

A Nonaqueous Route to Prepare Novel CuS Macroporous Material

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A novel nonaqueous route was applied to synthesize CuS macroporous material by the reaction between $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ and S via the reducing action of ethylene glycol solvent. The CuS macroporous material was formed by the irregular inter-growth of CuS thin layer crystals.

Macroporous materials represent a special class of porous materials and have attracted much attention from the fields of adsorption/separation and heterogeneous catalysis, because they combine the benefits of large internal surface area with the accessible diffusion pathways of macroporous networks.¹ One of the synthesis methods for obtaining macroporous materials is the route from varieties of layered materials by soft chemical approaches such as chemical template,² intercalation,³ and surfactant-mediated synthesis.⁴ Aqueous (including hydrothermal) route and nonaqueous (including solvothermal) route have been widely used to prepare inorganic materials with special morphologies.⁵ Since the preparation process of crystallites in aqueous or nonaqueous solution can be considered as a process of crystal growth, the morphology of the crystallites is expected to be controlled by optimizing the synthesis conditions such as temperature, supersaturation and pH value of the solution.⁶ CuS is of hexagonal symmetry (space group $P6_3/mmc$) at room temperature, the crystal structure is built up of layers consisting of CuS_3 triangles and CuS_4 tetrahedra, the layers are joined together by sulfur–sulfur bonds.⁷ CuS nanocrystals with special morphologies have been synthesized in aqueous or organic solutions, the morphologies can be controlled by choosing appropriate solvent as the reaction medium, selecting suitable copper source, and reaction time.⁸ In this paper, CuS macroporous material was prepared by a nonaqueous route using $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ and S as the reagents, ethylene glycol (EG, bp 199 °C) as the reaction medium. The formation mechanism of macroporous CuS, as well as the relationship between the crystal structure and the morphology, is discussed.

In a typical procedure, a mixture of 0.852 g of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ and 0.160 g of S powder was put into a glass tube of 50 mL-capacity, which was filled with 40 mL of EG (All of the reagents and solvent are analytical grade and commercially available without further purification). The tube was sealed by a rubber stopper and maintained at 120 °C. About two days later, black precipitate was obtained. The product was washed with distilled water and dried in vacuum at 70 °C. The obtained samples were characterized by scanning electron microscopy image (SEM, SEM images were obtained with a Hitachi X-650 scanning electron microanalyzer), and X-ray powder diffraction measurement (XRD, XRD measurements were carried out on a Rigaku D/max- γ A X-ray diffractometer with graphite-monochromatized Cu $K\alpha$ radiation ($\lambda = 1.54178 \text{ \AA}$) source.)

SEM image (Figure 1a) shows that the sample consists of loosely packed aggregates of CuS porous material with size of

50–100 μm , and magnified SEM image (Figure 1b) shows that the packed aggregates appear as a loose agglomeration of sheets irregular in size and shape, the interior hole are estimated to be about 5 μm .

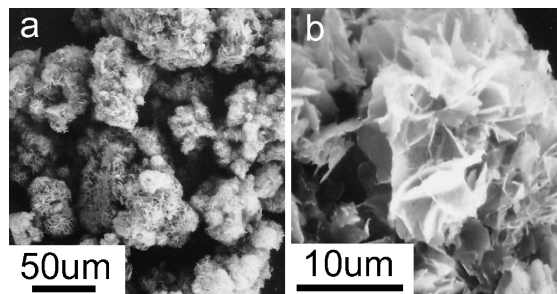


Figure 1. SEM images of CuS macroporous material (a) Low-magnification SEM image, (b) High-magnification SEM image.

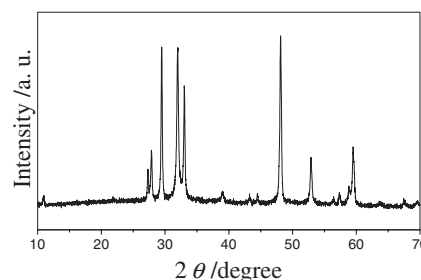


Figure 2. XRD pattern of the product (covellite CuS).

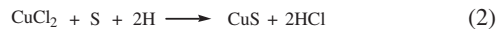
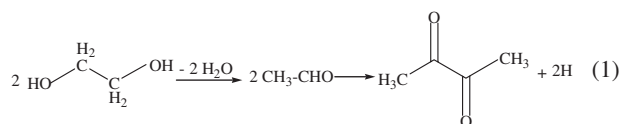


Figure 2 shows a typical XRD pattern of the obtained sample, all of the peaks could be indexed to covellite CuS (JCPCD Card No. 72-1966). Fievet et al. have investigated the reducing action of EG at high temperature.⁹ According to their investigations, acetaldehyde is produced by dehydration of EG at high temperature, the acetaldehyde can donate a hydrogen atom and acts as a reducing agent, as shown in Eq 1. By analyzing the composition in the EG solution after the reaction to synthesize CuS (HCl was determined by titration with NaOH solution and AgNO_3 solution), we found HCl was one of the major products, which suggests the reaction shown as in Eq 2 occurred under the reducing environment.

The preparation process of crystallites by nonaqueous route can virtually be considered as a process of crystal growth. Besides the morphology of a given crystal is affected by external

conditions such as temperature, supersaturation, pH value of the solution, it is also determined by the internal structure of the crystal. For example, trigonal Se and Te, with the helical chains parallel to [001] direction, have a strong tendency to grow along the direction;¹⁰ ZnO, ZnS, and CdS, are all of hexagonal symmetry, wurtzite structure type and polar crystal, well-pronounced polar growth along the *c* axis (polar axis) is the characteristic feature of these single crystals, one-dimensional nanostructured single crystallines of these materials have been synthesized.¹¹

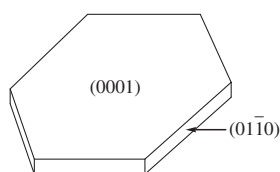
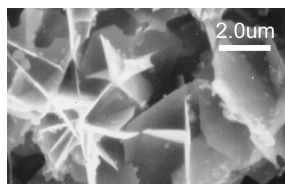
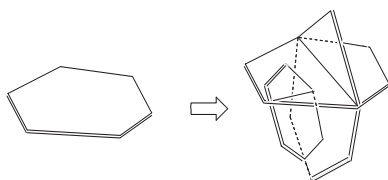


Figure 3. The morphology of CuS hexagonal flakes (top) and the schematic crystal faces of the flakes (bottom).



Scheme 1. The formation of house of cards structure by the irregular intergrowth of CuS flakes.

Fabrication of CuS macroporous material depends not only on the layer structure of covellite CuS, but also on the supersaturation of CuS in EG solution. In our experiments, CuS is easy to form hexagonal flakes (as shown in Figure 3), it is likely that growth along the (0001) surface of CuS crystal is energetically favorable. On the other hand, CuS is difficult to dissolve in EG solvent, the supersaturation of CuS in EG solution is high during the synthesis process. The formation of CuS macroporous material involves two processes, nucleation and crystal growth. When the above-mentioned reactions (Eqs 1 and 2) occur, CuS nuclei with random crystallographic orientation are formed due to its high supersaturation in EG solvent. With the deposition of growth units from the solution upon the surfaces of the nuclei, CuS crystal flakes grow along (0001) surfaces, and the irregular intergrowth of CuS flakes happened. As the results, CuS macroporous material with house of cards structure is formed. The overall processes are illustrated in Scheme 1.

For comparison, $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ (0.852 g) was substituted with CuCl (0.495 g) keeping the other conditions constant, the

obtained CuS have good crystallinity and regular polyhedral crystal faces of hexagonal CuS, the CuS flakes are thicker than these obtained by the reaction between $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ and S, but CuS with macroporous structure was difficult to form.

In conclusion, novel covellite CuS macroporous material has been obtained, the synthesis and growth mechanism were investigated. CuCl_2 reacted with S to form CuS via the reducing action of EG; the CuS macroporous material was formed by the irregular intergrowth of CuS thin layer crystals. The nonaqueous/aqueous route introduces a new method to synthesize macroporous materials with layer structure.

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