Atom-by-Atom Nucleation of Metal Nanocrystals from a Diatomic Seed

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Nucleation lies at the heart of the crystallization process and greatly determines the structure and size distribution of crystals. Understanding the mechanism of nucleation is essential to control and utilize the growth of crystals. To date, two theories have been developed to elucidate the nucleation of crystals from solutions which are described as 'classical nucleation theory' and modern 'two-step nucleation mechanism' (TSNM). The classical nucleation theory assumes that the atoms or molecules form ordered subcritical cluster by sequentially stacking single atoms or molecules in the initial state and subsequently grow into nuclei and crystals. While the TSNM suggests that liquid-like metastable clusters containing a few atoms or molecules form initially and then transform into nuclei.

A massive effort has been made to authenticate these two mechanisms, experimentally and theoretically [1-3]. Various analysis techniques, such as X-ray diffraction, atomic force microscopy, optical microscopyare applied to study the nucleation of organic and inorganic substances [4]. Technologies based on transmission electron microscope (TEM) such as in-situ liquid cell TEM and cryo-TEM, provide the possibility to intuitively glimpse the nucleation and growth of crystals from solutions. Nevertheless, the solution or the surrounding ice is reported to inevitably scatter electrons thus they seriously impair on resolution and contrast . Furthermore, the unfixed and random nucleation seeds, the three-dimensional matrix as well as the very short nucleation time make it unlikely to capture and record the nucleation process just from the level of the single atom.

In this study we observed the growth of an Φ#177;-Fe nucleus from a fixed diatomic seed inside a nano-test-tube, a single walled carbon nanotube, with atomic resolution. The TEM experiments have been performed using a FEI Titan 80-300 kV at 80 kV employing the electron beam simultaneously as an imaging tool and stimulus of the nucleation. 'Molecule injector' technique has been utilized to realize this in-situ nucleation experiment in vacuum. The nucleation of Φ#177;-Fe is identified into four stages, including diatomic seed, atom delivery process, liquid-like cluster and ordered crystalline nucleus. The disordered structure of cluster in the second and third stages conclusively proves the existence of metastable cluster. Thus it will be shown that the nucleation process agrees with the TSNM theory. In addition, the nucleation processes of Re and Au crystals were also investigated atom-by-atom and also agree with the TSNM theory.

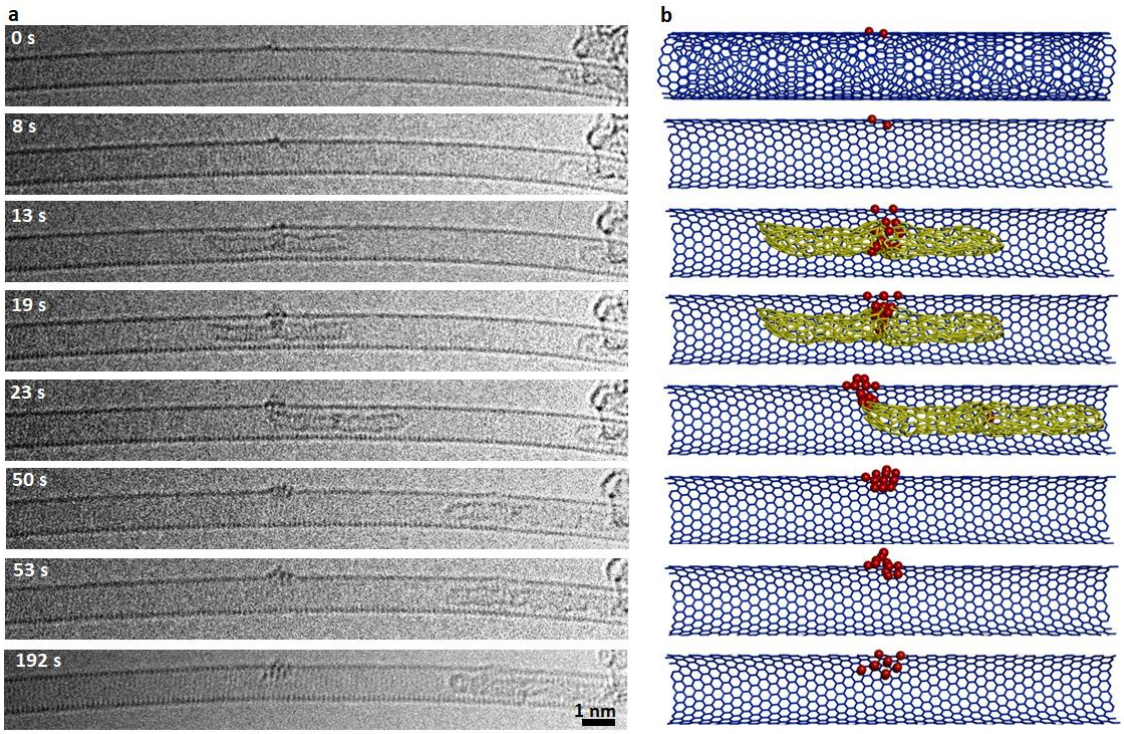

Figure 1: a. The time-series AC-HRTEM images showing the two-step nucleation of Φ#177;-Fe. b. The corresponding simulated structures for the time series in a.

References

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