

Synthesis of Nano-Germanium Oxid/SBA-15 Composite for Extremely Sensitive Semiconductor Gas Sensor

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Abstract: An easy way has been practical to make nano-Germanium oxid (GeO_2)/SBA-15 composites by damp impregnation of GeCl_2 by means of SBA-15 as the nanoporous sensor support. Following integration SBA-15 with GeO_2 , the mesoporous array of SBA-15 could still be well upholder. The sensor prepared of the nano- GeO_2 /SBA-15 composite display advanced sensitivities and the sensitivity to 1000 ppm of H_2 could be higher than 1300 which is almost 35 times extra sensitive than that of pure GeO_2 sensor. This judgment provides an inexpensive and effectual method to apply nanoporous materials to outstandingly improve the sensitivity of semiconductor metal oxide gas sensors.

Key words: GeO_2 , gas sensor, nano-germanium oxid/SBA-15, nanocomposites, mesoporous, array of labors

INTRODUCTION

From the time when the innovation of mesoporous silicates molecular strainer in 1992 (Kresge *et al.*, 1992), nanobased mesoporous materials have paying considerable attention for the reason that of their exceedingly pre-arranged pore structure as well as high surface area. A number of revisions have been intended at amending mesoporous materials in order to amplify the possible applicability of these materials (Xia *et al.*, 2000). Lately with the growth of semiconducting metal oxide gas sensors (Ashraf *et al.*, 2007), more labors are focal point on the research of mesoporous silica materials to amplify the assets of metal oxide gas sensors.

Numerous trails have been reported and comprehensived to the synthesis of a diversity of mesoporous metal oxides for gas sensing subsequent the discovery of MCM family of mesoporous silicates by means of supramolecular templating approach (Ramgir *et al.*, 2006), nevertheless, the majority of such mesoporous structured metal oxides were not steady after the elimination of surfactant and pore structure would fall down at high temperature (Michot *et al.*, 1998). A new way was to mechanically mixing with mesoporous material (Guo *et al.*, 2005) and the sensitivity of the mechanical mixture sensor to H_2 was improved about 4 times compared with that of pure GeO_2 gas sensor. Nevertheless, mechanical mixing could not give a uniform

dispersal of sensor component on the support. In current research, an easy chemical mixing way has been practical to get organized homogeneous nanosized GeO_2 /SBA-15 composites. GeCl_2 was chosen as the forerunner and SBA-15 as the nanoporous material. The sensors based on such composite illustrate much higher hydrogen sensitivity than those of pure GeO_2 sensor and the sensor prepared from a mechanical mixture of GeO_2 with SBA-15.

MATERIALS AND METHODS

Nanoporous SBA-15 material prepared as one literature procedure (Zhao *et al.*, 1998). Pluronic 123 triblock polymer ((EO)₂₀(PO)₇₀(EO)₂₀, Aldrich) was used as the surfactant and tetraethyl orthosilicate (TEOS, 98%, Aldrich) as the silicon source. After hydrothermal treatment in acidic condition, the sample was dried and calcined at 550°C for 10 h to remove the surfactant. For the preparation of GeO_2 /SBA-15 composite, 0.3 g of $\text{GeCl}_2 \cdot 2\text{H}_2\text{O}$ was dissolved in 20 mL of 0.2 N HCl solution. After stirring for 30 min, 0.3 g of SBA-15 was added to the solution and stirring was continued for another 6 h. The temperature was then raised to 100°C to remove water. Finally, the sample was calcined at 700°C in air for 4 h with a heating rate of 10°C min⁻¹ to oxidize GeCl_2 - GeO_2 . The sample is referred as GeO_2 (40% wt.)/SBA-15 where 40 wt% stands for the weight ratio of GeO_2 in the mixture. Pure GeO_2 in the absence of SBA-15 was synthesized using the same method. The N_2 adsorption-desorption isotherms measurements were performed on

quantachrome autosorb-1 analyzer. The XRD patterns were recorded on a SHIMADZU X-6000 X-ray diffractometer using Cu K α radiation as the X-ray source ($\lambda = 1.5418 \text{ \AA}$) with a scan speed of 2° min^{-1} . Sensors were fabricated by pressing the powder sample into pellet (10 mm in diameter and 1 mm in thickness) with 2 Pt wires embedded as electrodes. For Sensing test, the sensor was mounted into a specially designed quartz cell and the reducing gas used in this study was 1000 ppm of H $_2$. The sensitivity of the sensor is uttered as the ratio of the resistance of the sensor in air to the resistance of the sensor in H $_2$, i.e., $S = R_{air} / R_{H_2}$.

RESULTS AND DISCUSSION

Figure 1 shows the small angle XRD prototypes of unadulterated SBA-15 and GeO $_2$ (40% wt.)/SBA-15 composite. GeO $_2$ (40% wt.)/SBA-15 composite displays a very alike prototype as that of unadulterated SBA-15 with well resolved diffraction peaks which are indexed to the 100, 110 and 200 reflections of two-dimensional hexagonal mesostructure (Zhao *et al.*, 1998). The consequences point to that the attribute hexagonal mesoporous features of SBA-15 are still well maintained in the GeO $_2$ (40% wt.)/SBA-15 sample after mixing and calcination. Even though the greatness of (100) diffraction peak has reduced in GeO $_2$ (40% wt.)/SBA-15 composite, its 2θ angle is kept fairly constant.

The d-spacing which could be considered from the corresponding 2θ value does not budge, suggesting that the d100-spacing has not been affected by the incorporation with GeO $_2$. The wide-angle XRD prototype of GeO $_2$ (40 % wt.)/SBA-15 sample in Fig. 1 shows well-resolved diffraction peaks of the GeO $_2$ nanocrystals which can be indexed to a tetragonal structure (Hu *et al.*, 2002).

There is no new peak in the XRD spectra, representative that there is no new material formed. Furthermore, compared with the pure GeO $_2$ crystals synthesized in the absence of SBA-15, GeO $_2$ /SBA-15 has broader XRD peaks. The broad nature of the XRD peaks of GeO $_2$ (40 wt%)/SBA-15 show the attendance of very small crystallites of GeO $_2$ on SBA-15. This result advocated that SBA-15 not only acts as a support but also restrains the crystallite growth during calcination (Xu *et al.*, 2005).

Figure 2 shows the N $_2$ adsorption-desorption isotherms of pure SBA-15 and GeO $_2$ (40 wt%)/SBA-15 composite. GeO $_2$ (40 % wt.)/SBA-15 shows the same type IV isotherms with H1 hysteresis loops which are typical for nanoporous materials with two-dimensional hexagonal structures, indicating that the mesoporous structure could be retained. The BET specific surface area of SBA-15 is

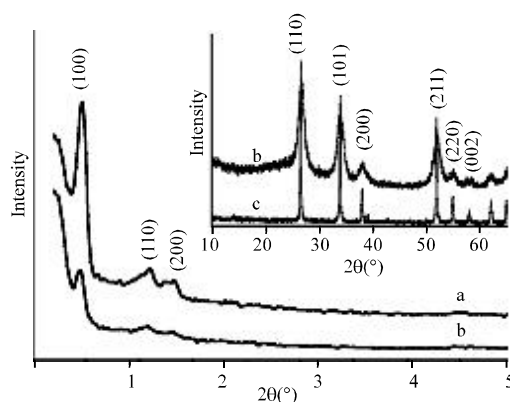


Fig. 1: XRD prototype of (a) SBA-15 (b) GeO $_2$ (40% wt.)/SBA-15 and (c) GeO $_2$

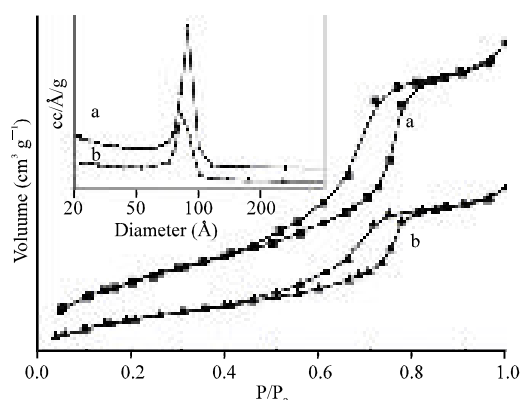


Fig. 2: N $_2$ adsorption-desorption isotherms and pore size allocation of (a) SBA-15 and (b) GeO $_2$ (40% wt.)/SBA-15

$850 \text{ m}^2 \text{ g}^{-1}$ and that of GeO $_2$ (40 % wt.)/SBA-15 composite reduces to $460 \text{ m}^2 \text{ g}^{-1}$. For the meantime, the pore diameter decreases from 86-81 \AA and total pore volume also decreases from 1.2-0.66 $\text{cm}^3 \text{ g}^{-1}$.

Since, the d100 spacing of SBA-15 has not been affected by mixing with GeO $_2$, the decrease of pore diameter indicates that the pore wall became thicker, showing that some GeCl $_2$ has entered into the mesopore of SBA-15 and nanocrystals of GeO $_2$ have been shaped and entrenched on the internal surface of nanoporous SBA-15 support (Xu *et al.*, 2005). Figure 3 shows the sensitivities of GeO $_2$ (40% wt.)/SBA-15 composite sensor and pure GeO $_2$ sensor to 1000 ppm of H $_2$. The utmost sensitivity of pure GeO $_2$ sensor to 1000 ppm of H $_2$ is 35. However, the sensing properties of nano-GeO $_2$ (40% wt.)/SBA-15 composite differ a lot. In fact, the GeO $_2$ (40% wt.)/SBA-15 sensor exhibits a much improvement of sensitivity to H $_2$, especially at 250°C where the sensitivity

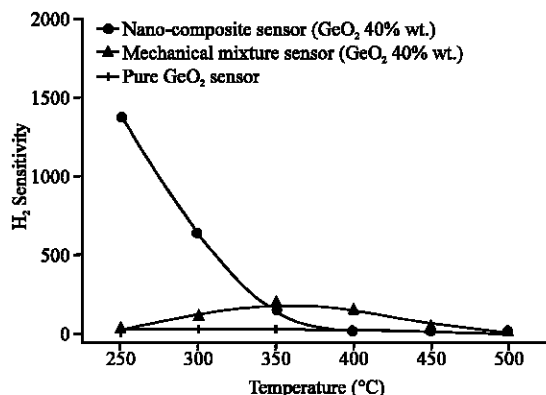


Fig. 3: Sensing property of the sensor equipped from GeO₂ with SBA-15

of the sensor to 1000 ppm of H₂ reaches as high as 1400, almost 40 times higher than that of the pure GeO₂ sensor.

It should also be renowned that the most favorable sensing temperature of GeO₂ (40% wt.)/SBA-15 sensor where the sensitivity is maximum is approximately 250°C which is lower than that of the pure GeO₂ sensor (350°C). For comparison, a mechanical mixture of GeO₂ with SBA-15 containing 40% wt. of GeO₂ is also prepared following literature method (Guo *et al.*, 2005) and the sensing property of the sensor equipped from the mechanical mixture of GeO₂ with SBA-15 is shown in Fig. 3.

It could be obviously seen that the sensor equipped from nano-GeO₂/SBA-15 composite possesses much higher sensitivity than that of the sensor equipped from the mechanical mixture of GeO₂ with SBA-15. This outcome shows the significance of preparation methods in authority the property of gas sensors as the GeO₂/SBA-15 composites sensor and the sensor equipped from the mechanical mixture of GeO₂ with SBA-15 have the same components but dissimilar gas sensing properties. It is well known that the conductivity of GeO₂ is mainly determined by the presence of singly charged oxygen vacancies.

When the reducing gas is introduced to the gas sensing system, it reacts with the surface oxygen ions and then the electrons are released to the semiconductor to increase the conductivity of the GeO₂ sensor. Since, SBA-15 is known to be a good adsorbent for gases (Senguttuvan *et al.*, 2006), GeO₂/SBA-15 composite would be able to adsorb more oxygen or hydrogen and promote the reaction between hydrogen and the surface adsorbed oxygen hence, increasing the amount of released electrons and increasing the sensitivity of the composite sensor.

Furthermore, since the sensitivity of the sensor is determined by the competition between surface adsorption and surface reaction (Ramgir *et al.*, 2006) and the adsorption of gases at lower temperature may be improved by the presence of mesoporous SBA-15, the optimum gas sensing temperature would shift to lower value.

Another probable motive for the improvement of the sensitivity of GeO₂/SBA-15 could be accredited to the presence of GeO₂ nanoparticles on GeO₂/SBA-15 composite materials since, the reduction of crystal size can cause a huge development of gas sensitivity (Senguttuvan *et al.*, 2006).

CONCLUSIONS

A lofty loading of nanocrystal GeO₂ supported on nanoporous SBA-15 material has been synthesized by a easy chemical mixing way. These GeO₂/SBA-15 composite gas sensors show extraordinarily improved sensitivities to reducing gases as contrast to that of the pure GeO₂ gas sensor. The consequences show the huge potential of use a material with high BET surface area and homogeneous nanopore as a sensor support to improve the sensitivities of semiconductor metal oxide gas sensor for prospect sensing claim.

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