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Preparation, characterization of WO_3–SnO_2 nanocomposites and their sensing properties for NO_2

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A B S T R A C T

WO_3–SnO_2 nanocomposites of various compositions have been successfully synthesized by a controlled two-step sol-precipitation method using tin chloride and ammonium metatungstate hydrate as precursors. The performances of the material were characterized by various analysis methods. The sensors based on the nanocomposites were used to detect the NO_2 at operating temperature range 100–300 °C, the response is defined as the ratio of the sensor resistance in an air–NO_2 mixture to that in air (Rg/Ra). The experimental results show that the 20 mol.% WO_3–SnO_2 nanocomposite based sensor exhibits the highest response of 186 to 200 ppm NO_2 at operating temperature of 200 °C. The responses were further enhanced to 251 and 418 by doping 3 wt.% Zn element as dopant and 3 wt.% MgO as surface modifier, respectively, and the optimum operating temperature reduced to 150 °C. The doping effect and sensing mechanism were also discussed by temperature-programmed desorption (TPD) and X-ray photoelectron spectroscopy (XPS) analysis.

1. Introduction

Nitrogen dioxide is one of the hazardous gases polluting the atmosphere in urban areas. The major sources of NO_2 are industrial combustion of fossil fuel and the exhaust of automotive engines. Metal oxide-based chemical sensors have been used extremely for the detection of toxic pollutant gases, combustible gases and volatile organic compounds (VOCs). The semiconductor gas sensors of metal oxides such as SnO_2, ZnO, TiO_2 and Fe_2O_3, were extensively studied in order to understand or improve their sensing properties to inflammable and toxic gases. Among a variety of oxide semiconductors, tin oxide (SnO_2) has been proven to be one of the most attractive sensing materials for gas sensor applications, owing to high sensitivity and chemical stability compared to other metal oxides for detection of reducing and oxidizing gases. It is well recognized that the grain size and thermal stability of the metal oxide significantly affect the performance of the sensor, and the microstructural changes over time lead to sensitivity decrease. To improve the thermal stability and gas-sensing performances of SnO_2 based sensors, in many works it was suggested to turn from single metal oxides to complex multi-component materials [1]. Recent much effort has been made to improve gas-sensitivity and to reduce operating temperature by incorporating oxide or introducing dopants. Yuasa [2] reported PdO loaded SnO_2 nanoparticles by reverse micelle method is highly sensitive to CO gas, and revealed that the electrical resistance as well as the sensor response is significantly dependent on dispersion states of PdO particles on SnO_2. The other hand efforts have been made in the controlled synthesis of oxide composites. Bai et al. [3] synthesized the ZnO–SnO_2 nanocomposites by reverse microemulsion and found that the nanocomposites exhibited the superior thermal stability against grain growth and high sensing properties to NO_2. Rumyantseva [4] reported the sensing and catalytic activity of SnO_2–Fe_2O_3 nanocomposites, and demonstrated that increase of Fe_2O_3 content reduces the amount of surface acid sites and enhances the oxidizing capability of nanocomposites in ethanol oxidation. Arbiol et al. [5] synthesized the SnO_2–MoO_3 nanocomposites using the sol–gel method and found it showed good response toward alcohols, $C_nH_{2n+1}OH$ ($n = 1$–4), and NH_3, and demonstrated this structural feature explains the saturation on the sensor response. The WO_3 is a wide band-gap n-type semiconductor, whose electron concentration is mainly determined by the concentration of stoichiometric defects, such as oxygen vacancy. The WO_3 is a promising candidate since it shows good sensitivity for the detection of oxidizing gases, such as NO_x and O_3, as a single-component oxide [6–8]. Thus, a novel preparation method of WO_3–SnO_2 nanocomposites was developed in this paper using ammonium metatungstate hydrate ($(NH_4)_6H_2W_{12}O_{40}{\cdot}4H_2O$) and $SnCl_4{\cdot}5H_2O$ as precursors, the resultant composite has high thermal stability and peculiar sensing performance for detection of NO_2. When dopant or

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surface modifier was introduced to the WO_3–SnO_2 nanocomposites, the sensor response to NO_2 were further enhanced [9] and the additive method, additives nature and loading were examined.

2. Experimental

2.1. Preparation of WO_3–SnO_2 nanocomposites

In this paper, we are interested in the development of a preparation technique that provides high-performing WO_3 composites in wide composition and be a good matrix for further studies such as doping and/or loading with a foreign element or oxide. WO_3–SnO_2 nanocomposites with various compositions were successfully prepared by the controlled two-step sol-precipitation method rather than a conventional co-precipitation method because the precursors of tungsten oxide and tin oxide could not co-precipitate at the same pH value. Tin chloride ($SnCl_4 \cdot 5H_2O$) was first dissolved in distilled water at a concentration of 0.05 M and then precipitated with ammonium hydroxide in solution of pH 8. The precipitated solution was aged for 4 h, followed by centrifugation and washing with distilled water to remove the chloride ions from the precipitate, and then the precipitated gel was dispersed in dilute acid solution at a concentration of 0.1 M. Appropriate amounts of the ammonium metatungstate hydrate ($(NH_4)_6H_2W_{12}O_{40} \cdot 4H_2O$), which was chosen as the precursor of tungsten oxide due to its high solubility in water, were added dropwise to the agitating solution. The precipitated slurry was aged for 24 h and allowed dry at 60 °C in air. The dried powders were ground in a mortar and pestle and calcined in air at 400–1000 °C for 6 h (ramp = 10 °C min^{-1}). The schematic diagram used to prepare the nanocomposites was illustrated in Fig. 1. If the ammonium paratungstate ($(NH_4)_{10}W_{12}O_{41} \cdot 4H_2O$) was chosen as the precursor of tungsten oxide, the pH value of the solution has to be adjusted to 0.5–1.0 with dilute nitric acid prior to precipitation, because the ammonium paratungstate is hardly soluble in water. A series of Zn, Cd and Sm-doped 20%WO_3–SnO_2 nanocomposites were prepared. The ammonium, chloride or nitrate salts of desired metal cations with nominal weight concentration were added to the precursor solution of the 20%WO_3–SnO_2 nanocomposite prior to precipitation, following after processes were as same as mentioned above. An impregnation method was used to obtain the nanocomposites coated 1 wt.%, 3 wt.% and 5 wt.% MgO. The dried precursor of the 20%WO_3 nanocomposite was added to $Mg(NO_3)_2$ aqueous solutions before the thermal stabilization treatment, and the slurry was evaporated to dryness at 60 °C on a hot plate. The resultant composites were calcined at 600 °C in air for 6 h to diffuse the specimen through the surface of the nanocomposite coated MgO achieving a uniform distribution [10]. It is concluded that the nitrate or chloride salts of desired metal cations added to the precursor solution prior to precipitation were considered as dopants, while those nitrate salts added through impregnating the dried precursor of nanocomposite were regarded as surface modifiers (or coatings).

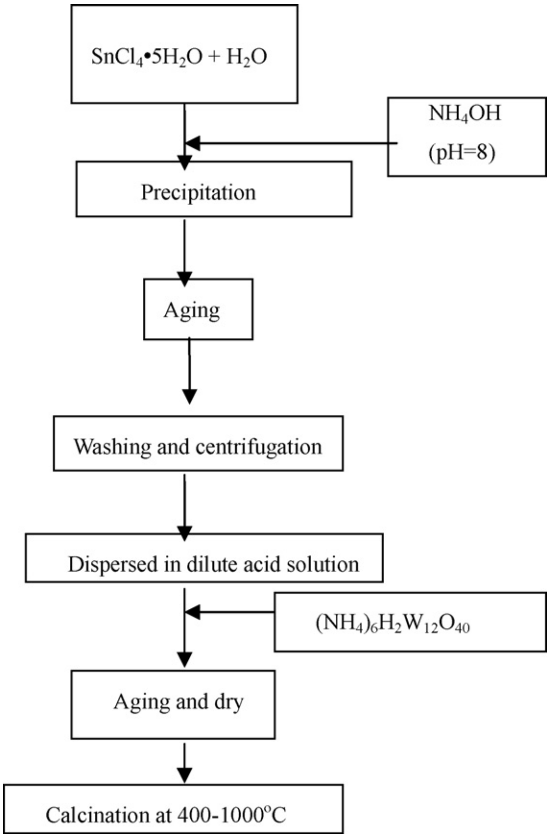

Fig. 1. Schematic diagram used to prepare the SnO_2–WO_3 nanocomposites.

2.2. Measurement of gas response

The nanocomposites synthesized by the method described above were used to fabricate NO_2 sensor element [11]. The annealed powders were pressed into a disc of 5 mm in diameter and 1.0 mm thickness under 10 MPa. The gold leads were applied on both sides of the disc to form the sensing element. The responses of the sensors were measured to NO_2 concentration in a range from 0.1 ppm to 200 ppm balanced with air in a temperature-controlled flow apparatus at the temperature range 100–300 °C. The sensor element was placed in a quartz tube, which was heated to 300 °C for several hours in a tube furnace to remove the adsorbates from the sensor surface prior to response measurement. The target gas and air were introduced through two flow meters to control the concentration of target gas in air. In a typical measurement of sensor response, a constant current of 10 μA was applied to each sensor. When air and ppm-level target gases were flown through the test tube, the corresponding steady-state resistance of the sensor in air (Ra) and in the presence of the target gases in air (Rg) were recorded using an EG&G potentiostat/galvanostat. The sensor response to oxidizing gases (NO_2, NO or O_3) is defined as the ratio of the sensor resistance in an air–NO_2 mixture (Rg) to that in air (Ra), while response to reducing gases (CO, CH_4 or C_2H_5OH, etc.) is defined as the ratio of Ra/Rg.

3. Results and discussion

3.1. Specific surface area and crystallite size of nanocomposites

The specific surface area of SnO_2–WO_3 powders was determined from nitrogen adsorption analysis by five-point BET (Brunauer–Emmitt–Teller) method on a Micrometric ASAP 2000 gas adsorption analyzer. The effects of complex composition on the specific surface area and crystallite size were shown in Fig. 2. The 20–40 mol.% WO_3 nanocomposites calcined at 600 °C have higher specific surfaces area (45.2–51.1 $m^2 g^{-1}$) than other compositions and the specific surface area decreased with WO_3 loading further increase. The existence of the secondary oxide (WO_3) also affected the phase structure. Phase identification of the nanocomposites was performed by powder X-ray diffraction (XRD) at room temperature with a SHIMADZU HR6000 diffractometer, operating at 40 kV and 30 mA, with a scan speed of 5° min^{-1} for 2θ in a range from 20° to 80° using nickel filtered Cu Kα radiation with λ of 0.15406 nm.