

Nanostructured semiconducting metal oxide gas sensors for acetaldehyde detection

Ali Mirzaei^{a*}, Hyoun Woo Kim^{b,c, **}, Sang Sub Kim^{d, *}, Giovanni Neri^{e****}**

^a Department of Materials Science and Engineering, Shiraz University of Technology, Shiraz 71557-13876, Iran

^b The Research Institute of Industrial Science, Hanyang University, Seoul 04763, Republic of Korea

^c Division of Materials Science and Engineering, Hanyang University, Seoul 04763, Republic of Korea

^d Department of Materials Science and Engineering, Inha University, Incheon 22212, Republic of Korea

^e Department of Engineering, University of Messina, Messina, 98166, Italy

Correspondences: Ali Mirzaei (mirzaei@sutech.ac.ir), Hyoun Woo Kim** (hyounwoo@hanyang.ac.kr), Sang Sub Kim** (sangsub@inha.ac.kr), Giovanni Neri**** (gneri@unime.it)

Abstract: Volatile organic compounds (VOCs) are among the most abundant air pollutants. Their high concentrations can adversely affect the human body and therefore, early detection of VOCs is of outmost importance. Among the different VOCs, in this review paper, we have focused our attention on the monitoring of acetaldehyde by chemiresistive gas sensors using nanostructured semiconducting metal oxides. These sensors not only can provide a high sensing signal for detection of acetaldehyde, but also high thermal and mechanical stability and low price. This review paper is divided into three major sections. First, we will introduce acetaldehyde as the target gas and importance of its detection. Then, the fundamentals of chemiresistive gas sensors will be briefly presented and, in the last section, a survey of literature on acetaldehyde gas sensors will be discussed. Acetaldehyde sensors working mechanism, their structures and configurations are reviewed. Finally, the future development outlook and potential applications are discussed, giving a complete panoramic view for researcher working and interested in acetaldehyde detection for different purposes in many fundamentals and applicative fields.

Keywords: Acetaldehyde; Chemiresistive gas sensor, Nanostructured metal oxide, Sensing mechanism.

1. Introduction

By definition, volatile organic compounds (VOCs) are organic compounds with a low boiling point, (50-100 °C to 240-260 °C), with saturation vapor pressures higher than 102 kPa at 25 °C [1]. They are air pollutants and mostly are emitted from industrial factories and vehicles. They accelerate the formation of secondary organic aerosols and under oxidized conditions will convert them to particles [2]. Accordingly, they cause different environmental issues and also have detrimental effects on the humans` health [3].

Aldehydes are a class of VOCs which are highly reactive and odorous. They are one of the most common source of pollution in air, because they are not only used in many chemical adhesives but also are produced in many industrial processes or incomplete combustions [4]. Formaldehyde (HCHO) and acetaldehyde (CH₃CHO) are considered two of the most important aldehydes [5] [6]. They are known as carcinogenic and probably carcinogenic agents, respectively [7] [8].

Acetaldehyde, with systematic name of ethanal [9], is a small molecule with low molecular weight as shown in Fig. 1. It has an aroma like orange, low boiling point (20.2°C) with solubility in water and lipids [10]. The indoor sources of acetaldehyde include laminate, building materials, wood ceilings, wooden varnished, etc., and the outdoor sources include power plants wood, trash, oil and gas extraction, cement kilns, refineries, and automobile exhausts [11]. It is also the most abundant carcinogen of tobacco smoke [12].

Acetaldehyde is widely employed to produce acetic acid, acetate esters, pentaerythritol, and pyridine bases [13]. In addition, it is used in dairy industry as synthetic flavoring component and food additive [14].

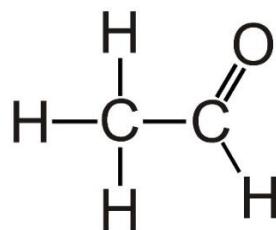


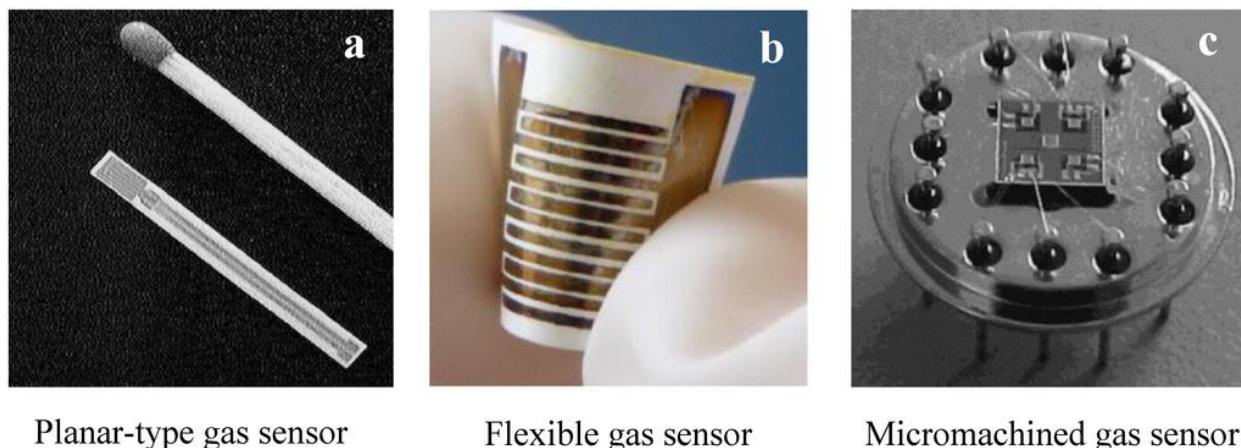
Fig. 1. Structure of acetaldehyde.

Acetaldehyde is a highly toxic compound [15]. The effects of acetaldehyde on the human body include eye irritation, headache, vomiting, liver diseases and detrimental effects on throat, skin, and the respiratory tract [16] [17] [18]. In particular, because of its pungent odor, it is extremely irritating at concentrations above 50 ppm [11]. Also, it can be a cause of “sick building syndrome (SBS)”, even in ppb level [19] [20]. Acetaldehyde has a strong electrophilic nature and can damage DNA in humans and is considered as a possible human carcinogen [21] [22]. Furthermore, it can easily react with Vitamin B1, leading to B1 deficiency. Accordingly, it can cause mental illness, visual disturbances and poor memory. A 100 ppm as a permissible exposure limit of acetaldehyde has been proposed for exposure to acetaldehyde [23].

2. Chemiresistive gas sensors

Nowadays gas sensors are widely utilized in different areas including public safety, industrial processes, domestic safety, underground mining, monitoring of environmental pollution and air quality in vehicles [24]. So far different types of gas sensors such as surface acoustic wave [25], optical [26], gasochromic [27], thermoelectric [28], electrochemical [29] and chemiresistive [30] [31] [32], gas sensors for detection of VOCs have been introduced. Among them, chemiresistive gas sensors are very popular owing to their high sensitivity, short response time, high stability, simple fabrication and operation and low costs [33] [34] [35]. Chemiresistive gas sensors were introduced for the first time about sixty years ago [36], in which the resistance of the sensing layer changes upon exposure to the target gas. Depending on the increase or decrease of the resistance and also amount of the resistance, gas concentration can be estimated [37] [38]. In chemiresistive gas sensors, surface area, morphology, chemical composition and sensing temperature are the main factors affecting the gas response [39] [40] [39].

A typical resistive-based gas sensor consists of a sensitive layer which is deposited on the surface of interdigitated electrodes (Fig. 2) printed on an (a) insulating ceramic, (b) plastics or (c) Si substrate [41]. A heater can be also used on the back of the substrate to rise the sensor temperature up to desired sensing temperature. However, in some cases, the sensor will be put in a gas chamber in a tubular furnace, where the temperature can be nicely controlled [42].



Planar-type gas sensor

Flexible gas sensor

Micromachined gas sensor

Fig. 2. Chemoresistive gas sensors with different configurations. Reprinted with permission from [36].

Fig. 3 schematically shows acetaldehyde sensing mechanism on both n- or p-type metal oxide chemiresistive sensors. For n-type ones such as ZnO , SnO_2 , initially in air, due to abstraction of the electrons by oxygen species, a so called electron depletion layer will be created on its surface. Because this, the resistance in this region is higher than that of the core-region of the sensing material (Fig. 3 (a) and (b)). Upon exposure to acetaldehyde gas, it reacts with already adsorbed oxygen ions and the released electrons come back to the surface of the gas sensor. As a result, the resistance of the gas sensor increases, leading to appearance of a sensing signal. For p-type metal oxides, such as CuO , initially in air, due to extraction of the electrons by oxygen species hole accumulation layer will be appeared on the surface of the gas sensor (Fig. 3 (c) and (d)). Since in p-type metal oxides the main charge carrier are the holes, the resistance in hole accumulation layer is lower than the core part. In acetaldehyde atmosphere, the released electrons come back to the surface of the gas sensor, leading to higher resistance of gas sensor and appearance of a sensing signal.

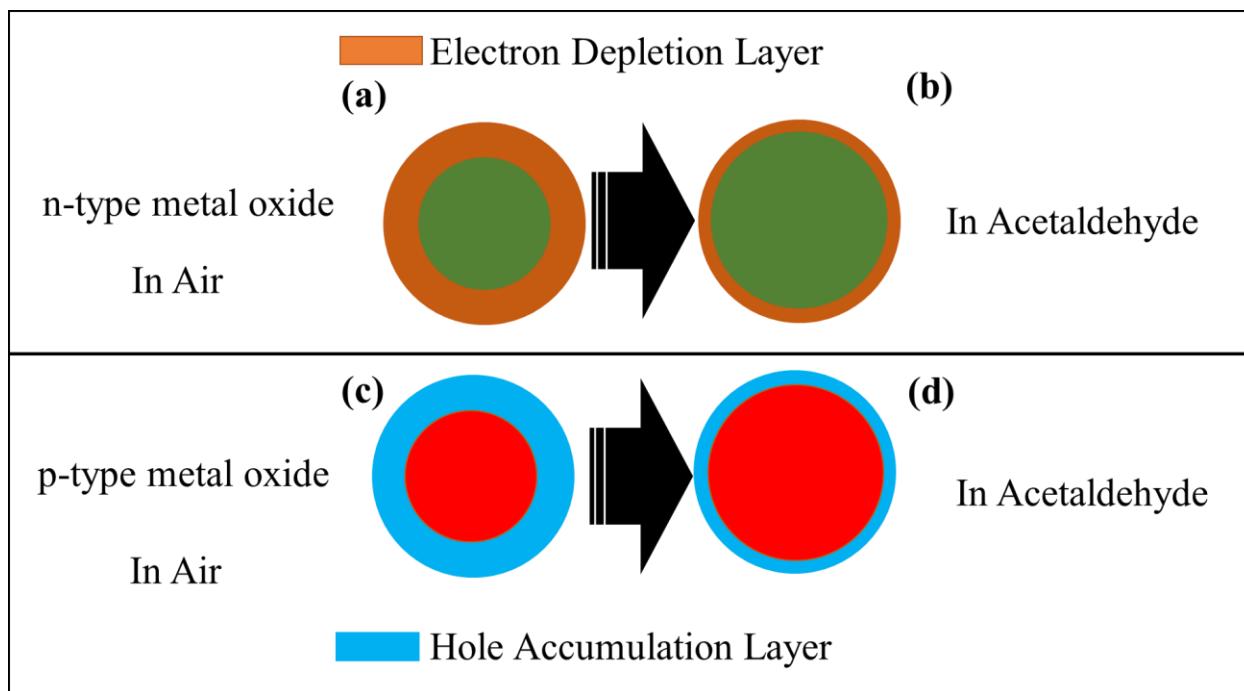


Fig. 3. Schematic of acetaldehyde sensing mechanism in (a) n-type metal oxide (b) p-type metal oxide.

3. Acetaldehyde detection on chemiresistive-based gas sensors

Traditional strategies to determine the concentration of acetaldehyde are use of gas chromatography, chemiluminescence, cataluminescence, etc. [43]. Even though such techniques are sensitive and accurate, they have some disadvantages for online monitoring, need expert operators and are bulky and expensive. Therefore, stable, fast, portable and simple operation sensors are highly needed for acetaldehyde detection [44] [45]. In the remaining parts of this paper we will discuss the chemiresistive acetaldehyde gas sensors on the basis of the metal oxides used as sensing material.

3.1 Zinc oxide-based acetaldehyde sensors

Zinc oxide (ZnO) is one of the most used sensing materials [34] [46] [47]. Morphology engineering is one of the best strategies to improve the sensing capabilities of metal oxide gas sensors [48] [49]. Accordingly, so far different morphologies of ZnO have been used for gas sensing studies. Different typologies ZnO nanostructures such as nanoparticles (NPs), tetrapods, nanobeads and nanotubes are shown in Fig. 4.

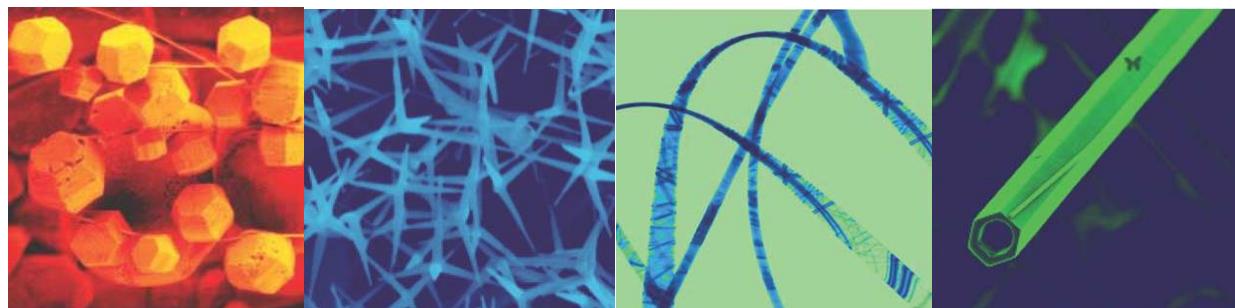


Fig. 4. Example of some typical ZnO morphologies. From right to left: nanoparticles, tetrapods, nanobeads and nanotubes. Adapted from [48].

For example, ZnO tetrapods with nanosized dimensions were synthesized for aldehydes detection [4]. The dynamic responses were obtained at different temperatures, showing that response/recovery times decrease when the temperature increases. The related calibration curves at different concentrations of acetaldehyde were also reported. At 400°C, the sensor revealed a higher response to propionaldehyde ($\text{CH}_3\text{CH}_2\text{CHO}$) compared to acetaldehyde. The higher response to propionaldehyde was due to the higher number of electrons return back to the ZnO, when the molecule was completely oxidized [4]:



As shown in above equations, the reaction of acetaldehyde and propionaldehyde with adsorbed electrons release 5 and 8 electrons, respectively. Accordingly, the response to acetaldehyde was slightly lower than the response to propionaldehyde. Interestingly, it was found that at $T > 350^\circ\text{C}$, the response was independent of the relative humidity (RH) value (0-75%).

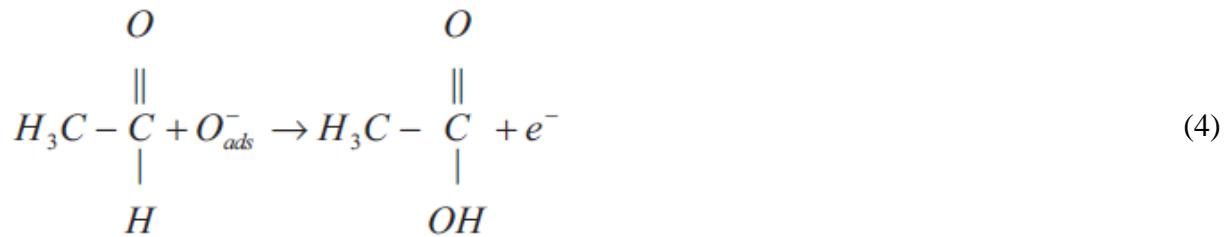
Also, the response of the sensor to ethanol was lower than that of acetaldehyde. It is well-known that aldehydes are intermediate products of alcohol oxidation, but often the kinetics of the first reaction is slow. For ethanol, a higher response than to acetaldehyde is expected. This is due to the fact that the reaction (3) is added to reaction (1) and a larger number of the released electrons are expected:



However, ethanol response was lower, because reaction (3) has a slow kinetics [4].

In this regards, flower-like ZnO nanostructures comprising of ZnO nanorods were fabricated through a hydrothermal synthesis method [50]. The high response the gas sensor to ethanol and acetaldehyde compared to CO gas was related to the electron donating effect of ethanol and acetaldehyde (10 electrons) which was higher than that of the CO gas (2 electrons). In another study, a fast acetaldehyde gas sensor was introduced using nanosheet-like ZnO nanostructures synthesized through a sonochemical method followed by subsequent etching [51]. The ZnO nanosheets had a high surface area, resulting in an enhanced sensing performance down to ppb level. At the optimal sensing temperature of 220°C, the sensor was able to detect even 50 ppb of acetaldehyde gas. Furthermore, the sensor revealed a linear response to acetaldehyde along with fast response and recovery times. The response and recovery times of the sensor to acetaldehyde was 8 and 60 s, respectively, which are so fast for practical applications. In fact, the presence of abundant channels and open space between the ZnO nanosheets accelerated the gas diffusion and decreased the response and recovery times.

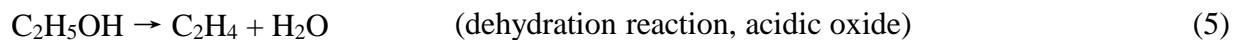
Generally, metal oxide NPs can be easily synthesized through different chemical synthesis methods. Accordingly, there are many literature regarding use of metal oxide NPs as gas sensors. For example, ZnO NPs-based gas sensor working at 450°C, revealed a response of 5.73 to only 2 ppm acetaldehyde. The high response of the gas sensor was attributed to the complete oxidation of acetaldehyde catalyzed by the surface, where with reaction with adsorbed oxygen, acetaldehyde transformed into acetic acid [11]:



In the humid condition, a decrease in the sensor response was resulted, due to the competition between water vapor and acetaldehyde. As a results, the number of available sites for acetaldehyde

adsorption were decreased. Also, the increase in RH led to decrease of the adsorbed oxygen species and accordingly, the conductivity was increased in humid air. Therefore, the baseline resistance decreased to a lower resistance for higher RH values [52].

Rai and Yu synthesized ZnO NPs by a citrate-assisted hydrothermal method for gas sensor studies [53]. The maximum response of the fabricated sensor was 45.75 at 400°C for 250 ppm of acetaldehyde gas. However, the selectivity of the sensor was not so good because it also revealed a high response to ethanol. The high response of the gas sensor to ethanol and acetaldehyde relative to CO gas was related to the electron-donating effects of target gases. Since the electron donating effect of ethanol and acetaldehyde (10 electrons) was higher than the CO gas (2 electrons), accordingly, a lower response to CO gas was obtained. In case of ethanol both dehydration and dehydrogenation reactions are possible as follows [53]:



Ethylene (C₂H₄) or acetaldehyde (CH₃CHO) intermediates are subsequently oxidized to CO, CO₂ and H₂O as follows [53]:



Since the ZnO has a basic nature, consequently the dehydrogenation reaction is preferred on the surface of ZnO and the number of the released electrons are comparable with those of acetaldehyde. Consequently, the higher response of acetaldehyde relative to ethanol was related to the long chain of reaction for ethanol gas which had a slow kinetic nature [53].

In another study, randomly interconnected ZnO NPs were prepared using a simple chemical spray pyrolysis method [47]. The sensor revealed a response of 50 to 50 ppm acetaldehyde gas with the response and recovery times of 60 and 40 s, respectively. Furthermore, the sensor showed a high selectivity to acetaldehyde relative to the interfering gases. This was related to the low bond dissociation energy for acetaldehyde (364 kJ mol⁻¹), which was smaller than those of other gases, resulting in a good gas selectivity. Even though the bond dissociation energy of formaldehyde was comparable with that of acetaldehyde, a lower response to formaldehyde was obtained. This was

related to the electron donating effects, where the number of electrons released during the reduction of acetaldehyde was more than that of formaldehyde [52]. In an interesting study, cotton fabrics were also used as gas sensors. Untreated and nanostructured ZnO added cotton fabrics were used to sense 100 ppm of acetaldehyde, ethanol and NH₃ at 25°C [54]. An improved acetaldehyde response was obtained for ZnO modified cotton fabric owing to the homogeneous distribution of ZnO NPs and the presence of high porosities between the inter-yarn pore.

UV light can be used to decrease the power consumption of the gas sensors [55]. In this regards, a ZnO NPs (50-70 nm)-based gas sensor was realized and used for acetaldehyde detection under UV light irradiation [56]. The sensor under UV light was able to detect 50 ppb acetaldehyde gas. Since acetaldehyde even at low concentrations is considered a carcinogenic agent, the developed sensor could be used for practical application of acetaldehyde detection with low power consumption [56].

Effects of noble metals on the acetaldehyde response of ZnO NPs were also studied. ZnO NPs (30-40 nm) metals were fabricated by using a chemical precipitation method, and subsequently were loaded with Rh, Mg, Y, Pd, V or La by impregnation method [57]. Among the different noble metal loaded gas sensors, the response of the Ru-ZnO sensor was higher to alcohol and acetaldehyde than to the other gases. Interestingly, it was found that the greater the response to acetaldehyde was, the higher the response to alcohol was. In addition, the response was higher toward acetaldehyde than to alcohol at all tested temperatures. Therefore, it was concluded that the presence of acetaldehyde favored the response to alcohol. To gain further insight, the catalytic oxidation of alcohol over ZnO NPs was studied in a reactor, and the reaction products were studied by gas chromatography technique. The response of the ZnO sensor to ethanol was dependent on the conversion of ethanol to intermediate products and acetaldehyde which was one of the intermediate products, increased the response to alcohol [57].

Not only loading of noble metals, but also doping can affect the sensing response to acetaldehyde. In this regards, Al-doped ZnO NPs were produced through a hydrothermal method for gas sensing application [58]. The sensing response ($R = 2250$) to 10 ppm acetaldehyde at 500°C was ~173 and 125 times higher than those of C₇H₈ and C₆H₆, respectively. Selectivity pattern of the sensor to different interfering gases, demonstrated the highest response of the gas sensor to acetaldehyde (Fig. 5). This was related to the larger dipole moment in the molecular structure of acetaldehyde

(2.7 D) than that in NO (0.16 D), NO₂ (0.32 D), TMA (0.61 D), benzene (0 D), NH₃ (1.47 D), toluene (0.31 D) and CO (0.122 D). The dipole moment of a gas molecule affects the attractive Van der Waals force between the target gas molecule and sensing layer [58]. Thus, the number of molecules of acetaldehyde that adsorbed on the surface of the gas sensor was more than those of other gases.

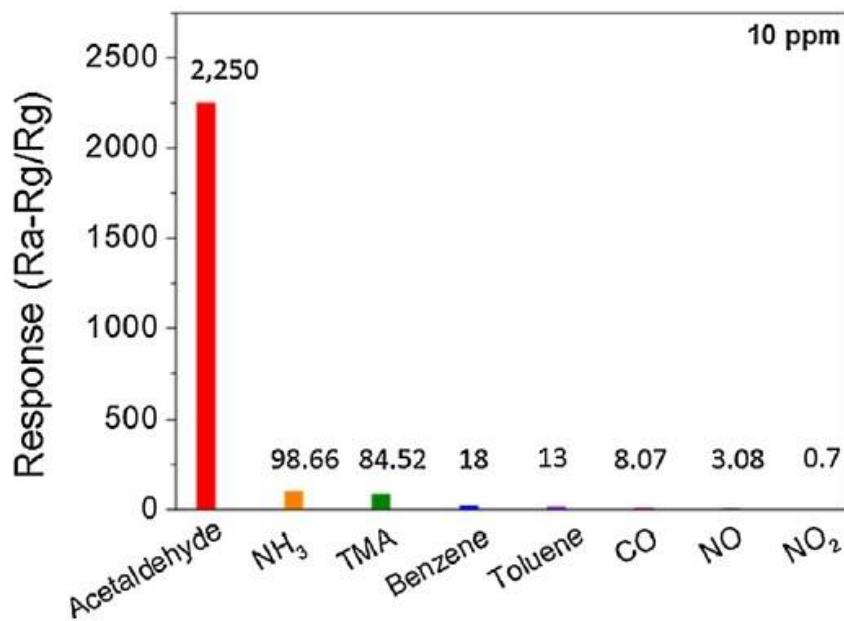


Fig. 5. Selectivity pattern of the Al-doped ZnO gas sensor to different gases. Reprinted with permission from [58].

When Al-doped ZnO NPs were in air (Fig. 6(a)), oxygen ions were adsorbed on the surface of the gas sensor, resulting in formation of a thick depletion layer on the surface of ZnO NPs. In acetaldehyde atmosphere (Fig. 6(b)), an electron exchange occurred owing to the interaction of acetaldehyde and the adsorbed oxygen species, resulting in the oxidation of acetaldehyde and the release of electrons into the sensor surface. Thus, the electrical resistance decreased. The response of the Al-doped ZnO NPs was 16 times higher than that in pristine ZnO NPs to acetaldehyde. The reasons for high response of Al-doped sensor were as follows: Firstly, the amount of oxygen vacancies which acted as adsorption sites for acetaldehyde on the surface of the ZnO NPs in the lattice of ZnO was found to increase after Al doping (Fig. 6(c)). Secondly, due to the presence of

additional carriers in Al-doped ZnO NPs and the shift of the Fermi level, the band gas was larger than that of pristine ZnO NPs. Increase of carrier concentration led to increase of ionized oxygen species on the surface of ZnO which reacted with acetaldehyde. Thirdly, the surface area of the Al-doped ZnO NPs (~ 42 m^2/g) was larger than that of the pristine ZnO NPs (~ 35 m^2/g). Accordingly, much more acetaldehyde molecules were adsorbed, resulting in a higher gas response in Al-doped ZnO gas sensor [58].

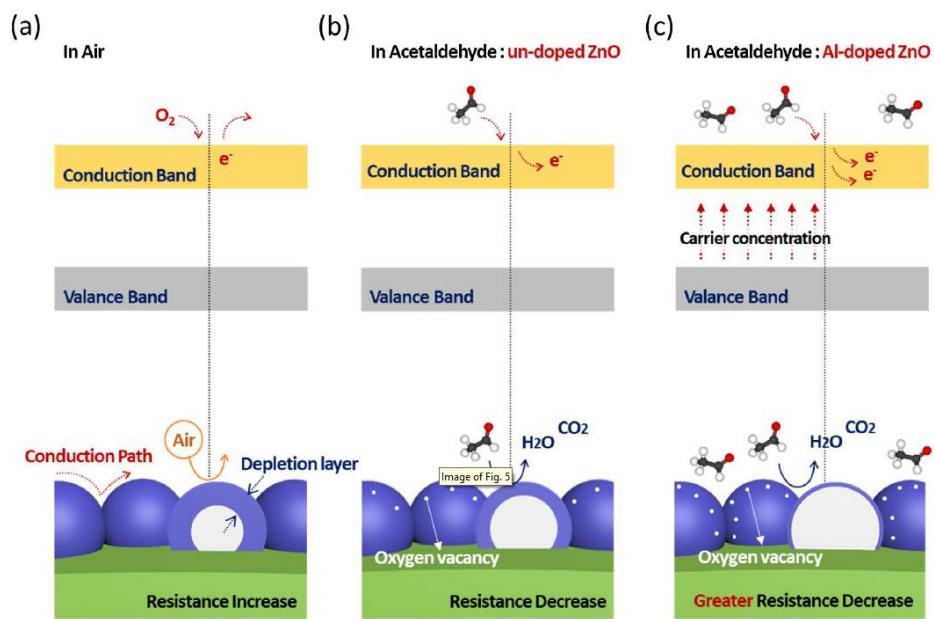


Fig. 6. The sensing mechanism in (a) pristine or Al-doped ZnO NPs in air, (b) pristine ZnO NPs and (c) Al-doped ZnO NPs in acetaldehyde atmosphere. Reprinted with permission from [58].

The p-type dopants (Cr, Co, Ni and Cu) have good potential for oxygen adsorption as well as good catalytic activity to VOCs[59] [60] [61]. In an interesting study, pristine and Co, Ni, Cu-doped ZnO nanostructures were realized by a chemical spray pyrolysis method [23]. The sensing response to 10 ppm acetaldehyde was 2.85, 800, 2.59 and 21.36 for the pristine, Co, Ni and Cu-doped ZnO-based sensors, respectively. The high response to acetaldehyde was due to the lower bond dissociation energy of acetaldehyde ($364 \text{ kJ}\cdot\text{mol}^{-1}$) than other gases and vapors such as ammonia ($435 \text{ kJ}\cdot\text{mol}^{-1}$), ethanol ($436 \text{ kJ}\cdot\text{mol}^{-1}$), methanol ($436.8 \text{ kJ}\cdot\text{mol}^{-1}$), formaldehyde ($364 \text{ kJ}\cdot\text{mol}^{-1}$) and toluene ($368 \text{ kJ}\cdot\text{mol}^{-1}$). The low response of Ni-doped sensor was due to morphology of this sensor which was different than other sensors. On the other hand, Co-doped

sensor showed the highest response to acetaldehyde due to its high catalytic activity to this gas. In addition, the initial resistance of pristine, Ni and Cu-doped ZnO sensors were lower than Co-doped ZnO gas sensor. Since the less number of electrons present on the surface of Co-doped ZnO sensor than the other sensors, the change in the width of the electron depletion layer during the exposure to acetaldehyde was higher than the other sensors [23].

Fluorine is a highly electronegative elements, and it can reduce the resistance of the sensing layer. Fluorine-doped ZnO film was produced using chemical spray pyrolysis technique [62]. At room temperature, it revealed a response of 4.8 to 100 ppm acetaldehyde gas. Also, the response increased with increasing of the fluorine dopant due to decrease of the grain size. With an increase in fluorine dopant, grain size was decreased and the higher surface area along with porous nature of the sensing layer led to an enhanced response to acetaldehyde.

In the end on this section, we present some ZnO-based sensors reported for sensing of acetaldehyde in the literature (Table 1). As it can be seen, ZnO based sensors with different morphologies are able to detect low and high concentrations of acetaldehyde gas at different sensing temperatures.

Table 1. Acetaldehyde sensors based on ZnO nanostructures.

Morphology	Concentration (ppm)	Operating temperature (°C)	Response (R_a/R_g)	Ref.
Al-doped ZnO	10	500	2250	[58]
ZnO powders	2	450	5.73	[63]
ZnO platelets	50	25	50	[64]
ZnO particles	250	400	~45	[53]
ZnO tetrapods	50		47.5	[65]
ZnO sheets	1	220	77	[66]
ZnO rods	250	400	5.30	[67]
ZnO flowers			8	[50]
ZnO petals	100	25	14	[23]
ZnO branched nanorods	10		2.85	
Co-doped ZnO branched nanorods	10		800	

3.2. Other metal oxides for acetaldehyde gas sensors

Apart ZnO, many other metal oxides can be used as sensing layer in chemiresistive sensors. For example, ultrafine CuO NPs were fabricated via a facile chemical route for acetaldehyde sensing studies [68]. At optimal temperature of 200 °C, the sensor showed a response ($\Delta R/R_a$) of 29.23 towards 100 ppm. The acetaldehyde sensing mechanism on the p-type CuO sensor is shown in Fig. 6. As presented in Fig. 7(a) initially in air a hole accumulation layer was formed on the surface of CuO NPs due to adsorption of oxygen ions. When the sensor was exposed to acetaldehyde (Fig. 7(b)), acetaldehyde molecules reacted with oxygen ions and the released electron back to CuO surface. Accordingly, the width of hole accumulation layer decreased and the resistance of the gas sensor increased. However, the sensor showed a reduced response in humid air because of the occupation of adsorption sites by water molecules.

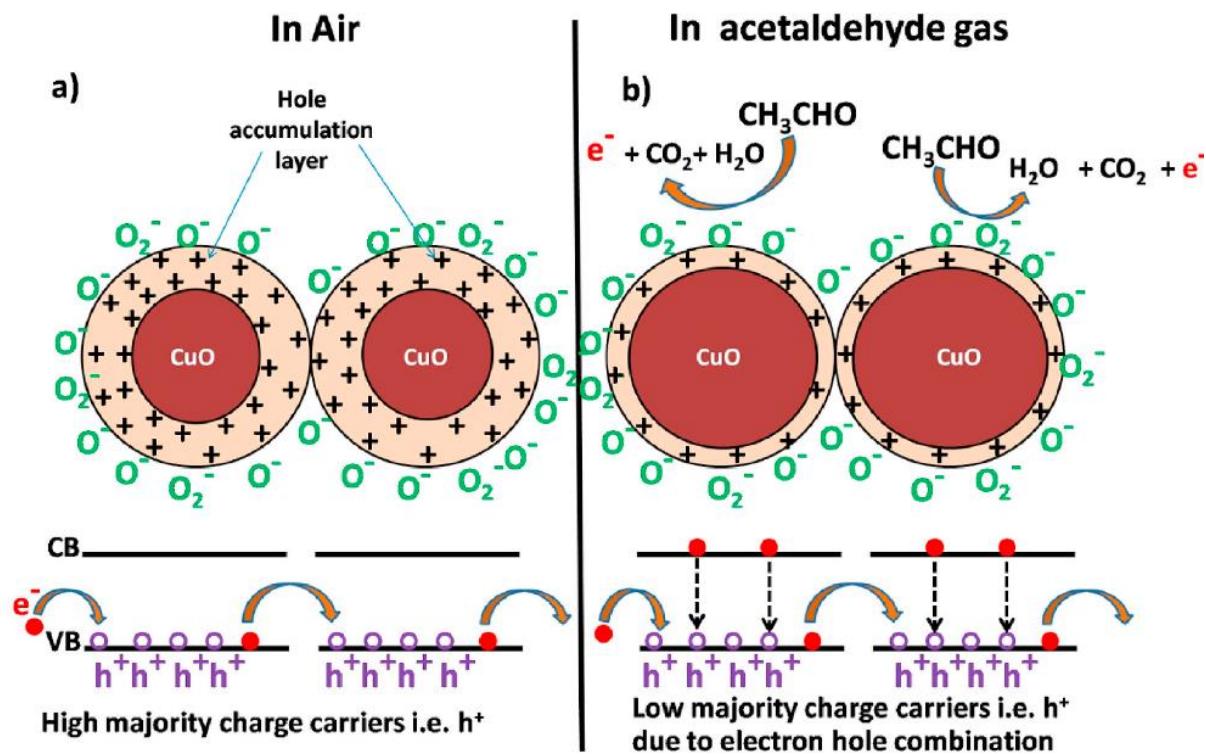


Fig. 7. Schematics of acetaldehyde sensing mechanism of CuO NPs (a) in air (b) in acetaldehyde atmosphere. Reprinted with permission from [68].

In another study, α -Mn₂O₃ thin films were deposited on silica substrates by spray pyrolysis technique [69]. The sensing tests showed that the sensing response was higher to acetaldehyde than any other vapors. The high sensing response at room temperature to acetaldehyde was related to the high electron donating ability of acetaldehyde as well as the catalytic effect of α -Mn₂O₃ towards oxygen. The α -Mn₂O₃ thin film sensor also showed a low response to interfering gases. Furthermore, the sensor showed fast dynamics and for 5 to 75 ppm acetaldehyde, it displays short response (9 s) and recovery (\sim 35 s) times.

Polyaniline (PANI)_x MoO₃ and poly(*o*-anisidine) (PoANIS)_xMoO₃ hybrid thin films were evaluated by Itoh and collaborators for aldehydes monitoring [20]. These materials were prepared by a modified intercalation method in which a [Na(H₂O)₂]_xMoO₃ thin film was soaked in intercalation solutions, namely PANI or PoANIS solutions. The intercalation solutions were filtrated to remove insoluble polymers which had a degree of polymerization. The hybrid-based sensors prepared by the modified method, could detect low concentrations of acetaldehyde gas up to several tens ppb level, whereas those prepared by the conventional method were not able to sense such a low concentrations of acetaldehyde due to the presence of insoluble PANI moieties adsorbed onto the surface of the hybrid thin films, which negatively affected the response of the gas sensor.

In an interesting study, SnO₂ NPs mixed with various amounts WO₃ and doped with Pt, Ru, Pd, Ag, Au, and In was also investigated for acetaldehyde sensing studies [52]. It was found that the 1 wt% Ru/10 wt% WO₃/SnO₂ gas sensor showed a response of 11 to 100 ppm acetaldehyde at 200°C.

Graphene is a well-known two-dimensional material with outstanding electrical conductivity [70], which can improve the conductivity of composites that is beneficial for realization of the gas sensors. In this regards, graphene (0, 0.1, 0.5, 1 and 3 wt%)-WO₃ nanocomposites were synthesized by a hydrothermal method [71]. It was revealed that the sensor based on 0.1 wt% graphene-WO₃ nanocomposite indicated the highest gas response of 5 to 1000 ppm acetaldehyde gas along with good selectivity at 100 °C. In acetaldehyde atmosphere, graphene absorbed a lot of gas molecules due to its high specific surface area. Furthermore, in the interfaces between

graphene and WO_3 , Schottky contacts were created. The graphene- WO_3 interface is a forward-biased Schottky barrier, leading to the easy capture and migration of electrons from WO_3 NP to graphene. Thus, the gas-sensing performance was improved in the presence of graphene.

Acetaldehyde gas-sensing performance of pristine and noble metal (Pt and Rh) loaded SnO_2 NPs were investigated by Shimizu and his collaborators [72]. Of the noble metals tested, Rh was revealed to be the best sensitizer, and the highest response to acetaldehyde was for the SnO_2 loaded with 0.1 wt % Rh at 350°C. In the case of pristine SnO_2 operating at 500°C, some amount of acetaldehyde was consumed during its diffusion through pores in the sensor into the interior region, therefore, the steady-state acetaldehyde concentration in the interior was lower than that in the ambient atmosphere. In addition, it was suggested that the sensitive acetaldehyde itself but arises mainly from the oxidation process of methane. This is another reason for its low sensitivity, since pure SnO_2 is usually less sensitive to methane. Similar oxidation behavior was expected even for 3.0Pt/ SnO_2 at a high temperature of 450°C, due to its ability for oxidizing acetaldehyde at low temperature. However, in the case of 0.1Rh/ SnO_2 at 350°C partial consumption of acetaldehyde during diffusion into the interior was small, and most of the acetaldehyde and its derivatives were oxidized almost completely only in the interior region. The temperature gradient associated with the heater location facilitated such a difference in oxidation behavior between the surface and the interior region of the sensor [72].

In_2O_3 NPs were synthesized through a one-step microwave hydrothermal route [73]. The NPs showed a response of 11.06 to 100 ppm acetaldehyde at 300°C. The sensing mechanism is shown in Fig. 8. Initially, in air, due to adsorption of oxygen species an electron depleted layer was formed. When In_2O_3 sensor was put in acetaldehyde atmosphere, the acetaldehyde vapor molecules reacted with the adsorbed oxygen ions on the surface of In_2O_3 NPs and the released electrons caused the significant change of the sensor resistance, contributing to the sensor response [73]. Table 2 lists some of acetaldehyde gas sensors based on metal oxides. As it can be seen, different metal oxides in pristine or composite forms can be used for the realization of acetaldehyde gas sensors. However, in general, their performance is lower those of the sensors based on ZnO .

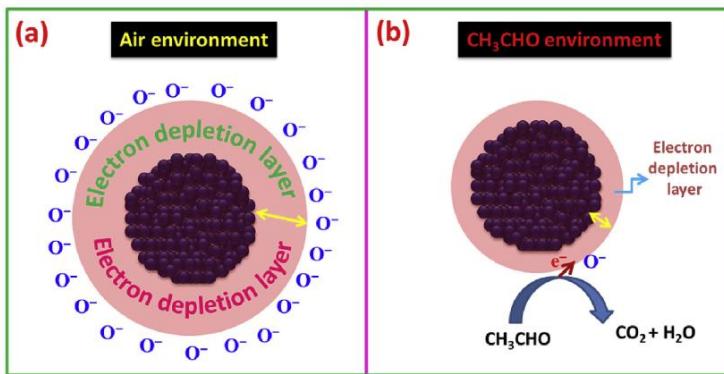


Fig. 8. Schematic of the acetaldehyde sensing mechanism for In_2O_3 gas sensor. Reprinted with permission from [73].

Table 2. Comparison of the performance of different metal oxides toward acetaldehyde.

Sensing material	Gas conc. (ppm)	T (°C)	Response (R_a/R_g)	Ref.
1 wt% Ru/10 wt% WO_3/SnO_2	100	200	11	[52]
CuO NPs	100	200	23.29 ($\Delta R/R_a$)	[68]
0.1 wt% graphene- WO_3	1000	100	5	[71]
In_2O_3 nanospheres	100	300	11.06	[73]
NiO nanotetrahedra	50	250	4	[74]
Au@ SnO_2 core-shell NPs	500	300	0.85	[75]

4. Conclusions and outlooks

Chemiresistive-based gas sensors for detection of acetaldehyde were reported and their functioning mechanism and performances were discussed, too. From the literature analysis search, these acetaldehyde sensors employ various semiconducting sensing materials. Among them, ZnO is the most widely used for acetaldehyde gas sensing by chemiresistive devices. The fundamentals of these sensors have been highlighted but, although there are some reports on acetaldehyde gas adsorption on transition metal oxides, the acetaldehyde sensing mechanism on chemiresistive sensors has not been completely explained till now. Indeed, research needs to understand the details of the change of the electronic properties of the sensing layer following the adsorption of acetaldehyde to enhance the sensor performances versus this gas. Regarding practical applications,

there are some challenges for realization of highly reliable and sensitive sensors for commercial purposes. Important parameters, such as sensitivity, selectivity, stability as well as reproducibility should be addressed by different strategies. Compared to traditional analytical techniques, these sensors have greater sensitivity, lower cost and improved portability. Another advantage is that no pretreatment is necessary, providing savings in the cost and time of analysis. These devices shows further straightforward integration with IC circuit devices. Microfabricated devices offer indeed reduced power consumption and increased portability, then they are also promising for mobile applications.

So, combining fundamental research on new sensing materials with technological advancement towards sensor miniaturization promises to address some of the challenges to wide-scale deployment of chemiresistive sensors for real-time monitoring of acetaldehyde in many applications.

Acknowledgments

This research was supported by the Basic Science Research Program through the National Research Foundation of Korea (NRF) funded by the Ministry of Education (2016R1A6A1A03013422). It was also supported by a National Research Foundation of Korea (NRF) grant funded by the Korean government (MSIT) (2019R1A2C1006193).

Author Contributions: Conceptualization, G.N, Original Draft Preparation, A.M., G.N, Writing -Review & Editing, G.N, A.M., H.K, S.K.

Conflicts of Interest: The authors declare no conflict of interest.

References

1. Qi, Y., Shen, L., Zhang, J., Yao, J., Lu, R., Miyakoshi, T. Species and release characteristics of VOCs in furniture coating process. *Environ. Pollution.* **2019**, *245*, 810-819.
2. Hou, H., Liu, H., Gao, F., Shang, M., Wang, L., Xu, L., Yang, W. Packaging BiVO₄ nanoparticles in ZnO microbelts for efficient photoelectrochemical hydrogen production. *Electrochimica Acta.* **2018**, *283*, 497-508.
3. Katsumata, K. I., Motoyoshi, R., Matsushita, N., Okada, K. Preparation of graphitic carbon nitride (g-C₃N₄)/WO₃ composites and enhanced visible-light-driven photodegradation of acetaldehyde gas. *J. Hazardous Mater.* **2013**, *260*, 475-482.
4. Calestani, D., Mosca, R., Zanichelli, M., Villani, M., Zappettini, A. Aldehyde detection by ZnO tetrapod-based gas sensors. *J. Mater. Chem.* **2011**, *21*(39), 15532-15536.
5. Delikhoon, M., Fazlzadeh, M., Sorooshian, A., Baghani, A. N., Golaki, M., Ashournejad, Q., Barkhordari, A. Characteristics and health effects of formaldehyde and acetaldehyde in an urban area in Iran. *Environ. Pollution.* **2018**, *242*, 938-951.
6. Santana, F. O., Campos, V. P., Cruz, L. P., Luz, S. R. Formaldehyde and acetaldehyde in the atmosphere of Salvador-Ba, Brazil, using passive sampling. *Microchem. J.* **2017**, *134*, 78-86.
7. Stefanov, B. I., Topalian, Z., Granqvist, C. G., Österlund, L. Acetaldehyde adsorption and condensation on anatase TiO₂: Influence of acetaldehyde dimerization. *J. Molec. Cata. A: Chemical,* **2014**, *381*, 77-88.
8. Kovács, I., Farkas, A. P., Szitás, Á., Kónya, Z., Kiss, J. Adsorption, polymerization and decomposition of acetaldehyde on clean and carbon-covered Rh (111) surfaces. *Surf. Sci.* **2017**, *664*, 129-136.
9. Lachenmeier, D. W., Salaspuro, M. ALDH2-deficiency as genetic epidemiologic and biochemical model for the carcinogenicity of acetaldehyde. *Reg. Tox. Pharm.* **2017**, *86*, 128-136.
10. Salaspuro, M. Key role of local acetaldehyde in upper GI tract carcinogenesis. *Best Practice & Research Clinical Gastroenterology*, **2017**, *31*(5), 491-499.
11. Giberti, A., Carotta, M. C., Fabbri, B., Gherardi, S., Guidi, V., Malagù, C. High-sensitivity detection of acetaldehyde. *Sens. Actuators B. Chem.* **2012**, *174*, 402-405.
12. Haussmann, H. J. Use of hazard indices for a theoretical evaluation of cigarette smoke composition. *Chem. Res. Toxicology*, **2012**, *25*(4), 794-810.
13. Sad, M. E., Peña, L. G., Padró, C. L., Apesteguía, C. R. Selective synthesis of acetaldehyde from lactic acid on acid zeolites. *Catalysis Today*, **2018**, *302*, 203-209.
14. Balagurunathan, B., Tan, L., Zhao, H. Metabolic engineering of *Escherichia coli* for acetaldehyde overproduction using pyruvate decarboxylase from *Zymomonas mobilis*. *Enzyme Microbial Tech.* **2018**, *109*, 58-65.
15. Turner, C., Španěl, P., Smith, D. A longitudinal study of ethanol and acetaldehyde in the exhaled breath of healthy volunteers using selected-ion flow-tube mass spectrometry. *Rapid Communications in Mass Spectrometry: An International Journal Devoted to the Rapid Dissemination of Up-to-the-Minute Research in Mass Spectrometry*, **2006**, *20*(1), 61-68.

16. Kanjanasiranont, N., Prueksasit, T., Morknoy, D. Inhalation exposure and health risk levels to BTEX and carbonyl compounds of traffic policeman working in the inner city of Bangkok, Thailand. *Atmospheric Environ.* **2017**, *152*, 111-120.
17. Zhang, X., Ye, L., Li, Y., Zhang, Y., Cao, C., Yang, J., Qi, F. Acetaldehyde oxidation at low and intermediate temperatures: An experimental and kinetic modeling investigation. *Combustion Flame*, **2018**, *191*, 431-441.
18. Smith, D., Wang, T., Sulé-Suso, J., Španěl, P., Haj, A. E. Quantification of acetaldehyde released by lung cancer cells in vitro using selected ion flow tube mass spectrometry. *Rapid Communications Mass Spectrometry*, **2003**, *17*(8), 845-850.
19. Tryba, B., Jafari, S., Sillanpää, M., Nitta, A., Ohtani, B., Morawski, A. W. Influence of TiO₂ structure on its photocatalytic activity towards acetaldehyde decomposition. *Appl. Surf. Sci.* **2019**, *470*, 376-385.
20. Itoh, T., Matsubara, I., Shin, W., Izu, N., Nishibori, M. Preparation of layered organic-inorganic nanohybrid thin films of molybdenum trioxide with polyaniline derivatives for aldehyde gases sensors of several tens ppb level. *Sens. Actuators B. Chem.* **2008**, *128*(2), 512-520.
21. Zhang, L., Zhou, M., Dong, S. A self-powered acetaldehyde sensor based on biofuel cell. *Analytical Chem.* **2012**, *84*(23), 10345-10349.
22. Verissimo, M. I., Gamelas, J. A., Simoes, M. M., Evtuguin, D. V., Gomes, M. T. S. (2018). Quantifying acetaldehyde in cider using a Mn (III)-substituted polyoxotungstate coated acoustic wave sensor. *Sens. Actuators B. Chem.* **2018**, *255*, 2608-2613.
23. Mani, G. K., & Rayappan, J. B. B. ZnO nanoarchitectures: ultrahigh sensitive room temperature acetaldehyde sensor. *Sens. Actuators B. Chem.* **2016**, *223*, 343-351.
24. Zhang, J., Liu, X., Neri, G., Pinna, N. Nanostructured materials for room-temperature gas sensors. *Adv. Mater.* **2016**, *28*(5), 795-831.
25. Gao, F., Boussaid, F., Xuan, W., Tsui, C. Y., Bermak, A. Dual transduction surface acoustic wave gas sensor for VOC discrimination. *IEEE Electron Device Letters*, **2018**, *39*(12), 1920-1923.
26. Zhao, Y., Zaghloul, M., Lilach, Y., Benkstein, K., Semancik, S. Metal Organic Framework-Coated Optical VOC Gas Sensor. In *2018 IEEE Photonics Conference (IPC)* **2018**, 1-2, IEEE.
27. Rizzo, G., Arena, A., Bonavita, A., Donato, N., Neri, G., Saitta, G. Gasochromic response of nanocrystalline vanadium pentoxide films deposited from ethanol dispersions. *Thin Solid Films*, **2010**, *518*(23), 7124-7127.
28. Rajanna, K. Development of thermoelectric gas sensors for volatile organic compounds. In *SENSORS, 2006 IEEE*, **2006**, 716-718). IEEE.
29. Mori, M., Nishimura, H., Itagaki, Y., & Sadaoka, Y. Potentiometric VOC detection in air using 8YSZ-based oxygen sensor modified with SmFeO₃ catalytic layer. *Sens. Actuators B. Chem.* **2009**, *142*(1), 141-146.
30. Kim, J. H., Lee, J. H., Mirzaei, A., Kim, H. W., & Kim, S. S. SnO₂ (n)-NiO (p) composite nanowebs: Gas sensing properties and sensing mechanisms. *Sens. Actuators B. Chem.* **2018**, *258*, 204-214.
31. Mirzaei, A., Park, S., Sun, G. J., Kheel, H., Lee, C., & Lee, S. Fe₂O₃/Co₃O₄ composite nanoparticle ethanol sensor. *J. Korean Phys. Soc.* **2016**, *69*(3), 373-380.
32. Mirzaei, A., Park, S., Kheel, H., Sun, G. J., Ko, T., Lee, S., Lee, C. Acetone Sensors Based on In₂O₃-Co₃O₄ Composite Nanoparticles. *J. Nanosci. Nanotech.* **2017**, *17*(6), 4087-4090.

33. Mirzaei, A., Leonardi, S. G., Neri, G. Detection of hazardous volatile organic compounds (VOCs) by metal oxide nanostructures-based gas sensors: A review. *Ceram. Inter.* **2016**, 42(14), 15119-15141.

34. Mirzaei, A., Neri, G. (2016). Microwave-assisted synthesis of metal oxide nanostructures for gas sensing application: A review. *Sen. Actuators B. Chem.* **2016**, 237, 749-775.

35. Mirzaei, A., Janghorban, K., Hashemi, B., Neri, G. (2015). Metal-core@ metal oxide-shell nanomaterials for gas-sensing applications: a review. *J. Nanoparticle Research*, **2015**, 17(9), 371.

36. Neri, G. First fifty years of chemoresistive gas sensors. *Chemosensors*, **2015**, 3(1), 1-20.

37. Mirzaei, A., Kim, J. H., Kim, H. W., Kim, S. S. Resistive-based gas sensors for detection of benzene, toluene and xylene (BTX) gases: a review. *J. Mater. Chem. C*, **2018**, 6(16), 4342-4370.

38. Mirzaei, A., Kim, S. S., Kim, H. W. Resistance-based H₂S gas sensors using metal oxide nanostructures: A review of recent advances. *J. Haz. Mater.* **2018**, 357, 314-331.

39. Leonardi, S. Two-dimensional zinc oxide nanostructures for gas sensor applications. *Chemosensors*, **2017**, 5(2), 17.

40. Mirzaei, A., Kim, J. H., Kim, H. W., Kim, S. S. How shell thickness can affect the gas sensing properties of nanostructured materials: Survey of literature. *Sens. Actuators B. Chem.* **2018**, 258, 270-294.

41. Mirzaei, A., Janghorban, K., Hashemi, B., Bonyani, M., Leonardi, S. G., Neri, G. A novel gas sensor based on Ag/Fe₂O₃ core-shell nanocomposites. *Ceram. Int.* **2016**, 42(16), 18974-18982.

42. Kim, J. Y., Lee, J. H., Kim, J. H., Mirzaei, A., Kim, H. W., Kim, S. S. Realization of H₂S sensing by Pd-functionalized networked CuO nanowires in self-heating mode. *Sens. Actuators B. Chem.* **2019**, 126965.

43. Yang, P., Lau, C., Liang, J. Y., Lu, J. Z., Liu, X. Zeolite-based cataluminescence sensor for the selective detection of acetaldehyde. *Lum. J. Bio. Chem. Lum.* **2007**, 22(5), 473-479.

44. Cao, X., Zhang, Z., Zhang, X. A novel gaseous acetaldehyde sensor utilizing cataluminescence on nanosized BaCO₃. *Sens. Actuators B. Chem.* **2004**, 99(1), 30-35.

45. Abideen, Z. U., Kim, J. H., Lee, J. H., Kim, J. Y., Mirzaei, A., Kim, H. W., Kim, S. S. Electrospun metal oxide composite nanofibers gas sensors: A review. *J. Korean Ceramic Soc.* **2017**, 54(5), 366-379.

46. Kim, J. H., Mirzaei, A., Kim, H. W., Kim, S. S. Low power-consumption CO gas sensors based on Au-functionalized SnO₂-ZnO core-shell nanowires. *Sens. Actuators B. Chem.* **2018**, 267, 597-607.

47. Gao, R., Cheng, X., Gao, S., Zhang, X., Xu, Y., Zhao, H., & Huo, L. Highly selective detection of saturated vapors of abused drugs by ZnO nanorod bundles gas sensor. *Appl. Surf. Sci.* **2019**, 485, 266-273.

48. Wang, Z. L. Nanostructures of zinc oxide. *Mater. Today*, **2004**, 7, 26-33.

49. Ahmad, R., Majhi, S. M., Zhang, X., Swager, T. M., Salama, K. N. Recent progress and perspectives of gas sensors based on vertically oriented ZnO nanomaterials. *Adv. Colloid Interface Sci.* **2019**, 270, 1-27.

50. Rai, P., Raj, S., Ko, K. J., Park, K. K., Yu, Y. T. Synthesis of flower-like ZnO microstructures for gas sensor applications. *Sens. Actuators B. Chem.* **2013**, 178, 107-112.

51. Zhang, S. L., Lim, J. O., Huh, J. S., Noh, J. S., Lee, W. Two-step fabrication of ZnO nanosheets for high-performance VOCs gas sensor. *Current Appl. Phys.* **2013**, *13*, S156-S161.
52. Mani, G. K., Rayappan, J. B. B. Novel and facile synthesis of randomly interconnected ZnO nanoplatelets using spray pyrolysis and their room temperature sensing characteristics. *Sens. Actuators B. Chem.* **2014**, *198*, 125-133.
53. Rai, P., Yu, Y. T. Citrate-assisted hydrothermal synthesis of single crystalline ZnO nanoparticles for gas sensor application. *Sensors Actuators B. Chem.* **2012**, *173*, 58-65.
54. Subbiah, D. K., Mani, G. K., Babu, K. J., Das, A., Rayappan, J. B. B. Nanostructured ZnO on cotton fabrics—A novel flexible gas sensor & UV filter. *J. Cleaner Production*, **2018**, *194*, 372-382.
55. Espid, E., Taghipour, F. UV-LED photo-activated chemical gas sensors: A review. *Critical Reviews in Solid State Mater. Sci.* **2017**, *42*(5), 416-432.
56. de Lacy Costello, B. P. J., Ewen, R. J., Ratcliffe, N. M., Richards, M. The characteristics of novel low-cost sensors for volatile biomarker detection. *J. Breath Research*, **2008**, *2*(3), 037017.
57. Xu, J., Han, J., Zhang, Y., Sun, Y. A., Xie, B. Studies on alcohol sensing mechanism of ZnO based gas sensors. *Sens. Actuators B. Chem.* **2008**, *132*(1), 334-339.
58. Yoo, R., Li, D., Rim, H. J., Cho, S., Lee, H. S., Lee, W. High sensitivity in Al-doped ZnO nanoparticles for detection of acetaldehyde. *Sens. Actuators B. Chem.* **2018**, *266*, 883-888.
59. Deng, S., Liu, X., Chen, N., Deng, D., Xiao, X., Wang, Y. A highly sensitive VOC gas sensor using p-type mesoporous Co₃O₄ nanosheets prepared by a facile chemical coprecipitation method. *Sens. Actuators B. Chem.* **2016**, *233*, 615-623.
60. Cho, S. Y., Yoo, H. W., Kim, J. Y., Jung, W. B., Jin, M. L., Kim, J. S., Jung, H. T. High-resolution p-type metal oxide semiconductor nanowire array as an ultrasensitive sensor for volatile organic compounds. *Nano Lett.* **2016**, *16*(7), 4508-4515.
61. Wang, L., Deng, J., Lou, Z., Zhang, T. Nanoparticles-assembled Co₃O₄ nanorods p-type nanomaterials: One-pot synthesis and toluene-sensing properties. *Sens. Actuators B. Chem.* **2014**, *201*, 1-6.
62. Gunasekaran, E., Ezhilan, M., Mani, G. K., Shankar, P., Kulandaishamy, A. J., Rayappan, J. B. B., & Babu, K. J. Fluorine doped ZnO thin film as acetaldehyde sensor. *Semiconductor Sci. Tech.* **2018**, *33*(9), 095005.
63. Giberti, A., Carotta, M. C., Fabbri, B., Gherardi, S., Guidi, V., Malagù, C. High-sensitivity detection of acetaldehyde. *Sens. Actuators B. Chem.* **2012**, *174*, 402-405.
64. Mani, G. K., Rayappan, J. B. B. Novel and facile synthesis of randomly interconnected ZnO nanoplatelets using spray pyrolysis and their room temperature sensing characteristics. *Sens. Actuators B. Chem.* **2014**, *198*, 125-133.
65. Calestani, D., Mosca, R., Zanichelli, M., Villani, M., Zappettini, A. Aldehyde detection by ZnO tetrapod-based gas sensors. *J. Mater. Chem.* **2011**, *21*(39), 15532-15536.
66. Fu, X., Liu, J., Han, T., Zhang, X., Meng, F., Liu, J. A three-dimensional hierarchical CdO nanostructure: preparation and its improved gas-diffusing performance in gas sensor. *Sens. Actuators B. Chem.* **2013**, *184*, 260-267.
67. Rai, P., Song, H. M., Kim, Y. S., Song, M. K., Oh, P. R., Yoon, J. M., Yu, Y. T. Microwave assisted hydrothermal synthesis of single crystalline ZnO nanorods for gas sensor application. *Mater. Lett.* **2012**, *68*, 90-93.

[68] Patil, P., Nakate, U. T., Nakate, Y. T., Ambare, R. C. Acetaldehyde sensing properties using ultrafine CuO nanoparticles. *Mater. Sci. Semiconductor Proc.* **2019**, *101*, 76-81.

[69] Srinath, A. K., Sankaranarayanan, L., Pandeeswari, R., Jeyaprakash, B. G. Thin films of α -Mn₂O₃ for resistance-based sensing of acetaldehyde vapor at ambient temperature. *Microchimica Acta*, **2015**, *182*(9-10), 1619-1626.

[70] Allen, M. J., Tung, V. C., Kaner, R. B. Honeycomb carbon: a review of graphene. *Chem. Rev.* **2009**, *110*(1), 132-145.

[71] Chu, X., Hu, T., Gao, F., Dong, Y., Sun, W., Bai, L. Gas sensing properties of graphene-WO₃ composites prepared by hydrothermal method. *Mater. Sci. Engineering: B*, **2015**, *193*, 97-104.

[72] Shimizu, Y., Yamaguchi, K., Fukunaga, K., Takao, Y., Hyodo, T., Egashira, M. Acetaldehyde gas-sensing properties and surface chemistry of SnO₂-based sensor materials. *J. Electrochem. Soc.* **1999**, *146*(3), 1222-1226.

[73] Chava, R. K., Cho, H. Y., Yoon, J. M., Yu, Y. T. Fabrication of aggregated In₂O₃ nanospheres for highly sensitive acetaldehyde gas sensors. *J. Alloys Comp.* **2019**, *772*, 834-842.

[74] Fu, Q., Ai, M., Duan, Y., Lu, L., Tian, X., Sun, D., Sun, Y. Synthesis of uniform porous NiO nanotetrahedra and their excellent gas-sensing performance toward formaldehyde. *RSC Adv.* **2017**, *7*(82), 52312-52320.

[75] Wang, Z., Hou, C., De, Q., Gu, F., & Han, D. One-step synthesis of Co-doped In₂O₃ nanorods for high response of formaldehyde sensor at low temperature. *ACS Sensors*, **2018**, *3*(2), 468-475.