Supplementary Information

Highly-efficient lonic Gating of Solid-State Nanosensor by the Reversible

Interaction between the pillar[6]arenes-AuNPs and Azobenzene

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Experimental Details

Materials: Poly (ethylene terephthalate) (PET, 12 μ m thick) membranes were irradiated with single heavy ion (Au) of energy 11.4 MeV/Nucleon at UNILAC linear accelerator (GSI, Darmatadt, Germany). Sodium hydroxide (NaOH), hydrochloric acid (HCl), formic acid (HCOOH), and potassium chloride (KCl) were purchased from Sinopharm Chemical Reagent Shanghai Co., Ltd. (SCRC, China). All solutions were prepared in MilliQ water (18.2 MQ). Current-voltage curves were measured by a Keithley 6487 picoammeter (Keithley Instruments, Cleveland, OH). Confocal images were acquired using a Zeiss confocal laser scanning unit mounted on a LSM710 fixed-stage upright microscope.

Fabrication of nanochannel:The nanochannel was prepared in PET films using the ion track-etching technique. Before etching process, each side of the PET membranes were exposed in UV light (365 nm) for 1h. To produce nanochannel, etching was performed from one sides. The PET membrane was embedded between the two chambers of a conductivity cell at 30 °C, one chamber was filled with etching solution (9 M NaOH), the other chamber was filled with stopping solution (1 M KCl + 1 M HCOOH). Then a voltage of 1 V was applied across the membrane. The etching process was stopped at a desired current value corresponding to a certain tip diameter.

SEM Characterization and size of single conical nanochannel:The diameter of the base was estimated from the multitrack membrane by field-emission scanning electron microscopy (FESEM) which was etched under the same conditions as the single-channel sample. In this work, before modification the base diameter was about 420 nm.

The diameter of large opening of conical nanochannel which was called base (*D*) was determined by scanning electron microscopy (SEM). The diameter of the small opening which was called tip (d_{tip}) was estimated by Supplementary Equation (1):

$$d_{tip} = \frac{4LI}{\pi k(c)UD}(1)$$

L is the length of the pore, which could be approximated to the thickness of the membrane after chemical etching; *I* is the measured ion current; *U* is the applied voltage; d_{tip} and *D* is the tip diameter and the base diameter respectively; k(c) is the specific conductivity of the electrolyte. For 1 M KCl solution at 25 °C, k(c) is 0.11173 Ω^{-1} cm⁻¹.

The tip diameter was estimated by the above relation, tip was about 22 nm.

Ion currents measurement: Ion currents were measured by a Keithley 6487 picoammeter (Keithley Instruments, Cleveland, OH). Ag/AgCl electrodes were used to apply a

transmembrane potential across the film. The film was mounted between the two halves of the conductance cell. In order to record the I–V curves, a scanning triangle voltage signal from -2V to +2V with a 40 s period was selected. Each test was repeated 5 times to obtain the average current value at different voltage.

Contact angles measurement: Contact angles were measured using an contact-angle system at room temperature and saturated humidity. To each sample, an about 2 μ L water droplet is dispensed onto the substrates. The average contactangle value is obtained at ten different positions of the same sample.

EOF experiments: The experiment used a porous film with a density of 10^7 cm^{-2} . Tip side of the cell was added with the mixture solution (~ 2 mL) of phenol and electrolyte solution (0.1 M KCl). The other side was added electrolyte solution (as permeated solution). Fluorescence intensity of the permeation solution measured with a fluorescence 11 spectrometry system every 30 min, and accumulated 150 min. Perform two comparison tests in this way, no voltage applied, and applied voltage.

Phenol, served as an electrically neutral molecular probe, is used for measuring the enhancement factor (E). By measuring the fluorescence emission of the phenol in the permeate solution to determine the rate of diffusion. Analogous experiments were completed to determine N_{diff} (the rate of diffusion in the absence of applied current and the N_i (the rate with applied current), Supplementary Equation (2):

$$E = \frac{N_i}{N_{diff}} \tag{2}$$

Peclet number (Pe) can be determined by Supplementary Equation (3):

$$E = \frac{P_e}{1 - e^{-P_e}} \tag{3}$$

The V_{eof} is determined using Supplementary Equation (4), where D is the diffusion coefficient for phenol and D = $8.9 \times 10-6$ cm² s⁻¹, L is the membrane thickness and L=12 $\times 10^{-4}$ cm. Supplementary Equation (4):

$$V_{eof} = \frac{P_e D}{L} \tag{4}$$

The ζ potential of the nanochannel walls can be determined by Supplementary Equation (5). Using the known values for the permittivity and viscosity of water ($\epsilon = 6.95 \times 10^{-10} \text{ c}^2 \text{ J}^{-1} \text{ m}^{-1}$, $\eta = 0.890 \text{ cp}$; J_{app} is the applied current density; and the measured resistivity of the electrolyte $\rho=2.23 \text{ K}\Omega \cdot \text{cm}$. Supplementary Equation (5):

$$V_{eof} = \frac{-\varepsilon \zeta \rho J_{app}}{\eta} \tag{5}$$

Surface charge density values (σ) can be estimated from the Gouy–Chapman equation (K⁻¹ =9.61 ×10⁻⁹ (z² c)^{-1/2}), Supplementary Equation (6):

$$\sigma = \frac{\varepsilon \zeta}{\kappa^{-1}} \tag{6}$$

Hence, the surface charge density can be calculated from above equation.

Finite-element computation: Finite-element computations were performed on the Poisson and Nernst–Planck equations using COMSOL Multiphysics 5.3. The equations are shown below:

$$J_i = D_i \Big(\nabla c_i + \frac{z_i F c_i}{RT} \nabla \varphi \Big) + u c_i \tag{7}$$

$$\nabla^2 \varphi = -\frac{F}{\varepsilon} \sum z_i c_i \tag{8}$$

$$\nabla \cdot J_i = 0 \tag{9}$$

Equation 7 is the Nernst–Planck equation that describes the transport property of a charged nanochannel. The electric potential and ionic concentration can be characterized by Eq. 8. Besides, the flux should satisfy the time-independent continuity Eq. 9 when the system reaches a stationary regime. The physical quantities J_i , D_i , c_i , φ , u, R, F, T, and crefer to the ionic flux, diffusion coefficient, ion concentration, electrical potential, fluid velocity, universal gas constant, Faraday constant, absolute temperature, and dielectric constant of the electrolyte solutions, respectively. The coupled equations can be solved by assuming appropriate boundary conditions. The boundary condition for potential φ on the channel wall is Eq. 10; and the ionic flux has zero normal components at boundaries (Eq. 11), where σ represents the surface charge density, and is given by the EOF experiment.

$$\vec{n} \cdot \nabla \varphi = -\frac{\sigma}{\varepsilon} \tag{10}$$

$$\vec{n} \cdot J_i = 0(11)$$

Electrolyte solution was 0.1 M KCl, and the diffusion coefficients of K⁺and Cl⁻ were set as $2.0 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$.