

"Seeing is believing"

Surface Catalysis in Crystal Nucleation and Epitaxy

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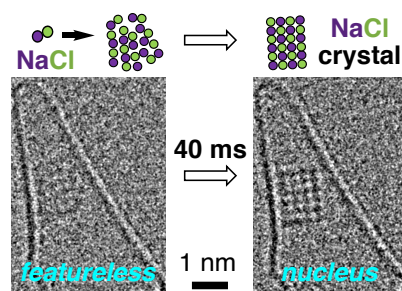
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An experimental technique called “single-molecule atomic-resolution time-resolved electron microscopy (SMART-TEM)” has been developed in the past 15 years and has realized our dream of watching chemical transformations of individual molecules with our eyes. In this lecture, I will report on the new paradigms of “cinematic chemistry” opened up by single-molecule atomic-resolution time-resolved electron microscopy (SMART-TEM). [1,2]

We get fine crystals upon stirring a concentrated salt solution, while large crystals upon letting it stand still. Here we show atomic resolution time-lapse images revealing in never-seen-before detail how the surface of the vessel catalyzes crystal nucleation and epitaxy. [3]

Many chemical reactions go through a cascade of events in which a series of metastable intermediates appear, and crystal nucleation is no exception. Although the consensus on the energetics of nucleation suggests the formation of metastable states preceding the crystal growth, little experimental evidence has been reported for their dynamics at an atomistic level. Operando imaging of two- and three-dimensional nucleation on a defect-free NaCl nanocrystal in carbon nanotubes using a millisecond angstrom-resolution transmission electron microscope revealed the formation of a metastable “floating island” (FI) that migrates thermally on the (100) facet of NaCl as the first intermediate of epitaxy. When a crystal tumbles in a container, a space repeatedly forms between the crystal and the container wall that hosts the FI. Tumbling repeatedly changes the surface energy and promotes the FI's conversion into a new epitaxial layer. We anticipate that this surface catalysis mechanism found on the nanoscale also operates in bulk heterogeneous nucleation where agitation and attrition accelerate crystallization. [4]



References

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- [2] Atomic-Resolution Transmission Electron Microscopic Movies for Study of Organic Molecules, Assemblies, and Reactions: The First 10 Years of Development, E. Nakamura, *Accts. Chem. Res.*, **50**, 1281–1292 (2017). DOI: 10.1021/acs.accounts.7b00076
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