Open Access Library Journal
2023, Volume 10, e9970
ISSN Online: 2333-9721
ISSN Print: 2333-9705

SnO_2 Modified by Quasi-Molecular Imprinting Method Gas Sensor for Formaldehyde

Wenfu Qin, Haiming Zhang*

School of Physical Sciences and Technology, Tiangong University, Tianjin, China
Email: *441598345@qq.com

How to cite this paper: Qin, W.F. and Zhang, H.M. (2023) SnO_2 Modified by Quasi-Molecular Imprinting Method Gas Sensor for Formaldehyde. *Open Access Library Journal*, **10**: e9970.
https://doi.org/10.4236/oalib.1109970

Received: March 6, 2023
Accepted: March 25, 2023
Published: March 28, 2023

Abstract

The stannic oxide (SnO_2) was modified using Quasi-Molecular imprinting method. The morphology and structure of the modified SnO_2 were characterized by X-ray diffraction (XRD), and transmission electron microscopy (SEM). The gas-sensing performance of the modified and unmodified SnO_2 sensors was compared, and the mechanism of MIP technique in improving the gas-sensing performance of SnO_2 was discussed. The selective test results showed that the improved SnO_2 gas sensor exhibited good gas sensitivity to formaldehyde. The SnO_2 gas sensor with good formaldehyde gas selectivity achieved precise measurement of continuous formaldehyde concentration. The response value to 100 ppm formaldehyde was 100˚C at 230˚C. The synthesis of SnO_2 was discussed, and the mechanism of improving gas-sensing performance after modification was analyzed.

Subject Areas

Physical Chemistry

Keywords

Stannic Oxide, Formaldehyde Detection, Quasi-Molecular Imprinting

1. Introduction

Nowadays, people pay more and more attention to volatile organic gases (VOCs) in various environments, the application of gas sensors is becoming increasingly important [1] [2] [3] [4]. For this reason, human beings have designed various gas sensors to detect various volatile flammable or toxic gases from different actual detection needs [5] [6]. Formaldehyde, which is colorless, odorless, and volatile, is one of the harmful gases that often appears in human daily activities, such as the home decoration industry. Long-term exposure to formaldehyde

leakage may lead to some diseases. Therefore, developing a gas sensor with excellent formaldehyde gas sensitivity has significant practical significance [7] [8].

The stannic oxide (SnO_2) has received widespread attention as a stable wide-band-gap n-type semiconductor in many applications [9]. Molecular imprinting technology provides great potential for identifying applications in various sensor applications [10] [11] [12] [13]. Molecular imprinting has specificity, as the molecularly imprinted polymer effectively and selectively binds to specific template molecules or their analogs. This provides a mechanism with significant target recognition and selectivity for the design of ultra-sensitive gas sensors [14] [15]. In order to detect formaldehyde, we designed a highly sensitive SnO_2-based formaldehyde gas sensor based on a quasi-molecular imprinting mechanism.

2. Experiment

2.1. Preparation of SnO_2 Water-Based Nanomaterials

Add 1.61 g of Tin Tetrachloride ($SnCl_4$) and 1.4 g of HMTA ($C_6H_{12}N_4$) to 40 ml of deionized water solvent, fully stir for 2 hours to fully mix the solution, then transfer it to 90 ml of polytetrafluoroethylene, put it into a metal autoclave, and conduct high-temperature hydrothermal heating at 120˚C for 12 hours. After the time, cool naturally and collect the sediment. Use deionized water and absolute ethanol to cross centrifuge and wash in a centrifuge at the speed of 4000 r/s for 3 times, then continue to collect the centrifuged products and dry them at 60˚C for 8 hours, and finally collect the products again and anneal them at 350˚C for 4 hours. After cooling to room temperature, collect powdered nano SnO_2 materials. Mark this group of samples as A.

2.2. Preparation of SnO_2 Formaldehyde-Based Nanomaterials

Add 1.61 g of Tin Tetrachloride ($SnCl_4$) and 1.4 g of HMTA ($C_6H_{12}N_4$) to 30 ml of deionized water solvent and 10 ml of formaldehyde mixed solution, fully stir for 2 hours to fully mix the solution. Other steps are the same as 2.1. After cooling to room temperature, collect powdered nano SnO_2 materials. Mark this group of samples as B.

2.3. Preparation of Gas Sensors with Quasi-Molecular Imprinting Method

A total of four groups of control experiments were established, which were named AW, AF, BW and BF. The first letter A of the four sample labels represents pure water mixing at the mixing stage, namely, water-based samples; The first letter B represents the addition and mixing of formaldehyde liquid in the hydrothermal mixing stage of nanomaterials; The second letter W represents the use of pure water in the coating aging stage; The second letter F represents the use of formaldehyde liquid in the coating aging stage. Therefore, sample A is coated with water and aged at 120˚C for 24 hours to obtain the gas sensor AW;

Sample A is coated with formaldehyde and aged at 120˚C for 24 hours to obtain the gas sensor AF; The gas sensor BW is obtained by aging the sample B with water at 120˚C for 24 hours; Group B samples were coated with formaldehyde and aged at 120˚C for 24 hours to obtain gas sensor BF. The three groups of AF, BW and BF can all be referred to as nano gas sensor materials improved by excimer imprinting technology.

3. Results and Discussion

3.1. Morphology and Structural Characteristics

X-ray diffraction (XRD) as shown in Figure 1, all distinguishable peaks match well with the tetragonal rutile structure of SnO_2 and are consistent with the JCPDS file 41-1445, indicating that the samples have good purity. There are no characteristic peaks of other impurities in any of the samples in Figure 1. The diffraction peaks of the samples are broad and low, indicating that their crystal grain size is small.

The microstructure of SnO_2 nano-materials before and after modification was observed by SEM. Nano-SnO_2 prepared on different substrates can be observed in (a)-(c) of Figure 2(a) is water-based sample A, (b) is sample AW of water-based sample coated with water, (c) is sample AF of water-based sample coated with formaldehyde, (d) is sample B of formaldehyde, (e) is sample BW of formaldehyde based sample coated with water, and (f) is sample BF of formaldehyde based sample coated with formaldehyde; It can be seen that the morphology and structure of all SnO_2 samples are basically similar, all of which are small spherical particles, but there are some differences in the size of the spherical structure. From the size of the spherical structure, the order is AW ≈ A > BW ≈ B > AF > BF, which shows that water coating has little effect on changing the size of spherical particles, but it is very feasible to improve the existing SnO_2 nanomaterials through three kinds of excimer imprinting, By this means, the diameter of spherical particles can be significantly reduced at the microscopic level.

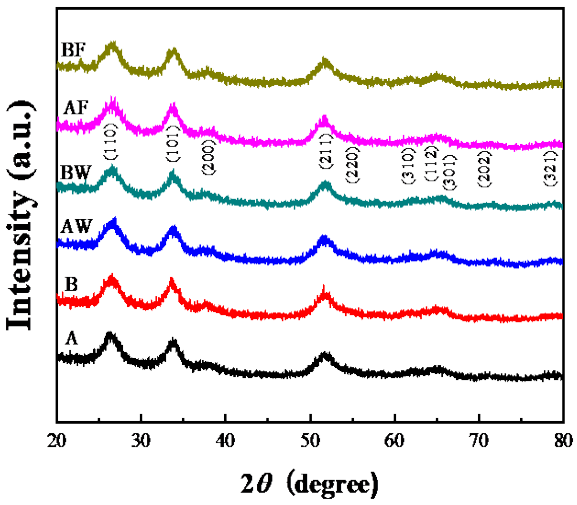

Figure 1. XRD patterns of different SnO_2.

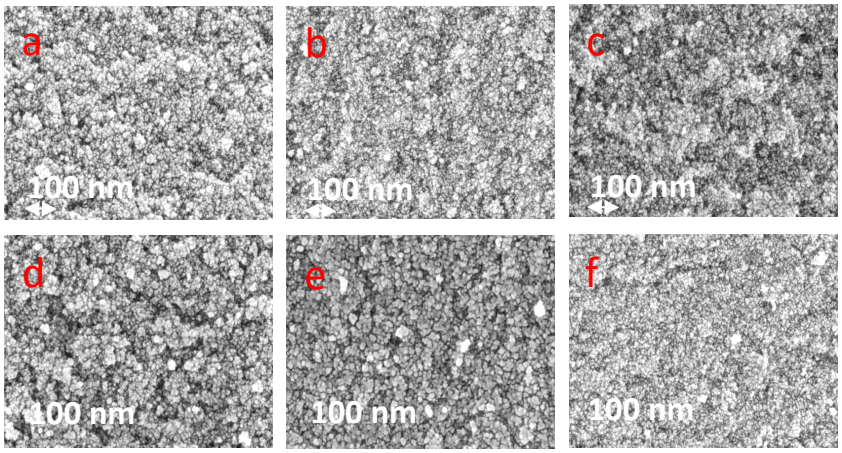

Figure 2. SEM images of SnO_2, (a) is A, (b) is AW, (c) is AF, (d) is B, (e) is BW, (f) is BF.

3.2. Gas-Sensing Property

Working temperature mainly affects the sensitivity of sensor and the time of gas adsorption and desorption [16] [17]. Consequently, the SnO_2 sensor was exposed to 10 ppm formaldehyde at 200˚C - 250˚C, and the best operating temperature was 230˚C. **Figure 3(a)** is the response of sensors made of Samples AW, **Figure 3(b)** is the response of sensors made of Samples AF, **Figure 3(c)** is the response of sensors made of Samples BW, **Figure 3(d)** is the response of sensors made of Samples BF. It can be shown that the response values of the four groups of sensors increase with the increase of temperature, reach the maximal response at 230˚C, and then decrease with the further increase of temperature. The unmodified response value is 50, and the modified best response value is 100, which upgrades the response performance by 2 times compared with that unmodified. The optimal working temperature of the sensor unmodified and modified does not change.

In recent years, with the advancement of gas sensor research, sensor 3S characteristics (sensitivity, stability, selectivity) research has become one of the important fields [18]. The stability verification of modified and unmodified SnO_2 sensors are shown in **Figure 4**. **Figure 4(a)** is the response of sensors to 10 ppm, and **Figure 4(b)** is the response of sensors to 100 ppm. It can be shown that the formaldehyde sensor retains basically the same response in the continuous test of the same concentration, and the mean error between the response values of the same concentration is less than 1.

Figure 5 shows the response of SnO_2 nanostructure sensor to a series of test gases (formaldehyde, methanol, ethanol, acetone, acetic acid, benzene and xylene) 10 ppm at the optimal working temperature of 230˚C. It can be seen that the unmodified SnO_2 gas sensor has the best selectivity to formaldehyde. After Quasi-Molecular imprinting method modification, the selectivity and response value of formaldehyde have been improved, especially the selectivity has been greatly improved, which has a good reference value for improving the selectivity of gas sensors.

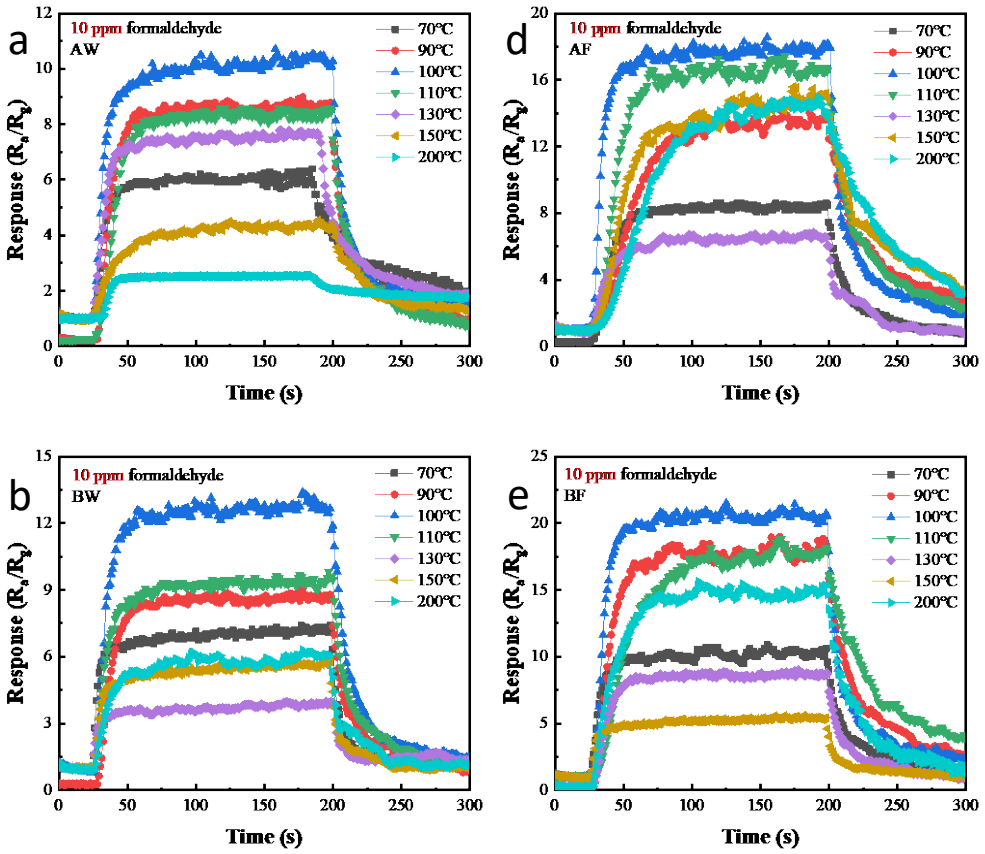

Figure 3. The response recovery curves of nano-SnO_2 sensors with different bases to 10 ppm formaldehyde at different operating temperatures (70˚C - 200˚C), (a) AW-based SnO_2 gas sensor, (b) BW-based SnO_2 gas sensor, (c) AF-based SnO_2 gas sensor, (d) BF-based SnO_2 gas sensor.

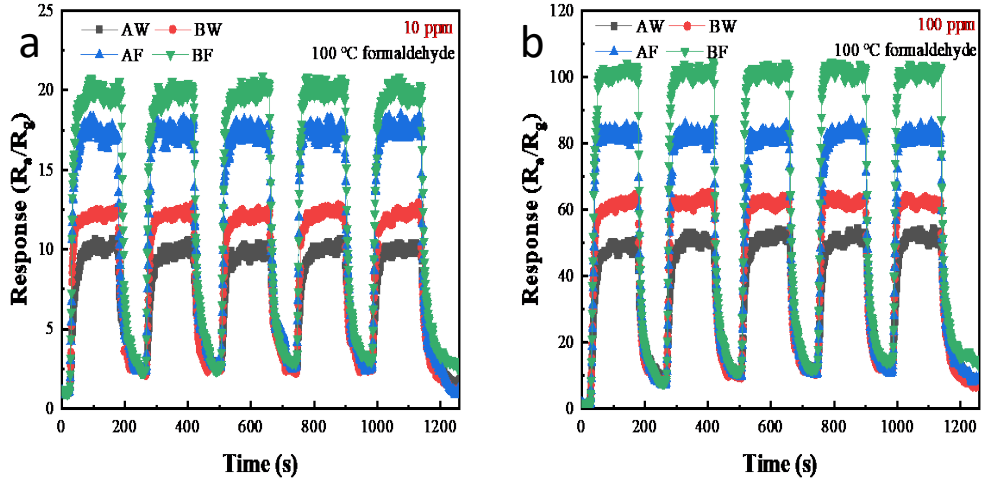

Figure 4. The stability verification of the SnO_2 modified and unmodified based sensor: (a) the response to 10 ppm; (b) the response to 100 ppm.

3.3. Gas-Sensing Mechanism

In the formaldehyde environment, the resistance value is mainly determined by the height of the barrier, as follows:

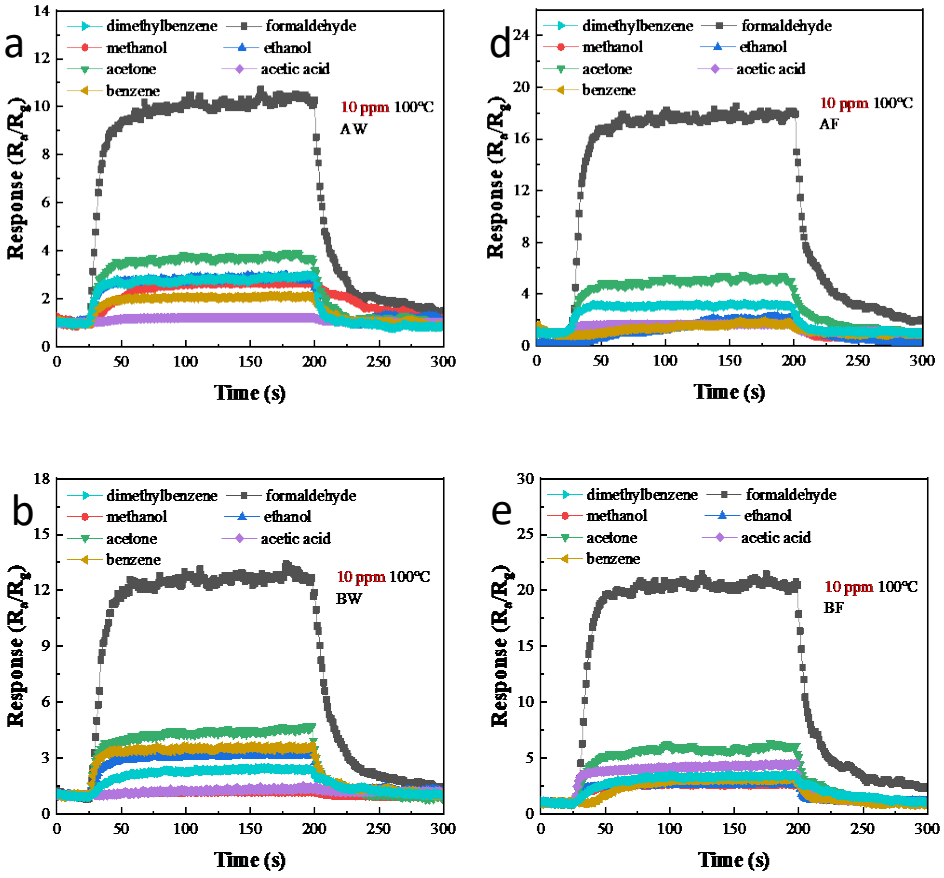

Figure 5. The response of the 10 ppm various test gases (formaldehyde, methanol, ethanol, acetone, acetic acid, benzene and dimethylbenzene) at 230˚C.

$$R_a = R_g \exp\left[\frac{qV_S(t)}{\kappa T}\right]$$

Here R_a is stable resistance in air, R_g is stable resistance in acetic acid, $qV_s(t)$ is the barrier height on the crystal surface, K is Boltzmann constant, T is temperature. The response recovery curve of SnO_2 sensor in the air and formaldehyde environment shows that there is an exponential relationship between Rg and Ra, and a small barrier change will lead to a significant change in the resistance of the sensor.

Formaldehyde clusters can interact with SnO_2 in solution during the synthesis of nanomaterials, which optimizes the pore structure of SnO_2 and is conducive to the adsorption of formaldehyde. The introduction of formaldehyde solution further optimized the pore structure of nano-materials. The etching process of formaldehyde clusters on nano-materials SnO_2 is similar to the molecular etching mechanism (defined as excimer cluster etching mechanism). Due to the introduction of formaldehyde in the process of nano-materials and device manufacturing, the sensor of BF based on AF makes BF alternately exposed to formaldehyde gas and clean air in the test process, and the formaldehyde gas absorbs more and diffuses faster, finally improving the sensing ability.

4. Conclusion

SnO_2 modified by Quasi-Molecular imprinting method gas sensor for formaldehyde. Modified SnO_2 showed good gas sensing performance to formaldehyde at 230˚C. The response of the modified SnO_2 to 100 ppm formaldehyde at 230˚C can reach 100, which is two times higher than the unmodified. The selectivity of modified SnO_2 to formaldehyde has also been greatly improved. The adsorb oxygen ability of Quasi-Molecular imprinting modified SnO_2 was enhanced due to the increase of the contact area with formaldehyde gas, which effectively improved the gas sensing performance. Therefore, it is helpful to use Quasi-Molecular imprinting method to improve gas sensing performance. This paper provides a modification strategy to improve the gas sensing performance of nano-materials with Quasi-Molecular imprinting method, which has certain reference value for the development of high-performance gas sensors.

Conflicts of Interest

The authors declare no conflicts of interest.

References

[1] Ali, A., Di, W., Liu, J., Ge, F., Wang, J. and Chu, X. (2022) The Detection of Ethanol Vapors Based on a P-Type Gas Sensor Fabricated from Heterojunction MoS_2-$NiCo_2O_4$. *Materials Chemistry and Physics*, **282**, Article ID: 125964. https://doi.org/10.1016/j.matchemphys.2022.125964

[2] Barsan, N., Koziej, D. and Weimar, U. (2007) Metal Oxide-Based Gas Sensor Research: How to? *Sensors & Actuators B*: *Chemical*, **121**, 18-35. https://doi.org/10.1016/j.snb.2006.09.047

[3] Deng, S, Tjoa, V., Hai, M.F., *et al.* (2012) Reduced Graphene Oxide Conjugated Cu_2O Nanowire Mesocrystals for High-Performance NO_2 Gas Sensor. *Journal of the American Chemical Society*, **134**, 4905-4917. https://doi.org/10.1021/ja211683m

[4] Fu, X., Yang, Q., Zhou, Q., Lin, Q. and Wang, C. (2015) Template-Monomer Interaction in Molecular Imprinting: Is the Strongest the Best? *Open Journal of Organic Polymer Materials*, **5**, 58-68. https://doi.org/10.4236/ojopm.2015.52007

[5] Patil, V.L., Vanalakar, S.A., Patil, P.S. and Kim, J.H. (2017) Fabrication of Nanostructured ZnO Thin Films Based NO_2 Gas Sensor via SILAR Technique. *Sensors & Actuators B*: *Chemical*, **239**, 1185-1193. https://doi.org/10.1016/j.snb.2016.08.130

[6] Tabassum, S., Kumar, R. and Dong, L. (2017) Plasmonic Crystal Based Gas Sensor Towards an Optical Nose Design. *IEEE Sensors Journal*, **19**, 6210-6223. https://doi.org/10.1109/JSEN.2017.2740176

[7] Tantipanjaporn, A., Kung, K.Y., Sit, H.Y. and Wong, M.-K. (2022) Quinoliziniu-Based Fluorescent Probes for formaldehyde Detection in Aqueous Solution, Serum, and Test Strip via 2-Aza-Cope Rearrangement. *RSC Advances*, **12**, 11543-11547. https://doi.org/10.1039/D2RA01397E

[8] Jian, S., Cheng, C., Wang, J., Lv, Y., Li, B., Wang, D., Wang, C., Tan, H. and Ma, B. (2022) Effect of Sulfonated Acetone Formaldehyde on the Properties of High-Fluid Backfill Materials. *Construction and Building Materials*, **327**, Article ID: 126795. https://doi.org/10.1016/j.conbuildmat.2022.126795

[9] Li, G., Fan, Y., Hu, Q., *et al.* (2022) Morphology and Size Effect of Pd Nanocrystals

on Formaldehyde and Hydrogen Sensing Performance of SnO_2 Based Gas Sensor. *Journal of Alloys and Compounds*, **906**, Article ID: 163765. https://doi.org/10.1016/j.jallcom.2022.163765

[10] Yu, J.B., Sun, M., Yu, M., Yang, M., Yu, H., Yang, Y., Dong, X.-T. and Xia, L. (2022) Preparation of Near Room Temperature Gas Sensor Based on Regular Octahedral Porous ZnO/SnO_2 Composite. *Journal of Alloys and Compounds*, **920**, Article ID: 165884. https://doi.org/10.1016/j.jallcom.2022.165884

[11] Gpel, W. and Schierbaum, K.D. (1995) SnO_2 Sensors: Current Status and Future Prospects. *Sensors & Actuators B*: *Chemical*, **26**, 1-12. https://doi.org/10.1016/0925-4005(94)01546-T

[12] Leite, E.R., Weber, I.T., Longo, E. and Varela, A. (2000) A New Method to Control Particle Size and Particle Size Distribution of SnO_2 Nanoparticles for Gas Sensor Applications. *Advanced Materials*, **12**, 965-968. https://doi.org/10.1002/1521-4095(200006)12:13<965::AID-ADMA965>3.0.CO;2-7

[13] Wang, B., Zhu, L.F., Yang, Y.H., Xu, N.S. and Yang, G.W. (2008) Fabrication of a SnO_2 Nanowire Gas Sensor and Sensor Performance for Hydrogen. *The Journal of Physical Chemistry C*, **112**, 6643-6647. https://doi.org/10.1021/jp8003147

[14] Tan, W.H., Yu, Q., Ruan, X. and Huang, X. (2015) Design of SnO_2-Based Highly Sensitive Ethanol Gas Sensor Based on Quasi Molecular-Cluster Imprinting Mechanism. *Sensors and Actuators B*: *Chemical*, **212**, 47-54. https://doi.org/10.1016/j.snb.2015.01.035

[15] Tan, W., Ruan, X., Yu, Q., Yu, Z. and Huang, X. (2014) Fabrication of a SnO_2-Based Acetone Gas Sensor Enhanced by Molecular Imprinting. *Sensors*, **15**, 352-364. https://doi.org/10.3390/s150100352

[16] Bhowmick, T., Ghosh, A., Nag, S. and Majumder, S.B. (2022) Sensitive and Selective CO_2 Gas Sensor Based on CuO/ZnO Bilayer Thin-Film Architecture. *Journal of Alloys and Compounds*, **903**, Article ID: 163871. https://doi.org/10.1016/j.jallcom.2022.163871

[17] Han, D. (2020) Sol-Gel Autocombustion Synthesis of Zinc Oxide Foam Decorated with Holes and Its Use as Acetic Acid Gas Sensor at Sub-ppm Level. *Ceramics International*, **46**, 3304-3310. https://doi.org/10.1016/j.ceramint.2019.10.036

[18] Zuliani, A., Bandelli, D., Chelazzi, D., Giorgi, R. and Baglioni, P. (2022) Environmentally Friendly ZnO/Castor Oil Polyurethane Composites for the Gas-Phase Adsorption of Acetic Acid. *Journal of Colloid and Interface Science*, **614**, 451-459. https://doi.org/10.1016/j.jcis.2022.01.123