

In-Situ Observation of the Kirkendall Effect of Cu₂O-Cu₂S Core-cage Structures and the Decomposition of Ag₂O by Transmission X-ray Microscopy

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Kirkendall effect is a phenomenon of two materials merging into a new one when their energy is enough. The most famous case is the formation of spinel, a solid-solid case. By contacting Al₂O₃ and MgO under thermal condition, they diffuse into each other with unequal speed and form MgAl₂O₄. However, our case is very different because our condition is in the aqueous solution and one of the reactants is the liquid phase (provide ions). Our purpose is to observe the turning process of pristine Cu₂O to Cu₂O-Cu₂S core-cage structures in situ. In Fig. 1, four images recorded at 120s, 345s, 360s, and 375s show the variation of the cubic structures. These core-cage were thin-shell at 120s and began to further consume their interior for several minutes as pointed by red arrows. The results of the formation process on materials with specific shapes had never been mentioned before in that they hadn't observed the reaction in solution in situ. This is really a breakthrough in the synthesis of nanomaterials.

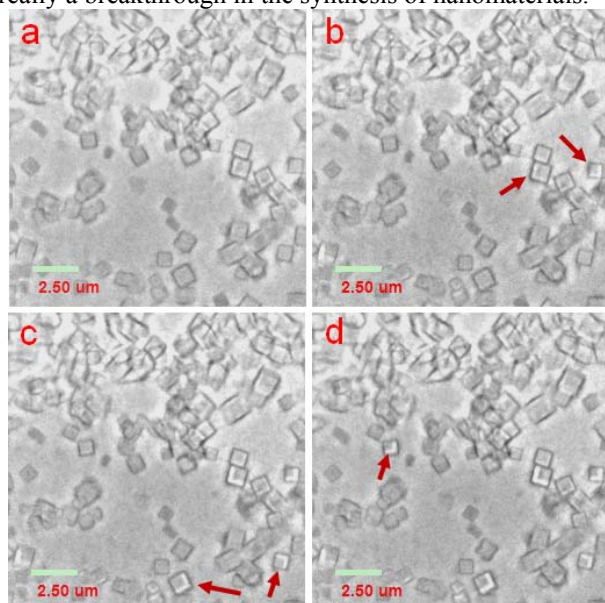


Fig. 1: TXM in-situ recorded the process of Kirkendall effect occurring between Cu₂O surfaces and sulfur anions in solution. The recording times were (a) 120s, (b) 345s, (c) 360s, and (d) 375s. At the stage of 345s, we clearly observed the consumption of the Cu₂O cores (pointed by red arrows), which went on for several minutes.

According to the same purpose, we used transmission X-ray microscopy to study the formation process of Ag₂O crystals. Unfortunately, the reaction rate is too fast to observe the entire process. However, something more interesting should be mentioned. In Fig. 2, there was no destruction on structures after one hour of irradiation, no change was observed when dried particles

were used (b1, b2). Surprisingly, Ag₂O crystals dispersed in water been to decompose as fragments after several minutes of X-ray irradiation (a1-a4). In spite of heating the cubic Ag₂O particles in 95 °C water for 1 h, didn't degrade and this suggested in fragmentation (c1,c2), that heat is not the factor for particle destruction under X-ray irradiation. Supposedly, X-ray excited semiconductor-Ag₂O [1] to produce electron-hole pairs, that generate hydroxyl radical [2]. Hydroxyl radicals attack Ag₂O and result in structural decomposition.

In conclusion, we have successfully obtained some evidence of the Kirkendall effect of Cu₂O-Cu₂S core-cage structures and the factor of Ag₂O decomposition. Further experiments are needed to investigate the two cases. Even though much improvement is necessary, there is no doubt that TXM is a powerful tool for the in-situ observation on crystal growth in solution.

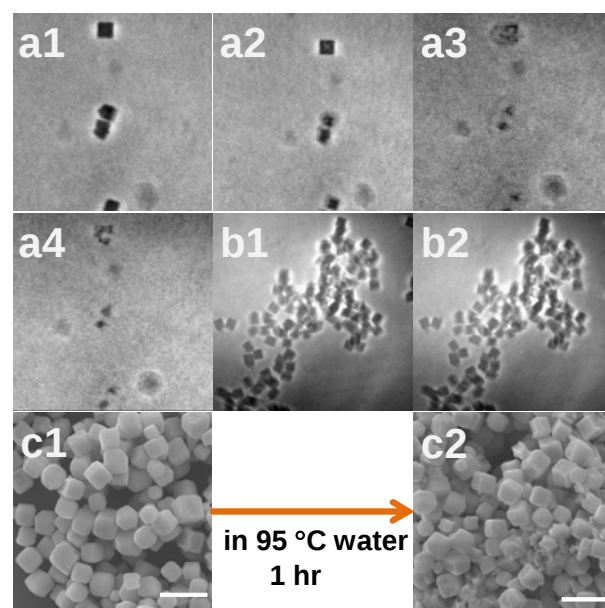


Fig. 2: Ag₂O cubic crystals dispersed in water were decomposed into fragments after several minutes of X-ray irradiation (a1–a4). Over the period of one hour of X-ray irradiation for the examination of possible structural change (b1, b2). Heating the cubic Ag₂O particles in 95 °C water for 1 h did not result in fragmentation, suggesting that heat is not the cause for particle fragmentation during X-ray irradiation (c1, c2). Scale bar = 1 μm.

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- [2] C. W. Yen, M. A. Mahmoud, and M. A. El-Sayed, *J. Phys. Chem. A* **113**, 4340 (2009).