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# In-Situ Atomic-Scale Observation of Intermediate Pathways of Melting and Crystallization of Supported Bi-Nanoparticles in the TEM

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Melting and crystallization are fundamental and practically important first-order phase transitions in condensed-matter physics, material science and climate change, yet a detailed understanding of their relevant kinetic pathways is still evolving [1,2]. To date, many theoretical models have been developed from homogeneous classical nucleation theory (CNT) model, but they rarely address the exact preferential nucleating sites and the potentially relevant role played by defects, surfaces, dimensionality and their combinations in phase transformations [3]. Recently, Samanta *et al*. conducted large-scale atomistic calculation of a phase transformation process of a metal from solid to liquid and predicted that the process takes place via multiple competing pathways involving the formation and migration of point defects or dislocations [4]. Although these calculations indeed provide a rare look at real phase transformations, much confusion still exists regarding the atomistic understanding of a dynamic process of a phase transformation due to the lack of direct experimental observations at the atomic scale as well as due to the experimental intricacies in tackling such a challenging topic.

Bismuth (Bi) is an ideal inorganic model material suitable for gaining insights into nucleation dynamics due to its low melting point (even down to room temperature due to size effect). Recently, Wang *et al.* used conventional transmission electron microscopy (TEM) to investigate a phase transformation induced by point defects in supported Bi nanoparticles under high electron dose irradiation at room temperature, and highlighted the fundamental role of defects in the phase transformation [5].

Here, we report in-situ atomic-scale observations of a real dynamic process of melting or crystallization in supported Bi nanoparticles under heating or cooling conditions using a heating holder within an aberration-corrected (scanning) transmission electron microscope. We provide direct evidence that pre-nucleation in either melting or crystallization takes places via multiple intermediate state pathways involving the formation and migration of domain boundaries (Figure 1), dislocations and the ordering of interface and surface at the atomic scale. The pre-melting of the nanoparticles initiates at a grain boundary and expands to interfaces and dislocations and finally undergoes a catastrophic transformation from a solid-liquid structure to a liquid droplet as a whole in a rather short time when their size exceeds a threshold value. When the size is smaller than the threshold value, the melting of nanocrystals takes place via two barrier-crossing pathways, i.e. pre-melting at grain boundary and a catastrophic solid-liquid transformation. Interestingly, pre-crystallization in a droplet occurs first at a solid-liquid interface and subsequently at the liquid surface, and eventually the droplet undergoes a fast complete transformation to a solid nanocrystal when undercooled (Figure 2).

Thus the ability to conduct *in-situ* atomic-scale observation of the evolutional pathways in phase transformations of supported nanoparticles represents a significant step forward in understanding microscopic mechanisms of phase transitions at the atomic scale. The findings in the present study demonstrate that the melting/crystallization processes cannot be viewed as a simple single barrier-crossing event but as a complex multiple intermediate state phenomenon, which enhances our general understanding of nucleation and growth, melting/crystallization phenomena, phase transformations and helps to clarify atomic origins of temperature dependent behaviours in other nanomaterials and thin films [6].

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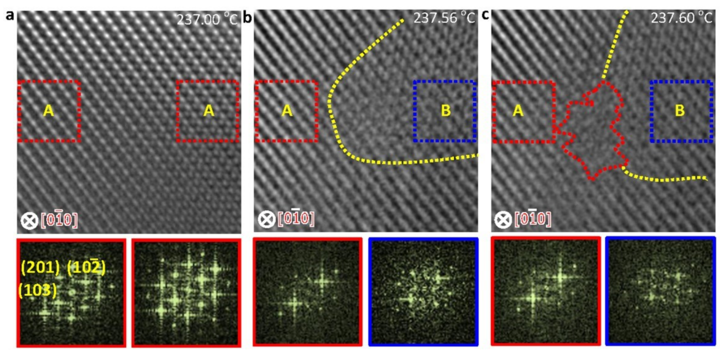


**Figure 1.** HRTEM images showing pre-melting at grain boundary.

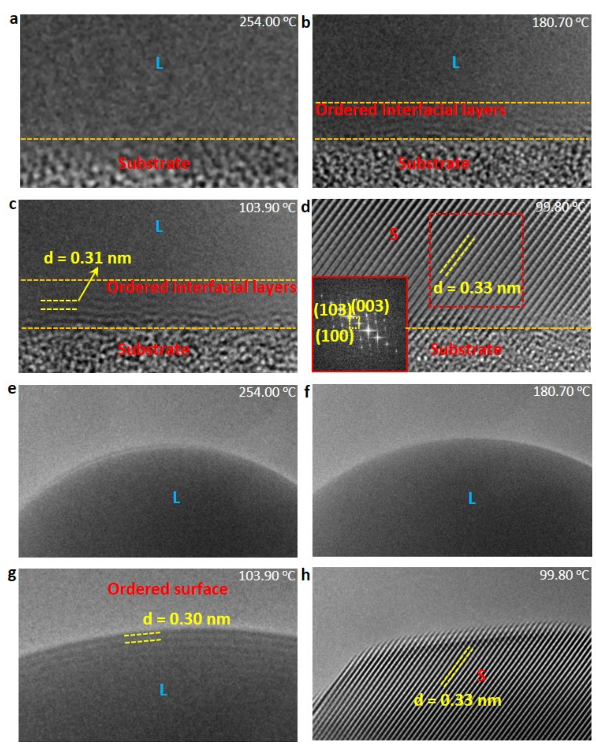


**Figure 2.** Sequential HRTEM images showing multiple intermediate states in the crystallization pathway of a supported droplet driven by undercooling.

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