Supplementary Information

Gated Proton Transport in Aligned Mesoporous Silica Films

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I. Synthesis of large-scale aligned mesopore thin films

The mesoporous silica(SBA15) films were synthesized by controlled dip-coating of the sol-gel precursor onto a substrate followed by programmed calcination at elevated temperatures(*1*, *2*). First, quartz or thermally-oxidized silicon substrates were successively cleaned with n-hexane, acetone, DI water, and piranha solution (H_2SO_4:H_2O_2 = 2:1 v/v). They were then rinsed with nanopure water, cleaned with 2-isopropanol assisted by ultrasonication, and dried in air. The synthetic approach for mesoporous SBA15 silica was based on a copolymer template method (Figure S1. a and b). Triblock copolymer P123 (0.081 g, 0.014 mmol) was dissolved in EtOH (2.85 g, 61.88 mmol) and the mixture was stirred at room temperature for 1 h in a capped vial. Another solution containing TEOS (0.30 g, 1.44 mmol), EtOH (3.0 g, 65.13 mmol), water (0.156 g, 8.67 mmol), and 0.1 M HCl (0.03 g, 0.003 mmol) in a separate capped vial was stirred at room temperature for 1 hr. These two solutions were then combined in an open container and further stirred at room temperature for 1 hr. Quartz or silicon substrates were immersed in the as-prepared solution for 5 sec and carefully withdrawn, and then aged at room temperature for 24 h and then annealed at 70 °C for 1 hr. The substrates were always held vertically in order to ensure the shear-induced alignment of mesochannels. The low concentration of sol-gel precursors led to the formation of a sufficiently thin layer through dip-coating (with a speed of ~1 cm/sec), which ensures the quality of transferred films as well as good micelle alignment induced by shear force (Figure S1.c). If the coated layer appears too thick, further dilution is needed to reach the

optimal thickness (~100nm). To remove the polymer template, calcination of the as-made thin films was performed by heating the samples in air with a very slow ramping rate (<1 °C/min) from room temperature to 500 °C, and then hold for 5 hours to burn off all organics. After calcination, the thin film appears smooth, uniform, and free of any crack or delamination, as shown in Figure S1d.

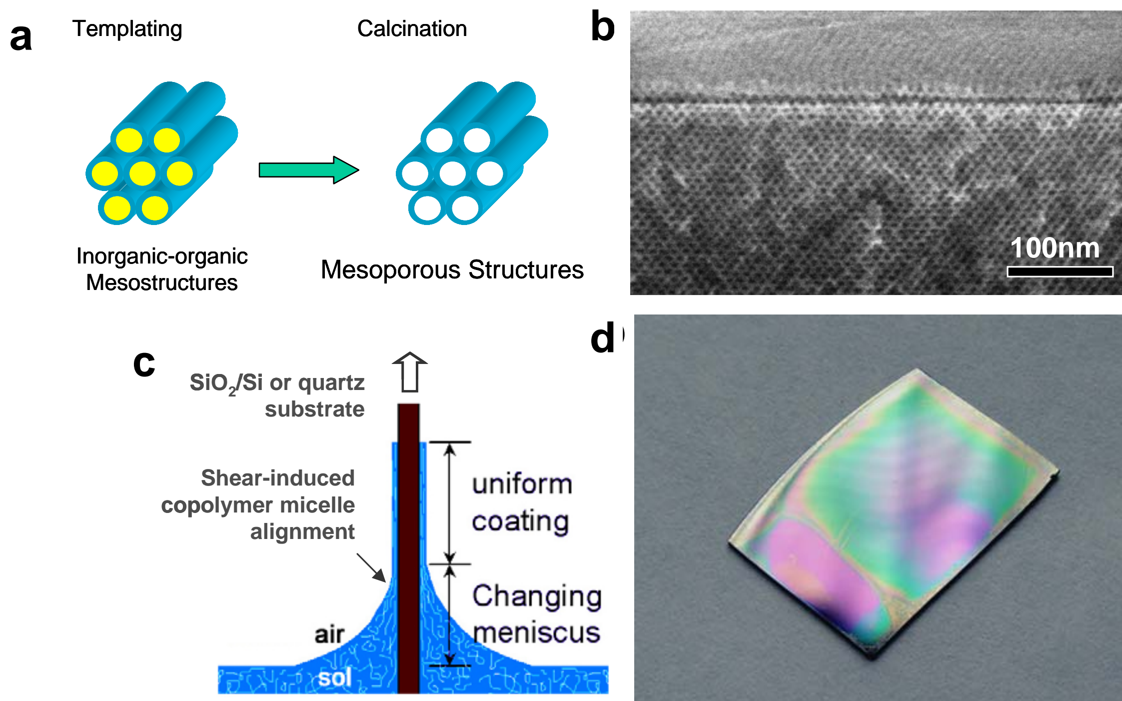

Figure S1 Controlled dip-coating approach to synthesize large-scale aligned mesochannel thin films. a, Schematic of block-polymer template synthesis. **b,** Scanning electron micrograph of calcined SBA15 materials. **c,** Schematic of shear-induced micelle alignment in dip-coating process. **d,** Picture of an aligned mesochannel thin film coated on SiO_2/Si substrate (size 1.5cmx2cm).

II. Coarse patterning of SBA15 thin film stripes for the measurement of concentration dependent ionic conductance

The calcined nanochannel thin film was patterned in form of macroscopic stripes(~2mm wide). Their edges are perpendicular to mesochannels. The fabrication process is detailed in the following. As-made SBA15 thin films on quartz or silicon dioxide substrates were coated with a layer of 2-µm thick G-line photoresist, and exposed using the Quintel mask

aligner (Berkeley Microfabrication Laboratory). After development, a low power (50W) oxygen plasma was used to remove the photoresist residue in the exposed area, and then photoresist was hard-baked at 120°C for 120min. Next, using these hard-baked photoresist stripes as etching mask, the pattern was transferred down to the mesoporous film by reactive ion etching in CHF_3/CF_4 plasma (Lam Research Inc.) at 850W for ~1-2 min, which produced parallel trenches into the substrates and opened the the cross-section of mesochannels to assess outside fluids.

Due to surface hydrophobicity and low surface charge densities in as-calcined SBA15 thin films. The nanochannels need to be activated by placing a drop of HCl solution (0.1-1M) in each trench for ~6 hrs and then thoroughly rinsed with DI water several times. In some experiments, a high voltage (+/-10V) was found to help accelerate this surface reactivation process. Once nanochannels are sufficiently hydrophilic, I/V curves become ohmic with negligible hysteresis, in contrast to the huge non-linear loop that is observed before reactivation. However, this process does not ensure 100% activation and a large portion of the nanochannels may remain non-wettable.

III. Fabrication of the mesochannel nanofluidic device that has metallic gate electrodes

The device was fabricated by integration of a PDMS microfluidic chip and the patterned SBA15 micropatches. First, the calcined SBA film on quartz or silicon dioxide substrates were coated with a layer of 2-μm thick G-line photoresist, exposed using Quintel mask aligner to form the square patterns (~400μmx400μm), developed with OCG 943 2:1 solution for 80sec, and finally de-scummed in oxygen plasma at 50W for 1min. The photoresist pattern was hard-baked at 120°C for 120min to produce a robust masking layer. Second, the mesoporous film patches were defined by reactive ion etching (RIE) in the CHF_3/CF_4 plasma at 850W for 1-2 min to etch through the entire thickness of SBA15 film. Afterwards, photoresist layer was stripped off using the PRS3000 photoresist remover (J.T. Baker) at 80°C overnight, and then the sample was descummed in oxygen plasma. Third, a Cr/Au (2nm/30nm) layer was sputter-deposited onto the entire substrate. A layer of G-line photoresist (1.3μm) was spun onto the Cr/Au coated sample, and then

exposed to define the position of gate electrode. Right after descum, a two-step wet-etching process - Au etching with a saturated KI/I_2 solution and Cr etching with a CR7 mask etchant - was performed to produce metal gate electrodes. The end-point for Au etching process was identified by color change, while the Cr layer was etched off by dipping into CR7 solution (Cyantek Coorperation) for 10sec. In the end, the photoresist was stripped off using PRS3000 or acetone. The fabrication process is shown in Fig. S2.

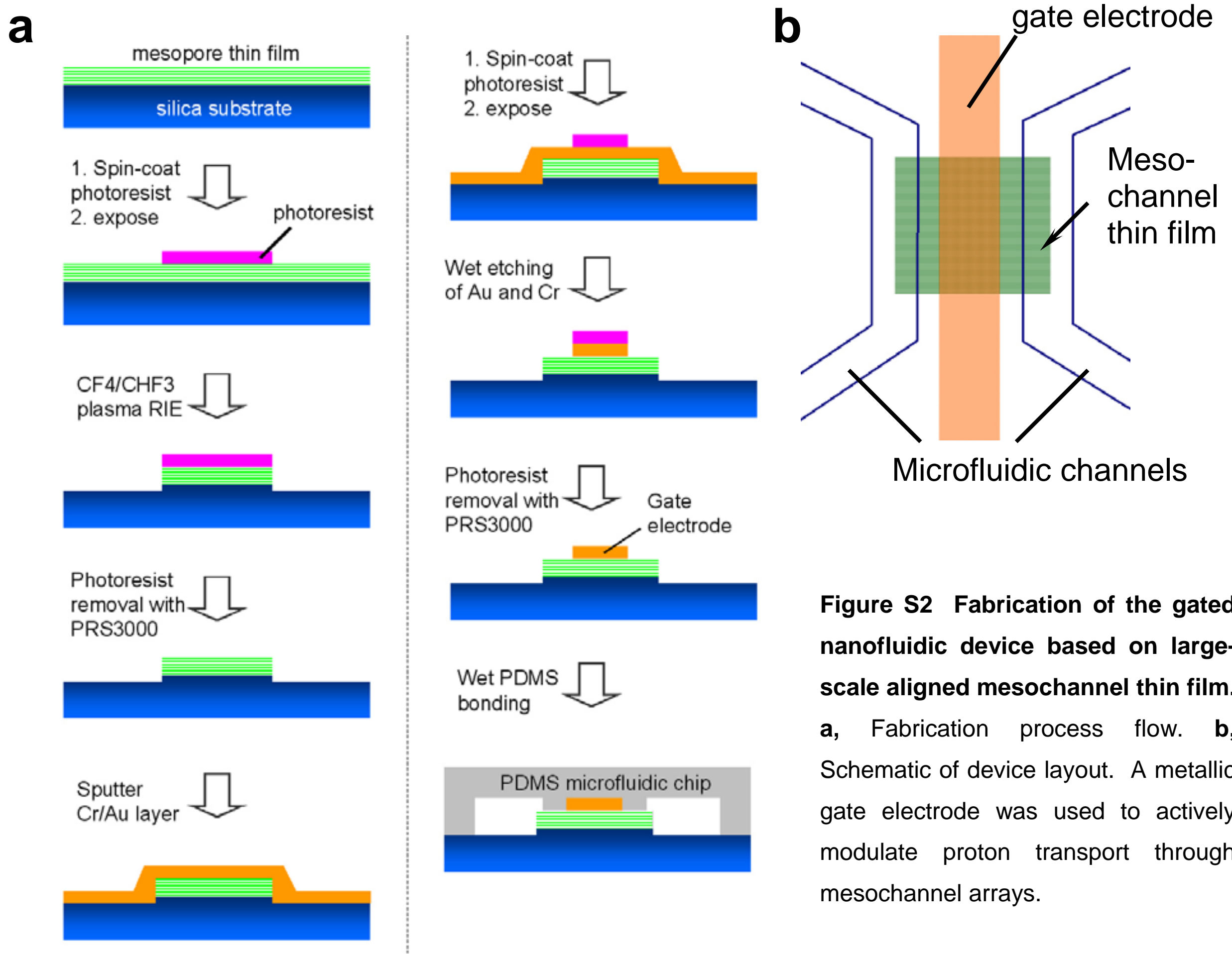

Figure S2 Fabrication of the gated nanofluidic device based on large-scale aligned mesochannel thin film. **a,** Fabrication process flow. **b,** Schematic of device layout. A metallic gate electrode was used to actively modulate proton transport through mesochannel arrays.

In the meantime, a PDMS microfluidic chip was separately fabricated by soft lithography(*3, 4*). First, a silicon hard mold was made using a 4μm-thick G-line photoresist as the etch mask. The photoresist on a 4″ silicon wafer was exposed with the Quintel aligner, descummed in oxygen plasma, hard-baked at 120°C for 120min, and then

treated with CF_4/CHF_3 plasma to remove native oxide. The pattern was transferred using the ICP-DRIE system (STS) through a series of SF_6 etching/C_4F_8 passivation cycles to reach a 100μm depth. Without the need of stripping off photoresist, this silicon master was ready for molding PDMS devices Next, a mixture of PDMS prepolymer (Sylgard 184, Dow Corning) and the initiator (10:1) was prepared, stirred, degassed and then applied to the silicon master that was pre-silanized with trimethylchlorosilane(TMCS) for 10min to aid the release of mold. After curing at 70°C for 1hr, PDMS microfluidic chips were peeled off the mold and cut to desired size.

Finally, the PDMS chip was bonded onto the mesoporous thin film sample using a wet-PDMS bonding method(*5*). First, the PDMS chip was cleaned with isopropanol (IPA) and DI water assisted by ultrasonication, and the access holes were drilled. Second, a thin layer of wet PDMS precursor/initiator mixture (10:1) was spun onto a clean silicon substrate at 8000rpm to yield a thin layer of wet PDMS (~5-20μm in thickness). A layer of wet-PDMS was transferred to the feature side of PDMS chip by direct contact. Within half an hour, this PDMS chip was carefully aligned and bonded onto the patterned mesopore micro-patch chip described above using a dark-field microscope. It was then moved into a convection oven and cured at 80°C for another hour to completely seal the whole device. This bonding method also ensures the insulation of gate electrode from both microfuidic channels. The completed device features three sets of mesopore patches (~400μmx400μm) each having a metallic gate electrode (~100-200μm wide) on the top and two microfluidic channels(~400μm wide, ~100μm deep) at both sides to create an integrated nanofluidic device.

To increase the wettability and surface charge density in the calcined SBA15 thin film, the mesopore film chip was hydrothermally treated in an autoclave using the vapor of a 0.1M HCl solution at 120°C for ~3hrs before it was bonded onto PDMS device. This step is critical to restore the silanol group on the silica surface such that the nanochannels become sufficiently hydrophilic and allow aqueous solutions to be pulled in via capillary action. This surface activation is critical to improve the effective proton conductivity.

IV. Electrical measurement of proton/ion conduction

All ionic conductance measurements were carried out in a Faraday shielding cage, which has the same ground with all other instruments used. The current-voltage (I/V) characteristics were measured with the Keithley 236 source-measure unit. The gate voltage was applied using the Keithley 230 voltage source. All instruments were controlled using a Labview program. The open circuit background noise at bias=1V is as low as 0.5pA when the leads were not connected to the nanofluidic device at all. A control experiment on a blank device without nanochannels gave rise to a typical noise level of ~1-2pA. In the typical setup, the source/drain electrodes were inserted into the plastic tubes that were used to deliver solutions into microfluidic channels, or simply inserted to the solution droplets in the outlet ports, to measure out DC ionic conductance. A syringe pump was used to control the delivery of solutions.

As metal contacts always play a key role in solid state electronics, the selection of electrodes here is also crucial. In the case of chloride solution and pure water, the Ag/AgCl electrodes worked properly with negligible potential barrier. In our experiment, Ag/AgCl electrodes were fabricated using an electrochemical method. A pure Ag wire and a counter Pt electrode were inserted in a 0.1M HCl solution. A voltage of ~ +0.35V was applied to the Ag electrode with Keithley 236 unit, giving rise to a typical ionic current of ~80μA. A few seconds later, gas bubbles emerged from the Pt counter electrode indicating the occurrence of electrochemical reactions. Usually, it takes ~5-10min to finish the electrochemical preparation of Ag/AgCl electrode. In the end, a thin, dense and dark-gray layer was coated on the surface of Ag electrode. This optimum voltage was found to be right before the onset of the first anodization peak in the cyclic voltammetric curve. A higher voltage will cause the reaction to proceed too rapidly. As a result, a porous, fragile and light gray coating layer was formed, which did not work well as a low barrier electrode and could easily delaminate from Ag electrode surface.

V. Estimation of single pore conductance

The sample geometry was precisely defined in the microscopic patch device described in Fig S3. A lithographically patterned thin film patch is 400μmx400μmx100nm (*LxWxH*). The measured conductance is ~10 nS at V_g=0V. According to the XRD data, inter-mesopore distance is ~8nm, which determines the total number of pores within the cross-section of the thin film patch is ~7.5x10^5. The proton conductance per pore is thus ~1.3x10^{-14} S. Because of cation enrichment due to unipolar environment in mesopores, we cannot use the bulk concentration to estimate the conductance per channel. Instead, an enhancement factor, 100, was used according to the concentration dependence study (Fig 2c). Given the mobility of free proton in aqueous solution (~3.45x10^{-7} m^2/Vsec), [refer to (a) Dean, J.A.. (1999). Lange's Handbook of Chemistry, 15th Edition, McGraw-Hill, New York. and (b) Vanysek, P. (2002), Ionic conductivity and diffusion at infinite dilution. *In*: CRC Handbook of Chemistry and Physics, 83rd Edn; ed. D.R. Lide, CRC Press, Boca Raton], and the mesopore diameter(~6nm), the estimate of ionic conductance per pore is ~2.35 x 10^{-14} S.

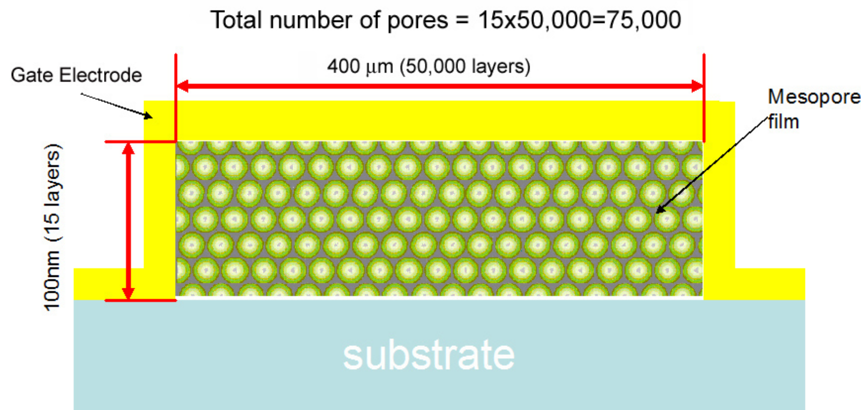

Figure S3. Schematic illustration for the dimensions of the lithographically patterned mesopore thin film patches

This implies that the effective number of activated mesopores is ~1/2 of the total number. Many factors including the incomplete activation of inner surfaces, the defects and discontinuity of mesochannels could contribute to the observed ionic conductance in actual devices. In addition, the longer the mesochannels, the more difficult the mesochannels can be completely activated and the higher probability the defects will

occur. This is evident by the lower conductance observed in the macroscopic mesoporous films (Fig 2c). Nevertheless, the observed proton conductivity is in the same order of magnitude as what one would expect.

VI. Leakage current consideration

In order to assess the influence of leak current across mesochannels, the drain-gate current at zero bias was always monitored in our experiments. For example, in the experiment with 0.1mM HCl, the measured leak current at $V_d=0$ ($[I-I_0]_{Vd=0}$), the total current at V_d=2V ($[I-I_0]_{Vd=2V}$), and the effective gatable current (total current – leak current) are plotted in Fig. S4, where V_d is the drain voltage, V_g is the gate voltage, I is the measured drain current, and I_0 is the system drift when both V_d and V_g are zero.

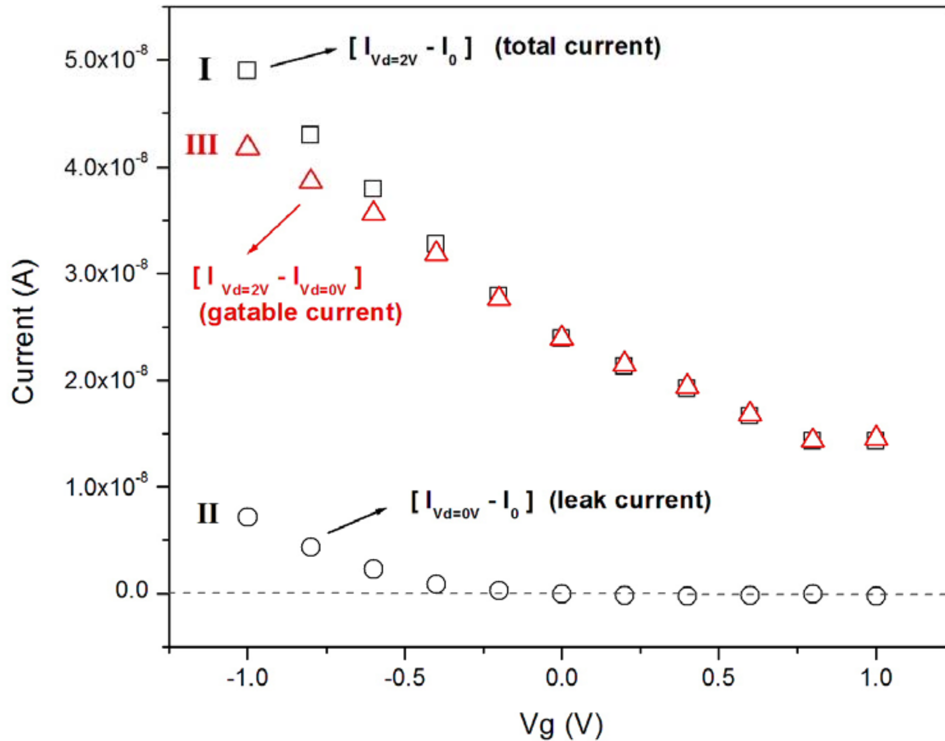

Figure S4. Leak current measurement and the effective gatable current. Total current (I) at forward bias of 2V, drain-gate leak current (II) and effective gatable current (III, red) vs. the gate voltage measured with the 0.1mM HCl solution are plotted. V_d is the drain voltage, V_g is the gate voltage, I is the measured drain current, and I_0 is the system drift when both V_d and V_g are zero. It shows that the gatable current (red triangle) is much greater than the leak current, and is subjected to gate modulation. To best present the data for the purpose of assessing gate control of ionic current, zero shift including both leak current and system drift has been subtracted in the measurement shown in Fig. 3c.

It shows that leak current is in general one order of magnitude lower than the drain current. By subtracting the leak current from the total current, the effective drain current (data III, red) still exhibits strong gate modulation that manifests the realization of gate control of ionic concentration and accordingly ionic conductance. By comparing the total measured current (I in Fig. S4) and the gatable current (III in Fig. S4), it is clear that proton conduction can be effectively modulated by gate voltage, while the leak current has minimum effect.

References

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