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Complex Concaved Cuboctahedrons of Copper Sulfide Crystals with Highly Geometrical Symmetry Created by a Solution Process

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In recent years, architectural control of nanoparticles with well-defined shapes and alignment of nanobuilding blocks into ordered superstructures have been key issues in modern colloids and material chemistry[1] and nanotechnology.[2] In addition, as a kind of new nanostructure, hollow nanostructures and core−shell nanostructures have received intense attention because of their improved physical and chemical properties over their single component.[3]

Copper monosulfide, one of the important semiconductor transition-metal chalcogenides, has gained more and more attention in material science because of its excellent optical, electronic, and other physical and chemical properties[4] and potential applications such as solar radiation absorber,[5] coating on the polymer surface to increase its conductivity,[6] high-capacity cathode material in lithium secondary batteries,[7] nanometer-scale switches,[8] and catalyst.[9] However, because copper sulfides have many different phase compositions and exist in a wide variety of compositions,[10] mixtures of different copper sulfides are usually obtained in many synthetic procedures.[11] CuS particles with different morphologies such as platelike,[12] rodlike,[13] and tubelike structures;[14] hollow spheres;[15] and flowerlike,[16] urchinlike, and snowflakelike patterns[17] have been synthesized. However, none of these diverse morphologies displays more complexity with a highly geometrical shape and no report has been yet focused on how they are assembled.

In this Communication, we report a chemical route for the synthesis of well-defined concaved cuboctahedrons of copper sulfide crystals by a solution reaction in ethylene glycol (EG). Each caved cuboctahedron is apparently "caved" with highly symmetric 14 cavities and is constructed by four identical hexagonal flakes while sharing the 24 edges in a dymaxion way.

In a typical synthesis, 0.5 mmol $Cu(NO_3)_2 \cdot 5H_2O$ was dissolved in 21 mL of ethylene glycol (EG) to form a clear blue solution, which was transferred into a 28 mL Teflon-lined stainless steel autoclave. Afterward, 1 mmol sulfur powder was added to this solution under vigorous stirring. The autoclave was sealed and maintained at 140 °C for 24 h. After the solution was cooled to room temperature, the obtained black solid products were collected by centrifuging the mixture; they were then washed with carbon disulfide and absolute ethanol several times each and dried in a vacuum at 60 °C for 4 h for further characterization.

The phase purity of the as-prepared products was determined by X-ray diffraction (XRD) using a Philips X'Pert PRO SUPER X-ray diffractometer equipped with graphite-monochromatized Cu−Kα radiation ($\lambda = 1.54178$ Å). The composition of the product was measured by an Atomscan Advantage inductively coupled plasma (ICP) spectroscopy with a pump flow of 1.85 mL min^{-1} and a flow rate of the auxiliary gas (Ar 99.99%) of 1.0 L min^{-1}. Scanning electron microscopy (SEM) and field emission scanning electron microscopy (FE-SEM) were applied to investigate the size and morphology and were carried out with a Hitachi X-650 scanning electron microanalyzer and a field emission scanning electron microanalyzer (JEOL-6700F), respectively. Transmission electron microscope (TEM) photos were taken with a Hitachi H-800 transmission electron microscope at an acceleration voltage of 200 kV. High-resolution transmission electron microscope (HRTEM) photos and selected area electron diffraction (SAED) patterns were performed on a JEOL-2010 transmission electron microscope.

The X-ray powder diffraction pattern can be indexed as pure hexagonal CuS (covellite, space group 194, $P6_3/mmc$) (JCPDS 6-464) (Figure 1A). The Cu:S atomic ratio was determined to be 1.1:1 by the ICP measurement. SEM images in Figure 1B clearly show that a majority of the particles

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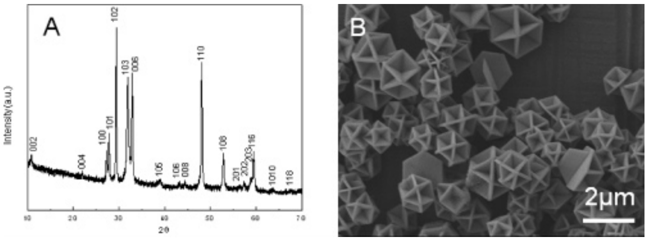

Figure 1. (A) XRD pattern of the CuS product prepared at 140 °C for 4 h. (B) General view of as-prepared CuS crystals after reaction at 140 °C for 4 h by a solvothermal process.

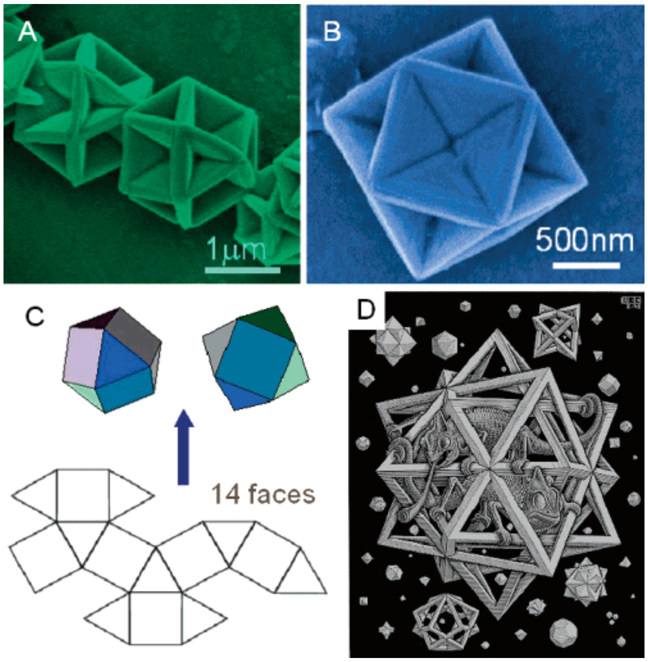

Figure 2. (A and B) SEM images of the typical caved cuboctahedral crystals, synthesized by the solvothermal process at 140 °C for 24 h. (C) Schematic illustration of a cuboctahedron with 14 faces (six squares and eight triangles), composing the structure by sharing the identical 24 edges in a dymaxion way. (D) Cuboctahedron appearing as one of the polyhedral "stars" in M. C. Escher's 1948 wood engraving *Stars*.[18]

are in a form of amazingly well-defined caved cuboctahedrons.

The particles synthesized at 140 °C for 24 h showed more complete cuboctahedral shape (Figure 2A,B). This novel structure can in fact also be described as comprising four identical hexagonal plates with an edge length of 1−1.5 μm and a thickness of ca. 200 nm. The dihedral angle for each set of two conjoined plates is measured to be about 70°, which is very close to the calculated value (70.5°) for a cuboctahedron (see the Supporting Information, Figure S1).

In fact, each cuboctahedron with 14 faces can be simplified as having a composition of six squares and eight triangles, and the overall structure shares 24 identical edges in a dymaxion way (Figure 2C). Because of the high esthetic quality of this structure, M. C. Escher took this symmetry element as an element in his 1948 wood engraving *Stars* (Figure 2D) as well as in the mezzotint *Crystal*.[18] It is appealing that a synthetic technique as simple as the one presented here can produce such beautiful objects that even a skillful craftsman cannot touch on the microscale level.

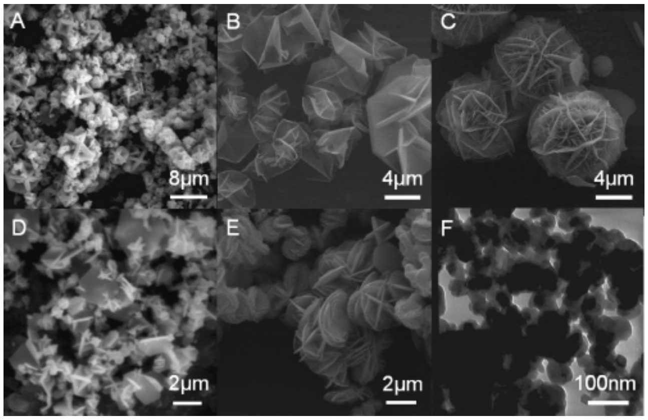

Figure 3. SEM images and TEM images of CuS particles obtained under different conditions. (A) In a mixed solvent (the volume ratio of V_{water}:V_{EG} = 1:1). Using different Cu^{2+} sources: (B) $CuSO_4 \cdot 5H_2O$, (C) $CuCl_2 \cdot 5H_2O$, and (D) $Cu(CH_3COO)_2 \cdot 5H_2O$. Using different sulfur sources: (E) thiourea (Tu) and (F) thioacetamide (TAA).

According to Fievet et al.,[19] the reactions happening in the present system can be expressed as the following

$$2HOCH_2CH_2OH \xrightarrow{-2H_2O} 2CH_3CHO \rightarrow 2H_3CCOCOCH_3 + 2H \tag{1}$$

$$S + 2H \rightarrow H_2S \tag{2}$$

Acetaldehyde is produced by the dehydration of EG at high temperature, where the acetaldehyde can donate a hydrogen atom and act as a reducing agent, as shown in eq 1. S^{2-} ions are then formed through the reduction of element S by H atoms, as shown in eq 2.

The reaction temperature was chosen to be 140 °C to exceed the melting point of sulfur (120 °C). In fact, no reaction occurred at 100 °C. The successful synthesis of phase-pure CuS is strongly dependent on the molar ratio of the precursors, and pure CuS can be obtained only when the molar ratio of S:$Cu(NO_3)_2$ is larger than 2:1. Under identical reaction conditions, no reaction occurred when water was used as the solvent, and a mixture of irregular particles and the well-defined crystals was obtained when a mixed solvent of ethylene glycol and water (V_{water}:V_{EG} = 1:1) was used (Figure 3A). So the solvent plays a great role in the formation of the caved cuboctahedron, and the way it works is still to be studied. Furthermore, neither the use of other Cu^{2+} sources with different anions such as $CuSO_4 \cdot 5H_2O$, $CuCl_2 \cdot 5H_2O$, and $Cu(CH_3COO)_2 \cdot 5H_2O$ nor the use of other sulfur sources such as thiourea and thioacetamide leads to particles with similarly high definition (Figure 3).

To understand how the structure setup in the closed autoclave occurred, we simulated the reaction in an oil bath (see the Supporting Information for experimental details). Smaller, less-defined, but single-crystalline plateletlike particles of pure CuS were obtained (Figure 4A,B). Selected area electron diffraction (SAED) patterns and HRTEM confirmed the single-crystalline structure of each platelet (Figure 4C,D), e.g., well-resolved 2D lattice fringes corresponding to the known distances (3.2 Å) within the hexagonal

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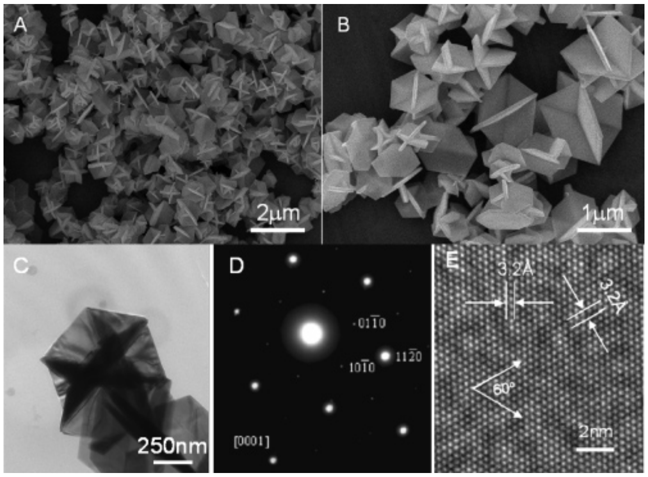


Figure 4. (A and B) FESEM images of the CuS particles obtained from reaction in an oil bath at 140 °C; (C) typical TEM image of the CuS particles obtained from reaction in oil bath; (D) selected area electron diffraction (SAED) pattern taken from a single platelet laying flat on the TEM grid; (E) HRTEM image taken from this platelet.

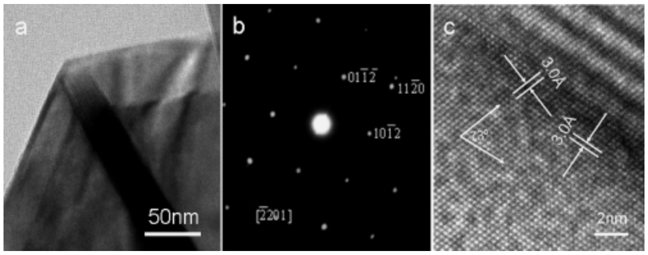


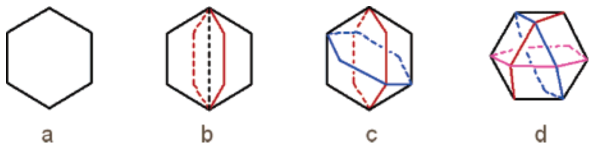
Figure 5. (a) Typical TEM image of a conjoined part of a concaved cuboctahedron CuS crystal obtained from reaction in oil bath; (b) selected area electron diffraction (SAED) pattern; and (c) HRTEM image taken from the conjoined part.

plane (Figure 4C−E). The preferential exposure of the [0001] plane is related to the intrinsic structural features of covellite, stacked CuS_4−CuS_3−CuS_4 layers that are held together by covalent S−S bonds.[20]

With further reaction, more and more defined branching points are observed in the products; the branched structure gets optimized until the caved cuboctahedron with their minimal exposure of edges are obtained. Obviously, optimization of structure relies on crystallization/dissolution processes, which can be optimized by the choice of temperature and solvent.

The electron diffraction pattern taken along the $\langle\bar{2}201\rangle$ direction on the conjoined place of two hexagonal plates indicated the highly crystalline nature (Figure 5a,b). The XRD pattern shown in Figure 1A also indicated that the peak of (102) is much stronger than that reported in the JCPDS card, implying the possible preferential orientation growth. The HRTEM image taken from the conjoined place of two hexagonal plates is shown in Figure 5c, from which we can

Scheme 1. Illustration of Possible Branched Structures Constructed from Hexagonal Plates.



(a) Single hexagonal plate; (b) constructed by two hexagonal plates; (c) constructed by three hexagonal plates; (d) well-defined concaved cuboctahedron constructed by four hexagonal plates

see that the two plates are of the same lattices fringes, which means that they grow from the same arris and along the same direction. The lattice spacing of 3.0 Å corresponds to the interplanar distance of $\{10\bar{1}2\}$. We presume that the well-defined concaved cuboctahedron could be formed by the growth of three other hexagonal plates along $\langle 10\bar{1}2\rangle$ from the diagonal direction of the basal plane, with the reaction going on as shown in Scheme 1. The exact formation mechanism of such complex concaved cuboctahedron needs more dedicated work in the future.

In summary, large scale synthesis of well-defined concaved cuboctahedral superstructures of copper sulfide by a solvothermal reaction in ethylene glycol (EG) is possible. Each caved cuboctahedron is apparently "caved" with 14 highly symmetric cavities and is constructed by four identical hexagonal flakes while sharing the 24 edges in a dymaxion way. This underlines that new facile mesoscale techniques of chemistry can access astonishing complexity, but also beauty as imagined by M. C. Escher.[18] The results demonstrate that the branching growth process in solution can be precisely manipulated for the controlled growth of amazingly complex crystalline structures with high geometrical symmetry, which is not reflected in the primary crystal symmetry. This new kind of caved cuboctahedron crystals with its 14 well-defined cavities could find potential applications because of their unique structure, e.g., as a micrometer-sized constructionelement or a new kind of potential container for carrying, filling in, or encapsulating other materials.

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Supporting Information Available: The detailed experimental procedures of the reaction in an oil bath and the detailed calculation of the dihedral angle of each of two conjoined plates for a cuboctahedron crystal. This material is available free of charge via the Internet at http://pubs.acs.org.

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