Oriented Attachment of Crystalline CuS Nanorods

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Oriented attachment growth was observed in CuS nanostructure for the first time. TEM and HRTEM were used to investigate the connections between the crystal pathway and microstructure of the attached CuS nanostructures.

Wet chemical processes including hydrothermal, solvent thermal, reflux, etc. have been widely used for synthesizing various nanomaterials. In these processes, the growth of nanometer-sized materials involves the process of precipitation of a solid phase in the supersaturated solutions, which consists of a nucleation step followed by particles growth stages.[1] Ostwald ripening is a classical mechanism for the growth stages which has been widely accepted and believed to be the main path of crystal growth.[2] Described by this mechanism, the growth stage is associated with coarsening which can be illustrated as a diffusion-limited growth of stable phase at the expense of unstable phase.[3]

Recently, oriented attachment, which is a new and attractive view of crystal growth, was proposed by Penn and Banfield.[4] It was substantiated in the work on ZnO,[5] TiO_2,[6] CuO,[7] ZnS,[8] etc.[9] Different from Ostwald ripening, the characteristic of the oriented attachment growth is that the primal units aggregate oriented along certain direction to form secondary crystalline structures. In the so-formed aggregates, the crystal lattice planes may be almost perfectly aligned to form a single-crystalline structure or some dislocations at the contact areas to form an almost single-crystalline structure.[5a] This growth mechanism is illustrated in the fusion growth of Ag nanoparticles into nanoprisms,[10] self-assembly of ZnO from nanodots to nanorods,[5a] oriented aggregation of a few hundred CuO nanoparticles into monocrystalline architecture,[7] formation of single crystalline attached ZnO nanorods, etc.[5b]

It is believed that oriented attachment along crystallographical direction which is different from random aggregation and self-assembly, would open a new access to the synthesis of more complex hierarchical single-crystalline structure. Great recent efforts have been devoted to shed light on oriented attachment growth mechanism in different materials. But so far as we know, this study is mainly focused on some kinds of oxide nanoparticle because of their special properties and corresponding synthetic route.[5a] As an important semiconductor in photothermal conversion, electrodes, solar cell devices, etc.,[12] CuS with different morphologies has caught much attenion.[13] To the best of our knowledge, there is still no any report on the oriented attachment growth in CuS nanostructures. In this paper, we report the findings of the oriented attachment growth in CuS nanostructure. It is expected that our findings can evoke materials scientist's interests in the growth mechanism in sulfide compounds.

In a typical procedure, 0.0852 g of $CuCl_2 \cdot 2H_2O$ was dissolved in 100 mL of de-ionized water. Then, 30 mL of NH_3 (0.15 M) solution was added to the $CuCl_2$ solution under constant stirring. A blue precipitate of $Cu(OH)_2$ was produced when NaOH (1 M) was added dropwise into the above solution to adjust the pH value to 12–13. After being stirred for 10 min, excess thioacetamide was added to the suspension. The blue precipitate turned into brown immediately. Then, the suspension was stirred for 12 h under the ambient temperature. The brown precipitates finally turned into black. The resultant was centrifuged, washed sequentially with de-ionized water and ethanol, then dried at 50 °C for 5 h under vacuum.

The X-ray powder diffraction (XRD) patterns were measured with a D/MAX 2250V diffractometer (Rigaku, Japan) using Cu Kα ($\lambda = 1.5406$ Å). Transmission electron microscopic (TEM) images were obtained on a JEOL JEM-2100F transmission electron microscope.

The powder XRD pattern of the product was showed in Figure 1. The obtained product displays the characteristic XRD peaks corresponding to the hexagonal covellite CuS [JCPDS 06-0464]. No characteristic XRD peaks arising from possible impurities are detected, indicating the preparation of pure phase CuS under the experimental conditions. The EDX and UV–vis adsorption spectra also confirm the pure phase CuS.

The morphology and structure of the product were investigated by the transmission electron microscope. Figure 2 are the TEM images of as-prepared product with different magnification. CuS nanocrystal with rod-like and irregular flake-like morphologies can be observed with a panoramic view from Figure 2a. The diameter of a single CuS nanorod can be measured to be about 4–5 nm in Figure 2b. These single CuS nanorods have the tendency to serve as the primal structure to form the secondary structures via the oriented attachment mechanism as shown in Figure 2b, from which four single CuS nanorods arrange along certain direction are observed. There is still a gap between the adjacent nanorods indicates that these nanorods are arranged but still not perfectly oriented attached. The driving force for the oriented arrangement and attachment is mentioned as the reduction of overall surface energy,[6b] which can be realized by eliminating the surfaces at which the crystallites join. Under this driving force, the oriented arranged CuS will further

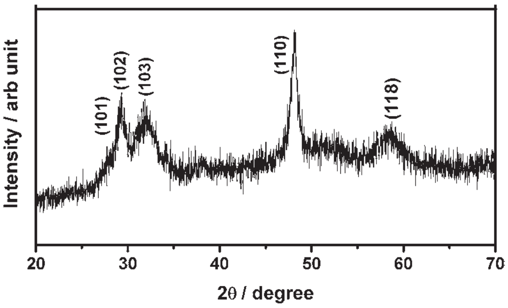


Figure 1. XRD pattern of the as-prepared CuS product.

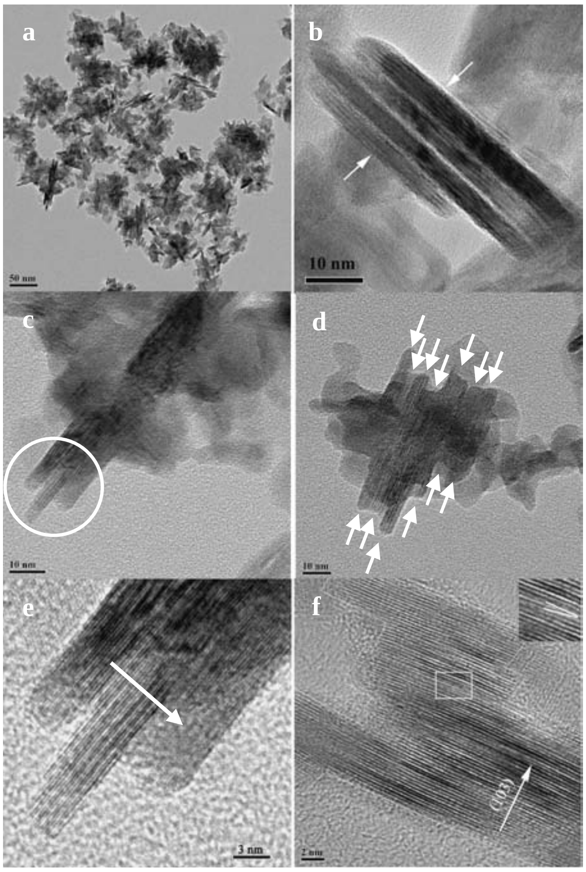
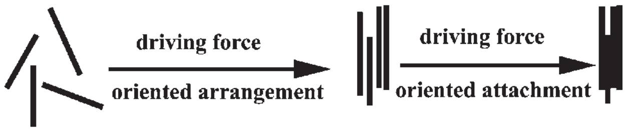


Figure 2. TEM images of a) CuS with low magnification; b) the arranged CuS nanorods; c) the attached CuS nanorods; d) more attached CuS nanorods. HRTEM images of e) the attached CuS nanostructure; f) the more attached CuS nanostructure. The upper inset is the reconstructed lattice image from the specified square area illustrates an edge dislocation. Scale bars: a) 50 nm; b) 10 nm; c) 10 nm; d) 10 nm; e) 3 nm; f) 2 nm.

attach to eliminate the surfaces and form the secondary structure. In Figure 2c, three CuS nanorods are attached in a coplanar manner using their side planes, while in Figure 2d, even more attached CuS nanorods are observed, there is no obvious gap between the adjacent nanorods compared to that in Figure 2b which indicates that these nanorods have arranged and further well oriented attached. To further reveal the microstructure and the growth mechanism of the attached CuS nanostructures, high-resolution TEM (HRTEM) images are recorded. Figure 2e is the HRTEM image of the circled part of attached CuS nanostructure in Figure 2c, from which the attachment of three nanorods via "oriented attachment" can be clearly observed. More attached CuS nanorods were shown in Figure 2f. The lack of obvious boundary between the adjacent rods indicates that the CuS nanorods are perfect aligned, which support that the attached CuS nanorods is a single-crystalline nanostructure. The average interfringe distance was measured to be 2.81 Å which could be assigned to the (103) planes with an interplanar distance of 2.81 Å. This result indicates the (103) being the bonding plane, and thus the oriented coalescence of several rods is along the [103] direction. The image of the specified square area (inset in Figure 2f) shows the existence of the dislocation at the bonding interface. This phenomenon can also been observed at other attached region in Figure 2f. It is well known that the formation of dislocation at the bonding interface is the direct consequence of the oriented attachment, because the oriented attachment occurrs by means of plastic deformation associated with the motion of dislocation until it reaches the thermodynamically favorable interface configuration.[11] The formation of oriented attached CuS nanostructure can be illustrated in Scheme 1.



Scheme 1. Schematic illustration of the formation of oriented attached CuS nanostructure.

In summary, we find that the CuS nanostructures can be formed via the oriented attachment growth mechanism. It is the first time for us to report this growth mechanism in copper sulfide. Further study will be taken to design the experimental conditions to fabricate even complex CuS single-crystalline nanostructures via oriented attachment which will provide us with opportunities to further observe and study this growth mechanism in CuS nanostuctures.

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