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Indium sulfide microflowers: Fabrication and optical properties

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1. Introduction

Nowadays, the controllable synthesis of micro- and nano-scale materials with unique morphology and hierarchy has stimulated intensive interest due to their importance in basic scientific research and technological applications [1–3]. Many efforts have been devoted to the fabrication of two-dimensional (2D) or three-dimensional (3D) micro-structure with 0D or 1D building blocks [4,5]. Generally, these hierarchical structures were fabricated via the oriented attachment mechanism, the Ostwald ripening process or both. However, due to the difficulties in controlling the nucleation and growth processes, the construction of well-defined 3D architectures with 2D components is still a great challenge [6–8]. These hierarchical structures may endow them with morphology-dependant properties and imply their potential application in various fields. Therefore, further research is warranted to realize the advantages of them.

As a mid-band gap semiconductor indium sulfide has two kinds of compositional forms (InS and In₂S₃) [9]. Furthermore, In₂S₃ is known to crystallize in three polymorphic forms as a function of temperature: e.g., a defect cubic structure called α -In₂S₃ (stable up to about 693 K), a defect spinel structure called β -In₂S₃ (stable up to about 1027 K) and a higher temperature layered hexagonal structure in the γ -form (above 1027 K). Among these three forms, β -In₂S₃ is known as an n-type semiconductor with a band gap of

ABSTRACT

With the assistance of urea, uniform 2D nanoflakes assembled 3D In_2S_3 microflowers were synthesized via a facile hydrothermal method at relative low temperature. The properties of the as-obtained In_2S_3 flowers were characterized by various techniques. In this work, the utilization of urea and L-cysteine, as well as the amount of them played important roles in the formation of In_2S_3 with different nanostructures. Inferred from their morphology evolution, a urea induced precursor-decomposition associated with the Ostwald-ripening mechanism was proposed to interpret these hierarchical structure formation. Furthermore, the optical properties of these In_2S_3 microflowers were investigated via UV-vis absorption and photoluminescence (PL) spectroscopies in detail.

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2.07 eV. Considerable attention has been focused on it because of its defect structure and the corresponding optical, acoustic, and electronic properties. It has motivated application researches such as green and red phosphors for color televisions, window materials in photovoltaic device, medical tracers for cancer diagnosis and dry cells [10–12]. Thus, many methods such as sonochemical method, precipitation, hydrothermal method, solvent reduction route, microwave assisted method and MOCVD method have been developed to fabricate In_2S_3 with different morphologies like urchin-like microspheres, dendrites, nanofibers, hollow microspheres, etc. [13–17]. However, there are few reports about the In_2S_3 secondary nanostructure fabrication. Hence, it is desirable to develop the controllable synthesis of In_2S_3 nanostructures with exceptional properties.

As a biomolecule, L-cysteine has several functional groups such as -NH₂, -COOH and -SH, which have a strong tendency to coordinate with inorganic cations. Inspired this, some metal sulfide nanostructures have been prepared in the presence of cysteine, which acted not only as a complex agent but also as a sulfur source and structure directing molecule [18–20]. To rupture the C–S bond, a high reaction temperature was utilized in these reports. Recently, to reduce the reaction temperature, some bases such as NaOH and NH₃·H₂O were selected [21,22]. In this paper, we develop a facile, one-step hydrothermal route to fabricate In₂S₃ microflowers with the assistance of urea and L-cysteine at a low temperature. Herein, urea served as both an inducement to the decomposition of Lcysteine and a structure-directing agent. Furthermore, the optical properties of them were investigated via UV–vis absorption and photoluminescence (PL) spectrum.

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2. Materials and methods

2.1. Materials

All chemical materials used (indium chloride tetrahydrate, Lcysteine, urea, etc.) were purchased from Beijing Chemical Corporation with analytical purities.

2.2. Synthesis of β -In₂S₃ microflowers

In a typical procedure to prepare β -In₂S₃ microflowers, 0.4 mmol of InCl₃·4H₂O, 1.8 mmol of L-cysteine and 0.8 mmol of urea were added to 24 mL distilled water. After stirring for 15 min, a transparent solution was formed and transferred into a 30 mL Telfon lined stainless steel autoclave. The autoclave was heated at 140 °C for 16 h, and then cooled to room temperature naturally. The yellow precipitates were collected, washed with distilled water for several times. In order to explore the influence of reaction parameters on the morphologies of β -In₂S₃, controlled experiments were designed, e.g., reaction time, different quantities of urea, L-cysteine, etc.

2.3. Characterization

X-ray diffraction (XRD) patterns of the prepared samples were recorded on a Rigaku-Dmax 2500 diffractometer equipped with graphite monochromatized Cu K α (λ = 0.15405 nm) radiation at a scanning speed of 4°/min in the range from 20° to 70°. Scanning electron microscopy (SEM) images were taken using Philips XL 30 and a JEOL JSM-6700F microscope. Energy dispersive X-ray analysis (EDX) was also done on the same instrument. Transmission electron microscopy (TEM) and selected area electron diffraction (SAED) measurement were carried out with JEM-2000 FX operating at 200 kV accelerating voltage. FT-IR spectra were recorded on a Bruker Vertex 70 FT-IR spectrometer. UV-vis absorption was characterized by Cary 50 UV-vis NIR spectrometer (Varian, USA). Photoluminescence (PL) emission measurements were performed using a LS-55 luminescence spectrometer (PerkinElmer).

3. Results and discussion

3.1. Compositions and morphologies of the products

The crystal structure and phase composition of the products were characterized by XRD and EDX analysis. As shown in Fig. 1a, according to the diffraction peaks location, the sample could be indexed to cubic β -In₂S₃ crystalline phase (JCPDS No. 65-0459) with a primitive cubic unit cell (*a* = 1.0774 nm). In addition, no other impurities, e.g., In(OH)₃, In₂O₃ or InS were detected in this pattern. Furthermore, the chemical composition was also investigated by EDS pattern (Fig. 1b). It was revealed that the final product consisted of In and S elements with a molar ratio of 2:3, confirming the formation of In₂S₃ nanostructure in our synthesis. (The element of Au was from the coating layer used for SEM imaging while Si was originated from the substrate.)

The hierarchical architectures of the products were recorded by the SEM and TEM. Fig. 2 showed the typical In_2S_3 images at different magnifications. From Fig. 2a, it was found that the spherical structures dominated in the full image, indicating a high yield for our products. In addition, their diameters were in a relative uniform range between 0.8 and 1.2 μ m. Detailed observations of these spherical morphologies were presented in Fig. 2b and c. It was noticed that all these spheres had flowery refined architectures, which were composed of dozen of nanope-



Fig. 1. (a) X-ray diffraction pattern (XRD) and (b) energy dispersive X-ray analysis (EDX) of the In_2S_3 sample (140 °C for 16 h).

tals. These nanopetals were connected to each other to build the 3D β -In₂S₃ flower-like structures (Fig. 2d). Fig. 3a showed the TEM image of β -In₂S₃ which was in good agreement with the results from SEM. In addition, under SEM magnification, the petal-like building blocks exhibited smooth surfaces. But based on the observation of TEM (Fig. 3b), the petals had rough surfaces. The selected area electron diffraction (SAED) (the inset of Fig. 3b) of the petal showed a set of diffraction rings, indicating the cubic β -In₂S₃ polycrystalline nature. These results were consistent with the XRD data shown in Fig. 1a.

3.2. Influence of urea on morphology

To investigate the influence of urea in the synthetic route. different quantity of urea was used in their preparation. As shown in Fig. 4, the quantity of urea played an important role in determining the morphology of In₂S₃. In the urea-free control reaction, the samples mainly showed spherical shapes with coarse surfaces in a broad size range (0.5-2 µm) (Fig. 4a). Further XRD characterization indicated their cubic phase of β -In₂S₃ in weak crystallinity (Fig. 4b). When 0.8 mmol urea was added, the uniform flowery architectures developed and became the dominant (Fig. 2). If we further increased the urea dose to 4 mmol, the resulting SEM image exhibited a 2D petal like In₂S₃ nanostructure (Fig. 4c). Detailed TEM image revealed that these flakes also combined together to construct flowery structures (Fig. 4d). However, the petals subunits are too filmy to support them on SEM substrate. The SAED pattern (the inset in Fig. 4c) also expressed the cubic β -In₂S₃ phase with polycrystalline nature. When 8 mmol urea was induced to the synthetic system, similar petal-like structures were



Fig. 2. FE-SEM images of the In₂S₃ flowers (140 °C for 16 h) at different magnification.

also recorded by SEM technology (Fig. 4e). The TEM image elucidated the real features of these petals as well as some integrated structures (Fig. 4f). The polycrystalline β -In₂S₃ nature was also indicated by the SAED pattern (the inset of Fig. 4e). Therefore, urea served as both an inducement to the decomposition of L-cysteine and a structure directing agents herein [23,24]. Neither a very low nor a very high quantity of urea is suitable for the construction of these flower-like nanostructures. Besides the concentration influence, the differences between alkaline sources were also investigated. When the alkaline source was replaced by NaOH, NH₃·H₂O and hexamethyleneteramine (HETA) respectively, the products showed different morphologies. As shown in Fig. 5a, when NaOH acted as the alkaline source, the samples exhibited flowery morphology, which were densely compacted and in a broad size range. If NH₃·H₂O was chosen, flowers with sparse petals dominated the whole image (Fig. 5b). When HETA was selected, the samples expressed spherical morphologies with coarse surfaces in narrow size range and connected each other (Fig. 5c). From the data above, we can draw the conclusion that not only the alkaline source but also the concentration of urea played important roles in the fabrication of these flowery superstructures.

3.3. Influence of L-cysteine on morphology

Besides the influence of urea, the effect of L-cysteine was also investigated in our research. As shown in Fig. 6a, if the dosage of Lcysteine was reduced to 0.8 mmol, the compacted flowery structures were formed (Fig. 6a). When the quantity of L-cysteine was increased to 3.2 mmol, the obtained samples showed a broad size distribution (Fig. 6b). If the sulfur source was substituted by mercapto propionic acid (MPA), which possessed the similar molecular structure except an amine group, the products exhibited spherical morphologies accreted by some $In(OH)_3$ microcubes (Fig. 6c) [24]. The reason for this phenomenon may be due to the lower coordination ability and the slower decomposition rate of MPA. Thus it was concluded that the selection of L-cysteine as well as its quantity played important roles in the fabrication of these 3D flower-like structures.

3.4. Growth mechanism of In₂S₃ flowery structure

In order to understand the fabrication process of the 3D flowerlike In_2S_3 nanostructures, time-dependent evolutions of morphology at 140 °C were elucidated by SEM and TEM (Fig. 7a–e). If the



Fig. 3. The typical TEM images of In_2S_3 flowers (140 °C for 16 h) at different magnification and SAED pattern of the samples.



Fig. 4. FE-SEM images ans the SAED patterns of the products obtained with different urea quantity: (a) 0 mmol, (c) 4 mmol, (e) 8 mmol; (b) the XRD pattern for the samples in (a); (e) and (f): the TEM images for the samples in (c) and (e) respectively.



Fig. 5. FE-SEM images of the products obtained with different basic source (a) 0.8 mmol NaOH, (b) 0.8 mmol NH₃·H₂O and (c) 0.8 mmol HETA.



Fig. 6. FE-SEM images of the sample obtained with different sulfur source: (a) 0.8 mmol cysteine; (b) 3.2 mmol cysteine; (c) 1.8 mmol MPA.



Fig. 7. FE-SEM images of the samples collected at different time period: (a) 2 h, (b) 4 h, (c) 6 h, (d) 10 h; (e): the typical TEM image for (d); (f) the XRD patterns for the samples above (*: the cubic In(OH)₃ phase).

reaction time was shortened to 2 h, the samples collected were in a low quantity. As shown in Fig. 7a, the products obtained at this stage consisted of spheres with smooth surfaces in a broad size range between 200 nm and 1.5 µm. When the reaction was conducted for 4 h, the yield of the precipitation increased. The surface of these spheres became rougher in a relative narrow size range between 700 nm and 1.2 μ m (Fig. 7b). After the reaction was performed for 6 h, those spheres were carved into flowery hierarchies with the same size (Fig. 7c). If the reaction were kept for 10 h, the flowers combined by several petals became the dominative structure (Fig. 7d). Further TEM characterization indicated the uniform size range and the detailed petal subunits (Fig. 7e). With the extension of reaction time, the products exhibited the flowery structures constructed by many petals in a narrow size range (Fig. 2). Afterward XRD were used to track the composition change of them. As shown in Fig. 7f, it was observed that at the embryo stage (2 h), the composition of the products were proved to be β -In₂S₃ and In(OH)₃ mixture. When the reaction time was prolonged to 4 h, the $In(OH)_3$ phase began to disappear. With the reaction time extended, the β -In₂S₃ crystalline increased and no other impurities were detected.

It was interesting to note that at the initial stage, the yield of the precipitation was quite low. Thus which states were in for those dissolved precursors was put forward as a question. Hence the upper solution was collected and a certain quantity of ethanol was added in it. Some white precipitates were gathered and washed for

SEM, XRD and FT-IR analysis. As shown in Fig. 8a, these white hybrid precursors exhibited irregular morphologies in nano-size about 50 nm. In addition, the corresponding EDS pattern indicated that five different elements (C, N, O, S and In) existed in the complex precursors (Fig. 8b). Quantitative analysis of the peak intensities indicated atom contents of 45.46% for C, 12.56% for N, 12.44% for O, 18.05% for S and 11.49% for In respectively. The sulfur element may be derived from L-cysteine. The C, N and O elements may originate from both L-cysteine and urea. The further XRD pattern provided amorphous nature of the hybrid complex (Fig. 8c). In addition, The FT-IR spectra of pure L-cysteine, urea and the hybrid composites were also shown in Fig. 8d. Several differences between these spectrum curves were detected. The characteristic amide I (1626 cm⁻¹, curve 3) band may attributed to the C=O stretching vibration and amide II (1496 cm^{-1}) band resulted from the combination of N-H bending and C-N stretching, different from 1677, 1604 and 1465 cm⁻¹ in curve 1. The characteristic $-NH_3^+$ band at 2016 cm⁻¹ (curve 1) and 2081 cm^{-1} (curve 2) disappeared. The typical signal of -SH at 2552 and 2508 cm^{-1} (curve 2) also disappeared indicating that S element of the complex originated from the -SH group of Lcysteine. Based on the above data, even though the precise chemical composition and molecular structure of the hybrid precursors cannot be deduced, it was pertinent to conclude that \ln^{3+} can coordinate with cysteine [18–21] and urea [23,24] to form embryo precursor complexes.



Fig. 8. (a) FE-SEM image, (b) the EDS pattern, (c) the XRD pattern and (d) the FT-IR characterization of the hybrid precursors obtained.

As discussed above, the growth mechanism can be proposed as urea induced precursor-decomposition associated with ripening mechanism. As illustrated in Scheme 1, at the initial stage, In³⁺ ions combined with L-cysteine and urea molecules in the mixed solution as a result of coordination effects (Fig. 8). These produced hybrid complex served as both the indium source and the sulfur source. With the increase of reaction temperature, urea molecules began to hydrolyze to give off ammonia, the pH value of the solution rose uniformly [25-27]. This prevented the occurrence of local supersaturation, favored the homogenous nucleation of tiny single crystals and meanwhile induced the decomposition of Lcysteine. However due to the unparallel decomposition rate between urea and L-cysteine, the irregular shaped nanoparticles were formed at this stage (Fig. 7a). Both the cubic In(OH)₃ phase and the cubic β -In₂S₃ phase was detected in the XRD pattern. As the reaction proceeded, the decomposition of L-cysteine dominated the reaction, and yielded unified spherical shaped particles (Fig. 7b). The solute particles were transferred to the crystal interface and were incorporated into the crystal by surface kinetics. Those spheres were carved into flowery hierarchies with the same size (Fig. 7c). Due to the lower solubility of β -In₂S₃ than that of In(OH)₃·(Ksp(In₂S₃) < Ksp(In(OH)₃), the In(OH)₃ impurities were transformed to β -In₂S₃ phase completely. In the following procedure, due to the excess existence of L-cysteine, the flowery structures turned into a concise form with thinner flakes (Fig. 7d). At the final period, due to the thermodynamic stability, the Oswald ripening process took place. The concise form compacted to a certain degree (Fig. 2).

Based on the mechanism above, the influence of the reaction parameters may also be interpreted. If the dosage of urea was reduced to 0 mmol, there would be not enough OH^- in the solution to induce the decomposition of L-cysteine. Thus the growth of the



Scheme 1. Schematic illustration of the growth mechanism for the 3D flowery In₂S₃.



Fig. 9. (a) UV-vis adsorption spectrum of the In₂S₃ flowers. (b) PL emission spectra of the above sample (excited by 335 nm).

flowery nanostructures was inhibited and spherical particles with coarse surfaces came into being in a broad size range. Besides, the poor crystalinity of them was also detected. When the urea concentration was increased, enough OH⁻ anions were supplied. These anions may bind on the surface to direct the flowers fabrication with thinner flakes to a certain extent. For the anions supply, if NaOH and NH₃·H₂O were selected, due to the local supersaturation, heterogeneous nucleation occurred and resulted in flowers in wide size range. When HETA was chosen, uniform spheres formed due to the homogeneous nucleation. However, due to the different coordination ability, these spheres linked together and failed to transform into flowery structures. Similar explanation was also applicable for the cysteine supply.

3.5. Optical properties of the flowery In_2S_3

As a promising semiconductor, its optical properties were also studied at room temperature. Fig. 9a represented the UV-vis absorption spectrum of the as-prepared In₂S₃ microflowers. Besides a weak broad absorption at 508 nm, a strong peak located at 291 nm was observed, which obviously revealed their blue shift compared with the reported data of 620.6 nm for bulk In_2S_3 materials [16,21]. The flower petals exhibited a thickness of about 20 nm, which was smaller than the Bohr exaction radius of In_2S_3 (33.8 nm). Consequently, this blue shift phenomenon of the absorption may be interpreted by the quantum confinement effect. In addition, we also carried out photoluminescence (PL) studies to investigate the optical properties of the stacked In₂S₃ flowers. This hierarchical superstructures showed good luminescence compared with the non-luminescent behavior of bulk In₂S₃. Under the excitation at 335 nm, a strong emission peak at 484 nm accompanied with several shoulders (420, 454 and 533 nm) was observed as shown in Fig. 9b. The blue luminescence at 484, 420 and 454 nm can be attributed to the presence of several deep trap states or defects in the structure. The weak green luminescence at 533 nm may be an emission from the indium interstitial sites, which corresponded to the report of Chen et al. [11].

4. Summary

In summary, 2D flakes based 3D flowery In₂S₃ architectures have been successfully synthesized by a simple hydrothermal method at relatively low temperature with the assistance of urea. In this case, urea not only acted as the alkaline source to induce the decomposition of cysteine but also directed the superstructure formation. In addition, it was intriguing to note that the sulfur source selected as well as the quantity had great influence on the final structure and composition control. Urea induced precursordecomposition associated with ripening mechanism was proposed to interpret their shape evolutions. These In₂S₃ novel architectures showed a quantum confinement effect in absorption spectra and exhibited a strong blue emission, which allowed to be utilized as promising materials for quantum electronic.

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