
Molecular-Scale Asymmetry Nanochannels for High-Efficiency Osmotic Energy Generation

Chao Liu,^{a,c,‡} Caichao Ye,^{b,‡} Jiali Wang,^a Ting Yang,^a Anqi Ni,^a Tianning Zhang,^a Kunpeng Mao,^a Long Chen,^a Shijian Wang,^c Jingwen Sun,^a Wenqing Zhang,^b Xin Wang,^a Jianfei Che,^a Pan Xiong,^{a,*} Guoxiu Wang,^{c,*} Junwu Zhu^{a,*}

^a Key Laboratory for Soft Chemistry and Functional Materials of Ministry Education, School of Chemistry and Chemical Engineering, Nanjing University of Science and Technology, Nanjing 210094, China.

^b Academy for Advanced Interdisciplinary Studies & Institute of Innovative Materials, Guangdong Provincial Key Laboratory of Computational Science and Material Design, Southern University of Science and Technology, Shenzhen, Guangdong 518055, China.

^c Centre for Clean Energy Technology, School of Mathematical and Physical Sciences, Faculty of Science, University of Technology Sydney, Sydney, NSW 2007, Australia.

ABSTRACT: Osmotic power as an example of iontronics, can convert ion gradient to electricity energy by membrane-based reverse electrodialysis technique. However, their efficiency in harvesting osmotic energy is mostly dependent on ion permeability and selectivity during the transmembrane diffusion. The two-dimensional (2D) heterogeneous interface establishes molecular-scale asymmetric structure and charge that is expected to exert a crucial effect on the ion permeability and selectivity, but remains unexplored. Here, we designed a 2D nanofluidic membrane with molecular-level asymmetric channels, which can achieve high cation selectivity while maintaining outstanding ion conductivity. When applied to osmotic energy generators, this membrane can exhibit a high cation selectivity coefficient of 0.985 and a superior energy conversion efficiency of up to 47.1%, coupled with an excellent output power density of over 20 W m⁻² in mixing the artificial seawater and river water. The Na⁺ ions transport through 2D heterostructured membrane via interface induced contiguous ion adsorption-diffusion mechanism is uncovered. The asymmetry pore structure and negative charge distribution enable highly selective adsorption of Na⁺ ions and subsequently fast transport in the molecular-scale asymmetry nanochannels. This work provides an in-depth understanding of ion transport in asymmetry nanochannels and further inspires their applications in other advanced energy-harvesting devices.

INTRODUCTION

Osmotic power, also known as blue energy, can be extracted from salt solutions of different concentrations based on reverse electrodialysis (RED) technology.¹⁻⁴ However, the current RED technology typically shows a low efficiency, primarily owing to the trade-off between ion conductivity and selectivity of the ion-selective membranes in use, which hinders its large-scale industrial applications. In recent years, two-dimensional (2D) nanofluidic materials such as graphene oxide (GO),^{5,6} boron nitride,⁷ molybdenum disulfide,^{8,9} MXene,^{10,11} covalent organic frameworks (COF)^{12,13} and so on, display great potential as ion-selective membranes for RED. For example, a monolayer MoS₂ membrane with a pore size of 10 nm and a porosity of 30% could theoretically achieve an unprecedented power density.⁹ In practice, the ultrathin nanoporous carbon membrane and COF membrane were also developed to produce a considerable power density.^{13,14} Nevertheless, these reported 2D membranes with ultrahigh power density were based on atomic thickness and the scalability was generally restricted by the low mechanical strength. Recently, an impressive output power density has been obtained in the GO nanofluidic channels, but the high-tech

nature and complex operation still constrain the practical application.⁵ Therefore, it remains a formidable challenge to construct stable, efficient and scaled salinity gradient power harvesting systems.

In biological systems, selective osmotic ion transport in the nanoconfined asymmetric channel has rendered the production of biological iontronic energy.¹⁵ For instance, the electric eel can produce voltages as high as 600 V and currents up to 1 A, which is attributed to the abundance of asymmetric “subnanoscale” protein ion channels embedded in electrolytes.^{16,17} To mimic the function of such a high-efficiency ion transport system, it is essential to fabricate artificial nanometric channels with similar structures. Therefore, many researchers have put several efforts to develop asymmetric channels based on the 2D materials, including MXene/block copolymer,¹⁸ GO/BP,¹⁹ vermiculite/polyvinylidene fluoride,²⁰ etc.^{21,22} These channels with asymmetric chemical, geometrical, and electrostatic structures show unidirectional ion transport characteristics, effectively preventing the dissipation of Gibbs free energy as Joule heat, thus improving the power generation.^{23,24} Nevertheless, the aforementioned asymmetric nanochannels exhibit bulk-scale

asymmetry in either structural configuration or surface charge, with their component layers usually possessing micron-scale thickness.^{21,25} This renders asymmetric nanochannel systems lacking the ability to effectively regulate the 2D heterogeneous interface, where only a limited number of heterogeneous interfaces between component layers make interactions with ions, resulting in comparatively low ion transport efficiency. As a result, the energy conversion efficiency and power density of asymmetric nanochannel membranes are mostly restricted below 35% (upper limitation of 50%) and 10 W m^{-2} , respectively. In this respect, we contemplated that if nanofluidic membranes are entirely composed of asymmetric nanochannels, the asymmetric properties can be fully utilized, potentially achieving energy conversion efficiency approaching theoretical limits.

Here, we report the use of a 2D heterogeneous interface to construct molecular-scale asymmetry nanochannels as a power generator (Figure 1a). Owing to the molecular configuration and surface charge asymmetries induced by the 2D heterogeneous interface, the membranes enable couple excellent ion selectivity and high conductivity together, contributing to a record energy conversion efficiency of 47.1% (close to the upper limitation of 50%) and exceptional Na^+ selectivity coefficient of 0.985 through the RED process. By mixing artificial seawater and river water, a remarkable power output of over 20 W m^{-2} is obtained, more than four times the commercial benchmark of 5 W m^{-2} . Importantly, the membrane with molecular-scale asymmetry nanochannels achieves an impressive output power density of 22.3 W m^{-2} under real seawater conditions throughout China and Australia, which proves its broad application viability. Furthermore, we propose the interface induced contiguous ion adsorption-diffusion mechanism based on the molecular-scale asymmetry nanochannels.

RESULTS AND DISCUSSION

Membrane design, preparation and characterization. Here, the 2D TiG-n membrane was employed as a proof-of-concept lamellar membrane for our design (Figure 1b). The 2D negatively charged titania ($\text{Ti}_{0.87}\text{O}_2$) nanosheets with Ti atomic vacancies, are synthesized by delaminating their parent layered titanates into molecular single sheets.²⁶⁻²⁸ Briefly, the layered titanates ($\text{K}_{0.8}\text{Ti}_{1.73}\text{Li}_{0.27}\text{O}_4$) were first prepared by a high-temperature solid-state reaction. Then, the $\text{K}_{0.8}\text{Ti}_{1.73}\text{Li}_{0.27}\text{O}_4$ was converted into the corresponding protonic form ($\text{H}_{1.07}\text{Ti}_{1.73}\text{O}_4 \cdot \text{H}_2\text{O}$) in HCl solutions. Finally, a stable suspension of $\text{Ti}_{0.87}\text{O}_2$ nanosheets with Ti atomic vacancies was obtained through exfoliation of $\text{H}_{1.07}\text{Ti}_{1.73}\text{O}_4 \cdot \text{H}_2\text{O}$ in tetrabutylammonium hydroxide solution. Distinct from Ti atomic vacancies in $\text{Ti}_{0.87}\text{O}_2$ nanosheets, the nanoscale holes are introduced into GO nanosheets via the improved Hummers' method during a strong oxidation process. Meanwhile, $\text{Ti}_{0.87}\text{O}_2$ nanosheets show a high negative charge density (1.46 C m^{-2}),^{27,29} primarily arising from the presence of Ti vacancies within the delaminated titania nanosheets, which results in a deviation from the stoichiometry of TiO_2 .³⁰ However, GO nanosheets possess a negative charge density of only 0.064 C m^{-2} ,^{28,31} which is generated by the protonation of the surface pendant groups.³² The significant differences in charge density between the two types of nanosheets can create heterogeneous channels with asymmetric surface charges. Due to the good compatibility, hydrophilicity and interfacial interactions between GO and $\text{Ti}_{0.87}\text{O}_2$ nanosheets (Figure S1), these two nanosheets enable face-to-face assembly to

form highly efficient 2D heterogeneous interfaces containing molecular-scale asymmetry nanochannels.³³⁻³⁵

The exfoliated $\text{Ti}_{0.87}\text{O}_2$ nanosheets are negatively charged, which can endow a stable colloidal aqueous solution with a noticeable Tyndall light-scattering effect (Figure S2a,b). The atomic force microscopy (AFM) measurement displayed the ultrathin thickness ($\sim 1.1 \text{ nm}$) of the unilamellar $\text{Ti}_{0.87}\text{O}_2$ nanosheet (Figure 2a). As shown in Figure S2c, transmission electron microscopy (TEM) observation manifested that $\text{Ti}_{0.87}\text{O}_2$ nanosheets possess a flat and nearly transparent morphology, again confirming that the as-synthesized $\text{Ti}_{0.87}\text{O}_2$ consists of monolayer nanosheets. Energy-dispersive X-ray spectroscopy (EDX) elemental mapping of the $\text{Ti}_{0.87}\text{O}_2$ nanosheets suggested that Ti and O were uniformly dispersed in the sample (Figure S2d-f). As illustrated in the high-angle annular dark-field STEM (HAADF-STEM) image, relatively weak dots correspond to Ti atomic vacancies, clearly visualizing their distribution in $\text{Ti}_{0.87}\text{O}_2$ nanosheets (Figure 2b).^{28,36} The line profile (Figure S3) further reveals variations in atomic column intensities, where sites of low intensity (indicated by black arrows) are attributed to Ti atomic vacancies.³⁷ Similar to $\text{Ti}_{0.87}\text{O}_2$ nanosheets, the GO nanosheets showed a high aspect ratio, which was favorable for the formation of uniformly ordered nanochannels. The aqueous suspension of GO nanosheets also exhibited a clear Tyndall light scattering and a broad ultraviolet absorption band centered at about 229 nm (Figure S4a,b). The AFM image of GO nanosheets is shown in Figure 2c, which reveals an even thickness of approximately 0.8 nm . The TEM measurement displayed the same morphology as was observed from AFM imaging and showed an atomically-thin thickness (Figure S4c-f). Figure 2d shows many light grey areas with higher transmittance of GO nanosheets, suggesting the presence of nanoscale defects.^{38,39} As reported in previous publications,^{38,40} the defect density could be roughly estimated by using the edge carbon atoms with double bonded oxygen. Accordingly, the defect density in GO is around 15.2% (Table S1).

We then used the obtained $\text{Ti}_{0.87}\text{O}_2$ and GO nanosheets (mass ratio=4:5) with different assembly ways to rationally construct 2D $\text{Ti}_{0.87}\text{O}_2/\text{GO}$ (TiG) membranes. The membranes were named TiG-x ($x=2, 4, 6, n$), where x denotes the number of 2D $\text{Ti}_{0.87}\text{O}_2$ -GO heterogeneous interfaces. Notably, n serves as a variable representing the highest number of 2D heterogeneous interfaces. TiG-2, TiG-4 and TiG-6 membranes were prepared via sequential filtration of $\text{Ti}_{0.87}\text{O}_2$ and GO dispersion, while TiG-n membrane was synthesized by direct filtration of the mixed suspension of $\text{Ti}_{0.87}\text{O}_2$ and GO (details in Supplementary Note 1). The chemical structure of the as-fabricated TiG-x membrane was identified by Fourier-transform infrared (FTIR) spectroscopy (Figure S5) and X-ray photoelectron spectroscopy (XPS) (Figures S6-S9). As illustrated in the top view scanning electron microscopy (SEM) image of Figure S10, the TiG-x membrane exhibited a homogeneous morphology of densely stacked 2D nanosheets, usually leading to additional and wider ion diffusion channels that enhance permeability.^{28,41} Cross-sectional SEM images indicated the TiG-x membranes with the same thickness of $\sim 13 \mu\text{m}$ (Figure S10). Meanwhile, all of the membranes showed a typical laminar structure. Impressively, the corresponding EDX mapping of the titanium element of TiG-x membranes directly revealed the 2D $\text{Ti}_{0.87}\text{O}_2$ -GO heterogeneous interface. Figure S11 suggests that the molecular-scale

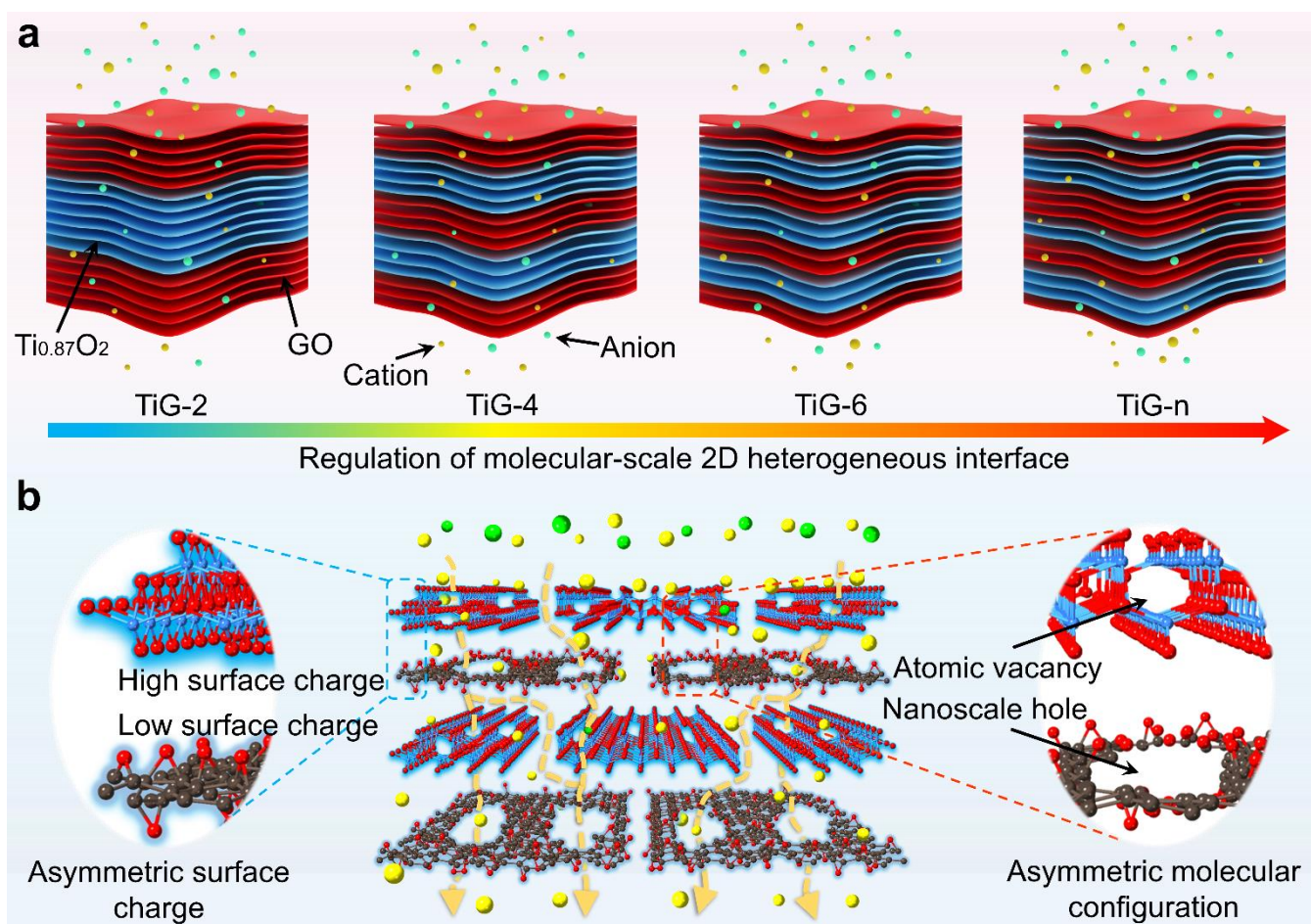


Figure 1. Molecular-scale asymmetry nanochannels with high-efficiency ion transport. (a) Schematic of the transmembrane ion transport of membranes with different 2D heterogeneous interfaces (TiG-2, TiG-4, TiG-6, and TiG-n membranes) in a salinity concentration gradient. (b) Molecular-scale asymmetry nanochannel design of TiG-n membrane for effective ion transport with high ion selectivity and permeability.

asymmetry nanochannel increases in the order of TiG-2, TiG-4, TiG-6, and TiG-n membranes. The X-ray diffraction (XRD) patterns of TiG-x membranes all exhibited layered $\text{Ti}_{0.87}\text{O}_2$ structures with dominant 010 peaks, which corresponded to an interlayer distance of ~ 1.75 nm (Figure 2e). However, the 010 peaks of TiG-x membranes showed distinctly different intensities, indicating the various stacking densities of $\text{Ti}_{0.87}\text{O}_2$ in these layered structures. We can find a sequential decrease in the intensity of the 010 peaks within the TiG-2, TiG-4, TiG-6, and TiG-n membranes, respectively. This result suggests that the 2D asymmetry nanochannel of TiG-2, TiG-4, TiG-6, and TiG-n membranes increases sequentially.^{42,43} Raman spectroscopy was performed to further investigate the heterointerface formation of TiG-x membranes. As shown in Figure 2f, the two characteristic D (1350 cm^{-1}) and G (1590 cm^{-1}) peaks of TiG-x membranes were observed, representing the hybridized vibrations of sp^3 defects and the in-plane vibrations of sp^2 carbon atoms, respectively.^{44,45} Generally, the intensity ratio of D peak to G peak (I_D/I_G) reveals the number of defects in the carbon material, which could contribute to the construction of abundant heterogeneous interfaces.⁴⁶ The I_D/I_G ratios calculated for TiG-2, TiG-4, TiG-6 and TiG-n membranes are 0.908, 0.914, 0.944, and 0.977, respectively. This result verifies the same trend of 2D asymmetry nanochannel numbers as the XRD analyses,

following the order of $\text{TiG-2} < \text{TiG-4} < \text{TiG-6} < \text{TiG-n}$ membranes. The interaction at the heterointerfaces between $\text{Ti}_{0.87}\text{O}_2$ and GO nanosheets was directly explored by XPS characterization. The Ti 2p spectra of pure $\text{Ti}_{0.87}\text{O}_2$ membrane showed two peaks at binding energies of 458.0 and 463.7 eV, which are attributed to the Ti $2p_{3/2}$ and Ti $2p_{1/2}$, respectively. In contrast, the TiG-n membrane displayed a slight shift towards higher binding energies in the Ti 2p spectra, from 458.0 to 458.1 eV and from 463.7 to 463.9 eV (Figure 2g). This slight shift indicates a moderate interaction between $\text{Ti}_{0.87}\text{O}_2$ and GO nanosheets of TiG-n membrane.⁴⁷ In addition, the Raman spectra of TiG-n and $\text{Ti}_{0.87}\text{O}_2$ membranes were illustrated in Figure S12. Compared with the $\text{Ti}_{0.87}\text{O}_2$ membrane, there was a redshift of the Ti-O vibrational mode in the TiG-n membrane. This result further indicates the presence of interactions at the interface between the $\text{Ti}_{0.87}\text{O}_2$ and GO nanosheets.⁴⁸ Moreover, the cross-sectional high-resolution TEM (HRTEM) image of TiG-n membrane exhibited a multilayered heterostructure of stacked $\text{Ti}_{0.87}\text{O}_2$ and GO sheets (Figure 2h), which provides numerous molecular-scale asymmetry nanochannels. The fringe spacing between $\text{Ti}_{0.87}\text{O}_2$ layers is 1.75 nm (inset in Figure 2h), which is in agreement with the d -spacing in the XRD pattern. For comparison, $\text{Ti}_{0.87}\text{O}_2$ and GO membranes with the same thickness of $\sim 13\text{ }\mu\text{m}$ were also constructed (Figures S13-S16). In addition, the

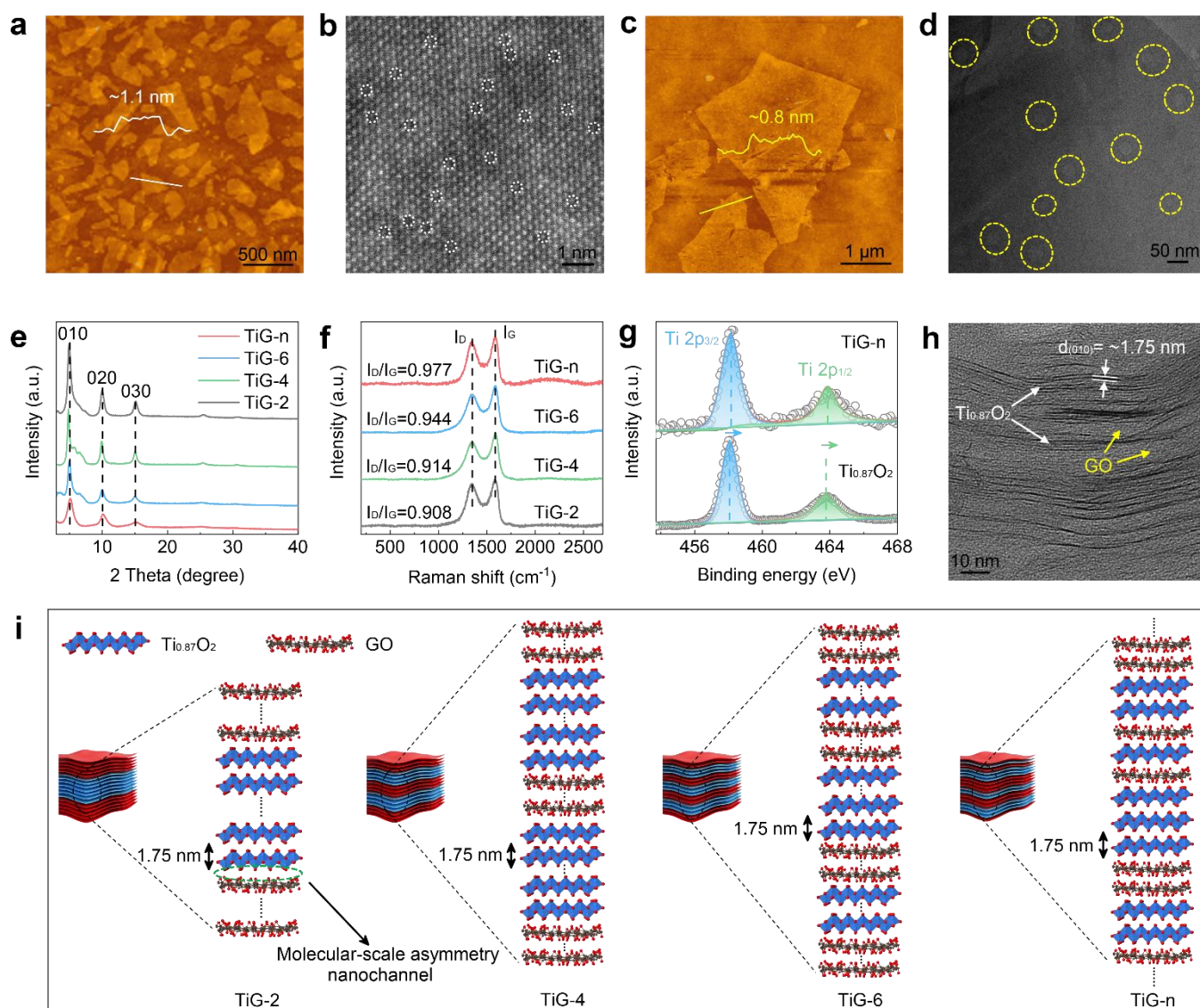


Figure 2. Preparation and characterization of TiG-n membrane. AFM image of (a) $\text{Ti}_{0.87}\text{O}_2$ and (c) GO nanosheets with their corresponding thickness. (b) HAADF-STEM image of a $\text{Ti}_{0.87}\text{O}_2$ nanosheet. (d) HRTEM image of GO nanosheets. (e) XRD patterns and (f) Raman spectra of TiG-2, TiG-4, TiG-6, and TiG-n membranes. (g) XPS peaks of Ti 2p obtained from $\text{Ti}_{0.87}\text{O}_2$ and TiG-n membranes. (h) Cross-sectional HRTEM image of a TiG-n membrane showing the multilayered structure of stacked $\text{Ti}_{0.87}\text{O}_2$ and GO sheets. (i) Schematic of the distinct restacking and same interlayer distance in TiG-2, TiG-4, TiG-6, and TiG-n membranes.

TiG-n membrane displayed high flexibility and excellent mechanical stability under different bending degrees (Figure S17). After long-term immersion in deionized (DI) water, the TiG-n membrane barely changed and remained structurally intact, while the GO membrane exhibited significant fragmentation (Figure S18). These can be ascribed to the interfacial interactions between $\text{Ti}_{0.87}\text{O}_2$ and GO nanosheets in the TiG-n membrane. Besides, the TiG-n membrane was more hydrophilic with a static contact angle of 21.7° compared with the $\text{Ti}_{0.87}\text{O}_2$, GO, TiG-2, TiG-4, and TiG-6 membranes (Figure S19). The high stability and enhanced wettability of TiG-n membrane are beneficial for subsequent ion migration tests in the aqueous electrolyte solution.

Ion conductivity and selectivity investigation. The transmembrane ion transport properties of TiG-n membrane were evaluated by fixing it in the middle of H-cell (Figure S20a). A pair of

Ag/AgCl electrodes was chosen to collect ionic current under NaCl electrolytes with various concentrations. As shown in Figure S20b, the current-voltage (I-V) characteristics of TiG-n membranes were explored in NaCl electrolytes at concentrations between 0.01 and 1 M. These current responses revealed a linear ohmic behavior, from which the transmembrane ion conductance could be obtained. Notably, the measured ion conductance of TiG-n membranes exhibited a different changing tendency with a wide series of NaCl concentrations (Figure S20c). In the higher concentration region ($>10^{-2}$ M), the ion conductances showed a linear relationship with the salt concentration, suggesting a bulk behavior. While the measured ion conductances deviated from the linear relationship in the lower concentration region ($<10^{-2}$ M), indicating a surface-charge-governed ion transport property (Figure 3a).^{7,49} In particular, the conductance values of the TiG-n membrane are obviously higher than those of TiG-6, TiG-4, TiG-2, $\text{Ti}_{0.87}\text{O}_2$, and GO

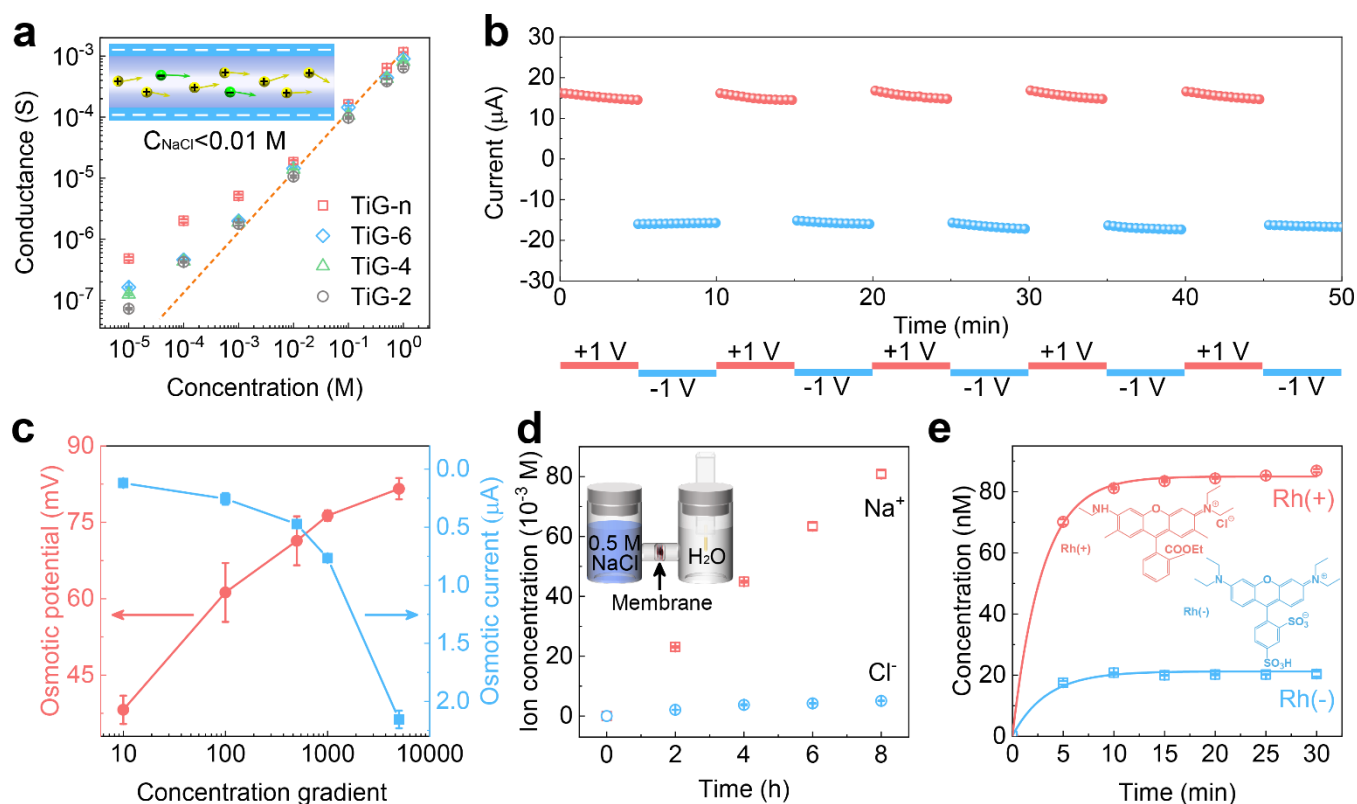


Figure 3. Transmembrane nanofluidic ion transport properties. (a) Transmembrane ionic conductance of TiG-2, TiG-4, TiG-6, and TiG-n membranes under various NaCl electrolytes. (b) I-T curves of TiG-n membrane in 0.1 M NaCl electrolyte with an external bias alternating ± 1 V. (c) I_{os} and V_{os} values of TiG-n membrane tested in various NaCl concentration gradients of 10, 100, 500, 1000 and 5000 ($C_{low}=0.1$ mM). (d) The Na^+ and Cl^- concentration in the right chamber of H-shaped cell with TiG-n membranes. (e) Permeation experiments of TiG-n membrane measured by rhodamine 6G (Rh (+)) and sulforhodamine (Rh (-)).

membranes, showing an ultrafast ion transport through the TiG-n membrane (Figures 3a and S21). Next, the current-time (I-T) test of the TiG-n membrane was carried out in 0.1 M NaCl electrolyte with an external bias alternating between +1 V and -1 V (Figure 3b). Each cycle lasted for 5 min without interruptions and was repeated for a total duration of 50 min. Both the negative and positive currents remained at the same level following each voltage polarity change, demonstrating the outstanding stability of the TiG-n membrane. To investigate the correlation between osmotic performance and salty concentration gradient, the I-V curves under a series of NaCl concentration gradients were performed to obtain both short-circuit current (I_{sc}) and open-circuit voltage (V_{oc}) from the intercepts on the coordinate axis (Figure S20d). Then, the osmotic current (I_{os}) and potential (V_{os}) can be obtained by subtracting redox potentials (V_{redox}) from the V_{oc} (Figure S22). In Figure 3c and Table S2, the values of I_{os} and V_{os} of TiG-n membrane both augmented with the concentration gradient increased. Moreover, the cation transference number of TiG-n membrane can reach up to 0.83 under a 10-fold concentration difference, indicating prominent cation ion selectivity (Figure S20e and Table S3).

The ion conductivity and selectivity of TiG-n membrane were further investigated by an ion diffusion experiment, which was measured using an H-type electrochemical cell filled with 0.5 M NaCl solution on the feed side and deionized water on the permeate side (Figure 3d). The feed and permeate sides were separated by the TiG-n, TiG-6, TiG-4, TiG-2, $Ti_{0.87}O_2$ and GO membranes, and the ion concentration of the permeate side was

monitored to examine the ion transport property. After ion diffusion of 8 hours, it was seen that the Na^+ ion concentration of TiG-n membrane was much higher than that of TiG-6, TiG-4, TiG-2, $Ti_{0.87}O_2$ and GO membranes (Figures 3d and S23). This indicated the excellent cation conductivity of TiG-n membrane. Meanwhile, the Cl^- ion concentration of TiG-n membrane could also be maintained at a low level, demonstrating its superior cation selectivity. The cation-selective property of TiG-n membrane was also examined by the permeation experiments of fluorescent dyes.^{50,51} As shown in the inset of Figure 3e, positively charged rhodamine 6G (Rh (+)) and negatively charged sulfonated rhodamine (Rh (-)) were selected due to their similar structures but opposite charges. The TiG-n membrane was sandwiched in the center of H-type electrochemical cells, which were filled with 1×10^{-4} M fluorescent dye solution and DI water. We monitored the side of the DI water with the assistance of Fluorescence spectroscopy for 30 min. As a consequence, the transport rate of Rh (+) is much larger than that of Rh (-), revealing the decent cation selectivity of TiG-n membrane (Figure 3e). EDX spectroscopy mappings were conducted to further explore the intrinsic ion selective feature of TiG-n membrane. We immersed the TiG-2, TiG-4, TiG-6 and TiG-n membranes in 0.1 M NaCl solution for 30 min, followed by rinsing with deionized water to remove residual ions. The corresponding EDX spectroscopy mappings displayed that the strength of Na signals is much higher than that of Cl, with the Na/Cl strength ratio following the trend of TiG-n > TiG-6 > TiG-4 > TiG-2 (Figures S24-S27). This result further reveals that the TiG-n

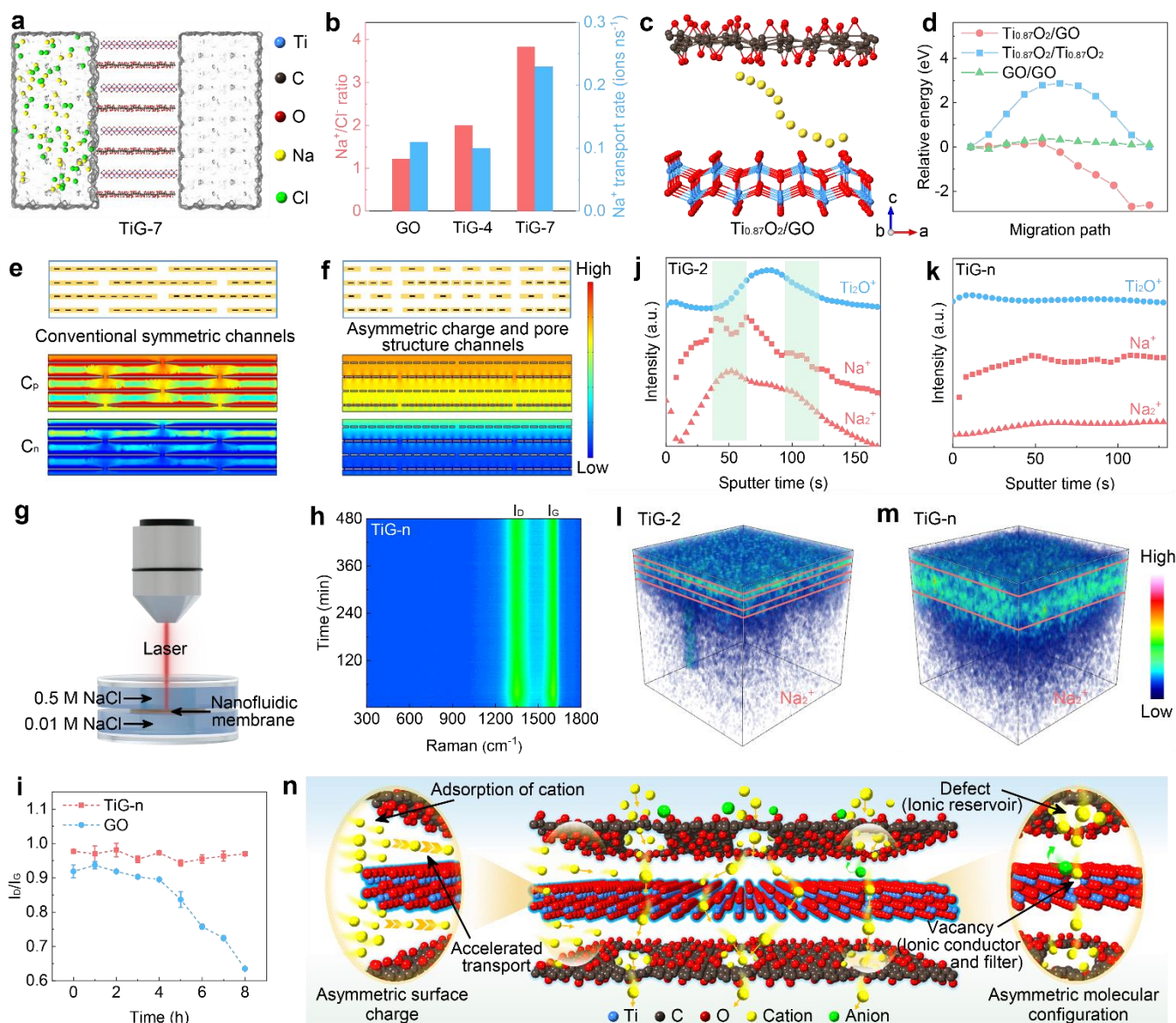


Figure 4. Interface induced contiguous adsorption-diffusion mechanism. (a) Typical simulation boxes exhibiting TiG-7 membrane and NaCl electrolyte. (b) Na^+/Cl^- selectivities and Na^+ transport rates calculated for Na^+ and Cl^- ions transferred across GO, TiG-4 and TiG-7 membranes. (c) Pathways for Na^+ ion diffusion in the interlayer of restacked $\text{Ti}_{0.87}\text{O}_2/\text{GO}$ bilayers from the side view. (d) Energy profile of Na^+ ion diffusion in the interlayer of restacked $\text{Ti}_{0.87}\text{O}_2/\text{GO}$ bilayers, $\text{Ti}_{0.87}\text{O}_2/\text{Ti}_{0.87}\text{O}_2$ bilayers and GO/GO bilayers. (e) Calculated cation and anion concentration of simulated (e) conventional symmetric channels and (f) asymmetric charge and pore structure channels. (g) Schematic illustration for the testing set-up of in situ Raman spectroscopy. (h) In situ Raman spectra of TiG-n membrane in the ion diffusion process of 480 min at 0.5 M/0.01 M NaCl salinity gradient. (i) The evolution of I_D/I_G ratios of TiG-n and GO membranes as a function of ion diffusion time. The 3D reconstruction distribution maps of Ti_2O^+ , Na^+ , and Na_2^+ secondary ions in (j) TiG-2 and (k) TiG-n membranes. ToF-SIMS depth profiles of Na_2^+ secondary ion in (l) TiG-2 and (m) TiG-n membranes. (n) Schematic illustration of interface induced contiguous ion adsorption-diffusion mechanism, where yellow balls represent cations, green balls represent anions, blue balls represent Ti, black balls represent C, and red balls represent O. The nanoscale defects on the GO layer can serve as ion storage spaces to capture a large number of cations, while Ti vacancies act as additional angstrom-scale confinement pore channels, functioning as ion filters and ion conductors to improve ion selectivity and permeability.

membrane possesses a decent cation selectivity due to the promotion effect of molecular-scale asymmetry nanochannels.

Interface induced contiguous adsorption-diffusion mechanism. To understand the origin of ion transport behavior in the molecular-scale asymmetry nanochannels, MD simulations were carried out to explore the ion diffusion mechanism of the TiG-n membrane. We first investigated the effect of

asymmetric surface charge within ion nanochannels. $\text{Ti}_{0.87}\text{O}_2$ and GO nanosheets with different surface charges were stacked in different orders to construct the eight-layer 2D interface membranes, namely $\text{Ti}_{0.87}\text{O}_2$, GO, TiG-4 and TiG-7 membranes (Figures 4a and S28). Two water boxes were placed on each side of the four modes, where the same amount of sodium and chloride ions was added to the left water box. Then, the ions were transported from the left water box to the right water box

along the lamination direction of nanosheets. Figure S29a-f shows the transfer quantity of Na^+ and Cl^- ions moving through the membranes during the simulation time. According to the transfer number of Na^+ and Cl^- ions, we further quantified the ion selectivity in nanofluidic membranes. Meanwhile, the corresponding Na^+ transport rate was obtained by calculating the total number of ions transferring across the membrane per unit time at a certain concentration gradient. Observed from Figure 4b, the Na^+/Cl^- selectivity and Na^+ transport rate across the membranes followed the order of $\text{TiG-7} > \text{TiG-4} > \text{GO}$, which was consistent with the trend of numbers of molecular-scale asymmetry nanochannels. This result indicates that nanochannels with asymmetry surface charge generated by 2D heterogeneous interfaces can improve the cation permeability and selectivity of nanofluidic channels. Noteworthy, only Na^+ ions but not Cl^- ions were transported through the $\text{Ti}_{0.87}\text{O}_2$ during the simulation time due to the strong ion- $\text{Ti}_{0.87}\text{O}_2$ electrostatic interaction (Figure S29g,h).⁵² Hence the $\text{Ti}_{0.87}\text{O}_2$ membrane possesses a high Na^+/Cl^- selectivity. However, the transport rate of Na^+ ions through $\text{Ti}_{0.87}\text{O}_2$ membrane was low, because some of them may be adsorbed on the membrane, hindering their further rapid diffusion due to electrostatic interaction arising from the symmetric high charge density.^{52,53} This further implies that the asymmetric surface charge of nanochannels plays an important role in the high-efficiency Na^+ ion adsorption-diffusion process.

Based on asymmetric surface charges, we also used DFT calculations to obtain an atomistic understanding of the role of asymmetric molecular configurations in the ion diffusion process. Three simulation structural models of $\text{Ti}_{0.87}\text{O}_2/\text{Ti}_{0.87}\text{O}_2$, GO/GO and $\text{Ti}_{0.87}\text{O}_2/\text{GO}$ were designed, to examine the interaction mechanism in nanochannels. As shown in Figure S30, the adsorption energy of Na^+ ions within the $\text{Ti}_{0.87}\text{O}_2/\text{GO}$ (-4.15 eV) is stronger compared to $\text{Ti}_{0.87}\text{O}_2/\text{Ti}_{0.87}\text{O}_2$ (-2.68 eV) and GO/GO (-3.27 eV). This phenomenon implies that the adsorption interaction between Na^+ ions and the $\text{Ti}_{0.87}\text{O}_2$ - GO ion channels with asymmetric surface charge formed at the 2D heterogeneous interface is significantly enhanced, thereby exhibiting a higher cation selectivity. Next, the diffusion process of adsorbed Na^+ ions driven by concentration gradient is examined by calculating the diffusion barriers in the interlayer of restacked $\text{Ti}_{0.87}\text{O}_2/\text{Ti}_{0.87}\text{O}_2$ bilayers, GO/GO bilayers and $\text{Ti}_{0.87}\text{O}_2/\text{GO}$ bilayers (Figures 4c and S31). Compared with the $\text{Ti}_{0.87}\text{O}_2/\text{Ti}_{0.87}\text{O}_2$ (~ 2.87 eV) and GO/GO (~ 0.39 eV) models, a much lower diffusion barrier of around 0.17 eV is obtained for the $\text{Ti}_{0.87}\text{O}_2/\text{GO}$ model (Figure 4d). Notably, in the latter stage of the migration pathway within the $\text{Ti}_{0.87}\text{O}_2/\text{GO}$ model, the diffusion energy of Na^+ ions obviously decreases due to the electrostatic attraction from surrounding Ti vacancies. This weakens the Coulombic repulsion between Na^+ ions and the $\text{Ti}_{0.87}\text{O}_2$ lattice, thereby promoting the transport of Na^+ ions through the Ti vacancies.^{28,54} These results suggest molecular-scale asymmetric $\text{Ti}_{0.87}\text{O}_2$ - GO ion channels formed at the 2D heterogeneous interface can induce the adsorption of Na^+ ions, followed by their fast diffusion.

COMSOL simulation based on the Poisson–Nernst–Planck (PNP) equations was further conducted to prove the effect of the asymmetric charge distribution and channel structure on the continuous ion diffusion behaviors of multilayer channels. By restacking traditional defect-free nanosheets and nanosheets with different defect sizes and charge densities, three simulation

structural models were constructed, conventional symmetric channels, asymmetric charge channels, and asymmetric charge and pore structure channels (Figures 4e,f and S32a). It was obviously seen that higher Na^+ concentration and lower Cl^- concentration could be attained in asymmetric charge channels compared with conventional symmetric channels (Figures S32b and S33a). This can be explained by the fact that symmetric high surface charges result in the local strengthening of the surface roughness, while symmetric low surface charges fail to well-overlap the electrical double layer, leading to limited ion-selective transport.^{53,55} In the case of conventional symmetric channels and asymmetric charge channels, Na^+ ions can only diffuse through the gaps between adjacent nanosheets. In contrast, Na^+ ions transport not only through the interlayer gaps but also in the various defects within single layers for asymmetric charge and pore structure channels. Thus, the Na^+ ion concentration of asymmetric charge and pore structure channels is much higher than that of the other two types of 2D channels (Figures S32b and S33), revealing that structural channels composed of alternately stacked nanosheets with asymmetric molecular configuration can facilitate cation contiguous adsorption-diffusion dynamics. Moreover, compared with other 2D channels, asymmetric charge and pore structure channels achieved a lower Cl^- concentration due to the size confinement sieving effect of angstrom-scale vacancy, which further validated their capability to effectively exert a strong exclusion of Cl^- ions and induce Na^+ ion adsorption and diffusion.

To reveal the ion transport mechanism in a deeper manner, in situ Raman spectra were measured during the transmembrane ionic transport process for the first time (Figure 4g). Figures 4h and S34 show the in situ Raman spectra of TiG-n and GO membranes under actual operation conditions (0.5 M $\text{NaCl}/0.01$ M NaCl) for 8 hours. The time-dependent Raman spectra for TiG-n and GO membranes both exhibited the appearance of the D and G peaks (Figure S35). As shown in Figure 4i, the I_D/I_G ratios of TiG-n membrane remained consistently higher than those of GO membrane in the process of ion diffusion, indicating that Na^+ ions are continuously adsorbed and subsequently diffused through the abundant molecular-scale asymmetry nanochannels.^{56,57} Moreover, during the ion diffusion process of 480 min, it was seen that the I_D/I_G ratios of GO membrane remarkably reduced. In contrast, the I_D/I_G ratios of TiG-n membrane did not exhibit significant changes, indicating its high structural stability. This can be attributed to the dynamic equilibrium of contiguous ion adsorption and diffusion within the molecular-scale asymmetry nanochannels.^{20,57,58} To demonstrate how the molecular-scale asymmetry nanochannels affect ion transport from a more microscopic point of view, time-of-flight secondary ion mass spectrometry (TOF-SIMS) was conducted to investigate elemental distribution occurring at the $\text{Ti}_{0.87}\text{O}_2$ - GO interface. Under a 0.5 M/ 0.01 M NaCl salinity gradient, TiG-2 and TiG-n membranes were characterized after ion diffusion for 3 hours. In the TiG-2 membrane, the Na^+ and Na_2^+ ionic fragments are primarily accumulated in the interface of $\text{Ti}_{0.87}\text{O}_2$ and GO (Figure 4j). On the contrary, both the same ionic fragments are uniformly distributed throughout the TiG-n membrane (Figure 4k), which is ascribed to the presence of molecular-scale asymmetry nanochannels formed by numerous heterogeneous interfaces within the membrane. The depth 3D distribution map further visually signified the same distribution trend as presented in the depth profiling data (Figures 4l,m and S36). These results

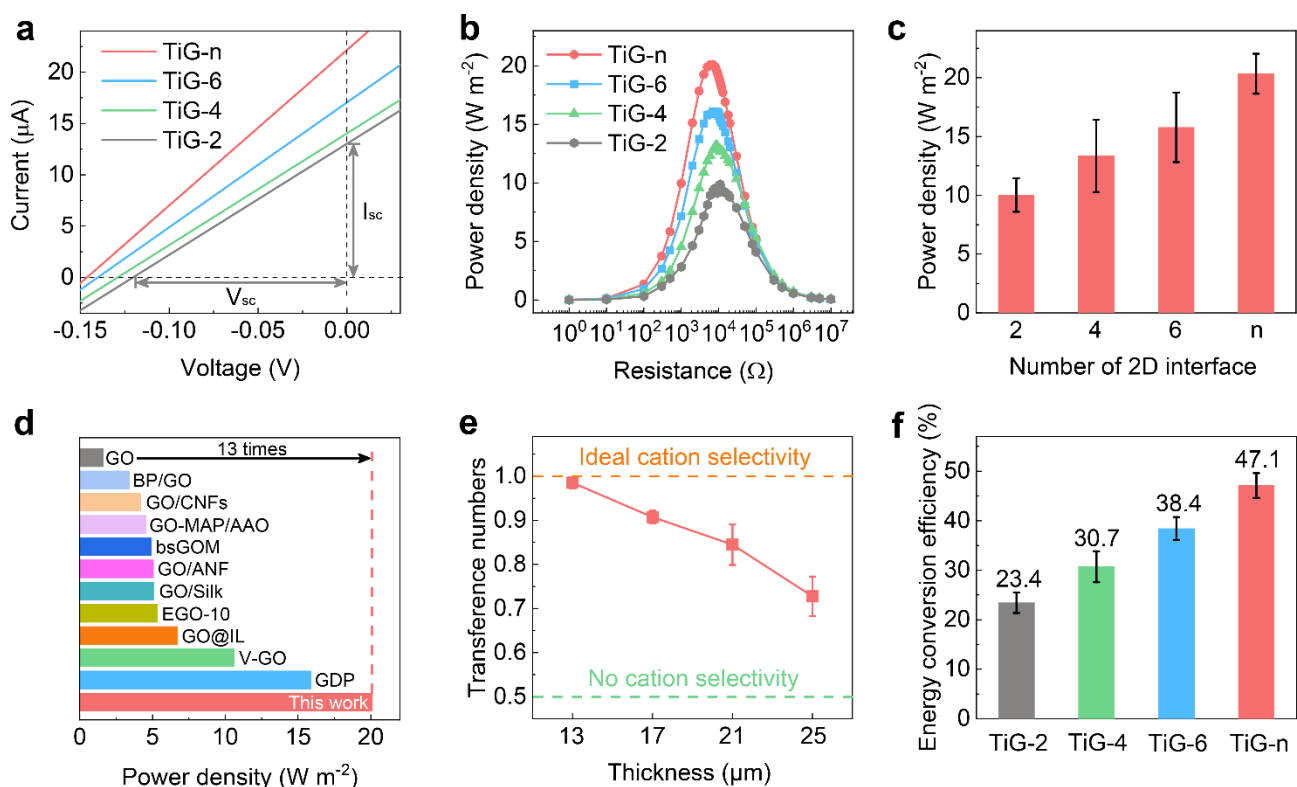


Figure 5. Osmotic energy conversion behavior. (a) I–V curves and (b) output power density of TiG-n, TiG-6, TiG-4 and TiG-2 membranes as a function of external load resistance for the artificial seawater/river water system. (c) Influence of the number of 2D interfaces on the power density. (d) Osmotic energy conversion of TiG-n outperforms all reported nanofluidic membranes based on GO materials. (e) Cation transference number of TiG-n membrane in different thicknesses under a 50-fold salinity gradient. (f) Energy conversion efficiency of TiG-n, TiG-6, TiG-4 and TiG-2 membranes under a 50-fold salinity gradient.

suggest the $\text{Ti}_{0.87}\text{O}_2$ -GO interface plays a critical role in facilitating the cation adsorption-diffusion process.

Therefore, we proposed the interface induced contiguous ion adsorption-diffusion mechanism for Na^+ ion transport in molecular-scale asymmetric GO- $\text{Ti}_{0.87}\text{O}_2$ nanochannels (Figure 4n). When Na^+ ions entered the negatively charged asymmetry nanofluid channels, they were initially selectively adsorbed due to electrostatic interactions. Then, the adsorbed Na^+ ions can be accelerated transport in the horizontal interlayer nanochannels, which is ascribed to asymmetric electrical double layer (EDL) formation induced by asymmetric surface charge.^{59,60} In contrast, symmetric high surface charge distribution in the channel can increase local surface roughness, reducing ion permeability, whereas symmetric low charges fail to ensure sufficient EDL overlap, thereby compromising ion selectivity.⁵³ In the vertical channels along the stacking direction, the nanoscale defects on the GO layer can act as ion storage spaces to trap a significant number of Na^+ ions, leading to the actual transmembrane transport concentration gradient being higher than the original concentration gradient.²⁰ Therefore, a higher chemical potential gradient could be obtained from GO layer to $\text{Ti}_{0.87}\text{O}_2$ layer, which resulted in a higher ion flux. This phenomenon can be verified by a numerical simulation. Figure S37 shows the cation concentration profile near the GO defect and Ti vacancy of hybrid channels, which is plotted from points A to B. It was seen that the cumulative ion concentration within the GO defect side exceeded that of the Ti vacancy side, indicating that defects of GO serve as the ion-enrichment space to enhance ion

permeability.⁶¹ When the Na^+ ion continued to diffuse through the $\text{Ti}_{0.87}\text{O}_2$ layer with rich Ti atomic vacancies, these vacancies served as additional angstrom-scale confinement pore channels, functioning as ion filters and ion conductors to enhance ion selectivity and permeability.^{27,62} Based on the calculation (Figure S38), we can see that the Ti vacancy-containing channels exhibited a higher cation concentration and lower anion concentration than the conventional channels, demonstrating the role of Ti vacancies in promoting ion selectivity and permeability. These simulation results are also consistent with the experimental measurements of ion transport rates (Figure S23). From the $\text{Ti}_{0.87}\text{O}_2$ to GO side, the smaller atomic Ti vacancies of $\text{Ti}_{0.87}\text{O}_2$ and the larger nanoscale defects of GO form a cone-shaped geometrical configuration capable of inducing fast ion transport.^{63,64} Due to the abundant molecular-scale asymmetric nanochannels in TiG-n membrane, such a cation adsorption-diffusion process can continuously occur. Combining the advantages of both asymmetric surface charge and asymmetric molecular configuration, the TiG-n membrane with molecular-scale asymmetric nanochannels possesses great potential in salinity energy conversion applications.

High-performance osmotic energy generation. The osmotic-energy-generation performance of TiG-n membrane was next investigated under a concentration gradient of standard artificial seawater (0.5 M NaCl) and river water (0.01 M NaCl). The typical I–V curves were recorded in the presence of a 50-fold concentration gradient. As shown in Figures 5a, S39b and S40b, the I_{sc} and V_{oc} values of TiG-n membrane were 22.17 μA and

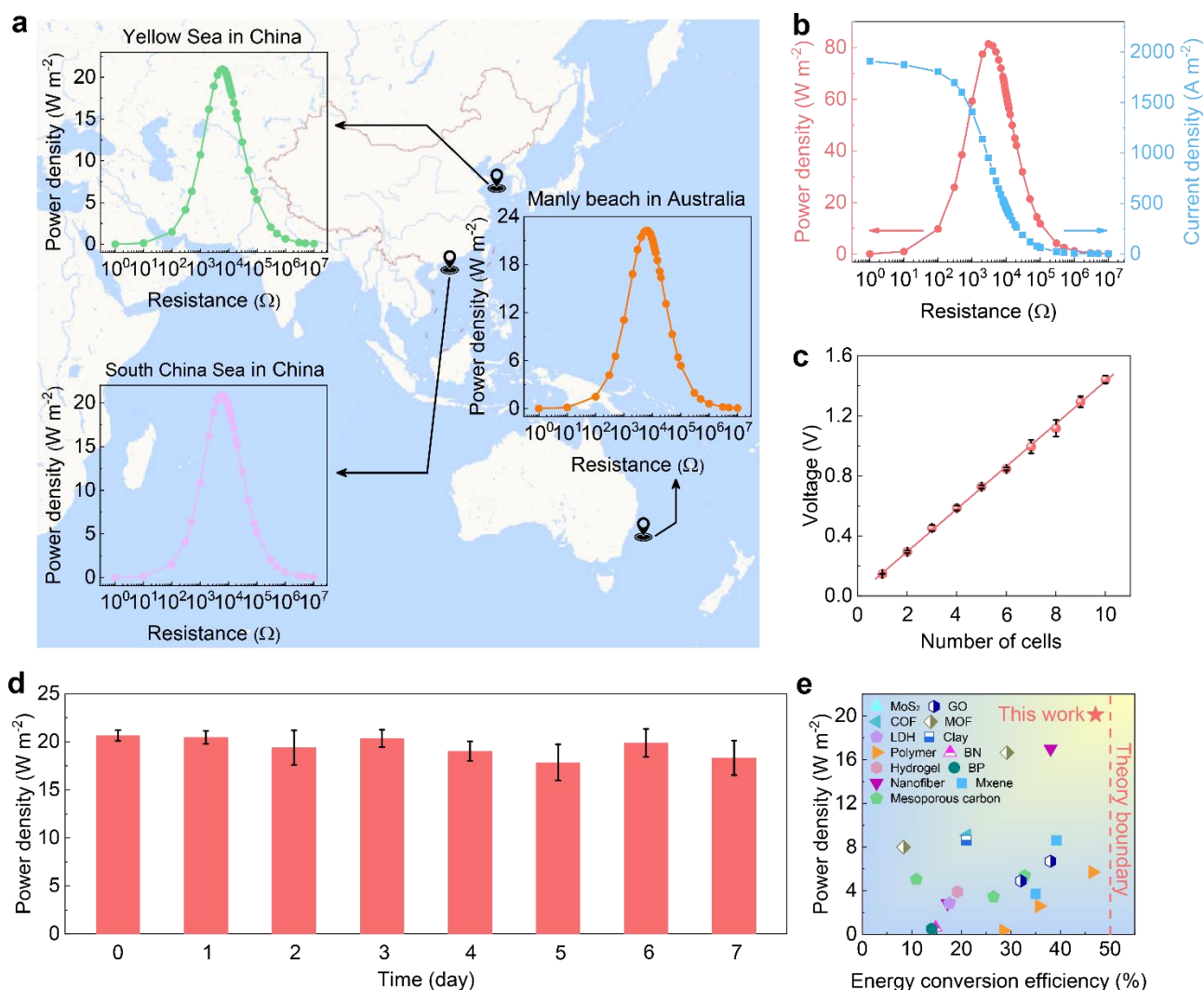


Figure 6. Application viability of the TiG-n membrane. (a) Output power density of TiG-n membrane in various natural seawater. (b) Output power density of TiG-n membrane as a function of external load resistance in artificial Dead Seawater/river water. (c) Linear correlation between the overall output potential of the tandem and the unit number. (d) The long-term stability of TiG-n membrane operating in artificial seawater/river water for 7 days with no electrolyte replenishing. (e) Comparison of the osmotic power harvesting capacity for the TiG-n membrane with reported macroscopic-scale membranes in terms of energy conversion efficiency and output power density. All values were collected under the same salinity gradient of 0.5/0.01 M NaCl and the same test area of 0.03 mm². Detailed data and references of all nanofluidic membranes are found in Table S5.

146.2 mV, respectively, which are higher than those of TiG-6, TiG-4, TiG-2, Ti_{0.87}O₂, and GO membranes. The harvested osmotic power can supply an external circuit with a load resistor (R_L), which was directly calculated by $P = I^2 R_L$. The current density gradually decreased as the R_L increased, and the TiG-n membrane exhibited a higher current density than TiG-6, TiG-4, TiG-2, Ti_{0.87}O₂, and GO membranes (Figures S39c, S40c and S41). Meanwhile, the peak power density output of the TiG-n membrane reached 20.1 W m^{-2} under a salinity gradient of 0.5/0.01M NaCl, outperforming TiG-6 (16.1 W m^{-2}), TiG-4 (13.2 W m^{-2}), TiG-2 (9.9 W m^{-2}), Ti_{0.87}O₂ (3.8 W m^{-2}), and GO (1.6 W m^{-2}) membranes (Figure 5b). We can conclude that the gradual decrease in power density is related to the number of 2D heterogeneous interfaces. As the number of these interfaces continues to increase, the osmotic power-generation performance further improves (Figure 5c). Notably, the TiG-n membrane with the highest number of heterogeneous interfaces

achieved a maximum output power density approximately 13 times higher than that of the GO membrane (Figure 5d). It could be seen from Figure 5e that the calculated Na⁺ transference number of TiG-n membrane was 0.985, very close to the ideal transference number ($t = 1$), which corresponds to a Na⁺/Cl⁻ selectivity ratio of around 65.7 under 0.5/0.01 M NaCl salinity gradient (details in Supplementary Note 9). This value surpassed those of most reported nanofluidic membranes under a 50-fold NaCl salinity gradient. We further calculated the energy conversion efficiency of TiG-n membrane to be as high as 47.1%, which is higher than those of TiG-6 (38.4%), TiG-4 (30.7%), and TiG-2 (23.4%) membranes (Figure 5f and details in Supplementary Note 10). Considering that ions can rapidly transport through vacancies, the influence of vacancy density on the osmotic energy generation performance was investigated. According to our previous studies,^{27,29} Ti_{0.91}O₂ nanosheets possess fewer Ti vacancies compared to Ti_{0.87}O₂ nanosheets

(Figure S42a,b). Then, $\text{Ti}_{0.91}\text{O}_2$ nanosheets were assembled with GO nanosheets to construct 2D $\text{Ti}_{0.91}\text{O}_2/\text{GO}$ membranes (Figure S42c,d). The $\text{Ti}_{0.91}\text{O}_2/\text{GO}$ membrane delivered a lower power density of 17.9 W m^{-2} than TiG-n membrane at a 50-fold NaCl salinity gradient (Figure S42e,f). The osmotic power-production performance was also found to be related to ambient temperature. The power density of TiG-n membrane continuously enhanced from 7.9 to 27.7 W m^{-2} with the increase in temperature from 10°C to 40°C (Figure S43), which is associated with improved ion mobility and suppressed ion concentration polarization.^{13,27} The thickness of the TiG-n membrane also influences the energy conversion performance with the optimal value at $13 \mu\text{m}$ (Figure S44). With increasing membrane thickness, the higher membrane resistance possesses a greater impact on transmembrane ion transport, resulting in a decrease in power density output.

Application viability and stability demonstration. In order to assess the practical application value of TiG-n membrane, osmotic energy harvesting performance was investigated by mixing real seawater and river water through RED. As shown in Figure 6a, the maximum power density was up to $\sim 20.95 \text{ W m}^{-2}$, 20.89 W m^{-2} , and 22.25 W m^{-2} for China's Yellow Sea, South China Sea, and Australian seawater, respectively, far superior to conventional permselective membranes and most of the reported nanofluidic membranes. Considering that the osmotic power is available in high salt lakes and industrial wastewater, the energy conversion of TiG-n membrane was tested in NaCl solutions with various concentrations. As can be seen from Figure S45a, with an increasing salinity gradient from 5- to 500-fold, the V_{oc} and I_{sc} both improved accordingly owing to the increased driving force of the concentration gradient. As a result, the corresponding maximum power density increased from 0.57 to 70.6 W m^{-2} (Figure S45b,c). We also measured its performance under 614-fold (artificial Dead Seawater/river water) concentration gradients, where the maximum output power density can further increase to 81.4 W m^{-2} (Figure 6b). In addition, the osmotic energy generation was evaluated by using different types of chloride salts. The V_{oc} and I_{sc} values tested with various salts followed the trend of $\text{KCl} > \text{NaCl} > \text{LiCl} > \text{CaCl}_2 > \text{MgCl}_2$ (Figure S46a), which shows a positive correlation with the diffusion coefficients of cations (Table S4). Thus, the highest peak power density of 22.0 W m^{-2} was achieved in the KCl electrolyte (Figure S46b). This result indicates the potential use of the TiG-n membrane in real-world multiple-ion environment applications. The antifouling property of nanofluidic membranes is equally significant for their practical applications. We examined the antifouling ability of the TiG-n membrane by measuring its osmotic energy conversion performance under a $0.1 \text{ M}/0 \text{ M}$ methylene blue gradient.^{27,65} It was found that the TiG-n membrane almost could not generate power in this case, which was ascribed to the incapacity of dye molecules to transport through the membrane (Figure S47). This result suggests that TiG-n membranes are able to effectively prevent organic pollution.⁶⁵

To test the scalability of energy conversion performance from an individual device to practical applications, a tandem device of the TiG-n membrane stacks was developed. As shown in Figure 6c, the individual cell delivered an average voltage value of approached 147 mV for $0.5 \text{ M NaCl}/0.01 \text{ M NaCl}$, and the total output voltage of the tandem device increased linearly with the

number of units. The output voltage reached up to $\sim 1.5 \text{ V}$ when 10 unit cells were connected in series, which could be used to power electronic devices (Figure S48). Furthermore, we tested the power-generation performance of TiG-n membrane under a large testing area. As illustrated in Figure S49, a maximum power density of 7.05 W m^{-2} was achieved with the testing area of 1 mm^2 . Such a size effect on the power density is observed by many previous publications,^{61,66} which can be ascribed to the non-linear increase of the total conductance and stochastic defect formation under a large membrane size.¹³ In addition, we also assessed the osmotic energy-conversion stability of TiG-n membrane for $0.5/0.01 \text{ M NaCl}$ solution. As shown in Figure S50, the measured current exhibited a negligible decrease after continuous testing within 40 h. More significantly, without electrolyte replenishment, the TiG-n membrane showed almost no attenuation in the measured power density after 7 days (Figure 6d). All these results verify the outstanding long-term working stability of our 2D heterogeneous interface membrane, TiG-n membrane, which can possess great application reliability in practical osmotic power generation. Impressively, the TiG-n membrane delivered an excellent energy conversion efficiency of 47.08% , which is the highest among all reported materials utilized in salinity-gradient power generation (Figure 6e and Table S5). Simultaneously, the high power density of TiG-n membrane far exceeded most state-of-the-art nanofluidic membranes to date and was over four-fold the commercialization benchmark value (5 W m^{-2}). This work underscores the critical role of channel structure in membrane design for osmotic energy harvesting, offering the inspiration for structural optimization and innovation of other advanced 2D systems, such as COF-based membranes.^{61,67} Through molecular-scale asymmetry nanochannel design, two monolayer nanosheets with distinct charge distributions and configurations were assembled into a high-efficiency nanofluidic system, which simultaneously enhances ion selectivity and permeability.

CONCLUSION

In summary, we have demonstrated the design of the 2D nanofluidic membrane with molecular-scale asymmetry nanochannels for high-performance osmotic energy conversion. Benefiting from its inherent heterogeneous geometry and electrostatic potential, the TiG-n membrane is able to couple exceptional selectivity and superior ion permeability together. Through simulations, calculations and in-situ characterization, the structure-performance correlation of 2D heterostructured membranes can be revealed. More importantly, owing to the decent energy conversion efficiency of 47.1% and high Na^+ selectivity coefficient of 0.985 , the TiG-n membrane exhibits excellent performance in various real seawater and hypersaline environments, highlighting its practical applicability. Also, our strategy not only offers a good candidate for generating osmotic energy, but also provides a general approach to modulate selectivity and transport resistance of 2D advanced nanochannel membranes for other related applications, including water purification, ion sieving, supercapacitors, and batteries.

ASSOCIATED CONTENT

Supporting Information.

The Supporting Information is available free of charge at <http://pubs.acs.org>.

Materials synthesis, characterization details, supporting data items, and supporting figures (PDF)

AUTHOR INFORMATION

Corresponding Author

Pan Xiong – Key Laboratory for Soft Chemistry and Functional Materials of Ministry Education, Nanjing University of Science and Technology, Nanjing 210094, China; Email: pan.xiong@njust.edu.cn

Guoxiu Wang – Centre for Clean Energy Technology, School of Mathematical and Physical Sciences, Faculty of Science, University of Technology Sydney, Sydney, NSW 2007, Australia; Email: guoxiu.wang@uts.edu.au

Junwu Zhu – Key Laboratory for Soft Chemistry and Functional Materials of Ministry Education, Nanjing University of Science and Technology, Nanjing 210094, China; Email: zhujw@njust.edu.cn

Author Contributions

*C.L. and C.Y. contributed equally to this work.

Notes

The authors declare no competing financial interest.

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