Effects of sintering temperature on sensing properties of WO₃ and Ag-WO₃ electrode for NO₂ sensor

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Pure WO₃ and Ag-WO₃ (mixed solid solutions Ag with WO₃) have been successfully synthesized by sol-gel method and the influences of calcination temperature on the particle size, morphology of the WO₃ and Ag-WO₃ nanoparticles were investigated. Powder X-ray diffraction results show that the hexagonal to monoclinic phase transition occurs at calcination temperature varying from 300°C to 500°C. SEM images show that calcination temperature plays an important role in controlling the particle size and morphology of the as-prepared WO₃ and Ag-WO₃ nanoparticles. The NO₂ gas sensing properties of the sensors based on WO₃ and Ag-WO₃ nanoparticles calcined at different temperatures were investigated and the experimental results exhibit that the gas sensing properties of the Ag-WO₃ sensors were superior to those of the pure WO₃. Especially, the sensor based on Ag-WO₃ calcined at 500°C possessed larger response, better selectivity, faster response/recovery and better longer-term stability to NO₂ than the others at relatively low operating temperature (150°C).

1. Introduction

Metal oxides have been very important materials in catalysis, gas sensors and energy conversions [1]. Tungsten trioxide (WO₃), a typical n-type semiconductor material with a band gap of
2.5–2.8 eV, has received much interest for applications including photocatalysis [2–5], electrochromic devices [6–8], solar energy conversion [9] and gas sensors [10], due to excellent catalytic, optical and dielectric properties, good physical and chemical stability. For gas sensing applications, WO₃ has attracted great attention for its distinctive sensing properties, and has been regarded as a promising material for detecting various gases, including CO [11], H₂ [12–13], SO₂ [14], NOₓ [15–19], H₂S [20] and organic vapours [21]. In addition, tungsten trioxide (WO₃) has been considered as a promising sensing material of solid-state semiconductor gas sensors for NO₂ monitoring because of its excellent sensitivity and selectivity. WO₃ nanoparticles can be fabricated by various techniques such as chemical vapour deposition [22], hydrothermal method [23–26], microwave irradiation method [27] and sol-gel process [28]. Sol-gel technique is the most common method of fabricating WO₃ nanoparticles because of the advantages of simple, quick process and easy control of particle size, crystal structure and morphology. In recent years, many attempts have been made to enhance the gas sensitivity of semiconductor gas sensors [29], one of which involved the doping of noble metal in the materials. It has been shown that the sensing performance of WO₃ can be substantially improved by loading particular elements [30–33]. Wang et al. [34] have shown that a high sensitivity was achieved when noble metals such as Pt, Au and Pd were deposited as activator layers on WO₃ films. Najim et al. [35] have mixed SnO₂ with WO₃ and prepared to synthesize nanostructured thin films by pulsed laser deposition as gas sensor. The sensors showed high sensitivity. However, there is still room for improvement in stability, selectivity and working temperature of the gas sensors [36].

In this work, WO₃ nanoparticles and Ag-WO₃ were prepared by a simple sol-gel method. The influences of calcination temperature on the particle size, morphology of the WO₃ and Ag-WO₃ nanoparticles were extensively investigated and NO₂ gas sensing properties of WO₃ and Ag-WO₃ nanoparticles were discussed.

2. Material and methods

2.1. Preparation and characterization

The WO₃ and Ag-WO₃ nanoparticles were prepared by sol-gel method. All of the chemical reagents were of analytical grade and used as received without further purification. In a typical synthesis, 3.5 g tungsten (W) powder was dissolved into 200 ml of deionized water under constant stirring for 30 min. Then, 100 ml of hydrogen peroxide (H₂O₂) were added into the above solution and stirred for 20 min. A homogeneous WO₃ precursor solution was produced by slowly dropping 30 ml of alcohol and stirred in the thermostatic water bath at 80°C until an opaque gel was formed. Ag-WO₃ precursor solution was also fabricated by dropping 4 ml of 0.1 mol l⁻¹ AgNO₃ aqueous solution into the WO₃ precursor solution. The pH value of the solution was fixed at 4.5 which was adjusted by using nitric acid (HNO₃) solution in the reaction process. After that, the transparent gel was transferred into a crucible and baked at 80°C for 12 h. Finally, the obtained products were calcined at 300°C, 500°C and 700°C for 2 h. A series of pure WO₃ and Ag-WO₃ powders were obtained.

2.2. Fabrication and measurement of gas sensor

The products’ crystallographic structures information were observed with small angle X-ray diffraction in Shimadzu diffractometer (XRD-6000, Japan) using Cu Ka line radiation at 40 kV and 40 mA. The XRD patterns were collected at 2 angles of 10–80° at a scan rate of 1° min⁻¹. A field emission scanning electron microscope (FESEM, JSM-6700F, Japan) was used to measure the particle size and morphology of WO₃ nanoparticles. Brunauer–Emmett–Teller (BET) method was used to determine the pore size distributions and surface areas. The gas sensing property of Ag-WO₃ nanoparticle film was measured by semiconductor characterization system (Keithley, 4200-SCS) with interdigital electrode structures. The concentration of Ag and W were measured by inductively coupled plasma–atomic emission spectroscopy (ICP-AES, Vista).

Side-heating gas sensors were built to measure the gas sensing properties of WO₃ and Ag-WO₃-based nanoparticles. Figure 1a shows the structure of thick film sensor, a commercial Si substrate with dimensions of 15 × 9 × 0.76 mm, and built-in Ag electrodes at 0.5 mm intervals. The WO₃ and Ag-WO₃ nanoparticles paste were coated in a 35 µm thickness via the screen-printing method and then sintered at 300°C for 15 days in air, in order to improve their stability and repeatability. The measuring electric circuit of gas sensing properties is shown in figure 1b. The operating voltage (Vheat)
was supplied to heat the sensor with a Ni-Cr heater, which can control the operating temperature from 100 to 500°C, and a test voltage ($V_{\text{test}}$) was supplied across. A load resistor $R_L$ was connected in series with the sensor, that resistance was measured and used for calculating and outputting the corresponding sensor resistance.

A sensor performance testing apparatus is shown in figure 2. The sensor was installed at a distance of 70 mm from the bottom of a 20 l (500 × 200 × 200 mm) chamber. The sensing electrodes were connected to the test circuit by copper probes. After the target gas was injected into the chamber with the fan on, the resistance was measured with an electrometer after the equilibrium concentration was reached. The sensitivity ($S$) of the sensing electrodes was defined as: $S = R_a/R_g$ for reducing gases or $S = R_g/R_a$ for oxidizing gases, where $R_a$ and $R_g$ represent the resistances of the sensing electrodes in air and in a target gas, respectively. Furthermore, the response and recovery times were defined as the times at which a total resistance change of 90% was achieved.

Figure 1. (a) Structure of thick film sensor and (b) measuring electric circuit of gas sensing properties.

Figure 2. Apparatus used for gas sensing experiments.
3. Results and discussion

3.1. X-ray diffraction

Figure 3 shows X-ray diffraction (XRD) patterns of (a) pure WO₃ and (b) Ag-WO₃ nanoparticle heated at 300°C, 500°C and 700°C for 2 h. As shown in figure 3a, the observed peaks at 300°C could be well matched to the pure hexagonal phase of WO₃, and agree well with the values in the standard card (JCPDS 33–1387). The main characteristic diffraction peaks at 500°C and 700°C correspond to the (002), (020), (200) and (202) planes at 2θ = 23.12°, 23.59°, 24.38° and 34.16°, respectively. These peaks match perfectly with the monoclinic structure of WO₃ according to the JCPDS file card (JCPDS 43-1035). Furthermore, the width of the peak at 700°C is sharper than that at 500°C. It indicates that the crystallite size of 700°C increases with temperature. No peaks of impurities can be found in XRD patterns of pure WO₃, illustrating the as-prepared samples were of high purity. The XRD patterns of Ag-WO₃ nanoparticles at different calcination temperatures are reported in figure 3b. All peaks are well matched with the diffraction lines documented for the hexagonal tungsten oxide (JCPDS 33-1387), monoclinic tungsten oxide (JCPDS 43-1035) and cubic Ag (JCPDS 04-0783). The diffraction peaks of Ag (111), (200), (220) and (311) at 38.1°, 44.0°, 64.5° and 77.5° can be observed obviously.

The effect of the calcination temperature and mixing Ag on the crystallite dimensions of WO₃ was also detected by XRD. The average crystal size of WO₃ was estimated by using the Scherrer equation:

$$D = \frac{\kappa \lambda}{\beta \cos \theta},$$

where $D$ is the crystalline size, $\kappa$ is the so-called shape factor and usually taken as 0.89, $\lambda$ and $\theta$ are the radiation wavelength (0.154056 nm) and Bragg’s angle, respectively, $\beta$ is the full width at half maximum (FWHM) of the diffraction peak. The average grain sizes of pure WO₃ and Ag-WO₃ particles at different calcination temperatures are reported in figure 3b. All peaks are well matched with the diffraction lines documented for the hexagonal tungsten oxide (JCPDS 33-1387), monoclinic tungsten oxide (JCPDS 43-1035) and cubic Ag (JCPDS 04-0783). The diffraction peaks of Ag (111), (200), (220) and (311) at 38.1°, 44.0°, 64.5° and 77.5° can be observed obviously. The effect of the calcination temperature and mixing Ag on the crystallite dimensions of WO₃ was also detected by XRD. The average crystal size of WO₃ was estimated by using the Scherrer equation:

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3.2. Field emission scanning electron microscopy

Figure 4 shows the SEM micrographs of pure WO₃ (a–c) and Ag-WO₃ (d–f) nanoparticles samples heated at 300°C, 500°C and 700°C, respectively. As illustrated in figure 4a–c the irregular mixture of sliced or granular structure at 300°C and 500°C, and mainly spherical particles of diameter 50–800 nm with irregular fringe are observed. When the calcination temperature increases to 700°C as shown in figure 4c, the powder presents three-dimensional (3D) irregular microspheres and some of them are interconnected with each other. Furthermore, larger size particles appear and tend to be of irregular
shape with straight edges, which can be attributed to the thermally promoted crystallite growth. Figure 4d–f shows the SEM images of Ag-WO₃ at different calcination temperatures. The images of the Ag-WO₃ powder calcined at 300°C is shown in figure 4d. Ag-WO₃ particles tend to form large agglomerates due to physical attraction between the particles with small sizes and irregular shapes. As the temperatures raise to 500°C, figure 4e, the particles showed good homogeneity and discreteness. Figure 4f shows the irregular mixture of sliced or granular structure with significant agglomeration at 700°C. The experiment results indicate that Ag-WO₃ of the sol-gel system for the fabrication of uniform nanoparticles of hexagonal and monoclinic WO₃ from condensed WO₃ gel is a key factor for controlling the final particle size and shape of the product.

Nitrogen gas sorption analyses were carried out to study the porosity of the composites. Figure 5a shows nitrogen adsorption–desorption isotherms and figure 5b pore diameter distribution curves of WO₃ and Ag-WO₃ calcined at 500°C. More details about nitrogen adsorption–desorption isotherms and pore diameter distribution curves can be found in the electronic supplementary material.

3.3. Gas sensing characteristics

Both of the nitrogen adsorption–desorption isotherms are type IV curves, characteristic of mesoporous materials [38,39]. The average values of the specific surface area and pore sizes calculated by the Barrett–Joyner–Halenda (BJH) method are illustrated in table 1. The specific surface area of the pure WO₃
powders decreased sharply with the increasing sintering temperature more than 500°C due to the grain sintering, phase transformation and growing up. The pore size of Ag-WO₃ is larger than the diameter of WO₃. The surface area increases slightly by mixing Ag at the same temperature, which may be due to the incorporation of Ag attached to the WO₃ framework affects the integrity and mesostructure [40]. Furthermore, the biggest specific surface area and pore size can be obtained with Ag-WO₃ calcined at 500°C.

The gas sensing properties of WO₃ and Ag-WO₃ at different calcination temperatures to 10 ppm NO₂ were measured at various operating temperatures, as shown in figure 6a. It is obvious that the response of these sensors to 10 ppm NO₂ varies with not only the operating temperature but also mixing Ag. It can be seen that all the sensitivity change shows a sharp upward trend at first and decreased rapidly with an increase in operating temperature. For all the Ag-WO₃ sensors, there is a maximum value at 150°C, while

![Figure 6. (a) Gas sensing response of the sensors based on pure WO₃ and Ag-WO₃ at different calcined temperatures to 10 ppm NO₂. (b,c) Responses of pure WO₃ and Ag-WO₃ sensors to different concentration NO₂ at 150°C.](image)

**Table 1. Physical properties of the WO₃ and Ag-WO₃ calcined at different temperatures.**

| sintering temperature (°C) | BET specific surface area (m² g⁻¹) | pore size (nm) |
|----------------------------|-----------------------------------|---------------|
| 300°C (pure WO₃)           | 5.4                               | 10.5          |
| 500°C (pure WO₃)           | 4.7                               | 9.7           |
| 700°C (pure WO₃)           | 4.4                               | 7.6           |
| 300°C (Ag-WO₃)             | 5.9                               | 24.7          |
| 500°C (Ag-WO₃)             | 6.7                               | 32.6          |
| 700°C (Ag-WO₃)             | 4.8                               | 14.5          |
all the pure WO3 sensors have the maximum gas response at 200°C. The operating working temperature of all the Ag-WO3 sensors is lower than pure WO3 sensors. In addition, the sensitivity of Ag-WO3 sensors exhibits much higher response than the pure WO3 sensors, compared with previous reports about NO2 sensors [41–43]. Especially, the Ag-WO3 sensor calcined at 500°C presents the largest response to NO2 at 150°C, which indicates that the sensitivities of the WO3 sensors are much enhanced by mixing Ag. Responses of pure WO3 and Ag-WO3 sensors calcined at different temperatures to different concentrations of NO2 (0.25–20 ppm) were measured at the same operating temperature (150°C) and are shown in figure 6b. All the responses have the same trend that they increased with the increase in the concentration of NO2. Furthermore, the gas response of all the Ag-WO3 sensors is higher than that of the pure WO3 sensors at the same condition. It can also be observed that Ag-WO3 calcined at 500°C exhibits the highest gas response, which may be due to the good crystallization and biggest specific surface area. The response of all sensors has the biggest increasing rate in the range of 5–10 ppm NO2, which indicated that the sensors have an excellent performance in monitoring NO2 gas, especially in low concentrations.

To highlight the highest performance of Ag-WO3 calcined at 500°C, Ag and WO3 components were separately synthesized by the sol-gel method and calcined at 500°C and then a control sample of the physical mixture of Ag and WO3 was tested for sensing NO2. Ag particles can be prepared by sol-gel method through Si(OC2H5)4, AgNO3 and HNO3 [44]. Two grams of silver particles was fully mixed with 200 g WO3 and its sensor performance is shown in figure 7. Physical mixture of Ag and WO3 has the same performance as Ag-WO3 and its operating working temperature is lower than pure WO3 sensors.

It is well known that semiconductor gas sensors are surely affected by the presence of ambient moisture [45]. When chemisorbed on material, water molecules influence the conductivity. The effect of humidity on semiconductor sensor is also related to the temperature and gas composition of the sensor. So all the experiments were measured in the same presence of ambient moisture.
The gas sensing mechanism of n-type semiconductor oxide is based on the change in resistance, which is primarily caused by the chemical adsorption and reaction of the gas on the surface of the sensing materials. When WO₃ is exposed in the atmosphere, oxygen molecules are adsorbed on the surface, and changed into chemisorbed oxygen species (O²⁻, O⁻) by capturing free electrons from conduction band. Presence of these oxygen species is decided by the operating temperature.

The oxygen ions predominantly exist in the form of O²⁻ below 100°C, O⁻ between 100 and 300°C. Above 300°C the O²⁻ are produced and get directly incorporated into the lattice. When the operating temperature of the material is 150°C, as represented in equations (3.1)–(3.3).

\[
\begin{align*}
\text{O}_2(\text{gas}) & \rightarrow \text{O}_2(\text{ads}), \\
\text{O}_2(\text{ads}) + e^- & \rightarrow \text{O}_2^-(\text{ads}) \\
\text{O}_2^- + e^- & \rightarrow 2\text{O}^-. 
\end{align*}
\]

Depletion region is formed on the surface of WO₃, leading to a decrease of carrier concentration and electron mobility [46]. Exposure to NO₂ gas results in a further decrease of the carrier concentration, for the electrons of WO₃ are captured [47], as represented in equations (3.4)–(3.6), and the depletion width further increases, which eventually decreases the conductivity of the sensor. When the Ag-WO₃ are exposed to NO₂, NO₂ as a polar molecule with positive charge localizes on the nitrogen

\[
\begin{align*}
\text{NO}_2(\text{gas}) + e^- & \leftrightarrow \text{NO}_2^-(\text{ads}), \\
\text{NO}_2(\text{gas}) + e^- & \leftrightarrow \text{NO}(\text{gas}) + \text{O}^- (\text{ads}) \\
\text{NO}_2(\text{gas}) + \text{O}_2(\text{ads}) + 2e^- & \rightarrow \text{NO}_2^-(\text{ads}) + 2\text{O}^-(\text{ads}).
\end{align*}
\]

and negative charge on the oxygen atoms, and electron interaction with the Ag will repel the negatively charged oxygen and attract the positively charged nitrogen [48]. The sensing properties of Ag-WO₃ materials are enhanced compared with pure WO₃ material due to the catalytic activity of Ag nanoparticles. The Ag additive serving as an active catalyst plays an important role in enhancing sensitivity, which can create more active sites [49]. Furthermore, the underneath areas of Ag particles will be less depleted by the electron flow from Ag to WO₃, for the work function of Ag (4.26 eV) is smaller than that of WO₃ (5.05 eV) [50].

As is known to all, response and recovery characteristics are important for estimating the performance of a sensor. The resistance changes of Ag-WO₃ powder calcined at 500°C were repeatable for three successive measures in 250 ppb NO₂. The response and recovery times in a single cycle were about 47 s and 103 s, respectively, as shown in figure 8a. Figure 8b shows relative responses of pure WO₃ and Ag-WO₃ power sensors calcined at 500°C on exposure to different gases (ethanol, CO, H₂, and NH₃ at 1000 ppm and NO₂ at 10 ppm) at 150°C. The responses of the two sensors exhibited a high performance of NO₂, while they are a little sensitive to four gases. Moreover, compared to the pure WO₃ sensor, the Ag-WO₃ sensor exhibited higher responses to all the testing gas, especially to NO₂. As a result, the Ag-WO₃ sensor can be a very promising sensor to monitor NO₂ at relatively low

![Figure 8. (a) Response and recovery characteristic of Ag-WO₃ sensor calcined at 500°C to 250 ppb NO₂ while cycling NO₂ gas in and out of the measurement environment three times at 150°C. (b) Responses of pure WO₃ and Ag-WO₃ sensor calcined at 500°C to various gases at 150°C (ethanol, CO, H₂ and NH₃ at 1000 ppm and NO₂ at 10 ppm). Responses: S = R_a/R_g for oxidizing gases or R_a/R_g for reducing gases.](rsos.royalsocietypublishing.org)
temperature; both sensitivity and selectivity are taken into consideration. The long-term stability is important to ensure the accuracy of detection for gas sensors. Consequently, a test for the long-term stability of sensor calcined at 500°C to 10 ppm NO2 was measured for three months. As shown in figure 9, it can be observed that the sensor still showed excellent response performance to NO2 gas even after three months, and the response values were just floating around 400, which indicated that the sensors based on Ag-WO3 have enough stability to detect NO2 gas for a relatively long period.

4. Conclusion

In summary, WO3 and Ag-WO3 (mixed solid solutions Ag with WO3) nanoparticles were successfully fabricated by sol-gel method. The XRD results show that the hexagonal to monoclinic phase transition takes place in the temperature range from 300°C to 500°C. The crystalline size of WO3 nanoparticles increases with increasing calcination temperature and decreased slightly by mixing Ag. The gas sensing properties of Ag-WO3 nanoparticles were measured and the experimental results exhibit that the gas sensor based on Ag-WO3 nanoparticle film has excellent selectivity and long-term stability to NO2 gas. The operating temperature and the amounts of additives play an important role in the

| sensing materials | operating temperature (°C) | NO2 concentration | response \((R_d/R_a)\) | ref. |
|-------------------|----------------------------|-------------------|-----------------|-----|
| Fe-WO3           | 120                        | 500 ppb           | 2.7             | [51]|
| ZnO@Au           | 250                        | 1 ppm             | 10.7            | [52]|
| WO3              | 220                        | 500 ppb           | 50.7            | [53]|
| mesoporous In2O3 | 150                        | 250 ppb           | 10.5            | [54]|
| In2O3 nanosheet   | 250                        | 50 ppm            | 164             | [55]|
| In2O3/NiO        | room temperature           | 15 ppm            | 3               | [56]|
| SnS2             | 120                        | 10 ppm            | 36.3            | [57]|
| MoS2             | 200                        | 1 ppm             | 5.8             | [58]|
| ZnO              | 290                        | 40 ppm            | 264             | [59]|
| ZnO/CNT          | 150                        | 1000 ppm          | 9.7             | [60]|
| (500°C) Ag-WO3   | 150                        | 10 ppm            | 408             | this work |
response of the sensors. The optimum performance was obtained at 150°C for the Ag-WO3 sensor calcined at 500°C and can be suitable for detecting NO2 at relatively low operating temperature.

Ethics. Research Ethics. We do not require any research ethical approval, licence or permission because it is not relevant to our work. Animal ethics. We do not require any animal ethical approval, licence or permission because it is not relevant to our work.

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