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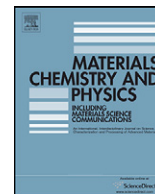


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Controlled synthesis and possible formation mechanism of leaf-shaped SnS₂ nanocrystals

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ABSTRACT

A sort of novel leaf-shaped SnS₂ nanocrystals have been synthesized by controlled reaction of CH₃CH₂OCS₂K with SnCl₄·5H₂O in aqueous solution in the absence of surfactant. The leaf-shaped nanocrystals consist of very thin sheets with several microns in length and 100–300 nm in width. The structure, composition, and morphology of the as-prepared leaf-shaped SnS₂ nanocrystals were characterized by XRD, Raman spectra, XPS, and FE-SEM, respectively. Elemental analysis, FT-IR spectra, and TEM were further used to study the formation mechanism of the leaf-shaped SnS₂ nanocrystals. A possible mechanism of producing lamellae – breaking into nanosheets – rolling and assembling was suggested for the leaf-shaped SnS₂ nanocrystals formation based on experimental results.

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1. Introduction

In the last decade, many efforts have been made to synthesize various low-dimensional nanomaterials, such as nanotubes, nanowires, nanorods, and nanobelts, due to their unique optical, electronic, magnetic and mechanical properties [1–5]. In recent years, size- and shape-controlled syntheses of nanocrystals have been focus of research because of unique physical and chemical properties dependent on these controllable nanocrystals [6–9]. There have been some typical examples of shape-controlled synthesis. By changing the ratio of the concentration of the capping polymer material to that of the platinum cations, the shapes of platinum nanoparticles could be controlled [10]. Alivisatos and co-workers reported a thermal decomposition of organometallic precursor approach in the two mixed surfactants to synthesize shape and size-controlled cobalt nanocrystals [11]. Using a surfactant template, the shapes of gold could be controlled through seed-mediated approach [12]. Based on a combination of colloidal lithography and etching techniques, shape-controlled large-area periodic nanopillar arrays had been fabricated [13]. A new biologic recognition approach was also used to fabricate shape-controlled Ag nanoparticles [14]. However, the development of facile, mild, and effective methods for controlling the shape of the product is still a key scientific challenge.

SnS₂ has exhibited abundant optical, electrical, and photoelectric properties [15–17]. It is a broadband gap semiconductor with band gap of 2.18 eV [18]. Owing to its photoconductivity, it is also regarded as a prospective candidate in solar cells and opto-electronic devices [19–21]. Its crystals consist of plane triple layers (sandwiches) S–Sn–S with strong ion-covalent bonding, weakly coupled to one another by van der Waals forces. One of the most salient properties of the layered SnS₂ is their ability to act as hosts for atomic and molecular guest species, which are accommodated at the empty sites bounded by van der Waals forces between adjacent close packed chalcogen layers [22]. Ascribing to this kind of property, lithium can be inserted into SnS₂ interbed and SnS₂ can become promising candidate as cathode material in the preparation of lithium batteries [23,24]. In addition, the absence of surface states associated with dangling bonds, which could act as recombination centers for photo-injected electrons, makes SnS₂ as an ideal model system for dye sensitization studies and also contributes to the high quantum yields [25].

Conventional methods for the synthesis of SnS₂ are chemical vapor deposition, laser ablation, molecular beam epitaxy, and spray pyrolysis [26–30]. Liquid-phase method has displayed prominent prospect in synthesis of inorganic nanoparticles due to its simple, reproducible, and controllable advantages. Some morphologies of SnS₂ such as nanowires, nanotubes, and nanobelts have been synthesized by it [31–33]. Herein, we present a simple direct hydrothermal route to synthesize leaf-shaped SnS₂ nanocrystals in the absence of surfactant and templates.

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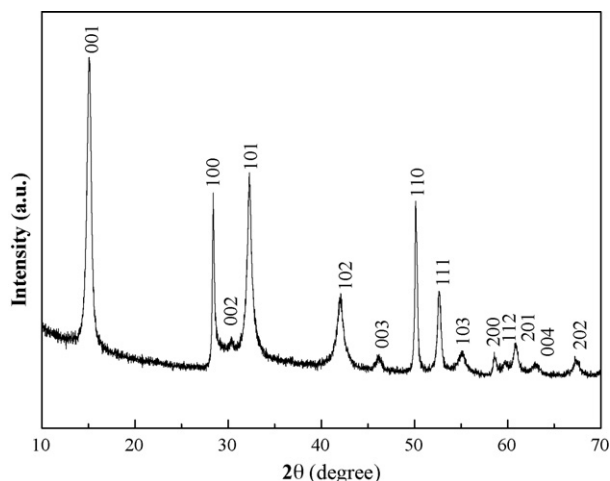


Fig. 1. XRD pattern of the as-prepared leaf-shaped SnS_2 nanocrystals synthesized at 200°C for 18 h.

2. Experimental

2.1. Materials

All chemicals used in this work, such as $\text{CH}_3\text{CH}_2\text{OCS}_2\text{K}$ (potassium ethylxanthate), $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$ (stannic chloride), are analytical grade reagents (from

ShangHai Chemical Co.). They were used as received without further purification.

2.2. Synthesis of leaf-shaped SnS_2 nanocrystals

In a typical procedure, 0.002 mol of $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$ was dissolved into 40 mL of distilled water. Then 0.008 mol of $\text{CH}_3\text{CH}_2\text{OCS}_2\text{K}$ was added into it under agitation. Immediately, much maize precipitate came into being. Stirring it for about 5 min, the precipitate was subsequently put into a Teflon-lined autoclave with a capacity of 60 mL. The autoclave was sealed and heated at 200°C for 18 h without shaking or stirring and allowed to air-cool to room temperature naturally. The products were filtered and rinsed with distilled water and absolute alcohol several times to remove impurities. After being dried in a vacuum at 50°C for 4 h, the golden powders were collected for characterization.

2.3. Characterization

X-ray diffraction (XRD) patterns were carried out with a Philips X'Pert PRO SUPER X-ray diffractometer equipped with graphite monochromatized $\text{Cu K}\alpha$ radiation ($\lambda = 1.541874 \text{ \AA}$) in the 2θ ranges from 10° to 70° . Elemental analysis was measured on a VARIO ELIII (German) element analytical instrument. FT-IR spectra were obtained on a Bruker Vector-22 FT-IR spectrometer recorded from 4000 to 500 cm^{-1} at room temperature. The samples and KBr crystal were ground together, and the mixture was pressed into a flake for IR spectroscopy. X-ray photoelectron spectra (XPS) were recorded on VGESCLAB MKII with X-ray as excitation source. The Raman spectrum was investigated with French Labram-HR confocal laser microRaman spectrometer and an argon-ion laser at 514.5 nm was used. Field emission scanning electron microscopy (FE-SEM) images were taken on a JEOL JSM-6700 SEM. The transmission electron microscopy (TEM) images and selected area electronic diffraction (SAED) patterns were performed on a Hitachi

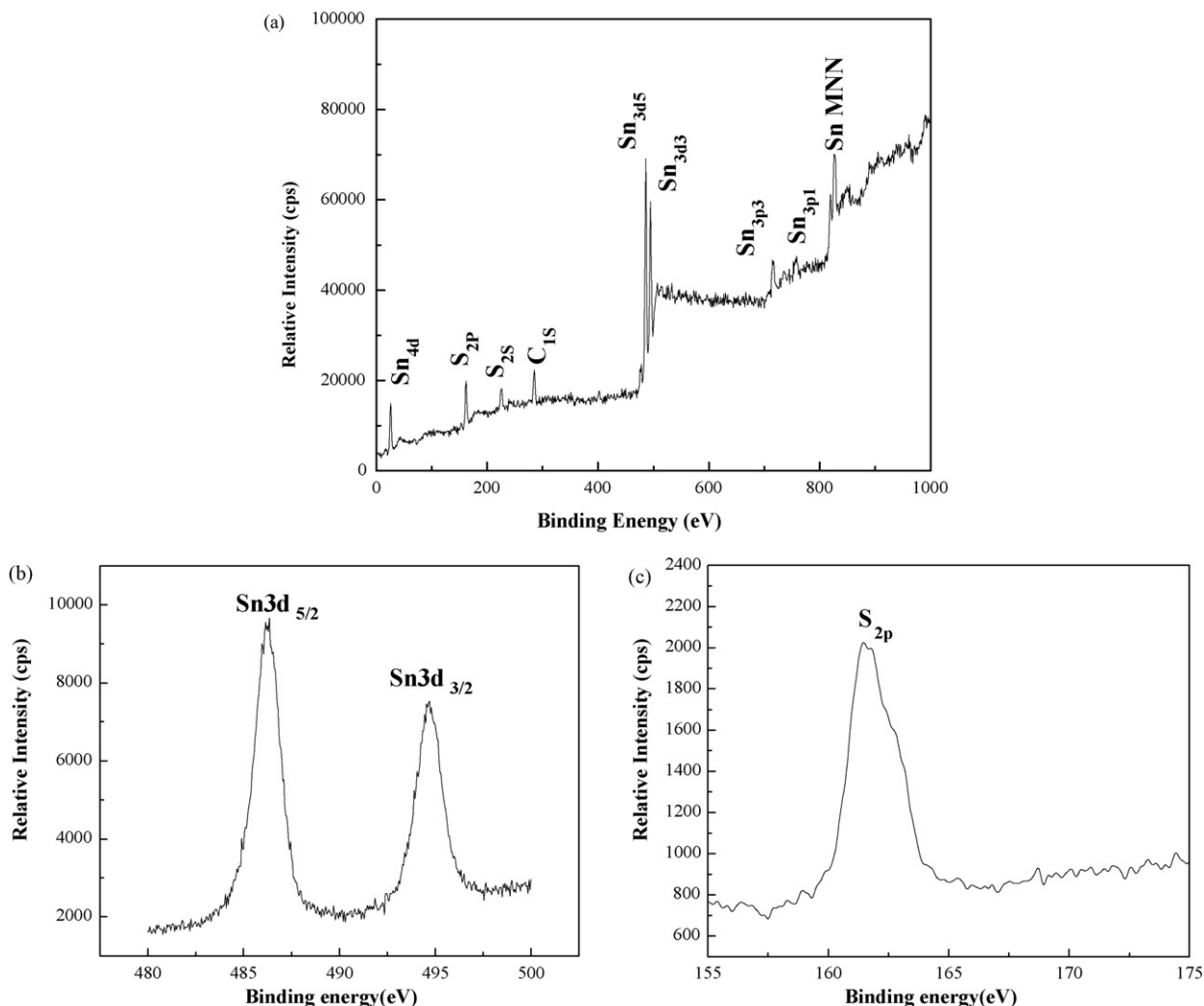


Fig. 2. XPS spectra of the final sample: (a) survey data of the sample, (b) $\text{Sn}3d$ core level spectrum, and (c) $\text{S}2p$ core level spectrum.

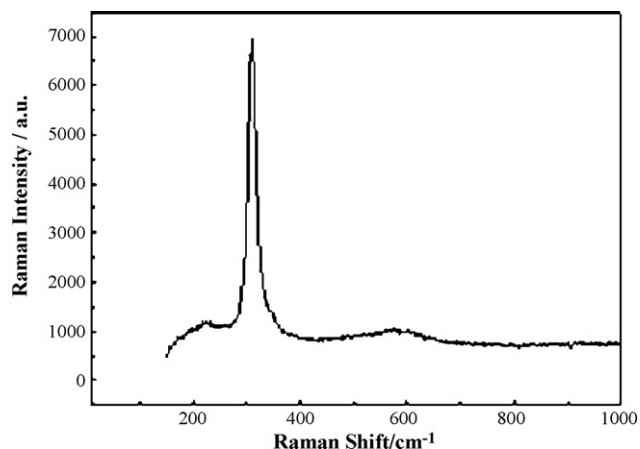


Fig. 3. Raman spectra of leaf-shaped SnS_2 nanocrystals at room temperature.

Model H-800 instrument with a tungsten filament, using an accelerating voltage of 200 kV.

3. Results and discussion

Fig. 1 shows a typical XRD pattern of the as-prepared leaf-shaped SnS_2 nanocrystals. All the diffraction peaks can be indexed to a pure SnS_2 hexagonal structure with lattice constant $a = 3.639 \text{ \AA}$, $c = 5.894 \text{ \AA}$, which are close to the reported data (JCPDS card 23-0677). The surface composition of as-prepared product was further confirmed by XPS as shown in Fig. 2. The survey XPS spectrum of the product is displayed in Fig. 2a. The binding energies obtained in the XPS analysis are standardized for specimen charging using C1s as the reference at 284.6 eV. The product SnS_2 had S 2p_{3/2} peaking at 161.50 eV and Sn 3d_{5/2} peaking at 486.40 eV, which is in agreement with the reported data [34]. No evidence of Sn^{2+} (binding energy at 485.8 eV) was detected in the spectra. Only peaks of Sn, S, and C were observed in the spectrum, which indicates the level of impurities is lower than the resolution limit of XPS. According to the integral area of S 2p to Sn 3d, the ratio of S to Sn is about 1:0.559, which is close to stoichiometric ratio of pure SnS_2 .

Raman spectrum was also carried out to characterize the as-synthesized leaf-shaped SnS_2 nanocrystals. As Fig. 3 shows, the stronger peak (310 cm^{-1} at 298 K) corresponded to A_{1g} mode and the very weaker peak (212 cm^{-1} at 298 K) to the E_g . A wide peak between 450 and 650 cm^{-1} may be attributed to second-order effects [35]. The downshift of the Raman peak of leaf-shaped SnS_2 nanocrystals (at 310 cm^{-1}) by seven wave numbers compared with that of bulk materials (at 317 cm^{-1}). The shift is probably attributed

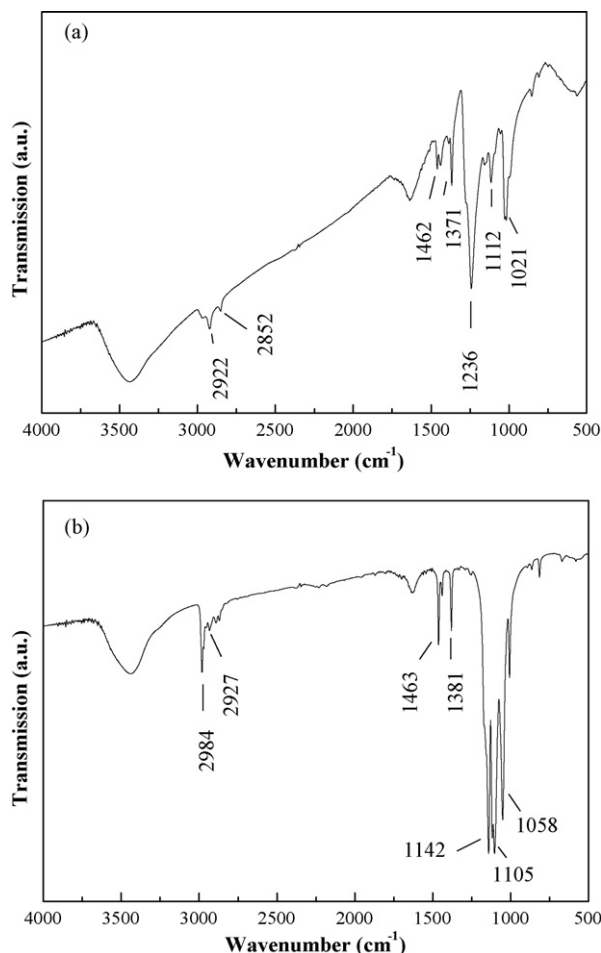


Fig. 5. FT-IR spectra: (a) the precursor and (b) the pure $\text{CH}_3\text{CH}_2\text{OCS}_2\text{K}$.

to nanosize effect [36]. The morphologies and microstructures of the products were investigated by FE-SEM. Fig. 4a and b are FE-SEM images of the products, which is magnified 6000 times and 35,000 times, respectively. The SnS_2 nanocrystals take on leaf-shaped morphologies at lower amplification times. The leaf-shaped nanocrystals have several microns in length and 100–300 nm in width. We observed that there were many microstructures on each leaves at 35,000 times magnification. A local magnification of an individual leaf-shaped nanocrystal shown in Fig. 4c (inserted in Fig. 4b) was again implemented. As a result, we clearly found that each leaves consisted of very thin nanosheets. At a rough estimate,

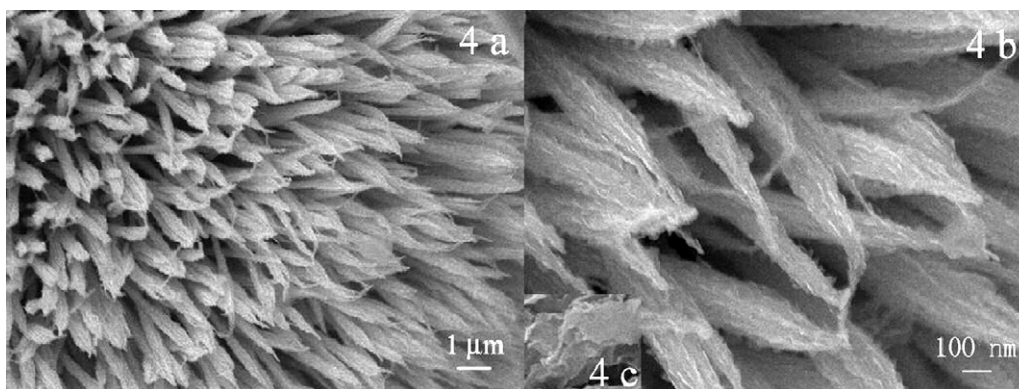


Fig. 4. FE-SEM images of the as-prepared SnS_2 nanocrystals: (a) at 6000 times, (b) at 35,000 times, and (c) local magnification of an individual leaf.

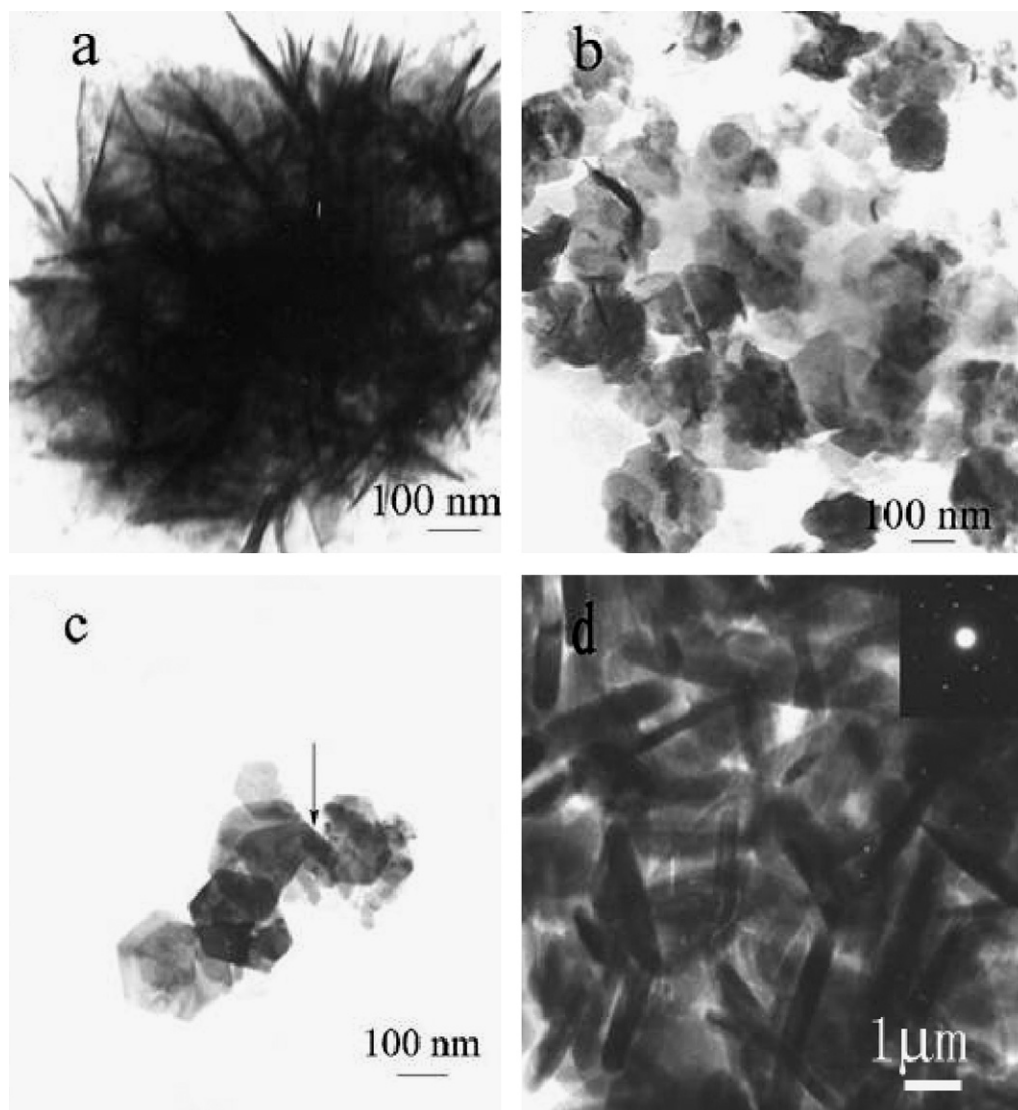
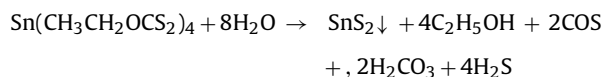
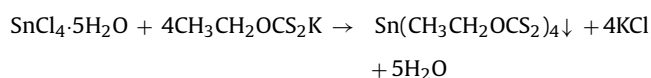


Fig. 6. TEM images of evolutive stages of the leaf-shaped SnS_2 nanocrystals at 200°C : (a) for 4 h, (b) for 8 h, (c) for 12 h, and (d) for 18 h.

the thickness of nanosheets is less than 10 nm. These nanosheets are linked and tangled with together and assemble into leaf-shaped nanocrystals.

When $\text{CH}_3\text{CH}_2\text{OCS}_2\text{K}$ was added into $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$ solution, immediately maize precipitate occurred. The precipitate was filtered and rinsed with distilled water and absolute alcohol for several times. After being dried in a vacuum at 50°C for 4 h, the powders were collected for elemental analysis and IR spectra study. Elemental tin and sulfur was determined through gravimetric analysis method. Carbon and hydrogen was measured on a VARIO ELIII element analytical instrument. The Sn:S:C:H ratio of as-prepared precursor is ca. 1:8:11:19. No Cl^- ion was detected by titration test of the precursor solution. According to this result, we deduce that the precursor may be $\text{Sn}(\text{CH}_3\text{CH}_2\text{OCS}_2)_4$. Fig. 5a and b describe FT-IR spectra of the precursor and pure $\text{CH}_3\text{CH}_2\text{OCS}_2\text{K}$, respectively. In Fig. 5b, the absorption peaks at 2984 , 1463 and 1381 cm^{-1} can be assigned to the vibration of C–H in $-\text{CH}_3$, 2927 cm^{-1} originating from the vibration of C–H in $-\text{CH}_2-$, 1142 cm^{-1} from the vibration of C=S, 1105 cm^{-1} from the vibration of C–O–C, and 1058 cm^{-1} from the vibration of C–S, respectively. Compared with Fig. 5b, Fig. 5a shows certain similarity and only the location of characteristic peaks of $\text{CH}_3\text{CH}_2\text{OCS}_2^-$ has a little shift. The absorption peaks

of C=S, C–O–C and C–S is shifted to 1236 , 1112 and 1021 cm^{-1} , respectively. Since Sn^{4+} substitutes for K^+ , the characteristic peaks of $\text{CH}_3\text{CH}_2\text{OCS}_2^-$ will be accordingly shifted. This further supported the formation of $\text{Sn}(\text{CH}_3\text{CH}_2\text{OCS}_2)_4$. Similar to Markens' report [37], the formation of SnS_2 may be explained by the following two reactions:



Firstly, much $\text{Sn}(\text{CH}_3\text{CH}_2\text{OCS}_2)_4$ precipitate were formed due to the reaction of $\text{CH}_3\text{CH}_2\text{OCS}_2\text{K}$ and $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$. Then the precursor precipitate will decompose slowly under hydrothermal conditions. Through the IR spectrum analysis of the final solid products, we did not observe any organic compounds in them. This shows that the precursor can completely change into SnS_2 at 200°C in close autoclave.

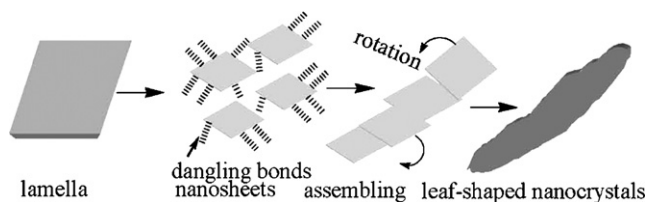


Fig. 7. Schematic illustrations for the formation of SnS_2 leaf-shaped nanocrystals.

We studied the evolutive process of the leaf-shaped SnS_2 nanocrystals through holistic analysis of TEM images of the products at the different reaction period of time. Fig. 6a–d are TEM images of the products at 4, 8, 12 and 18 h, respectively. All the products obtained at different intervals were SnS_2 by XRD characterization. At initial reaction stage, the products appear the lamellar morphologies. The lamella consists of several layers of petals. After reaction time was prolonged to 8 h, the lamella was broken into smaller nanosheets. These nanosheets show typical two-dimensional nanostructures. From Fig. 6c, it is known that these nanosheets began to roll (indicated by black arrowhead) and assemble. When reaction reached 18 h, the products displayed leaf-shaped morphologies. In the matter of fact, there are many microstructures on these leaf-shaped crystals. Selected area electronic diffraction pattern recorded on an individual leaf-shaped crystal (inserted in Fig. 6d) shows several concentric rings, which consists of diffraction spots. This shows that the products are well-crystalline and that there are some microstructures on it. Although there were many reports on formation mechanism of one-dimensional nanostructures, the formation mechanism of CdS nanorods and MnO_2 one-dimensional nanostructures give us much enlightenment [38,39]. CdS nanorods were built by a process of producing lamellae – breaking into fragments – growing into nanorods. To one-dimensional nanostructured MnO_2 , one rolling mechanism was suggested. Based on experimental results, we believe that a possible formation mechanism of producing lamellae – breaking into nanosheets – rolling and assembling is suitable for the leaf-shaped SnS_2 nanocrystals.

The possible mechanism may be defined as follows: (1) $\text{Sn}(\text{CH}_3\text{CH}_2\text{OCS}_2)_4$ precursors will form under stir at room temperature. (2) Under hydrothermal condition, $\text{Sn}(\text{CH}_3\text{CH}_2\text{OCS}_2)_4$ will be completely changed into SnS_2 clusters. The clusters will be grown into lamellae at 200°C for 4 h. (3) These bigger lamellae can be broken into small nanosheets at 200°C for 8 h. By contrast experiment, we also observed that lamellae could not be broken if temperature was lower than 180°C . (4) To these newborn nanosheets, they bore higher chemical activity. There are large numbers of dangling bonds on the edges of nanosheets, which are considered as a kind of driving force for these nanosheets assembling and rolling. (5) As time is prolonged to 18 h, plentiful leaf-shaped SnS_2 nanocrystals are produced. Although we do not know which step takes place firstly as far as assembling and rolling is concerned, the above-mentioned SnS_2 leaf-shaped formation mechanism suggested is believable based on our experimental results. A schematic illustration for the formation of SnS_2 leaf-shaped nanocrystals was shown in Fig. 7.

4. Conclusions

In summary, a soft solution process has been developed to synthesize leaf-shaped SnS_2 nanocrystals by the reaction of

$\text{CH}_3\text{CH}_2\text{OCS}_2\text{K}$ with $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$ in aqueous solution at 200°C for 18 h. This hydrothermal synthetic route, involving no catalysts, no seeds or templates and requiring no precise equipment, can be easily adjusted to prepare leaf-shaped SnS_2 nanocrystals on a large scale. The suggested formation mechanism is in good agreement with our experimental results. Since the leaf-shaped SnS_2 nanocrystals consist of very thin sheets, it can further be used to study dye sensitization and rechargeable lithium battery. We also believe that the present route may provide a general route to synthesize materials with specific morphologies, such as Sb_2S_3 , Bi_2S_3 , NiS and so forth.

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