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Research Article

Synthesis of Flower-Like Cu_2ZnSnS_4 Nanoflakes via a Microwave-Assisted Solvothermal Route

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Flower-like Cu_2ZnSnS_4 (CZTS) nanoflakes were synthesized by a facile and fast one-pot solution reaction using copper(II) acetate monohydrate, zinc acetate dihydrate, tin(IV) chloride pentahydrate, and thiourea as starting materials. The as-synthesized samples were characterized by X-ray diffraction (XRD), Raman scattering analysis, field emission scanning electron microscopy (FESEM) equipped with an energy dispersion X-ray spectrometer (EDS), transmission electron microscopy (TEM), and UV-Vis absorption spectra. The XRD patterns shown that the as-synthesized particles were kesterite CZTS and Raman scattering analysis and EDS confirmed that kesterite CZTS was the only phase of product. The results of FESEM and TEM show that the as-synthesized particles were flower-like morphology with the average size of 1~2 μm which are composed of 50 nm thick nanoflakes. UV-Vis absorption spectrum revealed CZTS nanoflakes with a direct band gap of 1.52 eV.

1. Introduction

I_2–II–IV–VI_4 quaternary compounds, such as Cu_2ZnSnS_4 (CZTS) and $Cu_2ZnSnSe_4$ (CZTSe) based solar cells, exhibit optical and electronic properties comparable to Cu(In, Ga)(S, $Se)_2$(CIGS) and CdTe materials while consisting entirely of nontoxic constituents and avoid the scarcity issues associated with indium, gallium, cadmium, and tellurium. CZTS has a direct band gap of 1.4~1.5 eV and large absorption coefficient in the order of $10^4\,cm^{-1}$ [1–3]. Previous reports show that many methods have been utilized for fabricating CZTS thin films, included sputtering [4], electrodeposition [5], coevaporation [6], and coating [7, 8]. The photoelectric conversion efficiency of CZTS-based thin film solar cells has been improved from 0.66% in 1997 [9] to 12.6% in 2013 [10]. Because the narrow thermodynamic window demonstrates that chemical-potential control was important for the growth of high-quality crystals CZTS [11], methods including coevaporation and sputter which obtained high efficiency in CIGS solar cells were not achieved good performance in CZTS thin film solar cells. However, the wet chemical processes based on printing technology have achieved the record efficiency of CZTS solar cell [10]. Therefore, synthesis of CZTS nanoparticles by hot injection [12], solvothermal [13], hydrothermal [14], and other wet chemical [15] has attracted more attention, and the as-synthesized nanostructures including plate-like [12], sphere-like [13], and spindle-like [16] have been also researched. Although various methods have been utilized to prepare CZTS particles, searching for a simple and rapid synthetic route was still worthy of further exploration. Herein, we report a microwave-assisted solvothermal method to prepare homogeneous and dispersible CZTS flower-like particles from the direct reaction between metal salts and thiourea in ethylene glycol.

2. Experimental

Preparation of the CZTS Particles. Typically, $Cu(CH_3COO)_2{\cdot}H_2O$ (0.050 M), $Zn(CH_3COO)_2{\cdot}2H_2O$ (0.025 M), $SnCl_4{\cdot}5H_2O$ (0.025 M), and NH_2CSNH_2 (0.200 M) were added in sequence to 30 mL of ethylene glycol at room temperature under magnetic stirring until the chemistries were completely dissolved. Then the mixture was loaded into a Teflon autoclave of 90 mL capacity and putted

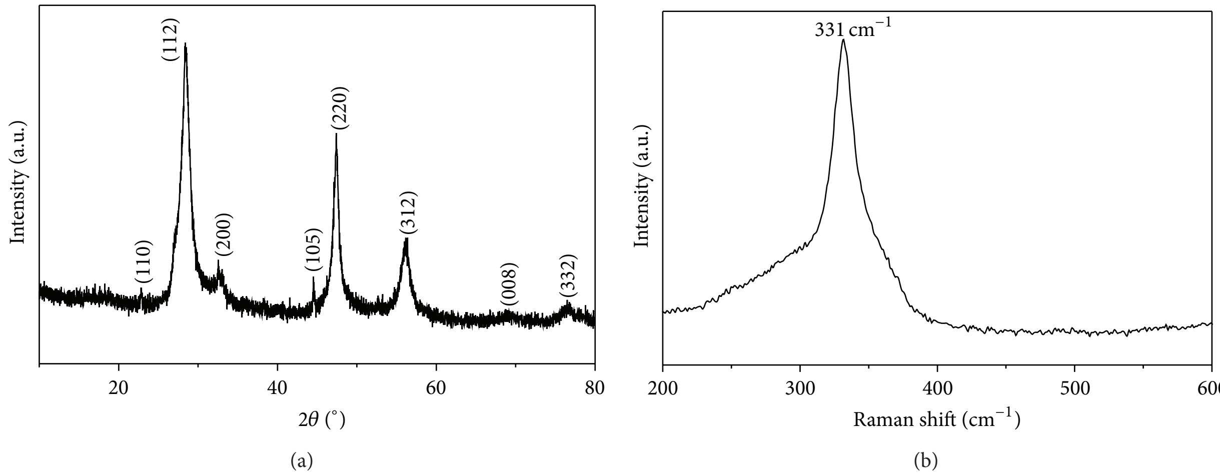

Figure 1: (a) XRD pattern of CZTS particles; (b) Raman scattering spectra of CZTS particles; the excitation laser wavelength is 532 nm.

into a microwave oven (2450 MHz, maximum power of 1200 W) heat to 230°C in 10 min and maintained for 1.5 h. The precipitates were centrifuged, washed by deionized water and ethanol for several times to remove by-products, followed by drying in a vacuum chamber at 80°C for 6 h.

Characterization of the CZTS Particles. The XRD patterns of as-synthesized particles were obtained on Panalytical X'Pert Pro with Cu Kα radiation (λ = 1.5406 Å) at 35 kV in a scanning range of 10°~80°. Raman spectra were recorded by using Thermo DXR Raman spectrometer at the room temperature, and the 532 nm line of an Ar^+ laser was used as the excitation source. FESEM images were observed by a Hitachi S-4800 field emission scanning electron microscope equipped with an energy dispersion X-ray spectrometer (EDS) and TEM images were recorded on JEOL JSF-2100 at 200 KV. Optical measurements were carried out with Shimadzu UV3600 UV-Vis spectroscopy.

3. Results and Discussion

The XRD pattern (Figure 1(a)) of the as-synthesized CZTS particles exhibits that the major XRD diffraction peaks appeared at 2θ = 28.44, 47.44 and 56.20 can be attributed to (112), (220), and (312) planes of the CZTS crystals (JCPDS card number 26-0575), respectively. However, the peaks of CZTS XRD patterns were similar to the ZnS (JCPDS card number 65-1691) and Cu_2SnS_3(JCPDS card number 27-0198), making it difficult to distinguish between them. So, Raman spectra have been carried out to confirm the products (Figure 1(b)), it exhibits a single intense peak at 331 cm^{-1}, which was consistence with previous study [17], and most importantly there was no peak at 275 cm^{-1}, 352 cm^{-1}, 267 cm^{-1}, 303 cm^{-1}, and 365 cm^{-1} suggest that the products absence of cubic ZnS and Cu_2SnS_3 [18].

The images of FESEM (Figures 2(a) and 2(b)) indicate that the as-synthesized CZTS particles were monodisperse superstructures with a uniform 3-dimensional flower-like morphology with the average size of 1~2 μm. Furthermore, these superstructures were built from intersectional nanoflakes with thickness about 50 nm (Figure 2(c)). The average composition of the products was Cu : Zn : Sn : S = 2 : 0.97 : 1.02 : 3.73 base on the result of EDS (Figure 2(d)), the slightly Sn rich and Zn poor composition deviated from stoichiometric may be due to different reactivity of starting materials.

The images of TEM, selected area electron diffraction (SAED), and high resolution transmission electron microscopy (HRTEM) of as-synthesized CZTS particles were shown in Figure 3. The average size of CZTS particles corresponds well with the FESEM images (Figure 2), and the flower-like particles were built from cross-nanoflakes (Figure 3(a)). SAED image reveals the polycrystalline nature of CZTS nanoflakes which was indicated by the presence of diffraction spots of (112), (220), and (312) planes. The HRTEM image of one nanoflake shows the interplanar spacing of 1.9 Å corresponding to the (220) planes.

The UV-Vis absorption spectrum of CZTS particles was shown in Figure 4. We determined the absorbance onset by plotting $(Ah\nu)^2$ versus $h\nu$ (A: absorbance, h: Planck's constant, and ν: frequency). From the long wavelength extrapolation of the band edge, the band gap was determined to be 1.52 eV which was in good agreement with the corresponding bulk materials [1]. This observation also eliminates existence of secondary phase of ZnS and Cu_2SnS_3. The good absorption in the visible light region may find its potential application in thin films solar cells.

4. Conclusions

Single phase kesterite CZTS has been prepared at 230°C for only 1.5 h via a microwave-assisted solvothermal without any surfactant; the CZTS particles with flower structure built from intersectional nanoflakes have been obtained, Cu : Zn : Sn : S = 2 : 0.97 : 1.02 : 3.73. Its founded microwave has strongly activated the process of solvothermal synthesis which significantly speeds up the reaction compared with

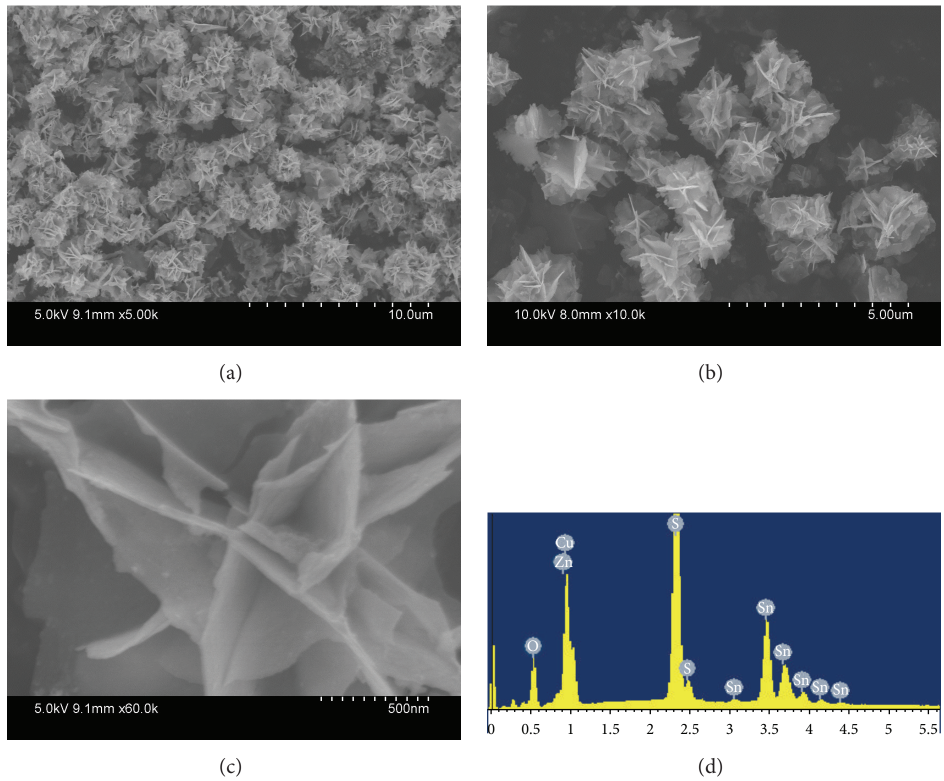

Figure 2: (a)–(c) FESEM images of CZTS particles; (d) EDS of CZTS particles.

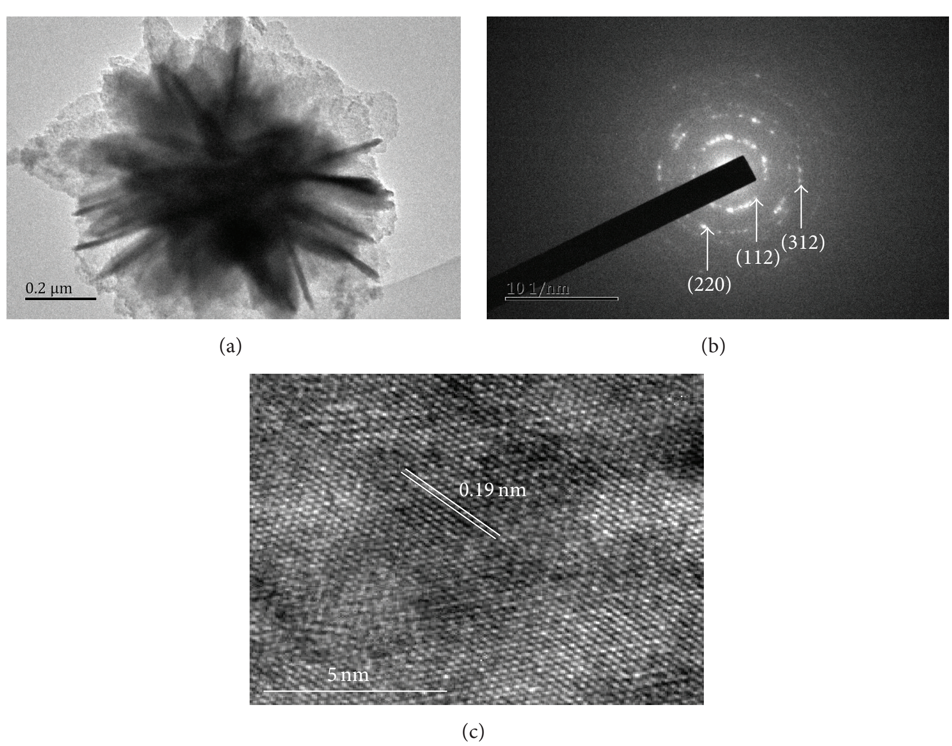

Figure 3: (a) TEM images of CZTS particles dispersed in ethanol; (b) SAED pattern; (c) HRTEM image.

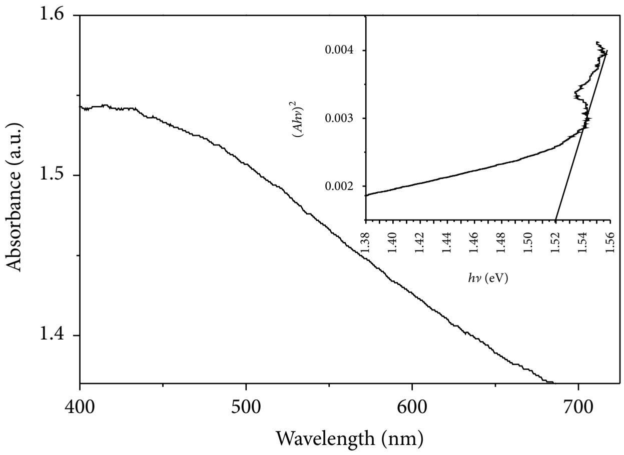

Figure 4: UV-Vis absorption spectrum of CZTS particles. The inset image shows a band gap of 1.52 eV.

traditional solvothermal synthetic methods. The UV-Vis absorption spectra of the products revealed that the band gap was 1.52 eV, which is optimal for photovoltaic applications.

Conflict of Interests

The authors declared that they do not have a direct financial relation with the commercial identities mentioned in this paper that might lead to any conflict of interest for any of the authors.

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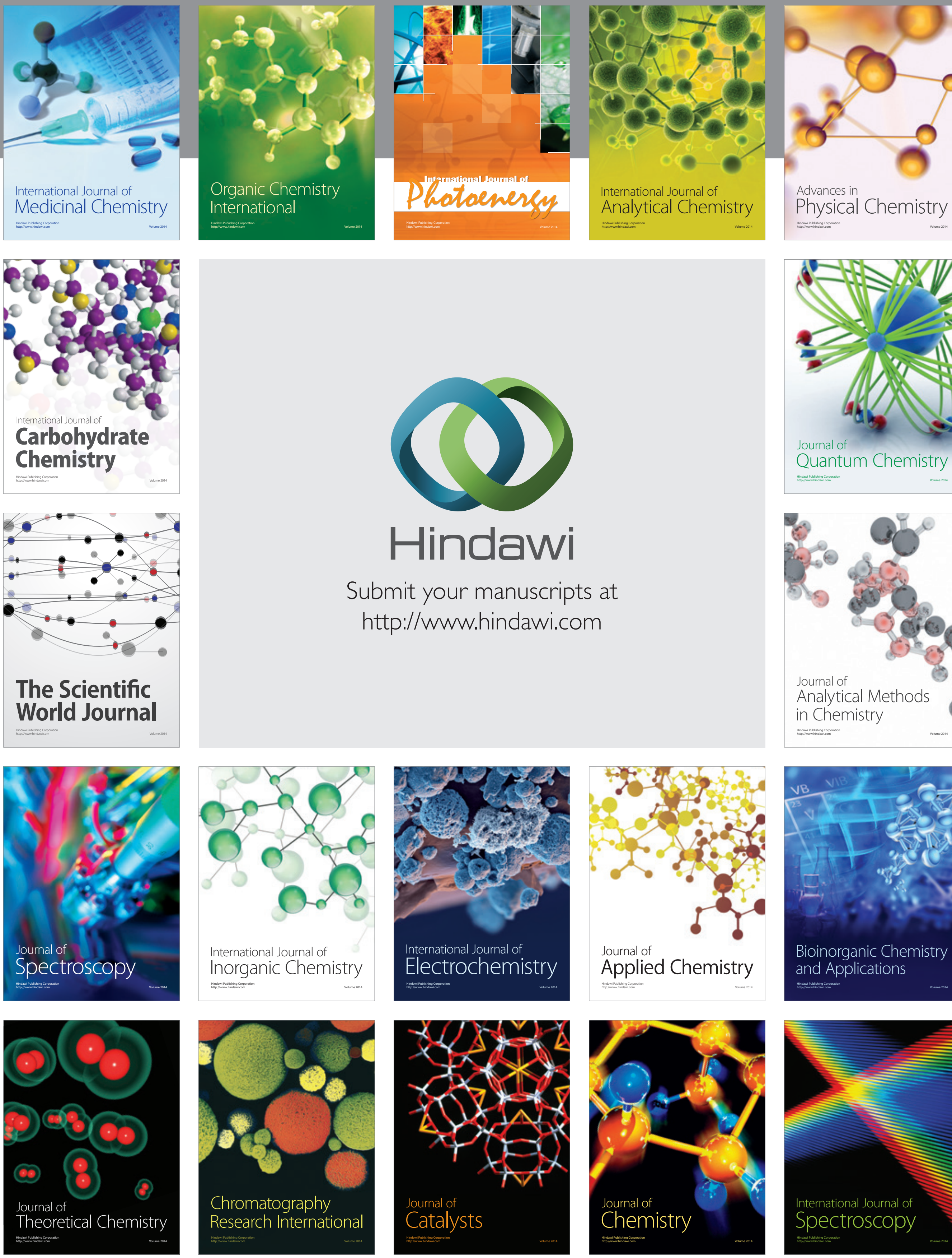
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