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Dynamic studies of solution-based reactions using operando TEM

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In-situ investigation of chemical reactions in liquid is attracting increasing interest in recent years, due to the unprecedented capabilities provided by the fast development of in-situ liquid-cell for scanning transmission electron microscopy ((S)TEM) technologies[1]. Using liquid-cell in (S) TEM, as shown in Figure 1.a), the solution-based structure and morphology evolutions can be studied. In this research, we use sandwiched silicon nitride liquid cell to study the effect of different electron dose rates and different liquid thicknesses on the e^--beam induced nucleation and growth of copper salts in solution.

In the experiment, we observe that copper salts can only be generated in the e^--beam exposure area, and its pre-nucleation time decreases as the dose rate increases over a threshold value. By studying the growth rate after nucleation, the different growth mechanisms of particles at thick and thin liquid-cell are revealed. In the thick liquid area (Figure 1.b)), the growth is mainly controlled by diffusion rate compared with the surface reaction-controlled growth when the liquid area is thin (Figure 1.c)). For thick liquid, the flower shaped amorphous precursor particles can be observed and identified by the diffraction patterns (DP). According to the different contrast of amorphous and crystalline phases in liquid, some crystals can be directly viewed to form in the center or at the edge of the amorphous particles and then expand. It proves that the amorphous phase exits during all the initial stages of the crystallization process. For the thin liquid cell, however, no amorphous phase was found. But some triangle, prismoid, rectangle and other regular shaped particles are formed in thin liquid. By changing dose rate and thickness of liquid, the morphology of new generated particles can be controlled. The dose rate and exposure time are directly related to pH variation and the radical products such as hydrogen, oxygen, and hydrated electrons, which are produced by e^--beam in aqueous solution[2]. Such findings demonstrate that the thickness of liquid cell largely affects the nucleation and growth of Cu salts, implying an underlying relationship between electron dose rate and phase transition that still needs to be explored. This research indicate how to use the liquid cell to study radiolysis effects on materials.

References:

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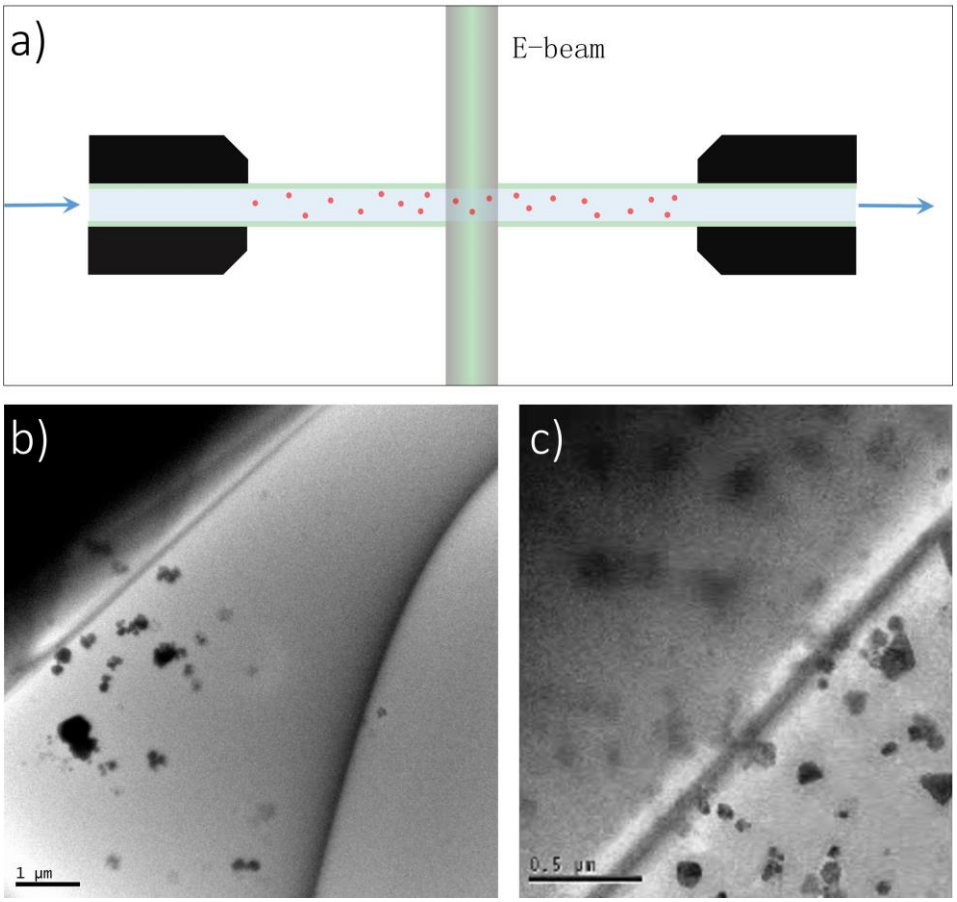

Figure 1. a) Schematic of the liquid holder in the TEM. A liquid cell is enclosed between two electron transparent windows made of silicon nitride. b-c) Different morphology of the particles formed inside the cell with different liquid thickness(b thick c thin).

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