

DESALINATION MEMBRANES

Sieving in order

Designing highly ordered and ultrathin nanoporous membranes achieves superior water flux, while maintaining high selectivity for NaCl rejection.

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With climate change and population growth, securing water resources has become one of the greatest challenges for the decades to come. To meet increasing demand, water must now be reclaimed and purified. Water treatment generally involves the use of sludge or biomass as a pre-treatment followed by filtration, while desalination technology alternatively uses distillation and reverse osmosis filtration¹. The development of membranes with superior selectivity and permeation rate is expected to reduce the energy footprint for reclaiming water and desalination, and would have a considerable societal and industrial impact. Traditional commercial porous membranes for molecular sieving are usually made of polymers or ceramic materials with specific pore sizes depending on the application. However, these membranes are still limited in terms of sieving performance and stability. Water filtration and desalination in reverse osmosis mainly rely on polyamide membranes based on thin-film composite designs, but the heterogeneity of the pores induces a trade-off between rejection efficiency and water flux^{2,3}.

Two-dimensional (2D) materials, with atomic thickness and large lateral dimensions, can be considered the ultimate membranes⁴. Traditional membranes made of 2D materials consist either of a monolayer with nanoholes, or of a stack of exfoliated nanosheets (Fig. 1)⁵. The challenge of using membranes consisting of a single layer of nanosheets is that ideal 2D materials generally lack atomic vacancies or intrinsic porosity. This prevents molecules from passing through, as well as most ions, although previous studies have shown that protons can cross materials with a single atomic thickness such as graphene and boron nitride⁶. The preparation of extrinsic nanopores on a monolayer has proved to be feasible but often at the cost of the membrane selectivity, especially when sieving small molecules and ions. Alternatively, nanoporous conjugated 2D polymers based on graphyne, polyphenylene or coronene have been explored as they

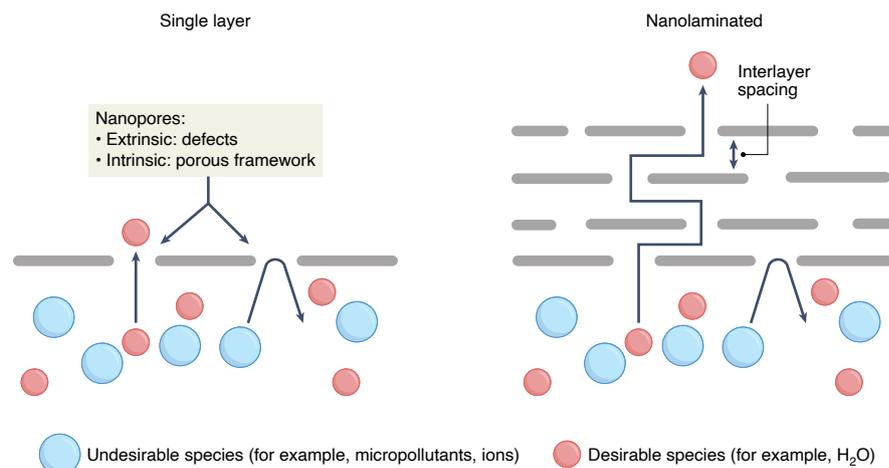


Fig. 1 | Transport mechanism through ultrathin membranes based on 2D materials. Ultrathin membranes can be either monolayers with intrinsic or extrinsic porosity, or multilayers where sieving occurs in the interlayer space.

offer intrinsic and well-designed porosity^{7,8}. However, the lack of growth control of nanoporous 2D carbon-based materials generally translates into uncontrollable pore orientation and membrane defects.

Now, writing in *Nature Materials*, Yu Han and co-workers at the King Abdullah University of Science and Technology report the growth of ultrathin ordered nanoporous membranes based on a conjugated polymer framework (CPF)⁹. With an optimal thickness of 8 nm, the membranes demonstrate a water flux as high as $112 \text{ mol m}^{-2} \text{ h}^{-1} \text{ bar}^{-1}$, equivalent to $\sim 2 \text{ l m}^{-2} \text{ h}^{-1} \text{ bar}^{-1}$ with a salt rejection of 99.5% when tested under forward osmosis.

The authors used 1,3,5-triethynylbenzene as a building block of the CPF, which controlled the planar growth of the framework and the formation of rhombic nanopores. s-CPF was grown on single crystalline Cu(111) as a catalyst for the coupling reaction via a chemical vapour deposition strategy (Fig. 2a, c). This results in improved film growth and reduced disorder. The crystallinity and stacking order were further confirmed by Raman and X-ray diffraction analyses, which are

consistent with an ABC stacking mode, similar to the rhombohedral stacking of graphite (Fig. 2b). The structural order was attributed to the chemical vapour deposition method and the use of single-crystal Cu as a substrate for film growth.

To evaluate the sieving properties in forward and reverse osmosis configurations, the researchers transferred the nanoporous film onto porous alumina used as a support. In forward osmosis with pure water as feed, the flux reached $215 \text{ l m}^{-2} \text{ h}^{-1} \text{ bar}^{-1}$, while a water/Na⁺ selectivity of $>6,800$ was demonstrated with a 0.1 M NaCl feed solution. Remarkably, the ultrathin membranes can withstand relatively high pressures up to 13 bar for 450 hours, and achieve a NaCl rejection of 83% and a water flux of $>9.5 \text{ l m}^{-2} \text{ h}^{-1} \text{ bar}^{-1}$ in reverse osmosis.

The team also used molecular dynamics simulation to better understand water transport through the nanoporous framework. Their results show that water can indeed pass through the $3.7 \times 10.3 \text{ \AA}$ rhombic windows formed by two stacked CPF layers (Fig. 2d). These nanopores are large enough to accommodate two to three water molecules. Interestingly, the stacking

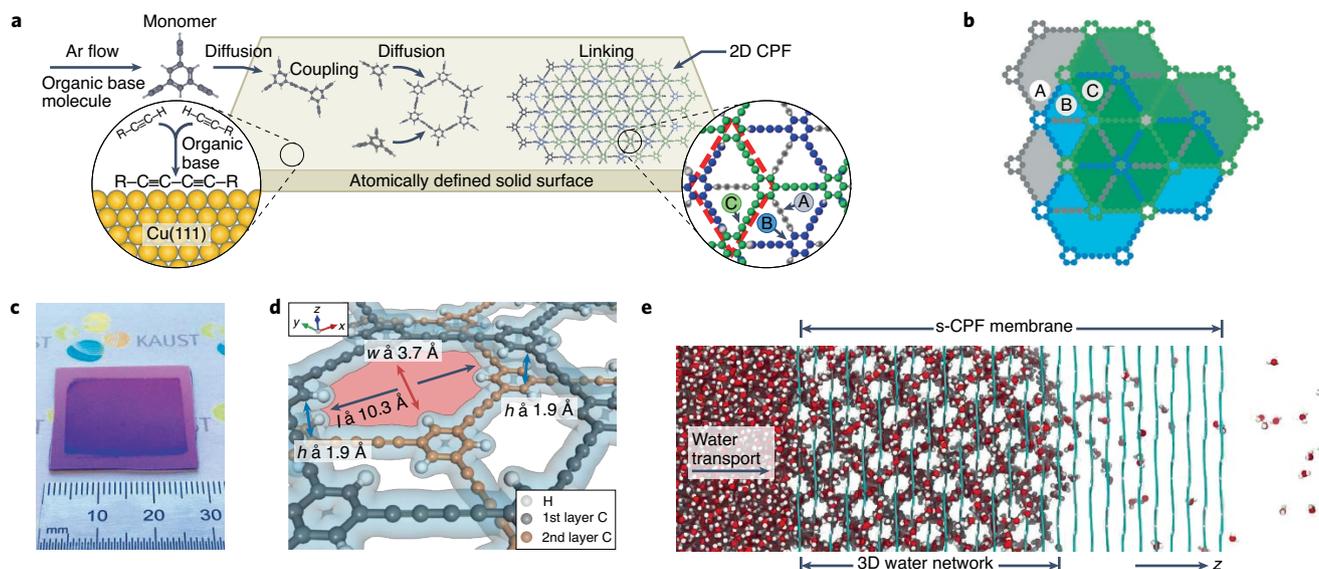


Fig. 2 | Synthesis and water transport in a CPF. **a**, Synthesis of ABC-stacked conjugated carbon framework. **b**, ABC stacking of the s-CPF. **c**, s-CPF films transferred on SiO₂/Si wafer. **d**, Rhombic nanopores formed by the stacked framework. *w*, window width; *h*, interlayer spacing; *l*, window length. **e**, Predicted water transport through the rhombic nanopores of the s-CPF membranes. Panels **a**, **c**, **d**, **e** reproduced with permission from ref. ⁹, Springer Nature Ltd.

of the successive ordered layers generates a 3D network, where the water molecules diffuse in three equivalent rhombic nanopores when passing between two successive layers (Fig. 2e), while the lateral diffusion of water within the interlayer space is prohibited.

To discriminate the contributions of the surface and chemistry of the nanopore, the researchers prepared the same CPF but on polycrystalline Cu (p-CPF). The films obtained showed a lower Young's modulus and a higher surface charge due to presence of oxygen from an incomplete C–C coupling of the monomers. The similar sieving properties between s-CPF and p-CPF indicated a size-controlled diffusion mechanism due to the well-controlled nanoporosity of the membrane. Excitingly, the ability to adjust the oxygen content of the film by selecting the growth substrate allows control of the surface charge, which may have applications in osmotic energy harvesting.

This work highlights the importance of controlling the design of the molecular building blocks of the polymer framework. Additional efforts are, however, expected to evaluate the full potential for the proposed strategy, especially towards realistic applications. While the desalination performance in forward osmosis configuration reaches satisfactory values, the NaCl rejection in reverse osmosis remains substantially lower than that of state-of-the-art thin-film composite membranes, the rejection of which typically exceeds 98% for seawater. The scalability of the process remains to be seen, in particular to meet industrial requirements in terms of membrane configurations such as spiral wounds or hollow fibres. Nevertheless, these findings are an important leap towards the synthesis of ultrathin carbon-based films with controlled and ordered porosity, and open new directions towards the realization of ultrathin porous conjugated polymer membranes. □

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Competing interests

The authors declare no competing interests.