

## 2D materials as an emerging platform for nanopore-based power generation

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**Abstract** | Osmotic power generation, the extraction of power from mixing salt solutions of different concentrations, can provide an efficient power source for both nanoscale and industrial-level applications. Power is generated using ion-selective channels or pores of nanometric dimensions in synthetic membrane materials. 2D materials such as graphene and MoS<sub>2</sub> provide energy extraction efficiencies that are several orders of magnitude higher than those of more established bulky membranes. In this Review, we survey the current state of the art in power generation with both 2D materials and solid-state devices. We discuss the current understanding of the processes underlying power generation in boron nitride nanotubes and 2D materials, as well as the available fabrication methods and their impact on power generation. Finally, we overview future directions of research, which include increasing efficiency, upscaling single pores to porous membranes and solving other issues related to the potential practical application of 2D materials for osmotic power generation.

Modern society, industry and research require ever increasing amounts of electrical power. With fossil fuel supplies shrinking<sup>1,2</sup> (*Annual Energy Outlook 2019*) and nuclear power facing negative public opinion<sup>3–5</sup>, researchers are turning their attention to the establishment of efficient and sustainable energy sources that could be both safe and ecological.

Besides solar and wind power, another type of energy is especially attractive<sup>6–8</sup>: that generated from water. Beside well-known hydropower generated by hydroelectric power plants (dams), scientists and engineers are exploring tidal energy, which exploits ocean waves friction to generate electricity (with triboelectric networks<sup>9–11</sup>), and blue energy<sup>12</sup>, which takes advantage of salinity gradients to harvest so-called osmotic energy. Blue energy (also known as osmotic or salinity gradient energy) — the extractable free energy of mixing of a concentrated salt solution with pure water — is promising, because the energy harvesting yield from mixing freshwater and seawater is estimated to be 3 kJ per litre mixed, which is equivalent to 0.8 kWh m<sup>–3</sup>, that could be harvested by prospective power generators<sup>13</sup>. The general estimate for the global potential of this energy source (*World Energy Resources 2016*) reaches up to thousands of terawatt hours<sup>14–18</sup>, with the possible added benefit of the integration of water desalination plants and, in certain cases, of mineral harvesting processes. Given the amount of freshwater and saltwater mixing sites on our planet (both natural and manmade, such as brines and wastewater), there is a huge potential

to develop a new, ecological and abundant source of energy. However, current prototypical implementations of osmotic energy generation give an energy production in the range of 1–5 W m<sup>–2</sup> (REFS<sup>19–23</sup>), which is not enough to power real-world devices<sup>24</sup>.

There are two general approaches to harvesting energy with membranes. Pressure-retarded osmosis (PRO)<sup>25–29</sup> uses a membrane permeable only to water to move water between a salty and a freshwater reservoir to decrease the concentration of salt (and increase the entropy), producing osmotic pressure that drives a turbine and, thus, generates power. Several implementations of PRO power plants were tested, but none had sufficient profit margins, giving a maximum of ~5 W m<sup>–2</sup> of generated power<sup>19–21</sup>. The second, more promising approach for power generation upscaling is osmotic energy harvesting using reverse electrodialysis (RED)<sup>30–36</sup>. In this concept, an ion-selective membrane is used between the salty and freshwater reservoir with minimal water flow. Owing to the ion selectivity of the membrane, the current of one type of ion is larger, producing a charge non-neutrality between the reservoirs that can be harnessed as a battery. The main bottleneck of both PRO and RED technologies lies in the low achievable power density<sup>24</sup> and high energy costs related to water pretreatment (to remove bulk particles and contamination that might clog the membrane) and pumping, as well as the intrinsic trade-off between energy harvesting efficiency and achievable power output<sup>37,38</sup>. Making these technologies practically useful requires

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producing novel, highly efficient membrane materials, which, ideally, should be semi-permeable and ion selective (for RED), allow good water fluxes (for PRO), not be susceptible to fouling or clogging (thus lowering the energy cost of water pretreatment) and have good mechanical stability and durability to endure the working environment<sup>37–41</sup>.

Several challenges face the field of membrane technologies for desalination and power generation<sup>42–45</sup>. Issues such as selectivity, material durability in aqueous conditions and fouling were taken into consideration to test and develop new membrane structures based on advanced materials, including novel ceramics<sup>46–52</sup>, polymers<sup>53–57</sup>, composites<sup>58–62</sup> and porous nanomaterials, such as nanotubes<sup>63–67</sup>, metal–organic frameworks (MOFs)<sup>62,68,69</sup>, stacked nanoflakes<sup>70–74</sup> and, finally, thin suspended films<sup>39,75–82</sup>. These materials were developed and tested in various configurations, including bulk intrinsically porous structures, precisely microfabricated nanochannels or nanopores on membranes (solid-state nanopores), stacked nanotubes and atomically thin, freestanding 2D materials (2D nanopores), which are now in the spotlight for blue energy harvesting.

The most substantial increase in generated power density was obtained by using nanotubes and then atomically thin materials. In 2013, the well-defined geometry of boron nitride nanotubes (BNNTs) was exploited to demonstrate power densities that could reach up to  $4\text{ kW m}^{-2}$  in a RED configuration in laboratory conditions<sup>83</sup>. Then, in 2016, the 2D material  $\text{MoS}_2$  was used to fabricate three-atom-thick membranes<sup>78</sup> that reached a power of  $\sim 1\text{ MW m}^{-2}$ . These results demonstrate improvements of orders of magnitude as compared with previously reported, ‘thick’ solid-state membranes, making thin nanomaterials (particularly 2D materials) especially promising for osmotic energy harvesting applications<sup>84</sup>. It remains to be clarified what are the underlying physical phenomena that make 2D materials so efficient in osmotic power generation, and how the material properties can be tuned to optimize efficiency and tackle practical issues with in-lab membranes.

To explore the role of 2D materials and their properties in osmotic power generation using RED, we first introduce the fundamental underlying phenomena and concepts, and then review relevant materials, starting with thick membrane materials before focusing on nanotubes and 2D materials and their properties. After surveying fabrication methods and important results on single-pore systems, we expand on avenues for the wafer-scale production of porous membranes for RED. Finally, the current challenges are discussed, including manufacturing methods, chemical and mechanical robustness, and upscaling to whole membranes.

### Understanding power generation

Most research on 2D materials as a platform for power generation membranes has focused, so far, on single pores under so-called laboratory conditions, with the aim to understand and characterize the important materials parameters. In laboratory conditions, one is constantly working at a fixed gradient, as the real total energy density per unit area is low, implying that the two solutions

do not have the opportunity to significantly mix, unlike in large-scale applications<sup>85</sup>.

Efficient power generation using ion-selective membranes demands optimizing three parameters<sup>86</sup>: the resistivity of the membrane, which must be reduced under gradient conditions; the selectivity of the membrane to anions or cations, which must be maximized; and the molar water permeation, which must be low so that there is minimal water flux from the high-concentration to the low-concentration chamber. In this section, we discuss the role of single-pore parameters in making efficient RED membranes, with an emphasis on selectivity and membrane resistance.

A typical design of an osmotic power generator involves a salinity difference between two reservoirs separated by a membrane, with a single pore providing a pathway for ions between the reservoirs (FIG. 1a,b). Assuming a linear response, an internal electromotive force  $\varepsilon_{\text{osm}}$  (the osmotic potential) produces a driving force through the pore with conductance  $G_{\text{osm}}$ , which generates an osmotic current  $I_{\text{osm}}$  (REFS<sup>50,87,88</sup>). When taking electrical measurements to characterize the system, one usually obtains current–voltage characteristics (FIG. 1c) with a distinct offset: a non-zero, open-circuit voltage  $\varepsilon_{\text{osm}}$  and a non-zero, closed-circuit current  $I_{\text{osm}}$ . The two electrodes have an inherent potential difference due to redox potentials that we ignore here; it is usually subtracted from measurement values<sup>50</sup> or experimentally eliminated using salt bridges on the electrodes<sup>89</sup>. What remains are the driving electromotive force  $\varepsilon_{\text{osm}}$  and the response function to this force, which we call osmotic conductance,  $G_{\text{osm}}$  (which is different from the membrane conductance  $G_{\text{m}}$  in the absence of a salt gradient between the reservoirs). In a naive picture, the resistance of a porous membrane comes from the parallel connection of pores with individual resistances  $G_{\text{m}}^{-1}$ . The higher the individual osmotic conductance of the pores, the more osmotic power is produced by the membrane under the same driving concentration gradient.

The driving force for osmotic power generation comes from the mixing of two solutions, one with a high concentration of salts  $c_{\text{h}}$  (salty water) and one with a low concentration of salts  $c_{\text{l}}$  (freshwater). In ideal solutions, the net flux of an ion species of valence  $z_i$  and diffusion constant  $D_i$  is given by the Nernst–Planck equation:

$$J_i = -D_i \left[ \nabla c_i + \frac{z_i e c_i}{k_B T} (\nabla \phi) \right] + c_i v_i \quad (1)$$

where the first term comes from the concentration gradient (diffusion), the second term from an electric field gradient (drift) and the last term is related to convection. In this section, we ignore liquid flow effects, leaving this discussion for the sections on nanotubes and 2D materials, and focus on symmetric salt solutions of valence  $\pm z$ . In a membrane with a pore (or channel) between the two sides, a net ion flux flows owing to the concentration gradient (FIG. 1d–f). Neglecting fluid flow and requiring charge neutrality, we find that a local electric field proportional to the logarithm of the local ion concentration

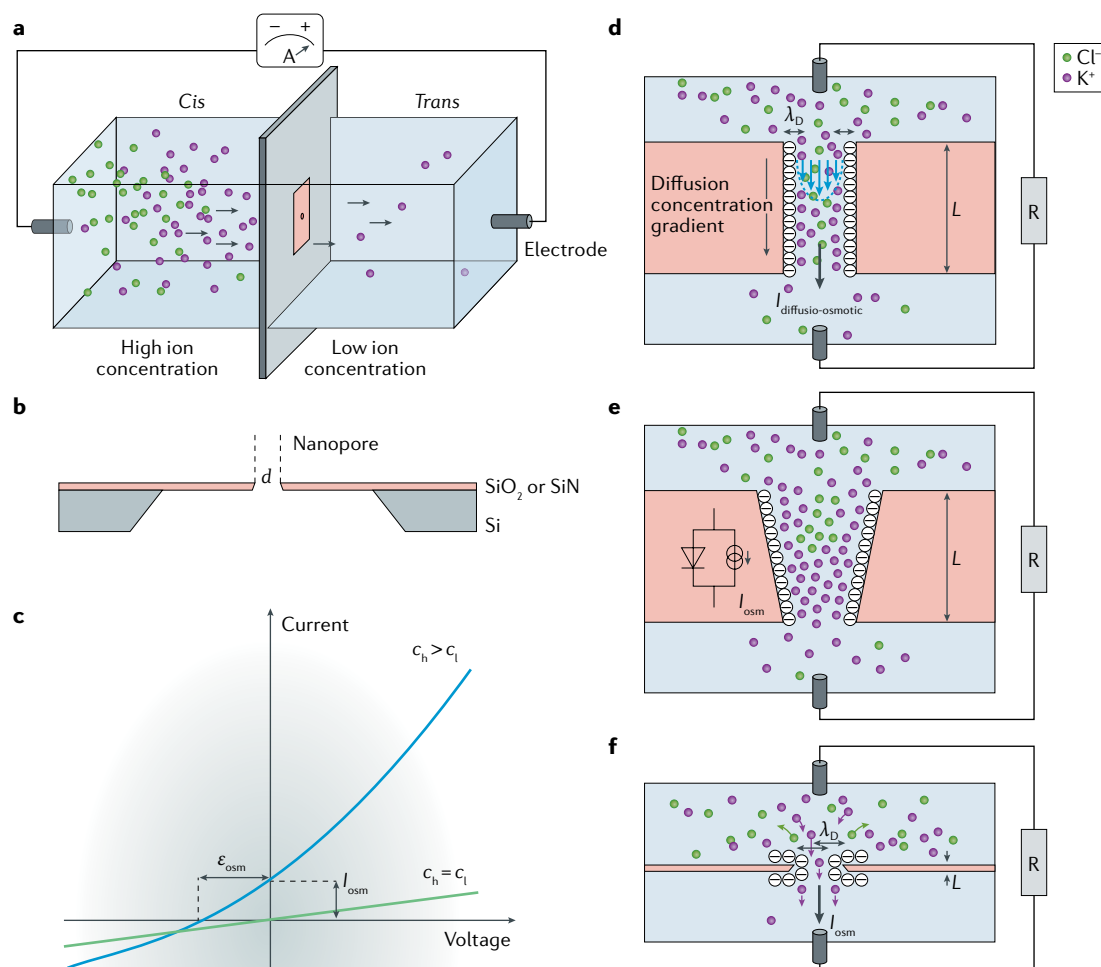


Fig. 1 | **Typical solid-state nanopore devices.** **a** | A thin membrane is placed between two reservoirs with a salt gradient that are connected via Ag/AgCl electrodes. **b** | The most commonly used design consists of etched, freestanding porous membranes of either SiN or SiO<sub>2</sub>, which can also act, in more complex experiments, as a supporting window for suspending monoatomic layers of flat materials with nanopores. **c** | Typical measured current–voltage curves under no osmotic gradient (green curve) and under an osmotic gradient (blue curve). **d–f** | Different ways to obtain power generation: a regime with salinity gradient (panel **d**), which causes a diffusio-osmotic flow, with the velocity profile inside the channel dragging the charges; an asymmetric nanopore cross section (panel **e**), which can result in an ionic current rectification behaviour; and a flat 2D membrane (panel **f**).  $\epsilon_{\text{osm}}$ , osmotic potential;  $c_h$ , concentration of the more salty solution;  $c_l$ , concentration of the less salty solution;  $I_{\text{osm}}$ , osmotic current;  $L$ , membrane thickness.

$E \approx \nabla \log(c(r))$  is produced to counteract the ion flux<sup>90</sup>. If we calculate the electric potential difference between the two sides of the membrane as measured by the electrodes, neglecting any fine effects related to the pore and differences in ion activities, we find that the osmotic electrostatic potential difference can be approximated as<sup>50</sup>:

$$\epsilon_{\text{osm}} = \frac{k_B T}{ze} S \ln \frac{c_h}{c_l} \quad (2)$$

where  $S = (D_+ - D_-)/(D_+ + D_-)$  describes the ion selectivity of the system;  $D_{\pm}$  is an effective diffusion constant, and  $k_B T/e \approx 25.7$  mV at 25 °C. We note that, if the effective diffusion constants of the cation and anion are the same, and there is no significant deviation from the ideal behaviour (which is usually manifested by a difference in the activity coefficients of different ions), there is no driving force for osmotic power and all the Gibbs free energy of mixing dissipates into heat. If the pore is ion

selective, then the flux of one charged ion species is larger than that of the other and produces a non-zero, short-circuit electrical potential difference, thus converting some of the Gibbs free energy of mixing into harvestable power<sup>87,91</sup>. A more general, model-independent way of defining the ion selectivity of channels is via the electrical current  $I_{\pm}$  carried by the two different ion species<sup>92</sup>, or via ion permeability,  $P_{\pm}$ , as:

$$S = \frac{I_+ - I_-}{I_+ + I_-} = \frac{P_+ - P_-}{P_+ + P_-} \quad (3)$$

which gives  $S = 1$  for a completely cation-selective channel,  $S = -1$  for an anion-selective channel and  $S = 0$  in case of no selectivity.

Eq. 2 provides insight, but it overestimates the osmotic potential at high salt gradients and selectivity, so care should be taken when comparing it with experimental results. A better model is based on the Goldman–Hodgkin–Katz

(GHK) voltage equation (here written for symmetric, monovalent salt solutions), which is valid for a constant electric field inside the pore<sup>93</sup>:

$$\varepsilon_{\text{osm}} = \frac{k_{\text{B}}T}{e} \ln \left( \frac{P_{+}c_{\text{h}} + P_{-}c_{\text{l}}}{P_{+}c_{\text{l}} + P_{-}c_{\text{h}}} \right) \quad (4)$$

with  $P_{\pm} = K_{\pm} D_{\pm}/L$  the permeability and  $K_{\pm}$  the partitioning coefficient in the pore<sup>93</sup>. The GHK voltage equation reduces to the Nernst equation for a perfectly selective pore. The Nernst potential in this case represents the maximal driving potential for osmotic power. In nature, water solutions contain a mix of different ions ( $\text{Cl}^{-}$ ,  $\text{Na}^{+}$ ,  $\text{Mg}^{2+}$ ,  $\text{SO}_4^{2-}$ ,  $\text{Ca}^{2+}$ ,  $\text{K}^{+}$ , ...) that can adversely influence RED performance; for example, multivalent ions have a low osmotic driving potential and can produce adverse effects such as uphill charge transport<sup>94</sup>.

### Ion selectivity

Ion selectivity under a salt gradient and its response to the driving force  $G_{\text{osm}}$  define the extracted osmotic current and, thus, power. Both are related to the characteristic length scales of the electrostatic screening and surface charges. The electrostatic screening length  $\lambda_{\text{D}}$ , also called the Debye length, determines the effective range of electrostatic interactions in the solution and is larger at smaller local salt concentrations. Owing to surface chemistry effects, all interfaces between solid materials and water have a certain surface charge density, which is usually also dependent on the local salt concentration and pH<sup>95</sup>. Aqueous salt solution tends to screen out these surface charges, forming a double layer on the surface with an increased local salt concentration. Charged ions in the solution will be repelled from the surface, producing local variations in the total charge. These local variations of ion concentration, coupled with the sample geometry, are responsible for selectivity and partially for osmotic conductance. Good selectivity is achieved when the characteristic length scale of the screened surface charge is comparable to the physical dimensions of the pore or if there is such a high level of confinement that the size of the ion hydration layer becomes relevant<sup>96–99</sup>. In general, selectivity increases with smaller pore sizes, longer pore or channel lengths and higher densities of surface charges on the pore walls<sup>87,92</sup>. Selectivity directly influences one important performance parameter, the energy conversion efficiency  $\phi$ .  $\phi$  is defined as the ratio between the Gibbs entropy of mixing and the extracted power, and is proportional to the square of the selectivity ( $\phi = S^2/2$ )<sup>50,91</sup>. Thus, one of the design strategies for 2D nanopore power generators is to maximize their ionic selectivity by decreasing the pore size and increasing the surface charge, although the atom-sized thickness would be expected to reduce the selectivity.

### Osmotic conductance

Maximizing the osmotic conductance is another design requirement, as this determines the extracted power density. The maximal power density of a membrane is defined as the maximal power divided by the surface area of the membrane; thus, to calculate it, single pore values

have to be extrapolated to the membrane scale assuming a certain maximal achievable pore density. The maximal power that can be extracted is  $P_{\text{max}} = 1/4 G_{\text{osm}} \varepsilon_{\text{osm}}^2$  when the power is transmitted to an external load with the same resistance as the power generator,  $G_{\text{osm}}^{-1} = R_{\text{L}}$ , and depends on both the osmotic conductivity and osmotic driving potential (selectivity)<sup>50,88</sup>. Even if the energy of mixing is efficiently converted, the power still needs to be transferred to an external load or it will dissipate within the system, for example, through current backflow through the pore. The ideal pore does not allow current backflow, behaving as an electrical diode with no resistance in the forward direction and infinite resistance in the backward direction. Such an ideal rectifying ionic power generator might be made to generate power depending only on the load<sup>84</sup>  $P_{\text{max}} \approx R_{\text{L}} I_{\text{osm}}^2$ . A high level of ionic current rectification  $r$ , defined as the ratio of the current at forward bias  $V$  to the current at reverse bias  $-V$ ,  $r = |I(V)|/I(-V)$ , is needed, particularly as the porosity of membranes for power generation is increased, thus decreasing their resistance to backflow. Ionic current rectification can be achieved in systems with an asymmetric geometry (FIG. 1e) or surface charge distribution<sup>100</sup>, and has been demonstrated in conditions of concentration gradients<sup>101,102</sup>. It is known that, in some conditions, ionic current rectification can be destroyed by hydraulic pressure<sup>103,104</sup>, but the influence of osmotic pressure is not yet completely understood. Importantly, ionic current rectification is accompanied by ion selectivity<sup>105</sup> and could be used to further enhance osmotic power generation using RED with 2D materials<sup>106</sup>.

Little systematic modelling has been done on the values of osmotic conductance and on its dependence on different parameters. It is known that, in long channels, the osmotic conductance is independent of the concentration gradient for pore sizes smaller than the Debye length, whereas for larger pores, it increases with increasing concentration gradients<sup>87,88</sup>. In the case of 2D materials, there are, to our knowledge, no detailed studies of these effects, so we have to relate the osmotic conductance to the conductance under no salinity gradients. Neglecting finite-size effects of ions, the conductance of a pore under symmetric salt concentrations can be approximated<sup>107–110</sup> as a combination of bulk surface conductance  $G_{\text{bulk}}$  and pore surface conductance  $G_{\text{s}}$ , so that the total conductance is  $G_{\text{bulk}} + G_{\text{s}} = \kappa \pi d^2/4L + \kappa_{\text{s}} \pi d/L$ , with  $\kappa$  the bulk conductivity,  $\kappa_{\text{s}}$  the surface conductivity and  $d$  and  $L$  the diameter and length of the pore, respectively.  $G_{\text{bulk}}$  and  $G_{\text{s}}$  are connected in series with two access resistances  $G_{\text{ac}}^{-1} = (d\kappa)^{-1}$ , leading to a total resistance of the pore  $G^{-1} = (G_{\text{bulk}} + G_{\text{s}})^{-1} + G_{\text{ac}}^{-1}$ . The access resistance is determined by the conductance of the region where the current converges towards the pore (which can be approximated as a hemisphere of diameter  $d$ ). The contribution of the surface conductivity with respect to the bulk conductivity is defined through the so-called Dukhin length,  $l_{\text{Du}} = \kappa_{\text{s}}/\kappa$ , which can be approximated as  $l_{\text{Du}} \approx |\Sigma|/2ec$ , where  $\Sigma$  is the surface charge density. In case of small salt concentrations, the surface charge can dominate and even modify the access resistance, as the semi-spherical cupola is influenced by the spatial

extent of the double layer, which leads to the following equation, which includes both effects<sup>111</sup>:

$$G = \kappa \left( \frac{4L}{\pi d^2} \frac{1}{1 + 4l_{Du}/d} + \frac{2}{\alpha d + \beta l_{Du}} \right)^{-1} \quad (5)$$

with  $\alpha \approx \beta \approx 2$ . This equation correctly accounts for the pore conductivity for a salt concentration of interest, but was never extended to salt gradient conditions. For nanopores in 2D materials, the access resistance is the most important contribution to the osmotic conductance, especially as the pore size decreases. In nanopores with diameters smaller than 2 nm, ion hydration effects and pore edge interactions can also contribute and provide strong nonlinear effects<sup>96–99,112</sup>, invalidating this simplified analytical model. Special care needs to be taken when extrapolating finite-element models to model 2D materials with pores in the nanometre range, as continuum modelling is expected to fail at these length scales<sup>95</sup>. We can conclude that larger pores in thinner materials increase the osmotic conductance, a competing requirement with that for small and long pores needed for high selectivity. In both cases, high levels of surface charge increase the energy extraction efficiency and power density.

### Materials for osmotic power generation

Most research on nanopore devices for blue energy harvesting emerged indirectly from research on membrane-based desalination devices<sup>18,31,43</sup> and solid-state nanopore biosensors<sup>81,113–120</sup>. The similarities in core concepts such as water permeability, ion selectivity, general stability and performance in aqueous solution lead to similar design across these devices. When considering osmotic power generators, one has to take into account general material properties such as mechanical durability under water pressure, pore edge termination, surface charges and fabrication protocols, which dictate the potential of practical usability and scalability. As opposed to conventional membrane technologies for power generation, 2D nanopore generators are still in the initial stages of research; hence, experiments are usually performed in a controlled, laboratory environment, and mostly with cation-selective membranes.

Typical nanopore devices are tested with either intrinsically porous materials, which directly yields the power density per membrane area, or with artificially made single or multiple nanopores or nanochannels. Because the power density is often used as a benchmark, single-pore measurements are usually parallelized and the results extrapolated to the theoretically achievable power density for a pore array with a certain porosity. The parameters and performance of different membranes, including commercial, solid-state and 2D membranes, are compared in TABLE 1. Their power densities are summarized in FIG. 2.

### Solid-state nanopores

Before the advent of 2D materials, most of the reported osmotic energy harvesting devices were based on nanofluidic channels and solid-state pores. Solid-state porous membranes are made of various materials, such

as stacked graphene oxide (GO)<sup>80,82,89,121,122</sup> flakes, zeolites<sup>123–125</sup> and single or aligned nanotubes<sup>83,126–130</sup>. Most of the solid-state nanopore devices for which power generation was reported are based on polymer<sup>57–59,62,131–133</sup>, silica and alumina membranes<sup>49–51,134–138</sup> (FIG. 3).

Polymer-based devices are typically obtained via ion irradiation, ion track etching of polyamide membranes or by using commercially available perfluorinated ion-exchange membranes<sup>55</sup> (Nafion 117; FIG. 3a). These fabrication methods often yield pores with asymmetric cross-sections<sup>57,133,139</sup>, which can lead to ionic diode behaviour, significantly enhancing energy harvesting. Furthermore, polymer membranes can show rich chemistry and enable unique designs, such as two-sided Janus membranes made of two different materials (such as polymer–polymer<sup>58,59,62</sup> or porous alumina–polymer<sup>138</sup>), often with different pore geometries and ion selectivity. So far, reported power densities of single polymeric membranes were in the range 2–20 W m<sup>−2</sup>, with pores of diameters from 10 nm to 50 nm (REFS<sup>56,57,91,132</sup>). The downside of this approach lies in its material limitations: the membrane thickness (directly linked to harvestable power) is usually in the range of micrometres<sup>55,56,139</sup> and can rarely be lower than 500 nm (REF.<sup>140</sup>), which limits the osmotic conductivity. Pore-etching techniques enable vast ranges of pore densities but also yield a pore size distribution, thus resulting in a lack of precise control over the device geometry. Other often investigated materials for power generation are porous alumina and silica<sup>49–51,134–138</sup> (FIG. 3b). Membranes made of these materials are intrinsically porous and have charged surfaces in solution. With present fabrication methods, it is possible to create columnar, uniform pore structures ranging from 4 nm to 200 nm in diameter, with an intrinsic porosity of up to 10<sup>11</sup> pores cm<sup>−2</sup>. However, the minimal thickness of these membranes is limited, ranging from 100 nm (REF.<sup>141</sup>) to tens or hundreds of microns<sup>49,52</sup>, leading to a bulk regime rather than a 2D regime. Reported power densities do not exceed 10 W m<sup>−2</sup>. A significant power increase, up to 945 W m<sup>−2</sup>, can be achieved by deliberately combining pores with a conical cross section with high surface charges<sup>133</sup> (for example, using polymer coatings inside pores). Such membranes exhibit extremely high power densities but are inherently limited by the base diameter of the conical pores (often in the range of a few microns<sup>57,133,139</sup>, which limits the effective pore density) and membrane thickness (limiting base osmotic conductance). All these findings indicate that, to improve the energy yield, it is necessary to increase the power density, as the energy conversion efficiency  $\phi$  is already approaching the theoretical maximum of 50%. Clearly, the osmotic conductance in such systems is small. Assuming that the non-gradient nanopore conductance scaling is valid in the osmotic gradient condition, the thickness of the membrane becomes an important factor for increasing the osmotic conductance, as the bulk conductance dominates in solid-state systems,  $G_{\text{osm}} \approx G_{\text{bulk}} = \kappa \pi d^2 / 4L$ . A good strategy could be to reduce the channel length or harness alternative conductance mechanisms, for example, by harnessing an increase of conductance from fluid flow in gradient conditions.



Table 1 | Properties and performance of different platforms for osmotic power generation

| Material                                    | Pore diameter                 | Pore Length       | Porosity                                                 | pH  | Type of experiment   | Power density at specific salt concentration                                | Power per pore                | Osmotic conductivity per pore | Electro-kinetic energy conversion efficiency | Refs  |
|---------------------------------------------|-------------------------------|-------------------|----------------------------------------------------------|-----|----------------------|-----------------------------------------------------------------------------|-------------------------------|-------------------------------|----------------------------------------------|-------|
| <b>Commercial applications</b>              |                               |                   |                                                          |     |                      |                                                                             |                               |                               |                                              |       |
| Statkraft PRO power plant                   | –                             | –                 | –                                                        | –   | –                    | 1 W m <sup>-2</sup>                                                         | –                             | –                             | –                                            | 19    |
| Mega-ton PRO power plant                    | –                             | –                 | –                                                        | –   | –                    | 13 W m <sup>-2</sup>                                                        | –                             | –                             | –                                            | 20    |
| Global MVP project                          | –                             | –                 | –                                                        | –   | –                    | 5 W m <sup>-2</sup>                                                         | –                             | –                             | –                                            | 21    |
| REAPower RED power plant                    | –                             | –                 | –                                                        | –   | –                    | 0.83 W m <sup>-2</sup>                                                      | –                             | –                             | –                                            | 22,23 |
| <b>Solid-state pores</b>                    |                               |                   |                                                          |     |                      |                                                                             |                               |                               |                                              |       |
| Silica                                      | 4 nm × 25 µm                  | 140 µm (Channels) | Nano-channels <sup>a</sup>                               | 5.6 | Experimental studies | 7.7 W m <sup>-2</sup><br>0.0001/1 M                                         | 0.16 pW<br>0.1/1 mM           | 73.4 pS                       | 31%                                          | 50    |
|                                             | 2–3 nm                        | 90 nm             | 4 × 10 <sup>12</sup> pores cm <sup>-2</sup>              | ~7  | Experimental studies | 0.024 W m <sup>-2</sup><br>0.01/0.5 M                                       | 6 × 10 <sup>-7</sup> pW       | 1.53 fS                       | –                                            | 141   |
| Porous alumina                              | 10–100 nm                     | 4 µm              | 10 <sup>8</sup> –10 <sup>9</sup> pores cm <sup>-2</sup>  | 5.4 | Numerical studies    | 9.9 W m <sup>-2</sup><br>0.001/0.1 M                                        | 0.14 pW<br>0.1/1 mM           | 256.8 pS                      | –                                            | 52    |
|                                             | 10 nm                         | 60 µm             | 1.18 × 10 <sup>11</sup> pores cm <sup>-2</sup>           | 5.4 | Experimental studies | 542 nW <sup>b</sup><br>10/100 mM                                            | –                             | –                             | –                                            | 51    |
|                                             | 100 nm                        | 60 µm             | 1.2 × 10 <sup>9</sup> pores cm <sup>-2</sup>             | 5.4 | Experimental studies | 0.98 mW m <sup>-2</sup><br>0.1/10 mM<br>0.59 mW m <sup>-2</sup><br>0.1/1 mM | 4.9–8.2 × 10 <sup>-5</sup> pW | 150–360 fS                    | 16%                                          | 49    |
|                                             | 200 nm                        | 60 µm             | 1.2 × 10 <sup>9</sup> pores cm <sup>-2</sup>             | –   | Experimental studies | 17.3 mW m <sup>-2</sup><br>0.017/0.51 M                                     | 1.5 × 10 <sup>-3</sup> pW     | 4.9 pS                        | –                                            | 246   |
| Alumina with porous carbon (Janus membrane) | 7/80 nm                       | 4.2 µm            | 10 <sup>9</sup> –10 <sup>10</sup> pores cm <sup>-2</sup> | ~7  | Experimental studies | 3.46 W m <sup>-2</sup><br>0.01/0.5 M                                        | 3.5 × 10 <sup>-2</sup> pW     | 87.9 pS                       | 37.30%                                       | 138   |
| PSS/MOF                                     | 60 nm                         | 85 µm             | 10 <sup>12</sup> pores cm <sup>-2</sup>                  | 11  | Experimental studies | 2.87 W m <sup>-2</sup><br>0.01/0.5                                          | 5.8 × 10 <sup>-4</sup> pW     | 472.9 fS                      | ~30%                                         | 62    |
| PCTE                                        | 15 nm                         | 20 µm             | –                                                        | 5.6 | Experimental studies | 58 mW m <sup>-2</sup><br>0.001/1 M                                          | 2.9 × 10 <sup>-4</sup> pW     | 729.7 fS                      | –                                            | 244   |
| Conical polymer pores                       | 10–50 nm (tip); 2 µm (base)   | 12 µm             | 10 <sup>8</sup> –10 <sup>9</sup> pores cm <sup>-2</sup>  | 5.6 | Experimental studies | 0.2 W m <sup>-2</sup><br>0.001/1 M                                          | 26 pW                         | 21.2 nS                       | 4%                                           | 56    |
|                                             | 10–40 nm (tip); 1.5 µm (base) | 12 µm             | Single pore                                              | 5.6 | Experimental studies | –                                                                           | 45 pW<br>0.001/1 M            | 36.7 nS                       | –                                            | 91    |
|                                             | 30–300 nm (tip); >1 µm (base) | 6 µm              | 2 × 10 <sup>6</sup> pores cm <sup>-2</sup>               | 7.6 | Experimental studies | 0.078 W m <sup>-2</sup><br>0.01/0.5 M                                       | 25 pW                         | 20.4 nS                       | –                                            | 176   |
|                                             | 400 nm (tip); 2 µm (base)     | 11 µm             | 10 <sup>6</sup>                                          | 6   | Experimental studies | 945 W m <sup>-2</sup><br>1/500 mM                                           | 120 pW                        | 120.1 nS                      | –                                            | 133   |
| Polymer Janus membrane                      | 10/17 nm                      | 500 nm            | –                                                        | 4.3 | Experimental studies | 0.7 W m <sup>-2</sup><br>0.01/0.5 M                                         | 7.0 × 10 <sup>-3</sup> pW     | 17.8 pS                       | 17.50%                                       | 58    |
|                                             | 9/18 nm                       | 11 µm             | 10 <sup>10</sup> pores cm <sup>-2,c</sup>                | ~8  | Experimental studies | 2.66 W m <sup>-2</sup><br>0.01/0.5 M                                        | 2.7 × 10 <sup>-2</sup> pW     | 67.6 pS                       | 35.70%                                       | 59    |
|                                             | 10/50 nm                      | 12 µm             | 10 <sup>11</sup> pores cm <sup>-2</sup>                  | ~8  | Experimental studies | 0.35 W m <sup>-2</sup><br>0.01/0.5 M                                        | 3.5 × 10 <sup>-4</sup> pW     | 889.9 fS                      | –                                            | 177   |

Table 1 (cont.) | Properties and performance of different platforms for osmotic power generation

| Material                         | Pore diameter | Pore Length         | Porosity                                  | pH  | Type of experiment   | Power density at specific salt concentration           | Power per pore            | Osmotic conductivity per pore | Electro-kinetic energy conversion efficiency | Refs   |
|----------------------------------|---------------|---------------------|-------------------------------------------|-----|----------------------|--------------------------------------------------------|---------------------------|-------------------------------|----------------------------------------------|--------|
| <b>Solid-state pores (cont.)</b> |               |                     |                                           |     |                      |                                                        |                           |                               |                                              |        |
| Nafion perfluorinated membrane   | >10 nm        | 24 × 500 μm         | 10 <sup>11</sup> pores cm <sup>-2,d</sup> | 5.6 | Experimental studies | 0.7 W m <sup>-2</sup><br>0.001/2 M                     | 7.0 × 10 <sup>-4</sup> pW | 471.4 fS                      | 36%                                          | 245    |
| hBN nanotube                     | 15–40 nm      | 1 μm                | Single pore                               | 11  | Experimental studies | 4 × 10 <sup>4</sup> W m <sup>-2,e</sup><br>0.001/1 M   | 20 pW                     | 16.3 nS                       | –                                            | 83     |
| <b>2D nanopores</b>              |               |                     |                                           |     |                      |                                                        |                           |                               |                                              |        |
| GO flake RED cells               | 0.9 nm        | 0.5–100 μm (stacks) | –                                         | 5.6 | Experimental studies | 0.77 W m <sup>-2</sup>                                 | –                         | –                             | 36.60%                                       | 243    |
| Graphene                         | 0.4–10.0 nm   | 0.34 nm             | Intrinsic defects                         | 7   | Experimental studies | 700 W m <sup>-2,f</sup><br>0.001/1 M                   | 10 pW<br>0.01/1 M         | 18.4 nS                       | –                                            | 89,122 |
| MoS <sub>2</sub>                 | 2–20 nm       | 0.65 nm             | Single pore                               | 11  | Experimental studies | 3 × 10 <sup>6</sup> W m <sup>-2,g</sup><br>0.001/1 M   | 1 nW                      | 815.4 nS                      | 20%                                          | 78     |
|                                  | 3 nm          | 0.65 nm             | Single pore                               | 7.4 | Experimental studies | 0.01/0.1 M                                             | 1.2–2.8 pW                | 22.5–51.4 nS                  | 8–44%                                        | 154    |
|                                  | 10 nm         |                     |                                           |     |                      |                                                        | 130–160 pW                | 238.5–293.6 nS                | 40–45%                                       |        |
|                                  | 1 nm          | 0.65 nm             | Single pore                               | 5   | Numerical studies    | 7.1 × 10 <sup>5</sup> W m <sup>-2,h</sup><br>0.001/1 M | –                         | –                             | –                                            | 153    |

<sup>a</sup>Etched singular nanochannels within the cell. <sup>b</sup>Power reported per whole cell. <sup>c</sup>Extrapolated from reported porosity of 14–22%. <sup>d</sup>Estimated pore density. <sup>e</sup>Estimation of 10<sup>10</sup> pores cm<sup>-2</sup>. <sup>f</sup>Estimation of intrinsic defects within the material. <sup>g</sup>Estimation of porosity of 30% porosity = 3 × 10<sup>12</sup>. <sup>h</sup>Estimation of porosity of 30% porosity = 3 × 10<sup>12</sup>. GO, graphene oxide; hBN, hexagonal boron nitride; MOF, metal–organic framework; PCTE, polycarbonate track etch; PRO, pressure-retarded osmosis; PSS, poly(4-styrenesulfonic acid); RED: reverse electrodialysis.

### Nanotubes

The first real step towards high-power-density membrane materials was reported using BNNTs in 2013 (REF.<sup>83</sup>). The device comprised a single-micron-long nanotube of 15–40 nm in diameter embedded by micro-manipulation and sealed under a scanning electron microscope into a silicon nitride membrane separating two reservoirs with varying concentrations of a KCl solution (FIG. 3c). Power generation densities reaching the record high value (for the time) of 4 kW m<sup>-2</sup> per single BNNT<sup>83</sup> cross-sectional area were reported. By applying hydraulic pressure, under no salinity gradient, the authors proved via zeta potential measurements (which probe the magnitude of the surface charge) and independent surface conductance measurements at low salt concentrations that there is an extremely large surface charge density of up to  $\Sigma = 1 \text{ C m}^{-2}$  at alkaline pH. Such a high surface charge density corresponds to about six elementary charges per nm<sup>2</sup>, implying hydroxilation of all possible surface sites. This surface charge is responsible for an enhanced double layer inside the BNNT, which varies considerably in width between the salty and fresh reservoir. Such variation in the double layer produces local charge non-neutrality, which varies along the tube length. Because there is a potential difference between the salty and the fresh reservoir, an electric field is produced, which exerts a net volume force on the liquid. This fluid flow is called diffusio-osmotic flow and forms a plug-like velocity profile (FIG. 1d) that scales as  $v_{\text{DO}} \approx \nabla \log(c(r))$ <sup>83,90</sup> and then drags the excess cations in the channel, producing a current proportional to the surface charge<sup>83</sup>:

$$I_{\text{osm}} \approx \frac{2\pi R \Sigma}{L} \frac{k_{\text{B}} T}{\eta \lambda_{\text{B}}} \Delta \log(C_{\text{s}}) \quad (6)$$

that is three orders of magnitude larger than the streaming current induced by hydraulic pressure. The term  $\Delta \log(C_{\text{s}})/L$  can be considered as an integral of the driving force over the membrane and  $\eta$  is the dynamic viscosity of the fluid.

Although the extracted power density is considerably larger than in solid-state pores (on the order of 1 kW m<sup>-2</sup>), the power generation demonstrated using BNNTs has a low energy conversion efficiency of  $\phi \approx 10$ –20%<sup>83</sup>. We interpret this low efficiency as coming from the large opening radii of the BNNTs, a critical parameter for selectivity<sup>87,92</sup> along with the high surface charge density<sup>92</sup>. In a linear model of power generation, the osmotic conductance scales as  $G_{\text{osm}} \approx R \Sigma / L \eta$  in the case of high surface charge densities and as  $G_{\text{osm}} \approx \Sigma^3$  for small values of the surface charge. The main conductance mechanism is fluid flow, which is usually neglected in the case of nanochannels and bulkier nanopores, and can be enhanced by the low surface friction of certain types of nanotubes (which results in large slip lengths)<sup>88</sup>. The diffusio-osmotic fluid flow goes in the opposite direction to the osmotic water flow and improves the water permeation of the membrane by reducing uncontrolled mixing<sup>85</sup>. The diffusio-osmotic current model predicts an increase in the generated osmotic power as the ‘membrane’ thickness  $L$  is reduced, but the exact value cannot be predicted for 2D materials, in which pore access resistance is expected to strongly influence

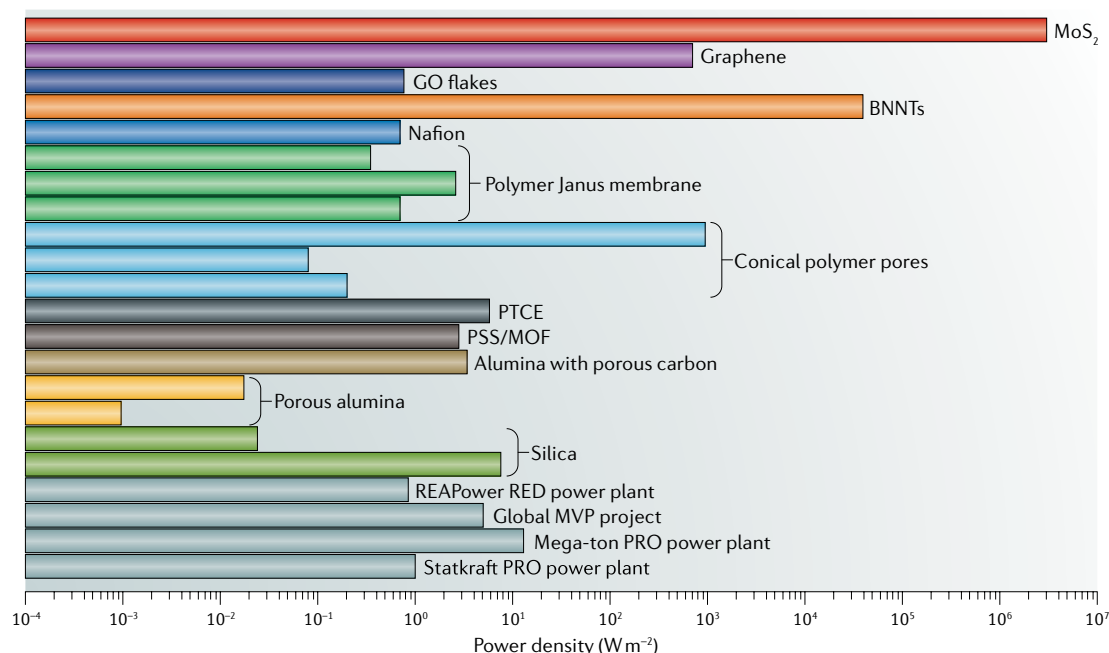


Fig. 2 | **Power densities per membrane area for different materials.** Reported and/or extrapolated values of power generation density for MoS<sub>2</sub> (REF.<sup>78</sup>), graphene<sup>89,122</sup>, graphene oxide (GO) flakes<sup>243</sup>, boron nitride nanotubes (BNNTs)<sup>83</sup>, polymers with conical pores<sup>56,91,133,176</sup>, Janus membranes<sup>58,59,177</sup>, poly(4-styrenesulfonic acid) (PSS) on a metal–organic framework (MOF)<sup>62</sup>, phenol-tetrachloroethane (PTCE)<sup>244</sup>, Nafion<sup>245</sup>, silica<sup>50,141</sup>, alumina<sup>49,51,138,246</sup> and for commercial projects<sup>19–23</sup>. The values for MoS<sub>2</sub>, graphene and BNNTs are estimates based on measurements in laboratory conditions.

conductance<sup>108,110</sup> and liquid flow<sup>142</sup>. Although nanotube systems can provide high levels of power generation, the complexity of the fabrication of aligned and stacked nanotube membrane<sup>83,143</sup>, along with their low energy conversion efficiency, makes upscaling unrealistic.

### 2D nanopores

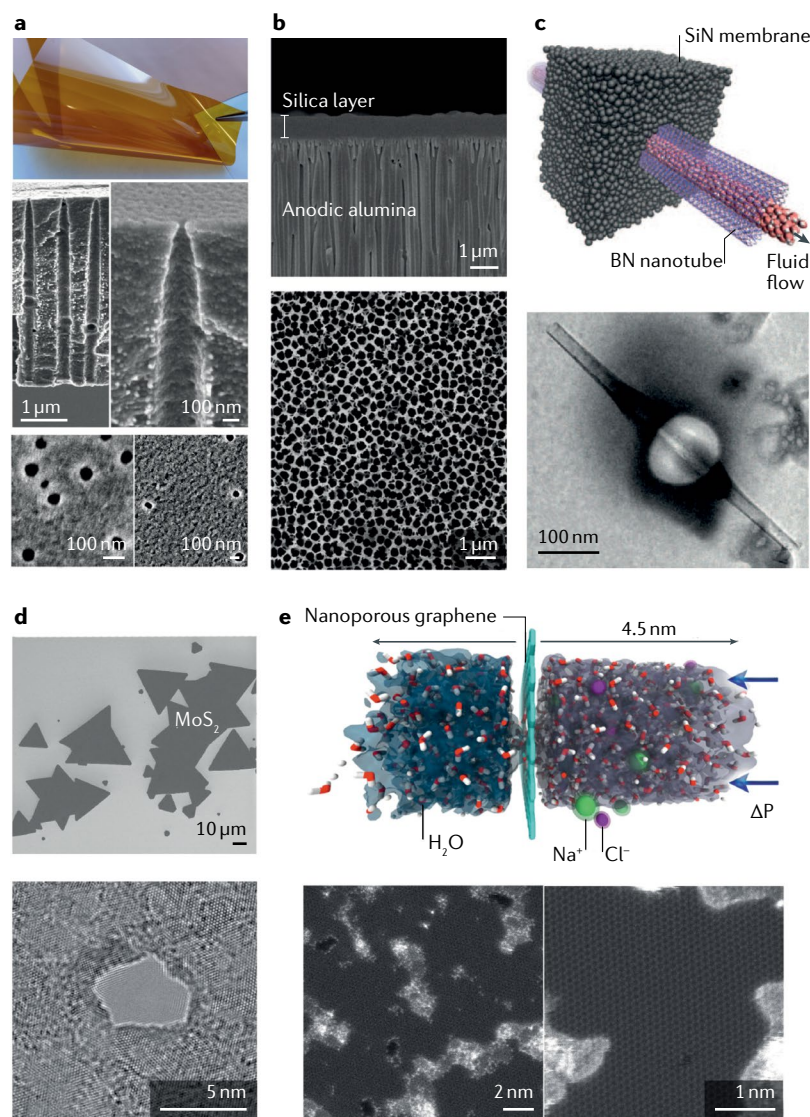
Power density is higher for thinner membranes (FIG. 2). By following this trend, eventually one encounters the final limit: atomic thickness. Synthesized or exfoliated single layers of van der Waals materials used as suspended porous membranes are especially interesting for osmotic power conversion, as they are expected to be more energy dense than other membrane materials (they support a higher power generation at the same level of porosity) and can be fabricated using well-established protocols<sup>79</sup>. In 2D materials, the dominant contribution to the osmotic conductance comes from the access resistance, whereas bulk contributions are negligible, thus the osmotic conductance (and osmotic power density) is larger than in typical solid-state nanochannels. From nanochannels, we know that selectivity and, thus, energy extraction efficiency, reduces as the thickness of the membrane tends to zero<sup>92</sup>. Yet, the selectivity and osmotic conductance of 2D materials such as MoS<sub>2</sub>, graphene and hexagonal boron nitride (hBN) can match or exceed that of BNNTs. In this section, we discuss why nanopore osmotic power generators based on 2D materials can be so efficient and power dense.

The highest reported power density — two orders of magnitude higher than that obtained with BNNTs — was measured in a nanopore power generator based on monolayer MoS<sub>2</sub>, showing an energy conversion

efficiency of up to  $\phi = 20\%$ <sup>78</sup>. MoS<sub>2</sub> is a van der Waals material actively researched for general nanopore applications<sup>79,115,116,144–146</sup>. A single-layer MoS<sub>2</sub> sheet is a semi-conducting, three-atom-thick film consisting of molybdenum atoms sandwiched by two sulfur atoms each<sup>147</sup>, similar to other transition metal dichalcogenide materials. MoS<sub>2</sub> with nanopores in the range 2–20 nm (FIG. 3d) displayed the maximal generated power at a pore size of ~10 nm, which, assuming a 30% porosity (roughly corresponding to 10<sup>12</sup> pores cm<sup>-2</sup>), translates to a generated power density of ~10<sup>6</sup> W m<sup>-2</sup> (REF.<sup>78</sup>). The strong influence of membrane thickness on generated power in MoS<sub>2</sub> was confirmed by molecular dynamics simulations<sup>78</sup> (FIG. 4a). Another candidate for 2D nanopore-based osmotic generators is graphene (FIG. 3e). Graphene is superior to solid-state membranes for water desalination and purification owing to its mechanical properties and high fluid permeability<sup>39,80,82,121,148–150</sup>, but does not perform as well in 2D pore-based power generators, as it is estimated, based on single-pore measurements, that the power density reaches only ~700 W m<sup>-2</sup> (REF.<sup>122</sup>), although with possible energy extraction efficiencies of up to  $\phi = 50\%$ <sup>89,122</sup>. Tests on single-layer hBN indicate a similar level of selectivity as in graphene<sup>122</sup>. Clearly, there are still unexplained differences between the performances of different 2D materials, which will need to be understood to identify the optimal 2D membrane.

**Selectivity and surface charges.** The selectivity of nanopores in 2D materials can be increased by reducing the pore size (FIG. 4b,c). The difference in pore radius is sufficient to explain the contrast in the energy extraction efficiency between 2D materials and BNNTs, because



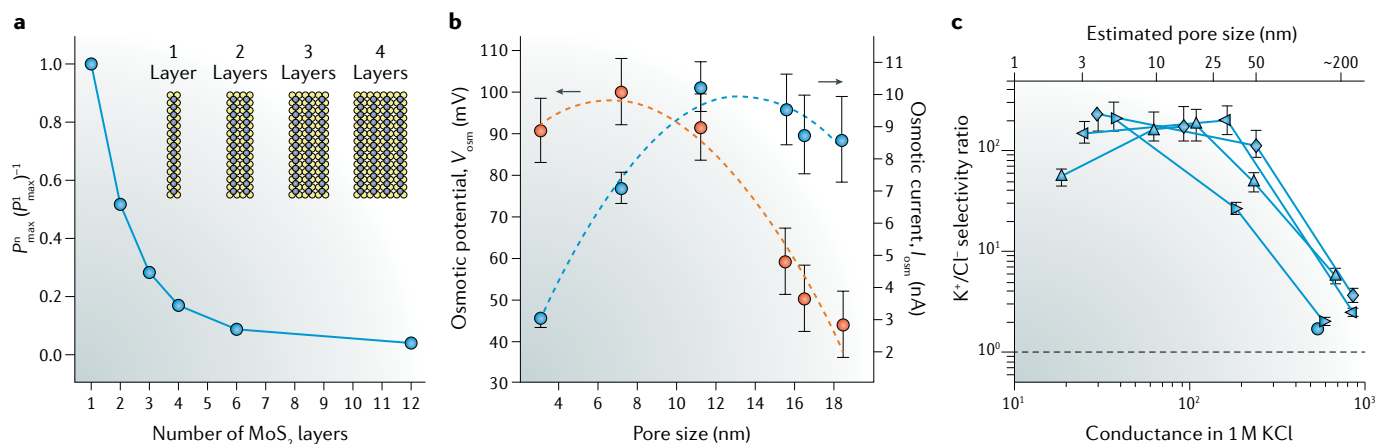


**Fig. 3 | Different materials used for nanopore power generation.** **a** | Polymer-based thin films made of polyimide, Nafion or polyethylene terephthalate (PET) allow large-area, inexpensive membrane synthesis. Nanopores are either intrinsically and densely packed during synthesis or defined later by ion beam techniques, as shown on the scanning electron microscopy images<sup>173</sup>. **b** | Scanning electron microscopy images of a cross-section and top view of highly porous membranes made of silica and anodic alumina<sup>49</sup>. **c** | Osmotic power generator based on a hexagonal boron nitride (hBN) nanotube embedded in silicon nitride with schematic water flow; a transmission electron microscope (TEM) image of the actual device is also shown<sup>83</sup>. **d** | Freestanding MoS<sub>2</sub>; the magnification shows a nanopore made by TEM irradiation<sup>78</sup>. **e** | A model of a porous graphene membrane and TEM images of a freestanding graphene membrane with nanopores made using Ar<sup>+</sup> irradiation<sup>82,121</sup>. Panel **a** is adapted with permission from REF.<sup>173</sup>, IOP Publishing. Panel **b** is adapted from REF.<sup>49</sup>, CC-BY-4.0. Panel **c** is adapted from REF.<sup>83</sup>, Springer Nature Limited. Panel **d** is adapted from REF.<sup>78</sup>, Springer Nature Limited. Panel **e** is adapted with permission from REF.<sup>121</sup>, Springer Nature Limited, and REF.<sup>121</sup>, ACS.

BNNTs have a pore diameter several times larger than the optimal diameter found in MoS<sub>2</sub> or graphene. This simple method for tuning selectivity provides an important advantage for 2D materials. From work on nanochannels and similar systems<sup>87,92</sup>, we know that the surface charge is a critical factor for selectivity and that its sign determines if the pore is cation or anion selective. The pore surface charge depends strongly on the

aqueous environment (pH) and steadily increases with increasing pH, with the highest surface charges obtained at alkaline pH values, well above the pH expected in natural water reserves (pH 7–8)<sup>151</sup>. It is a problem common to 2D materials and BNNTs that their surface chemistry does not support high charge densities at moderate pH. Graphene has a relatively low surface charge, as, in its pristine form, there are no chemically active surface groups. However, in the presence of externally attached surface groups (as in GO) or defects produced by plasma treatments, higher surface charges can be obtained (around 0.25 C m<sup>-2</sup> at pH 7)<sup>152</sup>, comparable to those in BNNTs (up to 1 C m<sup>-2</sup> at pH 11)<sup>83</sup>. This increased surface charge in graphene is expected to be highly sensitive to environmental conditions and unstable. The surface charge of MoS<sub>2</sub> at pH 5 was calculated to be in the range of -0.024 C m<sup>-2</sup> to -0.088 C m<sup>-2</sup> for 2–25-nm pores<sup>153</sup>, which is comparable to values for graphene (~-0.2 C m<sup>-2</sup> at pH 7)<sup>152</sup> and nanotubes (~-0.1 at pH 5.5)<sup>83</sup> at similar pH values. The surface charge can be enhanced by light irradiation, as was demonstrated for MoS<sub>2</sub>; thus, both selectivity and power generation are boosted in natural light conditions<sup>154</sup>. The surface charge, through the overlap of Dukhin lengths on the freshwater side of the membrane, is expected to provide the most significant contribution to selectivity<sup>92,106</sup>. Differences in surface charges and nanopore sizes might help to explain the differences in selectivity of MoS<sub>2</sub> and graphene, yet one must be careful in examining these values owing to variations in sample quality and measurement conditions. The values of surface charges are usually obtained using a fit to Eq. 5 for solutions of different salinity, and the same formula is often used to determine or confirm the size of nanopores produced in 2D materials. New approaches need to be developed to measure the surface charges of 2D materials and to reliably determine pore sizes, as well as to develop anion-selective membrane materials<sup>86</sup>, which would enable the creation of stackable RED cells and further upscaling of 2D nanopore power generators.

**Osmotic conductance.** Although selectivity is known to come from surface charges, the factors influencing the osmotic conductance in 2D materials are unclear, and materials with seemingly comparable surface charges (MoS<sub>2</sub> and graphene) show drastic differences in osmotic conductance. The osmotic conductance is ~10 nA V<sup>-1</sup> for graphene<sup>89</sup> and ~100 nA V<sup>-1</sup> for MoS<sub>2</sub> (REF.<sup>78</sup>) for 3-nm pores (at pH 11 with  $c_h = 1$  M and  $c_l = 1$  mM KCl), which is at the base of the high power density of MoS<sub>2</sub>. For comparison, BNNTs have an osmotic conductance of ~10 nA V<sup>-1</sup> for much larger pores (40 nm) in the same salt conditions<sup>83</sup>. Standard models for 2D pore conductance in graphene and MoS<sub>2</sub>, based on a combination of surface, bulk and access conductance contributions, cannot explain these differences between 2D materials unless there is a significant difference in surface charges and surface conductivity, something which is seemingly not supported by the observed similar selectivities. A possible explanation could be found in diffusio-osmotic flow<sup>83,90</sup>, the main reason why nanotubes can compete with thin 2D membrane materials despite



**Fig. 4 | Scaling properties of 2D nanoporous membranes.** **a** | Ratio of the maximum power obtained from multilayer membranes ( $P_{\max}^{\text{multilayer}}$ ) to the maximum power obtained from a single-layer material ( $P_{\max}^{\text{single-layer}}$ ) as a function of thickness, as obtained from molecular dynamics simulations<sup>78</sup>. **b** |  $\text{MoS}_2$  osmotic potential and current versus pore size. **c** | Pore-size dependence of the ion selectivity (permeability) ratio  $P_{\text{K}}/P_{\text{Cl}}$  in graphene<sup>89</sup>. The selectivity can then be calculated from this ratio using Eq. 3. Each curve corresponds to one device. The conductance was measured for one pore size, then the pore was enlarged in situ and conductance was measured again. Thus, the pore diameter is not measured directly but estimated based on the current conductance. Panels **a** and **b** are adapted from REF.<sup>78</sup>, Springer Nature Limited. Panel **c** is adapted from REF.<sup>89</sup>, CC-BY-4.0.

their micron lengths. It is known that adding flow effects increases the selectivity of nanochannels without salt gradients, with more pronounced effects in short and small channels<sup>92</sup>. In the case of extremely highly charged BNNTs with a surface charge of up to  $\sim 1 \text{ C m}^{-2}$ , this diffusio-osmotic flow is the major contribution to conductance and is responsible for high osmotic currents. For 2D materials, the flow through nanopores is dominated by hydrodynamic access resistance<sup>142</sup>, similar to the conductance, and, for small pore sizes, a large pressure drop between the membrane sides can build up due to electro-osmotic flow<sup>155</sup>. Recent work on diffusio-osmotic flow in 2D materials indicates that, apart from surface charges, any charge on pore walls can influence osmotic conductance; the same work calculated how solute and solution fluxes scale with pore parameters<sup>156</sup>. The graphene pore edge termination is charge neutral<sup>89</sup>, so it does not induce any surface charges that could boost osmotic current for small pores, in which edge effects are more relevant. By contrast, the pore edge of monolayer  $\text{MoS}_2$  can be terminated with either Mo or S atoms. Such termination could, in theory, be tuned<sup>157,158</sup> and might allow attachment of functional groups to increase the hydrophilicity of the pore interior. The character of pore-edge chemistry (for example, attached or adsorbed hydroxyl groups) can influence the electrostatic interactions inside the pore and, thus, additionally enhance ion selectivity<sup>82,122,157–159</sup>. We can even speculate that the nature of the material surface might help diffusio-osmotic flow in a similar way that hydrodynamic slip can boost osmotic power generation in nanochannels and nanotubes<sup>88,160</sup>, albeit care needs to be taken to include the effects of mobile surface charges<sup>160</sup>. Recent ab initio modelling indicates that there are differences in surface charge mobilities between 2D materials (graphene and hBN)<sup>161</sup>. In addition, if fluid flow has a major role in the osmotic conductance, graphene's high level of water

permeability<sup>82</sup> might become problematic, as, owing to osmosis, it would allow water to move in the opposite direction through the membrane, reducing the nanopore performance<sup>85</sup>. Differences in pore edge termination and surface charge mobilities might explain the much higher power output of  $\text{MoS}_2$  compared with graphene, especially if the effects of flow are included.

**Optimal materials parameters.** Understanding the selectivity and osmotic conductance of pores in 2D materials is critical for choosing the right material and pore size for power generation purposes. To achieve maximal power densities in  $\text{MoS}_2$ , the optimal pore size is  $\sim 6\text{--}10 \text{ nm}$  (REF.<sup>78</sup>). We propose that this is because the osmotic conductance grows with pore size as  $G_{\text{osm}} \approx d$ , based on experiments<sup>78</sup> on  $\text{MoS}_2$  and modelling in related systems<sup>88</sup>, and the selectivity (as seen from the osmotic potential) saturates with pore sizes below  $10 \text{ nm}$  (FIG. 4a). Recent theoretical work on the influence of access effects on diffusio-osmotic flow of uncharged solutes seems to corroborate these conclusions<sup>156</sup>. Yet, as the access resistance implies a similar scaling with pore parameters as with fluid flow, it is not clear how much of the osmotic conductance comes from diffusio-osmotic flow effects. Untangling the role of diffusio-osmotic flow in the osmotic conductance of 2D membranes requires careful study of flow effects through 2D membranes, which calls for large porous membranes with well-defined pore size distributions or new, precise measurement techniques applicable to single nanopores (such as minuscule flow rate sensors<sup>162</sup>).

### Fabrication of 2D materials and pores

To achieve power generation using 2D or solid-state pores, it is important to take into account the role of device fabrication protocols and their influence on membrane and nanopore properties. The membrane

material (typically, Si/SiN<sub>x</sub>, Si/SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, HfO<sub>2</sub>, TiO<sub>2</sub>, ...) has to be resistant to the working environment of the power generator, and either provide a stable support for porous 2D layers transferred on top or be thinned and processed to create pores. Generally, the fabrication processes are well established owing to the extensive and long-term use of 2D materials for solid-state nanopore sensing devices<sup>81,113–120,145,163–172</sup> and are based on photolithography followed by 2D material transfer and pore drilling.

### Membrane preparation

For solid-state pores, a typical fabrication process consists of membrane preparation (such as track etching of polymer films<sup>173–177</sup>), chemical synthesis of the porous material (such as alumina or silica with intrinsic pores<sup>49,51</sup>) or photolithography followed by wet and dry etching to obtain a substrate (such as Si, SiO<sub>2</sub> or SiN<sub>x</sub>) with defined porous membranes<sup>47,134–137</sup> (FIG. 5a–c). Such devices act either as a standalone solid-state pore system or host a monolayer material (or other porous material, such as Janus membranes) transferred on top. To host a suspended 2D film, a support membrane should ideally be mechanically and chemically stable under working conditions, exhibit good adhesion to the supported 2D layer and be easily fabricated, to allow potential upscaling (as is the case for low-stress SiN<sub>x</sub> membranes on Si chips)<sup>79</sup>.

### 2D layers synthesis and transfer

Usually, 2D layers are grown by chemical vapour deposition (CVD) or metalorganic CVD (MOCVD)<sup>178–191</sup>. Both approaches have good process scalability with high material quality and crystallinity. After growth, the 2D material is transferred onto a designated substrate (the supporting membrane) via wet or dry transfer methods<sup>178,189,192–194</sup>. Transfers are commonly performed by coating or dry stamping the as-grown material with a polymer (such as poly(methyl methacrylate), PMMA or polydimethylsiloxane, PDMS). As-grown 2D materials adhere to the polymer and can be separated from their growth substrate either by wet lift-off or by slow, careful peeling. The 2D material is then transferred on the final substrate, and the polymer is dissolved (PMMA) or peeled off (PDMS); this works even on the large scale of whole Si/SiN<sub>x</sub> wafers<sup>178,183,189,192,195,196</sup>. This process is relatively quick and robust; however, because the polymer and pristine monolayer are in contact, contamination of the monolayer is inevitable<sup>197</sup>, often lowering the fabrication yield and limiting the usable material area. To address this problem, a lab-scale CVD growth process allowing the growth of pristine monolayers over the supporting porous membrane was proposed<sup>198</sup>, allowing the transfer step to be skipped and achieving clean, suspended films. However, for large-scale processing and upscaling, 2D material transfer might be inevitable. Fortunately, with recent developments in CVD and MOCVD growth of various types of nanotubes<sup>199–203</sup>, hBN (REF.<sup>181</sup>), graphene<sup>204,205</sup>, MoS<sub>2</sub> (REFS<sup>178–191</sup>) and other 2D materials as well as new, cleaner transfer methods<sup>206</sup>, both the growth and transfer steps are no longer a bottleneck.

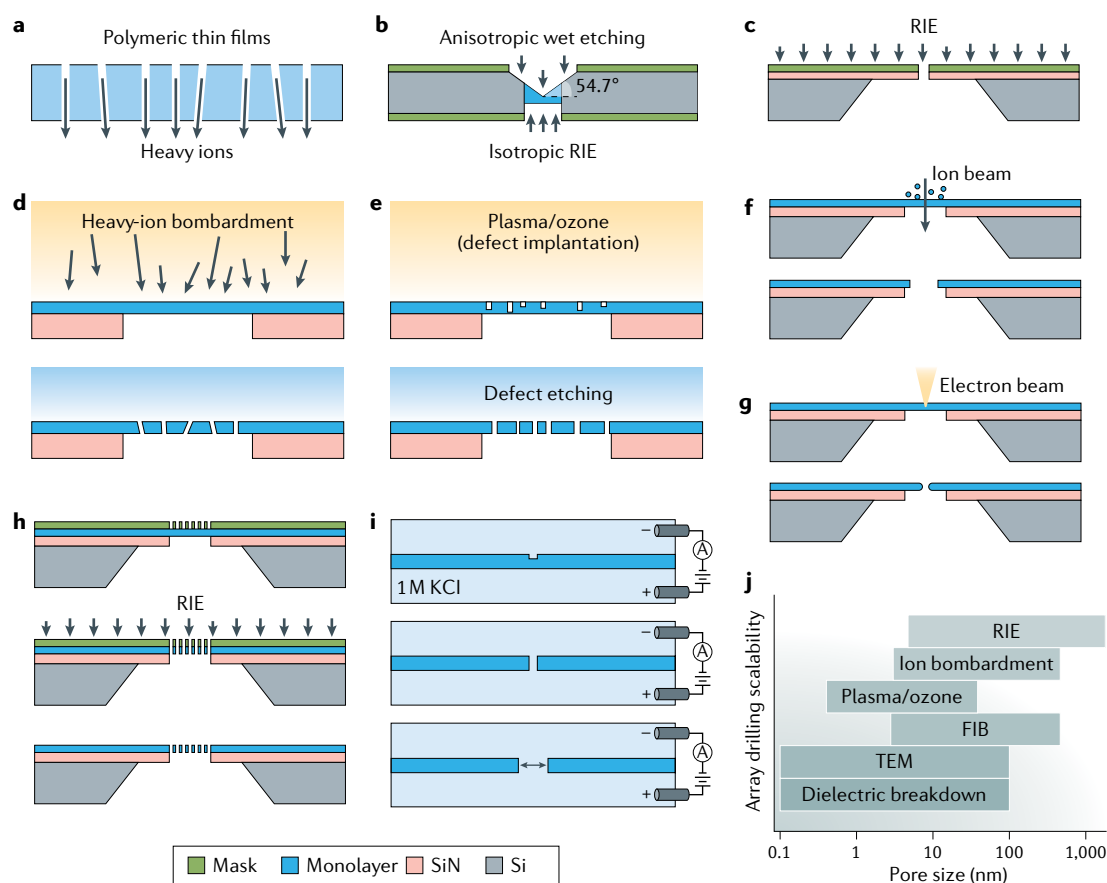
### Nanopore drilling

The nanopore size is one of the most important factors in determining the efficiency of the generator and, ideally, should be around 7–15 nm (REFS<sup>78,89</sup>). Drilling methods for solid-state pores and suspended thin films can be used to create 2D nanopores (on the lab scale); these include heavy-ion bombardment (FIG. 5d), plasma etching or ozone treatments (FIG. 5e) that produce randomly distributed pores with various diameters, and more precise techniques such as focused ion beam<sup>207–213</sup> (FIB; FIG. 5f) or transmission electron microscope (TEM) drilling<sup>78,79,134,135,214</sup> (FIG. 5g), in which highly focused electron or ion beams are used to create a hole through a suspended atomic membrane. Amongst these methods, TEM drilling, which exploits the controlled energy dose and a finely tuned spot size of the electron beam, offers the highest precision and enables the operator to open pores atom by atom and, more importantly, observe and measure them in situ. The downside of this technique is the susceptibility of monolayers to irradiation damage and carbon deposition<sup>215,216</sup>. This phenomenon might be interesting for graphene membranes, in which, with proper heating and tuning of the beam parameters, the nanopore size can be fine tuned, exploiting the competing processes of electron-beam-induced sputtering along nanopore edges and carbon adatoms generation<sup>217,218</sup>. For other materials, especially those sensitive to the electron beam, this process can be considered as contamination and might negatively influence membrane thickness and surface charges.

TEM drilling is time consuming and cost ineffective, and cannot be upscaled and automatized; thus, in principle, it is not the perfect tool for the mass fabrication of devices for experimental and potential industrial purposes. A compromise between scalability and pore size can be achieved by ion bombardment<sup>212,219,220</sup>. However, this method does not offer good control over pore location and size. The pore density, interpore distance and geometrical arrangement are crucial parameters for increasing the efficiency of the generator<sup>221,222</sup>, thus it is important to be able to control them. Ion techniques affording a higher precision, such as milling or low-energy ion irradiation using Ga<sup>+</sup>, Ar<sup>+</sup> or He<sup>+</sup> FIBs, might be effective in terms of batch fabrication of pore arrays or high pore densities<sup>47,207–212,223</sup>. Ion irradiation works in the low-energy regime, as opposed to electron beam irradiation, thus it does not cause direct knock-on or radiation damage but, rather, atomic displacements induced by the ion collision process. The size of the pores directly depends on the ion energy and its size. For solid-state (SiN<sub>x</sub> or SiO<sub>2</sub>) nanopores, an initial large hole can be shrunk effectively from dozens of nanometres to a subnanometric diameter, a phenomenon attributed to the local fluidization of amorphous SiN<sub>x</sub> or SiO<sub>2</sub> molecules under the ion beam, which directly leads to pore shrinking<sup>134</sup>. For a monoatomic layer, however, the pore size depends directly on the beam parameters, which have to be precisely tuned to achieve the smallest pore sizes.

Graphene nanopores were fabricated<sup>208</sup> using a helium ion microscope to precisely drill arrays of pores of 5–30 nm in diameter. The capability of the helium ion





**Fig. 5 | Nanopore drilling techniques. a–c** | Different nanopore drilling techniques for solid-state pores: ion track etching (panel a), based on using heavy-ion irradiation to perforate (mostly) polymeric membranes<sup>173–177</sup>; selective wet etching (panel b), based on photolithographic processing to define pore-to-be locations and taking advantage of anisotropic etching of Si by wet etchants to precisely obtain porous structures on a Si wafer<sup>247</sup>; and lithographic reactive-ion etching (RIE) on a masked membrane area of a Si/SiO<sub>2</sub> or Si/SiN<sub>x</sub> wafer<sup>134–136,207</sup> (panel c). **d–i** | Nanopore drilling techniques for 2D nanopores: heavy-ion irradiation<sup>212,213</sup> (panel d); plasma or ozone irradiation (panel e), which leads to the implantation of defects that can be further etched to obtain pores<sup>219,220,224</sup>; focused ion beam (FIB; panel f), based on heavy ions that mill through suspended thin films<sup>47,207–212,228</sup>; the focused electron beam of a transmission electron microscope (TEM) tuned to use local irradiation damage to sputter away single atoms<sup>78,79,116,118,214</sup> (panel g); e-beam lithography combined with RIE to obtain pore arrays<sup>137</sup> (panel h); and dielectric breakdown or electrochemical reaction (panel i), based on applying a critical voltage to a thin layer submerged in an electrolyte that creates a nanopore due to oxidation and expansion of intrinsic defect edges<sup>146,225</sup>. **j** | Overall obtainable pore sizes and process upscaling capabilities (going from dielectric breakdown techniques that only enable the drilling of one precise nanopore to RIE with ion bombardment, which enable theoretically unlimited and/or well-defined pore array sizes).

microscope for nanopore fabrication was further tested on other suspended 2D materials<sup>223</sup> and, by careful tuning of focus, irradiation time and ion dose, a precise and reproducible pore formation technique was obtained. With the achievement of 1.5-nm pores in graphene and pores smaller than 5 nm in MoS<sub>2</sub> and boron nitride, this semi-automatic drilling process shows great promise for batch production of lab-scale nanopore power generator devices. Another interesting approach is using lithographic processing on suspended 2D materials. By extremely careful processing and process control, it is possible to use polymer mask, e-beam lithography and dry etching to obtain precise porous arrays in graphene (FIG. 5h), with pore diameters down to 16 nm (REF.<sup>137</sup>). Alternatively, one can use defocused ion irradiation, plasma or ozone<sup>89,122</sup> treatment to nucleate defects that can be further enlarged to the desired diameter

by sputtering or chemical etching<sup>219,220,224</sup> to obtain the desired pore density. However, one has to be aware that increasing the fine defects density may significantly influence the surface charges as well as compromise the membrane's mechanical stability. Finally, dielectric breakdown can be used on an untreated material to enlarge already existing point defects<sup>146,225</sup> (FIG. 5i). This method is based on applying a specific critical voltage to a thin membrane in an electrolyte solution. Its ability to create a precise sub-nanometre pore is a considerable advantage for lab-scale experiments, but this technique inherently lacks scalability and control over the pore position and geometry. In the end, the choice of drilling method should be based on the type of 2D material and desired batch scale (FIG. 5j). Because all as-grown 2D materials exhibit intrinsic defects, it is important to use a technique that does not deteriorate the film further

(for example, most 2D layers are fragile to electron and ion beams, and excessive irradiation can render them useless) and allows controllable nanopore fabrication. Note that film deterioration is a problem only in suspended monolayer materials. In slightly thicker layered or stacked films, it is not necessarily an issue but can decrease the osmotic power generation performance.

## Outlook

### Upscaling of osmotic power generation

The viability of 2D nanopore-based osmotic power generators as power sources largely depends on the possibility of producing large-scale membranes with high power densities and high energy conversion efficiencies. In the previous sections, we have focused on single-nanopore power generators, because 2D materials are still an emerging technology without demonstrated large-scale applications. Platforms that can lead to high generated power per single pore include membranes with conical pores, nanotubes and 2D membranes. Yet, not all of these pores can be made of equal size (FIG. 6) and 2D materials have the smallest possible individual pores at the same osmotic conductance. For example, conical pores have a large cone base diameter, which can be in the micron range, and, as such, are not good candidates for achieving a high power density.

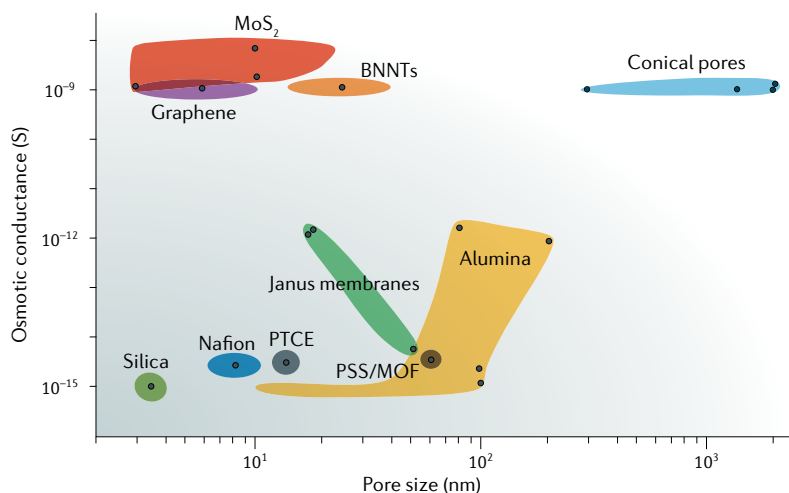
To achieve a large osmotic power density, an array of nanopores scalable up to industrial sizes is needed, with a high density of pores per unit area. One could naively imagine that the ionic conductance scales linearly with the number of pores  $N$  and as  $N \rightarrow \infty$ ,  $G \approx N G_{\text{osm}}$ . But for thin membranes with small aspect ratios, the pore conductance is predicted<sup>223</sup> to scale not linearly with the array size but sub-linearly with the number of pores  $N$ , and to depend on the topology of the network. The conductance is expected to scale like  $G \approx N/\log N$  for

a 1D line of pores and like  $G\sqrt{N}$  for a 2D array of pores (FIG. 7a). Such a reduction of osmotic power with increasing pore densities was also corroborated using numerical simulations for high pore densities while also including different pore sizes<sup>226</sup> (FIG. 7b). The physical mechanism is related to the interactions between neighbouring pore access resistances, which effectively reduce the cross-sectional area of individual pores in the array. This effect is expected to influence the hydrodynamic flow<sup>222</sup> but it is not yet clear if it influences the diffusio-osmotic flow, which originates from the local concentration gradient in the pore.

Numerical simulations of pore arrays in thick membranes<sup>226</sup> showed that osmotic power generation reaches a peak at a certain pore density ( $10^9$  pores  $\text{cm}^{-2}$ ) and then drastically decreases with increasing porosity due to the impairing of charge selectivity and strong ion concentration polarization. A nonlinear growth of diffusion current density with increasing pore density was also shown, suggesting that, with interpore distances shorter than 3,000 nm, the pore–pore interactions become important<sup>227</sup>. These simulations were confirmed by an experimental study carried out on 10-nm pores in a 1- $\mu\text{m}$ -thick polyethylene terephthalate (PET) film, and it was finally concluded that single-pore models for predicting power generation scaling are not valid for high pore densities (above  $10^7$  pores  $\text{cm}^{-2}$ ). These interaction effects originate from the overlap of charge concentration clouds of nanopores in the array, which reduces selectivity and osmotic current<sup>226</sup>. Consequently, care has to be taken when extrapolating single-pore power generator values to macroscopic membranes. Notably, these simulations did not include fluid flow effects and peculiarities of 2D materials. The effect of pore density on power generation has not yet been tested experimentally in 2D systems, but it is clear that there is interplay between the interpore distance, the Dukhin length of the system and pore entrance effects, and that individual pore osmotic generation is compromised at high pore densities. A conservative estimate for  $\text{MoS}_2$  with a porosity of  $10^7$  pores  $\text{cm}^{-2}$  gives a power generation density of  $\sim 1 \text{ kW m}^{-2}$ , which is still a considerable improvement on the best membrane materials in use today. The most cost-effective way to produce such high pore densities in 2D membranes would most likely involve using chemical etching or ion bombardment techniques, which are both currently under active development<sup>140,208,213,228</sup>.

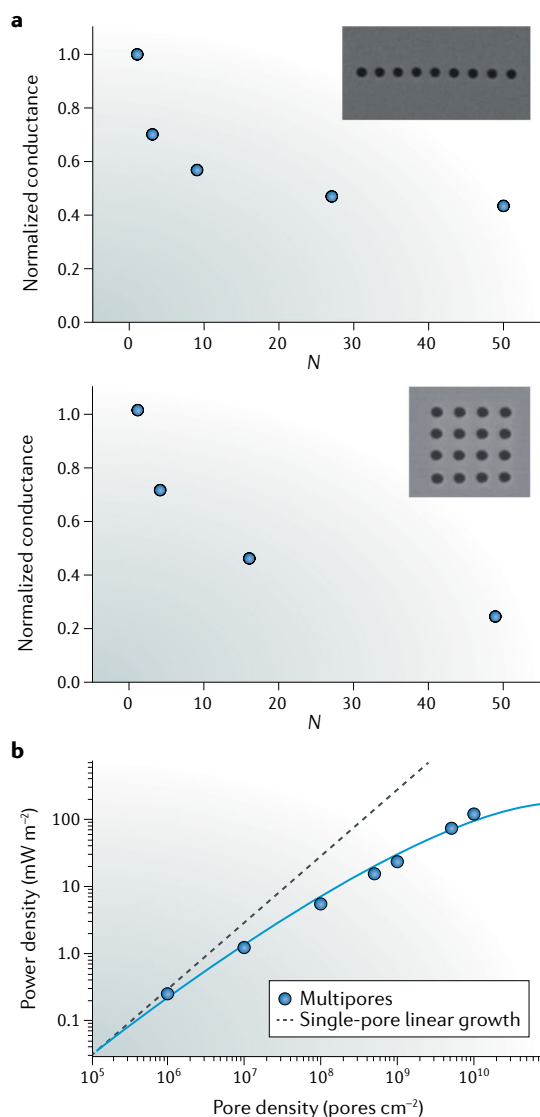
### Pore functionalization

Another interesting topic related to osmotic energy harvesting and its practical use is the exploration of the ionic diode behaviour of the nanopores to ensure efficient transmission of power to external loads and to enhance osmotic power generation performance. Substituting cylindrical for asymmetric conical pore shapes enhances the ion current flow in one direction, causes ionic current rectification due to geometry-induced concentration polarization<sup>104</sup> and can produce high power density and energy conversion efficiency<sup>133,176</sup>. With the ionic diode behaviour due to a preferential direction for ion flow, any back current is effectively suppressed. This kind of geometrical functionalization is typically



**Fig. 6 | Osmotic conductance per single pore as a function of pore size for different materials.** The pore size is interpreted here as the largest obtained diameter in a given experiment (that is, for conical pores, it is the base diameter that effectively limits the available pore density on membrane area). The values of the osmotic conductance are calculated from the following references:  $\text{MoS}_2$  (REFS<sup>78,154</sup>), graphene<sup>89,122</sup>, boron nitride nanotubes (BNNTs)<sup>83</sup>, conical pores<sup>56,91,133,176</sup>, Janus membranes<sup>58,59,177</sup>, poly(4-styrenesulfonic acid) (PSS) on a metal–organic framework (MOF)<sup>62</sup>, phenol-tetrachloroethane (PTCE)<sup>244</sup>, Nafion<sup>245</sup>, silica<sup>50,141</sup> and alumina<sup>49,51,138,246</sup>.





**Fig. 7 | Influence of pore density and size.** **a** | Normalized conductance in a 1D and 2D array as a function of the number of pores,  $N$ . These results show that pore–pore interactions influence pore array scalability. **b** | Power density as a function of pore density for small nanopores, showing a deviation from the ideal linear growth. Panel **a** is adapted with permission from REF.<sup>222</sup>, AIP Publishing. Panel **b** is adapted with permission from REF.<sup>226</sup>, Wiley-VCH.

explored in thicker, solid-state pores made of glass, SiN<sub>x</sub> or PET due to fabrication feasibility. The ionic diode behaviour can be further upscaled and adjusted by using various functionalization approaches to modify the pore walls, such as polyelectrolyte brushes<sup>133,176,229</sup>. PET conical pores were functionalized with polyelectrolytes<sup>133</sup>, which resulted in an osmotic energy yield of 120 pW (the same order of magnitude as the yield of a boron nitride nanotube) and an energy density of 945 W m<sup>-2</sup>. Other studies<sup>138,177,230</sup> also demonstrated the potential of using ionic current rectification in energy harvesting from desalination. In theory, this effect could be coupled with 2D materials by constructing a large array of conical pores acting as an access channel over which a

2D material with a large pore density would be placed. In addition to acting as a mechanical support for the membrane, such an array could boost the performance of osmotic power generators based on 2D materials.

Although pore-wall functionalization can be used in thick materials for tuning and enhancing ion selectivity, as well as producing ionic current rectification, its influence on atomically thin materials is limited. What can be done on this scale is to chemically modify the surface around the pore. Such functionalization is especially viable for graphene, which has relatively low surface charges, but, in principle, could also be implemented for MoS<sub>2</sub> and other materials to increase or induce specific positive or negative ion selectivity in the system. This was observed in graphene, in which surface functionalization using N or F atoms made the pores cation selective<sup>231</sup>. Such selectivity can be achieved by proper tuning of any neutrally charged pores. Cation selectivity in sub-nanometre neutral graphene, for example, was studied in connection with partial dehydration of K<sup>+</sup> ions and pore edge modifications<sup>232</sup>. Another functionalization approach is to dope the 2D layers with certain molecules to change or tune the surface charges, boosting the efficiency of the device<sup>233</sup>. Because the surface charge seems to have an enormous impact on osmotic energy generation, doped 2D materials might open up new ways to increase performance.

### Challenges for 2D porous materials

When considering the potential application of membrane-based energy harvesting systems in the river–seawater environment, one has to pay special attention to fouling. Nanometric pores tend to attract large particles and become clogged when exposed to volatile contamination. In such cases, cleaning 2D nanoporous membranes either chemically or mechanically is, least to say, problematic or even impossible. Besides that, monoatomic membranes (especially if they are porous and pretreated during fabrication) are fragile both on the micro and macro scale (at which unwanted defects can lead to lower power output and even to a material tear), which makes the whole device delicate and problematic to use in real environments. A compromise might be achieved with thicker nanopore membranes, with which the power output is traded for better mechanical and chemical stability and more feasible fabrication cost efficiency. A different pathway would be to engineer a design of conical channels supporting a highly selective 2D material to further increase the energy density. Interestingly, some 2D materials may exhibit anti-biofouling properties, which can be activated by material functionalization or light irradiation (for example, photocatalysis in MoS<sub>2</sub>)<sup>234–236</sup>. Light irradiation might additionally boost the power generation performance, especially for small pore sizes<sup>154</sup>. However, learning from solid-state PRO/RED research, without significant energy output, the power generator will not be efficient enough to either be commercially viable or to sustain itself, since defouling or (if necessary) water pretreatment processes usually require a massive amount of energy<sup>37,38,42</sup>. It is still unclear what requirements for water treatment 2D materials will have, but their

successful use in desalinization research is encouraging for developing practical applications.

There are techniques to remove larger particles from water sources, but the presence of multivalent ions constitutes a problem. Multivalent ions like  $\text{Ca}^{2+}$  or  $\text{Mg}^{2+}$  have been shown to reduce the power output of systems by up to 50%<sup>94</sup>, yet this simple fact is often ignored by the membrane community. The power output reduction happens because of several interconnected phenomena<sup>15,94</sup>: the osmotic potential is lowered because it is inversely proportional to the valance of the ion; there is 'uphill transport' of multivalent ions against the concentration gradient; and there is an affinity of the membrane to different ion charges. 2D materials can provide interesting solutions to these problems. The variation of pore size and surface charge can produce membranes with varying degrees of selectivity to monovalent or multivalent ions<sup>89</sup>, which can be stacked to first repel multivalent ions and then proceed to harvest the salinity gradient with monovalent ions<sup>15</sup>. The degree to which technical solutions can tackle fouling and the presence of multivalent species will determine the membrane's practical applicability. As this emerging technology starts to be implemented, its applicability might be limited to working with hypersaline solutions and brines, which are expected to provide better energy yields with smaller power consumption for water pretreatment<sup>38</sup>.

There is a huge scale gap between the research and development of solid-state membranes for PRO/RED technologies and that of 2D materials, due to the almost half a century of prior research on current membrane technologies. Although there are phenomena that we still do not fully understand or know how to exploit, we can learn lessons from 2D materials such as  $\text{MoS}_2$  and apply them to other systems. With thousands of possible monolayer van der Waals materials<sup>237</sup>, only a few have been explored in terms of osmotic energy harvesting<sup>179,238–240</sup>. A major step would be performing more detailed computational studies of important material properties (such as surface charge in solutions and pore edge terminations) of other monolayer materials. Other functional materials that have not yet been fully examined for osmotic energy harvesting applications might also be very promising as flat membranes. MOFs, made of a metal oxide cluster within an organic matrix, might be a candidate, as they offer outstanding functionalization possibilities and control over pore density and spacing, and have nanometric thickness and mechanical stability. MOFs are proven to perform as well as porous

membranes<sup>62</sup>, with the strong advantages of tuneable ion selectivity, extremely high possible porosity (up to 90%) and thickness as low as a few nanometres (for MFI zeolite nanosheets<sup>241,242</sup>). Another promising material group might be stacked monolayer materials. Such heterostructures are attractive because they allow yet another level of functionalization and material properties control. Proper composition of stacked 2D layers could hypothetically boost the efficiency of osmotic energy harvesting even beyond the best reported values. Yet, obtaining such stacks in a controllable, repeatable and contamination-free way to achieve pristine interlayer interfaces is still a challenge.

## Conclusions

2D membranes are an emerging technology that could be crucial for tapping into blue energy. Efficient membranes for osmotic power generation require high power densities and energy extraction efficiencies. 2D materials excel in both of these categories, providing power densities that are several orders of magnitude higher than those of current membrane materials that are undergoing large-scale testing. However, there are issues that still need to be addressed to fully understand the physics of osmotic power generation in these systems and, more importantly, to enable a wider and more practical usage of this technology. The nature of ion selectivity needs to be addressed with more systematic experimental studies of surface charge and pore size effects, particularly with the aim of obtaining also efficient anion-selective membranes via surface functionalization. A better understanding of the mechanisms for the generation of the osmotic conductance, and especially of the role of fluid flow in 2D materials, will enable the design of better membranes. Extensive experimental studies on the fabrication and upscaling of 2D pore arrays along with a diligent investigation of multipore systems will show how close we can get to the outstanding extrapolated estimations of power densities. 2D membranes would be best utilized in combination with other materials to remedy their inherent weaknesses, for example, materials with asymmetric pore geometries or supporting membranes with asymmetric cross sections. By learning from the fast advancement of graphene from discovery to practical applications in the past 15 years, we believe that 2D materials could find their place in real-world RED applications within a similar timescale.

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#### Author contributions

M.M. and S.M. wrote the manuscript; M.M., S.M. and A.R. researched the data for the article. V.N. contributed to the theory section. All authors discussed the contents and provided important contributions to the manuscript.

#### Competing interests

The authors declare no competing interests.

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