Supplementary Text

Direct observation of dynamics of nanometer-size hole in ultra-thin water film

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<u>Thickness estimate</u>: The thickness of the material imaged by electron microscope can be estimated from the image counts obtained during the TEM imaging using a simple relation:

$$\frac{I_{out}}{I_0} \approx \exp\left(-\frac{t}{l}\right)$$

where t-the thickness of the material and l-the mean free path (MFP) for a 120 keV electron going through this material, I_{out} and I_0 are the intensities of the output and incident electron beam.

In order to quickly check that camera is displaying proper counts that can be used for approximate thickness estimates we used gold nanoparticles sandwiched between two Si_3N_4 membranes and a free standing Si_3N_4 membrane (Fig. S1A). MFP for gold can be estimated using well known formula[1]:

$$l = \frac{106F\left(\frac{E_0}{E_m}\right)}{ln\left(2\beta\frac{E_0}{E_m}\right)}$$

where,

$$F = \frac{\left(1 + {}^{E_0}\!/_{1022}\right)}{\left(1 + {}^{E_0}\!/_{511}\right)^2}$$

$$E_m = 7.6Z^{0.36}$$

In the above expressions, E_0, Z amd β are energy of the incident electron in keV, atomic number of the material and semi convergent angle of the incident beam in mrad respectively. Using our microscope parameters (β =11 mrad, E_0=120 keV) and Z=79 for gold, we get l_{gold}=13 nm. The thickness of the gold based on the image intensities in Fig. S1A and the estimated MFP, t=-

$l\ln(I/I_0)$, is 6.4 and 5.5 nm between two and on top of a single Si_3N_4 respectively, which is in agreement with the lateral dimension of the nanoparticles of 7 and 8 nm, justifying the use of the image intensity as an approximate measure for the thickness.

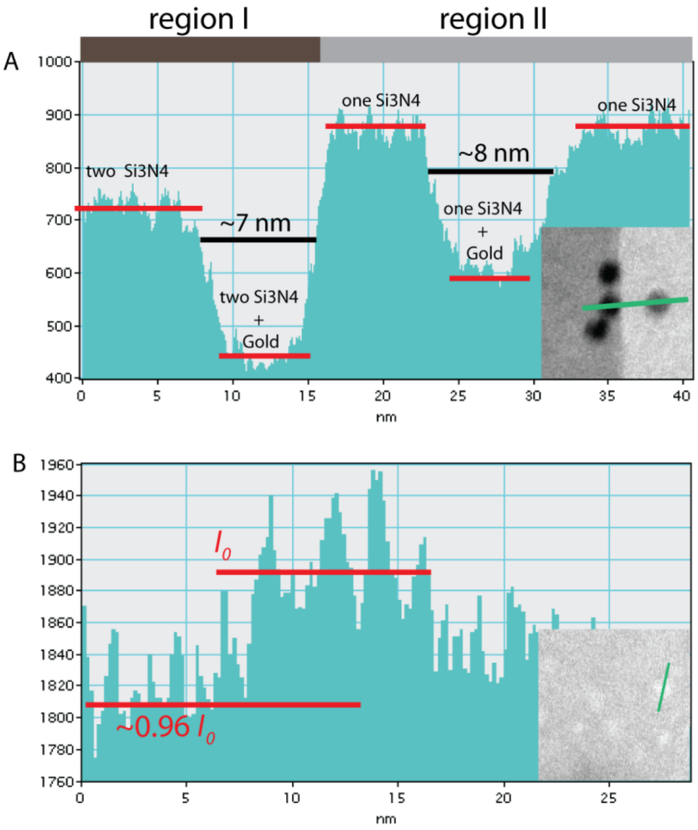

Figure S1. (A) Counts on pixels resulting from the electron beam passing through two Si3N4 and the gold nanoparticle sandwiched between two Si_3N_4 membranes (region I); and single Si_3N_4 and the gold nanoparticle on top of such Si_3N_4 membrane (region II). The count is taken across the line profile shown in the bottom right inset. (B) The beam intensity across the line profile going through hole as shown in the bottom right inset. The dynamic movement of the rims of the nanohole make the edges of the nanohole appear blurry.

Similarly, for thin water layer (Fig. S1B) we can estimate the thickness to be $t \approx -l_{water}\ln(0.96)=9.5$ nm, where $l_{water}=232$ nm for vitrified ice[2]. Line profiles of gray scale values of snapshots are rescaled so that the difference between the average pixel value of void and water film is ~4% of the average pixel value of void to obtain approximate depth profiles of the voids (Fig 2b and 4b).

<u>Estimate for the line tension energy</u>: Contact line tension for water can be estimated from the heat of vaporization[3]. For simplicity we consider the cubic arrangement for water molecules in the film so that each molecule is interacting with its six closest neighbors located a distance a away. Noting that the mass of water of volume V and density ρ is $m=\rho V$ and $m=NM/N_A$ (N-number of water, M-molar mass, N_A-avagadro number), we find that the volume occupied by a single molecule is $V=a^3=M/(N_A\rho)$, or a=3.1 Å. The bond energy between any two water molecules bond can be approximated to be $\sim H_{vap}/(6N_Aa)$, where

H_{vap}=40.7 kJ/mol is the heat of vaporization. At the rim of nanovoid in water film each water molecule has two less neighbors and thus ~ 2 $H_{vap}/(6N_A a)$ less energy. Then the line tension energy is simply:

$$\kappa = \frac{H}{3N_A a} = 7.3 \times 10^{-11} J/m$$

This number agrees nicely with the actual measured value of surface tension[4], κ=7×10^{-11} J/m.

References:

1. T. Malis, S. C. Cheng and R. F. Egerton, *Journal of Electron Microscopy Technique*, 1988, **8**, 193-200.
2. B. Feja and U. Aebi, *Journal of Microscopy*, 1999, **193**, 15-19.
3. H.-J. Butt, K. Graf and G. Kappl, *Physics and Chemistry of Interfaces*, 1st edn., Wiley-VCH, Weinheim, 2006.
4. T. Pompe and S. Herminghaus, *Physical Review Letters*, 2000, **85**, 1930-1933.

Supplementary Movies:

Movie 1: Bulk water is being pushed away by increasing the intensity of the beam (condensing the beam). Movie is recorded directly from the image screen of TEM.
Movie 2: Dynamics of nanovoid formation in ultrathin liquid film.
Movie 3: Unstable nanovoid (diameter remains less than estimated critical diameter).
Movie 4: Coalescence of two unstable nanovoids that leads to a formation of a larger nanovoid.