Hindawi Publishing Corporation
Journal of Nanomaterials
Volume 2011, Article ID 280216, 5 pages
doi:10.1155/2011/280216

Research Article

Simple Synthesis of Flower-Like In_2S_3 Structures and Their Use as Templates to Prepare CuS Particles

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Received 31 May 2010; Revised 2 August 2010; Accepted 6 September 2010

Academic Editor: Quanqin Dai

Flower-like structure In_2S_3 particles are prepared by a simple and rapid method. The reaction proceeds in a polyalcohol system without using any complex precursors. The phase and morphology of the In_2S_3 are investigated. Furthermore, flower-like structure CuS particles are synthesized via the reaction of Cu^{2+} ions with the obtained In_2S_3 as templates. Both the In_2S_3 and CuS particles can be used in preparing compound solar cell material $CuInS_2$.

1. Introduction

Indium sulfide (In_2S_3) is an important III-VI semiconductor and exists in mainly three phases: α-In_2S_3 which is a defective cubic structure and stable up to 693 K; β-In_2S_3 which is a defective spinel structure and stable up to 1027 K; γ-In_2S_3 which is a higher temperature structure and stable above 1027 K [1, 2]. Among these phases, n-type β-In_2S_3 with a band gap of 2.0–2.8 eV has the most wide applications. In particular, the nanostructure In_2S_3, owing to its unique catalytic, optical, electronic, and gas-sensing properties, can be used in many fields, such as catalysts, solar cells, optoelectronic devices, luminophores, and acoustic devices [3–12]. In particular, In_2S_3 nanostructures could be used as precursors to fabricate $CuInS_2$ thin film which is one of the most important thin film solar cells, and has been widely investigated in last two decades. So far, various shapes of nanostructure In_2S_3 have been reported, such as nanofibers, half shells, nanobelts, nanorods, flower-like structures, and hollow microsphere [13–17]. Among these structures, flower-like structure is a kind of 3D porous structure and has large surface area which will benefit for the application in catalysts and optoelectronic devices such as solar cells. Therefore, in recent years, flower-like structures have been prepared by different techniques, such as templates, surfactants, complex precursors, solvents, thermal decomposition, or hydrothermal synthesis [18–22]. However, those processes were complicated, and most fabricated flower-like In_2S_3 were larger than 1 μm in size.

Furthermore, In_2S_3 nanostructures exist as incompletely coordinated sulfur atoms and can serve as a host for other metal ions [8]. It was reported that Cu^{2+} and Zn^{2+} could displace In^{3+} in In_2S_3 nanostructures [23]. But, there are few reports about the synthesis of CuS nanostructures by using In_2S_3 as templates.

In this paper, we use a simple and rapid chemical method to synthesize In_2S_3 flower-like structures with a diameter about 300–600 nm. The synthesis proceeds in polyalcohol system below 150°C and does not use any complex agents. Furthermore, the obtained In_2S_3 are used as templates to synthesize flower-like CuS structures under room temperature. Both the In_2S_3 and CuS can be used in preparing compound solar cell material $CuInS_2$.

2. Experimental Details

2.1. Chemicals. All the used chemicals are analytical grade: indium(III) trichloride, $InCl_3 \cdot 4H_2O$; copper(II) dichloride, $CuCl_2 \cdot 2H_2O$; thiourea (TA); thioacetamide (TAA); hexadecyl trimethyl ammonium bromide (CTAB); diethylene glycol (DEG).

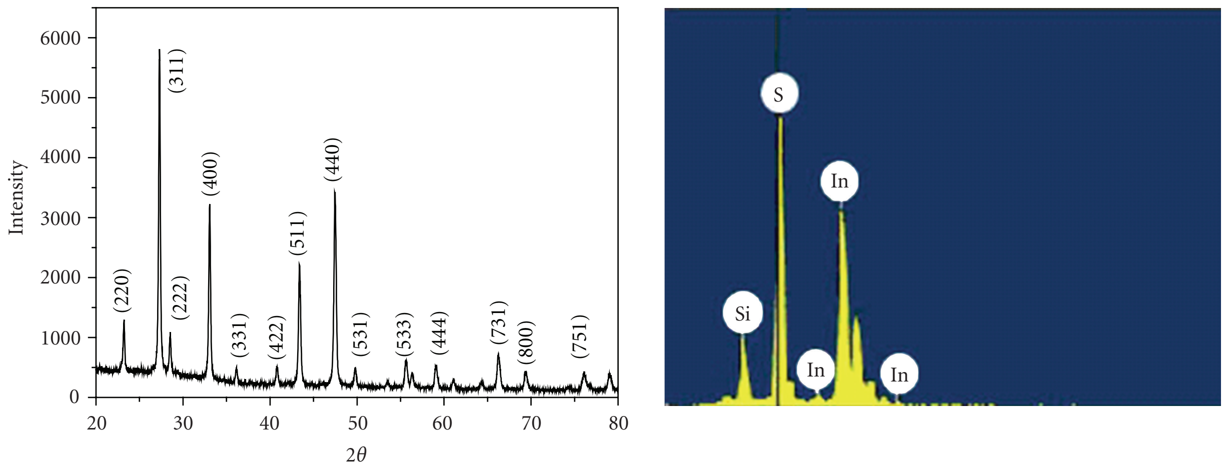


Figure 1: XRD pattern (a) and EDS spectrum (b) of the In_2S_3 particles reacting by $InCl_3$ and TA at 140°C for 60 minutes.

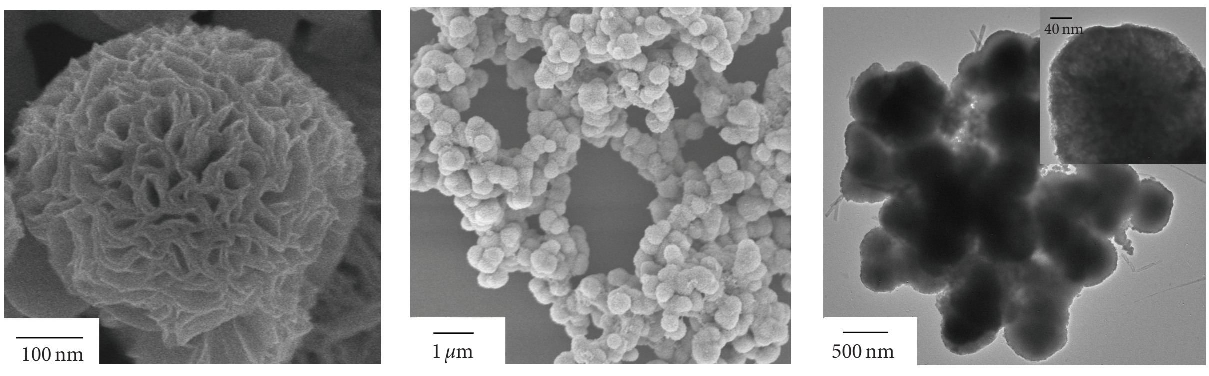


Figure 2: SEM ((a) and (b)) and TEM (c) images of the In_2S_3 particles reacting by $InCl_3$ and TA at 140°C for 60 minutes.

2.2. The Synthesis of In_2S_3 Particles. The In_2S_3 particles are synthesized through the following process. 1 mmol $InCl_3 \cdot 4H_2O$ is dissolved in 35 mL DEG in a three-neck flask. The solution is stirred under the protection of N_2 atmosphere at 140°C. Then 4 mmol TA or TAA dissolved in 5 mL DEG is slowly added into the solution. After 30–60 minutes reaction, the flask is removed from the heater and cooled to the room temperature. Then the particles are separated by centrifugation at 6500 rpm for 5 minutes and washed in ethanol for several times. At last, the particles are baked under 80°C for several hours.

2.3. The Synthesis of CuS Particles Using Obtained In_2S_3 as Template. The obtained In_2S_3 particles are dispersed in ethanol by a ultrasonic vibration equipment. Then 1 mmol $CuCl_2 \cdot 2H_2O$ power is added into the solution, reacting by ultrasonic vibration at room temperature for 30 minutes. The obtained particles are also washed and dried following a same procedure as that of In_2S_3 particles.

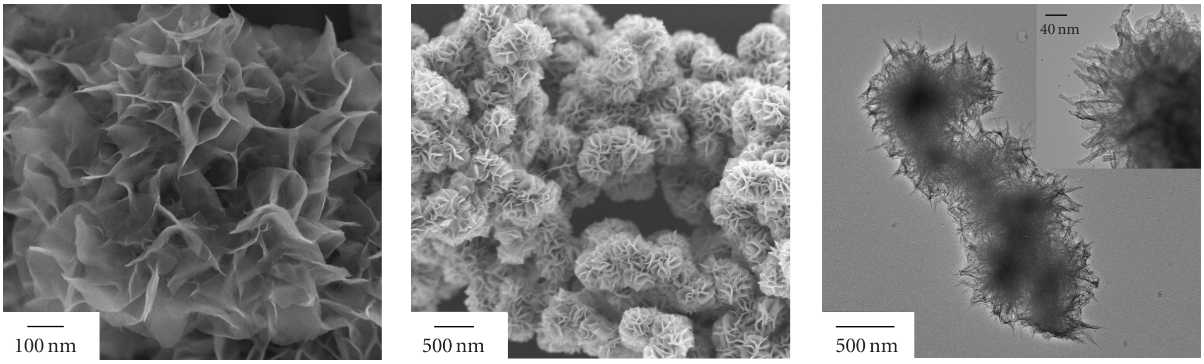
2.4. Materials Characterization. The particles are characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), and transmission electron microscopy (TEM).

XRD is carried out to study the crystal structures of all the samples, by using a X'Pert PRO (PANalytical) diffractometer equipped with a CuKα radiation source. Data is collected by step scanning of 2θ from 20° to 80° with a step of 0.02° and counting time of 1 s per step.

Morphology of the particles is investigated by SEM and TEM. The SEM images are taken by using a SEM Hitachi S4800. The compositions of samples are determined by energy-dispersive X-ray spectroscopy (EDS) attached with SEM. The operating parameters for EDS are as follows: acceleration voltage 20 kV, measuring time 80 s, working distance 15 mm, and counting rate 2.3 kcps. TEM Philips CM200UT is employed for TEM characterizations.

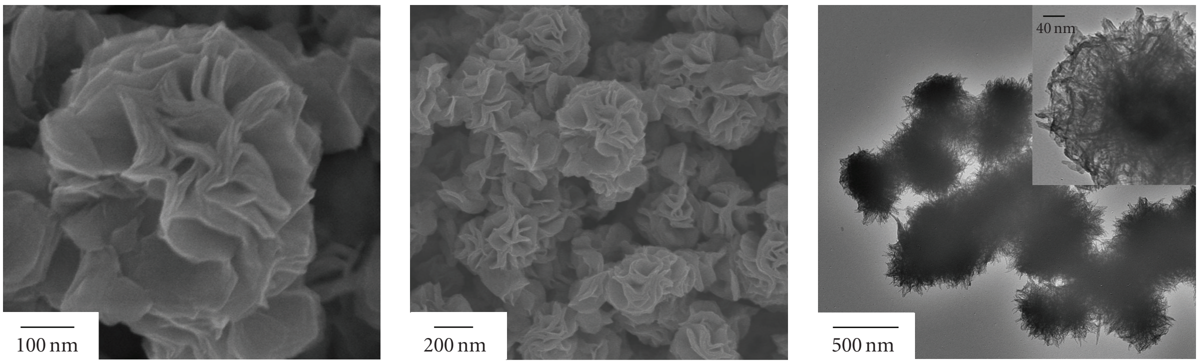
3. Results and Discussion

Size, shape, and dimensionality strongly affect the properties of nanomaterials [8]. In this paper, TA and TAA are used as two kinds of different S sources to synthesize In_2S_3. Due to their different release rates of S^{2-} ions, the obtained particles



(a) (b) (c)

Figure 3: SEM ((a) and (b)) and TEM (c) images of In_2S_3 particles reacting by $InCl_3$ and TAA at 140°C for 30 minutes.



(a) (b) (c)

Figure 4: SEM ((a) and (b)) and TEM (c) images of the In_2S_3 particles using CTAB as surfactant reacting at 140°C for 60 minutes.

may be different in surface morphologies. Besides, we use CTAB as a kind of surfactant to adjust the shape of the particles.

The XRD pattern and EDS spectrum of In_2S_3 particles via $InCl_3$ and TA reacting at 140°C for 60 minutes are shown in Figures 1(a) and 1(b). The similar XRD pattern by using $InCl_3$ and TAA as reactants has been obtained, which is not shown in this paper. All the peaks shown in Figure 1(a) can be readily indexed as a cubic phase of β-In_2S_3 without any other phase. The peaks are considerably narrow and strong, which indicates that the obtained particles are well crystallized. EDS spectrum of the In_2S_3 particles in Figure 1(b) shows that the samples are composed by In, S atoms (Si is from the substrate of the sample).

Figures 2(a) and 2(b) show the different magnification SEM images of the In_2S_3 particles reacting by $InCl_3$ and TA at 140°C for 60 minutes; and Figure 2(c) is their TEM image which further confirms the structure. It can be seen that the In_2S_3 particles are all flower-like porous structures with a diameter in range of 300–600 nm, while most of them are about 500 nm. The "petals" of the flowers are about 10–30 nm through careful examination.

Figures 3(a) and 3(b) show the different magnification SEM images of In_2S_3 particles reacting by $InCl_3$ and TAA at 140°C for 30 minutes. Similarly the images show that the In_2S_3 particles are also flower-like structures. But compared with Figure 2, it is found that the flake "petals" are much thinner, with a thickness of about 5–10 nm. Meanwhile, due to the thinner petals, leading to much more surface areas, the particles are conjugated to each other. Furthermore, the products using TA as S source are more spherical, whereas the products using TAA as S source are slightly fluffy. The TEM images which are shown in Figure 3(c) also prove this result.

For cubic β-In_2S_3, the crystallites are self-organized into spherical assemblies with protruding petals with a puffy flower-like manifestation [17]. TAA has faster release rates of S^{2-} ions than TA, leading to faster reaction speed with In^{3+}. This can be seen by the reaction phenomenon (the solution turns yellow quicker by using TAA). Thus, using TAA has a very fast growth rate along the petals. Therefore, the petals seem thinner and the whole flower-like structures are fluffier.

Furthermore, the CTAB is added to adjust and control the shape of the particles. Figures 4(a) and 4(b) show the SEM images of the In_2S_3 particles using $InCl_3$ and TA as reactants and using CTAB as surfactant. The TEM image is shown in Figure 4(c). It can be seen that the samples are still flower-like porous structures with a diameter around 300–600 nm and with a petal thickness about 10–30 nm. However, compared with Figure 2, the products get less flake petals,

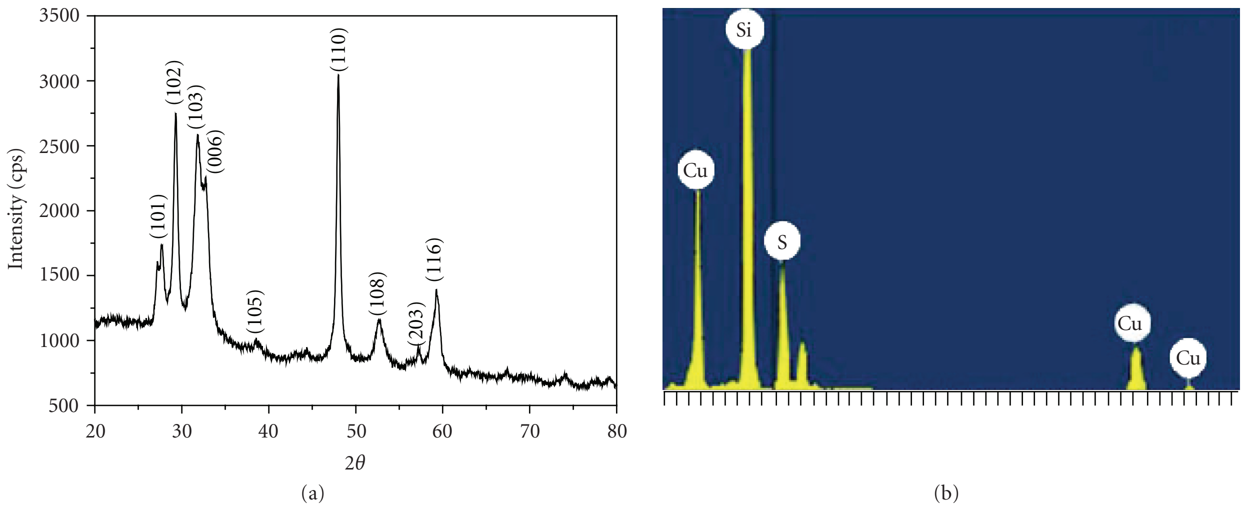


FIGURE 5: XRD pattern (a) and EDS spectrum (b) of the CuS synthesized by the reaction of In_2S_3 particles and $CuCl_2$.

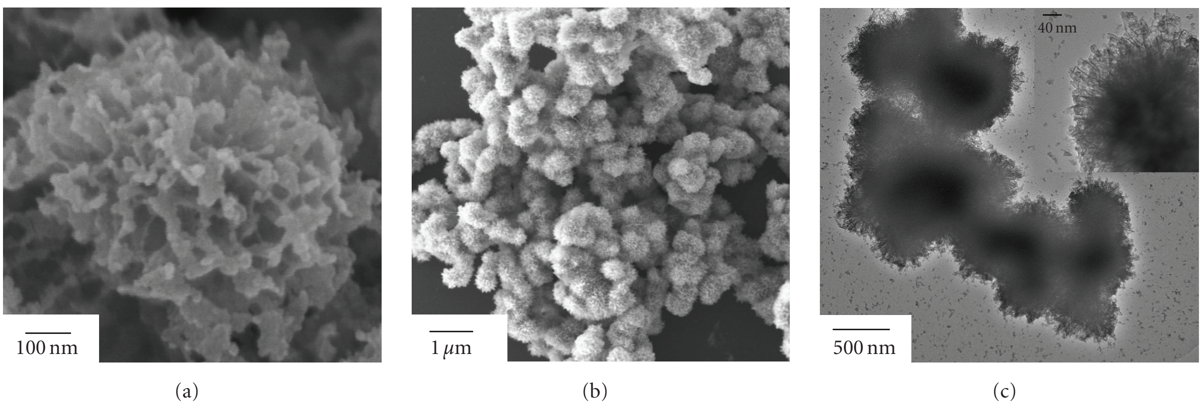


FIGURE 6: SEM ((a) and (b)) and TEM (c) images of the CuS synthesized by the reaction of In_2S_3 particles and $CuCl_2$.

as well as the bigger pores between the petals. Since CTAB is a kind of amphoteric surfactant and more tend to act as cationic surfactant, it is generally used to prepare hollow structures [24]. In this reaction, the CTAB and In^{3+} are together dissolved in the DEG first. CTAB may scatter around In^{3+}. Then when S sources are added, S^{2-} is easily attracted with one side of CATB. In the nucleation process, the other side of CTAB molecules may cause repulsion between flake petals and then make the flowers expand bigger.

Moreover, CuS particles are obtained by using the flower-like structure In_2S_3 as templates. In fact, CuS with flower-like structure has been fabricated by some methods such as polyol route or hydrothermal route [25, 26], and their structures are normally larger than 1 μm. In our experiments, the CuS flower-like structures with the diameter about 300–600 nm are synthesized at room temperature via $CuCl_2$ reacting with In_2S_3 particles as shown in Figure 2. Figures 5(a) and 5(b) show the XRD pattern and EDS spectrum of the CuS nanostructures synthesized by the reaction of In_2S_3 particles and $CuCl_2$. The XRD pattern shows that the obtained products are well-crystallized hexagonal phase CuS and no any In_2S_3 peaks are found, indicating that In_2S_3 is turned to CuS after reaction. EDS spectrum also verifies this since no hints of In are found.

Figures 6(a)–6(c) show the SEM and TEM images of the CuS synthesized by In_2S_3 particles and $CuCl_2$. It can be seen that the obtained CuS particles are also flower-like structures with a diameter around 300–600 nm, indicating the CuS particles are synthesized by In_2S_3 flower-like structures as templates.

The possible mechanism of this reaction is discussed as follows. In_2S_3 nanostructures exist incompletely coordinated sulfur atoms [8], and the flower-like structures appear a kind of porous surface and have large surface areas. Therefore there are numerous S^{2-} ions with high reactivity existing on the surface of flower-like In_2S_3 particles. And after Cu^{2+} ions are added, Cu^{2+} react with S^{2-} to form CuS. In addition, since the solubility degree of In_2S_3 is much bigger than that of ZnS and CuS, ions like Cu^{2+} and Zn^{2+} can displace In^{3+} in In_2S_3 nanostructure [23], whereas In^{3+} ions in the solution are washed away during the centrifugation process and that is the reason why we have not detected any hints of In. So at last, the flower-like CuS particles of pure phase are obtained.

4. Conclusion

In conclusion, In_2S_3 particles are prepared by a simple and rapid method. The obtained flower-like In_2S_3 structures have a diameter around 300–600 nm. By changing the S sources and, or adding surfactant, the In_2S_3 particles appear different in surface morphologies. Moreover, Cu^{2+} ions are added to react with In_2S_3 particles, and CuS with the similar structures and size are obtained. The mechanism of this reaction is probably due to the Cu^{2+} ions reacting with the high reactivity S^{2-} ions on the surface of flower-like In_2S_3 structures and in the same time displacing In^{3+} ions.

Acknowledgment

The authors would like to appreciate the financial supports from 973 project (no. 2007CB613403).

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