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Direct Observation of Crystallization Process in a Solution using Transmission Electron Microscopy

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Nucleation is a fundamental event that determines the size, number and morphology of produced crystals. Therefore, the nucleation process must be clarified to form products efficiently and to predict mineralization in various environments. The direct approach to understanding nucleation would be atomic-scale in-situ observation, for which a transmission electron microscope (TEM) would be a most powerful tool. However, the experimental conditions for TEM are limited, and there have been only a few reports on the in-situ observation of nucleation processes to date. In particular, since TEM needs a high vacuum, crystallization experiments in a solution are generally impossible. Recently, the processes of formation of nanoparticles and coalescence in a solution were finally observed using specially designed cells in a TEM [1-3]. However, live observation of the dynamics of the earliest stages of nucleation - those taking place before the formation of a stable crystal - had never been achieved before our recent work [4]. We overcame the difficulty by using an ionic liquid, which has negligible vapor pressure and is not charged up by the electron beam due to its relatively high electron conductivity, and by aiming to visualize the dynamics of nucleation under conditions very close to equilibrium, where the nucleation rate must be small but the conditions for TEM observation are more stable. We used two TEMs at an acceleration voltage of 200 kV (Hitachi H-8100, installed at Tohoku University, Japan) for the nucleation experiment and 300 kV (Hitachi H-9500, installed at Hitachi High-Technologies Corporation, Ibaraki, Japan) for the in-situ heating experiment.

An ionic solution could be observed stably under normal electron irradiation conditions as expected. Nucleation of sodium chlorate crystals was directly observed in the TEM at room temperature. Then, the sample was heated up in the TEM. The main results of the heating experiment were as follows:

1. Nanocrystals were not only dissolved but also newly formed even in the totally dissolving system, i.e., probably an undersaturated condition.
2. Both stable and metastable crystals nucleated independently of their respective solubility. However, metastable crystals were dissolved in a shorter residence time.
3. The total number of smaller particles decreased with the formation of new particles by the Ostwald ripening at or near equilibrium conditions.
4. High-density fluctuations may lead to nucleation even under equilibrium conditions.

We describe the ongoing results to elucidate the dynamics of nucleation at the nanoscale, as well as the growth, coalescence and dissolution of nanocrystals in a solution.

[1] Yuk, J. M., Park, J., Ercius, P., Kim, K., Hellebusch, D. J., Crommie, M. F., Lee, J. Y., Zettl, A. & Alivisatos, A. P. High-resolution EM of colloidal nanocrystal growth using graphene liquid cells. *Science* **336**, 61-64 (2012).

[2] Li, D., Nielsen, M. H., Lee, J. R. I., Frandsen, C. Banfield, J. F. & De Yoreo, J. J. Direction-specific interactions control crystal growth by oriented attachment. *Science* **336**, 1014-1018 (2012).

[3] Liao, H.-G., Cui, L., Whitelam, S. & Zheng, H. Real-time imaging of Pt_3Fe nanorod growth in solution. *Science* **336**, 1011-1014 (2012).

[4] Kimura, Y., Niinomi, H., Tsukamoto, K. & Garcia-Ruiz, J. M. In-situ live observation of nucleation and dissolution of sodium chlorate nanoparticles by Transmission Electron Microscopy. *J. Am. Chem. Soc.*, DOI: 10.1021/ja412111f. (2014).

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