Multifunctional wafer-scale graphene membranes for fast ultrafiltration and high permeation gas separation

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Reliable and large-scale manufacturing routes for perforated graphene membranes in separation and filtration remain challenging. We introduce two manufacturing pathways for the fabrication of highly porous, perforated graphene membranes with sub-100-nm pores, suitable for ultrafiltration and as a two-dimensional (2D) scaffold for synthesizing ultrathin, gas-selective polymers. The two complementary processes—bottom up and top down—enable perforated graphene membranes with desired layer number and allow ultrafiltration applications with liquid permeances up to $5.55 \times 10^{-8}$ m$^3$ s$^{-1}$ Pa$^{-1}$ m$^{-2}$. Moreover, thin-film polymers fabricated via vapor-liquid interfacial polymerization on these perforated graphene membranes constitute gas-selective polyimide graphene membranes as thin as 20 nm with superior permeances. The methods of controlled, simple, and reliable graphene perforation on wafer scale along with vapor-liquid polymerization allow the expansion of current 2D membrane technology to high-performance ultrafiltration and 2D material reinforced, gas-selective thin-film polymers.

INTRODUCTION

Upon the first isolation of graphene (1), perforated graphene (PG) has drawn vast attention for applications in efficient and high-performance filtration, owing, for example, to minimal flow impedances for gases (2–4) and liquids (5, 6). Furthermore, selective ion transport (7–9) in combination with its ability to withstand high pressures (10) enables graphene-based seawater desalination (11, 12). Therefore, PG has proven great potential in next-generation separation applications, so that considerable efforts have been devoted to manufacturing membranes for applications such as ultrafiltration, nanofiltration, gas separation, and desalination (13). As the latter two require very precise and small pores, the combination of PG, often having large pores, with dense polymer layers could bypass demanding manufacturing methods, improving performance by the intrinsic selectivity of the polymer while benefitting from the PG as an ultrathin mechanical scaffold.

Perforation of graphene is generally realized by two different approaches: bottom up and top down. The bottom-up synthesis of PG has been explored for preserving crystallinity and opening an energy bandgap. For this purpose, catalytically inactive materials (e.g., Al$_2$O$_3$ or SiO$_2$) are deposited on the catalyst, giving rise to graphene that is locally grown by the use of chemical vapor deposition (CVD) (14, 15). Very recently, an on-surface chemical reaction enabled 1-nm-wide nanopores in graphene sheets of 50 nm by 70 nm in size, potentially useful for nanosieving (16).

Among the top-down approaches, drilling a pore in mono- or multilayer graphene by focused electron or ion beam (4, 17, 18), chemical treatment of pristine graphene (12), or oxidation using nanoparticles (NPs) (19, 20) are the most widely explored methods to produce PG. Moreover, nanolithography-based methods using spherical block copolymer (s-BCP) allow patterning graphene (21) and metal films (22) without neutralization brushes that are otherwise required in BCP-based lithography (23).

Many of these methods are eligible for creating membranes with target pore sizes below 10 nm, suitable for desalination, direct gas separation, or nanofiltration. Nevertheless, they suffer from drawbacks such as complicated chemical processes, time-consuming prepatternning, low porosities, as well as void and crack formation. As a result, these challenges currently limit applications of graphene membranes in filtration and gas separation. Creating highly porous, wafer-scale PG with pores between 10 and 100 nm could, therefore, open a path for graphene membranes toward novel applications and devices.

Here, we demonstrate two complementary, simple, and reliable methods for the wafer-scale manufacturing of highly porous PG membranes for ultrafiltration, overcoming the limitations of current manufacturing methods and thereon enabling fabrication of ultrathin, PG-scaffolded, gas-selective polymers. The processes of graphene perforation rely on (i) a very simple, lithography-free, bottom-up synthesis of porous, single-layer graphene by catalyst engineering and (ii) the patterning of graphene using BCP for double-layer PG, highlighting the potential of self-assembled s-BCP–based wafer-scale nanolithography. We achieve high fidelity, uniformity, and pore size control in the range of sub-20 to 50 nm on average for samples up to 25 cm$^2$ using both methods. Showing these two distinct processes, we are able to elucidate their commonalities and differences, with focus on pore formation, structure, size, and density as well as their resulting performance in membrane applications. We are able to demonstrate high gas and liquid permeances using both PG types, surpassing the current state-of-the-art ultrafiltration membranes. Moreover, these PG layers enable the fabrication of 20-nm-thin, gas-selective polyimide membranes via vapor-liquid polymerization, underpinning their potential as an ideal, smooth two-dimensional (2D) scaffold. These graphene-polymer membranes exhibit on par selectivity with state-of-the-art membranes while having order-of-magnitude higher permeance.
two different carbides: the catalytically inactive carbide (W2C) or the presence of a carbon precursor at elevated temperatures, W can form distributed W NPs on the Cu surface after annealing (fig. S1). In the fully attain the conversion of as-deposited W thin films into evenly W2C should form rather than WC. If the WC forms predominantly, noncatalytic domains, whereas fast diffusion leads to WC. Slow diffusion into W favors the formation of W2C, effectively forming noncatalytic domains, whereas fast diffusion leads to WC. Slow diffusion of carbon to W is therefore desired, so we placed our tungsten/copper (W/Cu) catalyst in a “copper envelope,” a method very similar to that of Fang et al. (26), effectively limiting the diffusion of carbon precursor through the envelope to the W/Cu catalyst. If the copper envelope is omitted, then fully overgrown W/Cu samples are observed, supporting our hypothesis of slower diffusion of carbon into W.

Porous graphene is subsequently grown on a W/Cu catalyst system in a one-step, CVD process (Materials and Methods). It should be noted that the island-forming behavior of W on Cu is the only suitable combination for the porous growth in this work, as neither gold nor platinum, nor molybdenum, nor nickel exhibits the similar behavior (section S1).

Nanolithographic patterning based on BCP
Our patterning process for double-layer graphene on glass (Materials and Methods) is based on a simple and reliable method via s-BCP nanolithography directly applied to double-layer graphene without neutralization brushes (Fig. 1B). The 1 weight % s-BCP solution [polystyrene-block-polymethyl methacrylate (PS-b-PMMA), 195k-b-20k, in anhydrous toluene; Polymer Source Inc.] is spun directly on double-layer graphene to yield an approximately 50-nm-thick layer. Subsequent annealing in vacuum at 220°C induces microphase separation, forming a porous polymer after opening the PMMA spheres using oxygen plasma and their selective removal by acetic acid (section S2). Through the remaining polystyrene mask, we apply oxygen beam milling to anisotropically etch the underlying graphene, leading to a perforation of the graphene layer. The anisotropic etching of the s-BCP soft etch mask leads to a graphene pore diameter that depends on the etch depth due to the circular cross section of the polymer pore (section S3). We remove polystyrene residues via thermal annealing at 400°C in a reducing atmosphere, leaving behind patterned graphene on the glass substrates.

Transfer of PG to a polycarbonate track etched support
Transferring the porous and patterned graphenes onto a hydrophobic polycarbonate track etched (PCTE) layer (hydrophobic, 0.4-μm-wide openings; Sterlitech Inc.) results in PG suspended on PCTE using a modified direct transfer technique (Fig. 1C) (28). The PCTE is laminated on the PG at elevated temperature, followed by lift-off from the support by a release etch. The yield of this transfer method turns out to be as high as 99% for both porous and patterned graphenes (section S4), higher than ~70% of previous reports (10).

Characterization and comparison of PG membranes
We examined the as-produced porous and patterned graphene membranes using SEM and Raman spectroscopy to identify prominent Raman peaks (Materials and Methods). Table 1 summarizes the characteristics of the two types of PG.

The pore sizes of the porous graphene are determined by the size of dewetted W islands, which is controlled by the W film thickness between 2 and 10 nm, locally shielding the Cu surface during growth.
A thicker film turns to larger W islands on Cu after dewetting, thereby increasing areal porosity (Fig. 2, C and D, blue stars). The resulting pores are distributed normally, although a broadening is observed with increasing W thickness. The average pore size enlarges for porous graphene from $19 \pm 8$ to $54 \pm 20$ nm for 2- and 10-nm W, respectively. The pore size of the patterned graphene is controlled by ion beam etching durations (Fig. 2B and additional data in section S6). Increased etching duration of oxygen ion beam milling from 5 to 30 s resulted in an enlarged average pore size from $18 \pm 8$ to $31 \pm 18$ nm along with increased areal porosity (Fig. 2, C and D, red circles).

We observe a decreasing pore number density for porous graphene with increasing W thickness from $1.6 \times 10^{10} \pm 2 \times 10^9$ to $0.5 \times 10^{10} \pm 1 \times 10^9 \text{ cm}^{-2}$, which we attribute to the enlargement of the individual nanoislands by coalescence. For patterned graphene, the pore number density is constant up to 20 s of etching ($1.25 \times 10^{10} \pm 3.6 \times 10^9 \text{ cm}^{-2}$), where a sudden jump is recorded afterward to $2.1 \times 10^{10} \pm 4.6 \times 10^9 \text{ cm}^{-2}$, linked to the initial distribution of pores in the polystyrene mask (section S7). While both perforation methods are very different in their nature, we obtain very similar nanomorphologies, implying that similar applications are attainable. We further investigate graphene using Raman spectroscopy to unveil the differences in the crystal structure and nature of defects in both PG types.

The evolution of the Raman spectra of the porous and patterned graphene samples reveals notable differences: Porous graphene grown on substrates with domains of 2-, 5-, and 10-nm W is compared to pristine graphene (0-nm W) in Fig. 2E. The Raman intensity ratio of $I(D)/I(G)$ increases for larger tungsten domains, while $I(2D)/I(G)$ resembles closely that of pristine graphene, suggesting that the crystallinity of the porous graphene is maintained throughout the film to the pore edges. This finding is further confirmed by $I(D)/I(2D) = 3$ (Fig. 2F, blue squares), indicative of the grain boundary–originated line defects rather than vacancy-type defects (29). Transmission electron microscopy (TEM) and selective area electron diffraction (SAED) confirmed that the porous graphene maintains its hexagonal lattice structure throughout the layer (section S8). For the patterned graphene, the $I(D)/I(G)$ increases, indicating defect formation, whereas $I(2D)/I(G)$ decreases in comparison with the pristine double-layer graphene (Fig. 2G). The spectral evolution and the ratio $I(D)/I(2D) = 6.7$ closely resemble those observed for the formation of defects by ion irradiation (Fig. 2F, red circles) (18). We conclude that the patterned graphene—in contrast to the porous graphene—does not maintain its crystallinity throughout the film as the result of the ion etching, introducing amorphous regions around the pores and the basal plane.

We demonstrate the feasibility and uniformity of our manufacturing processes using wafer-scale samples up to 5 cm by 5 cm porous and patterned graphenes on PCTE (Fig. 2, H to K). We verified the uniform pore formation using SEM for porous (Fig. 2, H and I) and patterned (Fig. 2, J and K) graphene, checking spots in the center and at the edge of the sample.

### Table 1. Comparison of the membrane characteristics for both porous and patterned graphenes. The pore size, pore number density, and areal porosity of porous and patterned graphene membranes, all with standard deviation (SD), are shown. The pore statistics were obtained from the SEM graphs (section S5).

| PG type | Porous | Patterned |
|---------|--------|-----------|
| Number of layers | 1 | 2 |
| Pore size | $19.4 (\pm 7.7) - 54.1 (\pm 20.3) \text{ nm}$ | $18 (\pm 7) - 30.5 (\pm 18.3) \text{ nm}$ |
| Areal porosity | $5.5-13.9\%$ | $4.4-18\%$ |
| Pore number density | $0.5-1.5 \times 10^{10} \text{ cm}^{-2}$ (10-20% deviation) | $1.25-2.1 \times 10^{10} \text{ cm}^{-2}$ (20% deviation) |

*Figure 2C, blue stars. ‡Figure 2C, red circles. †Figure 2D, blue stars. §Figure 2D, red circles. ‡Section S7.*

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**Modeling and measurement of mass transport**

We performed gas and liquid flow transport measurements, after preparation of membranes (section S9), by pressure-driven transmembrane characterization. We used nitrogen ($N_2$) and water as respective testing fluids; the details of the characterization can be found in sections S10 and S11, respectively.

In the present work, we find the membrane to be intact after gas and water filtration experiments, although clogging of the membrane is observed after the deionized (DI) water measurement (section S11). Three samples for each membrane type are measured.

Modeling the transport through the graphene membrane on the PCTE support by the sum of two serial flow impedances allows theoretical permeance prediction, similar to that of O’Hern et al. (30). The total flow impedance can be modeled according to Eq. 1

$$R_{\text{tot}} = R_{\text{PCTE}} + R_{\text{graphene}}$$  \hspace{1cm} (1)

**Gas transport resistance**

The gas transport through our graphene membranes is dominated by diffusion, as the pore sizes are below 50 nm on average (4). Therefore, only the open porous area of the graphene needs to be considered, resulting in Eq. 2

$$R_{\text{Graphene, gas}} = \frac{\sqrt{2\pi MRT}}{A_{\text{open}}m_v}$$  \hspace{1cm} (2)

where $M$ is the molar mass of $N_2$, $R$ is the universal gas constant, $T$ is the temperature in Kelvin, $A_{\text{open}}$ is the open area of the membrane [porosity of graphene multiplied by porosity of PCTE (0.13)], and $m_v$ is the molar volume of a gas.

**Liquid transport resistance**

For liquids, a modified Sampson-Roscoe formula introduced by Jensen et al. (31) describes the average per-pore flow impedance in
**Fig. 2. Membrane characteristics and wafer-scale fabrication.** (A and B) Porous graphene (A) and patterned graphene (B) on PCTE support with a diameter distribution for each respective PG type. The dashed line in the histogram outlines a normal distribution. Scale bars, 500 nm. (C) Average pore size and SD for porous (blue stars) and patterned (red circles) graphene with respect to the respective process parameter. (D) Average porosity and SD for porous (blue stars) and patterned (red circles) graphene with respect to the respective process parameter. (E) Raman spectra evolution of porous graphene from nonporous (bottom) to 10-nm W (top). a.u., arbitrary units. (F) $I(D)/I(G)$ versus $I(D)/I(G)$ showing the different nature of defect in respective graphene films: ~3.3 for porous graphene reflects line defects (grain boundaries), and patterned graphene has an $I(D)/I(G)$ of ~6.7, indicating vacancy-like defects. (G) Raman spectra evolution of patterned graphene from unpatterned (bottom) to 30 s (top). (H) Photograph of wafer-scale porous graphene on PCTE support with pore formation in the middle and at the edge of the sample (I). (K) Wafer-scale patterned graphene on PCTE support (dashed circle) with pore formation in the middle and at the edge of sample (J).
the distribution of pores in the graphene membrane. The diameter of the pores is assumed to be normally distributed with average pore radius, \( r \), and SD, \( \sigma \). Equation 3 shows the overall flow impedance for \( N_{\text{open}} \), the number of open graphene pores

\[
R_{\text{Graphene, liquid}} \approx \frac{3\mu}{r^3N_{\text{open}}} \left[ \frac{1}{M_3} + \frac{A}{M_4} \right]
\]  

(3)

where \( \mu \) is the dynamic viscosity of water, \( M_3 \) and \( M_4 \) are the third- and fourth-scaled statistical momenta of the distribution, and \( A \) is the dimensionless thickness parameter (details are found in “Liquid flow permeance calculation” section under section S12). When calculating the theoretical permeance, \( A/M_4 \) is neglected because of the small thickness of graphene (<1 nm).

We have calculated the flow impedance for both types of graphene membrane, combining them with the PCTE impedance to give a total flow impedance \( R_{\text{tot}} \) (section S12), allowing calculation of the volumetric flow rate (\( Q_{\text{tot}} \)) for gases and liquids for all membranes using Eq. 4.

\[
Q_{\text{tot}} = \frac{\Delta P_{\text{tot}}}{R_{\text{tot}}}
\]

(4)

where \( \Delta P_{\text{tot}} \) is the overall pressure drop.

We measured the permeances through low-porosity (2-nm W, 10 s), intermediate-porosity (5-nm W, 20 s), and high-porosity (10-nm W, 30 s) PG membranes on PCTE supports. The measured permeances of the membranes show a strong correlation with the porosity of the graphene [Fig. 3, A and B, blue squares (porous graphene) and red circles (patterned graphene), respectively], reaching \( >6 \times 10^{-6} \text{ m}^3 \text{s}^{-1} \text{Pa}^{-1} \text{m}^{-2} \) for \( \text{N}_2 \) and \( >5 \times 10^{-8} \text{ m}^3 \text{s}^{-1} \text{Pa}^{-1} \text{m}^{-2} \) for water in case of the 10-nm W and 30-s samples, respectively. The theoretical prediction based on our model through the membranes agrees with the obtained permeances [Fig. 3, A and B, blue stars (porous graphene) and red stars (patterned graphene), respectively], confirming a correlation between permeance and porosity of membranes. The flow model slightly overpredicts the measured permeances for gas, while for the liquid permeances, a relatively nice match is observed. The simple model, therefore, is able to capture the governing physics overall, although some factors seem to additionally influence the flow rate, which are sources of uncertainty: variation in PCTE porosity and pore size, distribution of pore sizes, and numbers in graphene, as well as possible voids or cracks. An error bar is added to the prediction value for gas and liquid, based on the variation of pore characteristics of the graphene membranes (section S12), to account for some of these uncertainties.

For the high-porosity samples (>12%), the flow resistances of graphene membranes are similar to the bare PCTE resistance (section S12). This observation may seem remarkable, as the pore size of the graphene is typically one order of magnitude smaller than that of PCTE, but this effect can be explained by the atomic thickness of PG: The graphene minimizes the flow impedance for any passing fluid because of diminished interactions between the molecule and the pore wall. This finding indicates that a further increase of permeance
would require a more permeable support, as graphene is no longer the limiting factor for higher performance. Furthermore, the high-porosity samples exhibit large SDs of measured permeances, especially for the liquid flow measurements. We hypothesize that the local variation of porosity and pore size in PCTE, as well as PG, gives rise to this large permeance variations.

In membrane science, the unit Lmh/bar (liters per square meter per hour at 1 bar) is often used for permeance comparison of different membranes, especially in industry. With our membranes, we reach up to 20,000 Lmh/bar in this unit, which is among the highest measured given the size cutoff of these membranes. Compared with commercially available ultrafiltration membranes (PCTE, MF-Millipore) with similar size cutoff, the flow rate of 30-s membranes is higher by one to two orders of magnitude. As a result of massively increased porosity, 30-s membranes surpass those reported by Wei et al. (20), as well as carbonaceous nanofiber membranes (CNF-71; Fig. 3C) (32). Therefore, our PG membranes exhibit permeances well above commercially available technology and even surpass latest nanomaterial-based filtration membranes.

To further elucidate the application of these graphene membranes in ultrafiltration, we tested the size cutoff of a 2-nm W membrane, having smallest average pore size of all tested membranes, to filter gold NP (Au NP) from solution, demonstrating a size cutoff of 30 nm (section S13). The ultraviolet-visible (UV-vis) spectra (Fig. 3D) of the filtrate and the feed solution demonstrate the filtration of Au NP, as no peak around 520 nm, typical for Au NP of this size, can be obtained from the filtrate, underpinning the potential of PG/PCTE membranes in ultrafiltration with a size cutoff above 30 nm.

**Graphene-reinforced thin-film polymers**

In contrast to ultrafiltration, achieving highly porous, wafer-scale graphene membranes with pores allowing gas separation or desalination is typically very difficult because of the requirements for strict pore size cutoff below 1 and 2 nm (13). Polymers, on the other hand, have intrinsic selectivity but suffer from low permeance and mechanical instability or require dense, transport-impeding supports when manufactured thin (33–37). Combining polymeric materials with large-pore PG could result in highly permeable, freestanding, graphene-reinforced membranes, overcoming the limitations of both technologies. In a previous work, for example, a polydimethylsiloxane layer on ion-bombarded graphene has been deposited to enhance the gas separation by minimizing leakage flow (38); however, this layer was micrometer thick, notably reducing permeance.

Polyimides and polyamides have intrinsic selectivity due to the solution-diffusion-based transport and can be synthesized via interfacial polymerization on porous supports (39). Previous reports demonstrated the fabrication of ultrathin, highly selective polymer layers for gas separation via self-assembly (36) or liquid-liquid interfacial polymerization (40), but these methods typically suffer from defect formation. Furthermore, thin selective layers thus require dense polymeric supports, which mitigate leakage due to cracks and voids in the thin selective layer at the cost of added transport impedances. In the liquid-liquid interfacial polymerization on a porous support, the diffusion-limited reaction results in the formation of a rough nanofilm, with tens to hundreds of nanometers in thickness. In general, the parameters including diffusivity of the monomers from the support, uneven pore distribution, and support surface roughness influence the polymer film formation (41). Strategies such as using a template with densely and uniformly distributed pores successfully lead to smooth polymeric films exemplified in nanofiltration applications (37). Liquid-liquid interfacial polymerization has also been used to patch the microscale ruptures in graphene membranes (8).

We overcome the limitations of current liquid-liquid thin-film manufacturing methods by introducing the vapor-liquid polymerization on PG. In general, vapor-liquid interfacial polymerization is performed upon the diffusion of vapor through a porous support where it reacts with a liquid monomer, forming a polymer film on the porous support. Recently, the reaction of 6FDA [dianhydride,4’-hexafluoroisopropylidene] diphthalic anhydride with ethylenediamine (EDA) on CNT buckypaper has allowed the formation of polyimide membranes, exhibiting gas and hydrocarbon selectivity as well as desalination properties (42). Polymer membranes from the CNT buckypaper scaffold could be manufactured as thin as 100 nm. We have used this chemistry using triple-layer PG membranes on a silicon/silicon nitride frame (Fig. 4A and Materials and Methods). In this system, the thin and smooth PG plays the role of a permeable 2D scaffold for the controlled synthesis of a polymeric thin film.

This polycondensation reaction leads to a full coverage of the graphene surface by polyimide/polyamide (Fig. 4B), leading to the formation of a graphene-reinforced nanofilm in a freestanding sandwich structure. Since a single-layer PG is not stable enough to sustain the polymer synthesis and subsequent annealing, we have used a more resilient triple-layer porous graphene (section S14). We have successfully decreased the nanofilm thickness from 1000 ± 50 to 19 ± 3 nm by simply decreasing the monomer solution concentration (Fig. 4C). A self-sustaining, smooth polymer film is created using porous graphene combined with vapor-liquid interfacial polymerization, as confirmed using atomic force microscopy (AFM; section S15).

The gas transport through the 20-nm-thick polymer-graphene composite was characterized using hydrogen (H2), carbon dioxide (CO2), and methane (CH4) by separation of equimolar gas mixtures of H2/CO2 and H2/CH4 (section S16). Gas mixture selectivity for the uncoated PG membrane lies below the free molecular Graham selectivity (Fig. 4D), which is the theoretical selectivity value as a result of the effusive flow behavior. We attribute this lower selectivity to the transition from effusive to collective transport regimes in the porous graphene of the respective pore size (4).

After the nanofilm formation, the separation factor was enhanced above the Graham selectivity for both gas combinations (Fig. 4D). The permeance of all gases across the nanofilms decreased by one to two orders of magnitude in comparison with the noncoated PG membrane, while increasing the selectivity by a factor of 2. We conclude that the nanofilm shifts the transport from molar mass-dependent effusion to size-dependent diffusion, a manifestation of the typical structure of dense glassy polymers, such as polyamides (39). The gas permeance of the fabricated nanofilm is up to two-order-of-magnitude higher than that of the state-of-the-art polymeric membranes with similar selectivity (Fig. 4E), thereby showing the potential of graphene-reinforced polymers for gas separation.

**DISCUSSION**

The direct, single-layer, porous graphene synthesis and double-layer graphene patterning have been successfully established in this work. For the porous graphene, catalytically inactive W domains deployed on a Cu catalyst, formed by dewetting, allow direct, lithography-free, porous graphene formation during synthesis. The pore size and pore...
number density are controlled by the thickness of the initial W film. The crystal structure of porous graphene is well maintained, additionally illuminating a potential for electronic applications, such as sensor or wearable electronics.

The patterned graphene relies on a self-assembled s-BCP nanolithographic etch mask, formed directly on graphene and subsequent patterning by directional etching. The initial pore sizes are defined by the intrinsic characteristics (i.e., length of respective polymer chains) of the chosen BCP, while different pore morphologies can be created with increasing etching time as a result of circular cross sections of pores in the polymer etch mask. The layer number can be easily tailored using this process, so that applications requiring higher mechanical sturdiness, for example, are readily attainable.

Despite the different nature of pore formation, very similar pore morphologies are obtained using these two methods, and the detailed understanding of both processes yields membranes with pores from sub-20 nm to above 50 nm on average, achieving porosities up to >20% on areas as large as 5 cm by 5 cm. These findings mark a notable improvement over previous work in regard to membrane size and porosity. The manufacturing of our PG is simpler than previous methods as the number of required processing steps is reduced by omission of e-beam lithography for the porous growth or avoiding neutralization brushes for the uniform BCP formation on wafer scale. The demonstration of the two side-by-side processes enables to identify distinct features and characteristics of each method. These findings allow comparing both methods regarding their complexity and the resulting PG samples as graphene membranes.

Furthermore, the high-yield transfer of our PG to porous supports enables applications of PG as a selective layer in high-performance ultrafiltration: Fast gas and liquid permeances through these membranes—owing to the small transport resistance of our selective PG film—reaching up to 20,000 L/hm/bar for liquids with a controlled size cutoff down to 30 nm. Because of the self-assembly nature of both processes, scaling these methods up to industrial relevance is theoretically doable, which would, nevertheless, demand control of the W NP and BCP formation on areas of square meters with nanometer-scale precision, calling for dedicated manufacturing facilities and operation in semibatch/semicontinuous or fully continuous mode.

Furthermore, we overcome current limitations in thin-film polymer membrane fabrication for gas separation by the use of our PG as a 2D scaffold, enabling the creation of an ultrathin polymer membrane by vapor-liquid interfacial polymerization. This method creates graphene-reinforced polymer films as thin as 20 nm. These ultrathin polymeric membranes show gas separation characteristics on par with the state-of-the-art polymer membranes, while having up to two-order-of-magnitude larger permeances. PG, therefore, enables novel hybrid graphene-polymer membrane architecture. To further improve the performance of these graphene-polymer hybrid membranes, higher-porosity graphene is required that would enable thin-film formation while minimizing the flow impedance of the mechanical scaffold.
We believe that our work represents a major step toward the usage of PG membranes in real-world applications due to the simple, reliable, and wafer-scale manufacturing methods. Both methods for creating PG have their distinct advantages and characteristics, implying applications from filtration and separation to electronics. Furthermore, our graphene-polymer hybrid membranes expand the usage of PG toward 2D scaffolds for ultrathin nanomaterial-reinforced polymeric membranes.

**MATERIALS AND METHODS**

**Synthesis of porous graphene**

Porous graphene was synthesized using a W/Cu catalyst where W films of several nanometers in thickness had been prepared by e-beam evaporation (pressure, 2.0 × 10⁻⁴ to 2.0 × 10⁻³ mtorr; deposition rate, 2 Å/s) on top of the Cu catalyst (Alfa Aesar 46986; surface was milled to remove contamination). The synthesis of porous graphene was carried out in a custom-built quartz tube furnace (Graphene Square Inc., Republic of Korea). The sample was enclosed in a copper envelope to reduce the diffusion of carbon precursor into the W NPs during the actual growth steps. For this, the W/Cu sample was placed on a large copper foil and subsequently wrapped, where the edges of the foil were then folded to seal the envelope as much as possible. The annealing of the W/Cu was carried out at 1050°C, using 40 sccm (standard cubic centimeter per minute) hydrogen (H₂) at a pressure of 300 mtorr for 75 min, inducing dewetting of the tungsten thin film into tungsten NPs on top of the Cu foil. Graphene synthesis was subsequently carried out at 800°C by introducing 1 sccm of methane and 40 sccm of H₂ at 600 mtorr for 3 hours. The samples were lastly cooled down to room temperature while flowing 40 sccm of H₂.

**Synthesis and transfer of double-layer graphene for patterning**

**Synthesis**

Nonporous graphene for patterning was grown on copper foil (Alfa Aesar 46986; surface was milled to remove contamination). Graphene growth was performed at 1000°C in a custom-built quartz tube furnace (Graphene Square Inc., Republic of Korea). The copper foil was annealed at 950°C for 1 hour flowing 5 sccm of H₂ at 70 mtorr. Subsequently, 40 sccm of CH₄ was flown for 30 min to synthesize full coverage graphene on the Cu foil at 100 mtorr.

**Transfer to glass substrate**

The graphene sample was then spin-coated with PMMA (anisole, 2 weight %) to yield a 150-nm-thick film and baked for 5 min on a hot plate at 180°C. Ammonium persulfate solution (0.5 M; Sigma-Aldrich) was used as a copper etchant, and the PMMA/graphene/copper was floating-etched until the copper was removed entirely. The sample was then rinsed for 30 min in DI water and fished with another sample of graphene on copper to yield the double layer. The sample was again etched and rinsed in the same fashion. A glass slide [large cover glass (thickness, 190 to 250 μm), Ted Pella] was used to fish the double-layer PMMA/graphene. The sample was let dry in ambient and placed on a hot plate for 30 min to reduce wrinkling. The PMMA was subsequently removed in acetone and rinsed in isopropanol.

**SEM and Raman spectroscopy**

The SEM images were taken in two systems: FEI Helios Dual Beam (2 kV, 100 nA) and Hitachi Nova (5 kV, 10 μA). Raman spectroscopy was performed on NT-MDT Integra (473-nm laser, beam intensity of 0.5 mW cm⁻²). Typical Raman peaks are the D band around 1350 cm⁻¹, indicative of defects in the crystal lattice, the G band around 1585 cm⁻¹, corresponding to the graphitic signature of sp² hybridization, and the 2D band around 2730 cm⁻¹, arising from a second-order two-phonon process. The presence of a D’ peak evolving at 1620 cm⁻¹ indicates further degradation of the graphene lattice. Raman spectroscopy of the graphene was performed before transfer to the PCTE support.

**Triple-layer porous graphene on silicon/silicon nitride frames for interfacial polymerization**

Freestanding triple layers of the porous graphene were prepared by subsequent transfer of three single porous graphene layers (2-nm W) to a silicon/silicon nitride (Si/SiNₓ) frame with an array of multiple 4-μm-wide openings. Si/SiNₓ chips were used, as PCTE is not compatible with chemicals such as toluene and EDA. Manufacturing of Si/SiNₓ and graphene transfer were performed following Celebi, Buchheim et al. (4). Briefly, silicon wafers coated with 150-nm-thick SiNₓ were purchased from Si-Mat Wafer Inc. Photolithography and reactive ion etching allowed the formation of defined patterns on the front and back sides of the wafer so that by subsequent KOH etching, freestanding SiNₓ membranes were obtained, having an 8 × 8 array of 4-μm-wide holes. The porous graphene was transferred by spin-coating PMMA and subsequently etching Cu using 0.5 M ammonium persulfate. By repeating this procedure three times, three-layer porous graphene was obtained. The PMMA/graphene was rinsed in DI water for 30 min before the next layer or the final substrate fished the graphene stack. The PMMA was removed by thermal annealing under H₂ and Ar as carrier gas (atmospheric pressure, 9:1). The overall porosity of the triple-layer porous graphene was <0.1%. Triple-layer porous graphene is mechanically resilient enough to allow the postpolymerization thermal baking and subsequent handling of the membranes.

**Polymer nanofilm synthesis on graphene**

The solution of 6FDA monomer was prepared by dissolving the as-delivered monomer powder (TFC, Japan) in toluene to obtain a concentration of 0.004 g/ml and stirred for 3 hours at room temperature. The base solution is then further diluted with toluene to reach the target concentration.

The triple-layer porous graphene on Si/SiNₓ chip was mounted onto a lid of a cylindrical container with a 1 cm by 1 cm opening using Kapton tape. Liquid EDA (99%; Sigma-Aldrich) was injected into a crucible located in the container. The liquid EDA was vaporized at room temperature and condensed on the container wall, leading to saturated vapor condition. The vapor can escape through Si/SiNₓ trenches and, consequently, through nanopores of graphene because of the concentration difference between two sides of the PG membrane. EDA vapors may condense on both top and bottom sides of the graphene. pH paper was mounted on top of the graphene with no direct contact to the surface so that pH paper color change indicates passage of EDA vapor through PG. After an exposure of graphene pores to the saturated EDA for 2 hours, 1 μl of the 6FDA solution was added three times onto the surface of the PG membrane within a 3-min interval using a metallic capillary tube. The solution wetted both sides of graphene, and polyamide formation reaction occurred between 6FDA and EDA at the surface of graphene. Simultaneous to solution addition, a pressure-release lid was opened to avoid overpressurization of the forming nanofilm by the accumulated EDA vapor in the container.

The PG membrane was left exposed to EDA vapor for 20 min to complete the polycondensation reaction following a previously reported
reaction time scale of interfacially synthesized polyamide, which lies in the range of 1 to 10 min (36). Subsequently, nonreacted 6FDA was removed by toluene washing. The formed polyamide was then dried, cured, andimidized under N2 atmosphere at 190°C over 2 days. The heating and cooling rates were set to 0.5°C/min.

SUPPLEMENTARY MATERIALS

Supplementary material for this article is available at http://advances.sciencemag.org/cgi/content/full/4/11/eaau0476/DC1

Section S1. NP formation of tungsten on copper

Section S2. Patternng graphene using s-BCPtransfer to PCTE

Section S3. Effect of circular cross section of pores in s-BCP

Section S4. Graphene coverage on PCTE

Section S5. Pore size evaluation

Section S6. Full results of parameter study for patterned graphene

Section S7. Pore number density of porous andpatterned graphenes

Section S8. TEM and SAED of porous graphene

Section S9. Membrane preparation for gas and liquid flow measurements

Section S10. Gas flow permeance measurement

Section S11. Liquid flow permeance characterization

Section S12. Calculation of flow impedances through graphene on PCTE

Section S13. Gold NP filtration

Section S14. Polymer film formation on porous graphene

Section S15. Patterned double-layer graphene membrane (30 s) after DI water flow

Section S16. Liquid flow permeance measurement

Section S17. Properties of polymer/graphene membranes

Fig. S1. NP formation of W on Cu.

Fig. S2. Schematic of the manufacturing process of BCP patterning of graphene.

Fig. S3. Effect of circular pore cross section in s-BCP on graphene pore formation.

Fig. S4. Graphene coverage on PCTE.

Fig. S5. Pore size evaluation using SEM graphs.

Fig. S6. Full results of parameter study for patterned graphene.

Fig. S7. Pore number density of porous and patterned graphenes.

Fig. S8. TEM and SAED of porous graphene.

Fig. S9. Membrane preparation for gas and liquid flow measurements.

Fig. S10. Gas flow permeance measurement.

Fig. S11. Liquid flow permeance measurement.

Fig. S12. Extraction of liquid flow permeation from measurement.

Fig. S13. Patterned double-layer graphene membrane (30 s) after DI water flow.

Fig. S14. Polymer film formation on porous graphene.

Table S1.计算气体流速对于聚酰胺和PCTE的综合渗透性能基于组合掺杂膜的表面积和厚度

Table S2. Computed gas flow impedances for graphene and PCTE and the overall permeance based on the combined impedance model.

Table S3. Relative error functions based on the simplified error propagation model.

Table S4. Relative error for gas and liquid permeances computed based on the functions in table S3.

Table S5. Gas permeation and separation results of polymer/graphene membranes.

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