# Liquid Properties in Extended-nano Channels: Substrate material

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## ABSTRACT

When the channel size was reduced to 10-100 nm space, which we call extended-nano space, various unique liquid properties were observed in $SiO_2$ nanochannels for protonic solvents. SiOH groups on the substrate were verified to work as proton donors and affected the liquid property change. However, there is no investigation of the dependence on other proton-donor functional groups. In this presentation, the nanochannels were formed on a $TiO_2$ material (photocatalytic material), which also included TiOH groups as proton donors and was expected to show the similar unique liquid properties. Finally, we verified that the viscosity increased for water confined in the $TiO_2$ nanochannels as well. This results have a large impact on the nanofluidic sciences, when the various functional surface materials are used.

**KEYWORDS:** extended-nano channel, liquid property change, surface functional group

## INTRODUCTION

Recently, the size of the analytical space is downscaling to $10^1$-$10^2$ nm scale. From the view point of nanofluidic science, the space is a transient space from single molecules to bulk condensed phase, and unique liquid and fluidic properties can be expected. However, due to the extremely small space, which is even smaller than the wavelength of visible light, general chemical experiments were difficult in this space.

For these purposes, we developed state-of-the-art fundamental technologies.[1] These included glass nanofabrication, low temperature glass bonding, partial surface modification, aL-fL pressure driven flow control, and ultrasensitive detection of nonfluorescent molecules by thermal lens microscope. With these technologies, measurement of various liquid properties became possible such as viscosity, dielectric constant, proton mobility, proton concentration and chemical reaction. Then, many unique liquid properties were found.[2] Surprisingly, all the liquid properties changed when the channel size decreased from 500-800 nm, which were much larger than the size of solvent molecule (e.g. ~3Å for water). And we found that the liquid property changes were induced when the channel surface was $SiO_2$ and the solvent had proton-donating capability (e.g. water, ethanol, and methanol). Based on these results, we constructed a model that SiOH group worked as a proton donor (for forming hydrogen bonding), and the solvent worked as a proton acceptor. As a result of proton exchange, loosely-structured hydrogen bonding network was formed, which was expected to induce the liquid property change (Figure 1).

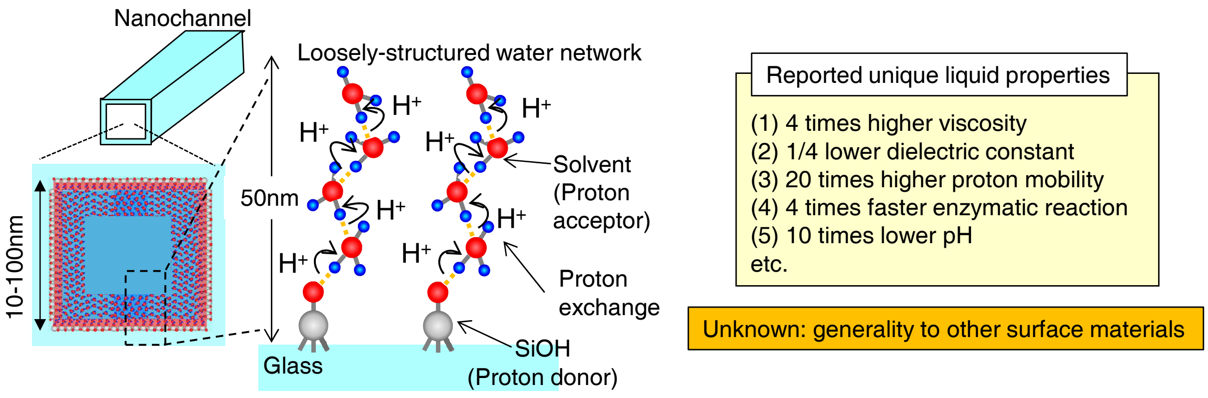

*Figure 1 Unique liquid properties in nanochannel*

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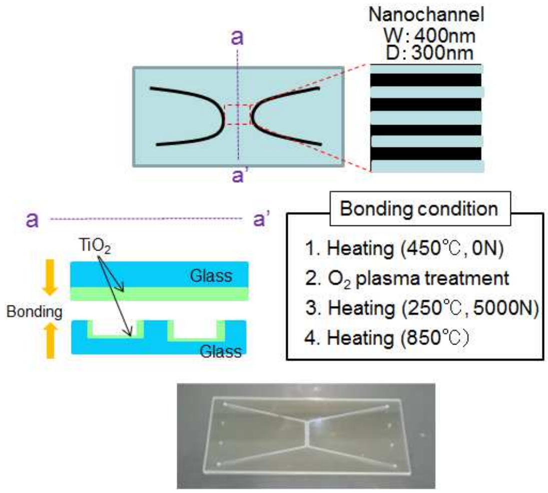
However, the generality to other surface materials was not investigated, while other materials were also important for catalytic reaction, filtering, fuel cell, etc. In this study, we focused on a $TiO_2$ as a surface material. For this purpose, we developed a new microchip with $TiO_2$ nanochannels.

## EXPERIMENTAL

The fabrication process of $TiO_2$ chip is shown in Figure 2. On a glass substrate, microchannels were fabricated by photolithography and dry-etching methods, and nanochannels were fabricated by electron-beam lithography and dry etching on the same substrate. The size of the nanochannel was 400 nm wide and 300 nm deep, which was sufficiently small to induce the viscosity change based on previous results. Another glass substrate was prepared for covering the channels. $TiO_2$ film was sputtered on each substrate with a thickness of 10 nm. The $TiO_2$ film, where nanochannel was not formed, was removed by a lift-off process, because bonding between $TiO_2$ substrates are currently difficult. Finally, we bonded the two substrates by our low temperature bonding method. (Figure 2) and successfully constructed the $TiO_2$ chip. Finally, in order to investigate the p*K*a (proton donor indicator) effect, the surface density of SiOH was reduced to $2/nm^2$ to be same with that of TiOH by heating the $SiO_2$ chip at 400 ºC. In this study, we measured the viscosity change by capillary filling method, which was reported by our group (Figure 3).[3] By changing the external applied pressure $P_{ex}$, which is controlled by air pressure with a pressure controller, capillary filling speed ($x^2/t$) was measured by a bright-field optical microscope. From the relationship, viscosity was calculated. The size of the nanochannel $D$ was determined before bonding by SEM.



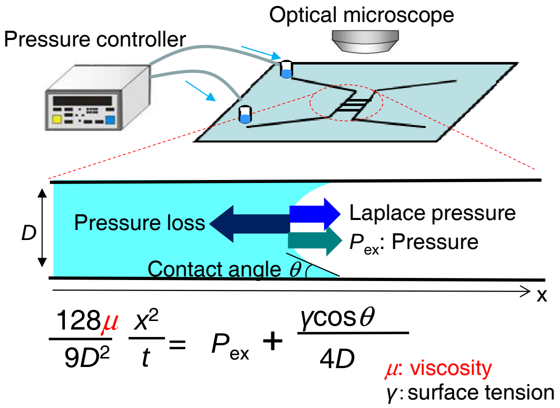


*Figure 2: Fabrication procedure of $TiO_2$ microchip*

*Figure 3: Viscosity measurement system*

## RESULTS AND DISCUSSION

By changing the external applied pressure $P_{ex}$, the capillary filling speed was measured for three solvents as shown in Figure 4: water (protonic and polar), acetonitrile (aprotonic and polar), and hexane (aprotonic and non-polar). As expected, The capillary filling speed showed linear relationship with the external applied pressure for all the solvents. By utilizing the slope of the curve, viscosity was calculated as shown in Figure 5. Similar to the $SiO_2$ surface, viscosity increase was also observed for the $TiO_2$ materials. However, the degree of the increase was smaller than that of $SiO_2$. The reason can be discussed based on the p*K*a values. The p*K*a of SiOH (2.7) is much smaller than that of TiOH (6.7). Then, it can be expected that the hydrogen bonding network becomes weaker for TiOH surfaces based on our previous model. That is why the viscosity change was smaller for TiOH surfaces. When we consider the dependence on the solvent, only water (protonic) showed the liquid property change similar to SiOH surface. This result also suggested proton-donor and proton-acceptor model from the surfaces.

Based on these results, the liquid property change was observed for other proton donor material for the first time. The results accelerate development of the nanofluidic science and unique devices using other functional materials

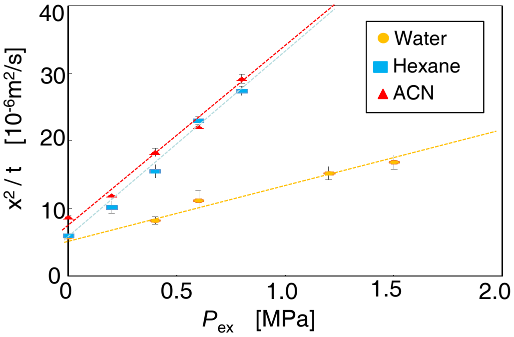


*Figure 4 Measurement of capillary filling speed depending on the external applied pressure Pex. From the slope, viscosity was calculated.*

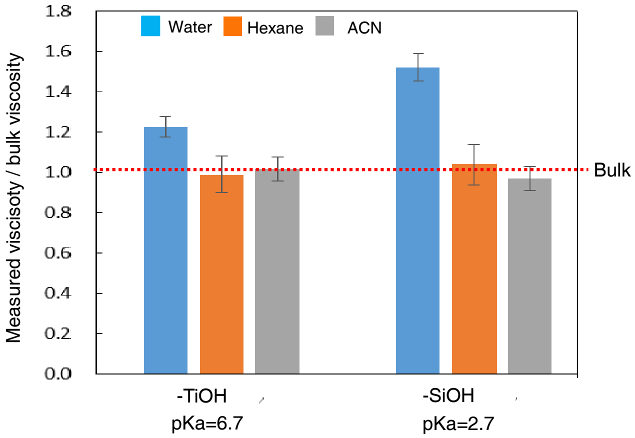


*Figure 5 Measurement viscosity change on $TiO_2$ chip and $SiO_2$ chip.*

## CONCLUSION

The unique liquid property was investigated in a channel with other surface functional group. TiOH group showed also liquid property change, which was consistent with our current model using proton-donor (surface functional group) and proton-acceptor (solvents). Metal oxides generally have –OH group on the surface and work as functional materials in many fields. These results will accelerate the utilization of unique liquid properties for novel functional devices and will be strategy of the device design.

## ACKNOWLEDGEMENTS

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