

## In-situ Observation of the Formation of Cu<sub>2</sub>O Nanocrystals by Transmission X-ray Microscopy

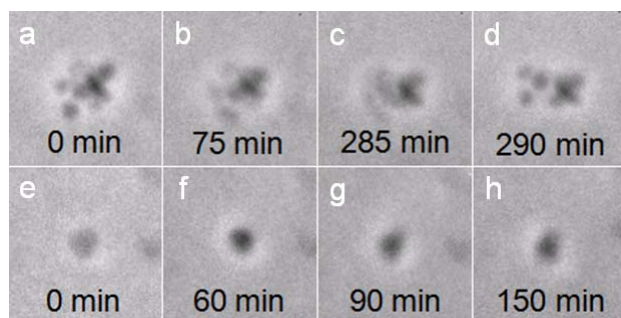
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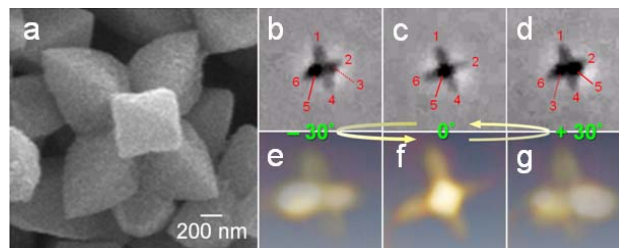
Cuprous oxide (Cu<sub>2</sub>O) is a *p*-type semiconductor with a direct band gap of 2.17 eV. Cu<sub>2</sub>O nanostructures have been demonstrated to possess properties useful for applications in gas sensing [1], CO oxidation [2], photocatalysis [3], photoactivated splitting of water [4], and organic synthesis [5]. Therefore, controlled growth of uniform Cu<sub>2</sub>O nanocrystals with highly active domains becomes a fundamentally important topic. We have used a synthetic procedure for the formation of Au@Cu<sub>2</sub>O core-shell plates (edge length 1–1.5 μm, thickness < 100 nm) to perform transmission x-ray microscopy (TXM) analysis, and reveal their growth mechanism, including nucleation, adsorption, aggregation and reconstruction processes. Besides, TXM is a powerful tool for obtaining tomography information. This can help us build a structural model for a complex crystal.

Figure 1 shows the selected images of the crystal formation processes taken from the movie, which was obtained by combining successive pictures, and gives the information of crystal growth. Here, Au nanoplates are used as the cores for easy observation during growth.

As the images in the upper row (a, b, c, d) show, several particles are in contact with each other and they gradually react in 4 hours. At 285 minutes, two particles “fuse” into the bigger core-shell particles. In another case, a triangular Au particle changes its contrast at a reaction time of 60 minutes (e, f, g, h). As the time passes by, the morphology of the core-shell particle starts to become distorted. This finally gives a core-shell particle with the same triangular shape but a deeper contrast). Although the observation provides some evidence of the growth mechanism, we cannot determine the correct mechanism conclusively because of the blurred images produced inherent to the resolution of TXM (60 nm). Nevertheless, we have made some progress and there is still room for improvement of the experiment including both sample preparation and resolution refinement.



**Fig. 1:** Selected in-situ images obtained from a movie recording the entire growth process. Upper row shows the aggregation stage from 0 to 290 minutes. Lower row gives the information about the variation of contrast and morphology during the formation of a Cu<sub>2</sub>O shell.



**Fig. 2:** Tomography investigation of a single Cu<sub>2</sub>O microcrystal with hexapods (a). By rotating the sample mount, we successfully got a movie which confirmed its hexapod structure (b, c, d). Its structure reconstruction was carried out by using Amira 4.0 (e, f, g).

Figure 2a displays a SEM image of a single Cu<sub>2</sub>O microcrystal with hexapods. Its complex structure is verified to result from the evolution of an octahedron with a higher growth rate along the [100] directions. To build up an exact crystal model, we need to get its tomographical information. In a typical procedure, we use the pre-synthesized Cu<sub>2</sub>O sample solution (dispersed in ethanol) and add 15 μL to the sample holder. By rotating the sample mount from  $-70^\circ$  to  $+70^\circ$ , successive motion of the Cu<sub>2</sub>O microcrystal was recorded. As the TXM images shown in 2b, 2c and 2d, its six arms are very clear and “arm 5” moves from left to right when it is rotated through 60 degrees (b, c, d). Subsequently, we constructed its exact tomographical model by using the Amira 4.0 program (e, f, g) and confirmed the structural homogeneity of this microcrystal.

In conclusion, we have successfully obtained some evidence of the growth process of Au–Cu<sub>2</sub>O core-shell plates. We have also acquired their tomographical information by using the TXM technology. Even though more improvements are necessary, there is no doubt that TXM is a powerful tool for the in-situ observation of solution samples with crystals.

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