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Molecular Level Analysis of Salt Crystallization Process Using Video Images

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Summary

The objective of this project is to obtain knowledge that contributes to the control of salt crystallization from transmission electron microscopy (TEM) video observations with atomic resolution. Crystallization is a scientific phenomenon that follows stochasticity and is difficult to control precisely even with today's mature science and technology. Crystallization control is a dream of mankind, and I believe that the lack of direct experimental methods and mechanistic research to solve this problem is a problem. Therefore, I hypothesized that the acquisition of an experimental picture of how atoms, molecules, and ions form aggregates, construct crystal nuclei, and grow into crystals would ultimately lead to the control of crystallization. The applicant's group has long been developing a method to precisely analyze the dynamic behavior of single molecules and molecular aggregates using TEM with atomic resolution (Single-Molecule Atomic-Resolution Time-resolved Electron Microscopy, SMART-EM). In 2021, based on the development of a new sample preparation method, we succeeded in capturing the moment when salt (NaCl) nucleation occurs. The subsequent crystal growth process was analyzed from molecular videos with a time resolution of 40 milliseconds. We have further developed this preliminary knowledge and conducted experiments to grasp the essence of the crystallization phenomenon in this application study.

In accordance with a previous study (T. Nakamuro, M. Sakakibara, H. Nada, K. Harano, E. Nakamura, J. Am. Chem. Soc. 143, 1763-1767 (2021)), NaCl was encapsulated in carbon nanotubes as the observation field. Atomic-resolution TEM observations were performed using a JEM-ARM200F instrument equipped with a spherical aberration corrector (point resolution: 0.10 nm) at 298 K, an acceleration voltage of 80 kV, and 1 x 10^{-5} Pa.

In this research, I aimed to obtain knowledge for controlling salt crystallization from video imaging with atomic resolution. For this purpose, I optimized the imaging conditions using the state-of-the-art K3-IS camera and succeeded in revealing the non-equilibrium dynamics during crystal growth through high-speed imaging at over 300 fps (~3 ms/frame). In the case of crystal growth, it was revealed for the first time that molecular aggregates do not attach to the crystal face of NaCl until their structure matures to a certain size, and that they dynamically float on the crystal face. We discovered an intermediate in crystal growth that we call the floating island (FI). Even in homoepitaxy, the structure of the crystal plane of bulk features and the molecular nucleation cluster is very different, and thus the floating nature of FI appears. Comparison with Monte Carlo simulations revealed that the diffusion occurs in the <110> direction (M. Sakakibara, H. Nada, T. Nakamuro, E. Nakamura, ACS Cent. Sci. 8, 1704-1710 (2022)).

Future issues include the possible influence of container size on crystallization behavior, which will be investigated. Although the present results can be interpreted as a good model for the behavior near the crystalline surface after desolvation, we will further investigate the influence of water through theoretical calculations in order

to control the crystallization behavior. Outreach activities are already underway and will be expanded to include education.