Highly porous nanofiber-supported monolayer graphene membranes for ultrafast organic solvent nanofiltration

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Scalable fabrication of monolayer graphene membrane on porous supports is key to realizing practical applications of atomically thin membranes, but it is technologically challenging. Here, we demonstrate a facile and versatile electrospinning approach to realize nanoporous graphene membranes on different polymeric supports with high porosity for efficient diffusion- and pressure-driven separations. The conductive graphene works as an excellent receptor for deposition of highly porous nanofibers during electrospinning, thereby enabling direct attachment of graphene to the support. A universal “binder” additive is shown to enhance adhesion between the graphene layer and polymeric supports, resulting in high graphene coverage on nanofibers made from different polymers. After defect sealing and oxygen plasma treatment, the resulting nanoporous membranes demonstrate record-high performances in dialysis and organic solvent nanofiltration, with a pure ethanol permeance of 156.8 liters m⁻² hour⁻¹ bar⁻¹ and 94.5% rejection to Rose Bengal (1011 g mol⁻¹) that surpasses the permeability-selectivity trade-off.

INTRODUCTION

Two-dimensional (2D) graphene offers tremendous opportunities for membrane separations (1). The atomic thickness of monolayer graphene is the thinnest possible among all existing materials, thereby holding great potential for high fluxes in membrane processes (2). Simulations revealed that introducing tailored nanopores into the graphene lattice can produce extremely high permeance and good selectivity for gas separation (3) and water desalination (4). Experimental results on nanoporous graphene sheet suspended on micrometer-sized pores (5–8) are in agreement with theoretical predictions. Suspended monolayer graphene is mechanically robust to withstand a hydraulic pressure of up to 100 bar (9) when properly supported, positioning the strength of the material in the practically useful range.

Among various membrane separation processes, one such area that has received intensive attention in recent years is organic solvent nanofiltration (OSN) (10, 11). In a typical pharmaceutical operation, solvent use accounts for 80 to 90% of the total mass consumption (12), contributing to substantial energy cost. Membrane-based OSN can potentially lead to up to 90% energy saving compared to the now-dominant evaporation or distillation process (13). To ensure long-term stability and operation safety, a membrane material that is intrinsically resistant to solvents is preferred. Thus far, most membranes developed for OSN are polymeric (11). Compared to many of the existing polymeric materials, the thermal and chemical stability of graphene makes it attractive for separations where resistance to high temperature or solvent is a must. However, the application of nanoporous graphene membranes for OSN has been rarely reported, and its scalable fabrication at the macroscale still remains a key technical bottleneck to realizing real-world applications.

Ideally, monolayer graphene that is typically grown by chemical vapor deposition (CVD) on copper should be transferred in a facile and defect-free approach to a porous support before a functional membrane becomes possible. Earlier efforts have focused on polymer-assisted transfer (14), where a sacrificial polymer layer is coated onto the graphene surface. In general, the polymer should have weak interactions with graphene to allow easy removal (15). The polymer-assisted method is theoretically applicable to any target substrate, but it suffers from limited scalability due to the complicated transfer procedures and requires substrates that are compatible with removal of the polymer layer that is typically done using solvents such as acetone or by high-temperature annealing. Alternatively, direct transfer enables the attachment of graphene onto a given substrate without the aid of any sacrificial material, providing benefits of process intensification in membrane production at scale. Often, it is achieved by mechanical forces that are sometimes coupled by thermal annealing, such as roll-to-roll lamination (16–19) and hot press (20, 21). The first functional membranes based on direct transfer was reported in 2012 by O’Hern et al. (22) through mechanical pressing where hydrophobic track-etched polycarbonate films were used as the supports. Recently, direct casting of a polyethersulfone solution onto the surface of graphene-copper foil has been experimented, followed by phase inversion to form a composite membrane (23–25). The Agrawal group developed porous carbon-supported monolayer graphene membranes by spin coating of a block copolymer and subsequent annealing at 500°C (25). In 2019, carbon nanotubes were deposited onto graphene to form a porous thin film, providing effective support for nanoporous graphene created with an in situ grown meso-SiO₂ template (26). Nonetheless, these methods are generally demonstrated on one specific type of polymer or material, which might limit their applications in different separations.

In addition, engineering porosity in the support is important. A highly porous support is required for efficient dialysis and forward osmosis, where internal concentration polarization can cause severe

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Detailed procedures are given in fig. S1. Nanopore creation by oxygen plasma under 37 W and 40- to 300-s exposure time. Etching of copper by 10 wt % ammonium persulfate (APS) solution. Electrospinning followed by hot press. Further evidence is given by scanning electron microscope (SEM) images in Fig. 2D, where fully porous PAN substrate is clearly covered by a transparent layer of graphene (with the presence of defects), with graphene exhibiting areal coverage of ~69% based on image analysis (Fig. 21 and fig. S6). The uncovered area might be attributed to the tears that are formed because of the wetting of PAN substrate during transfer. On the contrary, PVDF substrate alone does not allow stable attachment of graphene (Fig. 2, B and E), resulting in a low graphene coverage of ~30% (Fig. 21 and fig. S6).

Here, we demonstrate a facile method to directly transfer graphene onto highly porous electrospun nanofiber substrates made from different polymers via design of chemistry. As illustrated in Fig. 1, a graphene/nanofiber composite membrane was fabricated following four main steps: electrospinning with hot press, etching of copper, defect sealing by interfacial polymerization (IP), and selective nanopore creation by oxygen plasma. It is noticed that the limited contact area between cylindrical nanofibers and graphene surface poses a great challenge in maintaining the integrity of graphene-covered composite membranes. We show that by simply adding chemicals with suitable chemistry and configuration, nanofiber-supported graphene membranes based on both poly(acrylonitrile-co-vinyl acetate) co-polymer (abbreviated as PAN) and polyvinylidene fluoride (PVDF) can be realized. Highly selective pores have been created by oxygen plasma exposure, as is evident by effective molecular separations in both diffusion- and pressure-driven processes, with selectivity surpassing state-of-the-art membranes for dialysis and 94.5% rejection to Rose Bengal (RB) at a high ethanol permeance of 156.8 liters m⁻² hour⁻¹ bar⁻¹ for OSN.

RESULTS

Direct transfer of graphene onto nanofiber supports

PAN and PVDF are two of the most widely used low-cost polymers for commercial membranes (fig. S2). Here, they also serve as representatives of hydrophilic and hydrophobic polymers, respectively. Figure 2A and figs. S3 and S4 show the highly porous nanofibrous structure of these electrospun supports. When graphene on copper was used as the fiber collector, the nanofibers attach to its surface and provide mechanical support during the etching of copper in an ammonium persulfate (APS) aqueous solution (Fig. 2B). We observed wetting of the PAN nanofiber support during etching due to the hydrophilicity of PAN. Although wetting of the porous support has been considered an issue for high-fidelity direct transfer of graphene, graphene-covered PAN membranes were obtained, visually seen as a uniform gray square, representative of monolayer graphene on PAN (named as PAN-G, where G denotes that there is a graphene layer on the electrospun support). Further evidence is given by scanning electron microscope (SEM) images in Fig. 2D, where fully porous PAN substrate is clearly covered by a transparent layer of graphene (with the presence of defects), with graphene exhibiting areal coverage of ~69% based on image analysis (Fig. 21 and fig. S6). The uncovered area might be attributed to the tears that are formed because of the wetting of PAN substrate during transfer. On the contrary, PVDF substrate alone does not allow stable attachment of graphene (Fig. 2, B and E), resulting in a low graphene coverage of ~30% (Fig. 21 and fig. S6).

Molecular dynamics (MD) simulations (Fig. 3A and fig. S7) were performed to evaluate the interaction energies in the membrane fabrication process: (step 1) graphene and nanofiber were in contact with each other, under elevated temperature and pressure during hot press, (step 2) the pressure was released, and (step 3) the temperature was reduced to 25°C. For each system, the interaction energy decreases rapidly at the initial stage and then approaches a constant. Overall, the energy between graphene and PAN is lower than that with PVDF, suggesting stronger interaction and higher adhesion of the graphene-PAN pair. The difference is a result of the interaction strengths (ε) of oxygen (0.87) and nitrogen (0.71) in PAN as compared to that of fluoride (0.22) in PVDF. In Fig. 3B, a peak is present in the graphene-N and graphene-O radial distribution function profiles near graphene at the position of 0.35 to 0.4 nm, indicating that N and O tend to stay close to graphene, thus contributing to strong affinity between graphene and PAN, and the relatively higher surface coverage. An additional peak at 0.9 to 1.0 nm in the graphene-O profile might be due to steric effects. In contrast, no peak is observed in the profile of graphene-F, which implies the lack of strong interaction between PVDF and graphene.

To address membrane wetting and increase graphene coverage, three different types of polyhedral oligomeric silsesquioxane (POSS), including octaepoxycyclohexyl-dimethylsilyslyl (EP)−, trisnorbornenylisobutyl (NB)−, and octaphenyl (MS)−POSS (Fig. 2C and fig. S2), were added to the polymer solutions at a concentration of 2 weight % (wt %), with all other electrospinning and membrane fabrication procedures remaining unchanged (table S1). Note that MS-POSS is not miscible with PAN. The POSS molecules contain a

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**Fig. 1. Schematic illustration of the electrospinning-assisted direct transfer method for the fabrication of graphene-covered nanofiber membrane.** (A) Electrospinning followed by hot press. (B) Etching of copper by 10 wt % ammonium persulfate (APS) solution. (C) Defect sealing by IP using m-phenylenediamine and trimesoyl chloride as reactive monomers in the aqueous and organic phase, respectively. (D) Nanopore creation by oxygen plasma under 37 W and 40- to 300-s exposure time. Detailed procedures are given in fig. S1.
silicon oxide cage and one to two carbon-rich functional groups bonded to each silicon atom. Notably, the functional groups in EP-POSS are relatively flexible, while triangular norbornenyl and rigid structures are present in NB- and MS-POSS, respectively.

The presence of POSS in the nanofibers is confirmed by elementary analysis in fig. S8 and table S2. Upon the addition of POSS, the water contact angles of PAN-based supports are markedly increased from ~60° to >120° (Fig. 2H), transforming the membranes from...
hydrophilic to hydrophobic. The hydrophobicity of PVDF-based supports remained almost unchanged. Not surprisingly, no wetting was observed with any of the modified supports during the copper etching step (Fig. 2B). Figure 2 (B and D) and figs. S3 and S5 show that monolayer graphene is attached to most supports, in particular to those with EP-POSS. The surface coverage of graphene on PAN-EP-G (referring to graphene-covered PAN support containing EP-POSS) and PVDF-EP-G reaches 91 to 98% and 85%, respectively (Fig. 2I and fig. S6). The uniformity and low defect density of PAN-EP-G membrane were further demonstrated in fig. S9. MD simulations reveal that the lowest interaction energy of graphene is with EP-POSS, in comparison to PAN and PVDF, thus giving high surface coverage (Fig. 3A). The other two POSS additives are less effective, possibly due to the relatively sharp or rigid structures of their pendants to the silicon cage, as is evidenced by the highest interaction energy of MS-POSS with graphene (Fig. 3A). Our results suggest that hydrophobic molecules with structurally flexible chains may function as ideal “binder” additives to improve the attachment between nanofibers and graphene, thus enabling the preparation of monolayer graphene membranes based on supports made from different polymers.

**Nanoporous monolayer graphene membranes by defect sealing and oxygen plasma exposure**

After successful transfer of graphene onto nanofiber supports, we performed an initial evaluation of the membranes via potassium chloride (KCl) diffusion tests under continuous stirring at 1500 rpm (Fig. 4A). However, the graphene layer on PAN-EP nanofiber support was completely destroyed during the test as shown in fig. S10.

**Fig. 4. Sealing of defects on graphene membranes and creation of pores by oxygen plasma.** (A) Schematic illustration of the diffusion test. (B) Normalized diffusive fluxes of KCl for the membranes PAN-EP, PAN-EP-G, PAN-EP-G-IP’ (sealing after test), PAN-EP-G-IP-300s, PAN-EP-G-IP (sealing before test), and PAN-EP-G-IP-300s; 300s denotes the plasma treatment time (error bars represent SD and were calculated on the basis of at least three data points measured from different samples). (C) SEM images of top surfaces of PAN-EP-G-IP and PAN-EP-G-IP’ membranes, showing an intact graphene layer if sealing was done before test (PAN-EP-G-IP) and a dense polyamide layer if sealing was done after test (PAN-EP-G-IP’). (D) Raman spectra of the graphene membrane transferred onto silica wafer with and without treating by oxygen plasma. TEM images of (E) the pristine graphene and (F and G) nanoporous graphene with oxygen plasma exposure for 60 s.
which is verified by the high normalized KCl diffusion rate in Fig. 4B observed from the beginning of the test. It suggests that the high porosity and large pore size of the nanofiber support are unable to prevent the graphene layer from being torn under the action of the liquid meniscus.

IP was conducted to seal the defective sites of graphene using m-phenylenediamine (MPD) in the aqueous phase and trimesoyl chloride (TMC) in the hexane phase (Fig. 1, step 3) (30). When the sealing step was done after diffusion test, the membrane (PAN-EP-G-IP) becomes almost impermeable to KCl, even after 300 s of exposure to argon plasma (Fig. 4B). A new polymer layer is seen under SEM to have been formed on both the top and bottom surfaces of the membrane (Fig. 4C and fig. S11), again confirming the instability of graphene caused by defects. In contrast, most of the graphene layer remains clear and unblocked when defect sealing was done before diffusion tests (PAN-EP-G-IP). In addition, fig. S12 shows that after exposure to oxygen plasma for 300 s, a small number of polyamide plugs remain on the surface and inside the pores of the nanofiber support. Figure S13 further demonstrates the presence of polyamide plugs at the defective sites and the intact transparent graphene layer. In addition, the PAN-EP-G-IP membrane allows ~8% of the KCl flux of the bare support. Upon 300 s of exposure to plasma, the KCl diffusive flux is increased by >14 times to 88%, supporting the irreversible leakage through the defects but also prevents the growth of defects to maintain the integrity of graphene-covered nanofiber membranes. We hypothesize that the added polymer fills in to support the membrane (Fig. 4C and fig. S11), again confirming the instability of graphene caused by defects. In contrast, most of the graphene layer remains clear and unblocked when defect sealing was done before diffusion tests (PAN-EP-G-IP). In addition, fig. S12 shows that after exposure to oxygen plasma for 300 s, a small number of polyamide plugs remain on the surface and inside the pores of the nanofiber support. Figure S13 further demonstrates the presence of polyamide plugs at the defective sites and the intact transparent graphene layer. In addition, the PAN-EP-G-IP membrane allows ~8% of the KCl flux of the bare support. Upon 300 s of exposure to plasma, the KCl diffusive flux is increased by >14 times to 88%, supporting the irreversible leakage through the defects but also prevents the growth of defects to maintain the integrity of graphene-covered nanofiber membranes. We hypothesize that the added polymer fills in to support the free edges and other defects in the graphene layer, preventing them from being torn off under the action of the liquid meniscus.

Having obtained a stable, defect-sealed PAN-EP-G membrane, we now proceed to create nanopores in graphene by oxygen plasma. The formation of pores is qualitatively monitored by Raman spectroscopy. Figure 4D shows the characteristic 2D and G peaks on pristine graphene (0 s) without apparent D peak with a high intensity ratio $I_{2D}/I_G$ (>2), which proves the high structural quality of monolayer graphene. With longer exposure to oxygen plasma, defects are generated on graphene as is evidenced by the emergence of D peaks. Meanwhile, the width of D peak also increases, which might be caused by the formation of mixed sp² and sp³ bonds (27, 31). At an exposure time of 300 s, the intensity of signals is reduced, most likely due to the lower quantity of graphene that remains on the surface under plasma etching. When the nanopores were generated on PAN-EP-G-IP membrane, we notice that the integrity of graphene after 60 s of plasma exposure remains good (fig. S14), while 300-s plasma exposure completely destroys the graphene layer (fig. S12).

Figure 4 (E to G) and fig. S15 probe into the changes of graphene structure via spherical aberration-corrected transmission electron microscope (TEM). Pristine graphene shows clear, intact honeycomb-like lattice structure. After exposure to oxygen plasma for 60 s, a new layer of graphene sample was prepared from PAN-EP-G-IP-60s membrane, defects are formed. Most of those defects have a size of ~1 nm; in addition, a small portion of pores whose size is <0.5 or >1.5 nm also exists. An analysis of >10 TEM images reveals a defect density of ~1.1 × 10²² cm⁻².

**Ultrafast and selective diffusive separation and OSN**

The diffusive permeance and selectivity of PAN-EP-G-IP membranes (thickness ~ 30 μm; fig. S4) with different plasma treatment durations were examined in a diffusion cell with a selection of solutes in water, including KCl (75 g mol⁻¹), L-tryptophan (LT; 204 g mol⁻¹), Allura Red AC (AR; 496 g mol⁻¹), vitamin B12 (VB; 1335 g mol⁻¹), and lysozyme (LYS; 14,300 g mol⁻¹). The low permeances and high selectivities of PAN-EP-G-IP membrane for these solutes (Fig. 5, B and C) confirm the effective sealing by the polyamide plug. With increasing plasma exposure duration, the permeances of all solute species increase to different extents. The normalized diffusive fluxes of KCl and LT in Fig. 5A are distinctly higher than other solutes, consistent with their higher diffusion coefficients. Moreover, it can be seen in Fig. 5 (A and C) that the normalized fluxes of KCl and AR both increase fast, giving slightly decreasing selectivity upon increasing plasma exposure time up to 100 s. Meanwhile, the normalized flux of LT demonstrates a relatively sharp rise at 60 and 100 s of plasma treatment time, giving higher LT/AR selectivities of 8.03 and 6.24, respectively, suggesting that the size of most pores created by plasma within 100 s is distributed between LT and AR (204 to 496 g mol⁻¹). We notice that the sizes of LT and AR molecules are ~0.7 and ~1 nm, respectively (table S3). The observations are therefore consistent with the defect size that is revealed earlier by TEM images. Increased leakage rates of large molecules such as VB and LYS imply that a few large pores are also formed as is shown by TEM images in fig. S15, but overall, the selectivities are high within 100 s of plasma exposure time. For example, the KCl permeance reaches 6.59 × 10⁻⁸ m s⁻¹, while KCl/LYS selectivity and corresponding normalized selectivity are 93.06 and 9.54 at an exposure time of 100 s. A long plasma treatment time of 300 s, however, leads to extensive damage to the graphene layer, as is suggested by the low selectivity and the increase in permeance of LYS. Comparisons with other membranes (24, 27, 32) in literature works are given in Fig. 5 (E and F) and tables S4 and S5. Clearly, our membranes produce much higher permeance and selectivity than state-of-the-art commercial and laboratory-scale membranes, although at relatively large thickness of 30 μm. This is attributed to the high porosity of nanofiber supports that not only reduces concentration polarization but also exposes a large fraction of graphene to solute transport.

Next, the potential of nanofiber-supported monolayer graphene membranes for OSN was evaluated in a pressure-driven cell with ethanol as the solvent. Ethanol was chosen because it is among the top 10 solvents used in pharmaceutical plants (12). Figure 6A shows that ethanol is impermeable through PAN-EP-G-IP membrane. With plasma exposure for 40 s, a high pure ethanol permeance is achieved at 61.0 liters m⁻² hour⁻¹ bar⁻¹. The value is further boosted to 156.8 and 487.7 liters m⁻² hour⁻¹ bar⁻¹ at 50 and 60 s, respectively. It is also seen from Fig. 6B that the rejection to RB [1011 g mol⁻¹, 50 parts per million (ppm)] reaches 98.3% at 40 s and 94.5% at 50 s and decreases to below 80% at 60 s. This result is explained by TEM images in Fig. 4 (F and G) and fig. S15 as most nanopores are ~1 nm, which are larger than solvent molecules but smaller than RB (1.24 nm by 1.12 nm by 0.89 nm) (33). However, a few large pores (>1.5 nm) are also observed under 60-s exposure, leading to a slightly lower rejection. At increasing RB concentration in the feed, the rejection of PAN-EP-G-IP-50s membrane increases slightly to 96.0% at 500 ppm (fig. S16), while ethanol flux is mildly reduced. The decreased permeance is resulted from the higher osmotic pressure (34, 35) and additional transport resistance due to the accumulation of rejected dyes on the membrane surface (34, 36, 37), and the later factor is also responsible for the higher rejection (36, 37).
To get a better understanding of the transport properties of graphene membranes, dye molecules with different molecular weights were used, ranging from 320 to 1299 g mol\(^{-1}\) (table S3). Figure 6C shows an increasing rejection against molecular weight (using the 40-s plasma-treated membrane), suggesting size-based selectivity across the membrane. In addition, slightly higher rejection is observed with negatively charged dyes, which might be explained by the negative charges on oxygen-rich groups that are formed at the pore edges due to plasma treatment and subsequent oxidation in the air (38). In addition, we tested the permeances of different solvents including methanol, ethanol, isopropanol, water, hexane, and acetone (Fig. 6D). A comparison among different models (fig. S17) suggests that the total Hansen solubility parameter, solvent viscosity, and kinetic diameter (table S6), respectively. The experimental data are in good agreement with model description, suggesting that the transport of solvent molecules across graphene is affected by both graphene-solvent interactions and intrinsic properties of solvent (kinetic diameter and viscosity).

Finally, the long-term stability of single-layer graphene membrane was evaluated. Figure S18 shows steady permeance from the second day and rejection over a 10-day test.

A comparison of our membranes with state-of-the-art membranes, including the most recent work on other types of 2D membranes, is provided in Fig. 6E and table S7. Our membranes present

\[ p = \frac{k\delta_t}{\eta d_{kin}} \]  

where \( k \) is the proportionality constant, and \( \delta_t, \eta, \) and \( d_{kin} \) are total Hansen solubility parameter, solvent viscosity, and kinetic diameter (table S6), respectively. The experimental data are in good agreement with model description, suggesting that the transport of solvent molecules across graphene is affected by both graphene-solvent interactions and intrinsic properties of solvent (kinetic diameter and viscosity).

Fig. 5. Permeance and selectivity of graphene-covered nanofiber membranes in diffusive separation processes. (A) Normalized flux, (B) permeance, (C) selectivity, and (D) normalized selectivity of different solutes across the PAN-EP-G-IP membranes with different oxygen plasma treatment durations in the diffusion tests. Comparisons of the (E) permeance and (F) selectivity with literature work in (24, 27, 32). The normalized flux and normalized selectivity in (A) and (D) were obtained by using the flux and selectivity of the control nanofiber support as the references, respectively.
a record-high ethanol permeance that is ~3 to 10 times higher than literature work at comparable rejection (10, 39–47). It demonstrates that the atomic thickness of monolayer graphene, in combination with a highly porous support, can enable the fabrication of membranes that surpass the selectivity-permeability trade-off.

DISCUSSION
In this work, we demonstrated a facile and scalable approach to fabricate nanoporous monolayer graphene membranes on highly porous nanofiber supports. The electrospinning-based direct transfer method is not limited to one specific polymer but has proven its effectiveness across a range of polymers such as PAN and PVDF, by simply adding a “binder” with desirable chemistry. The membranes develop selective nanopores at oxygen plasma etching, showing high permeance and excellent selectivity in diffusion- and pressure-driven separations involving water or organic solvents. This work paves the way for applications of monolayer graphene membranes in biomedical dialysis, OSN, and other applications.

MATERIALS AND METHODS
Materials
CVD-grown monolayer graphene on copper foil was purchased from Graphenea, and copper was etched by APS (98%) solution. PAN [weight-average molecular weight ($M_w$) = 250,000 g mol$^{-1}$], PVDF (1,000,000 g mol$^{-1}$), dimethyl formamide (99%), EP-POSS (EP0430), MS-POSS (MS0840), and NB-POSS (NB1070) were used for nanofiber preparation. Ethanol (99%), hexane (anhydrous, 99%), TMC (99%), and MPD (99%) were used to seal defects via IP. KCl (99%), AR (90%), VB (99%), LYS (99%), LT (99%), methylene blue (99%), Victoria blue B (99%), Remazol brilliant blue R (98%), brilliant blue R (97%), RB (99%), and Alcian blue 8GX (98%) were the solutes for diffusion- and pressure-driven tests. A summary of the
fundamental properties of the solutes is provided in table S3. POSS molecules were purchased from Hybrid Plastics, and all other chemicals were acquired from Sigma-Aldrich unless otherwise stated.

**Preparation of nanoporous graphene membranes**

As is shown in fig. S1, nanoporous graphene membranes were prepared following four major steps: electrospinning (with hot press), etching, defect sealing, and pore creation. Briefly, the commercial graphene/Cu film was suspended onto a 10 wt % APS aqueous solution for 2 min to etch away the low-quality graphene side and then washed by deionized (DI) water and isopropanol for five times and one time, respectively. After air-drying, the graphene/Cu film was placed on an aluminum foil wrapped around the receiving drum of a customized electrospinning system (BlueOcean Memtech; fig. S19) and was subsequently covered by nanofibers during electrospinning at the rotation rate of 1000 rpm for a predetermined duration. Then, the aluminum foil with graphene/Cu and nanofiber were sandwiched between two steel plates in a heat press (STX11, Stahls Hotronix, USA) at hot-press at a specified temperature and pressure for 15 min. Details of the polymer solution, electrospinning, and hot press conditions are provided in table S1.

After cooling down, the aluminum foil was gently removed, and then the graphene-Cu nanofiber composite was suspended on an APS solution (10 wt %, degassed in a sonicator for 30 min) again to completely remove the residual copper. In the case of PVDF-based nanofibers, the edges of Cu/graphene film were covered by Scotch tape to prevent the intrusion of water into the interface between the Cu/graphene film and nanofiber support during the etching process. Thereafter, the composite membrane was washed by water and ethanol. After air-drying, the resultant graphene/nanofiber composite membrane was mounted on a Frank cell prefilled with a degassed MPD aqueous solution (10 mg ml⁻¹) at the lower half with graphene facing the aqueous solution and was then clamped by the top half of the Frank cell. Next, a TMC solution (5 mg ml⁻¹) in hexane was gently added into the top half-cell by a glass dropper to allow IP for 1 hour. Subsequently, the composite membrane was washed by hexane and ethanol, each for seven times, air-dried, and then exposed to oxygen plasma (FENTO, CUTE) to create nanopores across the graphene layer at a power of 37 W, a gas flow rate of 15 sccm (standard cubic centimeter per minute), and a pressure of 3.5 × 10⁻¹ torr.

**Membrane characterization**

The surface morphology of nanofiber supports and graphene-covered membranes was observed by field-emission SEM (JSM-7610F, JEOL, Japan), without precoating with Au or Pt. The water contact angles of the as-fabricated nanofiber membranes were measured by goniometer (G10, Kruss, Germany). The chemical properties of the as-fabricated nanofiber membranes were examined by x-ray photoelectron spectroscopy (Kratos AXIS UltraDLD, Kratos, England). The graphene transferred onto silica wafer with or without oxygen plasma treatment was examined by Raman spectroscopy (XploRAPlus, HORIBA, France). The graphene transferred from PAN-EP-G-IP and PAN-EP-G-IP-60s membranes onto the TEM grid was characterized by spherical aberration-corrected TEM (Titan Cubed Themis G2 300, FEI, The Netherlands) at 80 kV. The detailed procedure for the transfer of graphene onto the TEM grid can be found in the Supplementary Materials.

**Diffusion tests**

The diffusion tests were conducted using a side-bi-side diffusion cell (PermeGear Inc.), with KCl, LT, AR, VB, and LYS as the solutes, and an effective membrane area of 0.196 cm². The membrane was first mounted onto the cell, wetted by ethanol/H₂O mixture (50 wt %) filled in both sides of the diffusion cell for 5 min, and then replaced by degassed water for three times. Thereafter, 7 ml of degassed KCl solution (0.5 M) was added in the solute side facing graphene, and 7 ml of degassed DI water was filled in the dialysate side facing the nanofiber support, where the KCl concentration was monitored with a conductivity meter (FiveEasy, Mettler Toledo, Switzerland). Alternatively, 7 ml of 1 mM LT, AR, VB, or LYS in 0.5 M KCl solution was filled in the solute side, and 7 ml of 0.5 M KCl solution was filled in the dialysate side, where the solute concentration was tracked with an ultraviolet-visible (UV-Vis) spectrophotometer (Cary 60, Agilent, USA) under real-time monitoring. All the diffusion tests were stabilized for 30 min before data collection, and solutions in both sides were stirred rigorously at 1500 rpm. The diffusive permeance (P) of solutes is calculated on the basis of Eq. 2

$$ P = \frac{J}{\Delta C} = \frac{V \times \frac{dc}{dt}}{\Delta C \times S} $$  \hspace{1cm} (2)

where \( J \) is the diffusive flux, \( \Delta C \) is the solute concentration difference across the membrane, \( V \) is the volume in the feed side or the dialysate side of the diffusion cell, \( \frac{dc}{dt} \) is the slope of solute concentration in the dialysate side as a function of time, and \( S \) is the effective membrane area (0.196 cm²).

The normalized diffusive flux of each membrane was the ratio of the diffusive flux of the membrane (\( P \)) over that of the bare nanofiber support (\( P_0 \))

$$ \text{Normalized diffusive flux} = \frac{P}{P_0} $$  \hspace{1cm} (3)

The selectivity was calculated as the permeance ratio of two different solutes across the membrane according to Eq. 4

$$ \text{Selectivity} = \frac{P_1}{P_2} $$  \hspace{1cm} (4)

The normalized selectivity was determined by the ratio of solute selectivity between that of the nanoporous graphene membrane (Selectivity) and that of the bare nanofiber support (Selectivity₀)

$$ \text{Normalized selectivity} = \frac{\text{Selectivity}}{\text{Selectivity}_0} $$  \hspace{1cm} (5)

**OSN tests**

The pressure-driven tests were conducted by a custom-made dead-end permeation cell under stirring at 500 rpm (fig. S18). The membrane sample wetted by ethanol was mounted into the cell with an effective area of 0.196 cm². Next, the membrane was stabilized by ethanol with an applied pressure of 2 bar for 1 hour. After that, the pure ethanol permeance was measured. Alternatively, an ethanol solution containing 50 ppm of dye solutes was used to measure the permeance and rejection. The feed volume was 200 ml. At least 3 ml of permeate was discarded before another >3 ml of permeate was collected. The dye concentrations in the permeate and feed were determined by UV-Vis spectrometer (Agilent, Cary 60, USA). The pure ethanol permeance and ethanol permeance for the dye solution...
where $\Delta V$ is the volume of permeate collected over a period of $\Delta t$. $S$ and $\Delta P$ are the effective membrane area and the transmembrane pressure, respectively. $C_p$ and $C_t$ are the dye concentrations of the permeate and the feed measured by UV-Vis, respectively. Apart from the nanoporous graphene membrane, the OSN performances of PAN, PAN-EP-POSS, and PVDF nanofiber supports were also evaluated and corresponding results were shown in fig. S20.

**MD simulation**

To provide in-depth understanding of the interactions between graphene and polymer or fillers, we designed three MD simulations to mimic the three steps in experimental membrane fabrication process for each system (PAN-graphene, PVDF-graphene, EP-graphene, and MS-graphene): (i) Graphene and polymer or fillers were first contacted with each other at 100°C, and an external pressure (80 psi for PVDF and 30 psi for PAN and fillers) was applied through two graphene pistons for a time duration of 20 ns. (ii) Thereafter, the pressure on both sides of polymer/fillers was released at 100°C for 20 ns. (iii) Last, the temperature was reduced to 25°C within 7.5 ns and maintained at 25°C for 12.5 ns. All the MD simulations were carried out in a canonical ensemble using the GROMACS v5.0.6 package (48). PAN, PVDF, EP, MS, and graphene were described by the optimized potentials for liquid simulations—all atom force field (49). The Lennard-Jones parameters of cross-interactions were estimated by the combining rules: $\epsilon_{ij} = (\epsilon_i \epsilon_j)^{1/2}$ and $\sigma_{ij} = (\sigma_i \sigma_j)^{1/2}$, where $\epsilon$ is well depth and $\sigma$ is collision diameter. Each simulation system was subjected to energy minimization using the steepest descent approach. The initial atomic coordinates were generated by the Ewald summation method, while the dispersion interactions were truncated at 14 Å. The leap-frog algorithm was adopted to integrate the equations of motion at a time step of 2 fs. The temperature was maintained by the velocity-rescaling thermostat with a relaxation time of 0.2 ps. The periodic boundary conditions were applied in all three dimensions.
30. S. C. O'Hern, D. Jang, S. Bose, J.-C. Idrobo, Y. Song, T. Laoui, J. Kong, R. Karnik, Nanofiltration across defect-sealed nanoporous monolayer graphene. Nano Lett. 15, 3254–3260 (2015).
31. N. McEvoy, H. Nolan, A. K. Nanjundan, T. Hallam, G. S. Duesberg, Functionalisation of graphene surfaces with downstream plasma treatments. Carbon 54, 283–290 (2013).
32. A. Hirano, K.-i. Yamamoto, M. Matsuda, T. Ogawa, T. Yakushiji, T. Miyasaka, K. Sakai, Evaluation of dialyzer jacket structure and hollow-fiber dialysis membranes to achieve high dialysis performance. Ther. Apher. Dial. 15, 66–74 (2011).
33. J. Liu, G. Han, D. Zhao, K. Lu, J. Gao, T.-S. Chung, Self-standing and flexible covalent organic framework (COF) membranes for molecular separation. Sci. Adv. 6, eabb1110 (2020).
34. X.-L. Cao, Y.-N. Yan, F.-Y. Zhou, S.-P. Sun, Tailoring nanofiltration membranes for effective removing dye intermediates in complex dye-wastewater. J. Membr. Sci. 595, 117476 (2020).
35. L. G. Peeva, E. Gibbins, S. S. Luthra, L. S. White, R. P. Stateva, A. G. Livingston, Effect of concentration polarisation and osmotic pressure on flux in organic solvent nanofiltration. J. Membr. Sci. 326, 121–136 (2004).
36. Y. He, G. Li, H. Wang, J. Zhao, H. Su, Q. Huang, Effect of operating conditions on separation performance of reactive dye solution with membrane process. J. Membr. Sci. 321, 183–189 (2008).
37. I. Koyuncu, Reactive dye removal in dye/salt mixtures by nanofiltration membranes containing vinylsulphone dyes: Effects of feed concentration and cross flow velocity. Desalination 143, 243–253 (2002).
38. J. Chen, T. Shi, T. Cai, T. Xu, L. Sun, X. Wu, D. Yu, Self healing of defected graphene. Appl. Phys. Lett. 102, 103107 (2013).
39. L. Huang, J. Chen, T. Gao, M. Zhang, Y. Li, L. Dai, L. Qu, G. Shi, Reduced graphene oxide membranes for ultrafast organic solvent nanofiltration. Adv. Mater. 28, 8669–8674 (2016).
40. B. Liang, H. Wang, X. Shi, B. Shen, X. He, Z. A. Ghazi, N. A. Khan, H. Sin, A. M. Khattak, L. Li, Z. Tang, Microporous membranes comprising conjugated polymers with rigid backbones enable ultrafast organic-solvent nanofiltration. Nat. Chem. 10, 961–967 (2018).
41. Q. Yang, Y. Su, C. Chi, C. T. Cherian, K. Huang, V. G. Kravets, F. C. Wang, J. C. Zhang, A. Pratt, A. N. Grigorenko, F. Guinea, A. K. Geim, R. R. Nair, Ultrathin graphene-based membrane with precise molecular sieving and ultrafast solvent permeation. Nat. Mater. 16, 1198–1202 (2017).
42. L. Nie, K. Goh, Y. Wang, J. Lee, Y. Huang, H. E. Karahan, K. Zhou, M. D. Guiver, T.-H. Bae, Realizing small-flake graphene oxide membranes for ultrafast size-dependent organic solvent nanofiltration. Sci. Adv. 6, eaaz9184 (2020).
43. S.-D. Jiang, A. Y. K. Koh, K. H. Chong, S. Zhang, Opening organic solvent pathways by molybdenum disulphide in mixed matrix membranes for molecular separation. J. Membr. Sci. 585, 60–66 (2019).
44. T. Gao, L. Huang, C. Li, G. Xu, G. Shi, Graphene membranes with tuneable nanochannels by intercalating self-assembled porphyrin molecules for organic solvent nanofiltration. Carbon 124, 263–270 (2017).
45. M. H. D. A. Farahani, T.-S. Chung, Solvent resistant hollow fiber membranes comprising P84 polyimide and amine-functionalized carbon nanotubes with potential applications in pharmaceutical, food, and petrochemical industries. Chem. Eng. J. 345, 174–185 (2018).
46. B. Li, Y. Cui, S. Japip, Z. Thong, T.-S. Chung, Graphene oxide (GO) laminar membranes for concentrating pharmaceuticals and food additives in organic solvents. Carbon 130, 503–514 (2018).
47. M.-l. Liu, J.-l. Guo, S. Japip, T.-z. Jia, D.-d. Shao, S. Zhang, W.-j. Li, J. Wang, X.-l. Cao, S.-p. Sun, One-step enhancement of solvent transport, stability and photocatalytic properties of graphene oxide/polyimide membranes with multifunctional cross-linkers. J. Mater. Chem. A 7, 3170–3178 (2019).
48. D. Van der Spoel, E. Lindahl, B. Hess, G. Groenhof, A. E. Mark, H. J. C. Berendsen, GROMACS: Fast, flexible, and free. J. Comput. Chem. 26, 1701–1718 (2005).
49. W. L. Jorgensen, D. S. Maxwell, J. Tirado-Rives, Development and testing of the OPLS all-atom force field on conformational energetics and properties of organic liquids. J. Am. Chem. Soc. 118, 11225–11236 (1996).
50. D. Jang, J.-C. Idrobo, T. Laoui, R. Karnik, Water and solute transport governed by tunable pore size distributions in nanoporous graphene membranes. ACS Nano 11, 10042–10052 (2017).
51. A. Buekenhoudt, F. Bisignano, G. De Luca, P. Vandezande, M. Wouters, K. Verhulst, Unravelling the solvent flux behaviour of ceramic nanofiltration and ultrafiltration membranes. J. Membr. Sci. 439, 36–47 (2013).
52. B. Van der Bruggen, J. Schaep, D. Wilms, C. Vandecasteele, Influence of molecular size, polarity and charge on the retention of organic molecules by nanofiltration. J. Membr. Sci. 156, 29–41 (1999).
53. M. J. Lashaki, M. Fayaz, S. Niknaddaf, Z. Hashiho, Effect of the adsorbate kinetic diameter on the accuracy of the Dubinin–Radushkevich equation for modeling adsorption of organic vapors on activated carbon. J. Hazard. Mater. 241–242, 154–163 (2012).
54. Z. Fan, J. Chen, W. Guo, F. Ma, S. Sun, Q. Zhou, Crystallinity of regenerated cellulose from [B(nim)]Cl dependent on the hydrogen bond acidity/basicity of anti-solvents. RSC Adv. 7, 41004–41010 (2017).

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Competing interests: R.K. is an inventor on patents/patent applications/pending patents related to this work filed by the Massachusetts Institute of Technology (PCT/US2013/31963, filed on 15 March 2013, published on 19 September 2013; PCT/US2014/063301, filed on 31 October 2014, published on 7 May 2015; PCT/US2017/059984, filed on 3 November 2017, published on 21 June 2018; PCT/US2017/059984, filed on 3 November 2017, published on 21 June 2018; patent application no. US 16/457,349, filed on 28 June 2019, published on 2 January 2020). The authors declare no other competing interests. Data and materials availability: All data needed to evaluate the conclusions in the paper are present in the paper and/or the Supplementary Materials.

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