Artificial channels for confined mass transport at the sub-nanometre scale

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Abstract

Mass-transport at the sub-nanometre scale, including selective transport of gases, liquids and ions, plays a key role in systems such as catalysis, energy generation and storage, chemical sensing, and molecular separation. Highly efficient biological channels in living organisms have inspired the design of artificial channels with similar, or even higher mass-transport efficiency, which can be used at a much larger scale. In this Review, we highlight synthetic nanomaterials-enabled channels in the platforms of well-defined nanopores, 1D nanotubes, and 2D nanochannels, and discuss their design principles, channel architectures, and membrane or device fabrication. We focus on fundamental mechanisms of sub-nanometre confined mass-transport and their relationships with the structure-property-performance. We then present the practicalities of these channels and discuss their potential impact on the development of next-generation sustainable technologies for use in applications related to energy, environmental, and healthcare.

Short summary

Artificial channels that selectively transport small molecules at the sub-nanometre scale are used in many applications, but in particular, in molecular separation. This review discusses the design of channels, nanostructure, fabrication, mass-transport mechanisms, as well as outlining promising applications and the challenges ahead.

[H1] Introduction

Solid-state channels with a confined space that selectively transport small molecules (for instance, gases, liquids and ions) at the sub-nanometre (sub-nm) scale, have attracted growing interest over the past decades. In particular, these channels have shown tremendous potential for applications in the fields of energy storage and conversion, chemical sensing, and molecular separation. However, their practical applications have continuously faced challenges with respect to efficiency, stability and scalability. To develop sub-nm channels, an understanding of the confined mass-transport properties is required, which in turn may enable the rational design of the channels.

Synthetic channels can be inspired from natural channels that abound in biological systems. With different structures and functions, the biological channels in living organisms play essential roles in many of life's processes. The channels are formed from specific proteins that

can transport molecules and ions through membranes[1], in order to pump nutrients into cells, generate electrical signals, regulate cell volume, and secrete electrolytes across epithelial layers[2]. In fact, high transport efficiency has long been observed within these channels. For example, potassium ion channels exhibit a transport rate of 10^8 potassium ions per second (near to diffusion limit), but reject other types of ions (including sodium ions)[3]. Biological water channels, such as aquaporin-1 (AQP1), have been shown to possess a superb water permeability (~3×10^9 water molecules per subunit per second) and an excellent rejection of all ions, including protons[4]. AQP1 is also a physiologically important channel for CO_2 molecules transport, for which the permeability reaches ~1.2×10^5 molecules per AQP1 subunit per second[5]. The high mass-transport efficiency stems from the unique channel structure, the uniform sub-nm confinement, and the favourable interfacial properties[6,7]. However, these biological channels suffer from poor scale-up, low-efficiency and stability when used in large-scale industrial applications that create physical and chemical environments completely different from those existing in living organisms.

Researchers have sought to develop artificial channels with mass-transport properties similar to their biological counterparts. To date, there are three main types of channel architectures: nanopores, 1D nanotubes and 2D nanochannels (Fig. 1). These channels have persistent cavities that can discriminate between similarly sized analytes, on a molecular scale. Transient gaps in flexible polymers that are created by segmental packing and motion are not the focus of this discussion. Nanoporous materials are one of the key components of the channels, which can be classified as: inorganics (such as zeolites[8]), organics (for instance, microporous organic polymers[9,10], porous organic cages[11], and organic tubes[12]), hybrids (for example, metal-organic frameworks (MOFs)[13,14], metal-organic cages[15]), and carbons (such as carbon nanotubes[16], carbon molecular sieves[17]). Since the rise of graphene and related materials[18], 2D materials have been developed for the fabrication of porous mass-transport channels[19,20]. These synthetic channels are made of various sizes and adapted to different mass-transport mechanisms, at the (sub)nanoscale. They show unprecedented mass-transport rates and precise separation properties, that can even outperform their biological counterparts.

In this Review, we discuss artificial channels of the sub-nm scale (that is, the channels for selective transporting molecules or ions with sub-nm physical sizes or with size differences at the sub-nm scale) and review the progress that has been made in the design, fabrication and structural tuning of nanopores, 1D nanotubes and 2D nanochannels. We focus on confined mass-transport mechanisms, including details on how the architecture and the chemistry of the channels tune the transport behaviours of gases, liquids and ions. We also overview the development of processing these channels into membranes or devices for various applications, describe challenges and identify fruitful areas of future research.

[H1] Sub-nanometre scale channels

[H2] Sub-nanopores

Channels in the form of nanopores can be fabricated by using "bottom up" synthesized porous materials or by "top-down" creation of nanopores in non-porous materials[13,21-23]. Here, we focus on materials with sub-nanopores shown in Table 1, which summarizes their structural tunability, channels size, rigidity, and density for membranes or devices. Synthesized

nanoporous materials can be classified based on their crystallinity. Crystalline nanoporous materials include zeolites[8], MOFs[13] and related structures (such as metal-organic cages[15], and metal-coordinating microporous polymers (MMPs)[24]), covalent-organic frameworks (COFs)[25], and porous organic cages (POCs)[26]. While non-crystalline nanoporous materials are comprised of carbon molecular sieves (CMSs)[27], hyper-crosslinked polymers[28], polymers of intrinsic microporosity (PIMs)[29], conjugated-microporous polymers (CMPs)[30] and porous aromatic frameworks[31]. Compared with non-crystalline materials, crystalline materials, especially MOFs and COFs, have more ordered arrangements of pores, more uniform pore sizes, higher pore density, and generally, their pore structures are more tunable. As a result, the architecture and chemistry of pores influence the selectivity toward the desired molecules. It remains challenging to synthesize non-crystalline materials with well-defined sub-nm pores and narrow pore distributions[32]. However, hydrophilic PIMs with tight chain packing have been shown to form sub-nm pores (< 7Å) with narrow pore size distribution[33], which is beneficial for sieving ions. In addition, non-crystalline CMSs with rigid slit-like sub-nm (< 7Å) pores, show high efficiency for molecular transport even at high-pressure regime[27,32].

Porous 2D materials with atomically precise structures are promising nanoscale structures with selective mass-transport channels[22]. The atomic thickness of 2D materials enables the minimum resistance for mass-transport and maximum permeation flux. The intrinsic or created nanopores in the 2D lattices lead to precise sieving properties. The nanopores can be obtained by "bottom-up" synthesis of porous nanosheets or by "top-down" approaches using physiochemical perforation of inherently nonporous nanosheets[34]. "Top-down" fabricated 2D pores including graphene, MoS_2 and hexagonal boron nitride (hBN) with pore sizes from 3 Å to 76 Å made by either ion irradiation, chemical or plasma etching or post-functionalization, show high efficiency for gas, water and ion transport[22,34-36]. "Bottom-up" synthesized 2D pores such as 2D carbon nitride[37], MOFs[38,39], COFs[40,41] and zeolites[42] have been reported for selective mass-transport. Exploration of other "bottom-up" synthesized materials by using molecular precursors include nanoporous graphene[43], graphyne[44], stanene[45] and 2D polymers[46] is emerging.

[H2] 1D Nanotubes

[H3] Carbon nanotubes. Carbon nanotubes (CNTs) are the most studied 1D nanomaterial for selective mass-transport (Fig. 1b). Typically, the inner pore size of single-walled carbon nanotubes (SWCNTs) is ~8–20 Å. The openings and the exterior of CNTs can be chemically modified, however, there are currently no strategies to functionalize their interior space[47]. Instead, the inner surfaces of CNTs are molecularly smooth and enable ultra-fast molecular transport. Theoretical and experimental studies show that SWCNTs with diameters of 8.1 Å exhibit ultra-fast water transport in the channel[48,49].

[H3] Organic and inorganic nanotubes. The insides of the channel walls of organic and inorganic tubes are not atomically smooth because they can be single-molecule or an assembly of many molecules. However, these structures are more tailorable than CNTs in terms of pore chemistry, pore size (ranges from sub-nm to nanometre), alignment, processing, and performance. The length of the organic tubes is tunable through different assembly strategies. Sub-nm sized organic nanotubes for water channels have attracted increasing attention. For example, a 1D peptide appended hybrid[4]arene (PAH[4]), created by eight

phenylalanine tripeptides chains on hybrid[4]arene macrocycle molecules[12] (Fig. 1b), has sub-nm sized channels for fast water permeation (~10^9 water molecules per second) but efficiently rejects ions. Organic nanotubes can be constructed from molecular subunits via non-covalent interactions, such as hydrogen bonding, electrostatic, hydrophobic, π–π and ion–π interactions. Examples include nanotubes of octylureido-ethylimidazole[50], m-phenylene ethynylene[51], and helical macromolecules[52]. However, it is challenging to realize scalable processing to create robust membranes. Block copolymers (BCP) films fabricated by self-assembly have vertically aligned 1D channels with pore size from several nanometres to tens of nanometres for selective separation[53,54]. However, it is difficult to make sub-nm pore-sized BCP channels (down to ~1.2 nm so far[55]).

The inorganic tubes discussed here are mainly in the form of metal oxide, which are synthetic analogs of the nanotube mineral imogolite, including aluminosilicate or aluminogermanate-based nanotubes[56,57]. These nanotubes are synthesized by hydrothermal methods at low temperatures (~100°C) and at mildly acidic pH. For example, a single-walled aluminosilicate nanotube structure built with hexagonal aluminum hydroxide as the outer wall and pendant silanol groups aligned linearly as the inner wall has channels with inner diameters of ~6.5 Å and high rigidity (Fig. 1b)[58]. However, these inorganic tubes are rarely used in applications.

[H2] 2D Nanochannels

[H3] Graphene and graphene oxide. 2D graphene channels are formed by layer-by-layer stacking of graphene sheets. Graphene channels with hydrophobic, smooth, and frictionless surfaces enable the fast flow of fluids and may be used for water desalination[59,60], and gas separation[61]. Graphene oxide (GO) channels and membranes are another prototype, which, until now, are more practical for application at large scales of molecular separation. The excellent solution-dispersibility of GO enables its assembly into laminar macroscopic structures. Typically, the interlayer spacing in the GO laminate in a dry state is 9 ± 1 Å[62]. Considering the thickness of graphene is 3.4 Å, the interlayer empty space (*a*, that is, the space available for mass-transport) between GO nanosheets is 5.6 ± 1 Å, allowing one or two layers of moving water within the channels. The sub-nanosized GO channels have been widely demonstrated for molecular separation[63]. However, this distance is still not small enough for the separation of gas molecules, which requires the aperture sizes down to ~4−5 Å[32]. Additionally, GO channels are flexible, for instance, the channels swell to 13 ± 1 Å when immersed in water[62], sharply decreasing the selectivity for molecular or ionic separation. Different methods have been used to stabilize the interlayer channels, including chemically or thermally reducing GO[64], or by intercalation with other molecules or nanomaterials[65], or by graphene[66,67].

[H3] MXenes. Transition metal carbides or nitrides, termed as MXenes, are relatively new 2D materials[68]. Similar to GO, MXene nanosheets are hydrophilic and terminated with functional moieties, and show good solution-processability. $Ti_3C_2T_x$ (where T_x refers to functional moieties including –H, –O, and –F) is the most studied MXene, with interlayer spacing in the dry state of ~13.5–15 Å[69,70]. Considering the single-layer thickness of $Ti_3C_2T_x$ is ~10 Å, the *a* value is ~3.5–5 Å, which is a suitable channel size for gas molecules separation[69,70]. In water, *a* is ~6 Å for $Ti_3C_2T_x$ and the channels reject hydrated cations of a larger size[71]. The instability of the

structure resulting from oxidation is a major limitation for applications.

[H3] Other 2D materials. Other 2D materials assembled to form 2D channels include transition metal dichalcogenides (TMDs) (for example, MoS_2, WS_2, and WSe_2), hBN, and layered double hydroxides (LDHs). Similar to graphene, TMDs and hBN crystals are impermeable to molecules, but allow permeation between adjacent layers. Liquid-based exfoliation enables the assembly of laminar membranes using TMDs and hBN nanosheets[72,73]. These membranes, to some extent, outperform the GO membranes in terms of water stability because of the prevalence of van der Waals interactions between layers. Also, their smooth surface leads to low hydraulic resistance and thus, high water flux[74]. Particularly, MoS_2 with three-atomic layers exhibit higher rigidity in out-of-plane direction than GO[75]. However, using TMDs and hBN membranes for molecular separation requires the fabrication of high-quality, and defect-free membranes. Although it is intriguing that van der Waals assembled 2D channels (such as MoS_2 and hBN) with sub-nm size exhibit unexpected transport phenomena of hydrogen isotopes[76], gases[61], and ions[77,78], which challenges the classic mass-transport theory, and may boost applications. LDHs are composed of positively-charged brucite-like 2D sheets, charge-compensated anions and solvation molecules located in interlayer spacings[79]. Further research is required to control grain boundary defects, the orientation of layers, and the interlayer spacings of LDHs.

Large-area membranes or devices are required for the application of nanomaterial-enabled channels, particularly for molecular separation. Some fabrication techniques that are reliable and scalable are introduced in Fig. 2.

[H1] Channel structure and transport

Channels at different length-scales are dominated by a variety of mechanisms (Fig. 3a). An introduction of the mass-transport from nanometre (nm) to micrometre scale is provided in Supplementary Box S1. As the channel sizes decrease to sub-nm range, which is in the size range of gases, liquids and ions, the mass-transport behaviours vary based on distinct mechanisms (Fig. 3b). One of the most widely accepted mechanism is solution-diffusion theory (Supplementary Box S1 and Fig. S1), which explains transport phenomena such as gas separation, reverse osmosis (RO), forward osmosis (FO, driven by osmotic pressure difference), pervaporation (PV, separating liquids mixtures by partial vaporization through a selective membrane), and organic solvent reverse osmosis (OSRO, separating organic molecules with subtle molecular size differences in liquid organic mixtures). Aqueous nanofiltration and organic solvent nanofiltration (OSN) are a combination of solution-diffusion and pore-flow mechanisms[32,80]. Readers are referred to review articles[14,32,80,81] for discussions of these separation processes.

Current synthetic membranes, especially polymeric membranes, suffer from a trade-off between permeability and selectivity in almost all separation settings. Intrinsically, materials that have larger free volume (or pore size) are more permeable, however, they also have a wider distribution of free volume (or pore size), leading to a more open structure, and thus, lower selectivity. This trade-off was studied by upper bound models[82,83]. Channels with both high permeability and high selectivity to exceed the upper bound have emerged. Design of these channels is based on different mass-transport mechanisms, including molecular sieving, surface effect, electrical effect, channel-guest interaction, and quantum effect. (Fig. 3).

[H2] Sieving effect

Molecular sieving occurs when the channel sizes are exactly (or smaller than) the sizes of single molecules. For channels to separate molecules based on size, it is important to have channels of uniform size and high rigidity. Typically, high selectivity dominates when pore diameters are on the molecular scale (3−7 Å). Such an effect can be explained by coupling the solution-diffusion model and transition-state theory[32] (Supplementary Box S1), taking advantage of enthalpic and entropic factors.

Zeolites can act as molecular sieves with a clear "cut off", owing to their relatively fixed pore sizes. For example, membranes of NaA zeolite show high separation factors in alcohol dehydration separations[84]. In another study, single-layer MFI nanosheets are able to sieve *para*-xylene over *ortho*-xylene (kinetic diameters of 5.8 and 6.8 Å, respectively) with separation factors as high as 8,000−10,000[42]. However, the structures of zeolites can change at high temperatures or by the adsorption of guest molecules, leading to the loss of molecular sieving capabilities. Fortunately, NaA zeolite membranes synthesized by a modified seeding strategy show negligible defects even at 300 $^{\circ}$C with water vapour[85]. CMSs show excellent separation by molecular sieving because of high channel rigidity (Fig. 4a). The rigid pores originate from their manufacture by carbonization of polymeric precursors, leading to reduced swelling and plasticization compared with polymer membranes. As a result, the entropic factor (equation 1 in Supplementary Box S1) contributes to the molecular separation, endowing the CMSs with capabilities for the sieving of similar-sized gas molecules and OSRO process[27,32].

2D materials with sub-nm pores can also act as molecular sieves. Nanopores with size of ~3.4 Å created in few-layer graphene films by UV or ozone etching show preferential permeation of H_2 over N_2 with selectivity larger than 10,000[86], albeit the tiny testing film area of 1.96×10^{-5} mm^2. A graphene film of larger area (~1 mm^2) may have non-selective defects[87], and thus, shows a sharp reduction in selectivity (H_2 over CH_4 with selectivity of ~25). However, the graphene film still shows molecular sieving effect with the selectivity larger than the Knudsen selectivity of ~2.8. Single-layer graphene etched by oxygen plasma[88] has pores of ~5−10 Å (Fig. 4b, effective pore size of ~3−7 Å after considering the van der Waals diameter of a carbon atom). The porous graphene membranes act as molecular sieves with nearly 100% rejection of ions but allowing water transport. However, single or few-layer graphene membranes are yet to maintain molecular selectivity at high pressure. A recent work realizes the enhancement of mechanical robustness of graphene membrane through depositing CNTs networks on surface[89]. Such a hybrid membrane shows salt rejection of about 90% at a pressure of 0.5 MPa under RO testing.

MOFs are another class of molecular sieves that have been widely used for applications from gas purification to liquid separation[14]. The well-defined pore structure of MOFs can be directly observed by high-resolution transmission electron microscopy (HRTEM) at an atomic resolution[90-92]. For instance, the motion-corrected image taken along the [111] axis of a ZIF-8 crystal (Fig. 4c) shows the six-ring channels of ZIF-8 pores with the individual Zn atomic columns in triplet that are ~3.4 Å apart[91]. Such an array of sub-nm pores within membranes is favourable for selective mass-transport. However, MOFs do not always maintain the pore sizes as observed. Pore flexibility is often found in MOFs, causing the "gate-opening effect" followed by loss of sieving capability. Taking ZIF-8 as an example, although with a crystallographic

aperture size of ~3.4 Å (Figs. 1a and 4c), ZIF-8 pores have natural fluctuations in crystal structure (for instance, motion of ligands), which will reversibly expand to some extent. Actually, ZIF-8 is able to uptake guest molecules as large as ~7.6 Å (1,2,4-trimethylbenzene)[93]. Gas permeation through ZIF-8 membranes show that the effective pore size is 4.0−4.2 Å, sharply rejecting propane (4.2 Å) from propylene (4.0 Å) molecules with diffusion selectivity of ~140 (Fig. 4e)[32,94]. Similar to ZIF-8, the crystal triangular pore size of UiO-66 fluctuates between 3.7 and 9.2 Å, resulting from the three orientable benzene rings performing flips around the C2 symmetry axis[95].

Efforts have been made to improve the rigidity of MOFs nanopores by incorporating rigid linkers. A rare-earth MOF with a face-centred cubic (fcu) topology (Y-*fum*-**fcu**-MOF) featuring rigid pores with size of ~4.7 Å (Fig. 4d) has sieving behaviour with a sharp "cut-off" between n-C_4H_{10} and i-C_4H_{10} [96]. In addition, Y-*fum*-**fcu**-MOF has a higher diffusivity for n-C_4H_{10} than for ZIF-8 (by 3 orders of magnitude), which is commercially attractive[96]. Other examples include NbOFFIVE MOF[97] (NbOFFIVE indicates $(NbOF_5)^{2-}$ pillars) and $Ca(C_4O_4)(H_2O)$[98], which both show excellent sieving for alkenes over alkanes. However, the materials require further study to demonstrate membrane-based diffusion. In addition to pore flexibility, the absence of linkers or clusters[92,99], as well as coherent interface defects[91] weaken molecular sieving in MOFs pores. Thin films of ZIF-8 made by atomic layer deposition followed by ligand-vapour treatment may circumvent these problems[100]. The fabricated ZIF-8 membranes are shown to be defect-free, reproducible, capable of molecular-sieving, and may also be scalable.

The pore flexibility in MOFs can be tuned and hence, the mass-transport reversibly switched. For example, an external electric field (500V mm^{-1} perpendicular to the MOF layer) causes the lattice polarization of ZIF-8 (Fig. 4d), followed by switching the ZIF-8 crystal structure from cubic to monoclinic and triclinic polymorphs[101]. The monoclinic polymorph shows a pore diameter of 3.6 Å, which is larger than that of cubic polymorph (3.4 Å) of ZIF-8. However, the linker (2-methylimidazole) mobility in the monoclinic polymorph is more restricted than in the cubic polymorph, leading to stiffening of the ZIF-8 lattice and enhancing the molecular sieving of propene from propane (selectivity of propene over propane increases from 6 to 8). MOF pores can also be switched by assembling linkers containing photo-responsive groups (Fig. 4f) under light irradiation, showing reversible changes of gas separation[102]. Tuning the pore flexibility of MOFs may have implications beyond separation, such as tunable catalysis, drug delivery, and photo-actuated or electrically-actuated artificial tissues.

Other nanopores are also controlled by molecular sieving effect, for example, microporous polymers[103]. However, the pores of microporous polymers are considered to be semi-rigid, because nm or sub-nm scale motion occurring at the backbones of polymer networks may cause the loss of enthalpic and entropic contributions to molecular sieving. Sieving effects in COF pores[104], POC pores[105], and 1D organic or inorganic tubes[12,106] are observed but more study is needed, including the synthesis of materials and films, as well as mass-transport experiments.

2D nanochannels act as molecular sieves because of their assembled interlayer spacings. To study the mass-transport behaviours, nanofabrication was used to create van der Waals assemblies of 2D crystals with slit-like channels (with sizes down to several Ångstroms) (Fig. 5a). More specifically, two relatively thick (~100-nm) crystals (including graphite, hBN, and

MoS$_2$) are placed on top of each other, separated by stripes of another 2D crystal serving as spacers[60,78]. The trilayer assembly is kept together by van der Waals interactions, and the interlayer empty space (*a*) of the channels is the thickness of the 2D spacer layer. All the 2D crystals in the channel are obtained by mechanical exfoliation to provide flat 2D surfaces, which is vital for several reasons: first, the surface roughness at atomic scale endows the 2D channels with precisely controlled dimensions and channel height. Second, flat surfaces result in chemically inert channel with low ($\leq 10^{-4}$ C cm^{-2}) surface charge[78]. Finally, the channel height can be tuned by the spacer layer at atomic precision. For example, the use of bilayer graphene or monolayer of MoS$_2$ as the spacer layers, makes channels with *a* of ~6.6 Å[78]. Water transport and ion transport experiments indicate that these 2D channels allow water permeation but reject ions with diameters larger than ~10 Å. Small hydrated ions with diameter ~7 Å, such as hydrated K$^+$, Na$^+$ and Li$^+$, can permeate the slit-like channels, although they are larger than *a*. The permeation of the hydrated monovalent ions indicates that ions under nano-confinement are not mechanically hard, namely, the hydration shells may be partially distorted, flattened or shredded before entering the channels[78,107].

To enhance their sieving capability, 2D graphene channels with *a* ~3.4 Å are fabricated, using a monolayer of graphene as a spacer layer with water molecules inside the slits, which prevent channel collapse[59]. These slits show excellent sieving behaviour by almost completely rejecting ions while allowing water and proton permeation. Water molecules are predicted to be aligned as a 2D monolayer within the slits, enabling the transport of protons by jumping between water molecules (Grotthuss mechanism[59]). To be used in applications, these materials need to function at high pressure and at high concentrations of ions. These applications also require rigid channels because flexiblity results in the loss of selectivity as a consequence of the high chemical potential gradient that can force all molecules or ions pass through the channels[32].

Compared with van der Waals channels of uniform channel sizes, self-assembled 2D channels (such as the channels in GO membranes fabricated by filtration methods) have a wider distribution of sizes. However, these self-assembled channels still exhibit molecular sieving effects. For example, the GO membranes are reported to block solutes with sizes larger than 9 Å when immersed in water[62]. The swelling of GO channels in water impedes the use of GO to sieve small ions (hydrated diameter < 9 Å) and various strategies have been used to overcome this issue. One strategy is physical confinement; more specifically, using epoxy to encapsulate the GO membrane to restrict the swelling of laminates exposed in water (Fig. 5b). 2D GO channels with *a* ranging from 6.4 Å to 9.8 Å can be tuned by humidity before epoxy encapsulation. Such GO channels show rejection of ions when immersed in water[108]. Intriguingly, cations can determine the interlayer spacing of GO membranes, leading to the cationic control of 2D GO channels[107] (Fig. 5c). Because of the cation-π and hydrogen-bonding interactions between GO layers and hydrated cations, membrane spacings controlled by one type of cation can selectively exclude other cations that have larger hydrated volumes. For instance, GO membrane controlled by KCl can stably maintain the channel spacing at ~10 Å, and thus, reject other ions while still showing water flux of ~0.36 l m^{-2} h^{-1} under forward osmosis processes (Fig. 5c).

Another method is to chemically crosslink the GO nanosheets[65,109]. The crosslinkers, diamine monomers[65], react with oxygen functionalities on the GO via condensation and nucleophilic

substitution reactions (Fig. 5d). This crosslinking hinders the water-induced swelling of GO channels and the interlayer spacing is tuned to distinct values by changing the diamine monomers. Such GO membranes show sieving effects, with the pervaporative separation factor of water over ethanol as high as ~4,700 (which is ~70 times higher than that of pure GO membrane). Similar to the flexible MOFs pores, the height of GO channels can be tuned by stimuli from the environment, showing a smart gating-effect. Poly(N-isopropylacrylamide) (PolyNIPAM), a temperature-responsive polymer, has been covalently bonded to GO by free-radical polymerization (Fig. 5e)[110]. The intercalation of polymeric chains into GO channels switches the a value from ~18.6 Å to ~14.7 Å when temperature changes from 25 ^{o}C to 50 ^{o}C (or by illuminating infrared light). Water flux can be tuned between 12.4 and 1.8 l m^{-2} h^{-1} bar^{-1}.

[H2] Surface effects

The inner surfaces of 1D and 2D channels are atomically smooth walls, allowing fast molecular transport. For example, ultrafast water transport is found in CNTs channels, showing slip flow behaviour with flow rates that exceed the predictions of the Hagen-Poiseuille equation[111]. Early experimental studies on water transport through membranes of vertically-aligned multiwalled CNTs (~7 nm in diameter) have shown water slip lengths of 39 to 68 μm, indicating that the water flux is 4 to 5 orders of magnitude higher than the value predicted by the Hagen-Poiseuille equation with a no-slip boundary condition[112]. Recently, an enhancement of radius-dependent water flow has been demonstrated using single CNT channel measurements[113]. The slip length of water increases monotonically with a decrease in the CNT diameter from 100 nm to 30 nm. Interestingly, a further decrease in diameter, to a size approaching the van der Waals diameter of water molecules, can lead to a non-monotonic variation of slip length with CNT diameter[114]. CNTs with diameter of ~8 Å exhibit one order of magnitude higher water flux than 15 Å-CNTs, exceeding the water flux of AQP1 by a factor of 6 (REF.[49]). This extraordinary water transport can be attributed to the confined space and smooth graphitic walls. Water molecules are forced into a 1D wire configuration in 8 Å-CNTs (Fig. 6a), while they maintain a bulk-like arrangement in 15 Å-CNTs.

This enhancement of water transport results from the fewer hydrogen bonds per water molecule in the narrower CNTs pores[49]. In AQP1 channels, the amino acids slow down the water transport by kinetics of hydrogen-bond formation and breakage with water molecules. This mechanism is further demonstrated by showing 5-fold enhancement of water permeability through 8 Å-CNTs at acidic pH, where protonated carboxyl moieties at the nanotube rim hinder the hydrogen bonding with water. This 1D arrangement of water molecules occurs only on the sub-nm scale, and can facilitate proton transport via the Grotthuss mechanism[115].

2D van der Waals channels open another avenue to study the surface effects under confinement. Unlike 1D CNTs, 2D graphene channels show similar water slip lengths regardless of the interlayer channel spacing, with simulated values of ~60 nm[60] and experimental values of ~16 nm[116]. Fast water flow (up to 1 m s^{-1}) is observed in graphene channels, as a consequence of the low friction of water against the graphene wall[60]. Unexpectedly, the water flux increased significantly when the channel size approached ~10 Å. This increase may be because of the rapidly rising driving force (capillary pressure, above 1,000 bar), which is dominated by water-water interaction and water-carbon interaction under nano-confinement. Interestingly, the viscosity of water is found to increase by a factor of two

when the channel size decreases to the sub-nm scale. This increase can be ascribed to the formation of more aligned water layer between the sub-nm confined 2D graphene[60,117] compared with bulk water. This 2D layered water is different from bulk water, and has some intriguing phenomena. For instance, 2D square ice, an unusual phase of water, is observed in graphene nanocapillaries[117] owing to the existence of pressure caused by van der Waals interactions between graphene sheets. The same phenomenon seems to appear in the water confined between MoS_2 sheet and mica[118]. In addition, the dielectric constant (ε) of water confined in nanoscale channels (composed of a bottom layer of graphene and a top layer of hBN) can be as low as ~2, far below that of bulk water (~80)[119]. The behaviour of interfacial water could be important for investigating the water transport and ion transport in sub-nm scale channels.

Ion transport through 2D van der Waals channels is also controlled by surface effects. Driven by pressure, K^+ mobility through graphene channels (a of ~6.8 Å) reached up to 3×10^{-7} m^2 V^{-1} s^{-1}, which is even higher than the bulk potassium electrophoretic mobility (7.6×10^{-8} m^2 V^{-1} s^{-1})[77]. This high mobility for ions may arise from the anomalously fast transport of water[59,60,116] (Fig. 6a). But for anions, for instance, Cl^- are three times less mobile than K^+ in graphene channels (a of ~6.8 Å)[78], even though the ions have the same hydrated diameter and similar mobilities in bulk solutions. This observation may be a consequence of the polarization of water on the graphene channels surface, leading to the preferential orientation of −OH groups towards channel walls. The hydration shell of Cl^- has −OH groups pointing preferentially outside, while the exterior of K^+ is more covered by hydrogen atoms. Thus, the hydrated Cl^- has a stronger interaction with the graphene surface than hydrated K^+, leading to lower mobility of Cl^- [78]. Besides, van der Waals assembled graphene and hBN channels (both with a of ~6.8 Å) exhibited distinct K^+ diffusion behaviours, which can be attributed to the differences of molecular friction of water and ions on these two materials as well as the distinct electrical structures[77].

Results of intercalation of solid-state ions into van der Waals channels also show an ultrafast diffusion rate. For instance, the diffusion coefficients for Li^+ between the bilayer graphene can reach ~1.4×10^{-7} m^2 V^{-1} s^{-1} at room temperature[120]. In situ low-voltage TEM has proved that the intercalated Li^+ form a super-dense and ordered packing of Li atoms between the bilayer graphene, with the evidence of the appearance of crystalline 2D Li layers[121]. Instead of forming LiC_6, the close-packing of Li atoms leads to an increasing of Li storage capacity. Interestingly, Li^+ diffusion varies in the channels which are composed of different 2D materials, namely, the van der Waals heterointerface effect[122]. Compared with the channels interfaced by graphene/hBN or MoX_2/MoX_2 (where X=S or Se), the graphene/MoX_2 heterostructure channels (Fig. 6a) exhibited much higher Li^+ accumulation via the marriage of low-resistance electronic pathway by graphene and strong Li-binding affinity by MoX_2.

[H2] Electrical effects

Mass-transport, particularly ion transport, can also be tuned by electrical effects, including electrostatic interaction and applied electric potential. Electrostatic interaction is generated between the charged surfaces of channels and the flow of ions. In classical mean-field electrostatics theories, when the channels are narrower than the Debye length (λ_D) of the electrolyte, the surface charges repel the co-ions and attract counter-ions. An electrochemical

equilibrium, namely, the Donnan equilibrium, is established when an ionic solution is in contact with charged channels, forming the Donnan potential difference at the interphase of solution and channels. When a pressure gradient is applied for filtration, the Donnan potential excludes co-ions from the channels and must also exclude counter-ions owing to the electroneutrality requirement. It is important that λ_D is larger than channel size, and the channels are in the dilute solution, then the Donnan exclusion behaviour dominates. In a concentrated ionic solution, however, λ_D is comparable to the channel size and the rejection rate decreases rapidly.

Electrostatic interactions are a dominant factor for ion transport through nanopores[123,124], 1D[49,125] and 2D[20,66,126] nanochannels. The classic mean-field theories are less relevant for ion transport in channels under extreme confinement and in solution with high concentration of ions[114]. For instance, ion transport through sub-nm graphene pores is observed to exhibit heterogeneous contributions by different individual pores[123]. The sub-continuum ion dehydration coupled with electrostatic effects in sub-nm pores is found to dominate the observed rectified and nonlinear current–voltage characteristics. Cation to cation, or even cation to anion sieving is observed in graphene[123] and MoS_2[124] pores, 1D CNTs[49], and 2D GO channels[127]. The 8 Å-CNTs (Fig. 6b) with carboxy groups at the rims of nanopores[49], can reject almost all co-ions (Cl^-) when KCl concentration is 0.1 M at pH=7.5, and show a K^+: Cl^- ion selectivity greater than 184:1 at typical seawater salinity level of 0.6 M. In analogy with the biological channels based on the electrostatic interaction effects, the sub-nm CNT channels, intriguingly, function as voltage gates that open or close in response to the changes of transmembrane potential, and, like diodes, to transport ions only in one direction[49,128].

Ion separation enabled by electrostatic interaction can be regulated by manipulating the surface charges of channels. GO membranes with tunable surface charges can be obtained by coating the GO with positively or negatively charged polyelectrolytes[126] (Fig. 6b). The charge of the membrane surface, based on the protonation of amine groups or deprotonation of sulfonic, carboxy, or hydroxy groups in water, are finely tuned by the intensity and the amount of these ionizable functional groups. The selectivities of H_2O to $MgCl_2$ and H_2O to Na_2SO_4 can be enhanced, reaching as high as 2.2×10^5 and 5.4×10^5, respectively[126]. The divalent cation A^{2+} and anion B^{2-} with high interaction energy barriers are excluded by positively and negatively charged GO membranes respectively, and the electrostatically attracted low-valent counter-ions are rejected on the basis of electroneutrality requirements.

Graphene-based channels are intrinsically conductive, enabling their use as electrodes. Inspired by this trait, electric potential is applied across the channels to regulate the water and ion transport[129,130]. Water permeation can be affected by the ionization effect in water caused by an electric field[129]. With the application of an electric potential, the GO membranes containing moisture enable the creation of conductive filaments (conducting paths) within the channels (Fig. 6b). The electric field along the radical direction is as high as $\sim 10^7$ V m^{-1}, which can dissociate water molecules to produce hydronium (H_3O^+) and hydroxyl (OH^-) ions. Hydrogen bonding between H_3O^+ or OH^- ions and surrounding water molecules leads to the formation of large hydrated clusters, which can reduce water permeability from ~ 150 to ~ 10 mg m^{-2} h^{-1} (REF. [129]). Interestingly, interlayer spacing of the GO channels can be reversely switched from 9.2 Å to 8.5 Å, enabling their function as voltage gates for selective molecular transport.

Electric potential can also influence the transport of ions within charged channels by continuously changing the population and distribution of ions[131]. Simulations based on the Poisson–Nernst–Planck model[132] have shown that the flux of ions diffusing through the interfacial electrical double layers confined in nanochannels (size smaller than 2 nm) should decrease as the gate potential increases[130]. Surprisingly, experiments indicate that the flux of ions increases by up to 7 times when the voltage shifts from 0 to −0.5 V[130]. This observation may be because of the short-ranged, non-Coulombic correlation between the co-ions and counter-ions under nano-confinement, which disturbs the electrical double layers structure and attracts more co-ions to facilitate ion transport[133,134]. Such a strong ion-ion correlation is dependent on the ion type, indicating the possibility to realize the sieving of ions. Controlled water and ion permeation enabled by electric fields is also promising for smart molecular gates for applications including tissue engineering and field-effect transistors.

[H2] Channel-guest interactions

Selective mass-transport also occurs when the guest molecules show different channel-guest interactions. Typically, enhancing these interactions aids molecular transport of certain molecules as well as the selectivity over other molecules. For example, a NaA zeolite membrane exhibits fast transport of water vapour by favourable charge-dipole interaction between Na^+ and water, but rejects light gas molecules (H_2 and CO_2)[85]. Selectivity of H_2O over CO_2 reaches as high as ~11,000 even under high temperature and pressure (250 °C and 21 bar), boosting the conversion efficiency of CO_2 to methanol during CO_2 hydrogenation reaction. Transport of CO_2 molecules in 1D CNTs is enhanced by modifying the channel walls with divalent metal cations (Fig. 6c) [135]. These cations function as CO_2 carriers to facilitate CO_2 transport by providing suitable electronegativity to form π-complexation with CO_2 molecules.

MOFs are one of the most popular materials with tunable channel-guest interactions. Various chemical strategies can tune these interactions, such as open metal sites, secondary building units (SBU)-based interactions, hydrophobicity, and the presence of certain functional groups. For example, $Fe_2(O_2)(dobdc)$ MOFs ($dobdc^{4-}$: 2,5-dioxido-1,4-benzenedicarboxylate) show preferential binding of C_2H_6 over C_2H_4 by iron-peroxo sites through hydrogen bonding (Fig. 6c), realizing highly selective separation of C_2H_6 and C_2H_4 (C_2H_4 purity of 99.99% produced by column packed fixed-bed)[136].

If channel-guest interactions are too strong, the transport of molecules through membranes may be hindered. For example, the −NH$_2$ modified MIL-53 membrane shows high CO_2 adsorption capability, but low CO_2 permeance, and thus, high selectivity of H_2 over CO_2 [137]. The presence of certain functional groups can also influence the transport behaviour of aqueous ions. For example, modification of UiO-66 nanopores with $−N^+(CH_3)_3$ groups leads to anion to anion separation in solution under an electric field. F^- over Cl^- selectivity reaches ~240, which arises from the specific interactions between F^- ions and the binding sites in nanopores[138]. In addition, grafting amino acid groups (such as L-histidine and L-glutamic acid) into MOF pores enhances the discrimination between chiral molecules[139,140], and enabling chiral separation by MOFs-based membranes. Modification of nanopores with various functional groups has also been reported for COFs[25], POCs[23] and porous 2D materials[34].

Hydrophilicity facilitates water transport in 2D channels including GO, MXene, MoS_2 and amine-functionalized hBN. Water molecules are preferentially adsorbed onto the channel

surface, and then diffuse[19]. This process leads to water permeation rates in membranes comprising 2D channels ranging from dozens to thousands $L\ m^{-2}\ h^{-1}\ bar^{-1}$. These rates are significantly higher than commercial membranes with similar retention values. As well as electrostatic interactions, ions and 2D channels interact with each other through cation-π interaction[107] and metal coordination[141]. For example, 2D Na-Cl crystals can be formed within the confined reduced GO channels. This phenomenon originates from cation–π interactions between the ions and the aromatic rings in the graphitic surface[142]. Interestingly, unconventional stoichiometries of these 2D Na-Cl crystals are found under ambient conditions, including Na_2Cl and Na_3Cl. These stoichiometries can be explained by strong Na^+-π interaction and an excess of Na^+ caused by the charge transfer between the unoccupied valence orbitals of Na^+ and the delocalized π states of the aromatic ring structure in the graphene sheet[142]. This observation is useful for unravelling ion-transport mechanisms, as well as the magnetic, optical and mechanical properties of 2D ionic crystals.

Interactions between gas molecules and 2D channels are the leading effect for transporting gas molecules, especially for CO_2 molecules. Pure GO, MoS_2 and MXene channels show CO_2-philic properties, which inhibit the CO_2 transport within the channels[69,143,144]. However, forming 2D channels with interlocked stacking structures leads to preferential permeation of CO_2 over other gases including N_2, CH_4, and H_2. To switch gas permeation behaviours of MXene channels, borate and polyethylenimine (PEI) molecules are introduced to functionalize MXene layers (Fig. 6c). After this functionalization, MXene membranes have a densely interlocked structure and enhanced CO_2 sorption capability, making the transformation from "diffusion-controlled" to "solution-controlled" channels. These modified MXene channels are CO_2-selective rather than H_2-selective[70].

[H2] Quantum effects

The above mechanisms and theories do not explain mass-transport through Ångstrom-sized channels. In these cases, such as the selective permeation of light molecules (H_2, D_2, and He), quantum effects dominate. For isotope separation, typically, a heavier isotope with a shorter de Broglie wavelength λ_i (a smaller effective particle size) has a lower energy barrier for entry into the channels, leading to a difference of isotope transport rates. Various studies are conducted on the hydrogen-isotope separation using different materials, such as CMSs[145], zeolites[146], MOFs[147], COFs[148], POCs[149] and CNTs[150]. However, in most cases, relatively low temperatures (20 K−140 K) are needed for separation, requiring huge energy consumption. Alternatively, the isotope separation can be realized by 2D materials (such as graphene, hBN, and MoS_2) at room temperature[151,152].

Perfect monolayers of graphene and hBN with narrow hexagonal rings are impermeable for atoms and molecules. However, they are permeable for hydrogen ions (or protons)[153]. Proton transport occurs when the electron clouds are pierced by incident protons in the 2D materials. The difference in electron-density distribution of hBN, graphene and MoS_2 results in distinct rates of proton transport (Fig. 7a). In monolayers, the electron clouds of hBN (energy barrier E≈0.3 eV) are more "porous" than those of graphene (E≈0.8 eV), while MoS_2 does not have any 'pores' in its electron cloud, and so does not conduct protons[154]. In principle, isotopes are identical in molecular size but for isotopes of hydrogen ions, the size is exactly the size of nuclei, which is determined by the number of neutrons. As a result, heavy D^+ has a larger size

than H^{+}, resulting in a higher barrier while passing through graphene or hBN membrane. H^{+} and D[+] are electrically pumped to pass through the perfect graphene or hBN monolayer[152], and the separation factor of H over D is found surprisingly to be ~10. This efficient hydrogen-isotope separation is a consequence of the difference of zero-point energy (ZPE) of ~60 meV between H and D (Fig. 7b). Such proton transport can be enhanced by decorating the 2D layer with catalytic metal nanoparticles (for example, Pt) and by illuminating the layer with visible light[155]. With the response time in microseconds, the Pt-decorated graphene film generates ~10^4 protons per photon based on the unique photon-proton effect, holding potential for applications of fuel cell, light-induced water splitting, photocatalysis and photodetectors[155].

Quantum-confinement also occurs in the interlayer spacing of 2D van der Waals channels[61,76]. This spacing is ~3.34 Å for graphite and hBN, and ~6.15 Å for MoS_2. These spacings are larger than λ_i of protons (1.45 Å) or deuterons (1.02 Å) atoms at 300 K, which suggests that protons and deuterons may transport through the interlayer of graphite, hBN, and MoS_2. However, these interlayer spacings are filled with electron clouds and, until recently, it was unclear whether this small space could be used for mass-transport. Now, it has demonstrated that these interlayer spacings are impermeable to molecules but allow the transport of protons and deuterons[76]. The channels are created by reactive-ion etching of the 2D crystals (~500 nm thick), followed by coating with a ~ 50nm thick palladium film, which enables proton transport. This transport is a thermally-activated process, following an Arrhenius-type behaviour. The rates of proton transport through the channels decrease in the order, hBN > MoS_2 > graphite, and are dominated by the entry barriers (at the edge of channels) of the 2D interlayer, which increase in the order of graphite > MoS_2 > hBN. In fact, on the basis of the square-well confinement potential, the calculated effective widths for transporting H and D are ~0.52 Å for hBN and ~0.55 Å for MoS_2, which is significantly smaller than the λ_i for H and D[76]. As shown in Fig. 7c, the entry resistance of D (ρ_e^D) is smaller than H (ρ_e^H) for h-BN and MoS_2 interlayer channels (0.5 μm in length), which contrasts with transport in the direction perpendicular to the 2D crystals, showing larger entry resistance of D than H[152]. The difference of the entry barriers for H compared with D, ΔE_e, calculated as ~18 meV, is contributed by the differences of energy barriers in Pd layer ($\Delta\varepsilon_{Pd}$) and in the van der Waals channels ($\Delta\varepsilon_c$) (Fig. 7c). This result demonstrates a faster diffusion of D than H when entering the quantum confined van der Waals channels.

Interestingly, the quantum effect dominates gas permeation through van der Waals channels, and shows a reversed isotope effect. More specifically, the mass flow of H_2 is notably higher than that of D_2, which contrasts to the relation expected for classical flows[61]. 2D channels exhibits a specular reflection of helium molecules off atomically flat walls (of graphene or hBN channels)[61], allowing helium gas to flow almost two orders of magnitude faster than expected from Knudsen theory (based on random-angle molecular scattering)[61]. The helium permeability in graphene channels is 300−1,000 times higher than in MoS_2 channels, and is independent of channel length, indicating a ballistic transport of the helium atoms (Fig. 7d). Such a surface effect occurs because of the strong corrugations (~1 Å in height) of the MoS_2 atomic structure, which is comparable for λ_i of helium (0.5 Å) at room temperature. The van der Waals channels exhibit 30%±10% higher mass flow rate of H_2 than D_2, which differs to the prediction by Knudsen theory (the mass flow rate should be a factor of $\sqrt{2}$ larger for D_2 than H_2). This phenomenon may be caused by matter-wave effects that contribute to the specular

reflection, suppressing heavier atoms (deuterium) with shorter λ_i that are more likely to be hindered by channel surface roughness than the lighter atoms (hydrogen).

The flow of water through CNTs is enhanced by exciting the phonon modes of the nanotube[156]. Molecular dynamic simulations reveal that the friction force between water and double-walled CNTs oscillates regularly with time, as a consequence of the coupling of phonon modes of CNTs and water confined in the nanotube. The lowest odd-index longitudinal phonon modes can transfer momentum to the fluid, leading to an oscillating friction force and an increase of the transport rate of water via viscous diffusion (Fig. 7e). In particular, the increase of the water diffusion coefficient is highest (up to 300%) for the slowest modes (0.3 THz), indicating that very small excitations of the modes leads to a large increase in the diffusion of the confined water molecules[157]. The vibrations of CNTs may also be directly observed, in real-time, using a microcavity-based technique[158]. Discovering this coupling between CNT phonon modes and confined water opens a door for enhancing or tuning the mass-transport dynamics by physical excitation of the confined channels, which are important for applications of nano-electromechanics.

The photoelectric effect dominates ion transport in 2D GO channels[159]. Upon asymmetric light illumination, (that is, illuminating close to both ends of the GO membrane) cations are driven by light to flow through the negatively-charged GO channels with *a* of sub-nm (Fig. 7f). The GO membrane exhibits anti-gradient transport behaviour, depending on the light intensity, illumination position and surface charge density of GO channels. This phenomenon is because electrons and holes are excited by a photoelectric effect, and they will diffuse from the illuminated regions to non-illuminated regions driven by the concentration gradients. However, the diffusivity and mobility of holes are higher than that of the electrons in GO-based materials, leading to an electric potential difference along the axial direction. This difference can drive the cations from the non-illuminated regions to the illuminated regions.

[H1] Outlook

Artificial channels with unique mass-transport properties at the sub-nm scale need to be processed into membranes or devices for practical applications. Membranes comprising nanochannels with separation performances better than current commercialized membranes (mainly polymeric membranes), are promising for large-scale, energy-efficient separation technologies, including water desalination, gas separation, and organic separation (Supplementary Table S1). However, most membranes are only in the stage of concept or laboratory-scale, and efforts are needed to realize the success of artificial channels in real applications.

Fundamental research including the molecular-level design of channels is critical to ensure breakthroughs to boost selectivity and permeability of separation membranes. This design should involve the control of channel size, rigidity, and channel-guest interactions as well as combining the electrical effects and quantum effects. In addition, improvement of mechanical, chemical, and thermal stabilities of the channel materials in practical complex environments will help streamline the transition from laboratory to large-scale application.

Theoretical studies on transport mechanisms are still in their preliminary stage. Current studies are based on coupled thermodynamic and diffusion properties with focus being placed on

bulk-scale fluid mechanics. Moving forward, theories and principles at length scales ranging from atomistic to continuum will guide the rational design from single channel to assembled membranes. Experimental studies at the single-channel level are important to deepen our understanding on mass-transport mechanisms. Research to explain some unusual phenomena that happen within nano-confinement, including the phase transition[117], phase separation[114], the molecular deformation and alignment[59,60,117,142], and ionic Coulomb blockade effects[160,161], may help to reveal the nanostructure-property-performance relationships of channels.

For industry applications, membranes of areas > 1,000 m^2 and with a low concentration of defects are required (for gas separation, below about 1 cm^2 of defects for every 10^5 cm^2 of membrane surface area)[54]. These requirements for membrane-based separation, to some extent, are more stringent compared with other applications such as electronics. Better understanding of the origin of defects, not only during channels synthesis, but in the membrane fabrication process, will contribute to the realization of membranes on a large scale. Mixed matrix membranes (MMMs, formed by dispersing nanomaterials in continuous polymer matrix) is another way to achieve large-area fabrication. However, for MMMs, issues such as homogenous dispersion at high loading level and control of interface components need to be addressed. Optimizing the design of modules of membranes (in hollow fibre or spiral wound formats), and long-term testing of membranes under industrial-like conditions are necessary for artificial channels to realise practical membrane separation.

For water desalination technologies, including nanofiltration, RO, and FO, improving the water to solute (ions) selectivity (minimizing the solute passage) is more important than increasing the membrane permeance[80]. When designing nanochannels, the problems of membrane fouling, concentration polarization, oxidative stability (chlorine tolerant), and boric acid removal from seawater must be considered. For gas separation, the resistance to plasticization (that is, penetrant-induced swelling followed by the loss of separation properties) needs to be considered. Separations of organics at sub-nm scale include pervapouration and vapour permeation, and OSRO. Pervapouration and vapour permeation are likely to remain small-scale applications, because of the phase change-induced energy cost. Swelling (similar to what happens in gas separation membranes) problems of nanochannels should be addressed for the dehydration of organics (for example, removal of water from either ethanol or butanol) and organics pervapourative separation (for example, separation of xylene isomers, or separation of thiophene and n-octane). OSRO, more like "solvent to solvent" separation, is energy saving, and has potential for industrial applications including *para*-xylene recovery from xylene isomers, linear hydrocarbons from branched hydrocarbons, and alcohol and furan separations[32]. The high pressure required by OSRO needs to be considered before the membranes can be applied in this field.

In fuel cells, flow batteries, and Li–S batteries, nanochannels that assemble into membrane separators are being used to selectively transport ions, and improve ionic conductivity. A study shows that hydrophilic PIM membranes enable fast ion transport (for example, K^+) while block large redox active molecules (molecular weights in the range of 140–800 Da), showing the potential to function as membrane separators in aqueous organic flow batteries[33]. However, the issues of chemical degradation and poor electrolyte compatibility of membranes need to be solved.

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Asymmetric transport of ions through nanochannels can be used for osmotic energy harvesting[22]. Overlapping of Debye layers in nanoconfined channels leads to unipolar ion transport (selective transport of cations over anions), generating current flow. Concentration gradients of ions are one of the driving forces, for example, a single-layer of MoS_2 nanopores act as nanopower generators based on salt gradients[124]. Additionally, confined channels that can efficiently transport liquid and gas molecules are useful for heterogeneous catalysis[85,162] by enabling size-selective or shape-selective catalysis, and favourable channel-reactants interactions. Fast transport of molecules or ions in confined nanochannels can also find applications in sensing devices (for instance, ion, gas and humidity sensors)[163,164] and electrochemical actuators[165]. Interestingly, nanochannels have been demonstrated to discriminate biomolecules (DNA, RNA and peptides) with Ångstrom precision[166,167], which paves the ways for nanochannel-based single-molecule sensing and next-generation DNA sequencing technologies. The vibrant field of artificial channels at the sub-nm scale, will foster the development of advanced technologies, and benefit the fields of energy, environmental protection, electronics, and healthcare.

Acknowledgements

Table 1. Summary of promising sub-nm scale channels.

Materials	Selected sub-nm sized channels	Structural tunability, channels rigidity, and channel density for membranes or devices (high, moderate or low)
Sub-nanopores		
Zeolites	Zeolite A: 3 – 5 Å[8]; MFI zeolite: 5.8 – 6.8 Å[42]	Low tunability: tuned by temperature, cations, reaction time, and pH; high rigidity; high channel density
MOFs, MOCs and MMPs	MOFs: ZIFs series: ZIF-7 (3.0 Å), ZIF-8 (~3.4 Å), ZIF-90 (3.5 Å)[168]; copper-based MOF series: $Cu_3(BTC)_2$ (9 Å), CuBDC (5.2 Å)[168]; UiO-66 series: UiO-66 (~6 Å)[169]; RE-fcu-MOFs: Y-*fum*-fcu-MOF (~4.7 Å)[96]; NbOFFIVE-1-Ni MOF (3–5 Å)[97]; SIFSIX-3-Ni MOF (5–8 Å)[170]; Zn-BTM MOF (~3.6 Å)[171]; $Zn_2(bim)_4$ MOF (~3 Å)[38]; Ni_8(5-bbdc)$_6$(m-OH)$_4$ MOF (2.9 Å)[172] MOCs: MOP-*t*Bu (4–7 Å)[173]; MMPs: Cu-CA-PEI (~8 Å)[24]	High tunability: tuned by the secondary building units and organic linkers for desired functional groups, pore sizes and pore shapes; moderate rigidity; high channel density
Microporous organic polymers, cages and related structures	COF-300 (~7.2 Å)[174]; PIM-TMN-Trip (~7 Å)[175]; AO-PIM (<7 Å)[33]; POCs (3–5 Å)[176]; CMPs (6 – 8 Å)[177]	High tunability: tuned by the monomer design; low rigidity; high channel density
Carbon molecular sieves	Open micropores (pore size: 7−20 Å) connected by slit-like ultramicropores (pore size: <7 Å)[32]	Low tunability: tuned by the precursors and conditions for pyrolysis synthesis; high rigidity; high channel density
"Top-down" created 2D nanopores	Graphene, MoS_2, and hBN: 3−76 Å[19,34]	Low tunability: tuned by etching process; moderate rigidity; low channel density
"Bottom-up" synthesized 2D nanopores	2D carbon nitride: ~3.4 Å[37]; synthesized porous graphene (<10 Å)[43]; Graphyne (4–7 Å)[44]; Stanene (~4.6 Å)[169]; 2D polymers (~ 7 Å)[46]	High tunability: tuned by monomers design; rigidity unknown; high channel density
1D nanotubes		
Carbon nanotubes (CNTs)	Single-walled carbon nanotubes (~8–20 Å)[49,125]	Moderate tunability: tuned by growth conditions and pore sites functionalization; moderate rigidity; low channel density
Organic nanotubes	Peptide-appended hybrid[4]arenes (central cavity~3 Å, side window 5–7 Å)[12]; Octylureido-ethylimidazole channels (~2.6 Å)[50]; M-phenylene ethynylene nanotubes (~6.4 Å)[51]; Helical macromolecule channels (~5.5 Å)[52]	High tunability: tuned by monomers design; rigidity unknown; low channel density
Inorganic nanotubes	Single-walled aluminosilicate nanotubes (~6.5 Å)[58]	Low tunability: tune by functionalization of channel pore sites; high rigidity; channel density unknown
2D nanochannels		
Graphene	Graphene nanofluidic channels (3.4–100 Å)[59,60]	Low tunability: tuned by channel size; high rigidity; moderate channel density
Graphene oxide	Interlayer empty space (a) of ~4.6–6.6 Å (dry) and a ~8.6 – 10.4 Å (wet)[62]	Moderate tunability: tuned by oxidation degree, nanosheet size, and interlayer functionalization; low rigidity; moderate channel density
MXenes	For $Ti_3C_2T_x$: a of ~3.5–5 Å (dry)[69,70], a of ~6 Å (wet)[71]	Moderate tunability: tuned by nanosheets size, interlayer functionalization, and different types of MXenes; low rigidity; moderate channel density
Layered double hydroxides (LDH)	$ZnAl$-NO_3 LDH: ~4.1 Å[178], $NiAl$-CO_3 LDH: ~3.1 Å[178]	High tunability: tuned by metal cations in host layers, and anions in galleries; moderate rigidity; moderate channel density
Other 2D materials	MoS_2[143]: a ~3 Å (dry), a ~9 Å (wet); hBN[72]: a <1.9 Å (dry), after functionalization, a of ~8–18.3 Å	Moderate tunability: tuned by nanosheet size, and interlayer functionalization; moderate rigidity; moderate channel density

ZIFs, Zeolitic imidazolate frameworks; BTC, benzene-1,3,5-tricarboxylate; BDC, 1,4-benzene dicarboxylate; COF, covalent organic framework; UiO: University of Oslo; RE, Rare-earth; fcu, face centred cubic; fum, fumarate; NbOFFIVE, $(NbOF_5)^{2-}$ pillars; SIFSIX, $(SiF_6)^{2-}$; Zn-BTM, $Zn_2(btm)_2$ where H_2btm is bis(5-methyl-1H-1,2,4-triazol-3-yl)methane; bim, benzimidazole; 5-bbdc, 5-tert-butyl-1,3-benzenedicarboxylic acid; MOP-*t*Bu, Cu_{24}(5-*t*Bu-1,3-BDC)$_{24}$(S)$_{24}$; CA, 4-chloroisophthalic acid; PEI, polyethyleneimine; hBN, hexagonal boron nitride;TMN, tetramethyltetrahydronaphthalene; Trip, triptycene; AO, amidoxime.

Figure captions

Figure 1. Schematics and selected materials for mass-transport through nanopores, 1D nanotubes, and 2D nanochannels. a, A schematic of nanopores (left) and the structures of NaA zeolite, ZIF-8 MOF, and all-hydrogen passivated graphene nanopore (carbon, black; hydrogen, light grey) (middle and right). **b**, A schematic of 1D nanotubes (left) and the structures of a single-wall carbon nanotube (SWCNT), a peptide-appended hybrid[4]arene (PAH[4]), and a single-walled aluminosilicate nanotube (SWANT). **c**, A schematic of 2D nanochannels (left), and the structures of selected 2D materials. Panel **a** (ZIF-8 structure) is adapted from REF. [179], Springer Nature Limited; graphene structure is adapted with permission from REF. [180], ACS. Panel **b**, SWCNT structure is reproduced from REF. [48], Springer Nature Limited; PAH[4] structures are adapted from REF. [12], Springer Nature Limited; and SWANT structure is adapted with permission of REF. [181], ACS. Panel **c**, the structures of graphene, MoS_2 and hBN are adapted from REF. [182], Springer Nature Limited; LDH structure is adapted with permission of REF. [183], Royal Society of Chemistry.

Figure 2. Techniques for the fabrication of large-area membranes. a, Solvothermal growth involves immersing the substrate in a solution containing linkers or precursors, followed by heating. Large-area zeolite membranes are possible[184]. **b**, Layer-by-layer (LBL) assembly exposes the substrate to different solutions of linkers or materials in a circular manner. LBL in spray mode can achieve improved deposition compared with immersive mode because of the better materials distribution and alignment on the substrate[185,186]. **c**, Solution-casting, followed by drying, can fabricate membranes made from polymers of intrinsic microporosity (PIMs), porous organic cages (POCs), metal-coordinating microporous polymers (MMPs), and graphene oxide (GO)[24,33,187]. The thickness of the films (down to sub-micrometre) is controlled by a doctor blade. Mixed matrix membranes (embedding the nanochannels into a polymeric matrix) can be fabricated on a large scale. **d**, In liquid/liquid interfacial growth, a porous substrate at an interface functions as the microchannels for the diffusion and reaction of linkers, and the support for the membrane layer. Covalent organic frameworks (COFs), MOFs, and PIMs membranes can be made using this method. **e**, In gas/liquid interfacial assembly, a thin film is synthesized and compressed by barriers to ensure high-density packing. The film is then transferred to a substrate. **f**, Pressure filtration makes membranes of 2D nanochannels and 1D nanotubes. **g**, Graphene films with lengths <100 m can be fabricated using chemical vapour deposition (CVD)[123]. A technique combining CVD, roll-to-roll transfer and pore-drilling treatments (such as oxygen plasma[88]) is promising for mass production of graphene membranes. MOF membranes can also be fabricated by CVD[188]. **h**, Self-assembly of biological 1D channels into nanosheets with hexagonal 2D packing requires organic solvents and amphiphilic block copolymers[189]. The section of self-assembly in the lower right corner of this figure is adapted with permission of REF. [189], Springer Nature Limited.

Figure 3. Mass-transport controlled by different mechanisms. a, Mass-transport mechanisms at different length scales. **b**, Permeability of selective transporting gases, liquids and ions through channels with different sizes. Data points are adapted from typical channels. For gas channels, zeolites (MFI): REF. [190], MOFs (ZIF-8): REF. [100], porous organic cages: REF. [105], a polymer of intrinsic microporosity synthesized by triptycene containing a tetramethyltetrahydronaphthalene unit as the extended substituent (PIM-TMN-Trip): REF. [175], carbon molecular sieves: REF. [191], porous graphene: REF. [87], graphene oxide: REF. [144], MXenes: REF. [69], MoS_2: REF. [143], layered double hydroxides: REF. [183]. For liquid channels, AQP-1: REF. [54], zeolites (MFI): REF. [192], MOFs (UiO-66): REF. [193], porous graphene: REF. [88], single-wall carbon nanotube (CNT): REF. [49], organic tubes: REF. [51], graphene oxide: REF. [126], reduced graphene oxide: REF. [194], MoS_2: REF. [73], MXenes: REF. [71]. For ion channels, K^+ channel: REF. [54], porous MoS_2: REF. [124], porous

graphene: REF. [123], MOFs (UiO-66): REF. [138], single-wall CNT: REF. [49], graphene oxide: REF. [195], van der Waals 2D channel: REF. [77], 2D crystals (transport direction vertical to the plane): REF. [152].

Figure 4. The structures and sieving behaviours of carbon molecular sieves (CMSs), graphene, and MOFs. a, The structure of CMS channels (left), a helium ion microscopy image of the CMS membrane (middle) (CMS supported by porous substrate), and a transmission electron microscopy (TEM) image (right) showing the micropore size distribution in the CMS membrane. **b**, An aberration-corrected scanning transmission electron microscopy (STEM) image of a graphene film with pore size of ~5−10 Å. **c**, A high-resolution TEM image of ZIF-8 along the [111] axis. The upper right TEM image is the CTF (contrast transfer function)-corrected and denoised image; the lower right image is the symmetry-imposed and lattice-averaged image with a structural model of ZIF-8 embedded. Plot of the corrected diffusivities in ZIF-8 at 35 °C as a function of the molecular diameter of probe molecules (right). Blue squares represent estimated diffusivities for permeation through mixed matrix membranes. Green circles represent diffusivities calculated from kinetic uptake rate measurements. **d**, A comparison of the triangular window of rare-earth-**fcu**-MOFs for gas diffusion (fcu: face-centred cubic). In the Y-*fum*-**fcu**-MOF, the linear and rigid *fum* linker (fumarate) is constrained to a fixed aperture size of ~4.7 Å. In the Eu-*naph*-**fcu**-MOF, the bulky *naph* linker (naphthalene) with its rotational naphthalene group provides a flexible aperture with a maximum opening size of ~5.0 Å. d_i shown in the panel represents the molecular diameter of iso-butane. **e**, The pores of ZIF-8 can be tuned using an electric field (left) and a comparison of C_3H_6 and C_3H_8 separation performance before and after applying an electric field. I-43m and Cm represent the space groups of the cubic and monoclinic crystal systems, respectively. *P* and *α* indicate the permeance of gas and the selectivity of C_3H_6 over C_3H_8, respectively. **f**, The structure of $Cu_2(AzoBPDC)_2(AzoBiPyB)$ with the azobenzene groups in the trans state (left) and in the cis state (right) which is tuned by light irradiation of different wavelengths. AzoBPDC: 2-phenyldiazenyl-4,40-biphenyldicarboxylic acid, and AzoBiPyB: (E)-4,40-(2-(phenyldiazenyl)-1,4-phenylene) dipyridine. Panel **a** is adapted with permission from REF. [27], AAAS; Panel **b** is adapted from REF. [88], Springer Nature Limited. Panel **c** (left) is adapted from REF. [91], Springer Nature Limited. Panel **c** (right) is adapted with permission from REF.[196], ACS. Panel **d** adapted from REF. [96], Springer Nature Limited. Panel **e** adapted with permission from REFs [101,197], AAAS. Panel **f** is reproduced from REF. [102], Springer Nature Limited, CC-BY-4.0 (http://creativecommons.org/licenses/by/4.0/).

Figure 5. Controlling of 2D nanochannels structures. a, A schematic of 2D channels formed by van der Waals assembly (left). A high-magnification TEM image of the 2D van der Waals MoS_2 channel near its left edge, each bright horizontal line corresponds to a monolayer of MoS_2 (right). **b**, A schematic of the transport of water molecules and ions from top to down through physically-confined graphene oxide (GO) channels (left). Water molecules are shown in red and grey, ions are shown as green or blue spheres with a hydration circle. An optical micrograph of the cross-section of physically-confined GO channels, marked by a red rectangle showing 100-μm-thick GO laminates embedded in epoxy (middle). A scanning electron microscopy (SEM) image (right) of the marked region in the optical micrograph. **c**, A schematic of how K^+ ions in GO channels determine the interlayer spacing such that other cations are rejected while pure water can penetrate (left). Yellow pillars between the GO sheets depict the fixation of interlayer spacing by hydrated K^+. Upper right, the change of interlayer spacing before and after controlled by KCl. Dashed line indicates the interlayer spacing of GO membrane controlled by KCl. Lower right, Na^+, Ca^{2+} and Mg^{2+} permeation rates of GO membranes before and after controlled by KCl. Dashed lines indicate the detection limits of the different cations. **d**, A schematic of crosslinking GO channels, and the change of interlayer spacing. EDA, BDA, and PPD are crosslinking monomers of ethylenediamine, butylenediamine, and

p-phenylenediamine, respectively. **e**, A schematic of smart GO channel intercalated by poly(N-isopropylacrylamide) (polyNIPAM). Panel **a** is adapted from REFs.[61,198], Springer Nature Limited. Panel **b** adapted from REF.[108], Springer Nature Limited. Panel **c**, the schematic illustration and data are adapted from REF.[107], Springer Nature Limited.

Figure 6. Controlling channel structure and transport behaviour by surface, electrical and chemical effects. a, Surface effects with 1D water transport through a carbon nanotube (left); 2D monolayer of water and ion transport through graphene channels (middle); and surface friction and heterostructure effects of 2D nanochannels (right). **b**, Electrical effects with 1D CNT channels enables ion diodes based on electrostatic repulsion (left), tuning of the surface properties of 2D graphene oxide (GO) channels (middle), and water and ion transport tuned by applied electric potential (right). **c,** Chemical effects**.** Hydrogen-bonding between a $Fe_2(O_2)(dobdc)$ metal-organic framework nanopore and ethane molecules (left). $dobdc^{4-}$: 2,5-dioxido-1,4-benzenedicarboxylate. CO_2 facilitated transport by π-complexation interaction enabled by modification of Zn ions on the surface of CNTs (middle). Tunable molecular gas transport via polyethylenimine (PEI) and potassium tetraborate ($K_2B_4O_7$) modifying MXene ($Ti_3C_2T_x$) channels (right). Panel **a** (left) adapted with permission of REF. [49], AAAS. Panels **a** (middle, right) are adapted from REFs. [77,122], Springer Nature Limited. Panel **b** (left) is adapted with permission of REF.[128], AAAS. Panel **b** (middle) adapted from REF.[126], Springer Nature Limited, CC-BY-4.0 (http://creativecommons.org/licenses/by/4.0/). Panel **c** (left) adapted with permission of REF. [136], AAAS. Panel **c** (right) adapted with permission of REF. [70], Wiley-VCH.

Figure 7. Mass-transport controlled by quantum effects. a, The densities of the electron clouds around graphene, hexagonal boron nitride (hBN) and MoS_2 reveal successively lower porosities. **b**, A schematic of the energy barrier of a 2D crystal for proton and deuteron transport (out-of-plane direction). **c**, The ratio of the resistances of entry into the van der Waals channels (0.5 µm in length) for protons and deuterons (left), dashed lines indicate the average resistance ratio and the shaded areas show the standard errors for hBN and MoS_2 channels. A schematic of the entry mechanism (right). **d**, The intrinsic roughness of atomically flat surfaces (left), grey scale, electron density near graphene and MoS_2 surfaces; red curves, depth accessible for helium atoms with thermal energies. The dependence of helium transport on channel length (right), with interlayer empty space of 13.4 Å, the insets illustrate diffusive (top) and specular (bottom) scattering for MoS_2 and graphite, respectively. The data for MoS_2 are multiplied by 1,000 and the data for graphite are original. **e**, A schematic of the coupling of phonon modes of a carbon nanotube and water flow. The phonon modes of a carbon nanotube can transfer momentum to the confined water, and hence, the diffusion of water molecules is enhanced. **f**, Time traces of the photocurrent, according to the light illumination applied separately on three different positions (right, middle, or left). Panel **a** is adapted from REF. [154], Springer Nature Limited. Panel **b** adapted with permission of REF. [152], AAAS. Panel **c** is adapted from REF. [76], Springer Nature Limited. Panel **d** is adapted from REF. [61], Springer Nature Limited. Panel **e** is adapted from REF. [157], Springer Nature Limited. Panel **f** is adapted from REF. [159], Springer Nature Limited, CC-BY-4.0 (https://creativecommons.org/licenses/by/4.0/).

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