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Facile Fabrication of CuS Concaved Polyhedral Superstructures

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CuS concaved polyhedral superstructures have been successfully prepared by a simple solvothermal reaction without using any additional surfactants and template. CuS superstructures composed of single crystalline CuS nanoplates were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), selected area electron diffraction (SAED), high-resolution transmission electron microscopy (HRTEM), and UV–vis spectroscopy. A possible formation mechanism of CuS superstructures is discussed.

Copper monosulfide (CuS), as an important semiconductor transition-metal chalcogenide, has attracted much attention in materials science because of its excellent optical, electronic, and other physical and chemical properties[1] and potential applications such as solar radiation absorber, cathode material of lithium batteries, and catalyst.[2] Copper sulfide has been synthesized via different approaches, for example, wet chemical methods, solution methods, hydrothermal or solvothermal methods, and thermolysis methods.[3] Recently, many efforts have been devoted to the synthesis of CuS plate-based nanoarchitectures owing to their superior properties.[4] For example, Yu and co-workers have reported the well-defined concaved cuboctahedrons of CuS crystals composed of hexagonal plates by a solution reaction in ethylene glycol (EG).[5] Li et al. have also reported the solvothermal synthesis of CuS architectures which were composed of intersectional nanoplates in different solutions.[6] Although various CuS nanoarchitectures composed of nanoplates have been observed in solution-based processes, designing and developing simpler and more environmental friendly solution-based methods such as using ethanol as solution to synthesize CuS nanoarchitectures with high symmetry is still a challenge at present.

In this paper, we report one template-free solvothermal approach to fabricating CuS nanoplate-based architecture with high symmetry under ethanol solvents by using copper nitrate and sulfur without using any additional surfactants. The crystal structure of CuS superstructures was studied, and growth mechanism was additionally discussed.

In a typical synthesis, 0.25 mmol of $Cu(NO_3)_2 \cdot 3H_2O$ and 0.5 mmol of S powders were added into a 20-mL Teflon-lined stainless steel autoclave. Then 16 mL of absolute ethanol was added with vigorous stirring for about 30 min. The autoclave was stored at 180 °C for 12 h and then cooled on standing to room temperature. The black precipitates were centrifuged, washed with distilled water and ethanol three times, and dried under vacuum at room temperature for further characterization.

The crystal structures and phase purities of the samples were investigated by X-ray powder diffraction. The XRD pattern (Figure 1) shows that all the diffraction peaks can be indexed to the hexagonal phase of the covellite structure (JCPDS no. 6-464) with the $P6_3/mmc$ space group and a primitive hexagonal unit cell with $a = 3.792$ and $c = 16.344$ Å. No other characteristic peaks of impurities, such as $Cu_{1.8}S$, $Cu_{1.96}S$, Cu_2S, and CuO were detected. Energy-dispersive X-ray (EDX) analysis also verifies the coexistence of copper and sulfur in CuS superstructures (inset in Figure 1).

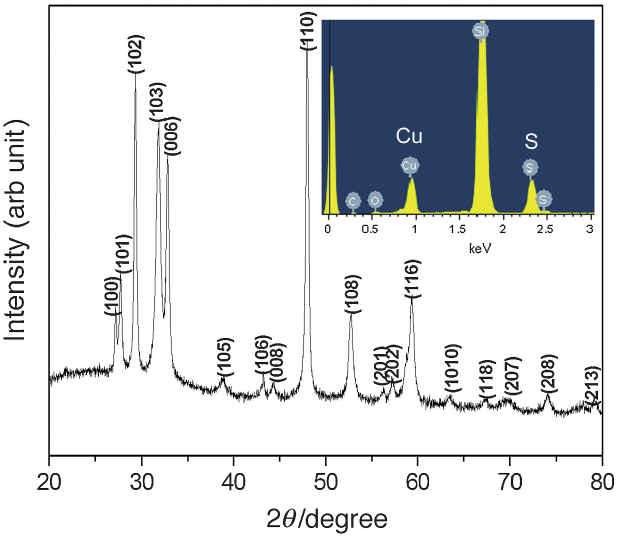


Figure 1. XRD pattern and energy-dispersive X-ray analysis (inset) of the CuS superstructrues obtained at 180 °C for 12 h.

Figure 2a displays a typical SEM image of the CuS superstructures obtained at 180 °C for 12 h. CuS superstructures with an average diameter of 1.5–2 µm are well dispersed and composed by nanoplates. Moreover, these CuS architectures are in a shape of amazingly well-defined caved architectures with high symmetry, which are constructed by intersectional nanoplates. When we changed the $Cu(NO_3)_2$ and S sources to materials such as $CuCl_2$, $Cu(CH_3COO)_2$, and thiourea or thioacetamide, the typical CuS superstructures could not be formed (Figure S1[9]). These results indicate that the nitrate and sulfur powders play key roles not only as the element sources but also other roles need further investigation. Figure 2b clearly shows the TEM image of CuS architectures consisted of intersectional nanoplates, the obvious contrast indicating the thin plates. The selected area HRTEM and electron diffraction from the platelet displayed in Figures 2c and 2d. The well-resolved 2D lattice fringes with plane distance of 0.32 nm and hexagonal plane indicated that the single platelet covered with (100) plane was grown along with [110] orientation. The FFT image (inset in c) and SAED pattern also demonstrates the single-crystal structure and preferential exposure of (100) plane of branched nanoplate.

We have also studied the influences of growth time and reaction temperature on the formation of CuS superstructures (Figures S2 and S3[9]). Concave polyhedral CuS superstructures

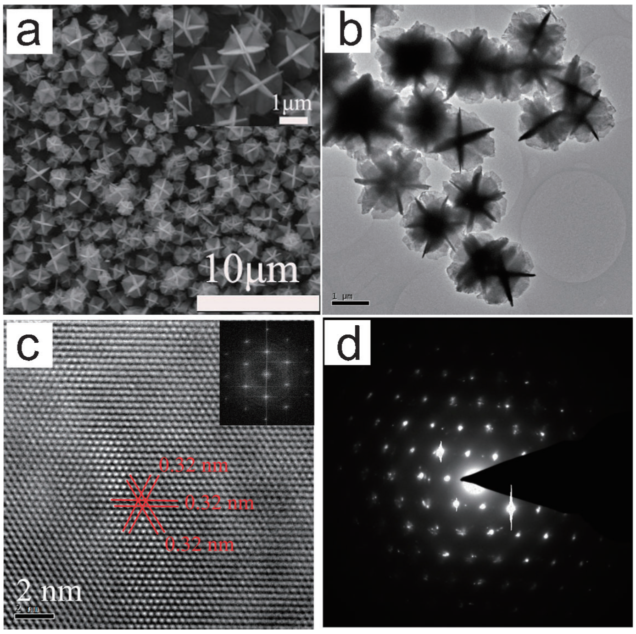
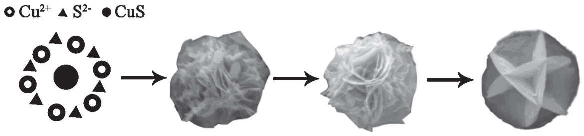


Figure 2. SEM image (a), TEM with low magnitude (b), high-resolution TEM (c), and selected electron diffraction pattern (d) of CuS architectures. Inset in c is the corresponding FFT image.



Scheme 1. Schematic illustration of the proposed formation mechanism of CuS concaved polyhedral superstructures.

took shape at 1 h and formed a well-defined sketch at 8 h. With increase of reaction temperature, especially exceeding 120 °C, CuS superstructures with defined concave polyhedron emerged. A possible formation mechanism based on three steps (nucleation, ripening, and mineral differentiation) for CuS nanoplate-based architecture is proposed in Scheme 1. First, tiny S nuclei initiated the precipitation reaction of Cu^{2+} and S^{2-} in solution and formed nanoparticles.[7] Small particles were spontaneously aggregated into large spheres through Ostwald ripening to minimize the surface energy. As the mass diffusion and Ostwald ripening process proceeded, the spherical microstructures became divided and evolved to concaved superstructures with a defined sketch. Yu et al. have reported similar CuS superstructures but different formation mechanism of branching growth process in solution. This may be due to ethylene glycol being used as solvent in Yu's case, as ethylene glycol has higher protective role and stability of directing the orientation growth than ethanol.

We have investigated the optical property of the CuS superstructures dispersed in ethanol by using UV–vis spectroscopy (Figure 3). The UV absorbance spectra is similar to what has been reported previously for the CuS structures,[8] they exhibit the short-wavelength absorption centered at approximately 450 nm and also an increased absorption in the near-infrared region. This indicates that the prepared CuS superstructures may find promising applications in photoabsorbant and photothermal conversion in the NIR region.[4]

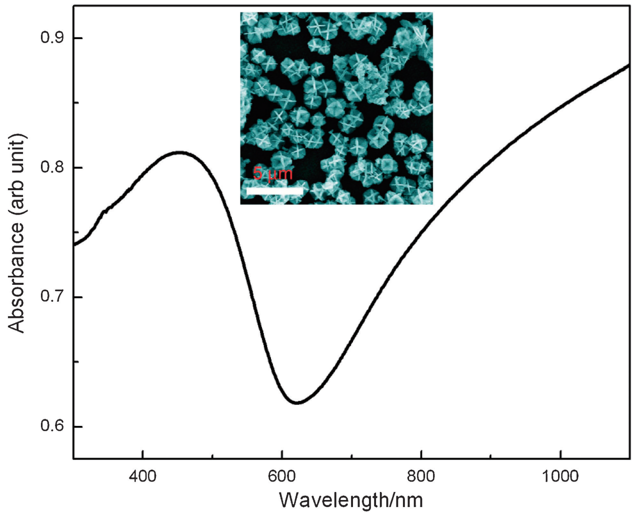


Figure 3. Absorption spectra of the aqueous dispersion (0.01 g L^{-1}) of as-synthesized CuS superstructures.

In conclusion, a simple and template-free solvothermal approach has been developed for preparation of CuS concaved polyhedral superstructures. CuS superstructures composed of single crystalline nanoplates were characterized, and a nucleation–ripening–mineral differentiation mechanism was proposed for CuS superstructures. Apart from conventional application in photocatalysis, the strong absorbance in near-infrared region makes CuS superstructures useful for NIR photothermal conversion in biomedicine.

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9 Supporting Information is available electronically on the CSJ-Journal Web site, http://www.csj.jp/journals/chem-lett/index.html.