Supplementary Information

Title: Stable Water Layers on Solid Surfaces

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Measuring thickness of water layers by electron energy loss spectroscopy (EELS)

The thickness of water layers could be measured directly via EELS log-ratio technique. And the log-ratio formula can be written as Equation S1 according to Poisson's law, [1]

$$\frac{t_{Si_3N_4}}{\lambda_{Si_3N_4}} + \frac{t_{water}}{\lambda_{water}} = \ln\left(\frac{I_t}{I_o}\right) \quad (1)$$

where t_{Si3N4} and t_{water} are the thickness of Si_3N_4 and water, respectively. λ_{Si3N4} and λ_{water} are mean free path of total inelastic scattering of Si_3N_4 and water, respectively. I_t and I_0 are the total area and zero-loss area under the EELS spectrum.

The first term is 2.29 ± 0.06 got from the EELS spectrum of microchannels only. The third term is 2.95 ± 0.10 got from EELS spectrum of microchannels with water layers. The standard deviation of the first and third terms were both gotten from 5 different data points as shown in Fig. S2. Therefore, the t_{water} could be deduced by substituting λ_{water} with 288 nm.[2] However, microchannels with full water could not be analyzed through log-ratio formula, because the I_0 is buried in noise.

Quantitative nanoparticle counting technique

When water layers with a gaseous void formed, the effective thickness of a water layer could be calculated from observed nanoparticle area density, as shown in Equation 2

$$\begin{aligned} \textit{Effective thickness of a water layer}\,(nm) &= \frac{\textit{observed nanoparticle area density}}{\textit{applied nanoparticle concentration}} \div 2 \\ &= \frac{\textit{observed nanoparticle per } nm^2}{\textit{applied nanoparticle per } nm^3} \div 2 \end{aligned} \quad (2)$$

where observed nanoparticle area density could be get from transmission electron microscopy (TEM) bright filed images, applied particle concentration is the concentration of applied solution, and dividing by 2 is because there are two layers of water.

1 wt % 100 nm PS beads (or 18 particles/μm^3) in water dried in microchannel with the gap size of 1 μm, 2 μm, and 5 μm, respectively. The imaged particle densities, as shown in Fig.3 (a)-(c), are 4.1, 4.8, and 5.9 particle/μm^2. Therefore, the effective thicknesses of a water layer are 114, 134, and 164 nm according to Equation 2.

Two water layers revealed by tilted TEM images

TEM images of water layers with PS beads in a 2 μm-gaped microchannel were shown in Fig. S3(a),(b), and those with 10° tilting were shown in Fig. S3(c),(d). By comparing TEM images before and after tilting for 10°, we found two sets of particles, one set appear stationary and the other set appear moved as a group. To aid the reader in visualizing these two sets, the stationary PS beads were marked with blue dots and moving PS beads were labeled with numbers, as shown in Fig. S3(b),(d).

The relative heights between these two groups are estimated as following: One group of PS beads keeps stationary and shows no relative movement between images taken at these

two angels. Hence, this group of particles is 5 ° below horizontal level before tilting and 5 ° above horizontal level after 10 ° tilting, as shown in Fig. S4. The moving distance of the other group is 480 nm. Therefore,

$$r\cos\alpha - r\cos(\alpha + 10°) = 480\,(nm)$$
$$\Rightarrow r\cos\alpha - r\cos\alpha\cos 10° + r\sin\alpha\sin 10° = 480\,(nm)$$
$$\Rightarrow 0.015r\cos\alpha + 0.174r\sin\alpha = 480\,(nm)$$

The relative height between these two groups is,

$$\begin{aligned} height &= r\sin(\alpha + 5°) \\ &= r\sin\alpha\cos 5° + r\cos\alpha\sin 5° \\ &= 0.996r\sin\alpha + 0.087r\cos\alpha \\ &\approx 5.72\times(0.015r\cos\alpha + 0.174r\sin\alpha) \approx 2700\,(nm) \end{aligned}$$

which is in reasonable agreement with the nominal 2 μm gap height.

This observation clearly showed two layers of water about 2.7 μm apart. It is reasonable to conclude that the water layers are adjoining to the gap walls. Other evidence suggesting two water layers was reported in a previous work.[23]

Capillary bridge and water layers

For the microchannel used in the work, there are side walls, where top and bottom water layers must connect (bridge). For simplicity, we ignore gravity here.

Based on the uniformity of nanoparticles, we conclude that the water layers are fairly uniform under the observation window. At the boundary of the void, the water surface must assume minimum curvature, which is circular. The profile is drawn in Fig. S5(a). Unfortunately, it is difficult to observe the profile in our silicon based microchannel. The profile of water in the area un-exposed to the window is only speculative.

It is reasonable to believe that the curvature of water surface profile is continuous from the bridge to the water layer. Thus the water layer surface is pulled up (thicker) by the bridge near the bridge. However, we argue that this pulling by the bridge cannot be the origin of this thick water layer. A scenario where water layer is completely formed by bridge pulling is depicted in Fig. S5(b), where the surface profile is elliptical.

First of all, the larger the pulling angle, the sharper the bend at the apex (bridge), which would make the elliptical an unlikely profile. Secondly, the water layer would exhibit a thickness gradient, which was not observed. Finally, this pulling effect would be strongly associated with gap heights. On the contrary, the layer thicknesses were insensitive to gap heights. We conclude that surface tension produced pulling cannot mechanically produce the water layer we observed.

Coulomb force (e.g. electrical double layer and surface charge)

In general, we reason that the mobility of ions and charged particles in liquid allows them to move and “leave the liquid behind”. They drift under the force of unshielded electric fields. At equilibrium, either the mobile charges are completely depleted, or the electric field is completely shielded in the liquid. In either case, it is unlikely to exhibit net force on the liquid. Thus, it is difficult for mobile charges to mechanically hold water layer in place against surface tension.

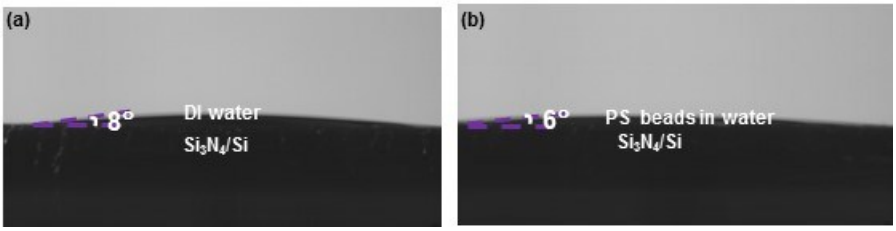

Figure S1. The contact angle of (a) DI water and (b) PS in water measured on the post-cleaned Si_3N_4 substrate.

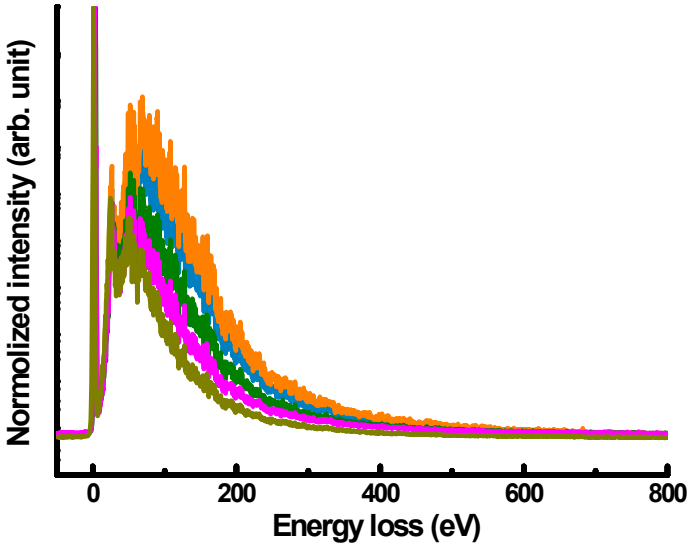

Figure S2. TEM EELS spectrum acquired from 5 different locations of 2 μm-gaped K-kit with water layers (nitride window films and water layer) show the total thickness of water layers is 203 ± 25 nm.

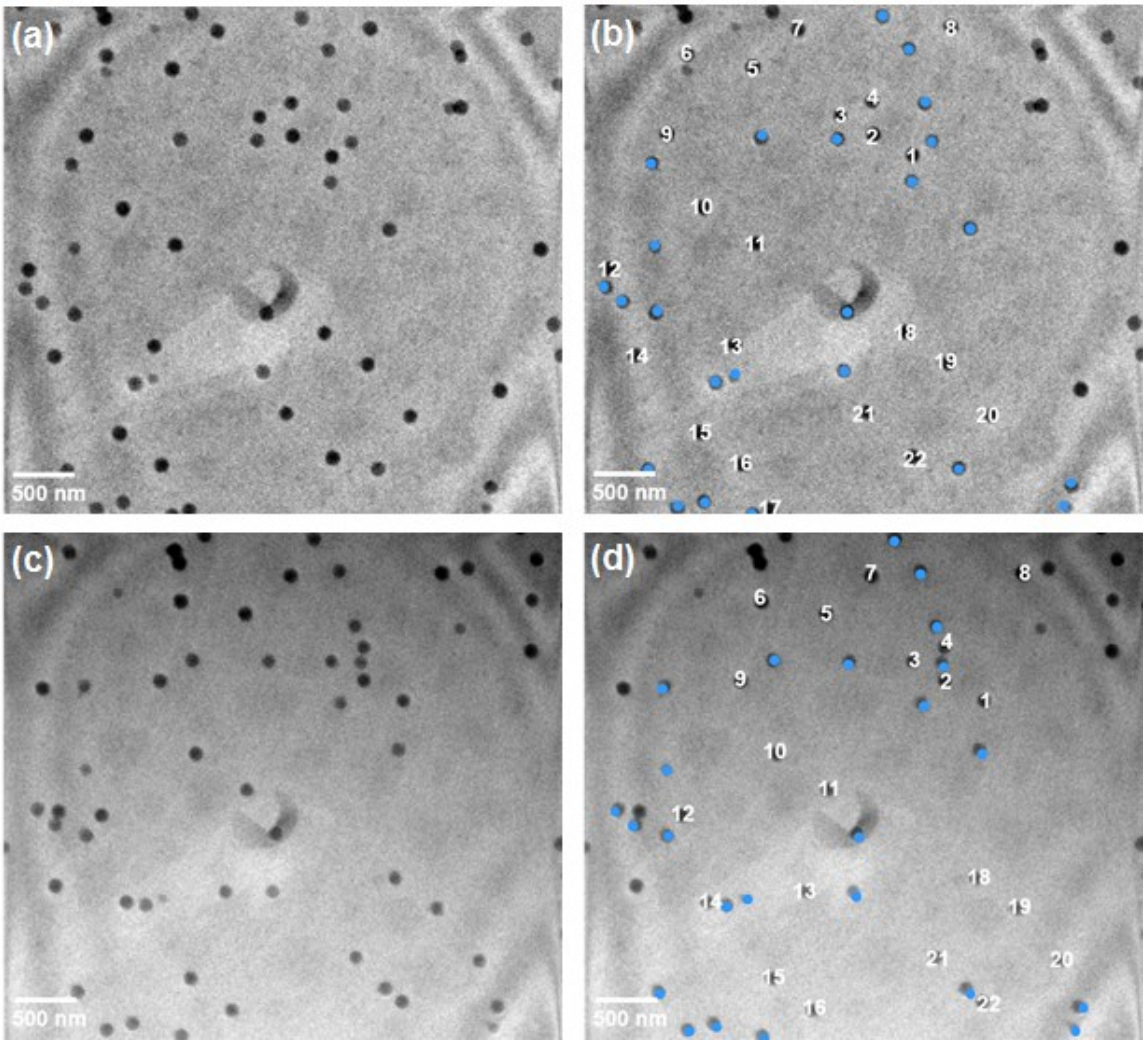

Figure S3. TEM images of PS beads in water layers in a 2 μm-gaped microchannel. (a),(b) Without tilting and (c),(d) with 10° tilting. The blue dots in (b) and (d) marked those stationary particles and the numbers in (b) and (d) labeled those moving particles.

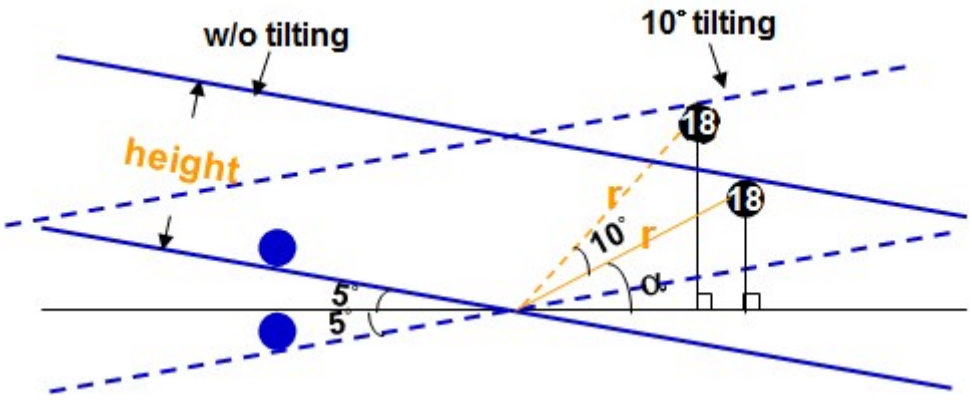

Figure S4. The schematic of relative height calculation. Blue dots represent stationary particles and black dots with a number represent moving particles.

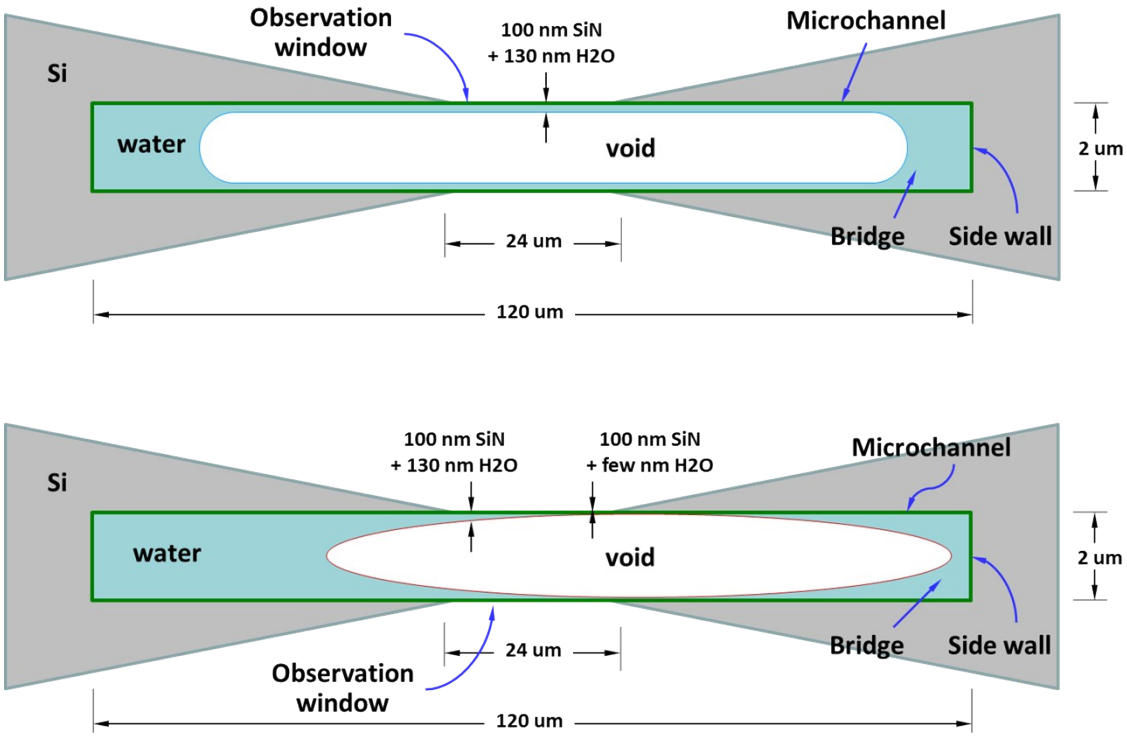

Figure S5. Cross-section schematics of (a) speculated water layers profile in a microchannel, and (b) a scenario where water layer is completely pulled by the bridge.

References

1. U. Buck, C. C. Pradzynski, T. Zeuch, J. M. Dieterich and B. A Hartke, Phys. Chem. Chem. Phys., 2014, 16, 6859-6871.
2. R. F. Egerton, Electron Energy-loss Spectroscopy in the Electron Microscope; Springer: New work, 1996.