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Research Paper

Rapid sensitive sensing platform based on yolk-shell hybrid hollow sphere for detection of ethanol

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ABSTRACT

The sensing layer composited from the inorganic particles, organic materials, polymers could be regarded as an important and functional component used in electronic devices, such as chemical sensor. Furthermore, it is very important for these materials to own hierarchical and porous structures leading to a large effective specific surface area. Among these, hybrid materials with yolk double-shelled architecture can further realize the required surface chemical reactions. However, it is rarely reported in gas sensors. Herein, a novel SnO_2-TiO_2 hollow nanostructure consisting of double shells was successfully designed and synthesized. Due to the special multi-shelled structure and abundant hetero-interface, the sensing layer based on SnO_2-TiO_2 realizes a rapid response rate within 1.7 s to ethanol gas and alluring reproducibility (15 days), which are superior over those for compact structure with similar sensors. The results indicated that the SnO_2-TiO_2 yolk double-shelled microsphere have the huge potential for designing high performance practical ethanol devices in environmental monitoring and drunk driving.

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1. Introduction

Recently, a great challenge to human beings was posed based on environmental problems, such as environment humidity, dust, toxic and hazardous gases. So, the rise of chemical sensors (CSs) is very important for monitoring the environmental change in real time [1–3]. For this purpose, high-performance chemical sensors are needed to be applied in various fields [4]. However, traditional gas sensing layers such as SnO_2, ZnO, and α-Fe_2O_3, suffered from several obstacles, for instance, poor sensitive selectivity, low catalytic activity, high cost, ultra-high working temperature and low electron conductivity [5–9]. To meet the ever-increasing demand for high performance sensing devices, it is imperative to design and fabricate efficient sensing materials that could provide a high sensing activity and effective utilization rate of surface area.

As we know, the gas reaction and sensing performance are highly relied on the exposed surface area [10,11]. That is to say, a high specific surface area could achieve more effective active sites, leading to a higher sensitivity [12]. Hence, assembling tunable shell on the valuable core not only reduces the consumption of precious materials but also increases the dispersibility, functionality and stability [13]. Compared with the micro-sized particles, 0D structured nanoparticles possess the shorter diffusion length and larger gas-sensing layer contact area. However, the low catalytic activity of single-component usually leads to poor sensing activity. Furthermore, hybrid structured nanomaterials usually exhibit higher reactive activity [14–17].

Inspired by the concept, we design a new type of SnO_2-TiO_2 hybrid materials with yolk double-shelled spheres that were prepared by using resorcinol-formaldehyde (RF) without any other additional surfactants. Systematic studies indicated that RF can not only passivate the surface of metal oxide semiconductor (MOS) particles to avoid aggregating but also act as precursor to form RF resin, which reveals dual functions. In this study, ethanol sensing behavior was significantly improved through the design of SnO_2-TiO_2 yolk double-shelled heterostructure. The aim of this study is to explore morphological effects as well as ethanol sensing performance of SnO_2-TiO_2 nanocomposites with an especial emphasis on improving sensing response and ultrafast response.

2. Experiment

2.1. Chemical materials

Tin (II) sulfate ($SnSO_4$, 99%), titanium (IV) sulfate ($TiSO_4$, 96%), resorcinol ($C_6H_6O_2$, 99.5%) and formaldehyde solution (HCHO, 37–40%) were the initial chemicals without any further purification after received. Moreover, deionized water was also used in this experiment.

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2.2. Chemical synthesis

Preparation of SnO_2-TiO_2 yolk double-shelled microsphere: SnO_2-TiO_2 yolk double-shelled microsphere was prepared by a facile and simple template-assisted hydrothermal method with a slight modification [18]. Typically, 1.6 g of $Ti(SO_4)_2$, 0.86 g of $SnSO_4$ and 0.64 g $C_6H_6O_2$ were added into the mixed solution of 12 ml of deionized water and 1.6 ml of formaldehyde under continuous stirring. Then, the mixture was transferred into a 20 ml Teflon-lined stainless steel autoclave and heated at 85 °C for uninterrupted 48 h. The obtained product was collected from the cooling autoclave and washed for 4 times using deionized water. After dried for overnight at 60 °C, the powder was transferred to the muffle furnace and heating at 500 °C for 3 h at a rate of 5 °C/min.

Preparation of SnO_2-TiO_2 nanoparticles: Solid SnO_2-TiO_2 nanoparticles (NPs) were prepared by a facile hydrothermal method. Typically, 1.6 g of $Ti(SO_4)_2$ and 0.86 g of $SnSO_4$ were added into the solution of 12 ml of deionized water and 1.6 ml of formaldehyde under continuous stirring. Then, the mixture was transferred into a 20 ml Teflon-lined stainless steel autoclave and heated at 85 °C for uninterrupted 48 h. The obtained product was collected from the cooling autoclave and washed for 4 times using deionized water. After dried for overnight at 60 °C, the powder was transferred to the muffle furnace and heating at 500 °C for 3 h at a rate of 5 °C/min.

2.3. Characterization

X-ray diffraction (XRD) was used to identify the crystal structures of the as-synthesized materials using Cu Kα radiation (λ = 0.154 nm) on a Rigaku TTRIII X-ray diffractometer (40 kV). Field-emission scanning electron microscope (FESEM) and high-resolution transmission electron microscope (HRTEM) were used to observe the micro-morphology on a JEOL JSM-7500F microscope and Tecnai G^2 20S-Twin microscope, respectively. The composition of the as-synthesized products was tested using a PREVAC X-ray photoelectron spectroscopy (XPS) system. And Brunauer-Emmett-Teller (BET) was carried on a JW-BK132F analyzer.

2.4. Fabrication and measurement of the gas sensor

Indirect-heating structure sensor was used in this work to obtain sensing properties (Fig. S1). The typical fabrication process was described as follows: the as-synthesized composite powder was transferred to an agate mortar and mixed with deionized water to form a paste coated onto the surface of a tube, which is made from alumina. A pair of Au electrodes was printed on the each side of the tube and four platinum wires were installed at each end. A Ni-Cr alloy wire was inserted crossing the alumina tube and used to control the working temperature. Then, the tube was connected to a bakelite base. Next, the gas sensor was aged for 24 h in air in order to ensure the stability and repeatability. The response to target gases is defined as: $S = R_a/R_g$, where R_g is the electrical resistance in the target gas and R_a is the resistance in the atmosphere. And the response/recovery time was defined as the time cost of changes of 90% resistance. What's more, in this experiment, the sensor was tested under the around 33% RH environment.

3. Results and discussion

3.1. Structural and morphological characteristics

The smart designed of SnO_2-TiO_2 composite has been illustrated in Scheme 1. The yolk double-shelled morphology results from the following processes: (1) formation of Sn^{2+}-Ti^{2+}@RF composite spheres by polymerization of the resorcinol and formaldehyde along with the decomposition of tin and titanium salts; (2) combustion of polymeric component, decomposition or oxidation of the outer part of Sn^{2+}-Ti^{2+}@RF sphere into SnO_2-TiO_2 outermost shell and then subsequent contraction of the inner Sn^{2+}-Ti^{2+}@RF sphere; (3) repeated procedure (2). For obtaining hierarchical structure, the Sn^{2+}-Ti^{2+}@RF colloidal spheres were obtained mainly through the process of polymerization of resorcinol in a mixture of formaldehyde and deionized water. Firstly, emulsion droplets were formed by the hydrogen bonding of resorcinol, formaldehyde and water firstly. Then Sn^{2+}-Ti^{2+}@RF polymer colloidal spheres generally grow into the bigger size through ageing polymerization. However, the Sn^{2+} and Ti^{2+} ions are considered to continuously interact with anionic SO_4^{2-} in the absence of RF, resulting in solid and compact particles because of aggregation. It seems that resorcinol acted two major roles in this synthesis system: (1) It served as a surfactant active agent, which could stabilize the as-prepared Sn^{2+}-Ti^{2+} core-particles, as no additional surfactants introduced; (2) It could form the resorcinol-formaldehyde (RF) resin shell through reacting with formaldehyde around the core-particles in the meanwhile. Therefore, the gas sensor based on SnO_2-TiO_2 yolk double-shelled microsphere is expected to display high response and rapid response speed in comparison with SnO_2-TiO_2 nanoparticles because of the sufficient content volume and porous surface. In short, the porous yolk double-shelled structure is promising for gas detection in the efficient industrial applications.

After the hydrothermal process, the final product was obtained. The as-fabricated structure of Sn-Ti precusor was observed with a diameter of about 3 μm, as shown in Fig. 1(a). Fig. 1(b) presents the XRD patterns of the Sn-Ti precusor and SnO_2-TiO_2 yolk double-shelled microsphere. XRD results reveal that the crystal structure of hierarchical product was coincident with of tetragonal SnO_2 (JCPDS No. 41-1445) and rutile TiO_2 (JCPDS No. 21-1272) after calcination. However, in the pattern of Sn-Ti precusor, only the (101) and (200) peaks of TiO_2 NPs could be observed, which was probably caused by the low intensity of other peaks of SnO_2 NPs. The thermal decomposition of the as-synthesized precursors was investigated using Thermogravimetric Analysis (TGA) (Fig. 1(c)). The heat-treatment project during TGA analysis was described as follows: the as-synthesized precursor was heated to 800 °C at a heating rate of 10 °C/min. The small weight loss (~6%) till ~270 °C could be explained by the removal of residual solvent. Heating in air flow to 800 °C results in a weight loss of about 66.5% because of the removal of adsorbed water and polymer, which indicated that the loading amount of tin and titanium oxide was about 33.5% in the initial as-synthesized composite. Moreover, about 63% weight loss appeared at 470 °C, and that is very close to the weight loss of that at 800 °C. Thus, the calcination temperature was fixed at 500 °C, and it could be confirmed that the impurity and organic matter removed completely. The porous surface of the structure of yolk double-shelled microsphere has been observed after calcination which is beneficial for the gas sensing reaction. The SEM and enlarged SEM images (Fig. 1(d and e)) reveal that the microsphere consists of lots of irregularly nano-sized particles, which leads to a larger number of channels. The inner shell could be observed clearly from the broken microsphere in Fig. 1(f and g). And large space appeared between the inner shell and outer shell, which results in a high surface area of 71.9 m^2g^{-1}. In addition, the most pore size of SnO_2-TiO_2 yolk double-shelled microsphere is 3.7 nm (Fig. 1(h and i)).

TEM and HRTEM images with the analysis of elements by EDS mapping were recorded (Fig. 2(a–d, f–i) and S2). More interestingly, the obtained microsphere presents a yolk double-shelled structure (Fig. 2(a and b)). In addition, the structure of the exterior shell was also investigated by HRTEM image (Fig. 2(d)). As can be seen, the as-synthesized hierarchical microsphere with porous shell owns large amount of cavities. The shell was rough and composed of

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