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Architecture of designed hollow indium oxide microspheres assembled by porous nanosheets with high gas sensing capacity

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ABSTRACT

Gas sensing properties could be remarkably enhanced by self-assembly of zero, one or two dimensional nano-size units into three dimensional (3D) complicated superstructures. In this work, the 3D hollow indium oxide (In_2O_3) microspheres (HIOMs) assembled with porous 2D sheets were successfully synthesized by solvothermal method in Oleic acid (OA) and trioctylamine (TOA) system with the help of glycerine (Gl) combined with subsequent heat treatment. The density of self-assemble porous 2D nanosheet could be regulated by changing the calcination temperature from 400 °C to 600 °C. The gas-sensing performance of the as-prepared HIOMs had been measured towards unstable organic compounds containing methanol, acetone, ethanol, dichloromethane (DCM) and tetrahydrofuran (THF). Experimental results revealed that HIOMs-400 showed the highest response and selectivity to ethanol, followed by HIOMs-500 and HIOMs-600. At an ethanol concentration of 600 ppm, the HIOMs-400 sensor had a sensitivity of up to 15.6, while the sensitivity was about 11.9 for HIOMs-500 and 6.7 for HIOMs-600. HIOMs-400 also presented long term stability and repeatability even after five months. Such outstanding gas sensing properties of HIOMs-400 benefited from the larger BET surface area, denser pore structure and excellent capabilities of surface adsorbed oxygen.

1. Introduction

Gas sensors have drawn prominent attention by their use in medical diagnosis, air quality detection, and flammable or toxic gases monitor [1–4]. Owing to possessing simple structure, low cost and high sensitivity, metal oxide semiconductors as gas-sensing materials have great potential for practical applications [5–7]. Generally, the sensing mechanism of metal oxides is chemical interaction of the semiconductor surface with gas molecules, which result in changes in the conductivity of semiconductor. Therefore, it is a surface-controlled process [8,9]. At present, a lot of engineering and scientific research is being devoted to regulate the surface of metal oxide to improve their gas selectivity, sensitivity and response rate. There are mainly three ways of improving the gas sensing activity of materials: (1) tuning the porous structure can shorten the diffusion pathways and offer minimized diffusion resistance to target gases [10–12]. For instance, Yang group reported a generalized "immobilized crystallization in silica nanoreactor" strategy for the synthesis of mesoporous SnO_2 particles, which exhibited enhanced gas-sensing properties than the nonporous SnO_2 due to their higher surface area [13]. (2) regulating the crystal facets and surface-to-volume ratio of working materials can increase the active surface area [14–18]. For example, our group had recently reported that trapezohedral In_2O_3 nanoparticles exposed with high-energy {211} surface showed higher gas sensitivity than octahedral In_2O_3 with low-index (111) facet [19]. (3) chemical modification of metal oxides surface by finely dispersed noble metal clusters or other metal oxides can also increase catalytically active sites to the surface of the base material [20–22]. Blackman et al. prepared WO_3 functionalized with Au or Pt using aerosol-assisted CVD method, which improved sensing characteristics, in particular to H_2 [23].

Recently, special attention had been paid to improve the gas sensing by designing of 3D hierarchical nanostructures built by 1D

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nano-rods or 2D nano-sheets owing to the merits of large specific surface areas and the existence of porous structure composed of the adjacent units, which could increase the chance of contact the semiconductor surface with the gas molecules and enhance gas diffusion rate in sensing materials. Therefore, 3D hierarchical nanostructures are thought to be the most impactful materials for enhancing the sensing performance [24,25]. For example, Guo group synthesized 3D flower-like SnO_2 nanospheres by one step hydrothermal reaction, which exhibited a short response/recovery time and good sensitivity [26]. Furthermore, the 3D microstructures with a robust architecture could well bear long-term working under high temperature, which could enhance the stability of material [27]. Therefore, developing different methods to control synthesis of 3D hierarchical structures with different sizes and morphologies is highly advisable for further improving gas sensing applications.

Indium oxide (In_2O_3) is a n-type semiconductor with a wide band gap of 3.6 eV, and has been widely used in many areas, including nanoelectronics [28], ultrasensitive gas sensors [29], biosensing [30]. Particularly, In_2O_3 has been acknowledged as promising gas sensor materials for toxic and harmful gas to our health and environment owing to its high electrical conductance and the strong interaction with certain gas molecules [31]. The gas sensing performance of In_2O_3 sensors is based on their morphologies and structures [32–37]. Until now, In_2O_3 nanostructures with different shapes such as nanobelt [32], nanowire [33,34], nanocube [35,36] and nanoctahedron [37], have been obtained to improve the gas sensing properties by various synthesis methods. However, it is the still a great challenge to construct a chiseled 3D hollow hierarchical nanostructures based on 0D nanoparticles forming porous 2D sheets, because it is still difficult to precisely controlling the nucleation and growth of nanomaterials.

In this article, we firstly report two-steps method for the synthesis of 3D hollow In_2O_3 microspheres (HIOMs) assembled with 2D porous flakes by solvothermal method combined with subsequent calcination treatment. The HIOMs have been studied for different volatile organic compounds sensing, showing high sensitivity, outstanding long term stability and repeatability even after five months.

2. Experimental details

2.1. Chemicals

The synthesis of HIOMs was carried out using commercially available reagents. Oleic acid (OA, 90%), Indium (III) acetate ($In(OOC_2H_3)_3$), trioctylamine (TOA, 98%) were bought from Alfa Aesar, Glycerine (Gl, 99%) was purchased from Chinese Sinopharm Chemical Reagent Co., Ltd.

2.2. Preparation of in–precursors

In a typical synthesis, TOA (1.5 mL, 3.4 mmol), OA (0.67 mL, 2.4 mmol) and Gl (1.5 mL, 0.02 mol) were mixed to form a solvent at 25 °C in a round bottom flask, then Indium(III) acetate (0.1 g, 0.34 mmol) was added to the above solvent, and then completely dissolved under ultrasonic treatment. The final white solution was reacted at 320 °C for 30 min. Finally, we got the white precipitate and the product was obtained by washing it with ethanol and centrifugation for 6 times, then the obtained sample was dried at 50 °C for 12 h.

2.3. Preparation of HIOMs

The as-prepared In-precursors were put into a porcelain boat and then calcined at 400 °C, 500 °C, 600 °C for 5 h. The white samples were changed into the gray powders.

2.4. Characterization tools and gas sensing measurements

The composition and phase of the as-prepared products were acquired by the powder X-ray diffraction (XRD) pattern using a Panalytical X-pert diffractometer with CuKα radiation. The morphology and crystal structure of as-prepared products were observed by scanning electron microscopy (SEM, SU8100), and high-resolution transmission electron microscopy (HRTEM, FEI Tecnai-F20) with an acceleration voltage of 200 kV. All TEM samples were prepared from depositing a drop of dilute suspension in ethanol on a carbon film coated copper grid. Thermogravimentric analysis (TGA) was carried on a TGA-Q500 thermoanalyzer with a heating rate of 10 °C/min under nitrogen atmosphere. PHI QUANTUM2000 photoelectron spectrometer (XPS) was used to characterize the surface compositions of the products. The surface areas of these samples were measured by the Brunauer-Emmett-Teller (BET) method using nitrogen adsorption and desorption isotherms on a Micrometrics ASAP 2020 system. The Barrett-Joyner-Halenda (BJH) method was used to calculate pore size distributions.

BET method: Adsorption isotherm equation: $\frac{1}{v[(p_0/p)-1]} = \frac{c-1}{v_m}\left(\frac{p}{p_0}\right)+\frac{1}{v_m c}$

p and p_0 are the equilibrium and the saturation pressure of adsorbates at the temperature of adsorption, v is the adsorbed gas quantity, v_m is the monolayer adsorbed gas quantity, c is the BET constant.

Adsorption isotherm equation is in a convenient form, since a plot of $p/v(p_0 - p)$ against p/p_0 should give a straight line, whose intercept is $1/v_m c$ and whose slope is $(c-1)/v_m c$. Thus from the slope and intercept the two constants v_m and c can be evaluated.

$S_{BET} = \frac{v_m N s}{Va}$; N is Avogadro's number, s is the adsorption cross section of the adsorbing species, V is the molar volume of the adsorbate gas, α is the mass of the solid sample or adsorbent.

The Barrett-Joyner-Halenda (BJH) method:

$$r_p = r_k + t$$

$$V_{pn} = R_n \Delta V_n - R_n \Delta t \sum_{j=1}^{n-1} c_j A_{pj}$$

r_p is the largest pore size, which defined as a distance between walls of the pore.
r_k: the inner capillary radium within the physically adsorbed layer.
t: the multilayer thickness which is normally built up at pressure p.
V: the pore volume.

$$R = r_p^2/(r_{k1} + \Delta t_i)^2$$

ΔV: the desorption of a measurable volume of adsorbed gas with reduction in relative pressure.
Δt: is reduction in thickness of the physically adsorbed layer with reduction in relative pressure.
c: a constant value.

$$A_p = 2V_p/r_p$$