Investigation of liquid cell transmission electron microscopy combined with antisolvent crystallization

*Tomoya Yamazaki[1], Yuki Kimura[1]

1. Institute of Low Temperature Science Hokkkaido University

Crystallization of salts in solutions is a quite common phenomenon in the earth and is important not only for production of materials but also for understanding geochemical processes. However, initial stage of crystallization, called nucleation, is not fully understood and numerous studies to understand the process have been reported. Recently, multistep nucleation pathway, which formations of one or more metastable phases are required on the route to a formation of a crystalline phase, have been proposed. Liquid cell transmission electron microscopy (TEM) is a promising method for observing the nucleation process directly because the spatial resolution of this method is under nanometer scale. More recently, multistep nucleation pathways of the crystals of calcium carbonate [1] and lysozyme protein [2] have been revealed by liquid cell TEM. However, capturing a moment of a nucleation event is quite difficult because the observable area of the method is small ($< 100\ \mu m^2$) and a nucleation event is typically very rare in the tiny volume within the area. In order to observe nucleation events efficiently, a supersaturation of a sample solution should be increased with observing the solution. To create the situation, we applied the anti-solvent crystallization technique, which crystallize the solute to add the solvent with the extremely low solubility of the solute (anti-solvent), to liquid cell TEM and tried to observe the nucleation event of a salt crystal.

We used the TEM holder (Poseidon 300, Protochips Inc.) and the liquid cells of silicon chips equipped with thin silicon nitride windows. Aqueous solution of sodium chlorate under equilibrium at room temperature was enclosed in the liquid cell. The TEM holder has two injection ports of liquid, and one of the ports was filled by acetone as the anti-solvent of sodium chlorate. After starting the observation of the sample solution, acetone was injected by syringe pump for mixing the aqueous solution in the liquid cell.

Using the methods, we succeeded in observing the nucleation events of crystals. In this presentation, we will report the detailed analysis of crystals and the nucleation processes.

Acknowledgement

This work was supported partly by Grant for Basic Science Research Projects from The Sumitomo Foundation (Grant Number 170738) and JSPS KAKENHI Grant Numbers JP15H05731 and JP18J01470. T.Y. is grateful for the JSPS Research Fellowship for Young Scientists.

References

[1] M. H. Nielsen *et al.*, *Science* **345** (2014), 1158.

[2] T. Yamazaki *et al.*, *Proc. Natl. Acad. Sci.* **114** (2017), 2154.

Keywords: liquid cell transmission electron microscopy, crystal growth, solution growth, anti-solvent crystallization

