

# **Electronic Supplementary Information for Mussel-inspired fabrication of porous anodic alumina nanochannels and graphene oxide interfacial ionic rectification device**

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**Chemicals and reagents.** Aluminum sheets (thickness 0.1 mm; purity 99.99%) were obtained from General Research Institute for Nonferrous Metals (Beijing, China). Analytical grade reagents of oxalic acid, sulfuric acid, phosphoric acid, perchloric acid, 36% hydrochloric acid aqueous solution, potassium hydroxide, potassium chloride, potassium persulfate, phosphorus pentoxide, graphite, stannous chloride, and ethanol were purchased from Sinopharm Chemical Reagent Co., Ltd. All solutions were prepared daily with deionized water ( $18.2 \text{ M}\Omega\cdot\text{cm}^{-1}$ , Milli Q). Prior to use, aqueous KCl solutions were all passed through a  $0.22 \mu\text{m}$  filter.

**Characterizations.** Scanning electron microscopy (SEM) images were acquired on a scanning electron microscope (S-4800 Hitachi, Japan). Transmission electron microscopy (TEM) result was obtained via FEI Tecnai G20. Atomic force microscopy (AFM) (AFM, Agilent Technologies 5500) was performed in tapping mode. Laser scanning confocal microscopy (LSCM) images were obtained on a laser scanning confocal microscope (TCS SP5 C1-Z, Leica, Germany) and excitation wavelength was 488 nm. X-ray photoelectron spectroscopy (XPS) was measured using a X-ray photoelectron spectroscopy (K-Alpha, Thermo Fisher Scientific, America).

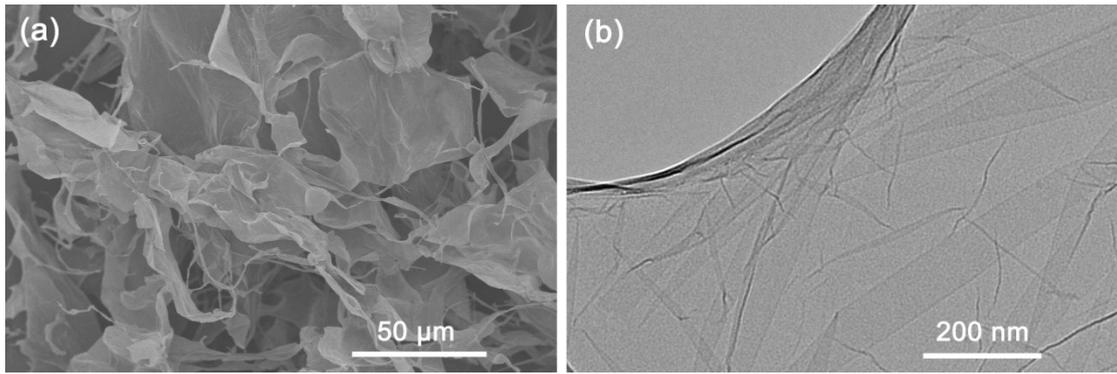
**Fabrication of PAA nanochannels.** PAA membranes used in this work were prepared via a two-step aluminum oxidation process. Aluminum sheet was cleaned in acetone and then electrochemically polished with perchloric acid/ethanol (1:9 v/v  $\text{HClO}_4$ : EtOH) at a constant voltage of 10 V for 10 min to achieve mirror finished surface. The temperature of the electrolyte was maintained at  $2 \text{ }^\circ\text{C}$ . Anodization process was performed in 0.3 M oxalic acid at  $20 \text{ }^\circ\text{C}$  at a constant voltage of 60 V for 0.5 h. Then, the PAA membrane was etched in an aqueous mixture solution of phosphoric acid (5 wt.%) and chromic acid (1.8 wt.%) at  $60 \text{ }^\circ\text{C}$  to remove the irregular oxide layer formed in the pre-anodization. Subsequently, the first anodization under the same conditions as that in the pre-anodization was performed for 4 h. Upon completion of the anodization, the barrier layer produced in anodization was thinned by chemical etching in 5 wt.% phosphoric acid at  $30 \text{ }^\circ\text{C}$  for 60 min.

**Preparation of GO.** Graphene oxide (GO) was prepared by using a modified Hummers method.<sup>25-26</sup> Briefly,  $K_2S_2O_8$  (1 g),  $P_2O_5$  (1 g) and graphite (2 g) were added into round bottomed flask (250 mL), and sulfuric acid (98%, 10 mL) were slowly added, then heated at 80 °C for 6 h. After that, the mixture was cooled to room temperature and diluted with distilled water carefully. Then, the preoxidation product was obtained by vacuum filtration under reduced pressure to neutral, sonicated in acetone solution for 1 h, and dried in a ventilated kitchen. Afterwards, preoxidated grapheme (0.2 g) were added to ice concentrated sulfuric acid (4.6 mL), potassium permanganate ( $KMnO_4$ , 0.6 g) were added slowly with magnetic stirring, stirring at 35 °C for 2 h, and added deionised water (9.2 mL). Then deionised water (28 mL) and 0.5 mL hydrogen peroxide solution (30%) were added. When the color of the solution turned to yellow with stirring, ended the reaction. GO was obtained by centrifugation (3000 rpm, 30 min). The crude GO was cleaned with hydrochloric acid (V:V = 1:10, 50 ml) to remove metal ions, dialyzing it till the dialysate was neutral. The dialyzed to neutral GO water sol was dried by freeze-drying to give dry GO. At last, the dialyzed to neutral GO water sol was dried by freeze-drying to obtain dried GO.

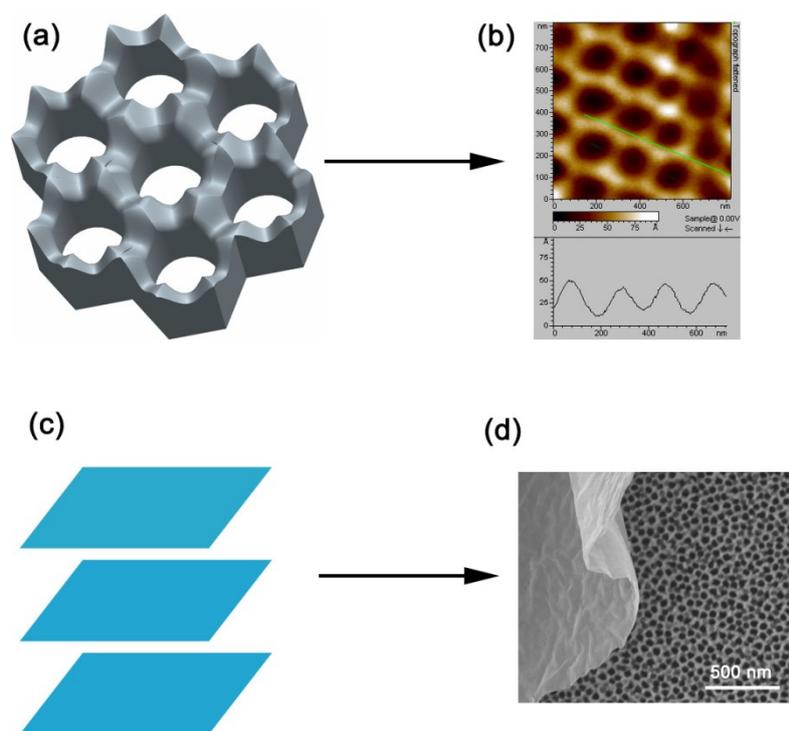
**Fabrication of PAA and GO composite membrane.** As shown in **Figure S1**, PAA membrane was clamped between two PDMS films and then placed in the middle of two Teflon cells without electrode. Dopamine solution (0.1 mM, pH=8.5) contained Tris-HCl (10 mM, pH=8.5) was injected into two electrolytic cells and stirred 10 min. Graphite oxide (0.2 mg/mL, dispersed in aqueous solution) was added into one electrolytic cell and reacted for 10 min. At last, two electrolytic cells including composite membrane were washed by ultrapure water.

**Measurement setup and *I-V* characterizations.** The scheme of ionic current measurement device featuring nanochannels array bridged two electrolytic cells is shown in **Figure S1**. The effective exposure area of nanochannels array was 3.14 mm<sup>2</sup> in the present study. The membrane was clamped between two PDMS films and then placed between two Teflon cells. All ionic current measurements were carried

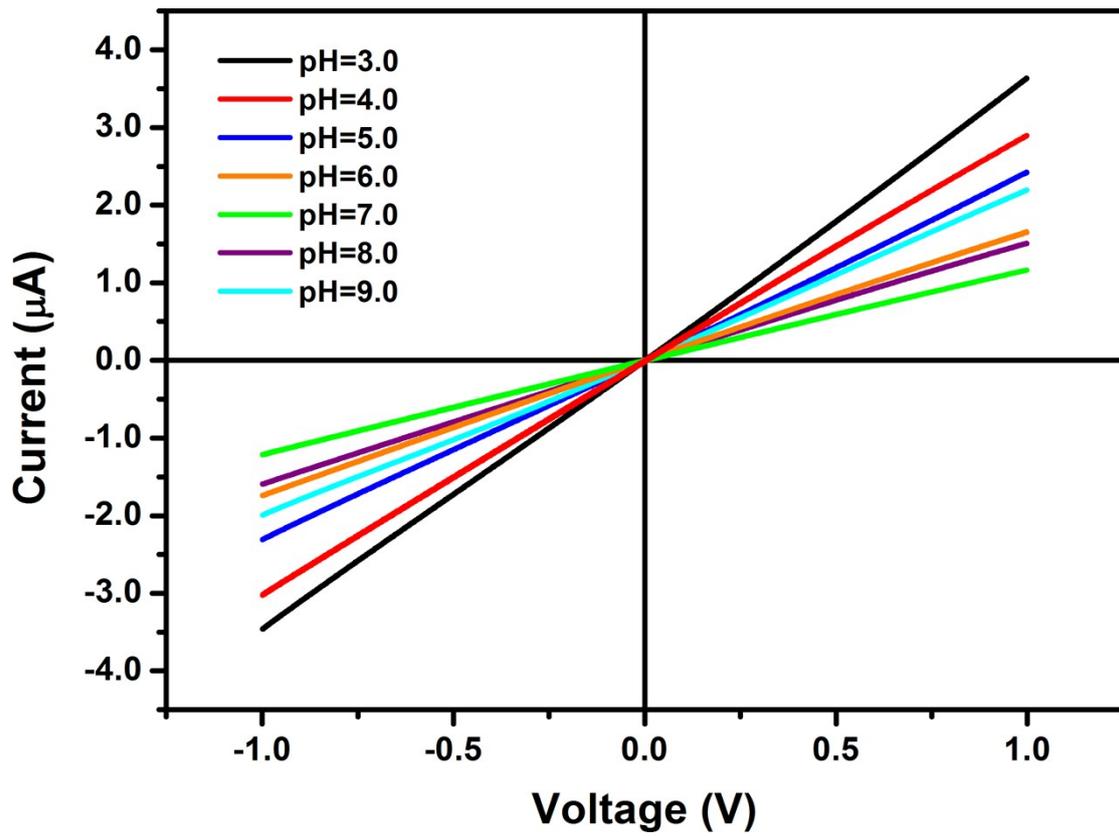
out in the same conductivity bath in a home-made Faraday shielding cage, which has the same ground with all other instruments used. Two Ag/AgCl electrodes were used for applying the trans-membrane potential and measuring the ionic current, since Ag/AgCl electrode is nonpolarizable and very stable. Linear sweep voltammetry was carried out on a CHI 660E electrochemical workstation (CHI Instrument Co. Ltd., USA). The ionic current through the nanochannel array was measured by scanning the voltage from  $-1$  V to  $+1$  V at a scan rate of  $100$  mV/s. Solution pH can be adjusted by either  $0.1$  M HCl or  $0.1$  M KOH.



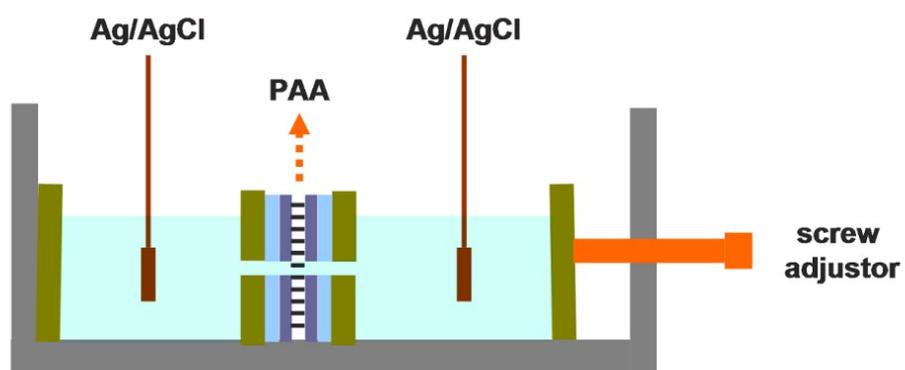
**Fig. S1** The microscopic structure images of GO. (a) SEM image. (b)TEM image.



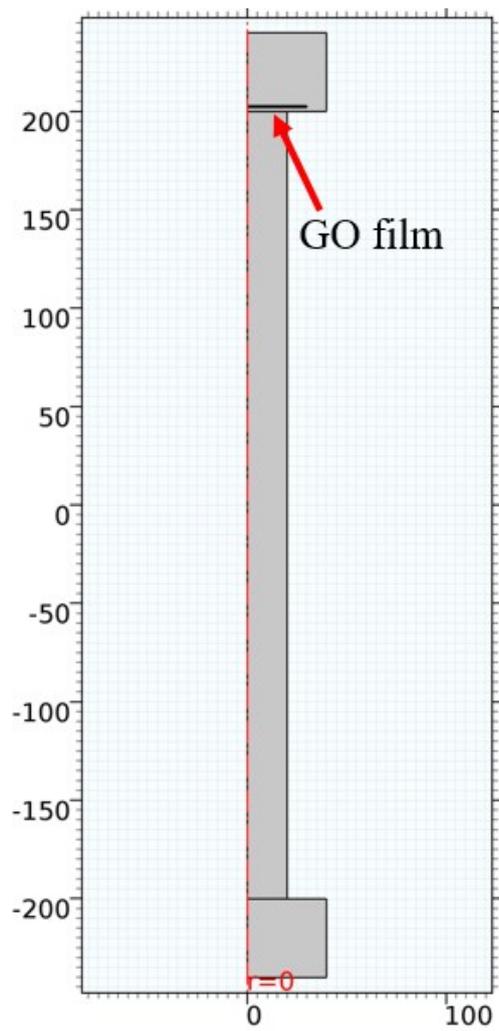
**Fig. S2** Microscopic structure images of PAA membrane and GO film. (a) Schematic diagram of the top surface of PAA membrane. (b) AFM image of the top surface of PAA membrane. (c) Schematic diagram of GO film. (d) SEM image of GO stripping from the surface of PAA membrane.



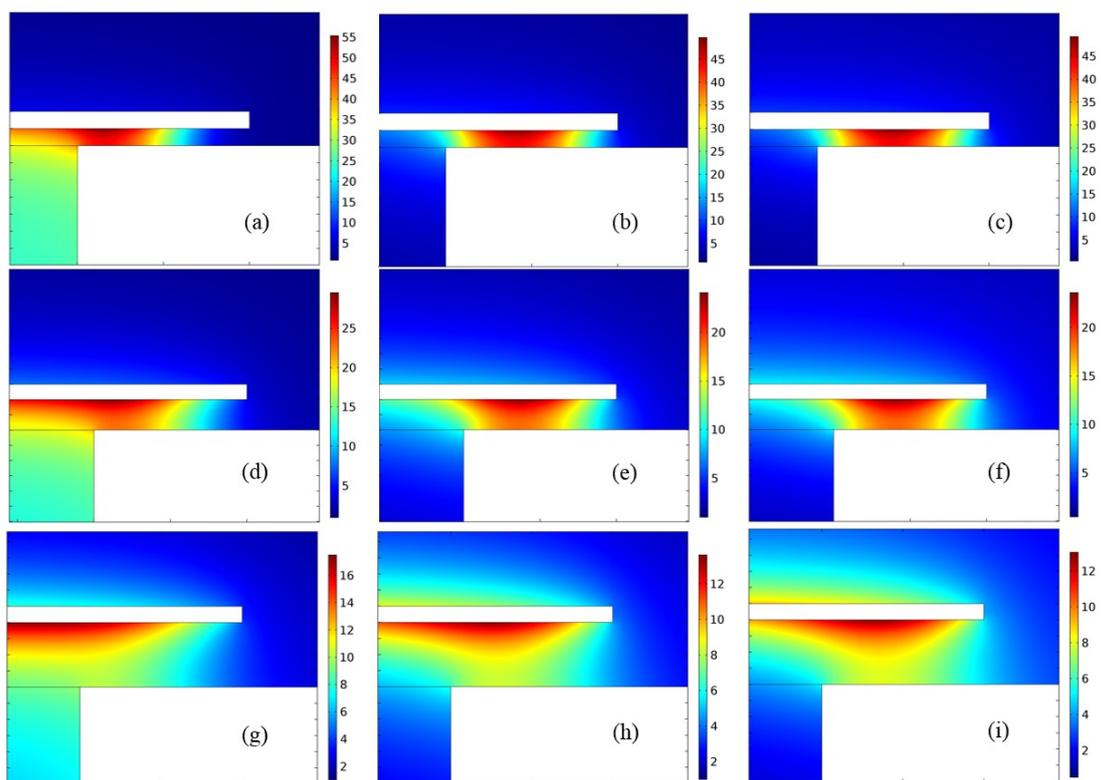
**Fig. S3** Current-voltage ( $I-V$ ) curves of the PAA membrane without GO film detected in 1 mM KCl with different pH values as indicated in the figures.



**Fig. S4** Schematic diagram of  $I-V$  measurement setup.



**Fig. S5** Geometry of model setup.



**Fig. S6** Potassium ion distribution at the interface with varying gap distance between GO film and PAA nanochannels. From top to bottom: Distance: 1 nm, 2 nm and 4 nm. From left to right: Biasing voltage: -1 V, 0 V and 1 V.