Synthesis and gas sensor application of nanostructure Cr$_2$O$_3$ hollow spheres

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Abstract. This paper prepared single phase Cr$_2$O$_3$ hollow spheres by the template method. The templates was carbon spheres prepared by glucose hydro-thermal method. The Cr$_2$O$_3$ hollow spheres were confirmed and characterized by TEM and N$_2$ adsorption-desorption. Then we investigated the gas sensor application of nanostructure Cr$_2$O$_3$ hollow spheres. The gas sensor properties of the Cr$_2$O$_3$ hollow spheres to some toxic flammable gases were investigated by resistance response method. The result showed that the sensor was extremely sensitive to the temperature, the resistance of sensor was increased linearly with the concentration of reductive gases varies from 50 to 250 ppm at optimum operating temperature (300$^{\circ}$C). The response and recovery of the sensor was fast with the time to reach 70% of the total resistance change was 16s and 7s.

1. Introduction

Hazardous and toxic gases from car and industrial exhausts are polluting the environment [1]. It is of great importance to detect these toxic gases. The sensing materials had been the focus of the research for decades. Some n-type metal oxide semiconductor, such as ZnO [2], SnO$_2$ [3], WO$_3$ [4], Fe$_2$O$_3$ [5], had been used as sensing materials. There were also many p-type metal oxide semiconductor, including NiO [6], MnO$_2$ [7], CuO [8], had been researched to be used for gas sensor because of their features such as ease of fabrication, high sensitivity.

As an important wide gap p-type metal oxide semiconductor, Cr$_2$O$_3$ has many outstanding properties, such as catalysis, electrochemical, magnetic, optoelectronic, mechanical and gas sensing properties [9]. So, Cr$_2$O$_3$ have been seemed to be a perspective material used for gas sensor. In this paper, a novel template method was used to synthesize Cr$_2$O$_3$ hollow spheres, which could provide big surface to volume ratio. It had be proved by the our N$_2$ adsorption-desorption. Then the sensor which had high sensitivity and fast response/recovery time based on the Cr$_2$O$_3$ hollow spheres powder was fabricated.

We use the resistance response method to investigate the sensor by the instrument Agilent B1500A Semiconductor Device Analyzer and special gas distribute system. The data showed that the resistance of sensor had close linear relationship to the gas concentration in a wide range from 50ppm to 250ppm at the optimum operating temperature 300$^{\circ}$C. Also, the result showed the gas sensor had fast response/recovery time and high sensitivity.
2. Experimental

2.1 Preparation of carbon microspheres
In a typical procedure, 9g Glucose Anhydrous was dissolved in a certain amount of deionized water to produce a resulting solution 50mL with the concentration of 1mol/L. Then the solution was transferred to a Teflon-lined autoclave and maintained at 180°C for 8h then cool it to room temperature. The purple brown products generated from the former process were then centrifuged and rinsed for at least 10 times with deionized water and ethanol to remove other organic impurities. Finally, a brown powder was generated from the cleaned solution after dried at 80°C for 12 h [10].

2.2 Preparation of Cr$_2$O$_3$ hollow spheres
For the preparation of the Cr$_2$O$_3$ hollow spheres powders, 0.5g of carbon microspheres obtained from 2.1 and 8g of Cr(NO$_3$)$_3.9$H$_2$O were dispersed in 40mL ethanol by ultra-sonication for 1h. After aged for 24h, the solution was rinsed with ethanol for 2 times and dried at 60°C for 12h. Next, the dried powder was calculated at 500°C for 2h in air with the temperature rising speed of 2°C/min. Now, the powders of Cr$_2$O$_3$ hollow spheres were obtained.

2.3 Characterizations
The prepared materials were characterized by transmission electron microscope (TEM: TF30, FEI USA). The element analysis was realized by EDX (TF30, FEI USA). The surface to volume ratio was investigated by N$_2$ adsorption-desorption.

2.4 Preparation of gas sensor
Sensors based on Cr$_2$O$_3$ hollow spheres were prepared as follows. First, 0.1g of the Cr$_2$O$_3$ hollow spheres was added into a mixed solution of Terminal and ethyl cellulose. After grinding for 1h and aged for 2h at room temperature, the resulted mixture was coated on an alumina substrate with eight pairs of gold interdigital electrodes. The width and clearance of the electrodes were 0.25mm. Then the resulted mixture with the interdigital electrodes was treated with two step annealing processes. First, they were heated to 60°C to remove the water, and then annealed at 500°C for 2h in air to remove the organic binders from the paste. Now, the Cr$_2$O$_3$ hollow spheres based sensor was fabricated. The sample need to be heated at 400°C in air for 1h before test. [11]

2.5 Gas sensing measurement
The gas sensing measurements were performed in a dynamic testing system, which has been reported in our former study [11]. A tubular oven was applied to achieve a precise working temperature for the sensor, and the concentration of target gas was controlled by four mass-flow controllers (MFC). An Agilent semiconductor analyzer (B1500A) was used to record and display the instantaneous variation of sensor resistance. Response of gas sensor (S) is defined: $S = \frac{R_g}{R_a}$, $R_a$ and $R_g$ are sensor resistance in air and target gas, respectively. The response time and recovery time were defined as the time to reach 70% of the total resistance change.

3. Results and discussions

3.1 Materials characterization
TEM was adopted to analyze micro topography of the Cr$_2$O$_3$ hollow spheres powder. The images were showed in Figure 1(a)-(b). The sample presents porous hollow spheres with rough surfaces and an average diameter distribution 10-20nm. HRTEM images of Cr$_2$O$_3$ were shown in Figure 1(c)-(d), which confirmed the high crystalline nature with a lattice spacing of 0.354nm and 0.267nm were corresponding to (012) and (110) of Cr$_2$O$_3$[12,13]. The formation mechanism of carbon nanoparticles and Cr$_2$O$_3$ hollow spheres were explained elsewhere[9]. As shown in Figure 1(e), We assume that the formation of the carbon spheres firstly involves the dehydration of the carbohydrate and carbonization
of the so-formed organic compounds, whose surface was hydrophilic and has a distribution of -OH and -C=O groups. In the step of 2.2, Cr\(^{3+}\) and its resulting nanoparticles were predominantly positioned near the hydrophilic shell of the carbon particles, which yields an increase in the diameter of the carbon spheres. After annealing, the carbon spheres were removed as carbon dioxide to the air, Cr\(^{3+}\) was oxidized and Cr\(_2\)O\(_3\) hollow spheres are obtained. The rough surface of the sample provides high surface to volume ratio and a great number of active sites for gas adsorption. All these morphology and microstructure results are approved this material will have a good gas sensing property. The EDX spectra of Cr\(_2\)O\(_3\) is shown in Figure 1(f), which indicates that the samples are composed of Cr and O elements, and further proves the impurity doping of Cr\(_2\)O\(_3\).

The inner porous architecture and the specific surface area of the Cr\(_2\)O\(_3\) porous microspheres are further characterized by nitrogen adsorption technique. Figure 2(a) shows the N\(_2\) adsorption/desorption isotherm curves and Figure 2(b) shows the corresponding BJH pore size distribution of Cr\(_2\)O\(_3\) hollow spheres. It could be seen from Figure 2(a) that the isotherms belong to a type-IV with a H3 type hysteresis loop (according to IUPAC classification) and exhibit no limited adsorption at high P/P\(_0\). As shown in Figure 2(b), the pore size distribution covered a range of 1–20 nm and showed a mesoporous structure. The sample showed a relatively high BET surface area of 49.0365 m\(^2\)/g, which indicated a kind of large textural porosity. And therefore, there might have some potential for the enhancement of gas sensing performances.

![Figure 1.](image)

Figure 1. (a)-(b) TEM images of Cr\(_2\)O\(_3\); (c)-(d) HRTEM image of Cr\(_2\)O\(_3\); (e) The formation model of the Cr\(_2\)O\(_3\) hollow spheres; (f) The EDX spectra of Cr\(_2\)O\(_3\)
3.2 Gas sensing properties

It is well-known that the response of gas sensors relies greatly on the working temperature. The response of the sensor on increasing concentration 50ppm to 250ppm of the C\textsubscript{2}H\textsubscript{5}OH vapor, was investigated to determine the optimum operating temperature and the response and recovery time. The test result and test condition were shown in Figure 3(a). When a certain concentration of the target gas flow into the tube, the resistance of sensor increased, which indicates typical p-type behavior [14]. The sensor response amplitude to C\textsubscript{2}H\textsubscript{5}OH remarkably increases with concentration. It can be seen from Figure 3(b) that the response of the sensor increases almost linearly with C\textsubscript{2}H\textsubscript{5}OH concentration within the range of 50-250ppm in each certain temperature. The sensor also showed best response to the C\textsubscript{2}H\textsubscript{5}OH at 300°C. The response and recovery time for the sensor to 50 ppm C\textsubscript{2}H\textsubscript{5}OH was found to be about 16s and 7s seen from Figure 3(c).

In order to comprehensively investigate the gas sensor performance to various gases at 300°C, 3 kinds of VOC gases, such as butyl-acetate, iso-propyl alcohol and methoxy-propanol, were employed to be the target gases. According to the experimental results that were showed in Figure 4(a)-(d), our prepared sensors showed improved properties to either C\textsubscript{2}H\textsubscript{5}OH or butyl-acetate, especially the latter. It could be seen that the relation between the response and the concentration of target gas was explicit linear. Compared with others, the response to iso-propyl was higher. This could explained by the reductive of the gases. Iso-propyl reacts more easily with the pre-adsorbed oxygen ions due to higher activity.
Figure 4. (a) Iso-propyl, (b) Methoxy-propanol, (c) Butyl-acetate test results at optimum operating temperature (300°C), (d) Compare of the response to different gas

3.3 Gas sensing mechanism
As we all know, the Cr$_2$O$_3$ is p-type metal oxide semiconductor. The gas sensing mechanism could be similar with that of other p-type metal oxide semiconductor, such as CuO. Gas molecules adsorbed on the surface of Cr$_2$O$_3$ particles have remarkable tuning effects on the electrical properties due to their high surface to volume ratio. The sensing property of Cr$_2$O$_3$ hollow spheres originates from the interaction between the target gases and the pre-adsorbed O$^-$ and O$_2^-$ on the Cr$_2$O$_3$ surfaces. When the Cr$_2$O$_3$ was exposed to the air, the charge exchange interactions between Cr$_2$O$_3$ and O$_2$ as following (1)-(4) did happen and generated the O$^-$ and/or O$_2^-$ on the surface of the Cr$_2$O$_3$. When such Cr$_2$O$_3$ is exposed to reductive molecules, taking ethanol as example, the adsorbed reductive molecules interact with the pre-adsorbed O$^-$ and O$_2^-$ as shown in (5)-(7). The reactions between the reductive molecules and the pre-adsorbed O or O$_2^-$ release free electrons and neutralize the holes (8), the majority carriers in p-type Cr$_2$O$_3$. This compensation results in a decrease in the holes in Cr$_2$O$_3$, and consequently, an increase in sensor resistance. Note that the oxygen molecules are continuously supplied from the dilute gas (synthetic air) and are adsorbed on the Cr$_2$O$_3$ surface while the interaction with reductive molecules to desorption from the surface, with the trend towards an equilibrium state. When the concentration of reductive target gas is decreased, more oxygen molecules in air will adsorb on the surface of Cr$_2$O$_3$, and the capture of electrons through the processes indicated in (1)-(4) will reduce the sensor resistance towards the initial stable surface state of Cr$_2$O$_3$.[15,16]

\[
\text{O}_2 (\text{gas}) \rightarrow \text{O}_2 (\text{adsorbed}) \quad (1) \\
\text{O}_2 (\text{adsorbed}) + e^- \rightarrow \text{O}_2^- (\text{adsorbed}) \quad (2) \\
\text{O}_2^- (\text{adsorbed}) + e^- \rightarrow 2\text{O} (\text{adsorbed}) \quad (3)
\]
\[ O^- (\text{Adsorbed}) + e^- \rightarrow O_2^- (\text{adsorbed}) \]  (4)

\[ C_2H_6O (\text{gas}) \rightarrow C_2H_6O (\text{adsorbed}) \]  (5)

\[ C_2H_6O (\text{adsorbed}) + 6O^- (\text{adsorbed}) \rightarrow 2CO_2 + 3H_2O + 6e^- \]  (6)

\[ C_2H_6O (\text{adsorbed}) + 6O^2^- (\text{adsorbed}) \rightarrow 2CO_2 + 3H_2O + 12e^- \]  (7)

\[ e^- + \text{hole} \rightarrow \text{NULL} \]  (8)

**Conclusions**

In summary, gas sensor based on template synthesis Cr₂O₃ hollow spheres have been successfully synthesized. A simple and practical test method for gas sensors with practical shelves is realized. 4 types of target gases were investigated. The optimum operating temperature was 300°C. The sensor have high sensitivity to reductive gases and great selectivity to the butyl-acetate. When reductive gases such as C₂H₅OH flow through the sensor, the resistance of sensor was increased. The sensitivity of the sensor was close linear correlated with the concentration of target gas. The response and recovery time was 16s and 7s.

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