Quaternary Cu_2CdSnS_4 nanoparticles synthesised by microwave irradiation method

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Published in Micro & Nano Letters; Received on 18th November 2013; Revised on 3rd March 2014; Accepted on 7th March 2014

Quaternary Cu_2CdSnS_4 (CCTS) nanoparticles were synthesised via a microwave irradiation method. The as-synthesised CCTS nanoparticles were characterised by X-ray diffraction, energy dispersive spectroscopy, scanning electron microscopy, transmission electron microscopy and UV–vis–NIR absorbance spectroscopy measurements. It is shown that the CCTS nanoparticles exhibit a sphere-like shape and a suitable bandgap ($E_g = 1.26$ eV), indicating they are a potential candidate for application as the absorber layer in thin film solar cells.

1. Introduction: Recently, there has been intense interest in research of chalcopyrite semiconductors owing to their suitable bandgaps and high optical absorption coefficient for potential application in thin film solar cells [1, 2]. For example, Cu(In,Ga)Se_2 solar cells have obtained the highest power conversion efficiency of nearly 20% [3]. Cu_2ZnSnS_4 (CZTS) is considered as a promising candidate because of some limitations of the scarcity of In and Ga [4]. To date, the high power conversion efficiencies of solar cells based on Cu_2ZnSnS_4 and $Cu_2ZnSn(S,Se)_4$ as high as 8.4 and 11.1% have been reported [5, 6]. Cu_2CdSnS_4 (CCTS) with a bandgap of 1.37 eV and a large absorption coefficient over 10^4 cm^{-1} is also considered as a possible photovoltaic material owing to its similar structure with CZTS [7, 8].

A few works on Cu_2CdSnS_4 compounds have been reported. Cui *et al.* [9] synthesised Cu_2CdSnS_4 semiconductor nanorods with a wurtzite structure by a solvothermal method. Cao *et al.* [10] prepared Cu_2CdSnS_4 nanoparticles by a simple solvothermal process. Liu *et al.* [11] used a facile solution chemistry method to prepare Cu_2CdSnS_4 colloidal nanocrystals with a tetrahedral coordinated structure. Ito and Nakazawa [7] reported the preparation of Cu_2CdSnS_4 thin films by atom beam sputtering. However, all these reported methods involve some limitations, such as a long reaction time, complicated operations or high vacuum, and so on. As a chemical process, microwave irradiation is the novel and economical method for short reaction times, simplicity and high yield. To the authors' knowledge, the microwave synthesis of CCTS has rarely been reported. In this Letter, we report a microwave irradiation method to synthesise CCTS nanoparticles. The structure, morphology and optical properties were also investigated.

2. Experimental details: $Cu(NO_3)_2{\cdot}3H_2O$ (Analytical Reagent, Nanshi-Reagent), $CdCl_2{\cdot}21/2H_2O$ (Analytical Reagent, Nanshi-Reagent), $SnCl_2{\cdot}2H_2O$ (Analytical Reagent, Nanshi-Reagent) and H_2NCSNH_2 (Analytical Reagent, Nanshi-Reagent) were used without further purification. In this experiment, $Cu(NO_3)_2{\cdot}3H_2O$ (0.06 M), $CdCl_2{\cdot}21/2H_2O$ (0.03 M), $SnCl_2{\cdot}2H_2O$ (0.03 M) and H_2NCSNH_2 (0.15 M) were added in 50 ml of ethylene glycol. A clear solution was formed after stirring at room temperature for two hours. Then the beaker containing the solution was put into a microwave oven (Midea, AG823LC7). The samples were microwaved with a power of 500 W for 3 min. The precipitates were washed several times with deionised water and absolute ethanol. The products were finally dried in vacuum at 80°C for 2 h.

The structural studies were carried out using a PANalytical X'Pert PRO diffractometer (XRD) with Cu K_α radiation having a wavelength $\lambda = 0.15406$ nm. The microstructure was recorded using a LEO-1530VP scanning electron microscope (SEM) and a Tecnai F20 transmission electron microscope (TEM). The chemical composition of the products was analysed by energy dispersive spectroscopy (EDS) attached to a SEM. The optical characteristics were measured using a Varian Cary 5000 spectrophotometer to calculate the bandgap energy.

3. Result and discussion: Fig. 1 shows the XRD pattern of the as-synthesised products. It can be seen that the XRD pattern matches well with the cernyite structure of CCTS (JCPDS No. 29-0537) in the tetragonal space group I-42 m. The diffraction peaks at $2\theta = 28.2°$, 47.4°, 56.2° and 76.2° can be attributed to the (112), (220), (312) and (413) plans of CCTS, respectively. No other characteristic peaks from other crystalline forms are observed. The lattice parameters calculated from the XRD pattern were $a = b = 5.47$ Å and $c = 10.82$ Å, which matches well with standard CCTS powder data. The plane also shows the broad full-width at half-maxima (FWHM), indicating the formation of nanocrystallinity. The average grain size calculated from the FWHM of the (112) plane using the Debye-Scherrer

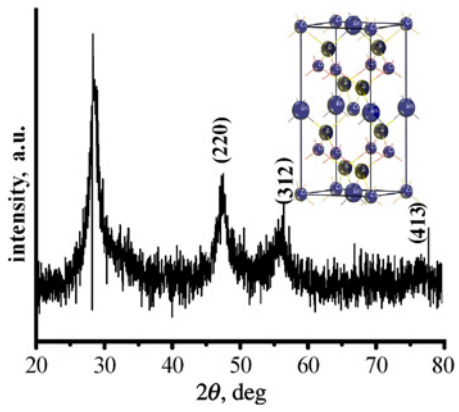

Figure 1 *X-ray diffraction pattern of the as-synthesised CCTS nanoparticles*

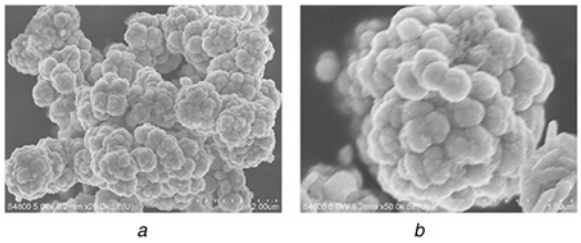

Figure 2 *SEM images of the as-synthesised CCTS nanoparticles*
a Low magnification
b High magnification

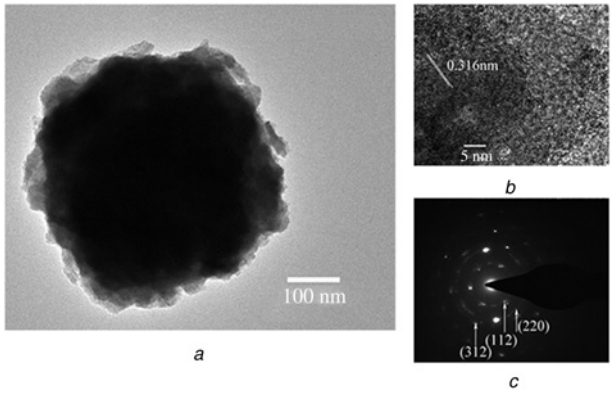

Figure 3 *TEM images analysis*
a TEM image of the as-synthesised CCTS nanoparticles dispersed in ethanol
b HRTEM image
c SAED pattern

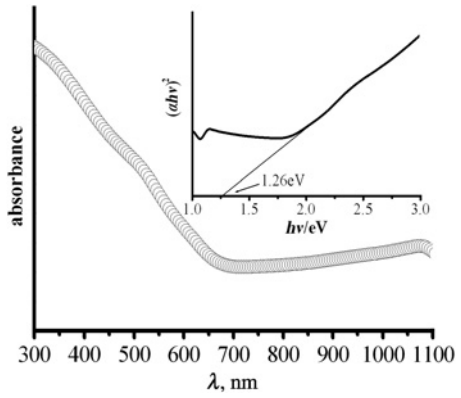

Figure 4 *UV–vis–NIR absorption spectrum of the CCTS nanoparticles*
Inset: Optical bandgap estimation of the as-synthesised CCTS nanoparticles

formula is about 6.35 nm. The average composition of the CCTS nanoparticles using energy dispersive spectrometry was determined to be 2.01:1.03:0.93:4.24, corresponding to the theoretical value of 2:1:1:4. The slightly Sn poor composition indicates the evaporation Sn during the reacting process.

Fig. 2 shows the SEM images of the as-synthesised CCTS nanoparticles. The SEM images (Figs. 2*a* and *b*) show that the product consists of a large amount of sphere-like particles with the average size of 200–400 nm. Furthermore, the higher magnification in Fig. 2*b* clearly shows that the sphere-like CCTS particles aggregate to a larger sphere-like shape. Fig. 3*a* shows the TEM image of the as-synthesised CCTS nanoparticles. It can be seen that the final CCTS nanoparticles are composed of small nanocrystals, which agree well with the XRD pattern. The high-resolution TEM (HRTEM) image in Fig. 3*b* shows the interplanar spacing of 0.316 nm that corresponds to the (112) plane of CCTS nanoparticles. The select area electron diffraction (SAED) pattern in Fig. 3*c* reveals the polycrystalline nature of the CCTS nanoparticles, as indicated by the presence of diffraction spots corresponding to the (112), (220) and (312) planes.

Fig. 4 shows the UV–vis absorption spectroscopy of the CCTS nanoparticles. It shows that the as-synthesised CCTS particles exhibit a broad optical absorption in the UV–visible region. As shown in the inset, the optical bandgap energy of the CCTS nanoparticles can be estimated from the $(\alpha h\nu)^2$ against $h\nu$ graph (α = absorbance, h = Planck's constant and ν = frequency) by extrapolating the linear absorption edge part of the curve. The optical bandgap of the CCTS particles is around 1.26 eV, indicating suitable optical properties for efficient solar energy conversion.

4. Conclusion: A microwave irradiation method has been developed for synthesising cernyite CCTS nanoparticles. The XRD, EDS, SEM and TEM characterisations confirm the structure, composition and morphology of the as-synthesised nanoparticles. The optical bandgap of the CCTS particles is around 1.26 eV, indicating suitable optical properties for solar cell applications.

5. Acknowledgments: This research is financially supported by the National Natural Science Foundation of China (no. 51202211), and the Research fund of Key Laboratory for Advanced Technology in Environmental Protection of Jiangsu Province (AE201364).

6 References

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doi: 10.1049/mnl.2013.0686