Fundamental transport mechanisms, fabrication and potential applications of nanoporous atomically thin membranes

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Graphene and other two-dimensional materials offer a new approach to controlling mass transport at the nanoscale. These materials can sustain nanoscale pores in their rigid lattices and due to their minimum possible material thickness, high mechanical strength and chemical robustness, they could be used to address persistent challenges in membrane separations. Here we discuss theoretical and experimental developments in the emerging field of nanoporous atomically thin membranes, focusing on the fundamental mechanisms of gas- and liquid-phase transport, membrane fabrication techniques and advances towards practical application. We highlight potential functional characteristics of the membranes and discuss applications where they are expected to offer advantages. Finally, we outline the major scientific questions and technological challenges that need to be addressed to bridge the gap from theoretical simulations and proof-of-concept experiments to real-world applications.

Membranes are thin barriers that permit selective mass transport, and form the basis of a number of separation processes typically driven by gradients in pressure, electric potential, concentration or temperature\(^1\). With the advantages of modularity, scalability, compactness and high energy efficiency, membrane separations have become pervasive\(^1\) in applications related to energy\(^1\), water\(^1\), food\(^1\), biotechnology\(^2\) and chemical processing\(^1\). Major applications include water desalination\(^4\),\(^6\), natural gas purification\(^7\), production of nitrogen from air\(^8\), haemodialysis\(^9\), bioprocessing\(^1\), solvent- and petrochemical-based separations\(^10\),\(^11\), and production of ultrapure water\(^9\). Beyond separations, membranes find use in fuel cells\(^1\), drug delivery\(^12\), bio/chemical sensors\(^13\) and energy harvesting from mixing processes\(^1\).

The performance of membrane-based systems (for example, energy efficiency, productivity or product recovery) depends on the constituent membrane characteristics, which place constraints on and define trade-offs in membrane process design. In addition to being economical and manufacturable, an ideal membrane should easily allow flow of the desired species (high permeance), reject undesired species (high selectivity) and exhibit robustness in operation (high chemical, mechanical and thermal stability, low fouling) (see Box 1).

Although remarkable progress has been achieved in membrane technology, persistent challenges remain, specifically (1) overcoming the trade-off between selectivity and permeability of the membrane material, (2) mitigation of fouling and (3) robust operation under harsh conditions. Specific examples include the need for chlorine-resistant membranes for water desalination\(^5\),\(^10\),\(^17\) and high-permeance membranes for production of oxygen from air\(^1\). To address these challenges, the past few decades have seen the exploration of various membrane structures and materials, including novel polymers\(^1\), inorganic membranes (zeolites\(^18\), silica, carbon\(^19\), ceramics), nanomaterials (metal-organic frameworks\(^20\), carbon nanotubes\(^21\) (CNTs), carbon nanomembranes\(^22\)) and polymer–inorganic ‘mixed-matrix’ membranes\(^23\),\(^24\) among others. These developments seek to achieve improved membrane performance by (1) the use of favourable membrane structures, for example, a thin selective layer, or (2) the use of materials with favourable properties, for example, antifouling properties and frictionless transport in CNTs\(^23\), or high permeability and selectivity of materials with intrinsic porosity\(^24\).

The rise of graphene and other atomically thin materials in the past decade\(^25\) has opened new possibilities in membrane technology. The atomic thickness of these materials makes them the thinnest possible barrier\(^26\), which, combined with their remarkable mechanical strength\(^27\), chemical robustness\(^28\) and ability to sustain selective, nanometre-scale pores\(^29\), evokes the possibility — at least in principle — of realizing an ideal nanoporous atomically thin membrane that could be tailored to a range of applications while offering high permeance, high selectivity and high chemical resistance. This review focuses on nanoporous atomically thin membranes (NATMs)\(^30\)–\(^37\) where transport is governed by flow across rigid pores in a continuous, atomically thin layer; for a discussion of membranes where other mechanisms influence transport, such as graphene oxide or carbon nanomembranes, the reader is directed to several excellent reviews\(^22\),\(^32\),\(^36\)–\(^41\).

Transport mechanisms

Membranes achieve selective transport through a variety of mechanisms operative over different length scales (Fig. 1a). At the smallest scale, dense polymeric membranes (without defined pores), such as reverse osmosis membranes for water desalination and many gas separation membranes, operate by a solution–diffusion mechanism\(^42\). Here, selectivity results from differences in species solubilities and diffusivities in the membrane material; solubility depends on the molecular structure, membrane porosity and chemical affinity, whereas diffusivity is governed by thermally activated rearrangements of the polymer chains that strongly favour size-dependent diffusion of smaller molecules. When selectivity
**Box 1 | Definitions, transport equations and length scales for NATMs.**

### Definitions of transport properties

**Permeance**  
\[ \text{Permeance} = \frac{\text{Mass, volume or molar flow rate across membrane}}{\text{Membrane area} \times \text{Pressure difference}} \]

where 'pressure difference' may also refer to a difference in chemical potential, concentration, electric potential and so on.

**Selectivity**  
\[ \text{Selectivity} = \frac{\text{Permeance of species A}}{\text{Permeance of species B}} \]

**Rejection**  
\[ \text{Rejection} = 1 - \frac{\text{Solute concentration in permeate solution}}{\text{Solute concentration in feed solution}} \]

**Pore permeation coefficient**  
\[ \text{Pore permeation coefficient} = \frac{\text{Mass, volume or molar flow rate across pore}}{\text{Pressure difference}} \]

**Pore effective area**  
\[ \text{Pore effective area} = \frac{\text{Pore permeation coefficient}}{\text{Ideal gas flux (incident on a surface)}} \]

### Some basic transport equations

**Ideal gas flux.**  
\[ J_{\text{ideal gas}} = \frac{\Delta P}{\sqrt{2\pi R M T}} \]

\( \Delta P \) is the gas pressure, \( M \) is the molecular weight of the gas, \( R \) is the universal gas constant and \( T \) is the absolute temperature.

**Permeation coefficient for viscous flow in pore.**  
\[ \Pi = \frac{R^2}{\mu R + 8 L_\mu} \]

where \( R \) is the pore radius, \( \mu \) is the dynamic viscosity and \( L_\mu \) (0.535 nm for graphene) is the pore length (from ref. 102). Sampson's model: \( \Pi = R^2/3\mu \); obtained for \( L_\mu = 0 \).

**Ion conductance of pore.**  
\[ G = \sigma \left( \frac{L_\mu}{\pi R^2} + \frac{1}{2R} \right)^{-1} \]

\( \sigma \) is the bulk ionic conductivity. This relation is valid for neutral pores.

### Length scales

**Graphene.** Carbon atom van der Waals diameter: \( d_{\text{vad}} = 3.4 \) Å. Carbon bond length in graphene: \( a = 1.42 \) Å. Area of a hexagonal ring in graphene is \( 5.24 \) Å².

**Pore geometry.** \( D_1 \) is pore diameter defined by centres of edge atoms. \( D_2 = D_1 - D_{\text{vad}}/\sqrt{2} \) is the pore diameter used for gas transport. \( D_p = D_2 - D_{\text{vad}} \) is the pore diameter adjusted for van der Waals size of pore edge atoms, used for water/ion transport.

**Gases.** Kinetic diameter (Å): He (2.6), H₂O (2.65), H₂ (2.89), CO₂ (3.3), Ar (3.4), O₂ (3.46), N₂ (3.64), CH₄ (3.8), SF₆ (5.5).

**Water molecule.** Mean van der Waals diameter: 2.8 Å.

**Ions.** Diameter of hydrated ion (Å): Li⁺ (7.64), Na⁺ (7.16), K⁺ (6.62), Mg²⁺ (8.56), Ca²⁺ (8.24), F⁻ (7.04), Cl⁻ (6.64), Br⁻ (6.60).

See Supplementary Section I for additional data, units and source references.

### Figure 1 | Membrane characteristics and length scales.

**Panel a** shows length-scale dependence of membrane transport mechanisms. Relative scales of gas and water molecules, hydrated ions and gas mean free path are depicted on bottom left. \( Q \), flux; \( D \), diffusivity; \( S \), sorption coefficient; \( m \), molecular mass; \( \mu \), viscosity. **Panel b** images adapted from: ref. 193, Elsevier (polyamide reverse osmosis (RO) membranes); ref. 194, RSC (carbon molecular sieves (CMS)); ref. 21, AAAS (CNT); ref. 195, IOP (anodized aluminum oxide (AAO)); ref. 40, AAAS (graphene oxide (GO)); ref. 196, RSC (metal organic framework (MOF) and zeolite); ref. 197, American Chemical Society (carbon nanomembrane (CNM)); ref. 198, Macmillan Publishers Ltd (NATM).
is governed by diffusion alone (as in many polymeric gas separation membranes)\(^4\), a more permeable material typically provides less selectivity and results in a trade-off between permeability and selectivity known as the Robeson limit in the context of gas separations\(^6\). Overcoming this trade-off requires incorporation of additional mechanisms such as chemical affinity or molecular sieving, where smaller molecules pass through while larger ones are sterically impeded (for example, in high free-volume polymers or carbon molecular sieves)\(^2,24\).

Due to the small free volume available, gas transport in membranes with pore diameters just beyond the molecular size is governed by phenomena such as diffusion, surface adsorption and condensation of gas molecules in the membrane pores\(^2,24\). In pores that are much larger than molecular size but smaller than the gas mean free path, gas transport is governed by Knudsen diffusion\(^6,46\), where molecules with lower molecular mass travel faster and have higher permeance. In liquid environments, transport in pores that are larger than molecules or ions is influenced by differences in species diffusivity, steric effects, chemical affinity and electrostatic interactions, including surface charge and dielectric effects\(^47\).

Although transport in membranes is complex, a thin selective layer with precisely controlled pores and chemical functionality — which is potentially realizable with NATMs — is ideal for achieving high permeance and high selectivity (Fig. 1b). Realization of NATMs requires an understanding of gas- and liquid-phase transport across pores in atomically thin materials, which we now discuss.

**Gas transport across atomically thin nanopores.** In 2008, Bunch et al.\(^26\) demonstrated that graphene is impermeable to helium and other gases, which opened the possibility of creating selectively permeable pores in graphene to realize selective membranes\(^26-28\). In their experiment, exfoliated pristine graphene ‘nanoballoons’ suspended on a SiO\(_2\) substrate retained gaseous helium to within detection limits (Fig. 2a). This impermeability was attributed to the fact that pristine graphene does not have gas-permeable defects. The space between the carbon atoms in graphene is too small to allow for transport of gases and the contribution of quantum tunnelling is negligible\(^26\).

A large number of theoretical studies\(^6-51\) have explored the transport of different gases (for example, CH\(_4\), CO\(_2\), H\(_2\), N\(_2\), CO, H\(_2\)S, O\(_2\), noble gases, alkanes and isotope) through graphene and other NATMs with pore edges terminated with atoms including C, H, N, F and O (Fig. 2b) (see Supplementary Section II for a detailed list of references). The majority of these studies have focused on graphene and similar materials with inherent nanoporosity, such as porous grapheme with various modifications\(^50-52\), graphdiyne\(^52,54\), graphyne\(^59\) and two-dimensional (2D) polymers based on polyphenylene\(^60-63\), porphyrin\(^64\) and cyclohexa-m-phenylene\(^45\); exploration of other materials including hexagonal boron nitride (hBN)\(^64\) has also begun.

These studies use one of two approaches to compute transport properties. (1) The energy barrier for a gas molecule to cross a pore is calculated using density functional theory (DFT)\(^51\) or other quantum mechanical methods\(^60-63\): permeance is then estimated using a transition state approach given the gas molecule kinetic energy distribution\(^6\), whereas selectivity is often estimated as the ratio of Arrhenius factors\(^6\). (2) The rate of molecules crossing the pore is calculated using classical (or first principles)\(^66\) molecular dynamics simulations, which directly yields the permeance\(^6,35,65\). These studies have shed light on transport mechanisms\(^6,67\), and revealed that permeance and selectivity can depend on differences in molecule size, mass, surface adsorption\(^44\), interaction with functional groups on the pore rim, conformational entropy\(^44\) and tunnelling rates\(^62,69,70\).

To a good approximation, gas transport across atomically thin pores can be understood by comparing the diameters of the gas molecule (\(D_m\)) and the pore (\(D_p\)), though one needs to exercise caution as diameter definitions vary (Fig. 2d). When the pore is slightly larger than the gas molecule, gas transport is similar to effusion, that is, molecular flow across a thin aperture smaller than the gas mean free path, where the pore presents an effective area \(A_{eff} = \pi a(D_m - D_p)^2\) (Box 1) that is smaller than the pore area \(A_{pore} = \pi aD_p^2\). Here, transport is dominated by steric considerations. When the pore size is approximately equal to or slightly smaller than the size of the gas molecule, the pore presents an energetic barrier to transport that depends on the molecule–pore repulsive interactions and any compliance due to bond stretching or flexing. We refer to this as the activated regime. If we assume a rigid pore with fixed atoms and approximate the molecule–pore interaction by the Lennard-Jones potential, the barrier height is given by

\[
E = \frac{\pi D_m^4}{4e} \left( \frac{\sigma}{D_m/2} \right)^{12} \left( \frac{\sigma}{D_p/2} \right)^{3} \approx \frac{4\pi \eta e D_m^4}{4a} \left( \frac{\sigma}{D_m/2} \right)^{12}
\]

where \(\sigma\) and \(\varepsilon\) are the Lennard–Jones parameters, \(D_m/2\) is the distance from the pore centre to the centre of the atoms constituting the pore, \(a\) is the distance between adjacent atoms on the pore rim and \(\pi D_m/\varepsilon\) gives the average number of atoms on the pore rim (Fig. 2d).

Assuming that all gas molecules with kinetic energies exceeding this value cross the pore, we obtain an Arrhenius-like expression for the effective pore size

\[
\frac{A_{eff}}{A_{pore}} \approx \frac{1}{2} \text{erfc} \left( \frac{E}{k_B T} \right)
\]

where \(k_B T\) is the Boltzmann factor (see Box 1 and Supplementary Section IV).

The effective pore areas predicted from simulations for different gas molecules across pores with different structures and functional groups, compiled from 33 literature reports, agree with this model and indeed collapse into two regimes (Fig. 2e), with a high permeance coefficient, with 0.0025 \(A_{eff}/A_{pore} < 1\) and \(\pi(D_m - D_p)^2/\varepsilon \geq 0.24 \AA^2\). \(A_{eff}\) and the permeance coefficient decrease rapidly in the activated regime as the pore size is reduced below the molecular size. For the majority (~75%) of simulated pores, effective pore areas and the corresponding permeation coefficients (see Box 1) of the most permeable molecule range from \(10^{-4} - 10^{-1} \AA^2\) and \(10^{22}-10^{31} \text{mol s}^{-1} \text{Pa}^{-1}\), respectively, which for a pore density of \(10^{12} \text{cm}^{-2}\), corresponds to a membrane permeance of \(10^{-2} - 10^{-3} \text{m}^{-2} \text{m}^{-1} \text{mol}^{-1} \text{Pa}^{-1}\) (10–100 GPU). For example, graphene pores with diameters of 3.6 and 4.8 \(\AA\) were reported to present effective areas of \(9.9 \times 10^{-14}\) and \(5.2 \AA^2\) (effective diameters of 0.11 and 2.57 \(\AA\)), permeation coefficients of 1.8 × 10\(^{-3}\) and 9.3 × 10\(^{-3}\) \text{mol s}^{-1} \text{Pa}^{-1} and permeance of 5.3 × 10\(^{-3}\) and 2.8 × 10\(^{-3}\) GPU, respectively, to hydrogen\(^68\) (kinetic diameter 2.89 \(\AA\)) (see Supplementary Section I for equations relating these parameters).

However, some simulations involve pore densities of up to 8.5 × 10\(^{-14}\) \text{cm}^{-2}, resulting in permeances up to \(10^{-1} \text{mol m}^{-2} \text{m}^{-1} \text{mol}^{-1} \text{Pa}^{-1}\) (100 GPU).

Given two different gas molecules, there are three possible regimes depending on pore size (Fig. 2d). (1) For large pores, transport is in the steric regime for both molecules and high selectivity is not possible. (2) Selectivity by molecular sieving accompanied by high permeance occurs when the pore size lies in between the sizes of the two gas molecules; transport of the smaller molecule is in the steric regime while that of the larger one is in the activated regime. (3) High selectivity at very low permeance occurs for small pores when transport of both molecules is in the activated regime. Interestingly, this simple steric exclusion and activated transport model predicts a trade-off between permeance and selectivity, analogous to the Robeson limit, and is consistent with published reports from theoretical studies (Figs 2f and 5f); smaller pore sizes lead to higher selectivity and lower permeance due to the highly nonlinear dependence of the energy barrier on pore size.
Molecular dynamics tends to better resolve high permeance, but has difficulty quantifying high selectivities (≥10^5) because of the limited number of observable molecule crossings imposed by a limited simulation time (∼100 ns). DFT-based approaches can resolve higher selectivities with reported values ranging up to 10^6, but some of these correspond to impractically low permeance.

Although the above model captures the basic dependence of permeance and selectivity on molecule size, other phenomena can contribute to higher selectivities with reported values ranging up to 10^7. Simulations using a limited simulation time (< 100 ns) and the limited number of observable molecule crossings imposed by DFT-based approaches can resolve higher selectivities with reported values ranging up to 10^7. Simulations using a limited number of observable molecule crossings imposed by DFT-based approaches can resolve higher selectivities with reported values ranging up to 10^7. Simulations using a limited number of observable molecule crossings imposed by DFT-based approaches can resolve higher selectivities with reported values ranging up to 10^7. Simulations using a limited number of observable molecule crossings imposed by DFT-based approaches can resolve higher selectivities with reported values ranging up to 10^7.
Figure 3 | Water and ion transport across NATM pores. a, Preferential configurations adopted by water molecules traversing hydrogen or hydroxyl terminated graphene pores are illustrated by water-oxygen density maps. Red denotes high density. b, Single-file water transport in a graphene pore. c, Nonlinear increase in ion flux with electric field illustrates the ion dehydration barrier. Addition of a negative pore charge enhances the flux of K⁺. d, Water permeation coefficient (m⁻¹ Pa⁻¹ s⁻¹) for experimentally measured values, and horizontal solid or dashed lines indicate the estimated range for experimentally measured values. GlpF, membranes from ref. 15. Solute is NaCl unless otherwise noted. e, Measured conductance (nS) and ion flux (ns⁻¹) for electrically driven transport of KCl compare well with continuum theory (see Box 1). f, Experiment: reported membranes. g, Forward osmosis: CNT, Song et al. 103

MD simulation: graphene
- Conductance theory (l_{pore} = 0.535 nm)⁰
- Conductance theory (l_{pore} = 0 nm)⁰
- Suk et al. ¹⁰¹
- Schneider et al. ¹¹⁸
- Charged pores
- 2 M KCl (MoS₂) ¹²⁶
- 1 M KCl (MoS₂) ¹²⁶
- 0.01 M KCl (MoS₂) ¹²⁶
- Charged pores ³⁸

MD simulation: other membranes
- CNT (ref. 199)
- MoS₂: mixed pores ⁹³
- MoS₂: Mo-only pores ⁹³
- MoS₂: S-only pores ⁹³
- Graphyne (n = 3, 4, 5) ⁶⁹
- Graphyne (n = 3) ⁵⁰
- Graphyne (n = 3) ⁵⁰
- GlpF (ref. 200)
- AQPI (ref. 201)
- BNNT (ref. 199)
- CTF (ref. 94)

MD simulation: other membranes
- Forward osmosis: CNT, Song et al. ¹⁰³
- CNT, Suk et al. (KCI) ¹⁹⁹
- BNNT, Suk et al. (KCI) ¹⁹⁹
- MoS₂: mixed pores, Heiranian et al. ⁹³
- MoS₂: Mo-only pores, Heiranian et al. ⁹³
- MoS₂: S-only pores, Heiranian et al. ⁹³
- Graphyne (n = 3, 4, 5) ⁶⁹
- Graphyne (n = 3, 4, 5) ⁶⁹
- Zhu et al. ⁸⁹
- CTF, Lin et al. ⁹⁴

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transport at low temperatures where the kinetic energy of gas molecules is much smaller than the energy barrier, which has been proposed for separating helium isotopes.

Experimental evidence of molecular sieving through NATMs was first reported in 2012 by Koenig et al. (Fig. 2c). Gas permeance of initially impermeable bilayer graphene nanoballoon membranes was monitored as nanopores were created in the graphene by ultraviolet/ozone etching, where a single pore is likely to dominate transport. One graphene membrane permitted selective transport of H₂ and CO₂ over the larger Ar, N₂ and CH₄ molecules (~3.4 Å pore) (Fig. 2c) and another membrane permitted transport of the above molecules but not only of larger SF₆ (~4.9 Å pore), with observed selectivities exceeding 10,000 (ref. 29). In subsequent studies with a single-layer graphene membrane, permeance was observed to decrease with increasing kinetic diameter for He, Ne, H₂ and Ar, but was anomalously high for N₂O and CO₂ (ref. 86), consistent with flux enhancement due to polar interactions. The permeation coefficients in these experiments were in the range of 10⁻²⁻¹⁻⁻¹² mol s⁻¹ Pa⁻¹ (pore effective area 5 × 10⁻²⁻⁴.0 Å²) in reasonable agreement with theoretical studies (Fig. 2e,f).

Although experimentally measured gas permeance generally agreed with simulations, transport through single-layer graphene pores was observed to fluctuate on a timescale of minutes, which was postulated to originate from thermally activated rearrangement of molecular bonds at the pore. Similar observations in multiple pores and in liquid environments suggest that dynamic fluctuations in transport across NATM pores may be common, although understanding their origin remains elusive. This also highlights the need for more controlled experiments and more realistic simulations that complement those on idealized model pores. For example, the majority of simulations fix the 2D lattice or the position and orientation of the gas molecules in calculating the energy barrier, although some methods take these into account. DFT calculations that permit lattice deformation or molecular dynamics simulations using the adaptive intermolecular reactive empirical bond order (AIREBO) potential that allows for deformation and thermal fluctuations indicate that assuming a fixed lattice can greatly over-predict selectivities.

Gas transport in larger pores is less complicated, but permeance is still very high owing to the atomic thickness of the membrane. Celebi et al. showed that graphene bilayer membranes with an array of 7.6-nm-diameter pores machined by a focused ion beam exhibited H₂/CO₂ selectivity consistent with effusion, but had more than three orders of magnitude higher permeance (~10⁻²⁻¹⁻⁻¹² mol m⁻² s⁻¹ Pa⁻¹, based on graphene area) than existing gas separation membranes with similar selectivity. Gas flow followed free-molecular effusion theory for small pores (≤50 nm) and a modified Sampson’s model (Box 1) for large pores.

Water and ion transport across atomically thin nanospheres. Motivated by applications in water desalination and purification, theoretical studies using classical molecular dynamics (or other methods) have focused on transport of water and ions driven by pressure, osmosis and electric fields across graphene with different pore terminations (refs 95,100,102,110,111), H (refs 96,98,99,103,106,109,112), hydroxyl (ref. 95), carbonyl (ref. 109), carboxyl (refs 95,106,109), amine (ref. 96), F (refs 99,103,105,109), N (refs 105,109), O (ref. 108)), variants of graphene (refs 99–101,104,113,114), MoS₂ (refs 93,97) and covalent organic frameworks.

Transport of water molecules (~2.8 Å van der Waals diameter) through NATM pores is largely determined by pore size. Graphyne-2 pores with ~2.9 Å diameter present a small barrier to water transport; pores larger than ~3 Å (which corresponds to atom-centre-to-centre diameters, Dₐ of ~6 Å) easily permit transport of water when the pore size is below ~2 nm. Transport of water is also influenced by hydrogen bonding and structuring of water molecules, which depends on the pore geometry and functional groups (Box 1 and Fig. 3f). The smallest pores in graphene (refs 100,102,105), graphyne (ref. 113) and MoS₂ (ref. 28) that permit water transport can accommodate only a single water molecule in their cross-section and therefore exhibit single-file movement of water molecules. In pores with diameter ≤1.5 nm (ref. 112), water molecules adopt certain preferential configurations as they pass through the pores (refs 108,112). Similar effects are also observed in other nanoscale conduits such as CNTs. In NATM pores, a significant fraction of the pressure drop occurs in the entrance and exit regions outside the pore. As, in many cases, entrance and exit resistance dominates transport in CNTs, flow rates through NATM pores are comparable to those in CNTs of similar diameter (refs 100,102,111). These flow rates are, in fact, predicted reasonably accurately (within an order of magnitude) by continuum no-slip hydrodynamics (see Box 1) for NATM pores. Flow enhancement is observed in molybdenum-terminated MoS₂ pores that mimic the conical shape of biological aquaporin channels and reduce the flow resistance at the entrance and exit. The effect of pore functional groups on water flow tends to be modest, with hydrophilic groups (for example, –OH, Mo, –N) reported to enhance permeation of water by up to twofold (~4.9 Å pore), with atomic thinness to the pore, compared with hydrophobic groups (for example, –H), which can present an entropic barrier to transport.

Transport of hydrated ions across atomically thin pores is influenced by electrostatic interactions, coordination with functional groups or charges at pore edges, and steric exclusion of the ion hydration shell (Box 1 and Fig. 3f). The diameters of the first hydration shell for Na⁺, K⁺ and Cl⁻ are ~6–7 Å, which require pore diameters exceeding ~7 Å (D > ~10 Å) for ions to pass through with an intact hydration shell. Neutrally charged pores smaller than the first ion hydration size therefore present a barrier to ion transport that depends on the energy required for dehydration and the electric polarizability of the NATM material. For example, Zhao et al. observed that 4-Å-diameter neutrally charged graphene pores completely excluded both K⁺ and Cl⁻, but 8 Å pores permitted passage of both ions. Ionic transport across larger, neutral pores is dominated by the ‘access resistance’ associated with the pore entrance and exit that is approximated well by continuum theory (Box 1 and Fig. 3f).

Pore functionalization can radically alter ionic transport, especially if the pore is smaller than the size of the hydrated ion. Charged or partially charged functional groups along the pore edge can lower the energy barrier for ions of opposite charge and increase the barrier for ions of like charge, leading to cation/anion selectivity. For example, Sint et al. showed that a ~5-Å-diameter graphene pore could be made cation selective by functionalizing the pore with electron-negative F or N atoms. Similarly, Zhao et al. observed that negatively charged, 4-Å- and 8-Å-diameter graphene pores permitted selective transport of K⁺, but the ionic flux increased nonlinearly with voltage as higher voltages facilitated partial dehydration of the K⁺ ion (Fig. 3c). Counterintuitively, by partially shedding their hydration shells, larger ions with lower hydration energies traverse pores more easily than smaller ions with tightly bound hydration shells. Ion transport can also drive fluid flow under an applied potential difference, a phenomenon called electroosmosis that finds use in fluidic pumping. Functionalized atomically thin pores that structurally resemble biological ion channels (Fig. 3d) show some similar behaviours, such as voltage gating and cation/cation selectivity, although the pores are much thinner than their biological counterparts. This raises the intriguing question as to what extent atomically thin pores can be tailored to achieve high ion selectivity, voltage sensitivity and other functionalities of biological channels.

The smaller size of water molecules compared with that of hydrated ions enables their separation when NATM pores are large enough to pass water, but small enough to block hydrated ions (Fig. 3g). Cohen-Tanugi and Grossman demonstrated rejection of Na⁺ and
Cl$^-$ ions for hydrogen- and hydroxyl-terminated graphene pores with diameters below 5.5 Å, even at realistic operating pressures for reverse osmosis (10–100 bar)$^{96}$, Heiranian et al.$^{93}$ showed that MoS$_2$ pores below 6 Å could reject NaCl while supporting high water flux. Pressure-driven separation has also been shown for trihalomethanes in 6 Å graphene pores$^{99}$, NaCl in graphene-3 (~4 Å)$^{99,90,92,101}$, NaCl in graphene-4 (~6 Å) with a fixed lattice$^{99}$(<100% rejection$^{99,92,101,104}$ with a non-fixed lattice), CuSO$_4$, benzene and CCl$_4$ in graphene-3 (ref. 101), and Mg$^{++}$, Ca$^{++}$, K$, Na^+$ and Cl$^-$ in graphene-3 and variants$^{99}$. Rejection of NaCl has also been demonstrated in forward osmosis in graphene$^{101,105,106}$ and graphene-3$^{104}$, consistent with selectivity governed by size effects. Compiled results indicate the theoretically predicted potential for high solute rejection and permeance of NATMs compared with existing membranes, although this performance remains to be experimentally realized (Fig. 3g).

A few experimental studies have probed transport across atomically thin pores$^{46,117-129}$, with particular focus on electrically driven ionic transport across pores in graphene$^{117-119,124}$, hBN$^{125}$ and MoS$_2$ (ref. 126), motivated by applications in DNA analysis. Ionic conductance of large pores (>2 nm) in graphene and MoS$_2$ agrees reasonably well with continuum descriptions of ion transport$^{110,117,124,126,127}$, although a surprisingly high K$^+$/Cl$^-$ selectivity was recently observed in large (20 nm) graphene pores, which was attributed to the surface charge on graphene$^{114}$. Experimental data on the behaviour of smaller pores (<2 nm) is limited (Fig. 3f). Hints of ion transport through subnanometre pore defects$^{109,110}$ smaller than the ion hydration shell were first seen in a study by Garaj et al.$^{117}$, who observed that salts of larger monovalent ions with lower hydration energies displayed higher conductance than salts of smaller ions. Jain et al.$^{98}$ attempted to isolate pore defects by suspending graphene across a silicon nitride nanopore. They observed linear, rectified and nonlinear current–voltage characteristics consistent with ion deidorization and electrostatic effects in subnanometre pores. Their observation of cation/cation selectivity and voltage-activated fluctuations$^{88}$ also hints at parallels between atomically thin nanopores and biological ion channels$^{107,108}$. Nonlinear current–voltage characteristics, effects of charge quantization and high ionic current driven by salt concentration difference were recently observed in MoS$_2$ nanopores$^{126,129}$, which may find use in energy harvesting from salinity gradients.

Ionic selectivity in macroscale single-layer graphene membranes was reported by O’Hallam et al.$^{121}$, who introduced subnanometre pores in graphene by ion bombardment followed by chemical etching. Although there was significant leakage through defects, the membranes exhibited some K$^+/Cl^-$ selectivity consistent with electrostatic exclusion of Cl$^-$ due to negatively charged pore functional groups$^{111}$, expected in oxidative etching; with further etching, the membrane permitted selective transport of KCl over a larger organic molecule (~1 nm size). Osmosis–driven water flux measured across similar graphene membranes with ~0.5 nm pores$^{122}$ was consistent with molecular dynamics predictions by Suk and Aluru$^{102}$. Water/ion selectivity was demonstrated by Surwade et al.$^{122}$ using oxygen plasma to introduce ~1 nm pores at a density of ~10$^{13}$ cm$^{-2}$ in single-layer graphene placed on a micrometre-scale aperture. For a certain plasma treatment, all NaCl ions were rejected and water permeated at high rates, though only one side of the membrane was wetted and evaporation may have played a role. Water transport has also been measured across larger (50–1,000 nm) pores in bilayer graphene, with results consistent with continuum theory$^{46}$. Although a picture of water and ion transport across atomically thin pores is beginning to emerge, experimental data are sparse, there are some discrepancies among the simulation results and ion selectivity remains to be understood (Fig. 3f).

Compared with water or ions, protons show distinct transport behaviours. Geim and co-workers discovered that monolayers of (nonporous) pristine graphene and hBN are permeable to protons$^{130}$ and have high selectivity (~10) over deuterons$^{131}$, opening new possibilities for deuterium/hydrogen separation. The observation that small, otherwise impermeable defects in graphene could also permit selective proton transport$^{132,133}$ suggests the possibility of creating high-permeance proton-selective NATMs from materials such as graphyne-1.

**Fabrication of NATMs**

Practical realization of NATMs requires synthesis of a continuous layer of atomically thin material with controlled porosity as well as...
NATMs can be fabricated ‘top-down’ by introducing pores in the catalytic substrate or chemical/plasma etching of an intrinsically porous material. Alternatively, thermal oxidation of graphene or graphite in oxygen produces subnanometre pores can be introduced in the initially nonporous atomically thin material, or by ‘bottom-up’ synthesis of an intrinsically porous material.

Top-down fabrication. Chemical vapour deposition (CVD) has emerged as a tunable and versatile method for producing continuous layers of 2D materials over large areas and lends itself easily to fabrication of NATMs. Within a year of the first demonstration of large-area CVD growth of monolayer graphene on copper by Li et al. in 2009, Samsung demonstrated roll-to-roll transfer of 30-inch sheets of CVD graphene and SONY later demonstrated roll-to-roll synthesis of 30-inch sheets of graphene, for which technical know-how is most advanced. Work on NATMs has therefore largely focused on exfoliated and CVD graphene, for which technical know-how is most advanced.

Forward osmosis: CNT (Song et al. 2006) left, Gore-tex Nextec (DuPont) middle, and SONY later demonstrated roll-to-roll synthesis of large sheets of graphene (right).

Figure 5 | Transport characteristics of NATMs. a, Pathways for transport of molecules of different sizes across membranes with tortuous pores (left) and unsupported and supported NATMs (right). b, Schematics of defect sealing in NATMs. Left: stacking of multiple layers. Right: sealing of small defects using atomic layer deposition (ALD) of hafnia, and of large defects by reaction of monomers that form plugs only at defects. Results are compared with continuum theory assuming only size exclusion. Scale bar, 0.5 cm. c, Forward osmosis: graphene (O’Hayre et al. 2012), DOW FILMTEC (brackish water) 205,206. d, Limits for H2 permeance due to Knudsen diffusion and Knudsen/steric hindrance. e, Graphene measurements. f, Comparison of experimental and simulation forward osmosis performance, for H2/CH4 separation across NATMs compared with a few other illustrative membranes.

The ability to handle the materials using suitable porous supports. NATMs can be fabricated ‘top-down’ by creating pores in an initially nonporous atomically thin material, or by ‘bottom-up’ synthesis of an intrinsically porous material.

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and was used for creating gas-selective pores in graphene nanoballoons\textsuperscript{29,96}. Oxygen plasma can also induce\textsuperscript{140,149} and grow nanometer-scale pores in suspended single-layer graphene\textsuperscript{122,123} at a high density ($\sim 10^{12}$ cm$^{-2}$, Fig. 4b). Nucleation of defects followed by growth can produce more uniform pores with controllable size and density\textsuperscript{141}. This was realized in graphene using oxygen and hydrogen plasma, respectively, to nucleate and grow pores\textsuperscript{99}. Ion irradiation can also controllably nucleate defects, which can be followed by electron-induced sputtering or chemical etching to create a high density ($\sim 10^{12}$–$10^{13}$ cm$^{-2}$) of subnanometre pores\textsuperscript{121,122,144} (Fig. 4a). Ion angle of incidence, energy and type determine the kind of defect, whereas the ion fluence determines their density\textsuperscript{140,144}. An energy threshold of $\sim 30$ eV is required to produce defects in graphene\textsuperscript{173}, indicating that ion impact could also play a role in plasma treatment\textsuperscript{146}. Whereas these methods produce a distribution of pore sizes\textsuperscript{140,145} and perhaps work well only in single-layer materials, focused ion beams can precisely machine a large number of individual pores down to $\sim 8$ nm in diameter\textsuperscript{48} (Fig. 4c). Electron beams focused below 1 nm can create precise subnanometre to few-nanometre pores\textsuperscript{170,186,159}. Other methods to create pores include the use of block copolymers\textsuperscript{49} or substrates\textsuperscript{49} as templates, reduction of graphene oxide\textsuperscript{146}, catalyst-induced etching\textsuperscript{163,164}, electrochemical machining by atomic force microscopy\textsuperscript{49}, or the use of electrical pulses to create pores with subnanometre accuracy in graphene\textsuperscript{166} or MoS$_2$, (ref. 165).

**Bottom-up fabrication.** In contrast to the creation of pores in an initially nonporous material, recent advances in the synthesis of intrinsically porous covalently cross-linked single or few-layer 2D polymers\textsuperscript{166,167}, including graphyne and its variants\textsuperscript{146,147}, have potential for creating a high density of atomically precise pores in tailor-made for specific applications, directly in a covalently bonded single-layer\textsuperscript{141,142,144}. For example, surface-assisted synthesis of porous graphyne by aryl–aryl coupling of polyphenylene-based precursors or cyclodehydrogenation using polyacrylatic aromatic hydrocarbons has been proposed\textsuperscript{141} (Fig. 4d). Graphdyne has been synthesized at the millimetre scale by cross-linking of hexaethynylbenzene on copper under nitrogen atmosphere\textsuperscript{146}, which may permit selective transport of hydrogen\textsuperscript{99}, and possibly water\textsuperscript{99} or protons. Recently, a 2D polymer with $\sim 0.8$ nm pores was synthesized by ultraviolet cross-linking of triptycene-based amphiphilic monomers self-assembled at the water/air interface in a Langmuir–Blodgett trough\textsuperscript{146} (Fig. 4e). The high quality of the resulting polymer and the ability to transfer centimetre-scale areas to porous supports makes it a promising route to realize NATMs.

Another potential route to NATM fabrication is by modifying synthesis processes that normally result in nonporous materials. Pores could potentially be created in a modified CVD process by controlling the ratio of the growth precursor and etchant (for example, CH$_4$ and H$_2$ for graphene)\textsuperscript{171}, introducing etchants during or post synthesis, templating of the catalytic substrate\textsuperscript{141} or substitutional doping to generate precisely defined pores\textsuperscript{172}. However, atomic precision and high porosity may be difficult to realize with these approaches.

**Scalability, quality and stability.** Among the top-down methods, pore creation in CVD-grown materials by chemical and plasma routes is amenable to fabrication of large-area NATMs (Fig. 4f). Machining using focused ion beams is less scalable and appropriate for smaller membranes, whereas electrochemical methods and machining using atomic force microscopy or tightly focused electron beams are suitable for creation of a few pores for microscale membranes. Bottom-up approaches remain relatively unexplored for membrane applications, and key challenges are to engineer practical processes for synthesis of continuous layers over sufficiently large areas\textsuperscript{96}. As of now, roll-to-roll processed 2D materials are not commercially available, and CVD-grown materials remain inherently polycrystalline with intrinsic vacancy defects, grain boundaries and wrinkles that contribute to leakage pathways\textsuperscript{120,173}. Compared with applications in electronics, the quality requirements for atomically thin materials for membrane applications are more stringent in some respects, as small pinhole defects can severely compromise selectivity. To address these issues, synthesis processes need to be tailored to minimize pinhole defects, and methods to assess quality for membrane applications need to be developed. In addition, polymer-based methods to transfer atomically thin materials tend to leave surface contamination, the effects of which on transport across the membrane are poorly understood. Techniques for clean transfer and control of surface contamination are also essential to ensure quality and reproducibility.

Mechanical stability of NATMs is essential to withstand handling, abrasion and high pressures. Graphene has a remarkably high fracture strength of 130 GPa ($\sim 44$ N m$^{-1}$) and tolerates strains of $\sim 25\%$ (ref. 27), which would facilitate its handling on a support. Although pores and defects can decrease the fracture strength by about an order of magnitude\textsuperscript{151,174}, it is more than sufficient to withstand high pressures when the atomically thin layer is properly supported. The ability to withstand pressure scales inversely with the support pore diameter, and molecular dynamics simulations indicate that nanoporous graphene can withstand a pressure of 570 bar when suspended over $1 \mu$m pores\textsuperscript{141}. Sufficiently high strengths are also expected of other atomically thin materials including MoS$_2$ (ref. 176), graphyne\textsuperscript{146,149} and covalent organic frameworks\textsuperscript{89}. Adhesion and abrasion resistance are other important considerations related to slippage, delamination and wear of NATMs. Graphene exhibits a high adhesion energy\textsuperscript{177} and good abrasion resistance\textsuperscript{188}, but abrasion resistance in the context of membranes is not well understood and protective coatings will be required if the atomically thin layer is damaged easily. Similarly, although NATMs are expected to be chemically stable\textsuperscript{142,152}, studies that specifically investigate this aspect are needed.

**From pores to membranes.** Provided that transport across a pore is not influenced by its neighbours, the net flux across NATMs is the sum of those across the membrane pores. Using this assumption, the predicted permeance ranges from $10^5$ to $10^8$ GPU and exceeds 1,000 l m$^{-2}$ h$^{-1}$ bar$^{-1}$ for gas separations and water desalination, respectively, significantly surpassing the permeance of polymeric membranes (Fig. 5e, f). These estimates constitute upper bounds, since real membranes will inevitably have a distribution of pore sizes and defects that are situated in parallel with each other (Fig. 5a). NATMs are therefore extremely sensitive to leakage through defects, and their size selectivity is determined by the largest pores\textsuperscript{172} — presenting a major engineering challenge that may well turn out to be the Achilles heel for some applications. It is for this reason that only a few studies have demonstrated selective transport across non-microscopic NATMs, which requires strategies to minimize the impact of defects by independent stacking of layers\textsuperscript{46,173}, sealing of defects\textsuperscript{123}, appropriate choice of the porous support\textsuperscript{173} or other mechanisms\textsuperscript{131} (Fig. 5b).

Celebi et al.\textsuperscript{46} stacked two layers of graphene on a silicon support to form a nearly impermeable layer, into which ordered arrays of pores with diameters of 8–1,000 nm were machined using a focused ion beam. The measured water flow rates (per unit graphene area) were five- to sevenfold greater than commercial ultrafiltration membranes, whereas vapour transport rates were two to three orders of magnitude higher than those in commercial membranes (Fig. 5c). Boutillier et al.\textsuperscript{173} showed that gas transport through stacked graphene layers can be explained by random alignment of defects, resulting in exponential decrease in gas permeance with selectivity approaching the Knudsen limit. Kim et al.\textsuperscript{173} stacked five layers of graphene on a polymeric membrane to enhance its barrier properties. The O$_2$/N$_2$ selectivity exceeded the Knudsen limit, and was attributed to defects and inter-layer transport. Although there are no reports of creating aligned subnanometre pores in multilayer materials, the stacking approach may be useful for materials like graphyne that have high intrinsic porosity.
O’Hern et al. created centimetre-scale single-layer graphene NATMs by multiscale sealing of defects. Nanoscale defects were sealed by atomic layer deposition, which tends to deposit preferentially on defects and wrinkles, whereas the impermeability of graphene was exploited to seal larger defects using interfacial polymerization, where monomers introduced on opposite sides of the graphene layer react to form polymer plugs only where graphene is missing (Fig. 5b). After introducing subnanometre pores by ion irradiation and etching, the resulting membrane exhibited water permeance based on graphene area comparable to polycarbonate reverse osmosis membranes, and rejected organic molecules (≥1 nm) and divalent MgSO₄ (but not NaCl) under osmotically driven flow (Fig. 5d).

Beyond these considerations, an appropriate support layer is essential to achieve high selectivity in the presence of imperfections and defects. An ideal support — or coating — will add a transport resistance in series to both selective pores and defects, thereby limiting leakage without adversely impacting the permeance. This resistive layer must provide parallel transport pathways or be thinner than the spacing between non-selective defects in the atomically thin layer. Such an approach was critical to early commercialization of gas separation membranes. Beyond its role in minimizing leakage, the support must have high surface porosity to make use of most of the NATM area, have high mechanical strength, good chemical resistance, higher permeance than the atomically thin layer, and provide stable adhesion and facilitate transfer or coating of the atomically thin layer. Most experimental studies have used specialized supports (for example, polycarbonate track-etched membranes or microfabricated silicon supports) with low surface porosity, which results in high permeance with respect to graphene area but low permeance based on total membrane area, and are suboptimal for practical separations. Although graphene NATMs have been fabricated on more practical supports such as poly(1-methylsilyl-1-propyne) and polypivinylidenefluoride, meeting all of the above requirements is challenging, especially for pressure-driven separations.

Potential applications of NATMs

The path for new membrane technologies to advance beyond the laboratory is tortuous. Membranes that are difficult to scale up have found use in research and analytical applications, whereas polyamide reverse osmosis membranes have grown to become the dominant desalination technology today. Although NATMs are still in the early stages of development, they present characteristics that are potentially advantageous for addressing persistent challenges in membrane separations.

A key advantage of NATMs is their high permeance that could enable higher energy efficiency and compact, high-productivity membrane separation systems. For seawater and brackish water, respectively, increasing the permeance of desalination membranes threefold could reduce the membrane area by 44% and 63% or reduce the energy consumption by 15% and 46% (ref. 182); the smaller gains for seawater are due to its higher osmotic pressure and build-up of the rejected salt at the membrane. More substantial gains in energy consumption and productivity are expected for applications involving low solute concentrations (for example, reverse osmosis treatment for drinking water, ultrapure water, and nanofiltration for water, pharmaceutical, food and beverage, and biotechnology industries), provided that fouling is not enhanced at higher fluxes. The combination of high selectivity and permeance is also desirable for a number of gas separations, such as O₂ or N₂ from air, CO₂/CH₄ for natural gas sweetening and H₂/O/air for dehumidification.

A second advantage of NATMs is their potential for increased robustness due to high chemical resistance and mechanical strength, which could prove useful for operation under harsh conditions. For example, NATMs may be able to better withstand chlorine and permit desalination of high-salinity water by high-pressure reverse osmosis, or allow for more aggressive cleaning procedures to maintain membrane performance and extend their useful life. NATMs may help to address the challenges of aging, compaction and influence of solvents in organic solvent nanofiltration, and potentially open new possibilities in the separation of liquefied gases and fuels.

Third, the molecular-sieving mechanism of transport is expected to lead to rejection of all species that significantly exceed the pore size. If NATMs could provide universal size-based rejection regardless of the solute or the fluid in which separation is performed, it would benefit applications involving a diversity of solutes such as in removal of persistent organic pollutants for water reclamation, removal of boron from seawater or in chemical processing.

However, actual application is contingent on commensurate advances in technology and practical membranes meeting these expectations. The predicted performance and most of the proposed applications have yet to be realized even at the lab scale. Significant advances including ensuring a tight pore size distribution, design of appropriate supports and minimizing leakage are prerequisite for proof-of-concept studies. Manufacture at appropriate scale and cost, packaging into modules that minimize concentration polarization, characterization of fouling and chemical resistance, and demonstration of long-term performance under realistic conditions are essential for large-scale applications such as water desalination and natural gas separations. Small-scale applications such as laboratory and analytical separations or nanofiltration — which have less stringent demands on selectivity but would benefit from the high permeance and chemical stability of NATMs — are likely to emerge first.

Beyond separations, NATMs could find use in a variety of other applications such as in fuel cells, microfluidics, energy harvesting, and a variety of biomedical applications, such as drug release, biosensing and immunosaturation. Nanopores in NATMs may find use in detection and analysis of single molecules, ions and binding events, or interrogating discrete steps in chemical reactions. In these applications, NATMs have the potential to offer higher selectivity, sensitivity, faster time-to-result or ease of fabrication. The more exotic capabilities of NATMs, such as isotope separation by quantum effects and perhaps undiscovered phenomena that do not have parallels in other membranes, could potentially open new applications. Finally, NATMs can provide fundamental insights into nanofluidic transport mechanisms that are relevant to atomically thin materials for barrier applications, for electron microscopy and in graphene oxide membranes.

Future perspectives

Regardless of the extent and timeframe in which NATMs will have an impact, they represent a unique class of membrane with tremendous potential for advancing membrane technology and are likely to persist far into the future.

Although theoretical studies have shed light on transport mechanisms in idealized pores, an understanding of the structure and behaviour of pores in real materials has only just started to emerge. Controlled experiments at the single pore level, complemented by theoretical studies on realistic pores, are required to probe the effects of different pore structures, functional groups, dynamic behaviours and the role of surface contaminants. Simulations are needed to advance pore creation techniques and explore different applications of NATMs, which can guide experimental developments. For example, there are pore structures that enable selective transport of water over boron, urea and other species that are difficult to reject using state-of-the-art membranes? Can NATMs separate water from ethanol? How effective are NATMs for separations in organic solvents?

Realization of practical membranes requires advances on four fronts. First, improved methods are needed to create a high density of uniform pores that will enable separations such as water desalination. Here, key challenges are achieving sufficiently precise pores using top-down techniques and scale-up of bottom-up synthesis methods. Second, better understanding of the origin of defects that
may arise during synthesis, handling or creation of selective pores, methods to limit leakage through defects, and quality control during synthesis are indispensable for realization of functional membranes. Theoretical studies are needed that shed light on how the distribution of pore size and defects as well as the membrane support structure determine the actual permeance and selectivity. Third, design or selection of an appropriate porous support layer and development of methods to promote adhesion and to coat the atomically thin layer on the support are essential for full utilization of the properties of NATMs. Fourth, packaging of membranes, design of modules tailored to NATMs, experimental and theoretical studies to understand fouling, chemical resistance, and potential degradation mechanisms, and cost-effective scale-up of membrane manufacturing are critical for advancing NATMs towards real-world applications. Finally, it is likely that there will be opportunities to use NATMs in novel formats or in novel devices. For example, NATMs could act as porous scaffolds to realize novel membranes with improved performance by coating100 or functionalizing101 them with ultrathin layers of materials102, perhaps by grafting polymers or materials that are difficult to cast into thin membranes. The fact that it is possible to make NATMs from conducting as well as insulating atomically thin materials raises the possibility of electrically actuated membranes that can actively modulate transport or pump ions2. Other intriguing possibilities arise due to the atomically thin nature that enables reactions across pores in NATMs — which could find use in selectively sealing leaky pores, functionalizing the membranes or performing chemical reactions across NATMs where pores control the stereochemistry.

Although significant technological challenges remain for practical applications, NATMs have provided us with the fascinating opportunity to explore fundamental questions in fluid flow at the smallest possible length scale. It is quite likely that these fundamental studies will continue to provide new — and perhaps surprising — insights into mass transport at the nanoscale. On the practical side, NATMs have tremendous potential, but also face considerable challenges that need to be recognized and addressed if the field is to move ahead. Only time will reveal whether NATMs live up to their promise.

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