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SYNTHESIS OF OCTAHEDRON Zn_2SnO_4 BY HYDROTHERMAL METHOD FOR HIGH PERFORMANCE ETHANOL SENSOR[#]

Nguyen Hong Hanh[1, 2], Lai Van Duy[1], Chu Manh Hung[1, *], Nguyen Van Duy[1], Nguyen Van Hieu[3, 4], Nguyen Duc Hoa[1]

[1]*International Training Institute for Materials Science (ITIMS), Hanoi University of Science and Technology, Ha Noi, Viet Nam*

[2]*Institute of Engineering Physics, 17 Hoang Sam Street, Cau Giay District, Ha Noi, Viet Nam*

[3]*Faculty of Electrical and Electronic Engineering, Phenikaa Institute for Advanced Study (PIAS), Phenikaa University, Yen Nghia, Ha-Dong district, Ha Noi, Viet Nam*

[4]*Phenikaa Research and Technology Institute (PRATI), A&A Green Phoenix Group, 167 Hoang Ngan, Ha Noi, Viet Nam*

[*]Email: *mhchu@itims.edu.vn*

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Abstract. The octahedron Zn_2SnO_4 was prepared through a facile hydrothermal method for ethanol gas-sensing application. The synthesized material was characterized by scanning electron microscopy (SEM) and powder x-ray diffraction (XRD). The gas-sensing characteristics were measured at various concentrations of ethanol at temperature ranging from 350 to 450 ºC. The gas response exhibits good linear relationship with increasing ethanol concentrations in the range of 50 -250 ppm. Gas-sensing measurements demonstrated that the synthesized octahedron Zn_2SnO_4 showed *n*-type semiconducting behavior, where the sensor resistance decreased upon exposure to ethanol. The findings pointed out that the sensors showed the highest response value at operating temperature of 400 ºC. The sensor response value was 30 at 250 ppm ethanol. Such outstanding gas sensing property might be attributed to the morphology of the octahedra which provided large contact area between Zn_2SnO_4 and target gas. The synthesized octahedron Zn_2SnO_4 is potential for detecting traces of ethanol.

Keywords: hydrothermal method, gas sensor, octahedron Zn_2SnO_4, ethanol sensing.

Classification numbers: 2.2.2, 2.4.2, 2.10.2.

1. INTRODUCTION

Ethanol is an important organic solvent used in industrial and pharmaceutical processes. However, ethanol is highly volatile and flammable and long-term exposure to ethanol can cause

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central nervous system disorders. Therefore, to detect the ethanol gas timely becomes a very important question considering the physical and production safety [1-6]. To date, many researchers hav*e dedicated their works on development of ethanol gas sensor using different metal semiconductor oxides such as ZnO [1], SnO_2 [2], SnO_2/ZnO [3], TiO_2 [4], In_2O_3 [5, 6], WO_3 [7]. However, they suffer from some limitations such as low sensitivity, poor selectivity and instability. In recent years, the complex oxides are of great interest as gas sensitive materials because they have many advantages over the common binary oxides including the chemically inert, thermal stable, as well as environmentally friendly. The complex oxides extensively used as sensor materials are $ZnFe_2O_4$ [8, 9] and Zn_2SnO_4 [10, 11] because of their multi-functional characteristics. Thanks to it advanced characteristics such as high electron mobility, high electrical conductivity, Zn_2SnO_4, as an interesting transparent conductive oxide material with a wide band gap of 3.6 eV [12], has been applied in various fields, such as photocatalysis [13], Li-ion batteries [14], solar energy conversion [15], and gas sensors [16-18]. Sensors based on Zn_2SnO_4 materials with different morphologies such as nanoparticles [19], nanowires [16], nanospheres [20], lamellar micro-spheres [21] have been tested over many gases including ethanol. An *et al*. fabricated Zn_2SnO_4 nanospheres for ethanol gas sensor [20]. Recent studies also pointed out that the gas-sensing performance of metal oxides is highly depended on their morphologies, crystalline size, porosity, defect level etc. [22]. Therefore, preparation of Zn_2SnO_4 nanostructures with novel morphology to further improve the response speed, selectivity and stability of devices is still challenging.

In this study, we developed a simple and inexpensive hydrothermal method to prepare octahedron Zn_2SnO_4 for gas sensor application. By using common chemicals available in the market, we could synthesize octahedron Zn_2SnO_4 with high quality and high crystallinity. The synthesized material is effective ethanol gas sensor towards industrial application.

2. EXPERIMENTAL

The octahedron Zn_2SnO_4 material was synthesized by a facile hydrothermal method. The synthesis of octahedron Zn_2SnO_4 was summarized in Figure 1.

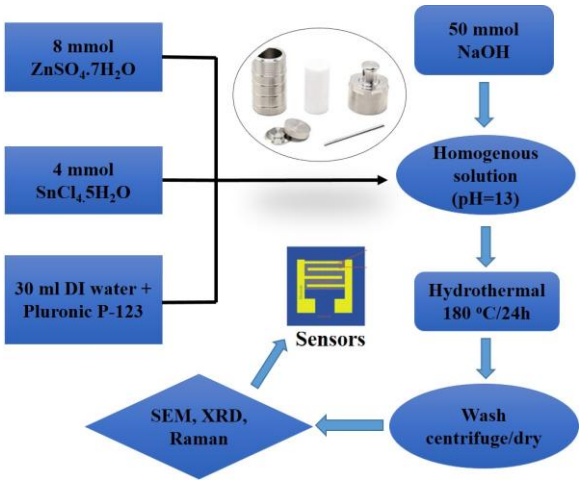

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Figure 1. Process for the hydrothermal synthesis of octahedron Zn_2SnO_4.

In a typical synthesis, $ZnSO_4.7H_2O$ (99.5 %) (8 mmol) and $SnCl_4.5H_2O$ (99 %) (4 mmol) were dissolved in a mixture of 30 ml of deionized water and Pluronic P-123 (99 %). After stirring for 15 minutes, 50 mmol NaOH (96 %) was added to this system, then continued stirring for 20 minutes until the pH value was about 13. After that, the above turbid solution was transferred to the 100 ml of inox autoclave at 180 °C for 24 hours. After natural cooling to room temperature, the precipitate was centrifuged and washed with deionized water several times. The precipitate in the flask was rinsed several times with deionized water and two times with ethanol solution with a centrifuge 4000 rpm. Finally, the white product was obtained and dried in an oven at 60 °C for 24 hours and calcining at 550 °C for 2 hours in air atmosphere. The synthetic materials are characterized by X-ray diffraction (XRD; Advance D8, Bruker) and emission field scanning electron microscope (FE-SEM), respectively.

3. RESULTS AND DISCUSSION

3.1. SEM images of the synthesized octahedron Zn_2SnO_4

The morphology and microstructure of the synthesized octahedron Zn_2SnO_4 were characterized by SEM observation. As shown in Figure 2A, a low-magnification SEM image of the as-prepared Zn_2SnO_4 reveals that the sample contains numerous octahedral blocks with different sizes ranging from 4 µm to 6 µm. In addition, there are many small sheets covered around those octahedral blocks, possibly due to the fragments of the sample.

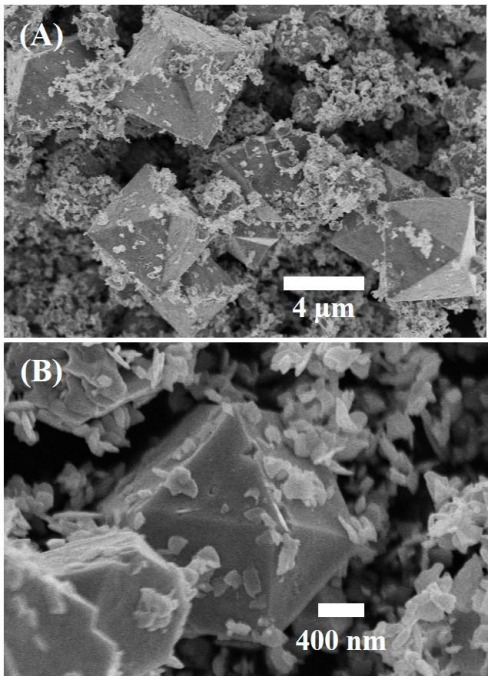

Figure 2. (A) Low and (B) high magnification SEM images of the synthesized octahedron Zn_2SnO_4.

A high-magnification SEM image (Figure 2B) of the octahedron Zn_2SnO_4 architecture shows that the small sheets have an average size of 400 nm in diameter and less than 100 nm in

thickness. Anyhow, these SEM images confirms the successfully synthesis of octahedron Zn_2SnO_4 by the hydrothermal method.

3.2. XRD pattern of the synthesized octahedron Zn_2SnO_4

The XRD pattern of the synthesized octahedron Zn_2SnO_4 was shown in Figure 3. It is clearly that all diffraction peaks are in good agreement with the profile of inverse spinel phase of cubic Zn_2SnO_4 (JCPDS: 24-1470). No impurity peak is detected that indicates the as-prepared sample is of high purity [23] or single phase of Zn_2SnO_4 with the accuracy of XRD. The intensity of (311) peak is strongest indicating the preferred growth orientation of the Zn_2SnO_4 crystals. The crystal size of the Zn_2SnO_4 crystal calculated by Scherrer formula via the prominent peak (311) to be about 25.77 nm. This value is much smaller than the size of octahedron Zn_2SnO_4 estimated by SEM image, suggesting that the octahedron is composed of nanocrystals, but not a single crystal.

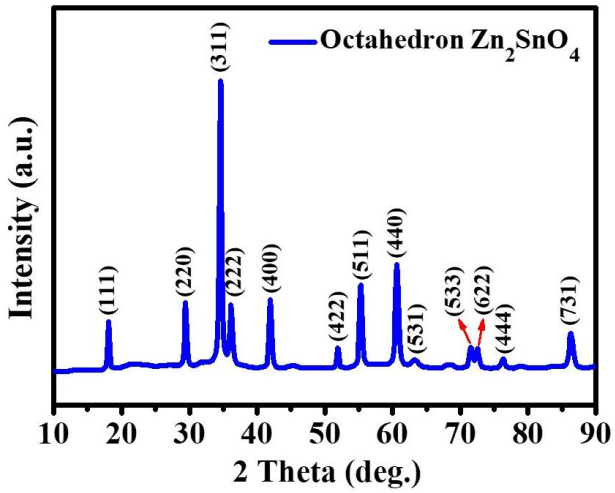

Figure 3. XRD pattern of the synthesized octahedron Zn_2SnO_4.

3.3. Ethanol sensing characteristics the synthesized octahedron Zn_2SnO_4

The ethanol sensing properties of the octahedron Zn_2SnO_4 based sensor were investigated at various working temperatures and ethanol concentrations. The transient resistance versus time upon exposure to different ethanol concentrations measured at temperatures ranging from 350 to 450 ºC are shown in Fig. 4A-C. The based resistance of the octahedron Zn_2SnO_4 decreases as the temperature rises and represents an obvious negative temperature coefficient of resistance in the measured range. With the increase of working temperature, the thermal energy excite electron from valent band to conduction band thus decreases the initial resistance of sensor. The base resistance of the sensor in the air are 403 kΩ, 182 kΩ, and 120 kΩ for temperatures of 350 ºC, 400 ºC, and 450 ºC, respectively. Upon exposure to ethanol, the sensor resistance decreases rapidly, indicating the fast response characteristic. When the analytical gas flow was stopped, the sensor resistance recovered to their original values confirming the total recovery phenomena. Such those characteristics display the reversible reaction of ethanol over the Zn_2SnO_4 surface. The reversible adsorption of the gas molecules on the sensor material surface is very important in the practical application and reusability of the gas sensor. The response of the sensor as a

function of ethanol concentrations for different working temperatures is shown in Fig. 4D. It is clear that the sensor response increases with increasing the concentration of ethanol from 50 to 250 ppm. This effect is more clearly when the sensors operate at the temperature of 400 ºC. At each ethanol concentration, the sensor response toward ethanol at 400 ºC is the highest comparing to the working temperatures at 350 ºC and 450 ºC. This is possibly due to the competition between the adsorption and desorption of gas molecules on the surface of sensing material [24]. At temperatures below 400 ºC, the adsorption of ethanol on the surface of Zn_2SnO_4 increases with an increment of temperate due to the increase of pre-adsorbed oxygen species. However, at temperature higher than 400 ºC, the desorption process is accelerated by thermal temperature, thus decreases the sensor response. As a result, the sensor showed the highest response values at a working temperature of 400 ºC. Therefore, we selected the working temperature of 400 °C to investigate other properties in the following experiments.

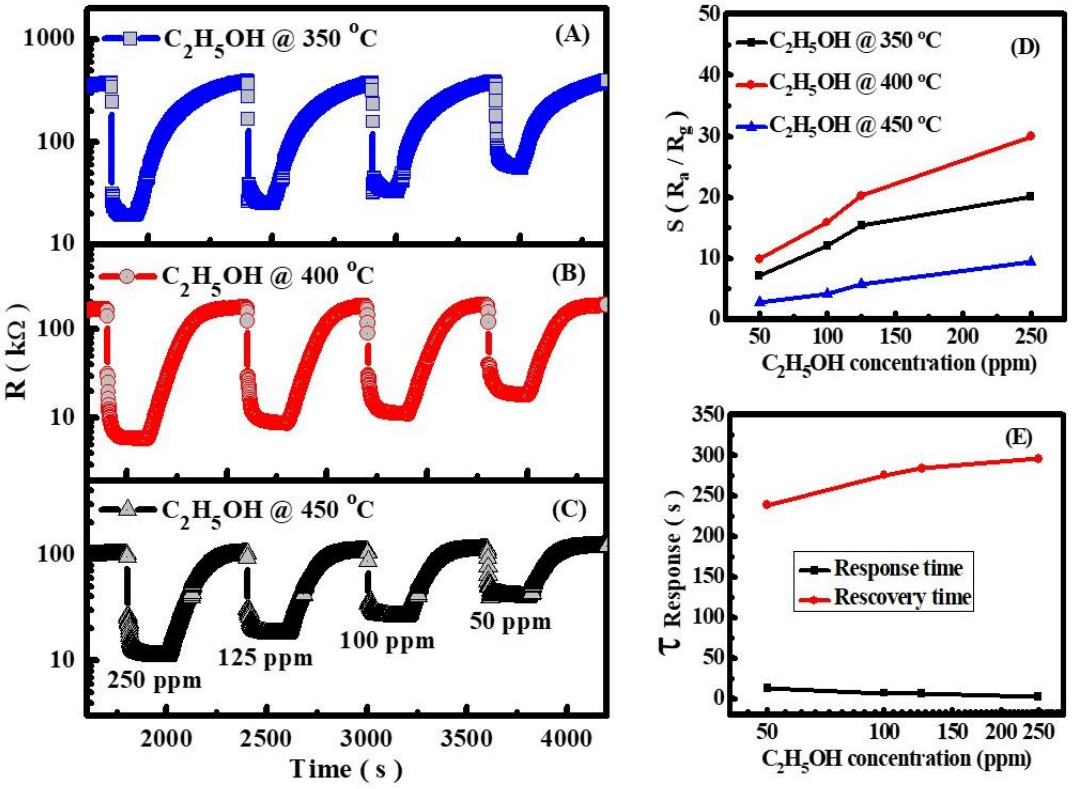

Figure 4. Ethanol sensing characteristics the synthesized octahedron Zn_2SnO_4: (A,B,C) transient resistance vs time upon exposure to different ethanol concentrations measured at various temperatures; (D) sensor response; (E) response and recovery time as a function of ethanol measured at 400 °C.

Specifically, the response value increases from 9.9 to 30 when the ethanol concentration increases from 50 to 250 ppm at a measured temperature of 400 ºC. Table 1 compares our result with recent studies about ethanol sensor using diffident materials and/or morphologies. The octahedron Zn_2SnO_4 showed the highest response value to ethanol among others. It is clearly that the materials and morphology strongly influence on the sensitivity of the sensor because different morphologies have different specific surface areas, and adsorption sites for gas molecules to adsorb. Herein, the excellent gas-sensing performance of the octahedron Zn_2SnO_4

structure might be attributed to its relatively high specific surface area. It leads to improve the effective adsorption sites, and gas diffusion into inside the gas sensing material to enhance the sensitivity [25-28].

Table 1. Comparative Ethanol gas response of different metal oxide sensors.

Metal oxide sensors	Temp. (^oC)	Gas conc. (ppm)	S (R_a/R_g)	Ref.
Zn_2SnO_4 nanoparticles	275	100	6	[25]
flowerlike SnO_2 nanorods	400	100	16	[26]
ZnO nanoplate	450	100	4	[27]
SnO_2 hollow sphere	450	100	5	[28]
Zn_2SnO_4 octahedron	400	250	30	This work

Figure 4E shows the response and recovery times of the sensor, which measured at different concentrations of ethanol at 400 ºC working temperature.. When ethanol gas concentrations increase from 50 to 250 ppm, the response time shortens because of reduced time for ethanol adsorption on active sites of octahedron Zn_2SnO_4; whereas, the recovery time increases due to the longer time required for ethanol gas desorption process. When the concentration of ethanol increases, while the response time declines, recovery time of the sensors enhances. The response time decreases from 13 s to approximately 3 s when the concentration of ethanol increases from 50 ppm to 250 ppm, respectively. In contrast, the recovery time of approximately 239 s at 50 ppm of ethanol increased to approximately 296 s when the concentration increases to 250 ppm.

4. CONCLUSIONS

We have introduced a facile hydrothermal synthesis of octahedron Zn_2SnO_4 for effective ethanol gas-sensing applications. The obtained particles performed a good crystallinity and dispersing level. The obtained octahedron Zn_2SnO_4 exhibit excellent gas sensing properties to ethanol, in terms of high response, fast response and recovery times. The sensor response value of 9.9 at 50 ppm level ethanol was obtained. The results also show that octahedron Zn_2SnO_4 can be a potential candidate for high performance ethanol gas sensing material.

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REFERENCES

1. Bhatia S., Verma N., and Bedi R. K. - Ethanol gas sensor based upon ZnO nanoparticles prepared by different techniques, Results Phys. **7** (2017) 801–806.
2. Ngoc T. M., Van Duy N., Duc Hoa N., Manh Hung C., Nguyen H., and Van Hieu N. - Effective design and fabrication of low-power-consumption self-heated SnO_2 nanowire sensors for reducing gases, Sensors Actuators B Chem. **295** (2019) 144–152.
3. Duc Khoang N., Dang Trung D., Van Duy N., Duc Hoa N., and Van Hieu N. - Design of

SnO_2/ZnO hierarchical nanostructures for enhanced ethanol gas-sensing performance, Sensors Actuators B Chem. **174** (2012) 594–601.

4. Rella R., Spadavecchia J., Manera M. G., Capone S., Taurino A., Martino M., Caricato A. P., Tunno T. - Acetone and ethanol solid-state gas sensors based on TiO_2 nanoparticles thin film deposited by matrix assisted pulsed laser evaporation, Sensors Actuators B Chem. **127** (2) (2007) 426–431.
5. Zhan Z., Lu J., Song W., Jiang D., and Xu J. - Highly selective ethanol In_2O_3-based gas sensor, Mater. Res. Bull. **42** (2) (2007) 228–235.
6. Park S., Kim S., Sun G. J., and Lee C. - Synthesis, Structure, and Ethanol Gas Sensing Properties of In_2O_3 Nanorods Decorated with Bi_2O_3 Nanoparticles, ACS Appl. Mater. Interfaces **7** (15) (2015) 8138–8146.
7. IONESCU R. - Low-level detection of ethanol and H_2S with temperature-modulated WO_3 nanoparticle gas sensors, Sensors Actuators B Chem. **104** (1) (2005) 132–139.
8. Van Hoang N., Manh Hung C., Duc Hoa N., Van Duy N., Park I., and Van Hieu N. - Excellent detection of H_2S gas at ppb concentrations using $ZnFe_2O_4$ nanofibers loaded with reduced graphene oxide, Sensors Actuators B Chem. **282** (2019) 876–884.
9. Van Hoang N., Manh Hung C., Duc Hoa N., Van Duy N., and Van Hieu N. - Facile on-chip electrospinning of $ZnFe_2O_4$ nanofiber sensors with excellent sensing performance to H_2S down ppb level, J. Hazard. Mater. **360** (2018) 6–16..
10. Xuan Thanh H., Dang Trung D., Quang Trung K., Van Dam K., Van Duy N., Manh Hung C., Duc Hoa C., Duc Hoa N., and Van Hieu N. - On-chip growth of single phase Zn_2SnO_4 nanowires by thermal evaporation method for gas sensor application, J. Alloys Compd. **708** (2017) 470–475.
11. Manh Hung C., Viet Phuong H., Van Duy N., Duc Hoa N., and Van Hieu N. - Comparative effects of synthesis parameters on the NO_2 gas-sensing performance of on-chip grown ZnO and Zn_2SnO_4 nanowire sensors, J. Alloys Compd. **765** (2018) 1237–1242.
12. Coutts T. J., Young D. L., Li X., Mulligan W. P., and Wu X. - Search for improved transparent conducting oxides: A fundamental investigation of CdO, Cd_2SnO_4, and Zn_2SnO_4, J. Vac. Sci. Technol. A Vacuum, Surfaces, Film **18** (6) (2000) 2646–2660.
13. Luiz Foletto E., Marimon Simoes J., Mazutti Marcio A., Jahn Sergio L, Irineu Muller E., Severo Fagundes Pereira L., Marlon de Moraes Flores E. - Application of Zn_2SnO_4 photocatalyst prepared by microwave-assisted hydrothermal route in the degradation of organic pollutant under sunlight, Ceram. Int. **39** (4) (2013) 4569–4574.
14. Zhu X. J., Geng L. M., Zhang F. Q., Liu Y. X., and Cheng L. B. - Synthesis and performance of Zn_2SnO_4 as anode materials for lithium ion batteries by hydrothermal method, J. Power Sources **189** (1) (2009) 828–831.
15. Liu M. *et al.* - Composite photoanodes of Zn_2SnO_4 nanoparticles modified SnO_2 hierarchical microspheres for dye-sensitized solar cells, Mater. Lett. **76** (2012) 215–218.
16. Tharsika T., Haseeb A. S. M. A., Akbar S. A., Sabri M. F. M., and Wong Y. H., - Gas sensing properties of zinc stannate (Zn_2SnO_4) nanowires prepared by carbon assisted thermal evaporation process, J. Alloys Compd. **618** (2015) 455–462.
17. Moon W. J., Yu J. H., and Choi G. M., - Selective CO gas detection of SnO_2–Zn_2SnO_4 composite gas sensor, Sensors Actuators B Chem. **80** (1) (2001) 21–27.

18. Jiang Y. Q., Chen X. X., Sun R., Xiong Z., and Zheng L. S., - Hydrothermal syntheses and gas sensing properties of cubic and quasi-cubic Zn_2SnO_4, Mater. Chem. Phys. **129** (1–2) (2011) 53–61.
19. An D., Wang Q., Tong X., Tong X., Zhou Q., Li Z., Zou Y., Lian X, Li Y. - Synthesis of Zn_2SnO_4 via a co-precipitation method and its gas-sensing property toward ethanol, Sensors Actuators B Chem. **213** (2015) 155–163.
20. An D., Mao N., Deng G., Zou Y., Li Y., Wei T., Lian X., - Ethanol gas-sensing characteristic of the Zn_2SnO_4 nanospheres, Ceram. Int. **42** (2) (2016) 3535–3541.
21. Xu T. T., Xu Y. M., Zhang X. F., Deng Z. P., Huo L. H., and Gao S. - Enhanced H_2S Gas-Sensing Performance of Zn_2SnO_4 Lamellar Micro-Spheres, Front. Chem. **6** (165) (2018) 1-5.
22. Yu Y., Xia Y., Zeng W., and Liu R. - Synthesis of multiple networked NiO nanostructures for enhanced gas sensing performance, Mater. Lett. **206** (2017) 80–83.
23. Miyauchi M., Liu Z., Zhao Z. G., Anandan S., and Hara K., - Single crystalline zinc stannate nanoparticles for efficient photo-electrochemical devices, Chem. Commun. **46** (9) (2010) 1529-1531.
24. Bie L. J., Yan X. N., Yin J., Duan Y. Q., Yuan Z. H. - Nanopillar ZnO gas sensor for hydrogen and ethanol, Sens. Actuators B **126** (2007) 604–608.
25. Li Y., Luo N., Sun G., Zhang B., Lin L., Jin H. H., Wang Y., Bala H., Cao J. L., Zhang Z. - In situ decoration of Zn_2SnO_4 nanoparticles on reduced graphene oxide for high performance ethanol sensor, Ceramics Inter. **44** (2018) 6836-6842.
26. Zhou X. W., Fu W., Yang H., Li M. H. - Synthesis and ethanol-sensing properties of flowerlike SnO_2 nanorods bundles by poly (ethylene glycol)-assisted hydrothermal process, Mater. Chem. Phys. **124** (1) (2010) 614–618.
27. Jing Z., Zhan J. - Fabrication and Gas-Sensing Properties of Porous ZnO Nanoplates, Adv. Mater. **20** (2008) 4547–4551.
28. Wang B., Sun L., and Wang Y. - Template-free synthesis of nanosheets-assembled SnO_2 hollow spheres for enhanced ethanol gas sensing, Mater. Lett. **218** (2018) 290–294.