Synthesis of CuS Millimeter-Scale Tubular Crystals

Chunrui Wang,[†,††] Kaibin Tang,*[†] Qing Yang,[†] Hai Bin,[†] Guozhen Shen,[†] and Yitai Qian*[†]
[†]*Structure Research Laboratory and Department of Chemistry, University of Science and Technology of China, Hefei, Anhui 230026, P. R. China*
[††]*Department of Physics, Huaibei Coal Industry Teacher's College, Huaibei, Anhui 235000, P. R. China*

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CuS millimeter-scale tubular crystals were synthesized for the first time via a hydrothermal method at 185 °C. A possible growth mechanism of CuS tubular crystals was proposed.

Copper(II) sulfides show semiconductor or metallic behavior depending on the stoicheiometry of the mineral phase.[1] At room temperature range, Cu_xS are known to exist in five stable phases,[2] with x = 1 (covellite), 1.75 (anilite), 1.8 (digenite), 1.95 (djurleite), and 2 (chalcolite). The study of copper sulfides Cu_xS (x = 1–2) and their alloy is of interest due to numerous technological applications such as the achievement of solar cells,[3,4] solar control and solar absorber coatings.[5–9] Recently nonlinear optical properties of Cu_xS nanoparticles have been reported in the literatures.[10–12]

Covellite (CuS) is a semiconductor which crystallizes with the hexagonal (space group 194, *P*63/*mmc*) type structure. The unit cell contains six formula units with two inequivalent sites for both Cu and S. One third of the Cu atoms in CuS are coordinated with three S atoms by a triangle, while the remaining Cu atoms are surrounded by four S atoms so as to form tetrahedron. Millimeter-scale hollow crystals of CuS have not been so far reported. Hollow crystals find importance for the fabrication of certain devices using electrodes attached to the inner and outer surfaces with favorable geometrical arrangement.

In this paper, we report for the first time growth of CuS millimeter-scale tubular crystals from a hydrothermal route. A possible growth mechanism of the CuS hollow crystals is discussed.

The synthesis was based on the follow reaction:[13]

$$2CuCl + S \rightarrow CuS + CuCl_2$$

Analytically pure CuCl (1.50 g) and S powder (0.60 g) were added to a Teflon-lined autoclave of 50 mL capacity, then a small amount of Cr powder was put into the autoclave. The autoclave was then filled with distilled water up to 85% of the total volume. The autoclave was maintained at 185 °C for 15 h and then cooled to room temperature naturally. The products were filtered off and washed sequentially with CS_2, absolute ethanol, diluted acid and distilled water to remove the residual impurities. After drying in a vacuum at 70 °C for 4 h, indigo blue crystals were collected.

X-ray powder diffraction (XRD) pattern was obtained on a Rigaku Damax γA X-ray diffractometer with Cu Kα radiation (λ=1.54178 Å). Figure 1 shows the XRD pattern of several CuS crystals that were crushed. The reflections could be indexed to the hexagonal CuS phase with lattice constants *a* = 3.790 Å, *c* = 16.341 Å, which are consistent with the value reported (JCPDS, 6-464).

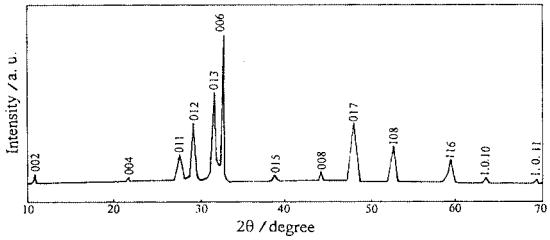

Figure 1. XRD patterns of several CuS crystals crushed.

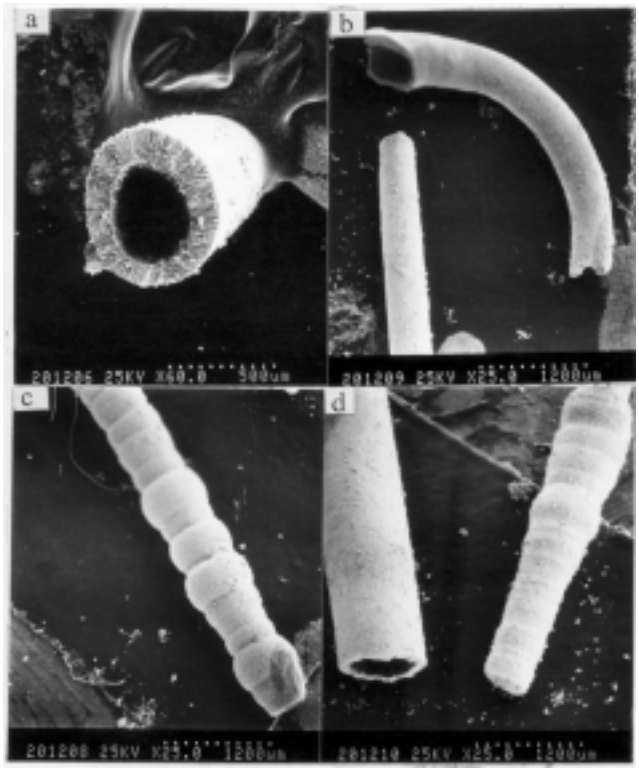

Figure 2. SEM images (a-d) of as-prepared CuS tubular crystals.

The scanning electron microscopy (SEM) images of as-synthesized CuS crystals are shown in Figure 2. CuS crystals exhibit hollow cylindrical structure (Figure 2a). Typically, the tubes are about 0.36–0.47 mm in diameter, 0.08–0.16 mm in thickness and length up to 1 cm. Figure 2b shows images of a bent tube and a closed end tube. Figure 2c and Figure 2d show images of bamboo-like closed end solid tubes. We can see the structure of the solid bamboo-like tube consists of sulfur (S) wrapped by CuS thin crystal flakes when it is broken. From

these SEM images, it can be seen that as-synthesized CuS tubular crystals are polycrystals.

The samples were also characterized by X-ray photo-electron spectra (XPS) (the spectras not shown). The results of XPS show the formation of CuS. No obvious impurities, e.g., chloride ion or element Cr, could be detected in the samples, indicating that the level of impurities is lower than the resolution limit of XPS and no Cr incorporation into CuS tubular crystals.

The reaction temperature was critical factors in the formation of CuS tubes. In the hydrothermal route, the essential temperature range for the formation of CuS tubes was at 185–190 °C.

Although the reaction mechanism of Cr on the formation of CuS millimeterscale tubes is not clearly. Element Cr also plays an important role in the formation of millimeter-scale tubes. In the absence of Cr, the obtained CuS displays a flake-like morphology only. In the presence of Cr, the obtained CuS shows a tubular-like morphology. Cr can be detected in byproduct of the reaction system by XRD.

The growth mechanism for the CuS millimeter-scale tubes is discussed as follow. When the starting materials are put into an autoclave, S powder floats on the water. CuS thin crystal flakes, which formed in the interface between S powder and water, are strongly undulated. The flake edge is bent. The reason for the flake edge folding can be understood in terms of relaxation of strain generated in the flakes during the growth. [14] In the same time, a cylindrical form is formed when S is wrapped by the flakes. The nucleation of cylindrical results in the growth of the tube, if the stacking order and orientation relationship between adjacent turns of the molecular layer is satisfied.[14] Cr may serve as a catalyst and promote the CuS thin crystal flakes folding on the formation of CuS millimeter-scale tubes.

In summary, CuS millimeter-scale tubes were synthesized successfully for the first time via a hydrothermal method at 185 °C. The possible growth mechanism of CuS tubes was proposed. It is expected that the hollow tubular crystals should have novel properties, and may offer exciting opportunities for both fundamental research and technological application. Deeper understanding of growth mechanism of CuS tubes and controlling the reaction kinetics are clearly needed.

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