Hindawi
Advances in Condensed Matter Physics
Volume 2017, Article ID 9720973, 6 pages
https://doi.org/10.1155/2017/9720973

Research Article

Mesoporous SnO_2 Nanowires: Synthesis and Ethanol Sensing Properties

Shan-Hong Li,[1] Fang-Fang Meng,[1] Zhong Chu,[1] Tao Luo,[2] Fu-Min Peng,[3] and Zhen Jin[2]

[1] *Department of Electronic Information and Electrical Engineering, Hefei University, Hefei, Anhui 230601, China*
[2] *Research Center for Biomimetic Functional Materials and Sensing Devices, Institute of Intelligent Machines, Chinese Academy of Sciences, Hefei, Anhui 230031, China*
[3] *College of Chemistry and Chemical Engineering, Anhui University, Hefei, Anhui 230039, China*

Correspondence should be addressed to Zhong Chu; chuzhonghfuu@163.com and Zhen Jin; ftbjin@hotmail.com

Received 3 October 2016; Accepted 9 January 2017; Published 14 February 2017

Academic Editor: Jinjin Li

The mesoporous SnO_2 nanowires composed of nanoparticles and nanopores have been successfully synthesized within the nanochannels of anodic alumina oxide templates by a facile sol-gel method. XRD, SEM, and HRTEM were used to characterize the synthesized mesoporous SnO_2 nanowires. The sensing property of the mesoporous SnO_2 nanowires in ethanol detection also has been studied. The as-prepared product displays excellent the high sensitivity, rapid response, and excellent repeatability to ethanol. The detection limit of the mesoporous SnO_2 nanowires to ethanol reaches 1 ppm. The sensing mechanism of the mesoporous SnO_2 nanowires has been further discussed. It is expected that the mesoporous SnO_2 nanowires might become a good sensing material for promising industrial applications.

1. Introduction

Due to the compact size, easy production, low cost, and simple measuring electronics, metal oxide gas sensors have been extensively exploited to detect volatile organic compounds [1–5]. A large number of investigations have shown that tin oxide (SnO_2) with large excitation energy, excellent electronic and photonic properties, is one of the most excellent sensing materials [6, 7]. Generally speaking, the performances of the metal oxide based gas sensors are mainly dependent on the sensing materials [8–10]. Thus, up to date, many efforts have been devoted to obtain high performance SnO_2 sensing nanomaterial by tailoring the morphologies and structures. Various SnO_2 nanomaterials with different morphologies like nanowires [11], nanotubes [12], nanobelts [13], and microspheres [14] have been synthesized. Among those SnO_2 morphologies, porous SnO_2 nanostructures with higher special surface area and slight agglomeration are favorable for the adsorption and diffusion of target gas molecules, thus introducing better gas sensing performance [15, 16]. However, until now, the synthesis of high performance porous SnO_2 nanomaterials is still a big challenge.

In present work, considering the advantages of the porous nanostructures to the gas sensing performance, we here present a facile sol-gel method to synthesis the mesoporous SnO_2 nanowires by using the anodic alumina oxide (AAO) membrane as the template. As the sensing materials, the mesoporous SnO_2 nanowires display high gas sensitivity to the ethanol, achieving the detection limit with a low concentration of 1 ppm. It is believed that the architect of the mesoporous SnO_2 nanowires would have the fundamental importance to environmental sciences and human health.

Synthesis of the Mesoporous SnO_2 Nanowires. The anodic alumina oxide membrane used as the template in this work was prepared by a two-step anodic oxidation process in a 0.3 M oxalic acid solution as described previously [17, 18]. The average diameter of the pores in the AAO template is about 70 nm.

For the preparation of porous SnO_2 nanowires, all of the reagents used in this experiment were of analytical reagent grade. Firstly, in a typical experiment, an amount of $SnCl_4{\cdot}4H_2O$ was dissolved into deionized water to form 0.01 M solution, and then urea was added to the solution. The mole ratio of urea to $SnCl_4 \cdot 4H_2O$ was 10 : 1 and the pH value of the solution was adjusted to near neutral by ammonia. The AAO template was put into a vessel that contained an appropriate amount of solution mentioned above. Then the vessel was kept at 70°C for 24 h. Then, the loaded AAO template was annealed at 500°C for 6 h in air and the mesoporous SnO_2 nanowires can be obtained.

Characterization. The morphologies of the as-prepared products are characterized by field-emission scanning electron microscopy (FE-SEM, FEI Sirion-200) and high resolution transmission electron microscopy (HRTEM, JEOL JEM-2011). The crystal structure of the as-prepared samples is determined by X-ray diffraction (XRD, Philips X'Pert PRO) with Cu Ka radiation.

Fabrication of the Gas Sensor and the Gas Sensing Measurement System. To fabricate the gas sensor, the mesoporous SnO_2 nanowires were dispersed in ethanol solvent and directly coated on the surface of a ceramic tube and then dried in an infrared drying oven followed by annealing in a muffle furnace at 300°C for 1 h in air.

The measurement of gas sensing property was carried out in a closed test chamber with a volume of about 1000 mL equipped with an inlet and an outlet for gas flow. Source/Measure Unit (SMU, Keithley 6487) was used to provide a power source as well as to record the response current. In the typical gas sensing test, a constant voltage was firstly applied onto the pair of electrodes between the sensing films. Then, a certain concentration of ethanol gas drawing from the headspace vapor was introduced into the test chamber using a microsyringe. Finally, the ethanol vapor in the testing chamber was released by inputting fresh synthesized air once the gas sensing measurement was over. The response currents of the sensors during the whole test process were measured by the SMU. Here, the gas response of the sensor is defined as

$$\text{Response} = \frac{I_g - I_a}{I_a} \times 100\%. \quad (1)$$

I_a and I_g are the currents of the sensor in air and target gas, respectively. The response time is defined as the time when the change of current reaches 90% of the balanced current on exposure to a target gas. Similarly, the recovery time is defined as the time reached a 90% reversal of the current.

2. Results and Discussion

Figures 1(a) and 1(b) show the top-side and cross-sectional SEM images of the AAO template, from which it can be clearly found that the AAO template consists of tremendous parallel hexagonal nanopores. The diameter of those nanopores is about 70 nm. Those nanopores are the perfect template for the synthesis of nanowires. Through a facile sol-gel method, the mesoporous SnO_2 nanowires can be easily synthesized. Figure 1(c) illustrates the top-side SEM image of the SnO_2 nanowires within the AAO template. It can be found that almost all of the nanopores are filled with SnO_2 nanowires. Figure 1(d) shows the profile SEM image of the SnO_2 nanowires after the removal of AAO template. It can be seen that the as-prepared SnO_2 nanowires are of rough surface and quite long. Figure 2 presents the corresponding XRD pattern of the SnO_2 nanowires. It can be clearly seen that the XRD pattern exhibit well resolved X-ray diffraction, which can be indexed to (110), (101), and (211) planes of the rutile structure of SnO_2 (JCPDS 88-0287).

The microstructure of the SnO_2 nanowires was further investigated in detail by TEM and selected area electron diffraction (SAED). Figure 3(a) and the inset show the low and high magnification TEM images of SnO_2 nanowires. It can be observed that the SnO_2 nanowire is composed of nanoparticles and pores, indicating the mesoporous structure of the SnO_2 nanowire. The stack of those nanoparticles is disordered. The diameters of the mesoporous SnO_2 nanowire are about 65 nm, which is corresponding to the pore size of the AAO template. Figure 3(b) provides the SAED pattern of the mesoporous SnO_2 nanowire. The polycrystalline diffraction rings (001), (110), and (111) of SnO_2 can be clearly observed. In our case, the AAO templates were dipped into the mixed solution of $SnCl_4$ and urea. Because of the capillary effect, the solution can be easily filled into the channels of the AAO template. When the solution was heated at above 60°C, the urea is undergoing hydrolysis, resulting in the increase of the pH value of the solution [19]. The generated OH^- ions then can be combined with Sn^{4+} ions to form $Sn(OH)_4 \cdot xH_2O$ gel particles [20]. This process took place not only in the solution, but also in the channels of the AAO template. Because of the confinement of the channels of the AAO template, mesoporous nanowires were synthesized by the assembly of $Sn(OH)_4 \cdot xH_2O$ colloidal nanoparticles. After the annealing process, the polycrystalline mesoporous SnO_2 nanowires can be obtained.

The sensing property of the mesoporous SnO_2 nanowires to ethanol also has been studied. Operating temperature is a key parameter for the sensing performance of metal oxide based gas sensors. Therefore, we firstly investigated the responses of the mesoporous SnO_2 nanowires to 100 ppm of ethanol vapor at different operating temperatures. In Figure 4, it can be seen that the responses of the mesoporous SnO_2 nanowires exhibited a peak at 250°C with increasing operating temperature. Therefore, we adopted 250°C as the optimal operating temperature for the following experiments of the mesoporous SnO_2 nanowire sensor. The surface reaction of the target gases with the adsorbed oxygen species lies on the activity of the adsorbed oxygen species [21]. There are different oxygen species including molecular (O_2^-) and atomic (O^-, O^{2-}) ions on the surface at different temperature. Generally, the molecular form dominates below 150°C, while the atomic species become increasingly important at higher temperature [22]. The optimal operating temperature of 250°C suggested that the sensor worked mostly depending on atomic species which are more reactive.

Figure 5(a) shows the real-time response curves of the mesoporous SnO_2 nanowires to different concentrations of ethanol. It can be obviously observed that, with the increasing of the ethanol gas concentration from 1 to 500 ppm, the current increases and rapidly drops as the ethanol gas is removed

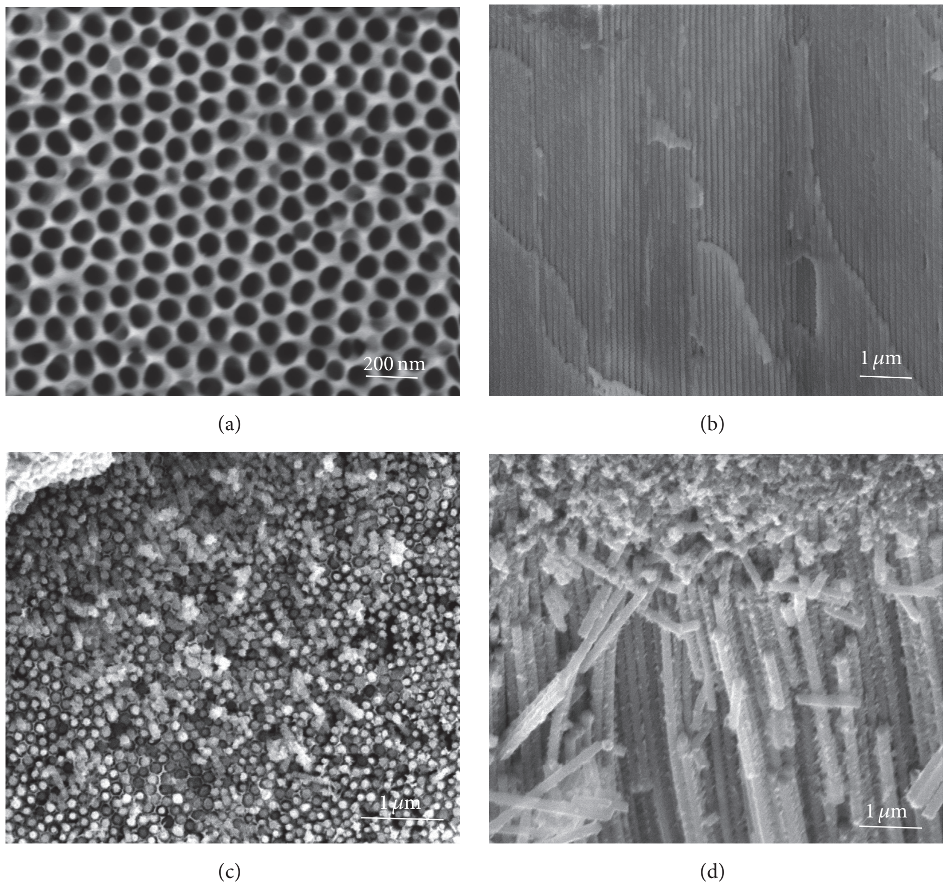


Figure 1: ((a), (b)) The top-view and cross-sectional SEM images of the AAO template, (c) the top-view SEM image of the mesoporous SnO_2 nanowires, and (d) the profile SEM image of the mesoporous SnO_2 nanowires after AAO template removal.

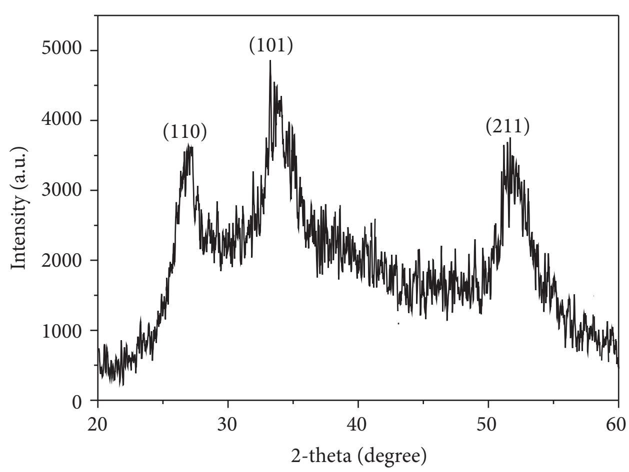
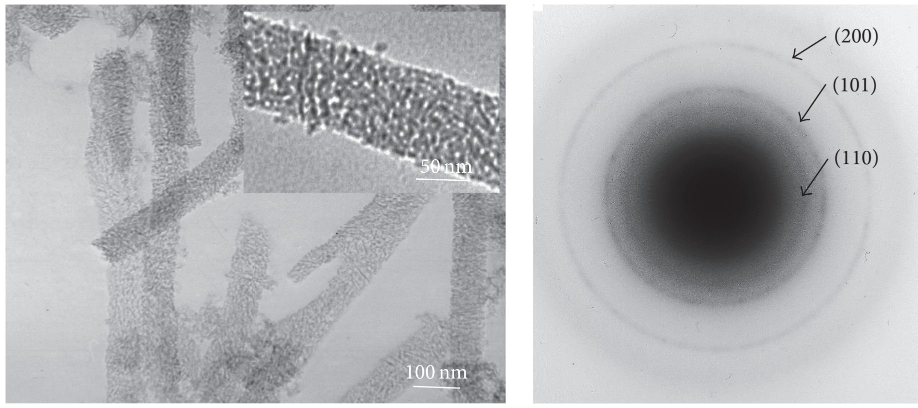


Figure 2: The XRD pattern of the mesoporous SnO_2 nanowires.

from the testing atmosphere. The mean response time is 18 s and the mean recovery time is 27 s. For comparison's sake, the sensing property of the commercial SnO_2 powders was also present in Figure 5(a). Evidently, the mesoporous SnO_2 nanowires possess higher sensing property than the commercial SnO_2 powders. Figure 5(b) displays the plot of the current intensity as a function of the ethanol of different concentration, revealing a linear range from 1 to 500 ppm. The least-squares fitting was $y = 1.88 + 0.0454x$ with a regression coefficient (R^2) of 99.6%. The results reveal that the mesoporous SnO_2 nanowires have good response to ethanol, and the sensitivity of the mesoporous SnO_2 nanowires is



(a) (b)

Figure 3: (a) The TEM image of the mesoporous SnO_2 nanowires; the inset shows the high magnification TEM images of the single nanowire. (b) The SAED pattern of the mesoporous SnO_2 nanowires.

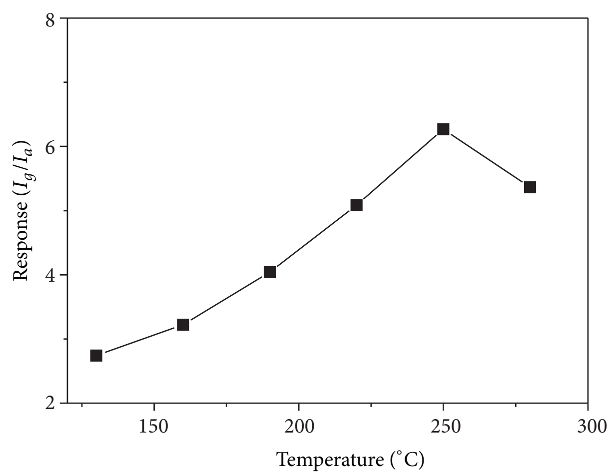
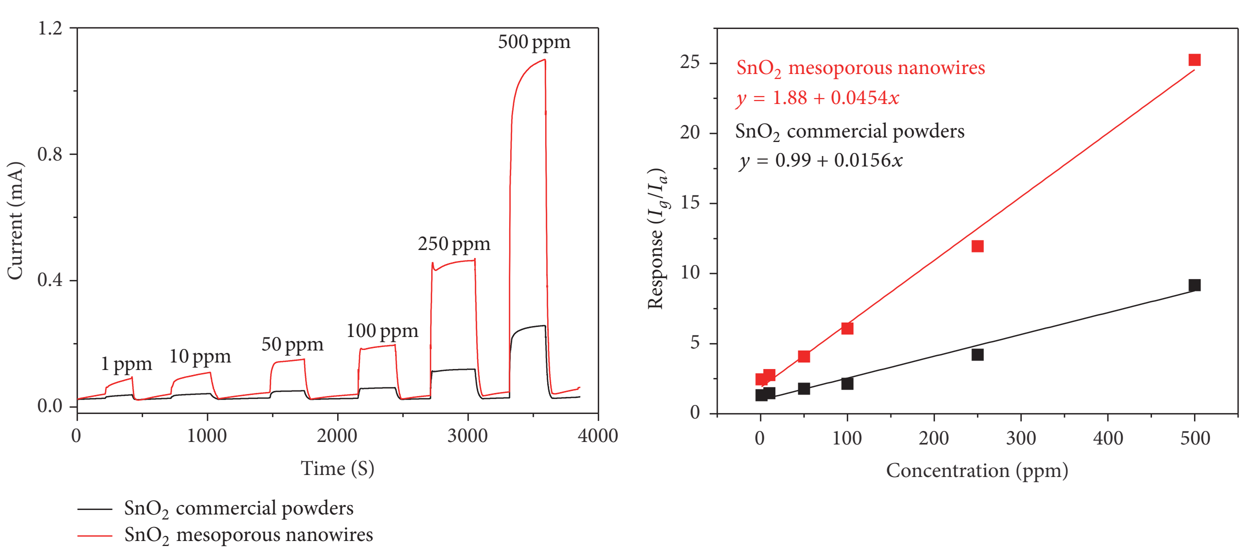


Figure 4: Responses of the mesoporous SnO_2 nanowires to 100 ppm of ethanol at different operating temperatures.



(a) (b)

Figure 5: Real-time response curves of the mesoporous SnO_2 nanowires and SnO_2 commercial powders, ethanol, and (b) the corresponding plots of the response versus concentration.

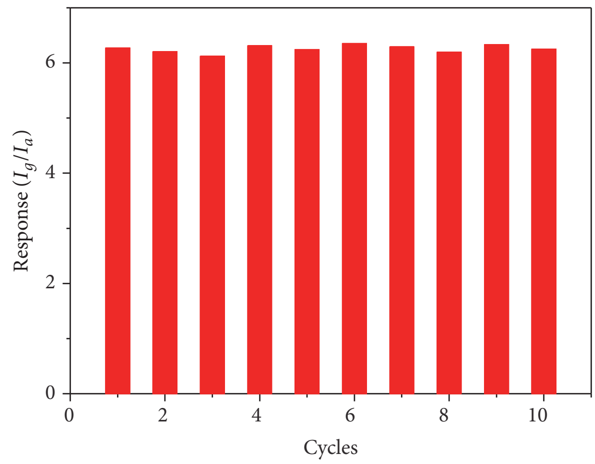


Figure 6: Response curves of the mesoporous SnO_2 nanowires to 100 ppm of ethanol after 10 cycles of gas on and off at 250°C.

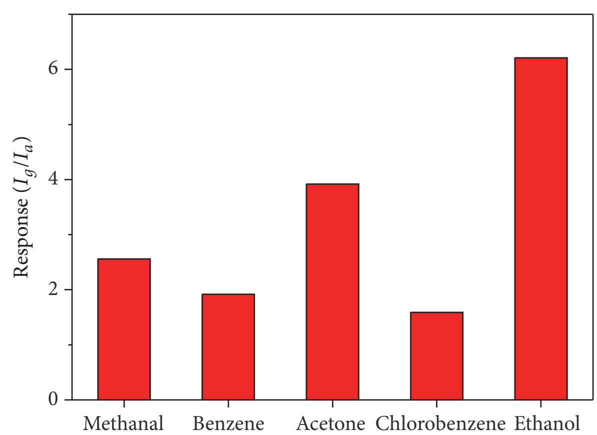


Figure 7: Comparison of the responses of the mesoporous SnO_2 nanowires to 100 ppm of different VOCs.

almost 3 times higher than that of the commercial SnO_2 powders. The high sensing performance of the mesoporous SnO_2 nanowires can be attributes to the large amount of mesopores. Those mesopores not only provided plenty of active sites for surface chemical reactions but also made gases diffuse into the sensing materials by molecular diffusion [23, 24]. The response was inversely proportional to the thickness of the sensing film. The increase of mesopores promoted the diffusion of the ethanol gas into SnO_2 nanowires by molecular diffusion, which was analogous to reduce the thickness of the film and consequently enhanced the gas response. Therefore, the mesoporous SnO_2 nanowires exhibited higher response and shorter response and recovery times.

For practical applications, the gas sensing stability of the sensor device is a very important parameter. For this reason, the reproducibility of the mesoporous SnO_2 nanowires based sensor has been investigated by the response curves of the mesoporous SnO_2 nanowires to 100 ppm ethanol after 10 cycles of gas on and off at 250°C. From Figure 6, it can be seen that the maximum deviation is an acceptable range. Selectivity is another important parameter for gas sensors. A good gas sensor should possess high selectivity. It has been reported that the SnO_2 based sensors have responses to many VOC gases, such as methanal, benzene, acetone, and chlorobenzene. However, as shown in Figure 7, it can be seen that the response of the mesoporous SnO_2 nanowires to 100 ppm of ethanol is much higher than that to 100 ppm of other VOC gases. This result speaks volumes for the excellent selectivity of mesoporous SnO_2 nanowires to ethanol. Based on the high sensitivity, good repeatability, and selectivity, the mesoporous SnO_2 nanowires might become a good sensing material for promising industrial applications.

3. Conclusion

In conclusion, large-scaled mesoporous SnO_2 nanowires composed of SnO_2 nanoparticles and mesopores have been synthesized within the channels of AAO templates through a facile sol-gel method. The mesoporous SnO_2 nanowires used as the gas sensing materials display excellent the high sensitivity, achieving the detection of ethanol with a low concentration of 1 ppm. Moreover, compared with commercial SnO_2 powders, the mesoporous SnO_2 nanowires have rapid response, good repeatability, and gas sensitivity to ethanol.

Therefore, we suggest that the synthesis approach to mesoporous SnO_2 nanowires and the achievement of detection to ethanol with a low concentration are of fundamental importance to environmental sciences and human health.

Competing Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

Acknowledgments

The authors appreciate the financial support of the Natural Science Research Project of Anhui Educational Committee (no. KJ2016A598 and no. KJ2016A600), National Natural Science Foundation of China (nos. 21407001 and U1432140), Key Project of Scientific Research Foundation of Hefei University (no. 10KY02ZD), and Scientific Research Foundation for Talents of Hefei University (no. 14RC11).

References

[1] T. Li, W. Zeng, H. Long, and Z. Wang, "Nanosheet-assembled hierarchical SnO_2 nanostructures for efficient gas-sensing applications," *Sensors and Actuators, B: Chemical*, vol. 231, pp. 120–128, 2016.

[2] W. G. Chen, T. Y. Gao, H. L. Gan, L. N. Xu, and L. F. Jin, "Improved C_2H_2 sensing properties of Ni doped ZnO nanorods," *Materials Technology*, vol. 30, no. 6, pp. 356–361, 2015.

[3] A. Chapelle, I. El Younsi, S. Vitale et al., "Improved semiconducting $CuO/CuFe_2O_4$ nanostructured thin films for CO_2 gas sensing," *Sensors and Actuators, B: Chemical*, vol. 204, pp. 407–413, 2014.

[4] S. S. Kalanur, I.-H. Yoo, Y.-A. Lee, and H. Seo, "Green deposition of Pd nanoparticles on WO_3 for optical, electronic and gasochromic hydrogen sensing applications," *Sensors and Actuators, B: Chemical*, vol. 221, pp. 411–417, 2015.

[5] F. Meng, N. Hou, Z. Jin et al., "Ag-decorated ultra-thin porous single-crystalline ZnO nanosheets prepared by sunlight induced solvent reduction and their highly sensitive detection of ethanol," *Sensors and Actuators, B: Chemical*, vol. 209, pp. 975–982, 2015.

[6] Y. N. Li, Q. Wei, P. Song, and Q. Wang, "Synthesis of porous SnO_2 nanocubes via selective leaching and enhanced gas-sensing properties," *Applied Surface Science*, vol. 360, pp. 1059–1065, 2016.

[7] J. Li, P. Tang, J. Zhang et al., "Facile synthesis and acetone sensing performance of hierarchical SnO_2 Hollow microspheres with controllable size and shell thickness," *Industrial and Engineering Chemistry Research*, vol. 55, no. 12, pp. 3588–3595, 2016.

[8] H.-M. Jeong, J.-H. Kim, S.-Y. Jeong, C.-H. Kwak, and J.-H. Lee, "Co_3O_4-SnO_2 hollow heteronanostructures: facile control of gas selectivity by compositional tuning of sensing materials via galvanic replacement," *ACS Applied Materials and Interfaces*, vol. 8, no. 12, pp. 7877–7883, 2016.

[9] S. Park, S. Kim, G.-J. Sun, W. In Lee, K. K. Kim, and C. Lee, "Fabrication and NO_2 gas sensing performance of TeO_2-core/CuO-shell heterostructure nanorod sensors," *Nanoscale Research Letters*, vol. 9, no. 1, article no. 638, 2014.

[10] F. L. Meng, N. N. Hou, Z. Jin et al., "Sub-ppb detection of acetone using Au-modified flower-like hierarchical ZnO structures," *Sensors and Actuators, B: Chemical*, vol. 219, pp. 209–217, 2015.

[11] T. Van Dang, N. Duc Hoa, N. Van Duy, and N. Van Hieu, "Chlorine gas sensing performance of on-chip grown ZnO, WO_3, and SnO_2 nanowire sensors," *ACS Applied Materials and Interfaces*, vol. 8, no. 7, pp. 4828–4837, 2016.

[12] W. J. Lee, M.-H. Park, Y. Wang, J. Y. Lee, and J. Cho, "Nanoscale Si coating on the pore walls of SnO_2 nanotube anode for Li rechargeable batteries," *Chemical Communications*, vol. 46, no. 4, pp. 622–624, 2010.

[13] F. K. Butt, C. Cao, R. Ahmed et al., "VLS and VS effect on ferromagnetic behaviour of SnO_2 nanobelts," *Journal of Experimental Nanoscience*, vol. 9, no. 1, pp. 17–26, 2014.

[14] F. Gyger, M. Hübner, C. Feldmann, N. Barsan, and U. Weimar, "Nanoscale SnO_2 hollow spheres and their application as a gas-sensing material," *Chemistry of Materials*, vol. 22, no. 16, pp. 4821–4827, 2010.

[15] C. H. Luan, K. Wang, Q. Q. Yu et al., "Improving the gas-sensing performance of SnO_2 porous nanosolid sensors by surface modification," *Sensors and Actuators, B: Chemical*, vol. 176, pp. 475–481, 2013.

[16] F. Li, Y. Chen, and J. Ma, "Porous SnO_2 nanoplates for highly sensitive NO detection," *Journal of Materials Chemistry A*, vol. 2, no. 20, pp. 7175–7178, 2014.

[17] H. Masuda and K. Fukuda, "Ordered metal nanohole arrays made by a two-step replication of honeycomb structures of anodic alumina," *Science*, vol. 268, no. 5216, pp. 1466–1468, 1995.

[18] M. S. Sander, R. Gronsky, T. Sands, and A. M. Stacy, "Structure of bismuth telluride nanowire arrays fabricated by electrodeposition into porous anodic alumina templates," *Chemistry of Materials*, vol. 15, no. 1, pp. 335–339, 2003.

[19] Z. Jin, F.-L. Meng, Y. Jia et al., "Porous TiO_2 nanowires derived from nanotubes: synthesis, characterzation and their enhanced photocatalytic properties," *Microporous and Mesoporous Materials*, vol. 181, pp. 146–153, 2013.

[20] Z. Jin, G. T. Fei, X. L. Cao, and X. W. Wang, "Fabrication and optical properties of mesoporous SnO_2 nanowire arrays," *Journal of Nanoscience and Nanotechnology*, vol. 10, no. 8, pp. 5471–5474, 2010.

[21] F. L. Meng, N. N. Hou, S. Ge et al., "Flower-like hierarchical structures consisting of porous single-crystalline ZnO nanosheets and their gas sensing properties to volatile organic compounds (VOCs)," *Journal of Alloys and Compounds*, vol. 626, pp. 124–130, 2015.

[22] N. Barsan and U. Weimar, "Conduction model of metal oxide gas sensors," *Journal of Electroceramics*, vol. 7, no. 3, pp. 143–167, 2001.

[23] G.-J. Li and S. Kawi, "Synthesis, characterization and sensing application of novel semiconductor oxides," *Talanta*, vol. 45, no. 4, pp. 759–766, 1998.

[24] L. Zhang, J. Zhao, H. Lu et al., "Facile synthesis and ultrahigh ethanol response of hierarchically porous ZnO nanosheets," *Sensors and Actuators, B: Chemical*, vol. 161, no. 1, pp. 209–215, 2012.