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Electronic Supplementary Information

Low-volume liquid delivery and nanolithography using the nanopipette combined with the quartz tuning fork – atomic force microscope

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S-1 Fabrication of the pulled nanopipette

The controlled delivery of a small volume of liquid onto a substrate was facilitated by the pulled nanopipette, which was fabricated using a commercial puller (P-2000, Sutter Instruments CO.). In general, three materials are used to produce nanopipettes: borosilicate, quartz and aluminosilicate. We chose borosilicate (outer diameter; 1 mm, inner diameter; 0.7 mm) in order to make smaller apertures and thinner shapes. Furthermore, we found that the borosilicate nanopipette tip had the least impact on the quality factor of the quartz tuning fork (see next section). After pulling, filling of the liquid solution is facilitated via the capillary force due to the filament that is pre-installed inside the glass pipette. The aperture sizes (resistance) and the liquid solution's behaviour is defined using an *I-V* converter (10^7 gain, 10 MΩ) combined with an optical microscope (Fig. S1-1). After the experiment, scanning electron microscopy (SEM) images were taken to determine the correlation with the current response. The resistance taken from the slope value of the measured *I-V* curve can be used to infer the aperture size of the pulled nanopipette without the SEM image. For example, the electrical resistance of the 30 nm aperture was 35.3 MΩ according to our measurement. The aperture size of the pulled nanopipette is controlled by varying the pulling power of the puller's parameter (Fig. S1-2).

S-2 QTF Sensor for studying the nano-scaled liquid solution's properties

The quartz tuning fork (QTF) can be used as a high-sensitivity force sensor.[1,2] Recent results show that it is sensitive enough to detect extremely small perturbations existing in the force (< 1 nN) of a nano-meniscus of water.[3] Generally, in atomic force microscopy (AFM), a silicon cantilever or a sharp metal tip is used to detect the long and short range atomic forces. Unfortunately, the conventional cantilever tip has a low spring constant, thus, it is susceptible to jump-to-contact damage as it approaches the surface. This behaviour caused by surface tension, van der Waals force, and the naturally formed meniscus limits experimental studies of the nano-scaled water. In contrast, the QTF has a high spring constant, generally $10^3 \sim 10^4$ N/m. The QTF tip is stiff enough to resist the jump-to-contact motion, which enables research of the physical properties of nano-scaled water columns and flows. Even when the nanopipette is glued to the prong edge of QTF, the quality factor of the QTF-nanopipette is still high enough for our measurements.

The QTF operates in two different modes: tapping and shear modes. The shear mode detects only the shear force interaction, while the tapping mode can detect various vertical forces such as the short-range van der Waals force and the long-range retardation force. The shear mode AFM operation, using the small amplitude modulation (AM), was utilized in the present work. This mode detects only the shear viscous forces that arise naturally from the surface tension, which plays a dominant role within the water nano-meniscus.

The QTF can be excited either by a mechanical or electrical oscillation and behaves as a simple harmonic oscillator in the small oscillation limit.[4] The QTF response can be easily interpreted by analysis of the following equation of motion:

$$m\ddot{x} + b\dot{x} + kx = F\cos\omega t + F_{perturb}\ , \qquad (1)$$

where m is the effective mass of the probe, b is the damping coefficient, k is the spring constant, F is the amplitude of the drive, and $F_{perturb}$ is the interaction force. The perturbation due to the presence of nano-scaled water changes the QTF's amplitude and phase signal. When one solves this equation, the visco-elastic force can be derived. The interaction force, which is calculated by inserting $x(t) = A\sin(\omega t + \theta)$ into Eq. (1), is used to determine the spring constant and the damping coefficient:

$$\begin{pmatrix} k = \dfrac{F}{A}\sin\theta + m\omega^2 - k_{\text{int}} \\ b = \dfrac{F}{A\omega}\cos\theta - b_{\text{int}} \end{pmatrix}, \quad (2)$$

where ω is the resonance frequency due to the interaction and A is the free oscillation amplitude.

S-3 Analysis of the field distribution near the apex of nanopipette

In the ink-jet printing technology, the electrostatic force is generally used to eject the liquid solution in a micro-sized droplet form from the nozzle and to guide the liquid droplets onto the substrate. However, this method is not directly applicable to the small-volume liquid ejection through the nano-apertured glass pipette, because the surface-tension force arising on the inner wall at the atmospheric pressure is highly enhanced for the nanometric apertures in ambient conditions. For example, to extract the liquid solution through the nano-aperture (diameter of 100 nm), the applied electric field should be more than ~ 10^7 V/m.[5] However, by the capillary-condensed nano-scaled water meniscus formed spontaneously in the nanopipette-combined QTF-AFM, the threshold electric field for the nano-liquid ejection is dramatically reduced to ~ 10^3 V/m, corresponding to the bias potential of ~ 10 V (Fig. S2-1). In this case, the FEM simulation is performed for the 12 V potential biased 1 mm above the ground surface. We observed that the electric-field gradient and energy density were much enhanced in the nano-meniscus region of the nanopipette-surface gap, which results in the low-field ejection, flow, and dispersion of the nano-liquids (Fig. S2-2).

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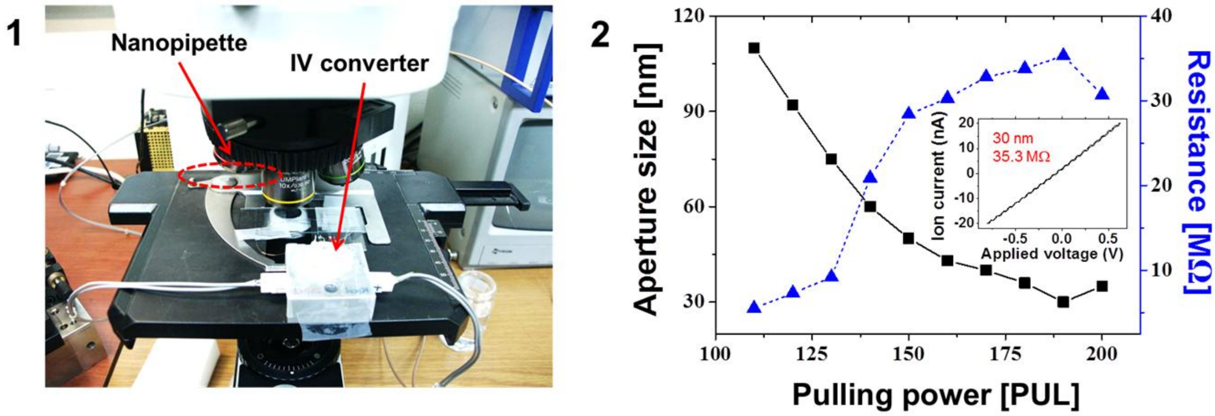

Figure S1

Figure S1. (1) The aperture sizes and resistance values of the pulled nanopipette were defined by using a typical current measurement system and SEM images. The *I-V* converter (10^7 gain, 10 MΩ) combined with an optical microscope (magnification factor of 500) is displayed. After filling the pulled nanopipette with the NaCl solution, the electrical current response (*I-V* curve) was measured. The electrolyte was an artificial 0.1M NaCl solution (conductivity of 1.068/Ω·m). (2) The controlled aperture sizes of the pulled nanopipette by varying the puller's parameter (laser power). The puller has five different control parameters: laser temperature (HEAT), beam spot diameter (FIL), velocity of pulling (VEL), delay time after melting (DEL), and pulling power (PUL). While the first four parameters were fixed, the nano-scaled aperture size was varied according to the last parameter (PUL). As increasing the pulling power of parameter, the aperture size is decreased (connecting lines are for eye guide). The 30 nm aperture (having equivalent resistance of 35.3 MΩ) was the minimum size that we could fabricate by using this puller, for which the typical pulling recipe consisted of HEAT=350, FIL=4, VEL=20, DEL=125, and PUL=190 (inset). One may further reduce the aperture size by optimizing all the parameters.

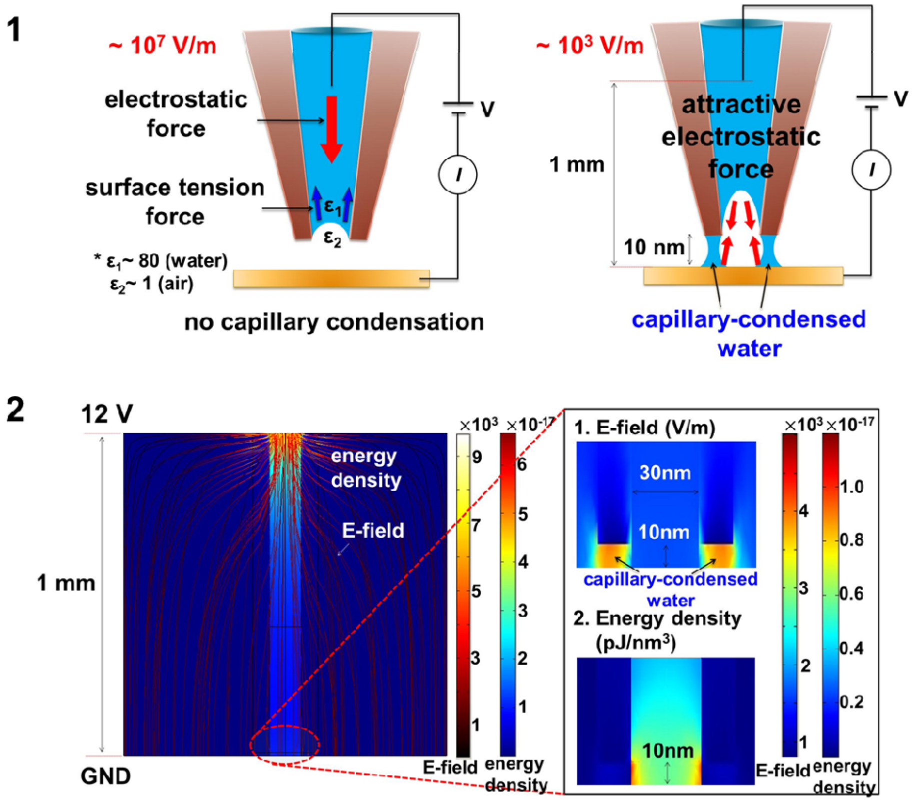

Figure S2

Figure S2. Analysis of the field distribution near the apex of the nanopipette. In the ink-jet printing technology, the electrostatic force is generally used to eject the micro-sized droplets of the liquid solution out of the nozzle and to guide the liquid droplets onto the substrate. However, this method is not directly applicable to the small-volume liquid ejection through the nano-apertured glass pipette because the surface-tension force arising on the inner wall at the atmospheric pressure is highly enhanced for the nanometric apertures in ambient conditions. Therefore, (1) to eject a liquid solution through the nanopipette without confined water meniscus in ambient conditions, an extremely high electric field (~ 10^7 V/m) should be applied for the electrostatic force (red arrow) to overcome the large surface-tension forces (blue arrows) on the inner wall of the nano-apertured glass pipette. However, the threshold electric field for nano-liquid ejection with the confined water meniscus is dramatically reduced to ~ 10^3 V/m, which corresponds to a bias potential of ~ 10 V. At this bias potential the liquid can start to flow through the formed liquid nanochannel onto the substrate. (2) The FEM simulation results of capillary-condensed water case are presented. The bias potential of 12 V is applied at 1 mm above the ground surface. One can observe the electric field gradient and the energy density are greatly enhanced near the nano-liquid meniscus, which allows for the low-field-induced ejection, flow, and dispersion of the nano-sized liquids.

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