Supplementary Information

Laser-induced fabrication of a supercooled liquid droplet embedded in an ice microcrystal

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S1. Numerical simulation using COMSOL

COMSOL Multiphysics Ver. 6.2 (http://www.comsol.com) was used for the numerical simulations of the temperature elevation and ice sublimation under illumination of a focused laser beam on an ice microparticle (MP). The calculation includes the following four steps:

1. Laser heating of the ice at the focal spot,
2. Heat transfer from the focal spot to the surroundings, via the ice surface,
3. Ice sublimation to water vapor at the MP surface,
4. Diffusion and the convective flow of the water vapor from the ice surface.

The steps 1 and 2 have been described previously.[1] The steps 3 and 4 were modified from a model "Droplet Evaporation on Solid Substrate" released by COMSOL.[2] We combined the steps from 1 to 4 into a single model. The modified model required both heat transfer and CFD modules that work under the COMSOL environment.

The schematic illustration of simulation geometry built for COMSOL is shown in Figure 6a. All the elements in the model: the ice MP (100-μm diameter hemisphere), air layer, and substrate (quartz glass) were included in the model using the experimental configuration. At the center of the ice MP was placed an elliptical volume representing a laser spot. The lengths of the minor and major axes for the laser spot were determined by the full width at half maximum (FWHM) intensity of the laser focus based on lateral and axial resolutions.[3]

$$\text{(lateral resolution)}\ \frac{0.51\lambda}{\text{NA}} \qquad \text{(axial resolution)}\ \frac{2n\lambda}{\text{NA}^2}$$

where λ is the laser wavelength (1064 nm), n is the refractive index of the surrounding air (1.0), and NA is the numerical aperture of the objective lens (0.7). Physical properties of ice, air, and substrate: thermal conductivity, viscosity, and heat capacity, and density were taken from the COMSOL Material library.[4]

The heat generation by laser illumination was assumed to occur by the absorption of laser light at the focal spot, i.e., the elliptical volume within the ice MP. The absorption coefficient of ice (water), α, at 1064 nm, 0.14 cm^{-1}, was taken from the literature,[5] and the heat generated at the laser spot, Q, was calculated with the following equation.[6]

$$Q = I\alpha$$

where I represents the intensity of the laser beam, which is defined as the average of the incident laser power at the elliptical volume that acted as a heat source. Next, we calculated the temperature distribution in a chamber using the heat transfer module.[7] Initially, the temperature distribution in the model was assumed to be uniform and equal to 253 K. The heat is continuously generated upon laser illumination and is transferred to the surroundings, resulting in an increased steady-state temperature distribution throughout the chamber. Time-dependent heat transfer in the model is given by the following equation: [5]

$$\rho C_P\left(\frac{\partial T(\mathbf{x},t)}{\partial t}+\mathbf{u}(\mathbf{x},t)\cdot\nabla T(\mathbf{x},t)\right)=\nabla\cdot\left(k\nabla T(\mathbf{x},t)\right)+Q(t)$$

where T(**x**, t) is the temperature at arbitrary position **x** at time t, ρ is the mass density, C_P the specific heat capacity at the constant pressure, **u**(**x**, t) the fluid velocity vector, k the thermal conductivity of the system at the position **x**, and Q(t) is the energy deposition term. In this case, the temperature elevation in the ice MP is assumed to exceed the melting temperature of ice at 273.15 K. Thus, we considered the latent heat of fusion and changes in physical properties at the the melting point of water. The detail of the phase change is described in the application note, "Phase Change", released by COMSOL.[7] In the calculation, the value of latent heat of fusion, 333.5 kJ kg^{-1} and that of the transition interval, 10 K were used.

The heat transferred from the focal point to the ice surface was used for ice sublimation. In other words, the ice surface can be regarded as a boundary heat source toward the air layer. The heat generated at the surface was defined as a product of an evaporative mass flux (kg $m^{-2}s^{-1}$)) and latent heat of sublimation, 2839 kJ kg^{-1}. [8] When the latent heat of sublimation is exceeded, sublimation occurred from the ice surface, and water vapor was released to the surrounding air. The vapor concentration of water at the ice surface was set to the saturation 0.0595 mol m^{-3} at 253 K, [9] the temperature of the air layer. The vapor concentration in the air was set to 0.05 mol m^{-3}, slightly less than the ice surface. Following the progress of ice sublimation, the ice surface retreated and finally the ice disappeared.

References:

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Figure S1 Raman spectrum after irradiation of pure ice

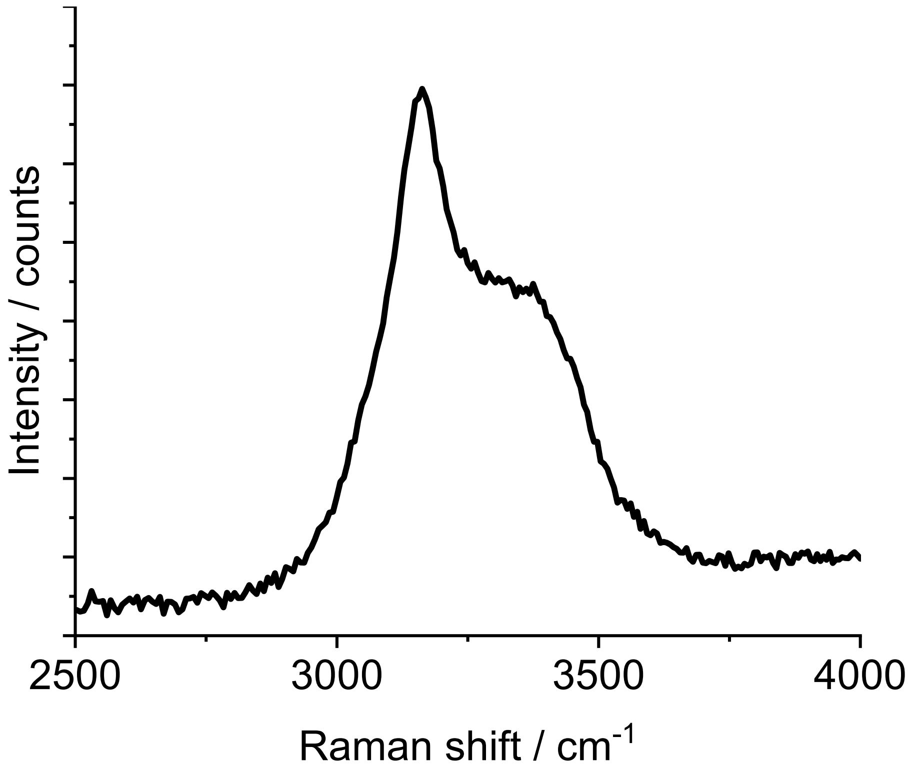
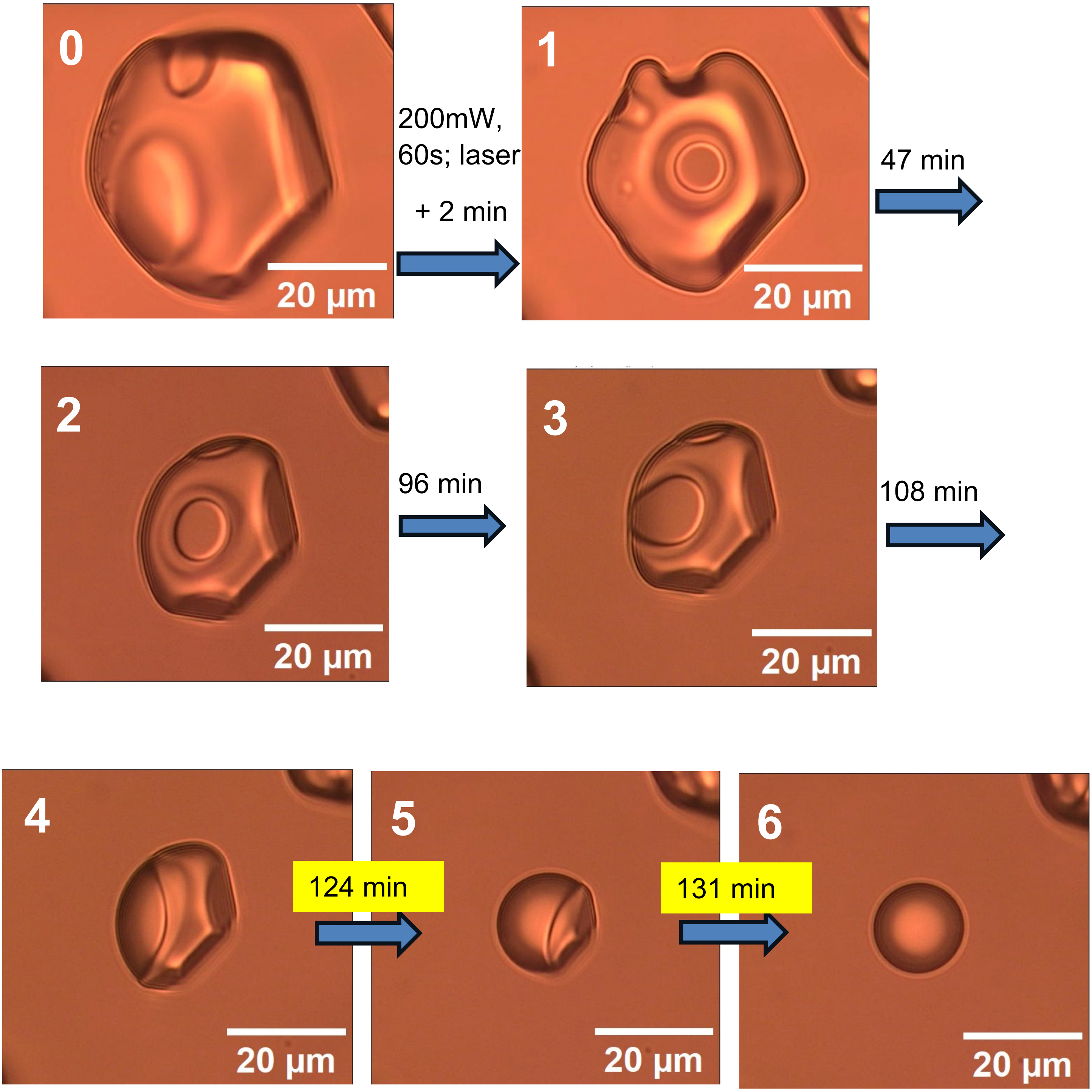
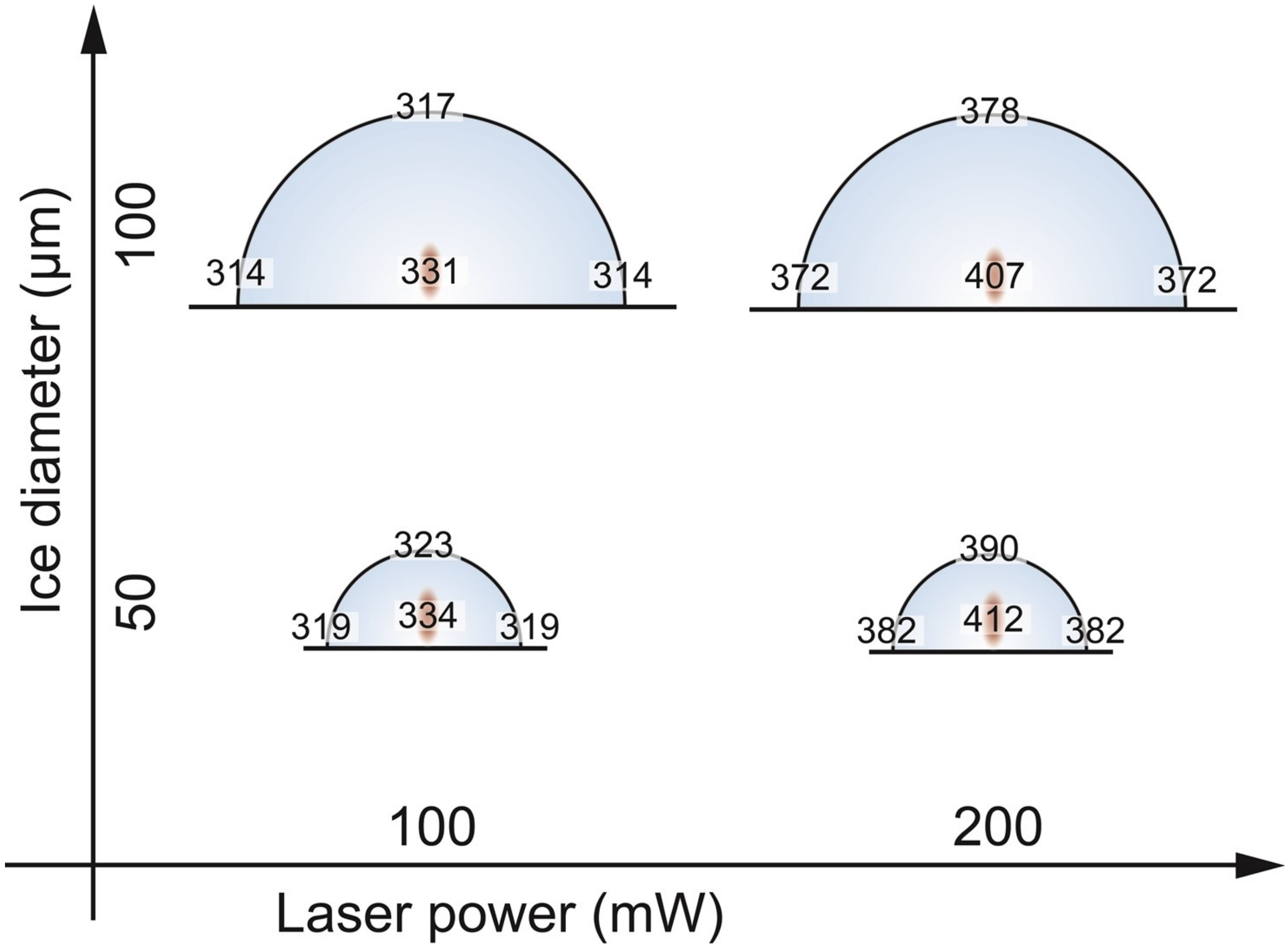


Figure S2 Laser-induced persistent melting



Time-evolution of particle images for laser-induced persistent melting of ice containing 0.1 M $(NH_4)_2SO_4$ at −15°C.

Figure S3 COMSOL simulation in the absence of sublimation



Temperature distribution of hemispherical ice particles (d=50 and 100 μm) supported on a quartz substrate in air when the particles were exposed to a focused laser illumination (100 and 200 mW) at 1064 nm and at –20°C (253 K).

Movie (MP4) showing laser-induced persistent melting.

Sample: ice particle at −14°C; ice was prepared from 0.1 M $(NH_4)_2SO_4$ aqueous solution.
Laser illumination: 1064 nm, 100 mW through an objective of 60×, numerical aperture of 0.70.
Period: for 50 s starting from laser illumination.