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Nanofluidics through a 30-nm Aperture Nanopipette by applying Electrostatic Field based on the QTF-AFM System

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***Abstract*-Nanofluidics of the liquid solution through a 30-nm aperture nanopipette was investgated using the QTF-AFM system. Used pulled nanopipette was attached on the edge of QTF to control the distance between the tip and substrate. Monitored QTF signal was changed by naturally formed water meniscus's force as tip approached to the sample within 10nm. After forming of water, electric field was applied for the purpose of a filled solution's extrusion onto the surface. Measured the fluid speed was 43.5 um/s and spread area was 136.6 um^2 after 5 seconds. During the experiment, temperature was 22 °C and humidity was 20.1 %. Checked thermal drift was 0.3 pm/s.**

I. Introduction

Nanofluidics's importance is increased in the field of Biotechnology. Even if simply changed thing is only "scale", the phenomena between macroscopic and microscopic system is definitely different. For example, if we change the size of the fluid's road from millimeter to micrometer one, we cannot easily predict the results of the microfluidics. Nano-scaled changing is more difficult to understand. Researchers are trying to know nanofluidics with nanopore [1], nanogap [2], nanochannel [3] and so on [4-10]. Combining nanotechnology and biotechnology suggest some solution about that problem. In this work we used liquid filled nanopipette. With this material we can research about microscopic regime through a nano-sized pore. nanopipette is a promising tool for manipulating individual cell [11], patterning nanometer-scaled features [12,13], and delivering materials with sub-femto liter volume in Bio-system as a nanosensor [14,15]. In this work, to control a nano-sized fluid throughout nano-scaled aperture, we used under a 30-nm apertured nanopipette based on the QTF-AFM (Quartz Tuning Fork - Atomic Force Microscope) system [16]. We used electric field to extrude out the liquid to substrate between electrode inside of nanopipette and surface.

II. Experimental System (QTF-AFM with Nanopipette)

A. *Pulled Nanopipette*

a 30-nm aperture nanopipette was fabricated by commercial pipette puller "P-2000" (Sutter Instruments). We used a borosilicate pipette which inner diameter was 0.7 mm. With this material, we can make nano-sized pore and also make high quality factor with QTF. We can make a 30-nm aperture nanopipette with pulling parameter (350, 4, 20, 125, 190) in the experiment. As you see, a middle of figure 1 (a) is scanning electron microscope image of the 30-nm aperture nanopipette, and we can control the aperture size of the pipette by varying the last PUL parameter (Table I). And we checked the resistance using IV-converter for electrical current signal. After pulling, the nanopipette was filled with liquid solution to see the phenomenon of nanofluidics like the liquid's spreading behavior. Then filled nanopipette was attached on the pipette holder, and Ag-electrode was inserted inside of nanopipette.

B. *Force Measurement Using QTF*

We used the Quartz tuning fork as force sensor [17]. The QTF can be assumed as simple harmonic oscillator with adding certain technique. We can drive the QTF with function generator. This QTF is generally used in NSOM system with attaching optical fiber. AFM system's Si-cantilever tip has so low spring constant. Cause of this low spring constant (k), this tip shows a jump-to-contact motion while tip approach to the surface. But QTF has very high spring constant (10^3~10^4 N/m). So, with this QTF tip we can make confined nano-water and can research about nano-scaled water's properties [18].

TABLE I
Resistance value of each pulled nanopipette according to the PUL parameters (HEAT 350, FIL 4, VEL 20, DEL 125, PUL ***)

PUL parameter	Apertured Inner Diameter	Nanopipette Resistance
160	43 nm	30.3 MΩ
170	40 nm	32.8 MΩ
180	36 nm	33.8 MΩ
190	30 nm	35.3 MΩ
200	35 nm	30.7 MΩ

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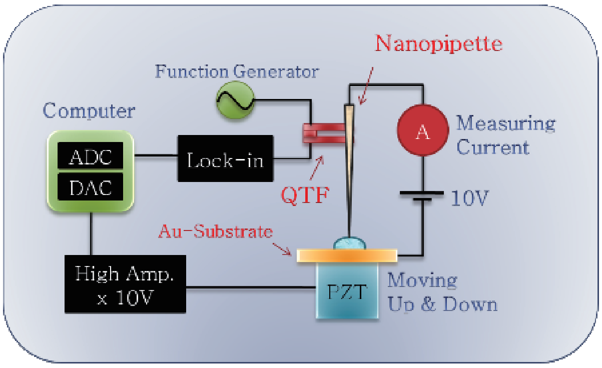
QTF can be easily interpreted with bellowed force equation

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

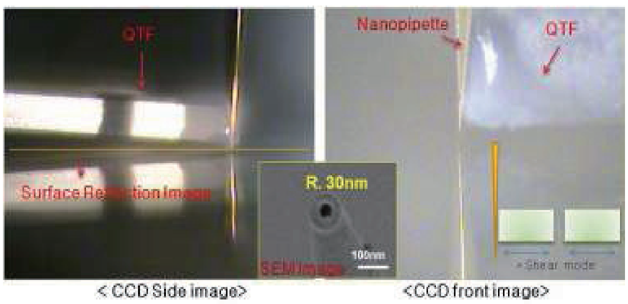
Where m is the effective mass of the probe, b is the damping coefficient, k is the spring constant, F is the amplitude of the drive, and $F_{perturb}$ is the interaction force. If we solve this equation, viscoelastic force can be derived [19,20].

C. QTF-AFM System with Nanopipette

We used this QTF system with shear mode. The shear mode system only detect the shear interaction. Cause of this property, we could monitor the signal came from naturally confined nano-water's shear perturbing force. Figure 1 (a) shows the diagram of the experimental system. Distance between tip and surface with high resolution could be controlled by the QTF-AFM system which was oscillated parallel to the substrate. We can get high quality factor (Q ~ 6000) with attaching the nanopipette tip on QTF as you see in figure 2 (b). And driving frequency was 32676.8 [Hz], and a dithering amplitude of the QTF was 0.7 nm. It's extremely small due to do not influence to the formed nano-scaled water meniscus. We can make the clearly simple harmonic oscillating QTF using current compensator circuit which removes the stray capacitance came from two electrodes on the QTF [21]. Figure 2 (a) and (b) are before and after removing stray capacitance of QTF. We used lock-in amplifier (EG&G 7265) to remove the noise came from QTF signal. Nanopipette was simply attached to the edge of the QTF as figure 1 (b). The reflection image was caused by clean Au-substrate. We also detect the output current signal

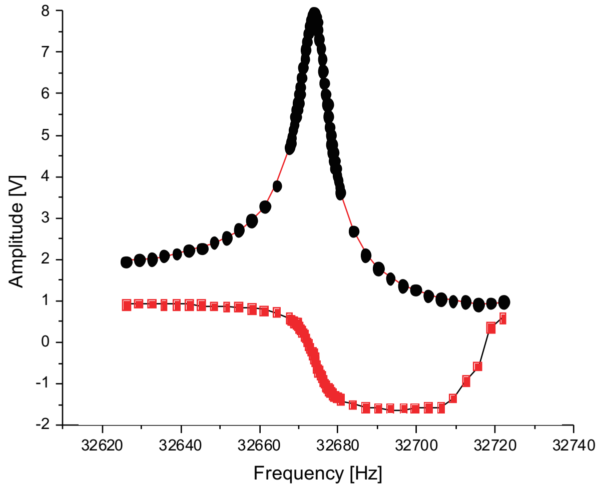


(a)

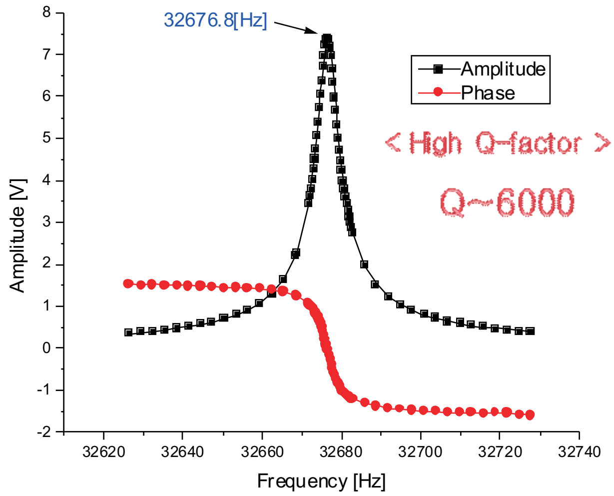


(b)

Fig. 1. Experimental Setup of the QTF-AFM system with Nanopipette. (a) Front and side CCD image of Nanopipette attached QTF (center; SEM image of a 30-nm aperture Nanopipette. (b) Diagram of Setup.



(a)



(b)

Fig. 2. Quartz tuning fork's resonance curve. High quality factor could be achieved. Driving frequency was 32676.8 [Hz]. (a) before removing stray capacitance (b) after removing stray capacitance

came from electrode inside of nanopipette with IV converter (LF356, 10MΩ) when voltage applied to the tip and Au-surface. Au-metal was coated on the Si-substrate by sputtering technique. The QTF can be easily affected by variation of temperature and humidity. So we used acryl box to sustain the temperature and humidity. We fixed temperature as 22 °C and humidity as 20.1 %. Checked thermal drift was 0.3 pm/s. We choose the acryl box for sustaining the temperature and humidity inside of the electromagnetic shielding box for protecting electrical noise.

III. Experimental Results

Experimental process is consisted of three steps. First nanopipette tip was approached to the surface within under 10 nm distance, second electric field was applied between inserted electrode inside of nanopipette and Au-surface, finally we capture the movie using high resolution CCD camera with x20 objective lens to see the speed of fluid and spread area range. Figure 3 shows the results of experiment. Both of two cases are output signal of QTF. Figure 3 (a) shows that naturally confined nano-water is suddenly formed within 10 nm distance from surface. And then tip was directly retracted from surface to rupture the nano-water formed between apex of nanopipette and surface. Measured rupture distance was 1 nm. At this forming point we applied voltage to system with 10V. Then filled liquid inside of nanopipette was extrude out came from 30-nm aperture to the surface. After extrusion of liquid, the nanopipette tip was retracted directly. Checked rupture distance was more than 100 nm as you see in the figure 3 (b). After procedure of figure 3 (a) electric field was applied and the tip was not retracted to see the fluid's property. Figure 4 shows the fluid speed and spread area of nano-scaled liquid according to time changing. We could capture the movie with CCD camera with 30 frames per second. Figure 4 (a) was captured spread area after 25 seconds. Diameter of spread area was nearly 80 um. Figure 4 (b) was each frame images per 5 seconds. After 5 seconds, the measured nano-scaled fluid's speed was 43.5 um/s and spread area was 136.6 um^2. Measured spread area and velocity was changed for each times and showed tendency of saturation in figure 4 (c). With increasing time, the speed and spread area would be decreased cause of widening of surface area.

IV. Discussion

We discussed out fluid velocity and speading picture with a 30-nm aperture nanopipette with QTF-AFM system with view point of nanofluidics. We need to define some parameters such as distance between the nanopipette tip and surface, temperature, humidity, and the nanopipette tip's aperture diameter in the future work. And we also try to confine this nanofluidic system to confocal microscope.

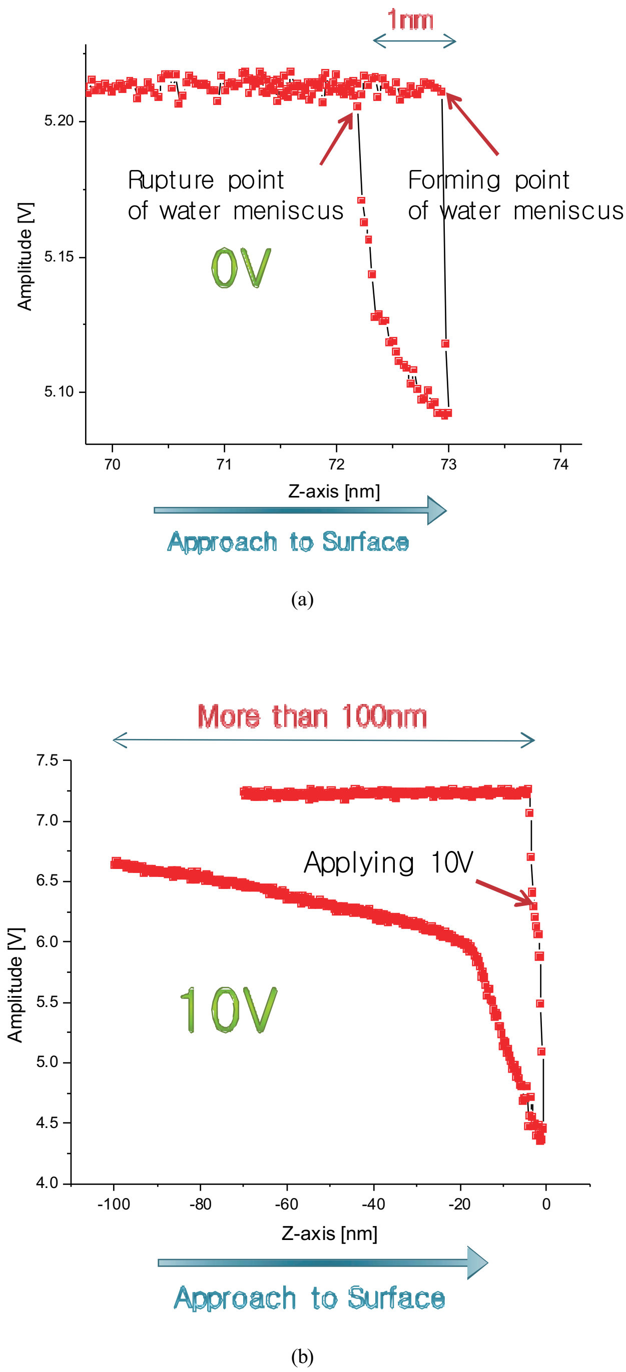
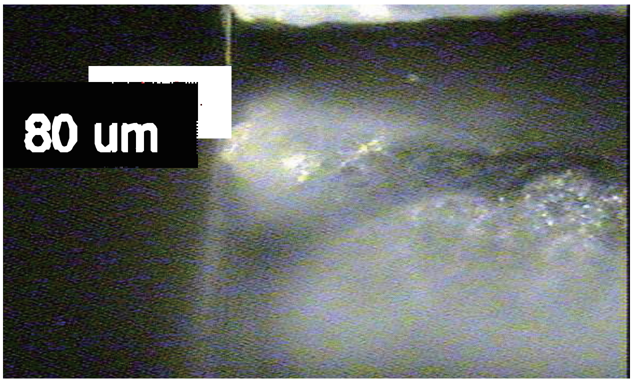
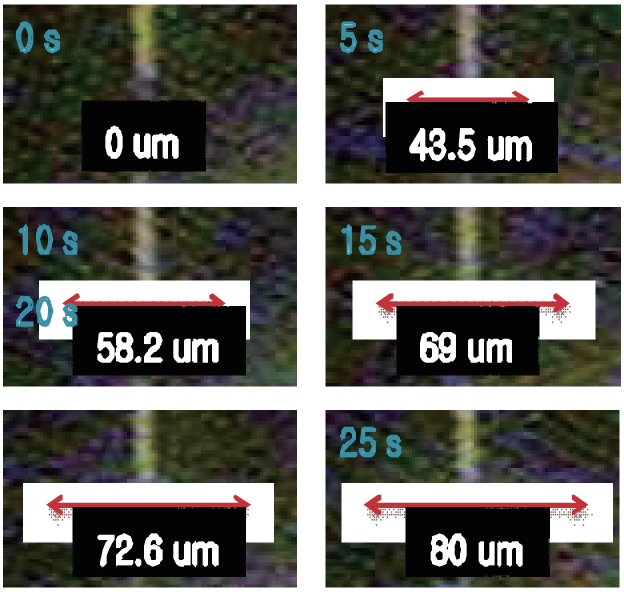


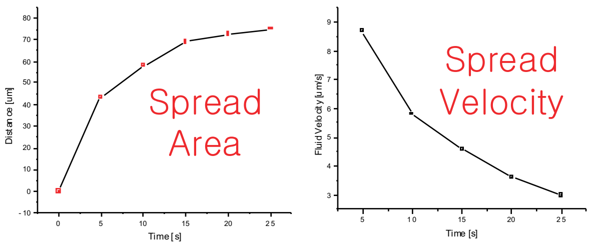
Fig. 3. Approach Curve of QTF-AFM system with Nanopipette. As distance between tip and sample is narrowed, a naturally confined nano-water suddenly can be formed within 10~20 nm. (a) Without applying voltage (0V), rupture distance was short, 1 nm. (b) With applying voltage (10V), rupture distance was very long, mopre than 100 nm.



(a)



(b)



(c)

Fig. 4. Ejected liquid solution came from a 30 nm aperture nanopipette spread on the surface. We could capture the movie with commercial CCD camera with 30 frames per second. (a) Captured CCD image after 25 seconds. Spread area was nearly 80 um. (b) Each frame images per 5 seconds (c) Measured spread area and velocity was changed for each times and showed tendency of saturation.

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