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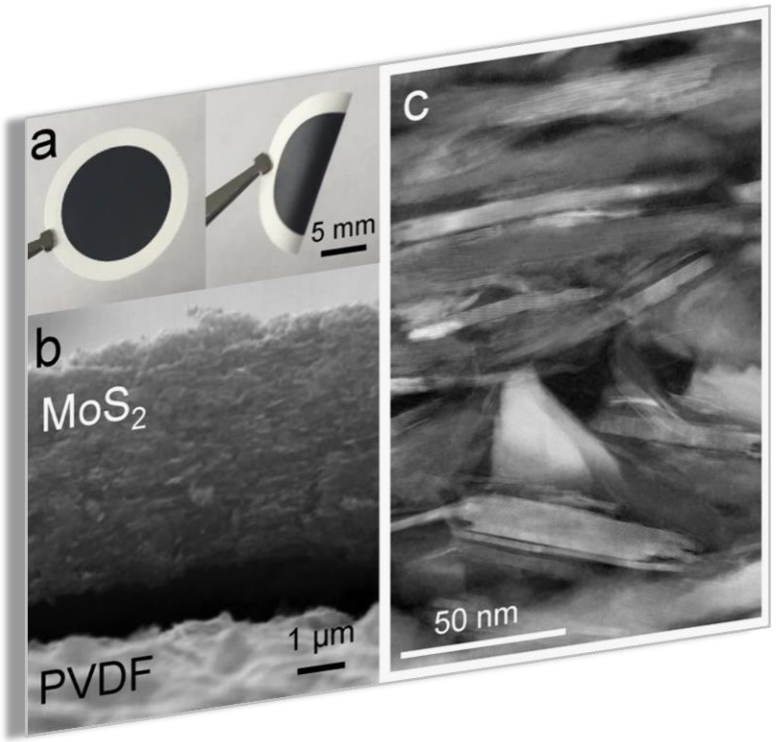

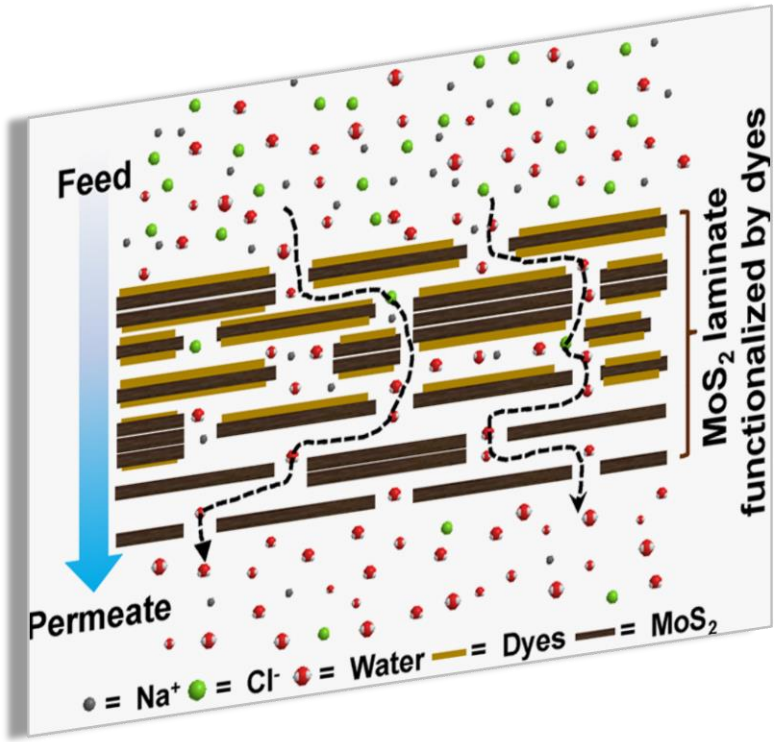

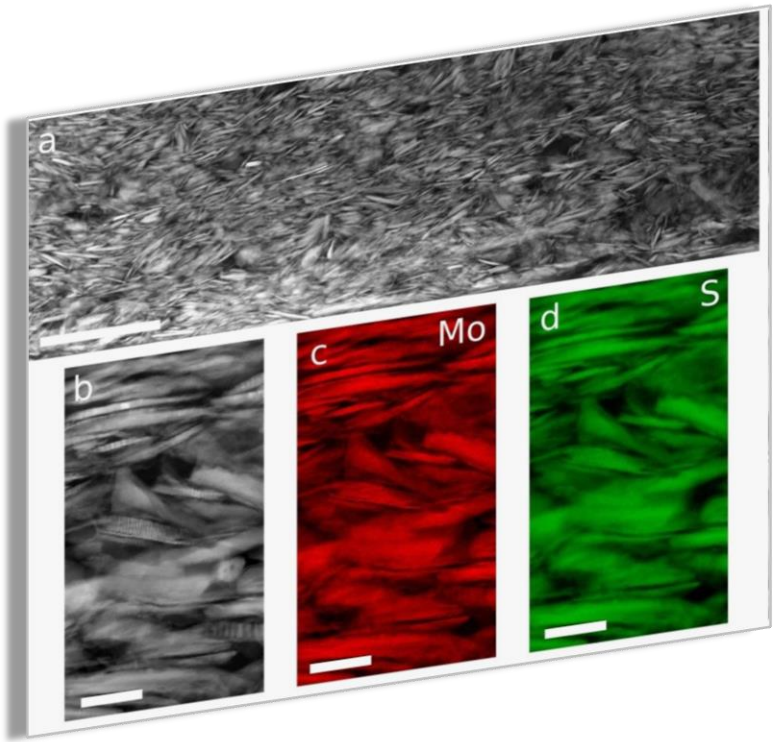

Desalination and Nanofiltration through Functionalized Laminar MoS_2 Membranes

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Swathy JR

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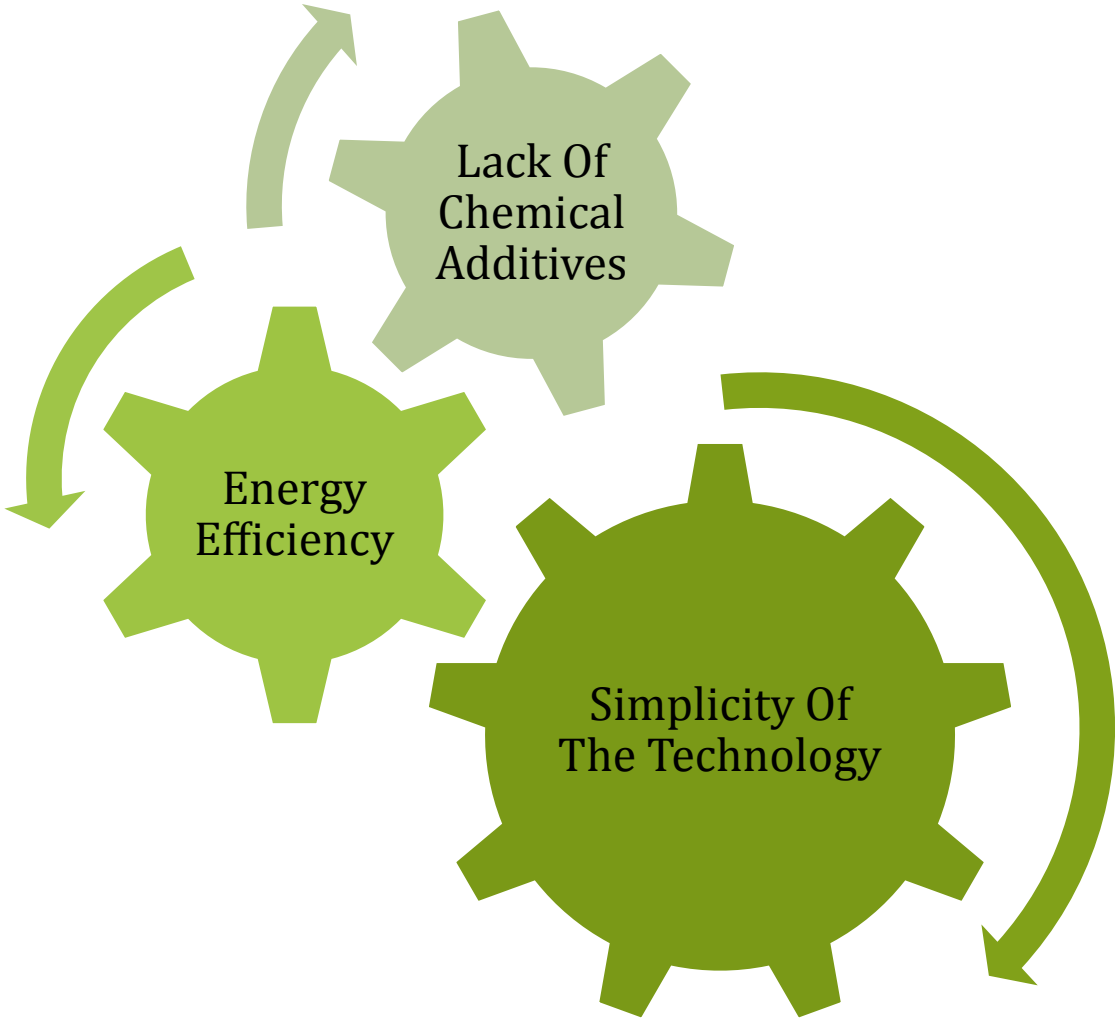
MEMBRANE TECHNOLOGY - FAVOURED OVER DISINFECTION OR DISTILLATION



Polymeric Materials

- High temperature - *Instability*
- Strongly acid / alkaline - *Low resistance*
- Organic solvents - *Sensitive*

Mesoporous Ceramics

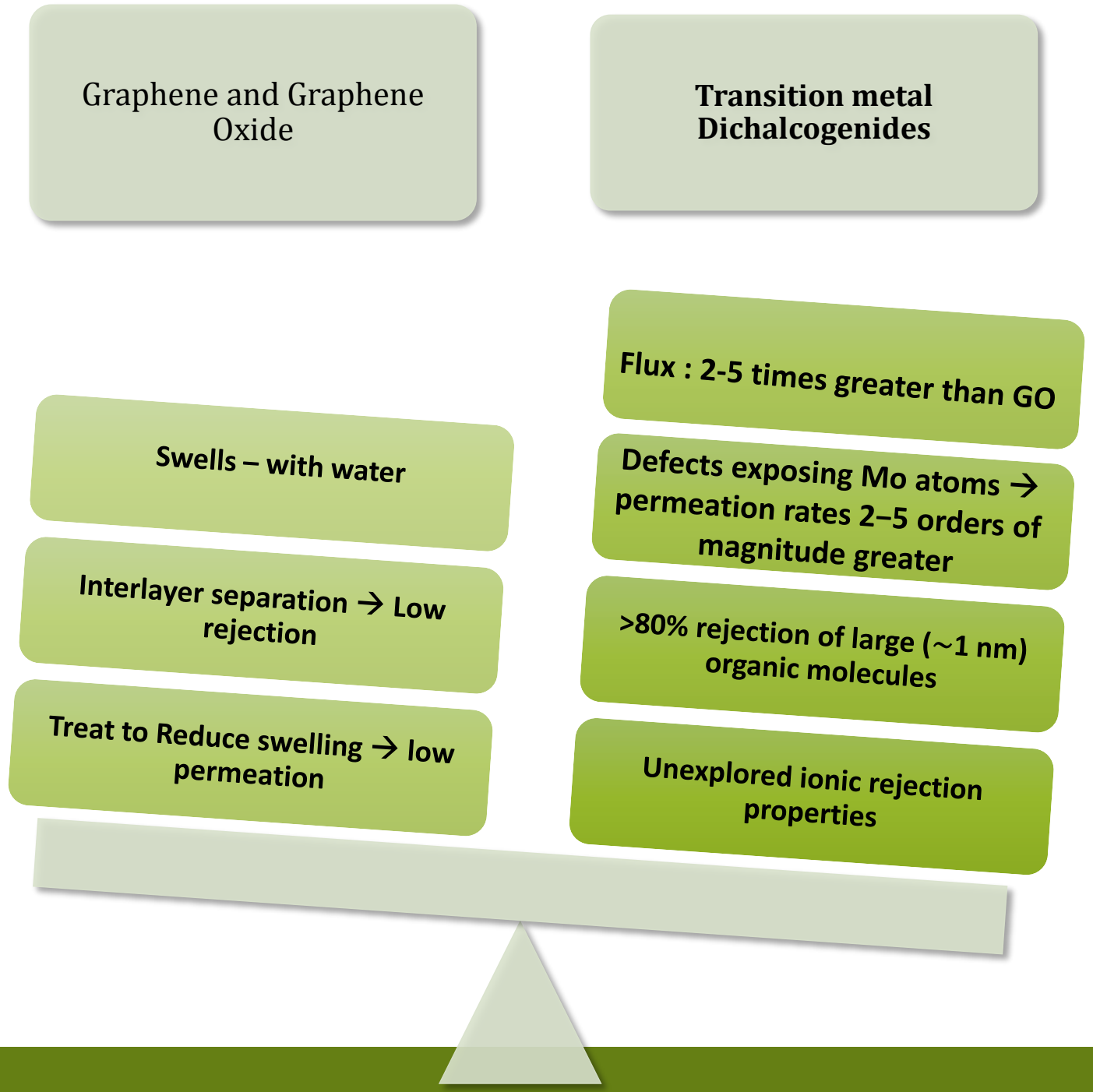
- Expensive for large-scale applications

Zeolite-based Materials

- Low water flux

2D MATERIALS

- ✓ Layered structure of **Nano-capillary channels.**
- ✓ **Tuneable** : solute rejection and solvent transport properties by preparation methods / surface functionality
- ✓ Much **higher water flux** than those of polymeric membranes,
- ✓ Demonstrating **ionic selectivity**.



THESE MOS_2 MEMBRANES EXHIBIT

- Excellent **ionic sieving** (e.g., Na^+, K^+, Ca^{2+}, and Mg^{2+})
- **High water permeation rates**.
- Impart **desired ionic sieving** by **chemical functionalization**
- **Long-term stability** with no change in the ionic rejection (6 months).
- Tolerant to **solvent exposure** (of varying polarity - no effect on the interlayer spacing)
- Suitable for a variety of **non-aqueous filtration** applications.
- Highly stable with **varying pH**.

IN THIS PAPER

Positives of Laminar MoS_2 membranes

RESULTS AND DISCUSSION

Producing Laminar MoS_2 Membranes

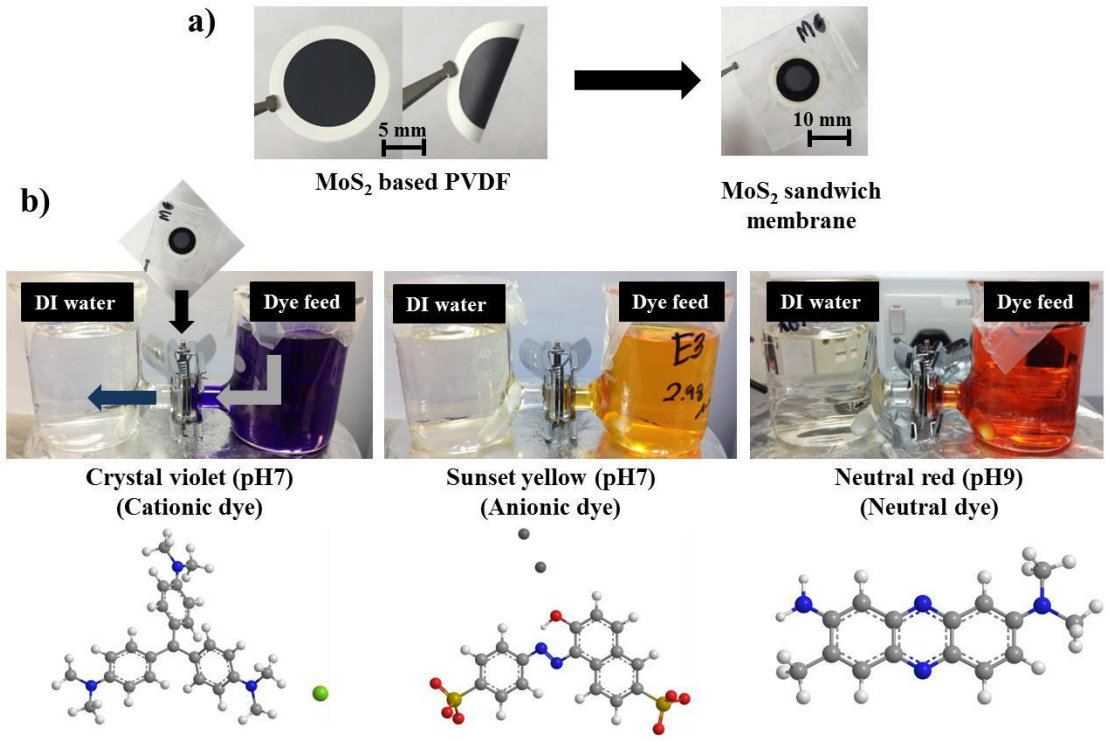
Filtration of solvent stabilized dispersions of exfoliated MoS_2 flakes

Filtered through polyvinylidene difluoride (PVDF) supporting membranes (100 nm pores).

Thicknesses in several (1-5) layer

range and lateral dimensions of 200-300 nm

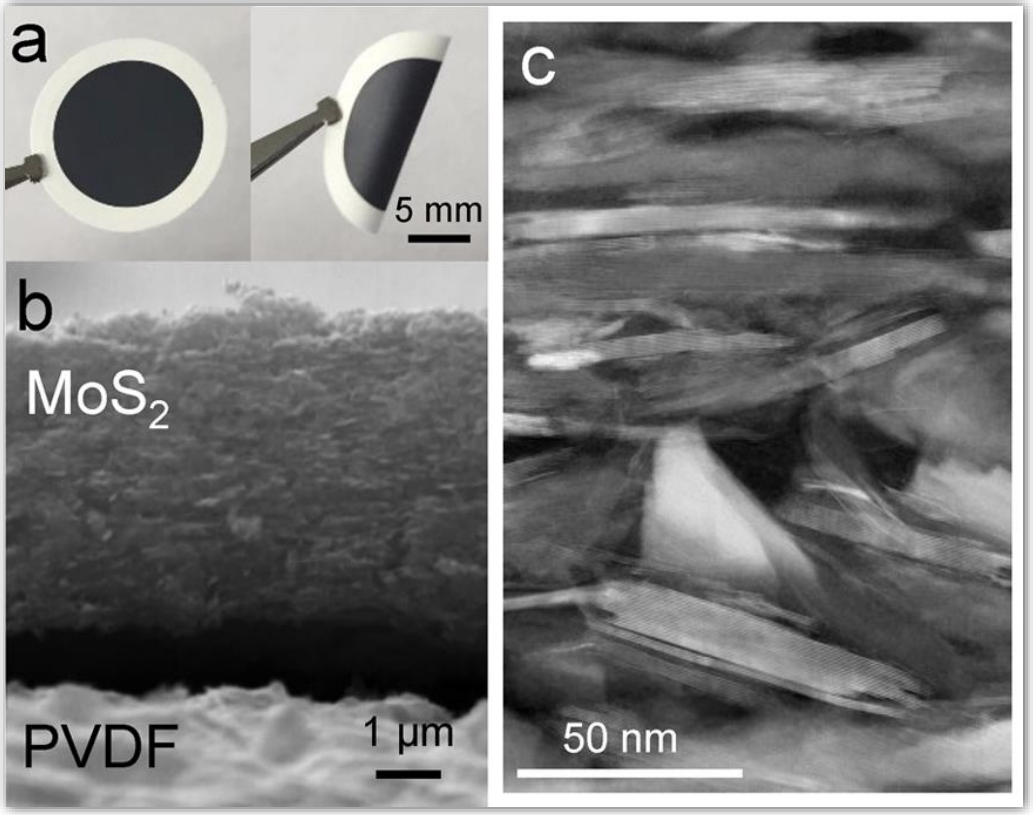
Membranes were functionalized by immersion in different dye solutions for extended periods (~21 days), in order to tune their permeation properties

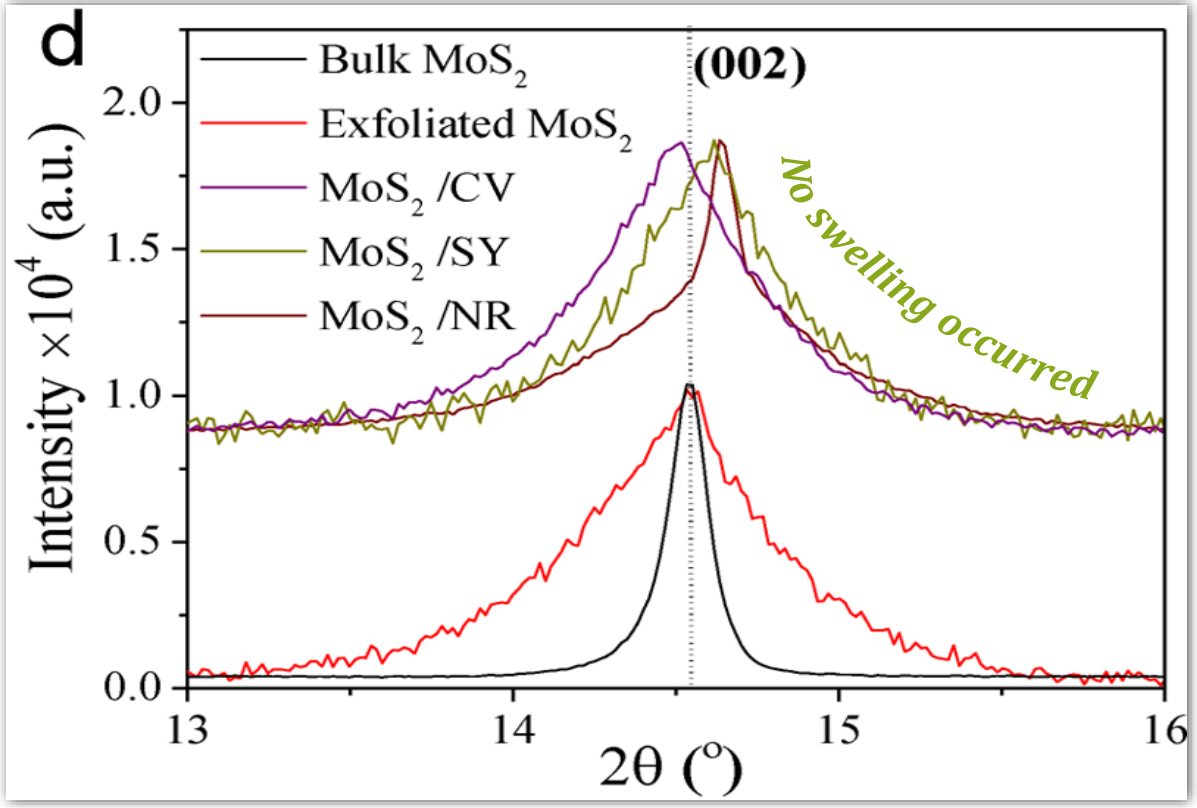


Various concentrations of dye solutions were prepared and added to MoS_2 dispersions. These solutions were then bath sonicated for 5 minutes to obtain a homogeneous dispersion.

Crystal Violet :
(tris(4(dimethylamino)phenyl)methylium chloride)
Sunset Yellow:
(disodium 6-hydroxy-5-(4sulfophenyl) azo]-2-naphthalenesulfonate)
Neutral Red:
(3-amino-7-dimethylamino-2methylphenazine)

Figure 1





(a) Photograph of the MoS_2 membrane supported by a polymer (PVDF) demonstrating their flexibility.

(b) Cross-sectional SEM image of the formed MoS_2 membrane supported on the PVDF showing the stacked layered nature of the MoS_2. Membranes were produced with thicknesses varying from 1 to 10 μm.

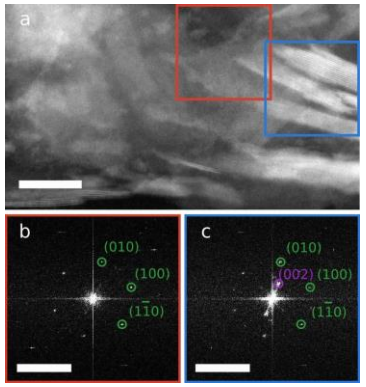
(c) Low-angle annular dark-field (LAADF) STEM image showing the cross-section of a laminate MoS_2 membrane. The thickness of individual flakes is ~1-10 layers, with the majority being few-layers (3-5).

(d) PXRD pattern of the (002) peak position for each of the functionalized membranes, pristine exfoliated MoS_2, and the bulk starting material.

Distribution in flake size - ultra sonication process reduces the size from several microns to a few hundred nm

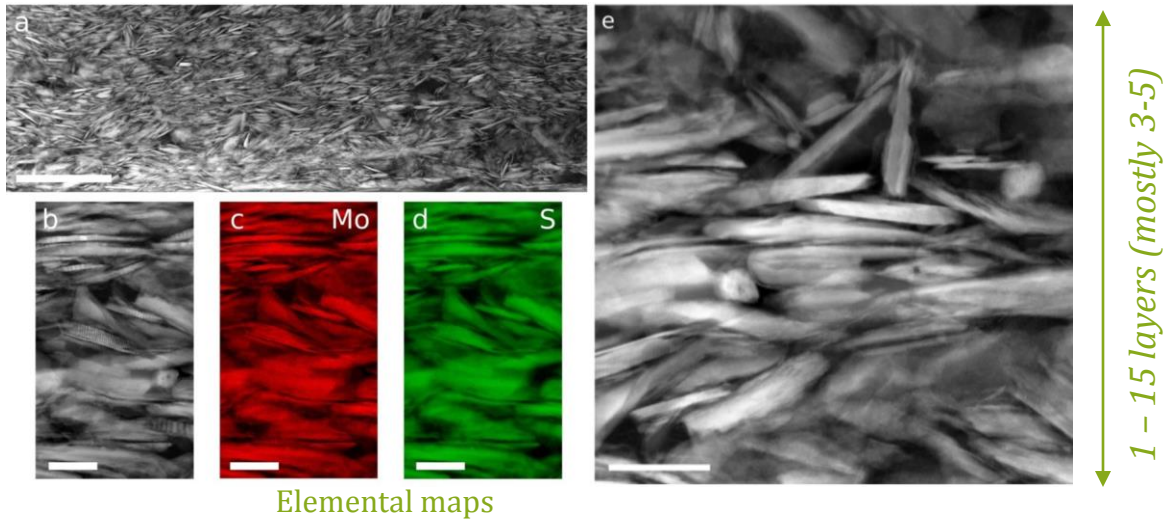
Figure 2, S5, S6

Cross-sectional STEM imaging of a functionalized membrane showing the distribution and orientation of MoS_2 flakes in the membranes.



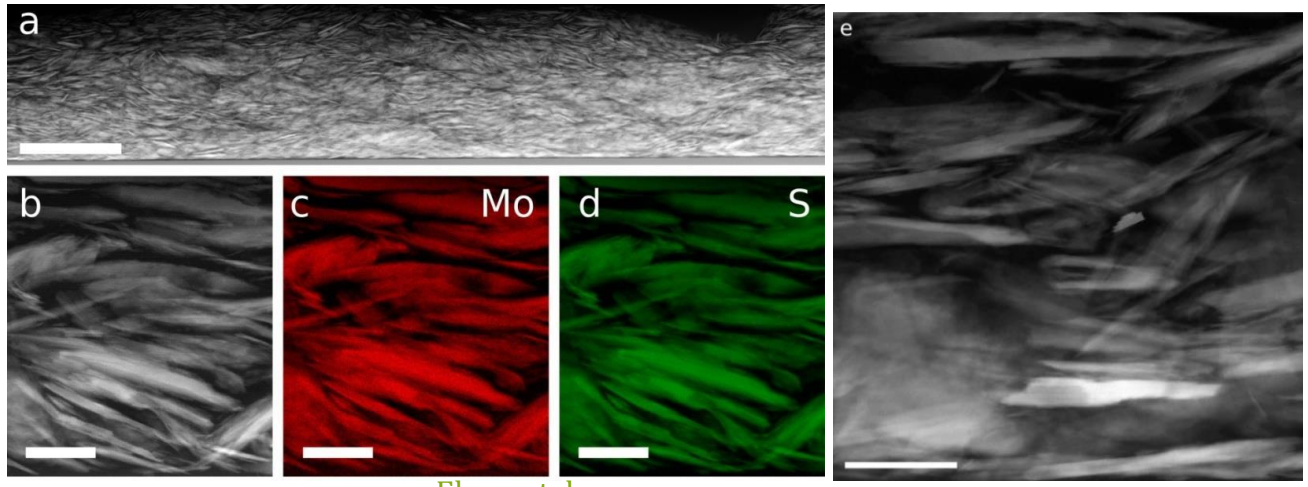
Flakes oriented in different directions

MoS_2/CV membrane



Elemental maps

pristine MoS_2 membrane



Elemental maps

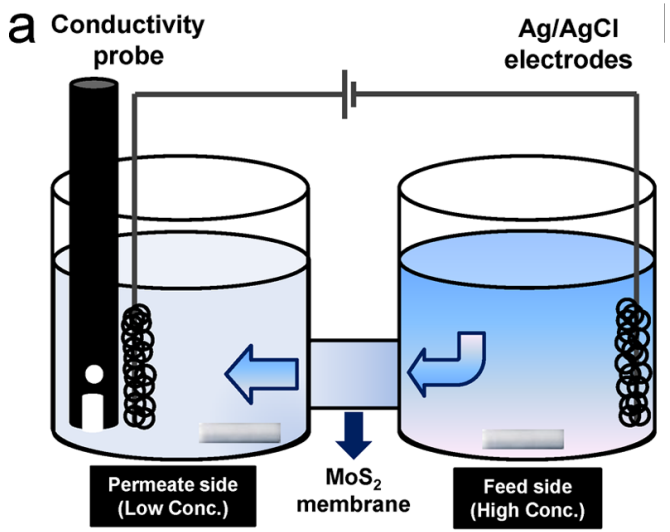
(a) Overview HAADF-STEM image of the membrane, the scale bar in (a) is 500 nm.
(b-d) HAADF image, Mo and S EELS maps
(e) high-resolution HAADF-STEM image of the membrane.

The scale bars in b-e are 50 nm.

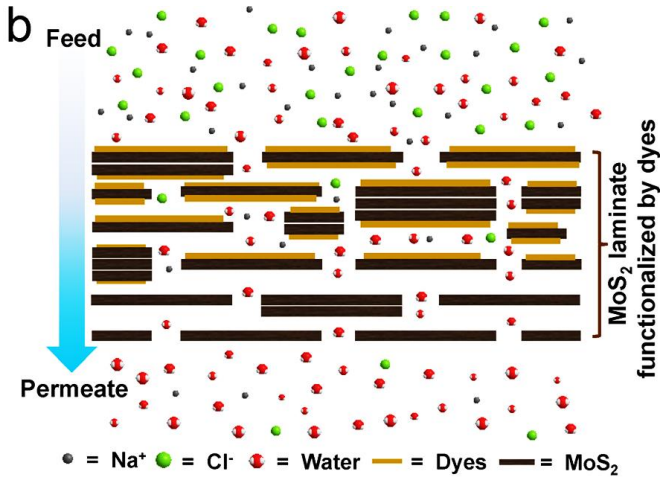
- Very high surface area
- Large amount of exposed edges
- Large number of nano-capillaries

Figure 3

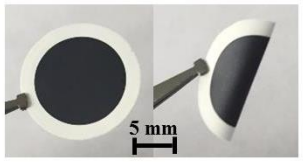
Bespoke H-beaker setup



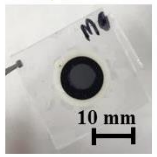
(a) Schematic of the experimental setup used for the ionic permeation experiments.



(b) Schematic showing the diffusion, driven by the large concentration gradient, of the solute (Na^+ and Cl^- ions) through the MoS_2 laminate membrane pre-functionalized by organic dye.



MoS_2 based PVDF



MoS_2 sandwich membrane

Membranes sandwiched between two polyethylene terephthalate (PET) sheets - to control exposed membrane area and reproducibility

Water Permeation Rates

OSMOTIC PRESSURE METHOD
(sucrose solution (1 M) vs distilled water)

MoS_2/CV membrane

3um thick	6 um thick
$40X10^{-3}$ $Lm^{-2}h^{-1}bar^{-1}$	$11.6X10^{-3}$ $Lm^{-2}h^{-1}bar^{-1}$

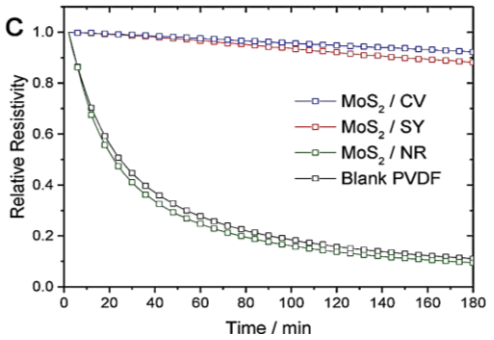
GO membrane
1um thick: ~$8X10^{-3}$ $Lm^{-2}h^{-1}bar^{-1}$

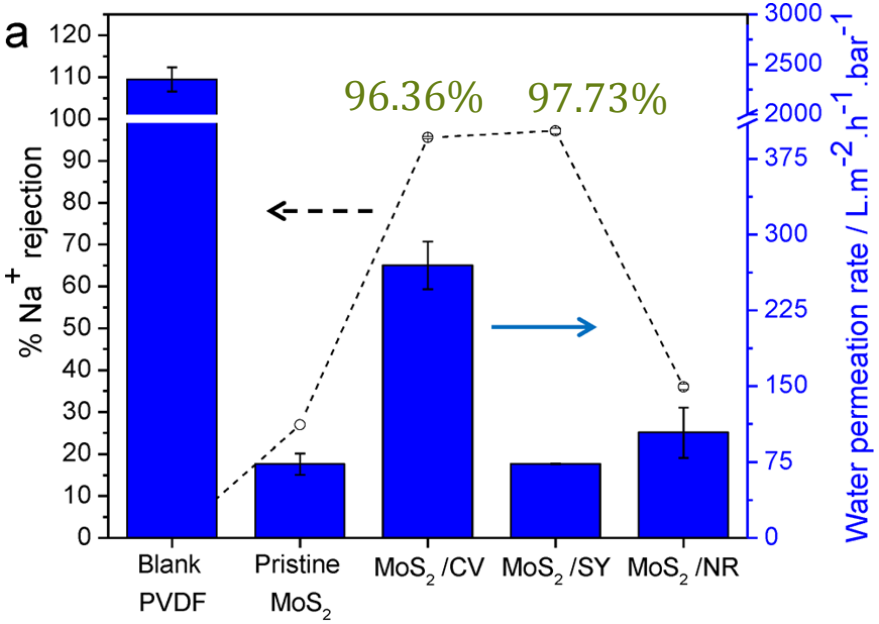
EXTERNAL PRESSURE METHOD
(1M NaCl)

MoS_2/CV	Pristine MoS_2
6um thick	1.7 um thick
269.5 $Lm^{-2}h^{-1}bar^{-1}$	245 $Lm^{-2}h^{-1}bar^{-1}$

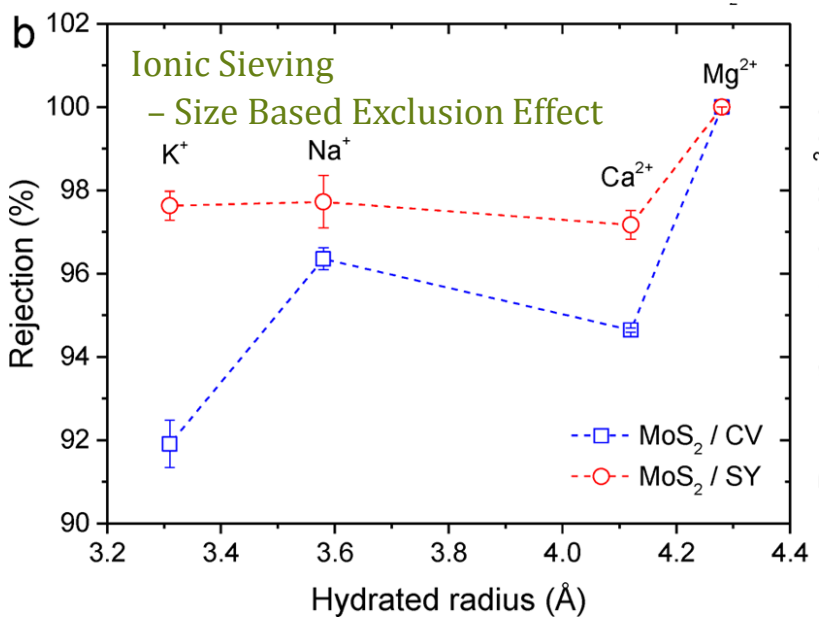
Figure 4

Plot comparing the change in **relative resistivity** of the permeate side



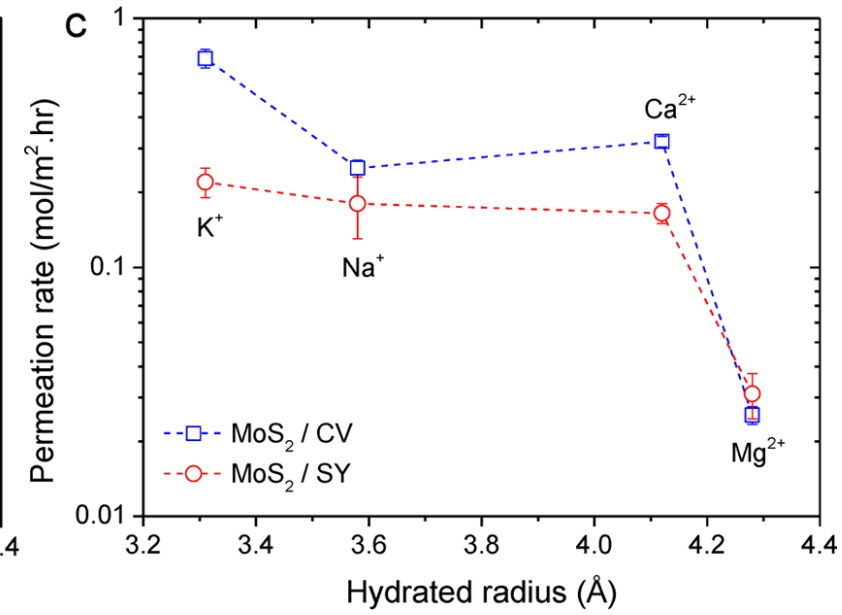


(a) Comparison of the **sodium ion (Na^+) percentage rejection** under diffusive pressure measured by ICP-OES after 180 min for each membrane (6 µm thick) as well as the water **permeation rate** measured with external pressure (1 bar).



(b) Plot of the **rejection properties** (R%=1- C_{MoS2}/C_{PVDF} membranes (6 µm thick) as a function of hydrated cation radius measured after 3 h.

C_{MoS2} / C_{PVDF} — increased concentration of solute ions in the permeate



(c) Plot of the **permeation rates** for the MoS_2/CV & MoS_2/SY membranes for the cationic species studied with a 1000X concentration gradient. Note the semilogarithmic scale.

Rejection properties for MoS_2/CV and MoS_2/SY membranes (6 μm Thick) for **synthetic seawater** containing mixed ionic solutes. Inset shows a schematic.

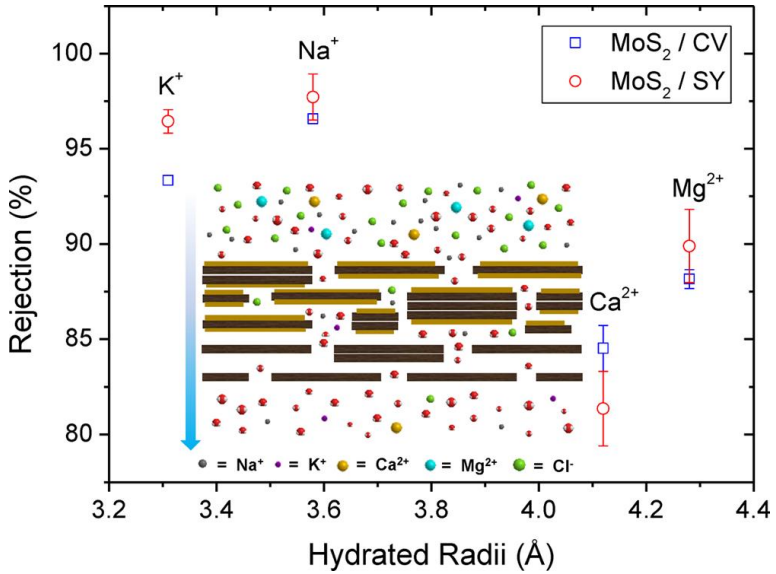
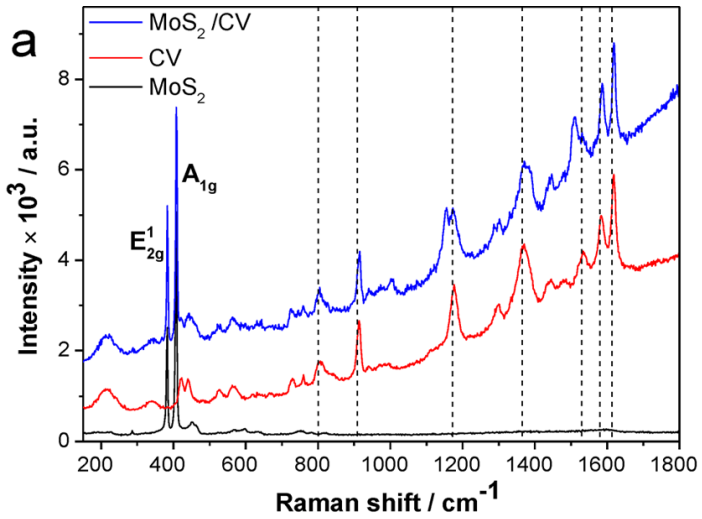
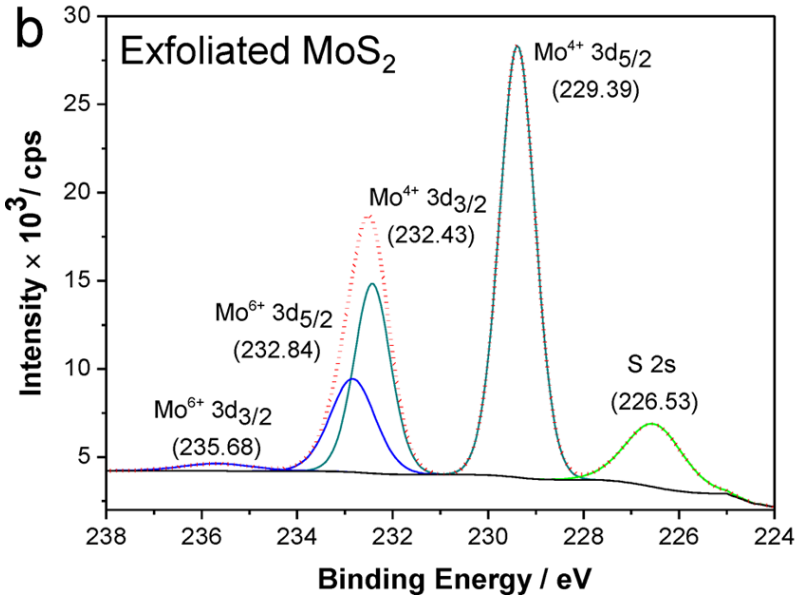


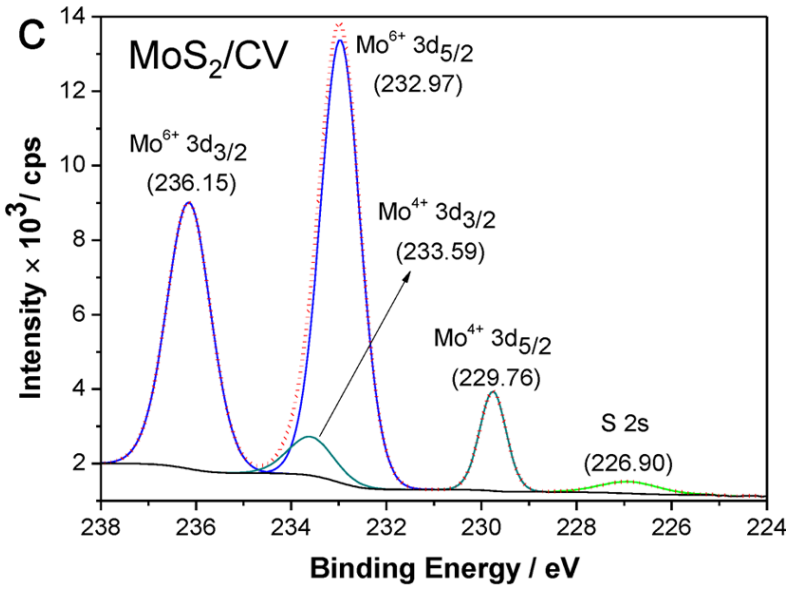
Figure 5, 6

(a) Raman spectra from the pristine MoS_2 membrane, crystal violet (CV) powder, and MoS_2/CV.



XPS spectra of the Mo_{3d} region for a pristine exfoliated MoS_2 membrane (b) and a CV-functionalized membrane (C).





Successful functionalization is confirmed by shifts in binding energy due to charge transfer in the sulfur peaks.

CONCLUSION

- A simple, low-cost route to produce membranes
- Removal of ions including NaCl, from water at room temperature.
- Works in seawater, drinking water or plant irrigation with a single pass through a membrane of few microns thick.
- The water fluxes are substantially higher than those of GO membranes of comparable thickness
- The approach is easily tunable via variation of the organic functionalization molecule

FUTURE DIRECTIONS

- Can we synthesize MoS_2 or other TMD membranes functionalized with specific clusters?
- MoS_2 membranes based filtration devices which are size tuned for purification of clusters in organic solvents

THANK YOU

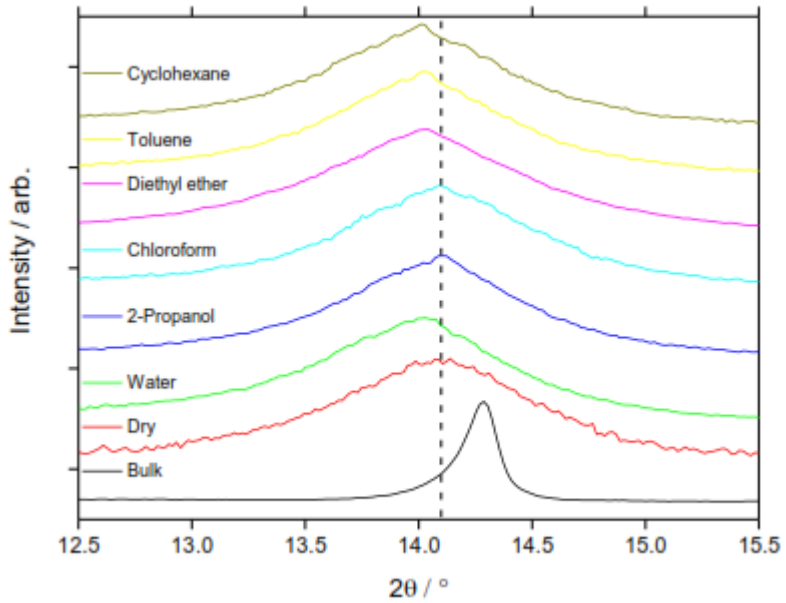


Figure S1: Comparison of the PXRD (002) reflection of a pristine MoS_2 membrane after immersion for ~72 hours in solvents with varying polarity,[1] ranging from water (relative polarity: 100), 2-propanol (P: 61.7), chloroform (P: 25.9), diethyl ether (P: 11.7), toluene (P: 9.9), and cyclohexane (P: 0.6).

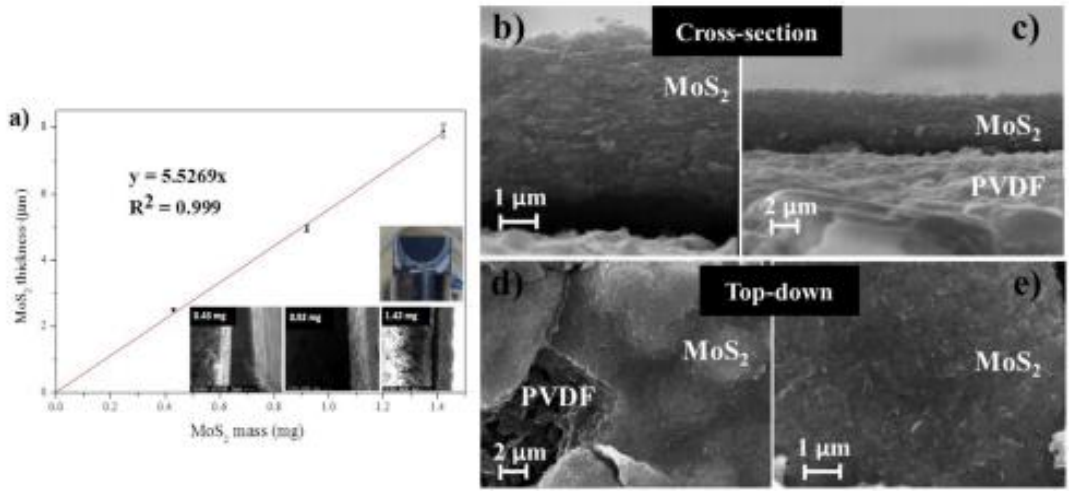


Figure S2: (**a**) Thickness calibration curve showing the linear relationship between MoS_2 mass and membrane thickness (determined from cross-section SEM). (**b-c**) Representative cross-section SEM images of a MoS_2 membrane. (**d-e**) SEM images showing the top-down morphology of the MoS_2 membranes.

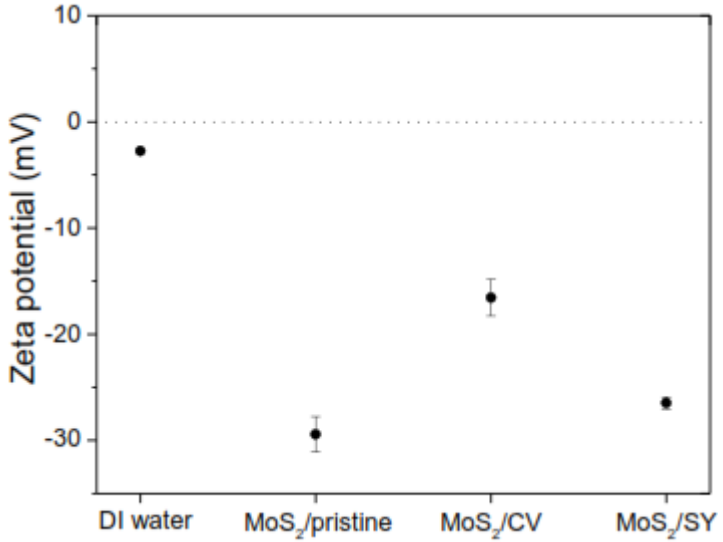


Figure S8: Measured zeta potential of dispersions of pristine and dye functionalized MoS_2

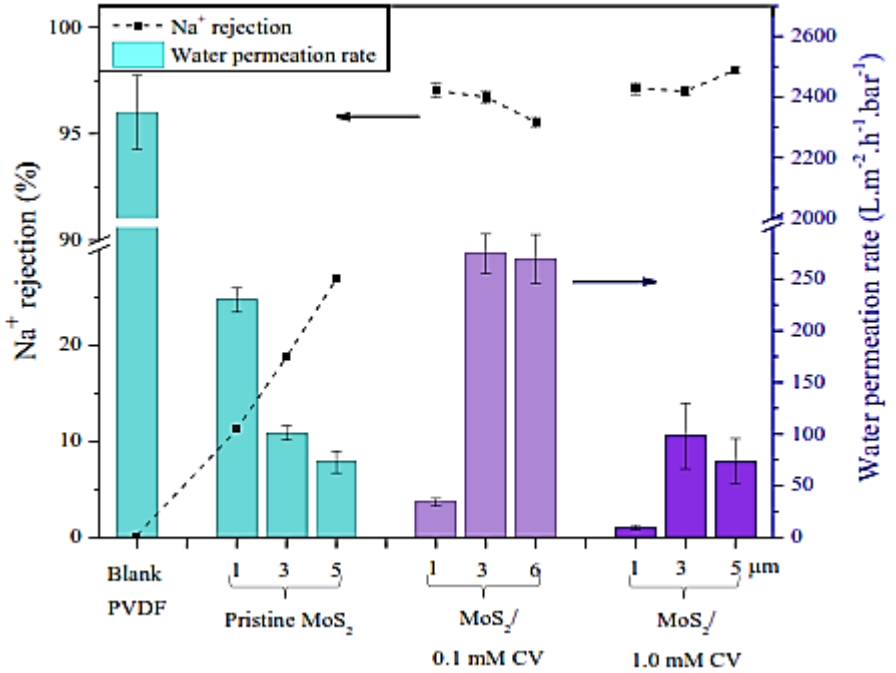


Figure S7: %Na^+ (NaCl) rejection and water permeation rates measured for pristine MoS_2, and for MoS_2 functionalized by 0.1 mM and 1.0 mM CV for 21 days; the dashed lines are %Na^+ rejection. Cyan, pale and dark violet columns are water permeation rate of pristine MoS_2, MoS_2 with 0.1 mM, and 1.0 mM CV, respectively. For all MoS_2 membranes different thicknesses are compared. All permeation rates were measured using external pressure at 1.0 bar.

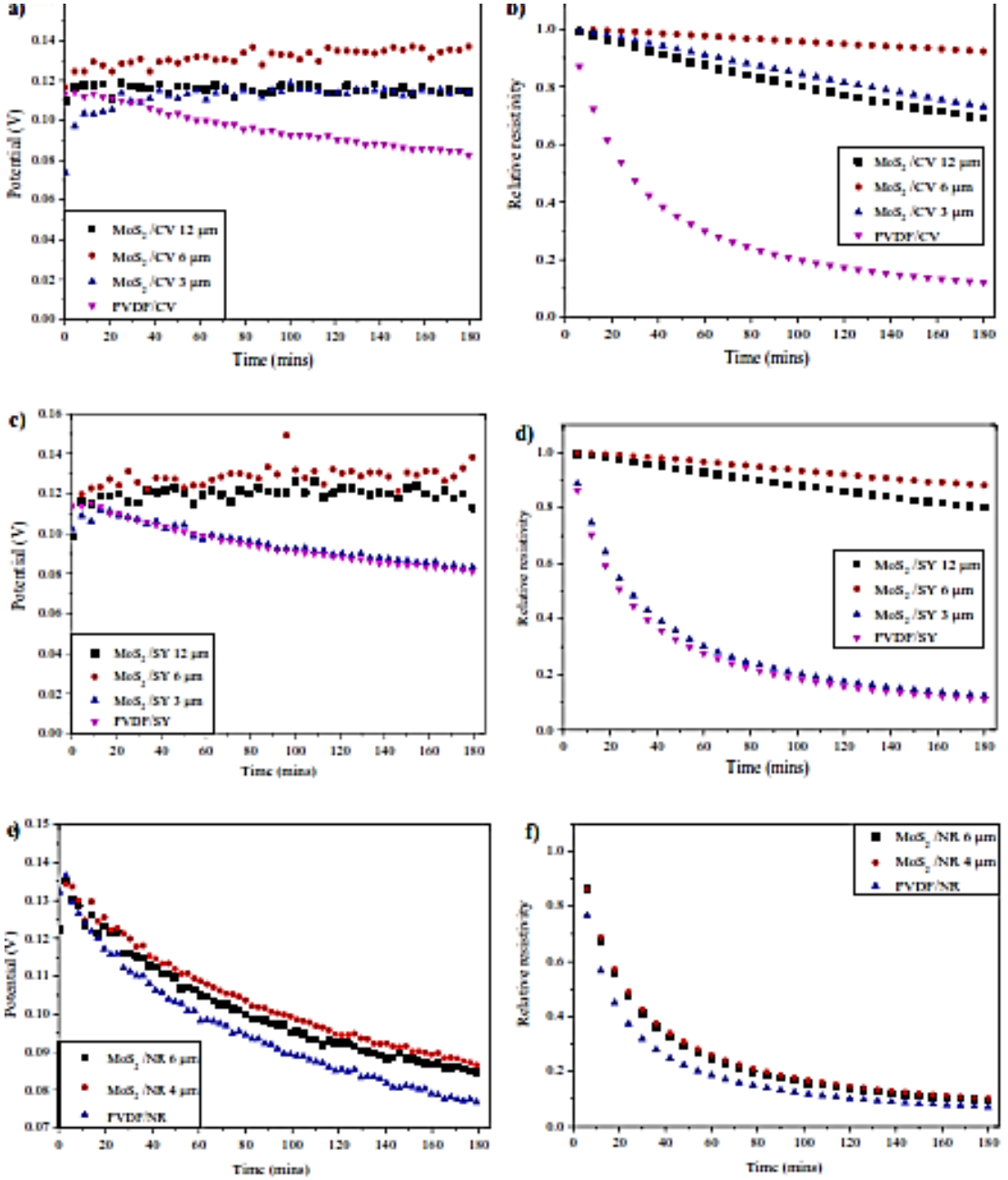


Figure S9: (**a, c, e**) Plots of measured potential between feed and permeate sides for the NaCl permeation test with MoS_2/CV, MoS_2/SY and MoS_2/NR membranes respectively. (**b, d, f**) Plots of relative resistivity of NaCl permeation as a function of time for up to 3 hours for MoS_2/CV, MoS_2/SY and MoS_2/NR membranes respectively. Relative resistivity of permeate solution is defined as 1 at beginning of experiment. All membranes were functionalized by 0.1 mM dyes for 21 days and comparative data for different membrane thicknesses and for similarly dye exposed bare PVDF filters is included for reference.

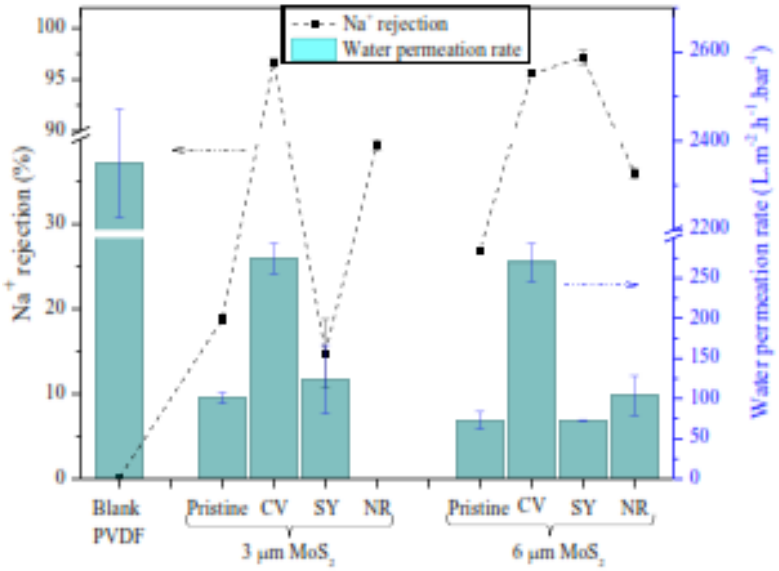


Figure S10: Plot of Na^+ rejection under osmotic pressure measure by ICP-OES after 3 hours and water permeation rates measured with external pressure (1 bar) for 3 μm and 6 μm thick membranes functionalized with different dyes; the dashed lines are Na^+ rejection (%) and bars are water permeation rate,. All membranes were functionalized by 0.1 mM dye for 21 days.

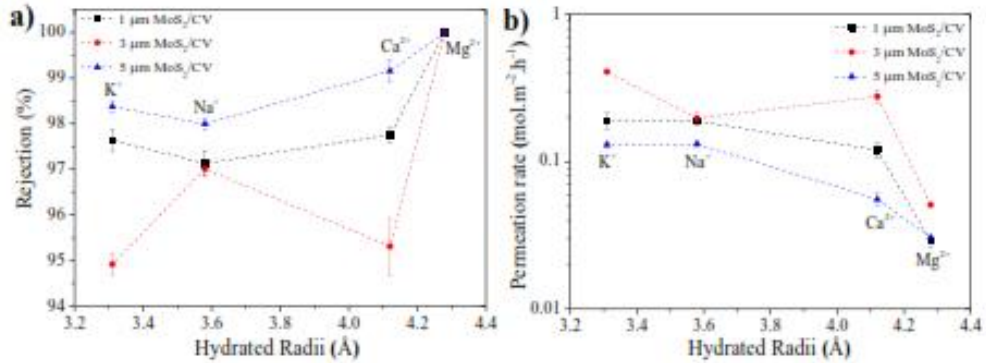


Figure S11: (a) Plot of the rejection properties of the 1.0 mM CV functionalized MoS_2 membranes at different thicknesses. **(b)** Plot of the permeation rate of each membranes functionalized by 1.0 mM CV for the different cationic species from KCl, NaCl, $CaCl_2$, and $MgCl_2$ studied with a 1000x concentration gradient. All increasing ion concentrations in the permeate sides were measured by ICP-OES after 3 hours.