Sensors and Actuators B 194 (2014) 33–37

Contents lists available at ScienceDirect

Sensors and Actuators B: Chemical

journal homepage: www.elsevier.com/locate/snb

Tungsten trioxide nanotubes with high sensitive and selective properties to acetone

Xiao Chi[a], Changbai Liu[b], Li Liu[a,*], Yu Li[a], Zhijun Wang[a], Xiaoqing Bo[a],
Lili Liu[a], Chang Su[a]

[a] State Key Laboratory of Superhard Materials, College of Physics, Jilin University, Changchun 130012, PR China
[b] College of Electronic Science & Engineering, Jilin University, Changchun 130012, PR China

ARTICLE INFO

Article history:
Received 2 August 2013
Received in revised form
16 December 2013
Accepted 20 December 2013
Available online 27 December 2013

Keywords:
Nanotubes
Gas sensing properties
Tungsten trioxide
Gas sensor
Electrospinning

ABSTRACT

WO_3 nanotubes have been successfully synthesized by electrospinning and followed by calcination. The synthesized WO_3 nanotubes have been characterized by scanning electron microscope (SEM) and X-ray powder diffraction (XRD). Based on the experimental results, the average diameter of the WO_3 nanotubes is about 200 nm. Gas sensors based on WO_3 nanotubes were made in order to investigate their gas sensing properties. The gas sensing measurements were evaluated toward different concentration of some gases including acetone, ethanol, methanol, ammonia, hydrogen, carbon monoxide and butane at 250 °C. The results reveal that the WO_3 nanotubes are promising acetone sensing material owing to their high response and good selectivity.

1. Introduction

Tungsten trioxide is an important n-type semiconductor with wide band gap of 2.5–3.0 eV [1]. A lot of efforts have been made to investigate its applications in electrochromic materials [2], photocatalysts [3] and electrodes for solar cells [4]. Besides, tungsten trioxide has been widely used to detect toxic gases and volatile organic compounds [5–7]. Recent years, due to the promising applications in the field of gas sensing, a lot of studies have been made to investigate WO_3 [8,9]. However, most studies were focused on WO_3 nanoplate [10], thick films [8] and nanofibers [11]. To the best of our knowledge, WO_3 nanotubes, especially made by electrospinning have never been reported. The morphology of materials has a big influence to their properties [12]. Tubular nanostructures often possess a big surface to volume, which have been demonstrated to present an excellent gas sensing performance. For instance, due to the nanotubes, ZnO [13], SnO_2 [14] and In_2O_3 [15] are all have been reported on their excellent gas response.

Acetone is a toxic and explosive gas. In the condition of 300 ppm acetone gas, acetone will do obviously harm to the mucous membrane. If an adult living in the circumstance with acetone (12,000 ppm × 4 h), the toxic symptoms will appear. Therefore, the acetone sensor with fast response and recovery time maybe has the value of practical application. In this work, we prepared WO_3 nanotubes via the electrospinning and followed by calculation. A possible formation mechanism of WO_3 nanotubes was proposed. Moreover, the gas sensor was made to investigate the gas sensing properties of WO_3 nanotubes. The results reveal that the WO_3 nanotubes can be the potential materials to detect acetone.

2. Experimental

2.1. Materials

Tungsten chloride (≥99%), N,N-dimethylformamide (DMF, ≥99.9%) and ethanol (≥99.5%) were purchased from Aladdin (China). Polyvinyl pyrrolidone (PVP, Mw = 13,00,000) was purchased from Sigma–Aldrich (U.S.A.).

2.2. Samples preparation and measurement

Tungsten trioxide nanotubes were synthesized through a single capillary electrospinning method. Firstly, 1 g tungsten chloride was mixed with 9 g N,N-dimethylformamide and magnetic stirred for 30 min vigorously. Then 2.2 g polyvinylpyrrolidone was added into the above solution and continued to stir for 30 min. Subsequently,

---

* Corresponding author. Tel.: +86 431 8502260; fax: +86 431 8502260.
E-mail addresses: liul99@jlu.edu.cn, liuli_teacher@163.com (L. Liu).

0925-4005/$ – see front matter
http://dx.doi.org/10.1016/j.snb.2013.12.078

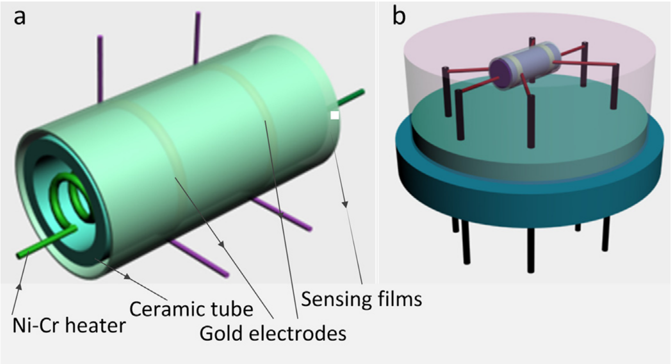

Fig. 1. The schematic of the sensor.

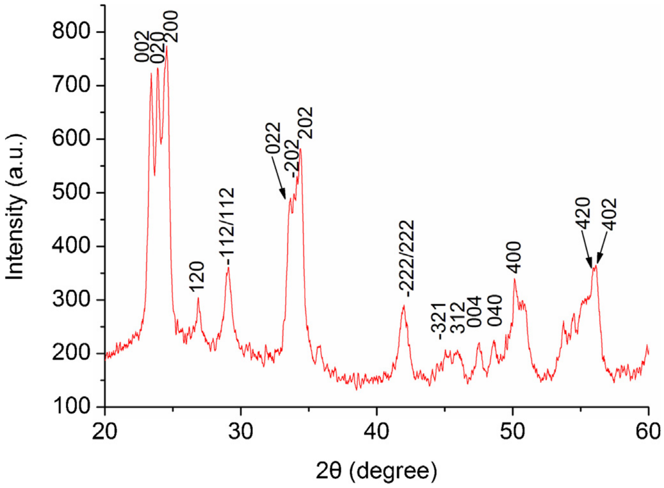

Fig. 3. XRD patterns of WO_3 nanotubes.

2.0 g ethanol was added into above solution and stirred for 10 h to obtain the precursor solution. At last, the precursor solution was load into a syringe and the pinhead was connected to a high-voltage power supply. 15 kV was provided between the syringe (anode) and the collector (a flat aluminum foil connected the cathode). The composite fibers in the form of non-woven mats were collected, followed by calcination at 550 °C for 3 h at the heating rate of 1 °C/min.

The structure of the nanotubes was analysis by X-ray diffraction conducted on XRD-6000 X-ray diffractometer (XRD, XRD-6000, SHIMADZU, Japan) with CuKα1 ($\lambda = 1.5406$ Å) radiation. The morphology of nanotubes was performed on a JSM-6701F instrument (SEM, JSM-6701F, JEOL, Japan).

The gas sensors were prepared as follows and also described in our previous work [16]. Firstly, the as-synthesized materials were mixed with deionized water in a weight ratio of 100:20 to form a paste. Then, the paste was coated onto a ceramic tube on which a pair of Au electrodes was previously printed. A Ni–Cr heating wire was placed through the tube to form a heater to provide the working temperature. The gas sensors were dried and aged before the first measurement. The sensor was aged at 260 °C for 7 days to make sure the sensitivity stable. The schematic of the sensor is provided in Fig. 1. The gas sensing properties tests of WO_3 were operated on CGS-8 intelligent gas-sensing analysis system (Beijing Elite Tech Co., Ltd., China).

The value of the response was defined as $S = R_a/R_g$. R_a was the resistance of the sensor in the air. R_g was the resistance of the sensor in the mixture of the target gas and air. The time taken by the sensor to achieve 90% of the total resistance change was defined as the response time in the case of response (target gas adsorption) or the recovery time in the case of recovery (target gas desorption) [17].

3. Result and discussion

3.1. Morphological and structural characteristics

The morphology of WO_3 nanotubes was characterized by SEM, which was shown in Fig. 2. From Fig. 2, it can be seen that the morphology of the WO_3 is one dimensional nanotube. The average diameter of nanotubes is about 200 nm. The surface of the nanotubes is rough and full of protuberances. The structural of nanotubes and protuberances can provide more space that makes electrons which on the surface of WO_3 react with target gas. This structural may have an enhancement for the sensitivity.

The result of typical power XRD pattern is shown in Fig. 3. From Fig. 3 we can see that all the prominent diffraction peaks are indexed to the pure monoclinic WO_3. The diffraction peaks are all agreed with JCPDS card of No. 72-0677, which indicating that the WO_3 nanotubes are high purity. The lattice constants of $a = 7.306$ Å, $c = 7.692$ Å. According to the Debye formula

$$D = \frac{K\lambda}{\beta\cos(\theta)} \qquad (1)$$

where D it the crystallite size, K is 0.89, λ is the wavelength of X-ray radiation ($\lambda = 0.15406$ nm) and β is the full width at half-maximum of diffraction peak at 2θ. From the XRD pattern, the highest three diffraction peaks (0 0 2), (0 2 0), (2 0 0) and (1 2 0) diffraction peaks

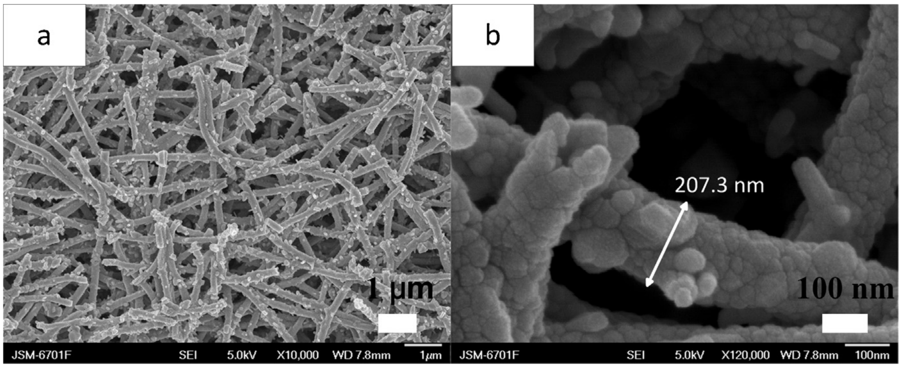

Fig. 2. SEM images of WO_3 nanotubes under (a) low- and (b) high-magnification.

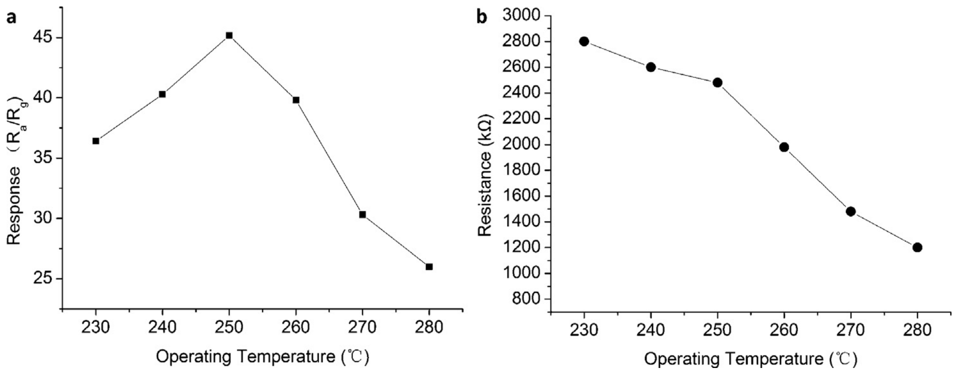

Fig. 4. Relationship (a) between the responses of gas sensors and operating temperatures to 100 ppm acetone, and (b) between the sensor resistances in the air and operating temperature.

were chosen to calculate the average size of WO_3 grains. The grain size is calculated by the four peaks, respectively. The average crystallite size of WO_3 nanotubes is about 15.1 nm, which was taken from the four peaks average value [18,19].

3.2. Possible formation mechanism

The formation of WO_3 nanotubes during electrospinning is maybe affected by the heating course. Especially the heating rate has a big effect to the formation of WO_3 nanotubes [13,20]. At the relatively low temperatures, the oxidation reaction rate on the surface is faster than that the inside due to the heating process was conduct externally. It makes the WCl_6 where on the surface was first oxygenated. Moreover, in the course of annealing, the incompletely volatile organic solvents in the nonwovens were also decomposed firstly on the fiber surface. This phenomenon leads to organic solvents with WCl_6 where in the fiber permeated toward the surface. Then more of the WCl_6 was oxygenated around the surface of fiber. With the increase of temperature, the inner WCl_6 was oxygenated and expanded for the strain strength. Gradually, WO_3 nanotubes were formed. The structural of protuberances may be ascribed to the decomposition of PVP annealing. During the course of annealing, PVP was broken down into some kinds of gas and released into the air from the fiber. The protuberant regions were formed due to the PVP decomposition from its surrounding. Besides, the interaction between the oxidation of WCl_6 and the decomposition of PVP may also have an effect to the formation of protuberances.

3.3. Gas sensing properties

Gas sensing experiments were operated to locate the optimum temperature condition for acetone test. Fig. 4a shows the relationship between the responses of gas sensors and operating temperatures to 100 ppm acetone. From Fig. 4a it can be seen that the highest response can be observed at 250 °C. The tendency of the constants show that the response of WO_3 nanotubes gas sensor increases and reaches its highest response at 250 °C, then decreases with the increasing temperature. The response is about 45.2 at 250 °C. 250 °C was chosen as the working temperature for the next experiments. Fig. 4b shows the relationship between the sensor resistance in the air (ambiance temperature was about 23 °C and the relative humidity was about 40%) and operating temperature. It can be observed that with the operating temperature increases, the resistance of sensor decreases. This phenomenon can be attributed to the carrier concentration growth rate exceeded the reduction rate of migration rate.

Response and recovery time are very important for the gas sensor practical application. Fig. 5 shows the response and recovery time curve for 0.5 and 40 ppm acetone. The responses of 0.5 and 40 ppm acetone are about 2.5 and 19.7. The response and recovery times are all about 5 s and 22 s, which are fast enough for practical application.

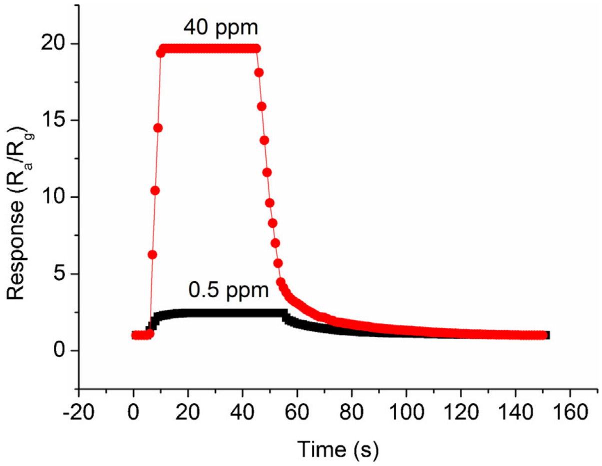

Fig. 5. Response–time curves of WO_3 nanotubes gas sensor to different concentrations of acetone at 250 °C.

Fig. 6 shows the responses of WO_3 nanotubes gas sensor to different concentrations acetone. Sensors were exposed to different

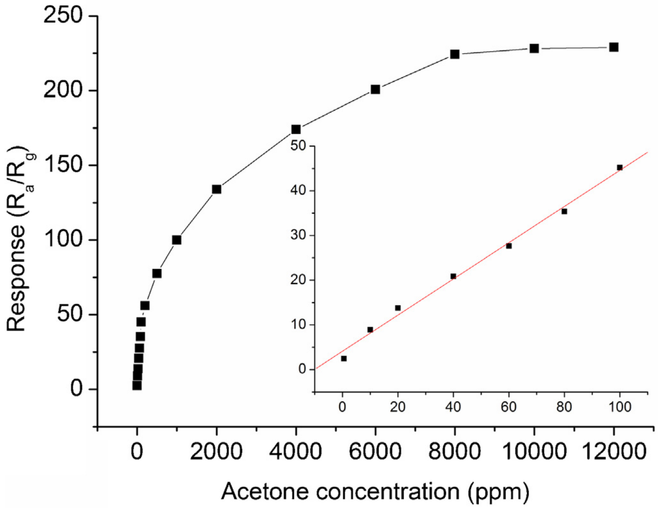

Fig. 6. Responses of WO_3 nanotubes gas sensor to different concentrations of acetone.

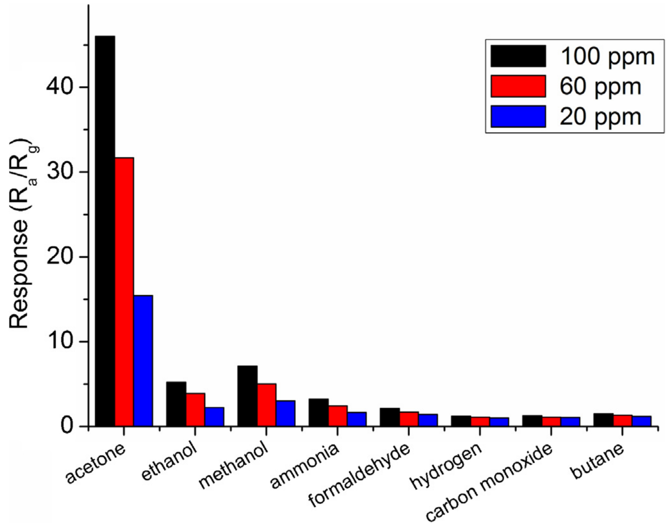

Fig. 7. Response of WO_3 nanotubes sensor to 100 ppm, 60 ppm, 20 ppm acetone, ethanol, methanol, ammonia, formaldehyde, hydrogen, carbon monoxide and butane at 250 °C.

acetone concentrations at 250 °C. The responses of WO_3 nanotubes gas sensor increase fast from 0.5 ppm to 100 ppm, which like a line. With the acetone concentrations increase further, the responses increase more and more slowly till 12,000 ppm near saturation. The results reveal that sensor possess a good sensitive to acetone even can detect 0.5 ppm acetone.

Selectivity is also an important characteristic of metal oxide gas sensors for practical application. Fig. 7 shows the responses of sensor to different kinds of gases. Fig. 7 indicates that WO_3 nanotubes sensor has a good selectivity to acetone at 250 °C. Thereinto, the response of sensor to 100 ppm acetone is more than 6 times to ethanol and methanol responses. The responses of WO_3 gas sensor to acetone are prior to other gases, which indicate the WO_3 nanotubes gas sensor have a good selective to acetone.

The rare structural of nanotubes with protuberances based on WO_3 possesses an excellent sensitivity to acetone at 250 °C. The sensing properties are prior in response, limit of detection, rate of reaction and selectivity. In this paper, the response is about 45.2–100 ppm acetone. The limit of detection is 0.5 ppm. The reaction time of sensor to 40 ppm acetone is about 5 s. The sensor possesses good selectivity to ethanol, methanol, ammonia, formaldehyde, hydrogen, carbon monoxide and butane. Hence, sensor based on WO_3 nanotubes with protuberances has a good gas sensing properties.

3.4. Gas sensing mechanism

Gas sensing mechanism of WO_3 nanotubes sensors can be explained as follows. The resistance change is controlled by the amount and species of chemisorbed oxygen (O^{2-}, O^-) on the surface. When sensor is exposed in air, O_2 is adsorbed on the sensor surface, which adsorbs electrons from the conduction band from the WO_3. The concentration of electrons in conduction band decreases and electrical conductance of the material decreases [6]. The process can be expressed as follows:

$$O_2(\mathrm{ads}) + e^- \rightarrow O_2^{\ -}(\mathrm{ads}); \tag{2}$$

$$O_2^{\ -}(\mathrm{ads}) + e^- \rightarrow 2O^-(\mathrm{ads}); \tag{3}$$

$$O^-(\mathrm{ads}) + e^- \rightarrow O^{2-}(\mathrm{ads}). \tag{4}$$

When the sensor is exposed in acetone vapor, the interaction of surface chemisorbed oxygen with acetone vapor, which exists in many forms such as O^{2-} (ads), $O_2^{\ -}$ (ads), O^- (ads) can react in some ways. The acetone vapor reacts with the chemisorbed oxygen and releases electrons back to conduction band and electrical conductance increases. The reaction is as follows:

$$CH_3COCH_3(\mathrm{gas}) + O_2^{\ -} \rightarrow CH_3C^+O + CH_3O^- + 2e^-; \tag{5}$$

$$CH_3C^+O \rightarrow C^+H_3 + CO; \tag{6}$$

$$CO + O^{2-} \rightarrow CO_2 + 2e^-. \tag{7}$$

CH_3CHO is the intermediate product in process of reaction [6].

The high sensitivity is due to the large specific surface area and the amount of chemisorbed oxygen. As far as I know, the open nanostructural has a good effect for oxygen adsorption and possesses the high response. The high sensitivity also can be owed to the morphology of nanotubes and protuberances. In our case, the nanotubes can provide a reaction not the outer but also the inner surface of the materials, which enhance the specific surface area. The structural of protuberances can also enhance specific surface area that makes electrons where on the surface of WO_3 react with acetone. Then the amount of electron which transport along the WO_3 nanotubes are improved. Hence, the gas sensitivity properties are improved.

The selectivity may ascribe to the different gases possessing different energies to adsorption and desorption on the surface of WO_3 nanotubes [21]. The sensor detects a certain gas at different temperatures has different responses. Thus the same sensor can detect different kinds of gases by different working temperature. In this paper, when the operating temperature reaches 250 °C, WO_3 sensor possesses the good selectivity to acetone.

4. Conclusions

WO_3 nanotubes are prepared via electrospinning and followed by calcination. The WO_3 nanotubes sensors have been confirmed to possess a good response to acetone with a short response time. The sensor can detect even down to 0.5 ppm acetone. Otherwise, sensor also possesses a good selective to acetone. All the advantages show that the WO_3 nanotubes nanomaterial have a good potential for gas sensing. WO_3 nanotubes nanomaterial has a potential for the practical application of metal oxide gas sensor.

Acknowledgements

The work has been supported by the Jilin Environment Office (2009-22), Jilin Provincial Science and Technology Department (20100344), and the National Innovation Experiment Program for University Students (2010C65188), Jilin Provincial Science and Technology Department (20140204027GX).

References

[1] D. Chen, X. Hou, T. Li, L. Yin, B. Fan, H. Wang, et al., Effects of morphologies on acetone-sensing properties of tungsten trioxide nanocrystals, Sens. Actuators B: Chem. 153 (2011) 373–381.

[2] N.A. Galiote, R.L.T. Parreira, J.M. Rosolen, F. Huguenin, Self-assembled films from WO_3: electrochromism and lithium ion diffusion, Electrochem. Commun. 12 (2010) 733–736.

[3] M. Sadakane, K. Sasaki, H. Kunioku, B. Ohtani, R. Abe, W. Ueda, Preparation of 3-D ordered macroporous tungsten oxides and nano-crystalline particulate tungsten oxides using a colloidal crystal template method, and their structural characterization and application as photocatalysts under visible light irradiation, J. Mater. Chem. 20 (2010) 1811–1818.

[4] L. Meda, G. Tozzola, A. Tacca, G. Marra, S. Caramori, V. Cristino, et al., Photo-electrochemical properties of nanostructured WO_3 prepared with different organic dispersing agents, Sol. Energy Mater. Sol. Cells 94 (2010) 788–796.

[5] N. Shankar, M.-F. Yu, S.P. Vanka, N.G. Glumac, Synthesis of tungsten oxide (WO_3) nanorods using carbon nanotubes as templates by hot filament chemical vapor deposition, Mater. Lett. 60 (2006) 771–774.

[6] Y. Zhang, W. He, H. Zhao, P. Li, Template-free to fabricate highly sensitive and selective acetone gas sensor based on WO_3 microspheres, Vacuum 95 (2013) 30–34.

[7] P. Van Tong, N.D. Hoa, V. Van Quang, N. Van Duy, N. Van Hieu, Diameter controlled synthesis of tungsten oxide nanorod bundles for highly sensitive NO_2 gas sensors, Sens. Actuators B: Chem. 183 (2013) 372–380.

[8] A. Boudiba, C. Zhang, P. Umek, C. Bittencourt, R. Snyders, M.-G. Olivier, et al., Sensitive and rapid hydrogen sensors based on Pd–WO_3 thick films with different morphologies, Int. J. Hydrogen Energy 38 (2013) 2565–2577.

[9] N.D. Hoa, V.V. Quang, D. Kim, N.V. Hieu, General and scalable route to synthesize nanowire-structured semiconducting metal oxides for gas-sensor applications, J. Alloys Compd. 549 (2013) 260–268.

[10] N.D. Hoa, N.V. Duy, N.V. Hieu, Crystalline mesoporous tungsten oxide nanoplate monoliths synthesized by directed soft template method for highly sensitive NO_2 gas sensor applications, Mater. Res. Bull. 48 (2013) 440–448.

[11] Y. Qin, F. Wang, W. Shen, M. Hu, Mesoporous three-dimensional network of crystalline WO_3 nanowires for gas sensing application, J. Alloys Compd. 540 (2012) 21–26.

[12] Q. Qi, T. Zhang, L. Liu, X. Zheng, G. Lu, Improved NH_3, C_2H_5OH, and CH_3COCH_3 sensing properties of SnO_2 nanofibers by adding block copolymer P123, Sens. Actuators B 141 (2009) 174–178.

[13] S. Wei, M. Zhou, W. Du, Improved acetone sensing properties of ZnO hollow nanofibers by single capillary electrospinning, Sens. Actuators B: Chem. 160 (2011) 753–759.

[14] N.G. Cho, D.J. Yang, M.-J. Jin, H.-G. Kim, H.L. Tuller, I.-D. Kim, Highly sensitive SnO_2 hollow nanofiber-based NO_2 gas sensors, Sens. Actuators B 160 (2011) 1468–1472.

[15] P. Song, Q. Wang, Z. Yang, Biomorphic synthesis and gas response of In_2O_3 microtubules using cotton fibers as templates, Sens. Actuators B: Chem. 168 (2012) 421–428.

[16] L. Liu, S. Li, J. Zhuang, L. Wang, J. Zhang, H. Li, et al., Improved selective acetone sensing properties of Co-doped ZnO nanofibers by electrospinning, Sens. Actuators B: Chem. 155 (2011) 782–788.

[17] L. Liu, Y. Zhang, G. Wang, S. Li, L. Wang, Y. Han, et al., High toluene sensing properties of NiO–SnO_2 composite nanofiber sensors operating at 330 °C, Sens. Actuators B: Chem. 160 (2011) 448–454.

[18] H. Shan, C. Liu, L. Liu, S. Li, L. Wang, X. Zhang, et al., Highly sensitive acetone sensors based on La-doped α-Fe_2O_3 nanotubes, Sens. Actuators B: Chem. 184 (2013) 243–247.

[19] V.D. Kapse, S.A. Ghosh, G.N. Chaudhari, F.C. Raghuwanshi, D.D. Gulwade, H_2S sensing properties of La-doped nanocrystalline In_2O_3, Vacuum 83 (2008) 346–352.

[20] L. Xu, B. Dong, Y. Wang, X. Bai, Q. Liu, H. Song, Electrospinning preparation and room temperature gas sensing properties of porous In_2O_3 nanotubes and nanowires, Sens. Actuators B: Chem. 147 (2010) 531–538.

[21] S.T. Navale, D.K. Bandgar, S.R. Nalage, G.D. Khuspe, M.A. Chougule, Y.D. Kolekar, et al., Synthesis of Fe_2O_3 nanoparticles for nitrogen dioxide gas sensing applications, Ceram. Int. 39 (2013) 6453–6460.

Biographies

Xiao Chi received his physical bachelor degree from Shandong University at Weihai in 2012. He is currently pursuing his master degree from the College of Physics, Jilin University. Now, he is engaged in researches in the field of sensing functional materials and gas sensor.

Changbai Liu is currently pursuing his bachelor degree from the College of Electronic Science & Engineering, Jilin University.

Li Liu received her PhD degree in the field of microelectronics and solid state electronics from the College of Electronic Science & Engineering, Jilin University in 2008. She was appointed a full professor in College of Physics, Jilin University in 2010. Now, she is interested in the field of sensing functional materials and chemical sensors.

Yu Li received her PhD degree from Jilin University in 2009 and became a lecturer in the same year. Now, she is interested in the field of sensing functional materials and chemical sensors.

Zhijun Wang received his MS degree from the College of Physics, Jilin University, China in 2004. Now, he is interested in the field of gas sensors and humidity sensors.

Xiaoqing Bo received her BS degree from Daqing Normal University in 2012. She is currently pursuing her master degree from the College of Physics, Jilin University. Now, she is interested in the field of sensing functional materials, gas sensors and humidity sensors.

Lili Liu received her BS degree from Zhengzhou University of Light Industry in 2013. She is a graduate student of the College of Physics, Jilin University for the moment. Now, she is interested in the field of sensing functional materials, gas sensors and humidity sensors.

Chang Su got his physical bachelor degree from Jilin in 2013. He is now pursuing his master degree at the College of Physics, Jilin University. At present, he is engaged in the field of sensing functional materials and gas sensor.