Three-dimensional imaging of a complex concaved cuboctahedron copper sulfide crystal by x-ray nanotomography

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By combining Fresnel zone-plate based transmission x-ray microscopy with computed tomography, the nanoscale features in materials with complex shapes can be imaged using synchrotron radiation. The tomographic data sets of a complex copper sulfide crystal were acquired in the angle range ±70° at photon energy of 8.0 keV and then were reconstructed by a standard filtered-back-projection algorithm. This experiment shows the quantifiable three-dimensional information of the copper sulfide crystal, which offers a complete understanding of the concaved cuboctahedron structure with 14 faces comprising of six squares and eight triangles. © 2008 American Institute of Physics. [DOI: 10.1063/1.2943337]

Objects with complex shapes and unique functions have always attracted attention and interest. Consequently, the synthesis of materials with controlled morphologies, unique structures, and complexity has become a hot research field.¹–⁴ Until now, micronsized and nanosized materials are commonly characterized by transmission electron microscopy (TEM) and scanning electron microscopy, which can provide important two-dimensional (2D) information due to their high spatial resolution. However, certain materials with complex three-dimensional (3D) shapes and thick ordered structures are a challenge for imaging since the overlap of complex features in projections will complicate image analysis. In particular, the measurement of volume structures is critical for understanding the function of materials and the synthesis mechanism of the controlled growth of crystalline structures under different reaction conditions. A TEM is mainly used for imaging thin sections of about 50–100 nm thickness or thin particles and macromolecules. It is difficult to obtain 3D information of such materials by TEM unless via serial sectioning of the samples. Furthermore, this method is time consuming and prone to introducing artifacts due to the destructive sample preparation. Thus, high-resolution imaging technique will be necessary for such investigations. In this paper, we show that x-ray nanotomography has the potential to accomplish these goals.

X-ray microscopy is widely used to image the interior of thick opaque specimens because of the large penetration depth of x rays. Due to the development of Fresnel zone plates (FZPs) (Refs. 5–9) and the availability of synchrotron radiation sources, a FZP based transmission x-ray microscope has resolved 2D structures better than 15 nm in the photon energy range of 0.25–1.8 keV.¹⁰ For harder x rays, a first-order lateral resolution below 40 nm has been achieved in the energy range of 7–18 keV.¹¹ An x-ray microscope with 30 nm resolution in the third order at 8 keV has been reported.¹² Computed tomography (CT) (Ref. 12) is a familiar tool for obtaining 3D information in diagnostic medical imaging as well as in nondestructive testing. By combining FZP based x-ray microscopy with CT, x-ray nanotomography has achieved tomographic reconstruction with a spatial resolution around 60 nm.¹³–¹⁵ It is relatively easy to accomplish with minimal sample preparation, which reduces, but does not eliminate, the introduction of artifacts by sample preparation. In combination with microscopy methods, x-ray nanotomography offers the possibility to obtain the 3D structures of micronsized and nanosized complicated materials. Here a complex concaved cuboctahedron of copper sulfide crystal discovered recently¹⁶ is used to demonstrate the feasibility of this methodology.

The experiment was performed on the x-ray microscope beamline U7A of National Synchrotron Radiation Laboratory (NSRL), Hefei, China. The schematic experimental setup of the transmission x-ray microscope is shown in Fig. 1. A 6 T superconducting wiggler is used as the x-ray source. A Si(111) double crystal monochromator tunes the photon energy in the range of 7–12 keV. It provides a monochromatic x-ray flux of 3.5×10⁹ photons/s at 8 keV at the stored ring current of 100 mA. An elliptically shaped capillary is used as the condenser with a focusing efficiency near 90%. Properly coupled with a beam stop and a pinhole aperture, the condenser provides a hollow cone illumination which matches the numerical aperture of the objective FZP. The objective FZP with a 45 nm outermost zone width operated at 8 keV is made by electroplating gold on the silicon nitride membrane. The diameter of the FZP is 80 μm while the thickness of the gold is 1.4 μm. Combined with the hollow cone illumination,¹⁶ it delivers a lateral resolution down to 50 nm and a 52 μm depth of field. The x-ray image is converted into a visible image with a scintillator. This image is further magnified by a factor of 20 using an imaging system

![FIG. 1. Principle of the transmission x-ray microscope at the beamline U7A of NSRL.](image-url)
for visible light, producing a total magnification of 880. The magnified image is recorded by a 1024×1024 charge coupled device camera, corresponding to a 15×15 μm² field of view. With an 880-fold magnification and a pixel size of 13.5 μm, one pixel corresponds to 15 nm. With a computer-controlled rotation stage and a stable mechanical design, the tomographic data can be automatically collected by the computer.

The concaved cuboctahedron CuS crystals were synthesized by the solvothermal process at 140 °C for 24 h as previously reported. The samples were moved onto a silicon nitride window fixed on the sample holder. Some golden particles at a scale of 500–800 nm were used as alignment reference markers. The total 71 sequential tomographic images were automatically collected from −70° to +70° in 2° intervals at 8.0 keV. Subsequently, these projections were aligned using the software developed by the Xradia Company which can calculate the rotation center of the projections from each angle. A standard filtered-back-projection algorithm was applied to reconstruct the aligned data.

The 3D rendering and reconstructed slices of the single concaved cuboctahedron CuS crystal are shown in Fig. 2 from different viewing angles. The original data of the single crystal was cropped from the numerous overlapping particles, because it is more convenient to distinguish the shape and the precise boundary of the crystal as well as to quantitatively analyze the generated volume structure. Figures 2(a) and 2(d) display the 3D rendering of the crystal, from which the low absorption of the silicon nitride is removed. We can easily identify that the crystal comprises four identical hexagonal plates (P1–P4). A reconstructed slice of the hexagonal plate P1 is displayed in Fig. 2(e). The edge lengths of the hexagonal plates were measured to be 1–1.5 μm while the thickness was measured to be around 200 nm. It can be directly counted from the tomographic reconstruction results that the crystal volume structure has 24 identical edges and 14 cavities. However, we found that plate P4 of the chosen crystal lacks an edge in Fig. 2(d). The reconstructed slice of plate P4 is shown in Fig. 2(i), in which the red box shows the lacking-edge region. It may be mainly because the branching structure of plate P4 had not grown optimized. The 14 cavities have 14 corresponding faces comprising six squares and eight triangles, which can be identified by the measured angles in Fig. 2. Figure 2(a) presents the 3D rendering of the CuS crystal from the top view of a triangle face, which is confirmed in the reconstructed slice of the same face [Fig. 2(f)]; while Fig. 2(b) displays the 3D rendering of the crystal from the top view of a square face, with the corresponding reconstructed slice of the same face in Fig. 2(g).

According to the experimental results, we show a schematic illustration of the CuS crystal in Fig. 2(j). Here we can describe the CuS crystal as a well-defined caved cuboctahedron with highly geometrical symmetry. Each cuboctahedron is apparently “caved” with symmetric 14 cavities and is constructed by four identical hexagonal plates through sharing 24 identical edges. In the schematic illustration, the value of the dihedral angle for each set of two conjoined plates is 70.5°. In the 3D rendering volume structure, we can measure this angle from a cross section of two conjoined plates. Figure 2(c) displays the 3D rendering of the crystal from the top view of two conjoined plates. The reconstructed slice of a cross section is shown in Fig. 2(b), in which the dihedral angle is measured to be 70.3°. In addition, the whole volume of the plates, as measured by means of the 3D image analysis of the reconstruction volume, is close to 38.7% of the whole space enveloped by the 14 faces. The 3D rendering of the whole enveloped space is shown in Fig. 3 from two different viewing angles. This means that the concaved cuboctahedron CuS crystals can sustain the whole enveloped space in a dymaxion way, which could find the possible usage as a small container for carrying, filling in, or encapsulating other materials as very recently demonstrated for loading silica spheres with diameters ranging from 30 to 730 nm.19

These results indicate that x-ray nanotomography is useful to image nanostructures of interest in materials with complex structures. In addition, it has also been applied to study cellular structures and organelles as well as integrated-circuit devices. The outstanding feature of this technique...
highlights its potential in a broad variety of fields, including materials science, environmental science, and the life sciences.

In summary, we demonstrate x-ray nanotomography with 50 nm spatial resolution on the complex concaved cuboctahedron of copper sulfide crystals with highly geometrical symmetry. The three-dimensional images of the crystal reconstructed by computed tomography offer a complete understanding of the cuboctahedron structure.

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19See EPAPS Document No. E-APPLAB-92-005824 for a video of the 3D rendering of the concaved cuboctahedron CuS crystal. For more information on EPAPS, see http://www.aip.org/pubservs/epaps.html.