Synthesis and gas-sensing properties of Ce-doped SnO₂ materials

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Abstract. Ce-doped SnO₂ (2, 5, 10%Ce) nanopowders were successfully synthesized by a sol–gel method and their gas sensing properties were investigated. The samples were characterized by X-ray diffraction (XRD), transmission electron microscopy (TEM), and thermogravimetric-differential thermal analyzer (TG-DTA). The results indicated that well-crystallized Ce-doped SnO₂ particles in size of about 30nm were obtained at annealing temperature 800°C. Ce-doped SnO₂ sensors showed a high response to H₂S, whose sensitivity is about sextuple of the undoped SnO₂ sensors to H₂S, and to ethanol, about triplication of the undoped SnO₂ sensors. These results were thought to be correlated with Ce distribution on the SnO₂ surface and its effective contribution towards the conductivity and crystallite size of the grains.

1. Introduction

Tin oxide semiconductor sensors are extensively used for the detection of various pollutant and combustible gases. The advantages of the sensors are high response, simple design, and low weight and cost. However, the major problems associated with SnO₂ sensors are their low selectivity and stability. Many attempts has been done to solve these problems by using suitable additives such as noble metals (Pd, Pt) and transition metal oxides [1]. On the other hand, rare earth doping in semiconductor materials such as TiO₂, Al₂O₃, etc [2-3], have obtained widespread interest, since the addition of rare earth ions can control morphology and size, which can contribute for technological innovation and development of new optoelectronic devices [4]. In this work, Ce-doped SnO₂ were successfully synthesized by a sol–gel method and succeedent annealing procedure. The gas-sensing properties of Ce-doped SnO₂ are also investigated.

2. Experimental

2.1. Synthesis of materials

In the typical process, SnCl₄·5H₂O and citric acid in a 1:1 molar ratio were added to the glycol solution to produce a tin citrate solution. The concentration of tin ion in the solution is 0.15 M. The Ce(NO₃)₃·6H₂O (Ce:Sn molar ratio is 0.02, 0.05 and 0.10, respectively) mixed with an appropriate volume of citric acid was added to the tin citrate solution to form a turbid mixture. NH₃·H₂O was
added until pH reached 1.5. The mixture was stirred for 4h at 55°C until the gel was formed, and then dried at 100 °C. The dried gel precursor was heated at 800°C for 3h, and the samples were obtained after ground into fine powders. For comparison, pure SnO₂ powders were also prepared with the same procedures described previously. All the chemicals used in the process are analytical grade.

The thermal analysis of the dried gel was obtained by thermogravimetric-differential thermal analysis (TG-DTA, ZRY-1) in ambient air with increasing the temperature at a speed of 15°C/min. The structure and morphology of the products were characterized using XRD (Bruker D8, Cu Kα radiation, λ=1.5418Å) and TEM (FEI TECNALG²).

2.2. Gas sensitivity test

The final powders were mixed and ground with an adhesive in an agate mortar to form a gas-sensing paste. The paste was coated on a ceramic tube on which a pair of Au electrodes was previously printed, dried under IR light for several minutes in air, and then sintered at 400°C for 1h. At last, a Ni–Cr heating wire was inserted to form a side-heated gas sensor. Its structure was shown in figure 1. The prepared gas sensors were aged at 300°C for 240h in order to improve their stability.

![Figure 1. The structure of the gas sensor.](image)

The test was operated in a measuring system of HW-30A (Hanwei Electronics Co. Ltd., Henan, China). The concentration of all gases was 50 ppm. The gas sensitivity was measured in static state. The circuit voltage was 10V, and outputs $V_{out}$ were the terminal voltage of the load resistor. The working temperature of a sensor was adjusted through varying the heating voltage. The resistance of a sensor in air or test gas was measured by monitoring $V_{out}$. The gas sensitivity (response magnitude) in this work was defined as $S = R_{air}/R_{gas}$, where $R_{air}$ and $R_{gas}$ were the resistances of a sensor in air and in a test gas, respectively. The response time was defined as the time required for the variation in conductance to reach 90% of the equilibrium.

3. Results and discussion

Figure 2 shows the TG-DTA curves of the dry gel precursor powder for the 2%Ce-doped SnO₂. In the DTA curve, there were broad exothermal peaks from 300°C to 750°C and no peak at other temperatures. The exothermic effects may correspond to the oxidation and decomposition of organic materials. Besides the weight loss at the temperature stage from 300°C to 750°C, a obvious weight loss can also be observed in TG curve from room temperature to 300°C. The weight change can be thought from the releasing of the adsorbed water, crystal water and other gases. From 750°C to 900°C, there is no obvious weight loss. In order to obtain the pure CeO₂-doped SnO₂, we chose 800°C as a appropriate calcination temperature.
Figure 2. TG-DTA curves of the dry gel precursor

Figure 3 showed XRD patterns of Ce-doped SnO₂ and undoped SnO₂ samples calcinated at 800 °C. From these patterns, it was observed that the strong diffraction peaks of the SnO₂ with tetragonal rutile structure became sharper with the increasing amount of Ce, which indicated doping Ce can improve the crystallization of the SnO₂ particles. When the Ce content was 5% and 10%, the reflections of CeO₂ appeared. As already reported [5], the second phase (CeO₂) of the tetragonal structure for 5%Ce-doped SnO₂ nanoparticles were also observed at temperature 1000 °C. Due to the large difference of the radius and charge between Ce⁴⁺ ions (0.092 nm) and Sn⁴⁺ ions (0.071 nm), it is difficult for Ce⁴⁺ ions to enter the lattice of SnO₂.

Figure 3. XRD patterns of Ce-doped SnO₂ and undoped SnO₂

Figure 4 shows TEM image of 2% Ce-doped SnO₂ nanoparticles. Sol-gel technology is an efficient synthetic method for SnO₂ nanocrystals with uniform shape and size. The image reveals that the doped materials present small particles with sizes about 30 nm, which is in accord with the XRD analysis by
Scherrer equation. Ce ion has a bigger radius than Sn ion (0.071nm), so it has a smaller solubility in the SnO₂ lattice, and the excess content simply acted as a stabilizer of the SnO₂ crystallites [6].

![Figure 4. TEM micrograph of Ce-doped SnO₂](image)

We selected 11 kinds of gases as detecting gases, including ethanol, formaldehyde, dimethylbenzene, acetonitrile, toluene, sulfureted hydrogen, hydrogen, ethene, methane and carbon monoxide. The gas sensing properties of samples were tested under heating voltage 5V (working temperature about 332°C). Figure 5 gives the sensitivities to gases of sensors based on SnO₂ and 10%Ce-doped SnO₂. As for pure SnO₂, it showed a certain response to almost all the gases, but the sensitivities are very low. But Ce-doped SnO₂ sensors showed a high response to H₂S, whose sensitivity is about sextuple of the undoped SnO₂ sensors to H₂S, and to ethanol, about triplication of the undoped SnO₂ sensors to ethanol. So that it may have excellent potential applications to detect sulfureted hydrogen and ethanol.

![Figure 5. Sensitivity of gas sensors based on SnO₂ and Ce-doped SnO₂](image)
Rare earth metal has a high alkalescence and good catalysis [7-8], which may be in favor of improving the sensitivities to H$_2$S and ethanol while did not favor that of other tested gases. Based on the spillover mechanism proposed by Morrison [9], the surface catalyst (in our case, Ce) dissociates the gas molecule, and reactive atoms formed are spilled over on the semiconductor surface and influence the conductivity. In the case of H$_2$S detection, the sensing mechanism was presumed as follows [10]:

$$2\text{H}_2\text{S} (g) + 3\text{O}_2 (ad) \rightarrow 2\text{H}_2\text{O} (g) + 2\text{SO}_2 (g) + 3\text{e}^-$$

(1)

When oxygen is adsorbed on the surface of Ce-doped SnO$_2$ grains, the high alkalescence formed by doping Ce species with strong localization can be available to dissociate H$_2$S gas molecules. The effects may be the reason that the materials had the high sensitivity to H$_2$S gas.

The reason of increasing response with the addition of Ce to ethanol should be similar to the above description to H$_2$S. The increasing of alkalescence of the surface of SnO$_2$ particles is good for enhancing the ethanol sensitivity [11-12]. The sensitivity of acetaldehyde by dehydrogenation and oxygenation from the surface of alkalescence is higher than that of ethylene by dehydrogenation and oxygenation from the surface of acidity.

On the other hand, the addition of Ce to SnO$_2$ can improve the crystallization of the SnO$_2$ particles, modified the particles size distribution and electrical conductivity. These changes also affected gas-sensing properties to some extent.

4. Conclusions

Tin dioxide (SnO$_2$) and Ce-doped SnO$_2$ were successfully synthesized by a sol–gel method using inorganic salts as raw materials. The Ce-SnO$_2$ powders were characterized by XRD, TEM, and so on. The results showed that well-crystallized nano-sized Ce-doped SnO$_2$ in size of about 30nm was obtained at annealing temperature 800°C. The gas-sensing properties were characterized. It was found that ceria doped SnO$_2$ showed the high sensitivity to ethanol and sulfureted hydrogen. The increase of alkalescence of the surface of SnO$_2$ particles is good for enhancing the response to ethanol and sulfureted hydrogen. It may have excellent potential applications to detect sulfureted hydrogen and ethanol.

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