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SYNTHESIS AND CHARACTERIZATION OF FLOWER-LIKE QUATERNARY CHALCOGENIDE Cu_2FeSnS_4 MICROSPHERES WITH A MIXED SOLVENT STRATEGY

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Self-assembly uniform flower-liked Cu_2FeSnS_4 (CFTS) microspheres have been successfully synthesized by a facial and promisingly mixed solvent method for the first time. In this study, we adopted ethylene glycol (EG) and deionized water (DIW) as the mixed solvent and controlled the specific volume ratio of these two solvent. Besides, the addition of polyvinyl pyrrolidone (PVP) for the formation of flower-like CFTS microspheres also play a crucial role. The as-obtained products were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), energy dispersive spectrometry (EDS) and transmission election microscopy (TEM).

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1. Introduction

Among quaternary chalcogenides, $CuIn_xGa_{1-x}(S,Se)_2$(CIGS) solar cells technology have obtained the unceasing development and progress, but the relative lack of indium and gallium elements is a bottleneck restricting the future commercialization of CIGS cells [1,2]. In order to solve this problem, researchers have payed more attention to the inexpensive, nontoxic and earth-abundant materials, such as Cu_2ZnSnS_4(CZTS) [3,4], Cu_2GeSnS_4 [5], Cu_2FeSnS_4(CFTS) [6] and so on. Relative to CZTS which has been continuously developing and made some achievements, CFTS has the similar crystal structure of CZTS and the earth's crust reserves of Fe element is about 5%, so CFTS is also a very promisingly alternative material to CIGS solar cells.

In recent years, several means have been developed for the synthesis of CFTS materials. For example, An et al. [7] and Gui et al. [8] prepared CFTS nanocrystals by hydrothermal reactions, Yan et al. [9] and Zhang et al. [10] used the hot-injection method for the formation of CFTS particles, Ai et al. [11] and Guan et al. [12] synthesized CFTS materials via a rapid microwave method and Jiang et al. [13] adopted the solvothermal synthesis. Herein, we report that through a mixed solvent method which derived from the development of the hydrothermal/solvothermal method, [14-19] self-assembly and uniform size flower-like CFTS microspheres was successfully synthesized in a relatively low temperature. And a serial of characterization of as-obtained CFTS were investigated.

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2. Experimental details

2.1 Materials

Copper (II) chloride dihydrate ($CuCl_2 \cdot 2H_2O$), iron (III) chloride hexahydrate ($FeCl_3 \cdot 6H_2O$), tin (II) chloride dihydrate ($SnCl_2 \cdot 2H_2O$), thiourea (CH_4N_2S), ethylene glycol (EG) and polyvinyl pyrrolidone (PVP) were purchased from Sinopharm Chemical Reagent Co.,Ltd. Double distilled deionized water (DIW, 18.2 MΩ) was obtain by Thermo purification system. All the reagents and solvents were used without further purification.

2.2 Synthesis of the flower-like CFTS microspheres

In a typical experimental procedure, 1mmol $CuCl_2 \cdot 2H_2O$, 0.5mmol $FeCl_3 \cdot 6H_2O$, 0.5mmol $SnCl_2 \cdot 2H_2O$ were dissolved in 4mL DIW under magnetic stirring. Then we added 2.5mmol CH_4N_2S and 28ml EG and 0.56g PVP into the solution. After stirring half an hour, the mixture was loaded into a Teflon-lined stainless steel autoclave of 50 ml capacity. The sealed autoclave was maintained at 180 °C for 24 h and then allowed to cool to room temperature. The precipitate was centrifuged and washed with deionized water and ethanol six times to remove by-products. The final product was vacuum-dried at 80 °C overnight.

2.3 Characterization of the flower-like CFTS microspheres

The phase and the crystalline structure of the samples were confirmed by powder X-ray diffraction (XRD) via an X-ray diffractometer (XRD, Rigaku smatrlab, Cu K_1 radiation λ=0.1542nm). The morphology and particle sizes were characterized by a scanning electron microscope (SEM, Cam Scan 2600 FE) and the elemental composition of the products were analyzed by energy dispersive spectrocopy (EDS) coupled with the SEM. The transmission election microscopy image of the samples were obtained by transmission electron microscopy (TEM, FEI Tecnai G20), and the selected area electron diffraction (SAED) and high resolution TEM (HRTEM) of the particles are studied.

3. Result and discussion

3.1 Influence of the ratio of the mixed solvent

In contrast to hydrothermal/solvothermal method, the characteristic of the mixed solvent method is that special morphologies or interesting nanostructure can be acquired by tuning the components and volume ratios of the mixed solvent. In our experiments, we found that changing the ratio of ethylene glycol (EG) and deionized water (DIW) can obtain the uniform flower-like CFTS microspheres, and the XRD patterns of the samples of different ratios (EG:DIW = 0:1, 1:3, 1:1, 3:1, 7:1 and 1:0 respectively) were shown in Figure 1a. Figure 1a indicated that only when EG in the mixed solvent took up most or all of the volume, the CFTS material could be successfully synthesized. Without DIW, the morphology of the product (Figure 1b) showed that the product was consisted of disorderly nanosheets assembly units. But when the ratio of EG and DIW was 7:1, the uniform flower-like CFTS microspheres could be obtained. Hence, the ratio of EG and DIW play a crucial role.

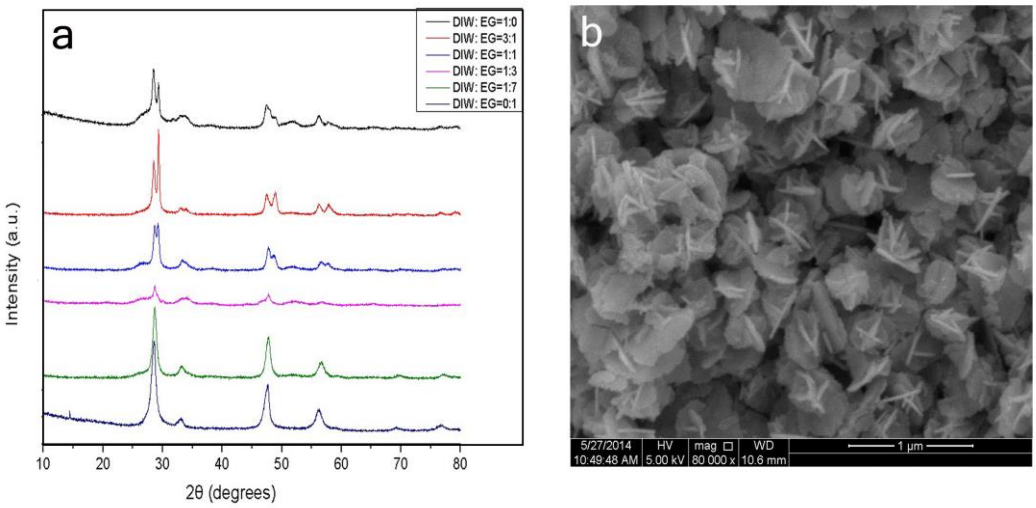

Fig.1 (a) XRD patterns of the samples of different ratios and
(b) the SEM image of the samples without DIW

3.2 Influence of the molecular weight of PVP

Polyvinyl pyrrolidone (PVP), as a common surface ligand, was also an indispensable factor in the synthesis of the uniform flower-like CFTS microspheres. With the purpose of verifying that the different molecular weight PVP influenced on the experimental product, we chose three different molecular weight PVP (K13-15, K30 and Mw=1300000) as raw materials for the contrast experiments. We can see form the XRD patterns of Figure 2a the products of three different PVP that the CFTS materials were prepared well. However, the TEM images (Figure 2b-c) of these products demonstrated that with the increasing of the molecular weight of PVP, the shape of the microspheres became more regular and the size of them trended to be uniform.

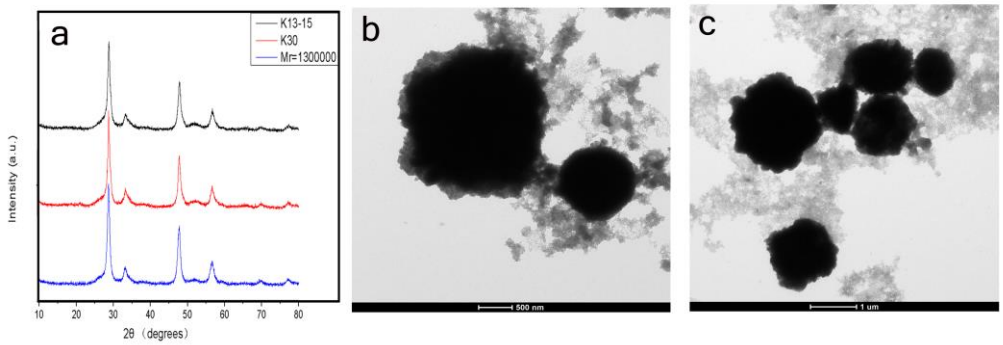

Fig.2 (a) XRD patterns of the as-obtained samples with three different PVP and (b,c) TEM images of the samples with K13-15 PVP and K30 PVP

3.3 Synthesis of the CFTS flower-like microspheres

The crystalline structure of the as-obtained sample was first confirmed by XRD. The diffraction pattern shown in Figure 3a was indexed to the stannite structure in the tetragonal space group $I\bar{4}2m$ and the three broad peaks of the XRD pattern are at 2θ= 28.5º, 47.4º and 56.3º corresponding to the (111), (202) and (311) planes. The transmission election microscopy (TEM) image of the samples shown in Figure 3b indicated that the size of the particle was about 2μm and the edge of the particle had the clear nanosheets. And in Figure 3c the selected area electron diffraction (SAED) pattern obtained from the nanosheets demonstrated that the CFTS microspheres was in the form of the single crystal and displayed good crystallinity. The Figure 3d was the High-resolution TEM (HRTEM) illustrating that the interplanar spacing of 0.31nm matched well with the (112) lattice plane of the tetragonal CFTS.

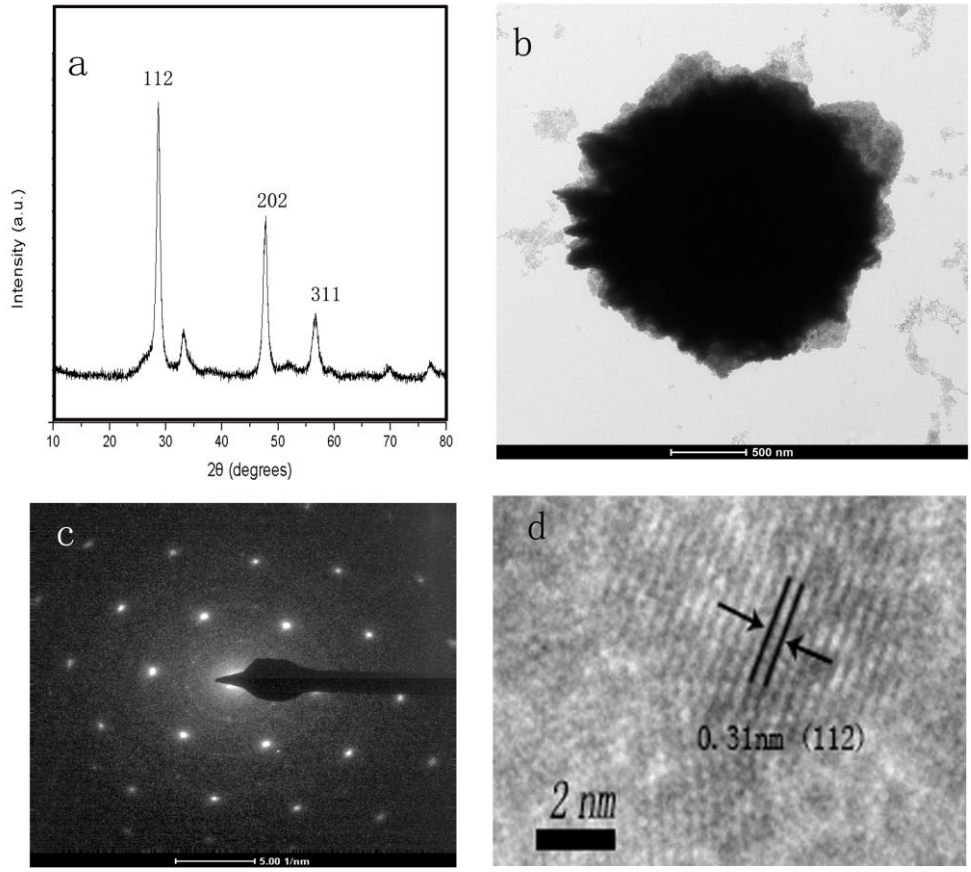

Fig 3. (a) XRD pattern, (b) TEM image, (c) SAED pattern and (d) HRTEM image of the as-obtained CFTS samples

Figure 4 is the scanning electron microscopy (SEM) images of the samples from which the morphology and size of the CFTS particles can be characterized. As shown in Figure 4a-b, the as-obtained sample was composed of nearly uniform flower-like microspheres. Figure 4c was the magnified image of an individual CFTS microsphere and we can see that the size of the individual was about 2μm. Every microsphere was consisted of nanosheets which were the agglomeration of amounts of nanoparticles and the thick of each nanosheet was about 100nm. The composition of

the CFTS sample was identified by energy dispersive spectrometry and the elemental analysis result in Figure 4d indicates that the sample only includes four elements and the atomic ratio of Cu: Fe: Sn: S was calculated to be 2.97:1:1.26:3.69. In consideration of the existential error of EDS detector, the above value basically matched well with the desired ratio of 2:1:1:4.

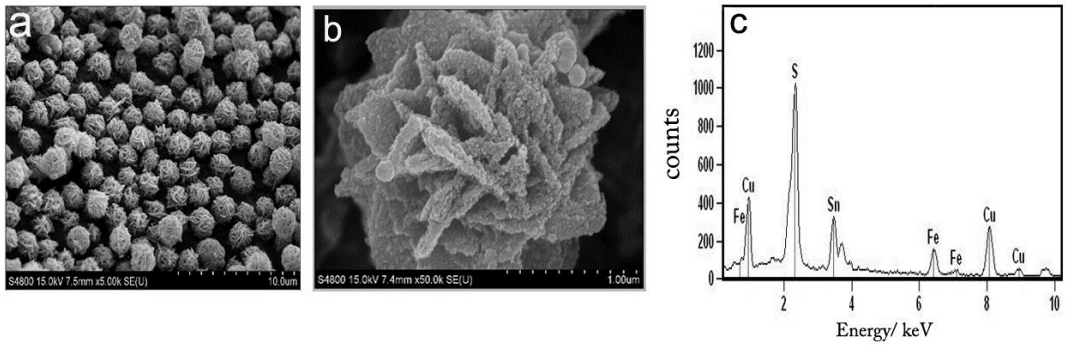

Fig 4. (a) SEM images, (b) SEM images with the high magnification and (c) EDS of of the as-obtained CFTS samples

4. Conclusions

In summary, the self-assembly uniform flower-like CFTS microspheres were successfully prepared by the mixed solvent method in a relatively low temperature for the first time. The ratio of EG and DIW confirmed by means of the trail of different ratio was 7:1 for the synthesis of the final product. What's more, we found that the molecular weight of PVP played a significant impact on the shape and the size of the experimental products. As the potential alternative to CIGS materials, CFTS still existed the big promotion space waiting for us to explore, such the properties, the mechanism and so on.

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