Enhanced ethanol response of La$_2$O$_3$-loaded SnO$_2$ nanorods prepared by an improved solid state reaction

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Abstract. La$_2$O$_3$-loaded SnO$_2$ nanorods with rutile structure were successfully synthesized by an improved solid state reaction with the surfactants in the presence of NaCl-KCl. The indirect-heating sensor was prepared using the products as sensing-material to study the response of the La$_2$O$_3$-loaded SnO$_2$ nanorods. The results showed that the performances of the SnO$_2$ nanorods to ethanol was greatly improved after loading La$_2$O$_3$. The significant improvement could be attributed to the excellent catalytic properties of loaded La$_2$O$_3$ and the high surface area.

1. Introduction

As a well-known substance used for detection of different VOC pollutants owing to chemical and thermal stability, good gas response and low cost [1], SnO$_2$ has been extensively studied for detection of a wide variety of flammable and toxic VOCs gases such as ethanol, acetone, isopropanol and so on [2]. However, it is also suffering a serious problem associated with maximum sensitivity, high operating temperature, lack of long-term stability and poor selectivity and so on. In order to overcome these shortcomings, a lot of exploratory work have been devoted to the new material with enhanced gas sensing performances. Recently, one-dimensional (1-D) nanostructured SnO$_2$ such as nanowires [3], nanobelts [4], nanorods [5] and so on, is attracting a great deal of attention to study the applications in sensor technology due to their high surface–volume ratio and enhanced surface reactivity. Another significant effort, doping Lanthanide has been used to overcome these limitations and improve the performances [6].

In this work, La$_2$O$_3$-loaded SnO$_2$ nanorods synthesized by an improved solid state reaction with surfactants in the presence of NaCl-KCl. Indirect-heating sensors based on nanorods were fabricated and investigated for the response to ethanol. The gas sensing experiments of La$_2$O$_3$-loaded SnO$_2$ nanorods were carried out compared against the no-loaded SnO$_2$ nanorods to research the effect of loading La$_2$O$_3$ on the sensing properties.

2. Experimental

All utilized analytical grade chemical reagents were purchased from the Sinopharm Chemical Reagent Co. No-loaded and La$_2$O$_3$-loaded SnO$_2$ nanorods were synthesized via an improved solid state reaction. Typically, a mixture of the SnCl$_4$·5H$_2$O added in an amount of LaCl$_3$·6H$_2$O (Did not add for no-loaded SnO$_2$ nanorods) was mixed with KBH$_4$ in the presence of KCl-NaCl and nonyl phenyl ether (9)/(5) at room temperature. Then, the mixture was fully ground to cause the solid phase reaction. The product kept in a porcelain crucible was annealed at 680 °C for 2h. After that, the resulting product was
washed with distilled water several times to remove NaCl and KCl, and was dried at 80 °C for 12 h for further characterization.

The X-ray diffraction (XRD) using a Rigaku D/MAX-3B powder diffractometer was performed to determine the crystalline structure and phase of SnO₂ nanorods. The morphology and detailed structure was characterized by an FEI Quanta 200 scanning electron microscope (SEM) and a transmission electron microscope (TEM, JEOL 2010, 200 KV). The indirect-heating sensor was elected to study the response of the SnO₂ nanorods [2]. The test of the gas-sensing properties carried out on a JF02F measurement system in a relative humidity range of 40–70%. The response was defined as the ratio of \( R_a / R_g \), where \( R_a \) and \( R_g \) is the resistance in atmospheric air and in target gas, respectively.

### 3. Results and discussion

The typical XRD patterns of the as-prepared SnO₂ nanorods were shown in Figure 1(a). As seen from Figure 1(a), all the diffraction peaks of the La₂O₃-loaded SnO₂ nanorods can be indexed to the rutile structured SnO₂ (JCPDS file No. 41-1445), which is almost similar to that of the no-loaded SnO₂ nanorods. However, it is obvious that two weak additional diffraction peaks located at 28.42° and 48.56°, which could be assigned to the crystalline phases of La₂O₃ can be detected. Moreover, the relative intensities of the SnO₂ nanorods sample decreased after loading La₂O₃, suggesting the growth of SnO₂ nanorod was prevented by La₂O₃.

Figure 1(b) and (d) showed the morphologies of the SnO₂ nanorods characterized by SEM. Being compared with the no-loaded SnO₂ nanorods (shown in Figure 1(d)), finer rod-like structured regular morphologies of the La₂O₃-loaded SnO₂ nanorods with the length in the range of 500 nm and several micrometers can be observed. It indicates that the La₂O₃ could prevent the nanorods further growth up [7]. The thinner nanorods could provide a large surface area, contributing to increase the probability of surface trapping to spur the surface reaction. The EDS spectrum of the La₂O₃-loaded SnO₂ nanorods shown in Figure 1(c) (inset) reveals the component of stannum (Sn), oxygen (O) and lanthanum (La), while the La is not observed in the EDS spectrum of the no-loaded SnO₂ nanorods shown in Figure 1(e) (inset).

![Figure 1. (a) XRD patterns of as-synthesized SnO₂ nanorods. (b) and (d) SEM images of SnO₂ nanorods. (c) and (e) EDS spectra of SnO₂ nanorods (inset).](image)

The TEM image of the La₂O₃-loaded SnO₂ nanorods shown in Figure 2 displayed that the product mainly consists of solid rod-like structures with diameters 20 nm and length up to several micrometers. Furthermore, it is obvious that many small La₂O₃ crystalline grains are attached to the SnO₂ nanorods surface. The HRTEM of individual SnO₂ nanorod shown in Figure 2b depicted the uniform structure and clear lattice fringes. The 0.342 nm space between two adjacent lattice fringes of the La₂O₃-loaded SnO₂ nanorod corresponds to the (110) lattice plane of SnO₂ in tetragonal cassiterite structure. The
Fourier transform electron diffraction pattern (FFT) (inset) indicated the single structure of the La$_2$O$_3$-loaded SnO$_2$ nanorod.

![Figure 2. TEM images of La$_2$O$_3$-loaded SnO$_2$ nanorod. (a) General TEM image. (b) HRTEM image. Inset: Fourier transform electron diffraction pattern.](image)

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Figure 3(a) showed the response dependence of the sensors on the operating temperature for 500 ppm ethanol. It showed that the responses increase with the temperature at first, after reaching a maximum value of 38 and 116 for no-loaded and La$_2$O$_3$-loaded SnO$_2$ nanorods at optimum operating temperature of 246 °C, and then decreased rapidly. This performance is associated with the kinetics and mechanism of gas adsorption and desorption of semiconducting metal oxides [8]. From the Figure 3(a), it can be seen that the SnO$_2$ nanorods sensors have a lower optimum temperature, and the response of La$_2$O$_3$-loaded SnO$_2$ nanorods is much larger than that of the no-loaded SnO$_2$ nanorods. Figure 3(b) showed the investigated response curves of La$_2$O$_3$-loaded SnO$_2$ nanorods sensor as a function of different ethanol concentration at the optimum operating temperature of 246 °C. It can be observed that the response increases rapidly in the range of 5 to 1000 ppm. The response increases slightly above 1000 ppm, indicating the sensors approach to saturation.

![Figure 3. (a) Response depending on the operating temperature. (b) Response to concentrations at 246 °C. (c) Dynamic response and recovery behaviours.](image)

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The repeatable characteristic of the response and recovery was shown in Figure 3(c) achieved by the La$_2$O$_3$-loaded SnO$_2$ nanorods sensor being orderly exposed to different concentrations at the optimized temperature of 246 °C. It is evident that the response amplitude of the sensors gradationally increases with the concentration changed from 5 to 1000 ppm. The sensor presents a considerable response to low ethanol concentration of 5 ppm. It is worth noting that the characteristics of the SnO$_2$
nanorods were remarkably improved after loading La$_2$O$_3$ compared with the no-loaded SnO$_2$ nanorods. The response ($t_{Res}$) and recovery ($t_{Rec}$) time is an important parameter to assess a gas sensor. Figure 4(a) and (b) showed the transient response–time data of the La$_2$O$_3$-loaded SnO$_2$ nanorods sensor to 500 ppm at 246 °C. It is easy calculated from the Figure 4(a) and (b) that the response time $t_{Res}$ values is 9 s, while the recovery time $t_{Rec}$ value is about 5 s. This result indicates the response ($t_{Res}$) and recovery ($t_{Rec}$) time is short enough for practical application. Furthermore, we performed a series of experiments of SnO$_2$ nanorods exposed to 300 ppm VOCs gas including acetone, ethanol, toluene, isopropanol, formaldehyde, petrol, carbinol and ammonia in order to explore the selectivity, and the result was shown in Figure 4(c). It showed that sensors exhibited a good selectivity to ethanol. Particularly, the response of the no-loaded SnO$_2$ nanorods is no greater than 36, while the response of the Ln$_2$O$_3$–loaded SnO$_2$ nanorods sensor achieves 84, which is more than 2 times larger than that of the no-loaded SnO$_2$ nanorods. The greatly improved response could be attributed to the excellent catalytic properties of loaded La$_2$O$_3$ and the restrained growth of the SnO$_2$ nanorods resulting in a high surface area, being beneficial to increase the amount of active sites on the SnO$_2$ nanorods surface [6].

**Figure 4.** (a) and (b) Enlarged response and recovery transient time examined. (c) Bar chart showing the response of La$_2$O$_3$-loaded SnO$_2$ nanorods to different gases.

4. **Conclusions**

In summary, La$_2$O$_3$-loaded SnO$_2$ nanorods with rutile structure were successfully synthesized by an improved solid state reaction in the presence of NaCl-KCl and surfactants. The response of the La$_2$O$_3$-loaded SnO$_2$ nanorods to ethanol showed high response, good selectivity, low detection limit, and short response and recovery time. The response improvement of the La$_2$O$_3$-loaded SnO$_2$ nanorods to ethanol is remarkable. Doping Lanthanide is effective and significant route to improve the performance of the SnO$_2$ nanorods for applications in detecting ethanol.

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**References**

[1] Wang Z J, Liu, S Y, Jiang T T, Zhang J, An C H and Wang C 2015 *RSC Adv.* 5 64582
[2] Qin G H, Gao F, Jiang Q P, Li Y H and Zhao H Y 2016 *Phys. Chem. Chem. Phys.* 18 5537
[3] Wang B, Zhu L F, Yang Y H, Xu N S and Yang G W 2008 *J. Phys. Chem. C* 112 6643
[4] Fields L L and Zheng J P 2006 *Appl. Phys. Lett.* 88 263102
[5] Yu L M, Fan X H, Qi L J, Ma L H and Yan W 2011 *Appl. Surf. Sci.* 257 3140
[6] Zhang G Z, Zhang S P, Yang L, Zeng D W and Xie C S 2013 *Sens. Actuators B* 188 137
[7] Ruiz A M, Cornet A, and Morante J R 2004 *Sens. Actuators B* 100 256
[8] Yamazoe N, Fuchigama J, Kishikawa M and Seiyama T 1979 *Surf. Sci.* 86 335