New method of synthesizing In_2O_3 nanoparticles for application in volatile organic compounds (VOCs) gas sensors

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In_2O_3 nanoparticles have increasingly attracted interest over the past decade due to their novel properties [1]. They are usually synthesized by using chemical routes such as sol-gel and solid-state reaction methods [2, 3]. However, there are some limitations such as a low yield rate, impurity pollution and agglomerates in these techniques. Recently, we have developed a new specific device in which inductive resource and continuous wave CO_2 laser beam were compounded to synthesize metal and their oxide nanoparticles, which can overcome the above-mentioned limitations [4]. Using this hybrid induction and laser heating (HILH) method, refractory cobalt amorphous or crystalline nanoparticles as well as Sb_2O_3 nanoparticles were synthesized [5, 6]. Also tetrapod-like ZnO nanowiskers were synthesized using this novel method and its yield rate can reach several kilograms per hour [7]. In this study, the In_2O_3 nanoparticles were synthesized by means of HILH, and the characteristics of the nanoparticles was systematically investigated by transmission electron microscope (TEM) and X-ray diffraction (XRD).

As a gas sensing material, In_2O_3 has been extensively applied to detect O_3, NO_2 and CO etc. [8–10]. We believe that the gas-sensing properties of In_2O_3 for volatile organic compounds (VOCs), especially toxic VOCs that are harmful to human health and the environment, have not been broadly studied. So the gas-sensing properties for five VOCs (benzene, toluene, xylene, acetone and alcohol) of thick films based on as-synthesized In_2O_3 nanoparticles were studied in this letter.

The experimental setup of HILH is described in the literature elsewhere [6]. The experimental procedures were as follows: the metallic indium was heated to a certain temperature by induction-heating in a vacuum chamber with a flowing mixed $Ar + O_2$ gas at a pressure of 1.0×10^4 Pa, where the oxygen partial pressure was kept fixed at about 2×10^3 Pa by controlling the oxygen flux. Subsequently, the continuous wave CO_2 laser beam was focused at the liquid surface. The focused beam diameter was 4 mm and the laser power was 1600 W, which gave a power density in the order of 10^4 W/cm^2. Finally the nanoparticles were obtained from the collection chamber for further examination. A JEM-2000 transmission electron microscope (TEM) was employed to observe the morphology of as-synthesized nanoparticles. Its phase structure was identified by X-ray diffraction (XRD) with Cu Kα1 incident radiation. The preparation of thick films based on nanoparticlers, and the measurement of resistance and gas-sensing properties for the thick film are described in detail in the literature [4]. The gas sensitivity, S, is defined as the ratio (R_a/R_g) of resistance in air (R_a) to that in detecting gas (R_g).

Fig. 1 presents the typical morphology of In_2O_3 nanoparticles prepared by the HILH method, indicating that the powders consist of small quadrate-like nanoparticles with size ranging from about 20–50 nm. The XRD pattern of the nanoparticles reveals that as-synthesized powder consists of a single In_2O_3 phase, as shown in Fig. 2. Chen *et al.* [11] reported that quasi-spherical In_2O_3 nanoparticles with maximal size of approx. 30 nm were produced by the atomizing-combustion technique, and the color of the powders was buff. Quan *et al.* [2] reported that the mean size of In_2O_3 powders prepared by the sol–gel method was about 50–60 nm. In literature [3], In_2O_3 powders with a mean grain size of about 25 nm were prepared by the solid-state reaction method.

Fig. 3 shows the resistance of In_2O_3 thick film as a function of working temperature. From Fig. 3, we can observe that the resistance of the thick films is about 10^5 Ω at room temperature, then it begins to drop steeply until the temperature exceeds 150°C. It is worth noting that the resistance of In_2O_3 thick films increases slowly in range of 150–270 °C, then drops slowly over the range of 270–420 °C. When the temperature is higher than 420 °C, the resistance drops steeply again.

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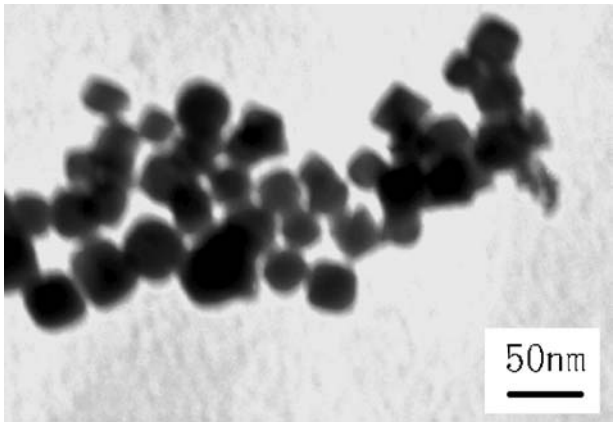

Figure 1 TEM image of In_2O_3 nanoparticles produced by HILH.

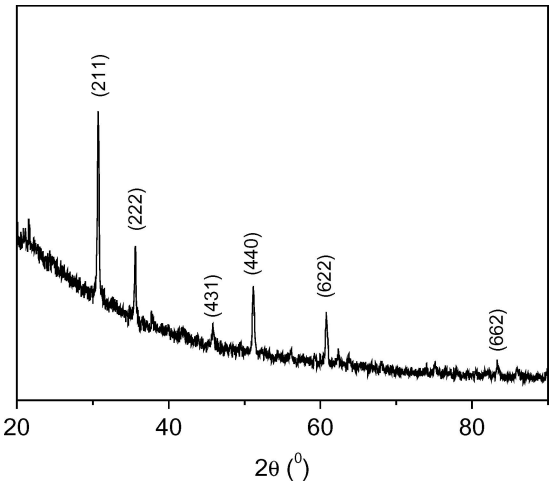

Figure 2 XRD pattern of obtained In_2O_3 nanoparticles.

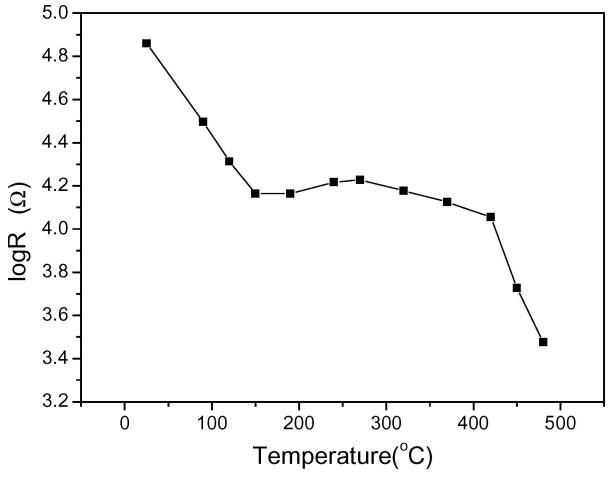

Figure 3 Temperature dependence of the resistance in air of In_2O_3 thick film.

It is obvious that the resistance change largely depends on the operating temperature, which is attributed to the change of intrinsic conductance and surface adsorbed oxygen with temperature.

In the case of In_2O_3 thick films, the electrons are extracted from the oxygen vacancies and the interstitial indium atoms [2]. The defect reactions are described as follows:

$$2In_{In}^{x} + 3O_{o}^{x} = 2In_{In} + 3V_{o}^{\cdot\cdot} + 6e' + \frac{3}{2}O_2(g) \quad (1)$$

$$In_2O_3 = 2In_i^{\cdot\cdot\cdot} + 6e' + \frac{3}{2}O_2(g) \quad (2)$$

With increasing temperature, the intrinsic conductance increases monotonously, but the grain surface of the thick film can adsorb much oxygen and the surface adsorbed oxygen captures electrons to produce O_2^-, O_2^{2-} and O^{2-}, which produce the resistance increase. So the resistance change of the films depends on the above-mentioned, two opposing factors. At lower temperature, the intrinsic conductance increase surpasses the conductance decrease caused by adsorbed oxygen, so the resistance continues dropping until $T > 150$ °C, where adsorbed oxygen or O^- acquires enough energy to transform into O^- or O^{2-}, causing the resistance to slowly increase from 150 to 270 °C, then slowly drop from 270 °C to 420 °C. When $T > 420$ °C, intrinsic conductance obviously dominates the situation again with the desorption of oxygen, making the curve fall steeply.

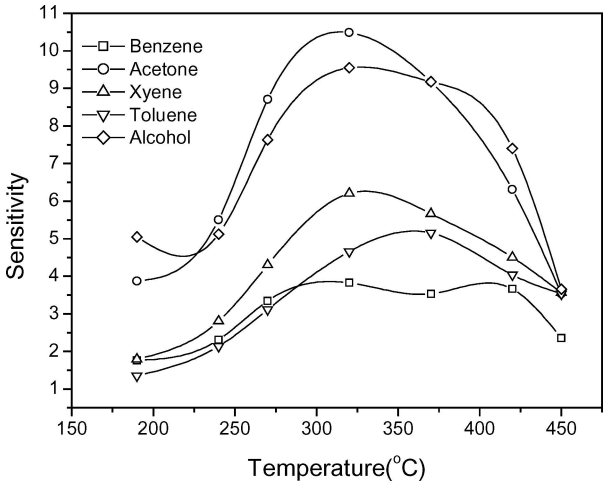

Figure 4 The sensitivity versus operating temperature of In_2O_3 thick film.

Fig. 4 illustrates the sensitivity to each of the five VOCs of acetone, benzene, alcohol, xylene and toluene tested as a function of temperature. Obviously, the sensitivity goes through a maximum at around 320 °C for all the organic vapors. The VOCs readily react with the oxygen ions and liberate electrons to the conduction band, accompanied by an increase in conductivity of the film, when they are in contact with the surface of the In_2O_3 film (at the proper elevated temperature). So the decreasing level of resistance, i.e. sensitivity, is dependent on the change of chemisobed oxygen ions on the surface. The process can be represented as follows:

$$VOCs + O^- \rightarrow VOCs{-}O + e^- \quad (3)$$

$$VOCs + O^{2-} \rightarrow VOCs{-}O + 2e^- \quad (4)$$

The increase in sensitivity with operating temperature can be attributed to the fact that the amount of

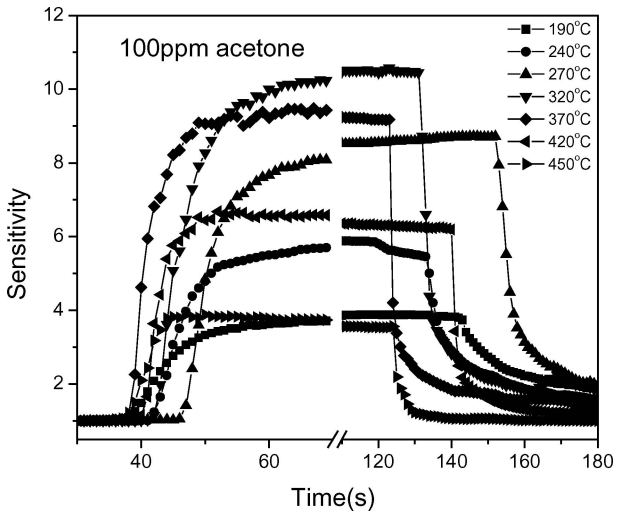

Figure 5 Sensitivity as a function of time of In_2O_3 thick film at various temperatures.

chemisorbed oxygen ions gradually increases as discussed above and the thermal energy obtained is high enough to overcome the activation energy barrier to the reaction, while the reduction in sensitivity above 320 °C is due to a gradual decrease in the amount of chemisorbed oxygen ions and/or the enhancement of desorption of oxygen.

The sensitivity is related to functional groups of organic vapor. Among the five organic vapors the films exhibit the highest sensitivity to acetone, next to alcohol. Of the three kinds of organic vapors with phenyl, xylene gives the highest sensitivity, followed by toluene, and the sensitivity to benzene is lowest, which coincides with the number of methyl groups involved.

Fig. 5 shows the typical change in sensitivity of the films as a function of time maintained at different operating temperatures, after injecting 100 ppm acetone into the chamber. The results show that the operating temperature influences not only the sensitivity, but also the response-recovery time of the thick films. It is observed that the response-recovery time is long at lower temperature, and it becomes short when the operating temperature is higher than or equal to 320 °C. Generally speaking, the response-recovery time of the films decreases with decreasing temperature because the VOCs adsorption, oxidation and desorption are all thermally activated reactions, which are sensitive to temperature. In addition, the response-recovery time of sensors also depends on the vapor species and its concentration.

In conclusion, In_2O_3 nanopowders formed by (HILH) consist of small quadrate-like particles with sizes ranging from about 20–50 nm. The operating temperature influences the resistance, sensitivity and response-recovery time for VOCs of In_2O_3 thick films. At 320 °C, the highest sensitivity is obtained, and the response-recovery time is shortest.

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