Study on the Gas Sensitivity Properties of TiO$_2$ Nanoparticles Modified by ZnO

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Abstract. TiO$_2$ nanomaterials and ZnO doped TiO$_2$ nanomaterials were synthesized by sol-gel method. The gas sensing properties of ZnO-doped TiO$_2$ nanomaterials were investigated by using a parathermal gas sensor. Studies have shown that the responsiveness of ZnO-doped gas sensor to ethanol gas is increased from 80% to 87%, and the response recovery time is shortened to (1.5s, 1s). This method improves the gas sensitivity of the sensor.

Introduction

With the increasing emphasis on environmental protection, higher requirements are placed on the detection and monitoring of industrial waste gas, toxic and harmful gases, and the research of gas sensor has become an important research topic [1-3]. Semiconductor gas sensors have been widely studied due to their small size, low cost, simple structure, simple preparation and long service life. At present, the widely used gas sensor materials are ZnO and TiO$_2$, which have good sensitivity to many gases such as ethanol, methane, hydrogen sulfide, carbon monoxide, etc. [4-9], semiconductors made of ZnO and TiO$_2$. Gas sensors can be widely used in the monitoring of toxic gases in various fields of production and living. Generally, gas sensing elements prepared by using pure semiconductor metal oxide powder have low sensitivity, high operating temperature, and difficult performance to meet applicable requirements. At present, the gas of semiconductor metal oxides is mainly improved by methods such as compounding and doping [10]. Sensitive performance. Taking TiO$_2$ as an example, the doping of elements can significantly change the band gap energy of TiO$_2$ and lead to diversified physicochemical properties, thereby improving the detection performance of the sensor on the target gas. By doping the TiO$_2$ gas sensitive material, the sensitivity can be greatly improved.

Experiment

The Preparation of ZnO Nanoparticles

a) Use electronic balance accurately weighed 8.2125 g zinc acetate and put into 30 ml of ethanol solution, stir with constant temperature magnetic stirrer and keep the temperature in 70°C, after 10 min stir, join 4.6 ml of ethanol amine drop by drop as stabilizing agent, stirring for 10 min, then cool to room temperature, using ethanol in 50 ml beaker titration, configured to 0.75 M level sol, finally in 70°C temperature magnetic stirrer stir for 1 hour to form transparent sol, let it stand aside for later use.

b) After drying the colloid, grind it into powder and anneal it in CVD at 700°C for 2 hours to obtain ZnO nanoparticles.
The Preparation of TiO$_2$ Nanoparticles

a) Firstly, take a certain amount of butyl titanate and blend it into anhydrous ethanol, and make the concentration ratio of the two become butyl titanate: anhydrous ethanol = 6ml:24ml, then stir it with magnetic stirrer at the speed of 130r/min for 30 mins.

b) Drop glacial acetic acid into 2ml of deionized water as a hydrolysis inhibitor, and drop about 0.4ml to keep the PH value at 2~3.

c) Mix the solutions obtained in steps a and b, stir for 1 hour, and let stand to form colloid.

d) The colloid was dried, ground into powder, and annealed for 2 hours in CVD at 700°C to obtain TiO$_2$ nanoparticles.

The Preparation of ZnO Doped TiO$_2$ Sensor

a) Same as the procedure a above, take a certain amount of butyl titanate and blend it into anhydrous ethanol, and make the concentration ratio of the two become butyl titanate: anhydrous ethanol = 6ml:24ml, then stir it with magnetic stirrer at the speed of 130r/min for 30 mins.

b) Dissolve ZnO powder with a mass fraction of 4%, namely 0.086g, in 2ml of deionized water, and then drop 0.4ml glacial acetic acid into the deionized water to maintain the PH value at 2~3.

c) Mix the solutions obtained in steps a and b, stir for 1 hour, and let stand to form colloid.

d) After drying the colloid, grind it into powder, and anneal it in CVD at 700°C for 2 hours to obtain nanoparticles doped by ZnO.

e) The prepared ZnO doped TiO$_2$ nanoparticles were slightly ground in an agate mortar, and the polished paste powder was coated on the surface of ceramic tube between Au electrodes, and then the ceramic tube was placed in a constant temperature drying box to dry. The final heat treatment was sintering of ceramic tube for 2 hours in CVD at a high temperature of 400 degree Celsius. As shown in figure 1(a), this side thermal gas sensor is mainly composed of ceramic tube, Au electrode and Pt electrode. As shown in figure 1(b), four platinum wire leads of the ceramic tube coated with samples are welded to the sensor base. Thus constitutes a side - thermal gas sensor. The sensor was aged for a period of time before gas sensitivity detection.

![Side thermal gas sensor structure diagram and its physical diagram.](image)

Figure 1. Side thermal gas sensor structure diagram and its physical diagram.

Reaction Mechanism

In the above reaction process, butyl titanate, anhydrous ethanol and water are configured with sol in a certain proportion: Ti(OC$_4$H$_9$)$_4$:CH$_3$CH$_2$OH:H$_2$O=2.5:10:1(volume ratio).

The hydrolysis reaction and condensation polymerization reaction of butyl titanate are as follows:

\[
\text{Ti(OC}_4\text{H}_9)_4 + 4\text{H}_2\text{O} \rightarrow \text{Ti(OH)}_4 + 4\text{C}_4\text{H}_9\text{OH}
\]

\[
\text{Ti(OH)}_4 + \text{Ti(OH)}_4 + 2\text{TiO}_2 + 4\text{C}_4\text{H}_9\text{OH}
\]

\[
2\text{Ti(OC}_4\text{H}_9)_4 \rightarrow 2\text{TiO}_2 + 4\text{H}_2\text{O}
\]
Results and Discussions

Figure 2 (a) illustrates the I-V characteristic curve of ZnO doped TiO$_2$ nanoparticles prepared by sol-gel method under dark and light conditions. As can be seen from the figure, the current and voltage curves show a linear relationship, indicating that ZnO doped TiO$_2$ nanoparticles have good ohmic contact with Au electrode. Figure 2 (b) states a function curve of sensor current changing over time under an environment of air and ethanol gas, from the graph, you can tell that the black curve at the bottom expresses minimum sensor current in the air, as ethanol steam continuously released slowly, gas concentration then gradually increased, a unceasingly increases of sensor current has also been detected. This indicates that the side thermal gas sensor prepared by ZnO doping TiO$_2$ nanoparticles has obvious response to ethanol gas.

![Figure 2](image1.png)

Figure 2 (a) The brightness I-V characteristic curve of ZnO doped TiO$_2$ nanoparticles prepared by sol-gel. (b) I-t characteristic curves of ZnO doped TiO$_2$ nanoparticles with ethanol in different concentrations.

Figure 3. XRD patterns of TiO$_2$ synthesized by sol-gel and ZnO doped TiO$_2$ nanoparticles.

It can be seen from figure 3 that the diffraction peaks of pure TiO$_2$ and ZnO modified TiO$_2$ nanoparticles correspond to each other. According to standard comparison card (JCPDS card No.21-1272), TiO$_2$ synthesized by sol-gel is anatase phase, and No ZnO diffraction peaks are found in the diffraction peaks, which may be related to the small amount of ZnO nanoparticles.

![Figure 3](image2.png)

Figure 4. SEM images of a)TiO$_2$ and b)ZnO doped TiO$_2$ nanoparticles synthesized by sol-gel.
The SEM diagram in figure 4 shows the distribution of pure TiO$_2$ synthesized by sol-gel is not uniform, and the particle diameter is large, the size is about 300-1500nm. However, ZnO doped TiO$_2$ nanoparticles are not only evenly distributed, but also has a uniform crystal size of 200 nm. This indicates that ZnO doping effectively inhibits the growth of TiO$_2$ grains, and makes a uniform distribution of particles and pores, and has a large specific surface area, which is conducive to gas adsorption.

Figure 5. Recovery time of the side-thermal gas sensor made of pure TiO$_2$ and ZnO doped TiO$_2$ nanoparticles prepared by sol-gel that response to ethanol gas at room temperature condition.

Figure 5 shows the gas-sensitive performance test curve of ethanol gas by a gas-sensitive sensor made of pure TiO$_2$ and ZnO doped TiO$_2$ nanoparticles prepared by sol-gel. For pure TiO$_2$ nanoparticles, as shown in figure 5(a), the response degree of gas-sensitive sensor is 80%, and the response time and recovery time are (2s, 2s) respectively. Under ZnO doping, as shown in Figure 5(b), the sensor's responsiveness was improved to 87%, and the response recovery time was also shortened to (1.5s, 1s). Confirming the above conclusion, the doping of ZnO makes TiO$_2$ nanoparticles smaller in size and evenly distributed, leading to an increase in the specific surface area, enhancing gas adsorption, and improving the gas sensitivity of TiO$_2$ nanoparticle sensor.

Conclusions
ZnO nanomaterials and ZnO doped TiO$_2$ nanomaterials were synthesized by sol-gel method, and the gas-sensitive properties of ZnO composite nanomaterials were studied by means of side-thermal gas-sensitive element. Due to the improvement of the specific surface area of the material surface modification doping, the gas-sensitive performance is improved. In the relatively short response recovery time (1.5s, 1s), its response to ethanol gas reaches the highest value of 87%.

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