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Synthesis of hierarchical CuS flower-like submicrospheres via an ionic liquid-assisted route

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Abstract. **A facile, ionic liquid-assisted route was developed to synthesize hierarchical CuS flower-like submicrospheres at 80°C for 24 h. The method was based on a reaction between $CuCl_2$ and thioacetamide (TAA) in aqueous solution with using ionic liquid 1-*n*-butyl-3-methylimidazolium chloride ([BMIM]Cl) as an assisted agent. The chemical composition, morphology and size of CuS product were characterized by XRD, SEM and TEM. The result shows that the as-prepared CuS consists of flowery spheres with a diameter of 0·6 ~ 1·0 μm, and these submicrospheres are, in fact, built by numerous nanoflakes with a thickness of 10 ~ 20 nm. The optical property of CuS product was examined by UV-Vis. In general, we suggested an ecologically and environmentally friendly route for the syntheses of hierarchical metal chalcogenides structures in this paper.**

Keywords. **Copper sulfide; ionic liquids; nanomaterials; semiconductors.**

1. Introduction

There has been considerable effort in synthesizing inorganic materials with hierarchical nano-/microstructures, which are desirable for many applications in optics, electronics, biology, medicine, and energy/chemical conversions. To date, a wide variety of inorganic materials, including metal (Teng and Yang 2005; Shen *et al* 2007), metal oxide (Liu and Zeng 2004), sulfide (Xie and Zhao 2002), hydrate (Zhang *et al* 2005) and other minerals (Murray *et al* 1995; Yu and Chen 2006), have been successfully prepared with hierarchical shapes.

Semiconductor materials have recently attracted much attention because of their novel properties and potential applications in manufacturing electronic and optoelectric devices (Duan *et al* 2001; Cui and Lieber 2001; Huang *et al* 2001). Besides being an excellent semiconductor, copper sulfide (CuS) also exhibits its commercial importance as pigment, catalyzer, solar energy conversion, and coloured indicator of nigrosine and so forth. On the basis of the versatile applications of the CuS material, a large effort has been focused on the synthesis and characteristics of the CuS nano-/microstructures. The reported methods for formation of CuS material mainly included sonochemical methods (Wang *et al* 2002), microwave-assisted methods (Liao *et al* 2003), electrosynthesis (Cordova *et al* 2002), hydrothermal methods (Tang *et al* 2004), solid-state reactions (Parkin 1996), and chemical vapour deposition (CVD) (Nomura *et al* 1996). However, a simple, mild and environmentally friendly preparation route for intriguing hierarchical CuS architectures still remains a highly sophisticated challenge.

Room temperature ionic liquids (RTILs) can be defined as electrolytes composed entirely of ions at ambient temperature, and have applications in organic synthesis (Bar *et al* 2001; Lee *et al* 2001; Potdar *et al* 2001), electrochemistry (Lin and Sun 1999; Tsuda *et al* 2001) and separation (Visser *et al* 2000; Anthony *et al* 2001; Dzyuba and Bartsch 2003). Their applications in inorganic field, however, are still in infancy. From theoretical points of view, ionic liquids can act as co-solvents for reactants and morphological templates for products at the same time, and facilitate the syntheses of inorganic materials with novel or improved properties.

In this paper, we reported the hydrothermal synthesis of hierarchical CuS flower-like submicrospheres at 80°C for 24 h in the presence of [BMIM]Cl, and demonstrated that this ionic liquid played an important role in the formation of CuS with the hierarchical flowerlike structure.

2. Experimental

2.1 *Synthesis of hierarchical CuS flower-like submicrospheres*

Ionic liquid 1-*n*-butyl-3-methylimidazolium chloride ([BMIM]Cl) was synthesized according to the literature (Huddleston *et al* 1998). All the other chemicals were purchased from commercial sources and used without

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further purification. In a typical synthetic procedure for CuS, 2 equivalents of 1-*n*-butyl-3-methylimidazolium chloride (4·8 mmol) and 1 equivalent of $CuCl_2 \cdot 2H_2O$ (2·4 mmol) were heated to 140°C for 10 min to get dark red, sticky liquid after cooling. The sticky liquid was dissolved in 40 mL of distilled water to form a homogeneous blue solution in a glass jar under constant stirring. Then 0·18 g of TAA was dissolved in 40 mL of distilled water, and subsequently added into the jar with $CuCl_2$ solution gradually without stirring or vibration. Then the jar was covered and maintained at 80°C for 24 h. The resulting black solid product was filtered, washed with distilled water and absolute ethanol in sequence, and then dried in a vacuum at 60°C for 6 h.

2.2 *Characterization of as-prepared CuS product*

X-ray diffraction (XRD) patterns were collected on a Philips-PW3040/60 X-ray diffractometer with Kα radiation ($\lambda = 0{\cdot}15418$ nm). Scanning electron microscopy (SEM) measurements were carried out with a HITACHI S-4800 field-emission microscope operated at an accelerating voltage of 5 kV. Transmission electron microscopy (TEM) was performed using a JEOL-2010 instrument at an accelerating voltage of 200 kV. An UV-2501 PC ultraviolet-visible light (UV-Vis) spectrophotometer was used to carry out the optical measurements of sample dispersed in ethanol in the wavelength range of 200 ~ 800 nm.

3. Results and discussion

The crystallinity and phase structure of the as-prepared CuS were examined by powder XRD. Figure 1 shows a typical XRD pattern of the product. All the diffraction peaks in the pattern can be indexed to pure hexagonal-phase CuS, which are consistent with the standard card (JCPDS Card 65-3556). No XRD peaks arising from impurities of CuO, $CuCl_2$ and Cu_2S can be detected, which indicates that pure CuS can be easily obtained under the current synthetic conditions. In addition, the sharp diffraction peaks reveal good crystallinity of the CuS sample.

The morphology of the as-synthesized CuS was investigated by SEM and TEM microscopies. Figure 2a shows the SEM image at a low magnification, and reveals that the product is composed of a large quantity of nearly monodispersed submicrospheres with a diameter of 0·6~1·0 μm. Figure 2b is the SEM image at a high magnification. It shows these CuS spheres have a flower-like hierarchical morphology and a nanoflakes-built superstructure. Figure 2c displays a representative TEM image of a single CuS sub-microsphere, where we can find the hierarchical sphere built by numerous nanoflakes with a thickness of 10~20 nm.

Figure 3 shows the UV-Vis absorption spectra of the as-prepared CuS flower-like submicrospheres dispersed in ethanol. It is interesting to note that two strong absorption peaks located at 255 and 503 nm occur in this spectra, which is obviously different from that of CuS nanoflakes (Xu *et al* 2006; Zhang and Zhang 2008), nanowires (Wu *et al* 2008), and hollow spheres (Yu *et al* 2007). In addition, the sample shows an increased absorption band in near-IR region, which is characteristic of covellite CuS (Haram *et al* 1996; Dixit *et al* 1998). The unusual phenomena in the UV-Vis absorption spectra may have potential applications in the optical field.

The influence of synthetic parameters, such as reaction temperature and [BMIM]Cl, on the morphologies of the products are investigated. Experiments at different hydrothermal temperatures such as 60, 70, 90, and 100°C were performed while keeping other reaction parameters constant, and the corresponding SEM images of products are shown in figures 4a–d. When the sample was prepared at 60°C, the ill-defined flower-like CuS aggregations assembled by some plates was obtained (figure 4a). This structure is loose with an irregular shape, and seems to be underdeveloped. Figure 4b illustrates a typical SEM image of the CuS quasi-spheres attained at 70°C. No individual nanoplates can be found, indicating the acquirement of hierarchical architectures. However, when the temperature was raised to 90 or 100°C, a majority of regular hierarchical flower-like structures were destroyed as seen in figures 4c–d, and many smaller irregular spheres formed. In the formation of hierarchical CuS flower-like submicrospheres, the reaction temperature played an important role. SEM observations suggest that the hierarchical CuS flower-like structures could only be perfectly constructed in the temperature range of 70~80°C.

A similar experiment was also done in the absence of any ionic liquid at 80°C for 24 h. As shown in figure 5, the final product has an ill-defined tubular structure com-

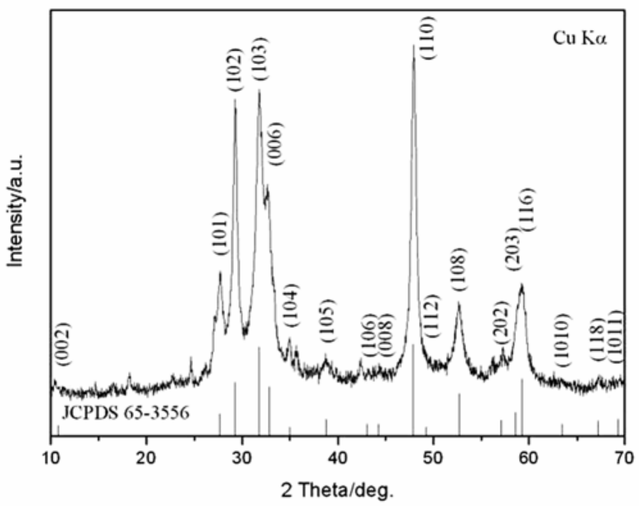


Figure 1. Powder X-ray diffraction pattern of hierarchical CuS flower-like submicrospheres.

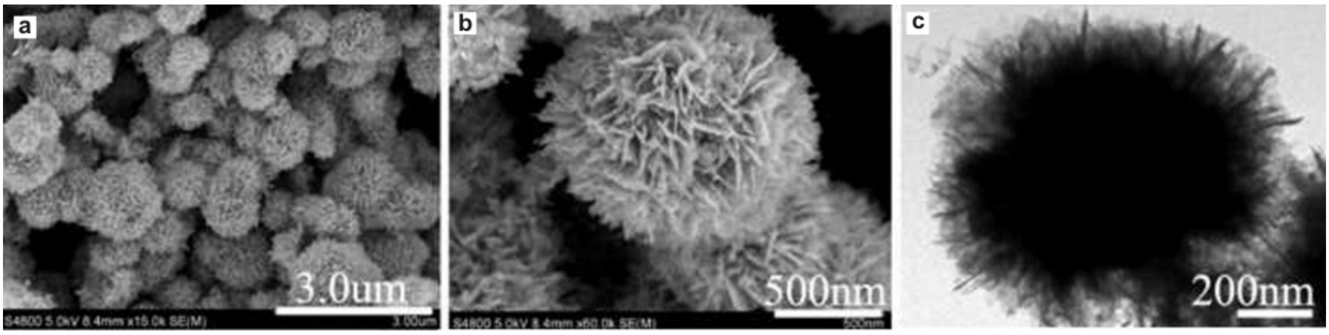


Figure 2. SEM (**a**, **b**) and TEM (**c**) images of hierarchical CuS flower-like submicrospheres.

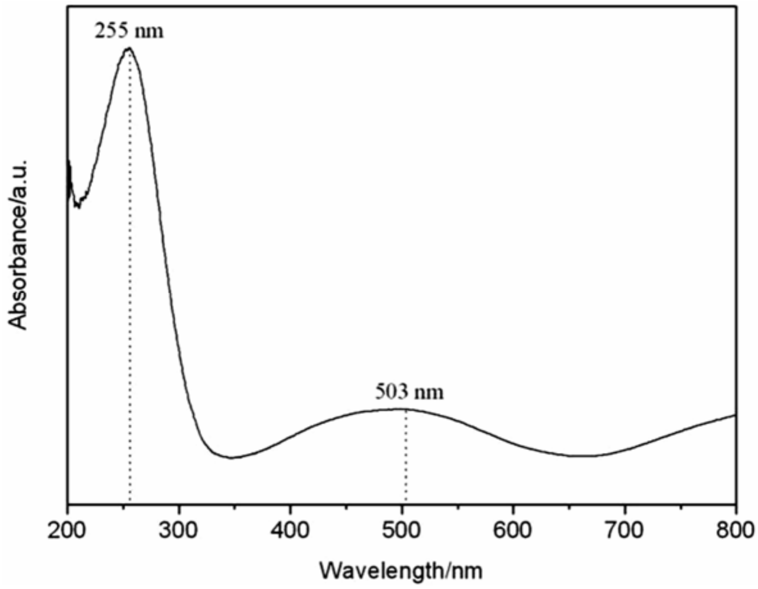
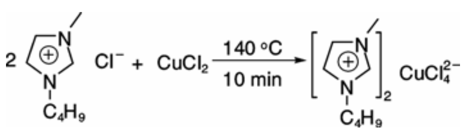


Figure 3. UV-Vis absorption spectra of hierarchical CuS flower-like submicrospheres.

posed of aggregated microspheres, where the total length of single tube is more than 10 μm and the extra diameter of the tube is about 4~5 μm. This morphology is obviously different from that of hierarchical flower-like CuS obtained in the presence of ionic liquid [BMIM]Cl. Thus, ionic liquid in our experiments also plays a vital role in the formation of the as-obtained hierarchical flower-like structures. Firstly, the strong combination between Cl^- and $CuCl_2$ results in the formation of an ionic liquid salt comprising of $CuCl_4^{2-}$ anions at 140°C for 10 min (Hardacre *et al* 2001; Neve *et al* 2001; Lee *et al* 2004). Then $CuCl_4^{2-}$ ions hydrolyze to release Cu^{2+} very slowly after being mixed with water due to the hinderance of the *bis*-lamellar cations, so here the cations are good buffer, which can keep a suitable hydrolysis rate of $CuCl_4^{2-}$ in this reaction system. Finally, suitable hydrolysis rate can control the formation and decomposition of precursor particles originating from the initial reaction between $CuCl_2$ and TAA, the nucleation speed of CuS nuclei, the growth rate of CuS nanoflakes, and their assembly into submicrospheres. In addition, the reformed ionic liquid [BMIM]Cl can act as the surfactant or morphological template, which may be responsible for such hierarchical structures as discussed previously in our report (Xu *et al* 2008). The probable reaction processes for the ionic liquid-assisted formation of CuS in aqueous solution can be summarized as follows:



(1)

$$CuCl_4^{2-} + 4H_2O \rightarrow Cu(H_2O)_4^{2+} + 4Cl^{-1}, \quad (2)$$

$$Cu^{2+} + TAA + H_2O + O_2 \rightarrow CuS + CH_3COO^- + NH_4^+ + H^+ + Cl^- + SO_4^{2-}. \quad (3)$$

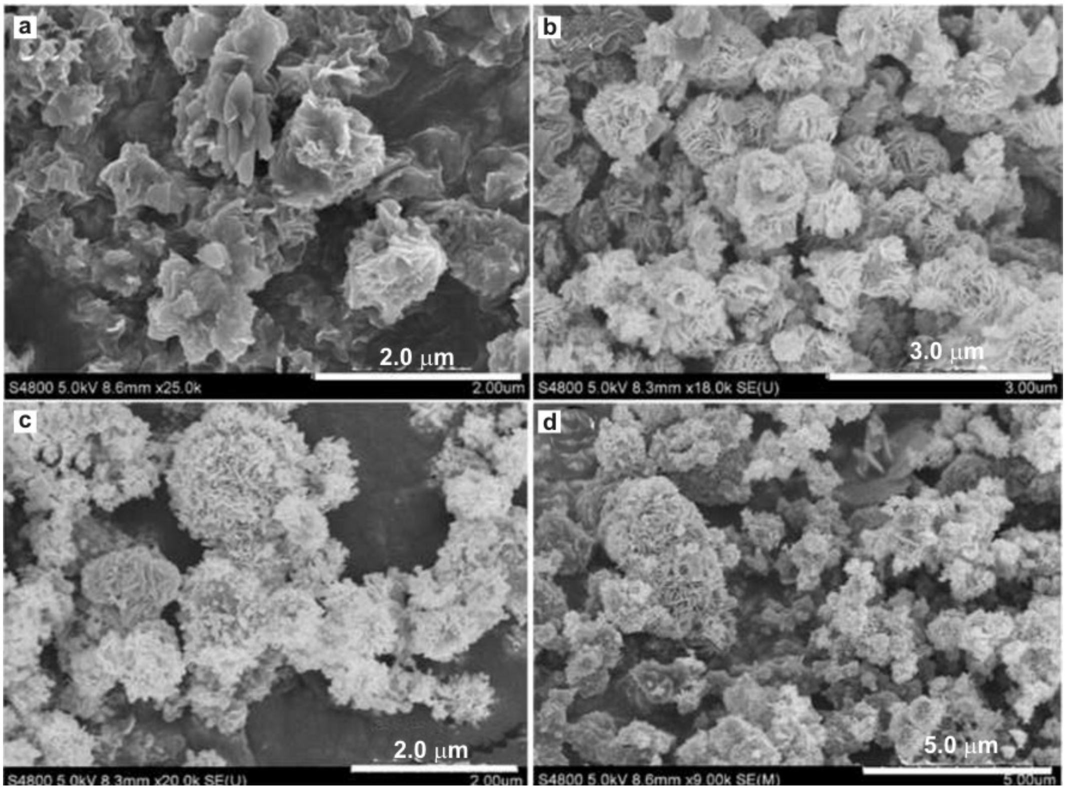


Figure 4. SEM images of CuS samples synthesized at different hydrothermal temperatures: **a**. 60, **b**. 70, **c**. 90 and **d**. 100°C.

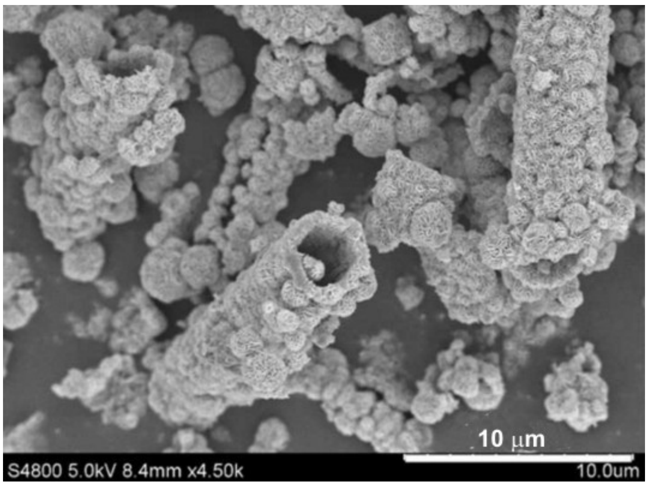


Figure 5. SEM image of CuS sample prepared in the absence of ionic liquid.

4. Conclusions

In summary, a mild method for the synthesis of the hierarchical CuS flower-like submicrospheres has been described. The intriguing hierarchical CuS structures were prepared using an ionic liquid [BMIM]Cl as an assisted agent at 80°C for 24 h, and characterized by XRD, SEM, TEM and UV-Vis. In addition, we found both the reaction temperature and ionic liquid played important roles on the morphology of CuS product. This simple, ecological and environment friendly preparation route is expected to extend to prepare other hierarchical metal chalcogenides structures.

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