Preparation and Gas Sensing Properties of SnO$_2$ Hollow Nanostructures

Junhai Wang, Xiutao Ge and Yuping Chen
Material Science Chemical Engineering School, Chuzhou University, Chuzhou 239000, China

Abstract. Gas sensor can be used to detect, monitor, analyze and alarm. It has very important application value in industry, national defense, food safety and medical examination. Among the gas sensors, the semiconductor resistance type gas sensor has many advantages, such as high sensitivity, fast response, small size, light weight, easy to carry, and so on. As one of the widely used gas sensing materials, SnO$_2$ has been a hot spot in the research and application in 60s, and it has been developing rapidly. SnO$_2$ is one of the most common gas sensitive materials, with physical and chemical properties of gas detection and stability; reversible adsorption and desorption time is short; low cost, energy saving and other advantages, is widely used in the detection of various gas sensitive devices. However, the disadvantages of high working temperature and poor selectivity of SnO$_2$ make it need to be further improved as gas sensitive material. The gas sensing mechanism of semiconductor gas sensitive material is mostly controlled by the surface, which is embodied in: increasing the specific surface area of the material and enhancing the gas sensing performance. At present, the main method of increasing the specific surface area of the material is nano scale. In this paper, the preparation and gas sensing properties of porous and hollow structure SnO$_2$ are mainly discussed on the basis of particle size. Porous structure facilitates the increase of the specific surface area of the material, providing a larger surface area and volume ratio for the material, which is of great benefit to the diffusion and transportation of the gas being measured. Nano hollow structure has a thin shell; the inner and outer surface provides a high surface area and volume ratio, so that the sensor has a faster response and recovery speed, and higher sensitivity. Using carbon micro spheres as hard templates, the structure of SnO$_2$ was successfully prepared by using different raw materials ratio and hydrothermal conditions. The composition and morphology of SnO$_2$ were characterized by XRD, SEM, TEM and so on. The study of gas sensitivity shows that the SnO$_2$ of the hollow classification structure can show good gas sensitivity, which has the advantages of high sensitivity, good selectivity and strong stability.

1. Introduction
With the rapid development of modern industry, such as chemical industry, automobile, medical treatment, petroleum and so on, human beings are in possession of great wealth, but also bear the serious environmental pollution. A large number of harmful toxic gases (such as carbon monoxide, nitrogen oxides, sulfur oxides, methane and so on) in human production and life, all the time, are not a threat to our health. Not only that, the pollution of the climate caused by the gas, for the safety of industrial and agricultural production has also planted hidden dangers. And with the improvement of living standards, the pursuit of the increase of material life makes the car as a convenient means of transport has developed rapidly. But in the car to bring people living facilities at the same time, because of drunk driving and traffic accidents caused by a serious threat to people's lives and property safety. The appearance of the above phenomenon, so that the gas detection equipment came into being.
Nowadays, the detection and analysis of gas is more time-consuming and expensive testing instruments, such as spectral analysis, chromatographic analysis, and so on. Gas sensor has many advantages, such as good selectivity, high sensitivity, fast response time, short recovery time, good stability and low cost, which is widely used. The use of gas sensor can accurately monitor the toxic and harmful gases, effectively prevent the occurrence of accidents, and protect the air environment [1]. The gas sensor is closely linked with our daily life, such as ethanol concentration detection, detection of pesticide residue, gas storage, flammable gas detection based on gas sensor are realized. With the research, development and application of the gas sensor, it has been widely concerned by people and put forward a great challenge to the scientific research personnel. Gas sensor is an important branch of the sensor, the mechanism is to use a variety of physical effects, chemical reactions, and the measured gas needs to be detected in the extraction of parameters. The gas sensing principle of typical representative metal oxide semiconductor is based on the change of the conductivity of semiconductor gas sensing material with the change of ambient atmosphere. So far, a lot of semiconductor metal oxides, such as iron oxide, Zinc Oxide, copper oxide and cerium oxide and so have been used as gas sensing materials. SnO$_2$ as the most sensitive material widely, with physical and chemical properties of stability, gas detection, reversible adsorption and desorption time is short, low cost, energy saving and other advantages, has long been favored by researchers. SnO$_2$ is a kind of important wide band gap n type semiconductor material, which contains oxygen vacancy or tin gap ion. The gas sensing effect is obvious. It is generally believed that the gas sensing mechanism is the control mechanism of surface adsorption. Because SnO$_2$ has a special crystal structure that is structural defects, high surface activity, large surface area and adsorption characteristics, so that their gas sensing performance compared with the traditional sensor showed a unique performance[2].

2. Experimental test methods
Scanning electron microscopy was used to observe and analyze the microstructure of the surface of the material. The block or powder particles are bonded to the conductive adhesive, and no conductive samples need to be sprayed with carbon or gold. The prepared samples were put on the test bench for observation. Observation of high magnification and high resolution by scanning electron microscope. Scanning electron microscopy is formed by electron beam through electronic grid scanning at the surface of the sample, the aggregation of electron beam and sample produced by the interaction of the two electron emission quantity with the specimen surface changes, two electronic signals are converted into electrical signals after being input to the kinescope grid, finally reflect the specimen surface the two electron image. Differential thermal analysis (DTA) is a thermal analysis method to determine the physical and chemical properties of the material by measuring the temperature difference between the sample and the reference. The sample in the heating occurs in the process of solidification, melting, decomposition, synthesis, crystal transformation, desorption, adsorption and other physical or chemical changes caused by variations in enthalpy, thermal effect, the temperature difference between the environment and the system. The heat weight method (TG) is based on the material in the process of heating, chemical changes will occur, which will be accompanied by changes in temperature. The change process can be studied by measuring the change of material quality. Transmission electron microscopy observation is often used to hollow structure material, its working principle: when the electron beam and the thin specimen interaction will inspire and sample can be used for imaging of electron beam scattering and transmission electron beam. The transmission electron beam through a lens focused like called bright field scattering, electron beam through lens focusing the image called dark field image. After the multi stage amplification, the image to be observed is presented on the screen. The principle of semiconductor gas sensor is based on the chemical reaction between adsorbed gas molecules and sensitive material. For the N type semiconductor, such as the SnO$_2$, the resistivity change mechanism and process: when the different morphologies of SnO$_2$ gas sensitive material preparation components when exposed to air, the molecular surface redox reactions occur with air, the oxygen molecules in the air conduction band won the gas sensitive materials in the form of electronic chemical adsorption oxygen (such as O$_2$-, O- and O$_2$-), which can reduce the carrier -SnO2 the number of electrons, the electron mobility is reduced, caused by decreased SnO2 conductivity. This system uses the voltage and current test method, the
basic test principle is shown in figure 1. The characteristic of the gas sensor is reflected by the voltage on the load resistance R1 which is connected in series with the gas sensing element. The circuit will be a known resistance load resistance R1 and gas sensor series access total voltage is 5V, is to change the relationship between voltages of gas sensor with time by measuring the load voltage Vout resistance under different conditions. When the heating wire is provided with the working temperature of the gas sensor, the different working temperature can be obtained by adjusting the different heating voltage[3].

![Figure 1. Schematic diagram of experimental device](image)

3. Copyright form

3.1. Preparation of porous structure by FA-template method SnO$_2$

The high porosity and high specific surface area of porous micro / nano materials show the superior physical and chemical properties compared with the bulk structure of the corresponding materials. These properties play an important role in photo catalysis, gas sensitivity, solar cells, lithium ion batteries and drug transport. Therefore, the development of the preparation of porous structure is a hot research topic in recent years. The preparation of porous materials by direct introduction of structural additives and the preparation of porous materials have been successfully achieved. Such as latex spheres, oxalic acid erosion, emulsion, block copolymers, surfactants, and so on, have played an important role in the process of preparing porous structures through crystallization and precipitation. Furfuryl alcohol (FA) as a chemical material, wide source. Research shows that in the acid (as Lewis acid) under the action of furfuryl alcohol can be catalyzing the formation of furfural resin (FAR). Heating in the air, the FAR will have a continuous reaction of polymerization carbonization combustion. Many metal cations can play a role in the Lewis acid, according to this principle, can the design and synthesis of the three-dimensional porous structure of metal oxide by furfural method. In this study, we used SnCl$_2$·2H$_2$O as the Lewis acid to catalyze FA to get a mixture of SnO$_2$-FAR, and then the porous structure was synthesized by combustion reaction control SnO$_2$. This preparation scheme, both as fuel and furfuryl alcohol conversion template. The preparation of porous structure has the advantages of furfuryl alcohol is easy to get raw materials, low cost and simple method, can be synthesized with high specific surface area and porosity of the porous material. Thermal analysis of porous structure SnO$_2$ by FA-template method is illustrated in Figure 2.

![Figure 2. Thermal analysis of porous structure SnO$_2$ by FA-template method](image)
3.2. Preparation of porous structure SnO$_2$ nano cubic block by phase separation method
Phase separation refers to the two kinds of incompatible oxide phase (the main frame material and the hole forming body) after mixing calcined into dense matter, then one of the constituents of selective eroded by chemical method or evaporation, thus leaving the equivalent gap in the main frame material. The porous metal oxides prepared by this method are MnO, TiO$_2$, TiN, ZrO$_2$ and so on. The phase separation method is proved to be an effective method to control the porous structure. In this paper, we use a simple wet chemical method, and prepared by poly - precipitation nano cubic precursor of CoSn (OH)$_6$ (CHS), and then calcining the mixture of Co$_3$O$_4$ and SnO$_2$, and finally get the pure porous structure of SnO$_2$ in pickling conditions. The whole reaction is the process of decomposition, aggregation and dissolution. For the selection of the best operating temperature of the test, we selected the measurement temperature range of 260-400. The sensitivity curve is drawn as shown in Figure 3. From the graph we can see that, with the increase of temperature, the sensitivity of the porous structure SnO$_2$ gas sensitive material to 200 ppm ethanol is gradually increased, and the sensitivity reaches the maximum value of 105 when the temperature reaches 300. In 300 C, with the increase of temperature sensitivity decreased linearly, so we selected 300 DEG C for optimum temperature response of gas sensors to ethanol gas, the temperature will also serve as a back test of different concentrations, different gas temperature[4].

3.3. Advantages of self-template method
Since the template method is by chemical erosion, Ostwald aging, Kirkendall effect mechanism will continue to consume the precursor template internal reaction, direct the formation of hollow structure. In this process, the precursor template is both a reactant and a product, without additional removal of the template. Hollow structure has been developed so far, the hollow particles prepared by the simple method are spherical and polycrystalline structure, because the non-spherical template is difficult to obtain, so people are still working hard to prepare non spherical single crystal particles. Wang et al have been using the self-template method to get the polyhedron Cu$_2$O hollow lattice by using the single crystal Cu$_2$O template. Preparation of non-spherical SnO$_2$ is very difficult, it is necessary to synthesize the non-spherical precursor under the aid of other metal elements, and then the introduction of the metal phase chemical erosion, the pure phase of non-spherical porous SnO$_2$. Due to the particle surface with free surface of high energy, so the reaction activity and reaction rate at the top corner of the large, so large vertex curvature is first dissolved, whole. Once a hole is formed, the OH- passes through the hole to penetrate into the inside of the cube. As the cube ZHS external than internal stability, so continue to carry out the decomposition reaction inside. Eventually, with the continuous generation and release of Zn (OH) 42- and 62- (Sn) OH, the formation of cubic hollow ZHS. The formation of the hollow structure can be understood: the central part of the interior cube, is in the raw material concentration and unbalanced conditions through the rapid precipitation polymerization reaction to form, as a result of the growth is relatively fast, so the structure is not stable, is in a metastable state.

4. Experimental result analysis
Through the electron microscope, it can be observed that there are a large number of solid fourteen surface ZHS generation, fourteen ZHS particles of uniform size, complete structure, smooth surface and no defects. The dispersion of particles is not very good, is often a few particles together to grow. The cause of this phenomenon may be caused by uneven stirring during the preparation process. Fourteen surface body structure size in 0.8-1 m or so. Can generate fourteen surface morphology because, with the existence of excess OH-, increase of OH- adsorption on a surface, inhibiting crystal growth on the surface of the shaft in the vertical direction, so that the surface area increases, the surface morphology is formed of fourteen polyhedron. After the erosion of the ZHS precursor and the erosion of the same, still maintained a fourteen surface appearance, and the internal ZHS has been reacted with an excess of OH-, the formation of a hollow structure. Scanning electron microscope photographs of the broken fourteen surface can clearly see the shell structure of the hollow spherical shell, the thickness of the shell layer is about 10 nm, the thickness is uniform, the surface is smooth, and the hollow diameter is around nm 400-600. Taking ZHS as precursor, the cubic and polyhedron morphology of solid and hollow structure were successfully prepared by self-template method. The results of XRD test showed that the solid and hollow structures were pure phase ZHS. The results of scanning electron microscope can be analyzed, and the solid and hollow cubic shape diameter is about nm 150-200, and the wall thickness of the hollow cube is about 40 nm. The diameter of solid and hollow fourteen surface is about 0.8-1 m, and the wall thickness of the hollow fourteen surface is about 10 nm, and the diameter is about nm 400-600. NaOH plays an important role in the process from cube to polyhedron and from solid to hollow. However, after the calcination and pickling, the morphology is badly damaged, and it is very different from the expected results[5].

5. Conclusion
In this paper, the SnO₂ hollow microspheres with hierarchical structure were prepared by hydrothermal method, and the SnO₂ hollow structure of Au was obtained by a simple thermal decomposition process. To study the effects of hydrothermal time on the size and morphology of SnO₂ microspheres, the formation mechanism of the hierarchical structure of SnO₂ hollow microspheres may product are discussed; in the preparation of hollow microspheres and solid SnO₂ microspheres for comparison, study its sensitivity to ethanol gas; from the hollow cubic ZHS particles prepared by template the well dispersed, the particle diameter of about nm in 150-200, wall thickness of about 40 nm. Fourteen surface morphology of hollow 0.8-1 m in diameter m, wall thickness of about 10 nm in diameter, hollow nm left 400-600 But did not generate the expected porous SnO₂. The yield of the hollow cubic CHS prepared by the self-template method is large, and the diameter of the particles is about 100 nm. But did not generate the expected porous SnO₂.

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7. References
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