Thioglycolic Acid-assisted Solvothermal Synthesis of $CuInS_2$ with Controllable Microstructures

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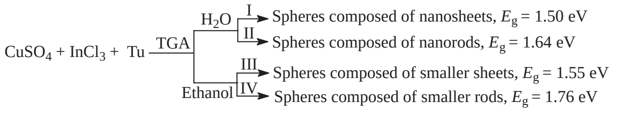
A facile solvothermal approach assisted by thioglycolic acid (TGA) was developed to control the morphologies and microstructures of $CuInS_2$. Furthermore, the band gap of the $CuInS_2$ microspheres was tunable in the range of 1.50–1.76 eV, depending on the synthetic conditions.

As a particularly promising candidate for photovoltaic applications, $CuInS_2$ has been intensively investigated in the past decade.[1] Up to now, $CuInS_2$ thin films and powders with different morphologies such as nanoparticles, foam-like nanocrystallites, nanorods, nanowires, nanotubes, nanocubes, and porous microspheres have been fabricated.[2–4] However, it still remains challenging to control over the microstructure and morphology through altering the synthetic conditions. Recently, we have reported the shape-controlled synthesis of ternary chalcogenide nano-/microstructures via a solution route.[5] In the present work, we describe a thioglycolic acid (TGA)-assisted solvothermal route (Scheme 1) to synthesize $CuInS_2$ with controllable surface microstructures and tunable band gap (E_g) by altering the solvents and the amount of TGA.

In a typical synthesis, stoichiometric amounts (1 mmol) of $CuSO_4 \cdot 5H_2O$ and $InCl_3 \cdot 4H_2O$ were dissolved in 10 mL of deionized water (or ethanol), in which appropriate amount of thioglycolic acid (50 or 500 μL) was added dropwise under magnetic stirring. Meanwhile, the initially light blue transparent solution turned into a yellow colloidal solution. Subsequently, 2 mmol of thiourea was added. After stirring for 30 min, the mixture was transferred into a Teflon-lined stainless steel autoclave of 20-mL capacity, maintained at 160 °C for 20 h, and then cooled to room temperature on standing. A black precipitate was filtered off and washed with distilled water and absolute ethanol for several times. Finally, the product was dried in vacuum at 60 °C for 4 h. The four products prepared according to Scheme 1 were named as sample I, II, III, and IV, respectively.

The products were characterized by X-ray diffraction (XRD, Rigaku D/Max-2500), field emission scanning electron microscopy (FESEM, JEOL JSM-6700F), and UV–vis diffuse reflectance spectroscopy (JASCO V-550).

Figure 1 shows the XRD patterns of the four products. All the diffraction peaks can be readily indexed to the pure tetragonal phase of $CuInS_2$ with chalcopyrite structure (JCPDS No. 27-0159). However, in the absence of thioglycolic acid, some binary sulfides such as Cu_2S, CuS, and In_2S_3 always coexist (the XRD pattern is not shown here), indicating that the addition of TGA in the solvothermal synthesis plays the dominant role in the structural control of $CuInS_2$.



Scheme 1. Synthetic route to $CuInS_2$ and the corresponding results.

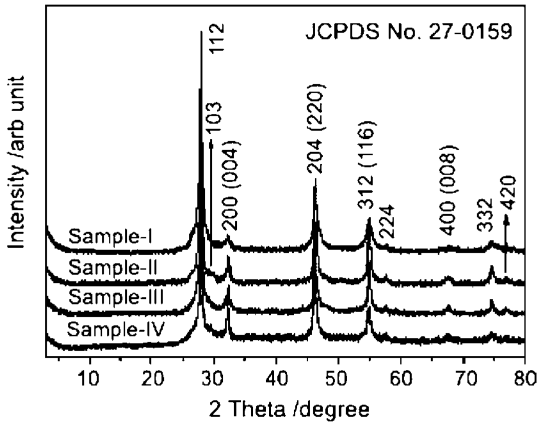


Figure 1. XRD patterns of the four products.

Figure 2 shows the FESEM images of the four samples obtained from both water and ethanol media, indicating that all the products were composed of highly monodisperse spheres with diameters of 2–5 μm. However, these sphere-like products at higher magnification show distinct surface microstructures, which are related to the preparation conditions. In the aqueous solution system, when the amount of thioglycolic acid was 50 μL, the resulting spheres (Sample I) were actually composed of nanosheets with thickness of about 80 nm and length of 2 μm (Figures 2a and 2b); While the amount of thioglycolic acid increased to 500 μL, the surface morphologies of the resulting spheres (Sample II) changed remarkably (Figures 2c and 2d). The surface of an individual sphere clearly revealed that the sphere was formed by numerous nanorods with a diameter of about 40 nm and length of about 200 nm. Similar phenomenon can also been observed by using absolute ethanol as the solvent (Figures 2e–2h), only the sizes of the building blocks such as nanosheets and nanorods are smaller than the corresponding sizes of those in the aqueous solution. Among the four $CuInS_2$ products, Sample I consisted of the largest nanosheets and Sample IV was composed of the smallest nanorods with a diameter of about 20 nm and length of 80 nm.

Figure 3 displays the band gap of the $CuInS_2$ samples estimated from their plots of $(\alpha h\nu)^2$ vs. $h\nu$ (where α is the absorption coefficient, h is Planck's constant, and ν is frequency), which were derived from their corresponding UV–vis diffuse re-

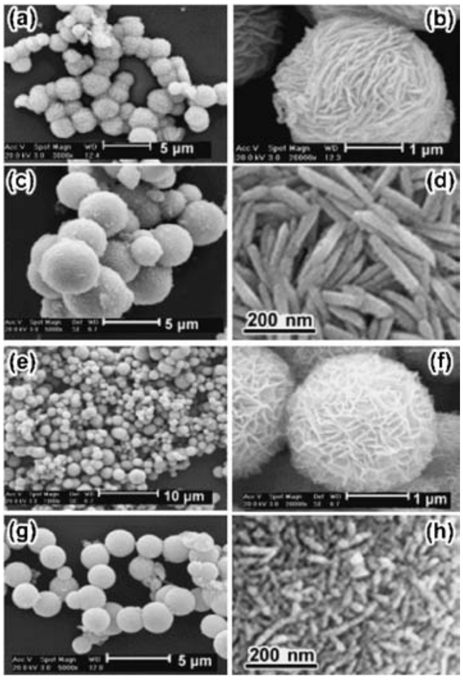


Figure 2. FESEM images of sample I (a, b), II (c, d), III (e, f), and IV (g, h) at different magnifications.

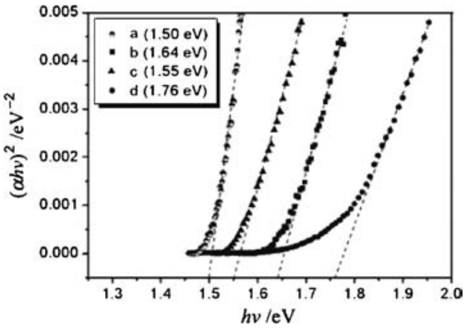


Figure 3. Band gap determination for $CuInS_2$ samples: I (a), II (b), III (c), and IV (d).

flectance spectrum (not shown here). As a whole, the band gap is in the range of 1.50–1.76 eV. Sample I has the narrowest band gap (1.50 eV) because of the largest nanosheets on the surface. Sample IV has the widest band gap (1.76 eV) owing to the smallest nanorods on the surface, which blue-shifted with quantum effect. Combining with the SEM observations (Figure 2), we can draw a conclusion that the band gap of the $CuInS_2$ products is relevant to their sizes of the building blocks and microstructures. Note that similar size- and shape-dependent optical properties have been reported in the CdSe system.[6]

Thioglycolic acid has been previously used as a stabilizer and capping agent to synthesize some binary chalcogenide nanocrystals with specific morphologies.[7–9] In the present case, we extend this synthetic method to synthesize ternary sulfide $CuInS_2$. As mentioned above, we could not obtain pure $CuInS_2$ without using TGA. Furthermore, when the concentration of TGA increased, the microstructures of $CuInS_2$ were based on nanosheets at first and then nanorods that self-organized into the form of spheres. It is possible that TGA functioned as a complexing agent and a stabilizer in the synthetic process of $CuInS_2$. Our experimental results show that TGA plays a critical role in controlling the composition and the microstructure of $CuInS_2$ under the solvothermal condition. However, studies in more depth are still needed to explore the exact mechanism.

In conclusion, we reported on a method for controlling the shape and size of building blocks of $CuInS_2$ microstructures by utilizing a simple thioglycolic acid-assisted solvothermal technique. The band gap of the resulting $CuInS_2$ materials was tailored in the range of 1.50–1.76 eV, which is of interest for photovoltaic applications, especially favored for production of highly efficient single-cell system with large open circuit voltages and of top cells in tandem systems. Further exploration about the potential applications of the resulting $CuInS_2$ materials with different microstructures and band gap values in solar cell is underway in our group.

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References

1 a) M. Nanu, J. Schoonman, A. Goossens, *Nano Lett.* **2005**, *5*, 1716. b) M. Grätzel, *Nature* **2001**, *414*, 338.

2 a) S. L. Castro, S. G. Bailey, R. P. Raffaelle, K. K. Banger, A. F. Hepp, *J. Phys. Chem. B* **2004**, *108*, 12429. b) G. Z. Shen, D. Chen, K. B. Tang, Z. Fang, J. Sheng, Y. T. Qian, *J. Cryst. Growth* **2003**, *254*, 75. c) Y. Jiang, Y. Wu, S. W. Yuan, B. Xie, *J. Mater. Res.* **2001**, *16*, 2805.

3 a) Y. Cui, J. Ren, G. Chen, Y. T. Qian, Y. Xie, *Chem. Lett.* **2001**, 236. b) Y. Jiang, Y. Wu, X. Mo, W. Yu, Y. Xie, Y. T. Qian, *Inorg. Chem.* **2000**, *39*, 2964.

4 a) K. Wakita, M. Iwai, Y. Miyoshi, H. Fujibuchi, A. Ashida, *Compos. Sci. Technol.* **2005**, *65*, 765. b) H. Hu, B. Yang, X. Liu, R. Zhang, Y. T. Qian, *Inorg. Chem. Commun.* **2004**, *7*, 563.

5 X. L. Gou, F. Y. Cheng, Y. H. Shi, L. Zhang, S. J. Peng, J. Chen, P. W. Shen, *J. Am. Chem. Soc.* **2006**, *128*, 7222.

6 T. Teranishi, M. Nishida, M. Kanehara, *Chem. Lett.* **2005**, *34*, 1004.

7 a) J. Li, X. Hong, D. Li, K. Zhao, L. Wang, H. Wang, Z. Du, J. Li, Y. Bai, T. Li, *Chem. Commun.* **2004**, 1740. b) H. Zhang, X. Y. Ma, Y. J. Ji, J. Xu, D. R. Yang, *Chem. Phys. Lett.* **2003**, *377*, 654. c) Z. Y. Tang, N. A. Kotov, M. Giersig, *Science* **2002**, *297*, 237.

8 a) C. L. Li, N. Murase, *Chem. Lett.* **2005**, *34*, 92. b) J. Guo, W. L. Yang, C. C. Wang, *J. Phys. Chem. B* **2005**, *109*, 17467.

9 a) H. Zhang, D. Y. Wang, H. Möhwald, *Angew. Chem., Int. Ed.* **2006**, *45*, 748. b) A. Purkayastha, F. Lupo, S. Kim, T. Borca-Tasciuc, G. Ramanath, *Adv. Mater.* **2006**, *18*, 496.

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