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FLOWER-LIKE Cu_2MnSnS_4 PARTICLES SYNTHESIZED VIA MICROWAVE IRRADIATION METHOD

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Flower-like Cu_2MnSnS_4 (CMTS) particles were synthesized by a microwave irradiation method. The as-synthesized CMTS particles were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM) and UV-vis-NIR absorbance spectroscopy measurements. The results showed that the CMTS particles exhibit flower-like microspheres in shape and a suitable band gap (E_g=1.06eV) which is optimal for photovoltaic applications.

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Keywords: Cu_2MnSnS_4; microwave; flower-like

1. Introduction

Recently, there has been intense interest in research of quaternary chalcopyrite semiconductors owing to their attractive semiconducting properties and potential applications in thin film solar cells [1-3]. For example, the highest power conversion efficiency of 20.3% has been achieved using $CuInGaSe_2$ (CIGS) as the absorption layer [4]. As two promising materials to replace CIGS, the power conversion efficiencies of solar cells based on Cu_2ZnSnS_4 (CZTS) and $Cu_2ZnSn(S,Se)_4$ as high as 8.4% and 11.1% have been also reported[5-6]. Related to CZTS, Cu_2MnSnS_4 (CMTS) is also considered as possible photovoltaic material due to its suitable band gap and the requisite optical characteristics. The ferroelectric and magnetoelectric properties of semiconducting CMTS have been studied. However, the optical properties were rarely explored. Liang *et al* synthesized CMTS with zincblende and wurtzite structures by a hot-injection approach [7]. Compared with hot-injection method, microwave irradiation is the novel and economical method for short reaction times, simplicity and high yields. Furthermore, microwave heating have a potentially industrially advantage in the large-scale production of high quality nanomaterials owing to scaled-up processes without suffering thermal gradient effects. Herein, we report a microwave irradiation method to synthesize CMTS particles. The structure, morphology and optical properties were also well studied.

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2. Experimental details

$Cu(NO_3)_2 \cdot 3H_2O$ (Analytical Reagent, Nanshi-Reagent), $Mn(CH_3COO)_2 \cdot 4H_2O$ (Analytical Reagent, Nanshi-Reagent), $SnCl_2 \cdot 2H_2O$ (Analytical Reagent, Nanshi-Reagent) and H_2NCSNH_2 (Analytical Reagent, Nanshi-Reagent) were used without any further purification. In a typical procedure, $Cu(NO_3)_2 \cdot 3H_2O$ (0.06M), $Mn(CH_3COO)_2 \cdot 4H_2O$ (0.03M), $SnCl_2 \cdot 2H_2O$ (0.03M) and H_2NCSNH_2 (0.15M) were added in 50ml ethylene glycol under stirring for 2h at room temperature. Then the beaker was placed in a microwave oven (Midea, AG823LC7). The samples were irradiated at 500W for 5min and allowed to cool to room temperature. The precipitates were washed several times with de-ionized water and absolute ethanol, and dried in a vacuum oven at 80℃ for 2h.

The structure were investigated using a PANalytical X'Pert PRO diffractometer (XRD) with Cu K_α radiation, λ=0.15406 nm. The morphology of the synthesized product was analyzed using LEO-1530VP scanning electron microscope (SEM) and Tecnai F20 transmission electron microscope (TEM). The absorption spectra were performed on Varian Cary 5000 spectrophotometer using ethanol as a reference. All tests were conducted at room temperature.

3. Result and discussion

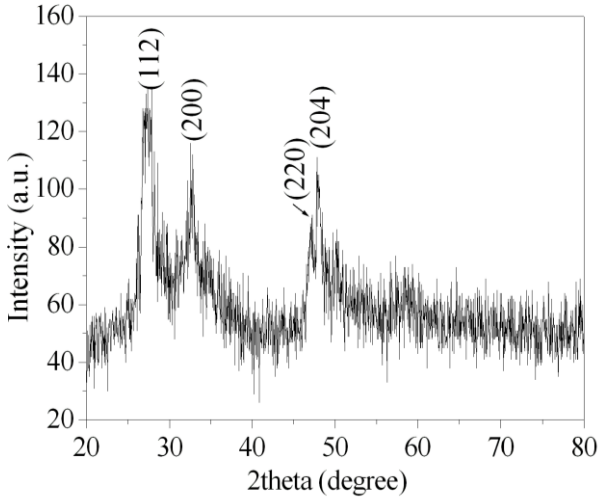

Fig.1 X-ray diffraction pattern of the as-synthesized CMTS particles

The XRD pattern of the as-obtained CMTS particles is shown in Fig.1. It can be seen that the XRD pattern matches well with the stannite structure of the CMTS particles (JCPDS NO.51-0757). The main diffraction peaks appeared at 2θ=28.1°, 32.8°, 46.8° and 47.1° corresponding to the (112), (200), (220) and (204) plans of CMTS, respectively. Except for these peaks, no other characteristic peaks of impurity phases are detected. The lattice parameters calculated from the XRD pattern were a=b=5.49Å and c=10.82Å, which is in good agreement with standard CMTS powder data. The plane also shows the broad full-width at half-maxima (FWHM), indicating the formation of nanocrystallinity. The average grain size, which is determined from X-Ray diffraction at grazing incidence using Debye-scherrer formula, calculated from the FWHM of the (112) plane is about 7.61nm.

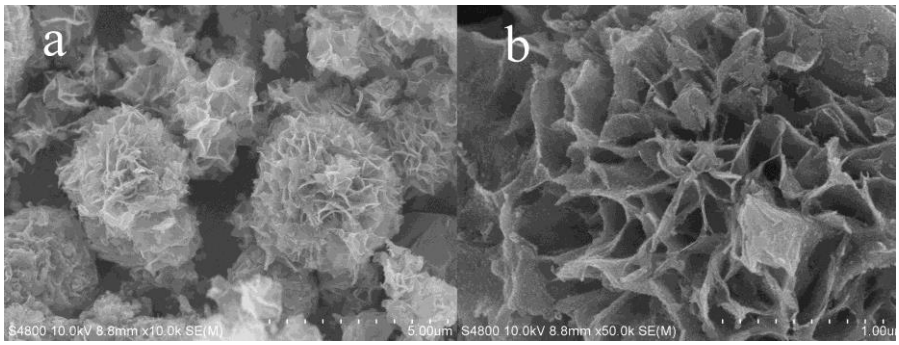

Fig.2 SEM images of the as-synthesized CMTS particles with low (a) and high (b) magnifications

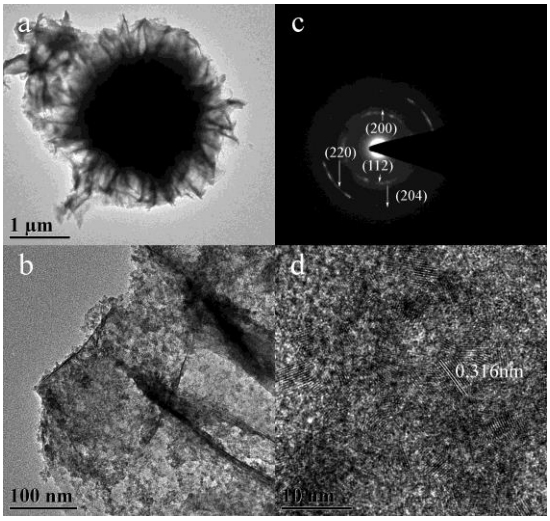

Fig.3 TEM images (a) and (b) of the as-synthesized CMTS particles dispersed in ethanol with SAED pattern (c) and HRTEM image (d)

Fig.2 shows the SEM images of the as-obtained CMTS particles. It indicates that the CMTS products are composed of large amount of flower-like particles with relatively uniform sizes of 2-3μm. Higher magnification in Fig.2 (b) reveals that the width of the petal is about 10nm. The TEM image, select area electron diffraction (SAED) image and high-resolution transmission electron microscopy (HRTEM) image of the as-obtained CMTS particles are shown in Fig.3. As shown in the TEM image, the CMTS particles that have flower-like microspheres in shape are composed of small nanocrystals with the average sizes of 5-10nm, which corresponds well with the XRD pattern. SAED image reveals the polycrystalline nature of CMTS particles which are indicated by the presence of diffraction spot corresponding to the (112), (200), (220) and (204) planes. The high-resolution TEM (HRTEM) shows the interplanar spacing of 0.316nm, which corresponds to the (112) plane. The possible formation mechanism of CMTS particles can be shown in Fig.4.

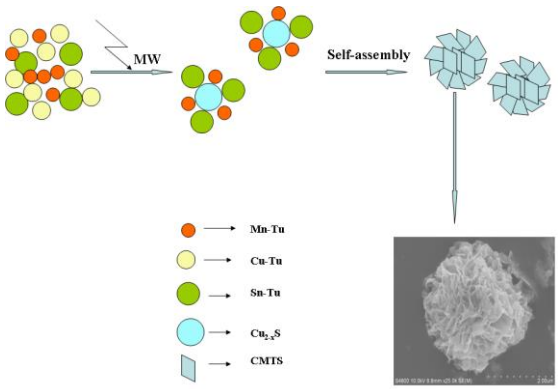

Fig.4 The growth mechanism of the as-synthesized CMTS particles

Fig.5 shows the UV-vis absorption spectroscopy of the CMTS particles in toluene, exhibiting a broad optical absorption in the UV-visible region. As shown in the inset, the optical bandgap of the CMTS particles can be estimated from the $(\alpha hv)^2$ versus hv graph, where 'α', 'h'and 'v'are the absorbance, Planck's constant and frequency, respectively, by extrapolation of the linear portion of the curve to $(\alpha hv)^2=0$. The value of the optical band gap is around 1.06eV. The value indicates the suitable optical properties for efficient solar energy conversion in a single-band-gap device.

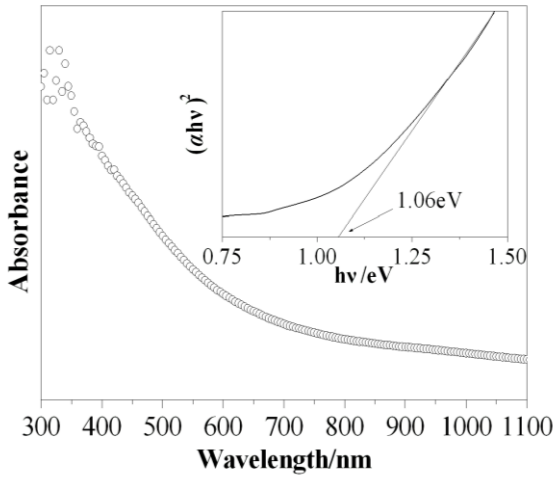

Fig.5 UV-vis-NIR absorption spectrum of the CMTS particles
Inset: Optical bandgap estimation of the as-synthesized CMTS particles

4. Conclusion

In summary, a microwave irradiation method was developed for prepare synthesizing flower-like CMTS particles. The structure, morphology and optical absorption were investigated by XRD, SEM, TEM and UV-vis spectroscopy. XRD confirmed the formation of CMTS phase with stannite structure. SEM and TEM showed that the CMTS particles are flower-like microspheres in shape. The optical bandgap of CMTS particles is around 1.06eV which is optimal for photovoltaic applications.

Acknowledgement

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