

Research Article

Preparation of Nanostructured Cu_2SnS_3 Photocatalysts by Solvothermal Method

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Nanostructured Cu-Sn-S powder was prepared by a relatively low-cost, simple, and green solvothermal method. Flower-like Cu_2SnS_3 nanostructures were successfully synthesized in 50 vol% ethanol water solution at 200 °C for 7.5 h. The structure and photophysical properties of the as-obtained samples were characterized by scanning electron microscopy, transmission electron microscopy, X-ray diffraction, and UV-Vis diffusion reflectance spectroscopy. Results showed that the cubic and tetragonal Cu_2SnS_3 was obtained by varying the ethanol contents. The band-gap energy of tetragonal Cu_2SnS_3 nanocrystals is near the optimum for photovoltaic solar conversion in a single band-gap device.

1. Introduction

With the energy crisis and environment problems becoming more and more serious, it is very urgent to explore new energy resource [1]. Solar energy is a promising new energy resource which is clean and sustainable. Cu-Sn-S, an important category of I-IV-VI chalcogenides functional materials, has attracted great attention because of their promising photocatalytic activity, photovoltaic property, nonlinear optical property, and outstanding optical-thermomechanical properties [2, 3]. Traditionally, these chalcogenides were prepared by solid-state reaction [4], which required high temperature, inert atmosphere protection, and a relatively long duration. Cu_4SnS_4 could be prepared by heating the starting materials of copper sheet, tin particles and sulfur powders at 900–1200 °C for 72 h in a silica tube [5]. Cu_2SnS_3 was obtained through a solid-state reaction by heating Cu_2S and SnS_2 at 900 °C for 48 h [6]. Similarly, Bouaziz et al. have synthesized Cu_2SnS_3 film through a solid-state reaction under vapor sulphur pressure at 530 °C for 6 h by using a sequentially deposited copper and tin [7]. Recently, solvothermal method has been used to prepare chalcogenides functional materials. Cu_2SnS_3 nanorods could be prepared by solvothermal reaction of Cu, Sn, S powders in the temperature range of 250–300 °C for 10–12 h [8]. Qu et al. [9] synthesized mesoporous

Cu_2SnS_3 spheres composed of nanoparticles via solvothermal route by using $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$, CuCl, thiourea as raw materials, PEG-1000 as surfactants, and ethanol as solvent. Qu et al. [10] also employed $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$, $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ as metal precursor, thioacetamide as sulfur source, and PEG-200 as surfactants and successfully synthesized cabbage-like Cu_2SnS_3 nanostructures.

Therefore, we dedicated to develop a low-cost, facile, and environmental-friendly solvothermal method to synthesize I-IV-VI chalcogenides. Cu_2SnS_3 nanostructures were prepared by varying solvents with different ethanol content through solvothermal method. $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$, $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$, and thioacetamide (TAA) were used as raw materials. Both the cubic and tetragonal Cu_2SnS_3 were obtained by varying ethanol content. The crystal structure, morphology, and photocatalytic property were also characterized.

2. Experimental

2.1. Preparation. All chemicals are analytical grade and used without further purification. Water is deionized water. A series of Cu_2SnS_3 were synthesized by the following process. 0.003 mol $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$ and 0.006 mol $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ were dissolved in 50 mL deionized water containing different

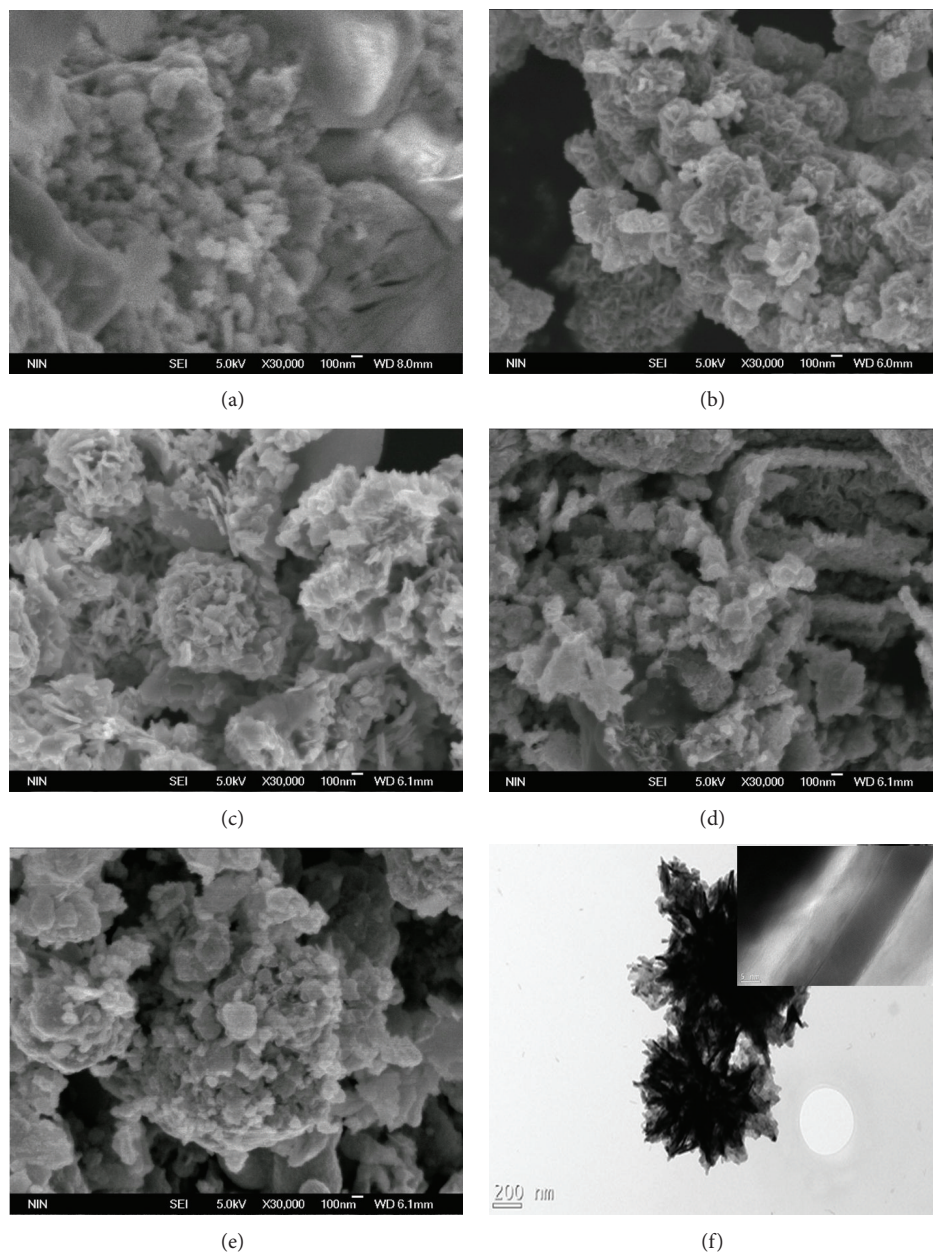


FIGURE 1: SEM images of the obtained samples at 200°C for 7.5 h as the function of different ethanol contents: (a) 100% H₂O, (b) 25% CH₃CH₂OH, (c) 50% CH₃CH₂OH, (d) 75% CH₃CH₂OH, and (e) 100% CH₃CH₂OH; (f) TEM image of sample from 50% CH₃CH₂OH (inset is TEM image of nanoflake).

concentrations of ethanol (0 vol%, 25 vol%, 50 vol%, 75 vol%, and 100 vol%) under magnetic stirring until they were dissolved completely. TAA was added and the mixture was transferred into a Teflon-lined stainless steel autoclave and sealed. The autoclave was maintained at different temperatures (180–220°C) for various durations (5.5–12.5 h) and then cooled down to room temperature. The precipitate was centrifuged and washed by deionized water and absolute ethanol for several times and finally vacuum-dried at 90°C for 5 h.

2.2. Characterization. The X-ray diffraction (XRD) patterns were recorded by a PANalytical X'pert Pro X-ray diffractometer equipped with CuK α irradiation at a scan rate of 0.02° s⁻¹. The accelerating voltage and the applied current were 40 kV and 40 mA, respectively. The morphology and microstructure of the samples were determined by field emission scanning electron microscope (SEM, JEOL JSM-6700F) and transmission electron microscope (TEM, JEM-2100). The UV-Vis absorption spectra were measured by a HITACHI UV4100 spectrometer, with the scanning range

from 100 nm to 800 nm. Raman scattering spectra were recorded on JobinYvon LabRAM HR800 spectrometer using 514.5 nm irradiation from an argon ion laser at 20 mW.

3. Results and Discussion

Figure 1 shows the SEM images of the as-obtained samples as the function of the different ethanol contents. Obviously, the morphology of the as-obtained samples is notably influenced by the solvents. When 25 vol% ethanol is employed, the morphology of the obtained samples consists of large quantities of flower-like nanocrystals as shown in Figure 1(b). As the ethanol content increases to 50 vol%, the flower-like Cu_2SnS_3 nanocrystals with the diameter of about 0.5–1 μm become bigger comparing Figure 1(a) with Figure 1(b). The Cu_2SnS_3 flowers are constructed by aggregation of large-scale thinner nanoflakes (Figure 1(f)) with the thickness of c.a. 15 nm (inset in Figure 1(f)). When the ethanol content increases more, the flower-like structure is broken and the as-obtained samples are not uniform in shape and microstructure as shown in Figures 1(d) and 1(e). It seems that the solvent plays a critical role in the process of preparing shape and crystallinity controllable Cu_2SnS_3 nanocrystals.

The XRD patterns of the as-obtained samples are shown in Figure 2. It is obvious that the ethanol content has a great effect on the crystallographic structure. The major XRD diffraction peaks that appeared at $2\theta = 28.5^\circ$, 33.0° , 47.6° , 51.7° , and 56.6° can be attributed to (112), (200), (220), (312), and (224) planes of Cu_2SnS_3 (JCPDS no. 89-4714), which is in good agreement with the standard data for the phase of the tetragonal Cu_2SnS_3 structure [11]. When the ethanol content is lower than 50 vol%, there appear some diffraction peaks which do not belong to the phase of Cu_2SnS_3 structure. The diffraction peaks of that synthesized in 50 vol% ethanol solution are the strongest, which indicates its highest crystallinity. In Particular, no obvious peaks attributable to other impurities are detected, confirming that the obtained sample is composed of pure tetragonal Cu_2SnS_3 structure. With the ethanol content increasing, the crystal phase of Cu_2SnS_3 changes. And the peaks corresponding to (111), (200), (220), (311), and (222) crystal planes appear, which match with the standard data for the pure phase of the cubic Cu_2SnS_3 structure according JCPDS no. 89-2877 [9]. It shows that the cubic Cu_2SnS_3 structure can be obtained when 100% ethanol was used as the solvent, but the crystalline structures are not as good as those of the tetragonal Cu_2SnS_3 structure because of the broaden diffraction peaks. In order to confirm the preparation of the pure tetragonal Cu_2SnS_3 , the Raman analysis is performed and the results are shown in Figure 3. Figure 3 is the Raman spectrum of the as-obtained Cu_2SnS_3 prepared in 50 vol% ethanol water solution at 200°C for 7.5 h. There are two peaks around 338 cm^{-1} and 298 cm^{-1} which are assigned to the tetragonal Cu_2SnS_3 [12]. Therefore, the pure tetragonal Cu_2SnS_3 with good crystallinity can be synthesized by the 50 vol% ethanol solvothermal method.

The reaction temperature and time are the other important parameters for the solvothermal method. The effect of the solvothermal temperature on the crystalline structures of

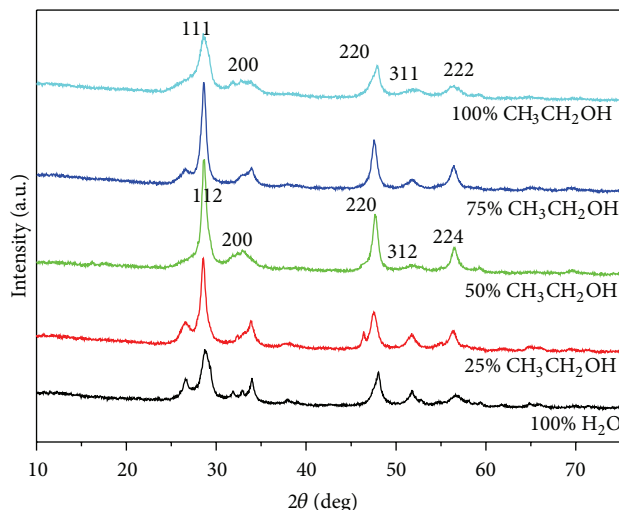


FIGURE 2: XRD spectra of the obtained samples at 200°C for 7.5 h as the function of different ethanol contents.

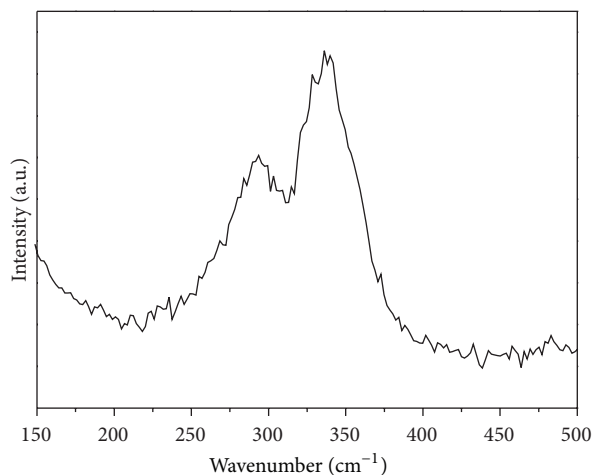


FIGURE 3: Raman spectrum of the obtained samples at 200°C for 7.5 h with 50 vol% ethanol.

Cu_2SnS_3 is investigated by fixing the reaction time of 7.5 h and the result is shown in Figure 4. As shown in Figure 4, the diffraction peaks of Cu_2SnS_3 prepared at 200°C match well with pure tetragonal Cu_2SnS_3 , and the peaks intensity of them is higher and sharper than that of those prepared at 180°C and 220°C . When the temperature increases to 220°C , many other peaks appear in the XRD patterns which imply the production of impurities. Then the best reaction temperature would be 200°C . Figure 5 shows XRD patterns of the as-obtained samples at 200°C for different reaction times. It is obvious that XRD intensity for pure Cu_2SnS_3 structure by treating 7.5 h is the strongest. Then we can conclude that the conditions for pure tetragonal Cu_2SnS_3 preparation by solvothermal method are 200°C for 7.5 h with 50 vol% ethanol in this study.

The optical band gap of the as-obtained tetragonal Cu_2SnS_3 nanocrystals can be evaluated from the UV-Vis

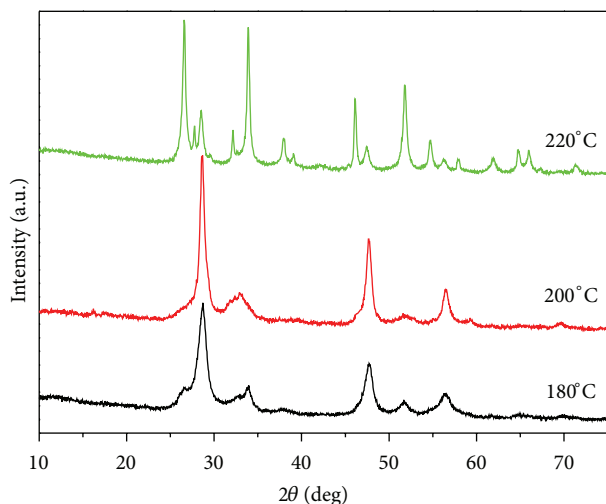


FIGURE 4: XRD spectra of the obtained samples for 7.5 h at the different temperatures.

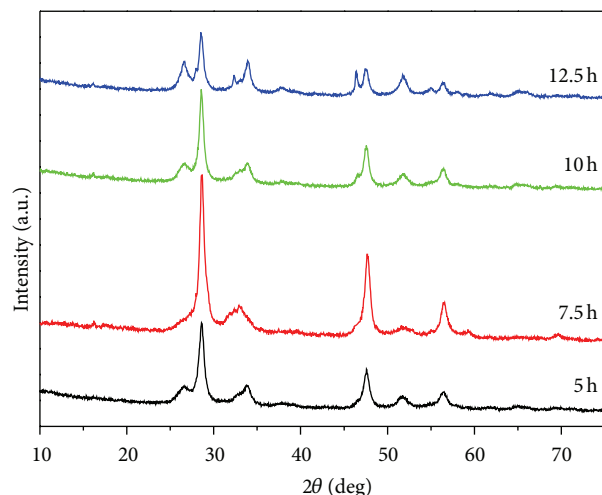


FIGURE 5: XRD spectra of the obtained samples at 200°C for the different reaction times.

absorption spectrum. Figure 6 shows the absorption spectrum of Cu_2SnS_3 prepared at 200°C for 7.5 h. From Figure 6, it can be seen that the as-obtained tetragonal Cu_2SnS_3 has broad absorption in the entire visible light region, and the absorption edge of about 872 nm is estimated from the intercept by extrapolating straight line to the horizontal axis. The band gap is calculated to be about 1.42 eV through the formula: E_g (eV) = 1240/ λ (λ = 872 nm). Obviously, the band gap of tetragonal Cu_2SnS_3 nanocrystals is near the optimum for photovoltaic solar conversion in a single band-gap device.

4. Conclusion

In this study, Cu_2SnS_3 nanocrystals were prepared through an environmental-friendly facile solvothermal method. It was found that the crystal structure and morphology of

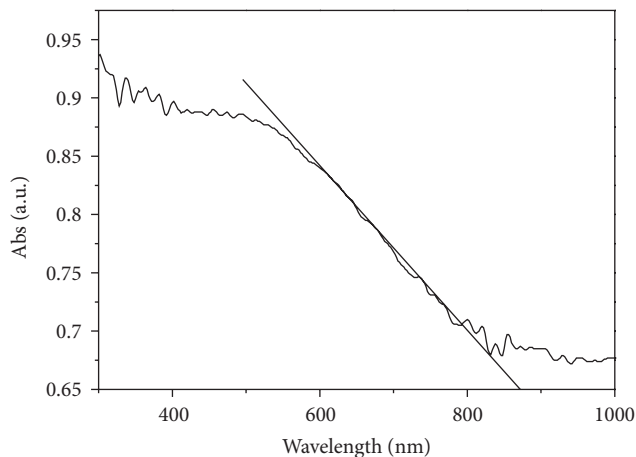


FIGURE 6: UV-Visible absorption spectrum of the obtained samples at 200°C for 7.5 h.

the productions were strongly influenced by the reaction conditions including solvents, temperature, and time. It is noticeable that the choice of ethanol water solution as solvents, which is a common, nontoxic, and low-cost solvent whose advantages are beneficial to sustainable development, is a key to successfully synthesize tetragonal Cu_2SnS_3 . The pure tetragonal Cu_2SnS_3 nanocrystals were prepared in 50 vol% ethanol solution at 200°C for 7.5 h, and the band gap is about 1.42 eV which is suitable to be solar cells materials.

Acknowledgments

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