

The alcohol-sensing behaviour of SnO₂ nanorods prepared by a facile solid state reaction

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Abstract. SnO₂ nanorods with the range of 12-85 nm in diameter were fabricated by a facile solid state reaction in the medium of NaCl-KCl mixture at room temperature and calcined at 600, 680, 760 and 840 °C, respectively. The XRD, TEM and XPS were employed to characterize the structure and morphology of the SnO₂ nanorods. The influence of the calcination temperature on the gas sensing behaviour of the SnO₂ nanorods with different diameter was investigated. The result showed that all the sensors had good response to alcohol. The response of the gracile nanorods prepared at a low calcined temperature demonstrated significantly better than the thick nanorods prepared at a high calcined temperature. The mechanism was attributed to the nonstoichiometric ratio of Sn/O and larger surface area of the gracile nanorods to enhance the oxygen surface adsorption.

1. Introduction

Gas monitoring and detection is significant for the applications in environmental protection, air quality control and healthcare. Gas sensor based on semiconductor metal oxides, including SnO₂, ZnO, In₂O₃ and TiO₂, play an important role to be used in the detection of volatile organic compound vapors (VOCs). As a typical gas sensing material, n-type semiconductor SnO₂ has gained prominent attention for the excellent electron conduction and good chemical and thermal stability [1]. In recent years, nanostructured semiconductor oxides are attracting a great deal of attention to improve the gas-sensing performances. Among them, one-dimensional (1D) nanostructure materials stood out as a gas-sensing materials due to their high surface–volume ratio, abundant surface states and enhanced surface reactivity [2]. Therefore, many novel one-dimensional nanostructures SnO₂ such as nanorods [3], nanobelts [4], nanowires [5], nanotubes [6] and nanofibers [7] have been found to show excellent response to VOCs. Although various chemical and physical methods were used for synthesis SnO₂ one-dimensional nanocrystals with different shapes, it is still challenging to fabricate SnO₂ nanostructures with controlled shape and crystallinity for obtaining excellent sensing performances. In this paper, SnO₂ nanorods with various diameters were fabricated by an adjusted solid state reaction in the presence of NaCl-KCl mixture annealed at different calcined temperature. The influence of calcination temperature on the alcohol-sensing behaviour of the SnO₂ nanorods was investigated. The mechanism of the enhanced response of gracile SnO₂ nanorod was discussed.

2. Experimental



All utilized analytical grade chemical reagents were purchased from the Sinopharm Chemical Reagent Co. without further purification. SnO₂ nanorods were prepared by calcining the precursor powders, using a route of solid state reaction between SnCl₄·5H₂O and KBH₄ mixed with surfactants (NP5+NP9) at room temperature, in which was participated by KCl-NaCl mixture. In order to obtain different diameters of the nanorods, the precursor mixture was annealed at 600, 680, 760 and 840 °C for 2h in the atmosphere (denoted as SA, SB, SC and SD, respectively). In this case, the 1:1 molar rate of the NaCl and KCl is the key condition due to they form flux at lower calcined temperature, which is conducive to adjust the calcination temperature in a wide range of 600-900 °C.

The structure and morphology of the SnO₂ nanorods were determined by powder X-ray diffraction (XRD, Siemens D5005 diffractometer with Cu Ka radiation) and transmission electron microscope (TEM, JEOL 2010, 200 kV). Meanwhile, the surface analysis of the nanorods was characterized by X-ray photoelectron spectroscopy (XPS) and the specific surface area was assessed by surface area analyzer (CHEMBET 3000) and the BET method. The indirect-heating sensor was elected to investigate the response of the SnO₂ nanorods [8]. The measurement of the gas-sensing properties was performed on a JF02F measurement system to obtain the electrical resistance of the sensor in atmospheric air and in the target gas in a relative humidity range of 40–70%. The response was defined as the ratio of R_a/R_g , where R_a and R_g represents the resistance in atmospheric air and in target gas, respectively.

3. Results and discussion

3.1 Characterization of SnO₂ nanorods

Fig. 1 shows a typical XRD pattern of SnO₂ products. The distinct and sharp reflection peaks observed from Fig.1 suggest the highly crystalline of all samples. All samples could be identified the rutile structured SnO₂ crystal, according to the peaks conformed to the standard data file of the JCPDS 41-1445. The curve (a) shown in Fig. 1 demonstrates the wide diffraction peaks of SnO₂ nanorods synthesized at 600 °C, indicating the small crystallite size of SnO₂ at lower calcination temperature. As the curves shown in Fig. 1b, 1c and 1d, the diffraction peaks of SnO₂ turn sharper gradually with the increase of the temperature from 680 °C to 840 °C, attributing to the growth up of the SnO₂ nanorods. The Scherer's formula was used to estimate the crystalline size of the SnO₂ nanorods employing XRD data of the (110) plane diffraction peak, and the result was about 11.8, 29.4, 53.2 and 79.1 nm, respectively. It betokens that the crystalline size of the SnO₂ samples gradually increases with the calcination temperature, which will be confirmed by the results of the TEM.

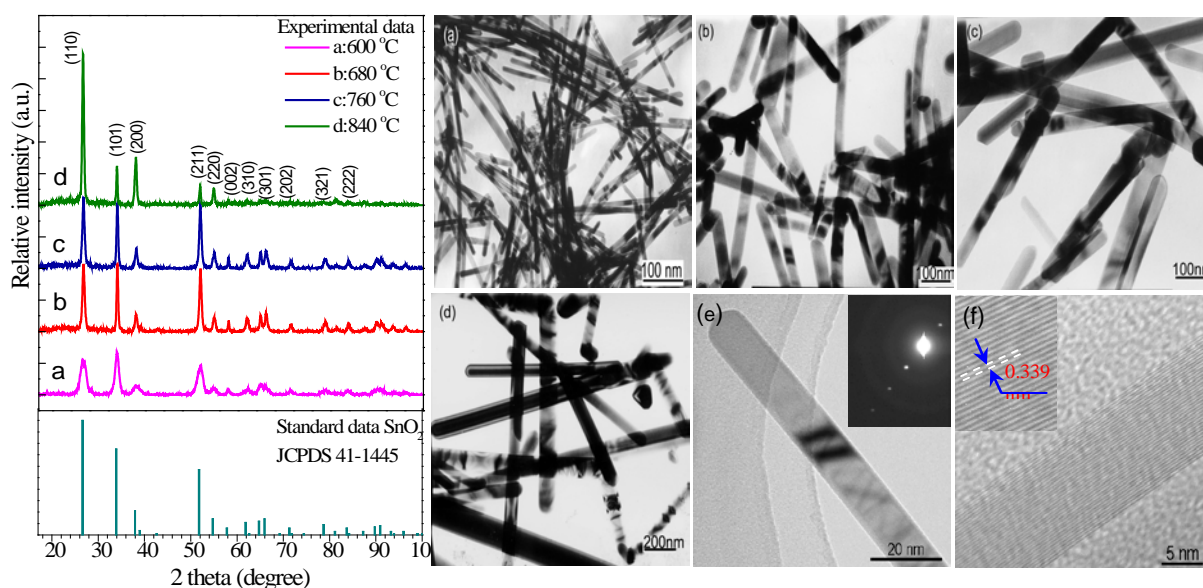


Fig.1. XRD patterns of SnO₂ nanorods prepared at different calcination temperatures.

Fig. 2. TEM images of SnO₂ nanorods prepared at different calcination temperatures. (a) 600 °C, (b) 680 °C, (c) 760 °C, (d) 840 °C, (e) A single SnO₂ nanorods prepared at 600 °C, (f) HRTEM image.

As shown in Fig.2, the morphology of the SnO₂ nanorods prepared at different calcination temperature depicts that the as-prepared samples mainly consist of solid rod-like structure SnO₂. The straight nanorod has a diameter of 10–100 nm and up to several micrometers long. As seen from the Fig. 2(a)-(d), the average diameter of the nanorods prepared at different calcination temperature was statistically estimated to be approximately of 12.2, 30.5, 52.4 and 81.6 nm, respectively. Evidently, as a function of calcination temperature, the diameter of the nanorod grew thick with the increase of the calcination temperature, which is in accordance with the XRD results. An enlarge TEM image individual SnO₂ nanorods shown in Fig. 2e demonstrates a smooth surface and an obtuse angle dome top of the nanorods. The corresponding SAED pattern (inset) indicates single-crystalline of the SnO₂ nanorods. Fig. 2f shows a high-resolution transmission electron micrograph (HRTEM) of an SnO₂ nanorod from SA sample. The uniform structure and clear lattice fringes revealing 0.339 nm space between two adjacent lattice fringe corresponds to the (110) lattice planes of SnO₂ in tetragonal cassiterite structure [9].

Fig. 3 shows the XPS spectra of Sn and O regions of the SnO₂ nanorods prepared at 600 °C. As shown in Fig. 3b, the high-resolution XPS spectra of Sn 3d demonstrates that Sn 3d_{5/2} peak and Sn 3d_{3/2} peak occur at 486.0 eV and 494.5 eV, respectively. The energy difference of 8.5eV between of them coincide with the energy splitting reported for SnO₂ [10]. The asymmetric O1s XPS spectrum survey shown in Fig. 3(b) indicates various states of oxygen nearby the nanorods surface region. The O1s peak was deconvoluted into two components located at 529.9 eV and 531.0 eV. The binding energy located at 529.9 eV is related to the crystal lattice O²⁻ anions corresponding to Sn-O bonds within the matrix of SnO₂ nanorods, while the binding energy sited at 531.0 eV causes for the adsorbed O⁻ or O²⁻ ions in the oxygen deficient regions within the matrix of SnO₂, which will react with the tested gas to enhance the response of SnO₂ nanorods for alcohol. In addition, the atomic concentration ratio of Sn and O was evaluated to be about 1:1.42 (≈0.704) using sensitivity factor, indicating serious deviation from the stoichiometry of SnO₂ composition (1:2). The XPS survey of other three samples calcined at 680, 760 and 840 °C was also measured (not shown). The atomic ratio of Sn/O was evaluated to be 1:1.57 (≈0.64), 1:1.71 (≈0.585) and 1:1.89 (≈0.53), respectively. It shows that the deviation from stoichiometry (0.5) of Sn/O atomic ratio changed from 0.7 to 0.53 caused by oxygen vacancies. The oxygen vacancy is conducive to improving the adsorption oxygen ions, which could contribute to the gas response. Thus, it can be speculated that the nanorods sample prepared at 600 °C would exhibit better gas-sensing response than other three samples.

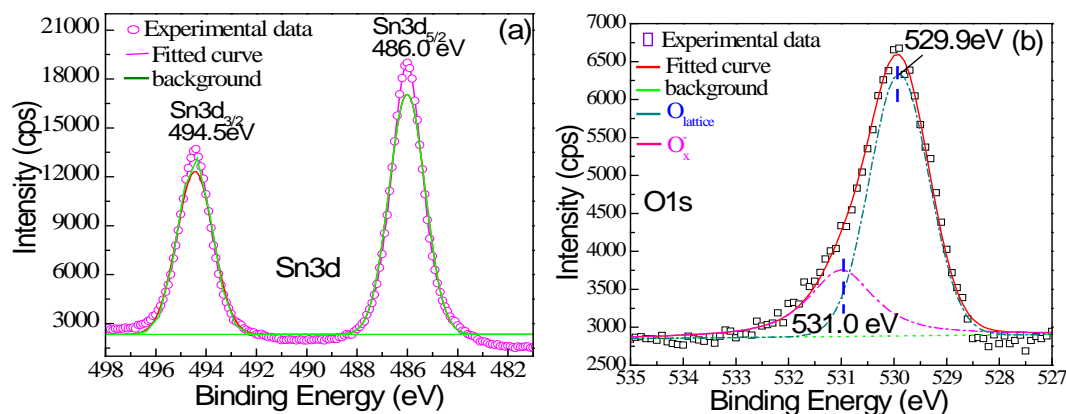


Fig. 3. XPS spectra of SnO₂ nanorods prepared at 600 °C: (a) Sn 3d, (b) O 1s.

The specific surface area of SnO₂ nanorods was determined by nitrogen adsorption–desorption measurements and Brunauer–Emmett–Teller (BET) analyzer method. The results show that the surface area of the SnO₂ nanorods was calculated to be 69.6, 53.14, 38.56 and 23.84 m²g⁻¹, respectively, indicating the decrease of the surface area with the increase of the SnO₂ nanorods diameter. It implies that the SnO₂ nanorods sample calcined at low temperature has a larger surface area than the sample calcined at higher calcination temperature. Generally, larger specific surface area may cause a better response due to more active sites to adsorb gas molecules.

3.2. Gas-sensing characteristics

The sensors were exposed to 1000 ppm ethanol at different operating temperature (175–425 °C) to determine the optimum working temperature and the result was shown in Fig.4(a). It can be seen from Fig. 4(a) that the response increase with the operating temperature and achieve a maximum value of 275 °C, and then the response rapidly descend with the increasing temperature again, which indicates the operable optimum temperature of the 275 °C. Fig. 4(b) depicted the response and recovery characteristics of the sensors based on SnO₂ nanorods prepared at 600, 680, 760 and 840 °C to 1000 ppm ethanol at 275 °C. For observing clearly, only one cycle was laid out. An overview from Fig. 4(b) is clear that the response amplitude of the sensor gradually increases with the diameter of SnO₂ nanorod decrease, indicating the sensing performance of sensor shows good dependence on the diameter of SnO₂ nanorods. Not surprisingly, the sensing performance of the SnO₂ nanorods with a diameter of about 12 nm exhibits an obviously better than the other sensors. It can be observed that the response and recovery time of SnO₂ nanorods calcined at 600 °C are about 6 s and 14 s, respectively, which is short enough for practical application.

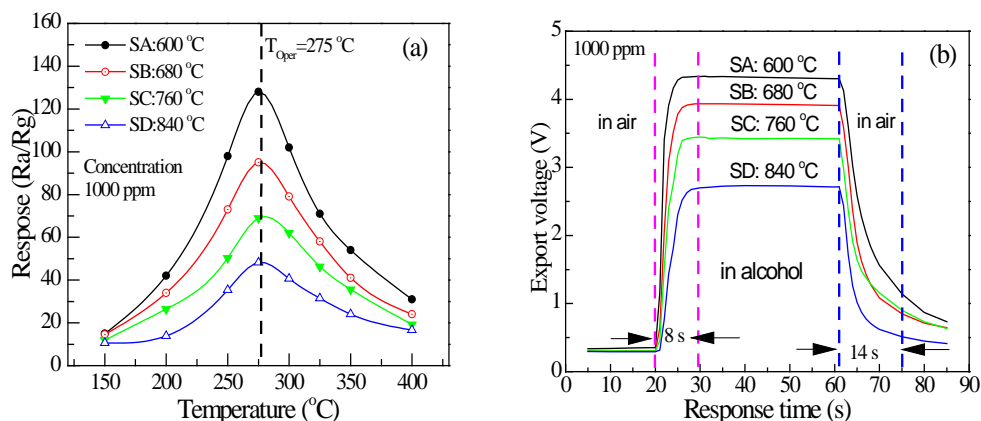


Fig. 4. (a) Dependence on the operating temperature of gas response. (b) Dynamic response and recovery behaviour of SnO₂ nanorods. (Only one cycle laid out).

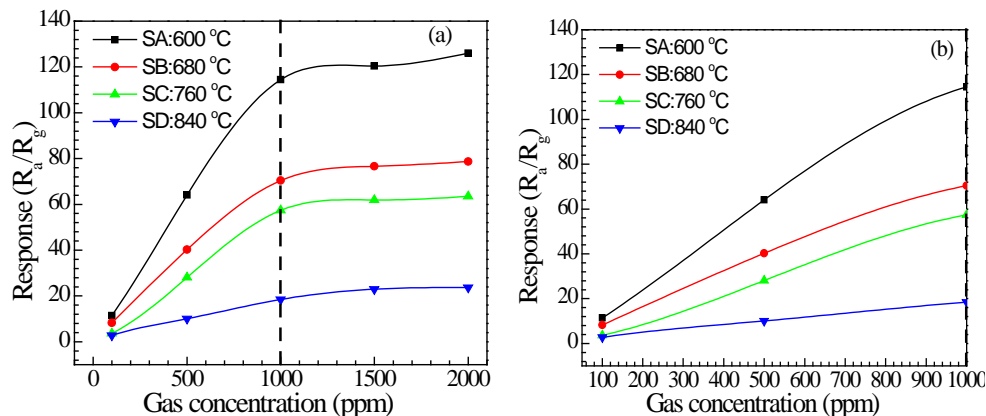
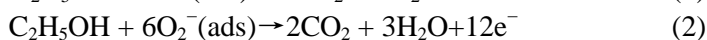
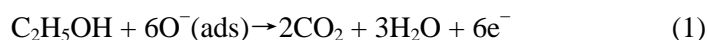


Fig. 5 (a) Gas response of sensors to ethanol concentrations at 275 °C. (b) Linear dependence of the response on concentration in the range of 100-1000 ppm.

The dependence of the response on the alcohol concentration at the optimum operating temperature of 275 °C was shown in Fig. 5. It can be seen from Fig. 5 that the response of all sensors increase with the alcohol concentration. Fig. 5(b) shows a good linear relationship between the response and alcohol concentration in the wide variation range of 100-1000 ppm. Above 1000 ppm, the response increase slowly with the increasing gas concentration, indicating the sensors achieve a saturated state. In particular, Fig. 5 presents that sensor based on the SnO₂ nanorods calcined at 600 °C exhibits much higher response to alcohol than other three SnO₂ nanorod sensors. For alcohol concentration of 100, 500, 1000, 1500 and 2000 ppm, the most sensitive SnO₂ sensor response is 11.38, 64.13, 114.46, 120.43 and 126.07, respectively. The higher response is probably ascribed to the absorption of more oxygen molecules to react with alcohol molecules.

As for the mechanism, the theory built on the change of the resistance caused by adsorption and desorption process of oxygen molecules on the SnO₂ nanorods surface is the widely accepted [11]. In atmospheric environment, oxygen molecules are chemisorbed on the surface and capture electrons from the conduction band of the SnO₂, causing an electron depletion layer in the SnO₂ nanorods surface layer and resulting in the resistance increase. When the alcohol molecules overstep the surface of the SnO₂ nanorods sensor, these gas molecules are oxidized by the adsorbed oxygen species to reduce the coverage of oxygen ions and the depleted electrons are fed back into the SnO₂ conductance band. It could result in a narrowed depletion layer and the decrease of the sensor resistance. Thus, an electrical signal is generated and output to the test system. The reaction between alcohol molecules and ionic oxygen species can be described in detail as Eq. (1) and (2) [12].



According to the above reactions, it is clear that a large specific surface area can provide more active sites for the gas adsorption to improve the adsorption capacity of oxygen molecules. In order to elucidate the influence of calcination temperature on the gas sensing behaviour of the SnO₂ nanorods with different diameter, we plot the specific surface area as a function of the average nanorods diameter (Fig. 6a), and the gas response measured at optimum temperature (275 °C) as a function of the atomic ratio of Sn/O (Fig. 6b), respectively. Fig. 6(a) implies that the SnO₂ nanorods prepared at low temperature has a larger surface area than the sample prepared at a higher calcination temperature. Larger specific surface areas have a more adsorption capacity of oxygen molecules, which lead to the enhancement of surface properties such as catalytic activity or surface adsorption. Moreover,

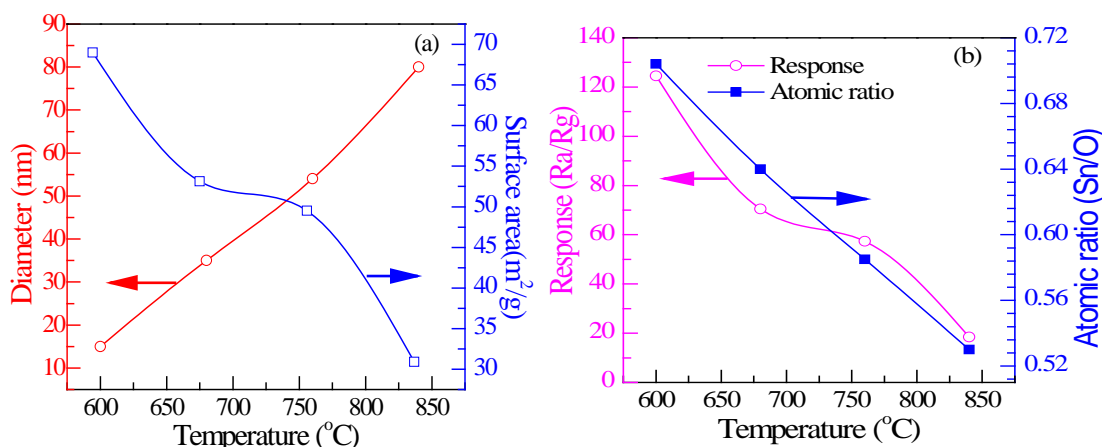


Fig. 6. (a) Correlation between the specific surface area (average diameter) and the calcinated temperature. (b) Correlation between the responses (or Sn/O atomic ratio) and the calcinated temperature.

depending upon the principle of crystallography, the calcination temperature affects the crystallinity of SnO₂ confirmed by the XRD results shown in Fig. 1. The low calcination temperature generally causes poor crystallinity of the SnO₂ crystal, resulting in a large number of oxygen vacancies in the surface layer of nanorods. It could enhance the absorption of oxygen molecules from the atmosphere. The results of the XPS shown in Fig. 3 have been confirmed that large amounts of oxygen molecules was adsorbed on the surface of gracile SnO₂ nanorods prepared at a low calcination temperature of 600 °C, which cause a positive effect on the gas response. The correlation between the response as a function of the Sn/O ratio of the SnO₂ nanorods with different diameter was shown in Fig. 6b. It can be seen that the gas sensitivity increases with the decrease of the Sn/O ratio deviation from stoichiometric ratio. Therefore, the gracile SnO₂ nanorods fabricated at lower calcination temperature shows a significantly better sensing performance, attributing to the larger effective surface area and the strongly stoichiometry deviation of the Sn/O ratio.

4. Conclusions

In summary, SnO₂ nanorods with different diameters were synthesized by an adjusted solid state reaction in the presence of mixed KCl-NaCl mixture and surfactants at room temperature and calcined at different temperature. The diameter of nanorods grew thick with the increase of the calcination temperature. The influence of the calcination temperature on the gas sensing behaviour of SnO₂ nanorods was investigated. All sensors showed good responses to ethanol gas. The response of the gracile nanorods prepared at low calcination temperature showed significantly better than the thick nanorods prepared at high calcination temperature due to the larger effective surface areas and the strongly deviated stoichiometric ratio of Sn/O. The experimental results indicate the great potential applications of utilizing gracile SnO₂ nanorods for fabricating gas sensor to detect ethanol.

Acknowledgements

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References

- [1] Sun G, Qi F X, Zhang S S, Li Y W, Wang Y, Cao J L, Bala H, Wang X D, Jia T K, Zhang Z Y 2014 *J. Alloy. Comp.* **617** 192
- [2] Comini E, Baratto C, Faglia G, Ferroni M, Vomiero A, Sberveglieri G 2009 *Prog. Mater. Sci.* **54** 1
- [3] Huang H, Lee Y C, Tan O K, Zhou W, Peng N, Zhang Q 2009 *Nanotech.* **20** 115501
- [4] Fields L L, Zheng J P, Cheng Y, Xiong P 2006 *Appl. Phys. Lett.* **88** 263102
- [5] Mohamed S H 2012 *J. Alloy. Comp.* **510** 119–124
- [6] Shi L, Lin H L 2011 *Langmuir* **27** 3977
- [7] Xu S, Kan K, Yang Y, Jiang C, Gao J, Jing L Q, Shen P K, Li L, Shi K Y 2015 *J. Alloy. Comp.* **618** 240
- [8] Luo L, Jiang Q P, Qin G H, Zhao K, Du G F, Wang H, Zhao H Y 2015 *Sens. Actuators B* **218** 205
- [9] Oviedo J, Gillan M J 2000 *Surf. Sci.* **463** 93
- [10] Dai Z F, Jia L C, Duan G T, Li Y, Zhang H W, Wang J J, Hu J L, Cai W P 2013 *Chem. Euro. J.* **19** 13387
- [11] Batzill M T, Diebold U R 2007 *Phys. Chem. Chem. Phys.* **9** 2307
- [12] Wang T T, Ma S Y, Cheng L, Luo J, Jiang X H, Jin W X 2015 *Sens. Actuators B* **216** 212