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Mesoporous SnO_2 sensor prepared by carbon nanotubes as template and its sensing properties to indoor air pollutants

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Abstract

An effort has been made to develop a kind of mesoporous SnO_2 gas sensor for detecting indoor air pollutants such as ethanol, benzene, meta-xylene. Mesoporous SnO_2 material has been prepared by sol-gel method joined into multi-wall carbon nanotubes as template. The field emission scanning electron microscope (FSEM) was used to characterize the samples, by which the mesoporous structure of SnO_2 was obviously observed. The investigation results suggest that the as-prepared mesoporous SnO_2 has a good response and reversibility to indoor environmental air pollutants. At last, the selectivity of the mesoporous sensor was investigated.

Keyword: mesoporous SnO_2, gas sensor, indoor air pollutants.

1. Introduction

In the past decades indoor pollution is one of the most crucial issues in the developing of economy. Indoor pollutants have led to many diseases, such as asthma, leukemia and chromosomal variation. The statistics implies that about 111 thousands people are died from indoor environment pollution every year. We have done lots of effort to deal with such problem, so the detection of indoor environment air pollutants is becoming a special need. The detection of indoor environment pollution is a quantitative measurement of environmental factor and concentration of indoor environment pollutes that are bad to health through intermittent or continuous form, using modern scientific techniques.

In environmental analytical chemistry area, many methods have been widely used such as gas phase chromatography (GC) [1], gas chromatography-mass spectrometry (GC-MS) [2-3], high-performance liquid chromatography (HPLC) [4, 5] and so on. However, these techniques require a complicated and tedious process and are time-consuming whereas they have many advantages. We need a simple, fast and high-sensitivity on-line

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detection device for the polluted gases. While, Gas sensor is one of the most effectual techniques and electronic devices for gas real-time monitoring.

Lots of materials such as conductive polymers and semiconductors have been developed as a sensitive film for the fabrication of gas sensor. Of which metal oxide semiconductors, including SnO_2, In_2O_3, TiO_2, ZnO, have been met with widespread interests due to broad and rapid target response. High sensitivity, rapid response and recovery, and selective detection are the most important parameters in designing semiconductor gas sensors. Tin oxide (SnO_2) is a typical n-type wide band gap semiconductor and has been widely utilized as a gas-sensing material. Nevertheless, the structure and morphology of SnO_2 sensitive film have significant effect on performance of the gas sensor. Recently a lot of researchers are paying close attention to SnO_2 nanostructure materials, such as nanoparticles [6-8], crystalline nanowires [9-12], nanobelts [13], nanorods, hollow spheres [14-16] and polycrystalline nanotubes [17, 18] or nanowires. More recently, mesoprous SnO_2 materials have attracted great research interest because of their large surface-to-volume ratio that can greatly facilitate gas diffusion and mass transport in sensor material. The mesoporous materials are considered to be promising host materials due to their highly-ordered pore structure and high specific surface area [19]. Moreover, a number of studies have been aimed to modify mesoporous materials in order to increase the potential applicability for gas sensor.

In our present work, we prepared a kind of mesoporous SnO_2 based on the template of Multi-wall carbon nanotubes which can detect indoor air pollutants including benzene, meta-xylene and ethanol. Otherwise, we also get some real-time curves for other volatile organic compounds (VOCs) to investigate the selectivity of the mesoporous SnO_2 sensor. Measurement results suggest that the as-prepared mesoporous SnO_2 sensor has many advantages such as high sensitivity, fast response and good reproducibility.

2. Experimental

2.1 Materials

Multi-wall carbon nanotubes (MWCNTs) with approximate diameter 20-30 nm were purchased from Chengdu Organic Chemicals Co. Ltd., Chinese Academy of Sciences. Tin(Ⅱ) dichloride ($SnCl_2 \cdot 2H_2O$) and ethanol were analytical grade and purchased from Shanghai Medicines Group Chemical Reagents Co., Ltd.

2.2 Purification of MWCNTs

The raw MWCNTs need to be purification before preparing SnO_2 mesoporous nanostructure. MWCNTs were calcined at 350°C for 2 h to remove amorphous carbon. The calcined MCNTs (1 g) were dispersed in 100 mL HNO_3 at the concentration of 7.0mol/L and via ultrasonic processing for 10 min, then refluxing at 120 °C for 12 h with stirring. The products were rinsed with deionized water until the solution was neutral, and finally dried under infrared lamp [20].

2.3 Preparation of mesoporous SnO_2 sensor

In the synthesis of mesoporous SnO_2 nanostructure, we adopted sol-gel method. In a typical process, 20 mmol $SnCl_2 \cdot 2H_2O$ were dissolved in 20 ml ethanol to form homogeneous mixture with stiring. Subsequently, 10 mg as-treated MWCNTs were dispersed in the previous solution by ultrasonication, then the mixture were heated to reflux for six hours with stiring. After that, place as-prepared products in oven at 60 °C for a while. We got the final solution followed by cooling to room temperature and keeping for 12 h to make it mature sufficiently. The as-prepared SnO_2/MWCNTs nanocomposites were coated on the outside surface of a ceramic tube directly and dried. The dried nanocomposites were calcined at 350 °C for 2 h and then heated to 650 °C and kept for 2 h with Ar as protection gas.

Fig.1 shows the structure of as-prepared gas sensor. Mesoporous SnO_2 is as the sensing materials that coated on the surface of a ceramic tube. Ni-Cr resistance wire is as heating wire and platinum wires are as electrodes.

2.5 Gas detecting system

The gas detecting system includes four parts i.e., carrier gas, sample evaporation chamber, detection and data transmission, as is shown in Fig.2. The high-pure air is carrier gas just as gas cylinder in the chart. The samples of the traditional SnO_2 sensor and the mosoporous SnO_2 sensor were placed in evaporation chamber. The evaporation chamber is connected to DC power as the heating system and picoammeter/voltage source as data acquisition device which is connected to a computer [21].

3. Results and Discussion

3.1 Morphology and structure of mesoporous SnO_2 materials

Traditional SnO_2 was prepared as follows: firstly, $SnCl_2{\cdot}2H_2O$ was dissolved into ethanol at the concentration of 1.0 mol/L. Then the solution was heated to reflux for 6 h. The subsequent treatment is programmed sintering to generate mosoporous structure. The as-prepared traditional SnO_2 materials and mesoporous materials were characterized by field emission scanning electron microscope (FE-SEM, Sirion200, operated at 5 kV). The FESEM images of them were shown in Fig.3. From the SEM images, the obvious difference can be found that the traditional SnO_2 particles are gathered and the size is relatively large, while the as-prepared mesoporous SnO_2 particles are felt each other and there are lots of mesopores on the film.

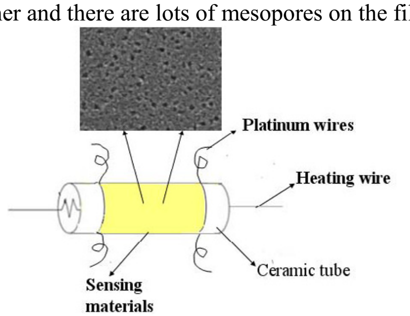


Fig.1. Structure of the mesoporous SnO_2 sensor.

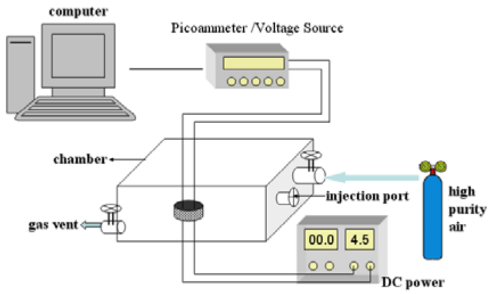


Fig.2. Schematic flow chart of the gas detecting system.

3.2 Comparison of the sensing properties between mesoporous SnO_2 and traditional SnO_2

We could discern significant differences, as shown in Fig.4. The comparison indicates SnO_2 mesoporous materials have better response to ethanol and benzene, especially benzene. In fact, the conclusion is true to other indoor environment-polluted gases. The key parameters to determine the gas sensing characteristics are thickness, permeability and surface morphology, while mesoporous structure has better permeability. During the response and recovery process, target gas molecules diffuse in and out of thin film of SnO_2 gas sensor. A diffusion equation assuming a first-order reaction of target gas is inducted to explain gas diffusion dynamics in the response process. The SnO_2 gas sensor is constructed by depositing a thin layer of the mesoporous SnO_2 material on a ceramic tube substrate. The molecules of sample gas diffuse into the surface of the mesoprous SnO_2 film and react with the surface oxygen of SnO_2 chains subsequently [22, 23]. The reaction of melecules occurs only on the out surface region of the traditional SnO_2 film. Since the SnO_2 mesoporous structure can increase response region and the inner parts become active, the mesoporous SnO_2 materials are more sensitive.

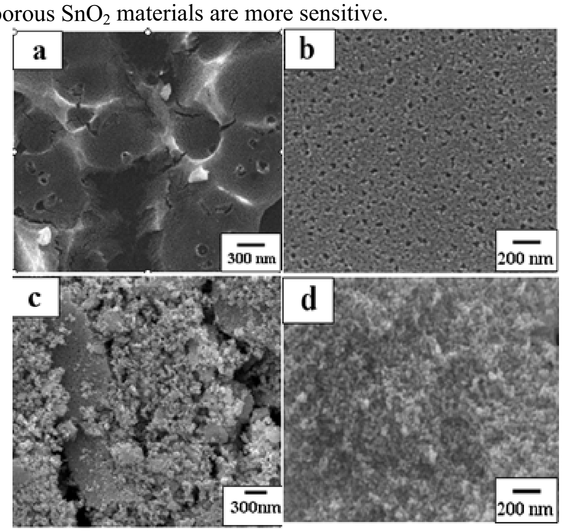


Fig. 3. FESEM images of (a), (b) the mesoporous SnO_2 and (c), (d) the traditional SnO_2 materials.

3.3 Gas sensing properties of mesoporous SnO_2 to indoor air pollutants

Fig.5 is the real-time response curves of the SnO_2 sensor upon exposure to different concentrations of ethanol. In the figures, two curves were putted in each picture in order to illustrate that the materials have better repeatability. The last is the plot of sensitivity *vs.* concentration. Generally, mesoporous SnO_2 sensor has a good linear response to ethanol.

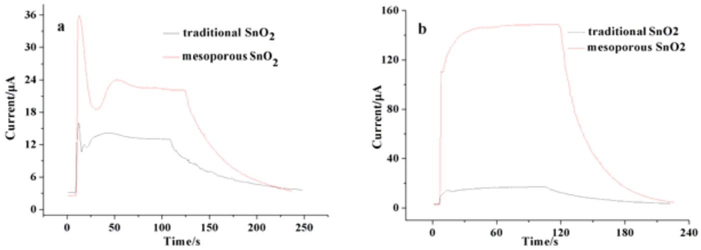


Fig.4. Response compares between the tradition SnO_2 sensor and the mesoporous SnO_2 sensor to (a) ethanol with concentration of 70 ppm (b) benzene with concentration of 280 ppm.

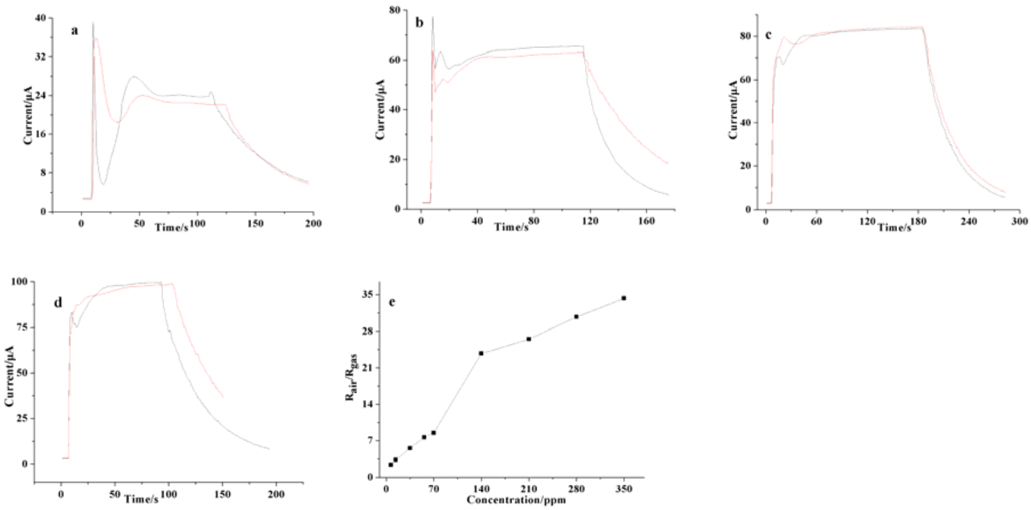
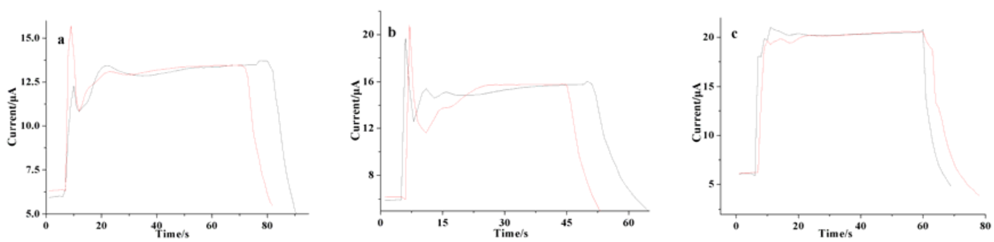


Fig. 5. Response curves of the mesoporous SnO_2 sensor to different concentrations of ethanol. (a) 73 ppm, (b) 146 ppm, (c) 219 ppm and (d) 292 ppm. (e) Plot of sensitivity *vs.* concentration.

Response curves of the mesoporous SnO_2 sensor to different concentrations of ethanol is shown in Fig.6, which are the curves of time-dependent changes of electric current. Benzene has less preferable response compared to ethanol at the same concentration. However, the response to benzene is quite obvious.



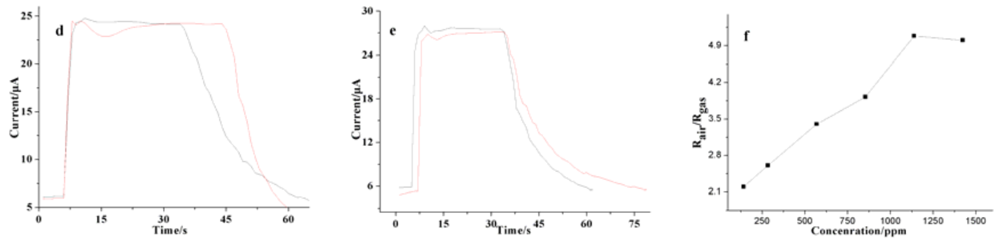


Fig. 6. Response curves of the mesoporous SnO_2 sensor to different concentrations of benzene. (a) 142 ppm, (b) 284 ppm, (c) 568 ppm, (d) 852 ppm and (e) 1138 ppm. (f) Plot of sensitivity *vs.* concentration.

Meta-xylene, which is an typical indoor air pollutant, is a homologue of benzene. The characteristic is also similar to benzene. The mesoporous SnO_2 sensor has a good linear response to meta-xylene just as the final curve in Fig.7. Good reproducibility can also be derived from the chart.

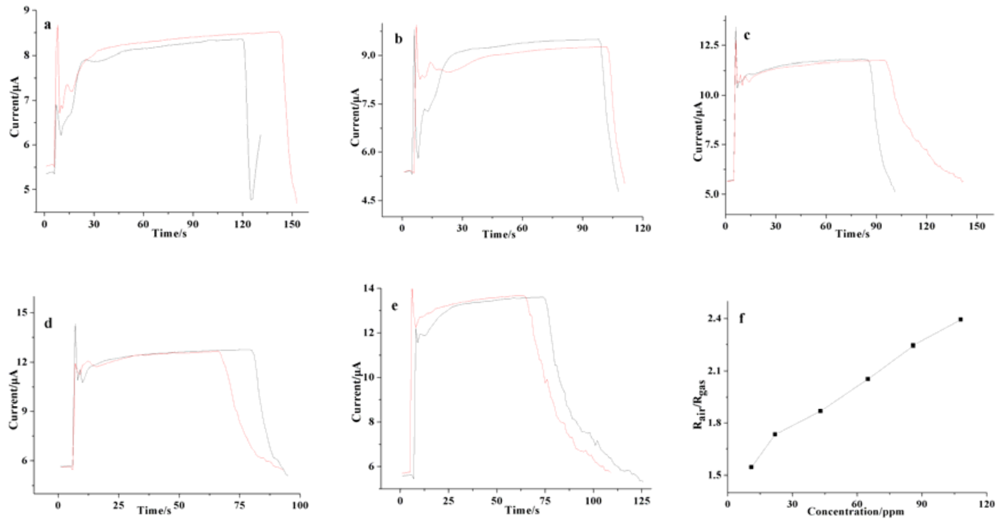


Fig. 7. Response curves of the mesoporous SnO_2 sensor to different concentrations of meta-xylene. (a) 10 ppm, (b) 20 ppm, (c) 60 ppm, (d) 80 ppm and (e) 100 ppm, (f) Plot of sensitivity *vs.* concentration.

Ammonia is a colourless, transparent and irritative liquid, which is an important chemical raw material and common reagent in chemical laboratory. In the housing construction process, ammonia may be generated because of building materials doped in expander and antifreeze agent that can produce ammonia. Ammonia is poisonous and irritating to nose, throat, and lungs if inhalation in body carelessly. It can cause the diseases of cough, shortness of breath, asthma and so on. In a word, ammonia as an indoor air pollutant is harmful to health. It is also noted from Fig.8 that the mesoporous SnO_2 sensor has a good response to ammonia.

3.4 Gas sensing properties of mesoporous SnO_2 to other volatile organic compounds (VOCs)

In order to explore the gas sensing properties, other VOCs including chlorobenzene, acetone, propyl alcohol, isopropanol were used for comparison as Fig.9. It may be concluded that the sensitivity of benzene, chlorobenzene and meta-xylene is similar. The results illustrate that the sensitivity of the sensor to ethanol is the highest, while the gas sensor is also sensitive to other VOCs.

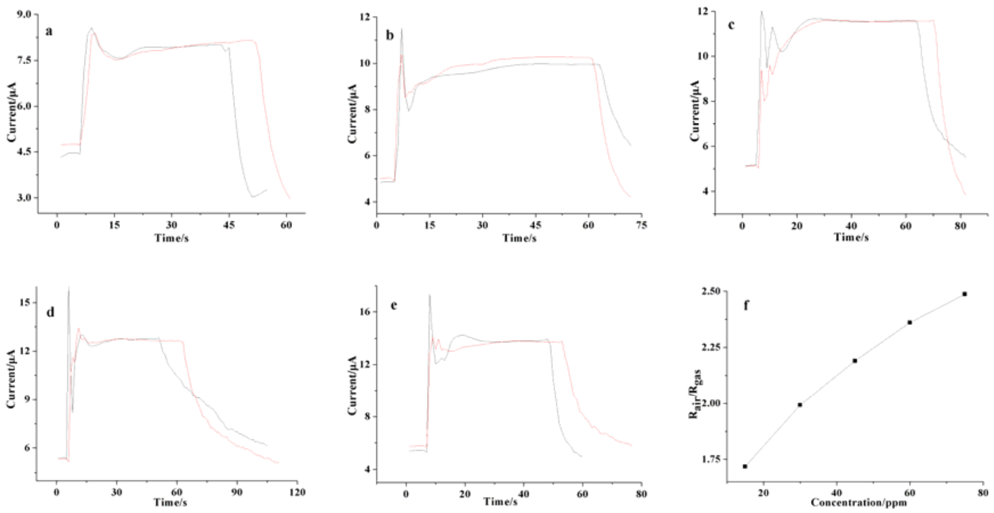


Fig. 8. Response curves of the mesoporous SnO_2 sensor to different concentrations of ammonia. (a) 15 ppm, (b) 30 ppm, (c) 45 ppm, (d) 60 ppm and (e)75 ppm. (f) Plot of sensitivity *vs.* concentration.

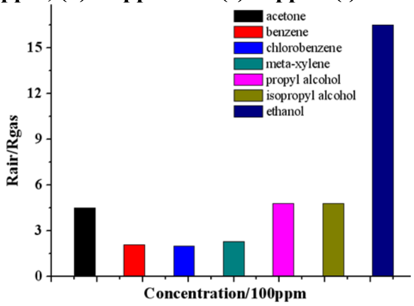


Fig. 9. Sensitivity of SnO_2 gas sensor to other VOCs at the same concentration of 100 ppm.

4. Conclusion

Mesoporous SnO_2 nanostructure was prepared by sol-gel process, using MCNTs with approximate diameter 20-30 nm as the template. Comparing to traditional SnO_2, mesoporous nanostructure has higher sensitivity and good repeatability towards the common indoor environment pollutants, especially to ethanol. The mesoporous gas sensors have potential applications in online monitoring of indoor air pollutants.

Acknowledgements

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