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Short Communication

Study of blueshift of optical band gap in stannic oxide nanosheets by an uncharged surfactant mediated alcohothermal process

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ABSTRACT

Two-dimensional (2-D) nanostructures have attracted great attention in recent years. Herein, we report the synthesis of 2-D nanosheets of stannic oxide (SnO_2) via an uncharged surfactant mediated alcohothermal process, by using stannic tetrachloride pentahydrate, alkali base pellets (caustic soda), ethyl alcohol as a solvent, and poly (oxy) ethylene glycol-200 as a surfactant. The powder X-ray diffraction (XRD) study shows the formation of the tetragonal rutile phase SnO_2. The Fourier transform infrared (FTIR) study confirms the formation of Sn–O bond. The morphology and sizes of the SnO_2 powder have been studied by the scanning electron microscopy (SEM) analysis. A strong absorption peak was observed in the ultraviolet region at 335 nm from the optical absorption spectrum.

1. Introduction

Semiconductor metal oxide (SMO) nanostructures such as rutile, zincite, copper oxide and stannic oxide have been the subjects of scientific and technological attention due to their various physical and chemical properties [1–3]. Of these materials, SnO_2 nanostructures have many attractive optical properties due to the broad band gap, compared to the other SMO nanostructures [1–3], and hence could be used for optoelectronic devices, solar cells, alkali-ion batteries, and catalysts, etc. [3–5].

SnO_2 is an n-type semiconductor with a broad band gap (3.6 eV), and it has a tetragonal rutile structure [6]. Several efforts have been made in the preparation and characterization of 1-D (nanotubes, nanowires, nanorods and nanobelts), 2-D (nanosheets, nanoplatelets) and 3-D (nanoflowers) SnO_2 nanostructures by different methods [3–11]. Among them, 2-D SnO_2 nanostructures are specially very promising for photothermal applications, light emitting devices, solar cells, etc. [3,4,9–10]. The synthesis of different SnO_2 nanostructures by using various methods, such as gas phase condensation method, pulsed laser deposition, spray pyrolysis, and chemical bath deposition method has been reported in the literature [11,12]. These methods are complicated, and also very difficult to produce 2-D SnO_2 nanostructures. Therefore, new methodologies are in great demand for the synthesis and production of 2-D SnO_2 nanostructures. Of all the synthetic methods, hydrothermal and /or alcohothermal is a better alternative with the advantage of simplicity and low cost, and there is no need for a special instrument or special conditions like an inert gas atmosphere [4,8–11].

Different surfactant-assisted 2-D SnO_2 nanostructures have been prepared by different methods, and their structural and optical properties investigated by many researchers [9–11]. The formation of SnO_2 nanostructures was mainly attributed to the presence of surfactants, and many different formation mechanisms were proposed [5,9–11]. It is noted that charged (cationic or anionic) surfactants are usually used in the reaction systems, and they all play critical roles in the morphological control of SnO_2 nanostructures.

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However, the use of cationic or anionic surfactants will inevitably increase the reaction complexity, and are disadvantageous from the viewpoint of green chemistry [5,9–11]. Thus, the development of a facile, effective, and uncharged surfactant-simple approach for the controlled synthesis of SnO_2 nanostructures is highly desirable [6,11]. It is well known that POEG (nonionic surfactant), as a kind of capping polymer material, usually acts as a surface modifier or steric stabilizer, and it could be easily adsorbed on the surface to confine more than one direction of the growing translucent metal-oxy precursor solution, if the amount of such polymers is increased a little [11].

In the present work, we have prepared stannic oxide (SnO_2) nanosheets by using stannic chloride ($SnCl_4.5H_2O$), caustic soda (NaOH) and poly (oxy) ethylene glycol (POEG-200) in ethyl alcohol (C_2H_5OH) as a solvent via alcohothermal synthesis, and investigated the characterization of these nanostructures by the XRD, FTIR, SEM and UV–visible absorption analysis.

2. Experimental

1 g and 0.40 g of $SnCl_4 \cdot 5H_2O$ and NaOH pellets were separately dissolved in 20 mL of C_2H_5OH. The stannic oxide precursor solution was prepared by mixing the two solutions after few minutes of vigorous stirring. Subsequently, 5 mL of POEG-200 was added to the stannic oxide precursor solution under stirring after 30 min, and it was transferred to the Teflon stainless steel autoclave maintained at 180 °C for 20 h at a ramping rate of 5 °C/min. The resultant precipitate was washed several times with distilled water and dried in a vacuum at 60 mmHg for 4 h.

The prepared sample, characterized by the powder XRD pattern, was collected on a Schmadzu model XRD 6000 with CuKα radiation ($\lambda = 1.5417$ Å). The functional groups were identified by the FTIR spectra (Nicolet 305 spectrometer). The morphological studies were carried out by the SEM (JOEL-JEM-2010). The optical properties were studied by the UV–visible absorption spectra (Varian cary 5E spectrometer).

3. Results and discussion

The crystal phase of the SnO_2 powder was characterized by XRD as shown in Fig. 1a. All the diffraction peaks have been identified. The observed reflection planes (110), (101), (200), (210), (211), (220), (002), (310), (112) and (300) in the XRD pattern, matched well with the previous literature on the tetragonal rutile phase of SnO_2 (JCPDS No. 41-1445) [11]. No other crystalline peaks such as stannous oxide and metallic tin were observed from the XRD pattern; this indicates the high purity of the prepared sample. Moreover, the strong and sharp peaks (Fig. 1a) reveal the well crystalline nature. The FTIR spectrum of the SnO_2 is shown in Fig. 1b. It shows the weak absorption peaks at ~1630 and ~3400 cm^{-1} that reveal the presence of H_2O and OH functional groups, respectively [6]. The broad band between 450 and 790 cm^{-1} is attributed to the tin–oxygen (Sn–O) bond in SnO_2 [5,6,9]. The presence of weak peaks at ~1119 and ~2990 cm^{-1} is attributed to the stretching mode of C–O–C [13]. These absorption peaks must be caused by POEG molecules absorbed on the surface of SnO_2 nanostructures [13].

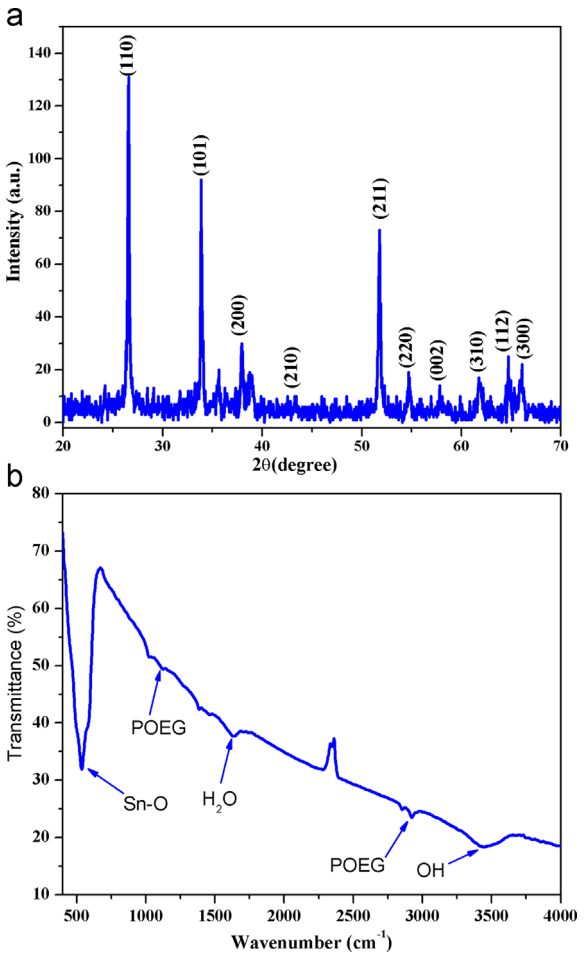

Fig. 1. (a) XRD pattern. (b) FTIR spectrum of the SnO_2 powders.

The morphology and average size of the SnO_2 is examined by the SEM analysis, as shown in Fig. 2a. It reveals the obvious sheet-like morphology. It is considered, that 2-D structures are effective in mitigating the agglomeration between nanostructures, and might be promising SnO_2 material in nanosheets form for optical and gas sensing devices [3,4]. Further, the observed SnO_2 nanosheets had an average length of ~150–260 nm and thickness of ~10–20 nm. The schematic formation of the SnO_2 nanosheet is shown in Fig. 2b. In our experiment, after mixing the two solutions containing $SnCl_4$ and NaOH, the precursor $Sn(OH)_4$ nuclei were formed by the translucent Sn^{+4} cations with OH^- anions. During the nucleation process, the POEG-200 molecules on the surfaces of the cylindrical droplets are adsorbed on to the surface planes of the formed $Sn(OH)_4$ nuclei, and they were transferred to the autoclave maintained at 180 °C for 20 h, subsequently dried in a vacuum at 60 mmHg for 4 h to lead to the formation of SnO_2 nanosheets [9,11]. Shen et al., [6] have reported a hydrothermal method for the preparation of nanocrystalline spherical SnO_2 particles through the reaction of $SnCl_4 \cdot 5H_2O$ with NaOH and POEG in water as a solvent. The mechanism for the formation of SnO_2 nanosheets in the present method may be similar to that proposed by Shen et al., except that ethyl alcohol was used as a solvent instead of