Watching cubic ice grow with molecular resolution

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Cubic ice, a distinct form of ice with a cubic crystal structure differing from the common hexagonal ice, has been postulated to be a natural phenomenon based on indirect evidence such as Scheiner's halo. Its existence has been a subject of longstanding debate owing to the challenges associated with distinguishing it from stacking-disordered forms of ice I. Recently, Huang et al.[1] employed state-of-the-art *in situ* cryogenic transmission electron microscopy (TEM) techniques equipped with low-dose imaging to investigate the nucleation and crystallization of cubic ice at the molecular level, as shown in Figure 1. This study provides a comprehensive analysis of the intricate structure of cubic ice at molecular resolution.

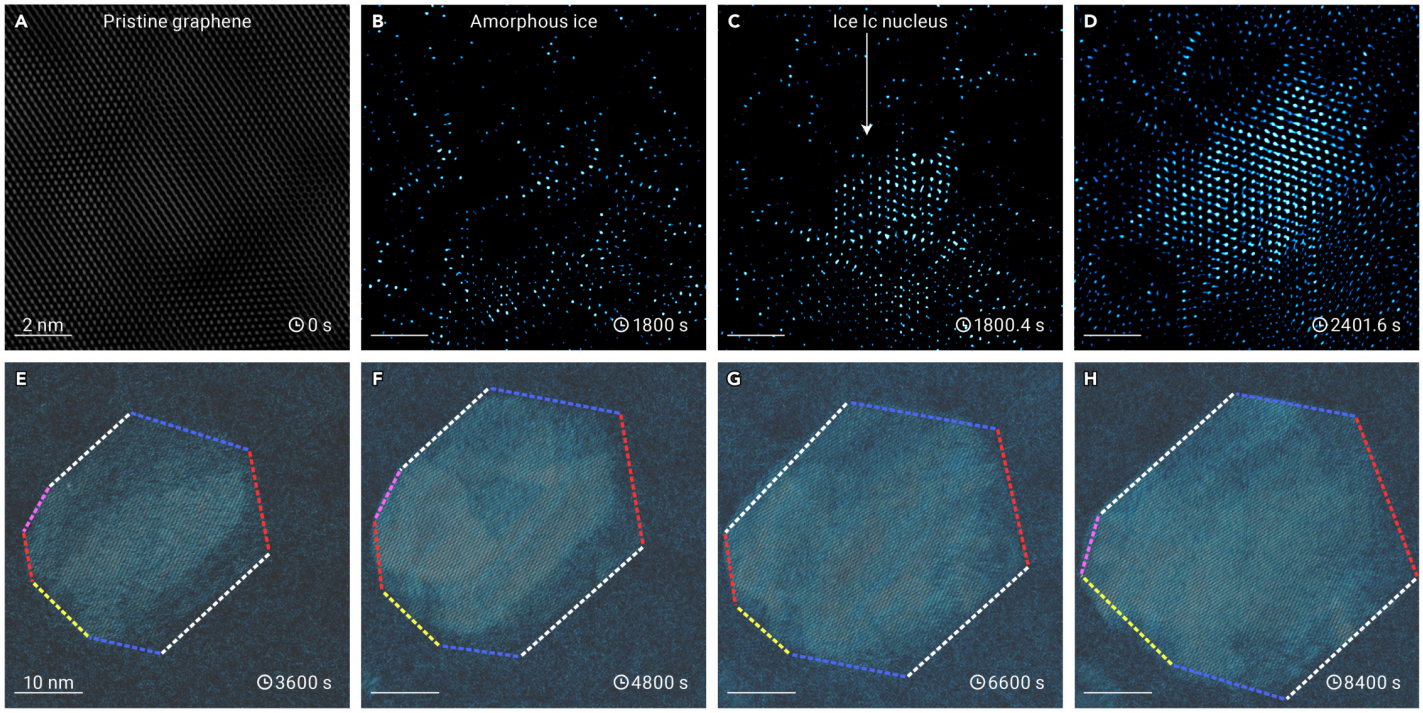

Figure 1. Microscopic growth process of cubic ice crystallite visualized by *in situ* transmission electron microscopy, adapted from Huang et al.[1] The corresponding-colored dashed lines in Figure E-H represent different crystal planes of the faceted crystallite. The legend for the colors is as follows: (001) plane is denoted by white, as $(1\bar{1}\bar{1})$ with red, $(1\bar{1}0)$ with yellow, $(1\bar{1}1)$ with blue, and $(\bar{1}13)$ with purple.

Recently, the application of *in situ* TEM has emerged as a powerful technique for studying atomic-scale reaction processes in materials under diverse external stimuli, such as strain, temperature, light, bias and cryogenic conditions. This technique is particularly valuable for investigating nucleation and crystallization processes occurring in complex interface systems, including gas–solid and liquid–solid interfaces. However, resolution constraints, hindering comprehensive observations during critical and intricate nucleation stages remarkably limit the existing studies on crystal growth. To address this limitation, TEM offers a feasible solution by providing ultrahigh spatial and temporal resolution. For instance, Wang et al.[2] employed graphene liquid-cell TEM to visualize the microscopic kinetics of NaCl nucleation. Their study revealed the formation of a transient metastable graphite-like phase preceding the transformation into a stable cubic rock-salt structure. This multistep nucleation process challenges the prevailing classical nucleation theories and underscores the remarkable advantages of *in situ* TEM techniques in characterizing crystal nucleation and growth processes in complex systems.

Among various types of crystals, the nucleation and growth of ice have attracted significant research interest due to its pivotal role in daily life and anomalous and volatile behavior. However, experimental research on ice encounters substantial challenges. The connectivity of oxygen tetrahedra in ice via hydrogen bonds renders it highly sensitive to external stimuli. Additionally, the presence of light elements in ice poses difficulties in imaging techniques that rely on adequate contrast. Quantum tunneling current–based scanning tunneling microscopy has made noteworthy contributions to the analysis of complex hydrogen bond configurations and ice imaging.[3] It has led to the discovery of unique two-dimensional ice structures on various surfaces.[4] Despite its ultrahigh spatial resolution, the limited spatial range of the tunneling current restricts these experimental detection methods to single or a few layers of ice. Previous research on the structure and phase of bulk ice has predominantly relied on diffraction methods.[5] However, these experiments often require large crystal samples and face challenges in identifying individual crystal particles for interpreting diffraction patterns in multiphase mixed-crystal status. Therefore, investigating ice with complex phase diagrams and elucidating microscopic kinetic pathways poses significant challenges.

The characterization of ice using TEM involves additional hurdles related to sample preparation. First, the stabilization of ice under low pressures within the TEM columns is a formidable task. Additionally, TEM necessitates extremely thin samples, causing difficulty in preparing ice samples below nanoscale. Despite the strong aspiration among the ice research community, using TEM to investigate the structure and growth of ice remains an elusive endeavor. Recently, Huang et al.[1] have overcome these challenges and

revealed intuitive imaging of ice using *in situ* TEM for the first time. In particular, they developed an *in situ* cryo-holder to cool a single-layer graphene substrate to ~102 K using liquid nitrogen. This ultralow temperature facilitated the condensation of the residual water vapor within the TEM column and promoted the nucleation and crystallization of ice on the graphene surface. The vacuum environment of the column with its low water vapor concentration remarkably influenced the nucleation and crystallization rate of ice. As a result, the researchers could precisely control the size of ice crystals at the nanoscale, which was essential for TEM observations.

The ultralow temperature of 102 K served two purposes: it facilitated the condensation of water vapor and reduced electron beam radiation damage. Additionally, the researchers employed a state-of-the-art low-dose imaging technique that directly detected individual electron signals. This approach allowed for the direct visualization of the water crystallization process at the molecular level in real space. More intriguingly, in stark contrast to diffraction-based probes, this *in situ* TEM method offers the prestigious advantage of real-space imaging, enabling the direct observation and tracking of single particles from the initial nucleation stages. Using this approach, the researchers unveiled the microscopic growth process of nucleation and crystallization of individual ice crystallites on a low-temperature substrate at 102 K. The results demonstrated the preferential nucleation of the metastable cubic ice phase on the cold substrate. In addition, high-resolution images captured by TEM revealed the presence of two distinct defect structures within cubic ice crystals: close-packed plane defects and stacking-disordered domains. Furthermore, using the electron beam as an energy perturbation source, the researchers systematically controlled and observed the structural dynamics of defect phase transitions in cubic ice. They discovered that close-packed plane defects in cubic ice exhibit a tendency for in-plane glide, similar to the defect dynamics observed in commonly encountered face-centered cubic metals. These findings offer detailed insights that cannot be obtained via traditional diffraction techniques, emphasizing the significance of real-space imaging for accurate structure characterization of ice.

The major findings of the investigation based on real-space TEM imaging reveal the spontaneous crystallization of water into single-crystal cubic ice coexisting and competing with hexagonal ice within a mixed environment. This finding prominently unveils the polymorphic and complex nature of water during phase transition. The rationalized *in situ* high-resolution real-space imaging completes the set of ice characterization techniques and ushers in a new era of microscopic research. With the continuous exploration of these structural characterization methods and their respective expertise, significant breakthroughs can be anticipated for understanding the most ubiquitous and elusive substance in nature, water, including its related complex phenomena of structural phase transitions. Furthermore, the newly developed *in situ* TEM technique for characterizing the water vapor–solid and liquid–solid interfaces can be readily extended to investigate other intricate systems such as the longstanding challenging field of liquid interface chemistry, which is fundamental to a wide variety of applications and will benefit from the ultrahigh spatial resolution offered by these novel techniques.

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DECLARATION OF INTERESTS

The author declares no competing interests.