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Studies on Principle, Expression and Characteristics of Gas Sensing Response of WO_3 Prepared by Hydrothermal Method*

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Abstract: WO_3 has gained considerable interest recently as a promising material for a variety of applications, especially in gas sensor field. This article provides a review of the principle and expression of gas sensing response as well as the current experimental efforts on the hydrothermal synthesis and gas sensing characteristics of WO_3. The morphologies and structures of WO_3 determine the gas sensing characteristics to a large extent. Because the increase of active surface area or surface-to-volume ratio would enhance the properties for detecting gases, small sizes of grains need to be decreased. Among the numerous preparation methods, hydrothermal synthesis is easily used to grow various desired morphologies and structures with small sizes. Adding some assisting agents helps to tune the size, surface morphology, shape and crystalline structure of WO_3 in the hydrothermal process. Most of work on gas detection has been devoted to the improvement of sensitivity, detecting low concentration target gas and the increase of gas types. In fact, well advancements have been gained in these aspects by optimizing the grow method, dopant, electrode and so on. However, these WO_3-based gas sensor just usually performed well above 150 ℃. Therefore, this paper also points out some trends for future investigation. Seeking new dopant material, controlling the preparation conditions accurately and making use of the very assisting agents to optimize the gas sensing characteristics of WO_3 are the widely approaches. Additionally, change the manner to detect the gases, such as recording the change of optical properties of WO_3-based sensor instead of the electrical properties.

Key words: WO_3; gas sensing characteristics; hydrothermal method
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Tungsten trioxide (WO_3), a transition metal oxide, is an important wide band gap (2.5 ~ 3.5 eV) n-type semiconductor material[1]. Nowadays, WO_3 has been widely applied in various fields such as gas sensors[2-6], electro-chromic devices[7], catalysts[8], photolysis[9], photo-electrochemical cells[10], memory devices[11], biosensor[12] and so on. In fact, gas sensors play an extremely important role in our daily life. The WO_3-based sensor can be used to monitor oxidizing inorganic gases (NO_2, O_3 and SO_2 etc.), reducing inorganic gases (H_2S, H_2, NO, CO and NH_3 etc.) and organic vapors (acetone, ethanol etc.). However, the gas sensing properties are mainly decided by its own material characteristics (size, surface morphology, shape and crystalline structure etc.), which strongly depend on the different growth methods. To date, many techniques, such as hydrothermal synthesis[13-16], thermal evaporation[17], electron-beam deposition[18], sol-gel route[19], pulsed laser deposition[20], reactive magnetron sputter-deposition[21], dip coating-pyrolysis method[22] and electro-spinning method[23] have been developed and used to grow WO_3. Among these methods, hydrothermal method is one of the important techniques used to fabricate different WO_3 structures because of its low cost, simple deposition equipment and operation manner[15].

This paper introduced the principle and expression of

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gas sensing response and summarized the latest progress on hydrothermal synthesis and gas sensing characteristics of WO_3.

1 Principle and expression of gas sensing response

The WO_3-based gas sensors operate on the principle that the sensor's resistance or conductivity changes in the presence of target gases[24]. When the gas sensing devices exposure under target gases, the gas molecules are adsorbed on the surface of WO_3 and electron transfer occurs between WO_3 and the adsorbent. As a result, a depletion or accumulation of charges occurs on the surface. Following that variation of surface potential barrier induces a change in the resistivity or conductivity[24-25]. Thus, this change suggests that WO_3 produces response to the target gases.

It is common to evaluate gas sensing characteristics by the parameters like sensitivity, response time, recover time, gas concentration and working temperature. The ideal sensor materials should be of high sensitivity to target gases, short response and recover time, low gas concentration and working temperature. The sensitivity (S) could be defined as the ratio between the respective variation of resistance in the air (ΔR_{air}) and in the target gases (ΔR_{gas}) according to

$$S = \Delta R_{air} / \Delta R_{gas}$$

ΔR represents the difference between the maximum and minimum values of the resistance during one complete period of aerating cycling[26]. However, we prefer to express the sensitivity with a more simple calculation route like this

$$S = R_{gas} / R_{air}$$
$$\text{or } S = R_{air} / R_{gas}$$

R_{air} and R_{gas} are the resistance of sensor in dry air and target gases, respectively. Usually, in oxidizing atmosphere, the oxide surface is covered by negatively charged oxygen adsorbate and the adjacent space charge region is electron-depleted: the oxide layer presents therefore a high resistance ($R_{gas} > R_{air}$). Under reducing conditions, the oxygen adsorbate is removed by the reaction with reducing gas species and the electrons are re-injected into the space charge layers: as a result, the oxide layer resistance decreases ($R_{gas} < R_{air}$)[27-28]. Besides, the voltage change of oxide may be used to illuminate the gas sensitivity at times[4]. Therefore, the change of resistance, conductivity or voltage could be used as the parameters to scale the sensitivity.

In addition, the response time is often defined as the time required for the conductance to reach 90% of the equilibrium value after the test gas is injected and the recovery time is the time necessary for the sensor to attain a conductance 10% above the original value in air[4].

2 Gas sensing characteristics of WO_3 prepared by hydrothermal method

2.1 Hydrothermal synthesis of WO_3

The adsorption of gases basically occurs at the surface level of sensing materials, and an increase in the active surface area of the semiconductor oxide would enhance the properties of the materials used for gas sensors[29]. Therefore, surface morphology of WO_3 influences the gas sensitivity in a great degree. It has been verified that, in the hydrothermal process, the morphology of the WO_3 can be tuned by some assisting agents such as surfactant, inorganic salt, complex agent and some dissoluble organic acid[15]. Upon this, various structural WO_3 prepared by hydrothermal methods with different synthesis procedures have been listed in Tab. 1 Obviously, the tungstate is widely used as tungsten sources. Tungsten trioxide can be produced by different chemical reactions. The addition of assistant reagents affects the structural morphologies and grain sizes of WO_3. Most final products are nanostructures and possess higher surface-to-volume ratio so that the sensor signal caused by the reaction with the target gas is stronger than the larger scale ones. Therefore, adopting hydrothermal method for the synthesis of WO_3 is conducive to improve the gas sensing characteristics of WO_3.

Fig. 1 shows somescanning electron microscopy images of WO_3 with different magnification. The every morphology looks so clearly and cleanly without other shapes. In addition, the synthesized WO_3 exhibits uniform size and morphology. Once the WO_3 is widely applied in the gas sensor filed, the hydrothermal method will be used for a mass synthesis of WO_3.

Tab. 1 The different syntheses and structures of WO_3 based on hydrothermal methods

Ref.	Tungsten Sources	Assisting Agents	Morphologies of WO_3	Comments