

High-surface-area functionalized nanolaminated membranes for energy-efficient nanofiltration and desalination in forward osmosis

Wensen Wang, Nicolas Onofrio, Eddy Petit, Bonito Aristide Karamoko, Huali Wu, Jiefeng Liu, Ji Li, Kun Qi, Yang Zhang, Christel Gervais, et al.

▶ To cite this version:

Wensen Wang, Nicolas Onofrio, Eddy Petit, Bonito Aristide Karamoko, Huali Wu, et al.. High-surfacearea functionalized nanolaminated membranes for energy-efficient nanofiltration and desalination in forward osmosis. Nature Water, 2023, 1 (2), pp.187-197. 10.1038/s44221-023-00036-1. hal-04284917

HAL Id: hal-04284917 https://hal.science/hal-04284917

Submitted on 14 Nov 2023 $\,$

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers. L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

High Surface Area Functionalized Nanolaminated Membranes For Energy Efficient Nanofiltration And Desalination In Forward Osmosis

2 3

4

5

6 7

1

Wensen Wang¹, Nicolas Onofrio¹, Eddy Petit¹, Bonito Aristide Karamoko¹, Huali Wu¹, Jiefeng Liu¹, Ji Li^{1,2}, Kun Qi¹, Yang Zhang^{1,3}, Christel Gervais,^{4,5} Luc Lajaunie^{6,7}, Chrystelle Salameh¹, Philippe Miele^{1,4}, Zhiyuan Zeng^{8,9}, Damien Voiry¹*

- ¹ Institut Européen des Membranes, IEM, UMR 5635, Université Montpellier,
 ENSCM, CNRS, Montpellier 34000, France
- ²College of Bioresources and Materials Engineering, Shaanxi University of Science &
 Technology, Xi'an 710021, P. R. China
- ³ Key Laboratory of Optoelectronic Devices and Systems of Ministry of Education and
- Guangdong Province, College of Optoelectronic Engineering, Shenzhen University,
 Shenzhen, 518000, China
- ⁴ Institut Universitaire de France (IUF), 1 rue Descartes, 75231 Paris Cedex 05
- ⁵ Sorbonne Université, Collège de France, Laboratoire de Chimie de la Matière
 Condensée de Paris (LCMCP), 4 place Jussieu, 75252 Paris cedex 05, France.
- ⁶ Departamento de Ciencia de los Materiales e Ingeniería Metalúrgica y Química
- 19 Inorgánica, Facultad de Ciencias, Universidad de Cádiz, Campus Río San Pedro S/N,
- 20 Puerto Real, 11510, Cádiz, Spain

⁷ Instituto Universitario de Investigación de Microscopía Electrónica y Materiales
 (IMEYMAT), Facultad de Ciencias, Universidad de Cádiz, Campus Río San Pedro
 S/N, Puerto Real 11510, Cádiz, Spain

- ²⁴ ⁸Department of Materials Science and Engineering, City University of Hong Kong,
- 25 Hong Kong 999077, P. R. China
- ⁹Shenzhen Research Institute, City University of Hong Kong, Shenzhen 518057, China
- 27

28 Abstract

29 Stacking two-dimensional (2D) nanosheets into laminar membranes to create

- nanochannels has attracted widespread attention at fundamental and practical
- **1 levels for separation technology. Constructing space-tunable and long-term stable**
- 32 sub-nanometer channels provide original systems for nanofluidic investigations
- 33 and accurate molecular sieving. Here, we report a scalable strategy for the
- 34 preparation of non-swelling covalently functionalized molybdenum disulfide
- 35 (MoS₂) membranes with tunable cohesion energy and interlayer space from 3.5 to

7.7 Å, depending on the nature of the functional groups attached to the MoS₂ 36 nanosheets. We evaluated the relationship between the capillary width, the surface 37 chemistry, the stacking disorder and the sieving behaviors of the membranes in 38 forwards osmosis (FO). By combining experimental investigations and numerical 39 simulations, we identified that the functionalization with aryl groups induces the 40 formation of a capillary width of 7.1 Å and interlayer stiffness as low as 5.6 eV Å⁻ 41 ², leading to controlled stacking defects. We report the fabrication of membranes 42 up to 45 cm², which demonstrate a salt rejection as high as 94.2% for a continuous 43 operating time of 7 days. Our work presents a desalination strategy in FO with a 44 specific energy consumption (SEC) of 4×10^{-3} kWh m⁻³, which compares favorably 45 with commercial FO membranes. 46

47

48 Introduction

The construction of selectively permeable membranes with sub-nanometer 49 channels has gained attention for artificial bionics and molecular sieving by taking 50 advantage of the sub-nanometer size of the pores formed between two successive 51 nanosheets. Two-dimensional nanolaminates are regarded from both fundamental and 52 practical points of view as mimicking systems of the biological protein transport 53 channels and building blocks of nanofiltration membranes^{1,2}. In nanolaminated 54 membranes, mass transport typically occurs within the physical gap between the layers 55 defined as the interlayer space or the capillary width. The fabrication of 2D sub-56 nanometer channels with controlled dimensionality and chemistry of the interlayer 57 space has therefore emerged as a mature topic in the field of 2D materials³⁻⁵. The 58 practical demonstration of nanolaminate membranes has not been achieved due to two 59 main bottlenecks, which are (i) the intrinsic instability of the interlayer space and (ii) 60

the difficulty in fabricating pinhole-free membranes on a large scale with controlled 61 thickness⁶⁻⁸. Currently, the most widely studied 2D building block of nanolaminate 62 membranes is graphene oxide (GO), which forms free spaces of around 5 Å in dry 63 condition. This allows a narrow molecular sieve size with sharp molecular cut-off for 64 rejecting large molecules and ions at the expense of the water flux⁹. Although the space 65 size can be modulated by encapsulating GO membrane into epoxy under different 66 humidity, the process is rather complex and prevents realistic applications¹⁰. Other 67 strategies for controlling the pore size of the nanolaminates include ion coordination¹¹, 68 polymer intercalation¹², crosslinking¹³. Inevitable swelling occurs in pristine GO 69 membranes when it is operated in an aqueous solution, which dramatically increases 70 the interlayer spacing, leading to a rapid degradation of the sieving performance¹⁴⁻¹⁶. 71 Besides GO, MoS₂ and MXene nanosheets are alternative building block candidates for 72 the construction of 2D nanochannels $^{17-20}$. MoS₂ laminated membranes have shown 73 outstanding water permeation in reversed osmosis (RO) and the improved stability 74 compared to GO and MXene membranes^{21,22}. Unfortunately, the molecular cutoff of 75 MoS₂ membranes depends on the presence of intercalated water molecules in the 76 laminated structure²³. We have recently reported a facile strategy to modify the surface 77 chemistry of the MoS₂ nanosheets and tune the interlayer space²⁴. Although the vast 78 majority of the efforts have focused on membranes for RO applications, forward 79 osmosis (FO) is regarded as a strategy to reduce the energy footprint associated with 80 water purification processes. To date, only few studies have however focused on the 81 production and testing membranes with sizes greater than 1 cm^2 due to the difficulty in 82 controlling the integrity of the membrane structures over large area (swelling, 83 delamination, formation of pinholes)²⁴⁻²⁶. 84

85

Here, using MoS₂ nanosheets as building units, we adopted a chemical

functionalization strategy to prepare FO membranes with controlled interlayer space 86 and interlayer stiffness in order to tailor the interlayer space and the stacking disorder 87 in the nanolaminated structure. The membranes are found to be resistant against 88 swelling, while the interlayer space can be adjusted with angström precision. We 89 demonstrated the fabrication of membranes with thickness from 100 nm up to 1 µm and 90 dimensions as large as 45 cm². The membranes achieved a water flux as high as 12 91 LMH with molecular cutoff of 180 Da and a salt rejection as high as 94.2%. When 92 tested against desalination, the functionalized MoS₂ FO membranes demonstrated 93 94 superior salt rejection performance for 7 days without significant loss of the water flux compared with GO-based membranes and commercial polymer FO membranes. The 95 nanofluidic behavior in various channels has been studied using physical 96 characterizations and molecular dynamic simulations to unravel the size entanglements 97 of the surface chemistry, the sub-nanometer interlayer space and the disorder of the 98 stacking of the nanosheets in the laminated structure. We finally evaluated the energy 99 consumption of our filtration system and found that the MoS₂ nanolaminate membranes 100 may allow for a lower electrical power consumption compared to commercial FO membranes thus opening avenues for practical applications of nanolaminate FO 102 membranes.

104 Characterization of Nanolaminated MoS₂ Membranes

Molybdenum disulfide nanosheets were exfoliated in water from a bulk crystal and further functionalized using alternatively organohalides or diazonium salts in order to covalently attach alkyl and aryl functional groups, respectively²⁷. Six types of molecules were selected offering different sizes and polarities. The functionalized MoS₂ nanosheets were first observed using electron microscopy in order to confirm the presence of attached functional groups and the crystallinity of the nanosheets (**Fig. 1a**,

b). The functionalized nanosheets were then characterized by performing Attenuated 111 total reflectance Fourier-transformed infrared (ATR-FTIR), Raman and ¹³C nuclear 112 magnetic resonance (¹³C NMR) spectroscopies as well as thermogravimetric analysis 113 (TGA) (Supplementary Note 1). Figures 2a, b show the chemical shifts of 114 functionalized MoS₂ nanosheets compared with those of the pristine organohalide or 115 diazonium salt reagents. The ¹³C signals of the aliphatic carbon (α -C) at -3.7 ppm²⁸ and 116 115.3 ppm²⁹ for ethyl iodoacetate and 4-bromobenzenediazonium respectively 117 disappear after functionalization and are shifted around 46 ppm and 126 ppm. The 118 119 significant perturbation of the α -C chemical shifts suggests a new chemical environment, which is attributed to the formation of S-C bonds. 120

The membranes were fabricated by vacuum filtering of the suspension of MoS_2 nanosheets on a porous support and the membrane thickness was adjusted between 100 nm and 1 µm (Supplementary Figure 5). The ordered interstitial structure was confirmed by the cross-section view of one typical functionalized membrane using scanning electron microscopy (SEM) and X-ray diffraction (XRD) (**Fig. 1c** and **Fig. 2c**, **d**).

127

Compared to pristine MoS_2 nanolaminates, which display an intense (002) peak at 128 $\sim 14.2^{\circ}$, the peaks of functionalized membranes shift to lower angles corresponding to 129 an increased interlayer space between the nanosheets. The capillary width was 130 estimated by subtracting 6.15 Å corresponding to the Mo-Mo distance between two 131 successive layers of MoS₂ in a bulk crystal. We obtained capillary width of 3.6 Å, 4.8 132 Å, 5.3 Å, 6.9 Å, 6.5 Å, and 7.1 Å for C2-, C3-, Ace-, Ben-, C3OH- and Aryl-133 functionalized MoS₂, respectively. Our XRD analyses therefore suggest that the 134 interlayer spacing can be fine-tuned to angström accuracy by employing different sizes 135

of functional groups. To visually observe the increase of the interlayer space, we measured the evolution of the membrane thickness before and after functionalization (**Fig. 2e** and Supplementary Figure 6). The thickness determined from our SEM crosssection analyses increases linearly with the d-space distance measured from XRD.

The structural stability of MoS₂ nanolaminates in aqueous solution was examined 140 by successive ex-situ XRD measurement at increased soaking time in water as well as 141 in saline solutions (Supplementary Figure 7-9). As shown in Figure 2f, the interlayer 142 space of hydrophobic nanochannel is found virtually stable in water for over 100 hours 143 144 with a swelling of only 8.6%, outperforming GO and MXene membranes (Supplementary Note 2). Our results indicate that stacking functionalized MoS₂ 145 nanosheets into membranes forms stable nanochannels with finely tunable interlayer 146 space and long-term stability. The changes of surface wettability after MoS₂ 147 functionalization were also examined by water contact angle (WCA) measurements 148 (Fig. 2g and Supplementary Figure 10, 11). Compared to pristine membranes, increased 149 WCA values were obtained in the case of hydrophobic groups grafted on the MoS_2 , 150 whereas hydrophilic groups caused a decrease in the WCA. The measurements of the 151 WCA brings direct evidence of the role of the surface chemistry to change the physical 152 and chemical behavior of the membranes. 153

154

155 Ionic and Water Transport in Functionalized MoS₂ Membranes

We first sought to evaluate the transport of the monovalent ions: Li^+ , Na^+ and K^+ across the functionalized MoS_2 membranes using a custom-made U-shape cell, where the two-compartments are filled with an electrolyte solution and DI water, used as permeate and feed solutions, respectively. We found that compared to water, the transport of Na^+ is more sensitive to the height of the 2D capillary, and shows an

exponential dependence with the capillary width (Fig. 3a and Supplementary Figure 161 12). The inhibition of Na⁺ transport with decreasing channel size arises from steric 162 hindrance of the pore. The permeation rate for Na⁺ decreased by 20 folds as the capillary 163 width decreased from 7.6 Å to 3.6 Å compared to 3 folds for water. In aqueous solution, 164 Na⁺, Cl⁻ and SO₄²⁻ have hydration shells with diameters of 7.16 Å, 6.64 Å and 7.58 Å, 165 respectively³⁰. This suggests that to enter inside a narrower channel, the ions will 166 necessarily strip more water molecules, which requires additional energy. It is worth 167 noting that the evolution of the permeation rates of Na⁺ with the capillary width, *i.e.* the 168 slopes in the middle and right panels of Figure 3a, is independent from the nature of 169 the counter ions (Cl⁻ or SO_4^{2-}). While the faster permeance of Na⁺ (about 3 times) in the 170 case of NaCl compared to Na₂SO₄ is attributed to the larger value of hydration energy 171 for SO_4^{2-} : -1330 kJ mol⁻¹ compared to -420 kJ mol⁻¹ and -350 kJ mol⁻¹ for Na⁺ and Cl⁻, 172 respectively³¹. We also found slightly higher permeance rates for Mg²⁺ compared to 173 Na⁺ despite larger ionic radius. This is attributed to the Gibbs-Donnan effect due to the 174 presence of remaining excess of charges on the functionalized MoS₂ nanolaminates, as 175 confirmed by our zeta potential measurements (Supplementary Table 1). Remarkably, 176 our results also indicated a stricter dependence of the permeance with the capillary 177 width, which is attributed to the larger hydrated radius and hydration energy of the Mg 178 ions. 179

The application of hydrostatic pressure in reverse osmosis conditions is known to affect the structure of the capillaries in the nanolaminated structure^{32,33}. Conversely, by operating in FO, we were able to precisely examine the influence of nanochannel structure and surface chemistry on water permeation. We first evaluated the water permeation across the functionalized MoS₂ membranes with different interlayer spaces under forward osmosis (FO) operation. Concentrated KCl (3M) and deionized (DI)

water were used as draw and feed solutions, respectively. Figure 3b shows the water 186 flux across the functionalized membranes with increasing stacking sequence from 160 187 layers up to 1600 layers in forward osmosis conditions. While pristine membranes were 188 found impermeable^{23,34} (Supplementary Note 3), water permeated through all the 189 functionalized MoS₂ nanolaminates, demonstrating the benefit of functionalization for 190 the diffusion of water. The water flux quickly increased with the decrease of stacking 191 layers due to the shortened pathway for water molecules. We found the highest flux of 192 ~12 L h^{-1} m⁻² (LHM) in the case of Aryl-functionalized membrane with a stacking of 193 194 160 layers. This flux is higher than the typical flux for forward osmosis, which is 5~10 LHM^{10,35}. 195

We then sought to discriminate the contribution of the capillary width and the 196 surface chemistry of the nanosheets on the water flux. For a fixed number of MoS₂ 197 nanosheets in the nanolaminate, the water flux showed a nearly linear relationship with 198 the capillary width with a \approx 3-fold increase when the capillary width increased from 3.6 199 Å to 7.6 Å. This confirms a size-dependent mass transfer process (Supplementary 200 Figure 14,15 and Supplementary Note 4). We extracted the different slopes values for 201 the functionalized membranes when increasing the number of MoS₂ nanosheets from 202 160 to 1600. The evolution of the water flux in LMH Å⁻¹ with the number of MoS_2 203 nanosheets revealed an exponential decrease tendency (Fig. 3b, inset). According to 204 the curve fitting, our results predict a flux larger than 100 LMH from a nanolaminate 205 membrane with a capillary width of 7 Å and a stacking sequence of 8 layers of MoS_2 , 206 corresponding to a thickness of ≈ 10 nm. To better understand the mechanism of water 207 permeation through the size-varied nanochannel, we estimated the activation energy of 208 water permeation³⁶ and found a linear decrease with capillary width (Fig. 3c, d and 209 Supplementary Note 5). Hydrophobic ethyl-functionalized membrane with the 210

narrowest channel demonstrated the highest transmembrane energy barriers for water 211 permeation in line with the fact that the membrane exhibits the lowest water flux. With 212 the increase of capillary width, the energy barriers rapidly and continuously decrease, 213 leading to improved water flux. Remarkably, we note that the activation energy of water 214 permeation is less affected by the nature of the functional groups (Supplementary 215 Figure 16). The results clearly point out the role of the sub-nanometer interlayer 216 217 distance for controlling the energy barriers and the water permeance under FO filtration. It is also worth noting that the Aryl-functionalized membranes showed the highest flux 218 219 for all thicknesses, while it had moderate energy barriers suggesting that the energy barrier is not the only parameter governing water diffusion in nanolaminates. 220

To elucidate the origin of the apparent high-water flux in Aryl-functionalized MoS₂ 221 membranes, we examined the structure of the nanolaminates by comparing the full-222 height at half-maximum (FWHM) of (002) XRD peaks. The FHWM of the diffraction 223 peaks is known to be a good indicator of the degree of disorder of a crystal and has been 224 used by extension to qualitatively assess the disorder in 2D nanolaminates^{24,37}. The FO 225 membranes made of Aryl-functionalized MoS₂ exhibit the largest FWHM at $1.74^{\circ} \pm$ 226 0.03°, indicating a large variation of capillary width of 1.57 Å (Supplementary Figure 227 17). For comparison, the variation of the capillary width of the corresponding pristine 228 MoS₂ membranes is of only 0.40 Å. The XRD analyses thus suggest a less ordered 229 stacking compared to the other functionalized membranes. A less ordered structure is 230 therefore likely to bring minor tortuosity, leading to a reduced effective path length for 231 water transport, thereby facilitating the water permeation³⁷. To further gauge the 232 influence of the stacking disorder on the water diffusion in the nanolaminate, we plotted 233 the water permeance as a function of capillary width and width variation for 234 nanolaminates with 400 and 1600 nanosheets (Figs. 3e, f). We observed that for the 235

thinnest membranes corresponding to a stacking number of 400, the water permeance 236 is controlled by the capillary width, while for thicker laminates the permeance is mainly 237 controlled by the variation in the capillary width. The reduction of the diffusion 238 pathway caused by the decrease of membrane tortuosity is negligible for the thinnest 239 laminates. As the transport pathway increases for thicker membranes, the effect of the 240 tortuosity on the diffusion becomes significant. In light of these results, we identify 241 different behaviors of the nanolaminate FO membranes as the number of two 242 dimensional capillaries increases, which is characterized by a transition from a size-243 controlled diffusion for the thinnest membranes to disorder-controlled diffusion of the 2.44 water molecules. Our investigations suggest that the control of both the interlayer space 245 and the stacking disorder in Aryl-functionalized MoS₂ nanolaminates is responsible for 246 the superior water flux in FO, making this membrane a relevant candidate for the 247 realization of practical FO filtration. 248

249

250 Mechanical properties of MoS₂ membranes from MD simulations

The stacking order of the nanolaminate membranes is directly related to the mechanical 251 properties of the layers. Therefore, to get further insight on the atomic origin of the 252 superior water flux of Aryl-functionalized membranes observed above, we performed 253 classical MD simulations of the interaction between functionalized layers (details in the 254 Methods section). Mechanical properties including surface energy and interlayer 255 stiffness can be evaluated by fitting the potential energy of two functionalized layers as 256 a function of interlayer distance, as depicted in Figure 4a. Here we use a simple 3-257 parameters Morse function to fit the potential energy. Our calculations predict surface 258 energies (D_e) of 24, 9 and 6 meV/ $Å^2$, and interlayer stiffnesses (k_e) of 113.7, 11.1 and 259 5.6 eV/ Å² for pristine, Ben- and Aryl-functionalized MoS₂, respectively (see Fig. 4b 260

and c). We obtained capillary width (δ =d₀-6.15, Fig. 4d) of 0.3, 7.4 and 7.8 Å for 261 pristine, Ben- and Aryl-functionalized MoS₂, respectively, in good agreements with 262 those measured from experiment (0.05, 6.9 and 7.1 Å, Fig. 2d). As expected, 263 functionalization leads to larger interlayer spacing, smaller surface energy as well as 264 smaller interlayer stiffness. Interestingly, we found that for Aryl- functionalized MoS₂, 265 both the surface energy and the interlayer stiffness are about 50 % smaller than for Ben-266 MoS₂. The small surface energy and the softness of Aryl-MoS₂ layers can be 267 appreciated by the small depth and the flat bottom of the potential well, respectively 268 (Fig. 4a). The combination of small surface energy and interlayer stiffness leads to an 2.69 increase of stacking defects, which contributes to the broadening of the diffraction 270 peaks measured experimentally. We also performed simulations with a lower extent of 271 functional groups and found that the mechanical properties were only slightly affected, 272 while the capillary width decreased significantly (Supplementary Table 2). Our 273 molecular analysis suggests a direct connection between surface chemistry of the 274 nanosheets and the macroscopic nanofluidic properties of the membranes and it 275 provides a framework for future screening of efficient functional groups for water 276 filtration and desalination. 277

279

Forward Osmosis Nanofiltration

To demonstrate the potential of the functionalized MoS₂ membranes, the molecular 280 sieving performance for micropollutants and salt were further evaluated. Four typical 281 micropollutants, a preservative (benzoic acid, BA), a psychoactive drug (caffeine), a 282 common drug (diclofenac sodium, DF) and an organic dye (phthalocyanine), with 283 varied Stoke diameter from ~5.64 Å up to ~14 Å (Supplementary Table 3), were 284 selected and the rejection was measured using high performance liquid chromatography. 285

Rejections of over 90% for all the micropollutants in functionalized membranes were 286 measured, suggesting excellent separation performance in FO. Particularly, the C₂-287 functionalized membrane with the narrowest channel presented the perfect repulsion of 288 \approx 100% for the four selected micropollutants. Figure 5a shows that the membrane 289 rejection improves with the increase of the molecular weight of the micropollutants in 290 line with the size-limited diffusion as the primary sieving mechanism (Supplementary 291 Note 6). When comparing the evolution of the rejection of the micropollutant with the 292 capillary width, we observe a sharp molecular cut-off of the FO MoS₂ membranes (Fig. 293 294 **5b**, **c**). This behavior highlights the importance of controlling the interlayer space and further evidences the absence of pinholes. To benchmark the performance of the 295 functionalized MoS₂ membranes, we also estimated the separation performance of the 296 graphene oxide (GO) nanolaminates and a commercial polymeric FO membrane 297 (Cellulose Triacetate, CTA) under the same conditions. As shown in Figure 5d, the 298 CTA membrane exhibited both a reduced flux and rejection for the smaller 299 contaminants. We determined a rejection of less than 80% for benzoic acid (BA) in 300 agreement with previous reports from the literature³⁸. Both the rejection and the water 301 permeance rapidly increase when filtering large molecules. This behavior is 302 surprisingly the opposite to those of both GO and MoS₂ FO membranes, which showed 303 a decreased rejection and an increased flux for the smaller micropollutants. The 304 decreased performance for sieving out the smallest molecules hints for a rapid fouling 305 due to the blocking of the one-dimensional nanopores of the polymer membranes. 306 Conversely, nanolaminates exhibit a fouling for the largest molecules due to the 307 deposition of the rejected molecules on the surface of the membranes, while the 2D 308 capillaries are not obstructed (Supplementary Figure 18). The surface fouling of the 309 nanolaminate can however be mitigated by operating under tangential crossflow 310

filtration (as described later in the article). GO membranes also exhibited a poor rejection of 65% for the smallest molecules of BA which is attributed to the large capillary width due to swelling. Overall, owing to the tailored and stable interlayer space, the Aryl-functionalized MoS₂ membranes exhibited superior performance both in rejection and flux than GO and commercial polymer membranes.

316

To properly estimate the molecular weight cutoff (MWCO) of the MoS_2 membranes, we evaluated the rejection performance of the nanolaminates for small neutral compounds: PEG 200 and D-Glucose. As show in **Figure 6a-c**, all the functionalized MoS_2 membranes exhibited high separation performance with rejection greater than 92%, demonstrating excellent cutoff for PEGs and sugar molecules (Supplementary Note 7).

We then examined the performance of the Aryl-functionalized MoS₂ membranes 323 towards desalination under realistic conditions. FO nanolaminated membranes were 324 prepared by vacuum filtration with sizes up to 45 cm² and a stacking of 400 layers, 325 corresponding to a thickness of ≈ 550 nm. We studied the pure water permeance of the 326 planar 45 cm² Aryl-functionalized membranes by employing a 2M sucrose as draw 327 solution. A stable water flux of 1.3 LMH was achieved under constant flow conditions 328 at room temperature for a period of 7 days (Supplementary Figure 19). The desalination 329 performance of the functionalized MoS₂ membranes was further evaluated on a pilot-330 scale tangential flow filtration cell under the forward osmosis operation using 0.1 M 331 NaCl as the feed solution (Fig. 6d). A water flux greater than 1.6 LMH was achieved 332 and was largely stable over a 7-day period, whereas salt rejection was maintained at 333 greater than \approx 94.2% and peaked at 96%. These robust desalination properties are 334 attributed to the control of the interlayer distance from the grafted functional groups 335

and the low interlayer stiffness. Remarkably, the interlayer space after 7 days of 336 continuous operation was almost identical to that of the as-prepared membranes 337 (Supplementary Figure 20). We note that the performance is slightly lower than those 338 obtained using smaller membranes, which demonstrated a water flux of 4.37 LMH with 339 a NaCl rejection of 93.9% suggesting that further improvements can be achieved. We 340 also evaluated the performance of GO membranes and obtained a poor salt rejection of 341 less than 50 % due to the large capillary width of 12.8 Å in line with the literature 342 $(Supplementary Figure 8)^{10}$. Importantly, the GO membrane could only run for one day 343 and then rapidly delaminated upon the application of the tangential flow which 344 highlights their intrinsic instability in water³⁹. Besides, commercial CTA polymer 345 membranes exhibited a rejection of around 89.1% with an average flux of 1.25 LMH 346 when tested under the same conditions– consistent with previous reports^{40,41}. Compared 347 with other 2D laminar membranes, the functionalized MoS₂ membranes exhibit a 348 higher water flux and superior salt rejection, exceeding the latest upper bound of state-349 of-the-art 2D laminar membranes (Fig. 6e). Importantly the desalination performance 350 is not significantly affected by the upscaling process and the Aryl-functionalized MoS₂ 351 membranes clearly outperform the best desalination performance from the literature 352 under forward osmosis operation (Fig. 6f). We finally evaluated the specific energy 353 consumption (SEC) of our FO system (Supplementary Note 8). Under a flow rate of 354 3.75 mL min⁻¹ (1.65 cm s⁻¹), the FO system recovered 148 mL of water in 20 h, 355 corresponding to a SEC of 0.004 kWh m⁻³. This value is lower than previous reports 356 for flat-sheet CTA membranes, which exhibit SECs of 0.008 kWh m⁻³ and 0.02 KWh 357 m⁻³, respectively^{42,43}. Although additional processing of the draw solution is requested 358 to obtain potable water, the present FO system shows a clear reduction of the energy 359 footprint compared to the other water recovery approaches such as traditional RO 360

- filtration $(1.5-2.5 \text{ kWh m}^{-3})^{44,45}$, thermal distillation technology $(16.3-27.3 \text{ kWh m}^{-3})^{44}$, and self-supplied FO with thermolytic ammonium bicarbonate $(0.1 \text{ kWh m}^{-3})^{46}$.
- 363

Overall this work presents a robust and scalable method to prepare stable 364 nanolaminated membranes with tunable sieving performance and high water 365 permeance in FO filtration. The structure of the functionalized MoS₂ membranes can 366 be precisely adjusted over a large range of interlayer spaces using alkyl and aryl groups 367 which offers angström-precision for the 2D nanochannels. Using this approach, we elucidated the contributions from the surface chemistry, the interlayer space and the 369 stacking tortuosity on the behavior of FO nanolaminate membranes. Our functionalized 370 membranes exhibit excellent water purification performance compared with the GO 371 and commercial membranes. In particular, we identified Aryl-functionalized MoS₂ 372 membranes as promising candidates for FO application and demonstrated its scalability 373 up to 45 cm^2 . 374

- 375
- 376
- 377

378 Methods

Preparation of single-layer MoS₂ nanosheets. The single-layer MoS₂ nanosheets were obtained by exfoliating the bulk MoS₂ powder using the lithium intercalation method. Typically, 400 mg MoS₂ powder and 4 mL n-butyllithium were mixed up in hexane solution and the mixture was stirred at 65°C for 48 h under argon protection. After that, the intercalated powders were collected by vacuum filtration and washed with excessive hexane to remove the unreacted reagent. Then the Li-intercalated powder was added to the water for exfoliation and the process was accelerated by the sonication. After one-

hour sonication, the solution was further centrifuged two times at 10,000 g to strip the 386 lithium cations from the nanosheets. In the end, the supernatant containing the single-387 layer MoS₂ nanosheets was collected after centrifugation twice at 1,400 g for 30 min. 388 Covalent functionalization of single-layer MoS₂ nanosheets. The single-layer MoS₂ 389 nanosheets were modified in solution by reacting with organohalide reagents and 390 391 diazonium. Six different molecules were selected: iodoethane, 1-iodopropane, ethyl iodoacetate, (2-iodoethyl) benzene, 3-iodo-1-propanol, and 4-bromobenzenediazonium. 392 First, dimethyl sulfoxide (DMSO) was added to the MoS₂ solution to achieve a volume 393 ratio of 3:2. Then the organohalide reagents or diazonium were directly added to the 394 mixture to react for 48h. The excessive organohalide reagents with ten times fold in 395 molar ratio than MoS₂ was added. While the charged diazonium with the same molar 396 amount as MoS₂ was separately added several times to avoid the electrostatic quench 397 and aggregation. Finally, the functionalized MoS₂ solutions were obtained. 398

*Preparation of functionalized MoS*₂ *membranes*. Vacuum filtration was employed to prepare the laminated membranes using diluted functionalized MoS₂ solution. Briefly, a certain amount of MoS₂ solution was filtered on Nylon filter paper with a pore size of 220 nm. To improve the uniformity of the nanolaminate, polyethersulfone (PES, 50 nm pore size) was used to prepare membranes larger than 10 cm². After filtration, the membranes were carefully washed 3 times to remove the unreacted reagents. The prepared membranes were dried at room temperature over 24 h.

Water permeation through nanolaminated MoS₂ membranes. The pure water flux of
nanolaminated MoS₂ membranes was measured using the forward osmosis devices,
which consist of two compartments filled with equal volumes (40 mL) of salt solution
(3 M KCl) and pure water. The MoS₂ membranes were placed in the middle to separate
those two compartments. The volume of salt solution as a draw solution would increase

due to the passed water. Based on the increased volume (ΔV) with permeation time (Δt), the water flux could be calculated following the equation:

413
$$J_w = \frac{\Delta V}{A\Delta t}$$
(2)

414 Where the A is the effective membrane area (1.13 cm^2) .

Ionic permeation through the nanolaminated MoS_2 membranes. The Na⁺/Mg²⁺ 415 permeation through the 400-layer stacked membranes was measured using two Teflon-416 made compartments, which were filled with the same volume of DI water and 1 M 417 NaCl/MgCl₂ or 0.5 M Na₂SO₄ solution, respectively. Magnetic stirring was used all the 418 time to eliminate possible concentration gradients around the membranes. The 419 conductivity of the feed side was recorded as a function of permeation time. According 420 to the measured conductivity, the salt concentration of feed side could be calculated 421 using the following equation: 422

423
$$C = \frac{\kappa}{\Lambda_m}$$
(3)

where C denotes the salt concentration, κ presents the measured conductivity and Am is the molar conductivity (NaCl: 126.4 S cm² mol⁻¹, MgCl₂: 258.6 S cm² mol⁻¹, Na₂SO₄: 259.8 S cm² mol⁻¹)⁴⁷. The salt permeation rate (J) was calculated by:

$$J = \frac{VC}{At}$$
(4)

where V is the solution volume in the feed side (200 mL), C is the calculated concentration from equation (3), A is the surface area of the membrane and t is the permeation time.

Water purification and rejection evaluations. The water purification performances of
the membranes were measured using the same apparatus as for the water permeation
measurements. However, the draw side and feed side were filled with 2 M sucrose
solution and 50 mM micropollutant solution (except for the dye solution, which was

3.3 mM), respectively. The two sides were constantly stirred to avoid the concentration
polarization. The draw side solution was collected after 20 h and the concentration of
micropollutant in sucrose solution was quantitatively analyzed by High-Performance
Liquid Chromatography-Ultraviolet (HPLC-UV). The flux was calculated by equation
(2) and the rejection was evaluated by the following equation:

$$R(\%) = \frac{C_F - C_P}{C_F} \times 100$$
(5)

Where C_F and C_P denote the concentration of the feed and permeate solutions, respectively. Unlike the reverse osmosis experiments, the permeated solution in forward osmosis system was diluted by the draw solution. The real concentration of the permeated solution was calculated using the following equation to eliminate the dilution effects:

440

$$C_p = \frac{C_D \times V_D}{V_P} \tag{6}$$

Where C_D and V_D are the measured micropollutant concentration in the draw side and the volume of the draw solution. The V_P presents the volume of permeated solution, which is the increased volume in the draw side.

Water desalination in tangential cross-flow filtration cell. We used the tangential 450 cross-flow filtration cell to estimate the water desalination performance of membranes 451 in long-term operation. The membranes with large surfaces prepared on the 452 polyethersulfone (PES) substrates were installed in the middle of the pilot-scale 453 forward filtration unit to separate the flowing draw and feed solution. The draw and 454 feed tank were filled with 2 M sucrose solution and 0.58 wt.% NaCl solution, 455 respectively. A peristaltic pump was utilized to provide a constant flow rate of 3.75 mL 456 min⁻¹. Two balances were used to monitor the mass changes of draw and feed tank and 457 458 the recorded data was further used to calculate the flux. The solutions in the tank were refreshed every 20 h. At the same time, the sucrose solution was collected and the salt concentration was analyzed by Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES). According to the increased mass and salt concentration in draw side, the salt rejection could be calculated using equations (5) and (6).

Molecular dynamics simulations parameter. Molecular dynamics simulations have 463 been performed with the LAMMPS package⁴⁸ and the OPLS interatomic potential⁴⁹. 464 To describe Mo-S interactions, we use the potential proposed by Blankschtein⁵⁰. We 465 developed OPLS parameters (harmonic bonds, harmonic angles and dihedrals) for S-C 466 467 interactions between fixed MoS₂ and various organic functional groups. We used a Monte Carlo procedure (similar to that presented in Ref. 51) to optimize OPLS 468 parameters against a training set of density functional theory calculations, as developed 469 in the Supplementary file. Molecular models consist of 2 layers of T' MoS₂ replicated 470 8 and 14 times in the x and y directions, starting from the rectangular unit cell. 471 Functionalization was achieved by randomly grafting functional groups to S atoms until 472 the fraction of 20% groups/S was reached. In order to obtain good statistics on the data 473 points corresponding to the potential energy surface shown in Figure 4, we scanned 4 474 times successively the interlayer distance (back and forth). One potential energy surface 475 corresponds therefore to 8 times (4 times back and forth) 300 interlayer distances. At 476 each interlayer distance, the functional groups were randomized by performing 10 ps 477 of NVT simulation at 600 K followed by an energy minimization. We used high 478 temperature MD to provide efficient randomization of the functional groups at each 479 interlayer distances. Although our force field could be used with a larger timestep, we 480 chose a timestep of 0.5 fs in order to properly integrate the equations of motion in the 481 rough conditions of the simulations. 482

485

486 **Data availability**

The data that support the plots within this paper and other findings of this study are available from FigShare (https://doi.org/10.6084/m9.figshare.21901638.v1).

489

490

491

492

493 Acknowledgments

This research study was supported by the French National Agency (ANR, program 2D-494 MEMBA - ANR-21-CE09-0034-01). D.V., K.Q., and H. W. acknowledge funding 495 from the European Research Council (ERC) under the European Union's Horizon 2020 496 research and innovation programme (grant agreement no. 804320). W.W., J.Liu and 497 J.Li acknowledge PhD scholarship from the China Scholarship Council (CSC). C.S. 498 acknowledged funding from the French National Agency (ANR, JCJC program, 499 MONOMEANR-20-CE08-0009). K.Q. and Y.Z. acknowledge financial support from 500 the China Postdoctoral Science Foundation (2018M633127) and the Natural Science 501 Foundation of Guangdong Province (2018A030310602). J.Li acknowledge financial 502 support by the National Natural Science Foundation of China (21808134). The French 503 Région Ile de France - SESAME program is acknowledged for financial support (700 504 MHz NMR spectrometer). This work was granted access to the HPC resources of 505 IDRIS under the allocation 2021-2022-A0110913046 and 097535 made by GENCI. 506 L.L. acknowledges funding from the Andalusian regional government (FEDER-UCA-507 18-106613), the European Union's Horizon 2020 research and innovation program 508

509	(grant agreement 823717 – ESTEEM3) and the Spanish Ministerio de Economia y
510	Competitividad (PID2019-107578GA-I00). The (S)TEM measurements were
511	performed at the National Facility ELECMI ICTS ("Division de Microscopia
512	Electronica", Universidad de Cadiz, DME-UCA).

- 513
- 514
- 515

516 Author Contributions

D.V. conceived the idea, designed the experiments and wrote the manuscript. W.W. 517 designed the experiments with D.V., synthesized the functionalized nanosheets, 518 519 fabricated the membranes and performed the experiments. D.V. and W.S. analyzed the data and wrote the manuscript. N.O. performed the atomistic calculations and discussed 520 the results with D.V. and W.W.. B.A.K. assisted W.S. with the measurements and 521 synthesized MXene. E.P. performed the liquid NMR and HPLC-UV to quantify the 522 membrane rejection, while H.W., J.Liu, J.Li, K.Q. and Y.Z. and assisted W.W with the 523 WCA, Raman, FTIR measurements. L.L. performed the (S)TEM measurements and 524 analyzed the data. C.G. performed the solid ¹³C NMR spectroscopy measurements and 525 discussed with results with C.S.. P.M. and Z.Z. discussed the results with W.W. and 526 D.V. All of the authors edited the manuscript before submission. 527

- 528
- 529
- 530

531 Competing financial interests

532 The authors declare no competing financial interests.

534

535

536 Additional Information

Supplementary information and chemical compound information are available in theonline version of the paper.

539 Correspondence and requests for materials should be addressed to D.V.
540 (damien.voiry@umontpellier.fr).

541

542

543

Figure 1 | Characterizations of the functionalized MoS₂ nanosheets. a, High-angle 544 annular dark-field (HAADF) STEM image of 4-bromobenzenediazonium salt 545 546 functionalized MoS₂ nanosheets and the corresponding EDX mapping for elements Br (in red) and S (in blue). The elemental mapping of Br in the functionalized MoS_2 547 nanosheets shows that the aryl groups are homogeneously grafted on the nanosheets 548 surface. **b**, HRTEM images of MoS₂ nanosheets functionalized with aryl groups. The 549 vertically aligned nanosheets form an interlayer spacing of ~13.2 Å, in line with the 550 XRD measurements. Meanwhile, the crystalline nature of the basal plane of Aryl-MoS₂ 551 nanosheets is confirmed by the diffraction pattern (inset). c, The SEM cross-section 552 view of laminated membrane prepared by vacuum filtration of Aryl-MoS₂ nanosheets 553 suspension. The highly aligned nanosheets in the vertical direction form 2D capillaries. 554 555

556

557

Figure 2 | Characterization of the functionalized MoS₂ membranes. a and b, ¹³C 558 CP MAS NMR spectra of the Ace-functionalized (a, bottom) and Aryl-functionalized 559 (**b**, bottom) MoS₂ nanosheets. ¹³C NMR spectra of pure chemical reagents namely ethyl 560 iodoacetate (a, top, solution) and 4-bromobenzenediazonium (b, top, solid-state) were 561 also recorded for comparison. The color dots are used to point out the positions of 562 carbon atoms in different chemical environments. c, Schematic illustration of the 563 separation process of stacked functionalized MoS₂ membranes with varied capillary 564 width for water purification and desalination. The values marked in the nanochannels 565 represent the effective layer space in aqueous solution through which water molecules 566 can shuttle. Atom color codes: Mo, pink; S, yellow; C, cyan; H, white; O, red; Br, 567 magenta; Na⁺, blue; Cl⁻, green; Micropollutant, ice-blue; water, transparent gray. **d**, X-568

ray diffraction pattern of pristine and functionalized MoS₂ membranes after vacuum 569 drying for 24 h. e, Measured thickness of MoS₂ membranes before and after 570 functionalization as a function of d-space. The slope k multiplied by 10 represents the 571 number of stacked layers. f, Evolution of the capillary width of functionalized MoS₂ 572 membranes in pure water over the soaking time. g, The contact angle of pristine and 573 functionalized MoS₂ membranes. Data are presented as mean values. All error bars 574 correspond to standard deviations (SD) based on at least three independent 575 measurements. 576

- 577
- 578

579

Figure 3 | Water permeation and ionic transport. a, The Na⁺/Mg²⁺ permeation rates 580 and water flux measured by using 400-layer stacked membranes at room temperature. 581 1 M NaCl/MgCl₂ or 0.5 M Na₂SO₄ were employed to provide the high ionic strengths 582 $(1 \text{ M Na}^+/\text{Mg}^{2+})$ for diffusion. The Na⁺/Mg²⁺ permeation rate depends exponentially on 583 the capillary width while the water flux varies linearly. Error bars are omitted for clarity. 584 The dotted lines are best fits. b, Water flux of functionalized MoS₂ membranes with 585 different stacking layers measured at room temperature under forward osmosis, where 586 3M KCl and DI water were used as the draw and feed solution, respectively. Inset: the 587 water permeance as a function of membrane thickness. The red curve is the best fit. c, 588 Temperature dependence of water permeation of 400-layer stacked membranes. Solid 589 lines are best fits to Arrhenius activation energies. d, Activation energy of water 590 permeation for the functionalized MoS₂ membranes as a function of capillary width. 591 The activation energy varied linearly with capillary width. The dotted line is the best 592 fit. Horizontal error bars represent the average half-height of the XRD peaks measured 593 after immersing the membranes in water for a long time (Supplementary Figure 7). e-f, 594 The plotted water permeance of membranes with different stacking numbers (400 layers 595 in e and 1600 layers in f) as a function of capillary width and width variation 596 (Supplementary Figure 17). The permeation rates were normalized by the permeance 597 of Aryl-functionalized MoS2 membranes. All vertical error bars correspond to SD and 598 based on at least five independent measurements. 599

600

601

602

Figure 4 | **Mechanical properties of functionalized MoS**₂ **nanosheets. a**, Potential energy as a function of interlayer separation. To obtain reliable data and statistics, the potential energy surface was scanned 4 times back and forth, as described in the Methods section. Dots correspond to averaged data points and some error bars are displayed (one error bar every 10 averaged data points). Lines correspond to Morse fits as defined by the equation $U(d) = D_e(1-exp(-\alpha(d-d_0)))^2$. **b**, Surface energy (D_e). **c**, Interlayer stiffness ($k_e = 2D_e\alpha^2$). **d**, Experimental capillary width as a function of those (d_0-6.15) extracted from the Morse fit.

611

612

613

Figure 5 | Water purification performance of the functionalized MoS₂ membranes. 614 a, Trace organic contaminants rejection measured with 400-layer stacked 615 functionalized MoS₂ membranes at 30°C under forward osmosis, where the 2 M sucrose 616 and 50 mM contaminants (3.3 mM for dye) were used as draw and feed solution. The 617 rejection is plotted as a function of the molecular weight of contaminants. Vertical error 618 bars represent SD of at least five independent measurements. The insets show the 619 molecular structure of contaminants and the gray, white, red, blue, green and yellow 620 balls denote C, H, O, N, Cl and S, respectively. b and c, Evolution of the rejection for 621 the benzoic acid (b) and caffeine (c) with the capillary width of membranes. The dotted 622 lines represent the effective hydrodynamic diameter of contaminant molecules (Stokes 623 diameter). The rejection sharply decreases after the capillary width of membranes are 624 larger than the effective diameter of the micropollutants, showing size-selective sieving. 625 The solid gray lines are guides to the eyes. d, Comparison of the water purification 626 performance from the functionalized MoS₂ membranes with GO and commercial FO 627 membrane (CTA). Each symbol represents the average flux and rejection calculated 628 from at least five independent measurements and the error bars are omitted for clarity. 629 The complete test data of all functionalized MoS2 membranes are shown in 630 Supplementary Figure 18. 631

632 633

634

Figure 6 | Molecular weight cut-off and water desalination performance of the 635 functionalized MoS₂ membranes. Evolution of the rejection for the PEG-238 (a), 636 PEG-282 (b) and D-Glucose (c) with the capillary width of membranes. The rejection 637 was measured with 400-layer stacked functionalized MoS₂ membranes at 30 °C under 638 forward osmosis, where the 2 M sucrose/50 mM PEG 200 and 0.92 M Na₂SO₄/50 mM 639 D-Glucose were used as draw/feed solution, respectively. Error bars correspond to SD 640 of at least five independent measurements. The dotted lines represent the effective 641 hydrodynamic diameter of PEG and D-Glucose (Stokes diameter). And the solid gray 642 lines are guides to the eyes. d, The desalination performance of Aryl-functionalized 643 MoS₂ membrane and the comparison with GO and commercial FO membrane. The 644 measurements were conducted in a tangential cross-flow cell using 2 M sucrose and 0.1 645 M NaCl as draw and feed solution. The GO membrane could only be run for one day 646

and then decomposed. e, Comparison of the desalination performance of Aryl-647 functionalized MoS₂ (red stars) with other 2D laminar membranes made of GO, MXene 648 and their hybrids. All the data listed in the figure were measured under separation 649 models in forward osmosis cells using sucrose and 0.1 M NaCl as draw and feed 650 solution. Our Aryl-functionalized MoS₂ membranes test data are marked with red stars, 651 while CTA and GO data are denoted by light-blue and green hollow diamonds. The 652 effective membrane area is labeled in white. The black line represents the upper bound 653 of state-of-the-art 2D laminar membranes due to the trade-off between membrane 654 permeability and selectivity. A comprehensive comparison of desalination performance 655 of 2D membranes estimated under diffusion or separation models can be found in 656 Supplementary Table 5. f, Comparison of effective membrane area measured in our 657 work with previously reported membranes. 658

659

660















669 **References**

- Shen, J., Liu, G., Han, Y. & Jin, W. Artificial channels for confined mass transport
 at the sub-nanometre scale. *Nat. Rev. Mater.* 6, 294-312 (2021).
- Werber, J. R., Osuji, C. O. & Elimelech, M. Materials for next-generation
 desalination and water purification membranes. *Nat. Rev. Mater.* 1, 1-15 (2016).
- Wang, S. *et al.* Two-dimensional nanochannel membranes for molecular and ionic
 separations. *Chem. Soc. Rev.* 49, 1071-1089 (2020).
- Kang, Y., Xia, Y., Wang, H. & Zhang, X. 2D laminar membranes for selective
 water and ion transport. *Adv. Funct. Mater.* 29, 1902014 (2019).
- 5 Cheng, L., Liu, G., Zhao, J. & Jin, W. Two-dimensional-material membranes:
 Manipulating the transport pathway for molecular separation. *Acc. Mater. Res.* 2, 114-128 (2021).
- 6 Safaei, J., Xiong, P. & Wang, G. Progress and prospects of two-dimensional
 materials for membrane-based water desalination. *Mater. Today Adv.* 8, 100108
 (2020).
- ⁶⁸⁴ 7 Liu, P. *et al.* Two-dimensional material membranes for critical separations. *Inorg.* ⁶⁸⁵ *Chem. Front.* 7, 2560-2581 (2020).
- 686 8 Cheng, Y., Pu, Y. & Zhao, D. Two-Dimensional Membranes: New Paradigms for
 687 High-Performance Separation Membranes. *Chem. Asian J.* 15, 2241-2270 (2020).
- 9 Joshi, R. *et al.* Precise and ultrafast molecular sieving through graphene oxide
 membranes. *Science* 343, 752-754 (2014).
- Abraham, J. *et al.* Tunable sieving of ions using graphene oxide membranes. *Nat. Nanotechnol.* 12, 546-550 (2017).
- Chen, L. *et al.* Ion sieving in graphene oxide membranes via cationic control of
 interlayer spacing. *Nature* 550, 380-383 (2017).
- Shen, J. *et al.* Subnanometer two-dimensional graphene oxide channels for ultrafast
 gas sieving. *ACS Nano* 10, 3398-3409 (2016).
- Hung, W.-S. *et al.* Cross-linking with diamine monomers to prepare composite
 graphene oxide-framework membranes with varying d-spacing. *Chem. Mater.* 26,
 2983-2990 (2014).
- ⁶⁹⁹ 14 Zheng, S., Tu, Q., Urban, J. J., Li, S. & Mi, B. Swelling of graphene oxide
 ⁷⁰⁰ membranes in aqueous solution: characterization of interlayer spacing and insight
 ⁷⁰¹ into water transport mechanisms. *ACS Nano* **11**, 6440-6450 (2017).

- Su, P., Wang, F., Li, Z., Tang, C. Y. & Li, W. Graphene oxide membranes:
 controlling their transport pathways. *J. Mater. Chem. A* 8, 15319-15340 (2020).
- 16 Han, Z.-y. *et al.* A review of performance improvement strategies for graphene
 oxide-based and graphene-based membranes in water treatment. *J. Mater. Sci.*, 130 (2021).
- Sun, L., Huang, H. & Peng, X. Laminar MoS₂ membranes for molecule separation.
 Chem. Commun. 49, 10718-10720 (2013).
- Guo, B.-Y. *et al.* MoS2 membranes for organic solvent nanofiltration: stability and
 structural control. *J. Phys. Chem. Lett.* **10**, 4609-4617 (2019).
- ⁷¹¹ 19 Ren, C. E. *et al.* Charge-and size-selective ion sieving through $Ti_3C_2T_x$ MXene ⁷¹² membranes. *J. Phys. Chem. Lett.* **6**, 4026-4031 (2015).
- 20 Ding, L. *et al.* A two-dimensional lamellar membrane: MXene nanosheet stacks.
 Angew. Chem. Int. Ed. Engl. 56, 1825-1829 (2017).
- ⁷¹⁵ 21 Wang, J. *et al.* Ion sieving by a two-dimensional $Ti_3C_2T_x$ alginate lamellar ⁷¹⁶ membrane with stable interlayer spacing. *Nat. Commun.* **11**, 1-10 (2020).
- Kim, S., Wang, H. & Lee, Y. M. 2D nanosheets and their composite membranes
 for water, gas, and ion separation. *Angew. Chem. Int. Ed. Engl.* 131, 17674-17689
 (2019).
- Wang, Z. *et al.* Understanding the aqueous stability and filtration capability of
 MoS2 membranes. *Nano Lett.* 17, 7289-7298 (2017).
- Ries, L. *et al.* Enhanced sieving from exfoliated MoS₂ membranes via covalent
 functionalization. *Nat. Mater.* 18, 1112-1117 (2019).
- 724 25 Mei, L. *et al.* Simultaneous Electrochemical Exfoliation and Covalent
 725 Functionalization of MoS₂ Membrane for Ion Sieving. *Adv. Mater.*, 2201416
 726 (2022).
- 26 Chu, C. *et al.* Precise ångström controlling the interlayer channel of MoS₂
 membranes by cation intercalation. *J. Memb. Sci.* 615, 118520 (2020).
- Eda, G. *et al.* Photoluminescence from chemically exfoliated MoS₂. *Nano Lett.* 11,
 5111-5116 (2011).
- Creemers, A. F. & Lugtenburg, J. The preparation of all-trans uniformly 13Clabeled retinal via a modular total organic synthetic strategy. Emerging central
 contribution of organic synthesis toward the structure and function study with
 atomic resolution in protein research. *J. Am. Chem. Soc.* 124, 6324-6334 (2002).

- Duthaler, R. O., Förster, H. & Roberts, J. D. Nitrogen-15 and carbon-13 nuclear
 magnetic resonance spectra of diazo and diazonium compounds. *J. Am. Chem. Soc.* **100**, 4974-4979 (1978).
- Nightingale Jr, E. Phenomenological theory of ion solvation. Effective radii of
 hydrated ions. J. Phys. Chem. 63, 1381-1387 (1959).
- Teychené, J., Roux-de Balmann, H., Maron, L. & Galier, S. Investigation of ions
 hydration using molecular modeling. *J. Mol. Liq.* 294, 111394 (2019).
- Wei, Y. *et al.* Declining flux and narrowing nanochannels under wrinkles of
 compacted graphene oxide nanofiltration membranes. *Carbon* 108, 568-575 (2016).
- Morelos-Gomez, A. *et al.* Effective NaCl and dye rejection of hybrid graphene
 oxide/graphene layered membranes. *Nat. Nanotechnol.* 12, 1083-1088 (2017).
- 34 Hoenig, E. *et al.* Controlling the Structure of MoS₂ Membranes via Covalent
 Functionalization with Molecular Spacers. *Nano Lett.* 20, 7844-7851 (2020).
- 748 35 Chekli, L. *et al.* A comprehensive review of hybrid forward osmosis systems:
 749 Performance, applications and future prospects. *J. Memb. Sci.* 497, 430-449 (2016).
- 36 Wang, K. Y., Chung, T.-S. & Qin, J.-J. Polybenzimidazole (PBI) nanofiltration
 hollow fiber membranes applied in forward osmosis process. *J. Memb. Sci.* 300, 612 (2007).
- 37 Lu, X. *et al.* Relating selectivity and separation performance of lamellar twodimensional molybdenum disulfide (MoS₂) membranes to nanosheet stacking
 behavior. *Environ. Sci. Technol.* 54, 9640-9651 (2020).
- Alturki, A. *et al.* Performance of a novel osmotic membrane bioreactor (OMBR)
 system: flux stability and removal of trace organics. *Bioresour. Technol.* 113, 201206 (2012).
- Andreeva, D. V. *et al.* Two-dimensional adaptive membranes with programmable
 water and ionic channels. *Nat. Nanotechnol.* 16, 174-180 (2021).
- 40 Al-aibi, S., Mahood, H. B., Sharif, A. O., Alpay, E. & Simcoe-Read, H. Evaluation
 of draw solution effectiveness in a forward osmosis process. *Desalination Water Treat.* 57, 13425-13432 (2016).
- 41 Li, G., Li, X.-M., He, T., Jiang, B. & Gao, C. Cellulose triacetate forward osmosis
 membranes: preparation and characterization. *Desalination Water Treat.* 51, 26562665 (2013).
- ⁷⁶⁷ 42 Zou, S. & He, Z. Enhancing wastewater reuse by forward osmosis with self-diluted

- commercial fertilizers as draw solutes. *Water Res.* **99**, 235-243 (2016).
- 43 Lambrechts, R. & Sheldon, M. Performance and energy consumption evaluation of
 a fertiliser drawn forward osmosis (FDFO) system for water recovery from brackish
 water. *Desalination* 456, 64-73 (2019).
- 44 Al-Karaghouli, A. & Kazmerski, L. L. Energy consumption and water production
 cost of conventional and renewable-energy-powered desalination processes. *Renew. Sustain. Energy Rev.* 24, 343-356 (2013).
- 45 Shannon, M. A. *et al.* Science and technology for water purification in the coming
 decades. *Nanoscience and technology: a collection of reviews from nature Journals*,
 337-346 (2010).
- 46 Qin, M. & He, Z. Self-supplied ammonium bicarbonate draw solute for achieving
 wastewater treatment and recovery in a microbial electrolysis cell-forward osmosiscoupled system. *Environ. Sci. Technol. Lett.* 1, 437-441 (2014).
- 47 Horvath, A. L. Handbook of aqueous electrolyte solutions. (Halsted Press, 1985).
- 48 Plimpton, S. Fast parallel algorithms for short-range molecular dynamics. J.
 Comput. Phys. 117, 1-19 (1995).
- 49 Jorgensen, W. L., Maxwell, D. S. & Tirado-Rives, J. Development and testing of
 the OPLS all-atom force field on conformational energetics and properties of
 organic liquids. *J. Am. Chem. Soc.* 118, 11225-11236 (1996).
- 50 Sresht, V. *et al.* Quantitative modeling of MoS₂–solvent interfaces: predicting
 contact angles and exfoliation performance using molecular dynamics. *J. Phys. Chem. C* 121, 9022-9031 (2017).
- ⁷⁹⁰ 51 Onofrio, N. & Ko, T. W. Exploring the Compositional Ternary Diagram of Ge/S/Cu
 ⁷⁹¹ Glasses for Resistance Switching Memories. *J. Phys. Chem. C* 123, 9486-9495
 ⁷⁹² (2019).
- 793
- 794
- 795