One-step Synthesis and Gas Sensing Properties of Hierarchical SnO₂ Materials

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Abstract  Hierarchical tin oxide(SnO₂) architectures were synthesized with a facile hydrothermal method. In the hydrothermal synthesis, sodium dodecyl benzene sulfonate(SDBS) surfactant plays an important role as structure-directing reagent. The synthesized samples were characterized by powder X-ray diffraction(XRD), field emission scanning electron microscopy(FESEM), transmission electron microscopy(TEM) and high-resolution transmission electron microscopy(HRTEM). The results clearly reveal that the hierarchical architectures of SnO₂ were composed of aggregated nanosheets with a thickness of about 100 nm. A possible mechanism for the formation of the SnO₂ hierarchical architectures was proposed. In addition, the gas sensing properties of the as-prepared products were investigated and it was found that the sensor based on the special SnO₂ hierarchical architectures exhibited a high response and good selectivity to NO₂ at the optimal working temperature of 160 °C.

Keywords  Tin oxide; Hydrothermal method; Sodium dodecyl benzene sulfonate(SDBS); NO₂

1 Introduction

Gas sensors based on the semiconductor oxides play an important role in environmental monitoring, chemical process control and personal safety. Semiconductor oxides, such as ZnO, SnO₂, WO₃ and In₂O₃, which were widely chosen as gas sensing materials exhibit excellent sensing properties[1―6]. Among those materials, tin oxide(SnO₂) has been extensively studied due to its high sensitivity and good long-term stability[7]. Besides, it has many applications in other fields such as optoelectronic devices[8,9], transparent conducting electrode[10] and catalyst supports[11]. In particular, two-dimensional SnO₂ nanosheets have attracted much attention due to their remarkable receptivity variation in gaseous environment, excellent lithium storage capacity and cycle performance[12―14].

In this work, novel SnO₂ hierarchical architectures were synthesized with a facile hydrothermal process and the as-prepared products were illustrated in terms of the crystallinity, morphology and structure. Moreover, the dependence of the morphology on reaction time was investigated, and a possible formation mechanism was proposed. Finally, the gas sensing properties of the sensors based on the novel hierarchical SnO₂ to NO₂ were investigated.

2 Experimental

In a typical synthesis process, 0.644 g of SnSO₄(3 mmol) was dissolved in 30 mL of deionized water with vigorous stirring for 30 min, then 0.697 g of sodium dodecyl benzene sulfonate(SDBS, 2 mmol) was added in the solution. Having been stirred for 1 h, the mixed solution was transferred into a 50 mL Teflon-lined stainless steel autoclave. The autoclave was maintained at 120 °C for 8 h and then cooled down to room temperature naturally. The product was collected by centrifugation and washed with distilled water and absolute ethanol, and then dried at 80 °C for 12 h in air. Finally, the product was obtained by calcining at 600 °C for 2 h.

The gas-sensing properties of the samples were determined under laboratory conditions(room humidity: 50%±10%, (23±1) °C). The measurement was processed by a static process in a test chamber. Environmental air was used as both a reference gas and a diluting gas to obtain desired concentrations of target gases. When the response reached a constant value, the upper cover of the test chamber was removed and the sensor began to recover in air. The response of the sensor was defined as $S = R_a/R_g$ for oxidizing gas or $R_g/R_a$ for reducing gas, where $R_a$ and $R_g$ are the resistances of the sensor in the air and target gas, respectively. The response time and recovery time are defined as the time taken by the sensor to achieve 90% of the total resistance change in the case of adsorption or desorption, respectively.
3 Results and Discussion

3.1 Structural and Morphological Characteristics of Prepared SnO₂

The crystal phase of the calcined product was characterized by powder X-ray diffraction (XRD) analysis [Fig. 1(A)]. It can be seen from Fig. 1(A) that all the peaks of the sample could be well indexed to the tetragonal rutile structure of SnO₂ with lattice parameters of \(a=0.4738\) nm and \(c=0.3187\) nm, which are consistent with the standard data (JCPDS File No. 41-1445). No characteristic peaks from other impurities were detected, indicating the high purity of the product. Furthermore, the strong and sharp diffraction peaks suggest that the products are highly crystalline.

Typical scanning electron microscopy (SEM) images of the SnO₂ microspheres are shown in Fig. 1(B)―(D) with different magnifications. The low-magnification SEM image of the sample in Fig. 2(B) exhibits dispersed microspheres with ca. 20 μm in diameter consisted of 3D flower-like nanostructures, while the high magnification SEM image in Fig. 1(C) further reveals the flower-like nanostructures constructed from numerous nanosheets. The thickness of each nanosheet is estimated to be about 100 nm according to Fig. 1(D).

Further detailed morphology information of the product was obtained with transmission electron microscopy (TEM) and high resolution TEM (HRTEM). The typical TEM images of as-prepared SnO₂ products shown in Fig. 2(A) and (B) indicate that the size and shape observed in TEM images are similar to those in the SEM images. The HRTEM image [Fig. 2(C)] shows that the spacing between adjacent lattice planes is 0.3347 nm, corresponding to the (110) planes of SnO₂. The selected-area

![Fig.1 XRD pattern(A), low-magnification(B) and high-magnification(C, D) SEM images of the as-prepared SnO₂ sample](image)

![Fig.2 TEM image of the as-prepared SnO₂ sample(A) and typical TEM image(B), HRTEM image(C) and SAED pattern(D) of an individual SnO₂ nanosheet](image)