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Thermal calcination fabrication of porous tin dioxide for new flexible ultraviolet photodetectors

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ABSTRACT

Porous tin dioxide (SnO_2) have been successfully synthesized by using in-situ thermal calcination precursors at different calcination conditions, including different calcination temperature, different calcination times, and zone heating. The as-synthesized SnO_2 samples were characterized by XRD, FESEM, TEM, UV–vis DRS and fluorescence spectrometry. Flexible photodetectors were then fabricated on PET (polyethylene terephthalate) substrate. The porous SnO_2-based flexible ultraviolet photodetectors have high flexible, lightweight, low-cost and high stability. Especially, the flexible device exhibits linear photocurrent behaviors and good sensitivity to ultraviolet light at wavelengths of 254 nm and 365 nm. Our result should be useful for creating high efficiency optoelectronic devices.

1. Introduction

Recently, tin dioxide-based nanostructures have got considerable attention due to their wide commercially used for environmental monitoring and protection, national defense, industrial and agricultural production, and so on [1–8]. Tin dioxide has a wide band gap (Eg = 3.6 eV, at 300 K) and a high exciton binding energy (1300 meV, at 293 K), is considered as a good material for lithium-ion batteries, solar cells, promising materials for gas sensing due to its cheap, nontoxicity, simple synthesis, high chemical and thermal stability, especially its excellent performance compared with other metal oxides [9–14].

Stimulated by its promising applications, there are many research activities devoted to the development of tin dioxide fabrication methods and revelent properties. So far, various tin dioxide nanostructures have been fabricated by different methods, such as hydrothermal method [12], precipitation method [13], vapor-liquid-solid process [14], solution-phase precursor route [15], microwave irradiation method [16], and so on. In the present work we have in-situ employed thermal calcination method to synthesize porous nanomaterials. Although the thermal calcination method is simple and inexpensive, yet the morphology of the nanomaterials can be modified by varying the reaction conditions to achieve the designed final samples. In addition to the reaction temperatures, hot calcination was another process which remain the morphology stable primarily of nanostructures. Calcination facilitates the movement of molecules and atoms through the mechanism of mass transport that may be surface diffusion, lattice diffusion and results in the grain growth which has influence on the properties of the nanomaterials. There are many papers that discussed the effect of calcination temperature and duration time on the size and relative properties of nanomaterials. For example, Prabhakaran et al. discussed the effect of calcination temperature on the structural, morphological, compositional and magnetic properties [17]. Saalinraj. S and his co-authors reported the nonlinear optical properties of TiO_2 nanoparticles calcined at various temperatures [18]. Nanoparticles of SnO_2 were synthesized through chemical route, and the calcination temperature effects the particle size and agglomeration were discussed by Singh et al. [19].

In the present work we report on the structural morphologies, electrical, and optical properties of tin dioxide by thermal calcination of as-synthesized porous tin sulfide nanomaterials at different calcination conditions. Influence of the various heating ways that control porous SnO_2 growth, including calcination

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temperature, calcination times, and zone heating, was discussed in detail. Additionally, the absorption activities, band gaps and photoluminescence spectra (PL) spectra of the prepared porous SnO_2 were tested. Besides, the successful fabrication of flexible ultraviolet photodetectors exhibited excellent photo sensing abilities toward 254 nm and 365 nm ultraviolet light, suggesting that this type of porous SnO_2-based device could be used in high-performance photodetectors and implantable optoelectronic devices.

2. Experimental section

2.1. Preparation of porous tin sulfide precursors

All chemicals used in the experiments are analytical grade, and they are used without further purification. The porous tin sulfide precursors were prepared by a simple polyol refluxing process. Briefly, appropriate amounts $SnCl_2$ and thiourea were dissolved in 50 mL ethylene glycol in a three-neck round bottom flask (equipped with thermometer and condenser). Stirring for 20 min, the flask was heated and kept at 160 °C for 1.5 h. The resulted dark precipitates were filtered, washed with distilled water and absolute ethanol thoroughly and finally dried in a vacuum oven at 60 °C for 3 h.

2.2. Synthesis of porous tin dioxide nanocrystals

Porous tin dioxide nanostructure were synthesized by a thermal calcination method using the tin sulfide precursors at around 350 °C - 450 °C to produce pure tin dioxide, with preserved morphology as the precursor(in Table 1). Finally, the white powders were collected for further characterization.

2.3. Characterization and photo-responsive measurements

Power X-ray diffraction patterns (XRD) of the as-prepared tin dioxide samples were obtained from an X-ray diffractometer (X′ Pert PRO, PANalytical B. V., the Netherlands) with radiation from a Cu target (Ka, $\lambda = 0.15406$ nm). The morphology and microstructure images were obtained with the field emission scanning electron microscopy (FESEM, JSM-6701F) and transmission electron microscopy (TEM, JEM-2010). The UV–vis absorption spectra were recorded on a UV–vis spectrometer (UV-2500, Shimadzu, measurement interval: 0.5 nm, resolution: 0.1 nm). Room temperature PL spectra were characterized by an HORIBA Jobin Yvon LabRAM Spectrometer HR 800 UV with the excitation wavelength of 325 nm.

The flexible ultraviolet photodetectors are fabricated to preliminarily measure the photoresponsive properties of the porous tin dioxide samples. In detail, a concentrated absolute ethanol and ethylene cellulose solution of porous tin dioxide samples was drop-cast on a flexible polyethylene terephthalate (PET) substrate and two deposited parallel silver wires severed as conductive electrodes ($Ag/SnO_2/Ag$ devices as shown in the inset of Fig. 6a, schematic illustration of a flexible SnO_2 ultraviolet photodetector as shown in Fig. 7a). Two LED lamps equipped with the output wavelength of 254 nm and 365 nm were used. Current-Voltage characteristics were recorded using a Keithley 2410-C.

3. Results and discussion

The representative morphologies and structures of the porous tin sulfide precursors were investigated by FESEM (Fig. 1a). The SEM images show that the porous products are constructed by many loose nanoflakes packed to each other without a clear center. Fig. 1b show the TEM and HRTEM images of the samples, which is corresponding to the SEM result and further exhibit the porous structure of the precursors. In addition, the lattice fringes of tin sulfide can be observed in HRTEM image (inset of Fig. 2b), a spacing of 0.40 nm can be seen, which correspond to the (110) plane of orthorhombic tin sulfide [20–22].

The Power X-ray diffraction (XRD) spectra of SnO2 products with calcination the porous tin sulfide precursors at different conditions are presented in Fig. 2a. All diffraction peaks in the pattern can be readily indexed to the pure tetragonal SnO_2 (JCPDS No. 41-1445, lattice constants: $a = b = 0.4738$ nm, $c = 0.3187$ nm). No peaks of any other phases are detected in this pattern, revealing that the crystal structure is pure tetragonal phase. The peak intensity of the samples increased with the increase of calcination temperature suggesting the enhancement in crystallinity.

The FESEM images in Fig. 2b and f shows the typical morphologies of the SnO_2 samples that in produced using the different reaction temperature and different reaction times. Fig. 2b, c and 2d show that the porous-like SnO_2 products still have the same structure as the tin sulfide precursors, the original morphologies were maintained. With the temperature increased, crystallinity of the samples become higher, but some broken porous formations have arisen (in Fig. 2e and f).

Based on the above morphologies and crystallinity result, we subsequently treat this as-prepared tin sulfide precursors at 350 °C for 1 h with a heating rate of 10 °C min^{-1}, then the temperature was further increased to 400 °C (450 °C for S7) at a rate of 10 °C min^{-1} and maintained for another 1 h (0.5 h for S7). Also in order to improve the crystallinity, we treat tin sulfide precursors at 380 °C for 6 h. The chemical composition of all calcined products are determined by XRD in Fig. 3a. All the diffraction peaks can be unambiguously assigned to tetragonal SnO_2 (JCPDS No. 41-1445). The relatively high peak intensities for those products indicate that the three samples are of high crystallinity. Fig. 3b and d shows the SEM images of as-prepared SnO_2 samples prepared at different calcination conditions, revealing structural perfection and uniform porous morphology for all of the products.

Obviously, at 400 °C, prolonging the calcination time was not

Table 1
Experimental conditions of the preparation of SnO_2 nanomaterials.

Sample No:	Oxidation temperature (°C)	Heating rate (°C/min)	Maintained time (h)	Oxygen flux (m^3/h)
S1	350	10	1	50
S2	400	10	0.5	50
S3	400	10	1	50
S4	400	10	2	50
S5	420	10	1	50
S6	350	10	1	50
	400		1	
S7	350	10	1	50
	450		0.5	
S8	380	10	6	50