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In_2O_3 microcrystals obtained from rapid calcination in domestic microwave oven

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ABSTRACT

'The simple way to prepare In_2O_3 microcrystals is reported in this paper. The precursor, $In(OH)_3$ microstructures, were obtained using the Microwave-Assisted Hydrothermal (MAH) Method. By annealing as-prepared $In(OH)_3$ precursor at 500 °C for 5 min in a domestic microwave oven (MO), In_2O_3 microcrystals were prepared, inheriting the morphology of their precursor while still slightly distorted and collapsed due to the $In(OH)_3$ dehydration process which was studied by thermal analysis. The $In(OH)_3$ and In_2O_3 were characterized using powder X-ray diffraction (XRD), field emission scanning electron microscopy (FE-SEM) and Raman spectroscopy. These techniques confirm the chemical dehydration of $In(OH)_3$ and the formation of In_2O_3 powders. The domestic MO promotes a rapid structural organization as compared with a CF (conventional furnace). The MAH method and the subsequent annealing in a domestic MO were shown to be a low cost route for the production of In_2O_3, with the advantages of lower temperature and smaller time.

1. Introduction

The synthesis of different dimensional nanostructures is of great importance in the study of physical properties of nanomaterials in the construction of functional nanodevices. Indium oxide (In_2O_3), an n-type semiconductor with a wide band gap of about 3.6 eV, has been widely used as a solar cell, a window heater, materials for a flat-panel display and gas sensors [1,2]. Nanostructures of this oxide (nanobelts [3,4], nanowires [5,6], nanofibers [7,8], octahedrons [9], nanocubes [5,10], nanotubes [11,12], and nanoparticles [13–15]) have been synthesized by different synthesis methods such as thermal evaporation of In_2O_3 [3], chemical vapor deposition [4], and wet chemical methods [16–19].

In_2O_3 materials have been obtained by heating their $In(OH)_3$ or InOOH precursors with the desired morphology using conventional hydrothermal and conventional furnace [13,20–23]. However, to produce In_2O_3 single crystals using these syntheses method, elevated calcination temperature and reaction time were required.

Recently, the domestic microwave oven (MO) has been successfully employed to obtain materials [24,25]. Advantages such as rapid heating, selective material coupling and enhanced reaction kinetics make the microwave process an attractive route for materials synthesis [26,27].

In this paper, In_2O_3 nanocubes were quickly synthesized after annealing a $In(OH)_3$ precursor at 500 °C for 5 min in a domestic MO. This process is simple and clean, does not require long annealing times and is more economical than conventional methods. The crystalline structure, morphology and particles size of the as-prepared $In(OH)_3$ precursor and In_2O_3 were investigated using powder X-ray diffraction (XRD), field emission scanning electron microscopy (FE-SEM) and Raman spectroscopy.

2. Experimental

The experimental procedure is as follows: 3.6 mmol indium (III) chloride (99% purity, Aldrich) was dissolved in 80 mL of deionized water under constant stirring for 30 min. The mixture was then transferred into a Teflon autoclave which was sealed, and the reaction system was heated under hydrothermal conditions of temperature at 140 °C for 60 min (heating rate fixed at 25 °C/min) using microwave irradiation (2.45 GHz, maximum power of 800 W). The pressure into the autoclave was stabilized at 3.0 atm. The white product obtained by the MAH treatment was centrifuged, washed with distilled water and ethanol to remove the ions remaining in the solid products and finally dried at room temperature. The as-prepared white powders were annealed in a boat crucible at 500 °C for 5 min with a heating rate at 25 °C/min using an adapted domestic MO [24,28].

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The thermal properties of the calcined $In(OH)_3$ powders were investigated by simultaneous thermogravimetric analysis (DTA and TG) using a Netzsch STA 409C/CD machine under synthetic air flow subjected to a heating rate of 10 °C/min from room temperature to 900 °C. Samples were placed in platinum crucibles, and a calcined alumina crucible was used as the reference material. The product was subjected to XRD using a Rigaku diffractometer (Model D/max-2500/PC) with Cu Kα radiation. Raman spectra were obtained using RFS/100/S Bruker FT-Raman equipment (scan range of 100–1400 cm^{-1}) with a 1064 nm exciting wavelength of a Nd:YAG laser. The morphology and size of the structures were observed by FE-SEM (Jeol JSM 6330F) images.

3. Results and discussion

The conversion process of the as-prepared $In(OH)_3$ cubic and rectangular-shaped microstructures during a calcination by MO in air was studied by thermogravimetry and differential thermal analysis, Fig. 1. An analysis of the $In(OH)_3$ TGA curve showed an abrupt weight loss occurring mainly in the temperature range from 180 to 600 °C, and a weight loss of about 17% attributed to chemical dehydration (see Eq. (1)). Above 600 °C, no obvious weight loss was observed. The DTA curve showed an endothermic reaction that can be attributed to the transformation of $In(OH)_3$ to In_2O_3 [20,29]. These results are in agreement with the results reported by Chen et al. [30] which indicate that InOOH is not formed during the chemical dehydration of the $In(OH)_3$:

$$2In(OH)_{3(s)} \rightarrow In_2O_{3(s)} + 3H_2O_{(g)} \uparrow \quad (1)$$

Fig. 2a shows X-ray patterns of the $In(OH)_3$ powders synthesized for 60 min using the MAH method. XRD data indicated single-phase formation. All the diffraction peaks could be indexed to the cubic lattice [space group $Im_3(204)$]. The calculated lattice constant was a = 7.9642(4) Å which is in good agreement with (7.979 Å) from the standard card (JCPDS No. 85-1338). After annealing the $In(OH)_3$ precursor at 500 °C for 5 min in a domestic MO, a crystalline single cubic phase of In_2O_3 was obtained. XRD patterns (Fig. 2b) showed all peaks were indexed to the In_2O_3 phase with a space group [Ia_3] and a calculated lattice constant of a = 10.1118(4) Å. These values are in agreement with (10.117 Å) as reported in the standard card (JCPDS No. 71-2194). The lattice parameters were calculated using the least-square refinement from the UnitCell-97 program [31].

Raman scattering spectra obtained at room temperature for $In(OH)_3$ and In_2O_3 powders are shown in inset of Fig. 2(a) and (b), respectively. There are five characteristic peaks for $In(OH)_3$ at 207, 309, 357, 392 and 667 cm^{-1} (inset of Fig. 2(a)). Peaks referent to In_2O_3 phase in the region of 131, 307, 367, 496 and 627 cm^{-1} are shown in inset of Fig. 2(b). The literature reported the Raman modes for a In_2O_3 standard commercial sample as approximately 308, 365, 504 and 637 cm^{-1} [32,33]. The Raman mode at ~307 cm^{-1} corresponds to In–O vibrations of InO_6 structural units and is very sensitive to the presence of oxygen vacancies [32,34].

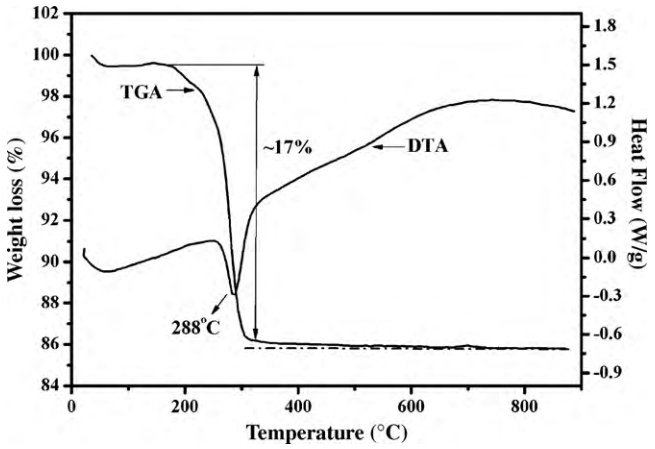

Fig. 1. TGA and DTA curves of the as-prepared $In(OH)_3$ precursor obtained by MAH.

Many researchers have reported chemical dehydration of the $In(OH)_3$ and the formation of In_2O_3 in a conventional furnace (CF) at different times and temperatures. However, in these syntheses method, elevated calcination temperature and reaction time were required according with Table 1.

In this present method the calcinations temperature and the reaction time were a smaller where compared to the previous works [13,20–23]. $In(OH)_3$ was obtained using the Microwave-Assisted Hydrothermal (MAH) method at 140 °C for 60 min and by annealing as-prepared $In(OH)_3$ precursor, in a domestic microwave oven (MO), In_2O_3 microcrystals were prepared at 500 °C for 5 min. In_2O_3 microcrystals inherited the morphology of their precursor while still slightly distorted and collapsed due to the $In(OH)_3$ dehydration.

Fig. 2(c) and (d) depict FE-SEM images of the $In(OH)_3$ (obtained at 140 °C for 60 min using the MAH method) and In_2O_3 (obtained at 500 °C/5 min using an MO), respectively. In these cubic and rectangular-shaped microstructures, a smooth and uniform surface where the angle between the adjacent edges is relatively close to 90° was observed (Fig. 2(c) and (d)). Fig. 2(d) images reveal that the In_2O_3 collapsed structures can be attributed to the rapid escape of a small amount of product water vapor. In situ release of water from oxyhydroxide materials during the chemical decomposition process would retain the morphology of their $In(OH)_3$ precursor [30]. FE-SEM micrographs facilitated the estimation of the average particle size distribution of $In(OH)_3$ powders by counting approximately 100 particles. $In(OH)_3$ powders prepared by the MAH method at 140 °C for 60 min resulted in the presence of microcrystals (Fig. 2(c)). An average particle height distribution from 0.75 to 4.75 μm (Fig. 2(e)) and an average particle width distribution from 0.75 to 4.25 μm (Fig. 2(g)) were observed. It was verified that approximately 70% of the particles exhibit an average width between 0.75 and 1.75 μm. After the calcination of the $In(OH)_3$ precursor at 500 °C for 5 min using a domestic MO, the volume shrinkage of the In_2O_3 microcrystals was observed (Fig. 2(d)). Fig. 2(f) shows the average particle height distribution in the range from 0.5 to 2.1 μm for the In_2O_3 powders calcined for 5 min. In this figure, 67% of the particles reached an average height between 0.7 and 1.3 μm. Fig. 2(h) shows the average particle width distribution in the range from 0.7 to 2.5 μm for the In_2O_3 powders. It was verified that approximately 82% of the particles exhibit an average width between 0.9 and 1.9 μm. The decrease in dimensions may be related to the chemical decomposition of $In(OH)_3$ during the rapid calcination process which caused the high density [35]. The results confirm that the chemical dehydration of the $In(OH)_3$ and the formation of In_2O_3 powders processed in a domestic MO presents a rapid structural organization as compared with the powders processed in a CF. This behavior can be attributed to the heating process in microwave radiation which occurs from the interior to the surface for $In(OH)_3$ powders. The microwave energy is transformed in heat through the interaction between molecules and atoms in the electromagnetic field. This interaction results in an internal and volumetric heating of the powders, promoting the formation of temperature gradients and heat flows [28]. In particular, the chemical decomposition of $In(OH)_3$ is employed for the preparation of In_2O_3 powders by collapsing the microcrystals.