Real-time, nanoscale observation of ice nucleation on TiO2 nanoparticles in water

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The understanding of heterogenous ice nucleation at water-solid interfaces is a subject of considerable interest owing to its extreme importance in geological, biological, and atmospheric sciences.[1-4] The existing experimental methods limit the temporal and spatial resolutions of ice crystals nucleation at nanointerfaces. Herein, we propose the in-situ graphene liquid cell (GLC) transmission electron microscopy (TEM) approach to investigate the real time heterogenous ice nucleation phenomenon at cryogenic temperature. The present study evaluates the heterogenous ice crystals nucleation at the nanointerface of water and anatase titanium dioxide (TiO_2) nanoparticles using cold stage TEM holder. Atomic resolution in-situ liquid TEM results showed the nucleation and growth of cubic phase ice crystals at the facets of anatase TiO_2 nanoparticle. Fast Fourier transform (FFT) analysis confirmed the predominant presence of characteristic (220) lattice planes of cubic phase ice crystals affiliated to 2.2 Å d-spacings. The observations of formation of cubic phase of ice crystals at TiO_2 nanointerface are in lined with the findings reported by Souda *et. al*[5], evaluated using reflection high energy electron diffraction (RHEED) characterization technique. The obtained atomic resolution in-situ liquid TEM results also provide insights on electron beam induced melting events of ice crystals. Cubic phase ice crystals were relatively stable at the TiO_2- water nanointerface in comparison with those in the bulk liquid, suggesting the possible influence of radical scavenging capability of TiO_2 nanoparticles mitigating the electron beam byproducts. Results also indicate that the absence of ice crystals around the gold nanoparticles likely attributed with their inherent hydrophobic surface properties. Moreover, the key dynamic events of cubic phase single ice crystal nucleation and growth and the ice crystal growth via multiple crystallites attachments along $(2\bar{2}0)$ active facets were evaluated in detail. Briefly, the present work demonstrates the capability of in-situ GLC TEM route to study the heterogenous ice nucleation and growth dynamic events at water-metal oxide nanointerface.

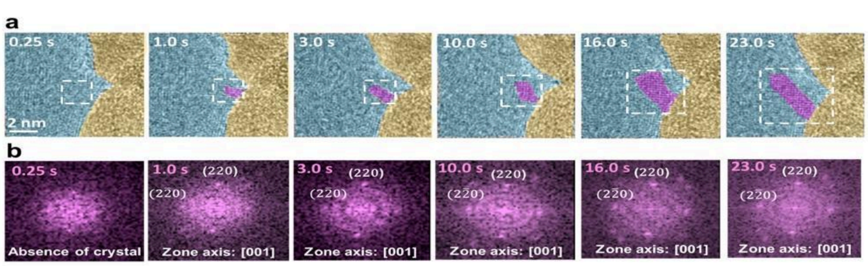

Figure 1. In-situ liquid TEM real time heterogenous ice nucleation at water-TiO_2 nanoparticle interface at cryogenic temperature. (a) TEM micrographs indicating temporal study of single ice crystal nucleation and growth events. (TiO_2 nanoparticles, ice crystal, and water are highlighted by gold color, purple color, and cyan color, respectively.) (b) Fast Fourier transform (FFT) analysis confirming the cubic phase of ice crystal.

References:

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