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Perspective

Constructing Two-Dimensional, Ordered Networks of Carbon–Carbon Bonds with Precision

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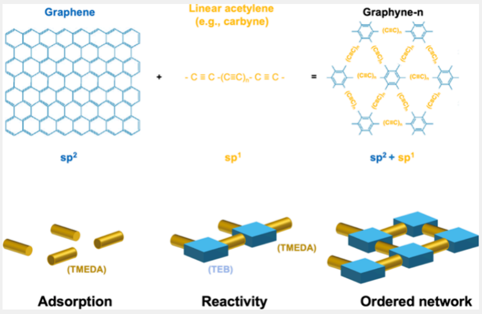

ABSTRACT: Organic semiconducting nanomembranes (OSNMs), particularly carbon-based ones, are at the forefront of next-generation two-dimensional (2D) semiconductor research. These materials offer remarkable promise due to their diverse chemical properties and unique functionalities, paving the way for innovative applications across advanced semiconductor material sectors. Graphene stands out for its extraordinary mechanical strength, thermal conductivity, and superior charge transport capabilities, inspiring extensive research into other 2D carbon allotropes like graphyne and graphdiyne. With its high electron mobility and tunable bandgap, graphdiyne is particularly attractive for power-efficient electronic devices. However, synthesizing graphdiyne presents significant challenges, primarily due to the difficulty in achieving precise and deterministic control over the coupling of its monomers. This precision is crucial for determining the material's porosity, periodicity, and overall functionality. Innovative approaches have been developed to address these challenges, such as the strategic assembly of molecular building blocks at heterogeneous interfaces. Furthermore, data-driven techniques, such as machine learning and artificial intelligence (AI), are proving invaluable in this field, assisting in screening precursors, optimizing structural configurations, and predicting novel properties of these materials. These advancements are essential for producing durable monolayer sheets that can be integrated into existing electronic components. Despite these advancements, the integration of graphdiyne into semiconductor technology remains complex. Achieving long-range coherence in bonding configurations and enhancing charge transport characteristics are significant hurdles. Continued research into robust and controllable synthesis techniques is essential for unlocking the full potential of graphdiyne and other 2D materials, leading to more efficient, faster, and mechanically robust electronics.

KEYWORDS: *organic semiconductors, two-dimensional, graphene, graphyne, graphdiyne*

■ INTRODUCTION

The exploration of organic semiconducting nanomembranes (OSNMs), especially those based on carbon, has been at the forefront of next-generation two-dimensional (2D) semiconductor research.[1,2] These materials offer remarkable promise by virtue of their diverse chemical properties and unique functionalities, paving the way for innovative applications across advanced semiconducting material sectors. Graphene is particularly noteworthy among the various carbon-based OSNMs due to its extraordinary mechanical strength, exceptional thermal conductivity, and superior charge transport capabilities unmatched by bulk graphite.[3] One notable advancement in graphene research is the creation of graphene nanomesh (GNM, Figure 1), achieved by perforating the basal plane of graphene through block copolymer lithography. GNM can be viewed as a highly interconnected network of graphene nanoribbons (GNRs). This structure can be precisely engineered with variable periodicities and neck widths as narrow as 5 nm by fine-tuning the lithographic process. GNM-based field-effect transistors demonstrate impressive performance, supporting currents nearly 100 times greater than those in individual graphene nanoribbon devices while maintaining an on–off ratio that is comparable to these devices and tunable by adjusting the neck width.[4] These attributes have sparked extensive research into graphene and inspired investigations into other 2D carbon allotropes, such as graphyne and graphdiyne, which consist of sp- and sp^2-hybridized carbons, respectively. These materials exhibit electronic properties that could potentially surpass those of graphene and GNM, making them highly suitable for efficient, high-speed transistor technologies.

Graphdiyne, for instance, stands out due to its theoretically high electron mobility, up to 10^5 cm^2/V-s, and a bandgap of

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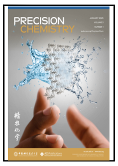

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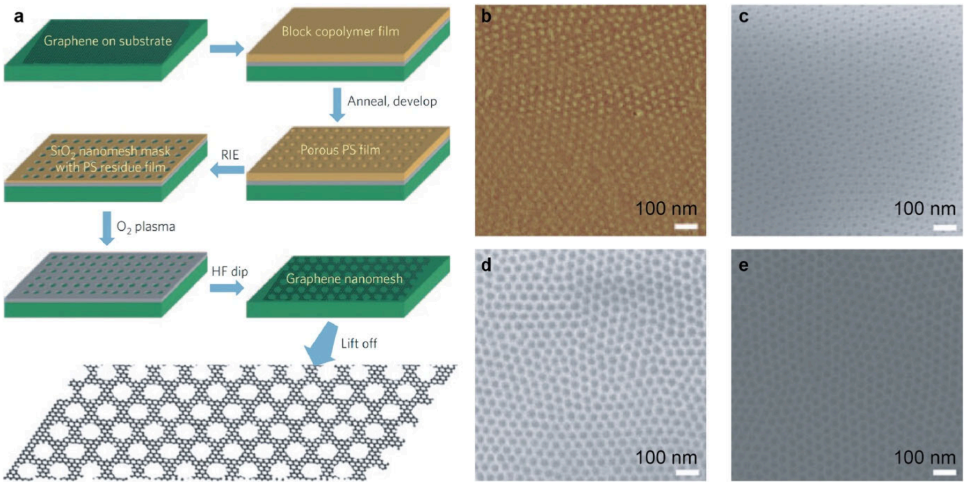

Figure 1. (a) Schematic representation of fabricating perforated graphene, nanomesh. The P(S-*b*-MMA) block copolymer is used for the nanopatterning process, which defines the neck width and periodicity of pores. (b) AFM phase contrast image of the annealed block copolymer film on graphene shows hexagonal-packed PMMA domains in the PS matrix. (c) SEM image of a porous PS film obtained by selectively removing the PMMA domains. (d) SEM image of the SiO_x nanomesh mask after reactive ion etching with the PS mask. (e) SEM image of a GNM structure after removing the top SiO_x mesh mask. Scale bars, 100 nm. Reproduced from ref 12. Copyright 2010 Springer Nature.

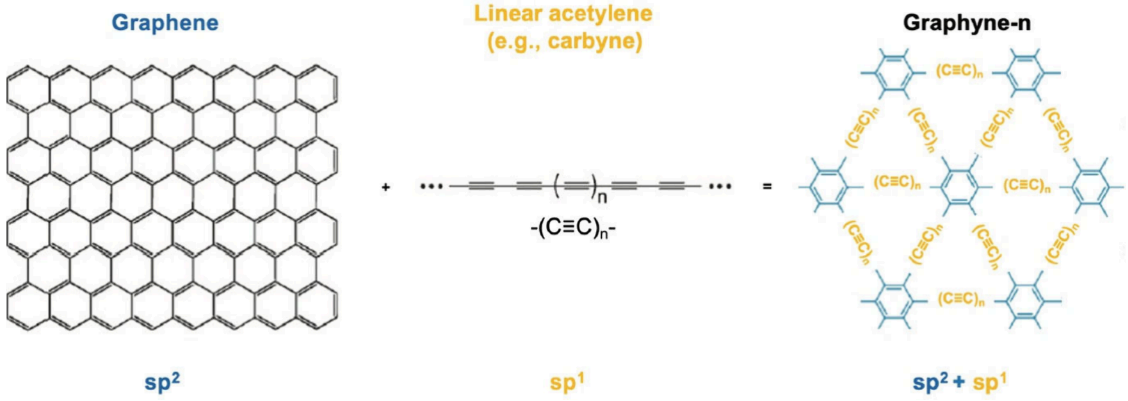

Figure 2. From a structural point of view, graphdiyne comprises the narrowest neck width (alkyne linkers) connected with benzene cores.

approximately 0.5 eV.[5] As shown in Figure 2, with the narrowest neck width (alkyne linkers) connected with benzene cores, graphdiyne shall gain enough bandgap for sufficient gate response and on−off ratio, and a denser mesh structure with molecularly well-defined periodicity and porosity can enable higher current delivery.[6−13] These properties make it particularly attractive for power-efficient electronic devices, offering a substantial contrast to the semimetallic nature of graphene nanomembranes, which limits their utility in certain semiconductor applications. Despite the promising characteristics of carbon-based OSNMs, the synthesis of 2D-ordered networks of carbon−carbon bonds extending beyond graphene remains a frontier challenge in contemporary chemistry.[14] Taking the solution-based synthesis of graphdiyne as an example, achieving the necessary precision in high-molecular-mass systems is fraught with difficulties, primarily due to their solubility and tendency to aggregate, complicating their synthesis via conventional bulk, solution-phase methods.[15] This often restricts the lateral dimensions of organic OSNMs to sizes barely exceeding the nanometer-scale scale, limiting their practical application. In parallel, rampant and random growth of the skeleton in the out-of-plane direction during the coupling of the monomer (hexaethynyl benzene, HEB) is often the result of free rotation between the alkyne−aryl single bonds. From an organic chemistry perspective, the concept of free rotation around alkyne−aryl single bonds is closely related to the conformational dynamics of the molecule.[15] Rotation around a single bond is relatively unhindered, allowing the molecule to adopt different conformations. The result is a disordered 3D structure with poorly defined micropores rather than the desired 2D structure, making the large-scale fabrication of the membrane unfeasible. Note that the use of HEB requires great care because it is highly reactive in ambient conditions.

■ INNOVATIVE APPROACHES TO SYNTHESIS

While solution-based synthetic schemes fail to circumvent the need for precision coupling at scale, the substrate-based technique takes advantage of the specially chosen platform to encourage the growth of graphdiyne with long-range, ordered networks. Innovative approaches have been developed to navigate these synthetic challenges, such as the strategic assembly of molecular building blocks at interfaces. Techniques like self-assembled monolayers (SAMs) and Langmuir−Blodgett films provide planar precursor films, which subsequently undergo intramolecular reactions between the molecular constituents, thus forming highly conjugated, robust

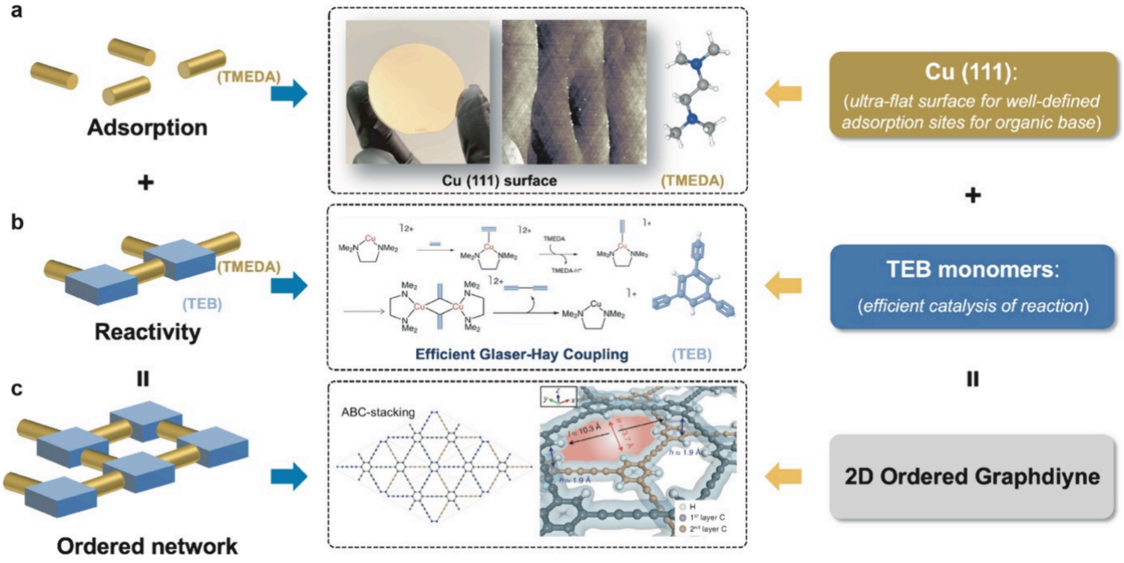

Figure 3. (a) Templating an organic base, tetramethyl ethylenediamine (TMEDA), on a thermally restructured, [111]-oriented copper (Cu) substrate provides spatially well-defined catalytic sites. (b) The spatially well-defined catalytic sites have proven to be the key factor in facilitating the Glaser−Hay coupling reaction while suppressing the free rotation between the alkyne−aryl single bonds of 1,3,5-triethynylbenzene (TEB) monomers. (c) The result is the ordered 2D mesh-like architecture formed throughout the entire growth substrate. Reproduced from ref 20. Copyright 2022 Springer Nature.

carbon-based nanomembranes.[16] These durable, monolayer sheets can be released and transferred onto substrates like silicon (Si) wafers and sapphires to seamlessly integrate with existing electronic components. Moreover, modifications such as low-energy electron bombardment have been utilized to create cross-linked matrices that transform functional groups.[17] This process, for nitroaryl thiols on gold, forms a dense, cross-linked matrix within the aryl segments and reduces the chain-end nitro substituents to amino groups. Upon detachment from the gold surface, the resulting Janus nanomembranes feature thiol groups on one face and amino groups on the other. This dual functionality holds significant potential for devices that require distinct electronic interfaces on the top and bottom surfaces.[18]

Tremendous progress with SAM-based alternatives began to shed light on achieving long-range coherence in the bonding configurations. The limiting step for synthesizing graphdiyne was simply achieving the desired configuration of carbon−carbon bonds by monomer coupling reactions at scale.[19] This would have greater implications for real-world applications but remain a formidable hurdle due to the uncontrollable growth. The focus of a great deal of research has thus shifted toward limiting the free rotation of the alkyne−aryl single bonds. One should consider three important design factors beyond scalability when considering the proficiency of any synthetic route to graphdiyne. First and foremost, a process must produce high regularity and well-defined porosity in the 2D crystal lattice to ensure mobility and selectivity. Second, the method must provide fine control over crystallite thickness and stacking so as to deliver uniform performance. Finally, and for ease of integration, any process should be compatible with existing technological platforms.

Recently, Jie Shen, Yichen Cai, Lain-Jong Li, Yu Han, and co-workers, in collaboration with our group, later showed that templating an organic base, tetramethyl ethylenediamine (TMEDA), on an ultraflat, single-crystalline [111]-oriented copper (Cu) substrate provides spatially well-defined catalytic sites.[20] Templating TMEDA on the atomic steps of Cu(111) has proven to be the key factor in suppressing the free rotation between the alkyne−aryl single bonds of 1,3,5-triethynylbenzene (TEB) monomers, thus promoting the formation of the ordered 2D mesh-like architecture throughout the entire growth substrate (Figure 3). The extended control in this phase minimizes variations in the material's porosity and periodicity, enhancing its electrical conductivity, mechanical strength, and chemical reactivity. One of the most exciting aspects of the TMEDA templating method is its reproducibility and scalability. Through the Glaser−Hay coupling reaction,[21] long-range coherence in 2D graphdiyne membranes is easily achieved and is only limited by the size of the TMEDA-templated Cu(111) substrate, making it possible to scale up production while maintaining high crystallinity. This scalability extends the potential applications of graphdiyne far beyond traditional semiconductor uses.

Indeed, the resulting 2D graphdiyne membranes can be facilely transferred onto porous support and exhibit excellent water transport and molecular sieving properties, which are superior to state-of-the-art membranes reported for water/monovalent-ion separation driven by osmotic pressure. Molecular simulations further reveal that seemingly vertical channels are connected by interlayer spaces to form a 3D network, thus allowing water molecules to pass rapidly through the membrane. Future advances in this area could explore new chemical pathways for monomer coupling, employ templating agents to guide monomer assembly, or refine reaction conditions to produce even more uniform and scalable products. These developments would significantly impact the scalability of graphdiyne production and pave the way for its adoption in various emerging fields, including catalysis, molecular sieving, lithium (Li) sequestration, sensor technologies, and its established role in semiconductors.

■ DATA-DRIVEN PRECISION FOR FUTURE WORK

Exfoliated 2D materials often possess unique properties surpassing their 3D counterparts, opening up a wide range of

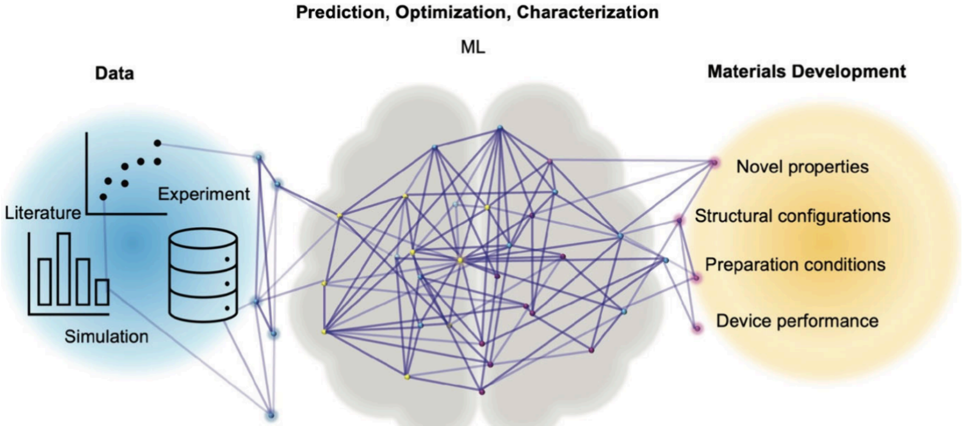

Figure 4. Schematic illustration of how ML accelerates the discovery and development of 2D OSNMs. ML models predict material properties, optimize synthesis conditions, and characterize structural configurations by processing large data sets efficiently. These techniques streamline the identification of promising candidates with desirable properties and enhance the precision of structural control, enabling the scalable production of high-quality 2D materials.

potential applications. However, using traditional theoretical and computational approaches to predict their properties can be highly resource-demanding and time-consuming. Despite their strengths, traditional methods like density functional theory (DFT) calculations and classical molecular dynamics (MD) simulations are often constrained by high computational demands and limited capacity to process large data sets efficiently. In the past few years, we have witnessed the rising trend in data-driven methods for expediting 2D material research, transforming how materials are discovered, designed, and developed. To this end, machine learning (ML) provides an alternative for investigating 2D organic OSNMs and speeding up their discovery.

ML models are extensively utilized to predict properties, optimize preparation conditions, and analyze structural configurations of 2D OSNMs, as illustrated in Figure 4. ML can identify promising material candidates with desirable properties such as high thermal conductivity, electron mobility, and exceptional mechanical strength by using algorithms that detect patterns and correlations in data sets. This approach not only streamlines the discovery process but also deepens our understanding of the fundamental physical and chemical mechanisms involved. There are two main approaches to predicting properties: one involves ML trained on databases comprising computational results and experimental data, and the other uses machine-learning interatomic potentials (MLIPs) trained over short ab initio molecular dynamics trajectories, offering an acceleration in evaluating forces and energies compared to DFT-based solutions. ML-based methods have predicted properties of carbon-based nanomembranes, such as thermal conductivity,[22,23] phononic properties,[24] and mechanical properties.[25−27]

ML can optimize preparation conditions by analyzing the impact of various factors on the resulting material structures and properties. For instance, we can predict the conditions for achieving precise control over monomer coupling in graphdiyne synthesis by adjusting temperature, pressure, and precursor concentration. This predictive capability is crucial for addressing the challenges of achieving long-range coherence and enhancing charge transport characteristics in 2D graphdiyne. In addition to optimizing preparation conditions, ML is also important for understanding and characterizing structural configurations. ML-based methods process data from advanced spectroscopy and microscopy tools, such as optical microscope (OM) and scanning tunneling microscopy (STM), to characterize structural configurations and find correlations that encode the underlying physics. ML has successfully identified the twist angles of bilayer graphene from Raman spectra corresponding to their vibrational properties,[28] and from STM corresponding to their local density of states.[29] It has also characterized graphene dispersions, such as flakes and sheet species, from polarized OM.[30] ML is proving to be a powerful tool for characterizing structural configurations and solving complicated inverse problems. Furthermore, AI has been effective in designing 2D layered materials with tailored properties for practical applications. Recent examples include but are not limited to the wafer-scale fabrication processes of electronic grade 2D OSNMs guided by ML and grid searching, ultimately optimizing the device performance.[31]

Using ML for screening precursors, optimizing structural configurations, and predicting the properties of carbon-based nanomembranes is promising. ML accelerates research by providing predictive insights, reducing the trial-and-error aspect of material synthesis. Additionally, the synergy between ML and traditional techniques enhances understanding of the mechanisms governing material behavior. This approach enables the development of robust and controllable synthesis methods, paving the way for scalable production of high-quality 2D graphdiyne with enhanced properties and expanded functionalities.

■ POSSIBLE APPLICATIONS

The potential applications of highly crystalline graphdiyne in semiconductor technologies are particularly promising due to its distinctive combination of properties. For instance, the TMEDA/Cu(111)-substrate-based methods for scalably producing 2D graphdiyne in a molecular precision at a low processing temperature (<200 °C), coupled with the thermal resistance up to 600 °C, presents a significant advantage in semiconductor manufacturing by reducing thermal budgets and associated costs. This characteristic is particularly valuable in applications where substrate sensitivity or integration with other low-temperature processes is crucial. Moreover, graphdiyne's tunable bandgaps offer the flexibility to engineer materials for specific electronic functions, ranging from visible-light photoactivity to charge transport layers in various electronic devices. This tunability allows for the customization of electronic and optical properties, making graphdiyne suitable for multiple applications, including photovoltaics, memories, and transistors. The high mobility of charge carriers in graphdiyne, which significantly exceeds that of many conventional semiconductor materials, enables devices to operate at higher speeds or with greater efficiency. This property is particularly critical in developing high-speed transistors and circuits, where rapid charge transport is essential for performance improvements. In parallel, the high mobility of charge carriers in graphdiyne contributes to efficient charge separation in heterojunction devices. For example, in graphdiyne/molybdenum disulfide (graphdiyne/MoS_2) heterojunctions, the electron repulsion of the alkyne-rich skeleton in graphdiyne facilitates effective electron−hole pair separation and transfer.

Additionally, graphdiyne's anisotropic thermal resistance is pivotal for applications requiring efficient heat dissipation, such as power electronics and high-performance computing devices. Efficient thermal management enhances device reliability and longevity by mitigating thermal degradation. Lastly, the mechanical properties of graphdiyne, including its robustness and flexibility, open up new possibilities for its use in flexible electronics and wearable devices. The material's durability under mechanical stress makes it an ideal candidate for applications where electronic components must maintain functionality under bending and stretching. Together, these attributes make highly crystalline graphdiyne a versatile and promising material for next-generation semiconducting channels in various electronic and optoelectronic devices. Its integration into current semiconductor technology could lead to more energy-efficient, faster, and mechanically robust electronics, significantly impacting the industry's landscape.

The periodic arrangement of the alkyne linkers connected to the benzene cores of graphdiyne closely resembles patterned graphene, making it possible to establish conditions for minimizing epitaxial lateral overgrowth of 2D and 3D semiconducting crystals. In this light, the atomic registry between the host substrate and the epilayer can be better matched through periodic porosity, thus facilitating the partially screened electrostatic potential of the substrate to interact indirectly with the adatoms during epilayer growth. Meanwhile, because of the formation of indirect chemical bonds, this remote interaction can lead to well-aligned nucleation of an epilayer that follows the orientation of the substrate.[22,23] Moreover, the interconnected networks of benzene cores provide a dangling-bond-free van der Waals (vdW) surface, enabling remote-epitaxial films to be detached at the interface through simple mechanical exfoliation with atomic precision.[24]

Moreover, theoretical explanations of the correlations between different descriptors and target properties are necessary to better understand these properties and improve ML model prediction efficiency and accuracy. Interpretable ML models, rooted in physical or chemical knowledge, enhance the reliability of predictions and can reveal unexpected correlations, offering new scientific insights into physical chemistry. Data-driven approaches can facilitate the discovery of graphdiyne derivatives with enhanced performance characteristics for use in flexible electronics, sensors, and energy storage devices.

■ CONCLUSION AND OUTLOOK

The engineering challenges and associated costs of developing 2D graphdiyne technologies are pivotal in ongoing research and manufacturing. Optimizing the production process of 2D graphdiyne may require a hybrid strategy that integrates various techniques, enabling the direct assembly and deployment of these materials in specific applications. The approach will need to be highly flexible and adaptable, tailored to the requirements of each intended use. Central to future advancements in 2D graphdiyne technology are the synthesis techniques employed. There is an urgent need for innovative methods that can expand the range of inorganic SNM materials beyond what is achievable with current techniques such as exfoliation, etching, epitaxial growth, and bonding. Like other classes of nanomaterials, the morphological and chemical properties of 2D graphdiyne surfaces are critical. In some cases, existing technologies for surface passivation may be adapted to create multilayer 2D graphdiyne structures, such as SiO_2/Si/SiO_2 configurations, which protect critical interfaces from environmental degradation.

In other instances, 2D graphdiyne surfaces may be deliberately exposed and functionalized for specific applications, such as sensors.[25] This functionalization is crucial for expanding the utility of 2D graphdiyne beyond traditional electronic and optoelectronic devices into a broader range of applications, including membranes in catalysis,[26] nanoelectromechanical systems (NEMS), photonic and plasmonic structures,[27,28] thermal and mechanical energy harvesting components, and micro/nanoscale sensors. Graphdiyne possesses a direct bandgap, a crucial characteristic of semiconductor applications. Tuning this bandgap offers significant advantages in device design and performance optimization. One notable approach is H-substitution, which can significantly widen the bandgap. For instance, H-substituted graphdiyne (H-GDY) exhibits an increased bandgap energy of approximately 2.5 eV. The bandgap of graphdiyne can also be tuned by modifying its structure. Different edge structures and widths in graphdiyne nanoribbons can lead to variations in the bandgap. With its wider bandgap, H-substituted graphdiyne (H-GDY) has shown enhanced photocatalytic hydrogen production when combined with TiO_2. The synthesis of functionally useful organic OSNMs beyond 2D graphdiyne poses significant challenges. Still, it offers tremendous potential, particularly through interfacial assembly and cross-linking techniques on monocrystalline substrates that are only limited by the dimensions of the annealing oven.[29−33] These approaches could lead to the fabrication of new materials with tailored properties for specific applications.

Understanding the physics of transport in shaped, chemically functionalized, and/or strain-engineered 2D graphdiyne could reveal additional properties, potentially exceeding those achievable with current materials and methods. Data-driven approaches will be essential in these advancements.[34−43] ML can dramatically reduce the trial-and-error process in material development by providing predictive insights and optimizing synthesis processes. Integrating ML with traditional techniques will deepen our understanding of material behavior, paving the way for scalable production of high-quality 2D materials.

The continued exploration of advanced 2D graphdiyne technologies could lead to groundbreaking applications across a broad spectrum of fields, including microfluidic devices, molecular sensors, sieves, and scaffolds for cell culture, among others. Each of these applications stands to benefit from the unique properties of 2D graphdiyne, which can be precisely tailored through advanced synthesis and functionalization techniques to meet specific operational demands.

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Notes

The authors declare no competing financial interest.

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■ REFERENCES

(1) Geim, A. K.; Novoselov, K. S. The Rise of Graphene. *Nat. Mater.* **2007**, *6*, 183−191.

(2) Tahara, K.; Yoshimura, T.; Sonoda, M.; Tobe, Y.; Williams, R. V. Theoretical Studies on Graphyne Substructures: Geometry, Aromaticity, and Electronic Properties of the Multiply Fused Dehydrobenzo[12] annulenes. *J. Org. Chem.* **2007**, *72*, 1437−1442.

(3) Diederich, F.; Kivala, M. All-Carbon Scaffolds by Rational Design. *Adv. Mater.* **2010**, *22*, 803−812.

(4) Franklin, A. D.; Chen, Z. Length scaling of carbon nanotube transistors. *Nat. Nanotechnol.* **2010**, *5*, 858−862.

(5) Long, M.; Tang, L.; Wang, D.; Li, Y.; Shuai, Z. Electronic Structure and Carrier Mobility in Graphdiyne Sheet and Nanoribbons: Theoretical Predictions. *ACS Nano* **2011**, *5*, 2593−2600.

(6) Nakada, K.; Fujita, M.; Dresselhaus, G.; Dresselhaus, M. S. Edge State in Graphene Ribbons: Nanometer Size Effect and Edge Shape Dependence. *Phys. Rev. B* **1996**, *54*, 17954.

(7) Son, Y.-W.; Cohen, M. L.; Louie, S. G. Energy Gaps in Graphene Nanoribbons. *Phys. Rev. Lett.* **2006**, *97*, 216803.

(8) Barone, V.; Hod, O.; Scuseria, G. E. Electronic Structure and Stability of Semiconducting Graphene Nanoribbons. *Nano Lett.* **2006**, *6*, 2748−2754.

(9) Aigner, S.; et al. Long-Range Order in Electronic Transport Through Disordered Metal Films. *Science* **2008**, *319*, 1226−1229.

(10) Kosynkin, D. V.; et al. Longitudinal unzipping of carbon nanotubes to form graphene nanoribbons. *Nature* **2009**, *458*, 872−876.

(11) Jiao, L.; Zhang, L.; Wang, X.; Diankov, G.; Dai, H. Narrow graphene nanoribbons from carbon nanotubes. *Nature* **2009**, *458*, 877−880.

(12) Bai, J.; Zhong, X.; Jiang, S.; Huang, Y.; Duan, X. Graphene Nanomesh. *Nat. Nanotechnol.* **2010**, *5*, 190−194.

(13) Lu, W.; Lieber, C. M. Semiconductor nanowires. *J. Phys. D: Appl. Phys.* **2006**, *39*, R387.

(14) Moreno, C.; et al. Bottom-up Synthesis of Multifunctional Nanoporous Graphene. *Science* **2018**, *360*, 199−203.

(15) Yu, H.; Xue, Y.; Li, Y. Graphdiyne and its Assembly Architectures: Synthesis, Functionalization, and Applications. *Adv. Mater.* **2019**, *31*, 1803101.

(16) Schultz, M. J.; et al. Synthesis of Linked Carbon Monolayers: Films, Balloons, Tubes, and Pleated Sheets. *National Academy Sciences* **2008**, *105*, 7353−7358.

(17) Geyer, W.; et al. Electron-induced crosslinking of aromatic self-assembled monolayers: Negative resists for nanolithography. *Appl. Phys. Lett.* **1999**, *75*, 2401−2403.

(18) Zheng, Z.; et al. Janus Nanomembranes: A Generic Platform for Chemistry in Two Dimensions. *Angew. Chem., Int. Ed.* **2010**, *49*, 8493−8497.

(19) Grill, L.; Hecht, S. Covalent on-surface polymerization. *Nat. Chem.* **2020**, *12*, 115−130.

(20) Shen, J.; et al. Fast water transport and molecular sieving through ultrathin ordered conjugated-polymer-framework membranes. *Nat. Mater.* **2022**, *21*, 1183−1190.

(21) Zhou, J.; Li, J.; Liu, Z.; Zhang, J. Exploring Approaches for the Synthesis of Few-Layered Graphdiyne. *Adv. Mater.* **2019**, *31*, 1803758.

(22) Kim, Y.; et al. Remote epitaxy through graphene enables two-dimensional material-based layer transfer. *Nature* **2017**, *544*, 340−343.

(23) Kong, W.; et al. Polarity governs atomic interaction through two-dimensional materials. *Nat. Mater.* **2018**, *17*, 999−1004.

(24) Chang, C. S.; et al. Remote epitaxial interaction through graphene. *Science Advance* **2023**, *9*, No. eadj5379.

(25) Cai, Y.; et al. Graphdiyne-Based Nanofilms for Compliant On-Skin Sensing. *ACS Nano* **2022**, *16*, 16677−16689.

(26) Yu, M.-J.; et al. Plasmon-Enhanced Solar-Driven Hydrogen Evolution Using Titanium Nitride Metasurface Broadband Absorbers. *ACS Photonics* **2021**, *8*, 3125−3132.

(27) Syong, W.-R.; et al. Enhanced Photogating Gain in Scalable MoS $_2$ Plasmonic Photodetectors via Resonant Plasmonic Metasurfaces. *ACS Nano* **2024**, *18*, 5446−5456.

(28) Ho, Y.-L.; et al. Finite-Area Membrane Metasurfaces for Enhancing Light-Matter Coupling in Monolayer Transition Metal Dichalcogenides. *ACS Nano* **2024**, *18*, 24173−24181.

(29) Fu, J.-H.; et al. Oriented lateral growth of two-dimensional materials on c-plane sapphire. *Nat. Nanotechnol.* **2023**, *18*, 1289−1294.

(30) Lu, A.; et al. Unraveling the Correlation between Raman and Photoluminescence in Monolayer MoS$_2$ through Machine-Learning Models. *Adv. Mater.* **2022**, *34*, 2202911.

(31) Wan, Y.; et al. Wafer-scale single-orientation 2D layers by atomic edge-guided epitaxial growth. *Chemistry Society Reviews* **2022**, *51*, 803−811.

(32) Fu, J.-H.; et al. Pieces of 2D materials: The next step to crystallize the polycrystalline domains. *Matter* **2023**, *6*, 2136−2152.

(33) Park, S.; et al. The Schottky−Mott Rule Expanded for Two-Dimensional Semiconductors: Influence of Substrate Dielectric Screening. *ACS Nano* **2021**, *15*, 14794−14803.

(34) Mortazavi, B.; Podryabinkin, E. V.; Novikov, I. S.; Roche, S.; Rabczuk, T.; Zhuang, X. Y.; Shapeev, A. V. Efficient machine-learning based interatomic potentialsfor exploring thermal conductivity in two-dimensional materials. *Journal of Physics-Materials* **2020**, *3*, 02LT02.

(35) Mortazavi, B.; Novikov, I. S.; Shapeev, A. V. A machine-learning-based investigation on the mechanical/failure response and thermal conductivity of semiconducting BCN monolayers. *Carbon* **2022**, *188*, 431−441.

(36) Mortazavi, B.; Novikov, I. S.; Podryabinkin, E. V.; Roche, S.; Rabczuk, T.; Shapeev, A. V.; Zhuang, X. Y. Exploring phononic properties of two-dimensional materials using machine learning interatomic potentials. *Applied Materials Today* **2020**, *20*, 100685.

(37) Singh, A.; Li, Y. M. Reliable machine learning potentials based on artificial neural network for graphene. *Comput. Mater. Sci.* **2023**, *227*, 112272.

(38) Lew, A. J.; Yu, C. H.; Hsu, Y. C.; Buehler, M. J. Deep learning model to predict fracture mechanisms of graphene. *Npj 2d Materials and Applications* **2021**, *5*, 48.

(39) Mortazavi, B.; Shahrokhi, M.; Shojaei, F.; Rabczuk, T.; Zhuang, X.; Shapeev, A. V. A first-principles and machine-learning investigation on the electronic, photocatalytic, mechanical and heat conduction properties of nanoporous C5N monolayers. *Nanoscale* **2022**, *14*, 4324−4333.

(40) Sheremetyeva, N.; Lamparski, M.; Daniels, C.; Van Troeye, B.; Meunier, V. Machine-learning models for Raman spectra analysis of twisted bilayer graphene. *Carbon* **2020**, *169*, 455−464.

(41) Sobral, J. A.; Obernauer, S.; Turkel, S.; Pasupathy, A. N.; Scheurer, M. S. Machine learning the microscopic form of nematic order in twisted double-bilayer graphene. *Nature Communication* **2023**, *14*, 5012.

(42) Abedin, M. J.; Barua, T.; Shaibani, M.; Majumder, M. A High Throughput and Unbiased Machine Learning Approach for Classification of Graphene Dispersions. *Advanced Science* **2020**, *7*, 2001600.

(43) Chen, X.; Xie, Y.; Sheng, Y.; Tang, H.; Wang, Z.; Wang, Y.; Wang, Y.; Liao, F.; Ma, J.; Guo, X.; Tong, L.; Liu, H.; Liu, H.; Wu, T.; Cao, J.; Bu, S.; Shen, H.; Bai, F.; Huang, D.; Deng, J.; Riaud, A.; Xu, Z.; Wu, C.; Xing, S.; Lu, Y.; Ma, S.; Sun, Z.; Xue, Z.; Di, Z.; Gong, X.; Zhang, D. W.; Zhou, P.; Wan, J.; Bao, W. Wafer-scale functional circuits based on two-dimensional semiconductors with fabrication optimized by machine learning. *Nature Communication* **2021**, *12*, 5953.