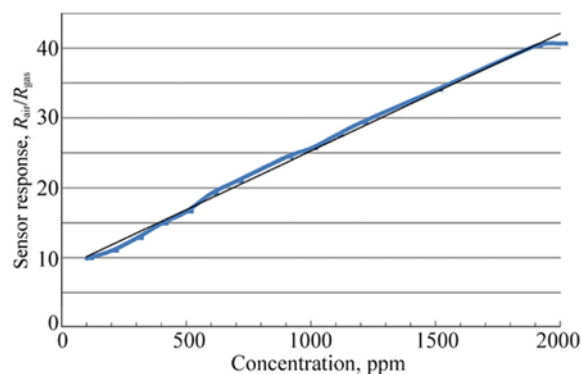


Fig. 8. Dependence of sensor response to acetone vapors concentration.

Various 1D heterostructural coaxial nanotubes were obtained. Such α -Fe₂O₃/MWCNTs heterostructural coaxial nanotubes may find great potential applications in photocatalysis, gas-sensing, and magnetic fields [51]. The Co_{1-x}Ni_xFe₂O₄/MWCNT nanocomposites ($x = 0.2, 0.4, 0.5, 0.6, 0.8$) were synthesized, they have a high selectivity for ammonia [52]. A composite film of cobalt oxide nanosheet and CNTs were manufactured, which adsorbed or desorbed CO gas at low concentrations (e.g. low ppm level) [53]. The advantages of such a sensor include work at room temperature, short response/recovery times and easy post process. The sensitivity of the CO sensor was about 0.19 at 34 mV/ppm, and the response and recovery times were 23 and 34 seconds at 200 ppm CO, respectively. Nanocomposite structures made of cobalt oxide and single-walled CNTs (SWCNTs) for a gas sensor application (NO_x and H₂) shown a response of ~200 % upon exposure to 4 % H₂ at room temperature [54].

Copper (II) oxide (CuO)/MWCNT thin film based ethanol-sensors were manufactured, their sensing response was the maximum at an operating temperature near 400°C [55]. Thin film gas sensors made from undoped and 1 wt% MWCNT-doped tungsten oxide (WO₃) were fabricated [56]. Hydrogen sensing properties of the thin films have been investigated at gas concentrations ranging from 100 ppm to 50,000 ppm. The results indicate that the WO₃/MWCNT thin film exhibited high sensitivity and selectivity to hydrogen at reduced operating temperatures [57-58].

Gas sensors made from doped- SnO₂ /CNT composites for NO₂ detection at room temperature were reported in [59]. It has been reported earlier [41, 60-61] that the incorporation of CNTs to a SnO₂ matrix results in a dramatic increase in sensor response at low operating temperatures and even at room temperature. Probably, the main reason for such response enhancement is the co-existence of two different depletion layers and associated potential barriers [41, 60]: one at the surface of the metal oxide grains and the other one at the interface between MWCNT and metal oxide. Nitrogen or boron doped CNTs were added into a SnO₂ matrix, it enhances the CNTs conductivity. Such a hybrid sensor was prepared to detect low ppb concentrations of NO₂ in air and shown at least 10 times higher response towards NO₂ at room temperature in comparison with the pristine SnO₂ and N- or B-substituted CNT sensors. Nitrogen doped MWCNTs sensors exhibited response and recovery times of the order of a few seconds.

It was also established [62] that sensors based on pure tin oxide nanoparticles and on pure plasma treated CNTs did not show responsiveness to nitrogen dioxide and carbon monoxide. In contrast, sensors made of SnO₂-decorated plasma treated CNTs are gas sensitive soon at room temperature. Recovery time to 1 ppm NO₂ was 4 min and 3 min when sensors are operated at room temperature and 150°C, respectively. Note that the CO response was far lower than the one

for NO₂. Response time was 5 min for 2 ppm of CO. Such sensors showed a decrease in resistance with exposure to CO when operated at room temperature. This experimental result is qualitatively consistent with what has been observed by Zhao, *et al.* [63], Yang, *et al.* [64] and Lu, *et al.* [65]. All these research teams have attributed such behavior to the decrease in the work function of SnO₂ in the presence of CO and a decrease in sensor resistance.

The SnO₂ / MWCNTs nanocomposite sensors are prepared and their response to ethanol, CO, NO and CH₄ are investigated in [66]. The COOH groups attached on the surface of CNTs lead to a significantly enhanced surface area. The enhancement in the response to methane up to 45 times is observed when 0.05 % MWCNTs were incorporated into SnO₂. Further increase in the MWCNTs content reduced its responses. Maybe, the MWCNTs agglomeration declines the effective contact between SnO₂ nanoparticles and MWCNTs-COOH. Addition of 0.05 wt% CNTs to SnO₂ reduces the optimum operating temperature from 200 to 150°C for ethanol and CO detection and also from 300 to 200°C for CH₄. An increase in the operating temperature drastically reduces the response of MWCNTs/ SnO₂ sensors. Maybe it attributed to the limited diffusion of the target gas through MWCNTs nanochannels and their change from the p-type semiconductor to metal at high temperatures, as well as the desorption of chemisorbed oxygen species.

Maximal Co₃O₄- SnO₂ sensor' response to CO [67] in the working temperature was found at 25 °C. Doping of 0.1 % CNT into Co₃O₄- SnO₂ enhanced the CO response of non-doped Co₃O₄- SnO₂. The sensor response varied under CO concentrations ranging from 20 to 1000 ppm.

The fast-LPG response of the α -Fe₂O₃/CNT nanocomposite thin film sensors was reported in [68] at room temperature. The composite film of nano-oxide cobalt and CNT (CoOOH/CNT) prepared by the precipitation-oxidation method changes the resistance when the film adsorbed and desorbed the carbon monoxide. The adsorption of its small quantity (the very low ppb level) has led to the significant change of the CNT conductivity. Such micro CO sensor was integrated with the corresponding circuit manufactured by the use of commercial 0.35 μ m MOS technology and the subsequent process. The sensor operated at room temperature, the small response and recovery times (23 s and 34 s at 200 ppm CO, respectively) were observed.

Pt-doped TiO₂/MWCNT composites have been synthesized in [69]. It was established that the TiO₂/MWCNT composite samples with nominal C/Ti molar ratio ranging from 3.5 to 17.0 were the best. Hydrogen monitoring takes place only with the Pt/TiO₂/ MWCNT ternary sensor, suggesting a synergistic action among metal oxide, noble metal and CNTs. Pt acts as a catalytic additive in the Pt-TiO₂/MWCNT-based sensors which were found to be sensitive to hydrogen at concentrations between 0.5

and 3 % in the air. They can be used as hydrogen leak detection devices.

So, we and other authors shown that the use of the metal oxide/ MWCNTs composition is very promising for manufacture and practical use of sensors of many gases having high sensitivity, selectivity and stability. The modification of the our nanosensors' surface with precious metals led to remarkable improve of the sensitivity and selectivity of sensors. They allow detect NH_3 , CO , NO_x , H_2 , H_2S , CO_2 , isobutane, O_3 , CH_4 , acetone, toluene as well as vapors of methanol and ethanol etc. We reported that our SnO_2 -MWCNTs sensor shown synergetic effect in process of detection of isobutane- it show large enhancement in sensitivity exceeding those of SnO_2 or MWCNTs [26].

6. Hydrogen Peroxide Vapors Sensors

Hydrogen peroxide vapors (H_2O_2) is characterized by a wide range of antibacterial properties, low toxicity [70-71]. However, hydrogen peroxide vapor belongs to the category of hazardous substances for humans with a certain maximum allowable concentration in the workplace. Hence, it is necessary to protect personnel outside the disinfected premises from accidental leakage of H_2O_2 fumes. Recently, the easily made peroxide based explosives most actively used by terrorists groups [72-75]. Thus, the development of sensors for detection of H_2O_2 vapors is actual and important.

Several techniques have been proposed today for the detection of hydrogen peroxide, such as chemiluminescent, spectrophotometric, fluorometric, calometric, and optical interferometry. All these techniques are complex, expensive and require considerable time consuming. In addition, these methods did not always allow to measure low concentrations of H_2O_2 . It is possible and promising the detection of H_2O_2 vapors using MWCNTs/ SnO_2 gas sensors [31]. We are expected that sensitivity of SnO_2 /MWCNTs based nanocomposite gas nanosensors of H_2O_2 will be high. We developed two types of such nanosensors, which are presented below- made from ruthenate nanocomposite obtained using hydrothermal method and non-ruthenate nanocomposite structures obtained using sol-gel technique.

The target final mass ratio of the SnO_2 /MWCNT nanocomposite components manufactured by hydrothermal method [12] was chosen 1:200. After annealing and cooling processes, the MWCNTs/ SnO_2 thick films were surface ruthenate SnO_2 /MWCNT Millimeter long MWCNTs grown by CVD were used to prepare membranes. Thick films were obtained on the base of SnO_2 /MWCNT nanocomposite powder made by sol-gel method with the 1:50 ratio of the components, respectively. The Multi-Sensor-Platform (purchased from TESLA BLATNÁ, Czech Republic) were used as substrates for printing the MWCNTs/ SnO_2 slurry (see Fig. 9).

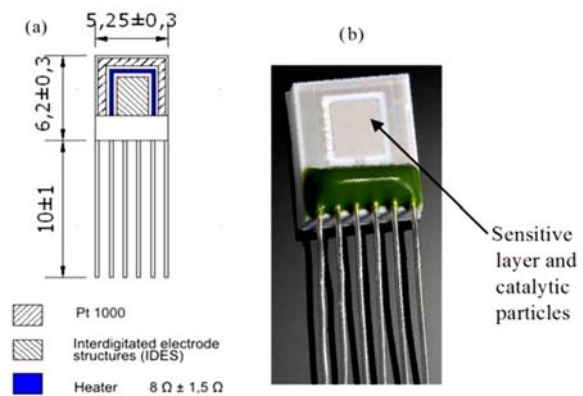


Fig. 9. The structure of the Multi-Sensor-Platform (a), and the sensor installed on the Multi-Sensor-Platform (b).

7. Characteristics of Hydrogen Peroxide Sensor

Measurement and testing of the developed hydrogen peroxide sensors' characteristics were carried out in YSU using developed automated setup. As a result of temperature measurements, the optimal operating temperature of the sensors around of 100°C was revealed. Response of ruthenate SnO_2 /MWCNT (1:200) H_2O_2 sensor vs vapor concentration measured at 100°C operating temperature is shown in Fig. 10. It can be seen from Fig. 10, the linear part of the signal on the H_2O_2 vapor concentration (double logarithmic scale) extends from 2 to 120 ppm gas concentrations, but the minimal registered H_2O_2 vapor concentration is ~ 875 ppb.

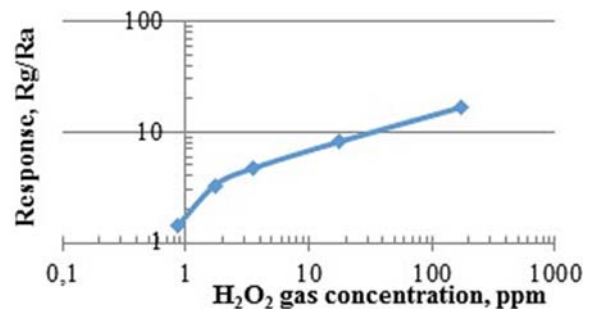


Fig. 10. Response of ruthenate SnO_2 /MWCNT (1:200) H_2O_2 sensor vs vapor concentration.

Values of the non-ruthenate SnO_2 /MWCNT (1:50) nanosensor response as well as response and recovery times under influence of the various concentrations of H_2O_2 in air are presented in the Table 1. Hereinafter τ_{res} and τ_{rec} are response and recovery times, respectively. Gas sensing performance of ruthenated SnO_2 /MWCNT (1:200) structures in the presence of different concentrations of H_2O_2 vapor in the air at the 100°C operating temperature are presented in Table 2.

Dependence of the response of the non-ruthenate SnO_2 /MWCNT (1:50) H_2O_2 vapor sensor on gas concentration measured at 100°C of the operating

temperature of work body is presented in Fig. 11. Obviously that the high level signal is about three others of magnitude higher, it is typical for non-ruthenate samples prepared by sol-gel technology.

Table 1. Gas sensing performance of the SnO₂/MWCNT (1:50) structures in the presence of different concentrations of hydrogen peroxide vapor in the air at 100°C operating temperature.

H ₂ O ₂ , ppm	R _g /R _a	τ_{res} , min	τ_{rec} , min
175	2856	4.4	8
105	2855	3	13
35	2688	2	4.5
17.5	595	3.5	5.7
3.5	1.89	1.5	4
1.75	1.33	0.8	4

Table 2. Responses of the sensor and time characteristics.

H ₂ O ₂ , ppm	R _g /R _a	τ_{res} , min	τ_{rec} , min
175	17	0.5	-
17.5	8.17	2.68	76.5
3.5	4.86	3.7	34.7
1.75	3.3	5.85	41.75
0.875	1.41	4.16	-

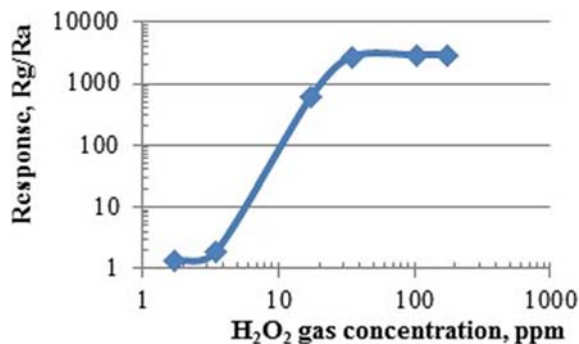


Fig. 11. The response of the non-ruthenate SnO₂/MWCNT (1:50) H₂O₂ sensor vs vapor concentration.

The linear part of the response vs concentration curve is in the range of about 3-13 ppm gas concentrations. Further, dependence of the response of the non-ruthenate SnO₂/MWCNT (1:50) H₂O₂ sensor on vapor concentration comes to the saturation. The latter most likely indicates that the H₂O₂ vapor reaches its saturation (dew point), after which the H₂O₂ vapor turn into a liquid state in the form of an aerosol in the air, or begins to condense on the surface [74].

As example, the response/recovery curve of the non-ruthenate H₂O₂ sensor measured at the presence of 17.5 ppm gas concentrations in air at 100 °C operating temperature is shown in Fig. 12.

Dependences of response times for both types of studied sensors vs H₂O₂ concentration in air are presented in Fig. 13.

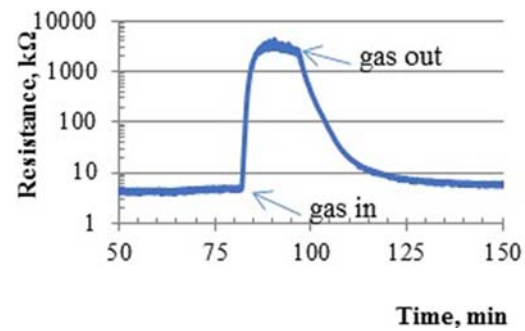


Fig. 12. The response/recovery curve of the non-ruthenate SnO₂/MWCNT (1:50) H₂O₂ sensor measured at presence of 17.5 ppm gas concentrations in air.

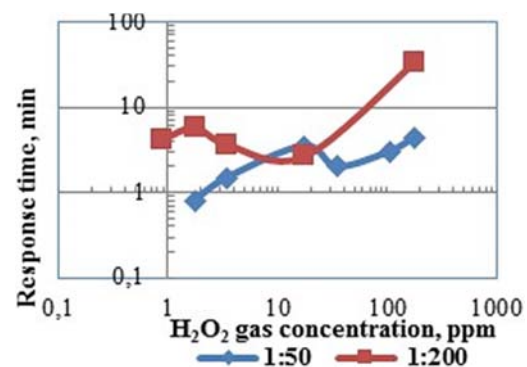


Fig. 13. Dependences of response times for both types of studied sensors vs H₂O₂ concentration in air measured at 100°C operating temperature.

It can be seen from Fig. 13 and Tables 1 and 2, response times for both cases are changed in the range of 0.8-5 min. But, recovery times of non-ruthenated SnO₂/MWCNT (1:50) H₂O₂ gas sensors are significantly smaller for ruthenate SnO₂/MWCNT (1:200) sensors.

8. Study of Propylene Glycol, Dimethylformamide and Formaldehyde Vapors Sensors made of the SnO₂/MWCNT Nanocomposite

Detection of harmful and hazardous vapors is very important for environmental protection, industrial manufacturing, medicine and national defense [76-77]. Propylene glycol (PG), dimethylformamide (DMF) and formaldehyde (FA) are known as industrial chemicals in foods products and antiseptics [76]. DMF, PG and FA have a huge impact on human organs (e.g. liver, skin, eyes and kidneys) [76, 78-82]. PG can cause nausea and vomiting, headaches, dizziness and fainting. Moreover, it is known as a combustible liquid, which can explode in fire. FA gas can cause burning sensations in the eyes, nose and throat as well as cause coughing, wheezing, nausea and skin irritation. Besides, exposure to relatively high amounts of FA can increase the risk of leukemia and even cause some types of cancer in humans.

We did not find scientific papers related to the development of resistive-type sensors for PG and DMF gases. There are only studies on sensors working on other principles (for example, sensors working on a modification of the color of the substance) [83-84]. As opposed to this case, there are various types of FA gas sensors made from graphene or polymers and working at a room temperature [85-86]. Pure metal oxide structures react on FA at higher operating temperatures (300–400 °C) [87-88] or room temperature with the assistance of UV LEDs [89-90].

We discussed below how carbon nanotubes (CNTs) used for gas sensors ([31, 91-94]). When CNTs' walls are covered with metal-oxide nanoparticles, the specific surface area of sensitive gas material enlarges. Furthermore, nanochannels in the form of hollows of CNTs promote penetration of gas molecules deeper down in the nanocomposite sensitive layer. Hence, it can be expected that application of nanocomposite structures composed of metal oxide functionalized with CNTs in the technology of gas sensors should improve gas sensor parameters, such as gas response, response, recovery times and operating temperature. The choice of SnO₂ as a component of SnO₂/MWCNT nanocomposite structure is conditioned by the fact that SnO₂ is a well-known basic material for metal oxide gas sensors [95-96]. The choice of processing technique, treating conditions and regimes for CNTs functionalization as well as modification of films surface with Ru catalyst, see above.

Here, we present characteristics of the PG, DMF and FA ruthenated SnO₂/MWCNT vapor sensors.

Remember that the gas response of the sensors determines as R_a/R_g , where R_a and R_g are the electrical resistance in the air and target gas–air atmosphere. The response and recovery times are determined when the time required for reaching the 90 % resistance changes from the corresponding steady-state value of the signal. Dependence of change in electrical resistance in the SnO₂/MWCNT structures vs operating temperature measured in air at 50 % RH is shown in Fig. 14.

The maximal response PG, FA and DMF vapors are detected in the range of 200–225 °C of operating temperatures (Fig. 15). Changes in the resistance of the structure vs PG and FA gas concentrations measured at the 200 °C operating temperature are presented in Fig. 16 and Fig. 17, respectively.

Dependencies of the response of MWCNTs/ SnO₂ sensors vs PG, DMF and FA vapor concentrations measured at the 200 °C operating temperature are shown in Fig. 18 and Fig. 19, respectively. Obvious that the sensor response occurs down to small target gas concentrations (13 ppm of PG and 5 ppm of DMF) and the response depends approximately linearly (on a double logarithmic scale in Fig. 18 and in a half logarithmic scale in Fig. 19).

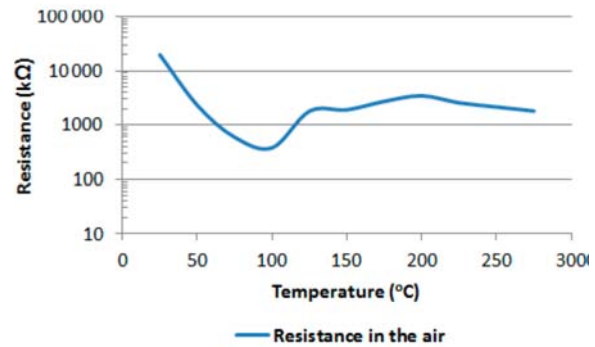


Fig. 14. Dependence of electrical resistance of SnO₂/MWCNT sensors vs pre-heating operating temperature.

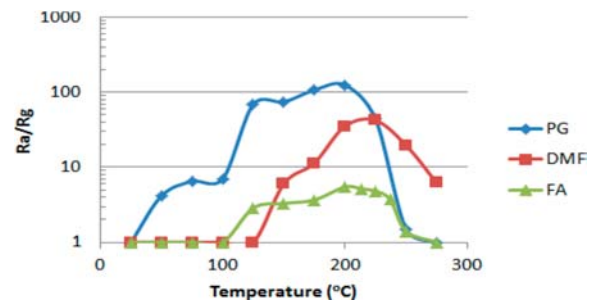


Fig. 15. Response of R_a/R_g vs. operating temperature at 650 ppm PG, 500 ppm DMF and 1160 ppm FA vapor exposure, respectively.

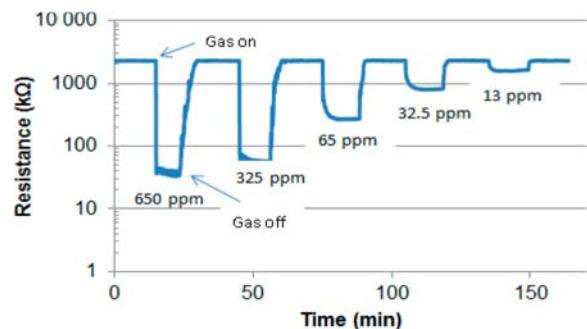


Fig. 16. The response–recovery curves observed at different PG concentrations.

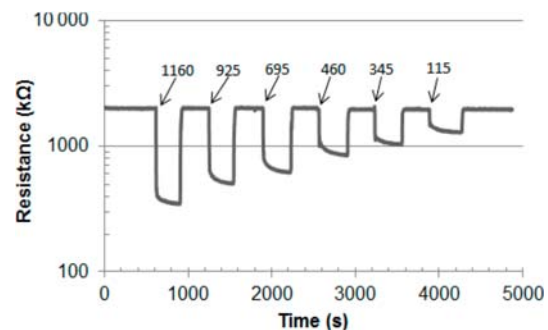


Fig. 17. The response–recovery curves observed at different FA concentrations.

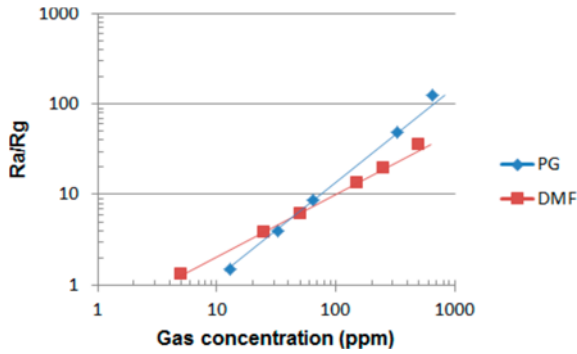


Fig. 18. Response of the SnO₂/MWCNT PG and DMF vapor sensor vs gas concentration.

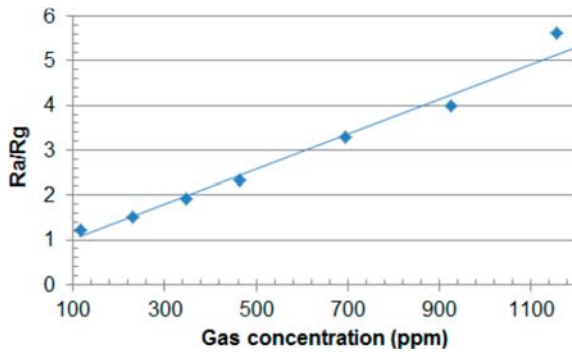


Fig. 19. Response of the SnO₂/MWCNT FA vapor sensor vs gas concentration.

Good repeatability of the sensor response can be seen from Fig. 20, where the electrical resistance changes in PG sensor vs. time measured upon cyclic exposure of 650 ppm PG vapors in air at 200 °C operating temperature is presented.

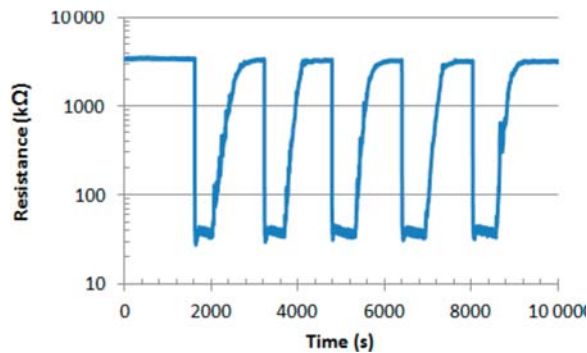


Fig. 20. The electrical resistance vs. time measured upon cyclic exposure of 650 ppm PG vapors in air.

Changes in the response and recovery times of the sensors depending on PG, DMF and FA vapor concentration are presented in Fig. 21, Fig. 22 and Fig. 23, respectively. Changes in the response and recovery times of the PG and FA vapor sensors depending on operating temperature are presented in Figs. 24-26. Comparison of responses of SnO₂/MWCNT sensors to 650 ppm PG, 500 ppm DMF and 1160 ppm FA vapor exposure vs. operating

temperature is shown in Fig. 27. As shown in this figure, sensors demonstrate the best response against PG and FA vapors at 200 °C operating temperature and against DMF vapor at 225 °C operating temperature.

Due to the reactivity of the target gas molecules is proportional to the speed of diffusion into the sensing layer, the target gas has the chance to penetrate sufficiently into the sensing layer and react with it. With an increase in operating temperature, desorption of the adsorbed ions from the surface of the sensor is growing. Therefore, the response falls at higher operating temperatures.

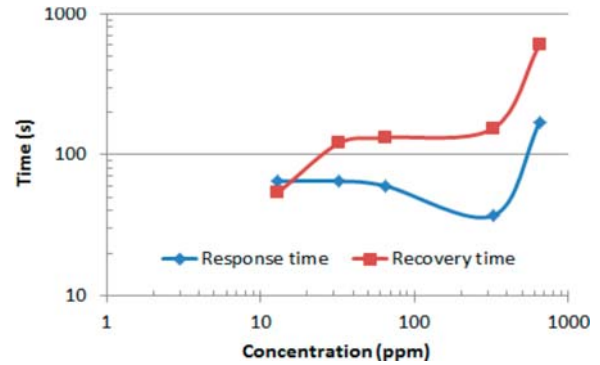


Fig. 21. Response and recovery times of SnO₂/MWCNT PG vapor sensor vs. gas concentration.

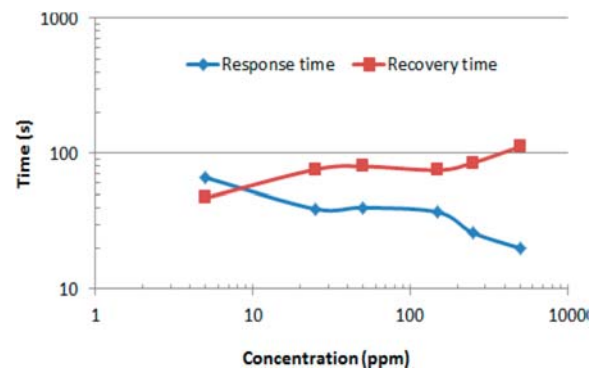


Fig. 22. Response and recovery times of SnO₂/MWCNT DMF vapor sensor vs. gas concentration.

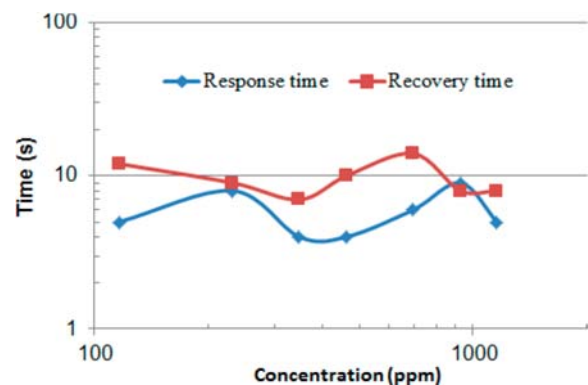


Fig. 23. Response and recovery times of SnO₂/MWCNT FA vapor sensor vs. gas concentration.

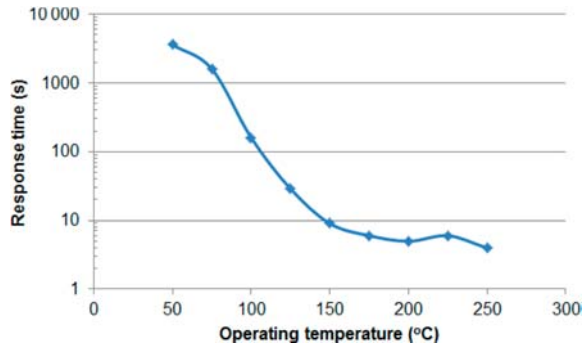


Fig. 24. Response time of SnO₂/MWCNT PG vapor sensor vs operating temperature.

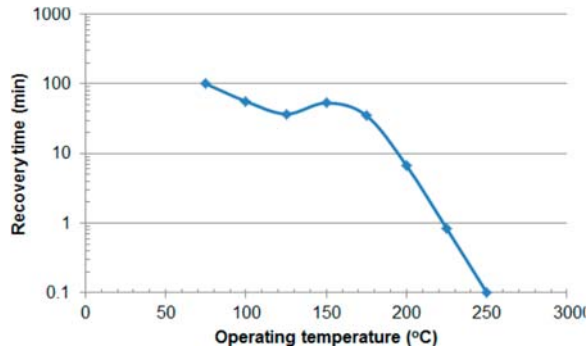


Fig. 25. Recovery time of SnO₂/MWCNT PG vapor sensor vs operating temperature.

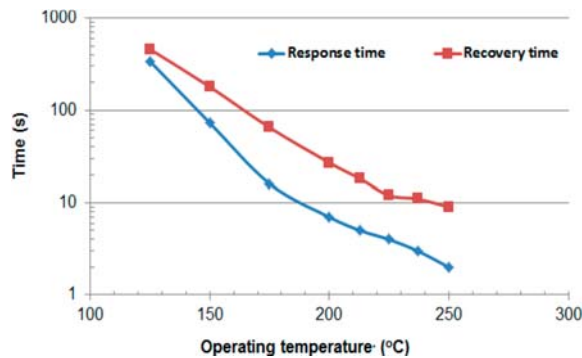


Fig. 26. Response and recovery times of SnO₂/MWCNT FA vapor sensor vs operating temperature.

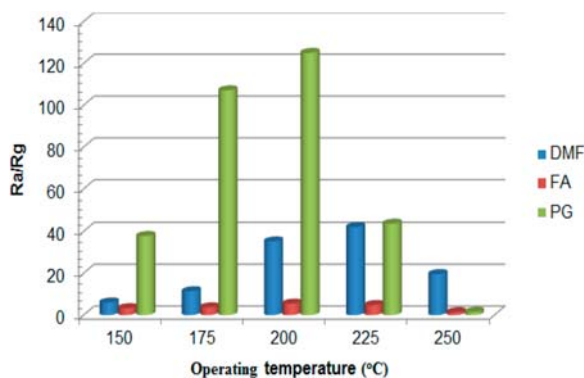


Fig. 27. Comparison of responses of SnO₂/MWCNT sensors to 650 ppm PG, 500 ppm DMF and 1160 ppm FA vapor exposure at various operating temperatures.

The molecular weights of investigated target gases are close to each other, the quantity of carbon atoms is just the same. Response from DMF-vapor exposure is smaller because the adsorbed oxygen ions demand the full oxidation reaction. Therefore, a chemical decomposition occurs. Nevertheless, the 1:200 weight ratios of the nanocomposite sensor components, with the relatively large amount of SnO₂ particles, promote an initiation of the sufficiently large quantity of ionized adsorption centers which, in turn, ensures a relatively high response to DMF gas exposure.

At exposure to low concentrations of both PG and DMF gases, recovery times become shorter than response times. We explain it by the fact that the chemisorption process is developing slower and on a larger scale than desorption of products, obtained during the chemical reaction. That is due to the necessity of having many adsorption centers for implementation of the oxidation reaction and because of desorption after the exposure by low concentrations of gases. Moreover, the presence of CNTs leads to a decrease in recovery times. We discussed in [33] why response and recovery times increased with concentration of propylene glycol. It is connected with its vaporization from the liquid. High-temperature heat source provides plenty of oxygen compared with a liquid state [98]. This promotes that at least part of the liquid can attain ignition temperature by heating (flash temperature is only just 64 °C) instead of plain vaporization. When combustion is complete, and there is plenty of oxygen pieces, the chemisorption reaction happens with formation just enough volatile CO₂ and water to release the conduction electrons. If the combustion is incomplete and there is not enough oxygen, intermediate formaldehyde is formed along with the most thermodynamically stable CO₂ and water [99]. We explain the sharp rise in PG response and recovery times at high PG vapor concentrations (beginning from about 300 ppm and higher) by intermediate formaldehyde formation. It is known that formaldehyde molecules are more stable than PG, but less stable than carbon dioxide [100]. We suppose that at least part of the formaldehyde gas molecules is adsorbed on the Ru catalyst. Based on the data of works [100-103], where decomposition of formaldehyde on Pt, Pd and Ru has been studied, we can assume that the catalytic decomposition of formaldehyde in our case on ruthenium also occurs.

9. Some Remarks about Theoretical Investigations of Metal Oxide Gas Sensors Decorated with CNTs

Note that that the sensitivity to gases of sensors made from metal oxides (MOs) functionalized with CNTs is mainly controlled by the MO due the adsorption of chemisorbed ions, while CNTs mostly reduced the resistance of sensors. A MO has the n-type of conductivity and MWCNTs have p-type and cover MO nanoparticles or aggregates. Therefore, the

response of the MO/CNTs sensors falls at higher operating temperatures. We discussed before and in [104] the oxidation reactions of PG and DMF vapors on nanocomposite surface taking into account that the reactivity of the target gas molecules is proportional to their speed into the sensing layer. Hence, the target gas has the chance to sufficiently penetrate into the sensing layer and react with an appropriate speed. The competition between the amount of adsorbed target gases and their oxidation rate supports maximum response and its sharp declining. Change in the operation temperature of work body of the sensor allows to have different sensitivity for different gases. For example, noticeable gas response at the 200 °C operation temperature was detected in the 1:200 weight ratio of SnO₂/MWCNTs sensor for ethanol and 250 °C for toluene vapor.

Theory of processes in MO sensors functionalized with MWCNTs is absent today. Note that a much simple case of MO gas sensors is considered by us in [105]. It is necessary to consider presence in the case of MO/CNTs of p-n heterojunctions inside of sensor, Schottky barriers between MWCNTs and MO matrix, adsorption and desorption phenomena in such a complicate system, sensitivity and selectivity to different gases in different ratio (wt%) of such sensors, operating temperature of work body of sensor, surface effects, etc. Situation will be more complicated when structures will be manufactured in future on the base of very thin (2d) layers of MOs or covering of the surfaces of MO and MWCNTs with different metals, COOH groups etc.

10. Conclusions

1. There are commercial metal oxide gas sensors, which are mainly based on measurement of large change of their resistivity after gas exposure. These sensors need in high pre-heating of the work body above 300°C, i.e. high consumption of energy, lack of selectivity and long-term stability which limit their applications. The main problem today is to develop new semiconductor gas sensors working at lower operating temperatures or without pre-heating. In addition, sensors should be cheap and easy to be inserted in future into microelectronic integral circuits. Investigations of ways to decrease the operating temperature are necessary.

2. Development of metal oxide hydrogen sensors in Yerevan State University showed that a decrease in metal oxide particle sizes led to an increase in the effective surface area for gas adsorption and large surface/volume ratio. Below a certain critical nanocrystalline size, the sensitivity of sensor increases sharply. This occurs when the nanocrystalline size becomes comparable with the double space-charge layer thickness of the semiconductors under consideration.

3. The development of CNT based gas sensors and sensor arrays has attracted an intensive research interest in the last years. But the use of pristine CNTs

as sensors is not promising, the functionalization of metal oxides with CNTs should be made. A special interest is displayed to investigations of different metal oxide composites functionalized (decorated) with CNTs. It allowed detect H₂, H₂S, CH₄, CO, O₃, C₆H₆, NH₃, NO₂ and C₂H₅OH, VOC gases (acetone, toluene, ethanol and methanol) down to their ppm level. We were shown that the sensibilization of CNT- SnO₂ composites in water solutions of Ru(OH)Cl₃ ensured high response to hydrogen, the synergistic effect during detection of isobutene as well as lower operation temperature of sensors. Sensors of H₂, NO_x and CO were manufactured from Fe₂O₃, cobalt oxide, Co_{1-x}N_xFe₂O₄, CuO and WO₃, TiO₂ functionalized with CNTs.

4. Research and development of nanosensors working without the pre-heating of their work body are started. The doping of metal oxides with CNTs leads to greater sensitivity to gases and a lowering of operating temperature to room one.

5. Different types of conductivity of CNTs and metal oxides, change in the work function (potential barrier), the modulation of formed heterojunctions should be taken into account during the analysis of complicate processes and phenomena in the gas sensitive structures reported above.

6. Influence of a change of operational temperature of work body of sensors to different gases on the sensitivity of metal oxide decorated with CNTs is investigated in details at first time. Results of such investigations are presented for hydrogen and carbon oxide sensors (see Fig. 1), methanol, ethanol, acetone, isobutane, and toluene (Fig. 6), H₂O₂ (Fig. 10), PE, FA and DMF (Figs. 15, 27). Choose of operating temperature of work body is very important.

7. Two types of the MWCNTs/SnO₂ nanocomposite nanosensors for measurements of concentration of hydrogen peroxide vapors with a sufficiently high response at low concentrations of H₂O₂ gas in the air were developed. The minimal gas concentration registered by our nanosensors is less than 1 ppm. Gas concentrations in the linear part of the response vs concentration curves of the ruthenate and non-ruthenate nanocomposite sensors measured at 100°C operating temperature can be around of 2-120 ppm and 3-30 ppm, respectively. With the increase in the concentration of H₂O₂ vapor in one order of magnitude, the response of the non-ruthenate sensors increases in three orders of magnitude, reaching 2.5×10³ and higher.

8. In this paper, we have investigated the ruthenate SnO₂/MWCNT thick-film nanocomposite sensors using hydrothermal synthesis and sol-gel technologies. It is revealed that such sensors give a sufficiently high response to harmful and hazardous gases like PG, DMF and FA at relatively low operating temperatures. The fast response of the sensors and acceptable recovery times are observed under all gas concentrations influence at 200°C operating temperature. The minimal PG, DMF and FA gas concentrations at which the perceptible signal is registered are 13, 5 and 115 ppm, respectively. Due to

the linear dependence of the response on the concentration of PG, DMF and FA vapors, it is possible to measure the concentration of mentioned gases in the atmosphere quickly.

Acknowledgements

Many thanks to Dr. Z. Adamyan, Profs. K. Hernady, B. Joost and L. Forro as well as Mrs. E. Khachatryan and G. Shahnazaryan, Drs. A. Sayunts, V. Arakelyan, M. Aleksanyan, A. Adamyan and other my colleagues and coauthors of joint publications from Armenia, Hungary, Switzerland and Czech Republic for collaboration and helpful discussions during many years.

This work was supported by Grants of Swiss National Science Foundation Project IZ73Z0 128037/1 and Swiss NSF SCOPES DecoComp project as well as NATO EAP.SFPP 984.587 Project. We are thankful for many years' support of State Committee of Science at the Ministry of Education and Science of the Republic of Armenia.

References

- [1]. N. Taguchi, A Metal Oxide Gas Sensor, *Japan Patent*, No. 45-38200, 1962.
- [2]. G. Korotcenkov, I. Blinov, M. Ivanov, J. R. Stetter, Ozone sensors on the base of SnO₂ films deposited by spray pyrolysis, *Sensors and Actuators B: Chemical*, Vol. 120, Issue 2, 2007, pp. 679–686.
- [3]. L. Berry, J. Brunet, Oxygen influence on the interaction mechanisms of ozone on SnO₂ sensors, *Sensors and Actuators B: Chemical*, Vol. 129, Issue 1, 2008, pp. 450–458.
- [4]. C.-T. Wang, M.-T. Chen, Vanadium-promoted tin oxide semiconductor carbon monoxide gas sensors, *Sensor and Actuators B: Chemical*, Vol. 150, Issue 1, 2010, pp. 360–366.
- [5]. V. Aroutiounian, Hydrogen sensors, in *Encyclopedia of Nanoscience and Nanotechnology*, S. E. Lyshevski (Ed.), *CRC Press*, 2014.
- [6]. V. M. Aroutiounian, Microelectronic technologies for preparation of solid-state chemical sensors, *Sov. Microelectron.*, Vol. 20, Issue 2, 1991, pp. 337–355.
- [7]. V. Aroutiounian, Porous Silicon Gas Sensors, in *Semiconductor Gas Sensors*, R. Jaaniso and Ooi Kiang Tan (Ed.), *Woodhead Publishing*, 2013, pp. 408–430.
- [8]. V. M. Aroutiounian, Use of Metal oxide, Porous Silicon and Carbon Nanotube Gas Sensors for Safety and Security, in *Advanced Sensors for Safety and Security*, A. Vaseashta, S. Khudaverdyan (Eds.), *NATO Science for Peace and Security Series B: Physics and Biophysics*, Ch. 9, 2012, pp. 408–430.
- [9]. V. M. Aroutiounian, H. V. Abovian, Z. N. Adamyan, K. R. Movsessian, A. A. Barsegyan, M. S. Panossian, Method of Making Smoke Detector, *US Patent 5382341*, January 17, 1995.
- [10]. A. Z. Adamyan, Z. N. Adamyan, V. M. Aroutiounian, Smoke sensor with overcoming of humidity cross-sensitivity, *Sensor and Actuators B: Chemical*, Vol. 93, Issue 1-3, 2003, pp. 416–421.
- [11]. V. M. Aroutiounian, V. M. Arakelyan, G. E. Shahnazaryan, Metal oxide photoelectrodes for hydrogen generation using solar radiation-driven water splitting, *Solar Energy*, Vol. 78, Issue 5, 2005, pp. 581–592.
- [12]. T. Huebert, L. Boon-Brett, G. Black, U. Banach, Hydrogen sensors – A review, *Sensor and Actuators B: Chemical*, Vol. 157, Issue 2, 2011, pp. 329–352.
- [13]. H. Gu, Zh. Wang, Y. Hu, Hydrogen gas sensors based on semiconductor oxide nanostructures, *Sensors*, Vol. 12, Issue 5, 2012, pp. 5517–5550.
- [14]. A. Z. Adamyan, Z. N. Adamyan, V. M. Aroutiounian, A. H. Arakelyan, K. J. Touryan, J. A. Turner, Sol-gel derived thin-film semiconductor hydrogen gas sensor, *Int. J. Hydrogen Energy*, Vol. 32, Issue 16, 2007, pp. 4101–4108.
- [15]. A. Z. Adamyan, Z. N. Adamyan, V. M. Aroutiounian, Study of sensitivity and response kinetics changes for SnO₂ thin-film hydrogen sensors, *Int. J. Hydrogen Energy*, Vol. 34, Issue 19, 2009, pp. 8438–8443.
- [16]. V. M. Aroutiounian, Semiconductor NO_x sensors, *Int. Sci. J. Alternative Energy and Ecology*, Vol. 4, Issue 1, 2007, pp. 63–76.
- [17]. V. M. Aroutiounian, Metal oxide hydrogen, oxygen and carbon monoxide sensors, *Int. Sci. J. Alternative Energy and Ecology*, Vol. 3, Issue 11, 2006, pp. 12–22.
- [18]. V. M. Aroutiounian, Semiconductor metal oxide hydrocarbon gas sensors, *Int. Sci. J. Alternative Energy and Ecology*, Vol. 4, Issue 3, 2007, pp. 33–42.
- [19]. G. Zhang, M. Liu, Effect of particle size and dopant on properties of SnO₂-based gas sensors, *Sensor and Actuators B: Chemical*, Vol. 69, Issue 1, 2000, pp. 144–152.
- [20]. C.-T. Wang, M.-T. Chen, Vanadium-promoted tin oxide semiconductor carbon monoxide gas sensors, *Sensor and Actuators B: Chemical*, Vol. 150, Issue 2, 2010, pp. 360–366.
- [21]. P. J. F. Harris, Carbon Nanotubes and Related Structures, *Cambridge University Press*, 1999.
- [22]. M. Endo, S. Iijima, M. S. Dresselhaus, Carbon Nanotubes, *Pergamon Press*, 1996.
- [23]. B. Mahar, C. Laslau, R. Yip, Y. Sun, Development of carbon nanotube-based sensors – A review, *IEEE Sensors J.*, Vol. 7, Issue 2, 2007, pp. 266–284.
- [24]. T. Zhang, S. Mubeen, N. V. Myung, M. A. Deshusses, Recent progress in carbon nanotube-based gas sensors, *Nanotechnology*, Vol. 19, 2008, pp. 1-14, 332001.
- [25]. Ch. Li, E. Thostenson, T.-W. Chou, Sensors and actuators based on carbon nanotubes and their composites: A review, *Compos. Sci. Technol.*, Vol. 68, Issue 7, 2008, pp. 1227–1249.
- [26]. Y. Wang, J. T. W. Yeow, A review of carbon nanotubes- based gas sensors, *J. Sensors*, 2009, 494904.
- [27]. A. Goldoni, L. Petaccia, S. Lizzit, R. Lariciprete, Sensing gases with carbon tubes: a review of the actual situation, *J. Physics: Condensed Matter*, Vol. 22, 2010, 0123001.
- [28]. M. Meyyappan, Carbon Nanotubes: Science and Applications, *CRC Press*, 2005.
- [29]. E. Couteau, K. Hernadi, J. W. Seo, L. Thien-Nga, Cs. Mikó, R. Gál, L. Forró, CVD synthesis of high-purity multiwalled carbon nanotubes using CaCO₃ catalyst support for large-scale production,

- Chemical Physics Letters*, Vol. 378, Issue 1-2, pp. 9-17.
- [30]. A. Magrez, J. W. Seo, R. Smajda, M. Mionić, L. Forró, Catalytic CVD Synthesis of Carbon Nanotubes: Towards High Yield and Low Temperature Growth, *Materials*, Vol. 3, Issue 11, pp. 4871-4891.
- [31]. V. M. Aroutiounian, A. Z. Adamyan, E. A. Khachaturyan, Z. N. Adamyan, K. Hernadi, Z. Pallai, Z. Nemeth, L. Forro, A. Magrez, E. Horvath, Study of the surface-ruthenated SnO₂/MWCNTs nanocomposite thick film gas sensors, *Sensor and Actuators B: Chemical*, Vol. 177, pp. 308-315.
- [32]. V. M. Aroutiounian, Z. N. Adamyan, A. G. Sayunts, E. A. Khachaturyan, A. Z. Adamyan, K. Hernadi, Z. Nemeth, P. Berki, Comparative study of VOC sensors based on ruthenated MWCNT/SnO₂ nanocomposites, *Int. J. Emerging Trends Sci. Technol.*, Vol. 1, 2014, pp. 1309-1319.
- [33]. Z. Nemeth, Z. Pallai, B. Reti, Z. Balogh, O. Berkesi, K. Baan, A. Erdohelyi, E. Horvath, G. Veréb, A. Dombi, L. Forró, K. Hernadi, Synthesis, Comparative Characterization and Photocatalytic Application of SnO₂/MWCNT Nanocomposite Materials, *J. Coating Sci. Technology*, Vol. 1, Issue 2, 2014, pp. 137-150.
- [34]. P. Berki, Z. Nemeth, B. Reti, Berkesi O., V. Aroutiounian, A. Margez, L. Forro, K. Hernadi, Preparation and characterization of multiwalled carbon nanotube/In₂O₃ composites, *Carbon*, Vol. 60, 2013, pp. 266-272.
- [35]. Z. N. Adamyan, A. G. Sayunts, E. A. Khachaturyan, V. M. Aroutiounian, Study of nanocomposite thick-film butanol vapor sensors, *J. Contemporary Physics*, Vol. 51, Issue 2, 2016, pp. 143-149.
- [36]. A. Star, V. Joshi, S. Skarupo, D. Thomas, J. P. Gabriel, Gas sensor array based on metal-decorated carbon nanotubes, *J. Physical Chemistry B*, Vol. 110, Issue 42, 2006, pp. 21014-21020.
- [37]. W. Li, N. D. Hoa, D. Kim, High-performance carbon nanotube hydrogen sensors, *Sensor and Actuators B: Chemical*, Vol. 149, Issue 1, 2010, pp. 184-188.
- [38]. J. Kong, N. R. Franklin, C. Zhou, M. G. Chapline, S. Peng, K. Cho, H. Dai, Nanotube molecular wires as chemical sensors, *Science*, Vol. 287, Issue 5453, 2000, pp. 622-625.
- [39]. V. M. Aroutiounian, V. M. Arakelyan, E. A. Khachaturyan, G. E. Shahnazaryan, M. S. Aleksanyan, L. Forro, A. Magrez, K. Hernadi, Z. Nemeth, Manufacturing and investigations of i-butane sensor made of SnO₂/multiwall-carbon-nanotube nanocomposite, *Sensor and Actuators B: Chemical*, Vol. 173, Issue 3, 2012, pp. 890-896.
- [40]. L. Zhao, L. Gao, Filling of multi-walled carbon nanotubes with tin(IV) oxide, *Carbon*, Vol. 42, Issue 15, 2004, pp. 3251-3272.
- [41]. B.-Y. Wei, M.-C. Hsu, P.-G. Su, H.-M. Lin, R.-J. Wu, H.-J. Lai, A novel SnO₂ gas sensor doped with carbon nanotubes operating at room temperature, *Sensor and Actuators B: Chemical*, Vol. 101, Issue 1-2, 2004, pp. 81-89.
- [42]. A. Wisitsoraat, A. Tuantranont, C. Thanachayanont, V. Patthanasettakul, P. Singjai, Electron beam evaporated carbon nanotubes dispersed SnO₂ thin films gas sensor, *J. Electroceramics*, Vol. 17, Issue 1, 2006, pp. 45-47.
- [43]. S. G. Wang, Q. Zhang, D. J. Yang, P. J. Sellin, G. F. Zhong, Multi-walled carbon nanotube-based gas sensors for NH₃ detection, *Diamond Related Materials*, Vol. 13, Issue 4-8, 2004, pp. 1327-1332.
- [44]. V. V. Krivetskiy, M. N. Rumyantseva, A. M. Gaskov, Chemical modification of nanocrystalline tin dioxide for selective gas sensors, *Russian Chemical Reviews*, Vol. 82, Issue 10, 2013, pp. 917-941.
- [45]. M. Arab, F. Berger, F. Picaud, C. Ramseyer, J. Glory, M. Mayne-L'Hermite, Direct growth of the multi-walled carbon nanotubes as a tool to detect ammonia at room temperature, *Chemical Physics Letters*, Vol. 433, Issue 1-3, 2006, pp. 175-181.
- [46]. E. Bekyarova, M. Davis, T. Burch, M. E. Itkis, B. Zhao, S. Sunshine, R. C. Haddon, Chemically functionalized single-walled carbon nanotubes as ammonia sensors, *J. Physics and Chemistry B*, Vol. 108, Issue 51, 2004, pp. 19717-19720.
- [47]. V. V. Kovalenko, A. A. Zhukova, M. N. Rumyantseva, A. M. Gaskov, V. V. Yushchenko, I. I. Ivanova, T. Pagnier, Surface chemistry of nanocrystalline SnO₂: effect of thermal treatment and additives, *Sensor and Actuators B: Chemical*, Vol. 126, Issue 1, 2006, pp. 52-55.
- [48]. J. Kaur, S. C. Roy, M. C. Bhatnagar, Highly sensitive SnO₂ thin film NO₂ gas sensor operating at low temperature, *Sensor and Actuators B: Chemical*, Vol. 123, Issue 2, 2007, pp. 1090-1095.
- [49]. K.-Y. Choi, J.-S. Park, K.-B. Park, Low power micro-gas sensors using mixed SnO₂ nanoparticles and MWCNTs to detect NO₂, NH₃, and xylene gases for ubiquitous sensor network applications, *Sensor and Actuators B: Chemical*, Vol. 150, Issue 1, 2010, pp. 65-72.
- [50]. V. M. Aroutiounian, V. M. Arakelyan, G. E. Shahnazaryan, M. S. Aleksanyan, K. Hernadi, Z. Nemeth, P. Berki, Z. Papa, Z. Toth, L. Forro, The ethanol sensors made from α -Fe₂O₃ decorated with multiwall carbon nanotubes, *Advance in Nano Research*, Vol. 3, Issue 1, 2015, pp. 1-11.
- [51]. X. Meng, M. Ionescu, M. N. Banis, Y. Zhong, H. Liu, Y. Zhang, S. Sun, R. Li, X. Sun, Heterostructural coaxial nanotubes of CNT@Fe₂O₃ via atomic layer deposition: effects of surface functionalization and nitrogen-doping, *J. of Nanoparticles Research*, Vol. 13, Issue 3, 2010, pp. 1207-1218.
- [52]. Y. Tang, Q. Zhang, Y. Li, H. Wang, Highly selective ammonia sensors based on Co_{1-x}Ni_xFe₂O₄/multi-walled carbon nanotubes nanocomposites, *Sensor and Actuators B: Chemical*, Vol. 169, Issue 1, 2012, pp. 229-234.
- [53]. C.-L. Dai, Y.-C. Chen, C.-C. Wu, C.-F. Kuo, Cobalt oxide nanosheet and CNT micro carbon monoxide sensor integrated with readout circuit on chip, *Sensors*, Vol. 10, Issue 3, 2010, pp. 1753-1764.
- [54]. W. Li, H. Jung, N. D. Hoa, D. Kim, S.-K. Hong, H. Kim, Nanocomposite of cobalt oxide nanocrystals and single-walled carbon nanotubes for a gas sensor application, *Sensor and Actuators B: Chemical*, Vol. 150, Issue 1, 2010, pp. 160-166.
- [55]. M. Parmar, R. Bhati, V. Prasad, K. Rajann, Ethanol sensing using CuO/MWNT thin film, *Sensor and Actuators B: Chemical*, Vol. 158, Issue 1, 2011, pp. 229-234.
- [56]. C. Wongchoosuk, A. Wisitsoraat, D. Phokharatkul, A. Tuantranont, T. Kerdcharoen, Multi-walled carbon nanotube-doped tungsten oxide thin films for hydrogen gas sensing, *Sensors*, Vol. 10, Issue 8, 2010, pp. 7705-7715.

- [57]. A. Bittencourt, Felten, E.H. Espinosa, R. Ionescu, E. Llobet, X. Correig, J.-J. Pireaux, WO₃ films modified with functionalized multi-wall carbon nanotubes: morphological, composition and gas response studies, *Sensor and Actuators B: Chemical*, Vol. 115, Issue 1, 2006, pp. 33–41.
- [58]. N. V. Hieu, L. T. B. Thuy, N. D. Chien, Highly sensitive thin film NH₃ gas sensor operating at room temperature based on SnO₂/MWCNTs composite, *Sensor and Actuators B: Chemical*, Vol. 129, Issue 2, 2008, pp. 888–895.
- [59]. R. Leghrib, A. Felten, J. J. Pireaux, E. L. Llobet, Gas sensors based on doped-CNT/SnO₂ composites for NO₂ detection at room temperature, *Thin Solid Films*, Vol. 520, Issue 3, 2011, pp. 966–970.
- [60]. Y. Chen, C. Zhu, T. Wang, The enhanced ethanol sensing properties of multi-walled carbon nanotubes/SnO₂ core/shell nanostructures, *Nanotechnology*, Vol. 17, Issue 12, 2006, pp. 3012–3017.
- [61]. J. Prasek, J. Drbohlavova, J. Chomoucka, J. Hubalek, O. Jasek, V. Adam, R. Kizek, Methods for carbon nanotubes synthesis—review, in *Carbon Nanotubes*, A. K. Mishra, Nova Science Publishers, Ch. 6, 2013, pp. 87–106.
- [62]. R. Leghrib, R. Pavelko, A. Felten, A. Vasiliev, Gas sensors based on multiwall carbon nanotubes decorated with tin oxide nanoclusters, *Sensor and Actuators B: Chemical*, Vol. 145, Issue 1, 2010, pp. 411–416.
- [63]. L. Zhao, M. Choi, H. S. Kim, S. H. Hong, The effect of multiwalled carbon nanotube doping on the CO gas sensitivity of SnO₂-based nanomaterials, *Nanotechnology*, Vol. 18, Issue 44, 2007, 445501.
- [64]. A. Yang, X. M. Tao, R. X. Wang, S. C. Lee, C. Surya, Room temperature gas sensing properties of SnO₂/multiwall-carbon-nanotube composite nanofibers, *Applied Physics Letters*, Vol. 91, Issue 13, 2007, pp. 133110-1 – 133110-3.
- [65]. G. Lu, L. E. Ocola, J. Chen, Room-temperature gas sensing based on electron transfer between discrete tin oxide nanocrystals and multiwalled carbon nanotubes, *Advances Materials*, Vol. 21, Issue 24, 2009, pp. 2487–2491.
- [66]. S. B. Naghadeh, S. Vahdatifar, Y. Mortazavib, A. A. Khodadadib, A. Abbasi, Functionalized MWCNTs effects on dramatic enhancement of MWCNTs/SnO₂ nanocomposite gas sensing properties at low temperatures, *Sensor and Actuators B: Chemical*, Vol. 223, 2016, pp. 252–260.
- [67]. R.-J. Wu, J.-G. Wu, M.-R. Yu, T.-K. Tsai, C.-T. Yeh, Promotive effect of CNT on Co₃O₄-SnO₂ in a semiconductor-type CO sensor working at room temperature, *Sensor and Actuators B: Chemical*, Vol. 131, Issue 1, 2008, pp. 306–312.
- [68]. B. Chaitongrat, S. Chaisitsak, Fast-LPG Sensors at Room Temperature by α -Fe₂O₃/CNT Nanocomposite Thin Films, *Journal of Nanomaterials*, Vol. 2018, Article ID 9236450.
- [69]. S. Trocino, A. Donato, M. Latino, N. Donato, S. G. Leonardi, G. Neri, Pt-TiO₂/MWCNTs Hybrid Composites for Monitoring Low Hydrogen Concentrations in Air, *Sensors*, Vol. 12, Issue 9, 2012, pp. 12361–12373.
- [70]. W. T. Hess, Hydrogen Peroxide, in *Kirk-Othmer Encyclopedia of Chemical Technology*, 4th Ed., Wiley, New York, Vol. 13, 1995, pp. 961–995.
- [71]. I. Taizo, A. Sinichi, K. Kawamura, Application of a newly developed hydrogen peroxide vapor phase sensor to HPV sterilizer, *PDA Journal of Pharmaceutical Science and Technology*, Vol. 52, Issue 1, 1998, pp. 13–18.
- [72]. F. Dubnikova, R. Kosloff, J. Almog, Y. Zeiri, B. R. Itzhaky, H. A. Alt, E. Keinan, Decomposition of Triacetone Triperoxide is an Entropic Explosion, *Journal of American Chemistry Society*, Vol. 127, Issue 4, 2005, pp. 1146–1159.
- [73]. S. Banerjee, S. K. Mohapatra, M. Misra, I. B. Mishra, The detection of improvised nonmilitary peroxide based explosives using a titania nanotube array sensor, *Nanotechnology*, Vol. 20, Issue 7, 2009, pp. 075502–07667.
- [74]. W. Xu, Y. Fu, Y. Gao, J. Yao, T. Fan, D. Zhu, Q. He, H. Cao, J. Cheng, A simple but highly efficient multi-formylphenol-amine system for fluorescence detection, of peroxide explosive vapour, *Chemical Communications*, Vol. 51, 2015, pp. 10868–10870.
- [75]. S. Reisert, B. Schneider, H. Geissler, M. van Gompel, P. Wagner, M. J. Schöning, Multi-sensor chip for the investigation of different types of metal oxides for the detection of H₂O₂ in the ppm range, *Physica Status Solidi A*, Vol. 210, Issue 5, 2013, pp. 898–904.
- [76]. M. A. Lefebvre, W. J. Meulingb, R. Engel, M. C. Coroamă, G. Rennerc, W. Pape, G. J. Nohynek, Consumer inhalation exposure to formaldehyde from the use of personal care products/cosmetics, *Regulation in Toxicology Pharmacology*, Vol. 63, Issue 1, 2012, pp. 171–176.
- [77]. A. Fiorito, F. Larese, S. Molinari, T. Zanin, Liver function alterations in synthetic leather workers exposed to dimethylformamide, *American J. Ind. Medicine*, Vol. 32, Issue 3, 1997, pp. 255–260.
- [78]. G. Malaguarnera, E. Cataudella, M. Giordano, G. Nunnari, G. Chisari, M. Malaguarnera, Toxic hepatitis in occupational exposure to solvents, *World J. Gastroentero*, Vol. 18, Issue 22, 2012, pp. 2756–2766.
- [79]. H. Y. Chang, T. S. Shih, Y. L. Guo, C. Y. Tsai, P. C. Hsu, Sperm function in workers exposed to N, N-dimethylformamide in the synthetic leather industry, *Fertility and Sterility*, Vol. 81, Issue 6, 2004, pp. 1589–1594.
- [80]. O. H. Robertson, C. G. Loosli, T. T. Puck, Test for chronic toxicity of propylene glycol and triethylene glycol on monkeys and rats by vapor inhalation and oral administration, *J. Pharmacology: Experiment and Theory*, Vol. 91, Issue 1, 1947, pp. 52–76.
- [81]. T. Salthammer, S. Mentese, R. Marutzky, Formaldehyde in the indoor environment, *Chemical Review*, Vol. 110, Issue 4, 2010, pp. 2536–2572.
- [82]. M. J. Ellenhorn, S. Schonwald, G. Ordog, J. Wasserberger, Ellenhorn's medical toxicology: diagnosis and treatment of human poisoning, 2nd Ed., *Williams & Wilkins*, 1997.
- [83]. G. F. Fine, L. M. Cavanagh, A. Afonja, R. Binions, Metal oxide semi-conductor gas sensors in environmental monitoring, *Sensors*, Vol. 10, Issue 6, 2010, pp. 5469–5502.
- [84]. G. Korotcenkov, S. H. Han, B. K. Cho, Material design for metal oxide chemiresistive gas sensors, *J. Sensor Sci. Technol.*, Vol. 22, Issue 1, 2013, pp. 1–17.
- [85]. W. Y. Chuang, S. Y. Yang, W. J. Wu, C. T. Lin, A Room-Temperature Operation Formaldehyde Sensing Material Printed Using Blends of Reduced

- Graphene Oxide and Polymethyl methacrylate, *Sensors*, Vol. 1, Issue 2, 2015, pp. 512-531.
- [86]. J. Flueckiger, F. K. Ko, K. C. Cheung, Microfabricated Formaldehyde Gas Sensors, *Sensors*, Vol. 9, Issue 11, 2009, pp. 9196-9215.
- [87]. C. Xu, J. Tamaki, N. Miura, N. Yamazoe, Grain size effects on gas sensitivity of porous SnO₂-based elements, *Sensor and Actuators B: Chemical*, Vol. 3, Issue 2, 1991, pp. 147-155.
- [88]. K. H. Park, D. S. Lee, A ppb-level formaldehyde gas sensor based on CuO nanocubes prepared using a polyol process, *Sensor and Actuators B: Chemical*, Vol. 203, Issue 1, 2014, pp. 282-288.
- [89]. F. C. Chung, R. J. Wu, F. C. Cheng, Fabrication of an Au@SnO₂ core-shell structure for gaseous formaldehyde sensing at room temperature, *Sensor and Actuators B: Chemical*, Vol. 190, Issue 1, 2014, pp. 1-7.
- [90]. X. Li, J. Wang, S. Lin, Highly sensitive and selective room-temperature formaldehyde sensors using hollow TiO₂ microspheres, *Sensor and Actuators B: Chemical*, Vol. 219, Issue 1, 2015, pp. 158-163.
- [91]. M. M. Arafat, B. Dinan, S. A. Akbar, A. S. Haseeb, Gas sensors based on one dimensional nanostructured metal-oxides: A Review, *Sensors*, Vol. 12, Issue 6, 2012, pp. 7207-7258.
- [92]. G. Korotcenkov, S. D. Han, B. K. Cho, V. Brinzari, Grain size effects in sensor response of nanostructured SnO₂ and In₂O₃- based conductometric thin film gas sensor, *Critical Review Solid State*, Vol. 34, Issue 1, 2009, pp. 1-17.
- [93]. S. A. Feyzabad, A. A. Khodadadia, M. V. Naseh, Y. Mortazavi, Highly sensitive and selective sensors to volatile organic compounds using MWCNTs/SnO₂, *Sensor and Actuators B: Chemical*, Vol. 166-167, Issue 1, 2012, pp. 150-155.
- [94]. N. V. Hieu, L. T. Thuy, N. D. Chien, Highly sensitive thin film NH₃ gas sensor operating at room temperature based on SnO₂/MWCNTs composite, *Sensor and Actuators B: Chemical*, Vol. 129, Issue 2, 2008, pp. 888-895.
- [95]. V. M. Aroutiounian, Metal oxide hydrogen, oxygen and carbon monoxide sensors for hydrogen setups and cells, *Int. J. Hydrogen Energy*, Vol. 32, Issue 9, 2007, pp. 1145-1158.
- [96]. P. Shankar, J. Bosco B. Rayappan, Gas sensing mechanism of metal oxides: The role of ambient atmosphere, type of semiconductor and gases-A review, *ScienceJet*, Vol. 4, Issue 126, 2017, pp. 1-17.
- [97]. A. Z. Adamyan, Z. N. Adamyan, V. M. Aroutiounian, Preparation of SnO₂ films with thermally stable nanoparticles, *Sensors*, Vol. 3, Issue 10, 2003, pp. 438-442.
- [98]. J. R. Walter, G. McClure, P. W. Brown, K. G. Galuk, An investigation of the degradation of aqueous ethylene glycol and propylene glycol solutions using ion chromatography, *Solar Energy Materials*, Vol. 11, Issue 5-6, 1985, pp. 455-467.
- [99]. R. P. Jensen, W. Luo, J. F. Pankow, R. M. Strongin, D. H. Peyton, Hidden Formaldehyde in E-Cigarette Aerosols, *New English J. Medicine*, Vol. 372, Issue 4, 2015, pp. 392-394.
- [100]. G. Ertl, J. Tornau, The catalytic decomposition of formaldehyde on palladium, *Zeitschrift fur Physics and Chemistry*, Vol. 104, Issue 4-6, 1977, pp. 301-308.
- [101]. M. A. Vannice, The catalytic synthesis of hydrocarbons from H₂CO mixtures over the group VIII metals: II. The kinetics of the methanation reaction over supported metals, *J. Catalysis*, Vol. 37, Issue 3, 1975, pp. 462-473.
- [102]. T. Borowiecki, J. Barcicki, Selectivity of the steam reforming of methane over metallic catalysts, *Reactions and Kinetics Catalysis Letters*, Vol. 12, Issue 1, 1979, pp. 101-106.
- [103]. V. M. Vlasenko, G. E. Yuzefovich, Mechanism of the Catalytic Hydrogenation of Oxides of Carbon to Methane, *Russian Chemistry Review*, Vol. 38, Issue 9, 1969, pp. 728-739.
- [104]. Z. Adamyan, A. Sayunts, V. Aroutiounian, E. Khachatryan, A. Adamyan, M. Vrnata, P. Fitl, J. Vlček, Study of propylene glycol and dimethylformamide vapors sensors based on MWCNTs/SnO₂ nanocomposites, in *Proceedings of the Second International Conference on Advances in Sensors, Actuators, Metering and Sensing (ALLSENSORS)*, 2017, Nice, pp. 44-49.
- [105]. H. Zakaryan, V. Aroutiounian, CO Gas Adsorption on SnO₂ Surfaces: Density Functional Theory Study, *Sensors & Transducers*, Vol. 212, Issue 5, 2017, pp. 50-56.

