Enhanced Butane Sensing performance of ZnO -TiO_2 nano composites

Bhargavi KS[1], Anindita Bose[1*]

1 Department of Physics, School of Engineering, Presidency University, Bangalore, India

Corresponding author:

Dr. Anindita Bose

Department of Physics, School of Engineering, Presidency University, Bangalore-560064, India.

Abstract

Metal oxide nano materials have huge scientific and industrial applications and proved to be good as sensing devices. ZnO - TiO_2 nano composites were synthesized by sol-gel method and tested as a chemi-resistive gas sensor. ZnO - TiO_2 nano composites with different weight percentages were prepared. Anatase structure was confirmed by XRD and surface morphology was confirmed by SEM. Dopant composition was analyzed by EDAX. Increased sensitivity was observed with increase in butane concentration for all samples investigated. Extensive experimentation for gas sensing with changing temperature was performed and optimum operating temperature was found to be 363K.

1. Introduction

Due to the living standards of industrial field, it is a big challenge to detect the toxic and hazardous gases which affect the environment and human health [1].It is necessary to synthesis of new materials to enhance the capability of gas sensors. Gas sensors are the powerful and effective devices used to detect inert and explosive gases. These are the essential devices, which converts gas concentration into electrical signals [2].Due to their high sensitivity and fast response time metal oxide semiconductors are used and have a great production for the gas sensors. Metal Oxide Semiconductors are very interesting because of the intricate and amiable nature of electrical properties. Metal oxides have various applications as solar cells, optoelectronics, antibacterial activity, spintronics, piezo electric and gas sensors [3].The working principle of semiconducting metal oxides is the change in the electrical properties with the exposure of target gas. Due to their low cost and simple synthesizing methods metal oxide semiconductors are gaining much attention in the field of gas sensing and also for the different applications [4]. ZnO and TiO_2 are the n – type semiconducting materials and multifaceted among the transition metal oxides and an effective consideration for several applications [5]. Due to the high temperature stability of TiO_2, it is most favorable material for gas sensing [6]. The idiosyncratic technological properties and unique sensing, photo catalytic applications of TiO_2 nano particles are engrossing in the recent research trend. TiO_2 has been investigated as an anticipated material for gas sensing [7]. The accessibility for the synthesis of TiO_2 nano particles has various morphologies like sheets, wires, rods, and aerogels through sol-gel method [8]. Enormous necessity of the emission of toxic gases, there is a great need in developing devices having vast electronic properties for the control of air pollution. In recent years semiconductor oxides are used in research over other materials due to their ease of fabrication, low-cost, good reliability/stability, high sensitivity and real time detection ability towards low concentration of toxic gases [9].The important parameters which are significant for the sensing mechanism are the grain size and crystallinity of metal oxides [10]. In these situations it is mandatory to put enormous efforts in developing gas sensors to detect the exhaust gases in the fields of disease diagnosis, military security, environmental and industrial production and additionally having a great demand due to its applications [11]. Due to simple synthesis, high response and low cost, semiconductor metal oxides are playing a dominant role in their applications [12].The design of gas sensor should be adjustable for both high and low temperatures and it should be helpful to detect toxic gases even at small concentration which is close to the oxygen partial pressure [13]. Because of its vast abundance and tolerance of harsh environments TiO_2 has a special attention in the field of gas sensing. TiO_2 improves its gas sensing activity when it is doped with some metals and with some non-metals [14]. An n-type semiconductor oxide with a large band gap is zinc oxide (ZnO) (3.37 eV). Due to its high sensitivity, it can detect gases in a variety of environmental settings. It is therefore frequently utilized in semiconductor oxide-type gas sensors. There are many different morphologies of ZnO nano materials, including rods, spheres, and flowers [15]. In this work one of the versatile semi conducting material ZnO with the weight percentages of 1,10,15 and 20 is doped with the titanium dioxide through the sol-gel method to detect the butane gas. Butane is a transparent, colorless liquid with a faint odor that is frequently used in industrial production [16]. Butane vapor exposure to open flames or high temperatures can result in combustion and explosion, which can lead to unintended harm or death [17]. Consequently, achieving early warning detection for butane sensors is crucial. These sensors cannot detect lower concentrations, operate at high temperatures, and have poor selectivity. Therefore, it's vital to develop better sensors to monitor butane performance.

2. Experimental Section:

2.1 Synthesis Procedure

(i) Synthesis of TiO_2:

Titanium dioxide and Zinc Oxide nano particles were synthesized by using sol-gel method. To prepare $TiO_{2,}$ Titanium tetra iso-propoxide (TTIP) solution was taken as precursor material. A 20 ml of TTIP solution was mixed to the solution of 10 ml of ethanol and 12ml of deionized water, After 1 hour of constant stirring at the temperature of 80^0C, concentrated nitric acid was added to maintain the pH of the solution, then the stirring was continued for 6 hours at 60^0C. White colored nano powder of TiO_2 was obtained after the calcination at 350^0C for 1.5 hours.

(ii) Synthesis of ZnO:

Nano particles of ZnO were synthesized by considering Zinc nitrate and KOH as precursors. (0.4M)KOH solution was added to the mixture of (0.3M)Zinc nitrate and de-ionized water at room temperature with a continuous stirring of 20 minutes. Then the precipitate was washed with Ethanol and calcinated at 600^0C for 2 hours to obtain the ZnO nano powder.

(iii) Synthesis of ZnO - TiO_2 nano composites

The nano composite with the weight percentage 1, 10, 15 and 20 of ZnO with respect to TiO_2 was fabricated by using the sol-gel process. To obtain the precipitation, As synthesized ZnO and TiO_2 nano particles with the proper weight ratio are dissolved in 20 ml of distilled water with the agitation for 4 hours at room temperature. After being aged for 24 hours it is filtered, washed with the distilled water, and dried for 12 hours at 150^0 C, the produced precipitate was then used. The final step was calcining the resulting powder for 2.5 hours at 700^0 C.

2.2 Material Characterization

Bruker powder diffractometer (Shimadzu-7000) with mono chromatized Cu-K (1.5406) radiation was used to characterize the synthesized ZnO-TiO_2 nano composites. The crystal size of the nano composites was determined using the Scherer formula. FTIR was used to investigate the stretching band frequencies. Scanning electron microscopy (SEM), a technique used to examine the morphology of nano composites, was carried out using a Zeiss electron microscope. The ability of the prepared nano composites to detect gases from an in-house gas sensing chamber was tested.

2.3 Gas sensing Measurements

Butane gas was used to characterize the metal oxide nano composites' gas sensing properties. The produced nano composite pellets' gas sensing abilities were tested using the flow through method. All measurements were made in a sealed room that was kept at a constant 25 degrees C humidity level. The operational temperature is ranged from 323 to 393K. The samples' resistance was continuously tracked. For testing the sensor's response to butane gas, the sensor was subjected to a gas sample for three minutes before air flow was resumed [18].

3. Results and Discussion:

3.1 Morphological Analysis: The structural analysis was done using X-ray diffraction analysis using Cu- Kα radiation (wavelengths of 1.5406). Fig 1 shows the ZnO - TiO_2 nano composites' room temperature (RT) X-ray diffraction spectra in the 2θ range of 10-90.

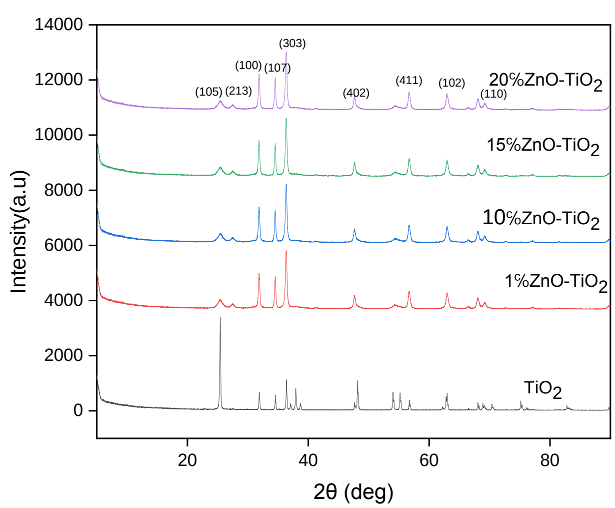


Fig 1: XRD spectra of ZnO - TiO_2 nano composite

ZnO's hexagonal wurtzite structure has been depicted by the strong peaks at the planes of (100), (102) (110) (107) with 2 Theta values of 31.73, 56.55, and 62.83 degrees (JCPDS Card No - 3-888). Additionally, the plane's peaks (213) (103) (303) (402) matched TiO2's anatase phase (JCPDS Card No - 1-562). The crystalline hexagonal phase of ZnTiO3 was also revealed by a single diffraction peak at the 2 theta value of 35.25 degrees. The asymmetry in ionic radii caused the corresponding TiO2 peaks to shift to higher 2 theta as the ZnO content increased. The average particle size was measured by using Scherer's equation.

$$D = \frac{K\lambda}{\beta Cos\theta}$$

Where d is the particle's size, θ is its glancing angle (2θ/2), β is its full width at half maximum, λ is the wavelength of X- ray's and K is the constant with a value of 0.89.

The range of the crystallite size measured by the Scherer's equation was 15nm to 18nm.

Table.1- Crystallite size of ZnO-TiO_2 nano composites calculated by Debye's Scherer's Method

Percentage of samples	Crystallite Size(nm)
1% ZnO- TiO_2	18
10% ZnO- TiO_2	16
15% ZnO- TiO_2	15
20% ZnO- TiO_2	15

3.2 Structural analysis

SEM image analysis was used to examine the prepared ZnO - TiO_2's structural investigation. Surface morphology was found to be homogenous, and particle shape was found to have a web-like structure. The photos revealed the particle aggregation. Fig 2 displays the high-magnification SEM images of the ZnO - TiO_2 nano composite.

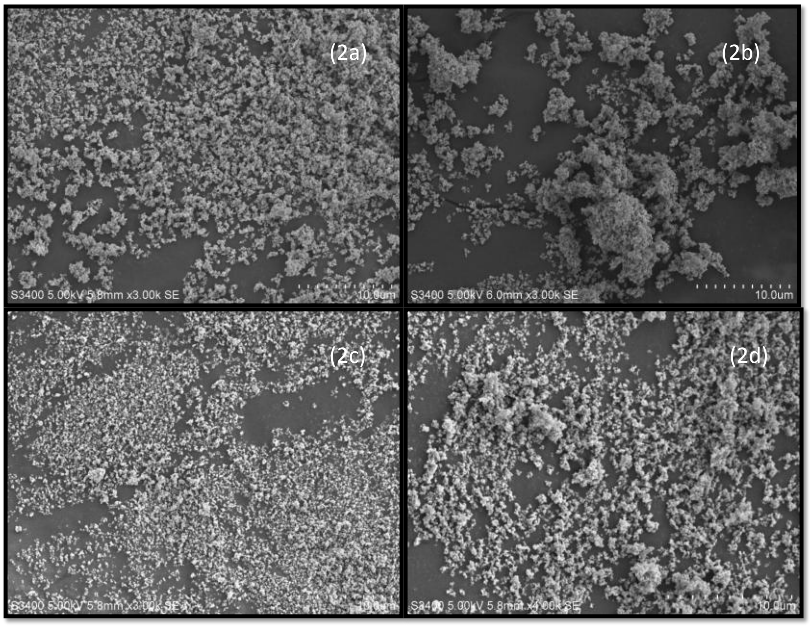


Fig 2: SEM analysis of (2a)1%ZnO, (2b) 10%ZnO, (2c)15%ZnO and (2d) 20% ZnO -TiO_2 nano composite

EDX spectra are used to show the chemical composition of the ZnO -TiO_2 nano composites, as shown in the fig 3. The spectra show that Zn, Ti, and oxygen elements are present.

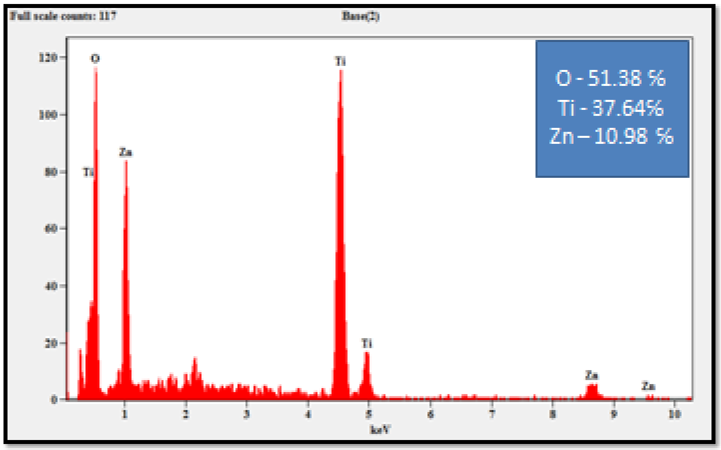


Fig 3 : EDX analysis of 10%ZnO-TiO_2 nano composites

3.3 FTIR analysis

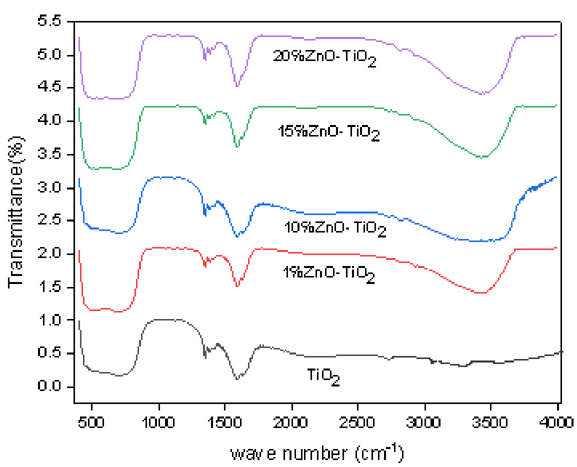


Fig 4: FTIR spectra of ZnO - TiO_2 nano composites

Fourier Transformation Infrared Spectroscopy in the range of 400–4000 cm^{-1} was used to analyze the ZnO/TiO_2 nano composite. Different TiO_2 signatures were detected by FTIR analysis at 493.53, 699.11, 1350.11, 2185.93, and 3433.88 cm-1. The IR peaks at 536.71, 692.65, 1590.01, and 3423.16 cm-1 represent the characteristic peaks of ZnO. The band at 3500 cm-1 is related to the presence of hydroxyl groups, and the band close to 1590 cm-1 is related to H-O-H bending vibration.

3.4 Gas sensing mechanism

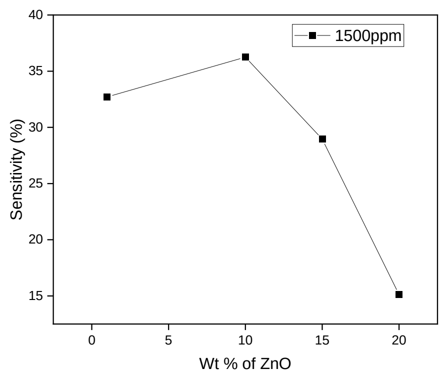
The entire system of an internally constructed gas sensing chamber, including a synthetic dry air unit and programmable DC power supply, is used for gas testing. The operating temperature of the sensors has an impact on their sensitivity because a change in temperature alters how the nanomaterials respond. By connecting a resistive wire through an electrode, the DC power supply controls and regulates the temperature to which the sensor is adapted. The digital multimeter displays and records the variation in the sensor's resistance during operation. The sensor is impacted by the entry and exit of the target gas from the confined chamber, and the magnitude of its resistance varies periodically. To test the sensing capabilities of the created nano composites, butane gas is used as the target gas. The following factors determine how the gas sensor reacts to the target gas:

$$S = [(R_g – R_a)/ R_a] \times 100\%$$

Where S denotes the gas sensor's sensitivity as well as its response value. R_g is the resistance value shown by the test gas's gas sensor. R_a is the resistance reading that the gas sensor in air displays.

The performance of the metal oxide gas sensor is explained by the chemi resistance principle, which peculiarly describes the change in electrical conductivity or resistivity of the samples upon exposure to a target gas. The kind of majority carriers in the metal oxide thin film controls whether or not the film's resistance rises or falls [19]. The properties of gas molecules and semiconducting film in a natural environment, whether they are oxidizing or reducing. N-type materials have thin films and have increased resistance to oxidising gases (acceptor) and decreased resistance to reducing gases (donor). On the other hand, with regard to p-type materials [20].

It has been studied how chemiresistor performance for explosive butane gas changes with operating temperature, gas concentration, and room temperature. It was found that the resistance value was in the 200 MΩ range. The butane gas response to various ZnO concentrations (1, 10, 15, and 20 c/o) of the chemi resistor at room temperature is shown in the inset of Fig. 5 with 32.71, 36.25, 28.96, and 15.13 percentages of sensitivity, respectively.



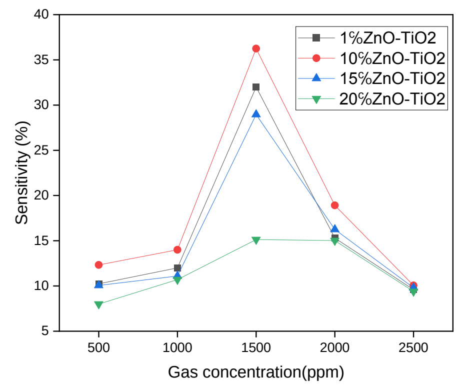


Fig.5: Different Wt percentage of ZnO Vs Sensitivity at room temperature

The results with butane gas concentrations ranging from 500 ppm to 2500 ppm versus sensitivity are shown in Fig. 6(a). It is demonstrating the high sensitivity of the 37 c/o at 1500 ppm. The maximum response to the butane gas to ZnO (10 c/o) doped TiO2 is shown in Fig. 6(b) as a bar chart of selective response to reducing gas (butane) as a function of operating temperature from 323K to 393K with 1500 ppm gas concentration. The optimal temperature was found to be 363 K.

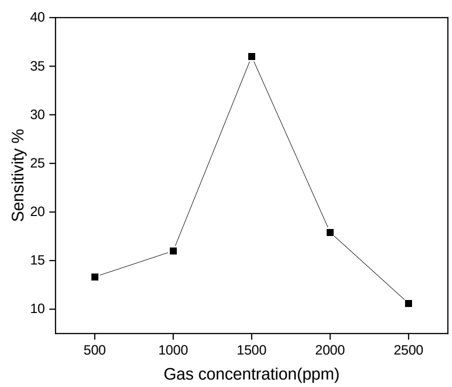


Fig.6(a) Gas concentration Vs Sensitivity(10% ZnO-TiO_2)

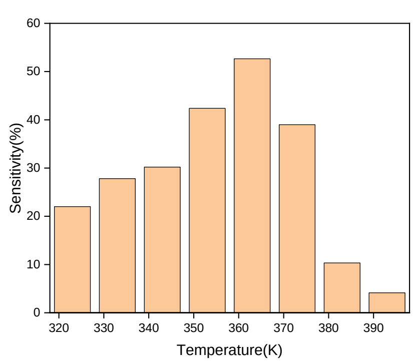


Fig.6(b) Temperature Vs sensitivity(10% ZnO-TiO_2)

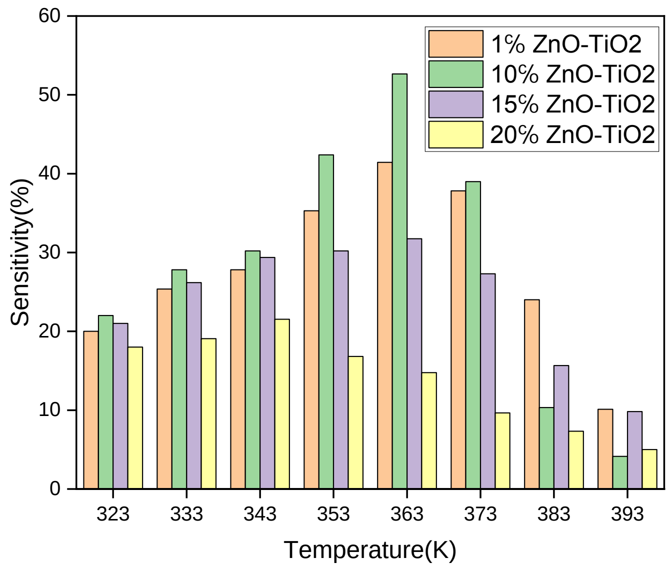


Fig.6: (c) Temperature Vs sensitivity of all concentrations of ZnO-TiO_2

Figure 7 depicts the cyclic reaction to the butane-reducing gas at the ideal temperature of 363 K with the surface concentration of gas absorbed (1500 ppm). The ZnO-TiO_2 nano composite sensor displays good gas sensitive performance for butane gas in terms of operating temperature when taking the results of the gas response. Its sensing response to butane gas at 1500 ppm was investigated for 60 days, with changes being noted every 10 days. The sensing capacity of manufactured samples was largely stable over the course of the time period, with only a very slight loss of sensing response for this sensor.

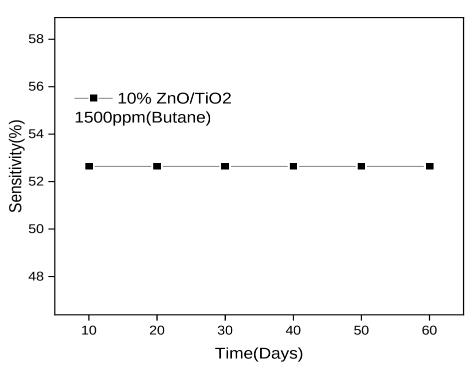


Fig 7: Stability analysis of (10%) ZnO-TiO2 nano composites at ideal temperature

Conclusion

By using the sol-gel method and varying the weight percentage of ZnO, ZnO-TiO2 nano composite materials of various crystallite sizes were successfully synthesized. By using XRD, SEM, EDAX, and FTIR, the prepared samples were characterized. 15.19 to 17.93nm was found to be the range for the average crystallite size. The temperature range of 323K to 393K was used for the butane gas sensing studies. According to the sensing studies, the ZnO-TiO2 nano composites' ability to detect butane gas is significantly influenced by ZnO concentration.

Conflicts of Interest

The corresponding author hereby declares on behalf of other authors that there is no conflict of interest among the authors.

Acknowledgement

The authors are thankful to the material research center and management of Presidency University, Bangalore.

References:

1. Colborn, Theo, Carol Kwiatkowski, Kim Schultz, and Mary Bachran. "Natural Gas Operation from a Public Health Perspective." *Human and ecological risk assessment: An International Journal* 17, no. 5 (2011): 1039-56.
2. Zhang, Jian, Ziyu Qin, Dawen Zeng, and Changsheng Xie. "Metal-Oxide-Semiconductor Based Gas Sensors: Screening, Preparation, and Integration." *Physical Chemistry Chemical Physics* 19, no. 9 (2017): 6313-29.
3. Laurent, S, S Boutry, and RN Muller. "Metal Oxide Particles and Their Prospects for Applications." In *Iron Oxide Nanoparticles for Biomedical Applications*, 3-42: Elsevier, 2018.
4. Deng, Yonghui. "Sensing Mechanism and Evaluation Criteria of Semiconducting Metal Oxides Gas Sensors." In *Semiconducting Metal Oxides for Gas Sensing*, 23-51: Springer, 2019.
5. Ranganatha, V Lakshmi, KS Nithin, Shaukath Ara Khanum, G Nagaraju, and C Mallikarjunaswamy. "Zinc Oxide Nanoparticles: A Significant Review on Synthetic Strategies, Characterization and Applications." Paper presented at the AIP Conference Proceedings, 2019.
6. Ferroni, M, V Guidi, G Martinelli, G Faglia, P Nelli, and G Sberveglieri. "Characterization of a Nanosized Tio2 Gas Sensor." *Nanostructured materials* 7, no. 7 (1996): 709-18.
7. Park, Jae Young, Sun- Woo Choi, Jun- Won Lee, Chongmu Lee, and Sang Sub Kim. "Synthesis and Gas Sensing Properties of Tio2–Zno Core- Shell Nanofibers." *Journal of the American Ceramic Society* 92, no. 11 (2009): 2551-54.
8. Sharma, Ajay, RK Karn, and SK Pandiyan. "Synthesis of Tio2 Nanoparticles by Sol-Gel Method and Their Characterization." *J Basic Appl Eng Res* 1, no. 9 (2014): 1-5.
9. Park, Jae Young, Ho-hyoung Kim, Dolly Rana, Deepika Jamwal, and Akash Katoch. "Surface-Area-Controlled Synthesis of Porous Tio2 Thin Films for Gas-Sensing Applications." *Nanotechnology* 28, no. 9 (2017): 095502.
10. Das, Sagnik, Subhajit Mojumder, Debdulal Saha, and Mrinal Pal. "Influence of Major Parameters on the Sensing Mechanism of Semiconductor Metal Oxide Based

Chemiresistive Gas Sensors: A Review Focused on Personalized Healthcare." *Sensors and Actuators B: Chemical* 352 (2022): 131066.

11. Eranna, G, BC Joshi, DP Runthala, and RP Gupta. "Oxide Materials for Development of Integrated Gas Sensors—a Comprehensive Review." *Critical Reviews in Solid State and Materials Sciences* 29, no. 3-4 (2004): 111-88.
12. Gao, Xing, and Tong Zhang. "An Overview: Facet-Dependent Metal Oxide Semiconductor Gas Sensors." *Sensors and Actuators B: Chemical* 277 (2018): 604-33.
13. Wang, Chao- Nan, Yu- Liang Li, Fei- Long Gong, Yong- Hui Zhang, Shao- Ming Fang, and Hao- Li Zhang. "Advances in Doped Zno Nanostructures for Gas Sensor." *The Chemical Record* 20, no. 12 (2020): 1553-67.
14. Tian, Xu, Xiuxiu Cui, Tingrun Lai, Jie Ren, Zhichao Yang, Mingjing Xiao, Bingsen Wang, Xuechun Xiao, and Yude Wang. "Gas Sensors Based on Tio2 Nanostructured Materials for the Detection of Hazardous Gases: A Review." *Nano Materials Science* (2021).
15. Vayssieres, L. Growth of Arrayed Nanorods and Nanowires of ZnO from Aqueous Solutions. Adv. Mater. 2010, 15, 464–466. [CrossRef]
16. Liu, X.; Qin, X.; Ji, H.; Wang, M. An enhanced butanone sensing performance of Er0.7Yb0.3FeO3 material with the proper electronic structure. J. Alloys Compd. 2018, 772, 263–271. [CrossRef]
17. Jiang, Z.; Guo, Z.; Sun, B.; Jia, Y.; Li, M.; Liu, J. Highly sensitive and selective butanone sensors based on cerium-doped SnO2 thin films. Sens. Actuators B Chem. 2010, 145, 667–673. [CrossRef]
18. Firdaus, CM, MSB Shah Rizam, M Rusop, and S Rahmatul Hidayah. "Characterization of Zno and Zno: Tio2 Thin Films Prepared by Sol-Gel Spray-Spin Coating Technique." *Procedia Engineering* 41 (2012): 1367-73.
19. Shankar, Prabakaran, and John Bosco Balaguru Rayappan. "Gas Sensing Mechanism of Metal Oxides: The Role of Ambient Atmosphere, Type of Semiconductor and Gases-a Review." *Sci. Lett. J* 4, no. 4 (2015): 126.
20. Masikini, Milua, Mahabubur Chowdhury, and Ouassini Nemraoui. "Metal Oxides: Application in Exhaled Breath Acetone Chemiresistive Sensors." *Journal of The Electrochemical Society* 167, no. 3 (2020): 037537.
21. Oliveira, T.; Zito, C.; Perfecto, T.; Azevedo, G.; Volanti, D. ZnO twin-rods decorated with Pt nanoparticles for butanone detection. *New J. Chem.* **2020**, *44*, 15574–15583.
22. Y. Lia and N. Chen, Formaldehyde detection: SnO2 microspheres for formaldehyde gassensor with high sensitivity, fast response/recovery and goodselectivity, Sens. Actuators, B, 2017, 238, 264.
23. Vioto, G.; Perfecto, T.; Zito, C.; Volanti, D. Enhancement of 2-butanone sensing properties of SiO_2@CoO core-shell structures. *Ceram. Int.* **2020**, *46*, 22692–22698.
24. Zhang, Q.; Zhang, H.; Xu, M.; Shen, Z.; Wei, Q. A WO_3 nanorod-Cr_2O_3 nanoparticle composite for selective gas sensing of 2-butanone. *Chin. Chem. Lett.* **2018**, *29,* 538–542.
25. Ppb-Level Butanone Sensor Based on ZnO-TiO_2-rGO Nanocomposites**.**