

Electronic Supplementary Information

**Gating of Responsive Multiple Nanochannels by Ultra-Low
Concentration of Saccharides**

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1. Experimental section

Materials. N-Isopropyl acrylamide, trichlorovinylsilane were purchased from Sigma-Aldrich. 2,2'-azobisisobutyronitrile (AIBN) were purchased from Sinopharm Chemical Reagent Co. Ltd. N-Isopropyl acrylamide (NIPAAm) was recrystallized in n-hexane three times. S-benzyl dithiobenzoate (BDTB) and 3-(acryloylthioureido) phenylboronic acid (ATPBA) was synthesized according to the literature.¹ Porous anodic alumina (PAA) membranes were purchased from Pu Yuan nano, China. Other reagents were of analytical grade. Milli-Q ultrapure water was used in all needed experiments.

Preparation of P(ATPBA-co-NIPAAm) copolymer. P(ATPBA-co-NIPAAm) copolymer was synthesized by reversible addition-fragmentation chain transfer (RAFT) polymerization according to literature.² Briefly, NIPAAm, ATPBA, BDTB and AIBN were charged in a Schlenk tube in the molar ratio of 170: 30: 2: 1. Certain amount of 1,4-dioxane/methanol (4:1) was added to dissolve the mixture. After the mixture was degassed three times, the tube was kept in an oil bath at 70 °C for polymerization. After 20 h, chloroform was added to terminate the polymerization. The P(ATPBA-co-NIPAAm) was precipitated by excess amount of hexane. The precipitate was re-dissolved in chloroform and then precipitated by hexane again. The precipitation process was repeated for at least three times. The purified products with light orange color were dried under vacuum overnight. The molecular weight M_w of products was 3500 ($M_w/M_n=1.10$) determined by gel permeation chromatography.

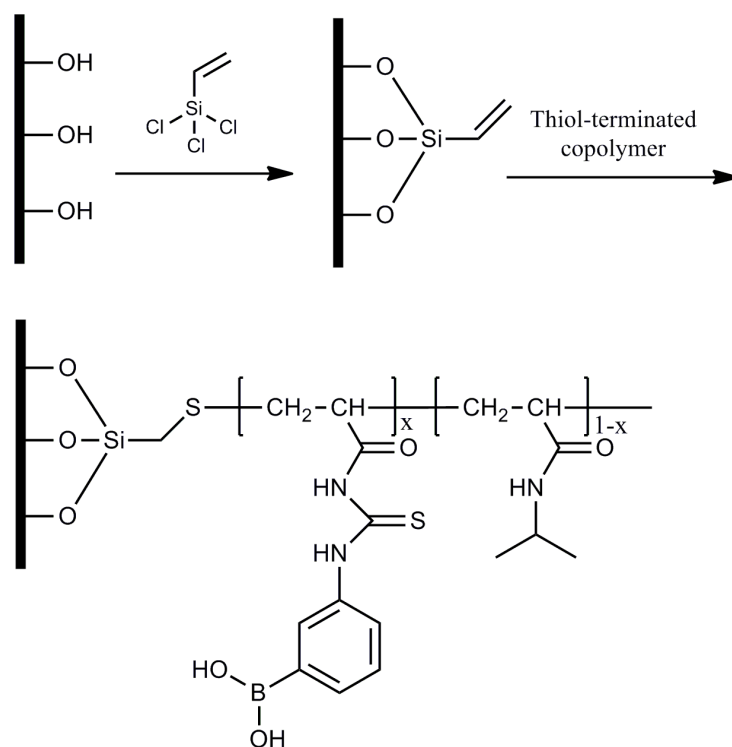
Modification of PAA with P(ATPBA-co-NIPAAm) copolymer. The PAA

membranes were treated by oxygen plasma at 200 W for 5 min to generate hydroxyl groups. Then the membranes were immersed in a mixture of 0.5 ml trichlorovinylsilane and 20 ml toluene at room temperature for 12 h to afford chemically bonded -CH=CH₂ group. The membranes were washed twice with methanol to remove the physically adsorbed trichlorovinylsilane. Then, the membranes were dried using N₂ and heated at 60 °C for 4h. Subsequently, a “thiol-ene” click reaction was carried out between the vinyl group on surface and thiol group of copolymers (Scheme S1). Briefly, 20 mg P(ATPBA-*co*-NIPAAm) copolymer powder was firstly dissolved in 10 mL methanol containing 2 mM NaBH₄ and incubated for 2 h. Then, the PAA membrane was immersed in the copolymer solution. The reaction was carried in N₂ atmosphere at for 12 h at 65 °C.

Characterization methods. Scanning electron microscope (SEM) images were obtained on a Hitachi S-4800 scanning electron microscope. X-ray photoelectron spectra (XPS) were recorded on a VG Multilab 2000 XPS system. Contact angle data were recorded on a Dataphysics OCA35 goniometer.

Electrical Measurements. A piece of nanochannel membrane was mounted in between a two-compartment electrochemical cell according to the literature.³ Ag/AgCl electrodes were used to apply a transmembrane potential across the membrane. The transmembrane ionic current was measured with a Keithley 6487 picoammeter/voltage source (Keithley Instruments) through Ag/AgCl electrodes. The effective area for ionic conduction measurements was ~20 mm². The electrolyte was 0.5 M NaCl solution.

2. Supplementary Figures



Scheme S1 Modification of nanochannels with saccharide-responsive copolymers P(ATPBA-co-NIPAAm) via “thiol-ene” click chemistry.

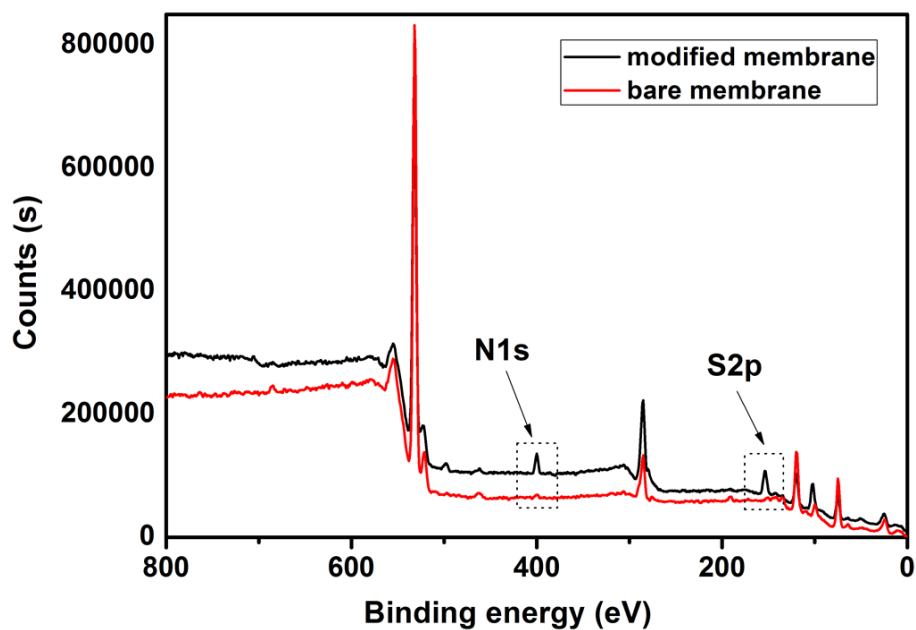


Fig. S1 XPS spectra of bare (red) and modified (black) PAA membranes.

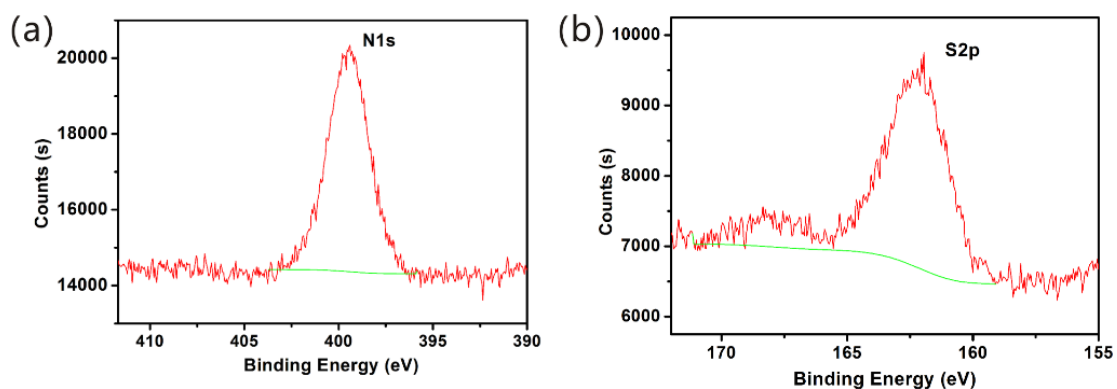


Fig. S2 The narrow scan XPS spectra of PAA membrane after copolymer modification. (a) N1s; (b) S2p.

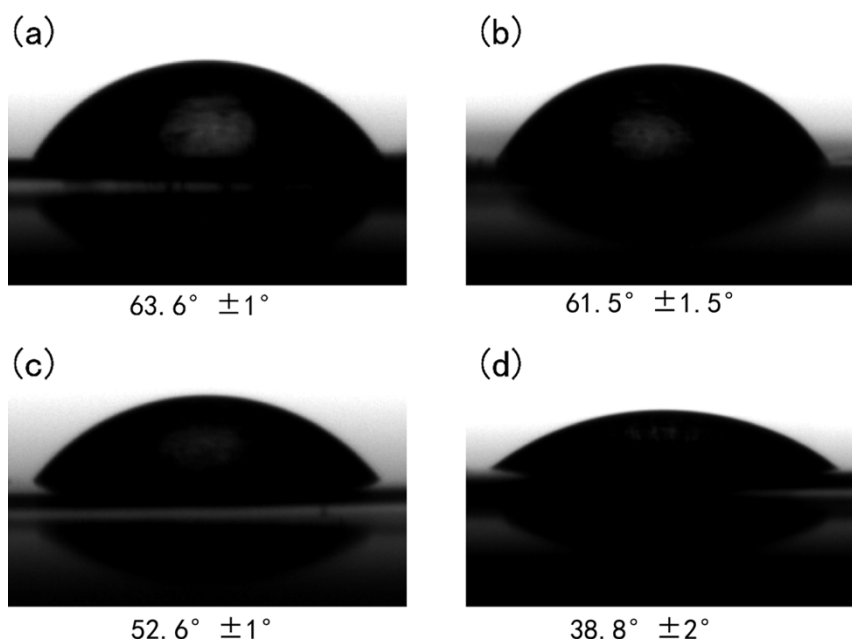


Fig. S3 (a-b) Water drop profiles for contact angle measurement on bare PAA membranes before (a) and after (b) immersion in glucose solution (10^{-2} M) for 10 min; (c-d) Water drop profiles on modified PAA membranes before (a) and after (b) immersion in glucose solution (10^{-2} M) for 10 min.

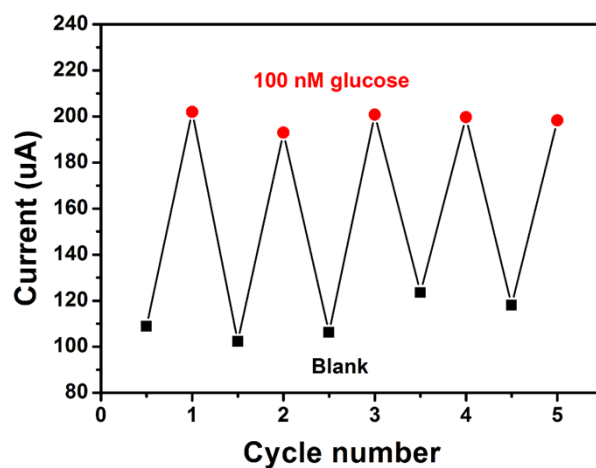


Fig. S4 Cycling experiment of modified nanochannels. A cycle includes the measurement of transmembrane ionic current at +0.2 V both after immersion of the membrane in blank electrolyte for 10 min and after immersion in 100 nM glucose solution for 10 min.

Reference

1. G. Qing, X. Wang, L. Jiang, H. Fuchs and T. Sun, *Soft Matter*, 2009, **5**, 2759.
2. M. Zhang, G. Qing, C. Xiong, R. Cui, D.-W. Pang and T. Sun, *Adv. Mater.*, 2013, **25**, 749.
3. P. Y. Apel, Y. E. Korchev, Z. Siwy, R. Spohr and M. Yoshida, *Nucl. Instrum. Meth. B*, 2001, **184**, 337-346.