

Supporting Information

Harvesting ionic power from neutralization reaction through heterogeneous graphene oxide membrane

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1. Supporting Notes

Fabrication of pGO, nGO, and pnGO membranes: The dispersed nGO or pGO nanosheets (contains 20 mg) self-assembled into a membrane upon vacuum filtration on polycarbonate (PC, an average pore size of 200 nm). After drying, the free-standing membranes could be easily exfoliated from the substrate. Heterogeneous pnGO membranes can be fabricated via a two-step vacuum-assisted filtration process. First, nGO layer (contains 10 mg nGO) were fabricated separately through a commonly used vacuum filtration method. Then the suspension solutions (contains 10 mg pGO) of the pGO are vacuum filtrated onto the nGO layer to obtain heterogeneous membranes.

Estimation of the interlayer spacing: The interlayer spacing can be calculated according to Bragg's law:

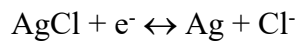
$$2d\sin\theta = n\lambda \quad (1)$$

where λ is the wavelength of the incident wave (1.54 Å) and $n=1$; θ is the angle between the incident wave and the scattering plane; d is the interlayer spacing. Given the theoretical 3.34 Å thickness of single layer GO nanosheet, the free interlayer spacing of nGO membrane and pGO membrane is calculated to be about 3.7 Å and 7.5 Å, respectively.

Electrical measurements: The ion transport properties of the nanofluidics were investigated by measuring the ionic current using the two-compartment electrochemical cell (Fig. S6). The electrical measurements are recorded with a Keithley 6487 source meter (Keithley Instruments, Cleveland, OH). The as-prepared membranes were fixed between a two-compartment electrochemical cell with two reservoirs filled with about 3 mL electrolyte solutions. A pair of homemade Ag/AgCl electrodes was used for recording the current-voltage (I-V) responses. For I-V measurements, testing area was 3.14 mm² and sweeping voltages from - 1.0 V to + 1.0 V was applied across the membrane with the step voltage of 100 mV. For measurements of ionic conductivity and energy conversion, the membranes were clamped by two silicon windows with a side length of 173 μm, which also played a role in limiting swelling through physical

confinement. When testing the ionic conductivity, open circuit voltage and short circuit current, sweeping voltages from - 0.2 V to + 0.2 V was applied across the membrane with the step voltage of 20 mV. For the ion transport test, the two compartments were filled with uniform concentration KCl solutions from 1 μ M to 1 M. For energy conversion test, the two halves of the electrochemical cell were populated with acidic solutions and alkaline solutions, respectively. The short-circuit current (I_{SC} , the current corresponding to zero external bias) and open-circuit voltage (V_{OC} , the potential corresponding to the zero current) of the nanofluidic energy conversion systems were read from the intercepts on the current and voltage axes, respectively.

Supporting electrolyte: Because nanofluidics demonstrate ion selectivity. The continuous asymmetric ion diffusion makes the low-concentration side negatively charged and leaves the high concentration side positively charged, generating a diffusion potential between the inlet and the outlet of the nanochannels. Therefore, to maintain the electroneutrality of the solutions in the two reservoirs, electrochemical redox reactions will occur on the electrode surfaces and the electrons will be transferred to an external circuit. The electrodes used in our experiment were Ag/AgCl electrodes and the redox processes is as follows,



The consumption of H^+ in HCl causes the electrode to undergo the oxidation reaction to consume Cl^- to maintain the electroneutrality of the solution, while the consumption of OH^- in NaOH causes the electrode to undergo a reduction reaction to produce Cl^- to maintain solution electroneutrality.

Considering the solubility product (K_{sp}) of the AgCl and AgOH (easily converted to Ag_2O). The K_{sp} (298.15 K) of AgCl and AgOH (Ag_2O) are 1.77×10^{-10} and 2.0×10^{-8} , respectively (CRC Handbook of chemistry and physical).

When $[\text{Ag}^+][\text{OH}^-] > K_{sp}(\text{AgOH})$, AgOH would form. When $[\text{Ag}^+][\text{Cl}^-] > K_{sp}(\text{AgCl})$, AgCl would form. Therefore, in order to keep AgCl in the precipitation process and keep AgOH (Ag_2O) in a soluble state, the following conditions need to be satisfied:

$$[Cl^-] > \frac{K_{sp}(AgCl)}{K_{sp}(AgOH)/[OH^-]} \quad (2)$$

The maximum concentration of NaOH used is 1 M, and the $[Cl^-]$ needs to be above 8.85×10^{-3} M to avoid the form of AgOH (Ag_2O). Therefore, 0.01 M NaCl is selected as the supporting electrolyte.

2. Supporting Figures

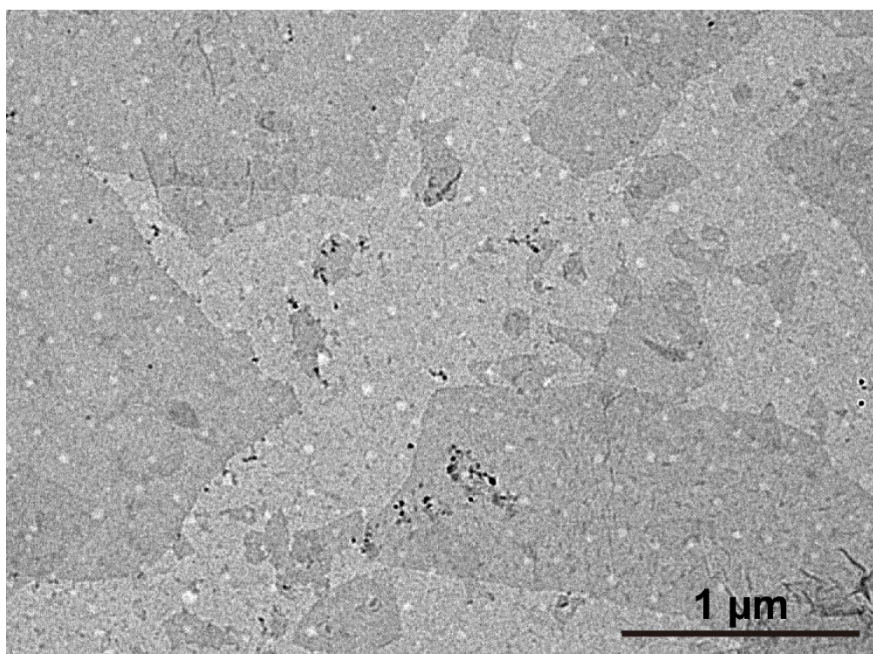


Fig. S1 A typical TEM image of the GO nanosheets.

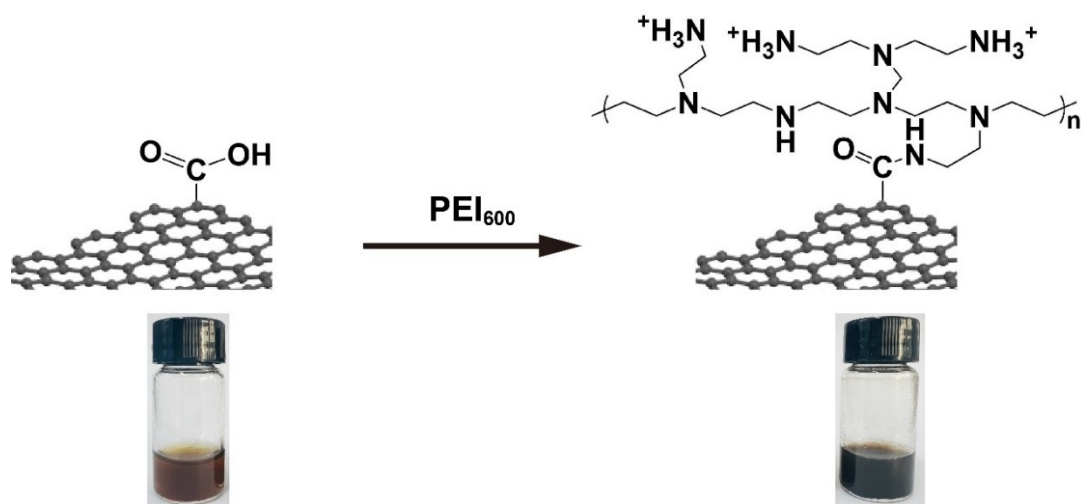


Fig. S2 Synthesis of pGO. Photographs of nGO and pGO dispersions (0.67 mg mL^{-1} , respectively).

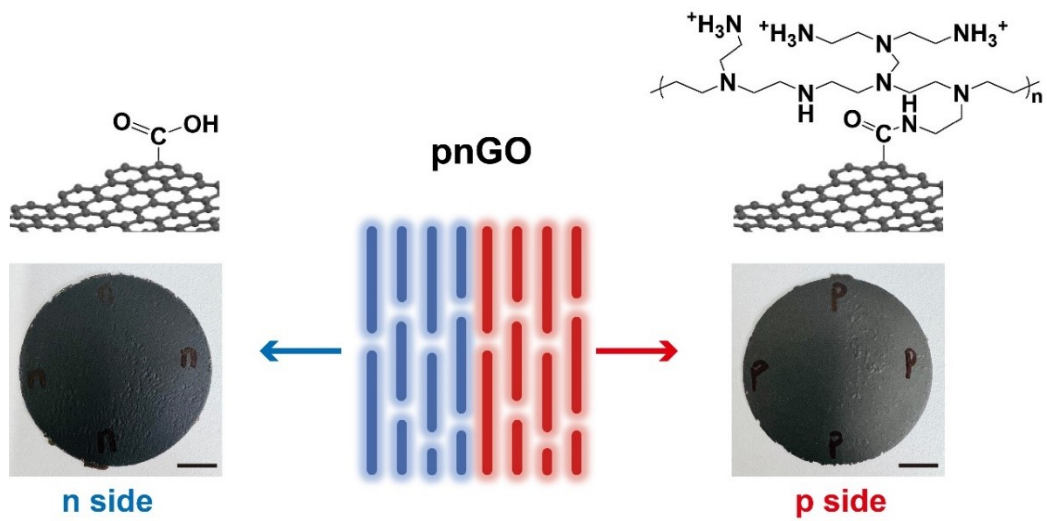


Fig. S3 Photographs of the two sides of the free-standing pnGO membrane (scale bar, 1 cm).

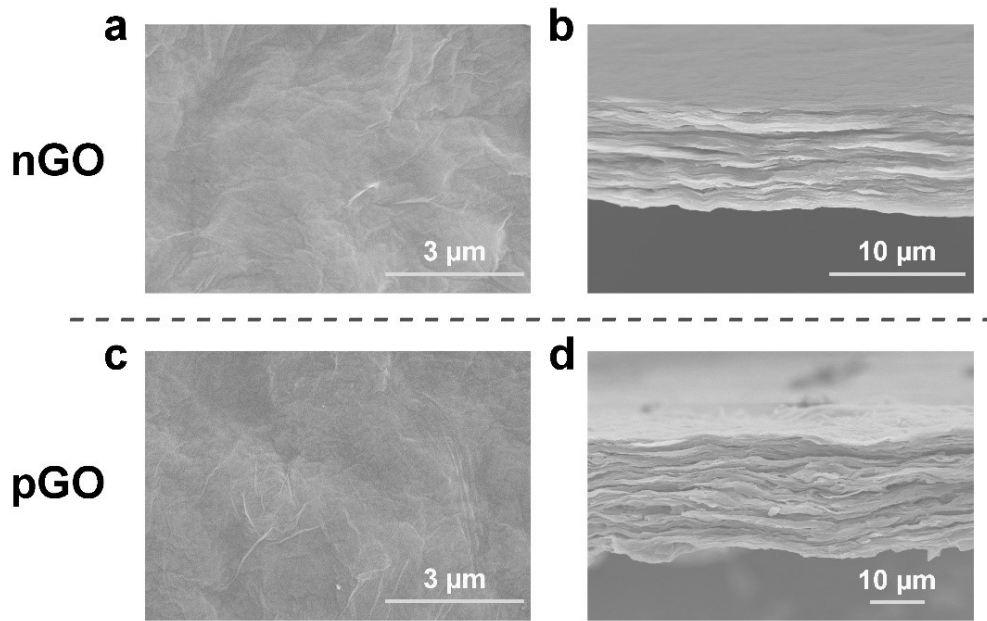


Fig. S4 Surface and cross-sectional SEM images of (a-b) nGO and (c-d) pGO membranes, showing the ordered lamellar structure.

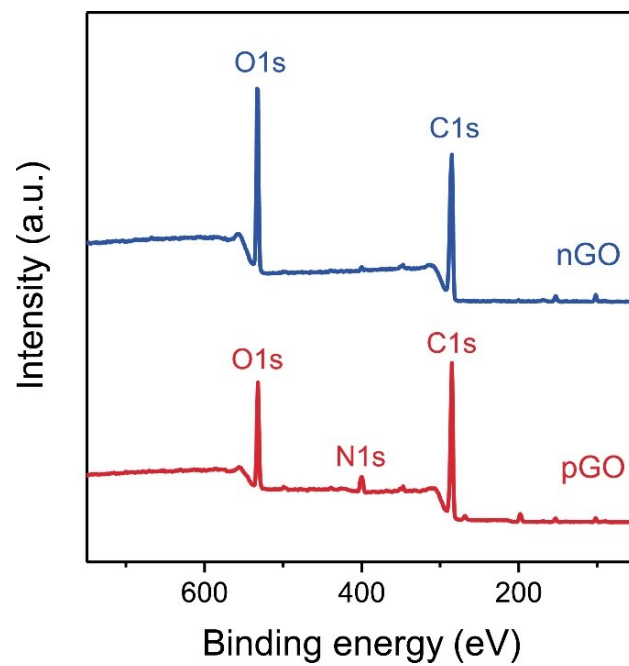


Fig. S5 X-ray photoelectron spectroscopy (XPS) scans of nGO and pGO membranes.

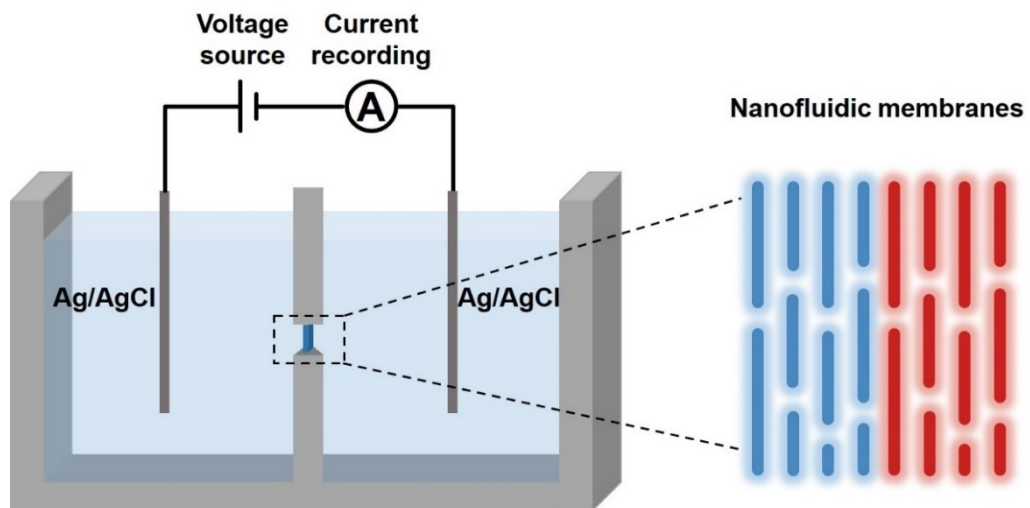


Fig. S6 Schematic of the two-compartment electrochemical testing setup.

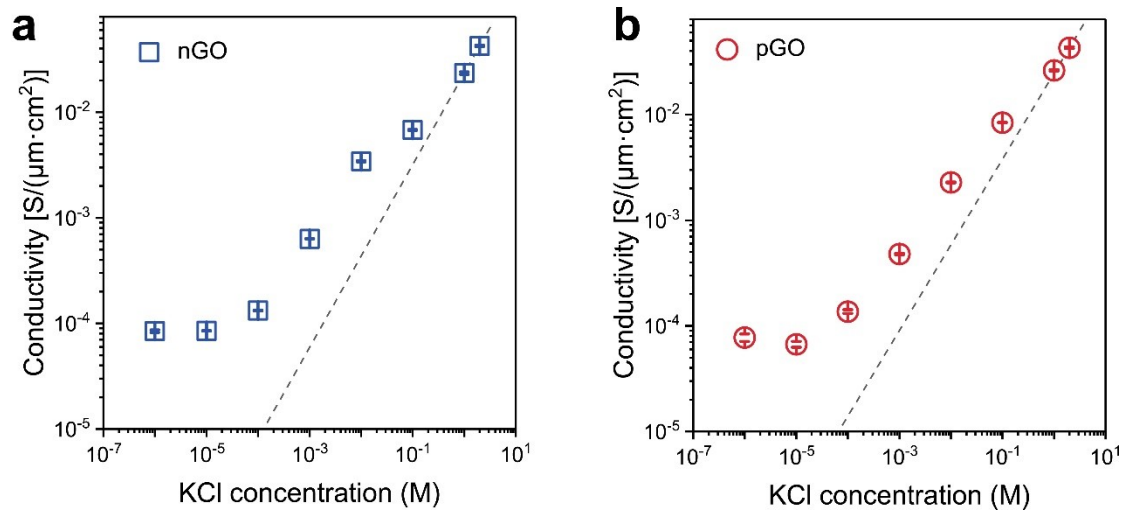


Fig. S7 Ionic conductivity as a function of concentration across the pGO and nGO membranes, respectively.

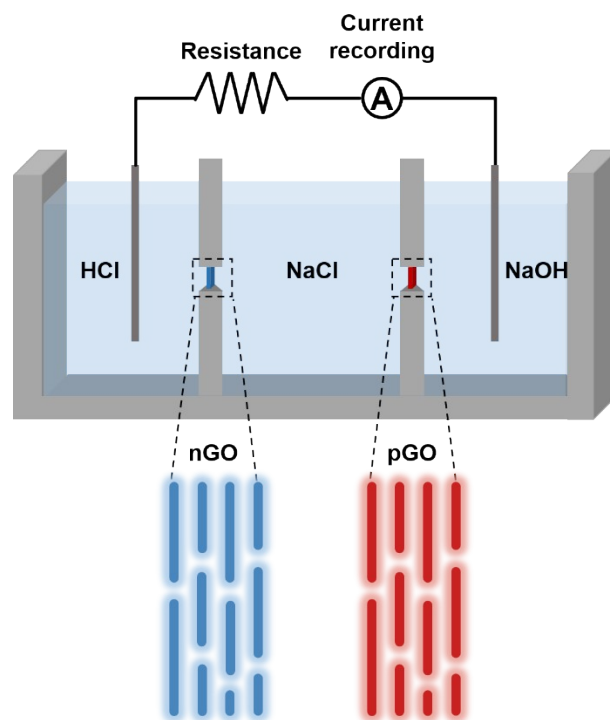


Fig. S8 Schematic of the three-compartment electrochemical testing setup: the cell pair of “cation-exchange membrane (nGO) + neutral compartment + anion-exchange membrane (pGO)”.

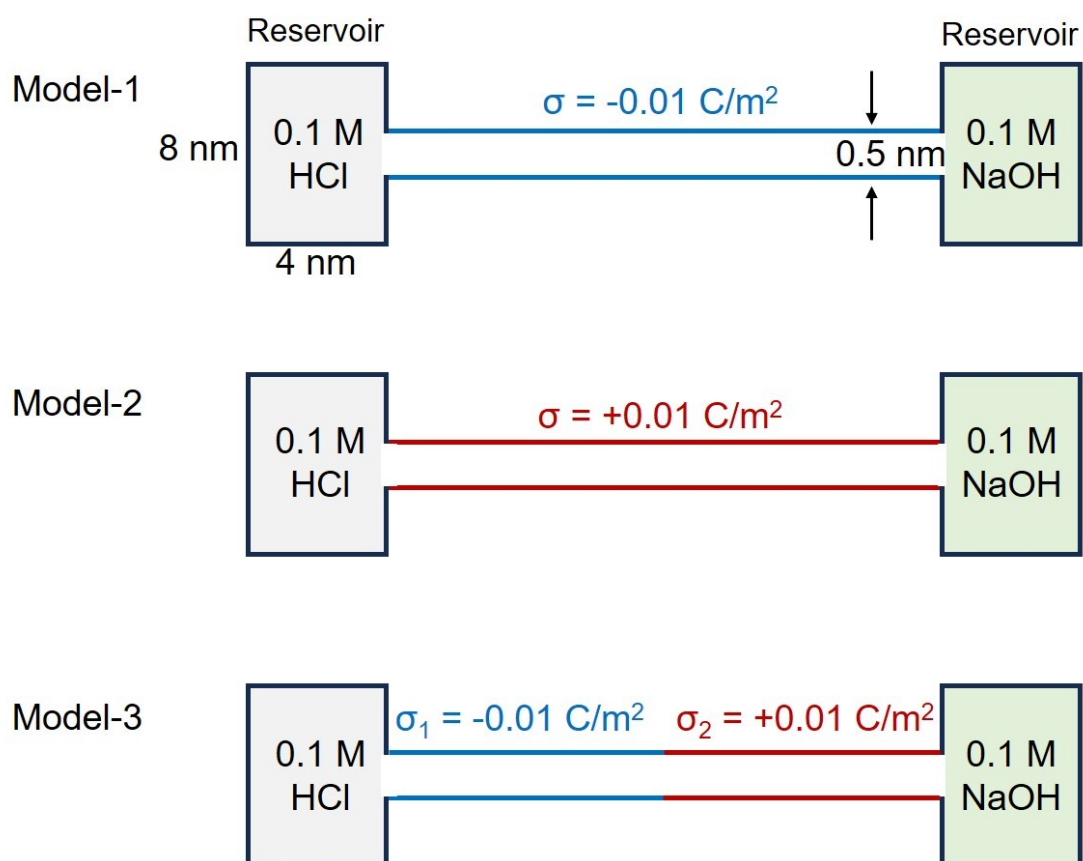


Fig. S9 Numerical simulation models. The simulation model contains a 15-nm length 2D channel with one kind of surface charge (Model-1 and Model-2) and two opposite kinds of surface charges (Model-3). (Drawing not to scale.)

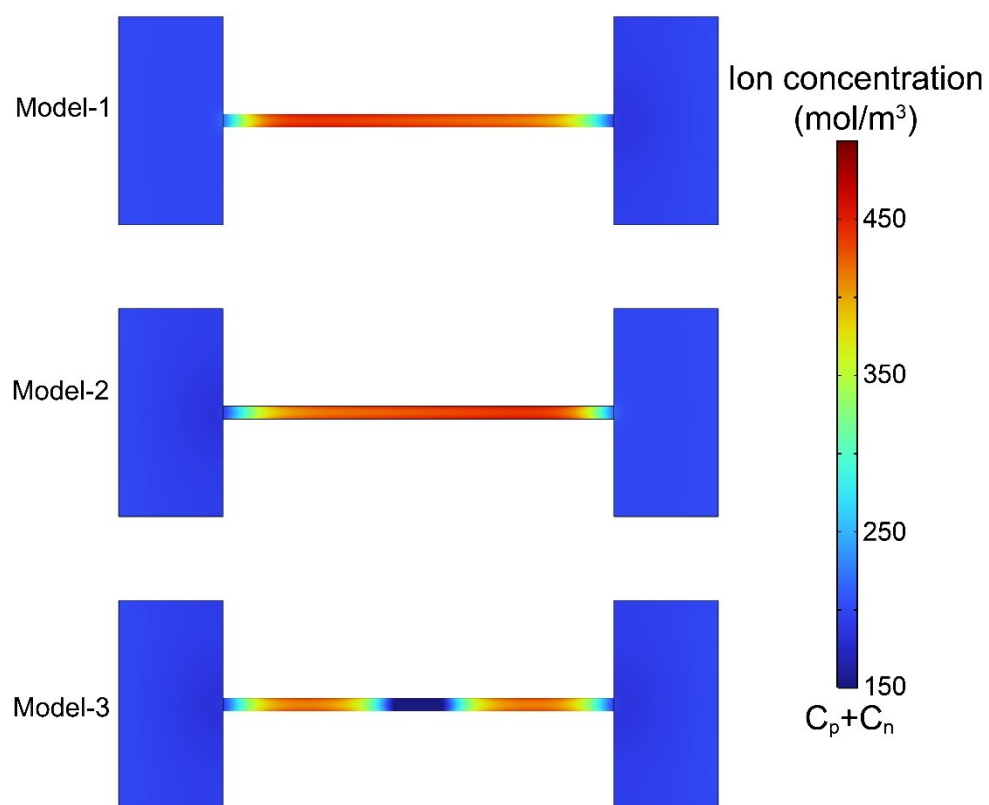


Fig. S10 The numerical simulations of ion concentration profiles in three models.

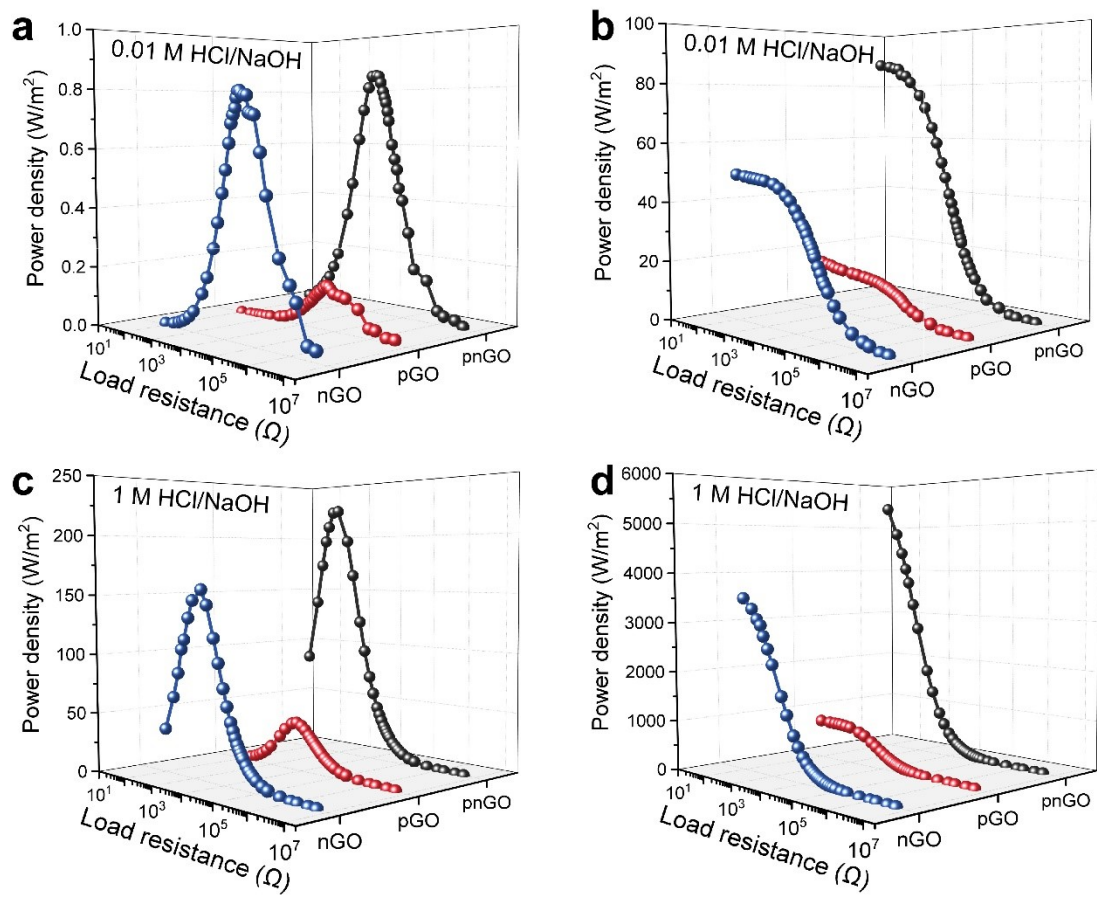


Fig. S11 (a, c) Output power density and (b, d) current density of nGO, pGO, and pnGO membranes with 0.01 M and 1 M ABP as functions of the load resistance.

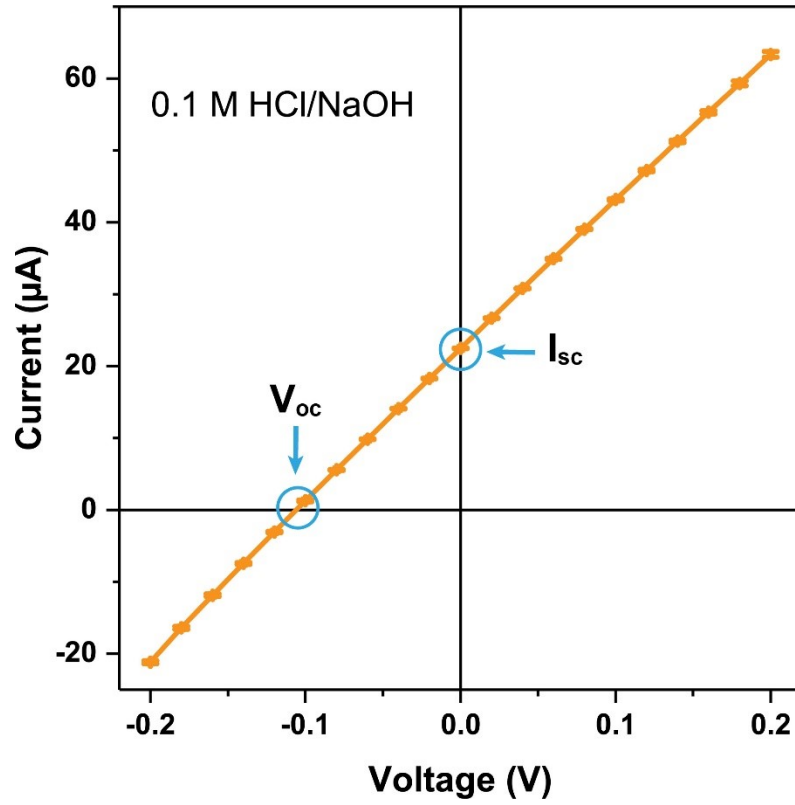


Fig. S12 I-V curve of the pnGO membrane recorded in 0.1 M ABP. The short circuit current (I_{SC} , the current corresponding to zero external bias) and open-circuit voltage (V_{OC} , the potential corresponding to the zero current) can be obtained from the observed intercept on the current axis and voltage axis, respectively.

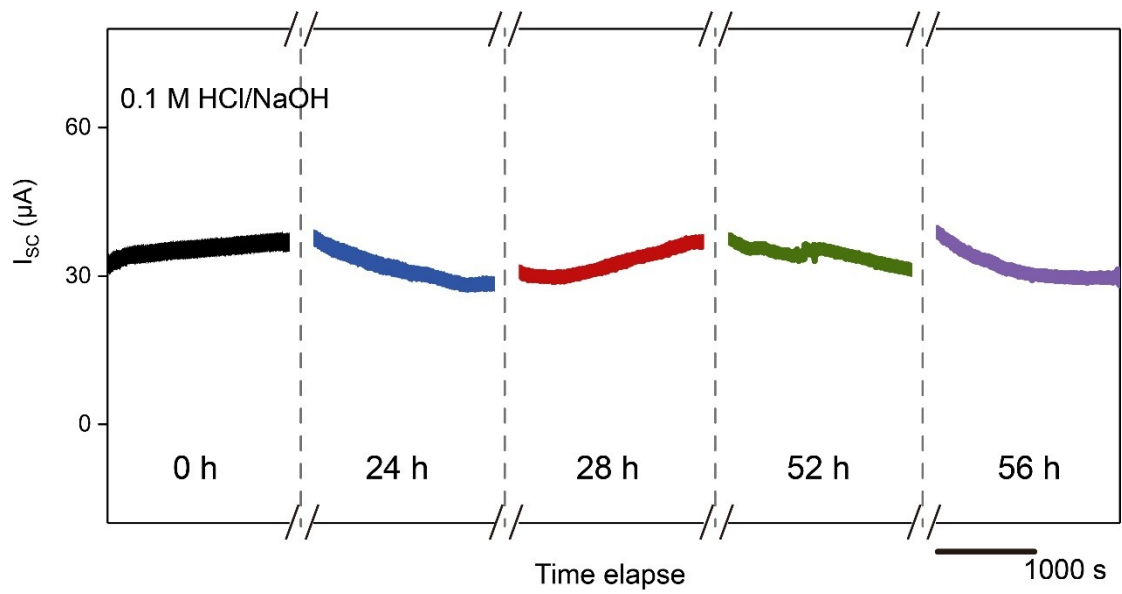


Fig. S13 Long-term operation test.

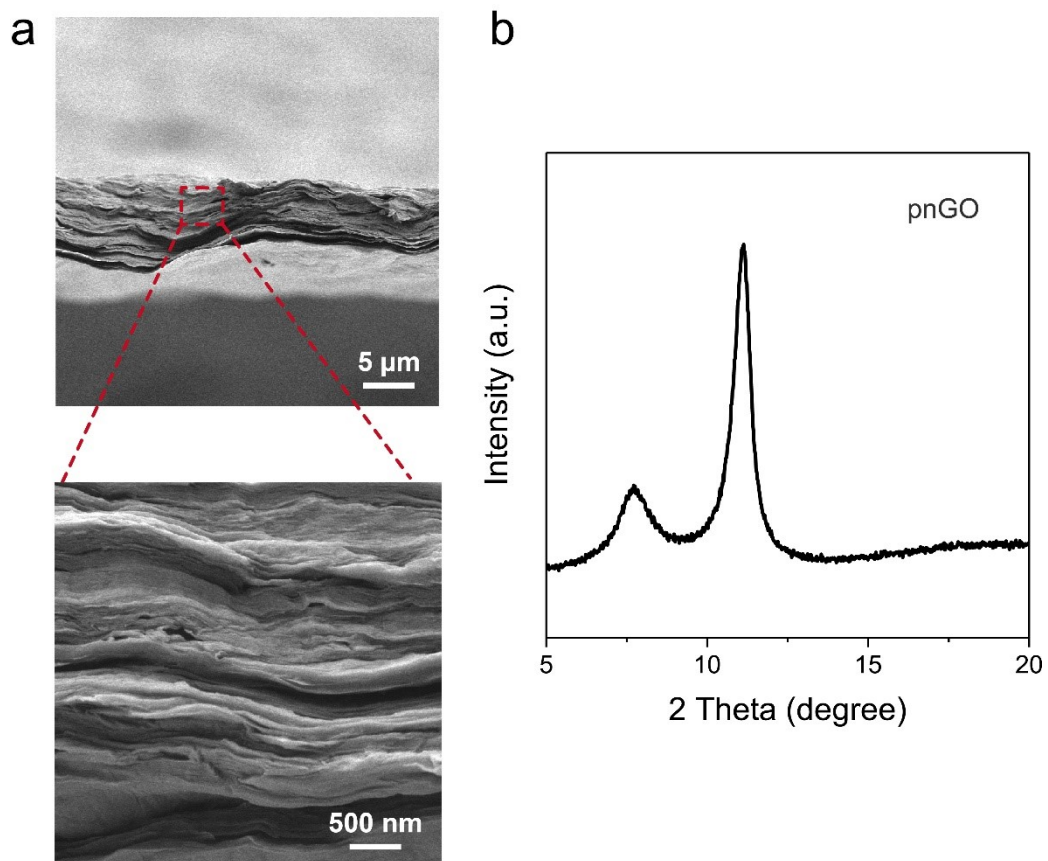


Fig. S14 (a) Cross-sectional SEM image and (b) XRD of the membrane after long-term operation test.

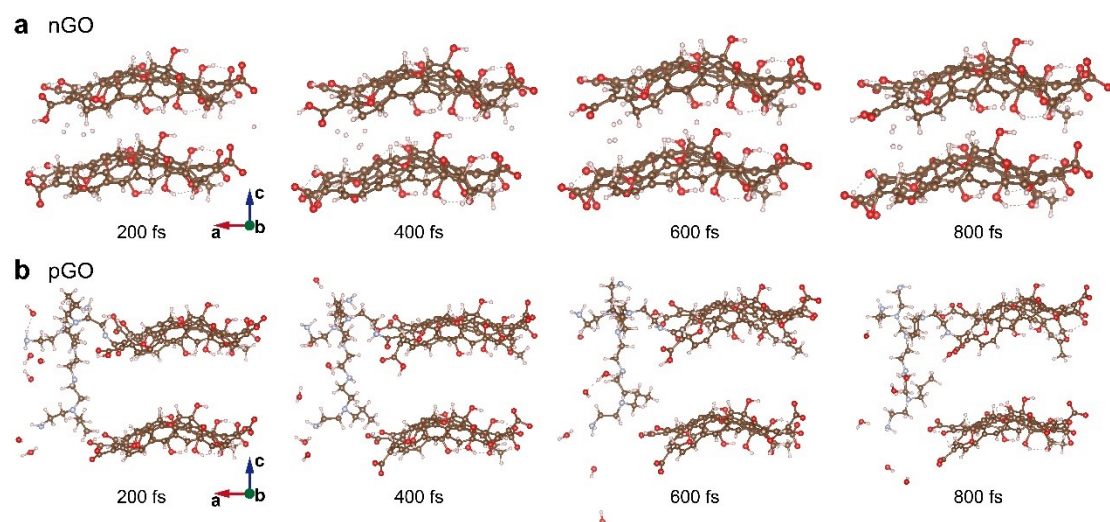


Fig. S15 Representative snapshots depicting the passage of H^+ and OH^- ions through the channels constructed by nGO and pGO nanosheets, respectively.

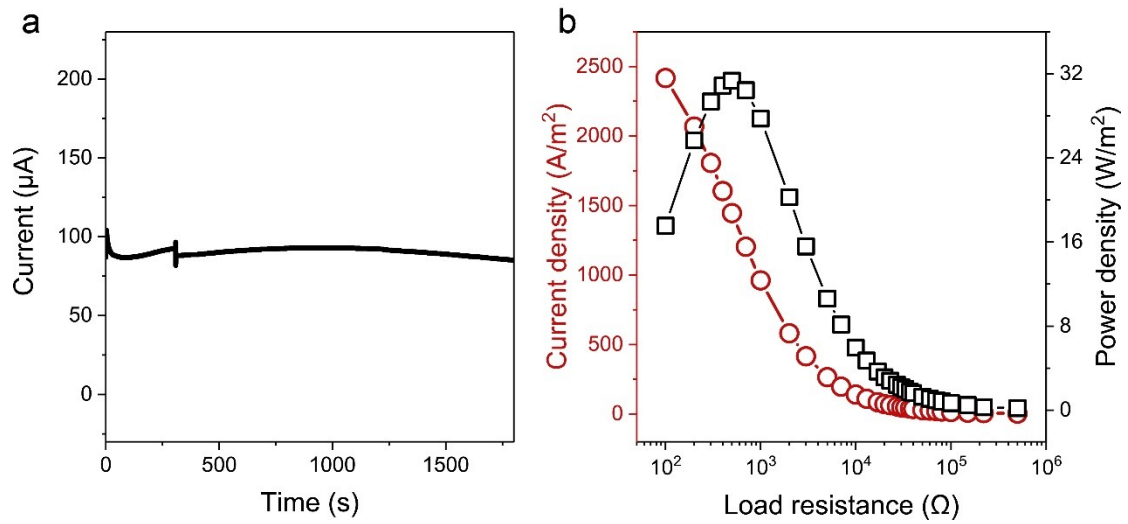


Fig. S16 Transmembrane ion transport and energy conversion behavior of pnGO membrane under the conditions of waste acids and bases of unknown composition and concentration from the laboratory.