Bottom-up synthesis of graphene films hosting atom-thick molecular-sieving apertures

Luis Francisco Villalobos^{a,1}, Cédric Van Goethem^{a,1}, Kuang-Jung Hsu^a, Shaoxian Li^a, Mina Moradi^a, Kangning Zhao (赵康宁)^a, Mostapha Dakhchoune^a, Shiqi Huang^a, Yueqing Shen (沈悦卿)^a, Emad Oveisi^b, Victor Boureau^b, and Kumar Varoon Agrawal^{a,2}

^aLaboratory of Advanced Separations, École Polytechnique Fédérale de Lausanne, Sion 1950, Switzerland; and ^bInterdisciplinary Centre for Electron Microscopy, École Polytechnique Fédérale de Lausanne, Lausanne 1015, Switzerland

Edited by Manish Kumar, The University of Texas at Austin, Austin, TX, and accepted by Editorial Board Member Pablo G. Debenedetti March 28, 2021 (received for review December 1, 2020)

Incorporation of a high density of molecular-sieving nanopores in the graphene lattice by the bottom-up synthesis is highly attractive for high-performance membranes. Herein, we achieve this by a controlled synthesis of nanocrystalline graphene where incomplete growth of a few nanometer-sized, misoriented grains generates molecular-sized pores in the lattice. The density of pores is comparable to that obtained by the state-of-the-art postsynthetic etching (10^{12} cm^{-2}) and is up to two orders of magnitude higher than that of molecular-sieving intrinsic vacancy defects in single-layer graphene (SLG) prepared by chemical vapor deposition. The porous nanocrystalline graphene (PNG) films are synthesized by precipitation of C dissolved in the Ni matrix where the C concentration is regulated by controlled pyrolysis of precursors (polymers and/or sugar). The PNG film is made of few-layered graphene except near the grain edge where the grains taper down to a single layer and eventually terminate into vacancy defects at a node where three or more grains meet. This unique nanostructure is highly attractive for the membranes because the layered domains improve the mechanical robustness of the film while the atom-thick molecular-sized apertures allow the realization of large gas transport. The combination of gas permeance and gas pair selectivity is comparable to that from the nanoporous SLG membranes prepared by state-of-the-art postsynthetic lattice etching. Overall, the method reported here improves the scale-up potential of graphene membranes by cutting down the processing steps.

intrinsic vacancy defects | nanocrystalline graphene | nanopores | graphene membrane | low-temperature growth

The direct bottom-up synthesis of two-dimensional (2D) films hosting molecular-sieving apertures is a longstanding goal in material chemistry. Materials with a high density of molecular-sized nanopores such as zeolites (1, 2), metal-organic frameworks (MOFs) (3, 4), covalent organic frameworks (5), graphitic carbon nitride (6), and protein channels (7) can be synthesized in a 2D topology, albeit in the form of nanosheets with lateral dimension limited to $\sim 0.1 \text{ } \mu\text{m}$, which prohibits the realization of porous, unit-cell-thick films by the bottom-up synthesis. On the other hand, the synthesis of high-quality atom-thick polycrystalline films of graphene (8) and hexagonal boron nitride (*h*-BN) (9) can be carried out in a scalable manner, with the production capacity of graphene films exceeding three million m^2 in 2017 (10). However, their lattice is impermeable in the absence of a sufficient electron-density gap for molecular transport with a reasonable energy barrier (11).

The lattice of graphene can be engineered by postsynthetic etching to obtain attractive separation performance, for example, by using an electron (12) and ion (13) beam or by chemical etching techniques involving O_2 (14), O_2 plasma (15, 16), O_3 (17–19), or UV/ O_3 (20). However, the postsynthetic lattice etching adds an additional and often complex processing step in the overall fabrication process. It is attractive to avoid this step from the point of view of membrane scale-up. This makes the bottom-up approach, capable of synthesizing a nanoporous graphene film in a single

synthesis step, extremely desirable. For example, Ullmann coupling is a highly promising route that yields porous lattice with a precise pore structure (21); however, significant advances are needed to enlarge the ordered domains, which are currently only a few nanometers in size. Another promising strategy is to engineer the catalyst to selectively avoid graphene growth where pores are desired. For example, Park and coworkers deposited 2 to 10 nm tungsten islands in a Cu foil to locally shield the Cu surface during growth giving rise to a porous graphene with 20 to 50 nm pores and a pore density of $\sim 10^{10} \text{ cm}^{-2}$ (22).

An attractive approach for the bottom-up synthesis of nanoporous graphene is to promote the incorporation of intrinsic vacancy defects in the graphene lattice during its crystallization. A proof of principle of this idea for molecular separation has been demonstrated by altering the chemical vapor deposition conditions of polycrystalline single-layer graphene (SLG) on a catalytic Cu foil (17, 18). Tuning the synthesis temperature (23), the precursor (methane, benzene) (24), and the roughness/orientation of the catalytic Cu foil (25) has been shown to yield intrinsic vacancy defects that could separate small molecules based on their size, for example H_2 from CH_4 . However, the SLG's true potential of ultrahigh molecular permeance could not be realized in these

Significance

The energy efficiency of gas separation is expected to benefit from the development of membranes yielding selective but large permeance. The ultimate limit of this is two-dimensional films hosting a high density of molecular-selective apertures (e.g., nanoporous single-layer graphene). Currently, pores are incorporated in single-layer graphene by postsynthetic etching route, and the direct bottom-up synthesis of nanoporous graphene, especially targeting a high pore density, remains a grand challenge attributing to a number of crystallization bottlenecks. We address this by increasing the density of molecular-sized intrinsic vacancy defects in graphene by developing crystallization conditions which promote the growth of misoriented grains, limiting the grains to a few nanometers in size and preventing a complete grain intergrowth while yielding mechanically robust films.

Author contributions: L.F.V., C.V.G., and K.V.A. designed research; L.F.V., C.V.G., K.-J.H., S.L., M.M., K.Z., M.D., S.H., Y.S., and E.O. performed research; L.F.V., C.V.G., K.-J.H., S.L., M.M., K.Z., M.D., S.H., Y.S., E.O., V.B., and K.V.A. analyzed data; and L.F.V., C.V.G., and K.V.A. wrote the paper.

The authors declare no competing interest.

This article is a PNAS Direct Submission. M.K. is a guest editor invited by the Editorial Board.

Published under the PNAS license.

¹L.F.V. and C.V.G. contributed equally to this work.

²To whom correspondence may be addressed. Email: kumar.agrawal@epfl.ch.

This article contains supporting information online at <https://www.pnas.org/lookup/suppl/doi:10.1073/pnas.2022201118/-DCSupplemental>.

Published September 7, 2021.

reports because the density of vacancy defects was low. To put this into perspective, the graphene lattice hosts 3.8×10^{15} atoms cm^{-2} , and the highest reported density of molecular-sieving vacancy defects is $\sim 5 \times 10^{10}$ cm^{-2} (24), whereas postsynthetic etching has been successfully used to incorporate defect density of 10^{12} cm^{-2} (16, 19, 26). Therefore, the development of a direct bottom-up method incorporating a high density of molecular-sized intrinsic vacancy defects in graphene would be highly attractive.

A major source of intrinsic vacancy defects in polycrystalline graphene is the incomplete intergrowth of misaligned grains (27–34). Therefore, to increase the density of such defects, one needs to reduce the grain size. Also, to make the vacancies large enough for selective molecular translocation, one needs to increase the misalignment between the grains. To the best of our knowledge, growth conditions that promote small, misoriented grains incorporating a high density of molecular-sized vacancies in graphene have not been reported. We note that while there have been several reports on nanocrystalline graphene, none of them reported a porous lattice. For example, a helium leak test carried out on sealed nanocrystalline graphene film, synthesized via the quenching approach, verified the absence of He-permeable vacancy defects in such films (35). Nanocrystalline graphene films have also been synthesized by electron-radiation-induced cross-linking of aromatic self-assembled monolayers on Au (36), graphitization of polymeric precursor on Ge (37), diffusion of carbon through Ni grain boundaries (38), quenching of Pt foil in a carbon solution (35, 39), etc. However, molecular-scale vacancy defects were not observed.

Herein, we report a graphene synthesis route based on the controlled precipitation and crystallization of carbon on Ni surface at a low temperature that limits the grain size in graphene to less than 5 nm and allows the realization of a high density ($\sim 10^{12}$ cm^{-2}) of molecular-sieving intrinsic vacancy defects or nanopores by the bottom-up synthetic route. The nanocrystalline graphene is few layered (two to four layers) except near the nanopores where the grains taper into a single layer and eventually terminate leading to vacancies (Fig. 1A). This nanostructure, which we refer to as porous nanocrystalline graphene (PNG), is highly attractive for the membrane-based molecular separation because the layered domains increase the mechanical robustness of the film, and the atom-thick apertures allow the realization of high-permeance attributing to the single rate-limiting transition state at the center of the pore (40).

The presence of high-density intrinsic vacancy defects led to extremely high H_2 permeance (38,000 gas permeation units or GPU; 1 GPU = 3.35×10^{-10} mol m^{-2} s^{-1} Pa^{-1}). The pores were commensurate with the size of H_2 indicated by activated transport of H_2 and attractive H_2/CH_4 , H_2/N_2 and CO_2/N_2 selectivities. The combination of permeance and selectivity is comparable to the state-of-the-art graphene membranes prepared by postsynthetic lattice etching (19, 41). Additionally, functionalization and masking methods previously demonstrated to improve the performance of postsynthetically etched graphene could be applied to PNG to fine-tune the application-specific performance. For example, oxygen functionalization of the pores increased H_2/CH_4 and H_2/N_2 selectivities by 150 and 130%, respectively. Masking PNG with CO_2 -phillic polymers led to attractive carbon capture performance with CO_2 permeance of 5,700 GPU and a CO_2/N_2 separation factor of 31.

Results and Discussion

Bottom-Up Synthesis of PNG Films. The synthesis of PNG is straightforward and scalable. It was carried out on a 25 μm thick Ni foil at ambient pressure by heating solid precursors under a reducing atmosphere (Ar/H_2 , 400/30 sccm) to 500 °C (a low temperature for graphene synthesis) at a rate of 1 °C min^{-1} , and holding the temperature for 1 h, followed by cooling at a rate of 1 °C min^{-1} . Briefly, during the heating step, the pyrolysis products of the precursors come in contact with Ni, deconstruct to single C

species, and dissolve in the Ni matrix. PNG grows from the precipitation of the dissolved C species while the porosity in the film is generated by a limited grain growth (discussed in detail later). This process leads to significant energy and time saving compared to state-of-the-art approaches for the synthesis of nanoporous graphene membranes which require 1) high temperature (900 to 1,000 °C) and high vacuum, and 2) postsynthetic etching.

PNG could be synthesized from several combinations of solid precursors (polystyrene-block-poly(4-vinyl pyridine) [PS-*b*-P4VP] or the corresponding homopolymers, and/or turanose) either by covering a reservoir of precursors by the Ni foil or by coating a thin film (100 to 1,000 nm) of precursors on the foil.

The first type of PNG we studied (referred as PNG-1) was synthesized by heating PS-*b*-P4VP (0.1 g) and turanose (0.2 g) inside a boat covered by Ni foil. PNG-1 films were extremely thin but had enough mechanical robustness to be self-standing in a water bath after the Ni foil was etched away. They could be washed and transferred to a transmission electron microscopy (TEM) grid without using a mechanically reinforcing layer (*SI Appendix, Fig. S1*). Crack-free areas of more than 200 μm^2 could be found in the TEM grid. Inspection of the aberration-corrected high-resolution TEM (AC-HRTEM) images revealed that the PNG-1 films were composed primarily of nanosized (<5 nm) few-layer-thick graphene grains (Fig. 1B and C and *SI Appendix, Fig. S2 A–C*). The grains were randomly oriented throughout the film as observed in the fast Fourier transform (FFT) images computed from 3×3 nm sections of Fig. 1B. The grains frequently tapered into single-layer domains and eventually into vacancy defects (Fig. 1B and C) with an unprecedented density for intrinsic vacancy defects (2.1×10^{12} cm^{-2}). The majority of defects had a van der Waals gap smaller than 1 nm, measured by subtracting the van der Waals diameter of a carbon atom (42) (*SI Appendix, Figs. S2D and S20 and Table S8*), making them attractive for molecular separation.

Fabrication of PNG Membrane with Mechanically Reinforcing Support in a Single Step.

We could also synthesize PNG films by spin-coating precursors on the Ni foil followed by heat treatment at 500 °C. An advantage of this approach, especially when turanose is added to the precursor, is that we could synthesize PNG film and a mechanically reinforcing nanoporous carbon (NPC) film on top of the PNG film in a single step. In the past, we have successfully used NPC film to transfer SLG on a macroporous support (W foil drilled with 5 μm sized holes) to study the gas permeation behavior (18, 43). Here, we refer to PNG film obtained in this route as PNG-2.

The following is a brief explanation for the synthesis of the hybrid PNG-2/NPC film. A wet film of PS-*b*-P4VP and turanose, coated on the Ni foil, phase separates into nanosized hydrophobic (PS) and hydrophilic (turanose hydrogen bonded to P4VP) domains upon drying (43). Pyrolysis of this film removes all PS, most of the P4VP, but only some of the turanose. This is because turanose is not degraded completely but rather yields an amorphous carbon backbone. So, when the phase-separated film is heat treated, the carbon residue of turanose forms the ~ 100 nm thick NPC films hosting 20 to 30 nm sized nanopores, while at the same time Ni catalyzes the synthesis of PNG-2 film from the vapor fraction of pyrolysis products (Fig. 2A–D).

We note that when the same process is done on a Cu, which does not catalyze graphene growth at 500 °C, only the NPC film is produced, and no evidence of a graphene was found (*SI Appendix, Figs. S3 and S5*). The structure of the NPC formed on Cu looked identical from both sides (*SI Appendix, Fig. S3 B, D and F*). In contrast, in the case of Ni foil, a thin film was observed on the side of NPC that was next to the foil (*SI Appendix, Fig. S3 A, C and E*). Nevertheless, the porous structure of the NPC could be observed below such thin film (*SI Appendix, Fig. S4*). Selected area electron diffraction (SAED) analysis of this film revealed that it was indeed nanocrystalline graphene (Fig. 2B and *SI Appendix, Fig. S5 A and B*).

Fig. 1. The nanostructure of PNG film. (A) Schematic of PNG showing the nanopores that form when three or more nanocrystalline graphene grains with different orientations meet. (B) AC-HRTEM image of the PNG-1 synthesized by exposing a 25 μm thick Ni foil to the pyrolysis products of PS-*b*-P4VP and turanose (1:2 weight ratio) at 500 $^{\circ}\text{C}$. The orange arrows point toward the nanopores, and the yellow squares indicate the areas used for computing the FFT images presented at the bottom of the panel. The scale bars in the FFT indicate 2 nm^{-1} , and the angles indicate the relative rotation of the graphene grains from an arbitrary reference point. (C) AC-HRTEM images of several nanopores. (Scale bar, 1 nm.) The PNG-1 samples were imaged directly after transferring to the TEM grid. No posttreatment or cleaning protocol was used before imaging.

It was not possible to observe the porous structure of NPC-supported PNG-2 using AC-HRTEM because the presence of NPC film deteriorates the resolution (Fig. 2D). Therefore, we used low-temperature scanning tunneling microscopy (LTSTM) of the PNG film suspended on $\sim 20\text{ nm}$ sized NPC pores to analyze the nanopores of PNG-2 (Fig. 2E–H). The pore density calculated from the LTSTM images was $1 - 4 \times 10^{12}\text{ cm}^{-2}$, in agreement with the pore density of PNG-1 films (calculated from AC-HRTEM images). The size of the observed vacancy defects ranged from 2.4 to 4.2 $\text{\AA}$ (SI Appendix, Fig. S6). Consistent with AC-HRTEM observations, the structure is made of a few nanometer grains, and the nanopores are located at the node of the grains (Fig. 2E, F, and H). To further probe the porosity and pore-size distribution in PNG-2, we carried out gas permeation experiments as discussed below.

Molecular Sieving from the NPC-Reinforced PNG-2 Films. We consistently observed gas-sieving behavior albeit with a varying degree of size-sieving effects for three PNG-2 membranes prepared

in the same way (Fig. 2I and SI Appendix, Table S1). For example, membrane 1 (M1) yielded large H_2 and CO_2 permeances of 26,000 and 9,300 GPU with gas pair selectivities slightly above that expected for effusion from atom-thick aperture, that is, H_2/N_2 and CO_2/N_2 selectivities of 4.0 and 1.4, respectively, compared to 2.8 and 0.8 expected from the effusive transport (13). Membrane 2 (M2) yielded lower H_2 and CO_2 permeances of 3,300 and 2,600 GPU, respectively, but with selectivities well above those expected from the effusive regime (H_2/CH_4 , H_2/N_2 and CO_2/N_2 selectivities of 11.4, 15.9, and 12.1, respectively). The performance of membrane 3 (M3) was somewhat in between M1 and M2 with H_2 and CO_2 permeances of 2,500 and 1,000 GPU, respectively, and H_2/CH_4 , H_2/N_2 and CO_2/N_2 selectivities of 6.3, 5.7, and 2.3, respectively. The membranes' performance was stable, evidenced by the retained performance measured after 50 d (SI Appendix, Fig. S7). Permeation experiments were done at 25 $^{\circ}\text{C}$ after heating the samples to 150 $^{\circ}\text{C}$ inside the membrane module for at least 3 h and then cooling down to 25 $^{\circ}\text{C}$ to avoid the influence of adsorbed contaminants.

Fig. 2. Molecular sieving from the intrinsic defects in PNG-2 membranes. Low-magnification TEM image (A), SAED pattern (B), and high-magnification TEM images (C and D) of the NPC-supported PNG-2. The SAED pattern is from an area of $\sim 25 \mu m^2$. (E and F) LTSTM images of PNG-2 film suspended on 20 nm sized NPC pores. White arrows point to nanopores. (G) Height profiles along the line a-a' in E. We note that it was challenging to obtain lattice resolution by LTSTM because the PNG film is suspended. For this reason, we chose a conservative threshold for defining vacancy defects ($> 2 \text{ \AA}$). Profiles for the rest of the marked pores are available in *SI Appendix, Fig. S6*. (H) Enlarged LTSTM image from panel F, marked with white lines representing three grains that merge to form the nanopore. (I) H_2/CH_4 , H_2/N_2 , and CO_2/N_2 ideal selectivities from the standalone NPC support and from three NPC-supported PNG-2 membranes (M1, M2, and M3). M2-O₃ indicates O-functionalized M2. The blue and red areas indicate 25 and 150 °C measurements, respectively. (J) Single-gas permeation data as a function of temperature for M2. (K) Gas permeation data at 150 °C as a function of the kinetic diameter before and after O-functionalization of M2. (L) A comparison of the H_2/CH_4 separation performance between PNG-2 membranes and SLG membranes in the literature.

The transport of gases (He , H_2 , CO_2 , N_2 , and CH_4) from these membranes was temperature activated, that is, they increased as a function of temperature (Fig. 2J and *SI Appendix, Table S2*), confirming the presence of an energy barrier for the transport of gases, indicating that the electron-density gap in the majority of the nanopores in PNG-2 were commensurate to the size of these gas molecules. For M2, H_2 permeance increased more than those of larger molecules, a phenomenon also observed in earlier studies (18, 19), and attributed to a narrower pore-size distribution, consistent with the higher selectivity from M2. As a result,

when the temperature was increased to 150 °C, H_2 permeance increased to 15,000 GPU, and H_2/CH_4 selectivity increased slightly to 12.4 (*SI Appendix, Table S4*). Another membrane (M4) displayed attractive combination of H_2 permeance (38,000 GPU) and H_2/CH_4 selectivity (17.2) at 150 °C.

In contrast, SF_6 permeance was not temperature activated, which indicated that the majority of the nanopores were smaller than the kinetic diameter of SF_6 (5.5 Å), and SF_6 mainly permeated from the tail end of the pore-size distribution. The activation energy for gas transport, E_{act} , was extracted by fitting an

Arrhenius-type relationship to the temperature-dependent gas transport and subtracting the heat of adsorption (*SI Appendix, Supplementary Note S3 and Table S5*). For M2, the E_{act} of H₂, CO₂, N₂, and CH₄ were 16.7, 19.2, 21.6, and 21.9 kJ · mol⁻¹, respectively. This indicates that the energy barrier for pore translocation increased monotonically for the larger molecules. Since the adsorption energies of N₂ (9.1 kJ · mol⁻¹) (44) and CH₄ (10 kJ · mol⁻¹) are higher compared to those of He (~0) and H₂ (4 kJ · mol⁻¹) (45), the apparent activation energies were higher for He and H₂ compared to those for N₂ and CH₄, explaining the higher selectivities at the elevated temperatures.

We note that the gas-sieving behavior observed here was certainly from the nanopores in PNG-2 film and not from the NPC film. A standalone NPC film without the PNG layer, hosting the similar-sized pores (20 to 30 nm) and thickness (~100 nm), yielded a transport characterized by Knudsen diffusion, marked by enormous permeances (>10 million GPU), which decreased with increasing temperature (*SI Appendix, Table S3*). The gas pair selectivity from the standalone NPC (Fig. 2I) was just lower than that expected from the Knudsen diffusion (18).

We could tune the gas pair selectivity of the PNG-2 film by functionalizing the pores with oxygen-functional groups using ozone (6% O₃ in O₂, 15 s exposure at 25 °C), at conditions which do not nucleate new pores, effectively shrinking the electron density gap, similar to our previous work on ozone-led functionalization of nanopores in SLG (18, 19). For example, the H₂/CH₄ selectivity from M2 enhanced by 150% (19.2) with H₂ permeance decreasing to 4,800 GPU at 150 °C (Fig. 2I and K and *SI Appendix, Table S2*). The decrease in permeance along with the drastic reduction in E_{act} for N₂ and CH₄ (*SI Appendix, Table S5*) points toward a shrinkage in the pore-size distribution where smaller pores became impermeable after further reduction in their effective size.

Overall, the gas separation performance of PNG-2 membranes was significantly better than that reported from intrinsic defects in SLG membranes. For example, H₂ permeances from PNG-2 membranes were 10- to 20-fold higher than those from the intrinsic defects in SLG membranes yielding similar H₂/CH₄ selectivities (Fig. 2L).

Factors Influencing PNG Growth. Ni is an excellent substrate to synthesize graphene at low temperatures because it has enough C solubility (0.01 to 0.04 AT%) in the range of 400 to 500 °C (46) to catalyze graphene growth. Ni can decompose C–C and C–H bonds in organic molecules at low temperatures down to room temperature (47). However, the incorporation of molecular-sized intrinsic vacancy defects, especially at high density, has not been reported in Ni-derived graphene (38, 48–50).

In order to understand how the precursors influence the synthesis of PNG, control pyrolysis experiments were conducted using three individual components of the precursor: PS, P4VP homopolymers, and turanose. This was motivated by the fact that each of these precursors has different pyrolysis behavior including 1) temperature window of pyrolysis, and 2) pyrolysis products themselves. Both of these parameters are expected to affect the growth because 1) dehydrogenation of the various pyrolysis products to form the carbon species is expected to take place at different rates, and 2) carbon solubility and bulk diffusivity in Ni is a function of temperature (both increase with temperature).

All three precursors led to thin carbon films, which were subsequently transferred to TEM grid for AC-HRTEM characterization (Fig. 3A–C and *SI Appendix, Fig. S8*). We observed crystalline as well as disordered domains from all precursors; however, important differences in nanostructure and mechanical robustness (ease of transfer to the TEM grid) could be noted. There were only a few crystalline domains in the turanose-derived film. Most of these domains were from thick graphitic areas (Fig. 3A, *Right*). While this type of thick crystalline domain was also occasionally

found in the PS- and P4VP-derived films, the latter also contained single- and few-layer nanocrystalline graphene domains (Fig. 3B and C, *Right*). In fact, the majority of the P4VP-derived film was composed of such single- and few-layer nanocrystalline graphene domains with a high density of nanopores. The majority of the PS-derived film was composed of thicker multilayer areas with occasional pores (Fig. 3C, *Left*).

Among the three precursors, turanose-derived film was the most fragile. The TEM specimen could only be prepared using a porous reinforcement film [lacey polymer film with sub-200 nm windows (51), see *Materials and Methods*], indicating a poor growth. AC-HRTEM images of the graphene film showed some multilayer areas with large pores (1 to 4 nm van der Waals gap) where the degree of order could not be ascertained (Fig. 3A, *Left*).

The graphene film derived from P4VP had a high percentage of single-layer domains, and the graphene lattice could be clearly observed. The pores had a van der Waals gap size of 0.4 to 3 nm (average = 1.1 nm, SD = 0.7 nm) and density was ~10¹² cm⁻² (Fig. 3B and *SI Appendix, Fig. S20 and Table S8*). The PS-derived film was thicker and pores were larger (0.5 to 6 nm van der Waals gap, average = 2.1 nm, SD = 1.6 nm). The density was lower: ~10¹¹ cm⁻² (Fig. 3C and *SI Appendix, Fig. S20 and Table S8*). As a result, it was easier to transfer to the TEM grid compared to the P4VP-derived graphene. A free-standing PS-derived PNG film could be directly transferred to a carbon-supported TEM grid with 2 μm holes (Fig. 3D, *Right*). The free-standing P4VP-derived film required a porous mechanical reinforcement film for its transfer (Fig. 3D, *Left*).

Differences in the thermal decomposition behavior of PS and P4VP in N₂ hinted at a possible explanation for the observed differences in the film nanostructure. Thermogravimetric analysis (TGA) showed that the decomposition of P4VP starts at 281 °C and finishes at 339 °C, whereas for PS, pyrolysis starts at 246 °C and ends at 376 °C (*SI Appendix, Fig. S9 and Supplementary Note S1*). When the carbon precursors were in direct contact with a Ni catalyst, their decomposition temperature shifted to lower values (266 to 302 °C for P4VP and 261 to 321 °C for PS; *SI Appendix, Fig. S10 and Supplementary Note S1*). At a lower temperature, both the solubility and diffusivity of C in the Ni is lower (52). Hence, the associated lower amount of C dissolved in the Ni and thus available for graphene growth could provide an explanation for the thinner, more porous PNG film observed for P4VP-derived graphene.

While the AC-HRTEM images clearly showed that the type of precursor influences the properties of the graphene, the transition from organic precursor to carbon by pyrolysis and dehydrogenation at the Ni surface is expected to be more complex than the precursor type alone. Pyrolysis of organic components typically results in three phases: a light gaseous and vapor fraction resulting from the cracking processes, a heavier hydrocarbon fraction, and a carbon residue that is left behind. Since vapor and small, oily fractions are more likely to contribute to dehydrogenated carbon, we probed the pyrolysis products of polymers in depth. For this, the condensable pyrolysis products of P4VP and PS were collected for further analysis.

NMR analysis of the collected condensable fractions revealed that PS and P4VP pyrolyzed into their monomer, dimer, and trimer fractions (*SI Appendix, Fig. S11*). 2D heteronuclear single quantum coherence ¹H-¹³C NMR (*SI Appendix, Figs. S12 and S13*) showed that the pyrolysis products of PS and P4VP have the same aromatic C/H, unsaturated C/H, and saturated C/H signatures as PS and P4VP polymers, respectively. And the diffusion ordered spectrum NMR (*SI Appendix, Figs. S12 and S13*) confirmed that three fractions with different diffusion constants were present (i.e., monomer, dimer, and trimer) in both cases. When the same analysis was done to PS-*b*-P4VP, a mixture containing monomers, dimers, and trimers from both homopolymers was produced (*SI Appendix, Fig. S14*).

Fig. 3. Nanostructure of polycrystalline graphene film from various growth experiments. AC-HRTEM images of the graphene grown by exposing a 25 μm thick Ni foil to the pyrolysis products of turanose (A), P4VP (B), and PS (C). The orange arrows point toward the nanopores. (D) Corresponding low-magnification TEM images of the graphene films from P4VP (Left) and PS (Right). (E) AC-HRTEM image of the graphene from PS, similar to panel C except that the PS film on top of the nickel foil was >1,000 thicker. (F) AC-HRTEM analysis of the graphene grown from PS on the 0.75 μm thick nickel film. The FFT image (Bottom Right) is from a 10 × 10 nm area (Top Right). No posttreatment or cleaning protocol was used before TEM imaging.

Therefore, we attribute monomers, dimers, and trimers as key precursors to PNG.

Our hypothesis on precipitation-based growth mechanism as against surface-growth mechanism (53) as the predominant mechanism is based on the fact that in the latter, the growth from C source, arriving from surface diffusion, generally leads to much larger grains (54). To substantiate this hypothesis, two control experiments, probing varying amounts of C/Ni ratios, were performed. The first experiment consisted of the deposition of a 1,000-fold thicker PS layer on the same 25 μm thick Ni foil. AC-HRTEM images of the resulting graphene (Fig. 3E) revealed a similar nanostructure (i.e., thick, multilayer misoriented nanocrystalline graphene) to that derived from the thinner PS layer (Fig. 3C);

however, the pore density was lower. The larger amount of precursor likely led to a higher uptake of C in Ni, which subsequently promoted a larger C precipitation, leading to a reduction in porosity. Given that precursors were only generated during the temperature-ramping step (<400 °C), the surface growth mechanism, if at all present, would only be active during the ramping period.

In the second experiment, the concentration of dissolved C was changed by using a much thinner Ni (0.75 μm instead of 25 μm). Our hypothesis here is that a thinner Ni would achieve a higher C supersaturation than a thicker foil because C concentration would get diluted by the diffusion in the bulkier Ni matrix in the latter case. AC-HRTEM images of the resulting graphene clearly showed a thicker, more ordered nanocrystalline structure

and a complete lack of porosity (Fig. 3F and *SI Appendix, Fig. S15*). A higher degree of graphene coverage with the thinner Ni points toward a precipitation-dominated growth mechanism, although one has to consider that the thin Ni on a sapphire substrate is composed of a larger fraction of (111) grains (98 and 88% of [111] grains in the 0.75 μm and 25 μm Ni, respectively) that are known to promote graphene growth; therefore, surface-catalyzed growth cannot be completely ruled out.

The precipitation-dominated growth mechanism is susceptible to the C concentration present in the Ni before the precipitation occurs. The presented graphene growth through precursor pyrolysis 1) loads C in the Ni matrix during the heating step [decomposition of precursors occurs below 500 $^{\circ}\text{C}$; the C solubility in Ni at 400 $^{\circ}$ is ~ 0.01 AT% (46)], 2) distributes the C in the Ni matrix during the isothermal step at 500 $^{\circ}\text{C}$, and 3) precipitates it to form PNG during the cooling step. An interplay between the

Fig. 4. PNG-3 from PS-*b*-P4VP precursor. Bright-field TEM image (A), SAED pattern (B), and AC-HRTEM image (C) of the PNG-3 film. (D) Distribution of the van der Waals gap. (E) Quantitative orientation maps of the grains at the edge of the pores. The 0 and 60 $^{\circ}$ angles indicate equivalent orientations, having a horizontal (11–20) plane orientation. Positive rotation is counterclockwise. Each grain shows a different color with sharp color interface. Soft color gradients indicate twisting of the grains. (F) Orientation of the graphene grains at the pore edge by a manual lattice fitting to the grains surrounding the pores. The model shows each grain in a different color and the bonds formed by the stitching of two grains with a color gradient. The angles indicate the mismatched angle between the two stitched graphene grains. (G) ADF-STEM image of the film. The numbers inside the yellow rectangles indicate the number of graphene layers in that area. (H) A linear correlation between the intensity and the number of graphene layers. (I) Intensity profile along the yellow line in G using an integration width of three pixels. The colored bands show the colors used in J to identify the number of layers. (J) Thickness map of the PNG-3 sample. The five tones correlate to the number of layers with the lightest being a pore and the darkest being four layers. The scale bars in E and F indicate 1 nm. No posttreatment or cleaning protocol was used before TEM imaging.

precursor decomposition kinetics and the increasing solubility and diffusivity of C in Ni with temperature determines the amount of C loaded. Given that the mean displacement of C in Ni in a timescale of 60 min is 2.9 μm at 500 $^{\circ}\text{C}$ and 0.4 μm at 400 $^{\circ}\text{C}$ (*SI Appendix, Supplementary Note S2*), one can expect a continuous dilution of the C concentration near the surface of the 25 μm thick Ni during the heating and isothermal steps. Contrarily, in a thinner 0.75 μm thick Ni, the loaded C has sufficient time to distribute homogeneously and reach a point where the concentration of C is constant throughout the Ni foil. As a result, graphene precipitation from a C-poor Ni reservoir (25 μm thick foil case) produces PNG, and a C-rich reservoir (0.75 μm thick Ni case) produces a thicker nonporous nanocrystalline graphene.

PNG from PS-*b*-P4VP. The above results suggest that polymer P4VP promotes the formation of high pore density, and PS improves the mechanical robustness of the film by promoting the formation of multilayers. Based on this, we pursued synthesis of PNG using PS-*b*-P4VP. We refer to this film as PNG-3. A low-magnification TEM image (Fig. 4A) shows the continuous PNG film decorated with the amorphous residues from the polymer decomposition (fibrous features) and thicker graphitic flakes (dark particles). SAED pattern from a 25 μm^2 area yielded a ring indicating the nanocrystalline nature of PNG-3 (Fig. 4B), which was confirmed by the lattice-resolution images (Fig. 4C and *SI Appendix, Fig. S16*) and the Raman characterization (*SI Appendix, Fig. S17*). Both single- and few-layer graphene, with a grain size of a few nanometers, could be observed with many areas displaying the characteristic hexagonal symmetry of the graphene lattice. As observed before, the grains varied in orientation leading to mismatched grain boundaries and a high density ($2.8 \times 10^{12} \text{ cm}^{-2}$) of nanometer-sized pores (Fig. 4D).

An advanced image analysis was performed to further investigate the grain orientation. Briefly, local FFT were calculated by scanning an area of 64 square pixels over the HRTEM image. For each pseudodiffraction pattern, the angular profile of graphene's (11–20) spots was extracted (details in *Materials and Methods*). In this way, the lattice orientation was calculated for each pixel of the HRTEM image and was encoded in a color map. Following this, grain orientations surrounding the pores were analyzed (Fig. 4E and *SI Appendix, Fig. S18*). It became clear that pores are surrounded by areas where multiple misaligned grains meet. A manual lattice fitting on the grains surrounding two pores corroborated this analysis and revealed the presence of 12 to 26 $^{\circ}$ mismatched angles between the graphene grains surrounding such pores and the presence of at least three different grains around the pores (Fig. 4F). These observations

confirm that the nanopores are the product of the incomplete coverage of nanocrystalline graphene. We note that these pores are not formed by chemical etching because dissociation kinetics of H_2 on Ni is extremely sluggish at 500 $^{\circ}\text{C}$ (55), and all the gases used for the synthesis were purified to remove traces of oxidizing impurities. Moreover, chemical etching is not expected to produce the observed vacancy defects surrounded by three or more different graphene grains.

Insight into thickness distribution of graphene was obtained from annular dark-field imaging in the scanning TEM (ADF-STEM) mode. The detector configuration was set to produce images in which the intensity correlates linearly with the number of graphene layers (Fig. 4G–I). Assigning a number of graphene layers to the correlated intensity thus allowed us to convert the ADF-STEM images (Fig. 4G) to a map of the number of layers (Fig. 4J) with an excellent fit ($R^2 = 0.9999$, Fig. 4H). The map revealed that the pores were mostly surrounded by single- and bilayer graphene whereas the thicker four layers were surrounded by tri- and bilayer graphene but rarely by SLG or pores. These observations are consistent with our hypothesis on the origin of pores.

Polymer Masking of Atom-Thick Apertures of PNG. The high pore density of PNG-3 film is attractive for high-flux gas separation; however, the mean van der Waals gap of 8.3 $\text{\AA}$ (Fig. 4D and *SI Appendix, Fig. S20 and Table S8*) is too large for the separation of light gas molecules. Indeed, PNG film masked with a dense 250 nm thick poly[1-(trimethylsilyl)-1-propyne] (PTMSP) film could achieve a high CO_2 permeance (38,000 GPU, SD = 3,700 GPU) at 35 $^{\circ}\text{C}$; however, the CO_2/N_2 ideal selectivity was 8 (SD = 1.2), typical of the dense PTMSP film (Fig. 5A and *SI Appendix, Table S6*). Inspired by our recent report on polymer-masked (41) and polymer-functionalized (56) membranes where CO_2 -selective polymer chains coated on top of graphene nanopores eliminate direct gas-phase transport and promote CO_2 adsorption, we deposited an ~ 10 nm thick film of polyethylene imine (PEI, $M_n = 10,000 \text{ g} \cdot \text{mol}^{-1}$) on top of PNG by spin coating. This was subsequently coated with 250 nm thick PTMSP for mechanical robustness for crack-free transfer of the film from the Ni foil to the macroporous W support. Finally, the back side of the graphene was exposed to an oligomer, poly(ethylene glycol) diglycidyl ether ($M_n = 500 \text{ g} \cdot \text{mol}^{-1}$), to swell PEI film to increase the gas diffusivity. The masking approach improved the gas separation performance with CO_2/N_2 ideal selectivity increasing to 36 (SD = 5) at 35 $^{\circ}\text{C}$. The corresponding CO_2 permeance was 3,900 GPU (SD = 1,400, Fig. 5A and *SI Appendix, Table S6*). A similar performance was achieved in mixed-gas

Fig. 5. Carbon capture performance of the PNG-3 and PEI/poly(ethylene glycol) diglycidyl ether (PEGDE)-masked PNG-3 membranes. (A) Single gas performance of PNG-3 and PEI/PEGDE-masked PNG-3 membranes supported by an ~ 250 nm PTMSP layer. (B) The CO_2 permeance and CO_2/N_2 separation factor as a function of temperature for one of the PEI/PEGDE-masked PNG-3 membranes.

experiments using a 20/80 (vol/vol) CO₂/N₂ mixture at two bars in the feed (Fig. 5B and *SI Appendix*, Table S7). The separation performance could be optimized as a function of temperature because CO₂ and N₂ permeances were temperature activated with apparent activation energy of N₂ larger than for CO₂ resulting in increasing CO₂ permeance and decreasing CO₂/N₂ separation factor with temperature. For example, at 50 °C, we could realize CO₂ permeance of 6,600 GPU and CO₂/N₂ separation factor of 22. These are attractive performances for highly competitive postcombustion carbon capture using membrane-based separation process (57–59).

Implications for the Bottom-Up Synthesis of Nanoporous 2D Film.

This work shows that it is possible to incorporate molecular-sieving pores in a graphene film by direct bottom-up synthesis, with a density comparable to that achieved by state-of-the-art etching methods, and using a low-temperature synthesis route. This was achieved by limiting the intergrowth of nanosized grains. The nanostructure of the film was dependent on C concentration in the Ni matrix, high enough so that there is sufficient grain stitching for a continuous film but not enough to form an impervious layer.

PNG films are multilayer in nature and have good mechanical robustness. The multilayered grains taper down to a single layer near the pores. This makes the pores essentially atom-thick apertures and allowed us to realize high-performance separation. The nanocrystalline graphene-based membrane reported here improves the gas permeance from carbon membranes that includes amorphous carbon nanomembranes (60–63) and carbon molecular sieves (64–66) (*SI Appendix*, Supplementary Note S4).

From a fundamental perspective, the pore structure in PNG is quite distinct from pores incorporated in SLG via the lattice-etching strategies. In the latter case, pores are generally surrounded by the same grain. On the contrary, pores in PNG are surrounded by three or more misaligned grains. As a result, the statistical probability of pore isomers, defined by pores made by the same number of missing carbon atoms but hosting a different structure, is altered. This opens another dimension to the isomer cataloging problem (67). Finally, the method reported here can be adopted for bottom-up synthesis of nanoporous films from other promising 2D materials such as *h*-BN.

Materials and Methods

Materials and methods for PNG synthesis from different precursors, fabrication and testing of PNG membranes, TEM and STM sample preparation and imaging, SEM imaging, TGA, and NMR analysis can be found in *SI Appendix*.

Data Availability. All study data are included in the article and/or supporting information.

ACKNOWLEDGMENTS. We acknowledge the host institution École Polytechnique Fédérale de Lausanne (EPFL) for generous support. We gratefully acknowledge Shell for financial support. Parts of the project were funded by the Swiss National Science Foundation, Assistant Professor Energy Grant (PYAPP2_173645), and European Research Council Starting Grant (805437-UltimateMembranes). K.-J.H. acknowledges the Taiwan-EPFL PhD Scholarship program funded by the Ministry of Education, Taiwan. C.V.G. is grateful to Research Foundation Flanders (FWO) for a junior postdoctoral fellowship (12ZQ420N). We thank Aurelien Bornet for his assistance in the NMR analysis.

1. K. Varoon *et al.*, Dispersible exfoliated zeolite nanosheets and their application as a selective membrane. *Science* **334**, 72–75 (2011).
2. M. Dakhchoune *et al.*, Gas-sieving zeolitic membranes fabricated by condensation of precursor nanosheets. *Nat. Mater.* **20**, 362–369 (2020).
3. Y. Peng *et al.*, Membranes. Metal-organic framework nanosheets as building blocks for molecular sieving membranes. *Science* **346**, 1356–1359 (2014).
4. T. Rodenas *et al.*, Metal-organic framework nanosheets in polymer composite materials for gas separation. *Nat. Mater.* **14**, 48–55 (2015).
5. A. P. Côté *et al.*, Porous, crystalline, covalent organic frameworks. *Science* **310**, 1166–1170 (2005).
6. L. F. Villalobos *et al.*, Large-scale synthesis of crystalline g-C₃N₄ nanosheets and high-temperature H₂ sieving from assembled films. *Sci. Adv.* **6**, eaay9851 (2020).
7. Y. M. Tu *et al.*, Rapid fabrication of precise high-throughput filters from membrane protein nanosheets. *Nat. Mater.* **19**, 347–354 (2020).
8. X. Li *et al.*, Large-area synthesis of high-quality and uniform graphene films on copper foils. *Science* **324**, 1312–1314 (2009).
9. J. S. Lee *et al.*, Wafer-scale single-crystal hexagonal boron nitride film via self-collimated grain formation. *Science* **362**, 817–821 (2018).
10. L. Lin, H. Peng, Z. Liu, Synthesis challenges for graphene industry. *Nat. Mater.* **18**, 520–524 (2019).
11. P. Z. Sun *et al.*, Limits on gas impermeability of graphene. *Nature* **579**, 229–232 (2020).
12. S. Garaj *et al.*, Graphene as a subnanometre trans-electrode membrane. *Nature* **467**, 190–193 (2010).
13. K. Celebi *et al.*, Ultimate permeation across atomically thin porous graphene. *Science* **344**, 289–292 (2014).
14. Y. Yamada *et al.*, Subnanometer vacancy defects introduced on graphene by oxygen gas. *J. Am. Chem. Soc.* **136**, 2232–2235 (2014).
15. S. P. Surwade *et al.*, Water desalination using nanoporous single-layer graphene. *Nat. Nanotechnol.* **10**, 459–464 (2015).
16. Y. Yang *et al.*, Large-area graphene-nanomesh/carbon-nanotube hybrid membranes for ionic and molecular nanofiltration. *Science* **364**, 1057–1062 (2019).
17. K. V. Agrawal *et al.*, Fabrication, pressure testing, and nanopore formation of single-layer graphene membranes. *J. Phys. Chem. C* **121**, 14312–14321 (2017).
18. S. Huang *et al.*, Single-layer graphene membranes by crack-free transfer for gas mixture separation. *Nat. Commun.* **9**, 2632 (2018).
19. J. Zhao *et al.*, Etching gas-sieving nanopores in single-layer graphene with an angstrom precision for high-performance gas mixture separation. *Sci. Adv.* **5**, eaav1851 (2019).
20. S. P. Koenig, L. Wang, J. Pellegrino, J. S. Bunch, Selective molecular sieving through porous graphene. *Nat. Nanotechnol.* **7**, 728–732 (2012).
21. C. Moreno *et al.*, Bottom-up synthesis of multifunctional nanoporous graphene. *Science* **360**, 199–203 (2018).
22. K. Choi, A. Droudian, R. M. Wyss, K. P. Schlichting, H. G. Park, Multifunctional wafer-scale graphene membranes for fast ultrafiltration and high permeation gas separation. *Sci. Adv.* **4**, eaau0476 (2018).
23. P. R. Kidambi *et al.*, Facile fabrication of large-area atomically thin membranes by direct synthesis of graphene with nanoscale porosity. *Adv. Mater.* **30**, e1804977 (2018).
24. M. H. Khan *et al.*, Hydrogen sieving from intrinsic defects of benzene-derived single-layer graphene. *Carbon* **153**, 458–466 (2019).
25. M. Rezaei, S. Li, S. Huang, K. V. Agrawal, Hydrogen-sieving single-layer graphene membranes obtained by crystallographic and morphological optimization of catalytic copper foil. *J. Membr. Sci.* **612**, 118406 (2020).
26. S. C. O'Hern *et al.*, Selective ionic transport through tunable subnanometer pores in single-layer graphene membranes. *Nano Lett.* **14**, 1234–1241 (2014).
27. J. Cervinka, C. F. J. Flipse, Structural and electronic properties of grain boundaries in graphite: Planes of periodically distributed point defects. *Phys. Rev. B Condens. Matter Mater. Phys.* **79**, 1–5 (2009).
28. X. Li *et al.*, Graphene films with large domain size by a two-step chemical vapor deposition process. *Nano Lett.* **10**, 4328–4334 (2010).
29. Q. Yu *et al.*, Control and characterization of individual grains and grain boundaries in graphene grown by chemical vapour deposition. *Nat. Mater.* **10**, 443–449 (2011).
30. K. Kim *et al.*, Grain boundary mapping in polycrystalline graphene. *ACS Nano* **5**, 2142–2146 (2011).
31. P. Y. Huang *et al.*, Grains and grain boundaries in single-layer graphene atomic patchwork quilts. *Nature* **469**, 389–392 (2011).
32. F. Banhart, J. Kotakoski, A. V. Krasheninnikov, Structural defects in graphene. *ACS Nano* **5**, 26–41 (2011).
33. A. W. Tsen *et al.*, Tailoring electrical transport across grain boundaries in polycrystalline graphene. *Science* **336**, 1143–1146 (2012).
34. T. Ma *et al.*, Tailoring the thermal and electrical transport properties of graphene films by grain size engineering. *Nat. Commun.* **8**, 14486 (2017).
35. E. Griffin *et al.*, Proton and Li-ion permeation through graphene with eight-atom-ring defects. *ACS Nano* **14**, 7280–7286 (2020).
36. A. Turchanin *et al.*, Conversion of self-assembled monolayers into nanocrystalline graphene: Structure and electric transport. *ACS Nano* **5**, 3896–3904 (2011).
37. R. Yekani *et al.*, Formation of nanocrystalline graphene on germanium. *Nanoscale* **10**, 12156–12162 (2018).
38. J. Kwak *et al.*, Near room-temperature synthesis of transfer-free graphene films. *Nat. Commun.* **3**, 645 (2012).
39. T. Zhao *et al.*, Ultrafast growth of nanocrystalline graphene films by quenching and grain-size-dependent strength and bandgap opening. *Nat. Commun.* **10**, 4854 (2019).
40. Z. Yuan *et al.*, Mechanism and prediction of gas permeation through sub-nanometer graphene pores: Comparison of theory and simulation. *ACS Nano* **11**, 7974–7987 (2017).
41. G. He *et al.*, Synergistic CO₂-sieving from polymer with intrinsic microporosity masking nanoporous single-layer graphene. *Adv. Funct. Mater.* **30**, 2003979 (2020).
42. L. Wang *et al.*, Fundamental transport mechanisms, fabrication and potential applications of nanoporous atomically thin membranes. *Nat. Nanotechnol.* **12**, 509–522 (2017).

43. A. T. Rodriguez, X. Li, J. Wang, W. A. Steen, H. Fan, Facile synthesis of nanostructured carbon through self-assembly between block copolymers and carbohydrates. *Adv. Funct. Mater.* **17**, 2710–2716 (2007).
44. G. He *et al.*, Synergistic CO₂-sieving from polymer with intrinsic microporosity masking nanoporous single-layer graphene. *Adv. Funct. Mater.* **30**, 2003979 (2020).
45. J. Schrier, Fluorinated and nanoporous graphene materials as sorbents for gas separations. *ACS Appl. Mater. Interfaces* **3**, 4451–4458 (2011).
46. T. Wada, H. Wada, J. F. Elliott, J. Chipman, Thermodynamics of the Fcc Fe-Ni-C and Ni-C alloys. *Metall. Mater. Trans., B, Process Metall. Mater. Proc. Sci.* **2**, 2199–2208 (1971).
47. R. T. Vang *et al.*, Controlling the catalytic bond-breaking selectivity of Ni surfaces by step blocking. *Nat. Mater.* **4**, 160–162 (2005).
48. H.-j. Kwon, J. M. Ha, S. H. Yoo, G. Ali, S. O. Cho, Synthesis of flake-like graphene from nickel-coated polyacrylonitrile polymer. *Nanoscale Res. Lett.* **9**, 618 (2014).
49. Z. Peng, Z. Yan, Z. Sun, J. M. Tour, Direct growth of bilayer graphene on SiO₂ substrates by carbon diffusion through nickel. *ACS Nano* **5**, 8241–8247 (2011).
50. S. J. Byun *et al.*, Graphenes converted from polymers. *J. Phys. Chem. Lett.* **2**, 493–497 (2011).
51. L. F. Villalobos *et al.*, Polybenzimidazole copolymer derived lacey carbon film for graphene transfer and contamination removal strategies for imaging graphene nanopores. *Carbon* **173**, 980–988 (2020).
52. J. J. Lander, H. E. Kern, A. L. Beach, Solubility and diffusion coefficient of carbon in nickel: Reaction rates of nickel-carbon alloys with barium oxide. *J. Appl. Phys.* **23**, 1305–1309 (1952).
53. L. L. Patera *et al.*, In situ observations of the atomistic mechanisms of Ni catalyzed low temperature graphene growth. *ACS Nano* **7**, 7901–7912 (2013).
54. L. Baraton *et al.*, On the mechanisms of precipitation of graphene on nickel thin films. *EPL* **96**, 46003 (2011).
55. S. T. Ceyer, The unique chemistry of hydrogen beneath the surface: Catalytic hydrogenation of hydrocarbons. *Acc. Chem. Res.* **34**, 737–744 (2001).
56. G. He *et al.*, High-permeance polymer-functionalized single-layer graphene membranes that surpass the postcombustion carbon capture target. *Energy Environ. Sci.* **12**, 3305–3312 (2019).
57. E. Favre, Carbon dioxide recovery from post-combustion processes: Can gas permeation membranes compete with absorption? *J. Membr. Sci.* **294**, 50–59 (2007).
58. T. C. Merkel, H. Lin, X. Wei, R. Baker, Power plant post-combustion carbon dioxide capture: An opportunity for membranes. *J. Membr. Sci.* **359**, 126–139 (2010).
59. S. Roussanly, R. Anantharaman, K. Lindqvist, H. Zhai, E. Rubin, Membrane properties required for post-combustion CO₂ capture at coal-fired power plants. *J. Membr. Sci.* **511**, 250–264 (2016).
60. A. Turchanin, A. Götzhäuser, Carbon nanomembranes. *Adv. Mater.* **28**, 6075–6103 (2016).
61. Y. Yang *et al.*, Rapid water permeation through carbon nanomembranes with sub-nanometer channels. *ACS Nano* **12**, 4695–4701 (2018).
62. P. Dementyev, D. Naberezhnyi, M. Westphal, M. Buck, A. Götzhäuser, Carbon nanomembranes from aromatic carboxylate precursors. *ChemPhysChem* **21**, 1006–1011 (2020).
63. Y. Yang *et al.*, Ultrahigh ionic exclusion through carbon nanomembranes. *Adv. Mater.* **32**, e1907850 (2020).
64. A. Ismail, L. David, A review on the latest development of carbon membranes for gas separation. *J. Membr. Sci.* **193**, 1–18 (2001).
65. K. M. Steel, W. J. Koros, Investigation of porosity of carbon materials and related effects on gas separation properties. *Carbon* **41**, 253–266 (2003).
66. P. Bernardo, E. Drioli, G. Golemme, Membrane gas separation: A review/state of the art. *Ind. Eng. Chem. Res.* **48**, 4638–4663 (2009).
67. A. Govind Rajan *et al.*, Addressing the isomer cataloguing problem for nanopores in two-dimensional materials. *Nat. Mater.* **18**, 129–135 (2019).