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Comparison of the enhanced gas sensing properties of tin dioxide samples doped with different catalytic transition elements

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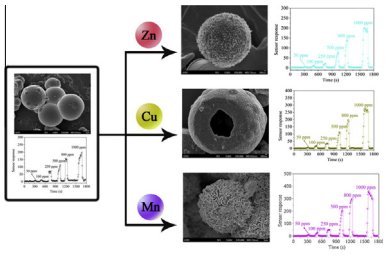
GRAPHICAL ABSTRACT



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ABSTRACT

In this work, non-doped SnO_2 samples, and SnO_2 samples doped with Zn(II), Cu(II), or Mn(II), having hierarchical microstructures, were prepared using an otherwise identical hydrothermal process, followed by annealing. The morphological and structural characteristics of the samples were systematically characterized by X-ray powder diffraction (XRD), field emission scanning electron microscopy (FESEM), transmission electron microscopy (TEM), Brunauer–Emmett–Teller (BET) measurements, and X-ray photoelectron spectroscopy (XPS). Ten gas sensors were constructed from each material, and compared as to detection of gas-phase ethanol, acetone, glacial acetic acid, methanol, and ammonia. The results indicated, for example, that SnO_2 containing 2.91% Mn dopant exhibited a 2.5-fold higher gas detection response toward ethanol at 100 ppm than that of the non-doped material. The fastest response time for 100 ppm ethanol was found for Cu(II)-doped SnO_2 (9.7 s), compared with 12.4 s for non-doped SnO_2. Graphs of sensor response versus operating temperature for SnO_2 containing different types and quantities of dopant exhibited quite different morphologies. The gas-sensing mechanism appears to involve reactions between the detected gases and the various oxygenous ions, such as O, O_2^-, and O^{2-}, present at the surface of the sensor.

1. Introduction

Gas sensors have attracted great interest and been extensively researched due to the widespread application areas of safety control requirements, environmental monitoring, detecting for inflammable (explosive or toxic) gases, chemical process control, medical and food quality analysis, and personal safety, etc. [1–5]. Metal-oxide

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semiconductors provide an appealing coupling of chemical, electrical, and optical properties that can be exploited in the design of gas sensors [6–9]. A prominent and well-studied example for metal oxide nanomaterials is tin dioxide (SnO_2), which is an important n-type wide-band gap (E_g = 3.6 eV, at 300 K) semiconductor with broad applications also in lithium rechargeable batteries [10], photocatalyst [11], and dye-sensitized solar cells [12].

Doping with extrinsic dopants is a facile and effective way to modify. The change in chemical, structural or electronic surface composition by doping provides many opportunities for creating surfaces with tailored physicochemical properties, for tuning the electronic properties of semiconductor material, and for enhanced detection of a target analyte. Hajati et al. reported graphene with a capability of gas sensing was shown to be drastically improved by inducing gentle disorder in the lattice through Ga^+ ion interaction [13]. Rare earth elements doping in metal-oxide semiconductors to improve gas sensitivity have been reported by Li et al. (Pr doped in SnO_2 [14] and Ce doped ZnO [15]), by Cheng et al. (Y-doped SnO_2 prismatic hollow nanofibers) [16], by Song et al. (Ce element doped in SnO_2) [17] and so on. In contrast, transition metals are abundant and can be cheap available. Transition metals ions are usually introduced into the nanomaterials due to increasing the available active site concentrations which are important factors in gas sensing performance. Indeed there is no shortage of published work concerning the catalytically active Zn (Cu or Mn) doped in SnO_2 or other semiconductor gas sensing material. Bohrer et al. [18] have reported the sensitivities of metallophthalocyanine (MPcs: M = Co, Ni, Cu, Zn, and H_2) chemiresistors to vapor phase electron donors and they found that the MPc sensor responses were correlated exponentially with binding enthalpy. Zn-doped SnO_2 nanorods or one-dimensional nanocones possess an enhanced gas sensing ability have been reported by Huang et al. [19] or Sun et al. [20]. Yang et al. [21] have reported their synthesized CuO nanoparticles (belongs to the p-type semiconductors) sensors are very sensitive to ethanol (EtOH) and can achieve strong and stable gas sensing signals. In coordination with the n-type SnO_2, the composite may provide desirable sensing property. Wei et al. [22] concerned the effects of Cu-doping on SnO_2 sensitivity toward H_2S and have studied it by means of the first-principles calculations based on the density functional theory. Ahmed et al. [23] have reported that gas sensing property of Mn-doped ZnO nanorods exhibited high sensitivity for oxygen detection as compared to un-doped ZnO. Rajeshwaran and Sivarajan [24] have studied the influence of Mn doping on acetone gas sensing properties of SnO_2 nanoparticles synthesized by a microwave technique.

As mentioned above that the selective doping of elements in semiconductor materials can extremely improve gas sensing activities. However, to the best of our knowledge, there is few comparative study of the sensing properties of several transition metals doped-SnO_2 in a published paper. It can be hardly discussed the effect of different elements doping on the gas sensing properties of SnO_2 or other semiconductors between numerous papers since the preparation methods and reaction conditions were dramatically different. This precludes predicting the final optimized functionality of gas sensing material by doping method.

In this research, pure and Zn (Cu/Mn) doped SnO_2 with hierarchical microstructures were synthesized via an easy and the same route. The microstructure and morphological properties of the as-synthetized a series of SnO_2 microspheres are analyzed by various characterizations. The comparative gas sensing tests of Zn, Cu, Mn and doped-free SnO_2 gas sensors were conducted. High sensitivity, fast response-recovery and a relatively good selectivity to EtOH are observed in our investigation. Finally, the gas sensing mechanisms of our sensors were also discussed.

2. Materials and methods

2.1. Materials and synthesis of hierarchical SnO_2 microstructures

All chemicals used in the facile hydrothermal process were analytically pure and used as received without any purification. In a typical synthetic procedure [25], 5 mmol $SnCl_2$ and 10 mmol sodium citrate ($C_6H_5Na_3O_7{\cdot}2H_2O$) were added into 40 ml of an EtOH–water mixture solution (20 ml EtOH and 20 ml deionized water) under vigorous stirring. Certain doping amount of zinc chloride ($ZnCl_2$; 0.99 at.%, 2.91 at.% and 4.76 at.%), copper chloride ($CuCl_2{\cdot}2H_2O$; 0.99 at.%, 2.91 at.% and 4.76 at.%) and manganous chloride ($MnCl_2{\cdot}4H_2O$; 0.99 at.%, 2.91 at.% and 4.76 at.%) were dissolved into the above solvents, separately. The vigorous stirring for each solution maintained for 1 h. After the stirring process, the solution was transferred to the 100 ml polytetrafluoroethylene-lined stainless autoclave, sealed, and heated to 180 °C for 12 h. After natural cooling to room temperature, the obtained product was washed with distilled water and EtOH sequentially. Finally, the products were annealed at 600 °C for 2 h with a heating rate of 6 °C min^{-1}. The undoped SnO_2 was denoted as S1 and the products obtained from the solution including $ZnCl_2$ (0.99 at.%, 2.91 at.% and 4.76 at.%); $CuCl_2{\cdot}2H_2O$ (0.99 at.%, 2.91 at.% and 4.76 at.%); $MnCl_2{\cdot}4H_2O$ (0.99 at.%, 2.91 at.% and 4.76 at.%) were denoted as S2, S3, S4; S5, S6, S7; S8, S9, S10, correspondingly.

2.2. Characterization

The crystal structure of our ten samples were characterized by X-ray diffraction (XRD) using a X'SPERT PRO diffractometer with Cu Kα radiation of 1.5418 Å wavelength at 2θ ranging from 20° to 80°. The images of Field emission scanning electron microscope (FESEM) were obtained on JSM-6701F with Au-sputtered specimens. Transmission electron microscopy (TEM, TECNAI G2 TF20), high resolution transmission electron microscopy (HRTEM) and selected area electron diffraction (SAED) patterns were also employed. X-ray photoelectron spectroscopy (XPS, PANnalytical MagixPW2403) measurement was carried out using the Al Kα line as the excitation source. The pore diameter distribution and surface area of the products were tested by the single point Brunauer–Emmett–Teller (BET) method through nitrogen adsorption/desorption analysis (ASAP 2010,USA Micromeritics).

2.3. Fabrication and gas sensing measurements of hierarchical SnO_2

The fabrication of gas sensor was given as follows: the SnO_2 and certain doping amount of selected element samples (powder form) were mixed with small mass deionized water to form a paste and then coated onto the outside surface of a ceramic tube. Then the sensors were aged at 350 °C for 2 h. Pair of Au electrodes and four Pt wires were previously installed at each end of ceramic tube with a diameter of 1 mm and length of 4 mm. A Ni–Cr alloy coil heating wire through the tube was employed as a heater to adjust the operating temperature (100–500 °C) by tuning the heating voltage. The structure of the sensor is further shown in Fig. 1a. The sensors were re-heated at different operating temperatures for about 1 h. The gas sensing measurements of all these sensors were conducted at the same time by the multichannel gas sensing platform, as shown in Fig. 1b. The high-precision gas sensing apparatus (WS-60A with a resolution ratio of 1 mV, Wei Sheng Electronics Science and Technology Co., Ltd.) was used to evaluate the gas sensing properties under a steady-state condition. The concise and basic electrical circuit for this instrument was given in Fig. 1c. V_c is the test circuit voltage, V_h is the heating voltage and V_{out} is the output voltage across the load resistance. The values of the sensor resistance can