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Facile synthesis of SnO_2 hierarchical porous nanosheets from graphene oxide sacrificial scaffolds for high-performance gas sensors

Changhui Zhao[a,b], Huimin Gong[a], Weizong Lan[a], Rajendran Ramachandran[a], Hu Xu[c], Sheng Liu[b,*], Fei Wang[a,d,*]

[a] Department of Electronic and Electrical Engineering, Southern University of Science and Technology, Shenzhen 518055, China
[b] School of Power and Mechanical Engineering, Wuhan University, Wuhan 430072, China
[c] Department of Physics, Southern University of Science and Technology, Shenzhen 518055, China
[d] State Key Lab of Transducer Technology, Shanghai Institute of Microsystem and Information Technology, Chinese Academy of Sciences, Shanghai 200050, China

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ABSTRACT

Facile synthesis of metal oxide semiconductors with controllable and novel nanostructures has attracted tremendous attentions due to their crucial importance in gas detection. In this work, we report the design and synthesis of tin oxide hierarchical porous nanosheets (SnO_2 HPNSs) via a graphene oxide (GO) assisted hydrothermal route, where the GO flakes act as scaffolds and fluoride ions (F^-) act as etchant to control the attachment growth of SnO_2 nanosheets. Highly wrinkled SnO_2/reduced graphene oxide nanosheets (such as SnO_2/rGO-5.0 mg) have been achieved with a proper addition amount of GO powders. The wrinkled ultrathin nanosheets are subsequently converted to the SnO_2 HPNSs after annealing at 500 °C in air, which are composed of the network interconnected SnO_2 nanosheets (or nanoparticles). Moreover, the SnO_2 HPNSs based gas sensors exhibit greatly enhanced ethanol sensing performance, with high response (77.1–100 ppm) and good selectivity at an optimum operating temperature of 250 °C, compared with the bare SnO_2 nanosheets (4.0–100 ppm, at 275 °C). A possible gas-sensing enhancement mechanism based on this novel hierarchical architecture is discussed.

1. Introduction

Over the past decades, most attention has been focused on the novel nanostructures for high-performance gas-sensing materials based on metal oxide semiconductors (MOSs), especially for hierarchical architectures that are constructed by nanosized building blocks (such as nanowires, nanotubes, and nanosheets) [1–5]. In general, sensing materials with a well-designed nanostructure may provide unprecedented opportunities to enhance their properties. Efforts have been made to assemble these building blocks, including hydrothermal/solvothermal [6,7], vapour phase deposition [8,9], and template-assist/free routes [10–12]. Obviously, the introduction of templates to a hydrothermal process should be considered as one of the most reliable and controllable routes to achieve the preconceived nanostructures. In recent years, 2-dimentional (2D) graphene oxide (GO) has been used as a template for the deposition of MOSs because of its high specific surface area and abundant functional groups. Additionally, a series of nanosheets (such as TiO_2, MnO_2, Si, SnO_2, Fe_2O_3, NiO, and Co_3O_4, etc.) have been prepared using GO as sacrificial templates [13–17].

As a robust n-type material, tin oxide (SnO_2, E_g = 3.6 eV at 300 K) has received immense attention in the field of gas detection due to its easy synthesis process and high sensitivity to several gases [18–20]. Various SnO_2 based hierarchical architectures such as flower-like, urchin-like, and hollow micro- and nanostructures have been reported, with their advantages of high specific surface area and porosity [21–26]. It has been demonstrated that porous SnO_2 nanosheets (or the hierarchical architectures consisting of these nanosheets) present excellent gas-sensing performance. However, there are few wrinkles in the plane of these nanosheets, which just show a relative smooth or porous surface. Therefore, it is still interesting to design and synthesize a new type of nanosheet with a wrinkled surface that can form a 3D hierarchical architecture by itself. To our knowledge, there are few reports about the gas sensors based on these novel SnO_2 hierarchical porous nanosheets (HPNSs). As a non-layered metal oxide, it is hard to obtain ultrathin SnO_2 nanosheets by the exfoliation of performed SnO_2 products (an up-bottom method). Takenaka et al. have prepared a type of

* Corresponding authors.
E-mail addresses: victor_liu63@126.com (S. Liu), wangf@sustc.edu.cn (F. Wang).

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ultrathin SnO_2 nanofilms using GO as a template (a bottom-up method) [17]. Nevertheless, the metal alkoxides used in this route still has some limitations for practical application (due to its high-cost, time-consuming, and low-yield). Guo et al. have also studied a generalized strategy to obtain 2D metal oxide nanosheets by using GO flakes as templates [27]. Driven by this, a facile and controllable method should be developed to meet the demands for attachment growth of SnO_2-based building blocks (nanosheets or nanoparticles) on the surface of GO scaffolds.

In this work, we have proposed a GO-assisted hydrothermal route to synthesize highly wrinkled SnO_2/rGO nanosheets, where rGO flakes acted as sacrificial scaffolds. The effects of GO amounts and fluoride ions (F^-) on the morphology transformation of SnO_2/rGO precursors were investigated in detail, which also greatly affected the morphology and microstructure of the final SnO_2 products. As expected, SnO_2 HPNSs could be achieved by annealing SnO_2/rGO-5.0 mg precursors at 500 °C in air. Gas-sensing characterizations demonstrated that the SnO_2 HPNS-based sensors exhibited a significantly enhanced gas-sensing performance, which was mainly due to their novel 3D hierarchical porous architectures.

2. Experimental section

2.1. Materials

All chemicals were purchased in analytical reagent grade and used without further purification. GO powder was purchased from Nanjing XFNANO Materials Tech. Co., Ltd. In a typical hydrothermal process, stannous chloride dehydrate ($SnCl_2{\cdot}2H_2O$), sodium fluoride (NaF), and GO were used as precursors. Briefly, 0.643 g $SnCl_2{\cdot}2H_2O$ and 0.36 g NaF (F/Sn atomic ratio of about 3) were dissolved in 20 mL of deionized water. At the same time, various amount of GO powder (0.5, 1.0, 3.0, and 5.0 mg, respectively) was dispersed in 10 mL of deionized water with the aid of ultrasonic agitation. Then the above two solutions were mixed and stirred for 30 min, followed by transfer of the mixture to a 50 mL polyphenylene-lined stainless steel autoclave, and maintained in an oven at 180 °C for 24 h. After cooling down to room temperature, the black precipitates were centrifuged and washed three times in deionized water, and twice in absolute ethanol, and dried overnight at 60 °C in a vacuum oven. The preformed SnO_2/rGO precursors were noted as SnO_2/rGO-x, where x is the weight of GO powder. Finally, the rGO was removed by annealing the precursors at 500 °C for 2 h in air. The obtained products, in order, were marked as SnO_2-1, SnO_2-2, SnO_2-3, and SnO_2-4, respectively. For comparison, bare SnO_2 samples were also prepared with and without NaF under the same condition, respectively.

2.2. Characterizations

The crystal structures of the samples were recorded by X-ray diffraction (XRD, Rigaku Smartlab) using Cu-Kα radiation in the 2θ range of 10–80°. The morphologies of as-prepared samples were observed by a field emission scanning electron microscope (FESEM, Zeiss Merlin) and a high-resolution transmission electron microscope (HRTEM, FEI Tecnai G2 F30). Nitrogen (N_2) adsorption-desorption analyses were carried out on a Micromeritics ASAP 2020 analyzer at 77 K. The Brunauer–Emmett–Teller (BET) surface area was determined by the multi-point BET method using the adsorption data in the relative pressure (P/P_0) range of 0.05–0.30. Desorption isotherm was used to determine the pore-size-distribution by the Barret-Joyner-Halender (BJH) method. The surface chemical states of samples were identified by X-ray photoelectron spectroscopy (XPS, ESCALB 250Xi) with Mg Kα radiation.

2.3. Fabrication and measurement of gas sensors

Firstly, the obtained materials were mixed with a proper amount of ethanol to form a slurry, which was thereafter coated onto a thermally oxidized Si (SiO_2/Si) substrate with comb-like Cr/Au electrode arrays (Cr/Au fingers with 200 μm width and 200 μm spacing), as shown in Fig. 1a. After drying at room temperature, all coated sensors were annealed again at 400 °C for 2 h and aged at 300 °C for a week to improve their stability. Gas-sensing measurements were performed on a commercial CGS-4TPs system (Beijing Elite Tech CO., Ltd., China). Fig. 1b shows the digital pictures of the sensors and test bench, where the sensors were placed on an aluminium plate with controlled temperature and were connected by a pair of probes. During the test, the operating temperature was ranging from 150 to 300 °C at around 40% relative humidity (*RH*). The sensor response is defined as R_a/R_g, where R_a is the resistance of sensor measured in air and R_g in the target gases. The response/recovery time (t_{res}/t_{rec}) is defined as the time required for reaching 90% of the sensor resistance change in the case of the target gas in/out, respectively.

3. Results and discussion

3.1. Structures and morphologies

The crystal structures of samples before and after annealing at 500 °C were characterized by XRD. Fig. 2a shows the XRD patterns of the SnO_2/rGO precursors with different amounts of GO powders. All peaks can be well indexed to the rutile SnO_2 phase (JCPDS No. 41-1445). The peaks at 2θ of 26.4, 33.9, 37.9, 51.8, 54.8, 61.9, 65.9, and 78.7° are correspond to the (110), (101), (200), (211), (220), (221), (301), and (321) plane, respectively. No characteristic peak of rGO can be observed even in the curve of SnO_2/rGO-5.0 mg precursors, which is mainly due to the weak intensity of rGO. After annealing at 500 °C, all diffraction peaks in Fig. 2b become sharper. The appearance of four new peaks such as (111), (002), (112), and (202), (numbering from left to right), also implies an improvement in the crystallinity of the SnO_2.

To study the roles of GO scaffold in the SnO_2/rGO-x composites, Fig. 3a–h show the SEM images of precursors with GO powders in various addition amounts (0.5, 1.0, 3.0, and 5.0 mg). When a small amount of GO is added (Fig. 3a and b, SnO_2/rGO-0.5 mg), uniform flower-like architectures with an average diameter of about 4 μm are obtained (similar to the bare SnO_2 nanosheets in Fig. S1). All SnO_2/rGO-0.5 mg precursors are entirely made up of ultrathin nanosheets. When the amount of GO increases to 1.0 mg, the SnO_2/rGO-1.0 mg (Fig. 3c) precursors also present a flower-like architecture. With smaller but denser leaves, the adjacent flowers can attach to each other, which may be connected by the rGO flakes. From the enlarged SEM images (Fig. 3d), it can be seen that the size of SnO_2 nanosheets can be decreased significantly by increasing GO scaffolds. With further increase in the GO amount, the flower-like architecture is severely destroyed, only some small nanosheets can be observed (Fig. 3e and f, SnO_2/rGO-3.0 mg). Meanwhile, it is also hard to find some wrinkled nanosheets (until 3.0 mg GO was added), indicating that all of rGO flakes can be completely covered by SnO_2 nanosheets (which is further observed by TEM, as shown in Fig. S2). Fig. 3g and h exhibit the morphology of SnO_2/rGO-5.0 mg precursors with high-yield and highly wrinkled nanosheets, which is apparently different from the bare SnO_2 nanosheets. It should be noted that if the addition amount of GO is more than 5.0 mg (such as 7.0 mg, not mentioned in this article), the resultant precursors would be densely agglomerated during the drying process, which is assumed to be mainly caused by the excessive amount of rGO flakes (partially covered by SnO_2). In this situation, the surface of