Supporting Information:

Condensation Mode Determines the Freezing of Condensed Water on Solid Surfaces

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Preparation of ZnO nanorod array films

The ZnO nanorod array films were prepared by the method of the low-temperature wet chemical bath deposition. Typically, glass cover slips with the thickness of ca. 130 mm was cleaned ultrasonically for 10 min in acetone and ethanol, followed by another 10 min in ultra-pure water. A thin film of zinc acetate was then coated on the substrate by immersing the glass cover slips into the solution of 10 mM zinc acetate dehydrate (98 %, Beijing Co. Ltd.) in ethanol and drying at 140 °C. This process was repeated 10 times. Then, the cover glass with a thin film of zinc acetate was annealed at 350 °C in air for 2 h to obtain the ZnO seeds layer. For the growth of ZnO nanorods on the substrate with seeds, the equimolar aqueous solution of $Zn(NO_3)_2$ (98 %, Beijing Co. Ltd., 0.1 M) and hexamethylenetetramine (HMTA, 0.1 M) were quickly mixed at room temperature, and then glass cover slips with the ZnO seeds were immersed vertically into the mixture. Each reaction vessel was sealed and kept at 90 °C for 2 h. After that, the substrates were taken out and rinsed in ultra-pure water by ultrasonication, and dried in an oven at 80 °C.

The as-prepared ZnO nanorod array film was stored in the dark for two weeks to achieve sample 2, and sample 1 was one exposed to UV light (40 mW/cm^2) for 20min. Furthermore, the samples with ZnO nanorod arrays were placed in a desiccator, which contained the heptadecafluoro-1, 1, 2, 2-tetradecyltrimethoxy- silane (FAS-17) vapor, for different duration (3 min for sample 3; 1 h for sample 4) at the room temperature. Then, the samples were placed in an oven at 60 °C for 1 h to get sample 3 and 4.

Characterization of samples

The morphologies of samples with ZnO nanorod arrays were characterized by a field emission scanning electron microscope (FESEM, Hitachi S-4800). The water CA on the samples was measured by a CA System (DSA100, Kruss Co. Germ.) at ambient temperature and the volume of droplets was 2.0 μl. An average CA value was obtained by measuring the same sample at least three times. And the CA hysteresis was measured by the adding first and then retrieving method.

X-ray photoelectron spectroscopy (XPS) data on samples were collected on an

ESCALab220i-XL electro spectrometer from VG Scientific using 300 W Al Kα X-ray source (1486.6 eV photons) with a takeoff angle of 90 °. The base pressure was about 3×10^{-9} mbar.

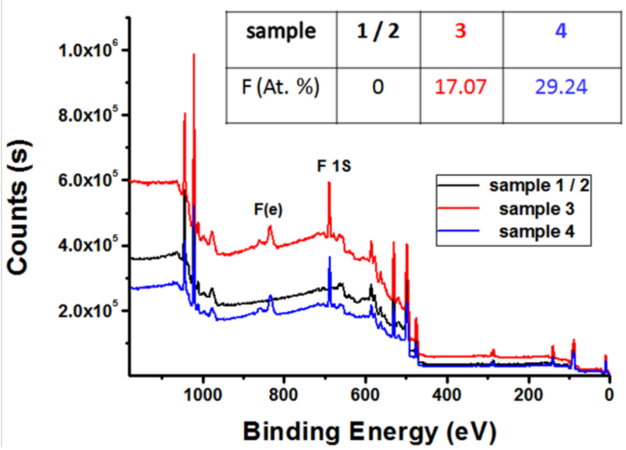

Fig. S1 XPS spectra of different Specimens. Inset: atomic percent of F in different samples.

Measurement of the freezing of CWMDs

The instrument (Fig. 2) used to measure freezing temperatures of CWMDs consists of a commercial optical microscope (Olympus BX51), a high speed camera (Phantom V7.3), and a Linkam Heating and Cooling stage (Linkam THMS 600), on which the closed sample cell was loaded. In this work, the temperature of sample surfaces was controlled by the commercial Linkam cooling/heating system. The temperature of the sample surfaces was calibrated.

Firstly, the sample was placed on a circular cover glass. A 0.7 μl ultra-pure water droplet was then placed at the edge of the sample surface. A second cover glass with a spacer (O-rings, 2.65 mm × 1.4 cm) was placed over the first cover glass to produce a sample cell after purging with the argon flux. The spacer ensured that the droplet between the cover slips was not in contact with the top cover slip, and the sample cell was sealed with vacuum the silicon grease to try to ensure the water vapor amount in the cell during experiment progress. The sealed sample cell was transferred to the silver stage. The sample cell was then heated to +50 °C and remained at this temperature for 5 min to completely evaporate the macrodroplet. Then the sample surface temperature was lowered at 2 °C/min, and CWMDs were formed on sample surfaces. When the surface temperature was further lowered, freezing of CWMDs occurred. And the temperature of sample surfaces was calibrated according to the standard procedure of the commercial Linkam system.

In our experiment, at least 4 cycles of condensation and evaporation performed on each sample to obtain adequate data. And the wettability of samples remained almost the same before and after all cycles of condensation and evaporation (Table 1).

Furthermore, different objective lenses were used in order to unambiguously observe the freezing of condensed microdroplets on various samples; objectives were 10 X, 50 X, 50 X and 50 X for sample 1, 2, 3 and 4, respectively.

Record videos in this experiment showed the freezing process of condensed water microdroplets on different surfaces. The freezing of each condensed water microdroplet was characterized by the rapid onset of opacity of the microdroplet, and the temperature of sample surface at this moment is the freezing temperature of the CWMD. Analysis of the videos recording the freezing of CWMDs on each surface, together with the temperature curve of the Linkam system, yielded the freezing temperature of each CWMD. More than 200 freezing events of the CWMDs were measured on each surface (except the superhydrophilic surface, sample 1, because of the limited number of CWMDs in the image window as well as the shape irregularity of these CWMDs as shown in Fig. 3a). And the freezing temperature was the mean values of the freezing temperature of all investigated CWMDs on each sample surface.

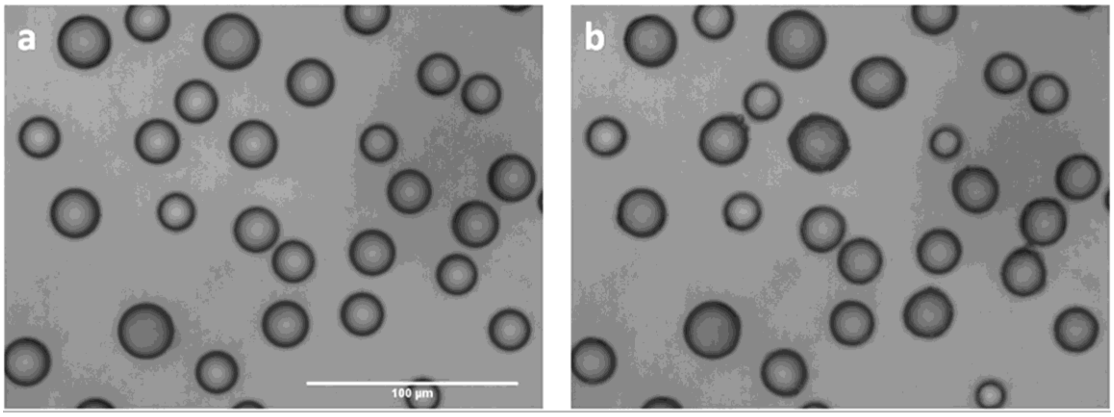

Fig. S2 Optical microscope images of condensed water microdroplets on sample 4 before (a) and after (b) freezing. The scale bar is 100 μm.

Additionally, we supply the videos to show the freezing process of condensed water microdroplets on sample 1 and 4, which also clearly indicate the duration of all CWMDs with filmwise condensation and that of dropwise ones respectively. The used rate of high-speed camera was 100 fps and the interval of between original images was 10 ms. The video are post-processed to demonstrate the freezing duration of all condensed water droplets on each sample. If anyone wants to receive recorded videos of other samples, please email author.

Video 1: The freezing process of condensed water microdroplets on sample 1 in the sealed sample cell.

Video 2: The freezing process of condensed water microdroplets on sample 4 in the sealed sample cell.

To further verify the effects of the condensation mode on the freezing of CWMDs, freezing of condensed water on these four surfaces was investigated in a in a real environment and freezing delay time was compared. The environmental temperature was 26 ^{o}C with a relative humidity (RH) of 35 %. The sample surface temperature was kept at – 5 ^{o}C. Water condensation was first observed on cold surfaces and then condensed water microdroplets grew until the freezing occurred as indicated by the rapid onset of opacity of the condensed water. Condensed water formed via filmwise condensation on sample 1 and 2 froze simultaneously, but the freezing of condensed water droplets formed via dropwise condensation on sample 3 and 4 did not affect each other. Freezing delay of condensed water on sample 3 and 4 was more than 2000 s, which was at least one order of magnitude longer than that on sample 1 and 2 (about 200 s). Furthermore, liquid water droplets could still be observed 15 min after the initial freezing of microdroplets on sample 3 and 4 as shown in Fig. S 3c and S 3d.

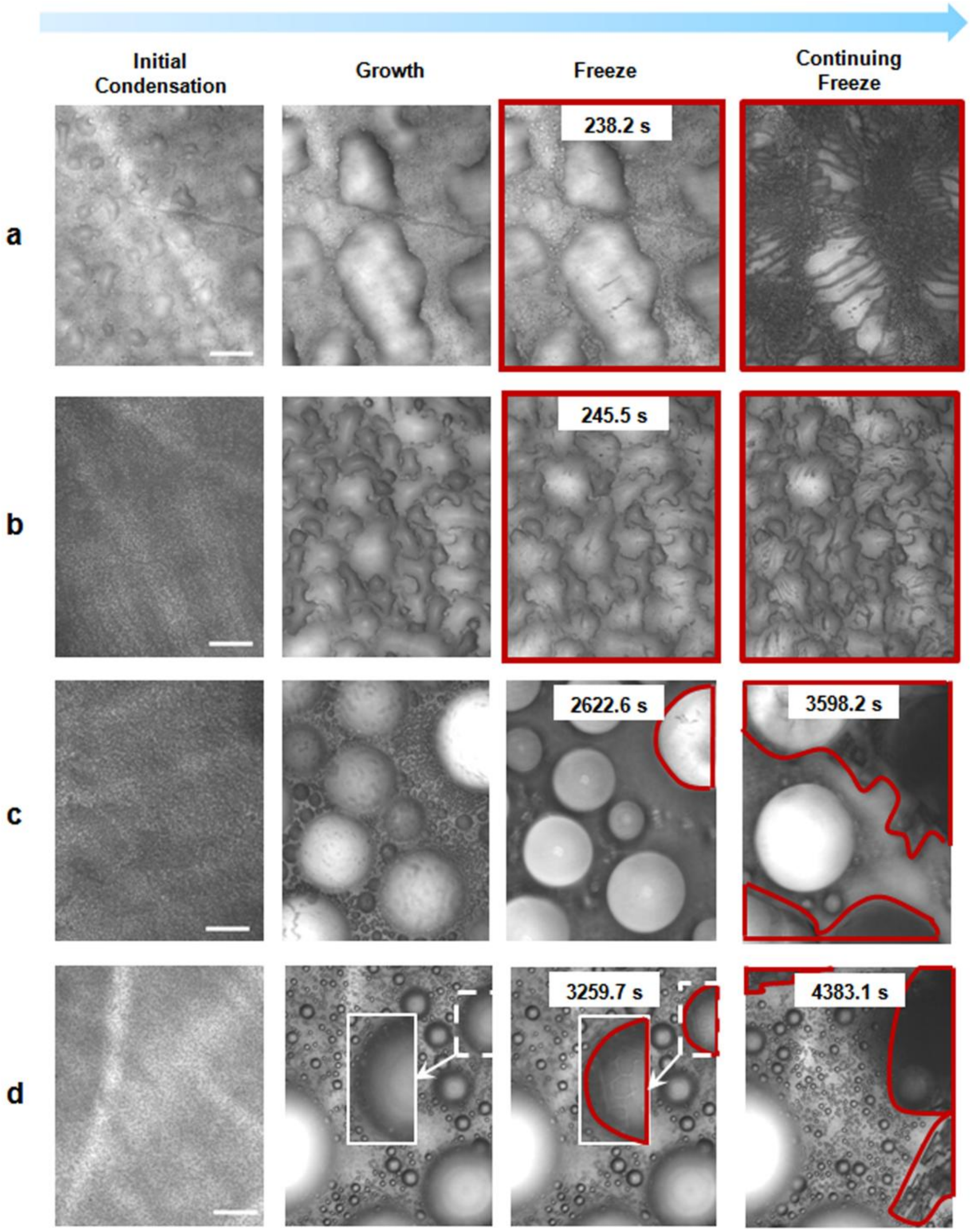

Fig. S3 The process of the ice formation on different sample surfaces. The numbers show the freezing delay of condensed water on these surfaces and the regions highlighted by red lines represent the ice formed. Insets in (d) are the corresponding high magnification images of liquid microdroplets and the afterwards formed ice particles, where ice formed is characterized by the rough ice structures. The scale bar is 100 μm. (a) and (b) freezing of CWMDs with filmwise condensation occurred spontaneously on sample 1 and 2; (c) and (d) freezing of CWMDs with dropwise deposition occurred independently on sample 3 and 4. And the freezing delay on smaple 3 and 4 was one order of magnitude longer than that on sample 1 and 2.