Support based novel single layer nanoporous graphene membrane for efficacious water desalination

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ABSTRACT
Among promising novel membrane materials for enhancing desalination performance, graphene has been realized as a high potential candidate due to its unique properties. However, large area graphene membrane, dominantly available through wet transfer and assistance of polymers, has inevitable features like defects, holes and cracks that could limit realistic prospects of industrial-scale production of desalination membranes. Here, using hole arrays in silicon as a secondary and a fine mesh grid as an initial support, we experimentally designed a mobile nanoporous graphene membrane with tunable salt rejection and water permeation by favourably limiting the undesired effects of defects and holes on the graphene. A model is also presented to support the experiments and give more insight into the possible superpositions (i.e. motifs) that occur by movements of graphene/grid over silicon hole arrays. Using the moveable assembly of graphene/grid/hole arrays and the consequent motifs, a range of high permeation ($4.34 \times 10^7$–$5.90 \times 10^7$ Lm⁻²h⁻¹bar⁻¹) and NaCl rejection (58%–100%) values were obtained. The moveable assembly of graphene/grid on fixed silicon hole arrays opens possibilities of fabrication of scalable atomically thin membranes for water desalination and can be applied for many other separation purposes specifically ion selectivity and filtration of multivalent ions or larger molecules.

1. Introduction
Realization of nanoporous graphene and other atomically thin membranes unwraps new opportunities in membrane technology. Atomic thickness [1], significant mechanical stability [2], sustainability to nanoscale pores in their rigid lattice [3] and chemical robustness [4] make these materials ideal candidates for a range of applications including water desalination [5–7], ultrapure water production [8] and...
natural gas purification [9]. Key advantages of nanoporous atomically thin membranes are their high permeance that enables higher energy efficiency and productivity in applications involving water desalination [10] and molecular-sieving. Therein, the mechanism of transport is expected to lead to rejection of all species that significantly exceed the pore size [11,12]. Mechanical stability of these membranes is also essential to endure handling and high pressures. Graphene has remarkably high fracture strength of 130 GPa and bears strains of ~25% [2], which would expedite its handling on a support. Although pores and defects can decrease the fracture strength by about an order of magnitude [13,14], it is more than sufficient to tolerate high pressures when the atomically thin layer is properly supported. Molecular dynamics simulations show that nanoporous graphene can withstand a pressure of 57 MPa when suspended over 1 μm pores. As the support pore diameter increases, the membrane tolerance to pressure decreases [15].

Experimental approaches to fabrication of nanoporous atomically thin graphene membranes include synthesis of a continuous large layer mainly through chemical vapour deposition (CVD) with controlled porosity and the ability to handle the membrane by utilizing suitable porous supports [16,17], with key challenges to tackle in each section. To date, large area roll-to-roll processed graphene [18,19] is not commercially available, and CVD-grown graphene is inherently polycrystalline with intrinsic vacancy defects, grain boundaries and wrinkles that contribute to leakage paths [20,21], as small pinhole defects for instance, can reduce selectivity. In addition, polymer-based methods to transfer graphene [22–24] leave surface contaminations that add up the probability of defects and pinholes present on the surface. Using an appropriate support layer is essential to minimize these unfavourable effects not only for fabrication of large scale single layer graphene membrane but even for graphene suspended over few hundred microns for a research level desalination experiment. An ideal support will limit ion leakage without unfavourably impacting the permeance. In the presence of undesired imperfections and defects, the support will add a transport resistance in series to both selective pores and defects to obtain high selectivity [21]. In addition, the support with high surface porosity allows efficient usage of the nanoporous membrane area, and exhibit high mechanical strength and chemical resistance; therefore it will provide stable adhesion and facilitate the transfer of the atomically thin graphene layer [16]. Most experimental studies have used particular supports like polycarbonate track-etched membranes [37] and micro-fabricated silicon (Si) supports [33] with low surface porosity or more practical supports such as polypyrrole and polyvinylidenfluoride [41], but meeting all the requirements mentioned for an ideal support, especially for pressure-driven separations, is difficult.

Subnanometer pores can be introduced in the atomically thin sheets of graphene using ion irradiation [25–27] or chemical/plasma etching [3,28–31]. While these methods produce a distribution of pore sizes [25,32], and probably work best in single-layer materials, focused ion beams can create precise pores down to 8 nm in diameter [33] and focused electron beams can create subnanometer-few nanometer pores [34]. Other methods to generate pores include electrochemical machining by atomic force microscopy [28], or the use of electrical pulses to create pores with subnanometer accuracy in graphene [35]. However, machining using focused ion beams is less scalable and more suitable for smaller membranes, while electrochemical methods and machining using atomic force microscopy or focused electron beams are suitable for creation of a few pores for microscale membranes. A few experimental studies have probed water and ion transport across atomically thin graphene pores [20,25,29,33–38] while experimental data on the performance of smaller pores (≤2 nm) is limited. The smallest pores in graphene that permit water transport only allow a single water molecule in their cross-section [39,40]; nevertheless, Surwade et al. [29] reported high rates of water permeation with ~100% NaCl ions rejection across pores of 1 nm.

Here, to demonstrate the effectiveness of single layer graphene as a desalination membrane, a research level experimental setup is prepared introducing a novel yet simple idea of using an initial porous support that holds and suspends the sheet directly and a secondary porous support that allows tuning of desalination parameters. For the initial support, commercial 2000 mesh nickel grids were used as a reliable inexpensive mechanical substrate by limiting the side effects of pinhole defects previously shown in [42]. Large total area suspended single layer CVD graphene membrane was produced and extended to $4.87 \times 10^4 \mu m^2$ comparing to the literature [43–45] where the overall area of the suspended single layer graphene did not exceed a few hundred $\mu m^2$. For the secondary support, we fabricated porous Si with hole arrays of different sizes and spacings. Si at this level, provided the opportunity of limited number of holes with variation of the hole size where alternative commercial supports with similar specifications were not easily accessible and quite expensive. Knowing that realistic graphene membrane with the undesirable features (e.g. holes, defects, cracks and wrinkles) from polymer assisted transfer has inevitable ion leakage, the integration of the secondary fixed support with the mobile graphene/grid membrane allows enhancement of the desalination performance and facilitates tuning of the permeation and rejection parameters by significantly limiting the leakage while maintaining very high permeation rates. Not only 100% NaCl rejection rate was achieved at some motifs, but a range of rejection rates was obtained that can be useful for selectivity applications or separations of larger ions or molecules. Moreover, a range of permeations was attained much higher than the values for commercial desalination filters and higher than values predicted for graphene membranes. Models analogous to experimental assembly were considered to explore more motifs and give insight into the permeation and rejection tuning.

2. Experimental

2.1. Preparation of hole arrays in $Si_3N_4/Si$ wafers

Single side polished $Si_3N_4/Si$ wafers (Supplementary), Si/Ni thereafter, were gone through a combination of wet and dry etching processes with the nitride layer as a hard mask as seen in the schematics in Fig. 1(a). The un-polished bottom nitride layer was first patterned through photolithography and etched away with sulfur hexafluoride (SF$_6$) plasma in a reactive ion etching system (RIE R320 RF, Yar Nikan Saleh, Iran) at 100 W for 3 min. Si was then removed through anisotropic wet etching using 40% KOH as the etchant and 1 cm$^3$ of isopropyl alcohol (IPA) for the improvement of the etching process for 8 h at 80°C. This process stopped when 2–3% of the Si had remained. Fig. 1(b) shows a FESEM image of a membrane with anisotropic walls decorated with microstructures mainly due to the unpolluted nature of the bottom side of SiN/Si. Patterns of the hole arrays with various hole size and spacing were first prepared by Corel software and reduced to 1/5 of their original size on chrome coated glass by a reduction photolithography system (Litho-mask Reduction LA10, Nano Pajuhan Raga, Iran). The polished top side of SiN/Si was patterned through photolithography using the chrome coated glass masks and the nitride layer was removed via RIE with similar conditions as the bottom side. Fig. 1(c) shows a hole with the nitride layer etched vertically by RIE. These holes were further etched in the same KOH etchant for 20–30 min depending on the thickness of the membrane for removal of another ~1% Si. However, < 1% of the Si was remained to provide mechanical support for the top nitride layer and make it less fragile. As seen in Fig. 1(d), hole arrays were formed with a circular SiN mask on top and four anisotropic Si walls underneath. The hole on top of the nitride side was always larger than the hole on the bottom Si side. The width of the holes and the distance between hole centers varied by 6.5–75 μm and 21.4–238 μm, respectively. The dimension of the hole arrays was designed to extend beyond the membrane area to ensure the membrane area was fully covered with the array. The samples were characterized by optical microscope, scanning electron microscope (SEM, TESCAN...
VEGA3 TSS136MM, Czech Rep.) and field emission scanning electron microscope (FESEM-4160, Hitachi, Japan).

2.2. Graphene membrane preparation

Single layer CVD graphene obtained from Graphenea (Supplementary) was used for preparation of the membranes. The supporting material for the membranes was nickel TEM grids with very fine 2000 mesh purchased from TAAB (Supplementary) named as G2000 hereafter. Standard CVD transfer process was carried out with polymethyl methacrylate (PMMA) assistance as follows: PMMA was spun on the graphene/Cu foil and baked for 2 min at 120 °C. The PMMA/graphene/Cu foil was treated in oxygen plasma to remove the back side partial graphene. The foil was then carefully cut into 2.5 × 2.5 mm² square pieces and the copper was subsequently etched away using a FeCl₃ solution. This was followed by repeated washing in deionized water. The floating PMMA/graphene sheets were scooped out with nickel TEM grids and left overnight to fully dry. This was to ensure reasonable conformation of graphene to the grids. The transferred graphene onto grids is named as G/G2000 hereafter. The grids were held at an angle, and acetone was dropwise added on to the surface to remove the PMMA. The surface was let to fully dry after every five drops and the next five drops were added and this continued for 10 times. To minimize mechanical damages (e.g. cracks and pinholes) on the graphene surface, we did not immerse the PMMA/graphene sheet in an acetone bath. Also, heat treatments (> 150 °C) for PMMA removal as recommended in the literature was not applied to G/G2000. Heating the G/G2000 beyond 100 °C could result in a lift off of the graphene sheet from the grid surface due to the softness and flexibility of the grids and partial expansion caused by heat. The grids were handled with care throughout the transfer process to avoid bending of their edges. After the transfer of graphene sheets and removal of PMMA, each sample was carefully examined under optical microscope with enhanced contrast for identification of large ruptures. Samples with major ruptures were exempted from any further measurement. We did try other transfer methods using thermal release tape (TRT) or polylethylene terephthalate (PET)/silicone. However, our observations indicated that graphene transfer with PMMA ended in more continuous sheets and lower density of unintended micro- and nano-meter sized cracks, defects, wrinkles and holes.

2.3. Nanopore formation and membrane characterization

Reactive ion etching of oxygen was used to create intended nanopores on the surface of the free-standing graphene membranes. We followed the protocol of [29] and placed our samples into the plasma cleaner earlier mentioned at 20W power in a vacuum chamber with a flow of pure oxygen at 550 mTorr. The samples were at the same position for 1 s. Prior to each run, the chamber was cleaned with a test run with the same flow of oxygen and power for a minute. The surface of oxygen plasma treated graphene membranes was inspected and characterized with transmission electron microscopy (TEM, Philips CM30), field emission scanning electron microscope (FESEM, JEOL JSM-7610F) and atomic force microscopy (AFM, NT-MDT TS150).

2.4. Design of moveable assembly of G/G2000 over SiN/Si hole arrays

Fig. 2(a) shows schematics of a moveable assembly of G/G2000 over SiN/Si hole array. Using Plexiglas sheets and cylinders we designed a home-made setup for mounting the G/G2000 membranes onto SiN/Si hole arrays, in a manner that while both the membrane and SiN/Si hole arrays were fixed onto their holders, the G/G2000 could be moved on top of the SiN/Si hole arrays. For an accurate amount of movement, a ruler with 100 μm precision was laser etched on x and y directions of the holders of G/G2000 and SiN/Si hole arrays (as schematically shown in Fig. 2(b, c)). Full details of mounting, movement procedure of G/G2000 over SiN/Si hole arrays and the zero leakage assembly are described in the Supplementary. Fig. 2(d) shows a center/center coverage of G/G2000 with SiN/Si hole arrays and Fig. 2(e) shows 100 μm displacement of G/G2000 in both x and y directions with respect to the center of SiN/Si hole arrays. The limiting parameter that could not allow displacements beyond ~200 μm for G/G2000 was the mesh diameter of G2000 which is the only size commercially available. If the mesh area of G2000 was larger, the SiN/Si hole array could be designed larger to fit larger displacements. For water related measurements, we overlaid G/G2000 on SiN/Si hole arrays in five different situations; i) complete overlap of center/center of the holders containing G/G2000 and SiN/Si hole arrays, ii)~v) 100 μm displacement of G/G2000 holder to the left, to the right, to the top and to the bottom of SiN/Si hole array holder, respectively.

Fig. 2(f) shows schematics of single layer graphene covered with randomly distributed features on G2000. This random distribution model will be used in the results and discussion section to give insight into the impact they have on desalination performance. In this model, only micron sized features can be seen. In pristine graphene, the defect density is < 1 per 0.5 × 0.5 μm² [29]. Here, the density of large defects is 22 per ~250 × 250 μm² where large defects can be decomposed into several small defects and significantly increase this value. Small holes
usually occur near defects and we deliberately did not show an adjacent defect near a hole to avoid overcrowding the image. The density of small holes over the sheet is 140 per ~250 × 250 μm² and can meaningfully increase the density of defects on the surface. Fig. 2(g) shows the superposition of the single layer graphene with random distribution of features in Fig. 2(f) with G2000 where the size of holes and bar regions in the grid are scaled exactly as the real G2000. Note that transport is only possible through the holes although the bar area is not shaded.

2.5. Experimental setup for water related measurements

In a homemade experimental setup (Supplementary), salt rejection rates and water permeation values were measured for different samples. A 1 m column of salty water was used as the driving force for water transport across the membranes producing ~10 kPa hydrodynamic pressure. For salt rejection and water permeation measurements of all samples, 10 mM NaCl in deionized water was prepared. Conductivity/total dissolved solids (TDS) of salty water before (feed solution) and after the filters (permeate solution) were measured by portable conductivity/TDS meter (HANNA Instruments HI8731, Romania). The probe of the instrument was held firmly in beakers containing feed solution and permeate solution until conductivity and TDS values were stable and recorded. The conductivity and TDS values of 10 mM NaCl feed solution were 1240 μS and 620 ppm, respectively. Since salt concentration in Brackish water is 500–3000 ppm and in moderate saline water is 3000–10,000 ppm, 620 ppm stands at lower range of Brackish water definition [46]. Salt rejection rate (%) was measured as

\[
1 - \frac{\text{TDS permeate Solution}}{\text{TDS feed solution}} \times 100.
\]

3. Results and discussions

3.1. SiN/Si hole arrays and G/G2000 membrane characteristics

Arrays of holes on SiN/Si were fabricated as described in the Experimental Section 2.1. The size and spacing of the holes were chosen to vary to cover a range of possibilities of their superposition with G/G2000 (Fig. 3(a)i–v) which will be thoroughly discussed in the next subsection. (3 × 3) part of larger arrays ((22 × 22), (7 × 7), (60 × 60), (6 × 6)) in Fig. 3(ai–iii) were selected to better compare the arrangement of holes. The slight misalignments in the holes orientation in Fig. 3(aiii and iii are due to slight misalignment of the membrane with the lithographic mask. Fig. 3(aiii) shows a tilted FESEM image of a larger area of array (60 × 60) with hole width D = 6.5 μm and spacing d = 60 μm. The inset of this figure is a magnified FESEM image of a single hole in the array. The characteristics of the holes originate from the wet and dry etching processes they have undergone. The top circular opening of the holes is due to the vertical etching of the SiN layer with RIE and the sloped walls that join a drain are the result of anisotropic etching in KOH. The combination of these two features may have an impact on the salt rejection and water permeation with and without a graphene layer on top.

FESEM tilted images in Fig. 3(b, c) show G/G2000 surface with some defects. As expected from the characterization of the CVD graphene (Supplementary), the sheet over grids was uniform and most of the regions were monolayer while areas of bilayer or few layers were
hardly found. From optical microscopy, AFM and FESEM character-
izations, mainly defects and wrinkles were evident on the surface of G/
G2000. The presence of holes, cracks and in-plane strain was less evi-
dent in these characterizations. However, the combination of the
mentioned features has been seen in many graphene membranes sus-
pended over larger sized holes and regardless of the number of gra-
phene layers [43–45]. It has been shown in [42] that as the hole area
decreases, the graphene sheet conforms better to the surface of grid bars
and flattens itself reducing strain, wrinkles and curvature in the sus-
pended area. Another reason for the low distribution of micron sized
cracks and holes and significantly low strain is the presence of a high
number of holes in G2000 (> 59,700). In the transfer process, when the
graphene sheet is scooped out from water via the grid, the water drains
fast through the holes and therefore the ef-
effect of trapped water is
negligible compared to graphene transferred onto non-porous surfaces.

Fig. 3(e, f) shows TEM images of treated G/G2000 surfaces with
oxygen plasma at 20 W RF for 1 s. Our characterization over large areas
(100 μm scale and above) showed that there was a range of pores in
size. However, the density of smaller pores was higher. 1–5 pores of
~1 nm width were found in every 10 × 10 nm² unit area while larger
holes of up to 5–8 nm width were distributed less densely (~1 in every
25 × 25 nm² unit area). In a comparison with [29], at 1 s exposure
time, pore size of 1 nm was reached, similar to [29], but larger pores
were also found while in [29], almost uniform pores were formed on
the surface. The distribution of the pores was more than five times
higher than what reported in [29] in a similar area (10 × 10 nm²).
These differences can be attributed to generally higher number of de-
fects on the surface of our samples prior to oxygen plasma treatment.
Here, the only removal method for PMMA was dropwise washing with
acetone as mentioned in Experimental section, while in [29], in addi-
tion to acetone cleaning, each sample was annealed and outgassed in
ultra-high vacuum (UHV) for several hours. The kinetic radius of the
Na⁺ and Cl⁻ ions are reported as 0.102 and 0.181 nm while this
quantity for water is 0.28 nm [16]. Since, NaCl is highly soluble in
water, the ions become hydrated and therefore larger; diameter of hy-
drated Na⁺ and Cl⁻ ions are: 0.716 and 0.664 nm [16]. Theory predicts
that the required pore size for rejecting NaCl is around 0.5 nm, but
recent experiments [29] show for pore size of 1 nm, almost 100% re-
jection is possible. Therefore, 1 nm pore size is small enough to reject
NaCl and allow water molecules pass through.

3.2. Tuning water permeation in mobile G/G2000 on SiN/Si hole arrays

Permeation of water relates to the volume of the water passing
through an area in a certain time and at a specific pressure. For su-
perpositions of G/G2000 over SiN/Si arrays of holes width D and
spacing $d$, at constant pressure 10 kPa and 10 cm$^3$ salty water, the area and time being in the denominator, interplay oppositely in water permeation. We note that area and time relate inversely with each other, i.e. the higher the area the lower the time required for water transport. The array in the first column in Table 1 is the effective size that fits in the membrane area 1.2 $\times$ 1.2 mm$^2$, and smaller than the actual patterned array. For example, original array (22 $\times$ 22) has been reduced to (20 $\times$ 20) to fit the membrane area. The other parts of the array have stayed out of the membrane, and do not play any role in the transport of water or rejection of salt since they are not fully drilled. Without G/2000 on top, the area that lets water through SiN/Si hole arrays is described as the ‘total area of bare holes’ varying from 1.33 $\times$ 10$^4$μm$^2$ to 2.72 $\times$ 10$^5$μm$^2$ and summarized in Table 1. To clarify how the permeation values were calculated, we first demonstrate possible superpositions (i.e. motifs) of G2000 with each hole array. Note that in the experiments, the grid and the Si came very close together and the air between them was sucked out followed by fully tightening with nuts and screws. In the model, we considered zero gap between the grid and the Si. This minimized the possibility of tortuous water passage in between the two supports and therefore had negligible impact on desalination parameters. However, a comprehensive simulation study is required to fully analyse the mechanism of water flow if submicron gaps are considered between the two supports and for different superstructures. Fig. 4(a)-iii shows motifs for G2000 over a section of array (20 $\times$ 20); D = 6.5 μm; d = 60 μm. The width of the array holes is the same as the width of the grid holes. The first motif shows full coverage of a grid hole on an array hole while in the other two, the array holes are partially covered with the grid holes. These three motifs are the only possible situations that can occur for the superposition of G2000 array and array (20 $\times$ 20); D = 6.5 μm; d = 60 μm. Three out of ten motifs of G2000 superposition with hole array (56 $\times$ 56); D = 10.5 μm; d = 21.4 μm are depicted in Fig. 4(b)-ii. A careful inspection of a large area of G2000 and this array shows that there is a unit cell array (4 $\times$ 7) of overlap features that is repeated periodically and form the whole superstructure (Fig. S2, Supplementary). By adding up the area of partial bits of grid holes, each array hole is approximately covered by the area of a single grid hole. Overlay of G2000 on other hole arrays of D = 19, 30 and 75 μm and the possible motifs are respectively shown in Fig. 4(c-e). Using these motifs, the total area of G2000/holes (μm$^2$) letting water through, were calculated for all the relevant experimental cases and models in Table 1. G2000 has a meshed area of 3.14 × 10$^4$μm$^2$ that consists of holes and bar regions. Knowing this, center to center distance of holes (9.5 μm), the width of the bars (3 μm) and the width of holes (6.5 μm) we calculated the area of a unit cell consisting of a hole and bar as 52.61 μm$^2$. The number of holes, the total area of holes and the total area of bar regions for G2000 were calculated as 60,230, 1.99 × 10$^6$μm$^2$ and 1.14 × 10$^6$μm$^2$, respectively. With these simple calculations, 36% of the overall meshed area is blocked via the bar regions. While a large proportion of SiN/Si membrane area is already impermeable by water, the bar area of G2000 may additionally limit the transport from the top depending on the motifs of G2000/holes.

Using TEM images of 1 s oxygen plasma treated graphene, we statistically measured the total area 586 ± 15 nm$^2$ of nanopores with sizes from 1 nm to 8 nm in every 100 $\times$ 100 nm$^2$ unit area and found a ratio of 0.0733 to the total area of nanopores across grid holes overlaid on array holes, described as the ‘total area of G/G2000/holes’ in Table 1. Assuming that transport across a pore is not influenced by its neighbours, the net permeation across the whole membrane is the sum of those across the membrane nanopores. Permeation values were calculated for the experimental configurations knowing the pressure, the volume and the time for passing 10 mM NaCl solution and using the total area of G/G2000/holes values. As described in the Experimental section, for each hole array, G/G2000 was aligned over the array in five different positions, not specifically identifying the motif of the superposition. A range of time (s) values was obtained from the measurement for water transport in each case. Referring to Fig. 4, there are not too many motifs of G/G2000/holes for each array and therefore, we related the minimum and maximum of the time values to the maximum and minimum of total area of G/G2000/holes, respectively. The resulting range of permeation values confirms the effectiveness of the mobile graphene membrane on Si holes. For array (20 $\times$ 20); D = 6.5 μm; d = 60 μm, the difference between the lowest and highest permeations is 1.57 $\times$ 10$^7$Lm$^{-2}$h$^{-1}$bar$^{-1}$ which is significantly large. This is because the difference in time and in total area of G/G2000/holes motifs is significantly large. For array (56 $\times$ 56); D = 10.5 μm; d = 21.4 μm, we did not find a significant difference in time measurements for the five configurations of G/G2000 over this array. As seen in Fig. 4(b), with an approximation, the motifs of these configurations did not significantly differ in a large area and overall,

<table>
<thead>
<tr>
<th>Ref.</th>
<th>Array</th>
<th>Hole size (μm)</th>
<th>Spacing (μm)</th>
<th>Total area of bare holes (μm$^2$)</th>
<th>Total area of G2000/holes (μm$^2$)</th>
<th>Total area of G/G2000/holes (μm$^2$)</th>
<th>Time (s)</th>
<th>Permeation of G/G2000/holes (Lm$^{-2}$h$^{-1}$bar$^{-1}$)</th>
<th>Permeation of G/G2000/holes (g m$^{-2}$s$^{-1}$atm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>[42]</td>
<td>(20 $\times$ 20)</td>
<td>6.5</td>
<td>60</td>
<td>1.33 × 10$^4$</td>
<td>1.33 × 10$^4$</td>
<td>9.73 × 10$^4$</td>
<td>8560–25,112</td>
<td>4.33 × 10$^7$–5.90 × 10$^7$</td>
<td>1.20 × 10$^2$–1.64 × 10$^2$</td>
</tr>
<tr>
<td>[29]</td>
<td>(5 $\times$ 5)</td>
<td>238</td>
<td>75</td>
<td>1.10 × 10$^5$</td>
<td>3.47 × 10$^4$</td>
<td>2.54 × 10$^4$</td>
<td>3181–3326</td>
<td>4.36 × 10$^6$–4.37 × 10$^6$</td>
<td>1.20 × 10$^2$–1.21 × 10$^2$</td>
</tr>
<tr>
<td>Ref. [29]</td>
<td>(6 $\times$ 6)</td>
<td>30</td>
<td>200</td>
<td>2.54 × 10$^4$</td>
<td>2.17 × 10$^4$</td>
<td>1.59 × 10$^4$</td>
<td>4640–5564</td>
<td>4.34 × 10$^7$–4.38 × 10$^7$</td>
<td>1.19 × 10$^2$–1.22 × 10$^2$</td>
</tr>
<tr>
<td>Ref. [29]</td>
<td>(12 $\times$ 12)</td>
<td>100</td>
<td>30</td>
<td>1.02 × 10$^5$</td>
<td>4.87 × 10$^4$</td>
<td>3.57 × 10$^4$</td>
<td>NA</td>
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</table>

Table 1: A description of SiN/Si hole arrays, calculated values for total areas of bare holes, bare G2000 holes over array holes and G/G2000 over hole arrays, experimental values for time of 10 cm$^3$ (10 mL) NaCl solution transport from G/G2000/holes at 10 kPa and finally the calculated permeation values of the transport of the same solution over G/G2000/holes. The following model arrays have no experimental analogue: (20 $\times$ 20); D = 19 μm; d = 60 μm, (12 $\times$ 12); D = 30 μm; d = 100 μm.
each array hole was fully covered by a grid hole. The permeation for this array lies in the range of the permeation values for array ($20 \times 20$), with much higher total area of G/G2000/hole and much lower time. For array ($6 \times 6$); $D = 30 \mu m$; $d = 200 \mu m$, the range of permeation value is again related to different configurations of G/2000 over this array. The values of permeation in this array are close to the lowest values for array ($20 \times 20$) considering the larger total area of G/ G2000/hole and lower time. Similarly, for array ($5 \times 5$); $D = 75 \mu m$; $d = 238 \mu m$, the range of permeation relates to different configurations of G2000 over this array and the values are close to the values of array ($20 \times 20$). However, the differences in the permeation ranges for arrays ($5 \times 5$) and ($6 \times 6$), are $10^6 \text{L} \cdot \text{m}^{-2} \cdot \text{h}^{-1} \cdot \text{bar}^{-1}$ and $4 \times 10^5 \text{L} \cdot \text{m}^{-2} \cdot \text{h}^{-1} \cdot \text{bar}^{-1}$ which are still quite high but an order of magnitude lower than the difference in permeation values of array ($20 \times 20$). There are two other rows in Table 1 that refer to model arrays. These models were defined to explore more configurations of hole arrays and enhance the analysis of the experimental results for both water permeation and salt rejection. Model array ($20 \times 20$); $D = 19 \mu m$; $d = 60 \mu m$ with similar values of total area of G/G2000/hole as array ($5 \times 5$) is predicted to have similar values of permeation. Model array ($12 \times 12$); $D = 30 \mu m$; $d = 100 \mu m$ with total area of G/ G2000/hole almost twice as array ($6 \times 6$); $D = 30 \mu m$; $d = 200 \mu m$, is expected to let water pass through faster but not necessarily twice as fast. Therefore, the effect of area and time do not fully compensate and therefore lower permeation values are expected for array ($12 \times 12$). In Ref. [42], the permeation value for transport of 10 cm$^3$ of 10 mM NaCl solution at 10 kPa over nanoscale of single layer CVD graphene on a single SiN/Si hole with $D = 200 \mu m$ is $2 \times 10^5$ lower than the lowest permeation value reported here. Overall, the permeation values for G/ G2000/holes in all these arrays are an order of magnitude higher than [29], where graphene was suspended over a single 5 μm wide SiN/Si hole under 17 kPa pressure and reported as the first successful graphene membrane for water desalination. Furthermore, the obtained values of permeation are higher than what D. Cohen-Tanugi et al. [47] has reported. In Ref. [47], the water permeability calculated for 0.231 nm$^2$ hydrogenated pore and 0.163 nm$^2$ hydroxylated pore ranged from 39 to 66 L·cm$^{-2}$·day$^{-1}$·MPa$^{-1}$. Our permeation values translated into the same units range from 1.03 $\times$ 10$^5$ to 1.41 $\times$ 10$^6$L·cm$^{-2}$·day$^{-1}$·MPa$^{-1}$, around two orders of magnitude larger than what was predicted for hydrogenated and hydroxylated pores. This large difference could be due to larger pore size, and several times higher number of pores which allow more water pass through per time per area at a given pressure. Additionally, it is arguable that after plasma treatment, the graphene has been decorated with oxygen-containing groups that can turn graphene hydrophobic and make water enter the interface energetically more favourable. Note that permeation for commercial filters lies between 0.1 and 1 L·cm$^{-2}$·day$^{-1}$·MPa$^{-1}$ [47]. O’Hern et al. [37] created centimetre-scale single-layer graphene nanoporous membrane by multiscale sealing of defects. After introducing subnanometer pores by ion irradiation and etching, the resulting membrane exhibited water permeance based on graphene area comparable to polyamide reverse osmosis membranes. Celebi et al. [33] stacked two layers of graphene on a Si support to form a nearly impermeable layer with ordered arrays of pores with $D = 8–1000$ nm machined using a focused ion beam. The measured water flow rates (per unit graphene area) were five to seven times greater than commercial ultrafiltration membranes.

3.3. Tuning salt rejection in mobile G/G2000 on SiN/Si hole arrays

The model of G/G2000 with a random distribution of defects, holes, wrinkles and cracks, introduced earlier in Fig. 2(g), is overlaid on various hole arrays (Fig. 5) to give more insight into salt rejection process of G/G2000/holes. To keep the schematic model simple, we assume that the graphene sheet has nanopores with size and distribution obtained from 1 s oxygen plasma treatment as discussed in Section 3.1. It is obvious that at this scale, we cannot show the nanopores in the schematic model. With nanoporous graphene decorated randomly with various features on top, there are now many possibilities that one could imagine for the superposition of G/G2000 over the hole arrays, where several situations can occur. Each SiN/Si hole covered with nanoporous graphene may have (I) no feature, (II) only micron sized holes, (III) only defects, (III) only wrinkles, (V) only cracks and (VI) a combination of two or more features, which will determine the salt rejection. In the case of (I), the salt rejection would be 100%. However, it is not simple to predict the salt rejection in the other five situations. In our model, regardless of the possibility of still having some rejection across the features in real case, we assumed 0% rejection. With this assumption, we obtained a range of rejection % for various motifs of G/G2000/hole arrays.

We chose a SiN/Si cell of $254 \times 254 \mu m^2$ dimension to fit the random model of G/G2000. This cell was ~22 times smaller than the experimental case and only part of each SiN/Si hole array fitted in the
cell. Due to limitations of the size of the cell, the size of the modelled G/G2000 and the width and spacing of the hole arrays, we could only focus on a few motifs in some of the cases. Fig. 5(a) shows a motif of G/G2000 over array (4 × 4); D = 6.5; d = 60 μm, with a squared dashed box on the top left corner selecting 49 grid holes. Each grid hole was superimposed on the center of the top left corner SiN/Si hole making a motif. The other three squared dashed boxes result in similar motifs as the first one. We did not consider half coverage or quarter coverage of a hole array with a grid hole, i.e. we only considered the situation of Fig. 4(a)ii. For array (10 × 10); D = 10.5 μm; d = 21.4 μm, using the same method, 25 motifs were formed (Fig. 5(b)). Here, we only considered the situation in Fig. 4(b). Even a smaller number of motifs (only 8) were formed for array (2 × 2); D = 30 μm; d = 200 μm where situation in Fig. 4(d) was considered. However, 385 motifs could be formed for array (1 × 1); D = 75 μm; d = 238 μm, but we only considered 200 motifs as shown in Fig. 5(d). To count these motifs, we used the situation in Fig. 4(e)ii. The number of possible motifs in Fig. 5(e) for array (4 × 4); D = 19 μm; d = 60 μm, was 84. Unlike array (4 × 4); D = 6.5 μm; d = 60 μm, each SiN/Si hole could cover three grid holes. We used situation in Fig. 4(c) with three grid holes fitting in the SiN/Si hole, with two configurations: 1) one hole on the top row and two holes on the bottom row, or 2) two holes on the top row and one hole on the bottom row. For array (3 × 3); D = 30 μm; d = 100 μm in Fig. 5(f), the number of motifs was only 8 with situation in Fig. 4(d)ii used.

For each motif, we manually counted the number of situations where (I) did not occur and divided it by the number of holes that could practically let water pass through in the cell and multiplied it by 100 as the rejection %. For each array, we counted the number of motifs that gave a certain rejection % and divided it by the number of all possible motifs and multiplied it by 100 to express it as a percentage. In this way, we could compare the percentage of motifs in different hole arrays. For (4 × 4); D = 6.5 μm; d = 60 μm in Fig. 6(a), the rejection % ranged broadly from 59.5% to 100%, while the highest percentage of motifs gave rejections 75–81%. For (10 × 10); D = 10.5 μm; d = 21.4 μm in Fig. 6(b), the rejection % range narrowed down to 73.5%–86%, while the highest percentage of motifs gave rejections of 78–80%. In Fig. 6(c), the rejection % range was 66%–87%, with the highest percentage of motifs giving rejections 73–76%. In Fig. 6(d), the rejection % ranged from 63% to 87%, with a peak of percentage of motifs at rejections 65–71%. For the model array (4 × 4); D = 19 μm; d = 60 μm, the rejection % range was 58.3–85% with highest percentage of motifs giving rejections 73–77% rejection. Finally, for array (3 × 3); D = 30 μm; d = 100 μm, the rejection % ranged from 72% to 81% showing a peak of percentage of motifs at rejections 74.2–75%. It is evident that as D increases, the highest percentage of motifs gives lower rejection rates. It is also concluded that the range of rejection % is broader for the smaller D. Motifs with maximum rejection % are shown in Fig. S3 (Supplementary), for all the arrays in Fig. 5.

Experimental results for salt rejection of G/G2000 over the 1.2 × 1.2 mm² SiN/Si membrane with hole arrays are presented in Fig. 6 for comparison. A range of rejection % in experimental results confirms that tuning of desalination parameters is possible by controllable movement of G/G2000 over SiN/Si hole arrays. As discussed in the previous subsection, G/G2000 was aligned in five motifs over SiN/Si hole arrays and measurements were carried out. Prior to comparing these results, there are several notes to make: I) the random distribution model of defects, cracks, holes and wrinkles on G/G2000 resembles the experimental G/G2000 samples but it is not identical. Even two experimental G/G2000 samples are never identical since the distribution of features is always random. II) The number of motifs for the model ranged from 8 to 200, but the number of experimental motifs were limited to 5. III) The area in the experimental case was 22 times larger than the model, but since the model is random, it can be
compared to a large area in experiment with an approximation. III) The motifs in the models were obtained by very small displacements (a few μm) but the motifs in the experimental cases were made by 100 μm displacements. Since the SiN/Si hole arrays are regular and the graphene model on G2000 is random, the overlay of the two, would still be random and any size of movement would result in a different motif. Therefore, there is no periodicity in the occurrence of the motifs and hence, no specific quantity and direction of G/G2000 displacement over SiN/Si hole arrays is favoured over any other quantity or direction. IV) In the model, we assumed a hole covered by graphene with any kind of feature would have a rejection of 0% while in experiment even bare grids have 5−7% rejections and bare SiN/Si hole arrays with D = 5−200 μm (Fig. 6(g)), have rejections of 29−14%, therefore it is predicted that a graphene sheet over a grid hole (D = 6.5 μm) decorated partially with a crack, a hole or defect, should not completely be permeable to the salt. Furthermore, in reality, a small or even a large wrinkle does not necessarily rupture the graphene membrane without application of stress or strain and therefore it may not impact the salt rejection as long as it has not damaged the sheet. VI) The structure of SiN/Si hole arrays (with anisotropic side walls and micro features on the walls) and their size and spacing contribute to salt rejection while this effect was neglected in the model. VII) A crack usually occurs if wrinkles are too large or there is sufficient amount of strain over the graphene membrane as observed in graphene suspended over holes with D = 10−75 μm [42]. According to our FESEM analysis, we did not observe cracks on the surface of G/G2000 since the strain was very low. Only if the e-beam was focused on an area, a crack was deliberately created. In the model, we have considered several small and large cracks on G/G2000 surface to generalize the usage of this model for larger suspended structures. According to the last three notes, the rejection % obtained from motifs in the models is expected to be lower than their experimental analogues especially in arrays with smaller D.

To demonstrate the effect of cracks on salt rejection in Fig. 6(i), we have eliminated the cracks on the model (Random Features B), overlaid it on the smallest hole arrays (4 × 4); D = 6.5 μm; d = 60 μm, and compared the results of salt rejection % with the original random distribution containing cracks (Random Features A) in Fig. 6(h). The comparison shows that the minimum rejection % shifts to higher values and the percentage of motifs at higher rejection % increases. The results of Random Features B are closer to the experimental results for this hole array. As D increases to 30 and 75 μm, the G/G2000 membrane loses more of the supporting effect of SiN/Si surface. The larger the area of hole-free SiN/Si surface, the more it will cover and limit the undesired areas of graphene membrane. A comparison shows that for arrays with smaller D (6 and 10.5 μm) in experimental cases, more motifs have higher rejection % and the minimum rejection % is significantly higher with respect to analogous model results. For experimental arrays with larger D (30 and 75 μm), the minimum rejection % are lower compared to equivalent model results.

Comparing our salt rejection results with literature, Surf et al. [29] demonstrated water/ion selectivity using oxygen plasma to introduce ~1 nm pores at a density of ~1012 cm−2 in single-layer graphene placed on a 5 μm aperture. For 1 s plasma treatment, 20% of the samples rejected all NaCl ions at 40 °C thereby evaporation may have played a role. Centimetre-scale single-layer graphene membrane by multiscale sealing of defects created by O’Hern et al. [37] rejected organic molecules (≥1 nm) and divalent MgSO4 (but not NaCl) under osmotically driven flow with subnanometer pores created by ion irradiation and etching.

We did not explore the effect of using bilayer or few layer graphene on desalination performance; however, according to Ref. [48], if layer separation and pore alignment in few layer graphene membranes could not be controlled experimentally, their performance for desalination could be less effective than in single layer. To date, there are no reports of creating aligned subnanometer pores in multilayer materials [16], though assuming that creating the pores on each layer stepwise with oxygen plasma is possible, but there is still a lack of experience in controlling layer separation and pore alignment in bi or few layer graphene that can be left for future work.

3.4. Microporous supports for realistic desalination plants

Si with different array of holes was fabricated here at a research level and as a secondary support for graphene to find the optimum size and distance of the holes in order to favourably limit the leakage of the ions and keep the permeation values high. However, for realistic desalination plants, Si may not be an ideal support. With the current technology, porous Si cannot be fabricated without the introduction of a thin membrane. Not only the effective area of the wafer reduces to the membrane extent, but the thin membrane area decorated with pores of micron sizes, becomes fragile and may not withstand the pressures required for reverse osmosis (RO) in desalination plants. Though Si may be useful for plate and frame desalination module and for low volume applications, it is not flexible to be rolled and fitted into the pressure vessels for some specific modules of desalination plants like spiral wound module. Besides, microfabrication of Si and the price of the wafer itself is not cost effective for industrial scale applications. However, the idea of a fixed secondary porous support specifically for atomically thin membranes (e.g. graphene and MoS2 as two popular candidates with inevitable defects from transfer), can be envisaged with Si replacement candidates. One such example is thin nickel foil (>50 μm), where the flexibility allows rolling up of the whole assembly, the surface can be chemically etched for the creation of hole arrays, the material does not corrode when applied to large volume of salty water and the material is accessible and less expensive for large area fabrication. Additionally the overall weight of thin nickel foils in an element would not be much higher than the commercial membranes.

Nevertheless, the main challenge is the limitations of large area fabrication of single layer graphene and creation of nanopores at an industrial scale. Assuming that the current spiral wound module is the ideal RO element, the largest graphene sheet of 30 in. on copper produced by roll to roll method [18] can be fitted into a commercial element with small diameter and small length. For this we propose to grow the graphene directly onto thin nickel foil as an alternative catalyst, using the same large diameter quartz tube in [18] and without adding any polymer. Next step is to pattern the backside of the foil into numerous holes (<6 μm) and chemically etch the holes to obtain large total area of suspended graphene. While bar regions of the nickel still support the sheet mechanically as is in grids, the holes allow water flow. From simulations, nanoporous flat graphene sheet in a plate and frame module can withstand pressures an order of magnitude higher than the required RO membranes and no curvature is expected to happen to it, however a concern in rolling graphene membranes for spiral wound module is the quantity of the stress/strain applied in plane or out of plane of the rolled sheet that might cause instability for the membrane. For instance if the strain exceeds 25%, the graphene sheet might rupture. Therefore it is left to in depth future studies to predict the strain via simulations or find approximate experimental values or find methods of step by step rolling of the sheet to keep the strain below the threshold values.
Table 2

<table>
<thead>
<tr>
<th>Element (diameter × length)</th>
<th>Effective area of membrane (m²)</th>
<th>Dow Filmtec (TFM) GPD</th>
<th>Ami membranes (TFM) GPD</th>
<th>G/Ni/Ni</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.5″ × 14″</td>
<td>0.65</td>
<td>$144 (200)</td>
<td>$137 (200)</td>
<td>$1200</td>
</tr>
<tr>
<td>2″ × 26″</td>
<td>0.65</td>
<td>$169 (220)</td>
<td>$141 (220)</td>
<td></td>
</tr>
<tr>
<td>2.5″ × 21″</td>
<td>1.2</td>
<td>$165 (325)</td>
<td>$140 (325)</td>
<td></td>
</tr>
<tr>
<td>4″ × 40″</td>
<td>8</td>
<td>$299 (900)</td>
<td>$256 (3000)</td>
<td></td>
</tr>
</tbody>
</table>

Next step is creating nanorods; the front side of the large graphene sheet can be exposed to plasma treatment to introduce nanorods in unique systems like Corial 360RL RIE or Corial D500 PECDV, where plasma can form between large plates accommodating sheets as large as 50 cm × 50 cm. In order to tune the salt rejection and water permeation, the secondary nickel foil with hole arrays can be used. After several trials of various alignments between the two supports and rejection tests to obtain the optimum values, both sheets can be glued together with the best alignment and the ensemble can be rolled with spacers to fit a RO desalination element with certain dimensions. One of the smallest RO elements commercially available (Dow Filmtec, ami membranes) have an effective membrane area of 0.65 m². In order to fully fit an element with graphene membrane, we would need two such ensembles to make up this effective area. An accurate evaluation of the total cost for the fabrication of two ensembles with 30 in. graphene on two nickel foils, is not at hand even though the materials may have total cost for the fabrication of two ensembles with 30 in. graphene on fully.

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References


