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Single-source approach to the synthesis of In_2S_3 and In_2O_3 crystallites and their optical properties

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Abstract

Novel urchin-like In_2S_3 microspheres constructed with nanoflakes were synthesized via a single-source approach using indium diethyldithiocarbamate as precursor under hydrothermal conditions. In_2O_3 nanoparticles with the average diameter of 20 nm were obtained by calcining the as-synthesized In_2S_3 microspheres at 500 °C under ambient pressure. The samples were characterized by XRD, IR, TEM, and XPS. The optical properties of In_2S_3 micro-spheres and In_2O_3 nanoparticles were also investigated. UV-vis spectra indicate that there exists obvious blue shift compared with the In_2S_3 and In_2O_3 bulk materials. PL spectra demonstrate that the as-prepared In_2S_3 and In_2O_3 crystallites can emit at 355 and 380 nm, respectively.

1. Introduction

Tetragonal In_2S_3 is an n-type semiconductor with a band gap of 2.00–2.20 eV [1,2], perhaps owing to its defect structure, giving it optical properties [3], optoelectronic properties [4], acoustic properties [5], and electronic properties [6], which has inspired applications in the preparation of green and red phosphors for color televisions [7–9], dry cells [10] and heterojunction for use in photovoltaic electric generators [11]. Meanwhile, In_2O_3 , an important transparent conductive oxide (TCO) with a wide band gap close to GaN, has been extensively employed as microelectronic device materials in solar cells, flat-panel displays, sensors, architectural glasses and so forth [12–15].

Several kinds of methods have been developed to fabricate In_2S_3 and In_2O_3 with different morphologies. For instance, In_2S_3 nanoparticles were synthesized through sonochemical method [16], precipitation [17], hydrothermal method [18], and solvent-reduction route [19]; In_2S_3 dendrites were prepared via an oxidization–sulfidation growth route [20]; In_2S_3 nanorods were obtained by metal–organic chemical vapor deposition approach [2]. Similarly, In_2O_3 nanofibers were synthesized by annealing InOOH nanofibers at 490 °C [21]; In_2O_3 nanowires were fabricated through mesostructured frameworks [22], ethylene glycol-mediated approach [23] and chemical vapor deposition [24,25]; In_2O_3 nanoparticles were synthesized via microwave irradiation method [26] and thermal decomposition [27]. To our knowledge, there is no report on the formation of nanostructured In_2O_3 through the oxidation of In_2S_3 crystallites under ambient pressure.

Herein, we present a single-source approach to fabricate In_2S_3 microspheres by the thermal decomposition of an indium diethyldithiocarbamate complex obtained by mixing sodium diethyldithiocarbamate (NaS₂CNEt₂ or NaDDTC) and InCl₃ in absolute ethanol. In₂O₃ nanoparticles were further obtained by calcining the

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as-synthesized In_2S_3 microspheres at 500 °C. It was previously reported that NaDDTC could be used as complex reagent to form Sb_2S_3 [28] and Ni_3S_4 [29], but there is no report on the preparation of In_2S_3 formed with the aid of NaDDTC. The optical properties of In_2S_3 micro-spheres and In_2O_3 nanoparticles were also investigated.

2. Experimental

All the analytical reagents are purchased from Shanghai Chemical Reagents Company and used without further purification.

3. Synthesis of indium diethyldithiocarbamate complex

The indium diethyldithiocarbamate complex was prepared from stoichiometric amounts of 1 mmol $InCl_3 \cdot$ $4H_2O$ and 3 mmol NaDDTC in 50 mL absolute ethanol. The obtained yellow precipitate was filtered off, washed with distilled water and absolute ethanol several times and dried at room temperature.

4. Synthesis of In₂S₃ microspheres

In a typical procedure, $0.4 \text{ g In}(\text{S}_2\text{CNEt}_2)_3$ complex and 40 mL distilled water were added into a Teflon-lined stainless steel autoclave with a capacity of 50 mL. The autoclave was sealed, maintained at 180 °C for 12 h, and then cooled to room temperature naturally. The yellow-orange precipitate was filtered off, washed with distilled water and absolute ethanol several times and dried in vacuum at 50 °C for 6 h.

5. Synthesis of In₂O₃ nanoparticles

Part of the as-prepared In_2S_3 sample was heated to 500 °C in air with a ramping rate of 10 °C min⁻¹ and then calcined at 500 °C for 4 h under ambient pressure, which results in white powder.

6. Instruments and characterization

X-ray powder diffraction (XRD) patterns were determined using a Philips X'Pert PRO SUPER X-ray diffractometer equipped with graphite monochromatized Cu K α radiation ($\lambda = 1.541874$ Å). Transmission electron microscopy (TEM) images were characterized by Hitachi H-800 transmission electron microscope with a tungsten filament and an accelerating voltage of 200 kV. Fourier transform infrared (FT-IR) spectroscopy of the as-prepared products was recorded at room temperature with a KBr pellet on a VECTOR-22 (Bruker) spectrometer ranging from 400 to 4000 cm⁻¹. X-ray photoelectron spectra (XPS) were examined on an ESCALab MKII X-ray photoelectron spectrometer, using non-monochromatized Mg K α X-rays as excitation source. The thermal gravimetric analysis (TGA) was conducted using a Shimadzu TGA-50H analyzer (purified air stream 50 mL/min; heating rate 10 °C/ min). Ultraviolet and visible (UV–vis) and photoluminescence (PL) spectra were recorded on a JGNA Specord 200 PC UV–vis spectrophotometer and Hitachi 850 fluorescence spectrophotometer, respectively.

7. Results and discussion

IR spectra of the as-prepared In-DDTC complex and pure NaDDTC are characterized at room temperature (not shown here). The characteristic absorption peaks of the as-prepared In-DDTC complex at 1492 and 984 cm⁻¹ can be assigned to the stretching vibrations of C–N and C–S, respectively [28–30]. And the frequency of the C–N stretching vibration of the complex shifted from 1477 cm⁻¹ in the pure NaDDTC to 1492 cm⁻¹. The shift of the C–N stretching vibration implies that the sulfur in the diethylthiocarbamate coordinates with the metal ion in the complex [31]. Based on the IR spectra, it is believed that the In(DDTC)₃ complex is successfully synthesized via the reaction of NaD-DTC and InCl₃ · 4H₂O in absolute ethanol.

Fig. 1 is the typical XRD patterns of the as-prepared In_2S_3 (a) and In_2O_3 (b). All the peaks in Fig. 1a can be indexed as tetragonal In_2S_3 with lattice parameters of a = 7.615 Å and c = 32.322 Å, which are in agreement with the reported value of a = 7.619 Å and c = 32.32 Å



Fig. 1. XRD patterns of the as-prepared products: In_2S_3 (a) and In_2O_3 (b).

(JCPDS Card No. 25-0390). Similarly, all the peaks in Fig. 1b can be indexed to cubic In_2O_3 with the lattice parameters of a = 10.105 Å, which is consistent with the reported data of a = 10.11 Å (JCPDS Card No. 71-2194). No other characteristic peaks can be detected in Fig. 1.

Representative TEM images and SAED patterns of the as-prepared In_2S_3 and In_2O_3 are shown in Fig. 2a– d, respectively. It can be seen in Fig. 2a that there exists a large number of In_2S_3 microspheres with novel urchinlike morphology. Based on the observation of the magnified image in Fig. 2b, In_2S_3 microspheres are constructed with nanoflakes. Fig. 2c is the typical TEM image of In_2O_3 nanoparticles with the average diameter of 20 nm obtained by calcining the as-synthesized In_2S_3 microspheres at 500 °C. The selected area electron diffraction (SAED) pattern of the In_2O_3 nanoparticles in Fig. 2d is consistent with cubic In_2O_3 with strong ring patterns due to (222), (400), (440), and (622) planes.

Further evidence for the quality and composition of the as-prepared In_2S_3 was obtained by the XPS analysis (not shown here). No peaks of other elements except C, S, and In are observed on the survey spectrum. The binding energies for In $3d_{5/2}$ and S $2p_{3/2}$ are of 444.3 and 161.6 eV, respectively, which agree with the reported data in In_2S_3 [20]. The contents of In and S are quantified by In 3d and S 2p peak areas, and a molar ratio of 1:1.46 for In:S is given. No obvious peaks for other elements were observed.

In order to depict the nature of the as-prepared In_2S_3 sample, thermogravimetric analysis (TGA) measurement was carried out. Fig. 3 shows the weight loss of



Fig. 2. TEM images of the as-prepared products: In₂S₃ (a,b) and In₂O₃ (c,d).



Fig. 3. TGA curve of the as-prepared In_2S_3 sample.

the sample as a function of temperature. TGA shows two distinct weights loss steps in the temperature range of 30–500 °C, with an overall weight loss of 15.12%, which is approximately equal to the ideal weight loss of 14.72% when In_2S_3 is oxidized into In_2O_3 in air. The weight-loss process ceases at 500 °C, and the stable residue can be reasonably ascribed to In_2O_3 .

To investigate the optical properties of the-synthesized In_2S_3 microspheres and In_2O_3 nanoparticles, UV-vis spectra and photoluminescence (PL) spectra were recorded with ethanol used as reference. Fig. 4 shows the typical UV-vis spectra of the-synthesized In_2S_3 (a) and In_2O_3 (b). There are strong and broad absorption peaks located at 270 and 320 nm in Fig. 4a and b, respectively, which obviously reveals their blue shift compared with the reported data of 620.6 nm for In_2S_3 bulk materials [4] and 338 nm for In_2O_3 bulk materials [32], indicating the strong quantum confine-



Fig. 4. UV-vis spectra of the as-synthesized In₂S₃ (a) and In₂O₃ (b).

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Fig. 5. PL spectra of the as-synthesized In_2S_3 (a) and In_2O_3 (b).

ment of the excitonic transition expected for the In_2S_3 microspheres and In_2O_3 nanoparticles.

The photoluminescence (PL) spectra of the-synthesized In_2S_3 and In_2O_3 are shown in Fig. 5. Under PL excitation at 260 nm, the urchin-like In_2S_3 sample emits blue light located at 355 nm, indicating the blue shift in contrast to bulk In_2S_3 [33]. It was reported that the bulk In_2O_3 could not emit light at room temperature [34]. However, the room-temperature photoluminescence spectrum in Fig. 5b shows that there exists an obvious emission peak at located 380 nm excited at 325 nm, which is mainly attributed to the existence of oxygen vacancies [35].

8. Conclusion

In conclusion, a single-source approach has been developed to fabricate In_2S_3 microspheres with novel urchin-like morphology using indium diethyldithiocarbamate as precursor under hydrothermal conditions. Meanwhile, In_2O_3 nanoparticles were obtained by calcining the as-synthesized In_2S_3 microspheres at 500 °C. The optical properties of In_2S_3 micro-spheres and In_2O_3 nanoparticles were also investigated. This single-source approach might open an opportunity to prepare other transition metal sulfides in the future.

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