



Complexing Agent Controlled Synthesis of CuInS₂ Microcrystals with Hierarchical Architectures†

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Three different kinds of hierarchical three-dimensional (3D) copper indium sulfide (CuInS₂) microstructures (nanosheet-based microflowers, nanoplatelet-based solid microspheres and nanoflake-based porous microspheres) were synthesized by a facile ethanol solvothermal treatment from CuCl₂·2H₂O, sodium diethyldithiocarbamate (DDTC-Na), InCl₃·4H₂O and NH₂CSNH₂, where DDTC-Na acted as a complexing agent and structure-directing agent. The crystal structure, composition and morphology of the as-prepared products are characterized by X-ray diffraction, energy dispersive X-ray spectrometry, field-emission scanning electron microscopy. The morphology of CuInS₂ microcrystals were greatly affected by the concentration of DDTC-Na. When the concentration of DDTC-Na was increased from 0.0125, through 0.025-0.05 mol L⁻¹, the morphology of CuInS₂ could be changed from microflowers, through solid microspheres to porous microspheres. Based on the investigation on the influence of DDTC-Na, the possible mechanism for the formation of CuInS₂ microstructures is simply discussed.

Key Words: CuInS₂, Microstructures, Solvothermal technique, Nanomaterials.

INTRODUCTION

Nanoscale to microscale materials often exhibit physical and chemical properties that differ greatly from their bulk counterparts¹ and have attracted much attention because of their structural, electronic and optical properties and their potential applications. In recent years, self-assembled structures with highly specific morphology are of great interest to chemists and materials scientists. In particular, hierarchical self-assembly of nanoscale building blocks, such as nanotubes, nanowires, nanobelts and nanoplatelets, is an important process for the fabrication of functional electronic and photonic nanodevices²⁻⁵.

As an important I-III-VI₂ ternary semiconductor, copper indium disulfide (CuInS₂) is regarded to be effective light-absorbing materials for photovoltaic solar cells due to its direct band gap of 1.53 eV and a large absorption coefficient ($\alpha \sim 10^5 \text{ cm}^{-1}$)⁶⁻⁸. In addition, CuInS₂ is a candidate for the cathode material of photochemical devices owing to its high performance and high output stability⁹. Over the past decades, considerable effort has been focused on synthesizing various morphologies of the CuInS₂ nanomaterials using different preparing methods. Castro *et al.*¹⁰ prepared colloidal CuInS₂

nanoparticles through thermal decomposition of the molecular single-source precursor (PPh₃)₂CuIn(SEt)₄ in the presence of hexanethiol in dioctylphthalate. Jiang *et al.*^{11,12} synthesized CuInS₂ nanorod and nanotubes by a elemental solvothermal reaction. Qian *et al.*¹³ synthesized uniform CuInS₂ porous microspheres on a large scale using CuCl₂·2H₂O, InCl₃·4H₂O and KSCN as starting reagents in ethylene glycol at 200 °C for 12 h. Chaudhuri *et al.*⁷ prepared CuInS₂ flower vase-like nanostructure arrays on Cu-tape substrates by a self-catalyzed vapour-liquid-solid (VLS) technique. Tang *et al.*¹⁴ prepared hollow CuInS₂ microspheres *via* a simple solution-based route without employing templates and surfactants. Xiang *et al.*¹⁵ synthesized CuInS₂ microspheres *via* a mild solvothermal approach involving CuCl₂·2H₂O as the copper source, InCl₃ as the indium source, L-cysteine as the sulfur source and N,N-dimethylformamide as the reaction medium. Herein, we developed a facile complexing agent controlled solvothermal process to synthesize hierarchical 3D CuInS₂ microstructures by the reaction of copper chloride dihydrate, indium chloride tetrahydrate and thiourea at 200 °C for 30 h. During the process of synthesis, copper reagent (DDTC-Na) was introduced into the reaction system. Diethyldithiocarbamate is a bidentate ligand with two anchor sulfur atoms, which can complex with

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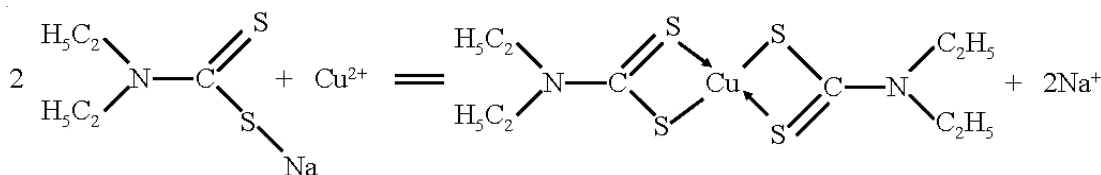


Fig. 1. Reaction process of complexation

Cu²⁺ to form coordination complex Cu(DDTC)₂¹⁶. The complexing reaction is shown in Fig. 1. The morphology of the synthesized CuInS₂ could be easily controlled by adjusting the adding amount of DDTC-Na. When the concentration of DDTC-Na was increased from 0.0125, through 0.025-0.05 mol L⁻¹, the morphology of CuInS₂ could be changed from microflowers, through solid microspheres to porous microspheres.

EXPERIMENTAL

All chemicals (analytical grade reagents) were purchased from Shanghai Chemical Reagents Co. and used without further purification.

General procedure: In a typical experimental procedure, 1 mmol CuCl₂·2H₂O, DDTC-Na (0.5, 1.0 or 2.0 mmol), 1 mmol InCl₃·4H₂O and 2 mmol NH₂CSNH₂ were added into a 50 mL Teflon-lined stainless steel autoclave. It was filled with absolute ethanol up to 80 % of the total volume. The obtained reaction mixture was stirred for an additional 50 min. The autoclave was sealed and maintained at 200 °C for 30 h. After the reaction was completed, the resulting black solid products were filtered off, washed with absolute ethanol and distilled water for several times and then finally dried in a vacuum at 60 °C for 4 h.

Detection method: The phase purity of the as-synthesized products was examined by X-ray diffraction (XRD) using a Dandong Y-2000 X-ray diffractometer equipped with graphite monochromatized CuK_α radiation (λ = 1.54178 Å). Field-emission scanning electron microscope (FESEM) images of the samples were taken on a field-emission microscope (Sirion 200, 15 kV) attached with the energy dispersive X-ray spectrometry (EDX).

RESULTS AND DISCUSSION

The typical XRD patterns of the as-prepared CuInS₂ products (sample A: 0.5 mmol DDTC-Na, sample B: 1 mmol DDTC-Na and sample C: 2 mmol DDTC-Na) are shown in Fig. 2(a). Four prominent XRD peaks can be indexed to the CuInS₂ crystal planes of (112), (004), (204)/(220) and (312), which give a tetragonal structure with the measured lattice constants of *a* and *c* of 5.524 and 11.15 Å, respectively, consistent with the standard values of the reported data (JCPDS File, 27-0159, *a* = 5.523 Å, *c* = 11.14 Å). No characteristic peaks belonging to other impurities were detected. The sharp diffraction peaks indicate the good crystallinity of the as-prepared products.

The purity and composition of the as-prepared sample are reflected by EDX analysis (Fig. 2(b)). The result exhibits only the presence of Cu, In and S elements in products. The molar ratio of Cu:In:S obtained from the peak areas is 1.02:0.98:1.97, which is in agreement with stoichiometry of CuInS₂, confirming the XRD analysis. No impurities were

detected in the EDX survey spectrum of CuInS₂ (sample A). The two peaks assigned to Al and O come from aluminum specimen stage.

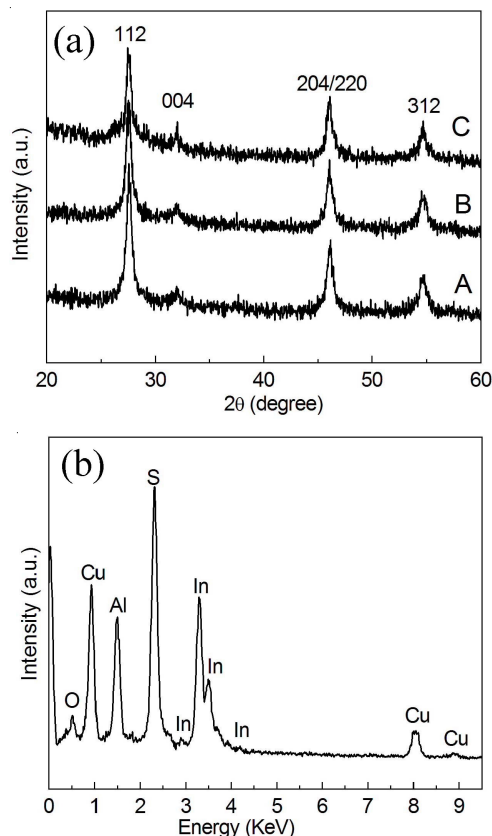


Fig. 2. XRD pattern (a) and EDX result (b) of the as-prepared sample

Based on the FESEM observation, we discover that the obtained products (samples A, samples B and samples C) take on different morphologies, which are shown in Fig. 3. Fig. 3(a) and (b) give the pictures of sample A obtained by adding 0.5 mmol DDTC-Na (0.0125 mol L⁻¹). Fig. 3(a) is the low-magnification image, which indicates that the products are mainly composed of flower-like microstructures with diameters ranging from 2-5 μm. The enlarged image (inserted at the lower left corner of Fig. 3(a)) clearly demonstrates that the prepared CuInS₂ microflowers are composed of nanosheets with thickness of 45 nm. Fig. 3(b) shows a single beautiful flower-like microcrystal with diameter of 3 μm, which is assembled by many nanosheets with certain thickness radiating from the same nuclei center.

Fig. 3(c) and (d) show the morphologies of sample B obtained by adding 1 mmol DDTC-Na (0.025 mol L⁻¹), which indicates that the CuInS₂ products are sphere-like microcrystals with considerably rough surfaces constructed of nanoplatelets. These microspheres are compact and solid. The

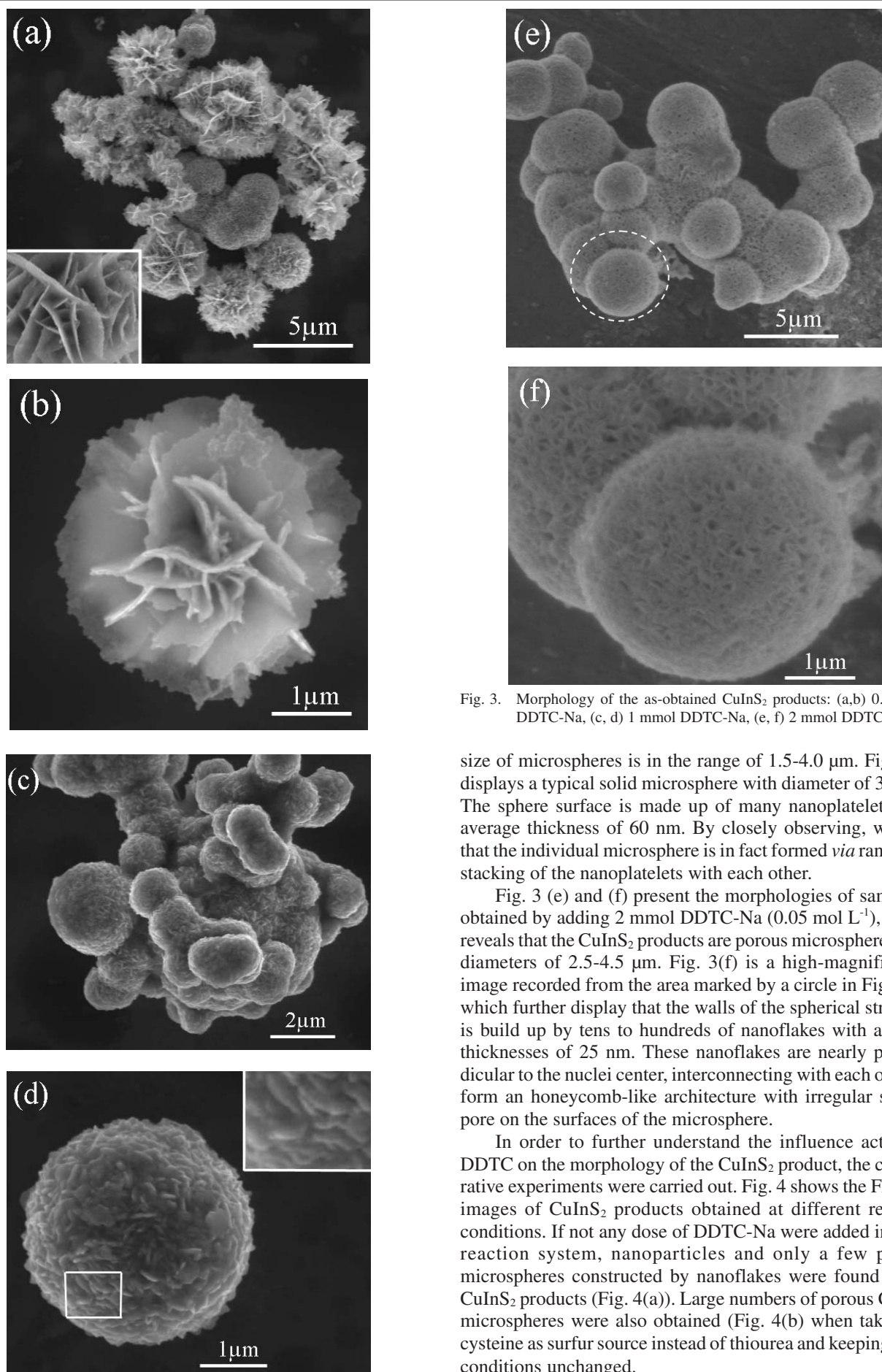


Fig. 3. Morphology of the as-obtained CuInS₂ products: (a,b) 0.5 mmol DDTC-Na, (c, d) 1 mmol DDTC-Na, (e, f) 2 mmol DDTC-Na

size of microspheres is in the range of 1.5-4.0 μm . Fig. 3(d) displays a typical solid microsphere with diameter of 3.2 μm . The sphere surface is made up of many nanoplatelets with average thickness of 60 nm. By closely observing, we find that the individual microsphere is in fact formed *via* randomly stacking of the nanoplatelets with each other.

Fig. 3 (e) and (f) present the morphologies of sample C obtained by adding 2 mmol DDTC-Na (0.05 mol L^{-1}), which reveals that the CuInS₂ products are porous microspheres with diameters of 2.5-4.5 μm . Fig. 3(f) is a high-magnification image recorded from the area marked by a circle in Fig. 3(e), which further display that the walls of the spherical structure is build up by tens to hundreds of nanoflakes with average thicknesses of 25 nm. These nanoflakes are nearly perpendicular to the nuclei center, interconnecting with each other to form an honeycomb-like architecture with irregular shaped pore on the surfaces of the microsphere.

In order to further understand the influence action of DDTC on the morphology of the CuInS₂ product, the comparative experiments were carried out. Fig. 4 shows the FESEM images of CuInS₂ products obtained at different reaction conditions. If not any dose of DDTC-Na were added into the reaction system, nanoparticles and only a few porous microspheres constructed by nanoflakes were found in the CuInS₂ products (Fig. 4(a)). Large numbers of porous CuInS₂ microspheres were also obtained (Fig. 4(b)) when taking L-cysteine as sulfur source instead of thiourea and keeping other conditions unchanged.

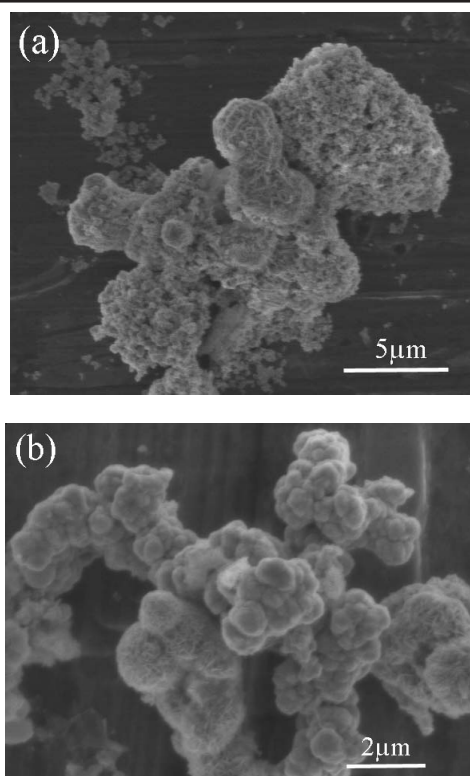
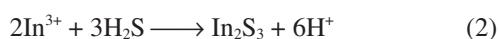
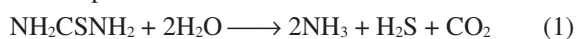


Fig. 4. FESEM images of CuInS₂ products obtained at different reaction conditions: (a) no DDTC-Na, (b) using L-cysteine as surfur source

In the present reaction system, as a copper reagent, DDTC-Na can react with metal Cu²⁺ to form Cu(DDTC)₂ complexes at low temperature¹⁶. Under solvothermal (elevated temperature and pressure) conditions, the preformed Cu(DDTC)₂ complexes decompose to release dissociative *meta* ion Cu²⁺. Meanwhile, Cu²⁺ was reduced to Cu⁺ by H₂S which comes from the hydrolyzation of thiourea. Then, free In³⁺ ion react with S²⁻ to form (InS₂)⁻ dissolved in solution. Finally, Cu⁺ combines with (InS₂)⁻ at the growth site to form CuInS₂ products¹³. The whole reaction process can be described as follows:



Based on the comparative experiment results above, a conclusion can be drawn that DDTC-Na may be essential for the formation of 3D CuInS₂ microstructures. It is speculated that the copper reagent (DDTC-Na) not only may act as a complexing agent but also may act as a structure-directing agent for the growth of 2D building blocks (nanosheets, nanoplatelets, nanoflakes) and their subsequent orientated aggregation growth into 3D microstructures. Production of Cu(DDTC)₂ complexes could reduce the concentration of free Cu²⁺ ions in solutions and provide enough time and opportunity for the growth of CuInS₂ 2D building blocks. Moreover, the adsorption of the DDTC to specific surfaces of the crystals may also affect the morphology of the final product. It is believed that the orientated aggregation growth of CuInS₂

nanosheets, nanoplatelets or nanoflakes along the special stabilized lattice face under solvothermal conditions may lead to the growth of 3D hierarchical CuInS₂ architectures. More in-depth studies are still needed to explore the exact formation mechanism and some correlative works are in process.

Conclusion

Copper indium sulfide microcrystals with three kinds of hierarchical architectures have been successfully fabricated by a complexing agent controlled solvothermal technique. The experimental results revealed that complexing agent (DDTC-Na) is an important factor influencing the growth of CuInS₂ microstructures. By changing the concentration of DDTC-Na, nanosheet-based microflowers, nanoplatelet-based solid microspheres and nanoflake-based porous microspheres have been controllably synthesized *via* a kinetically controlled process. The controllable shape and size distribution makes the application of CuInS₂ materials more feasible. Furthermore, the present technique can be extended as a facile synthetic route to access other inorganic compounds with desired hierarchical architectures.

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