Sn/In/Ti nanocomposite sensor for CH$_4$ detection

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Article info
Article history:
Received 22 December 2007
Received in revised form 18 June 2008
Accepted 18 June 2008
Available online 9 July 2008

Keywords:
CH$_4$ sensor
Sn–In–Ti
Nanocomposite
Sensing properties

A B S T R A C T

Novel CH$_4$ gas sensors made of the nanocomposites of Sn/In/Ti oxides were investigated. The nanosized crystalline oxides and their composites were successfully prepared by a sol–gel and controlled precipitation method, respectively, through manipulating the salts concentration, precipitation pH value, aging time and composition of composites. The derived precursors exhibited superior thermal stability. To ensure sufficient crystallinity and insignificant grain growth of the materials, the appropriate calcination temperatures were 600$^\circ$C for 4 h and 700$^\circ$C for 2 h for the precursors of oxides and composites, respectively. The performance and structure of the composites were characterized by EDX, TEM, BET, TG–DTA and XRD. The sensing tests showed that these nanocomposites exhibited high response and selectivity for the detection of CH$_4$ at operating temperatures between 200$^\circ$C and 250$^\circ$C and the response depended on the composition of composites, calcination temperature, operating temperature and gas concentration in air. The gas sensing mechanism of the sensor was also discussed by X-ray photoelectron spectroscopic (XPS) and temperature-programmed desorption (TPD) studies.

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1. Introduction

Tin oxide is an important semiconductor gas sensing material due to its good chemical stability and high sensitivity at lower operating temperature, compared to other oxides for detection of reducing and oxidizing gases [1]. With a decrease in crystallite size, a large interfacial area, homogeneity and highly reactive surface of the nanocrystalline particles have attracted much attention for electronic, catalytic and optical applications. The grain size reduction is one of the main factors enhancing the sensitivity of semiconductor sensors. Xu et al. [2] suggested a model concerning the grain size ($D$) and the thickness of space charge layer ($L$) to explain the effect of particle size on the response of a sensor. The model has widely been accepted to explain the sensing mechanism of semiconductor oxide gas sensors. Unfortunately, sensor fabrication process requires higher calcination temperature, even when nanocrystalline SnO$_2$ is used as the starting sensing material. This would result in significant grain growth after sensor fabrication, greatly compromising the sensitivity of the resulting device. In order to enhance the thermal stability and response towards a specific gas, nanocomposites have been considered as sensing materials.

de Lacy Costello et al. [3] studied a highly sensitive mixed oxide sensor for detection of ethanol; the proportion for the most sensitive response was 25%SnO$_2$–75%ZnO. Serra et al. [4] reported the sensing properties of a new sensor for NO gas; the sensing material was made of a composite of In–Se oxide crystallites which were obtained by thermal evaporation of polycrystalline In–Se and subsequent thermal annealing in an oxygen flow. Ishihara et al. [5] examined mixed oxides of Al$_2$O$_3$–V$_2$O$_5$ as sensing materials for detection of NO and NO$_2$ gases. Chen and coworkers [6] synthesized SnO$_2$–ZnO nanocomposites which exhibited superior thermal stability, and achieved superb response to CO and NO$_2$ gases through introduction of metal (Cd) or Al$_2$O$_3$ coating.

This paper aims at enhancing the CH$_4$ response through introducing TiO$_2$ into binary composites of SnO$_2$ and In$_2$O$_3$. The structural symmetry and high temperature firing nature of CH$_4$ molecules determine its low reactivity and response. The cross-sensing between CH$_4$ and CO is still one of major problems for CH$_4$ sensors because of the same reducing characteristics of both gases. To further improve the response and selectivity and also to decrease the optimal operating temperature of the present CH$_4$ sensor, a small amount of Pd or Pt or a MgO coating was employed as a dopant or a surface modifier. The design of a CH$_4$ sensor possessing good response and selectivity is very important for the safe detection in household and coal mines as well as for industrial process control of natural gas combustion.

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doi:10.1016/j.snb.2008.06.051
2. Experimental

2.1. Preparation of sensing materials

Nanocrystalline powders of SnO2, In2O3 and TiO2 were prepared by sol–gel processing, controlled precipitation method and thermal decomposition methods [7]. A solution of 0.1 mol% SnCl4 in ethylene glycol was prepared under vigorous stirring at 80 °C until a colorless and transparent solution was obtained. The solution was then heated to 120 °C to evaporate water and hydrochloride. When the solvent was completely removed, a dark brown gel was obtained. The gel was aged for 30 min and then dried at 120 °C for 8 h. The dried xerogel was calcined at a temperature of 600 °C for 2 h, and nanosized SnO2 powders were obtained. Highly pure In was dissolved in nitric acid. After being dried, it was decomposed at 500 °C for 2 h to get In2O3. TiO2 was prepared by hydrolysis of TiCl4. The above three kinds of nanosized oxide powders were mixed together in various proportions and ball-milled to produce precursor composites. The precursor powders were calcined at 600 °C for oxides and at 700 °C for composites. Thus, the CH4 sensitive matrix material was obtained. In the doping process, an additive was introduced in the solution prior to precipitation. Pt or Pd was added, in a nitrate or chloride form, at a nominal weight concentration of 1–3%. In the coating process, the dried precursor was impregnated with a Pt or Pd nitrate solution at 1–3 wt%. After impregnation, the powder was subjected to thermal treatment at 700 °C. Preparation parameters, such as precipitation pH value, aging time, calcination temperature and time, and the composition of composites, were critical for controlling the grain size and crystallinity of the materials derived since they governed the nucleation and crystal growth rates.

2.2. Characterization of sensing materials

Energy-dispersive X-ray spectroscopy (EDX) on JEOL JSM-840A/PGT IMIX (accelerating voltage: 20 kV) was used to measure the chemical composition of the nanocomposites. To determine the particle size and morphology, the calcined powders were analyzed by a transmission electron microscope (TEM) equipped with a JEM 200CX instrument. Specific surface area of the nanocrystalline powders was measured from nitrogen adsorption analysis by the Brunauer–Emmett–Teller (BET) method on a Micromeritics ASAP2010 gas adsorption analyzer. Phase structure was characterized by powder X-ray diffraction (XRD) with a Shimadzu HR 6000 diffractometer using the nickel filtered Cu Kα line at 0.15406 nm; an accelerating voltage of 40 kV, an emission current of 30 mA and a scanning speed of 5° min⁻¹ were used. Crystallite size was estimated from the width of XRD peaks by the Scherrer formula, \( D = \frac{k\lambda}{\beta\cos\theta} \), where \( \beta \) is the full width at half maximum of the peak, \( \lambda \) is the X-ray wavelength (1.5406 Å), \( \theta \) is the Bragg angle, and \( k = 0.89 \). Temperature-programmed desorption (TPD) studies were carried out to investigate the desorption properties over the SnO2 and nanocomposite. About 100 mg of a sample was placed in a tube and pre-treated in a 20 ml min⁻¹ He atmosphere at 300 °C for 2 h to remove any surface adsorbates, followed by cooling down to room temperature in He, and then the sample was exposed to CH4 for 2 h. Desorption of adsorbed species was performed during heating from 50 to 700 °C (rate: 10° min⁻¹) in flowing helium at a rate of 20 ml min⁻¹ and the amounts of gases desorbed from the surface of the sample were measured using a TPD/R/O 110 series analyzer (Thermo Electron S.P.A., Italy). X-ray photoelectron spectroscopic (XPS) analysis was conducted on a PHI-5600 spectrometer (PerkinElmer, USA).

2.3. Measurement of sensor response

The fabrication method of CH4 sensors used in this study was different from our previous reports [9]. The sensing element was prepared starting from the paste obtained by adding 2 wt% of acid asbestos to the calcined nanocomposite to enhance the adhesion strength of the interface between the paste and an alumina substrate. The paste was covered on an alumina tube (4 mm length and 1 mm diameter) provided with two Au wire electrodes to form the sensor. Or, the ceramic sensor was obtained by covering a Pt wire coil with pastes obtained by adding an inorganic vehicle to the powders together with 1–2 wt% of glass frit for improving the adhesion of material to the Pt wire, then fired at 600 °C for 2 h. The element was enclosed in a quartz tube, which was heated to 50–350 °C in a tube furnace. Prior to gas response testing, the element was heat treated for 8 h. The target gas and air flows were then introduced by gas flow meters to control the gas concentration. A constant current was applied across the element and steady-state resistance of the element was measured in air \( (R_a) \) and in the presence of a target gas in air \( (R_g) \). Sensor response to a reducing gas was defined as the ratio of the sensor resistance in air \( (R_a) \) to that in an air–gas mixture \( (R_g) \).

3. Results and discussion

3.1. Sensor response and selectivity of nanocomposites to CH4

The responses of various ternary composites to 850 ppm CH4 were measured over an operating temperature range of 100–350 °C and correlated with their composition and operating temperature. The response data are presented in Figs. 1 and 2. These results indicated that the 20%TiO2–20%In2O3–60%SnO2 nanocomposite calcined at 700 °C had the largest response value of 27.4 to 850 ppm CH4 at 250 °C; thus, it was the optimum composite for the detection of CH4. The high response was attributed to the enhancement of thermal and phase stability of SnO2. A TEM image of the optimum composite (Fig. 3) showed that the grain size was quite uniform, about 30 nm, and the crystallite size was estimated to be 19 nm from the width of XRD peaks by the Scherrer formula. From BET surface area measurement, the decrease in

**Fig. 1.** Response of ternary composites calcined at 700 °C to 850 ppm CH4. (a) 10% TiO2–10% In2O3–80%SnO2, (b) 20% TiO2–10% In2O3–70%SnO2, (c) 30% TiO2–10% In2O3–60%SnO2 and (d) 40% TiO2–10% In2O3–50%SnO2.
crystallite size was accompanied by an increase in specific surface area from 25 m² g⁻¹ for SnO₂ to 54 m² g⁻¹ for the composite through introduction of In and Ti oxides. The response of the composite decreased with further increasing the amount of TiO₂, which suggested that SnO₂ was the major sensing component in the composite. It could be explained by XRD analysis that two crystalline phases of SnO₂ and In₂O₃ were observed for the composite (Fig. 4), while the crystalline phase of TiO₂ was not observed. This implies that the TiO₂ was substituted into the SnO₂ crystal lattice in the calcination process because the Ti⁴⁺ ionic radius (0.62 Å) was near to the Sn⁴⁺ ionic radius (0.69 Å), while the In₂O₃ was not substituted into the SnO₂ lattice because the ionic radius of In³⁺ (0.81 Å) was considerably different from that of Sn⁴⁺ (0.69 Å). If In³⁺ ions were substituted into the SnO₂ lattice, the unit cell parameters of SnO₂ in the composite were negligible. Enoki et al. [8] also reported that the solubility of In₂O₃ in SnO₂ was 3.9–5.6 mol% at temperatures below 1200 °C and the solubility varied only slightly with the temperature, as shown by an energy-dispersive X-ray micro-analyzer with STEM.

So, the In₂O₃ existed acted as a barrier against the advancement of grain boundaries of SnO₂ to suppress the crystallite growth of SnO₂ and loss in surface area. These results are in good agreement with those observed from BET specific surface and TEM photograph.

In addition to response, selectivity is one of the most important gas sensing properties of gas sensors. The cross-sensing between CH₄ and CO is still one of the major problem for CH₄ sensors due to the same reducing character of both gases. Fig. 5 shows that the response of the binary nanocomposite of 40%In₂O₃–60%SnO₂ to 850 ppm CO was larger than that to CH₄ under the same conditions. For the ternary nanocomposite of 20%TiO₂–20%In₂O₃–60%SnO₂, the response to CH₄ was larger than that to CO at the same operating temperature and gas concentration (Fig. 5). The CH₄ selectivity against CO at the same gas concentration of 850 ppm for the ternary nanocomposite is shown in Fig. 5, according to the definition of selectivity \( K = S_{CH_4}/S_{CO} \). The selectivity of the optimum com-
posite for CH$_4$ achieved 9.8 and 9.4 at operating temperatures of 200 °C and 250 °C, respectively. Even when the sensor was operated at 50 °C and 100 °C, the response to CH$_4$ was 3.7 and 7.9, respectively, but without response to CO.

3.2. Effects of calcination temperature and gas concentration on the CH$_4$ response

A sufficient degree of crystallization and ultrafine grain size are required to attain the desired sensing properties for gas sensor application. The sensing materials have to be calcined at appropriate temperature to achieve crystallization and structural evolution. In order to investigate the crystallinity and particle size dependence of sensor performance, the precursor powders were annealed at different temperatures (400–1000 °C). When calcination temperature was lower than 700 °C, for example 400 °C, the nanocomposite had the largest specific surface area over 100 m$^2$ g$^{-1}$, but the sensor response was lower. This is because the nanocomposite calcined at 400 °C does not satisfy the requirement of sufficient crystallinity for sensor application. However, when the calcination temperature was above 700 °C, the response decreased, because SnO$_2$ in the nanocomposite underwent substantial crystal growth and therefore the surface area decreased. The optimum nanocomposite was calcined at 700 °C for 2 h, which was found to be an appropriate calcination temperature as it ensured SnO$_2$ crystallization in the nanocomposite without significant crystallite growth (19 nm), thereby achieving the largest specific surface of 54 m$^2$ g$^{-1}$ and the highest sensor response of 27.4. In contrast, pure SnO$_2$ underwent substantial growth of the crystallite size to 38 nm and the specific surface decreased to 25 m$^2$ g$^{-1}$. It suggests that incorporation of In$_2$O$_3$ as a secondary component had a dramatic effect on the thermal stability of SnO$_2$ in heat treatment up to 700 °C, as confirmed by TEM and XRD analysis. The calcination temperature is thus an important parameter for gas sensing materials and in designing sensors.

The response of the nanocomposites was related not only with the composition of composite and the calcination temperature but also with the operating temperature and test gas concentration. The response increased with increasing the gas concentration in air at an operating temperature. It is clear from response data (e.g. Fig. 1) that the gas response increases with an increase in operating temperature and reaches to a maximum at 250 °C and falls with a further increase in operating temperature. At 250 °C, a larger amount of oxygen would be adsorbed on the surface of the sensing material, which would facilitate the sensor to oxidize CH$_4$ molecules, immediately giving faster and larger gas response. The adsorption amount of gas on the composite surface will gradually increase with temperature because chemisorption needs activation energy until the rate of desorption becomes equal to the rate of adsorption, or an equilibrium is established. If the temperature is further enhanced over 250 °C, the amount of adsorbed gas will decrease with temperature, as shown in Fig. 8. Hence, the gas response may decrease above 250 °C.

3.3. Effect of additives to CH$_4$ response

The addition of surface deposits and dopants has proven to greatly improve the gas sensing properties and reduce the operating temperature requirements in semiconductor gas sensors [9,10]. In this study, the method of additive introduction as well as the nature and loading of additives were examined for the optimum nanocomposite. Nitrate or chloride salts of desired metal cations introduced 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 modification or “coatings”. This section aims at enhancing the response to CH$_4$ at lower operating temperature and reducing the operating temperature of maximum response to CH$_4$. Metal oxides such as MgO, Al$_2$O$_3$ and CeO$_2$, which are known to be effective catalysts for CH$_4$ oxidation and/or adsorbs, were introduced in this study as surface coatings to the optimum nanocomposite sensor. Fig. 6 shows the effect of the MgO loading level on the CH$_4$ response. The loading of 1 wt% MgO enhanced the CH$_4$ response at low temperature and reduced the optimal operating temperature from 250 °C to 150 °C, and the response value was 7.2 and 5.9 at operating temperatures of 70 °C and 50 °C, respectively. In order to further reduce the operating temperature and enhance the response at low temperature, Pt and Pd were introduced as dopants, as shown in Fig. 7. It is found that the CH$_4$ sensing properties were substantially improved; particularly, an optimal Pt loading of 1 wt% was found to reduce the optimal operating temperature from 250 °C to 100 °C and enhance the response from 8.0 to 30 toward 850 ppm CH$_4$ for the optimum nanocomposite at an operating temperature of 100 °C. The response to CH$_4$ still
had a value of 6.5 even at 30 °C. Use of noble metals as dopants could enhance the catalytic properties of sensing materials for CH₄ oxidation [11], improving the CH₄ sensing performance. The optimum Pt-doped nanocomposite was a highly sensitive material for CH₄ detection over an operating temperature range of 30–100 °C and displayed an impressive improvement in CH₄ detection. Consequently, the CH₄ sensor will have more convenient application.

4. Gas sensing mechanism

The sensing response of semiconductor gas sensors is based on the conductivity (or resistance) change of the materials due to the interaction between the semiconductors and the test gases. The interaction includes chemical and electronic functions. The chemical interaction involves the adsorption and reaction of the test gases on the semiconductors. Oxygen molecules in air adsorb on the surface of an n-type semiconductor to form chemisorbed oxygen anions (O_ads⁻) by capturing electrons from the conductance band, resulting in the formation of a depletion layer, known as the space charge layer, on the surface of the sensor material.

\[ \text{O}_2 + 2\text{e}^- \rightarrow 2\text{O}_{\text{ads}}^- \]

When test gases were adsorbed, electrons were added to or removed from the space charge layer, leading to a change in electrical conductivity of the sensor. Upon exposure to a reducing gas (e.g. CH₄), the test gas (G) reacts with the surface oxygen anions, causing the electrons to return to the semiconductor and leading to an increase in concentration of electrons.

\[ \text{G} + \text{O}_{\text{ads}}^- \rightarrow \text{GO}_{\text{des}} + \text{e}^- \]

This eventually increases the conductivity of the material (or a decrease in resistance), which has been shown to increase the response for the detection of reducing gases, such as CH₄. In contrast, n-type semiconductors change their resistance from low to high in the presence of oxidizing gases (e.g. NO_x) because the gases captures electrons and are reduced [12]. TPD studies showed that the optimum nanocomposite had enhanced CH₄ adsorption capability in comparison with that of pure SnO₂ (Fig. 8), which was consistent with the larger CH₄ response of the optimum nanocomposite than that of pure SnO₂. In the case of surface modified, the capture of the CH₄ molecules by the additive atoms first be assumed. This capture probability will depend on the active site concentration and the capture energy barrier at this temperature. Posterior interaction of the additive with the supporting composite could take place on these active sites on the interface of the composite with additive, which is required either to transfer the chemical effects of interaction or directly to transduce on electrical signal from the additive into the composite base material. It causes a modification of the electrical characteristics of composite. 1 wt% MgO coating supplied a large surface area and a large amount of surface active sites for both gas adsorption and surface reaction, resulting in an increase in CH₄ response and reduced optimal operating temperature. Use of a noble metal of Pt or Pd as a dopant could decrease the activation energy of chemiadsorbed and enhance the rate of surface reaction for test gases, leading to an increase in CH₄ response or decrease in optimum operating temperature for the optimum composite. Therefore, the sensing temperature was further decreased to 100 °C and the response to CH₄ of 6.5 was achieved at an operating temperature of 30 °C. XPS analysis was performed on the optimum nanocomposite and used to examine the nature of In₂O₃ and TiO₂ in the nanocomposite and the electronic states of Sn, In, Ti and O in the nanocomposite calcined at 700 °C. Significant positive chemical shift of 0.6 eV and 0.9 eV in the Ti 2p₃/₂ and O 1s peaks relative to the peaks for pure TiO₂ were observed for the optimum nanocomposite. This suggested that electronic interactions existed between SnO₂ and TiO₂ in the nanocomposite. The shifts in binding energies reflected the shifts in the Fermi energy of SnO₂ due to electronic interaction with TiO₂, which was responsible for the enhanced gas response of the nanocomposite. It also suggested that the electronic interactions of metal oxide semiconductors played an important role in enhancing the CH₄ response. In contrast, a negligible chemical shift in binding energy of 0.1 eV was noted in the In 3d₅/₂ peak of the optimum nanocomposite relative to pure In₂O₃. This indicated that the electronic interaction between In₂O₃ and SnO₂ in the nanocomposite might not be detectable. The enhanced gas response by introducing In₂O₃ was explained due to the enhanced thermal stability of SnO₂. Thus, the sensing performance of the sensor was attributed to chemical and electronic synergistic effects between the nanocomposites and the gases.

5. Summary

CH₄ sensors based on the ternary nanocomposites of Sn, In and Ti were investigated over an operating temperature range of 30–350 °C. The nanocomposite containing 20%TiO₂–20% In₂O₃–60% SnO₂ exhibited the largest response value of 27.4 at an operating temperature 250 °C, and selectivity of 9.8 against CO at an operating temperature of 200 °C. Surface modification with 1 wt% MgO by coating or impregnating and doping of 1 wt% Pt enhanced the response at lower temperature and further reduced the optimum operating temperature to 100 °C. The response value of 30 and 6.5 were achieved even at operating temperatures of 100 °C and 30 °C, respectively. So, enhancement of gas sensing properties for semiconducting CH₄ sensor could be attributed to the smaller crystallite size of SnO₂, more adsorption amounts and active sites on surface of composites, and faster rate of surface reaction for test gases as well as lower oxidizing temperature of CH₄ on surface of composites.

Acknowledgements

This research work was supported by the National Natural Science Foundation of China (Nos. 20577001, 50872007 and 50702004) and Beijing Natural Science Foundation (Nos. 8062011, 8082018 and 8072018).
References


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