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Preparation and gas-sensitivity of ultra-fine zinc-oxide powders from roasted zinc-blended

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Ultra-fine zinc oxide is an important versatile semiconductor material, which has attracted attention for its wide range of applications such as solar cell, luminescent and chemical sensors that detect the combustible or toxic gases by virtue of their high sensitivity and stability [1]. The gas sensing mechanism involves the chemisorption of oxygen on the oxide surface followed by charge transfer during the reaction between the chemisorbed oxygen reducing and target gas molecules, leading to a change in surface resistance of sensor element. Numerous techniques have been developed for preparation of ultra-fine zinc oxide powders, which include sol–gel method [2], hydrothermal method [3], and evaporative decomposition of solution [4]. Some methods such as noble metal or rare-earth element doping, surface decoration have already been reported [5]. Recently the liquid phase reaction has been of considerable interest, because it allows a very fine and reactive regular homogeneous powder to be prepared, and the powder characteristics can be easily modified by changing the conditions during powder synthesis and in which the reaction regent can be recycled, and the powders' shapes are regular ect. In this experiment ultra-fine ZnO powders with particle size of 20–30 nm have been prepared from industrial roasted zinc blended *via* liquid phase synthesis of basic zinc carbonate by chemical direct precipitation method followed by thermal decomposition. The transformation of phase structure, particle size, and morphology of ZnO powders was investigated. The gas sensing properties of ZnO sensor to ethanol, gasoline, cyclo-hexane, and *n*-hexane were measured using distribution in static state. The results show that the low cost film of ZnO prepared by this method exhibits a higher degree of gas sensitivity at low temperature compared with the other form of sensor elements reported till now, and is a stable continuous operation and has quick response and recovery characteristics to ethanol gas.

Roasted zinc-blended and sulfuric acid solution were used as starting materials and coarse $ZnSO_4$ solution was obtained under water bath at 80 °C for about 1 hr. Fine $ZnSO_4$ solution was obtained by removing some of the Fe, Cu, Cd, Ni, Mn, and Cr elements from the coarse $ZnSO_4$ solution under certain pH values and in the boiling water bath. Basic zinc carbonate was synthesized by adding ammonium carbonate solution (analytical grade) into fine $ZnSO_4$ solution in which the concentration of Zn^{2+} is 1 mol/l and the mole ratio of $(NH_4)_2CO_3$ to $ZnSO_4$ is equal to 1.15. The precipitation was carried out at 40 °C for 35 min with the final pH of resulting slurry being about 7.0. The system was further stirred for another 0.5 hr. The as-prepared powder was filtered, washed thoroughly with deionized water and then with ammonia and ethanol, respectively, till the ${SO_4}^{2-}$ was not capable of being detected with the saturated $BaCl_2$ solution and then dried at room temperature under vacuum. The calcinations of as- powders were carried out at several selected temperatures from 250 to 900 °C for 2 hr in air during which the as-prepared powders were decomposed as follows:

$$Zn_4CO_3(OH)_6 \cdot H_2O \rightleftharpoons 4ZnO + CO_2 + 4H_2O \quad (1)$$

The crystalline phase in the as-prepared and calcined powders at various temperatures were identified by an X-ray diffraction (XRD) with a Rigaku D/MAX-IIIB diffractometer using CuKα radiation. The particle morphology and sizes of the as-prepared and calcined powders were examined by transmission electron microscopy (TEM) using a jeol JEM-2010 electron microscope. The calcined powders were dry-ground with an agate mortar and then wet ground with organic binder to make a paste. Then the paste was coated daub in the pottery onto an Al_2O_3 tube on which two gold electrodes had been placed at each end, and then were heat treated at certain temperature for 1 hr in air, and aged at 300 °C for 240 hr. Sensor resistance in air (R_a) or in detecting gas (R_g) was examined in the temperature range from the room temperature to 350 °C, which is adjusted by the heating power from 2.0 to 5.5 V. The gas sensitivity degree S_r was expressed by the ratio of R_a to R_g:$S_r = R_a/R_g$, where R_a and R_g are the electronic resistances of the sensor in air and under the test gas, respectively. The selective coefficient K of A gas to B gas was defined as K = Sr(A)/Sr(B). Gas sensitivity studies were carried out on a HW-30A gas sensor detection system made in HeNan Hanwei Electronics

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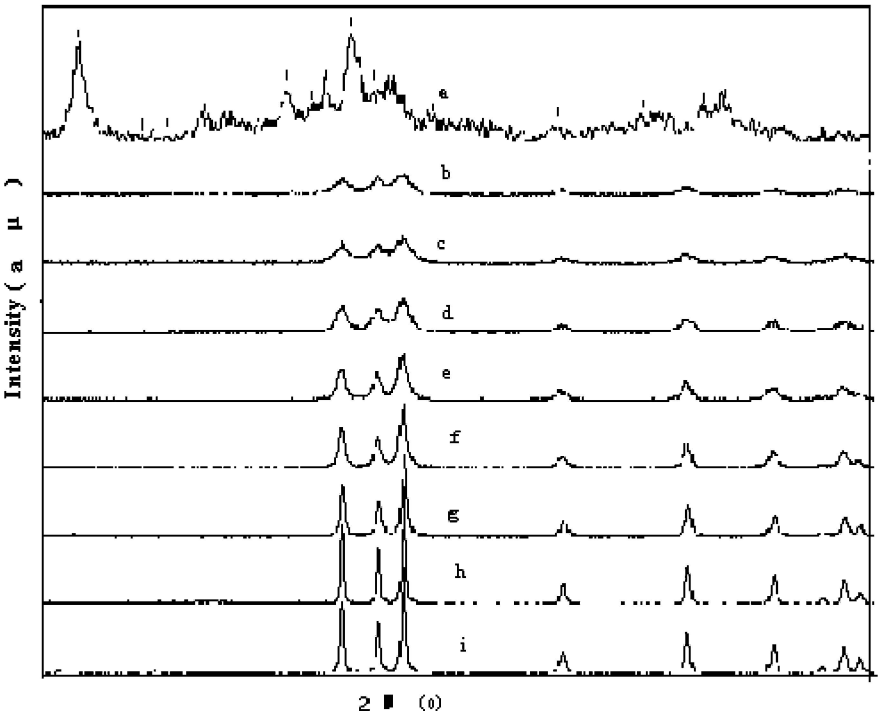

Figure 1 XRD pattern of the (a) as-prepared powders and (b) calcined powders obtained at different temperatures 250 °C, (c) 300 °C, (d) 400 °C, (e) 500 °C, (f) 600 °C, (g) 700 °C, (h) 750 °C, (i) 900 °C.

Co. Ltd. The sensing properties to ethanol, gasoline, cyclo-hexane, and *n*-hexane were measured using distribution in static state. The response and recovery characteristics were also studied as a function of time.

Fig. 1 shows the XRD pattern of the as-prepared powders and calcined powders. The crystalline phase presenting in as-prepared powders is $Zn_4CO_3(OH)_6 \cdot H_2O$, which were decomposed after being calcined at a certain temperature. The diffraction peak of $Zn_4CO_3(OH)_6 \cdot H_2O$ becomes significantly reduced with the increase of the calcining temperature, and hexagonal wurtzite zinc oxide appears as the predominant phase in calcined powders after 400 °C, and the diffraction peaks become narrow as the calcination temperatures increase.

The results show that the particle sizes of the calcined powders at 250 °C are smaller than the as powders, which means a lot of the as powders have been decomposed and have been transformed into the ZnO powders. However, the particle size became larger with the increase of the calcination temperature after 300 °C, which were consistent with the XRD pattern in Fig. 1. This maybe due to the particles' growth and spheroidization and a lot of small particles' aggregation after being high-temperature sintered. As is shown in Fig. 2, the morphology of calcined powders at 500 °C derived from the basic zinc carbonate present oval shape and the particle size is about 20 nm.

Fig. 3 shows that the gas sensitivity degree increase rapidly with the augmentation of concentration of ethanol within the range being determined. The sensitivity degree reaches the maximum value 98.32 when the concentration of ethanol is 100 ppm, (0.01 vol./%). The low detectablity is due to small particle size and the relative large specific surface area. As a result, it is easy for the reducing gas molecule to be absorbed on the surface of ZnO powders and to diffuse through the multicrystals.

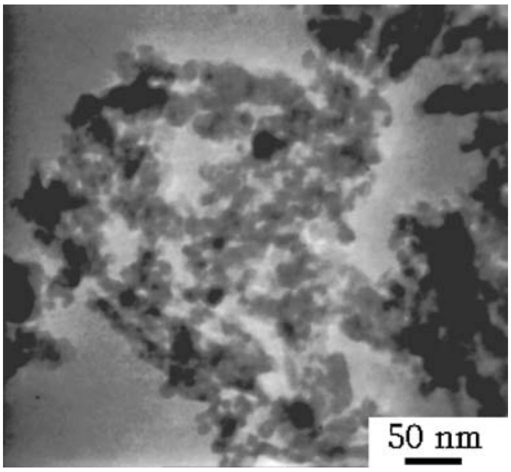

Figure 2 TEM image of the ZnO powders calcined at 500 °C.

Fig. 4 shows that the gas sensitivity of ZnO powder enhanced as the calcination temperatures increased, and the sensitivity degree increased to maximum when the calcined temperature was 600 °C, which is the optimal calcination temperature. From then on the sensitivity decreases as the calcination temperatures increase. Being calcined at the higher temperature and being annealed in air renders more oxygen vacancy generation, which enhances the material's gas sensitivity. The electric resistance of the sensor is too high for the too low calcination temperature, which cannot be suitable for the gas sensor. However, after the calcining temperature of 600 °C, the particle size of calcined powders becomes larger which means the small specific surface area after being sintered at too high temperature, which

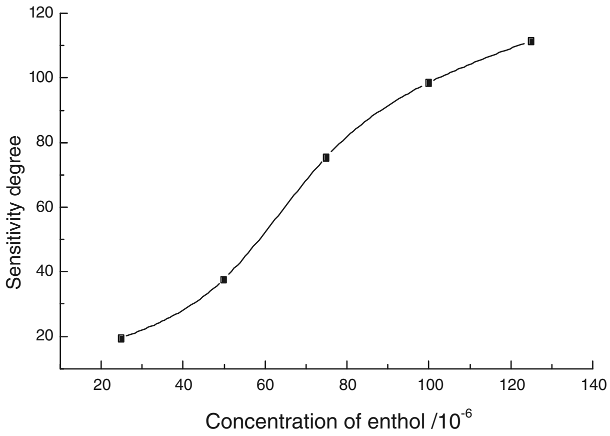

Figure 3 Dependence of sensitivity on concentrations of ethanol at 340 °C.

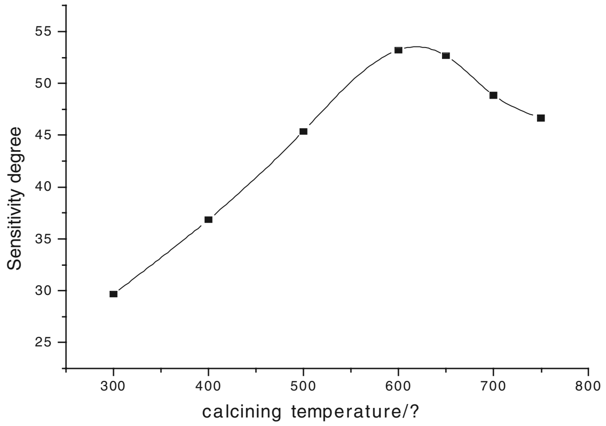

Figure 4 Sensitivity of sensor vs. the calcining temperatures.

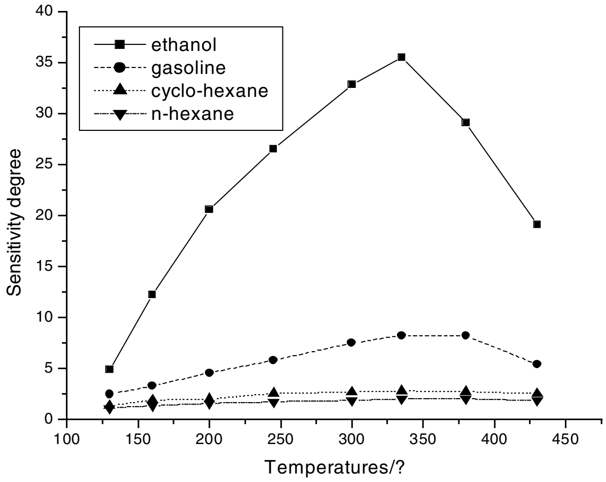

Figure 5 Sensitivity degree–heating V curves of various gases.

leads to the decrease of gas sensitivity, as the result, 600 °C is the optimal calcination temperature.

Fig. 5 shows the relationship between the gas sensitivity and temperatures in the atmosphere of ethanol, gasoline, cyclo-hexane, and *n*-hexane, respectively. When other conditions are the same, all the concentration of the measured gases is 50 ppm. In ethanol gas, the sensitivity increased with the augmentation of the testing temperature. When the testing temperature is 335 °C, the sensitivity increased to the maximum, which for ethanol is 37.45. The variation of sensitivity degree with temperature is not so obvious in other test atmospheres, and at this point the selectivity coefficient of the gas sensor for ethanol to petrol, cyclo-hexane, *n*-hexane is 4.61, 15.80, and 27.13, respectively.

TABLE I The response and recovery times of ZnO in various kinds of gas circumstances

Category of gases	Ethanol	Gasoline	cyclo-hexane	*n*-hexane
T res/s	9	19	16	15
T rec/s	14	26	24	18

The response and recovery characteristics were examined by the change of load voltage U_L: when the component is exposed to the test gas, load voltage increases by virtue of the component resistance being reduced. On the contrary, after the gas taking off the sensor, load voltage declines by virtue of the component resistance increasing [6].

As shown in Table I, when all the concentrations of tested gas are in 0.01 vol.% the average response and recovery times of zinc-oxide sensor ethanol are shorter than that in other test atmospheres at room temperature. The results reveal that ZnO powder sensors prepared from the roasted zinc blended have quicker response and recovery characteristics to ethanol gas at room temperature, and can be used as the materials at room temperature.

Zinc-oxide is typical *n*-type semiconductor in which the excess zinc ion exists in the interval place of the crystal.

$$\mathrm{Zn}_i^{\bullet} = \mathrm{Z\dot{n}}_i + \mathrm{e}^- \qquad (2)$$

The gas sensitivity enhancement was based on improving the three mechanisms: electron activations, oxygen adsorption, and oxygen desorption. Observed low temperature activation barriers can be attributed to donor states associated with oxygen vacancy according to the ionization processes listed below [7]

$$\mathrm{Vo} = \mathrm{Vo}^+ + \mathrm{e}^-, \quad \mathrm{Vo}^+ = \mathrm{Vo}^{2+} + \mathrm{e}^- \qquad (3)$$

The small particle size means the relative large specific surface area to volume, which increases absorbing of the reducing gas and oxygen gas on the sensor surface [8, 9]. Some of the transition metals whose ionic radius is in proximity to that of Zn^{2+}, which were formed as the impurity donor, trace quantity of high-charge ion such as Fe, Pb, Ga, Al, and Cr, which were detected by the SHIMADZU AA-6800 atomic absorption spectrophotometer. High-charge ions such as Fe^{3+}, Al^{3+}, and Ga^{3+} take the place of Zn^{2+} lattice. Negative charge will be increased by these vacancies to compensate for the equivalent electron charge of some defects in multicrystal particles to keep the electricity neutral of the powders, which contribute a lot of electrons [10]:

$$\mathrm{Al_2O_3} + \mathrm{ZnO} = 2\mathrm{Al}_{\mathrm{Zn}}{}^{\bullet} + 2\mathrm{O_o} + \mathrm{O_2} + 2\mathrm{e}^- \qquad (4)$$

Some impurity elements such as Fe, Ni, Cr, and Cd have electricity negativity nature, which is higher than the zinc element. Then the ionic bond between oxygen and metal element is so weak that it is easy for oxygen vacancy to be formed. All these factors attributed to crystal surface to absorb the reducing gas and oxygen molecules in the atmosphere lead to enhancement of the gas sensitivity of the semiconductor of ZnO to reducing gas as follows [11]:

$$\begin{aligned} O_2(g) &\rightarrow O_2(ph) \rightarrow O_2^-(ch) \rightarrow 2O^-(ch) \\ &\rightarrow 2O_2^-(ch) \rightarrow 2O_2^-(lat) \end{aligned}$$

In summary, the ultra-fine ZnO with the particle size of 20 nm sensing materials were prepared from $Zn_4CO_3(OH)_6{\cdot}H_2O$ using roasted zinc-blended and sulfuric acid as starting materials at low cost *via* liquid chemical precipitation. The excellent gas sensitivity and selectivity was achievable at relatively low temperatures, and quick response and recovery properties were exhibited in the ethanol, circumstances that benefit from the ultra-fine particle size and appropriate element doping from the zinc ore mining debris.

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