Preparation of SnO_2Nanoparticles by an Electrodeposition-Based method for Use in Gas Sensor

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Abstract: A new electrodeposition-based method was introduced to prepareSnO_2 nanoparticles for use in resistive-type gas sensor. Different from most electrodeposition methods, the product formed in electrolyte rather than on the electrode was collected and used. This product was easier to be coated onto a substrate to construct a gas-sensor. After a calcination process, SnO_2 nanoparticle sensing film could form. To optimize the sensor, polyethylene glycol(PEG) was introduced in the electrodeposition process. It was proved thePEG modification wasan effective way to obtain SnO_2 nanoparticles with decreased working temperatureandincreasedsensing performances.

Introduction

SnO_2 is one of the most excellent semiconductive material in gas sensing materials. [1] It has many advantages, such as easy fabrication,environment-friendly, strong stability, etc. Electrodepostion is a common and effective fabrication method of various materials with specific morphologies.[2] However, the electrodeposited materials usually grow on a electrode, which obviously causes the difficulty in the supsquent constrution of a gas-sensor.To obtain a sensor, the electrodeposed materials must be scaped off and then coated onto a non-coductive substrate.[3,4]This is not only complicates the manipulation process, but also damages the morphology of the materials and the performance of the sensor.Here, a new electrodeposition-based method was introduced to prepare SnO_2 nanoparticles for use in gas-sensor. Electrodeposed nanoparticles were controlledto be formedand dispersed near the electrode in the electrolyte, and then they (rather than the particles on the electrode)were collected to be further used in constructing a gas-sensor. The morphology of the particles had little damage during the construction of the sensor, which was benefit to build a more reasonable relationship between the sensing performance and the morphology. Polyethylene glycol(PEG), asa surfacant, added in the electrolyte could lead to the formation of spherical SnO_2 nanoparticles. The obtained sensor exhibited more excellent sensing performances than the constructed from SnO_2 prepared without the asisitance of surfacant[5]. This method provides a new way to prepare sensing materials and a new idea for the use of electrodepostion technique in gas-sensor.

Experimental

The electrolyte was prepared by dissolving 0.135 g $SnSO_4{\cdot}7H_2O$, 0.255 g $NaNO_3$and 0.15 g PEG(Mw=400)in 30 mL 0.075 M HNO_3 aqueous solution.The electrodeposition was carried out at 5 mA in a cell consisting of a graphite anode and an ITO glass cathode.White product formed on the cathode and in the electrolyte near this electrode, simultaneously.1.5 hrs later, product in the electrolyte was separated by centrifugation and washed with distilled water. This product was called as PEG-SnO_2 because PEG was involved in the formation of it. To construct a gas-sensor, the

product was made into paste with deionized water,coated on a gas-sensing ceramic tubeand calcined at 400℃ for 2 hrs.The gas sensing test was carried on a WS-30A system (Weisheng Instruments Co., Zhengzhou, China).As a comparison, SnO_2product was also prepared by the same process, except for the addition of PEG in the electrolyte.

Results and discussion

According to the electrodeposition process, H^+ ions in the electrolyte were preferably reduced at the cathode, leading to a rise in the pH value near the electrode. Sn^{2+} would then be easily hydrolyzed to $Sn(OH)_2$ on the cathode and in the electrolyte. As shown in Figure 1, the XRD patterns of SnO_2 and$PEG\text{-}SnO_2$products directly obtained in the electrolyteshowed only a weak and wide peak at 26~32°, which should be attributed to the amorphous $Sn(OH)_2$. After calcined, the amorphous $Sn(OH)_2$ was transferredinto crystalline SnO_2.Peaksat26.1°,33.8°,and51.5°correspondtothe(110), (101), and (211) crystal faces of tetragonal SnO_2, respectively (JCPDS no. 41-1445).The similar XRD patters of the two products explained the addition of PEG have nearly no influence onthe crystal structure of SnO_2.

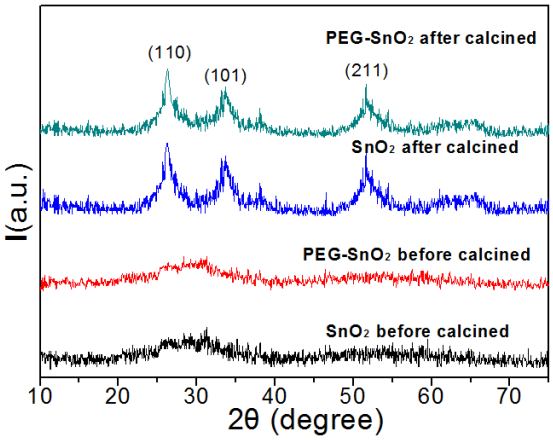

Figure1 XRD pattern of the $PEG\text{-}SnO_2$and SnO_2 products before and after calcined

After these products were coated onto the ceramic tube, nanoparticle films formed, as shown in Figure 2. For SnO_2 film, particles had sizes of about 100~300nm and irregular shapes before calcined(Figure 2a); after calcined (Figure 2b) almost all particles were endowed with spherical shapes but sintered into together and left a little ratio of spherical surfaces exposed.However, for $PEG\text{-}SnO_2$ film (Figure 2c), particles appeared nearly uniform spherical shapes. After calcined (Figure 2d) their spherical structure was changed a little, exposing more spherical surfaces. Obviously, PEG in the electrolyte promoted the formation of spherical $Sn(OH)_2$and the final spherical SnO_2particles. The reason might be explained as follows.In the electrodeposition process, PEG molecules would be adsorbed onto the $Sn(OH)_2$ nuclei and every crystalline plane of a nucleus would have the same growth rate, leading to isotropic growth of the crystal nucleus and the formation of spherical particles.During the subsequentcalcinations, in addition to the H_2O gas from the dehydration of $Sn(OH)_2$, more gases generated from the decomposition of PEG would prevent the sintering of particles and the spherical shape of particles would be kept better. At the same time, the decomposition of PEG might helpto the additional generation of porous structure.

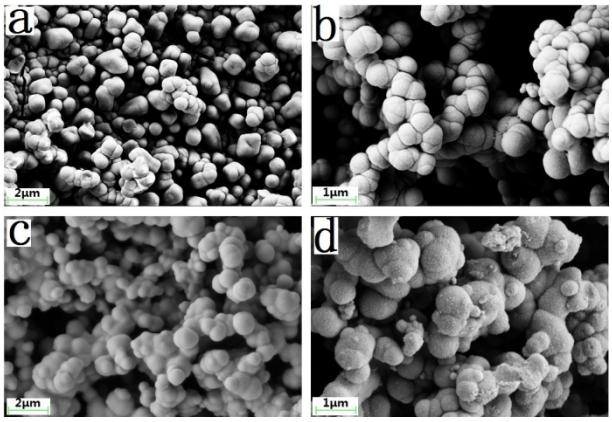

Figure 2 SEM images of SnO_2film before (a) and after(b) calcined and PEG-SnO_2film before(c)and after(d) calcined.

Both calcined SnO_2 and PEG-SnO_2 nanoparticle filmson the ceramic tubes wereemployed as resistive type gas sensors. The two sensors could rapidly response toethanol gas. Taken the detection of 50 ppm ethanol gas as an example, the sensitivity of the sensors at working temperature of 140-260 ℃ were recorded (Figure 3a).The optimum working temperature of the PEG-SnO_2 sensorwas thereby determined as 200℃,which was 20℃lower than that of the SnO_2 sensor. Moreover, the sensitivity of the PEG-SnO_2 sensor was always higher than that of the SnO_2 sensor at a same temperature. Figure 3b showed the response of the sensors to ethanol gas with concentration of 1-50 ppm at the working temperature of 200℃.Their response and recovery time were almost limited in the range of 10~15 s. The sensitivity of both sensors graduallyincreased with the increase of the ethanol gas concentration.For SnO_2 sensor, the sensitivity increased from 1.7 to 6.1, while for the PEG-SnO_2 sensor, it increased from 3.1 to 16. In detection of the gas with the same concentration, the PEG-SnO_2 sensor had the higher sensitivity, for example, in detection of 50 ppm gas (Figure 3c) three measurements always displayed the sensitivity of the PEG-SnO_2 sensor was around 2.7 times of that of the SnO_2 sensor. The higher sensitivity should be attributed to its specific morphology of the nanoparticle film shown in Figure 2. Due to the assistance of PEG, the prepared nanoparticles had more exposed spherical surfaces and might have additional porous structure, which increased the actual surface area and the sensitivity of the PEG-SnO_2 film.The sensor was stable, which could also be explained by the almost consistent sensitivity in three measurements. Moreover, the sensors had good selectivity in detection of ethanol gas, as shown in Figure 3d. By comparing with responses of the sensors to some other reductive gases, such as HCHO, CH_3OH, C_2H_5OH, NH_3 and CH_3OCH_3, the response to ethanol gas was obviously higher a lot. The PEG-SnO_2 sensor was superior to the SnO_2 sensor.

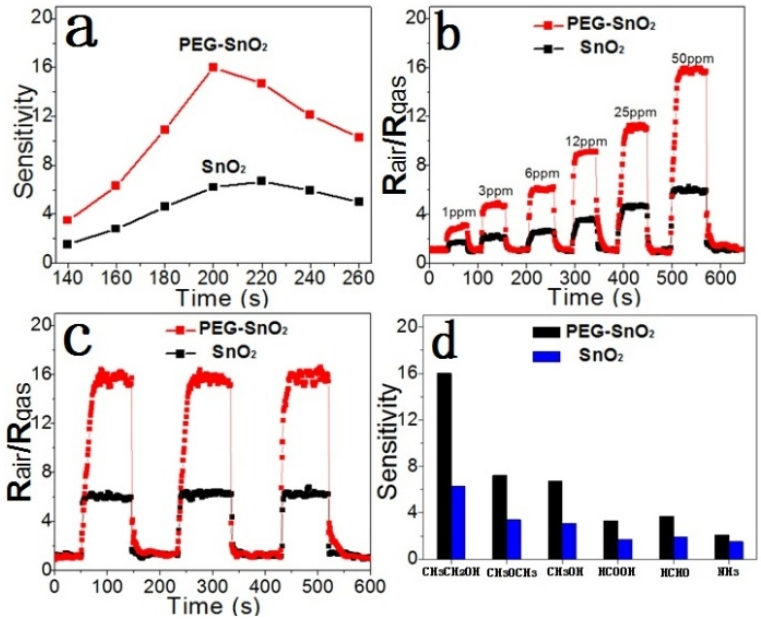

Figure 3 (a)Sensitivity of sensors in detecting 50 ppm ethanol gas at different working temperature;(b) responses of sensors to different concentration of ethanol gas; (c)the response of sensors to 50 ppm ethanol gas in 3 measurements test; (d) response of sensors to 50 ppm different gases.In obtaining the data of b-d, the working temperature was always controlled at 200℃.

Conclusions

In summary, PEG-SnO_2 and SnO_2 nanoparticles were prepared by an electrodeposition-based method. Amorphous $Sn(OH)_2$particles were firstly formed in the electrolyte and then coated onto ceramic tube to be transferred into corresponding crystalline SnO_2 nanoparticle sensing films by a calcination process. Both kinds of naonoparticles showed spherical shapes and the corresponding sensors exhibited excellent responses to ethanol gas. The detection limit concentration of the gas could reach as low as 1 ppm. Due to the assistance of PEG, the PEG-SnO_2 nanoparticle film displayed higher sensitivity, lower working temperature and better selectivity.

Acknowledgements

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