Electronic Supplementary Material (ESI) for Chemical Science.

Supplementary Information for

Investigating States of Gas in Water Encapsulated between Graphene Layers

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Figures S1 to S11

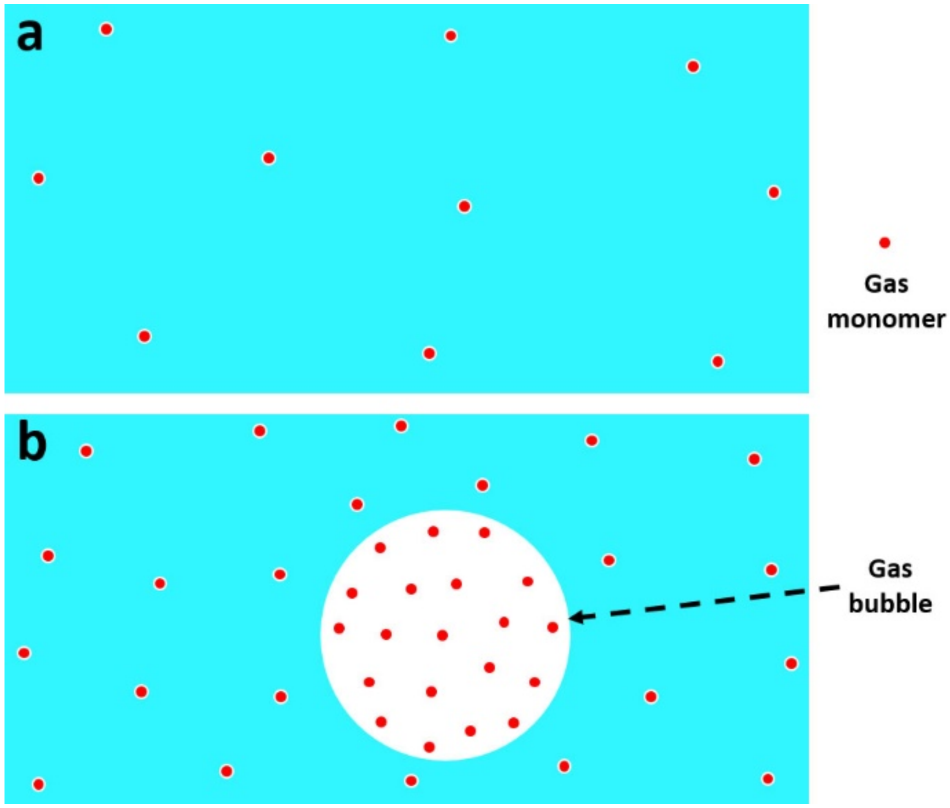

Fig. S1 Schematic of the paradigm of gas dissolved in water. Conventionally, there are two states for gas in water: (a) well-dispersed gas monomers in water and (b) gas bubbles with gas in the vapor phase.

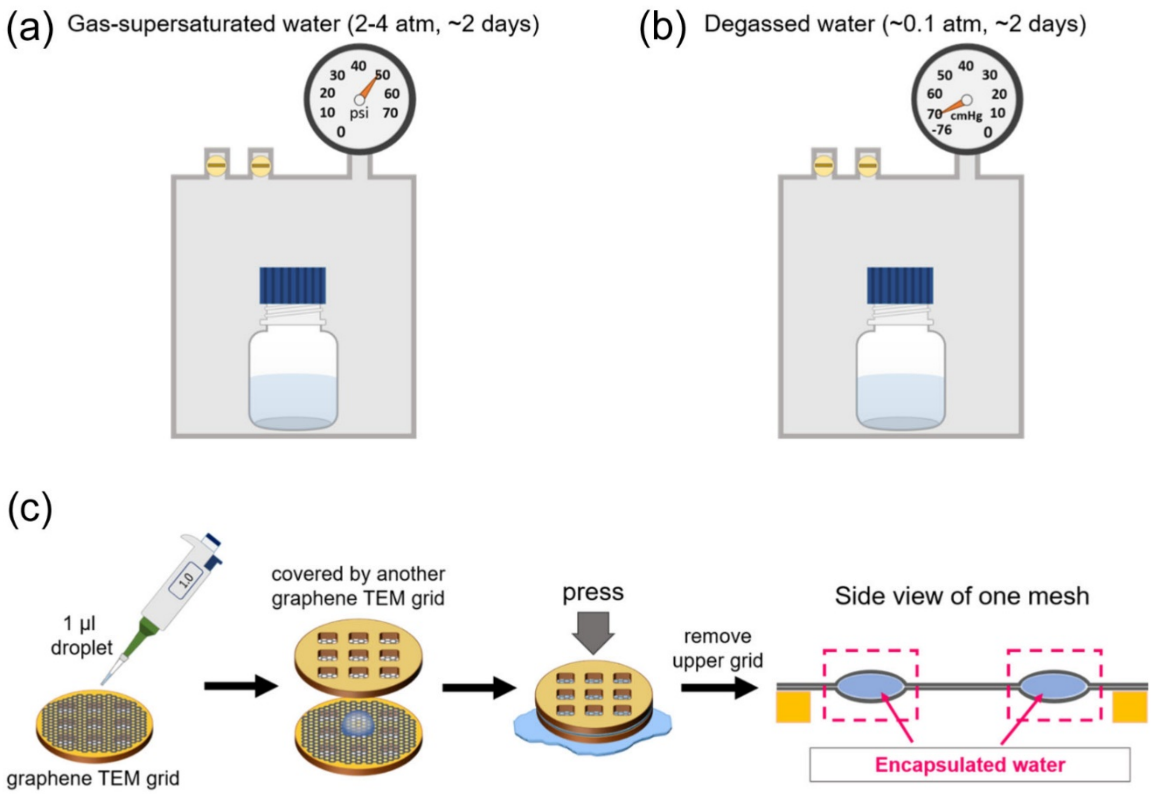

Fig. S2 Schematic of the method for preparing (a) gas-supersaturated water and (b) degassed water. A cap is on the bottle but does not seal it, enabling the gas in the tank to equilibrate with gas inside the bottle. (c) Schematic of the method for preparing GLC samples for TEM observations.

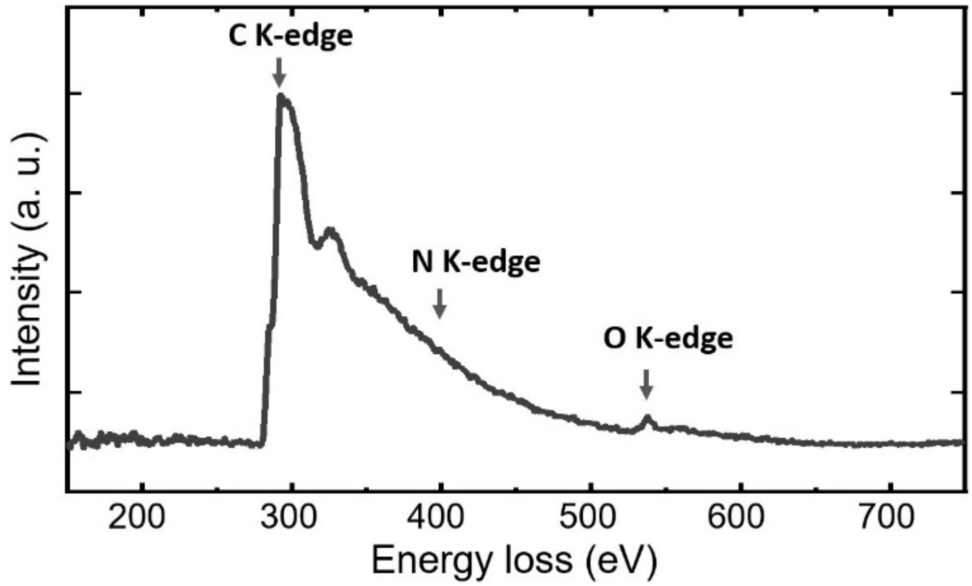

Fig. S3 Representative EELS spectra acquired from a pocket of degassed water. Spectra from 284 to 310 eV (carbon K-edge) are associated with the graphene layers. The peak at ~540 eV (oxygen K-edge) arises from water. No spectra for a nitrogen K-edge are evident.

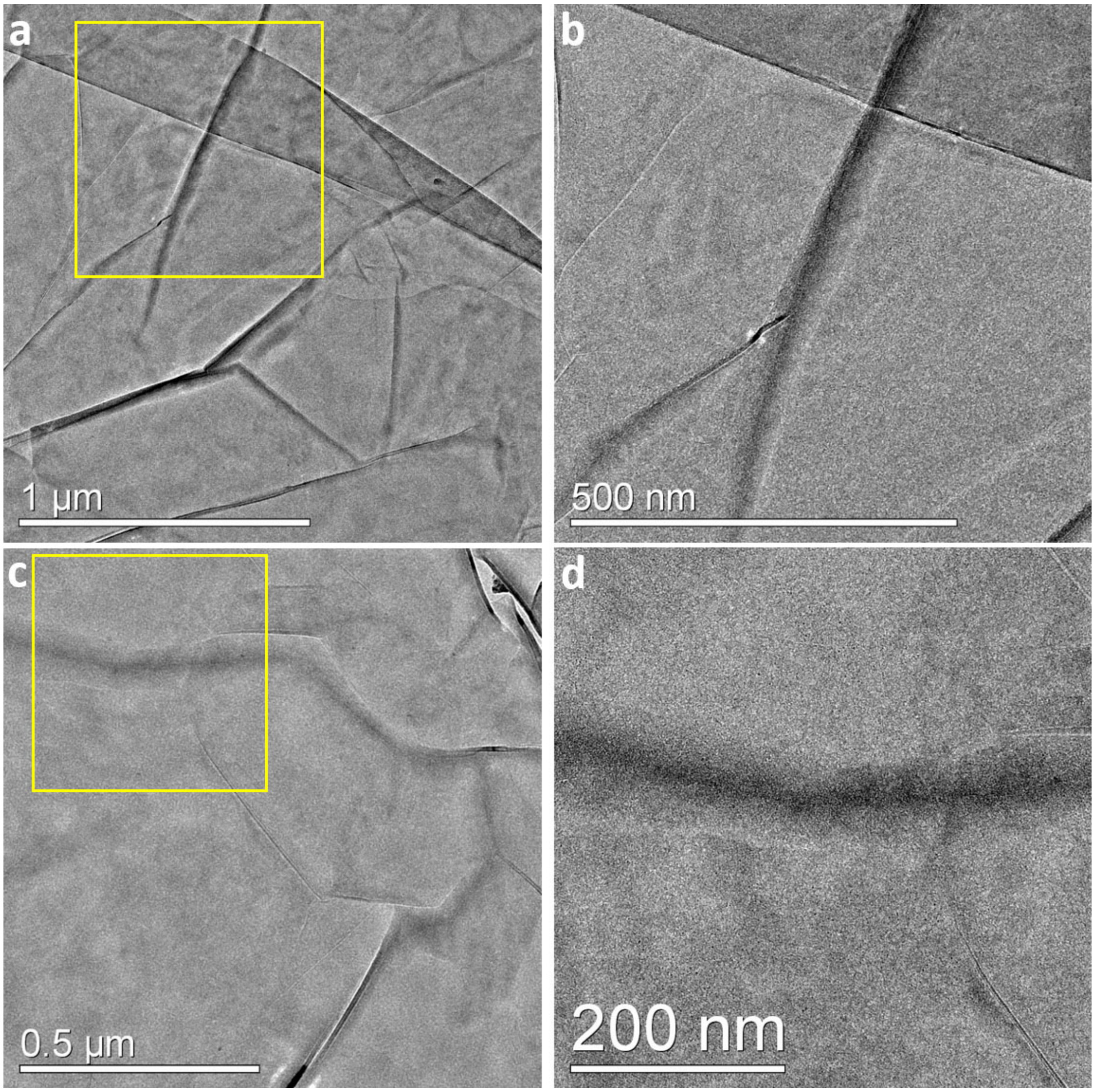

Fig. S4 Representative TEM of GLCs containing deionized water. (a) Bright-field image showing a few encapsulated water regions. (b) Higher-resolution image of the region outlined in yellow in (a). (c) Bright-field image of another sample. (d) Higher-resolution image of the region outlined in yellow in (c).

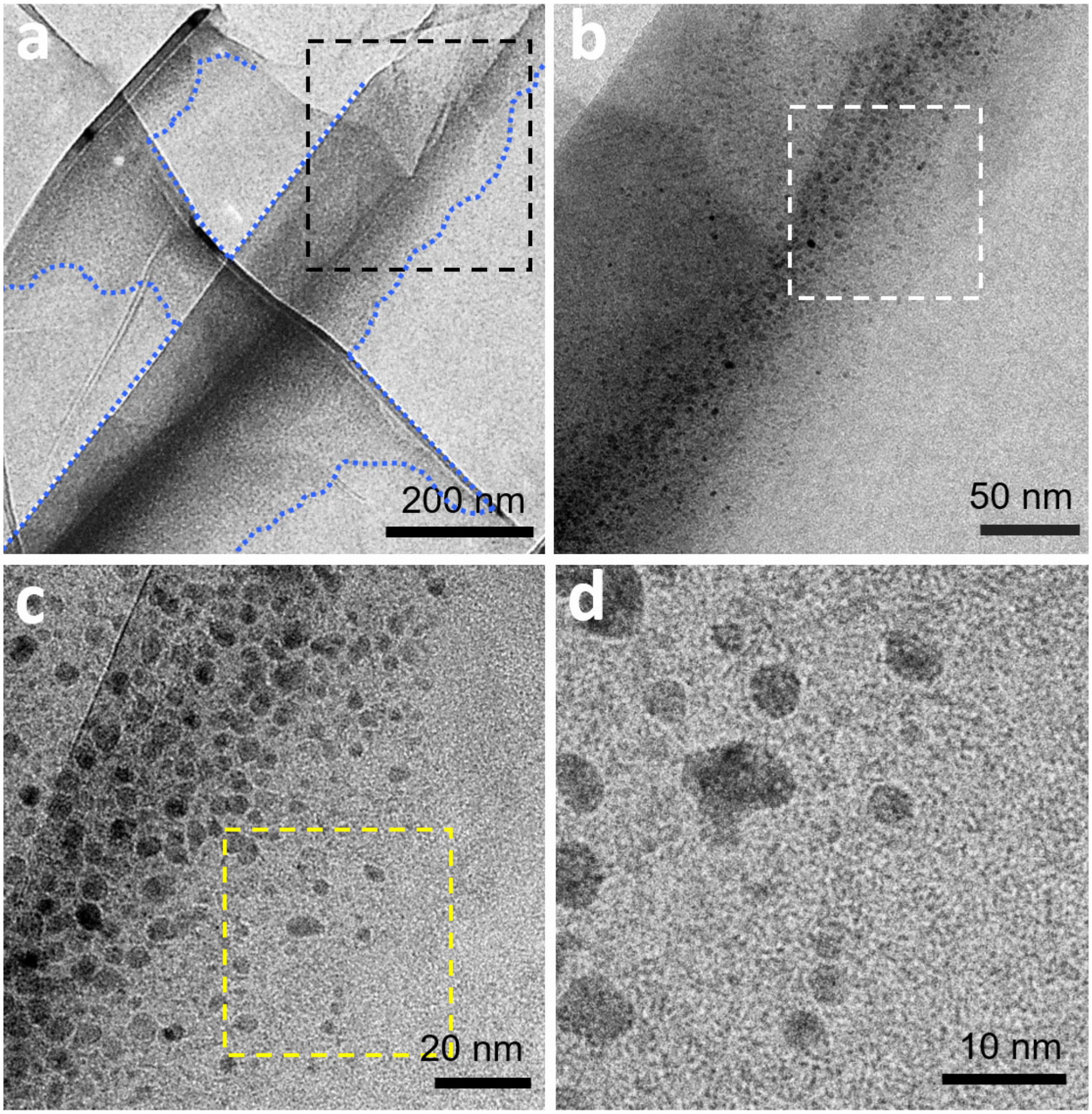

Fig. S5 TEM of GLCs containing N_2-supersaturated water. (a) Bright-field image of a few encapsulated water regions. The blue dashed lines outline the water pockets. (b) Higher-resolution image of the region outlined in black in (a). Small dark particles of several nanometers are evident. (c) Higher-resolution image of the region outlined in white in (b). (d) Higher-resolution image of the region outlined in yellow in (c).

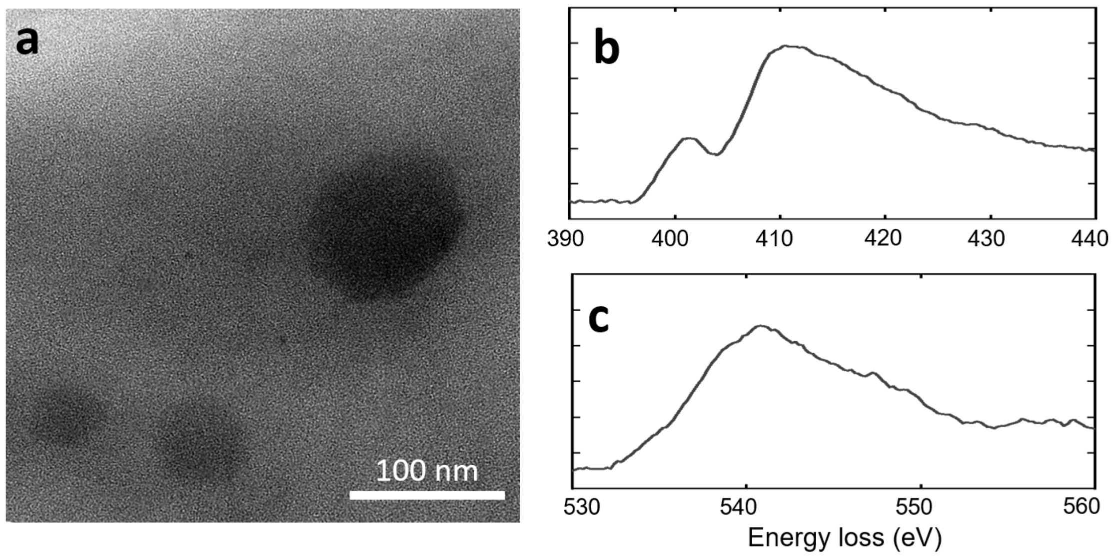

Fig. S6 EELS of a water pocket containing nitrogen nanoparticles in N_2-supersaturated water. (a) Bright-field image. (b) Background-subtracted EELS spectra showing a nitrogen K-edge on the largest particle in (a). (c) Background-subtracted EELS spectra showing an oxygen K-edge.

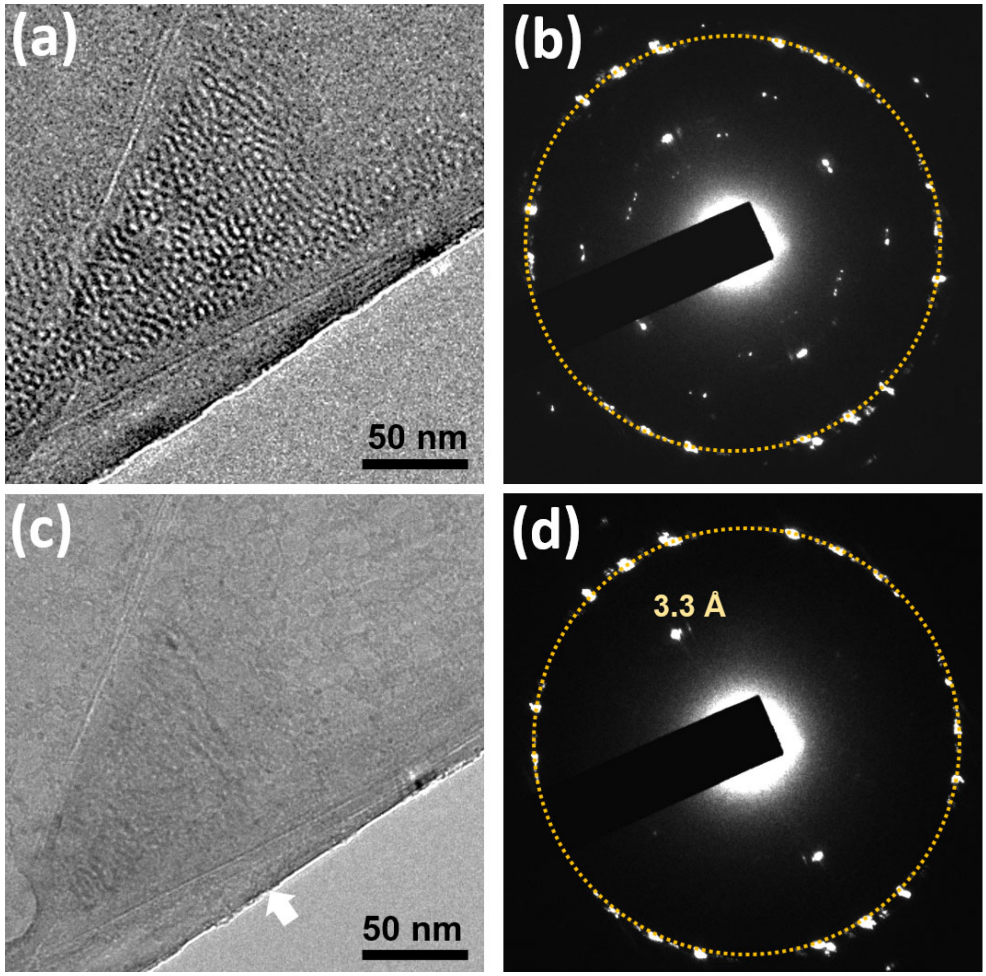

Fig. S7 Draining of liquid inside a pocket in CO_2-supersaturated water after high-magnification imaging. (a) Bright-field image of a pocket containing clathrate structures before high-magnification imaging. (b) SAED pattern of the region in (a). Many diffraction spots associated with the clathrate structures were seen. The orange circle indicates the first-order diffraction spots of the multi-layer graphene. (c) Bright-field image of the water pocket in (a) after imaging at high-magnification (×250,000) for ~10 min. All cell structures have disappeared. The region appears brighter because nearly all of the material inside the pocket has flowed out of the region. (d) SAED pattern of the region in (c). All diffraction spots related to the clathrate structures have disappeared. The remaining spots with d-spacing of 3.3 Å are associated with the graphene wrinkle indicated with an arrow in (c).

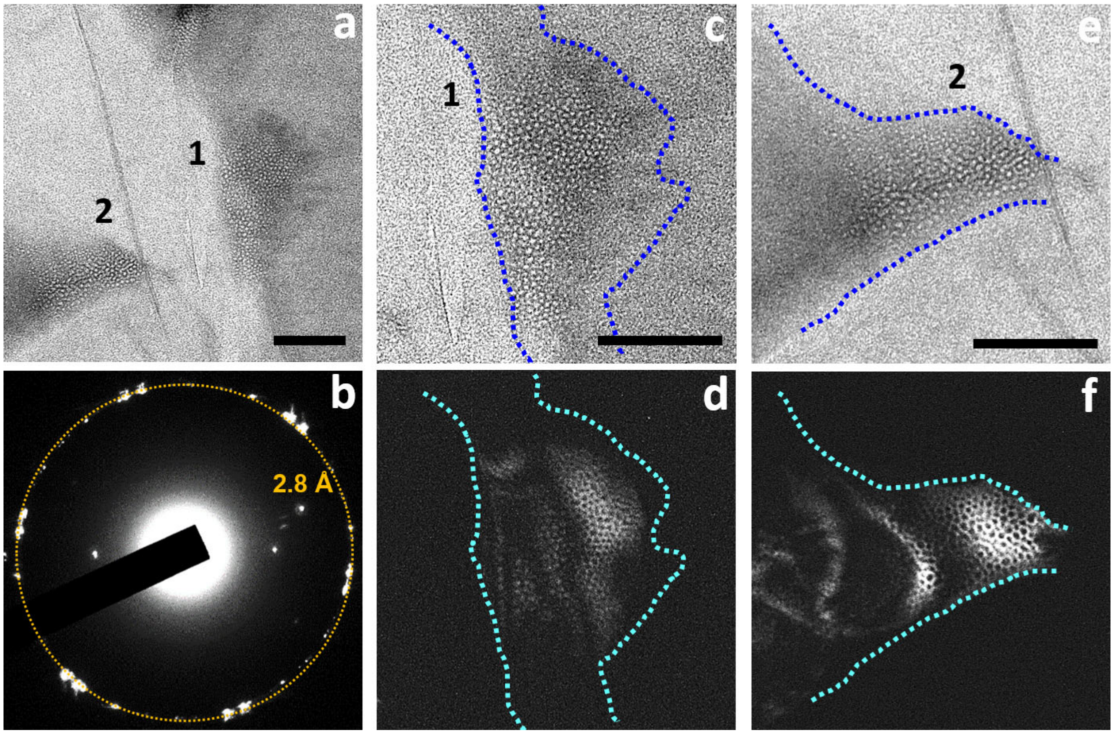

Fig. S8 Bright-field and dark-field imaging of clathrate structures in O_2-supersaturated water encapsulated in a GLC. (a) Bright-field image. The sample was tilted by +6.7° around the X-axis. (b) SAED pattern of the region shown in (a). The orange circle indicates the first-order diffraction spots of the multi-layer graphene. (c) Enlarged view of Region 1 in (a). (d) Dark-field image of Region 1 acquired from the diffracted beam indicated with d-spacing of 2.8 Å in (b). The blue dashed lines outline Region 1. (e) Enlarged view of Region 2 in (a). (f) Dark-field image of Region 2 acquired with the image shown in (d). The blue dashed lines outline Region 2. Scale bars: 100 nm.

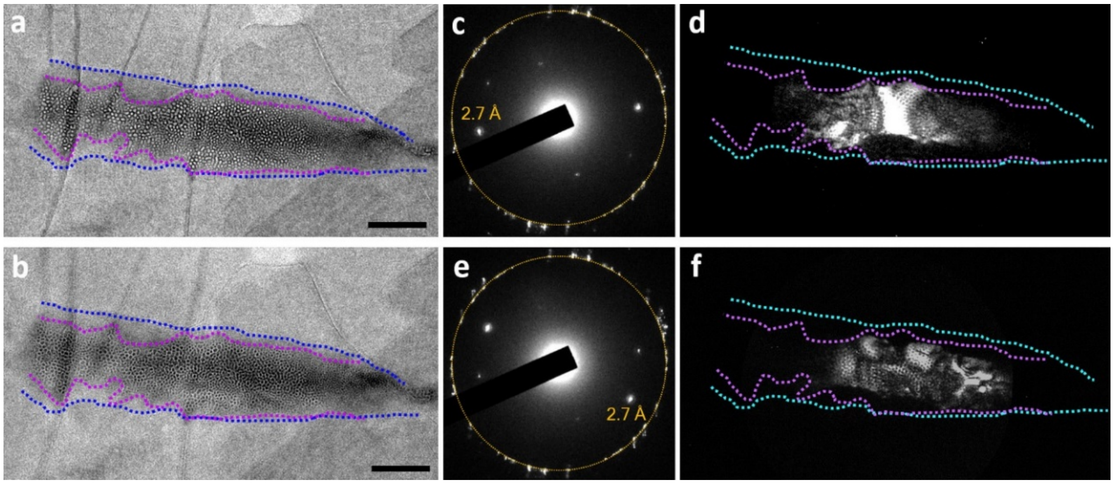

Fig. S9 Bright-field and dark-field imaging of a clathrate structure in Ar-supersaturated water encapsulated in a GLC. (a) Underfocus and (b) overfocus images were acquired before the sample was tilted. The purple dashed lines outline the region of the clathrate structure; the blue lines outline the entire water pocket. This region is the same as that shown in Fig. 4 i-k. (c) SAED pattern of the region shown in (a) after the sample was tilted to +7.1° around the X-axis. The orange circle indicates the first-order diffraction spots of the multi-layer graphene. (d) Dark-field image acquired from the diffracted beam indicated with d-spacing of 2.7 Å in (c). Dashed lines are as in (a) and (b). (e) SAED pattern of the region shown in (a) after the sample was tilted to +12.2° around the X-axis. (f) Dark-field image acquired from the diffracted beam indicated with d-spacing of 2.7 Å in (e). The region outside the clathrate structure (outside the purple dashed lines but inside the blue dashed lines) is liquid water and exhibits dark contrast in the dark-field images. Scale bars: 100 nm.

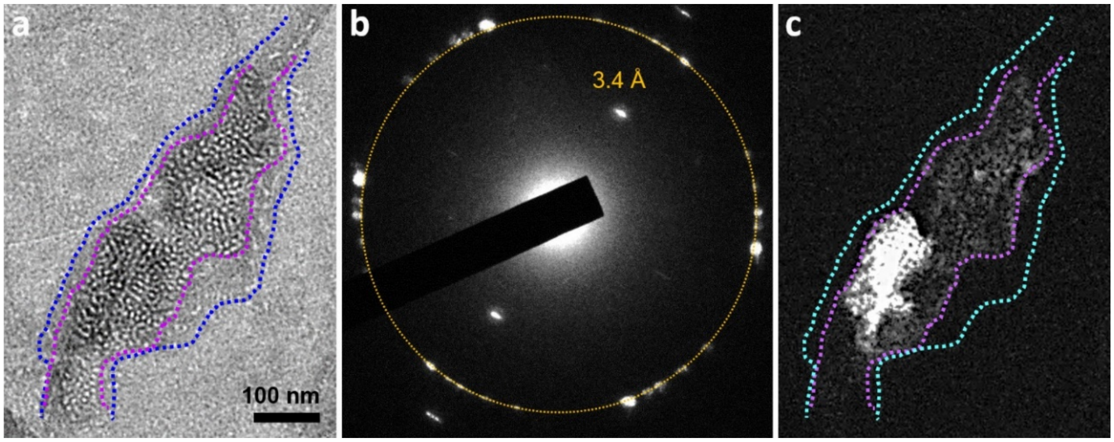

Fig. S10 Bright-field and dark-field images of a clathrate structure in Ar-supersaturated water encapsulated in a GLC. (a) Bright-field image. The purple dashed lines outline the region of the clathrate structure; the blue lines outline the entire region of the water pocket. (b) SAED pattern of the region shown in (a). The orange circle indicates the first-order diffraction spots of the multi-layer graphene. (c) Dark-field image acquired from the diffracted beam indicated with d-spacing of 3.4 Å in (b). Dashed lines are as in (a). The region outside the clathrate structure (outside the purple dashed lines but inside the blue dashed lines) is liquid water and exhibits dark contrast in the dark-field image.

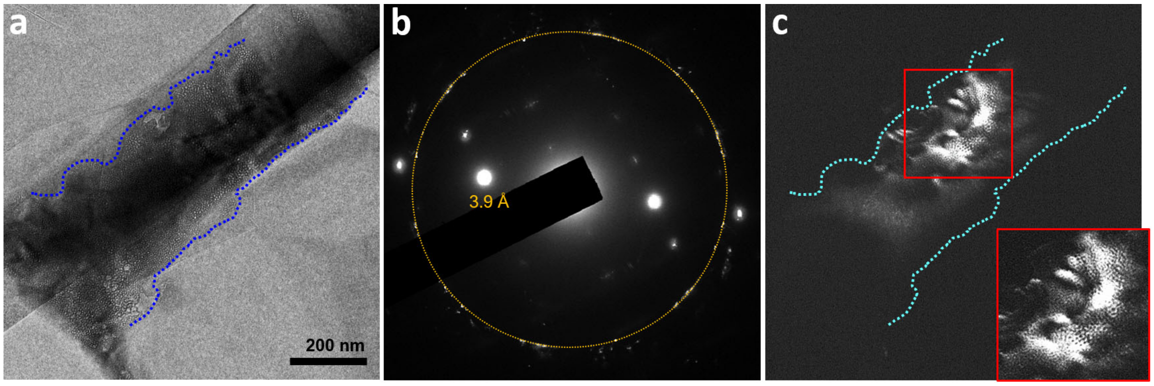

Fig. S11 Bright-field and dark-field study of a clathrate structure in CO_2-supersaturated water encapsulated in a GLC. (a) Bright-field image. The blue dashed lines outline the region of the clathrate structure. (b) SAED pattern of the region shown in (a). The orange circle indicates the first-order diffraction spots of the multi-layer graphene. (c) Dark-field image acquired from the diffracted beam indicated with d-spacing of 3.9 Å in (b). Inset: enlarged view of the region outlined in red.