Supporting Information

Kirigami Nanofluidics

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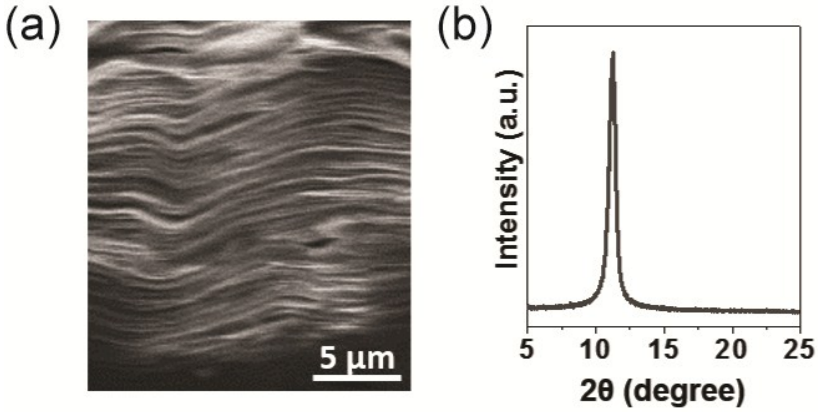

Figure S1. Characterization of the lamellar GO film. The GO is in dry state. (a) Cross-sectional SEM view of the GO paper suggesting lamellar microstructure of the GO paper. (b) XRD pattern of the GO paper indicates a d-spacing of 0.8 nm, which upon hydration can readily expand to around 1.5 nm (see Ref 6a for more details).

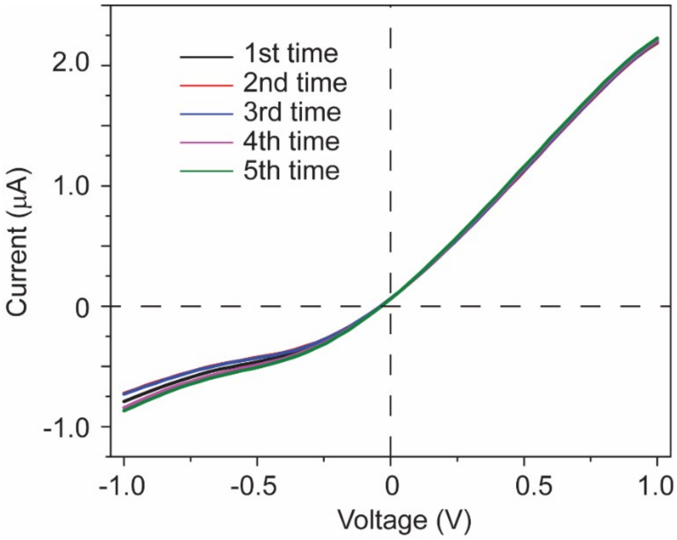

Figure S2. I-V curves are measured 5 times in succession, showing good consistency.

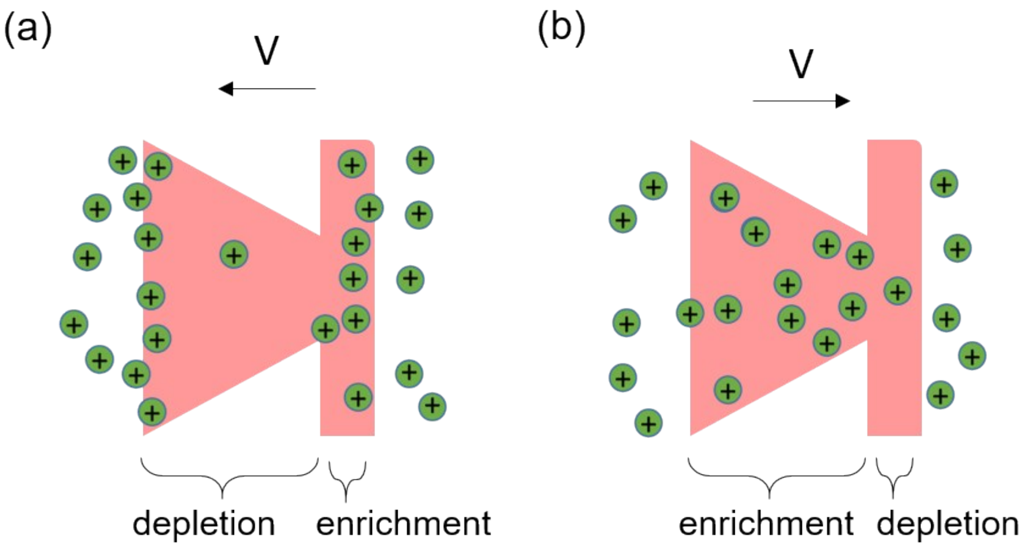

Figure S3 Enrichment-depletion argument predicts ionic rectification for "diode-sign" shaped membrane. The "diode-sign" has a trapezoid part on the left and a rectangle on the right. Under the asymmetric ion flux argument, the trapezoid and rectangle parts should have opposite depletion/enrichment states under either bias. Since the "neck" was intentionally designed to be off-centered, the overall state in (a) should still be "depletion", and (b) "enrichment". Therefore, the "diode-sign" should rectify.

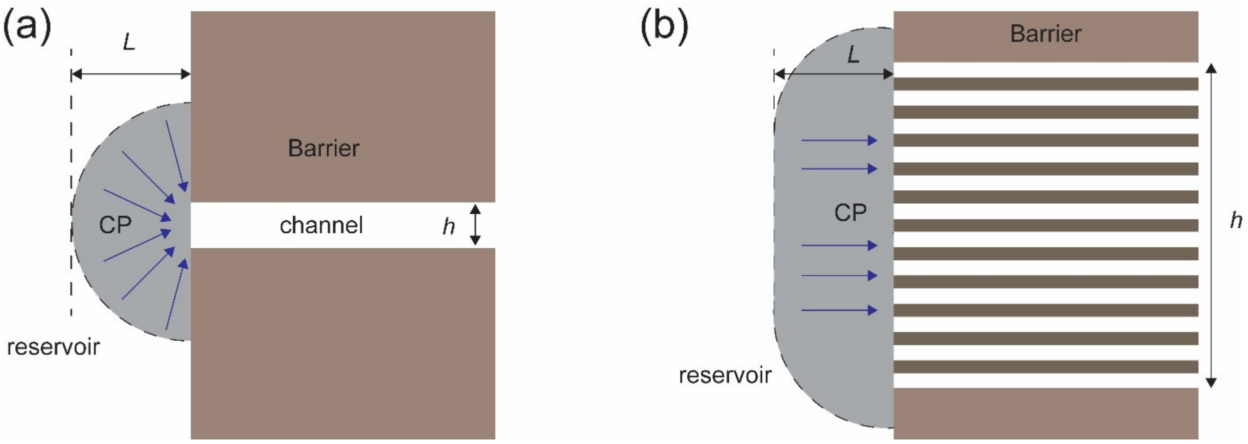

Figure S4. Direction of the currents in the CP layer for (a) *L*>>*h*, and (b) for *L*<<*h*, where *L* is the size of the CP diffusion layer and *h* is the height of a single nanochannel in (a) and the total height of a stacked nanochannel membrane in (b). The blue arrows indicate the direction of the ion current in the CP layer in either case, and shows how the stacked nanochannel system in (b) renders the geometry in the CP layer quasi one-dimensional.

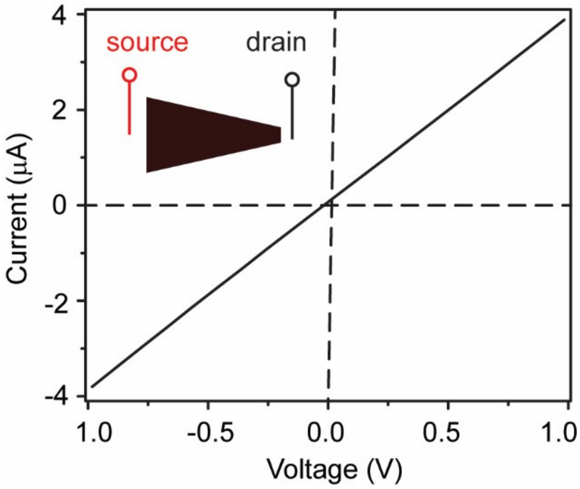

Figure S5. No current rectification when the channels are no longer charge selective. At high electrolyte concentration (e.g., ≥ 50 mM), the Debye layer is screened by electrolyte, causing the channels to lose their charge selectivity. The concentration-polarization mechanism predicts the absence of ionic rectification in this region. Indeed, a trapezoid GO nanofluidic device loses its diode-like property when KCl concentration is 50 mM.

Supporting Note 1: Nonlinear effects and CP-layer geometry

Previously, it has been observed that asymmetric CP zones can induce rectification through a single array of nanofluidic channels, but only when extremely high electrical field is applied ($>10^4$ V/m).[1] By contrast, in our system, rectification starts at around 10 V/m (see Figure 2). Here we offer a more detailed analysis than what was written in the main text.

Strong nonlinear effects can be observed in systems where the resistance of the CP zone is significant, which occurs when the current density J reaches beyond a limiting value J^*.[2] From the onset of strong nonlinear effects (asymmetric in V) in our I-V curves a limiting current $J^* \approx 3$ A / m^2 can be estimated, which puts the upper bound of size of the CP layer to a few microns at the onset of limiting behavior. The GO membrane is approximately 10-20 μm thick, which is relatively large in comparison to the size L of the CP layer. Because of this, we could use here the conventional one-dimensional expression for the limiting current density, $J^* = cF/(2DL)$, with c the bulk concentration, F Faraday's constant and D the diffusion constant. On the other hand, for small nanofluidic systems, such as those made of a single array of 1D nanochannels[1] or just a single 2D nanochannel (illustrated in Figure S4), radial focusing of the current for such small systems would yield a limiting current density

$$J^*_{radial} = J^*4\pi(L/h)\log(L/h),$$

from which a critical current density J^*_{radial} is estimated to be about two orders of magnitude larger than J^* for the same L. As such, in our quasi-one-dimensional CP system, the critical voltage to trigger strong CP effect is drastically lower than in the small systems suffering radial focusing.

The above analysis again highlights one of the main advantages of 2D nanofluidic systems – their scalability. It is the ease to scale up these 2D channels that enables one to observe these CP zone effects at such low applied electric voltages/fields. The above analysis also explains why the restrictive channels at the membrane-electrolyte interface must be introduced in the simulation, which was done on just a few 2D channel (Figure 3b), to more accurately represent our experimental system that contains massive arrays of channels.

Supporting Note 2: Supporting simulation methods

Particle excluded volume was modeled using the shifted-truncated Lennard-Jones potentials of diameter σ = 0.66 nm and strength $\varepsilon = 0.83k_BT$, where the temperature T = 300 K. The solvent was modeled as a continuous dielectric medium with a dielectric constant of 80 and electrostatic energies and forces were calculated using particle–particle particle–mesh Ewald summation with a relative accuracy of 10^{-4}. Brownian effects and thermostatting were modeled implicitly using a Langevin thermostat with damping time 0.5τ, with τ = nm $(m/\varepsilon)^{1/2}$ the Lennard-Jones unit of time, with m the average mass of K^+ and Cl^-.

To model experiments in which the bulk concentration is independent of the applied bias, the bulk region is continually replenished during equilibration until its concentration remains fixed at 7.6 mM, at which point the particle number is kept constant and production begins. Average behavior and statistical errors are determined by at least eight separate simulations with different random-number seeds for each set of parameters.

Supporting References

1. Yossifon, G., Mushenheim, P., Chang, Y.-C. and Chang, H.-C. Nonlinear current-voltage characteristics of nanochannels. *Phys. Rev. E*, **2009**, *79*, 046305.

2. Rubinstein and L. Shtilman, *J. Chem. Soc., Faraday Trans. 2,* **1979**, *75*, 231; I. Rubinstein and B. Zaltzman, *Phys. Rev. E,* **2000**, *62*, 2238.