# ENHANCEMENT OF PROTON TRANSFER BY SURFACE SILANOL GROUPS IN EXTENDED NANOSPACE

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## ABSTRACT

Understanding liquid properties in extended nanospace (10-1000 nm) is important for nanofluidic devices. Our group found unique liquid properties in fused-silica extended nanochannels and surface silanol groups have been considered to play a key role in these properties. Here, we controlled surface silanol density in extended nanochannels and evaluated proton transfer in water molecules confined in the channels. The result of NMR measurements strongly suggests that surface silanol groups enhance proton transfer in extended nanospace. Our result contributes to development of nanofluidic devices.

**KEYWORDS:** Water, Proton transfer, Silanol group, Nanochannel, NMR

## INTRODUCTION

As micro/nanotechnologies developed, the microfluidic research field is moving its focus to extended nanospace (10-1000 nm) for developing innovative devices. Our group found unique liquid properties in extended nanospace such as higher proton mobility [1], and successfully applied extended nanospace to high efficient fuel cell device by using extended nanochannels as proton conductor [2]. To explain these phenomena, we suggested proton transfer phase with loosely coupled water molecules within 50 nm of the surface, which induces fast proton hopping through hydrogen bond network (Figure 1).

In this model, the surface silanol groups are considered to work as proton donor in the formation of proton transfer phase. Recently, we found the enhancement of proton dissociation from silanol group and the increase in proton concentration in extended nanospace [3], [4]. However, the role of silanol groups as dominant factor of proton transfer phase has not been understood.

In this study, we controlled surface silanol density in extended nanochannels and verified the hypothesis that surface silnol groups in extended nanospace induce the structure of loosely coupled water molecules and enhance proton transfer. In detail, we evaluated proton transfer in water molecules confined in extended nanospace using NMR.

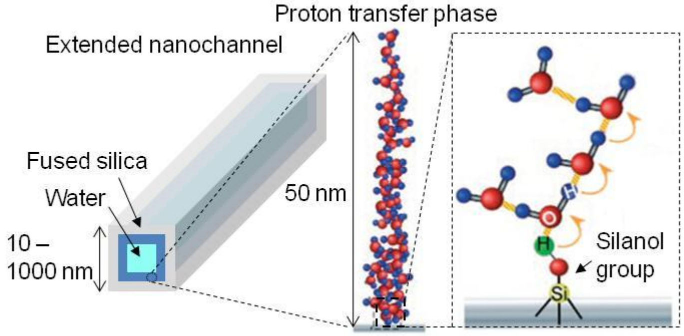

*Figure 1. Schematic illustration of proton transfer phase. The proton is transferred through hydrogen bond network with loosely coupled water molecules within 50 nm of the surface.*

## EXPERIMENTAL

First, it was required to control surface silnol density. The idea of using dehydration reaction between silanol groups (-SiOH + -SiOH → -SiOSi- + $H_2O$) was conceived. A microchip equipped with extended nanochannels (width: 190 nm, depth: 170 nm) on fused silica substrate was fabricated (Figure 2) and the surface silanol density was controlled by heat-treating at several temperature. The silanol density was evaluated

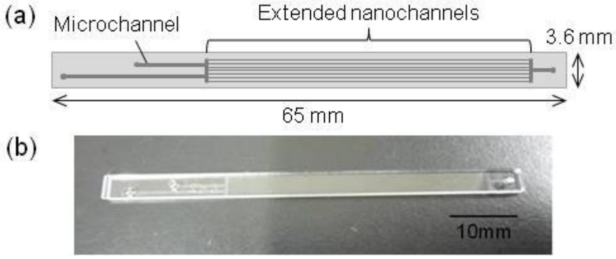

*Figure 2. (a) Schematic illustration of a microchip equipped microchannels for injection and extended nanochannels (Width: 190 nm, Depth: 170 nm, Length: 42 mm). (b) Picture of the microchip.*

using XPS and success in control of the density was confirmed.

Then, we evaluated proton transfer in water confined in the extended nanochannels where the surface silanol density was controlled. In addition, a microchip modified with trimethylsilyl-imidazole (TMS-im) was prepared, where whole silanol groups in the extended nanochannels were blocked. We assumed that the surface has no silanol group ([SiOH/Si] = 0).

Using NMR, $^1$H-NMR spin-lattice relaxation rate ($1/T_1$) of water confined in the extended nanochannels was measured and the activation energy ($E_a$) was estimated from the temperature dependence of $1/T_1$. $E_a$ corresponds to the energy required for breaking and re-forming of hydrogen bonds between water molecules and low $E_a$ means fast proton transfer (Figure 3).

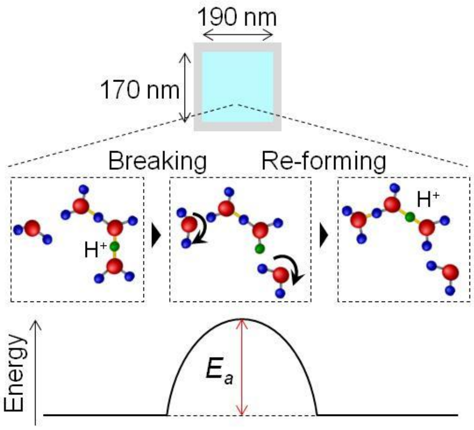

*Figure 3. Schematic illustration of the activation energy ($E_a$).*

## RESULTS AND DISCUSSION

The result of NMR measurements is shown in Figure 4. The $E_a$ decreases with increasing surface silanol density, and is 3 times lower than that in bulk at the highest density. This indicates proton transfer in water molecules confined in extended nanochannel is more enhanced at the higher surface silanol density. This result strongly suggests that surface silanol groups are dominant factor of proton transfer phase and enhance proton transfer in extended nanospace.

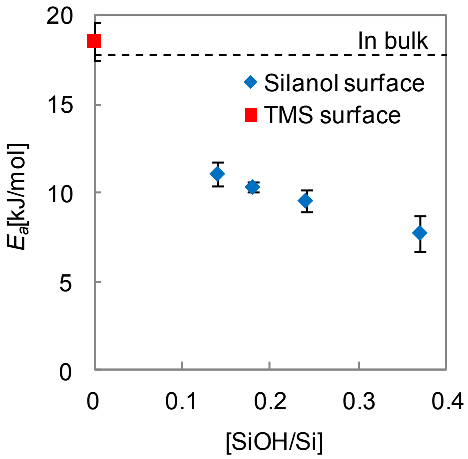

*Figure 4. Dependency of the activation energy ($E_a$) on surface silanol density ([SiOH/Si]). Dotted line refers the value in bulk (17.8 kJ/mol).*

## CONCLUSION

We evaluated proton transfer in extended nanochannels where the surface silanol density was controlled. The result of NMR measurements show 3 times lower $E_a$ than they in bulk at the highest silanol density, and strongly suggest the enhancement of proton transfer by surface silanol groups in extended nanospace. This study provides important information for designing charge transfer such as high efficient micro fuel cell.

## ACKNOWLEDGEMENTS

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