

Supporting information

Experimental section

Fabrication of nanopores

The nanopores were fabricated on a SiN_x (100 nm)//Si (500 μm, heavily doped)//SiN_x (100 nm) substrate (10 mm × 10 mm). A microscale window (70 μm square) was firstly produced by combining photolithography, reactive ion etching, and wet etching procedures. In the center of this window, an approximately 4-μm-wide hole was subsequently opened by using focused ion beam (FIB, Nova200 NanoLab). A square hole (80-μm-wide), far away from the microscale window, was also opened for the following polarization process. On the other hand, 3 wt% P(VDF-TrFE) (70/30) diethyl carbonate solution was spin-coated (4000 rpm) on a Cu foil (10 mm × 10 mm) with CVD-growth graphene monolayer. This P(VDF-TrFE)/graphene layer (approximately 100 nm) was subsequently transferred onto previous SiN_x substrate by a conventional wet graphene transfer technique (see ref ^[16]). Graphene was at the bottom which contacted directly with Si layer. To increase the strength of the transferred polymer film, an additional P(VDF-TrFE) layer (approximately 100 nm) was spin-coated. As-prepared film was then annealed at 135°C for 4 hrs in a quartz tube furnace with flowing argon gas (400 sccm). An array of nanopores (approximately 50 nm in diameter) was subsequently produced by using FIB where these nanopores perforated the suspended 200 nm P(VDF-TrFE)/graphene layer. After an additional annealing process, the nanopores were finally obtained.

Electrical characterization of nanopores

The nanopores conductance as a function of KCl concentration and solution pH was characterized by clamping the nanopore slide between two homemade Teflon cells. Prior to filling KCl solution, isopropanol was employed to improve the wettability of these polymer nanopores. Subsequently, KCl aqueous solution with 5% isopropanol (PH 7.0) was immediately added and replaced by using new saline solution for three times. Two homemade Ag/AgCl electrodes were separately placed into the cells and the current-voltage characteristics (bias range, -0.3 V to 0.3 V and sweep rate, 1 mV/s) were then recorded by using a program-controlled Keithley 2636B source-meter. To reduce the impact of environmental fluctuation, the whole test device was encapsulated into a noise-shielding metallic box. The measurements were carried out from low (0.1 μ M) to high (1 M) KCl concentration where at each concentration, 5 measurements were performed. The pH of KCl solution was adjusted by using 0.1 M KOH (increase) or 0.1 M HCl (decrease) solution. The conductance was finally calculated by considering the channel dimensions.

Charge density–electric field hysteresis loop measurement

Before performing hysteresis loop measurement, P(VDF-TrFE) ferroelectric capacitor (C_F) was firstly fabricated. An 8 mm \times 8 mm P(VDF-TrFE)/graphene layer (approximately 500 nm) was transferred onto a 10 mm \times 10 mm highly doped silicon substrate by the conventional wet graphene transfer technique. Gold top electrode (20 nm thick) was deposited by using e-beam deposition through a 5 mm \times 5 mm shadow mask. The graphene/Si (Ohmic contact) and the gold layer were used as two

electrodes respectively. The polarized charge density as function of electric field was subsequently characterized by using a Sawyer–Tower circuit (**Figure 1f**). In this circuit, a P(VDF-TrFE) capacitor (C_F) was serially connected with a linear ceramic capacitor C_R (1 μ F), which was used as a reference capacitor to sense the charge in the P(VDF-TrFE) capacitor. A program-controlled Keithley 2636B source-meter was employed to generate triangle voltage signals ($V_T, f = 0.02$ Hz) and the voltage (V_Q) on the reference capacitor was recorded. During measurement, the electric field E across the ferroelectric layer could be calculated by $E = (V_T - V_Q)/d$, where d is the thickness of the ferroelectric film. The charge density could be calculated by using $P_r = C_R \cdot V_Q/A$, where A is the cross section area.

PFM characterization of nanopores

Piezoresponse force microscope (PFM, Bruker Multimode-8) was employed to confirm the effectiveness of polarization of C-AFM method. An area of approximately $15 \times 12 \mu\text{m}^2$ was firstly polarized by placing -75 V. Subsequently, a positive 75 V bias was placed (an area of approximately $15 \times 6.5 \mu\text{m}^2$) to flip the polarization state (see Fig.1 g upper dark region). The out-of-plane PFM image was subsequently recorded by using a Pt/Ir-coated Si cantilever and an AC potential at room temperature. The parameters of cantilever were: tip radius, approximately 30 nm, force constant, approximately 40 N/m, and resonant frequency, approximately 280 kHz. The amplitude and frequency of the AC potential were 0.5 V and 17 kHz respectively.

Polarization and inverse polarization for a nanofluidic rectifier

The polarization of P(VDF-TrFE) polymer nanopores was conducted by using a conductive atomic force microscopy (C-AFM, Bruker M-Pico). The bottom graphene/Si electrode was grounded and a constant bias was placed on the top conductive probe electrode. The nanopores were then polarized by scanning the probe (30 $\mu\text{m/s}$) in the whole region of 4- μm -wide hole. Placing a positive bias denoted a positive polarization. For depolarization, -75 V , 60 V , -50 V , 40 V , -30 V , 20 V , and -10 V were sequentially placed onto a positive (75 V) polarized layer. For inverse polarization, -75 V was placed to switch the dipole orientation.

Logic circuit measurements

The basic logic circuits, ‘AND’ and ‘OR’, were integrated by combining two nanofluidic rectifiers and a resistor. We fabricated two types of logic circuits, two-states and three-states circuits, based on the numbers of output states. In the two-states circuits, namely, two output states (high and low potentials), the input ‘0’ and ‘1’ were high (0.8 V) and low (0 V) potential imposed on the circuits respectively. In the three-states circuits (output high, medium, and low potentials), the input ‘ -1 ’, ‘0’, and ‘1’ represented the polarization conditions of nanofluidic rectifiers. Specifically, ‘ -1 ’ was negatively polarized, ‘0’ was absence of polarization, and ‘1’ was positive polarized. ‘ -1 ’, ‘0’, and ‘1’ condition could be reversibly switched in the same device. The potential supply was 0.8 V and the resistance of load was $1\text{ G}\Omega$.

Theory details

A coupled Poisson and Nernst-Planck equations were employed to model the P(VDF-TrFE) nanofluidic rectifier. Under electrostatic field, the ion flux J_i could be described by using a Fickian diffusion term and a drift term:

$$\frac{\partial c_i}{\partial t} = -\nabla \cdot J_i \quad 1 \ll i \ll N \quad (1)$$

$$J_i = -D_i(\nabla c_i + c_i \nabla \phi z_i e / k_B T) \quad (2)$$

Where the index i corresponds to the i^{th} ionic species; c_i , z_i , and D_i are the concentration, charge, and diffusion coefficient of species i respectively; ϕ is the electrostatic potential; e is the elementary charge; k_B is the Boltzmann constant; T is the absolute temperature. The electrostatic potential depends on the “anchored” charges on the wall of polymer nanopores and the mobile charges arising from the space-dependent ion concentrations through the Poisson equation:

$$-\nabla \cdot (\epsilon \epsilon_0 \nabla \phi) = \sum_i z_i e c_i \quad (3)$$

Where ϵ_0 is the vacuum dielectric constant and ϵ is the relative dielectric constant. For simplicity, we considered a two dimensional domain $[0, L_x] \times [0, L_y]$. The initial and boundary conditions could be summarized as:

$$\phi(x, y = 0, t) = 0; \phi(x, y = L_y, t) = \phi_0;$$

$$c_i(x, y = 0, t) = c_i(x, y = L_y, t) = c_i^0;$$

$$\phi(x, 0 < y < L_y, 0) = 0; c_i(x, 0 < y < L_y, 0) = 0$$

where ϕ_0 was given by the potential difference along the nanopore; the ion concentrations both at the top and bottom sides were set the same as the bulk value.

The coupled equations (1) and (3) were then solved numerically by using a commercial finite element solver (COMSOL 5.1) to obtain the distribution of ion concentrations and electrostatic potential. The current through the nanopores was finally integrated by:

$$I = \sum_i \int_L z_i e D_i \left(\frac{\partial c_i}{\partial y} + c_i \frac{\partial \phi}{\partial y} z_i e / k_B T \right) dy \quad (4)$$

where L was a cut line at any cross section inside the nanopore region.

The calculation was subsequently performed on a single 200 nm height conical nanopore where the top and bottom opening are 50 and 35 nm respectively. The KCl concentration was 100 μ M. The charge density of bottom surface contacted with graphene layer was set as 0 because of charge screening effect. At the absence of polarization (corresponding to $P = 0$ in Fig. 3), a homogeneous surface charge distribution with density of $\sigma_s = -1.2$ mC/m² (see Fig. 1d) was chosen for the calculation. Upon polarization, the top face and the bulk body of nanopore (150 nm) were set with surface charge distributions calculated according to the electrodynamic formula $\sigma = \vec{P} \cdot \vec{n}$, where σ , \vec{P} , and \vec{n} were the surface charge density, the intensity of polarization, and a unit normal vector to the surface of dielectric. For a nanopore being completely polarized, \vec{P} was normal to the ferroelectric film and the absolute value was set with the remnant charge density (60 mC/m²) according to the ferroelectric hysteresis loop measurement (Fig. 1e). At the top and bottom opening regions (25 nm for each) were set with linear-gradient surface charge distributions. The parameters were: $D_K = 1.96 \times 10^{-9}$ m²/s, $D_{Cl} = 2.03 \times 10^{-9}$ m²/s; $\epsilon = 70$ (solution), 8 (polymer film); $\epsilon_0 = 8.85 \times 10^{-12}$ F/m; $T = 300$ K.