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Hydrothermal synthesis of highly crystalline Zn_2SnO_4 nanoflowers and their optical properties

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ABSTRACT

The primary focus of this work is to identify the ideal conditions for synthesizing highly crystalline Zinc Stannate (Zn_2SnO_4) nanoflowers through green hydrothermal synthesis by optimizing the reaction time and temperature. The X-ray diffraction pattern of the samples show an enhanced crystallinity and phase formation of Zn_2SnO_4 nanoflowers with increase in reaction temperature and time, and the most beneficial condition was observed and validated at 220 °C for 48 h. Subsequent SEM and TEM investigations revealed that the samples exhibit nanoflower morphology composed of nanosheets and nanoneedles. The circular ring like pattern observed from selected area electron diffraction (SAED) establishes the well crystalline nature of nanoflowers. Optical absorption study revealed the band gap energy was slightly higher than that of the bulk Zn_2SnO_4, and the 400 °C annealed samples exhibited a red shift of the absorption edge compared with the as synthesized samples. The emission bands recorded at UV region and low visible region using room-temperature photoluminescence characterization indicated their high structural and optical quality.

1. Introduction

Nanostructured ternary oxide, Zinc Stannate (Zn_2SnO_4) has emerged as a promising material in advanced applications owing to their high electrical conductivity, high electron mobility, low visible absorption and attractive optical and electrical properties. Contrary to binary oxides such as ZnO, TiO_2 and SnO_2, complex ternary oxides like Cadmium Stannate (Cd_2SnO_4), Zinc Stannate (Zn_2SnO_4) and Zinc Titanate ($ZnTiO_3$) have received much attention for having higher electron mobility and superior optical transparency. Further, ternary oxides have more freedom to tune the band gap of the materials by varying their compositions. Zn_2SnO_4 is indeed a promising material with a band gap of $E_g = 3.6$ eV and electron mobility of 10–15 $cm^2 V^{-1} s^{-1}$ [1]. Wu et al. [2] reported that Zn_2SnO_4 possesses good chemical and thermal stability aside from their attractive optical and electrical properties. On the real application side, Zn_2SnO_4 functions as transparent conducting oxide (TCO) [3]; as photoelectrode material in dye-sensitised solar cells (DSSCs) [1,4–7]; as negative electrode material for Li-ion battery [8,9]; as sensors [10,11] and as photocatalytic materials [12,13]. Compared to binary oxides, the ternary oxide Zn_2SnO_4 is an ideal nanoparticle for applications involving extreme conditions because of its good integration of chemical and physical properties.

Zinc Stannate has two different oxides with different crystallographic structures and Zinc to tin ratios: metastable $ZnSnO_3$ has the face-centered perovskite structure, whereas the orthostable Zn_2SnO_4 has the cubic spinel structure [13,14]. During crystallization through solid state reaction, metastannate may be obtained by thermal dissociation of Zinc hydroxystannate, at temperatures ranging from 300 to 500 °C. This metastannate decomposed into the stable Zinc orthostannate when heated above 600 °C, and exhibits both a diamagnetic and semiconductor properties [15]. The processing routes to synthesize Zn_2SnO_4 are many such as high temperature solid state reaction [16], mechanical grinding [17], thermal evaporation [18,19], co-precipitation method [20], sol–gel synthesis [21,22] and hydrothermal method [7,23,24]. However among all these, hydrothermal method is much preferred today for its simple operation, cost effectiveness, capability for mass production and environmental friendliness [25,26]. It is also an attractive green process as the nucleation and growth of the crystal happens under mild conditions in aqueous medium [13]. Shigeyuki et al. [27] had reported that hydrothermal technique is one of the best methods to produce pure fine oxide powders in large scale. Review of literature reveals that alkaline concentration, synthesis temperature and the reaction time are the major factors that determine particle size, morphology and crystallinity which influence the performance of the product. Researchers are now concentrating on controlling the morphology of hydrothermally grown Zn_2SnO_4 nanostructures as the interest in complex oxides for innumerable applications keep growing.

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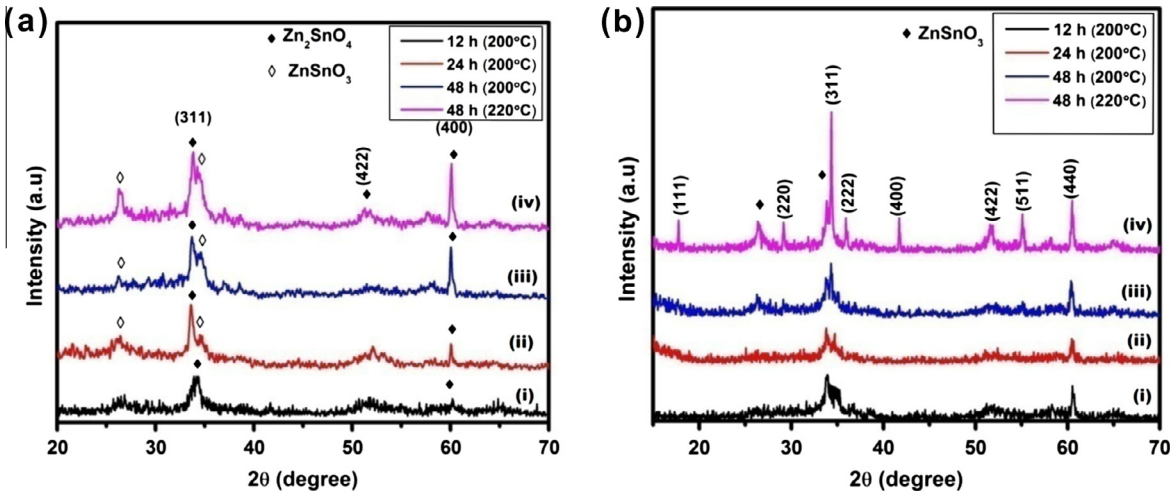

Fig. 1. (a) XRD patterns of as synthesized Zn_2SnO_4 nanoflowers and (b) Zn_2SnO_4 nanoflowers annealed at 400 °C for 1 h for different reaction times (i) 12 h at 200 °C, (ii) 24 h at 200 °C, (iii) 48 h at 200 °C and (iv) 48 h at 220 °C.

In this manuscript, we demonstrate a green hydrothermal method for synthesizing ternary Zn_2SnO_4 nanoflowers under optimal reaction temperature and time. The synthesized nanoparticles were characterized by XRD, SEM, TEM, and their optical properties were studied using UV–vis spectroscopy and PL measurement.

2. Experimental details

2.1. Synthesis of Zn_2SnO_4 nanoflowers

All reagents were of analytical grade purchased from Merck and used without further purification. Zinc chloride ($ZnCl_2$) and tin chloride dihydrate ($SnCl_2{\cdot}2H_2O$) were used as precursors and NaOH as the mineralizer for the hydrothermal synthesis of Zn_2SnO_4 nanoflowers. The process began with dissolving $SnCl_2{\cdot}2H_2O$ (3 mmol) and $ZnCl_2$ (3 mmol) into 20 mL of double distilled water separately to form two transparent solutions. There after 20 mL NaOH (1 M) solution was added little by little facilitated by magnetic stirring into the tin chloride dihydrate transparent solution. Zinc chloride solution was added drop by drop into above mixed solution under vigorous stirring using magnetic stirrer at room temperature until the formation of white precipitate of the hybrid complex. Finally, the white hybrid complex was transferred into a 100 mL Teflon-lined stainless autoclave with a fill factor of approximately 70%. The autoclave was sealed and maintained in a furnace at 200 °C as well as at 220 °C for varying time durations, in order to examine the influence of the reaction time on the product structure and morphology. The autoclave was cooled naturally to room temperature. The obtained precipitate was washed several times in double distilled water and absolute ethanol by repeated centrifugation and ultrasonication. Finally, the product was dried in an oven at 80 °C for 20 h and used for further characterization.

2.2. Characterization

Phase formation of synthesized samples were identified by using SEIFERT JSO DEBYEFLEX 2002, German make X-ray diffractometer with CuKα radiation (λ = 1.540598 Å) operated at 40 kV and 30 mA in the 2θ range 10–70°. Morphologies were characterized by field emission scanning electron microscope (FE-SEM, S-4200, Hitachi) operated at 15 k. EDX characteristics were recorded using FEI Quanta FEG 200-High Resolution Scanning Electron Microscope (HRSEM). Transmission electron microscopy (TEM) observation was performed with JEOL model JEM 2011 at an accelerating voltage of 200 kV. UV–vis absorption studies were conducted on the Varian Cary 500 UV–VIS–NIR spectrophotometer in the wavelength range of 200–700 nm. The room temperature photoluminescence spectra were recorded using Fluromax-4 spectroflurometer in the spectral range of 300–700 nm.

3. Results and discussion

3.1. XRD analysis of Zn_2SnO_4

Fig. 1a and b shows the X-ray diffraction patterns of as prepared and 400 °C (1 h) heat treated Zn_2SnO_4 nanoflowers for different reaction times and temperatures. These figures show typical peak patterns, which can be indexed as the Zn_2SnO_4 cubic structure in the standard data (JCPDS, 24-1470). Besides the cubic phase of Zn_2SnO_4 another secondary phase of $ZnSnO_3$ (JCPDS, 28-1486) was also observed in the XRD pattern. Particle size was estimated from the XRD peaks of Zn_2SnO_4 nanoparticles using Scherrer formula ($\Phi = k\lambda/\beta\cos\theta$) applied to the prominent peaks corresponding to the plane (3 1 1). The estimated average grain size is about 34 nm in all the synthesized samples at different reaction times of 200 °C and 220 °C for 48 h corresponding to the most prominent peak to the plane (3 1 1). The diffraction peaks gradually become intense with the increase in reaction time, demonstrating that the crystallinity of the product improved significantly with increasing reaction time. However, longer reaction time and increase in temperature enhance the phase formation and grain growth, but there still existed small amount of $ZnSnO_3$ phase. As shown in Fig. 1b the crystallinity and intensity of XRD spectra for the heat treated samples at 400 °C for 1 h are enhanced than that of the synthesized samples and their cubic phase too is enhanced. In the initial stage of the hydrothermal reaction, some complex formations such as $Sn(OH)_6^{2-}$, $ZnSn(OH)_6$ and $Zn(OH)_4^{2-}$ are formed in the presence of NaOH. Further, high temperature and high pressure of hydrothermal treatment leads to the decomposition of these complex formations into Zn_2SnO_4 nanoparticles [23]. However the exact growth mechanism is not clear and needs further investigation. Further, the estimated lattice parameter for the heat treated sample at 200 °C for 48 h is about 8.658 Å which is in good agreement with the reported value of 8.657 Å in JCPDS card no: 24-1470.

3.2. Morphology of Zn_2SnO_4

The size and morphology of the Zn_2SnO_4 synthesized nanoflowers were examined by field emission scanning electron microscopy (FESEM) and transmission electron microscopy (TEM). Fig. 2a–d show the different magnification SEM images of the Zn_2SnO_4 nanoflowers synthesized at 200 °C and 220 °C (reaction time of 48 h). The images reveal high-yield growth of assembled Zn_2SnO_4 structures. The morphology and the average size of the assemblies were substantially uniform in each case. At low magnification the samples synthesized for 48 h at 200 °C and 220 °C exhibit a morphology that is composed of uniform, beautiful bouquet of flowers, but at 220 °C the presence of flowers appear denser and brighter than at 200 °C (Fig. 2a and c). The reason for the characteristic difference is because higher temperature enhanced the atomic