Electronic Supplementary Information (ESI)

Optoelectronic modulation of ionic conductance and rectification through heterogeneous 1D/2D nanofluidic membrane

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1. Chemicals and reagents

Meso-Tetra(4-carboxyphenyl)porphine (TCPP) were purchased from J&K Frontier. Potassium chloride (KCl) were purchased from Beijing Chemical Works. N, N-dimethylformamide (DMF) obtained from Sinopharm Chemical Reagent Co.. Ltd. were (3aminopropyl)triethoxysilane (APTES) and aluminum chloride hexahydrate (AlCl₃·6H₂O) were purchased from Aladdin. The anodized aluminum oxide (AAO) membranes were purchased from PuYuan Nano (Hefei, P. R. China). The graphene oxide (GO) aqueous dispersion (2 mg/mL) were purchased from XF Nano (Nanjing, P. R. China). Chemical reagents were all used as received. Aqueous solutions were all prepared with pure water from a Milli-Q water system (Millipore, 18.2 M Ω cm). Unless stated otherwise, all experiments were carried out at room temperature.

2. Chemical modification of the nanoporous membrane

The AAO membranes were firstly cleaned in ethanol with ultrasound treatment for 5 minutes and then dried with nitrogen. Afterwards, the membranes were immersed into ethanol solution with 5% APTES for 10 hours. Finally, the membranes were thoroughly washed in ethanol and dried in oven.¹

3. Synthesis of MOF powder

The synthesis of MOF powder was conducted with a hydrothermal method.^{2, 3} Briefly, TCPP (23.3 mg) and AlCl₃· $6H_2O$ (50 mg) were dispersed in 5 ml of H₂O. Then the mixture was sonicated for 15 min and transferred into a sealed glass microwave vessel. The sealed vessel was heated to 160°C for 40 min under microwave irradiation. The MOF powder was obtained through centrifugation, and washed six times with DMF and six times with H₂O, then dried under vacuum to remove remaining solvent.

4. Fabrication of GO@MOF and GMM

Firstly, 4 mL of 0.2 M AlCl₃ solution was added into 5 mL GO aqueous dispersion (2 mg/mL). After sonication for 40 minutes, the mixed solution were left overnight under stirring. Then, the obtained solution was centrifuged at 8000 rpm to collect the GO-Al precipitation.^{4, 5} After that, GO-Al (2 mg/mL) and TCPP (18.7 mg) were dispersed in 4 mL water by sonication. And then the mixed solution was added to a sealed glass microwave vessel, which was heated to 160°C for 40 minutes under microwave irradiation.² After the reaction, the obtained solution was centrifuged at 8000 rpm to collect GO@MOF precipitation, which was washed with DMF and pure water extensively. Finally, GO@MOF dispersion (GM, 0.1 mg/ml, Fig. S1) was deposited onto the AAM membrane with positive charge via vacuum filtration following a previously reported procedure.⁶



Fig. S1 Photographs of GO@MOF and GO dispersions used for experiments.

5. Zeta potential of GO@MOF powder

We measured the Zeta potential (ζ) of GO@MOF powder in H₂O and 10 mM KCl. As shown in Fig. S2, both are negatively charged. Zeta potential measurement was conducted on a Zetasizer Nano ZS ZEN3600.



Fig. S2 Zeta potential of the GO@MOF in H₂O and 10 mM KCl solution.

6. Size distribution of the AAM

The pore diameter of AAM is about 75±4 nm (Fig. S3). The statistic results are given by averaging 100 measurements with the scanning electron microscopy (SU8020, HITACHI) images (Fig. 2a).



Fig. S3 Nanochannel size distribution of the AAM.

7. Characterization of GOM

GO membrane (GOM) was gained following a previously reported procedure.⁶ Briefly, GO dispersion (1 mg/ml, Fig. S1) was deposited onto the AAO membrane via vacuum filtration. Then, the resulting GOM was dried at 80 °C for 24 hours in an vacuum oven.⁶ The morphology of GOM was characterized by SEM and transmission electron microscope (TEM, JEM 2010). The lateral size of the GOM is about 15 mm, and thickness is about 30 µm.



Fig. S4 Characterization of the GOM. (a) Photograph of the self-standing GOM, the lateral size is about 15 mm. (b) SEM image of GOM from top view. The membrane surface is homogeneous with no pinholes. (c) TEM image of single-layer GO platelet. (d) Cross-section view of GOM with thickness of ca 30 μ m.

8. Characterization of MOF power

The morphology of MOF powder was provided in Figure S5. The average size of MOF powder is about 551 ± 71 nm. The statistic results were given by averaging 50 measurements with the SEM image. By comparison, we found that the average size of MOF nanosheets growing on GO is about 59 ± 13 nm, which is smaller than MOF powder (Fig. 2b). For the synthesis of MOF powders, the metal source is abundant in the hydrothermal solution. However, for MOF nanosheets growing on GO, the metal source is only aluminum ions adsorbed on GO substrates, leading to the smaller size compared to the bulk MOF powders.



Fig. S5 SEM image of MOF power.

9. Stability of GMM

To improve the stability, the GMM were thermally annealed at 80 °C for 24 hours in an vacuum oven, following a previously reported procedure.⁶ The thermally treated GMM could maintain structure integrity in pure water for 30 days (Fig. S6).



Fig. S6 The thermally annealed GMM shows high stability in water for 30 days.

10. Measurement setup

For *I-V* tests, a piece of mixed AAM/GMM was mounted in between a two-compartment electrochemical cell. The working electrode was placed on the GMM side, and the reference one was set on the AAM side. The testing membrane area was about 0.2 mm². The light was illuminated from the photo-responsive side of GMM. The transmembrane ionic current was measured with a source meter (Keithley 2636B) through Ag/AgCl electrodes, which were covered with black Teflon tube to avoid the light influence.



Fig. S7 *I-V* measurement device with light illumination.

11. Current-voltage (I-V) curves of AAO/GMM and AAM/GMM

As control groups, we investigated the ion transport properties of AAO/GMM and AAM/GMM membrane in 10 mM KCl solution. The tested condition was the same as that provided in the main text. As shown in Fig. S8, an obvious ICR was observed with AAM/GMM. However, the mixed AAO/GMM membrane shows no ICR because of the weak surface charge of blank AAO membrane. Previous study reported that the ICR effect in the synthetic nanofluidic systems stems from the presence of asymmetric element either in the device structure, or in the environmental conditions.⁷ For the device structure, not only the nanopore geometry and composition is of much importance, but also the surface charge distribution is crucial.



Fig. S8 (a) Representative *I-V* responses of AAO/GMM in 10 mM KCl electrolyte. (b) Representative *I-V* responses of AAM/GMM in 10 mM KCl electrolyte.

12. I-V responses through AAM/GMM under different KCl concentrations

The transmembrane ionic current of AAM/GMM were measured in various KCl solutions with concentrations ranging from 0.1 mM to 100 mM. As shown in Fig. S9, the ionic current rectification is sensitive to electrolyte concentration. When the electrolyte concentration is 10 mM, the AAM/GMM exhibits a remarkable ionic current rectification characteristic.



Fig. S9 *I-V* responses through AAM/GMM heterogeneous membrane with different concentrations of KCl solutions ranging from 0.1 mM to 100 mM.

13. Ion transport through GMM with and without light illumination of 420 nm wavelength

We measured the *I-V* responses of GMM without and with light illumination of 420 nm wavelength. As shown in Fig. S10, linear *I-V* curves were obtained through the homogeneous GMM. The ICR ratio had no change and kept around 1 with and without light illumination, indicating that the rectification is caused by the heterogeneous AAM/GMM membrane. Meanwhile, an obvious increasement of the conductance can be observed due to photo response of GMM.



Fig. S10 Ion transport through GMM membrane. (a) Representative *I-V* responses of GMM with and without light illumination in 10 mM KCl electrolyte. The light wavelength is 420 nm, and light power intensity is 44.2 mW/cm^2 . (b) The calculated conductance ratio and ICR with *I-V* curves in (a). The error bars indicate the standard deviation of three independent measurements.

14. Ion transport through GMM membrane before and during light illumination with different wavelengths

The *I-V* responses of GMM before and during light illumination with different wavelengths under the same light power intensity were carried out, as shown in Fig. S11. The light power density is 44.2 mW/cm². We found that the responsive ionic current also showed dependence on the light absorption property of MOF nanosheets. For comparison, we calculated the ICR ratio and conductance ratio by using the results in Fig. S11a. The results show that the ICR ratio of GMM with light illumination of different wavelengths had little change, confirming that the ICR would not appear with the individual GMM. Although the conductance ratio showed some increase with different light wavelengths, the changes were still less compared with that of 420 nm wavelength.



Fig. S11 Ion transport through GMM membrane under light illumination with different wavelengths. (a) Representative *I-V* responses of GMM before and during light illumination with different wavelengths under the same light power intensity. (b) The calculated conductance ratio and ICR with *I-V* curves in (a). The error bars indicate the standard deviation of three independent measurements.

15. *I-V* curves and corresponding conductance ratio of the blank electrochemical cell, AAM, and GOM with light illumination

As control groups, we also tested ion transport property through blank electrochemical cell, AAM, and GOM with light illumination of 420 nm wavelength. As shown in Fig. S12, there existed no difference for the blank electrochemical cell and AAM with light illumination and without light illumination, indicating that the electrodes and AAM have no photo response. However, a minor increasement for the GOM can be observed due to the unique characteristic of GO, which is in agreement with the reported results.⁸



Fig. S12 Light response of ion transport with different materials under the same experimental conditions. Representative *I-V* responses of blank electrochemical cell (a), AAM (b), and GOM (c) with and without light illumination in 10 mM KCl electrolyte. The light wavelength is 420 nm, and light power intensity is 44.2 mW/cm². (d) The calculated conductance ratio with *I-V* curves in (a, b, and c). The error bars indicate the standard deviation of three independent measurements.

16. *I-V* curves of the AAM/GMM with varied light power intensity and corresponding conductance ratio at -1 V

Light modulated ionic current through AAM/GMM with different light power intensity was recorded. As shown in Fig. S13, the current shows step-wise increasement with enhanced light illumination intensity. However, the enhancement ratio is different at bias voltage of ± 1 V. The conductance ratio at -1 V is much smaller compared with the ones at +1 V (Fig. 4a) with increasing light illumination intensity.



Fig. S13 (a) Representative *I-V* responses of AAM/GMM heterogeneous membrane recorded with varied light power intensity and before light illumination. (b) Conductance ratio calculated from *I-V* curves at -1 V in (a). The error bars indicate the standard deviation of three independent measurements.

17. The reversibility and stability of AAM/GMM with light illumination

The *I-V* responses of AAM/GMM with and without light illumination were recorded. Three independent cycles were carried out through the mixed membrane, showing no difference and indicating the stability of the nanofluidic device.



Fig. S14 Three independent cycles of ion transport through AAM/GMM heterogeneous membrane with and without light illumination. The results showed excellent reversibility and stability of the complex membrane.

18. ICR ratio and conductance ratio through AAM/GMM with light illumination in different KCl concentrations

The change of ICR ratio and conductance ratio through AAM/GMM with light illumination in various concentrations KCl solutions were shown in Fig. S15. The ICR is sensitive to electrolyte concentration and has the same trend in all concentrations, which shows decrease with light illumination compared to that before light illumination. However, the AAM/GMM exhibits a remarkable ICR property when the electrolyte concentration is 10 mM. Fig. S15b shows that the conductance ratio almost remains at about 2.0 with light illumination of the same light power intensity regardless of the ion concentration.



Fig. S15 (a) ICR ratio of AAM/GMM in different concentrations of KCl solution with and without light illumination. (b) The calculated conductance ratio of AAM/GMM with light illumination. The error bars indicate the standard deviation of three independent measurements.

19. References

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