

# Ag-Decorated/Loaded Gas Sensors

Subjects: **Agricultural Engineering**

Contributor: Ali Mirzaei , Mehrdad Shahbaz

Ag is one of the cheapest noble metals which is extensively used in the decoration or doping of semiconducting metal oxides (SMOs) to boost the overall gas-sensing performances of nanostructured SMOs. This is due to the electronic and chemical sensitization of Ag nanoparticles.

Ag

decoration/loading

doping

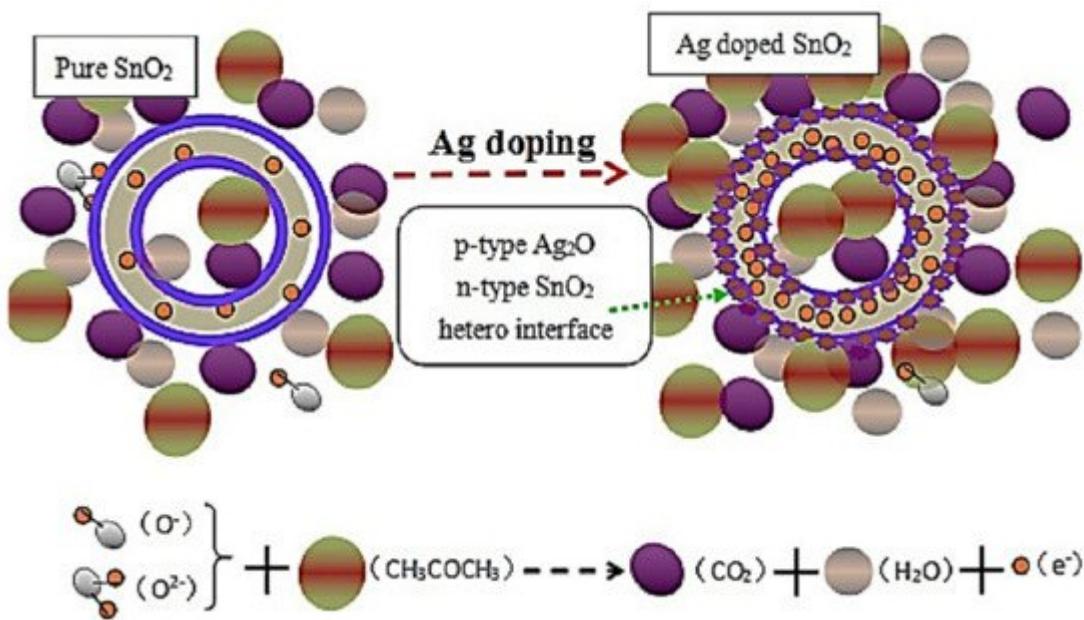
gas sensor

sensing mechanism

## 1. Ag-Decorated/Loaded Acetone ( $\text{CH}_3\text{COCH}_3$ ) Gas Sensors

$\text{CH}_3\text{COCH}_3$  belongs to the family of volatile organic compounds (VOCs) that are employed as solvents in various industries.  $\text{CH}_3\text{COCH}_3$  at higher levels may have a negative impact on the central nervous system and may be harmful to the eyes and nose. Therefore, the occupational threshold limit value for  $\text{CH}_3\text{COCH}_3$  was set at 250 ppm considering a time-weighted average of 8 h [1]. Accordingly, the development of sensitive  $\text{CH}_3\text{COCH}_3$ -sensing devices is required from the perspective of safety. In this regard, some attempts have been made to establish selective  $\text{CH}_3\text{COCH}_3$  sensors by adding Ag into SMOs. For instance, Xu et al. [2] described the synthesis of Ag-decorated  $\text{SnO}_2$  hollow nanofibers (NFs) with large surface areas and their  $\text{CH}_3\text{COCH}_3$  sensing properties. Typically, noble metals have higher electrical conductivities that enable the rapid transfer of electrons and catalysis of the oxidation of reducing gas molecules such as VOCs [3][4][1][2]. Thus, noble metal-incorporated sensing materials can be suitable candidates for detecting VOCs. The developed Ag-decorated  $\text{SnO}_2$  sensor showed an excellent response and higher selectivity for  $\text{CH}_3\text{COCH}_3$  at 160 °C. A schematic of the sensing interactions between the  $\text{CH}_3\text{COCH}_3$  gas molecules and pure and Ag-decorated  $\text{SnO}_2$  is shown in **Figure 1**. Owing to the presence of p-type  $\text{Ag}_2\text{O}$  crystals, p-n heterojunction interfaces formed between p-type  $\text{Ag}_2\text{O}$  crystals and n-type  $\text{SnO}_2$ , generating a broader depletion layer on the  $\text{SnO}_2$  side, thereby increasing the initial resistance of the sensing material. Upon exposure to  $\text{CH}_3\text{COCH}_3$ , significant modulation of the heterojunctions occurred and contributed to the sensor response. The Ag NPs produced  $\text{Ag}_2\text{O}$  in air, which has facilitated the development of highly electron-depleted layers while removing electrons from  $\text{SnO}_2$ . This process has increased the total resistance and the area adjacent to the Ag– $\text{SnO}_2$  interfaces, thus increasing the sensitivity of  $\text{SnO}_2$  to  $\text{CH}_3\text{COCH}_3$ . Furthermore, one-dimensional (1D)  $\text{SnO}_2$  hollow nanostructures fabricated via electrospinning considerably facilitated the diffusion and transport of electrons in  $\text{CH}_3\text{COCH}_3$  molecules, thereby rapidly and substantially changing the sensor resistance. Additionally,  $\text{SnO}_2$  hollow NFs with both outer and inner surfaces exhibited high surface areas and eventually contributed to high  $\text{CH}_3\text{COCH}_3$  responses. In summary, the significantly high  $\text{CH}_3\text{COCH}_3$  sensing performances of Ag/ $\text{SnO}_2$  composites are attributed to the Ag dopant and 1D NF structures of  $\text{SnO}_2$ . Ag with high electrical conductivity enabled the rapid transfer of electrons and catalyzed the oxidation of the reducing  $\text{CH}_3\text{COCH}_3$  gas molecules. Moreover, the  $\text{SnO}_2$  NFs with higher surface areas led to an effective

dispersion of catalyst particles and possessed a porous tube-like structure that promoted rapid gas flow and a superior ability to store and release oxygen ions.



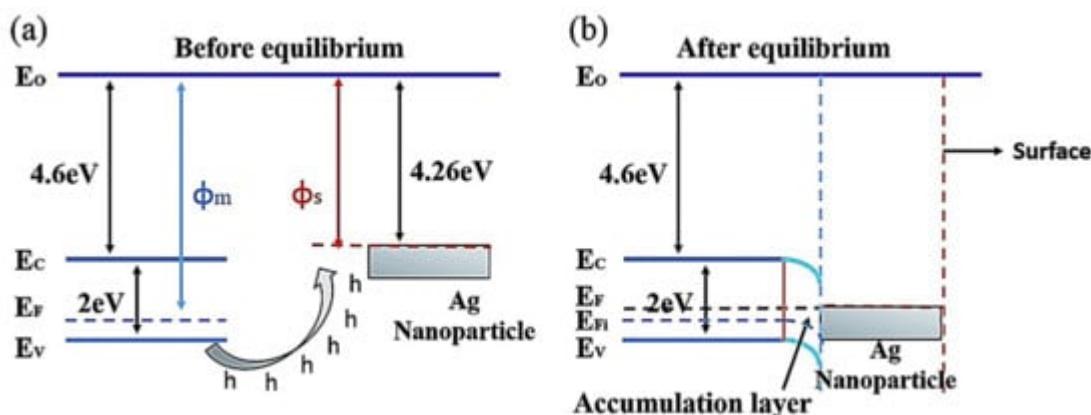
**Figure 1.** Schematic representing the  $\text{CH}_3\text{COCH}_3$  sensing mechanism of pure and Ag-doped  $\text{SnO}_2$ . Reprinted from reference [2] with permission from Elsevier.

In another study, Kilic et al. [5] reported the  $\text{CH}_3\text{COCH}_3$  sensing characteristics of Ag-loaded  $\text{TiO}_2$  nanorods (NRs). They used a seed-mediated hydrothermal approach to grow  $\text{TiO}_2$  NRs and subsequently loaded Ag onto  $\text{TiO}_2$  NRs by thermally evaporating metallic Ag at different times of 30, 45, and 90 s. The authors demonstrated that the enhancement in the  $\text{CH}_3\text{COCH}_3$  detection performance of the Ag-loaded  $\text{TiO}_2$  (45 s) sensor was due to the catalytic activity of Ag. Actually, Ag loading increased the number of adsorption sites on the surface of  $\text{TiO}_2$  and accelerated the rate of electron exchange between the  $\text{TiO}_2$  surface and  $\text{CH}_3\text{COCH}_3$  molecules. Under a  $\text{CH}_3\text{COCH}_3$  atmosphere, the bonds between  $\text{CH}_3\text{COCH}_3$  molecules were easily dissociated by Ag, allowing these molecules to quickly interact with the chemisorbed oxygen species. Moreover, the decoration of Ag NPs onto  $\text{TiO}_2$  NRs pinned the Fermi level of  $\text{TiO}_2$  because of the transfer of electrons from  $\text{TiO}_2$  to Ag. This led to surface band bending and induced a more pronounced electron–hole separation effect, thereby enhancing the sensitivity of the sensor to  $\text{CH}_3\text{COCH}_3$ . The lower  $\text{CH}_3\text{COCH}_3$  response of the Ag-loaded  $\text{TiO}_2$  (90 s) sensor was associated with the accumulation of Ag clusters on the  $\text{TiO}_2$  surface, which impeded  $\text{O}_2$  diffusion within  $\text{TiO}_2$  and reduced the catalytic activity of Ag.

## 2. Ag-Decorated/Loaded Chlorine ( $\text{Cl}_2$ ) Gas Sensors

$\text{Cl}_2$  gas is very hazardous to the human respiratory mucous membrane at concentrations in the range 0.2–3.5 ppm. It causes psychological disorders, skin infections, and even liver damage. Hence, the early detection and successive monitoring of hazardous  $\text{Cl}_2$  by reliable gas sensors are highly important. Few studies have been

reported on the  $\text{Cl}_2$  detection properties of Ag-loaded sensors. Li et al. [6] illustrated the effect of Ag loading on the  $\text{Cl}_2$  response of bismuth ferrite ( $\text{BiFeO}_3$ , BFO) nanospheres (BFO NSs); they synthesized BFO NSs using a sol-gel route and successively loaded Ag NP onto BFO NSs via a photodeposition technique. Typically, BFO has a distinct surface reactivity,  $\text{O}_2$  adsorption ability, and a narrow band gap, which are beneficial for improving the gas-sensing characteristics. Therefore, BFO NSs are important candidates for the detection of  $\text{Cl}_2$ . The observed response of the optimum 4 mg  $\text{AgNO}_3$ -modified BFO sensor to 10 ppm  $\text{Cl}_2$  was 72.62 at a working temperature of 240 °C. This response was 2.5 times that of the pure BFO sensor. A schematic of the energy band structure and hole transfer after the loading of Ag NPs is shown in **Figure 2**. Upon the loading of Ag NPs onto BFO, the positive charges on BFO reduced, and downward band bending occurred because the holes on the BFO NSs transferred to the Ag NPs. Along with the separation of electrons and holes, the electrons probably combined with  $\text{O}_2$  and  $\text{Cl}_2$  on the surface of the gas sensor. No barriers were formed because of the reduction in the number of conduction band electrons, thus supporting the progress of the reaction. Moreover, the Fermi levels of Ag and BFO correspond to one another at the same level, following contact because BFO ( $\phi_m$ ) has a lower work function than that of Ag ( $\phi_s$ ). Here, Ag NPs might also be used as distinct adsorption sites for  $\text{O}_2$  and  $\text{Cl}_2$ . Furthermore, at the Ag/BFO interface, a Schottky junction was created that decreased the intergranular barriers and enhanced the interfacial effect [6].

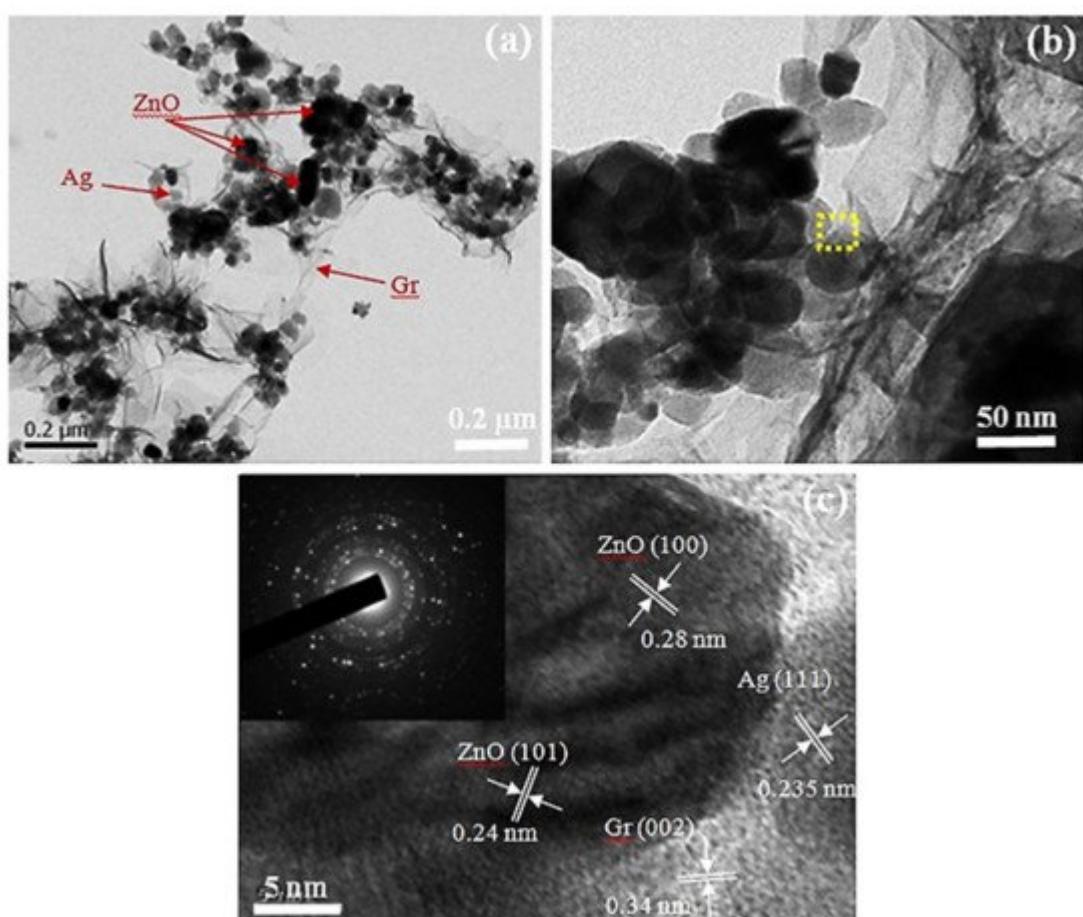


**Figure 2.** Energy band diagram and hole transfer in Ag NP-decorated BFO NSs (a) before and (b) after equilibrium [6]. Reproduced from <https://pubs.rsc.org/en/content/articlelanding/2018/ra/c8ra06247a> (accessed on 26 September 2018) from RSC. (This article is licensed under a Creative Commons Attribution-NonCommercial 3.0 Unported Licence).

In contrast, the number of electrons at the reaction sites increased, and the reaction quickly saturated because of the rapid transfer of charge carriers from BFO to Ag. Consequently, the gas response significantly improved, and the response time shortened. However, the amount of adsorbed O ions decreased when high amounts of Ag were loaded onto the BFO NSs, which reduced the reactions of  $\text{O}_2$  and  $\text{Cl}_2$ , thereby decreasing the sensor response. Thus, this study demonstrates that the addition of noble metals presents a new way of enhancing the sensitivity of p-type semiconductors toward  $\text{Cl}_2$  gas.

### 3. Ag-Decorated/Loaded Acetylene ( $\text{C}_2\text{H}_2$ ) Gas Sensors

$C_2H_2$  is a flammable and colorless gas with a peculiar odor and is commonly utilized as a fuel in oxyacetylene welding and metal cutting and as a raw material in various industries.  $C_2H_2$  poses serious threats due to its inherent instability, primarily in the cases of liquefaction, pressurization, heating, or mixing with air. This means that  $C_2H_2$  can cause massive explosions if it leaks. Accordingly, from environmental and safety perspectives, the development of highly efficient  $C_2H_2$  sensors is becoming increasingly important [7][8][9]. In this regard, Uddin et al. [8] described the  $C_2H_2$  sensing properties of chemically synthesized 0–5 wt.% Ag-loaded ZnO-reduced graphene oxide (ZG-Ag) ternary hybrids. Generally, herein, the use of rGO was preferred over that of graphene because of difficulties in the large-scale production of graphene and lack of functional groups and band gaps in graphene [10]. Transmission electron microscopy (TEM) and high-resolution TEM (HRTEM) images (Figure 3) support the Ag/ZnO/Gr configuration of these heterostructures.

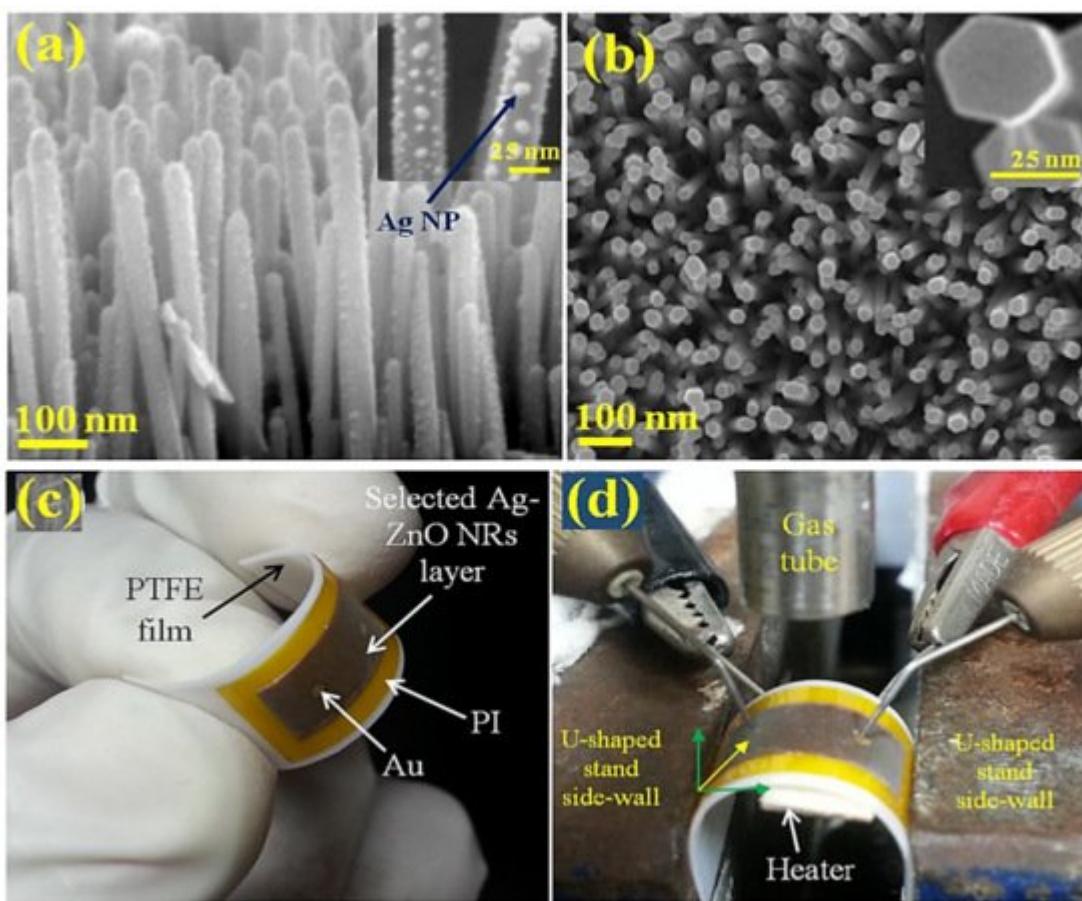


**Figure 3.** (a) TEM and (b,c) HRTEM images of the ZG–Ag3 hybrid (inset shows the equivalent SAED pattern). Reprinted from reference [8] with permission from Elsevier.

The Ag-loaded sensor based on ternary hybrids showed a higher response than that of the sensor without Ag. The sensor without Ag could detect 16–100 ppm  $C_2H_2$  at 250 °C. The response of the 3 wt.% Ag-loaded ZnO–Gr (ZG–Ag3) sensor was 22 at 150 °C, indicating that 3 wt.% was the optimum loading amount of Ag. The loading of 3 wt.% Ag onto the ZnO–Gr sensor not only enhanced the sensor response but also reduced the optimum sensing temperature. Ag has a superior capacity to dissociate  $O_2$  than ZnO, and it catalyzes the dissociation of molecular

$\text{O}_2$  on the sensor surface, which generates higher  $\text{C}_2\text{H}_2$ -sensing active sites and thereby a higher sensor response. The development of depletion layers around the  $\text{ZnO}$  NPs due to the presence of Ag was mostly correlated with the modulation of nano-Schottky barriers, thereby improving the low-temperature surface reactivity. Upon the loading of Ag onto the  $\text{ZnO}$ –Gr sensor, further dynamic sites generated at the sensing layer/Ag interfaces because of the spillover effect, and a larger number of  $\text{C}_2\text{H}_2$  molecules adsorbed on the sensor surface. Therefore, a high sensor response was obtained when the loading amount of Ag was optimal. Nevertheless, when an excess amount of Ag was loaded, the  $\text{O}_2$  molecules dissociated on the surface and surpassed the percolation threshold, which caused an overlapping spillover zone, ultimately affecting the efficient transfer of  $\text{O}_2$  and decreasing the chances of  $\text{C}_2\text{H}_2$  adsorption; this reduced the sensor response.

In another study associated with the detection of  $\text{C}_2\text{H}_2$ , Uddin et al. [11] designed a  $\text{C}_2\text{H}_2$  sensor using Ag-decorated  $\text{ZnO}$  NRs supported by a flexible polyimide (PI)/polytetrafluoroethylene (PTFE) substrate (**Figure 4**).



**Figure 4.** Images of (a) cross-section and (b) in-plane view of 8 s Ag-loaded  $\text{ZnO}$  NRs, (c) the Ag-decorated  $\text{ZnO}$  flexible gas sensor, and (d) the experimental setup at one bending angle. Reprinted from reference [11] with permission from Elsevier.

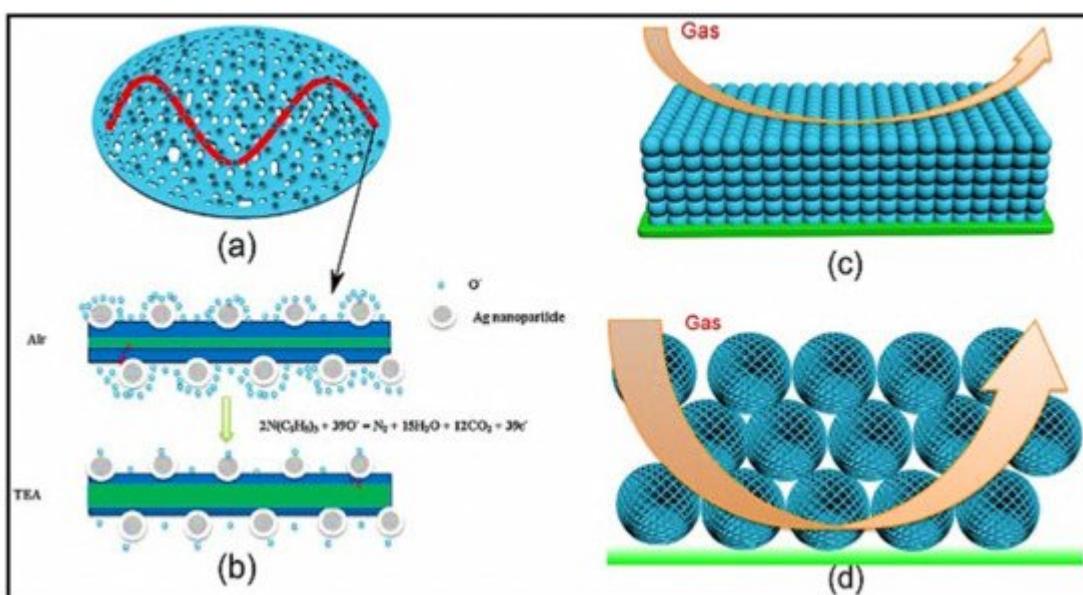
Flexible gas sensors should have the following characteristics: (i) the ability to detect gases at low concentrations and (ii) low- or room-temperature operation [12]. In this study, radio frequency magnetron sputtering (125 W, 7 mTorr) was applied to load Ag NPs onto the sensing layer of  $\text{ZnO}$  NRs in an Ar environment at different loading

times of 6, 8, and 10 s. Gas-sensing analysis demonstrated that the flexible sensor developed using 8 s Ag-loaded ZnO NRs showed a higher response of 13.8 toward 100 ppm C<sub>2</sub>H<sub>2</sub> at 200 °C than those of the pristine (3.21), 6 s (9.33), and 10 s (9.57) Ag-loaded sensors. Furthermore, upon repeated bending and relaxation for up to 5 × 10<sup>4</sup> cycles, the sensor response only slightly decreased, which demonstrated the outstanding sustainability and mechanical strength of the designed flexible sensor. This performance improvement was attributed to the integration of the Ag–ZnO structure with the flexible PI substrate, which improved the physical binding and adherence of the Ag–ZnO structure to the supporting substrate. ZnO NRs with small diameters ensured an improved surface area and a larger aspect ratio of the resulting sensor. This caused inadequate surface atomic coordination and higher surface energy, leading to better adsorption of O ions and hence improved sensor response. Furthermore, because of catalytic interactions, the Ag NP/ZnO NR interface might produce further charge carriers or O vacancies on the sensor surface. In the case of Ag-loaded ZnO NRs, the ZnO surface transformed from an electron-depletion state to an almost flat band state along with a redox change at Ag. Additionally, the improved C<sub>2</sub>H<sub>2</sub> sensing activity observed at an optimum temperature of 200 °C was ascribed to the height of the Schottky barrier between the ZnO grains and Ag in the Ag-loaded ZnO NRs. The improvement in the performance of the Ag-loaded ZnO NRs may also be controlled by changing the Ag concentration for the sensitive variation of the Ag oxidation state during exposure to C<sub>2</sub>H<sub>2</sub>. When the Ag loading amount was high, a thick Ag layer developed on the ZnO NR surface, which decreased the efficacy of the open surface porosity of ZnO, thereby reducing the gas sensor response. Herein, the observed higher selectivity of the Ag/ZnO NR sensor toward C<sub>2</sub>H<sub>2</sub> was attributed to the chemical sensitization effect. Since Ag has excellent catalytic activity, it acts as a certain adsorption site for the dissociation of O<sub>2</sub> and separation of H<sub>2</sub> molecules owing to the spillover effect.

## 4. Ag-Decorated/Loaded Triethylamine (TEA) Gas Sensors

TEA, a clear and flammable liquid with a strong odor of ammonia, is widely used in chemical industries [13]. However, TEA can cause many severe health issues, such as pulmonary edema, gastroenteritis, headaches, and even death, because of its toxicity [14]. Additionally, dead fish and other decaying marine products may release TEA, and the concentration of TEA is expected to progressively increase over time [15]. Consequently, TEA may serve as a chemical indicator to assess the quality of marine food [16]. Therefore, designing an advanced sensor for the detection and monitoring of TEA is required. In contrast, recently, three-dimensional (3D) structural nanomaterials have received considerable attention in gas-sensing applications. In fact, 3D structures may offer highly efficient specific surface areas that improve the response of the corresponding gas sensor. Accordingly, Shen et al. [17] reported the TEA sensing characteristics of Ag-loaded 3D porous ZnO microspheres. Their morphological studies indicated that the ZnO microspheres (3–5 μm in size) were assembled by numerous thin and porous nanosheets with sizes of ≈20 nm. The developed sensor exhibited better cross-selectivity toward TEA, which was significantly attributed to the differences between the reactivity of the target gases caused by their different bond energies and chemical molecular structures. The reported C–N, C–O, C–H, C=C, C=O, and O–H bond energies are 307, 326, 414, 610.3, 798.9, and 458.8 kJ/mol, respectively. As a result of the lower C–N bond energy, the TEA molecules were more easily reduced by Ag–ZnO.

In this case, the baseline resistance of the Ag-loaded sensor (2737.8 M $\Omega$ ) was higher than that of the pristine sensor (28.5 M $\Omega$ ). Furthermore, O species may more readily adsorb on the Ag NPs via a known spillover effect. Thus, highly active negative O ions spilled on the ZnO surface, which extracted the electrons from the conduction band of ZnO, thereby increasing the thickness of the electron-depletion layer and consequently the sensor resistance. Furthermore, the active O species accelerated the reaction of the sensor with TEA. Overall, the widely dispersed Ag NPs were highly favorable to the spillover effect and might catalyze the sensing reaction to increase the response of the sensor to TEA (Figure 5a,b). Finally, the special hierarchical 3D porous nanostructure comprised hundreds of porous nanosheets was an additional meaningful component for the excellent TEA sensing properties of the Ag-loaded gas sensor. This unique structure with a high surface area and large pores (Figure 5c,d) increased the regions of the sensing reaction and promoted the TEA sensing performance of the sensor.

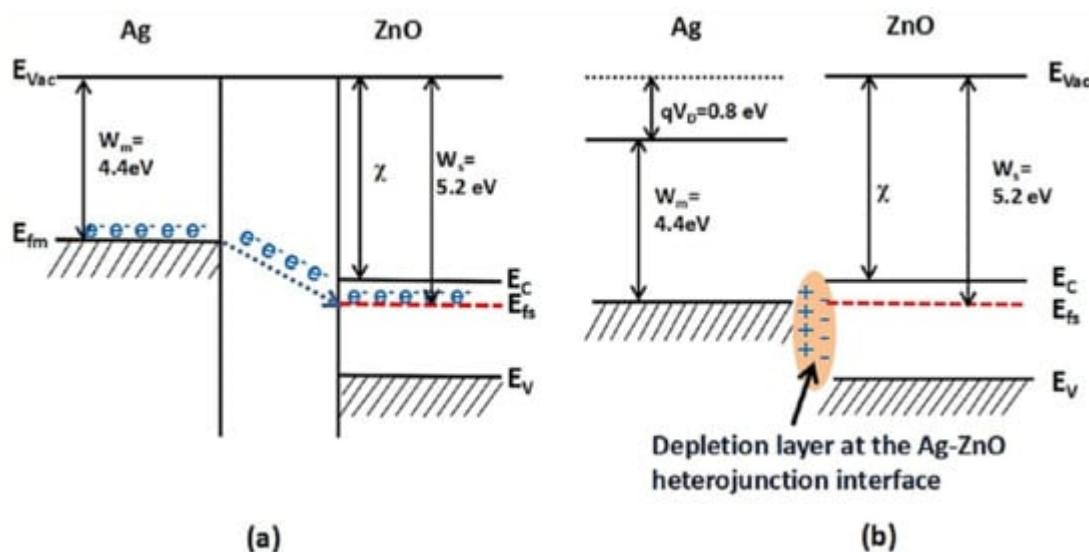


**Figure 5.** Schematic of the (a,b) TEA gas-sensing mechanism of the Ag–ZnO sensor and (c,d) structures of the microspheres with the illustration of large pores. Reprinted from reference [17] with permission from Elsevier.

## 5. Ag-Decorated/Loaded Formaldehyde (HCHO) Gas Sensors

HCHO is extensively utilized in several industrial applications. Typically, HCHO is a colorless gas with a pungent odor, and it easily evaporates from the products into the indoor air. Many health-related issues, including headaches, nausea, cancer, and mucosal and respiratory irritation, are associated with exposure to HCHO [18][19][20][21]. Therefore, the development of highly sensitive HCHO gas sensors is urgently required to ensure the safety of people. In this regard, Xing et al. [22] prepared highly porous 1–5 at % Ag-loaded ZnO for application in HCHO sensors. In this study, the sensor fabricated using 1 at % Ag-loaded ZnO exhibited the maximum response to HCHO (170.42) at an optimal temperature of 240 °C. Unique hierarchically structured porous Ag-loaded ZnO provided an adequate surface area for interaction between the HCHO molecules and the sensing material. The high response of the optimal gas sensor to HCHO was ascribed to the production of heterojunctions between Ag and ZnO in addition to the catalytic activity of Ag. Schematics of the energy bands of Ag/ZnO in the presence of air

and HCHO gas are shown in **Figure 6a,b**, respectively. Herein, the electrons transferred from Ag to ZnO because the work function of Au ( $W_m = 4.4$  eV) is smaller than that of ZnO ( $W_s = 5.2$  eV), generating an electron-depletion layer because of the increase in the concentration of electrons at the Ag/ZnO interface. When the Ag/ZnO sensor was exposed to air, the electrons released from ZnO were captured by the adsorbed O ions to form  $O_x^-$ , which showed strong oxidation activity. This process reduced the sensor resistance. Upon exposure to HCHO, the previously adsorbed  $O_x^-$  strongly reacted with the HCHO molecules and oxidized HCHO into  $CO_2$  and  $H_2O$ , thereby decreasing the sensor resistance. This study reveals that the HCHO sensing performance of the sensor is directly influenced by the Ag/ZnO heterojunction and the developed  $O_x^-$ .



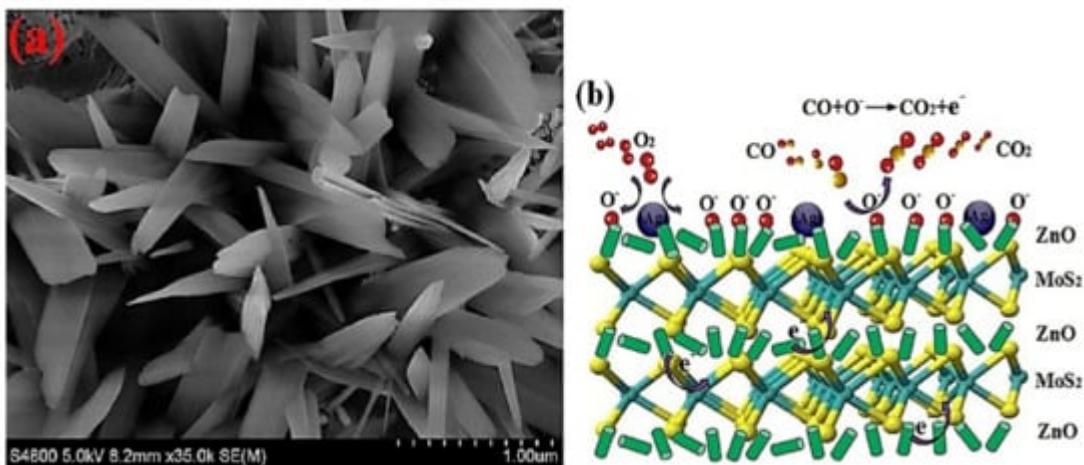
**Figure 6.** Schematics of the band structures of Ag-loaded ZnO in (a) air and (b) HCHO. Reprinted from reference [22] with permission from Elsevier.

Furthermore, Wang et al. [23] reported the HCHO sensing activity of a two-step solution-processed Ag-loaded sunflower-like hierarchical  $In_2O_3$  nanoarchitecture. The observed HCHO sensing performance was attributed to the highly porous and hierarchically designed sunflower-like nanostructure and the catalytic activity of Ag. The exclusive hierarchical 3D sunflower-like nanostructures possess numerous radial nanobranches with irregular surfaces, which offer a larger exposed surface area and additional paths for the exchange of electrons during the entire gas diffusion and surface reaction processes. An appropriate Ag loading amount plays an important role in chemical and electronic sensitization during the detection of HCHO by the Ag-loaded  $In_2O_3$  sensor. Chemical sensitization favored gas reactions by dissociating HCHO via a spillover effect, and electronic sensitization substantially enhanced the direct exchange of electrons between  $In_2O_3$  and Ag. However, higher Ag loading amount resulted in the conduction of electrons along the metallic Ag NPs irrespective of chemoresistive variations, thereby deteriorating the sensor response.

## 6. Ag-Decorated/Loaded Carbon Monoxide (CO) Gas Sensors

CO is among the most hazardous gases as it is invisible, tasteless, odorless, and colorless and thus cannot be detected by human sensory organs [24]. Consequently, numerous efforts have been made to detect CO gas by various materials and strategies. Molybdenum disulfide ( $\text{MoS}_2$ ) is a distinct graphene-like two-dimensional (2D) layered transition metal dichalcogenide. In addition to a conventional band gap of 1.8 eV, it has a large surface area-to-volume ratio with excellent physical/mechanical properties [25]. Nevertheless, the gradual degradation of  $\text{MoS}_2$  nanosheets occurs under ambient conditions owing to atmospheric oxidation and surface contamination, which may eventually decrease their sensing performances. Thus, to achieve an appropriate CO sensing performance of pure  $\text{MoS}_2$  nanosheets, sensing should be performed under an inert  $\text{N}_2$  atmosphere, significantly restricting their commercial applications. To overcome this limitation, Zhang et al. [26] fabricated a novel ternary Ag-loaded  $\text{ZnO}/\text{MoS}_2$  nanocomposite via layer-by-layer self-assembly for the detection of CO gas.

The presence of  $\text{ZnO}$  NRs, Ag NPs, and  $\text{MoS}_2$  nanosheets was verified by morphological investigations (the scanning electron microscopy (SEM) image is shown in **Figure 7a**). The developed nanocomposite sensor demonstrated excellent room temperature CO sensing performance. This confirmed that the existence of  $\text{MoS}_2$  might reduce the operating temperature and energy consumption probably because of the higher specific surface area and better conductivity of  $\text{MoS}_2$  along with the synergistic effect between  $\text{ZnO}$  and  $\text{MoS}_2$ . Ag effectively improved the catalytic activity of the sensor and mobilities of the carriers for the interaction of gas with the surface of  $\text{MoS}_2$  or  $\text{ZnO}$  by modifying the energy band structure and surface morphology of the sensing material. Furthermore, substantial dynamic sites for CO adsorption might be generated upon Ag loading. After Ag modification, the interactions of CO molecules with O ions dramatically reduced the resistance of the Ag– $\text{ZnO}/\text{MoS}_2$  nanocomposites as compared to that of the  $\text{ZnO}/\text{MoS}_2$  film, resulting in a high CO response of the sensor. A schematic of the interactions between the CO molecules and the Ag– $\text{ZnO}/\text{MoS}_2$  sensor is depicted in **Figure 7b**. Herein, Ag and Pt were employed to improve the CO sensing performance of the  $\text{ZnO}/\text{MoS}_2$  composite sensor. The Ag-loaded sensor exhibited the maximum response as compared to that of the Pt-loaded sensor under similar experimental conditions. The higher response of the Ag-loaded sensor was explained with respect to the work function. Upon the introduction of a noble metal into  $\text{ZnO}/\text{MoS}_2$ , the electrical characteristics of  $\text{ZnO}/\text{MoS}_2$  may be influenced by the existence of a Schottky barrier. Therefore, noble metals with lower work functions are preferred to reduce the Schottky barrier and thus improve the response of the corresponding  $\text{ZnO}/\text{MoS}_2$  sensor. As Ag has a lower work function (4.26 eV) than that of Pt (5.65 eV), the Ag– $\text{ZnO}/\text{MoS}_2$ -based sensor demonstrated higher CO sensing performance.



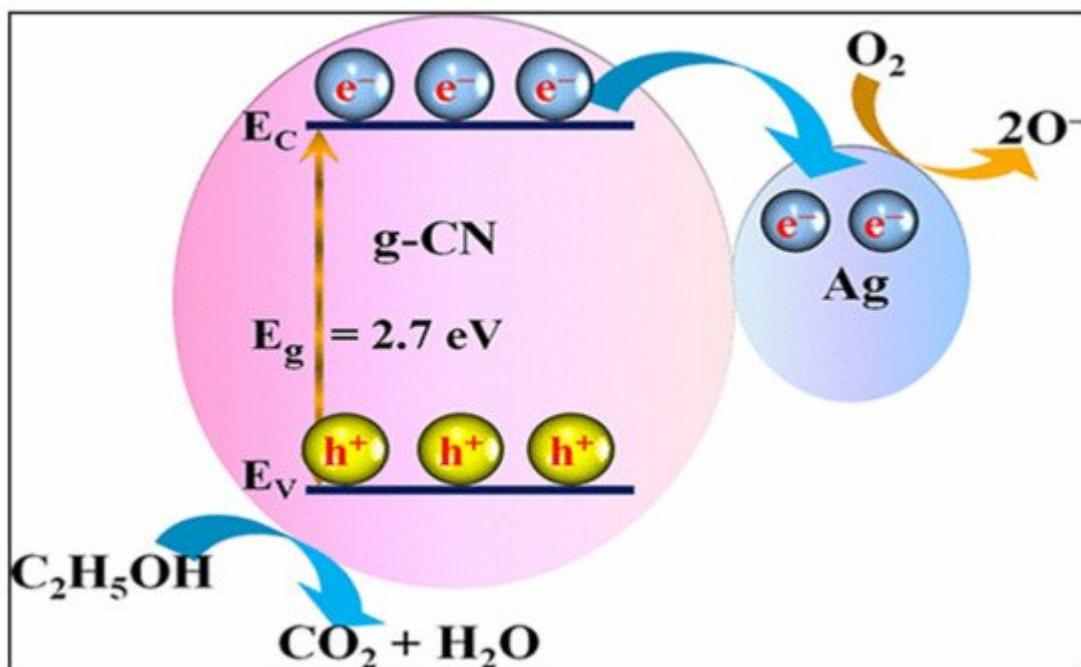
**Figure 7.** (a) SEM image of Ag–ZnO/MoS<sub>2</sub> and (b) schematic of the CO sensing mechanism of Ag–ZnO/MoS<sub>2</sub>. Reprinted from reference [26] with permission from Elsevier.

In another study, Ag-modified flower-like ZnO microspheres were prepared using a combination of solvothermal strategy and an impregnation approach [27]. Dual selective sensing of methane (CH<sub>4</sub>) and CO using 1.5 at % Ag-loaded ZnO by monitoring the working temperature was reported in this study. Ag exhibits high catalytic activity for low-temperature oxidation of CO. However, the low-temperature oxidation of CH<sub>4</sub> is very difficult to achieve, as CH<sub>4</sub> is a thermally stable sp<sup>3</sup>-hybridized non-polar molecule. Accordingly, no considerable low-temperature response of the sensor to CH<sub>4</sub> was observed. In contrast, at higher temperatures, CH<sub>4</sub> was sufficiently activated by Ag because there was adequate thermal energy to overcome the barrier, thereby increasing the sensor response. Consequently, the sensor fabricated using 1.5 at % Ag-loaded ZnO exhibited temperature-modulated dual selectivity toward CO and CH<sub>4</sub> at 130 and 200 °C, respectively.

## 7. Ag-Decorated/Loaded Ethanol (C<sub>2</sub>H<sub>5</sub>OH) Gas Sensors

C<sub>2</sub>H<sub>5</sub>OH is one of the most commonly used VOCs. Exposure to C<sub>2</sub>H<sub>5</sub>OH vapors may cause headache, drowsiness, eye irritation, liver damage, and breathing difficulties. Furthermore, the consumption of C<sub>2</sub>H<sub>5</sub>OH is the leading cause of motor vehicle accidents worldwide, and alcohol-impaired driving fatalities account for 31% of the total number of traffic-related deaths in the United States [28]. Thus, the design of low-temperature operating and selective sensors for the detection and monitoring of C<sub>2</sub>H<sub>5</sub>OH is required from the viewpoint of safety. Graphitic carbon nitride (gC<sub>3</sub>N<sub>4</sub>, g-CN) is a non-metallic polymer semiconductor with a 2D layered structure. As a result of its unique physicochemical characteristics, suitable band gap, and outstanding thermal and chemical stabilities, g-CN can be utilized as an active sensing element in gas-sensing applications. In this regard, Tomer et al. [29] fabricated well-ordered mesoporous Ag-decorated meso-CNs using a hard template by nanocasting to detect C<sub>2</sub>H<sub>5</sub>OH at trace levels. The response of cubic meso-CN to C<sub>2</sub>H<sub>5</sub>OH gas was approximately two times that of conventional g-CN. This improvement was caused by the higher meso-CN surface area along with uniform pore channels through which the target gas penetrated the deep portions of the sensor. The response of the 3 wt.% Ag-decorated meso-CNs to C<sub>2</sub>H<sub>5</sub>OH gas was two times that of meso-CN. A schematic of the C<sub>2</sub>H<sub>5</sub>OH sensing mechanism of the Ag/g-CN sensor is shown in Figure 8. In this case, the electrons transferred from g-CN to Ag due to the lower work

function of g-CN (4.3 eV) than that of Ag (4.7 eV), thereby creating a potential barrier. This barrier prevented the transfer of electrons through the mesoporous sensor, and the electrons existing on the sensor surface developed dynamic sites for the adsorption of  $O_2$ , thereby increasing the sensor response. Moreover, the loading of Ag NPs strongly accelerated catalytic oxidation and chemical sensitization, which ultimately enhanced the number of dynamic O species on the surface of meso-CN. In fact, the chemical sensitization effect (namely, spillover effect) of Ag NPs improved the rate of adsorption–desorption of molecular  $O_2$  on the sensor surface and transformed molecular  $O_2$  into O ions. Furthermore, the excellent catalytic activity of Ag NPs accelerated the decomposition of  $C_2H_5OH$  gaseous molecules into active radicals, thus enhancing the interactions between the chemisorbed O ions and  $C_2H_5OH$  molecules. Owing to the transfer of electrons from meso-CN to Ag NPs, a negatively charged layer was produced around the Ag/meso-CN interface. Under a  $C_2H_5OH$  atmosphere, the electrons returned to the sensing layer via the  $Ag_2O/Ag$  redox reaction, and thus, the areas along the Ag/meso-CN interface became very sensitive to  $C_2H_5OH$ .



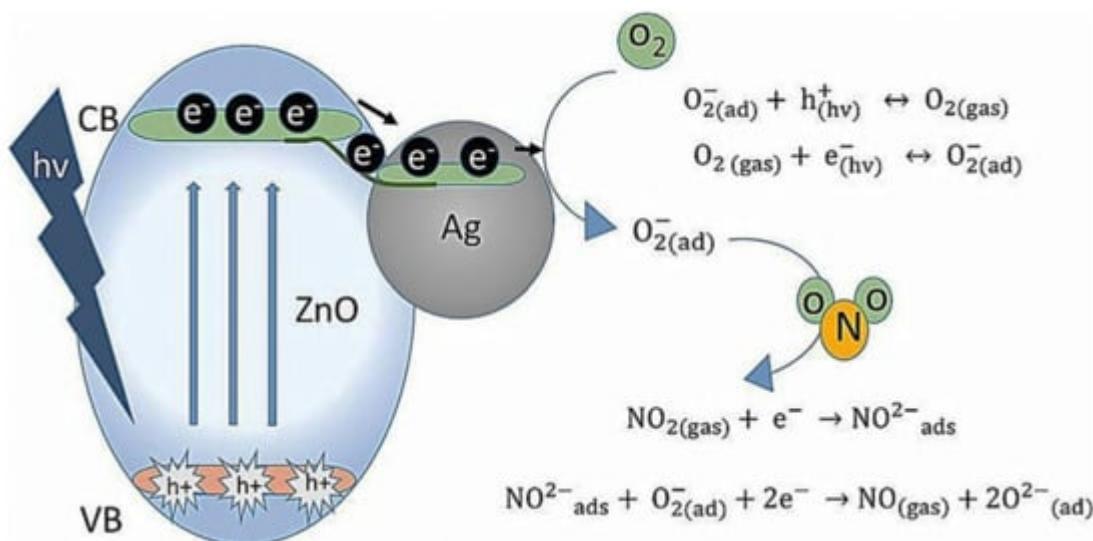
**Figure 8.** Band diagram of the Ag/g-CN sensor, elucidating the  $C_2H_5OH$  sensing mechanism of the sensor [29]. Reprinted from <https://pubs.acs.org/doi/10.1021/acsomega.7b00479> (accessed on July 14, 2017) with permission from ACS (further permissions related to the material excerpted should be directed to the ACS).

## 8. Ag-Decorated/Loaded Nitrogen Dioxide ( $NO_2$ ) Gas Sensors

$NO_2$  is a highly poisonous and polluting gas that produces acid rain and photochemical smog [30]. As a result of its highly toxic nature, detection and monitoring systems for  $NO_2$  are needed. Accordingly, Wang et al. conducted  $NO_2$  gas-sensing studies employing Ag-loaded mesoporous  $WO_3$  designed using 3D cubic KIT-6 as a hard template [31]. Herein, Ag at different molar ratios of 0.2, 0.5, and 1.0% was loaded onto mesoporous  $WO_3$ . The sensor developed using 0.5% Ag exhibited a higher response of 44 to 1 ppm  $NO_2$  at 75 °C because of its larger surface area and

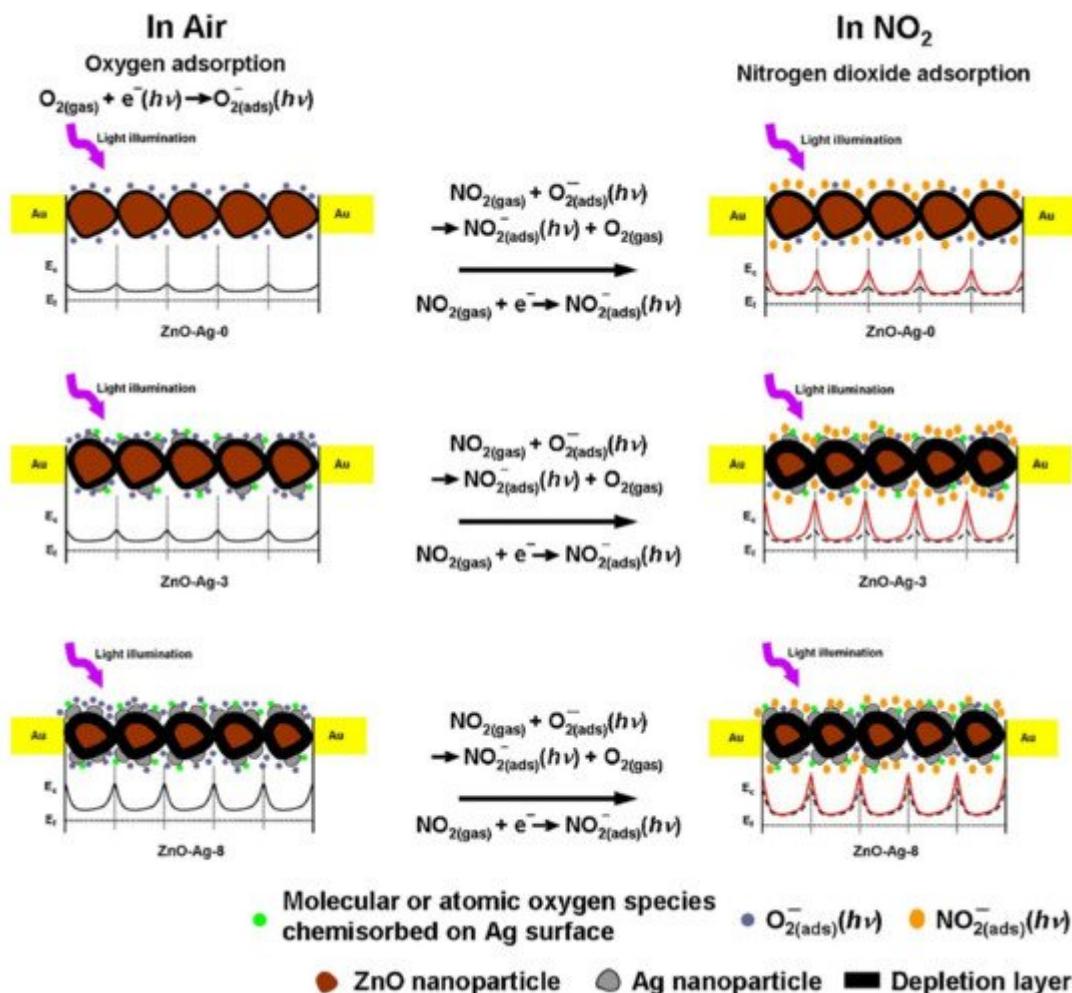
diffusion paths.  $\text{NO}_2$  is a polar molecule having a positive charge localized on the N atom and a negative charge over the O atom. The interaction of electrons with Ag repels the O atom and attracts the positively charged N atom. Ag was used as a dynamic catalyst to create more active sites for the detection of  $\text{NO}_2$ . Although the addition of Ag may enhance the sensing properties of the material, the loading of Ag at excessively high concentrations can decrease the catalytic performance of the material. When the Ag concentration exceeded 0.5%, the total surface area reduced, and interconnected Ag NPs changed the electron path to be from Ag instead of  $\text{WO}_3$ .

The advantages of UV-activated sensors are their high stabilities, abilities to detect flammable gases, and low energy consumptions. In a typical UV-based gas-sensing device, the UV wavelength and power intensity determine the energy of the photons arriving at the exposed surface. This energy influences the steady-state surface reactions and plays a significant role in the response curve. Espid et al. [32] explained the  $\text{NO}_2$  gas detection characteristics of Ag-loaded  $\text{ZnO}$  nanoellipsoids, which were synthesized by a simple coprecipitation method, under UV illumination. When the surface of the gas sensor was irradiated with the photons released from a UV light-emitting diode, the electrons of the sensor hopped from the valence band to the conduction band, leaving holes in the valence band. A schematic of electron mobilization and the related reactions of the Ag-loaded  $\text{ZnO}$  sensor with  $\text{NO}_2$  gas under UV illumination is depicted in **Figure 9**. Photogenerated electron/hole pairs supported the direct adsorption of  $\text{O}_2$  molecules. Under an air atmosphere,  $\text{O}_2$  interacted with the excited electrons and adsorbed in the ionic form on the sensor surface. This slightly increased the sensor resistance. Under a  $\text{NO}_2$  atmosphere, the gas molecules reacted with the chemisorbed oxygen ions or directly adsorbed on the sensor surface by accepting electrons. A change in the electron flow stimulated by these reactions modulated the electrical resistivity. Under continuous UV irradiation, when the  $\text{NO}_2$  flow was stopped, the accelerated photons eliminated the  $\text{NO}_2$  species from the sensor surface. The observed enhancement in the  $\text{NO}_2$  detection performance of  $\text{ZnO}$  nanoellipsoids after Ag loading was associated with the synergistic effects of the semiconductor composite and Ag. Additionally, the improvement of the sensing response in the presence of Ag was linked to the increased electron utilization ratio and the decreased recombination rate of photogenerated electrons and holes due to the trapping of electrons in the Ag NPs during excitation. Similarly, the adsorption ability was directly correlated with the number of unoccupied oxygen sites. When Ag was embedded in the  $\text{ZnO}$  lattice, O-vacancies formed because of the differences between the charges of  $\text{Ag}^+$  and  $\text{Zn}^{2+}$  ions, which indicated that additional adsorption sites were created, resulting in a higher sensor response.



**Figure 9.** Schematic of electron mobilization and related reactions of the Ag–ZnO sensor in the presence of  $\text{NO}_2$  gas [32]. Reproduced from <https://iopscience.iop.org/article/10.1149/2.0141807jss> (accessed on 10 April 2018) from IOPScience (This is an open access article distributed under the terms of the Creative Commons Attribution Non-Commercial No Derivatives 4.0 License (CC BY-NC-ND, <http://creativecommons.org/licenses/by-nc-nd/4.0/> (accessed on 10 April 2018))).

Furthermore, Zhang et al. [33] designed a room-temperature light-assisted  $\text{NO}_2$  gas sensor using Ag-decorated ZnO NPs. The sensor developed using 3 mol.% Ag exhibited the highest  $\text{NO}_2$  response. A schematic of the  $\text{NO}_2$  detection mechanism of pure and Ag-loaded ZnO NPs under various light conditions is shown in **Figure 10**. Herein, characterization studies revealed the development of a heterojunction between Ag NPs and ZnO NPs. Nevertheless, the improved  $\text{NO}_2$  detection performance of the sensor after Ag loading was ascribed to prominent interactions between Ag NPs and the O vacancies. In this study, Ag NPs and surface oxygen vacancies acted as electron sinks to boost charge separation and catalytic activities of Ag NPs for promoting the adsorption of gas molecules. The effective separation of photogenerated electron–hole pairs due to the interfacial charge transfer between ZnO and Ag and charge-carrier trapping through the surface oxygen vacancies enabled further accumulation of unpaired electrons on the surfaces of ZnO NPs. Moreover, Ag NPs and oxygen vacancies on the surface enhanced the adsorption of gas molecules, and thus, more oxygen molecules adsorbed on the sensor surface. An excess of Ag NPs reversibly acted as charge-carrier recombination centers, leading to negatively charged electrostatic attraction between Ag and the positively charged holes, thereby reducing the photoquantum efficiency. Additionally, sometimes, it is difficult to completely desorb the molecular or atomic oxygen species chemisorbed on the Ag surface through light irradiation at room temperature. In brief,  $\text{O}_2$  molecules play an essential role in the absorption/desorption of  $\text{NO}_2$  molecules on the surfaces of ZnO NPs. Specifically, the exposure degree of  $\text{O}_2^-(\text{ads})$  ( $\text{hv}$ ) directly stimulates the sensing characteristics, such as response and response/recovery speeds, of light-assisted  $\text{NO}_2$  sensors.

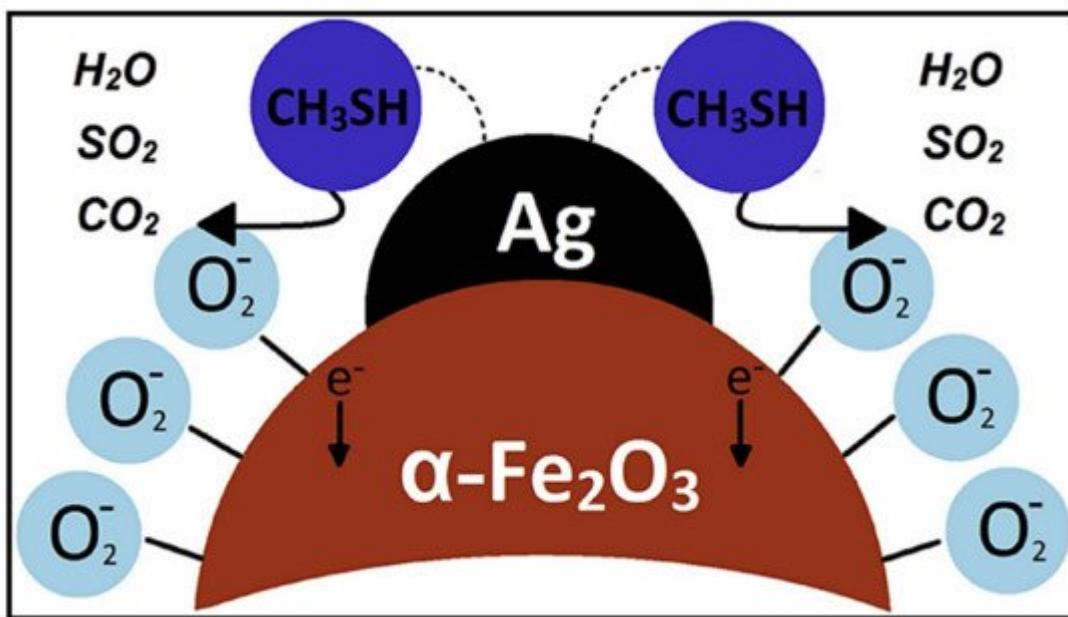


**Figure 10.** Schematic of the NO<sub>2</sub> gas detection mechanism of pristine and Ag-loaded ZnO NPs irradiated with light of 365–520 nm wavelengths. Reprinted from reference [33] with permission from Elsevier.

## 9. Ag-Decorated/Loaded Methyl Mercaptan (CH<sub>3</sub>SH) Gas Sensors

CH<sub>3</sub>SH is a gas that is commonly used as an additive to other gases including propane and natural gas. The rotten egg odor of CH<sub>3</sub>SH facilitates the detection of CH<sub>3</sub>SH leakage. The recommended airborne exposure limit for CH<sub>3</sub>SH is 0.5 ppm during an 8 h work shift. Exposure to higher levels of CH<sub>3</sub>SH results in eye and throat irritation, drowsiness, and even bronchitis [34]. Consequently, designing a sensor that can detect CH<sub>3</sub>SH at low levels is highly desirable. Additionally, CH<sub>3</sub>SH gas-sensing properties of SMOs have rarely been reported. In this regard, Garcia et al. [34] constructed a sensor using mesoporous Ag-loaded hematite ( $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>) to detect CH<sub>3</sub>SH at room temperature. Herein, the loading of 3 wt.% Ag onto  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> significantly enhanced the sensor response owing to the deeper electron-depletion layer. Ag loaded onto the surface of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> served as a catalyst to accelerate the rate of conversion of O<sub>2</sub> into ionic O. Therefore, more electrons were trapped, which generated a thicker depletion layer. When the Ag-loaded  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> sensor was exposed to CH<sub>3</sub>SH, the CH<sub>3</sub>SH molecules favorably chemisorbed due to the strong affinities of thiol groups for metallic Ag. Ag loading accelerated the reaction of CH<sub>3</sub>SH with oxygen

ions via a spillover effect (Figure 11). In this case, the deep electron-depletion layer converted into a flat layer, which resulted in a better sensor response. However, when the concentration of Ag exceeded 3 wt.%, the Ag NPs generated a connected network on the surface of  $\alpha\text{-Fe}_2\text{O}_3$ , and consequently, the resistance of the sensor reduced. Thus, the adsorption of  $\text{O}_2$  and the gas– $\text{O}_2$  interaction substantially reduced, causing an inferior response of the sensor to the target gas.



**Figure 11.** Schematic of the chemical influence of Ag NPs on the sensing mechanism of the  $\alpha\text{-Fe}_2\text{O}_3$  sensor. Reprinted from reference [34] with permission from Elsevier.

## 10. Conclusions

The gas-sensing performances of chemiresistive sensors, such as SMOs and related composites, can be enhanced by Ag doping owing to the catalytic activity and electronic/chemical sensitization effects of Ag. As an effective catalyst, Ag can attract abundant  $\text{O}_2$  molecules from the air and transfer them to the surfaces of SMOs, accordingly promoting the capture of electrons from SMOs by  $\text{O}_2$  molecules. Moreover, the higher electrical conductivity of Ag NPs facilitated rapid electron transfer and thereby improved the sensor response. Therefore, Ag may be an excellent choice as a sensitizer to improve the sensing performances of chemiresistive sensors as it offers additional active adsorption sites and charge transfer pathways to enhance surface reactions. Generally, the introduction of Ag in an optimal amount into the sensing material can lead to the best sensing properties, and a bell-shaped relationship typically exists between the sensor response and the addition amount of Ag. Due to the low cost of Ag than that of other noble metals, the incorporation of Ag into gas sensors is a highly promising strategy to not only reduce the overall price of these sensors but also enhance their sensing properties.

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