CONSPECTUS: Gas separation is one of the most important industrial processes and is poised to take a larger role in the transition to renewable energy, e.g., carbon capture and hydrogen purification. Conventional gas separation processes involving cryogenic distillation, solvents, and sorbents are energy intensive, and as a result, the energy footprint of gas separations in the chemical industry is extraordinarily high. This has motivated fundamental research toward the development of novel materials for high-performance membranes to improve the energy efficiency of gas separation. These novel materials are expected to overcome the intrinsic limitations of the conventional membrane material, i.e., polymers, where a longstanding trade-off between the separation selectivity and the permeance has motivated research into nanoporous materials as the selective layer for the membranes. In this context, atom-thick materials such as nanoporous single-layer graphene constitute the ultimate limit for the selective layer. Gas transport from atom-thick nanopores is extremely fast, dependent primarily on the energy barrier that the gas molecule experiences in translocating the nanopore. Consequently, the difference in the energy barriers for two gas molecules determines the gas pair selectivity. In this Account, we summarize the development in the field of nanoporous single-layer graphene membranes for gas separation. We start by discussing the mechanism for gas transport across atom-thick nanopores, which then yields the crucial design elements needed to achieve high-performance membranes: (i) nanopores with an adequate electron-density gap to sieve the desired gas component (e.g., smaller than 0.289, 0.33, 0.346, 0.362, and 0.38 nm for H₂, CO₂, O₂, N₂, and CH₄, respectively), (ii) narrow pore size distribution to limit the nonselective effusive transport from the tail end of the distribution, and (iii) high density of selective pores. We discuss and compare the state-of-the-art bottom-up and top-down routes for the synthesis of nanoporous graphene films. Mechanistic insights and parameters controlling the size, distribution, and density of nanopores are discussed. Fundamental insights are provided into the reaction of ozone with graphene, which has been successfully used by our group to develop membranes with record-high carbon capture performance. Postsynthetic modifications, which allow the tuning of the transport by (i) tailoring the relative contributions of adsorbed-phase and gas-phase transport, (ii) competitive adsorption, and (iii) molecular cutoff adjustment, are discussed. Finally, we discuss practical aspects that are crucial in successfully preparing practical membranes using atom-thick materials as the selective layer, allowing the eventual scale-up of these membranes. Crack- and tear-free preparation of membranes is discussed using the approach of mechanical reinforcement of graphene with nanoporous carbon and polymers, which led to the first reports of millimeter- and centimeter-scale gas-sieving membranes in the year 2018 and 2021, respectively. We conclude with insights and perspectives highlighting the key scientific and technological gaps that must be addressed in the future research.

INTRODUCTION

The conventional gas separation processes are energy intensive because they rely on thermal energy. Membrane-based gas separation is attractive because it does not rely on thermal energy for separation. It is environment-friendly as no waste is produced. Nanoporous two-dimensional (2D) films when applied as the selective layer of the membrane can overcome several limitations of the conventional polymeric membranes. Nanoporous 2D films are especially attractive for breaking the intrinsic performance trade-off of the polymeric materials. In addition, they help realize chemically and thermally robust membranes that do not have issues such as aging and plasticization. Several chemically and thermally robust 2D materials, e.g., single-layer graphene (SLG), hexagonal boron nitride, transition metal dichalcogenides, graphitic carbon nitride, graphynes, etc. (Figure 1A) are attractive for this purpose. Atom-thick nanopores can be incorporated into these...
Nanopores in SLG constitute the thinnest possible permselective layer. Single-atom thickness of the nanopore translates into extremely small molecular diffusion path length and consequently high permeance. Molecular-sized nanopores differentiate gas molecules based on the relative size difference of gas molecules with respect to the nanopores, a concept termed molecular sieving.

Nanoporous SLG (N-SLG) has been widely studied for gas separation given the high chemical, thermal, and mechanical robustness of graphene. Experimental studies have shown that porous graphene suspended over a submicron-sized support pore can sustain transmembrane pressure up to several bars. Unique for an inorganic material, graphene is flexible attributing to its 2D lattice. Large-scale roll-to-roll synthesis of graphene have been already demonstrated for application in electronics.

The first theoretical paper on gas transport from graphene nanopore was reported by Jiang et al. in the year 2009, which discussed the tremendous potential of graphene for gas separation based on molecular sieving. They showed that a pore-10, where 10 indicates the number of missing carbon atoms in the pore, can sieve H₂ from CH₄ with an exponential selectivity (10⁸−10²³ depending on the edge functional groups). Subsequent theoretical studies have predicted that high gas permeance is expected, on the order of 10⁴−10⁵ gas permeation units or GPU where 1 GPU = 3.35 × 10⁻¹⁰ mol m⁻² s⁻¹ Pa⁻¹, if a high density of nanopores can be incorporated in the lattice (∼10¹³ cm⁻²). Gas adsorption plays a significant role when the molecule of interest has a strong affinity with graphene lattice or functional group along the pore edge. Therefore, pore functionalization can be used to manipulate the transport properties of gas molecules.

A proof-of-concept experiment for gas sieving from graphene nanopore was demonstrated in the year 2012 by Bunch and co-workers. They measured the deflation rate of a pressurized graphene microballoon to estimate the gas flux. Pores were incorporated by oxidation of graphene with UV/O₃. Further advances in this field faced a stiff challenge from preparing larger area membranes in a crack-free manner. It was not until the year 2018 that the size-sieving behavior was demonstrated from nanopores in SLG by directly measuring the composition of mixed gases crossing the nanopores. Crack-free transfer protocol ignited experimental advancements in gas separation and has allowed the development of uniform and

Figure 1. Atom-thick nanopores for gas sieving. (A) Examples of 2D materials with atom-thick nanopores suitable for gas separations. (B) Schematic of N-SLG showing the three general kinds of pores for a given separation. (C) Lognormal PSD that is typically produced in N-SLG by etching techniques. (D) Example of a PSD for CO₂/N₂ separation consisting of pores with 1−16 missing carbon atoms. Smaller pores do not contribute to permeation (large energy barrier), and pores larger than 16 missing carbon atoms are not selective (no energy barrier). (E) Energy barrier for gas transport through graphene nanopores and its corresponding relative transport rate.

| E_{\text{trans}} (eV) | Relative transport rate |
|----------------------|------------------------|
| 0.5                  | 0.00001                |
| 0.2                  | 1                      |
| 0                    | ~2000                  |

accounts of materials research pub.acs.org/amrcda article https://doi.org/10.1021/accountsmr.2c00143 acc. mater. res. 2022, 3, 1073−1087
scalable chemical etching approaches. However, challenges still linger ahead especially related to advancing the gas separation performance and to the scalable fabrication of large-area membranes.

In this Account, we summarize recent developments in this field focusing on the approaches for the incorporation of vacancy defects, a toolbox for modulating gas transport, characterization of nanopores, and finally practical aspects that are crucial in scaling up membranes. We conclude this Account with a perspective highlighting the key scientific and technological gaps, which must be addressed in the future.

**GAS SIEVING FROM GRAPHENE NANOPORES**

Achieving gas sieving from N-SLG membranes requires four key design elements:

(i) Å-scale pores to sieve gases based on their relative size with respect to the nanopore (Figure 1B). The gas flux is directly proportional to the energy barrier that a molecule experiences at the transition state while crossing the pore. Therefore, to realize size sieving, the pore size should be commensurate to the molecule of interest.

(ii) A narrow pore size distribution (PSD). It is currently not possible to incorporate monomodal pores in graphene, and typically a log-normal PSD is observed by the state-of-the-art pore incorporation techniques (Figure 1C). Molecules do not experience an energy barrier while crossing larger nanopores at the tail end of the distribution (Figure 1D,E). As a result, these pores yield large permeance and poor selectivity.

(iii) A high density (10^{12}–10^{13} cm^{-2}) of gas selective nanopores to maximize gas permeance.

(iv) Adequate surface and edge functional groups to favor interactions with the targeted molecules.

Pores can be incorporated into graphene either by postsynthetic lattice etching (top-down route) or by direct crystallization of nanoporous graphene lattice (bottom-up route). Postsynthetic etching of the graphene lattice is promising for achieving a fine control over PSD. Direct crystallization of porous graphene is attractive to improve the scalability of graphene membranes. In this section, we review advances in this area (Figure 2).

Postsynthetic etching can be achieved by (i) physical etching involving knocking out carbon atoms by energetic electron or ion beams (Figure 3A–C) and (ii) oxidative chemistry involving gasification of carbon atoms into CO/CO\_2 using O\_2, O\_3 plasma, and UV/O\_3 (Figure 3D–G). We note that the incorporation of a high density of gas-sieving nanopores is challenging because often reaction conditions that generate new pores (nucleation event) also expand the existing pores; i.e., the pore nucleation and expansion steps are coupled. So while pore density can be increased by a prolonged etching, it also generates a broader PSD. Therefore, decoupling pore nucleation and expansion is an extremely attractive research goal.

Physical etching can be used to precisely control the position of the nanopore by selecting the location for knocking out carbon atom using energetic beams. Recent advances have shown the incorporation of pores in the size range of a few nanometers. However, this route is challenging to incorpo-
rate Å-scale pores needed for gas sieving because the energy barrier for knocking out a carbon atom from graphene’s basal plane is much higher (∼20–21 eV) compared to that needed from an edge (∼14 eV, Figure 3B). As a result, the rate of pore expansion is much faster than the rate of nucleation (Figure 3C).

Chemical etching is highly promising because it can be carried out uniformly over a large area of graphene in a scalable way. It provides an opportunity to control the pore size at the Å scale by controlling the chemical transformation of the lattice at the atomic level. Chemical etching can be described by the following general steps:\(^{32,33}\) (i) chemisorption of the etchant forming oxidative groups such as epoxies, (ii) evolution of epoxy groups into energy minimizing clusters, and (iii) gasification of carbon atoms from the cluster leading to the formation of a vacancy defect. In this case, the energy barriers for pore nucleation and expansion are similar (O(1 eV)).

We have recently shown that O\(_3\) gas can chemisorb on graphene even at room temperature, making O\(_3\) a user-friendly and scalable gaseous etchant.\(^{14}\) Etching starts with the formation of an epoxy group. The energy barrier for

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**Figure 3.** Postsynthetic etching. (A) Illustration of physical etching, such as the ion/electron beam, on graphene lattice with corresponding nucleation and expansion energy barriers. Reprinted with permission from ref 29. Copyright 2017 American Chemical Society. (B) Energy barrier of pore expansion extracted from the trajectory of graphene pore growth with increasing electron dose. (C) Pore size distribution of nanopores etched by electron beams in TEM. Panels B and C reprinted with permission from ref 28. Copyright 2012 National Academy of Sciences. (D) Evolution of defects in graphene by oxidation: epoxy and ether groups cluster and finally lead to C=C bond breakage (energy is in eV unit). Reprinted with permission from refs 30 and 31. Copyright 2006 The American Physical Society and 2012 American Chemical Society. (E) High-resolution transmission electron microscopy (HRTEM) images of nanopores in graphene lattice after O\(_3\) etching treatment (2 min at 80 °C). Reprinted with permission from ref 14. Copyright 2018 The Authors. (F) Narrow PSD of nanoporous graphene after O\(_3\) etching treatment. (G) Carbon capture performance of nanoporous graphene etched by O\(_3\) and O\(_2\) compared to that from the state-of-the-art membranes. Panels F and G reprinted with permission from ref 20. Copyright 2021 American Association for the Advancement of Science.
chemisorption of O$_3$ into epoxy has been predicted by ab initio calculations to be 0.75 eV.\textsuperscript{32} We recently estimated an energy barrier of 0.67 eV based on counting the concentration of oxygen functional groups on a graphitic lattice as a function of O$_3$ exposure conditions using X-ray photoelectron spectroscopy (XPS).\textsuperscript{20} The epoxy groups have been reported to form cyclic trimers and finally cluster as a honeycomb network of cyclic trimers to minimize the net energy of epoxy/graphene system (Figure 3D).\textsuperscript{34} Subsequently, a significant strain present in the cluster leads to the cleavage of C–O–C bond, leading to the formation of a pair of semiquinone groups.\textsuperscript{31,35} This is followed by gasification of the edge atoms as CO/CO$_2$.\textsuperscript{33} Understanding and controlling the formation of clusters and subsequent transformation into vacancy defects is key to controlling the PSD in graphene.

Recently, we showed that CO$_2$-sieving pores can be incorporated into graphene by etching in a millisecond time scale (Figure 4A–C).\textsuperscript{19,20} A short millisecond reaction limits pore expansion while a high oxidation temperature (250–300 °C) promotes chemisorption increasing the pore density. By varying the O$_3$ exposure, we could prepare membranes with attractive gas separation performance (Figure 4D,E). Recently, by using multiple pulses of O$_3$ in a short time, we were able to increase pore density resulting in improved CO$_2$-sieving (CO$_2$...
permeance of 4400 GPU and CO₂/N₂ selectivity of 33.4, Figure 4F). Briefly, pore nucleation was promoted by a higher O₃ pressure in multipulse exposure. This is because chemisorption, and therefore, nucleation is proportional to the O₃ pressure, $P$. However, pore expansion is proportional to $P^n$, where $n$ is less than 1 because an O₃ molecule can yield more than one functional group at the pore edge. As a result, a higher O₃ dose in a short time leads to a narrower PSD (Figure 4F).

The direct bottom-up synthesis is highly attractive for scalable production of nanoporous graphene. The presence of porosity in graphene in the form of intrinsic vacancy defects has been known for some time now. Intrinsic defects in graphene are both grain-boundary defects (arising from imperfect grain stitching) and intragrain defects (formed by...
lattice etching in the presence of O2 in the CVD reactor. We recently visualized these two kinds of defects by expanding them with CO2 at 800 °C.36 We could identify several grain-boundary defects as well as intragrain defects although the density of the former was significantly higher (Figure 5A). The relative population of these defects is sensitive to the CVD conditions, including the leak rate of the CVD reactor.

Intrinsic vacancy defects can be regulated by varying growth temperature, carbon precursor, and the catalytic substrate. CVD temperature affects graphene grain growth, its morphology, and the resulting “quality” and, hence, the defect density. Kidambi et al. reported an increased defect density upon lowering CVD temperature from 1000 to 900 °C.37 We recently reported benzene-derived SLG where the average graphene grain size reduces from 20 to 1 μm by reducing the CVD temperature from 1000 to 825 °C (Figure 5B,C).38 This was also reflected in increased H2 permeance (600 to 1000 GPU, Figure 5D).38 The carbon precursor controls the grain morphology because it controls the nature and the concentration of active growth species. A favorable dehydrogenation kinetics of an unsaturated molecule (e.g., benzene) promotes growth at a lower temperature. Comparing H2 transport from intrinsic vacancy defects in graphene synthesized using methane and benzene, one observes a relatively higher H2 permeance and lower H2/CH4 selectivity from the benzene-derived graphene (5–8 and 6–25 for benzene- and methane-derived graphene, respectively).13,38

The catalytic CVD substrate catalyzes precursor breakdown into active species and ultimately controls grain morphology.39 For CVD on copper, the entire sequence of reaction and diffusion of the precursors takes place on the external surface (surface growth mechanism).39 However, substrates with a significant C solubility (e.g., Ni or Rh) crystallize graphene via the precipitation route.31 We recently exploited this route to prepare porous graphene with a high density of intrinsic vacancy defects. Depositing a small amount of carbon precursor on the foil as a thin polymer film followed by a short heat treatment at 500 °C, produced porous nanocrystalline graphene (PNG) (Figure 5E).42 The heat treatment resulted in the pyrolysis of the polymer, which built a C reservoir in the Ni matrix. Upon cooling, the C solubility decreased, which led to a high degree of supersaturation and eventual precipitation of C as graphene grains on the surface of the foil. Because of the intentionally limited C loading, complete intergrowth of the graphene grains forming the PNG film was not achieved. Rather, films with a high density of grain-boundary defects (2.1 × 1012 cm−2; measured from AC-HRTEM images) similar to that obtained by the state-of-the-art postsynthetic etching techniques, were obtained. The type of vacancy defects (nanopores) predominantly found in PNG films are intergrain defects produced by the incomplete stitching of three or more grains (Figure 8H–J).

**TOOLBOX FOR TAILORING GAS TRANSPORT**

The transport of gas molecules through N-SLG can be tailored by postsynthetic modification, by nanopore functionalization, by masking, and by adjusting the PSD (Figure 6).

Nanopore functionalization can reduce the electron-density gap and alter molecular interactions either by modifying the molecular diffusivity or by enhancing molecular affinity to the lattice. The effect of functionalization is best studied using mixtures because competitive interactions often dominate the transport of molecules. Molecular dynamic insights have shown that relatively large nanopores can be converted to CO2-selective nanopores either by inducing a surface charge or by depositing a film of ionic liquids (IL).44 Recently, Guo et al. verified experimentally that coating a nonselective N-SLG with a thin layer of IL could produce membranes with CO2/N2 selectivities of up to 32.45

We showed that a room temperature O2 treatment can graft O-functional groups at the pore edges, resulting in improved gas-sieving performance.14 A decreased H2 permeance accompanied by an increased H2/CH4 selectivity (by 1.5-fold). This behavior is consistent with a reduced electron-density gap in the pore after atomic-scale functionalization. The reduction depends on the size of the functional groups grafted at the edge of the nanopores. For example, a semiquinone group would reduce the electron-density gap by 1.2 Å. To enhance adsorption affinity, we grafted N-SLG with polyethyleneimine (PEI) chains hosting CO2-phlic groups46 (Figure 7A). PEI was grafted on the graphene lattice via the ring-opening chemistry of epoxy groups in oxidized graphene.
Figure 7. Modification of graphene nanopores. (A) Illustration of polymer-functionalization by the ring-opening reaction leading to a 10 nm thick PEI film. Portions of panel A reprinted with permission from ref 46. Copyright 2019 The Authors. (B) N 1s XPS data confirming functionalization. (C) Comparison between PSD of O$_3$-etched and O$_2$ plasma-etched nanopores. (D) Carbon capture performance of polymer-functionalized graphene compared to nanoporous graphene and the state-of-the-art membranes. Panels B–D reprinted with permission from ref 18. Copyright 2021 The Authors. (E) CO$_2$/N$_2$ separation performance when graphene is masked by PIM-1. CO$_2$ (F) and N$_2$ (G) transport as a function of pore size using different transport pathways. Panels E–G reprinted with permission from ref 48. Copyright 2020 Wiley-VCH. (H) Schematic illustration showing the advantage of controlling nucleation and expansion rates. Reprinted with permission from ref 36. Copyright 2022 The Authors. (I) Effect of O$_2$ etching on the gas permeance of MGR-based N-SLG. Reprinted with permission from ref 20. Copyright 2021 The Authors.

(Figure 7B). PEI chains were swollen with poly(ethylene glycol)–dimethyl ether to improve gas diffusivity. Ten nanometer thick selective layers prepared by this strategy yielded attractive CO$_2$/N$_2$ separation performance (CO$_2$ permeance of 6180 GPU and CO$_2$/N$_2$ separation factor of 22.5). Improving the PSD by controlled O$_3$ etching followed by PEI functionalization further improved the separation performance (CO$_2$ permeance of 8730 GPU with CO$_2$/N$_2$ separation factor of 33.4, Figure 7C,D).

An advantage of depositing polymeric chains on graphene is that the pores are masked by the chains. As a result, the direct access to the pores from the gas phase is blocked. This helps to reduce the rapid effusion through any large nonselective nanopore. We demonstrated this by depositing a polymer of intrinsic microporosity (PIM-1, Figure 7E). An obstruction of direct gas-phase transport reduced the N$_2$ transport much more relative to CO$_2$, thanks to a stronger adsorbed-phase
transport of CO$_2$ (Figure 7F,G). In general, this route can be applied using several high-permeability polymers.\(^{18}\) Controlled pore expansion can be used to manipulate PSD and molecular cutoff. We recently demonstrated this with O$_2$.
or low-concentration O$_3$ (Figure 7H). A controlled expansion of pores was achieved by an in situ exposure to O$_2$ at 200 °C inside a membrane module (Figure 7I), where a concerted increase in CO$_2$ permeance and selectivity with N$_2$ was achieved. A model of pore expansion predicted an expansion rate of 0.14 Å h$^{-1}$ under these conditions, consistent with shifting the molecular cutoff in favor of a rapid permeation of CO$_2$. This was also evidenced by the fact that O$_2$/N$_2$ selectivity increased during this slow expansion in O$_2$. Recently, we demonstrated that CO$_2$ could be used as an etchant for existing pores in N-SLG where only pore expansion events take place and new nucleation events are prohibited. This is because nucleation of new defects on the basal plane of graphene requires surpassing a prohibitive energy barrier (5 eV). A controllable etching rate of 0.6 to 280 nm min$^{-1}$ could be achieved by varying the etching temperature between 750 and 1000 °C. This etching strategy is promising for various separations ranging from gas to ions. We note that etching at such high temperatures did not produce cracks when done on Cu-supported graphene, but cracks could develop if the graphene is supported on a porous substrate with a different coefficient of thermal expansion.

### UNDERSTANDING THE STRUCTURE OF NANOPORES

Developing a robust understanding of gas transport observed from the N-SLG membranes requires linking nanopore structure with the observed transport properties. However, current understanding is limited because of the lack of understanding of the "real" pore structure, including functional groups around the pores that participate in the gas transport.

The most common characterization for nanopore structure is based on aberration-corrected high-resolution transmission electron microscopy (AC-HRTEM). It is a powerful tool to resolve the structure of porous lattice, and therefore, pore size, shape, and density. However, preparing a contamination-free specimen for AC-HRTEM is challenging. Also, the electron beam can affect sample integrity when the energy transferred is higher than the knockout energy of carbon atoms in the basal plane (20–22 eV) or at the nanopore edge (14 eV). These issues can be avoided to some extent by working at an acceleration voltage of 80 kV or below. While it is not possible to prevent the rearrangement of edge atoms because such events take place with a small energy barriers, imaging at a low acceleration voltage (30 kV) is promising to minimize such events.

Over the past three years, we have developed several specimen preparation strategies to minimize surface contamination, to clean a contaminated lattice, and to perform pore formation experiments directly on the TEM grid. These advancements facilitated the high-throughput analysis of graphene nanopores and helped elucidate etching of graphene by O$_2$ and CO$_2$. A good specimen preparation technique should allow the formation of suspended graphene without any residual contamination from the graphene transfer step. This is crucial for nanoporous graphene samples because contaminants interact more strongly with nanopores compared to the basal plane. Recently, we developed a polymer-free transfer approach that reinforces nanoporous graphene with a premade lacy carbon film with 20–1000 nm openings to produce samples with high coverage and robust enough to withstand further cleaning steps (Figure 8A–D). We also demonstrated that a high-temperature treatment (900 °C) in the presence of activated carbon and using overpressure of H$_2$ (to avoid an O$_2$ leak) can remove surface contamination from nanoporous graphene samples without generating new nanopores. An alternative technique to circumvent the contamination issue is to first transfer pristine graphene to a TEM grid, and then subsequently produce the nanopores on the suspended graphene. To achieve this, we adapted the paraffin transfer method developed by Leong et al. to transfer pristine graphene to a holey silicon nitride grid (Figure 8E).
allowed the study of the CO$_2$ nanopore etching kinetics by imaging the nanopores before and after an etching step (Figure 8F,G). While it is crucial to develop sample preparation techniques that allow imaging of a large volume of nanopores per sample, it is equally important to develop computational methods capable of efficiently analyzing the increasingly large volume of data. Recently, in this direction, we introduced an advanced image analysis to investigate the grain orientation in nanocrystalline nanoporous graphene samples by calculating the local FFT around each pixel of the HRTEM and using these data to produce an orientation map (Figure 8H–I).

While the advances mentioned above allow characterization of porous graphene lattice, it is currently extremely challenging to resolve functional groups around the nanopores, which tend to gasify during sample preparation and imaging. Ongoing developments in (i) atomic resolution using low electron accelerating voltages, (ii) high-speed imaging by coupling ultrafast isolated electron pulses with direct counting electron detectors, (iii) in situ cleaning protocols, and (iv) scanning atomic electron tomography, will open venues for studying the dynamics of structural changes and the three-dimensional position of atoms and functional groups at the edge of graphene nanopores.

Scanning tunneling microscopy (STM) is emerging as a highly complementary characterization tool for nanoporous graphitic lattice. STM can investigate the surface of nanoporous lattice without modifying the sample including functional groups because of a nondestructive interaction with the sample. As a result, STM facilitates an understanding of pore geometry (PSD, density, functional group surrounding the pores, etc.) by the topography image. Additionally, under low-temperature imaging conditions, one can also probe the nature of functional groups by scanning tunneling spectroscopy. We have used low-temperature STM (LTSTM) operating at 4 K to unravel the mechanistic insights from O$_2$-based etching of the graphene lattice. We could analyze the density and distribution of epoxy clusters and vacancy defects (Figure 8K–M) and could observe various stages of evolution of clusters into vacancy defects (Figure 8N–P).

Advances in sample preparation and improved availability of STM could position it as an extremely popular technique for analyzing the N-SLG lattice.

## SCALE-UP POTENTIAL

The high performance of N-SLG membrane makes its scale-up a compelling task. N-SLG membranes have come a long way from the first proof-of-principle on micrometer-sized graphene in the year 2008 (Figure 9A). Millimeter-scale and centimeter-scale gas-sieving N-SLG membranes were reported in 2018 and 2021, respectively (Figure 9B–D). Still, several challenges remain in improving the scalability of graphene membranes. Most important of these are a scalable synthesis of N-SLG, transfer on a porous support, and a design of a high-packing-density module. The key technological barrier is the high cost of catalytic metal foil, complex pore generation techniques, and the complex graphene transfer protocol onto a porous support.

CVD is routinely used for synthesizing high-quality SLG (Figure 10). It is an established process and is widely used in the semiconductor industry. Being a vapor-phase technique, obtaining uniform films in a scaled-up reactor is feasible. Efficient packing of copper foils while ensuring a rapid external mass transfer of carbon precursors to Cu, can be used to synthesize large-area graphene, O(100–1000 m$^2$), in a single batch in a single day inside an industrial CVD reactor (typical diameter of 1 m, length of 1–2 m).

Our group has shown that the cost of copper foil can be reduced by optimizing the surface smoothness of low-cost foils by thermal annealing. Further reduction in the cost of foil can be achieved by developing methods allowing reuse of the foil. Among the pore generation technique, O$_2$ and O$_3$ treatments can be adapted to generate pores in a scalable manner. For example, they can be introduced directly inside the CVD reactor after the synthesis of graphene to generate porosity.

The largest hurdle in the scale-up of N-SLG membranes is the transfer of graphene on porous support without inducing cracks and tears. The concept of a gas-permeable mechanical reinforcing layer that can be left permanently on graphene is an
effective strategy for avoiding cracks and tears. The desirable characteristics of the reinforcing materials are strong adhesion to graphene, high intrinsic gas permeance, and robust thermal and chemical stability. We first demonstrated this concept by forming the NPC film on graphene by the pyrolysis of a block copolymer templated turanose (Figure 9B).\textsuperscript{14} The NPC film has a perforated lamellar (PL) nanostructure where gas transport takes place in the Knudsen regime via an interlamellar spacing of \(\sim 2\) nm.\textsuperscript{15} The film terminates with a pore opening of \(\sim 20\) nm, over which a graphene layer is suspended. Submicron-thick NPC films have a negligible gas transport resistance (H\(_2\) permeance up to 1 million GPU) because of a rapid transport of gas through the PL nanostructure of NPC. The NPC film bonds strongly to graphene, and as a result, graphene membranes with a total area of \(1\) mm\(^2\) could be prepared on a laser-drilled metal foil support that could be subsequently pressurized to several bars. We extended this approach by further improving the strength of the mechanical reinforcing layer by adding a layer of multiwalled carbon nanotubes (MWNTs) on top of the NPC film (Figure 9C).\textsuperscript{16} As a result, centimeter-scale membranes could be prepared on low-cost woven stainless-steel support. Apart from the porous carbon film, an alternative for the mechanical reinforcement layer is gas-permeable dense polymeric films. Highly permeable nanoporous polymeric films that interact well with graphene can allow crack-free transfer of graphene to a porous substrate (Figure 9D).\textsuperscript{20,47} This method has the advantage that not only does the polymeric film act as a support but it also acts as a defect sealing film blocking the direct gas-phase transport, and in some cases, can enhance adsorption selectivity. We are now extending this strategy to develop meter-scale membranes under an industry-sponsored pilot plant project for postcombustion capture targeting a capture rate of 10 kg CO\(_2\) per day.\textsuperscript{58}

\section*{Perspective}

Membranes with an atom-thick selective layer, such as N-SLG, hold great promise for gas separation because one can avail a large permselective flux, reducing the needed membrane area to reduce the process footprint and capital cost. However, currently, there are several fundamental and engineering challenges in implementing these membranes on a large scale.

The key scientific challenges relate to the synthesis of N-SLG with a high density of pores while maintaining a narrow PSD. For the top-down etching technique, developing a decoupled pore nucleation and pore expansion technique would allow independent control of density and PSD. This can be achieved by generating pore precursors (epoxy clusters) while avoiding gasification events. For the bottom-up direct crystallization route, improved control of grain growth down to the nanometer scale will help tune the size of the grain-boundary defects. This can be achieved by improving the mechanistic understanding of grain growth and subsequently optimizing control handles such as carbon precursor concentration and growth temperature profile. Further control of selectivity can be obtained by postsynthetic modification such as polymer masking or pore functionalization. Here, an extremely desirable direction is to carry out atomic-scale functionalization at the nanopore edge such that the diffusivity across the membrane is not compromised.

As sample preparation and imaging techniques advance, the need for high-throughput computational strategies to identify and analyze a high number of graphene nanopores will be needed to build a better understanding of the structure–property relationship. Currently, the analysis requires a great degree of human intervention to achieve trustworthy results. Further advancements to automatically identify nanopores and to analyze their structure and the neighboring lattice orientation are needed.

From the scale-up point of view, it is important to note that the “quality” of graphene plays a very important role in achieving high-performance membranes. High-quality graphene in this context is single-layer graphene films with a low \(I_D/I_G\) ratio (ideally less than 0.05) before any intentional etching step. They should be devoid of any particulate contamination (especially larger than \(100\) nm), which typically arises when CVD synthesis is carried out in quartz tube reactors. These conditions can be met in a large area CVD reactor by bringing design elements that ensure a good temperature uniformity while avoiding contaminations from the reactor wall.

To advance the technology readiness level of graphene membranes for gas separation, studying separation performance using a realistic gas mixture, e.g., flue gas for postcombustion capture, under relevant operation conditions (temperature, pressure) is needed. Luckily, graphene nanopores are chemically and thermally robust. Proof-of-concept studies have reported attractive separation performances under simulated flue gas conditions (humid feed,\textsuperscript{46} elevated temperature,\textsuperscript{20,42,46} variable feed pressure\textsuperscript{4,16}).

In a recent perspective of membrane separation technology by Beuscher, Kappert, and Wijmans, the need for more holistic research encompassing not only material development but also module and process research was pointed out.\textsuperscript{59} Therefore, the fabrication of N-SLG membranes on low-cost supports that can be assembled in a module with a high-packing-density-mimicking spiral wound module (300–1000 m\(^2\)/m\(^3\)) is needed. Developing roll-to-roll transfer techniques for graphene onto low-cost supports, while at the same time peeling off catalytic substrate for reuse, will be transformative for the field.

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\section*{PERSPECTIVE}

Membranes with an atom-thick selective layer, such as N-SLG, hold great promise for gas separation because one can avail a large permselective flux, reducing the needed membrane area to reduce the process footprint and capital cost. However, currently, there are several fundamental and engineering challenges in implementing these membranes on a large scale.

The key scientific challenges relate to the synthesis of N-SLG with a high density of pores while maintaining a narrow PSD. For the top-down etching technique, developing a decoupled pore nucleation and pore expansion technique would allow independent control of density and PSD. This can be achieved by generating pore precursors (epoxy clusters) while avoiding gasification events. For the bottom-up direct crystallization route, improved control of grain growth down to the nanometer scale will help tune the size of the grain-boundary defects. This can be achieved by improving the mechanistic understanding of grain growth and subsequently optimizing control handles such as carbon precursor concentration and growth temperature profile. Further control of selectivity can be obtained by postsynthetic modification such as polymer masking or pore functionalization. Here, an extremely desirable direction is to carry out atomic-scale functionalization at the nanopore edge such that the diffusivity across the membrane is not compromised.

As sample preparation and imaging techniques advance, the need for high-throughput computational strategies to identify and analyze a high number of graphene nanopores will be needed to build a better understanding of the structure–property relationship. Currently, the analysis requires a great degree of human intervention to achieve trustworthy results. Further advancements to automatically identify nanopores and to analyze their structure and the neighboring lattice orientation are needed.

From the scale-up point of view, it is important to note that the “quality” of graphene plays a very important role in achieving high-performance membranes. High-quality graphene in this context is single-layer graphene films with a low \(I_D/I_G\) ratio (ideally less than 0.05) before any intentional etching step. They should be devoid of any particulate contamination (especially larger than \(100\) nm), which typically arises when CVD synthesis is carried out in quartz tube reactors. These conditions can be met in a large area CVD reactor by bringing design elements that ensure a good temperature uniformity while avoiding contaminations from the reactor wall.

To advance the technology readiness level of graphene membranes for gas separation, studying separation performance using a realistic gas mixture, e.g., flue gas for postcombustion capture, under relevant operation conditions (temperature, pressure) is needed. Luckily, graphene nanopores are chemically and thermally robust. Proof-of-concept studies have reported attractive separation performances under simulated flue gas conditions (humid feed,\textsuperscript{46} elevated temperature,\textsuperscript{20,42,46} variable feed pressure\textsuperscript{4,16}).

In a recent perspective of membrane separation technology by Beuscher, Kappert, and Wijmans, the need for more holistic research encompassing not only material development but also module and process research was pointed out.\textsuperscript{59} Therefore, the fabrication of N-SLG membranes on low-cost supports that can be assembled in a module with a high-packing-density-mimicking spiral wound module (300–1000 m\(^2\)/m\(^3\)) is needed. Developing roll-to-roll transfer techniques for graphene onto low-cost supports, while at the same time peeling off catalytic substrate for reuse, will be transformative for the field.

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Notes

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Kuang-Jung Hsu received his Master degree in chemical engineering at National Taiwan university in 2018 and is now a Ph.D. candidate at EPFL. His research interests are engineering and functionalization chemistry on Å-scale nanopores on single-layer graphene for gas separation. He is also interested in developing the atomic thin membranes for the postcombustion carbon capture.

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Kumar Varoon Agrawal is an assistant professor and GAZNAT chair of Advanced Separation at EPFL. His research interests focus on material chemistry and engineering at Å-scale for the development of energy-efficient inorganic and hybrid membranes for molecular separation. He has keen interest in the fundamental aspects of nanoporous 2D materials as well as in the scale-up of high-performance membranes based on these materials.

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