FLOWER-LIKE Cu_2FeSnS_4 PARTICLES SYNTHESIZED BY MICROWAVE IRRADIATION METHOD

HAO GUAN[a,b,*], YUFEN SHI[a], BAOXIANG JIAO[a], XU WANG[a], FANGLI YU[a]

[a] *School of Materials Engineering, Yancheng Institute of Technology, 9 Yinbing Street, Yancheng 224051, PR China*

[b] *College of Materials Science and Technology, Nanjing University of Aeronautics and Astronautics, 29 Yudao Street, Nanjing 210016, PR China*

Cu_2FeSnS_4 particles were prepared by using a microwave irradiation method. X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM) and UV-vis-NIR absorbance spectroscopy measurements show that the Cu_2FeSnS_4 products exhibit flow-liked particles with spherical structure and idea band gap (E_g=1.52eV), indicating a potential candidate for application as absorber layer in thin film solar cells.

(Received October 31, 2013; Accepted December 19, 2013)

Keywords: Cu_2FeSnS_4; Microwave; Flow-like; Solar cells

1. Introduction

In recent years, chalcopyrite semiconductors such as Cu_2ZnSnS_4 and $Cu_2ZnSnSe_4$ have aroused strong concern due to near-optical direct band gaps around 1.5eV and high absorption coefficients (＞$10^4 cm^{-1}$) for potential application in thin film solar cells[1-6]. The highest power conversion efficiencies of 8.4% and 11.1% for solar cells based on Cu_2ZnSnS_4 and $Cu_2ZnSn(S,Se)_4$ have been achieved[7-8]. Cu_2FeSnS_4 (CFTS), another possible earth-abundant alternative to Cu_2ZnSnS_4, is also considered as possible photovoltaic material because of its suitable band gap of 1.2-1.5eV and large absorption coefficient of ～$10^4 cm^{-1}$ [9-10].

Several methods have been used for the preparation of CFTS particles, such as hot-injection method [11], solvothermal method [12] and microwave irradiation method [13]. Among these methods, microwave irradiation is the novel and economical method for short reaction times, simplicity and high yield. Ai *et al* [13] synthesized CFTS hollow chain microspheres using a rapid microwave nonaqueous strategy. In this paper, we report a microwave irradiation method to synthesize flower-like CFTS particles. The structure, morphology and optical properties were also investigated.

2. Experimental details

$Cu(NO_3)_2·3H_2O$ (Analytical Reagent, Nanshi-Reagent), $Fe(NO_3)_3·9H_2O$ (Analytical Reagent, Nanshi-Reagent), $SnCl_2·2H_2O$ (Analytical Reagent, Nanshi-Reagent) and H_2NCSNH_2

*Corresponding author: guanhao1980@sina.com

(Analytical Reagent, Nanshi-Reagent) were used without further purification. In this experiment, $Cu(NO_3)_2\cdot3H_2O$ (0.06M), $Fe(NO_3)_3\cdot9H_2O$ (0.03M), $SnCl_2\cdot2H_2O$ (0.03M) and H_2NCSNH_2 (0.15M) were added in 50ml ethylene glycol. Clear solution was formed after being stirred at room temperature for two hours. Then the beaker containing solution was put into microwave oven. The samples were microwaved under different conditions. The precipitates were washed several times with de-ionized water and absolute ethanol. The products were finally dried in vacuum at 80℃ for 2h.

The structure studies were carried out using a PANalytical X'Pert PRO diffractometer with Cu K_α radiation having wavelength λ=0.15406 nm and JY-T64000 Raman spectrometers. The microstructure was recorded using LEO-1530VP scanning electron microscope and Tecnai F20 transmission electron microscope. The optical characteristics were measured using Varian Cary 5000 spectrophotometer to calculate band gap energy.

3. Result and discussion

Fig.1 presents the XRD patterns of the as-synthesized samples for different power and time. It can be seen that the power and time have important influence on the formation of the CFTS particles. The XRD pattern of the product, obtained under the condition of 50W/4min, matches well with the stannite structure of CFTS (JCPDS NO.44-1476). The diffraction peaks at 2θ = 28.7°, 32.8°, 47.4° and 55.9° can be attributed to the (112), (200), (204) and (312), respectively. The plane shows the broad full-width at half-maxima (FWHM), indicating the formation of nanocrystallinity. The average grain size calculated using Debye-Scherrer formula is about 6.08nm. The lattice parameters calculated from the refined pattern were a=b=10.46Å and c=5.72Å, which matches well with standard CFTS powder data. The possible formation mechanism of CFTS particles can be explained as follows: At first, Cu_2SnS_3 was obtained by the reaction of CuS and SnS phases. Then Cu_2SnS_3 reacted with FeS to form CFTS. With the increasing of the power and time, the product temperature increases faster, leading to the decomposition of CFTS.

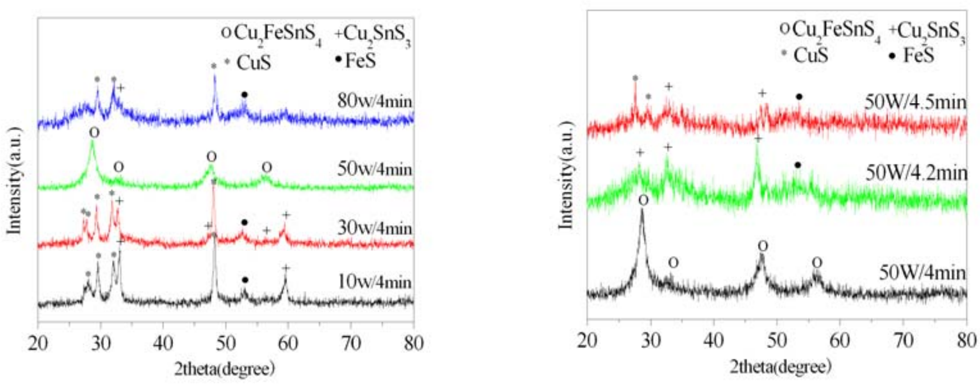

Fig.1 The XRD patterns of the as-synthesized samples for different power and time

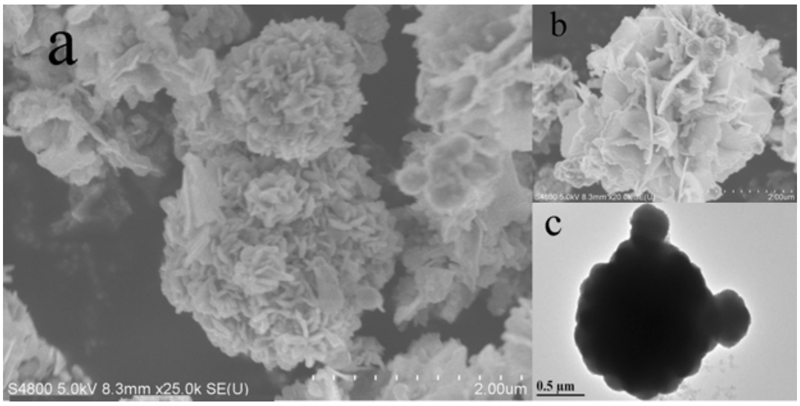

Fig.2 (a) Low, and (b) high magnification SEM images of CFTS particles,
(c) TEM images of CFTS particles

The different magnification SEM images of the CFTS products are shown in Fig.2 (a) and Fig.2 (b). The results reveal that the CFTS products are composed of flower-like particles. Further observation of the TEM image (Fig.2 (c)) shows spherical structure. It is believed that the CFTS products display a flow-like morphology with spherical particle.

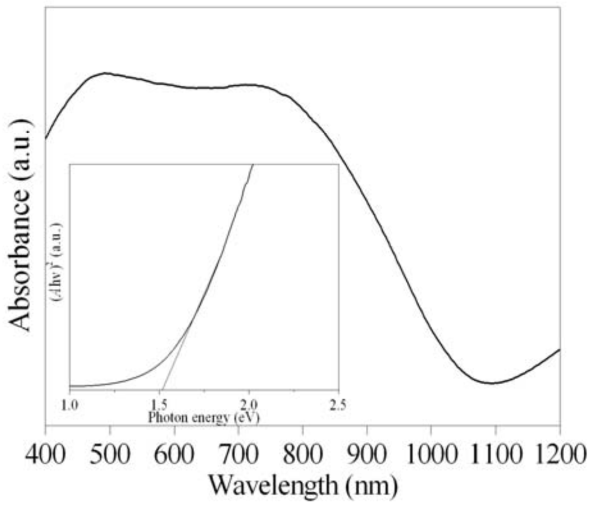

Fig.3 UV-vis-NIR absorption spectrum of the CFTS particles
Inset: Optical bandgap estimation of the CFTS particles.

The UV-vis-NIR absorption spectrum of the CFTS particles is shown in Fig.3. The as-synthesized CFTS particles exhibit a broad optical absorption in the UV-visible region. As shown in the inset, the optical bandgap energy of the CFTS particles can be estimated from the $(Ahv)^2$ versus hv graph (A=absorbance, h=Planck's constant and v=frequency) by extrapolating the linear absorption edge part of the curve. The optical bandgap of the CFTS particles is around 1.52eV.

4. Conclusion

In conclusion, a microwave irradiation method was developed for prepare synthesizing stannite CFTS particles. The prepared CFTS products display flow-liked particles with spherical structure. The optical bandgap of CFTS particles is around 1.52eV, indicating the suitable optical properties for solar cell applications.

Acknowledgement

This research is financial supported by the National Natural Science Foundation of China (No.51202211), Research fund of Key Laboratory for Advanced Technology in Environmental Protection of Jiangsu Province (AE201364).

References

[1] J. Y. Chane-Ching, A. Gillorin, O. Zaberca, A. Balocchi, X. Marie, Chem. Commun. **47**, 5229 (2011)
[2] S. K. Swami, A. Kumar, V. Dutta, Energy Procedia **33**, 198 (2013)
[3] O. Volobujeva, J. Raudoja, E. Mellikov, M. Grossberg, S. Bereznev, R. Traksmaa, J. Phys. Chem. Solids **70**, 567 (2009)
[4] J. Zhou, L. You, Q. Yi, Z. Ye, Mater. Lett. **107**, 225 (2013)
[5] R. A. Wibowo, E. S. Lee, B. Munir, K. H. Kim, Phys. Status Solidi A **204**, 3373 (2007)
[6] F. Liu, Y. Li, K. Zhang, B. Wang, C. Yan, Y. Lai, Z. Zhang, J. Li, Y. Liu. Sol. Energy Mater. Sol. Cells **94**, 2431 (2010)
[7] B. Shin, O. Gunawan, Y. Zhu, N. A. Bojarczuk, S. J. Chey, S. Guha, Prog. Photovolt. Res. Appl. **21**, 72 (2013)
[8] T. K. Todorov, J. Tang, S. Bag, O. Gunawan, T. Gokmen, Y. Zhu, D. B. Mitzi, Adv. Energy Mater. **3**, 34 (2013)
[9] X. Zhang, N. Bao, K. Ramasamy, Y. H. A. Wang, Y. Wang, B. Lin, A. Gupta, Chem. Commun. **48**, 4956 (2012)
[10] L. Li, X. Liu, J. Huang, M. Cao, S. Chen, Y. Shen, L. Wang, Mater. Chem. Phys. **133**, 688 (2012)
[11] C. Yan, C. Huang, J. Yang, F. Liu, J. Liu, Y. Lai, J. Li, Y. Liu, Chem. Commun. **48**, 2603 (2012)
[12] X. Jiang, W. Xu, R. Tan, W. Song, J. Chen, Mater. Lett. **102-103**, 39 (2013)
[13] L. H. Ai, J. Jiang, J. Mater. Chem. **22**, 20586 (2012)