Supplementary Information

Modifying Surface Charge Density of Thermoplastic Nanofluidic Biosensors by Multivalent Cations within the Slip Plane of the Electric Double Layer

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1. Fabrication of polymer nanochannels

1.1 General fabrication steps

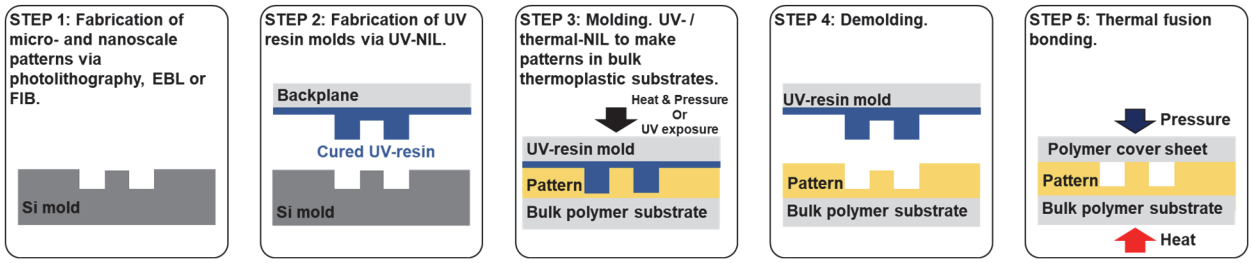

Figure S1. Steps to fabricate polymer based in-plane nanopore via NIL using UV-resin mold: (1) fabrication of Si mater mold; (2) fabrication of UV-resin mold; (3) thermal/ UV imprint into polymer substrate using UV-resin mold; and (4) UV-resin mold demolding from patterned substrate. (5) thermal bonding of the imprinted structure with cover sheet to make complete devices. For imprinting, PEGDA was exposed to flash-type UV light (250-400 nm) for 1 min at an intensity of ~1.8 W/cm^2 by using a PMMA substrate as a backbone structure in STEP 3. PMMA and COC were thermally imprinted at 135 °C, 3.5 MPa and 160 °C, 5 MPa for 15 min, respectively. For bonding, imprinted nanofluidic devices on PEGDA, PMMA and COC are bonded to a thin COC cover sheet at 70 °C, 1 MPa for 15 min.

1.2 Polymer nanochannels for conductance measurement

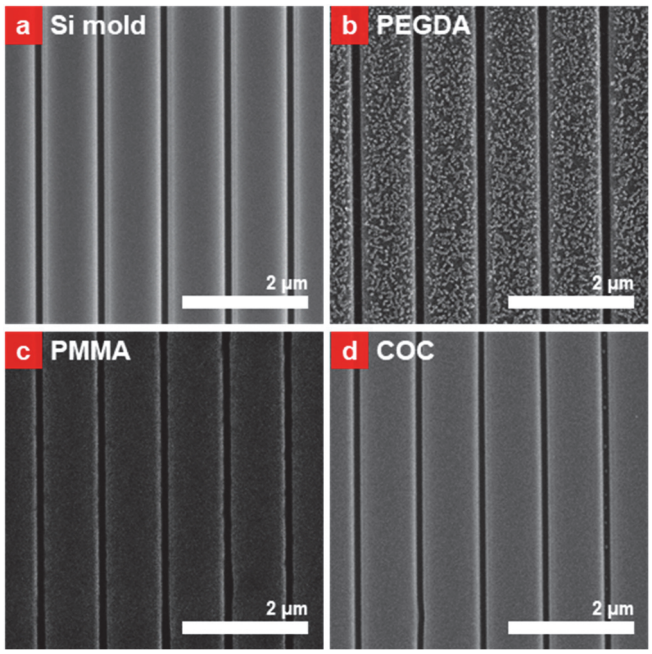

Figure S2. SEM images of nanochannel devices for conductance measurement. (a) Si master mold, (b) UV imprinted nanochannels on PEGDA substrate, (c) thermal imprinted nanochannels on PMMA substrate, and (d) thermal imprinted nanochannels on COC substrate.

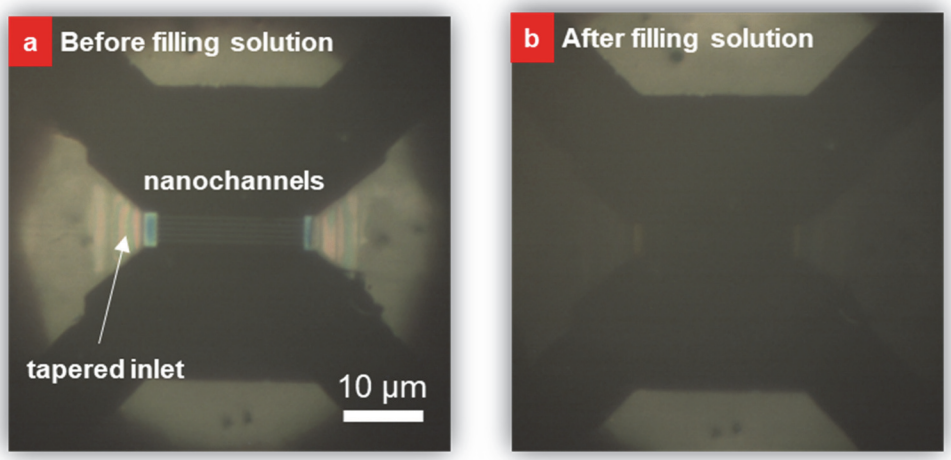

Figure S3. Optical images of nanochannels before and after filling salt solution. (a) before filling salt solution, five imprinted nanochannels were observed, (b) after filling solution, we inspected the nanochannels and the micro-inlet area to make sure there was no trapped air bubbles and the devices were wet completely.

2. Stability of Al^{3+} modified COC substrate

2.1 Nanochannel conductance vs withdraw-and-refill cycles

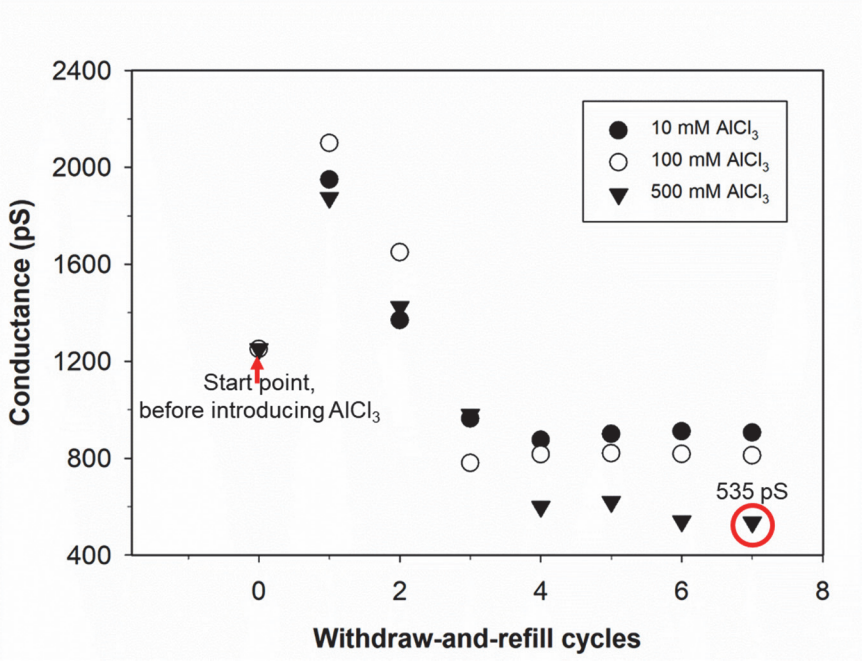

Figure S4. COC nanochannel conductance as a function of withdraw-and-refill cycles. Within the first two cycles, nanochannel conductance was even higher than the reference due to remaining high concentration $AlCl_3$ in nanochannel. After four cycles, nanochannel conductance reduced to a saturated value, which reflected its effective surface charge density, $\sigma_{eff,\ AlCl3}$. After the seventh cycle, nanochannel conductance reach to 535 pS as indicated in the red circle.

2.2 Modification stability

Table S1. Conductance of 500 mM $AlCl_3$ modified COC nanochannel after continuously measurement under a bias of 1V for 0.5 hour, 1 hour, 1.5 hours and 2 hours.

Time	0.5 hour	1 hour	1.5 hours	2 hours
Conductance (pS)	570	576	581	585

3. Translocation of λ-DNA through $AlCl_3$ modified COC in-plane nanopore

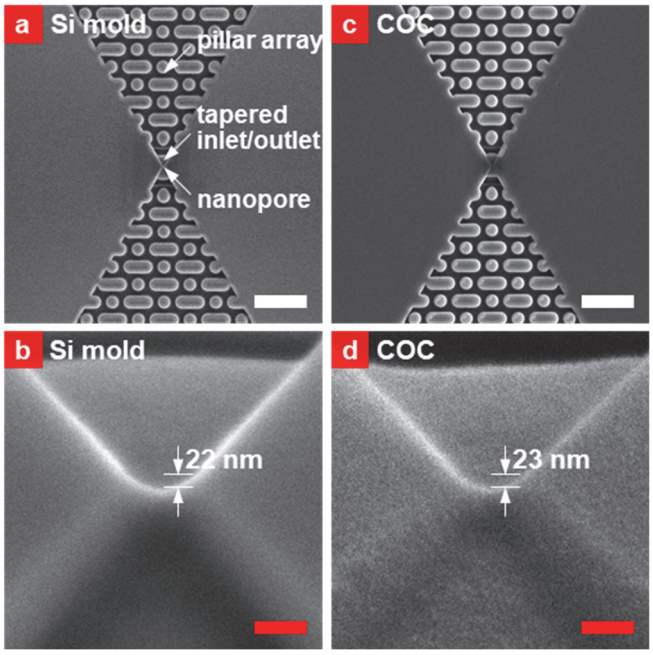

Figure S5. SEM images of Si master mold (a, b) and imprinted in-plane nanopore on COC (c, d) substrates. Nanopillar arrays with 300 nm gap and tapered inlet/outlet with an angle of 60° are designed to pre-stretch DNA. Scale bars, 3 μm in white and 100 nm red. Imprinted planar nanopore has an equivalent pore diameter of 10.3 ± 3.3 nm.

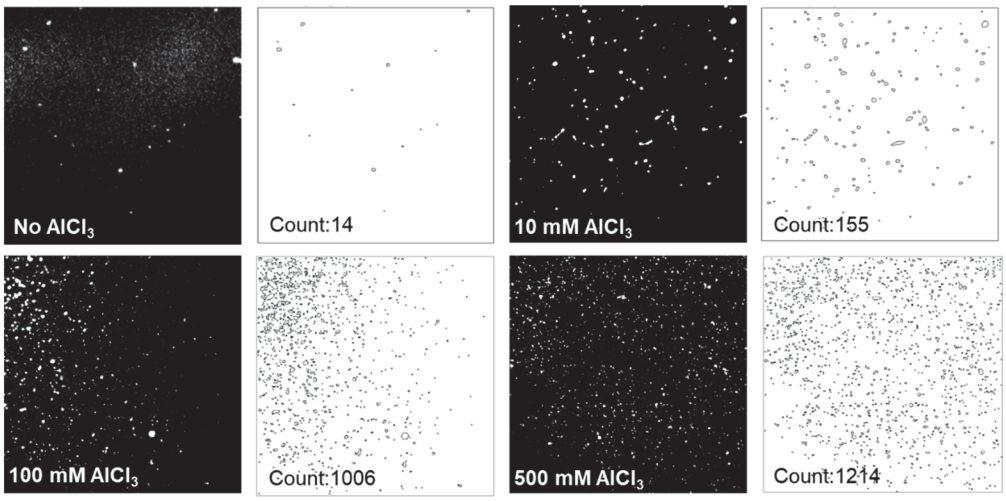

Figure S6. Fluorescence images of λ-DNA binding to COC microchannel wall modified by $AlCl_3$ having different concentration and their ImageJ images to count the number of DNAs bound at the surface.

4. Conductance vs. Surface charge density

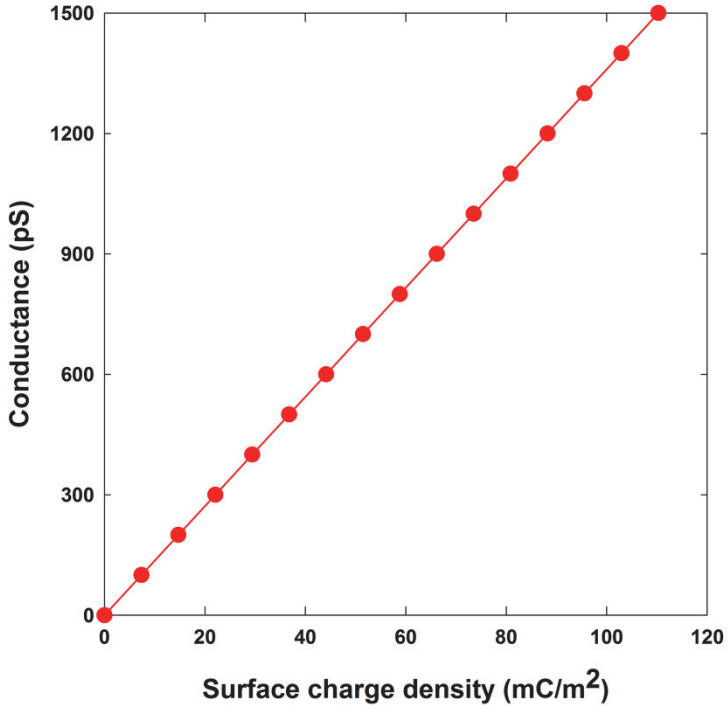

Figure S7. The calibration plot between conductance and surface charge density calculated using Equation (1).

Since we simply used the equation (1) to relate the measured conductance values to the surface charge density, they should show a linear relationship.