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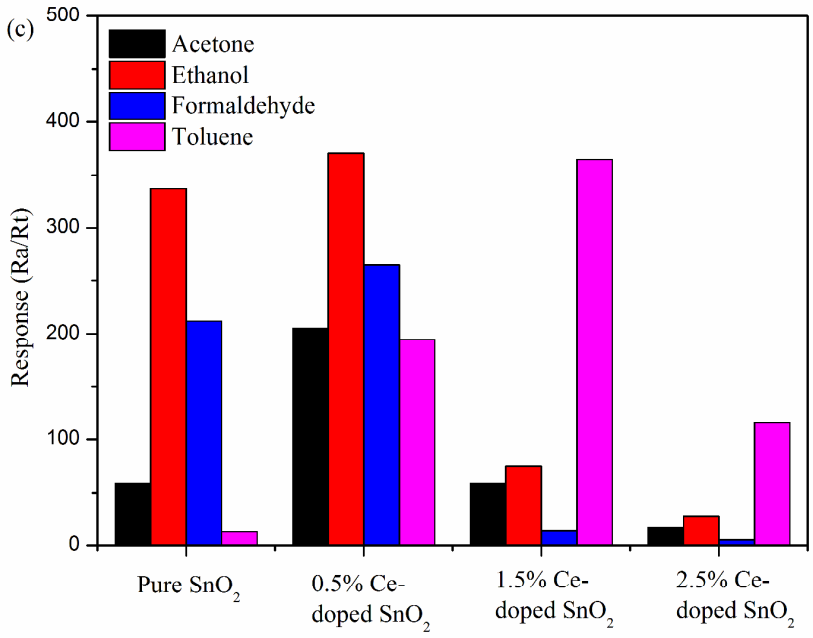

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Cite this: DOI: 10.1039/c0xx00000x

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ARTICLE TYPE

Highly sensitive and selective toluene sensor of Ce-doped coral-like SnO_2

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Received (in XXX, XXX) Xth XXXXXXXXX 20XX, Accepted Xth XXXXXXXXX 20XX

DOI: 10.1039/b000000x

Abstract: Coral-like SnO_2 nanostructure was synthesized via a simple hydrothermal treatment in the presence of glucose. The characterization results showed that the size of coral-like SnO_2 powders is about 13 nm with porous structure. The special surface area and the average size of pores are about 46.9 $m^2 \cdot g^{-1}$ and 7.61 nm, respectively. Subsequently, we investigated the gas-sensing properties of the sensors based on the coral-like SnO_2. We choose CeO_2 as a dopant and made three CeO_2 doped sensors with 0.5%, 1.5%, and 2.5% for the mole ratio of Ce to Sn. The gas sensing tests indicated that CeO_2 as the dopant can dramatically enhance the gas selectivity to toluene, and the sensor with 1.5% mole ratio showed the highest sensitivity to toluene at 190°C, which is much higher than to other VOCs gases such as ethanol, acetone, and formaldehyde. The efforts in the research have proved that the CeO_2 doped SnO_2 could be a promising candidate of highly sensitive and selective gas sensors for toluene.

Keywords: Sensors; Semiconductors; Porous materials; doping

Introduction

Toluene has potential to cause severe neurological harm as it is easily inhaled, ingested and absorbed by the skins of human being.[1] At present, toluene sensitive sensors can be categorized into organic semiconductor sensors, [2] metal oxide semiconductor sensors, [3-4] solid electrolyte type sensors, [5] optical sensors, [6] and bacterial biosensors, [7] etc. Among them, metal oxide semiconductor sensors could detect the concentration at ppm level, [8] and they are considered as the most promising materials due to their low-cost and reliability.

Among these metal oxides, SnO_2, a nontoxic and inexpensive n-type semiconductor, has been proved to be an excellent gas sensing material for detection of both toxic and combustible gases, such as CO, [9] H_2, [10] acetone, [11] and ethanol. [12] Although numerous efforts have been done to improve the gas-sensing performance of a single semiconductor, their properties are still limited by some shortcomings, such as high operating temperature, low sensitivity, poor selectivity and stability. Extensive studies have found many basic factors concerning the sensing properties of semiconductor gas sensors. (1) grain size of particles, [13] (2) microstructure of the sensing body. [14,15] (3) surface modification of particles. [16-17]

Recently, some researchers revealed that SnO_2 is also a very promising candidate to sensing toluene. Qi et al. found a kind of SnO_2 nanofiber, which are well selective to toluene at quite high temperature at 350°C. [18] Huang et al. synthesized porous flower-like SnO_2 and porous SnO_2 microcubes. They investigated their gas-sensing properties to volatile organic compounds (VOCs) [19-20] and found that both materials exhibited good responses to toluene. However, the selectivity was not satisfied. Doping as an efficient method to improve selectivity of gas sensor was widely used. Ceria as a dopant has received great attention due to its peculiar properties arising from the availability of the 4f shell. For example, Ce-doped SnO_2 nanomaterials have been used to improve ethanol response selectivity in presence of CO, LPG and CH_4. [21] Based on Ce-doped SnO_2 thin films, Fang et al. [22] prepared a high sensitivity H_2S sensor at room temperature. Nevertheless, there are few reports on the sensors based on Ce-doped SnO_2 for detecting toluene.

The paper focuses on the investigation of Ce-doped SnO_2 sensors for detecting toluene. A coral-like SnO_2 with a hollow architecture was prepared by using a facile wet-chemical approach integrated in an annealing process. [23] It is reported that nano coral-like architecture can provide many quick passages to absorb and desorb gas, which enhance gas sensing showing high response to several VOCs gas at low operating temperature. As expected, Ce dopant can improve response to VOCs gas. We made some sensors by doping CeO_2 to the coral-like SnO_2 and tested their sensitivity and selectivity to toluene. The results showed that CeO_2 dopant improved selectivity to toluene.

Experimental

The coral-like SnO_2 was prepared by hydrothermal treatment combined with an annealing process as we have reported in previous research paper. [24] The crystal structure and morphology of SnO_2 were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM) and transmission electron microscopy (TEM). The specific surface area and the average size of pores were obtained upon the multi-point Brunauer–

Emmett–Teller (BET) analysis of N_2 sorption isotherms recorded at 77 K with a Nova 2000e surface area and pore size analyzer.

Gas sensor was produced as a side heated structure. $Ce(NO_3)_3 \cdot 6H_2O$ ethanol solution was added to the as-prepared coral-like SnO_2 powder with CeO_2 molar ratio of 0.5%, 1.5% and 2.5%, respectively. And then ground until obtained a printable paste. The paste was afterwards transferred onto an alumina ceramic tube (4 mm in length, 1.2 mm in external diameter and 0.8 mm in internal diameter) on which Au electrodes and Pt wires have been fixed at both ends. After sintered at 400℃ for 2 h in a muffle furnace, A Ni-Cr heater strip with resistance of about 35 Ω was placed across the ceramic tube centre and welded to the element tubes to control the operating temperature. Finally, the element was aged at an operating temperature of 400℃ for 24 h to improve their stability.

Gas sensing properties were measured under room condition (humid range 30 - 60%) using a static test system made by Henan Hanwei Electronics Co. Ltd, which included a test chamber (about 18 L in volume) and a data acquisition/processing system. The resistances of sensors were measured via direct current bridge method. The operating temperature of a gas sensor was adjusted through varying the heating voltage, because each heating voltage has its corresponding operating temperature. The magnitude of the response in this paper was defined as S = Ra / Rt, where Ra and Rt are the resistance of the sensor in air and in tested gas, respectively.

Results and discussions

Structure and morphology

Fig. 1(a) is the XRD patterns of coral-like SnO_2 that all peaks correspond well to tetragonal rutile structure of SnO_2 (JCPDS card No. 41-1445). No other crystal phase is detected, indicating the high purity of the final products. The average particle size of coral-like SnO_2 is about 13 nm, which is calculated by Topas Soft ware package. [25]

The TEM and SEM images exhibit the product is coral-like morphology as shown in Fig. 1(b) and (c). The formation of the coral-like porous SnO_2 should be owe to $Sn(OH)_4$ colloid obtained by hydrolyzed Sn^{4+} on the surface of carbonaceous sphere which is conglomerated from small carbonaceous spheres by OH groups. [26]

The nitrogen adsorption–desorption isotherms and the pore size distribution curves of porous coral-like SnO_2 are shown in Fig. 1(d). The isotherm of the SnO_2 sample exhibits a hysteresis loop at the P/P_0 ranges of 0.69–0.98, which is associated with the filling and emptying of microspore by capillary condensation. The result clearly indicates that the coral-like SnO_2 sample exhibits a large textural porosity. The pore size distribution of the coral-like SnO_2 sample shows a peak in pore size region of 7-12 nm. The calculated pore-size distribution indicates that the material contains an average pore size of 7.61 nm. The BET surface area of the porous coral-like SnO_2 sample is calculated to be 46.9 m^2/g.

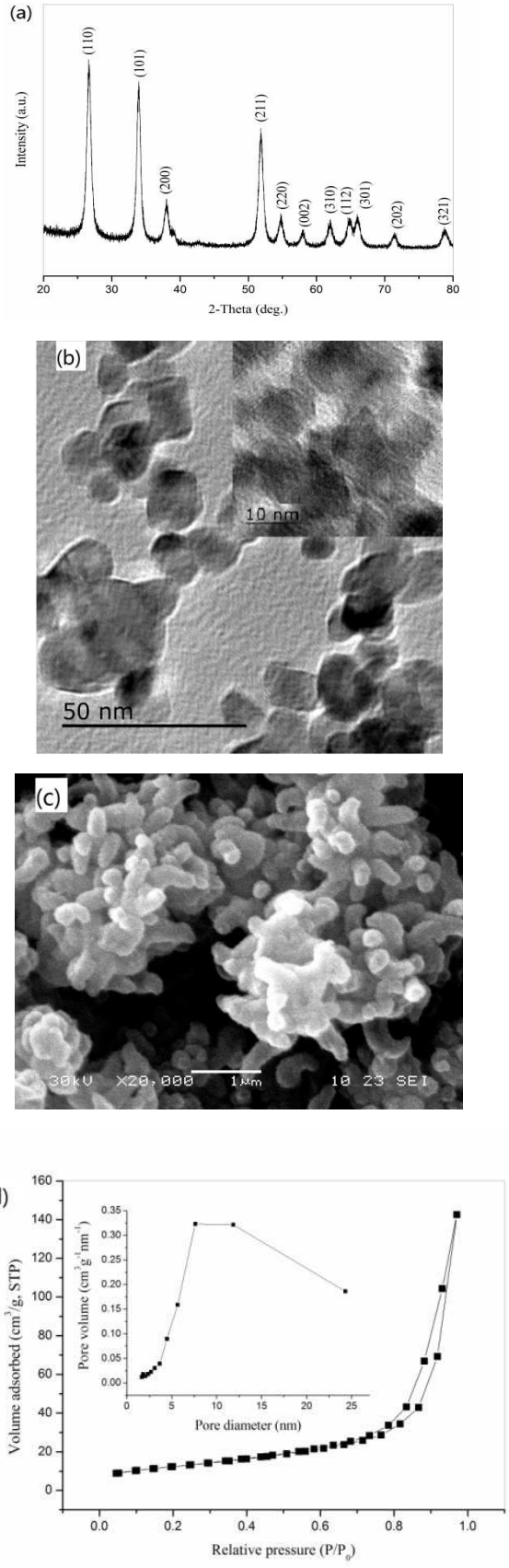

Fig. 1 XRD (a), TEM (b), SEM(c), and nitrogen adsorption isotherms and corresponding pore size distribution (inset) (d) of prepared coral-like SnO_2.

Gas sensing studies

The responses to 50 ppm toluene of the pure and CeO_2 doped SnO_2 sensors at different operating temperature are shown in Fig. 2(a). It is obvious that the response of pure SnO_2 sensor decreases with increasing operating temperature. The CeO_2 doped sensors exhibit high responses to toluene under temperatures 190°C and the corresponding responses are much higher than that of the pure SnO_2 sensor. The response value of sensor based on 1.5% CeO_2 doped SnO_2 was calculated to be 365 at 190°C, 28 times higher than the pure SnO_2. Therefore, 190°C was chosen as the optimum operating temperature for the following tests.

Fig. 2(b) shows the response curves of the pure and CeO_2 doped SnO_2 sensors to toluene with concentration from 5 to 100 ppm. It can be seen that the CeO_2 can dramatically improve the sensor response to toluene. Clearly, the dopant content has a great impact on the sensitivity of sensors, 1.5% CeO_2 doped SnO_2 shows the best gas sensing performance .

To further investigate the practicability of these sensors, the selectivity of the sensors was tested by exposing them to various 50 ppm gases, as shown in Fig. 2(c). Apparently, the responses of pure SnO_2 and 0.5% CeO_2 doped SnO_2 sensors followed this order: C_2H_5OH > HCHO > CH_3COCH_3 > $C_6H_5CH_3$. The only difference between them is that the sensitivity of the 0.5% CeO_2 doped sensor was higher than that of pure SnO_2, especially for toluene. When the dopant content further increased to 1.5%, the responses of the sensors to ethanol, acetone and formaldehyde decreased remarkably, however, the response to toluene was enhanced. The responses to all test gases were decreased when the CeO_2 dopant increased to 2.5%. Namely, the pure SnO_2 and 0.5% CeO_2 doped SnO_2 exhibited the low response and selectivity to toluene, the 1.5% and 2.5% CeO_2 doped SnO_2 showed high selectivity to toluene, the responses ratio of toluene to other interference gases were over 4. It is obvious that CeO_2 can catalyze the reaction of toluene with adsorbed oxygen. This has been confirmed by Barakat et al. [27] The sensor based on 1.5% CeO_2 doped SnO_2 exhibits the highest response to toluene.

The sensing mechanism of the CeO_2 doped SnO_2 sensor is based on the surface chemical reaction. The response of sensor derives from the change of electrical conductivity when the gas molecules react with adsorbed oxygen ion on the surface of SnO_2. CeO_2 dopant can improve the capability of oxygen adsorption. [18] When SnO_2 is doped by CeO_2, the number of adsorbed oxygen ion on SnO_2 surface increases, so the gas sensing reaction of gas molecules with adsorbed oxygen ions enhances, which results in the response value increase. But as the amount of CeO_2 increasing further, the adsorbed oxygen ions become excess and occupy the limited active sites at SnO_2 surface, which blocks test gas molecule such as ethanol, toluene contacting with active sites to react with oxygen ions, so the response value decreases. Owing to the two aspects of influence, there is an optimum doping amount. Due to the oxygen consumption of toluene larger than ethanol, acetone and formaldehyde, the optimum doping amount to toluene should more than that to ethanol, acetone and formaldehyde. The maximum response to ethanol, acetone and formaldehyde appears in the sensor based on 0.5% CeO_2 doping SnO_2, and the maximum response to toluene appears in 1.5% CeO_2 doping SnO_2.

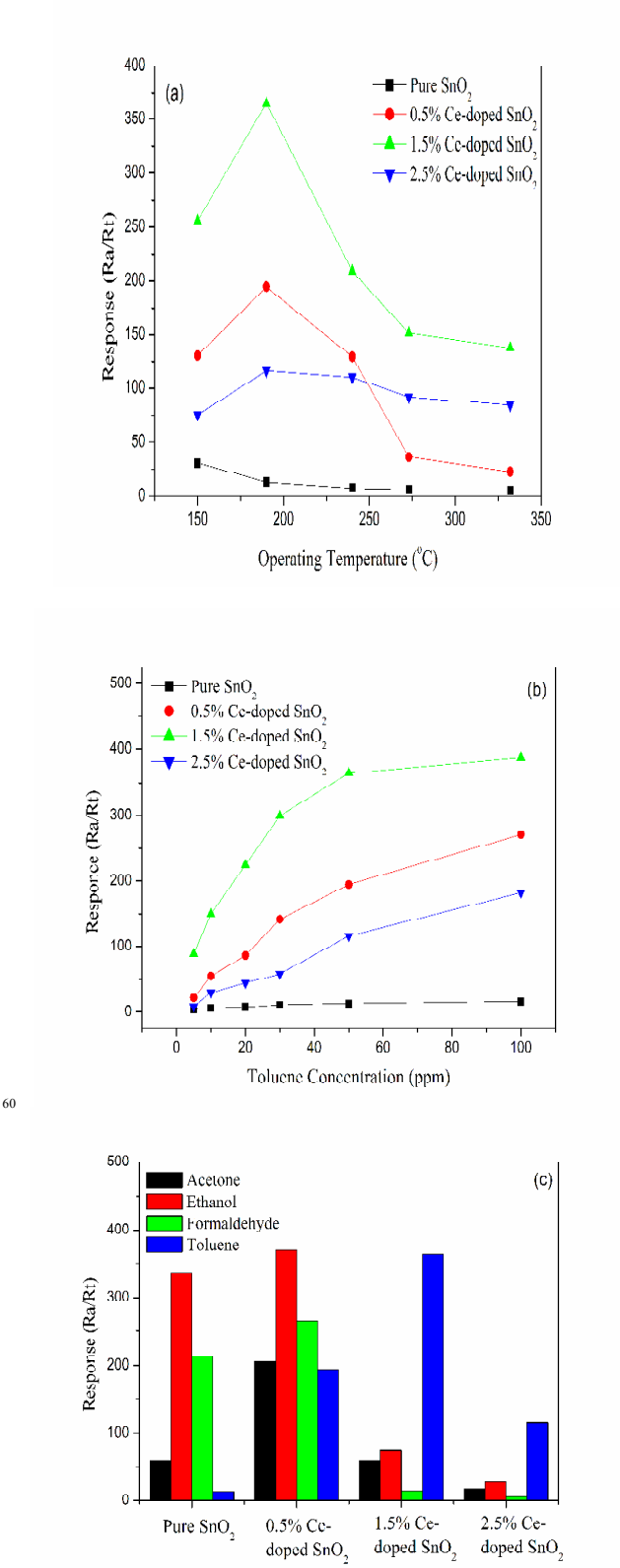

Fig. 2 Responses of the sensors to 50 ppm toluene at different operating temperatures (a); responses of the sensors to different concentrations of toluene at 190 °C (b); responses of the sensors to 50 ppm different test gases at 190 °C (c).

In addition, the sensors of pure and Ce-doped SnO_2 exhibited

good repeatability (Figure S1), reproducibility and long-term stability. The gas responses of the sensors were similar as that examined in two months, as shown in Fig. 3.

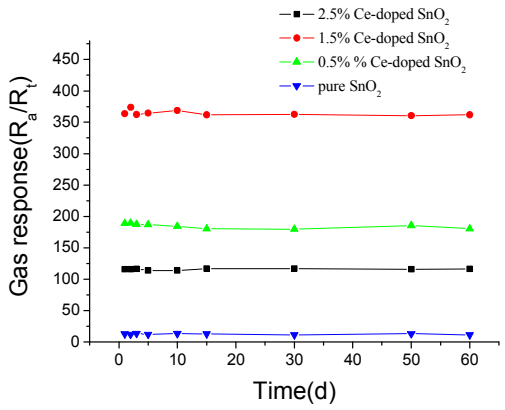

Fig. 3. Gas responses of pure and Ce doped SnO_2 sensors change as time changes at 190 ˚C to 50 ppm toluene.

Conclusion

The sensors based on CeO_2 doped SnO_2 were fabricated with different doping content of CeO_2, and exposed to various gases. The results indicated that CeO_2 dopant can dramatically enhance the toluene gas performances, CeO_2 seemed to be a potential addictive in fabricating toluene sensor as well as toluene catalyst. The results also revealed that CeO_2 content has a great effect in sensor properties. The 1.5% CeO_2 doped sensors showed the best gas sensing properties to toluene with relative high sensitive and selective, which is a promising toluene sensor.

Acknowledgements

The research was financially supported by the National Natural Science Foundation of China (21307035).

Notes and references

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