Supporting Information

Real-time TEM observations of ice formation in graphene liquid cell

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Experimental methods

Fabrication of graphene-coated TEM grids

Graphene-coated TEM grids were prepared using the protocol of Hauwiller *et al*.[1] Briefly, monolayer commercial CVD grown graphene-coated copper foil (Grolltex, monolayer graphene on copper foil 6" x 6") was used as graphene source. 1cm x 1cm pieces of graphene-coated copper foil were cut using a surgical-grade scalpel. Wrinkles of the graphene-coated copper foils were removed with glass slides and nonwoven wipes (Texwipe, TX629). Quantifoil micromachined holey carbon coated 200 mesh gold grids (SPI supplies, 4220G-XA) were placed on the flattened graphene-coated copper foil, assuring the carbon side of the grids remained in contact with the graphene layer. Successively, 15 μL of iso-propyl alcohol was dropped on the graphene-coated copper foil to improve van der Waals interactions between graphene and the holey carbon layer of the TEM grids. After 2 hours of drying in air, the graphene-coated copper foil adhered to the TEM grid, which was then placed in a copper etchant containing sodium persulfate solution (Millipore Sigma, 216232) for 12 hours. After the etching process, the floating gold TEM grids were transferred into HPLC grade water (Millipore Sigma, 7732-18-5) using glass slides. The rinsing process was repeated 3 times and the graphene-coated TEM grids were air dried.

STEM-EELS analysis of water encapsulated in GLC nanovessels

An aberration-corrected JEOL ARM200CF transmission electron microscope (200kV) equipped with cold field emission gun was used for performing *in-situ* GLC STEM-EELS analysis at cryogenic temperatures. To prepare GLC grids, a 0.3 μL of solution containing ultrapure water with dispersed anatase TiO_2 nanoparticles (Millipore Sigma, Product No. 637254) was encapsulated in between two graphene-coated TEM grids. The GLC grids were then loaded on a cold-stage TEM holder at room temperature. The TEM emission current was set at 10 μA. An electron beam convergence angle of 22 mrad at 19 pA probe current was used for acquiring STEM- STEM-low angle annular dark field (LAADF) images with 512 x 512 pixel scanning resolution. STEM-EELS analysis was performed at 17.8 mrad convergence semi-angle and at 53.4 mrad collection semi-angle. Energy dispersion of 0.3 eV/Ch with 5 mm entrance aperture was used for STEM-EELS acquisition. The EELS spectrum was acquired at 0.05 s pixel dwell time with 4.2 nm x 4.2 nm pixel size.

HR-TEM analysis of ice crystals

In-situ HR-TEM imaging of ice crystal nucleation and growth events at cryogenic temperature was performed using the aberration-corrected JEOL ARM200CF microscope operated in TEM mode. The electron beam emission current was set at 10 μA. An Orius CCD camera was used for the acquisition of HR-TEM real-time videos and micrographs. *In-situ* liquid TEM analysis in the GLC was performed by limiting the electron dose rate to 0.022 $e^-/Å^2/s$.

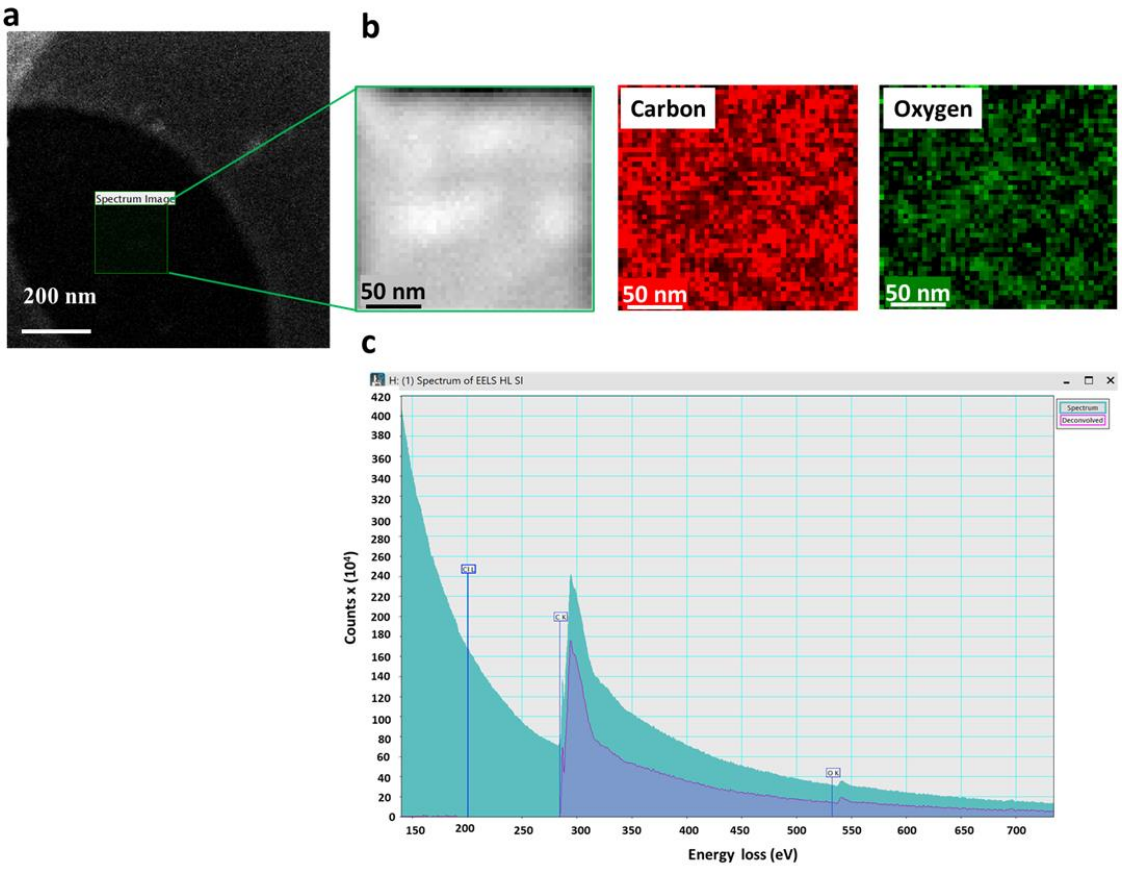

Figure S1. STEM-EELS analysis of water encased in a GLC nanovessel, which confirmed the absence of any possible contamination of chloride salts. (a) The STEM-LAADF image marks the region of interest in a GLC nanoreactor, where the signal was acquired. (b) Corresponding ADF micrograph along with STEM-EELS elemental mapping of carbon and oxygen. (c) Acquired high energy loss EELS spectrum revealing carbon and oxygen K-edges and the absence of chlorine L_3-edge.

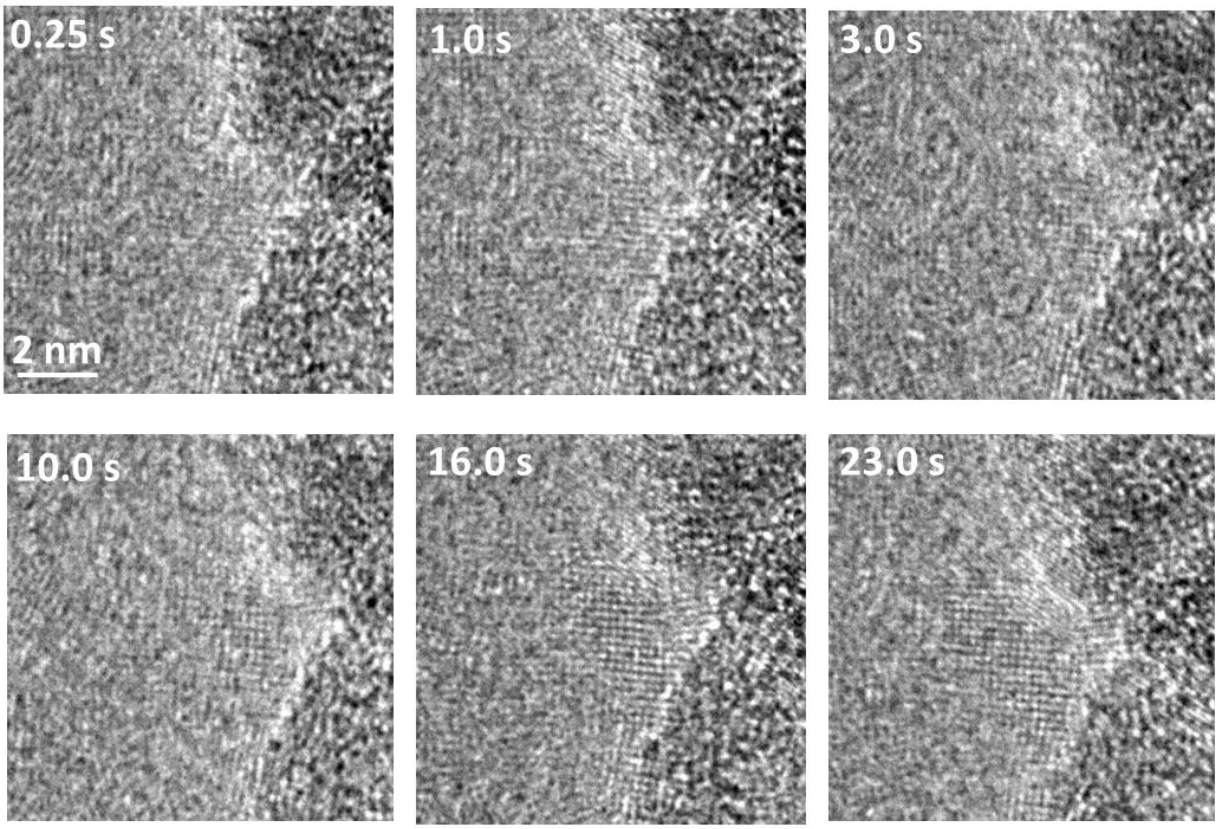

Figure S2. Time-sequenced TEM micrographs representing real-time ice crystal heterogeneous nucleation and growth events at a TiO_2-water nanointerface in GLC at cryogenic temperature. The respective false-colored TEM micrographs and crystal phase information can be found in the manuscript, **Figure 2**.

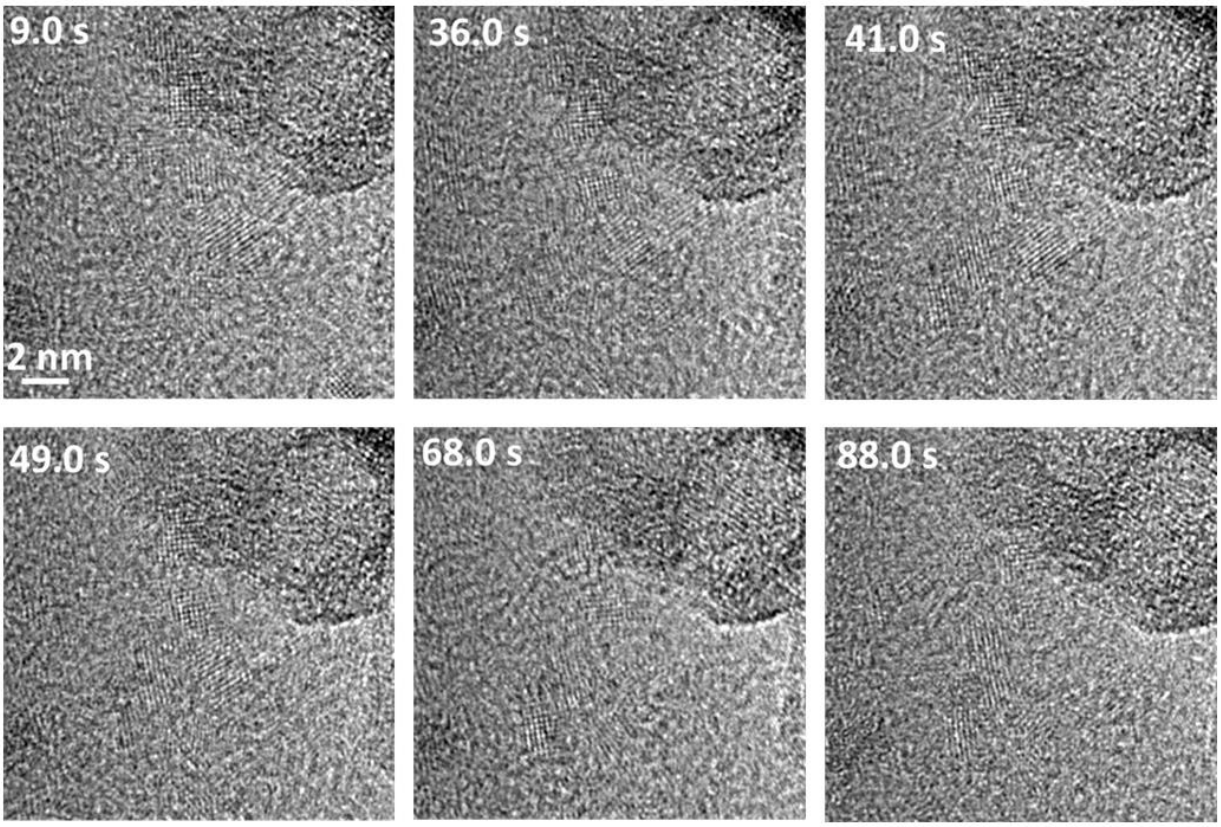

Figure S3. Time-sequenced TEM micrographs representing multiple ice nuclei growing via oriented attachment. The respective false-colored TEM micrographs and crystal phase information can be found in the manuscript, **Figure 3**.

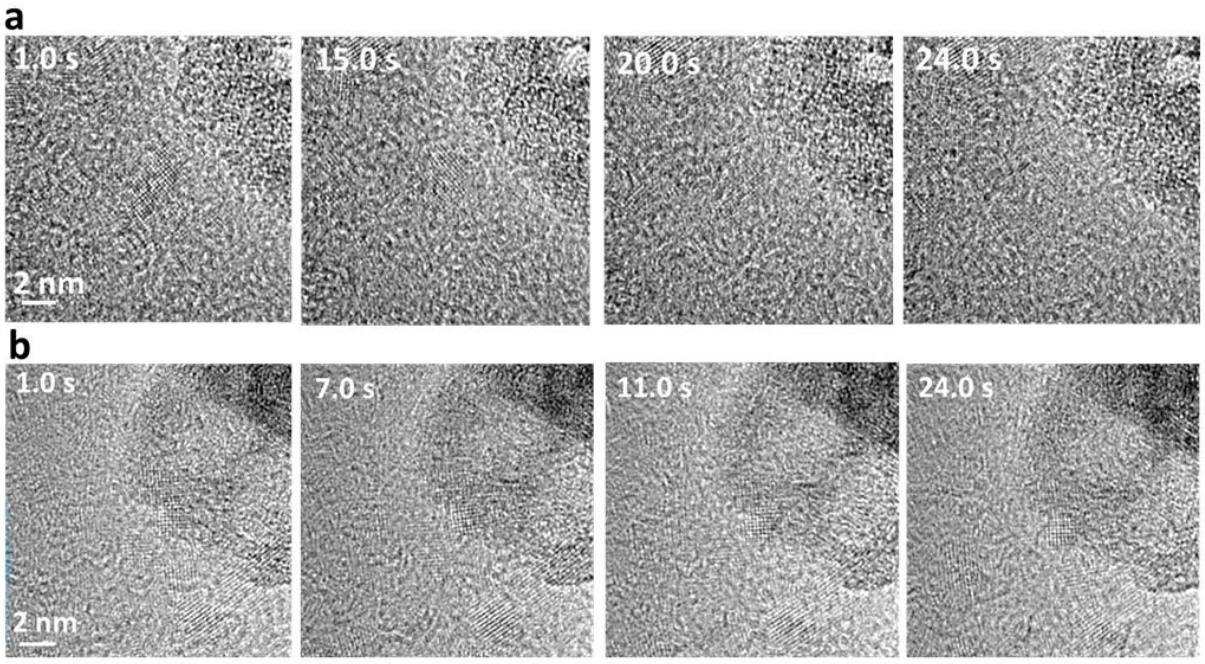

Figure S4. Ice crystal dissolution sequence at the TiO_2-water nanointerface and away from it in GLC, observed after 45 minutes of electron beam exposure at cryogenic temperature. (a) Time-sequenced TEM micrographs of ice-crystal dissolution away from the TiO_2 nanoparticle interface, confirming the gradual reduction in ice crystal size. (b) Time-sequenced TEM micrographs of an ice crystal formed at the TiO_2 nanoparticle surface, which confirmed the ice crystal's stability. The respective false-colored TEM micrographs and crystal phase information can be found in the manuscript, **Figure 4**.

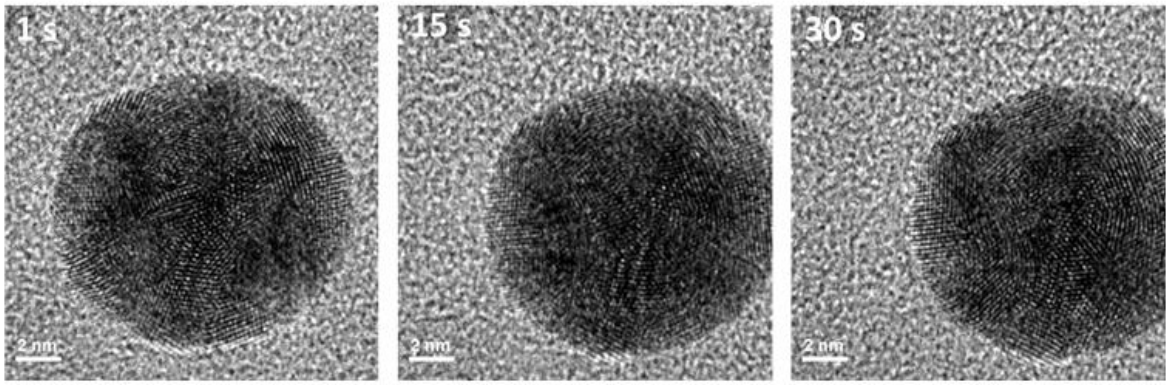

Figure S5. Time-sequenced TEM micrographs reveal no ice crystals on or near a gold nanoparticle in water in GLC at cryogenic temperature.

Table S1. List of supplementary videos

Video #	Video speed	Caption
Video S1	1X	TiO_2 nanoparticle/water nanointerface in GLC at 25°C TEM holder temperature
Video S2	1X	Multiple homogeneously grown ice crystals in the vicinity of TiO_2 nanoparticles in GLC at -176°C TEM holder temperature
Video S3	1X	Real-time heterogeneous nucleation and ice crystal growth at a TiO_2-water nanointerface in GLC at -176°C TEM holder temperature
Video S4	1X	Ice crystal growth by oriented attachment of ice nuclei in GLC at -176°C TEM holder temperature
Video S5	1X	Electron beam-induced dissolution of ice crystals away from the TiO_2 nanoparticle surface in GLC at -176°C TEM holder temperature
Video S6	1X	Stable ice crystal at the TiO_2-water nanointerface after prolonged exposure to the electron beam in GLC at -176°C TEM holder temperature
Video S7	1X	Sequence showing no ice crystals at gold (Au) nanoparticle-water nanointerface in GLC at -176°C TEM holder temperature

Reference

1. Hauwiller, M. R.; Ondry, J. C.; Alivisatos, A. P., Using graphene liquid cell transmission electron microscopy to study in situ nanocrystal etching. *Journal of Visualized Experiments* **2018,** (135), 57665.