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Solvothermal synthesis and characterization of copper indium diselenide microflowers

Huiyu Chen [a,b,*], Dan Nie [a,b], Chunju Xu [a,b], Guizhe Zhao [a,b], Yaqing Liu [a,b,*]

[a] *Research Center for Engineering Technology of Polymeric Composites of Shanxi Province, North University of China, Taiyuan 030051, China*
[b] *School of Materials Science and Engineering, North University of China, Taiyuan 030051, China*

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Novel flower-like copper indium diselenide ($CuInSe_2$) microstructure has been successfully prepared via a solvothermal process at 180 °C for 36 h. Selenium powder, copper (II) chloride, and indium (III) chloride were employed as the starting materials. Ethylenediamine was served as both solvent and reducing reagent, and no surfactant or any template was employed during the entire synthetic process. The $CuInSe_2$ microflowers with size ranging from 25 to 30 μm were constructed by many platelet-like petals with thickness of 150 nm. The assembled petals with coarse and smooth surface could be obtained with different solvothermal durations, and shape evolution process was proposed on the basis of time-dependent experiments. The band gap was calculated to be 1.04 eV according to the UV–vis absorption spectrum.

1. Introduction

Ternary I–III–VI_2 chalcopyrite semiconductors have triggered great interest due to their promising photovoltaic applications. One good example is copper indium diselenide ($CuInSe_2$), which has unique structure and excellent electrical properties including direct band gap (~1.05 eV) at the red edge of solar spectrum, high optical absorption coefficient (~10^5/cm), and good radiation stability [1,2]. Therefore, this material is an ideal candidate for the production of photochemical devices. Thin film solar cells made of $CuInSe_2$ based chalcopyrite are able to achieve conversion efficiencies as high as 21.5% [3]. Up to now, $CuInSe_2$ micro-/nanostructures with various shapes such as nanoparticles [4,5], nanorods [6], nanowires [7,8], nanotubes [9], and dandelion-shaped microstructures [10], were successfully prepared via different routes. In addition, Chang et al. [11] fabricated $CuInSe_2$ nanoflowers in a mixture of trioctylphosphine oxide, trioctylphosphine and aliphatic amine used both as a capping agent and a reaction solvent, and the surface of these nanoflowers are composed of many small nanoparticles. To the best of our knowledge, there is still no report about the synthesis of perfect flower-like $CuInSe_2$ microstructures assembled by petals in single type of solvent so far.

Herein, we report a solvothermal approach to prepare $CuInSe_2$ microflowers in the solvent of ethylenediamine without using any template or surfactant. Elemental selenium powder, copper (II) chloride, and indium (III) chloride were employed as the starting materials. Flower-like $CuInSe_2$ microstructures composed of many platelet-like petals with coarse and smooth surface could be obtained with different solvothermal durations. The present facile method is mild and effective for large-scale production of $CuInSe_2$ microstructures.

2. Experimental procedure

Materials and method: All reagents were analytical grade and were used without further purification. In a typical procedure, 0.395 g of Se powder was dissolved in 40 mL of ethylenediamine at 80 °C with magnetic stirring, after 1 h, 0.427 g of $CuCl_2.2H_2O$ and 0.553 g of $InCl_3$ were introduced. The mixture was transferred into a Teflon-lined stainless-steel autoclave of 50 mL capacity, sealed and maintained at 180 °C for 36 h. Finally, the product was collected, rinsed with distilled water and absolute ethanol several times, and dried at 35 °C in an electronic oven for several hours. Controlled experiments were conducted by changing the reaction time while the other synthetic parameters were kept unchanged.

Characterizations: XRD pattern was recorded on a Bruker D8 focus diffractometer with Cu Kα radiation. FESEM images were taken on a JEOL JSM6700F scanning electron microscope equipped with an EDS attachment and TEM image was obtained by a JEOL JEM2100F transmission electron microscope with an accelerating

* Corresponding authors at: Research Center for Engineering Technology of Polymeric Composites of Shanxi Province, North University of China, Taiyuan 030051, China. Tel./fax: +86 3513559669.
E-mail addresses: hychen09@sina.com (H. Chen), zfflyq98@sina.com (Y. Liu).

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voltage of 200 kV. XPS measurements were conducted on an ESCA 2000 spectrometer using Al Kα X-ray as the excitation source. UV–vis-NIR absorption spectrum was measured with a SHIMADZU UV-3600 spectrophotometer.

3. Results and discussion

Fig. 1a displays the XRD pattern of the product prepared at 180 °C for 36 h. All peaks can be indexed as chalcopyrite tetragonal $CuInSe_2$ by comparison with the JCPDS no.40-1487. No peaks of impurities are detected, indicating that the product is rather pure. The chemical composition was analyzed by EDS (not shown here) and has a Cu/In/Se molar ratio of 0.99/1/1.96, nearly stoichiometry of $CuInSe_2$. The valence states of the above $CuInSe_2$ sample were further examined by XPS. Fig. 1b showed the Cu 2p core-level spectrum and two intense peaks were located at 932.5 and 952.4 eV, which corresponded to Cu $2p_{3/2}$ and $2p_{1/2}$, respectively. Additionally, the typical satellite peak for Cu^{2+} (942 eV) did not emerge. It implied that the chemical valence state of copper is +1 and well consistent with the literature report [4]. Meanwhile, the binding energies for In 3d (445.2 and 452.7 eV) and Se 3d (54.4 eV) were given in their core-level spectra (Fig. 1c and d), which were in good agreement with the previously reported values for $CuInSe_2$ [4,12].

The shape and microstructure of the obtained $CuInSe_2$ was investigated by SEM and TEM. Fig. 2a displayed the panoramic view of the sample, from which flower-like architectures with high quantities can be seen. A minute amount of particles or patches also coexisted. A close-up view of Fig. 2b showed a typical $CuInSe_2$ microflower with the overall size of about 30 μm, and a few small particles attached on the assembled petals. From the magnified SEM image in the inset, we find that the surface of the platelet-like petals was coarsed and many nano-pricks protruded out. The thickness of the petals was uniform with average values of about 150 nm. A representative TEM image (Fig. 2c) displayed several $CuInSe_2$ microflowers aggregrated together, and the diameters ranged from 25 to 30 μm, almost consistent with the SEM observations. The SAED pattern in the inset possessed several discrete spot rings, indicating the polycrystalline nature of the $CuInSe_2$ product. The features of platelet-like petals were sufficiently revealed by the appearance of the clear edges (Fig. 2d), and the observed lattice spacing in HRTEM image (inset of Fig. 2d) was calculated to be 0.34 nm, corresponding to that of the (112) planes of $CuInSe_2$.

In order to investigate the formation process of such novel flower-like $CuInSe_2$ microstructures, time-dependent experiments were carried out and samples solvothermally treated for 6, 15, 24, and 48 h were characterized by SEM. Particles with size in the range of 200–500 nm were produced on a large scale when the reaction proceeded for 6 h (Fig. 3a). These particles have a strong tendency to aggregate in order to reduce the interfacial energy, and the size grew larger when the reaction time was extended to 15 h. As shown in Fig. 3b, $CuInSe_2$ microparticles with coarse surface were dominant, and a few micropatches also coexisted together. As the solvothermal treatment was continued, the surface of the microparticles became much rougher and some undeveloped petals emerged (Fig. 3c). The edges of undeveloped petals could be clearly seen and protruded out. The overall size of such microparticles is about 20 μm. The petals grew into platelet-like shape with coarse surface when the reaction was further prolonged (Fig. 2a). Interestingly, smooth surface was finally obtained with a time of 48 h and the thickness was increased to ca. 250 nm (inset of Fig. 3d). The diameter of these flower-like $CuInSe_2$ microstructures with smooth petals is about 30–35 μm. From the SEM observations of the above several samples, the Ostwald ripening process was proposed for the growth of $CuInSe_2$ microflowers. Small particles were formed firstly with size in a relatively wide range, and in the following steps, these small particles could serve as seeds for the growth of microflowers at the expense of smaller particles through the Ostwald ripening.

Many factors including temperature, concentrations, pH values, and types of starting materials, would influence the shapes and size of final products. In our previous work, we obtained $CuInSe_2$

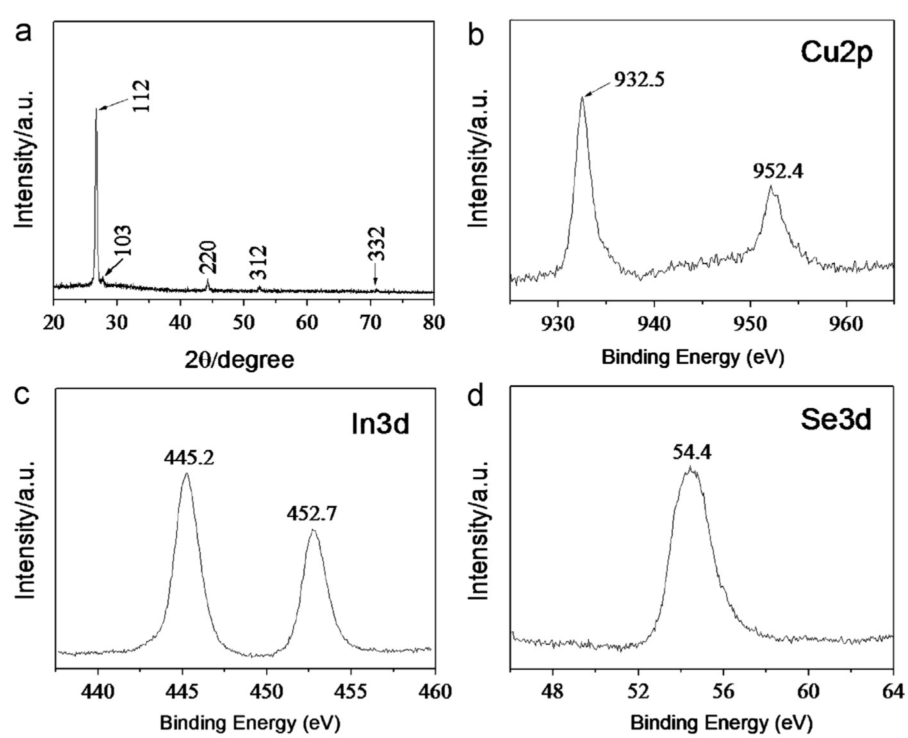

Fig. 1. (a) XRD pattern, (b) Cu 2p, (c) In 3d, and (d) Se 3d XPS core-level spectrum of flower-like $CuInSe_2$ microstructures synthesized at 180 °C for 36 h.