



An emerging carbon allotrope: Graphyne—from diverse structures, controllable synthesis, and systematic characterizations to multifunctional applications

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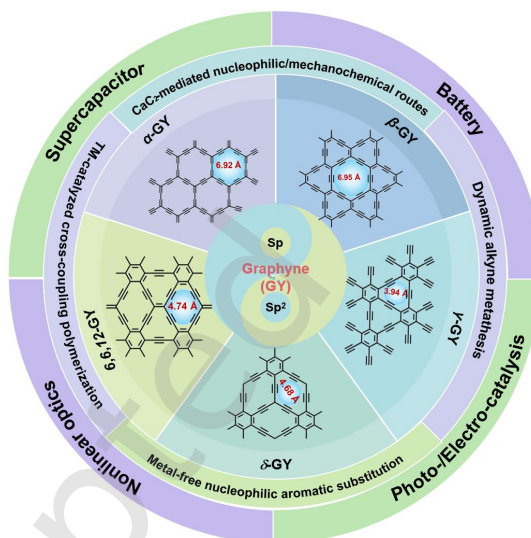
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Graphyne (GY), an emerging carbon allotrope constructed from *sp*- and *sp*²-hybridized carbons, is systematically overviewed based on its structural diversity, controllable synthesis strategies, and multifunctional applications. Representative allotropes including α -GY, β -GY, γ -GY, δ -GY, and 6,6,12-GY are introduced, along with their characteristic pore structures and synthesis routes (CaC₂-mediated nucleophilic/mechanicochemical routes, transition metal-catalyzed cross-coupling polymerization, metal-free nucleophilic aromatic substitution, dynamic alkyne metathesis). Their key applications are further explored across four domains: supercapacitors and batteries for electrochemical energy storage, photo-/electro-catalysis for redox reactions, and nonlinear optics for advanced functional technologies.

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ABSTRACT

As a frontier complement and extension to the well-developed graphdiyne, graphyne (GY) is a distinctive carbon allotrope featuring single acetylene ($-C\equiv C-$) linkages bridging adjacent benzene rings, which represents a cutting-edge direction in the development of emerging two-dimensional carbon materials. This review first summarizes the structural classification, lattice parameters, and intrinsic properties of GY based on theoretical calculations. The controllable synthesis methods for almost all GY are then categorized by precursor type—including CaC_2 -mediated nucleophilic/mechanochemical routes, transition metal(TM)-catalyzed cross-coupling polymerization, metal-free nucleophilic aromatic substitution, dynamic alkyne metathesis—with critical discussion of their respective advantages, limitations, and underlying mechanisms. Furthermore, we provide a detailed summary of characterization techniques covering structural, compositional, and additional advanced analyses, alongside a thorough overview of multifunctional applications covering supercapacitors, batteries, photo-/electro-catalysis, and nonlinear optics. Finally, this review critically assesses the key challenges and future opportunities spanning from GY synthesis to practical applications, emphasizing the urgent need for direct experimental evidence to elucidate the crucial role of $-C\equiv C-$ bonds in different applications.

KEYWORDS

Graphyne; Carbon allotrope; Two-dimensional material; Synthesis methodology; Structure–property relationship; Multifunctional applications

1. Introduction

The development and utilization of novel materials are essential for unlocking multifunctional capabilities in emerging applications, ranging from advanced energy systems to next-generation electronics. In this regard, emerging carbon based architectures have gained extensive interest owing to their unique physicochemical properties and wide-ranging application prospects [1-3]. The remarkable structural diversity of carbon arises from its capacity to engage in three fundamental hybridization motifs: tetrahedral (sp^3), trigonal (sp^2), and linear (sp) [4,5]. Specifically, sp^3 -hybridized carbon (e.g., diamond)

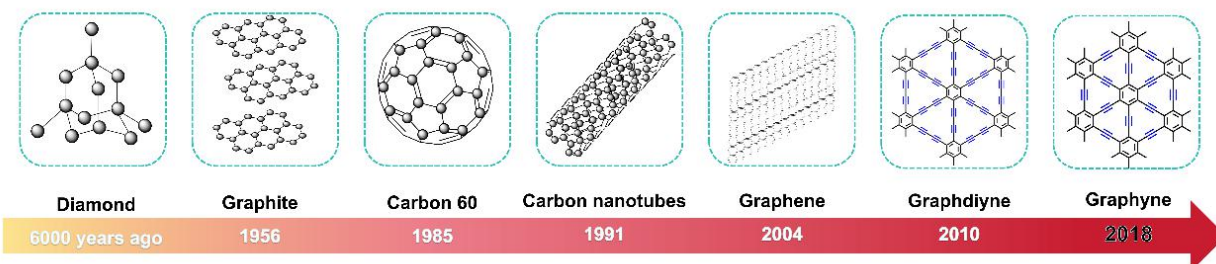
forms stable three-dimensional (3D) networks that impart high mechanical strength [6]; sp^2 -hybridized carbon (e.g., graphene) enables high electrical conductivity [7]; and sp -hybridized carbon forms conjugated π -systems that regulate charge distribution and optimize porous structure. Traditional carbon allotropes, including diamond, carbon nanotubes (CNTs), and graphite, are well-established, yet they are dominated by single sp^2 or sp^3 hybridization. Rational combination of sp^3 , sp^2 and sp hybridization enables the deliberate construction of a vast hierarchy of carbon allotropes. However, a systematic understanding of the coexistence of sp^3 , sp^2 and sp hybridized carbon domains within a

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(a) Timeline shows representative research of carbon materials



(b) Timeline shows representative research of graphyne and its analogues

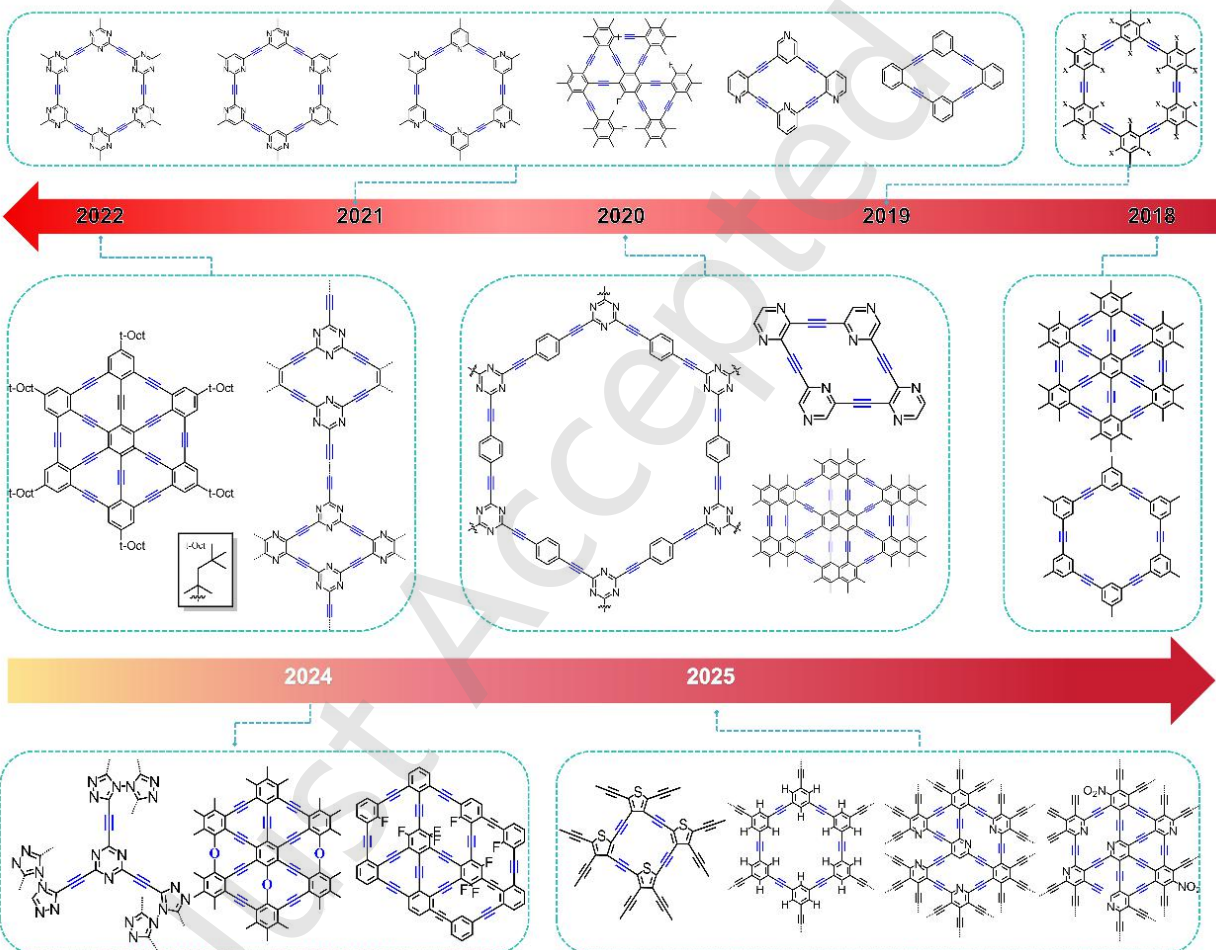


Figure 1 (a) Timeline illustrating significant research developments in carbon materials. (b) Timeline highlighting key research milestones related to GY and its analogues.

single architecture remains limited.

The evolution of carbon materials has paralleled the history of human advancement and occupies an important place in materials science (**Fig. 1a**). The graphyne family (GYs), first put forward by Baughman et al. in 1987 via computational modeling of their baseline crystallographic architectures, possesses a hybrid-bonding network of sp - and sp^2 -hybridized carbons [8]. They are constructed by substituting some carbon-carbon single bonds of graphene with acetylenic ($-C\equiv C-$) groups to generate diverse two-dimensional polymorphs. Since then, considerable investigation spanning first-principles

computations and bespoke synthetic campaigns have been aid to explore the synthetic feasibility and intrinsic electronic characteristics of GYs, thereby expanding their application potential across diverse research fields [9-12]. A milestone breakthrough occurred in 2010, when Li and colleagues successfully realized the experimental synthesis of graphdiyne (GDY), wherein neighboring phenylene rings are covalently interlinked via butadiynyl ($-C\equiv C-C\equiv C-$) spacers [13]. Following this pioneering work, a series of controllable synthetic methods, including spanning solution-phase coupling, interfacial polymerization, and vapor-assisted growth, have been

progressively established to enable the routine procurement of phase-pure, large-area GDY films. Intensive investigation over the last decade has consequently converged on GDY, leading to the development of a large number of GDY-based nanostructures with benchmark performance metrics in oxygen reduction/evolution reactions, lithium/sodium storage systems, photoelectrochemical cells, affinity-based biosensors, and advanced oxidation processes for water treatment [14-18]. In addition, GDY can be further functionalized through heteroatom doping and molecular modification to optimize its metallic/semiconducting transition thresholds, frontier-orbital hybridization gaps, drift-diffusion transport parameters, and solid-liquid junction charge-separation yields [19-21]. This seminal GDY advance has both galvanized sustained inquiry into its structural congeners and established a versatile platform for the targeted construction and characterization of a broader spectrum of GY-based analogues.

Generally, the GYs includes pristine GY, GDY, and higher-order GY_n structures ($n \geq 2$), where the remarkable structural polymorphism originates directly from the variable length of the oligoyne $(-\text{C}\equiv\text{C}-)_n$ bridging units that interconnect successive benzene-derived junctions. Theoretical simulations have demonstrated that expanding the internal ring porosity and reducing the contiguous sp^2 domain size simultaneously attenuates the structural integrity and increases the propensity for bond scission under thermal perturbation [22]. Consequently, the experimental synthesis and performance exploration of graphtriyne and other high-order GYs remain relatively insufficient compared with conventional GY and GDY. As a frontier complement and extension to the well-developed GDY, GY is a distinctive carbon allotrope featuring single acetylene $(-\text{C}\equiv\text{C}-)$ linkages bridging adjacent benzene rings, representing an archetypal two-dimensional (2D) carbon allotrope that occupies a structurally strategic position within the broader graphyne family, bridging the gap between fully sp^2 hybridized graphene and the more highly alkyne-populated GDY lattice. Computational results further reveal that GY possesses an ultra-high theoretical specific surface area of $3440 \text{ m}^2 \text{ g}^{-1}$. This data considerably eclipses that of conventional activated carbon ($2000 \text{ m}^2 \text{ g}^{-1}$) and registers a significant enhancement relative to both the theoretical ($2620 \text{ m}^2 \text{ g}^{-1}$) and experimental ($1500 \text{ m}^2 \text{ g}^{-1}$) capacities of GDY [5]. Benefiting from excellent structural robustness, intrinsically wide band gap, and electronically tunable architecture positions GY as a compelling material for next-generation electrocatalytic, optoelectronic, and adsorptive technologies.

In parallel with pure carbon-based GYs, metal integration has emerged as an effective strategy to introduce extrinsic functional motifs into GY skeletons,

enabling the construction of metallated GY (MGY) derivatives [23-26]. MGYs represent a novel class of multifunctional 2D carbon materials that integrate the inherent advantages of pristine GY with diversified metal-centered electronic and catalytic characteristics. The rational implantation of metal ions enables precise modulation of the electronic configuration, surface polarity, and chemical reactivity of GY substrates, thereby greatly broadening their applicability in nanoelectronics, molecular devices, and catalytic systems. A variety of metallic species, including Hg^{II} , Ni^{II} , Pd^{II} , Pt^{II} , and Co^{II} , have been successfully anchored within GY architectures to serve as active centers and nonlinear optical functional sites, substantially improving the catalytic performance of MGY systems [23-26]. Combined density functional theory (DFT) simulations and experimental characterizations have systematically clarified the underlying electronic evolution and interfacial reaction mechanisms of these metal-modified GY materials, providing reliable theoretical and experimental support for their future practical applications. At present, continuous research attention is still focused on exploiting new high-efficiency modification strategies and precisely tailoring the microstructures of GY derivatives, aiming to achieve targeted structural engineering for high-performance functional applications (**Fig. 1b**).

Over the past decades, research fields related to GDY and GY have exhibited an overall increasing trend in terms of both publications and citations (**Fig. 2**). To date, numerous reviews have focused on GDY [27-30], whereas only a handful are dedicated specifically to GY. Moreover, existing GY-related reviews suffer from certain limitations, leaving a notable gap in the systematic investigation of this emerging carbon allotrope (**Table 1**): (1) Narrow material coverage: Most existing reviews focus on specific GY variants e.g., all carbon γ -GY [31, 32] and pristine, composite, hybrid, and coordinated γ -GY materials [33], lacking systematic comparison across all GY allotropes including α -GY, δ -GY, and 6,6,12-GY; (2) Limited research scope: Some reviews are confined to limited aspects, including specific energy storage and photocatalytic behavior applications [34, 35], the mechanochemical synthesis of GY [32], and specialized characterization techniques [36], lacking a systematic and comprehensive overview of GY covering diverse structures, controllable synthesis, and multifunctional applications. (3) Insufficient review studies: Systematic and dedicated reviews focusing exclusively on GY remain extremely scarce [37, 38]. Most existing reviews only briefly discuss partial properties and applications of GY as a secondary research content, rather than providing targeted and in-depth summaries. To date, fewer than ten comprehensive reviews specifically focus on GY, lacking a holistic overview to guide the further development of GY-related research.

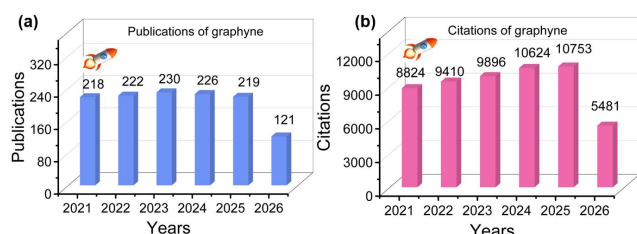


Figure 2 (a) Yearly publications and (b) citations for GY-related research from 2021 to 2026 (data from Web of Science).

In this review, we focus on the most recent advances in almost all types of primary GY and MGY, covering various synthesis methods and multifunctional applications, with the aim of systematically understanding their structure-activity relationships. The remainder of this work is divided into five sequential parts, each dedicated to a distinct facet of GY chemistry, ranging from synthesis to application-oriented performance evaluation. The review begins with an introduction in Section 1, which delineates the broader research landscape and the specific knowledge gaps that motivate our systematic survey. Section 2 systematically catalogs the theoretically predicted ground-state geometry of GY, drawing attention to its most characteristic physicochemical features. Section 3 focuses on various synthesis methods for over a dozen of GY materials, categorizing them based on the precursor molecules involved. This section

comprehensively dissects the performance advantages and practical deficiencies of each system in terms of stability, functionality, and processability. Section 4 provides a detailed overview of the reported characterization methods employed to investigate GY materials at various levels. By utilizing these techniques, researchers have gained valuable insights into the crystal structure, surface functional group chemistry, phonon dispersion characteristics, and elastic response of these materials. Section 5 explores the multifunctional applications of GY, highlighting its potential in supercapacitors, lithium/sodium/potassium-ion batteries, photo-/electro-catalysis, nonlinear optics. In-depth research into GY applications can clarify the structure-activity relationship and provide valuable insights for future design efforts. Finally, we critically assess the remaining synthetic hurdles and emerging application opportunities for GY-based materials, proofing the functional roles of acetylenic bridges and mixed-hybridization motifs in actual device-relevant environments, coupled with the absence of standardized protocols for property benchmarking. By weaving together the collective insights from theoretical, synthetic, and applied research streams, we endeavor to furnish a definitive reference that not only encapsulates the current frontiers of GY science but also furnishes a clear roadmap for translating its intrinsic material advantages into tangible technological breakthroughs.

Table 1 Some of the previously published papers in the proposed area.

Previous reviews	Focus/Strengths	Limitations/Weaknesses
M. Golzani, A. Tadjarodi, M. Golzani, M. Poliki, R. Z. Dorabei and K. Dashtian, <i>Coord. Chem. Rev.</i> , 2024, 510, 215838.	Synthesis, properties and applications of γ -graphyne-based coordination, composite, and hybrid materials.	Only γ -graphyne-based examples.
L. Wang, Z. Hao, S. Chen, H. Chen, Y. Lou, C. He, Y. Chen and X. Cui, <i>Prog. Mater. Sci.</i> , 2024, 146, 101327.	Reactive mechanism, specific disadvantages and future improving directions of mechanochemical synthesis of full-carbon graphyne.	Only focus on full-carbon graphyne and mechanochemical fabrication method.
G. Narang, D. Bansal, S. Joarder, P. Singh, L. Kumar, V. Mishra, S. Singh, K. Tumba and K. Kumari, <i>FlatChem</i> , 2023, 40, 100517.	Synthesis, properties, and applications of graphynes.	Limited examples; Focused only limited applications on water remediation, sensors, and electrocatalysis.
J. Li and Y. Han, <i>Giant</i> , 2023, 13, 100140.	Synthesis, properties, and applications of γ -graphyne.	Only limited to γ -graphyne and introduces its potential applications based on predicted properties.
F. Yao, W. Wang, H. Shi, Z. Xu, M. Zeng, Y. Hu, L. Liu and X. Ji, <i>ACS Catal.</i> , 2021, 11, 14122-14147.	Electronic properties, synthesis, and catalysis applications of graphynes.	Only limited to catalysis applications.

X. Liu, Y. Zhao, J. Du and D. Wang, <i>Sci China Mater.</i> , 2024, 67, 729-751.	Synthesis, characterizations, and applications of crystalline graphdiyne.	Only crystalline graphdiyne examples.
X. Zheng, S. Chen, J. Li, H. Wu, C. Zhang, D. Zhang, X. Chen, Y. Gao, F. He, L. Hui, H. Liu, T. Jiu, N. Wang, G. Li, J. Xu, Y. Xue, C. Huang, C. Chen, Y. Guo, T. B. Lu, D. Wang, L. Mao, J. Zhang, Y. Zhang, L. Chi, W. Guo, X. H. Bu, H. Zhang, L. Dai, Y. Zhao and Y. L. Li, <i>ACS Nano</i> , 2023, 17, 14309-14346.	Synthesis, structure, properties, and applications of graphdiyne.	Only graphdiyne examples.
B. Li, S. Yu, M. Zhou, C. Chen, C. Lai, M. Zhang and H. Lin, <i>J. Mater. Chem. A</i> , 2022, 10, 3905-3932.	Synthesis, structures, properties, and applications of graphynes-derived single atoms nanomaterials.	Focused only on limited applications of energy storage and conversion.
Y. Fang, Y. Liu, L. Qi, Y. Xue and Y. Li, <i>Chem. Soc. Rev.</i> , 2022, 51, 2681-2709.	Foundation and application of graphdiyne and graphdiyne-based materials.	Only graphdiyne examples
C. Huang, Y. Li, N. Wang, Y. Xue, Z. Zuo, H. Liu and Y. Li, <i>Chem. Rev.</i> , 2018, 118, 7744-7803.	Basic properties, preparation, characterization and potential applications of graphdiyne-based materials. History, synthesis and application of graphdiyne-based materials.	Only graphdiyne examples
R. Sakamoto, N. Fukui, H. Maeda, R. Matsuoka, R. Toyoda and H. Nishihara, <i>Adv. Mater.</i> , 2019, 31, 1804211.		
Y. Li, L. Xu, H. Liu and Y. Li, <i>Chem. Soc. Rev.</i> , 2014, 43, 2572.	Theoretical predictions and applications of graphdiyne and graphyne.	Published ~ 11 years ago, concentrated on theoretical prediction of graphyne structures.

2. Diverse structures of GY

2.1 Structural classification of GY

GY represents a significant advancement in carbon materials science. Differing from conventional carbon allotropes, GY possesses a unique structure in which partial C-C single bonds of graphene are replaced by $-C\equiv C-$ linkages [39]. This crucial alteration not only introduces intriguing properties but also enables a range of potential applications across various fields. GYs can be subdivided into several well-defined categories based on the extent of acetylene bond incorporation within their sp^2 -hybridized carbon frameworks. The principal types include GY itself, GDY, graphtriyne, and more generally, graph- n -ynes, where ' n ' indicates the number of $-C\equiv C-$ linkages per structural unit (**Fig. 3**) [40]. For instance, GY features a relatively lower number of $-C\equiv C-$ linkages, while GDY and graphtriyne incorporate progressively more $-C\equiv C-$ units. This increase in $-C\equiv C-$ units results in a finely tunable series of characteristics: charge-carrier mobilities vary with band dispersion, elastic moduli scale with alkyne density, and optical bandgaps shift predictably with the number of $-C\equiv C-$ units, collectively endowing GY derivatives with exceptional application requirements.

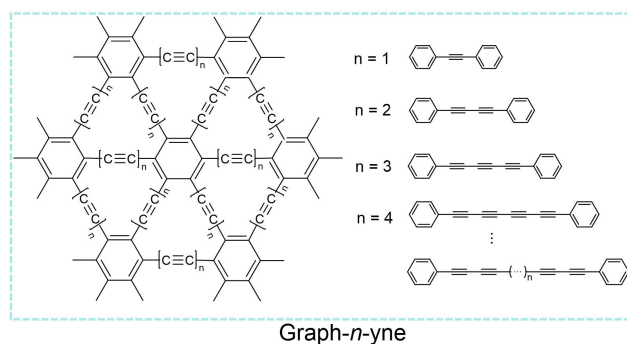


Figure 3 Schematic illustration of the chemical structures of graph- n -yne.

Among the family of GYs, GY occupies the ground-state energy minimum, exhibiting the highest resistance to structural decomposition rivals that of graphene, with formation energy comparable to well-known carbon structures such as C_{60} , C_{70} , and fullerenes [41]. The stability of GY is primarily attributed to its unique composition, which coordinates sp -carbon ($C-sp$) and trigonally coordinated sp^2 -carbon ($C-sp^2$). This is achieved by strategically inserting $-C\equiv C-$ moieties into the sp^2 -hybridized graphene lattice, resulting in a hexagonal symmetric structure ($P6m$) that endows GYs with distinctive properties [5]. Unlike traditional 2D

carbon materials, such as graphene, GY monolayers exhibit three distinct types of chemical bonds: (1) C=C/aromatic bonds, which involve C- sp^2 connecting to other C- sp^2 ; (2) C-C bonds, which connect C- sp^2 and C- sp ; and (3) C $\equiv$ C bonds formed between two C- sp [41, 42].

According to previous reports, different types of GY-like structures can be realized by inserting $-C\equiv C-$ moieties into various positions within pristine graphene [42, 43]. The various types of GY, including α -GY, β -GY, γ -type, δ -GY, and 6,6,12-GY, display remarkable differences in their arrangements of C- sp and C- sp^2 , leading to diverse electronic and physical properties [44]. α -GY adopts a distinct geometric configuration arising from its specific arrangement of C atoms. The bond lengths vary depending on the hybridization state of the C atoms (**Fig. 4**). The C $\equiv$ C triple-bond linkages formed by sp -hybridized carbon exhibit shorter bond lengths compared with sp^2 -hybridized C-C bonds [45]. The angles between the bonds also contribute to the overall structure. α -GY often exhibits a relatively compact arrangement with a certain degree of symmetry. In contrast, β -GY presents a different set of structural parameters. It has a more open structure with longer C-C bond lengths in some regions. The degree of conjugation is higher in β -GY, leading to enhanced optical and catalytic properties. The angles between the bonds are adjusted to accommodate the specific arrangement of C atoms, creating a unique spatial configuration. γ -GY is characterized by its unique pore structure and surface area. The bond lengths and angles are optimized to create these natural pores [46]. C atoms are arranged to maximize the surface area available for interaction with other substances.

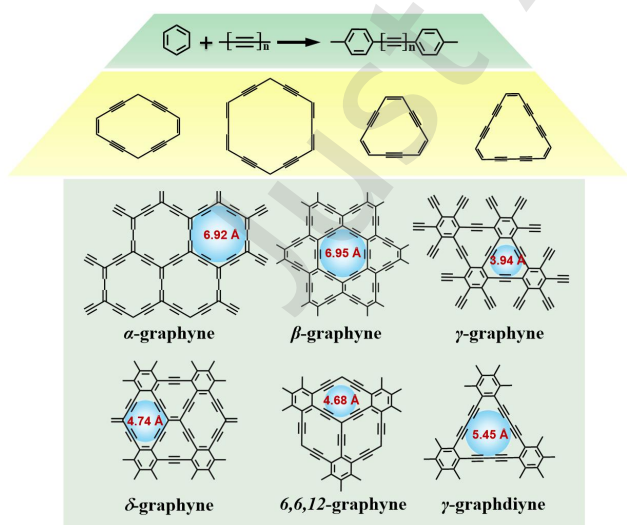


Figure 4 Schematic illustrations of the chemical structures for α -GY, β -GY, γ -GY, δ -GY, 6,6,12-GY, and α -GDY.

2.2 Lattice parameters of GY

Each distinct type of GY including α -type, β -type, γ -type, δ -type, and 6,6,12-type exhibits unique

arrangements of C- sp and C- sp^2 , resulting in a fascinating array of electronic and physical properties that make them highly valuable in materials science and nanotechnology. The various types of GY share certain similarities in their structural parameters. For instance, the C- $sp\equiv C-sp$ bond length, which represents the triple bond between C sp , typically ranges from 1.20 Å to 1.25 Å across all types [47]. Similarly, the C- $sp-C-sp$ bond length, denoting the single bond between C- sp and C- sp^2 , generally falls within 1.34 Å to 1.40 Å for all variants. The lattice parameters of α -, β -, and γ -GY were systematically investigated by Ruiz-Puigdollers and co-workers using first-principles density functional theory (DFT) calculations, being 6.996 Å, 9.480 Å, and 6.890 Å, respectively. The optimized bond lengths of C- $sp\equiv C-sp$ in α -, β - and γ -GY are 1.230 Å, 1.232 Å, and 1.223 Å, respectively, and the optimized bond lengths of C- $sp-C-sp^2$ in α -, β - and γ -GY are 1.396 Å, 1.389 Å, and 1.408 Å, respectively, and the optimized bond lengths of C- $sp^2=C-sp^2$ in β - and γ -GY are 1.457 Å, and 1.426 Å, respectively, which showed close agreement with previous theoretical results [48]. Furthermore, the C- sp^2-C-sp^2 bond length, signifying the bond between two C sp^2 , consistently measures between 1.39 Å and 1.42 Å. These similarities suggest that the fundamental bonding characteristics remain relatively stable across the different forms of GY. Moreover, the C-C-C bond angle is consistently around 120°, indicating a stable hybridization state within the structure. The interlayer spacing among distinct GY types also falls within a relatively narrow range of 3.3 Å to 3.5 Å, contributing to the structural integrity and layered nature common to all forms of GY [49].

Despite their shared fundamental features, GY allotropes differ significantly in structural parameters that dictate their electronic, mechanical, and optical properties, thus enabling diverse applications. Pore sizes vary: α -GY (6.92 Å), β -GY (6.95 Å), γ -GY (4.74 Å), δ -GY (3.94 Å), and 6,6,12-GY (4.68 Å), influencing gas storage and filtration. Lattice parameters also differ: α -GY (6.966 Å), β -GY (9.480 Å), γ -GY (6.890 Å), δ -GY (6.710 Å), and 6,6,12-GY (9.130 Å), affecting packing density and mechanical stability. Cohesive energies, calculated by DFT and summarized in **Table 2** [48], range from 6.23 eV (6,6,12-GY) to 7.21 eV (γ -GY), reflecting bonding strength and influencing thermal stability, conductivity, and reactivity. Collectively, these variations define the physicochemical fingerprint of each allotrope, tailoring them for specific applications from molecular sieving to energy storage.

2.3 Intrinsic properties of GYs

Among the distinct GY allotropes (α -, β -, γ -, δ -, and 6,6,12-type), the first three are well-studied [45,50].

γ -GY, in particular, is frequently investigated due to its exceptional electronic and mechanical properties, arising from its hybrid hexagonal/triangular carbon ring structure. In contrast, δ - and 6,6,12-GY remain at early theoretical/experimental stages because of synthetic challenges. DFT calculations reveal that α - and β -GY are metallic (zero band gap), while γ -GY is a direct-gap semiconductor with valence band maximum and conduction band minimum both at the M point (Fig. 5) [48,51]. The band gap of γ -GY varies widely (0.46–1.22 eV), depending on the functional used (e.g., 0.46 eV with GGA-PBE vs. 0.96 eV with HSE06) [44]. Optically, γ -GY exhibits superior visible-light absorption and reflectivity [52, 53], while its in-plane stiffness (170–240 N m⁻¹) [54] is lower than graphene but still robust. These properties make γ -GY a promising candidate for nanoscale electronic and optoelectronic devices.

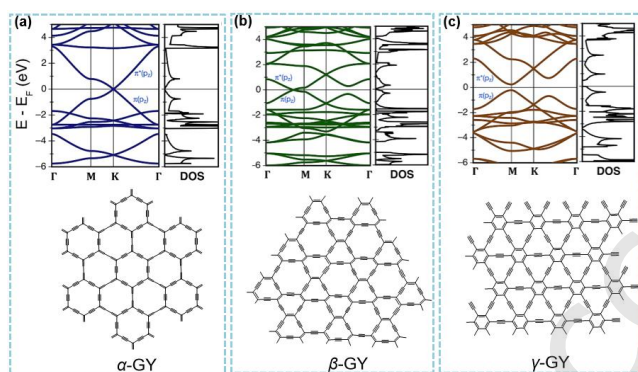


Figure 5 Band structures and total density of states (DOS) for (a) α -, (b) β -, and (c) γ -GY. The Fermi level is set to 0 eV. Reprinted with permission from ref. [48], © 2015 Elsevier Ltd

Therefore, the structural diversity of GY allotropes encompassing α -GY, β -GY, γ -GY, δ -GY, and 6,6,12-GY originates from the strategic insertion of $\text{--C}\equiv\text{C--}$ linkages into the graphene lattice, creating hybrid sp/sp^2 carbon networks with precisely tunable electronic and physical properties. First-principles DFT calculations have systematically elucidated the structural parameters that distinguish these allotropes: lattice constants range from 6.710 Å (δ -GY) to 9.480 Å (β -GY), pore sizes vary between 3.94 Å (δ -GY) and 6.95 Å (β -GY), and cohesive energies span 6.23 eV (6,6,12-GY) to 7.21 eV (γ -GY), reflecting the thermodynamic stability hierarchy that prioritizes γ -GY as the most energetically favorable configuration. The electronic structure analysis reveals fundamentally different transport behaviors: α - and β -GY exhibit metallic character with zero band gaps, while γ -GY manifests semiconducting behavior as a direct-gap semiconductor with valence-band maximum and conduction-band minimum converging at the M point of the hexagonal reciprocal lattice. Notably, the calculated band gap of γ -GY shows significant functional dependence (0.46–1.22 eV), underscoring the necessity of benchmark-quality computational approaches for reliable device simulation. The optical properties further distinguish γ -GY through

superior visible-light absorption and reflectivity, while mechanical assessments demonstrate in-plane stiffness values of 170–240 N m⁻¹—lower than graphene yet sufficient for robust nanoscale device integration. This systematic structure-property mapping establishes that the GY family offers a versatile platform where subtle modifications to the acetylenic bridge density and arrangement enable tailored functionality for specific applications. However, the δ -GY and 6,6,12-GY allotropes remain predominantly theoretical constructs, highlighting the critical need for experimental validation and synthesis development to fully exploit the structural diversity inherent to this emerging carbon allotrope family.

DFT calculations reveal fundamentally different transport behaviors among GY allotropes, α -GY and β -GY exhibit metallic character with zero band gaps. While γ -GY manifests as a direct-gap semiconductor with valence-band maximum and conduction-band minimum converging at the M point of the hexagonal reciprocal lattice. The calculated band gap shows significant functional dependence, underscoring the necessity of benchmark-quality computational approaches for reliable device simulation. Theoretical predictions indicate that the insertion of acetylenic linkages modulates charge-carrier mobilities in a predictable manner, varying systematically with band dispersion across different GY allotropes. Experimentally, among all GY allotropes, only γ -GY has been successfully synthesized experimentally to date, primarily through mechanochemical routes. Experimental characterization confirms its semiconducting nature with a band gap of 2.58 eV as determined by UV-Vis DRS spectroscopy, which is significantly higher than theoretically predicted values. This discrepancy likely arises from structural defects, finite domain size, and the presence of impurities in the synthesized samples.

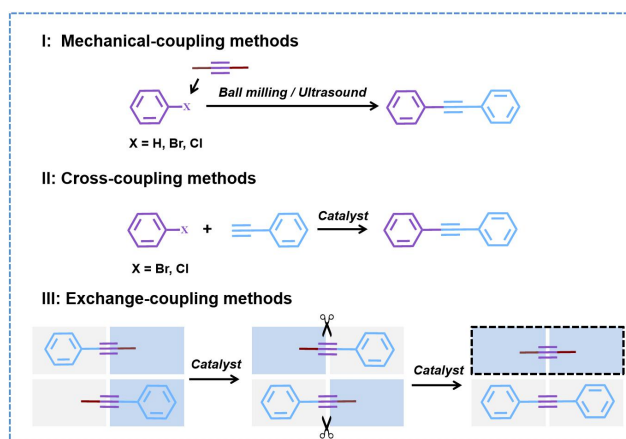


Figure 6 Schematic illustration of various synthesis methods for GY: arylene mechanochemical method, arylene coupling method, and arylene exchange method.

3. Controllable synthesis

The past decade has experienced a marked surge of theoretical prediction of GY structures and properties. However, the experimental realization of these predictions remains a major challenge [55]. To bridge this gap between theory and reality, researchers have been exploring different synthesis techniques to produce GY materials with specific characteristics. A central goal in current GY research is to achieve a facile and high-yield synthetic protocol that overcomes the intrinsic limitations of conventional cross-coupling methods. Based on the actual bond-forming chemistry, the reported synthetic routes can be categorized into four main classes: (i) CaC_2 -mediated nucleophilic/mechanochemical routes, (ii) transition metal-catalyzed cross-coupling polymerization, (iii) metal-free nucleophilic aromatic substitution (S_{NAr}), and (iv) dynamic alkyne metathesis. Within each category, different processing environments (solid-state, solution-phase, interfacial) are discussed as implementation strategies rather than independent reaction classes. Fig. 6 provides a schematic overview of these synthetic strategies [56–58].

3.1 Calcium Carbide-Mediated Nucleophilic/Mechanochemical Routes

The CaC_2 -mediated nucleophilic/mechanochemical route leverages mechanical force or ultrasound irradiation to activate precursor molecules and enhance their reactivity [59, 60]. This method is further divided into two subcategories based on the aromatic precursors: (i) aryl

halides with CaC_2 , and (ii) aromatics with CaC_2 . The high-energy collisions between particles lead to bond breaking and the formation of new bonds, resulting in the desired product [61]. Critical to the success of this synthetic sequence is the electronic interplay between the halo-substituted arene (electrophilic at the C–X bond) and the calcium-based activating agent; this polarization, characterized by a partial negative charge on the halogen and a partial positive charge on the adjacent carbon, orchestrates the nucleophilic attack that sets the cascade in motion. The high levels of mechanical energy significantly reduce the activation energy (E_a) by activating the reactants through mechanochemistry [32], making it easier to perform the reaction compared to traditional methods (Fig. 7). This process inevitably leads to the formation of calcium halides as byproducts. Despite challenges such as byproduct formation and residual impurities, this method remains widely adopted due to its operational simplicity and scalability. One of its key advantages is its ability to carry out reactions without the need for traditional solvents or harsh reaction conditions, making it an environmentally friendly and sustainable alternative to conventional synthesis methods [62–64]. Additionally, the mechanochemical route distinguishes itself by allowing independent modulation of the physical and chemical reaction coordinates, such as reaction time, temperature, collision energy, and precursor molar ratio, ensuring high efficiency and improved yield [57, 65].

Table 2 Structural parameters of different GY allotropes: lattice parameters, pore sizes, bond lengths, and cohesive energies.

GY Type	Pore Size (Å)	Bond Length (Å)	Lattice Parameter ($a = b$, Å)	Cohesive Energy (eV atom ⁻¹)
		$\text{C}_{\text{sp}} \equiv \text{C}_{\text{sp}} / \text{C}_{\text{sp}} - \text{C}_{\text{sp}2} /$ $\text{C}_{\text{sp}2} = \text{C}_{\text{sp}2}$		
α -GY	6.92	1.230/1.396/	6.966	6.93
β -GY	6.95	1.232/1.389/1.457	9.480	7.01
γ -GY	4.74	1.223/1.408/1.426	6.890	7.21
δ -GY	3.94	/	6.710	6.50
6,6,12-GY	4.68	/	9.130	6.23

C_{sp} and $\text{C}_{\text{sp}2}$ denote sp and sp^2 -hybridized carbon atoms, respectively.

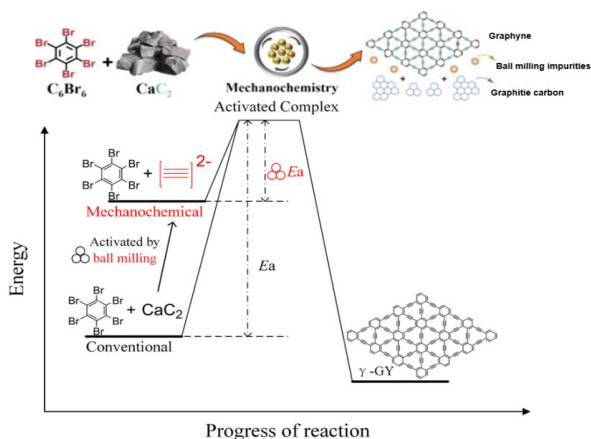


Figure 7 E_g analysis for the mechanochemical reaction between hexabromobenzene and CaC_2 . Reprinted with permission from ref. [32], © 2024 Elsevier Ltd.

3.1.1 Aryl Halides with CaC_2 Mechanochemical synthesis of γ -GY from hexabromobenzene

The aromatic mechanochemical method uses halogenated aromatics (e.g., benzene, naphthyl derivatives) that undergo bond cleavage and reformation under mechanical force during grinding or milling, yielding GY compounds [65]. This sustainable approach avoids harsh conditions and toxic reagents, extending mechanochemistry into a versatile platform for inorganic [66] and organic [67].

Li et al. advanced alkynyl carbon material (ACM) synthesis via aromatic mechanochemistry (**Fig. 8a**) [68]. By milling CaC_2 with polyhalogenated hydrocarbons (PHHCs) at room temperature, they produced multiple ACMs. Using $\text{C}_6\text{Br}_5\text{CH}_2\text{CH}_2\text{C}_6\text{Br}_5$ as an example, the two-step process involves: (1) sealing CaC_2 and PHHCs with ~250 g of steel balls in a stainless-steel vessel for continuous planetary ball milling under vacuum; (2) acid washing, microfiltration, ultrapure water rinsing, and vacuum drying at 100 °C to afford high-yield ACM. Li et al. further reacted CaC_2 with six fully halogenated hydrocarbons (CCl_4 , C_2Cl_6 , C_2Cl_4 , C_6Cl_6 , C_6Br_6 , $\text{C}_{14}\text{H}_4\text{Br}_{10}$) to yield ACM-1 to ACM-6, analyzing their carbon content, specific surface areas, and thiophenic sulfur adsorption [69]. Cui et al. synthesized hydrogen-substituted GY via vacuum ball milling of CaC_2 and 1,3,5-tribromobenzene (PhBr_3), removing impurities with dilute nitric acid and benzene. The resulting material features hexagonal pores between benzene rings linked by alkynes, facilitating molecular/ionic migration (**Fig. 8b**) [70]. Using PhBr_6 (hexabromobenzene) overcame steric hindrance from six substituents, enabling the first experimental synthesis of GY with single alkynyl linkages in 2018. Cui et al. milled CaC_2 and PhBr_6 to produce GY with composition and lattice constants matching theoretical predictions (**Fig. 8c**) [56]. The material is a *p*-type semiconductor ($E_g = 2.58$ eV), indicating electronic application potential. Concurrently, ultrasound-assisted synthesis has emerged as a versatile strategy. Gao et al. prepared γ -GDY by sonication of CaC_2 and PhBr_6 in anhydrous ethanol under Ar at 25 °C for >30 h, followed by washing and drying [71]. Acoustic cavitation generates extreme local conditions that promote bond formation/rearrangement, with tunable power and frequency enhancing selectivity, reproducibility, and reaction rates [72–75].

It is important to note that the structural identity of mechanochemically synthesized γ -GY has recently been called into question (**Table 3**). A replication study [76] reported that attempts to reproduce the mechanochemical synthesis of γ -GY from hexabromobenzene and CaC_2 failed to produce the

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<https://doi.org/10.26599/NRE.2026.9120280>

claimed graphyne product. The replication study found that the reaction products consisted primarily of carbonaceous impurities and unreacted precursors, with no evidence of the characteristic graphyne structure as determined by XRD, Raman spectroscopy, and elemental analysis. The authors suggested that the reported characterization data from the original studies may be insufficient to unambiguously confirm the formation of γ -GY. While the original studies reported consistent characterization results (including XRD peaks matching theoretical predictions, Raman bands characteristic of *sp*-carbon, and XPS evidence of C–C and C≡C bonds), the replication study highlights the need for more rigorous structural characterization and careful control of reaction conditions. Key differences between the studies include precursor purity (the original work used commercial hexabromobenzene without further purification, while the replication used purified hexabromobenzene), milling conditions (ball size, rotation speed, and atmosphere may have varied), and purification procedures (the effectiveness of acid washing and annealing in removing impurities may differ). This controversy underscores the critical need for independent confirmation of structural assignments in GY research and the importance of establishing standardized synthesis and characterization protocols.

Ultrasound-assisted synthesis of GY

The prevalent methods for preparing GY currently include ultrasonic irradiation and mechanical ball milling. Notably, Wang et al. have introduced a novel solvent-free dry grinding technique for GY synthesis [77] (**Fig. 8d**). This refined mechanochemical approach not only retains the inherent benefits of traditional methods, such as simplicity and cost-effectiveness, but also significantly minimizes impurity levels and enhances the quality of GY, underscoring the potential of ultrasound-assisted synthesis as a versatile and efficient route to functional carbon frameworks. The introduction of the calcination step proved to be a crucial breakthrough in the research conducted by Cui et al. (**Fig. 8e**) [78]. Calcination after ball milling effectively mitigates structural defects in GY, enhancing its Li^+ storage capacity and cycling stability in lithium-ion batteries. This thermodynamically controlled heat treatment improves structural integrity and overall material performance, demonstrating a viable route for high-quality GY production via mechanochemical synthesis. Meanwhile, synthesizing *sp*-hybridized carbon allotropes remains challenging, with polyaromatic alkynes emerging as a promising direction. Li et al. achieved an alkynyl-linked naphthyl structure through a solvent-free mechanochemical reaction of CaC_2 and perchloronaphthalene, yielding high conversion efficiency and enabling green, cost-effective production (**Fig. 8f**) [79]. Mechanistically, intense mechanical stress activates CaC_2 , generating reactive $[\text{C}\equiv\text{C}]^{2-}$ species that undergo nucleophilic substitution with halogenated monomers. This process proceeds rapidly, akin to click chemistry,

ultimately forming GY while converting organic halogens into inorganic salts.

Heteroatom-doped GYs via mechanochemistry

Heteroatom doping of carbon materials can alter their valence, enhance conjugation, and boost physicochemical properties, facilitating applications in optical [80],

electrocatalysis [81], photocatalysis [82], and batteries [83, 84]. Inspired by this, Cui's research group extended their investigation to the synthesis of N-doped GY (N-GY) [85]. They selected D_{2h} -symmetric tetrahalogenated organics, specifically 2,3,5,6-tetrachloropyridine and 2,3,5,6-tetrachloropyridine, as precursors for their

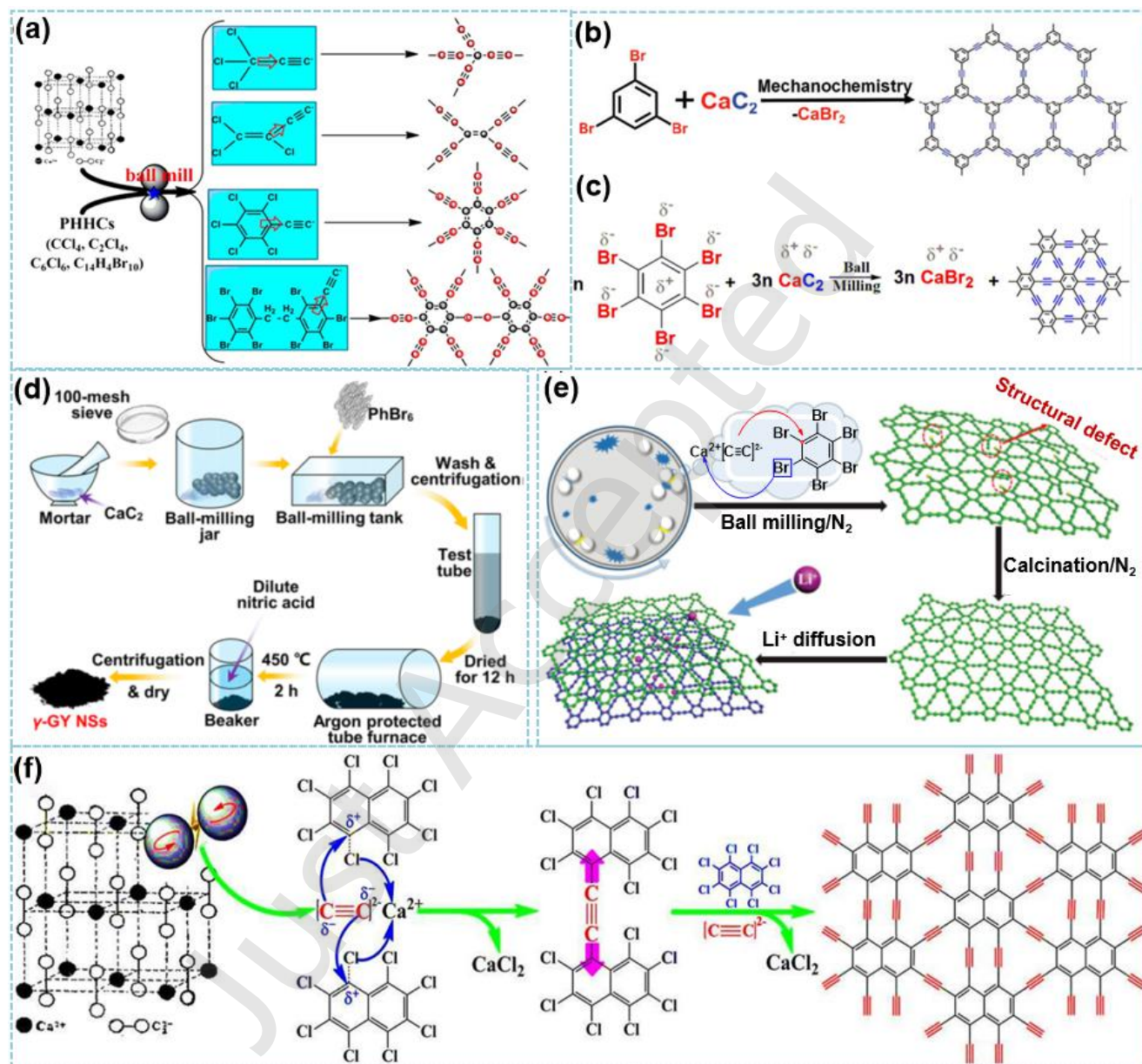


Figure 8 (a) The aromatic mechanochemical reaction between PHHCs and CaC_2 . Reprinted with permission from ref. [68], © 2017 American Chemical Society. (b) The aromatic mechanochemical reaction between PhBr_3 and CaC_2 . Reprinted with permission from ref. [70], © 2018 Elsevier Ltd. (c) The aromatic mechanochemical reactions between PhBr_6 and CaC_2 . Reprinted with permission from ref. [56], © 2018 Elsevier Ltd. (d) The aromatic mechanochemical reactions between PhBr_6 and CaC_2 using a solvent-free dry grinding technique. Reprinted with permission from ref. [77], © 2023 Royal Society of Chemistry. (e) Schematic illustration of preparation and Li^+ diffusion of GY by adding a calcination process. Reprinted with permission from ref. [78], © 2019 WILEY-VCH. (f) The proposed mechanochemical synthesis pathway between CaC_2 and C_{10}Cl_8 . Reprinted with permission from ref. [79], © 2020 American Chemical Society.

groundbreaking rhombic GY constructions (Fig. 9a). This choice aims to introduce heteroatom modifications at specific sites to fine-tune the electronic distribution and enlarge the interlayer gallery height. As a result, the final structures reveal tightly packed rhombic pores, which faithfully preserve the aromatic backbone of the benzene

or pyridine rings, alongside the original hydrogen substituents and pyridinic N species. This approach not only improves the coherence of the overall structure but also provides a more dynamic and versatile electron configuration. The addition of NH_4HCO_3 as a nitrogen source in the synthesis process allowed for the controlled

incorporation of nitrogen into the GY structure (**Fig. 9b**) [85]. Nitrogen doping tunes electron distribution in N-GY, improving electrochemical performance. Li et al. synthesized S-GY via mechanochemistry. As shown in **Fig. 9c**, the gray-to-black color change during reaction of CaC_2 with $\text{C}_4\text{Br}_4\text{S}$ is supported by GC evidence of $\text{C}_4\text{Br}_4\text{S}$ consumption and Br^- formation. A near-theoretical yield (102%) and 99.8% debromination confirm efficient nucleophilic substitution, following $\text{C}_4\text{Br}_4\text{S} + 2\text{CaC}_2 \rightarrow \text{C}_8\text{S} + 2\text{CaBr}_2$ [86]. **Fig. 9d** shows that mechanical activation generates reactive $[\text{C}\equiv\text{C}]^{2-}$, which substitutes C-Br bonds to form alkynyl-linked thiophene units and the S-GY framework. This solvent-free approach reduces energy input and cost while remaining environmentally friendly.

Dual doping offers synergistic advantages over single doping [87]. Cui et al. prepared N/S co-doped GY via mechanochemistry (**Fig. 9e**). During ball milling, alkynyl groups from CaC_2 react with aromatic monomers, while BDS produces S radicals forming C-S-C bonds. After annealing and purification, N/S-GY exhibits increased active sites and optimized electron distribution (e.g., pyridinic-N-induced channels and S-driven electron modulation), enabling faster Li^+ transport and enhanced electrochemical performance.

Heteroatom doping and composite modification represent powerful strategies for expanding the functionality of GY materials. Nitrogen doping introduces pyridinic-N, pyrrolic-N, and graphitic-N configurations that modulate the electronic structure, enhance

conductivity, and create active sites for catalysis [88, 89]. Sulfur doping, achieved through the mechanochemical reaction of CaC_2 with tetrabromothiophene, introduces S atoms that modify the electron distribution and enhance Hg(II) adsorption capacity [86]. Boron and phosphorus doping, while less explored, offer potential for further tuning the electronic properties and chemical reactivity of GY. Composite modification, including the incorporation of metal nanoparticles, metal oxides, and other carbon nanomaterials (graphene, CNTs), creates synergistic effects that combine the advantages of GY with those of the second component. For example, GY/ TiO_2 composites exhibit enhanced photocatalytic activity through improved charge separation at the heterojunction interface. The rational design of doped and composite GY materials offers a versatile platform for achieving optimized performance in energy storage, catalysis, and optoelectronic applications.

Notably, recent advances in other 2D materials have demonstrated the promise of heteroatom doping and composite modification for expanding biomedical applications. For instance, chemical-exfoliated borophene has been explored for light-induced tumor theranostics [90], black phosphorus-based nanomaterials have shown great potential in photothermal therapy and immunotherapy [91], vertical graphene has been employed in photoelectrochemical biosensing platforms [92], and ultrathin nonlayered tellurium nanosheets have demonstrated excellent photoresponse performance [93].

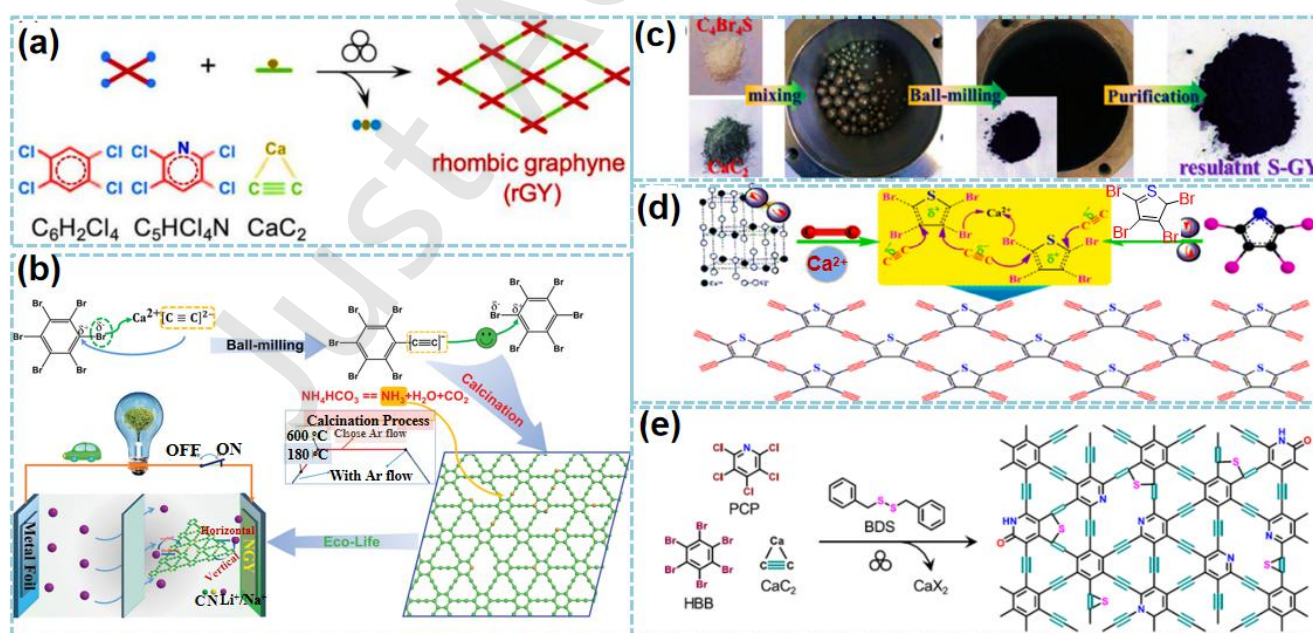


Figure 9 (a) Schematic illustration of the preparation of *r*-GY. Reprinted with permission from ref. [70]. (b) Schematic illustration of the preparation of N-doped GY using NH_4HCO_3 as a N_2 source. Reprinted with permission from ref. [85], © 2020 WILEY-VCH. (c) Procedure analysis and proposed mechanism for the solvent-free mechanochemical synthesis of S-doped GY, and (d) proposed mechanochemical reaction pathway for the synthesis of S-doped GY. Reprinted with permission from ref. [86], © 2024 Elsevier B.V. (e) Reaction route for the mechanochemical synthesis quasi-pyridinic N/S co-doped γ -GY from CaC_2 , HBB, PCP, and BDS precursors. Reprinted with permission from ref. [87], © 2024 Elsevier B.V.

Table 3 Comparison of original and replication experiments.

Parameter	Original Study (Cui et al., 2018–2020)	Replication Study (Kone et al., 2025)
Precursors	Hexabromobenzene (PhBr ₆ , 99% purity, used as received) + CaC ₂ (98%)	Hexabromobenzene (purified) + CaC ₂ (reagent grade)
Milling conditions	Planetary ball milling; 600 rpm; stainless steel vessel; vacuum; various ball-to-powder ratios	Detailed replication of conditions described in Carbon 2018, Small 2019, and J. Mater. Chem. A 2019
Post-treatment	Acid washing (dilute HNO ₃), filtration, water rinsing, vacuum drying at 100 °C; optional annealing at 260 °C under N ₂	Same purification procedures as reported
XRD evidence	Broad peaks matching calculated γ -GY lattice (6.89 Å); interlayer spacing ~0.36 nm	No diffraction pattern matching γ -GY; only amorphous carbon features
Raman spectroscopy	Bands at ~1380 cm ⁻¹ (D) and ~1570 cm ⁻¹ (G); additional bands attributed to sp-carbon	Partially consistent D/G bands but no detectable sp ¹ carbon signals
XPS evidence	C 1s peaks at ~284.6 eV (C–C), ~285.5 eV (C≡C)	Consistent with amorphous carbon; no definitive C≡C signature
FTIR evidence	C≡C stretching at ~2200 cm ⁻¹	No detectable C≡C absorption
Structural assignment	Claimed formation of γ -GY based on combined spectroscopic data	Products are "heavily contaminated, amorphous chars with no detectable sp ¹ carbons"

3.1.2 Aromatics and CaC₂

In addition to the case of aryl halides and CaC₂, the combination of CaC₂ with various aromatic compounds represents another aromatic mechanochemical method. CaC₂ is a versatile reagent that can undergo a range of reactions, including acetylene formation. When mixed with aromatic compounds and subjected to mechanical forces, CaC₂ reacts with the aromatic molecules to form new compounds. The energy generated during the grinding or milling process promotes the reaction, leading to the formation of GY materials. Cui et al. presented a gram-scale mechanochemical route to convert benzene into GY through employing benzene and CaC₂ as the reactants in a solid–liquid interfacial system (**Fig. 10a**) [88]. GY was synthesized via a controlled mechanochemical process. A mixture of benzene, CaC₂, ethanol, and stainless-steel balls was milled in a planetary mill (600 rpm, 8 h; then 450 rpm, 8 h) under insulating conditions with intermittent operation to limit heat buildup. The product was annealed at 260 °C under N₂ to enhance crystallinity, followed by two-step acid washing and ultrasonic treatment to remove impurities, yielding purified GY powder.

The functional properties of GY for energy

technologies can be strategically augmented via substitutional doping, with N atom serving as a particularly efficacious heteroatom that concurrently modulates the electronic band structure, surface hydrophilicity, and charge-transfer kinetics of the host lattice. This doping-induced electronic perturbation not only facilitates electron transport and redox activity but also expands the electrochemically accessible surface area and improves interfacial compatibility with aqueous electrolytes. As a compelling case in point, Ding, Anandan, and their research team reported a mechanochemical route to N-GY—proceeding via a single-step ball-milling of CaC₂ with pyrazine—that enables the selective incorporation of nitrogen at well-defined crystallographic positions within the γ -GY framework, as evidenced by structural and spectroscopic analyses (**Fig. 10b**) [89]. A plausible nucleophilic substitution mechanism was proposed to illustrate the preparation of N-GY (**Fig. 10c**): Firstly, ball milling promotes thorough and intimate contact between the reactants due to the reduced particle size and strong mechanical forces. This ensures efficient mixing of CaC₂ and pyrazine. Additionally, the high energy generated during ball milling facilitates the reaction

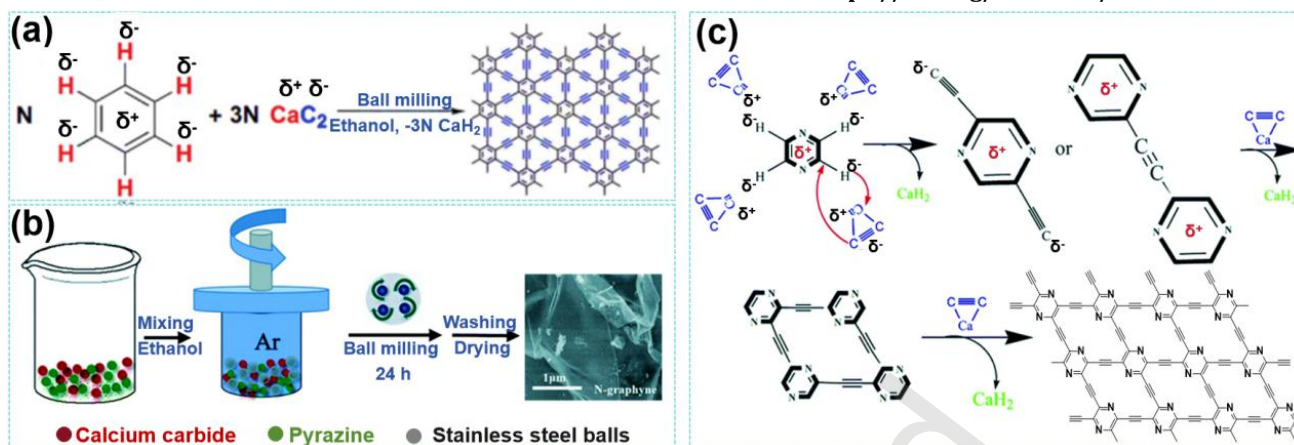


Figure 10 (a) The proposed mechanochemical synthesis pathway between CaC₂ and benzene. Reprinted with permission from ref. [88], © 2019 The Author(s). Published by the Royal Society of Chemistry. (b) Schematic illustration of the fabrication of N-GY. (c) A plausible mechanism for the preparation of N-GY. Reprinted with permission from ref. [89], © 2020 The Author(s). Published by the Royal Society of Chemistry.

between CaC₂ and pyrazine. It is shown that the alkyne groups formed from CaC₂ carry negative charges and can act as nucleophiles. Since the electron-withdrawing propensity of nitrogen, whose Pauling electronegativity (3.04) is appreciably higher than that of carbon, the $\text{--C}\equiv\text{C--}$ groups target the C atoms with positive charges in the pyrazine ring rather than the N atoms. As a result, the H atoms on pyrazine are substituted by $\text{--C}\equiv\text{C--}$, leading to the formation of C–C bonds. Overall, the synthesis of N-GY using CaC₂ and pyrazine through ball milling is a highly effective and innovative approach. The ball milling process ensures optimal mixing and provides the necessary energy for the reaction to occur.

3.2 Transition Metal(TM)-Catalyzed Cross-Coupling Polymerization

The TM-catalyzed cross-coupling polymerization method involves the coupling of two specific functional groups within one or two molecules to form a larger and more intricate GY structure (Fig. 6b). This method relies on the reactivity of these functional groups, which can undergo various coupling reactions, such as Sonogashira–Hagihara, Stille, or cyclotrimerization reactions, offering the capability to dictate not only the site-specific attachment but also the stereoelectronic orientation of the incorporated functional entities, leading to the creation of highly tailored structures. By carefully selecting the appropriate coupling partners and reaction conditions, remarkable transformations can be achieved, enabling the construction of molecules with desired properties. This approach can be further divided into intramolecular and intermolecular coupling reactions.

3.2.1 Intramolecular coupling reaction

Intramolecular coupling reactions are widely employed techniques that involve bringing two functional groups within the same molecule together, resulting in the

formation of a covalent bond. This reaction is particularly advantageous because it is most effective when the two functional groups are in close proximity, allowing for a more efficient and precise coupling process. To fully understand the unique properties of this reaction, it is crucial to synthesize large-size atomically precise GY fragments. By doing so, we can further explore the distinguishing characteristics that set GY apart from other materials. Wu and his team reported the construction of a 6-fold symmetric GY spoked wheel via a palladium(0)-catalyzed cyclotrimerization of a triyne intermediate, followed by a 12-fold intramolecular Stille coupling manifold (Fig. 11a) [94]. The synthetic strategy hinges on a star-shaped hexayne core, which is conventionally prepared via 6-fold Sonogashira or Negishi coupling of hexabromobenzene—a route that is frequently plagued by competitive debromination due to steric congestion.

The long-standing challenge of bulk γ -GDY synthesis was overcome by Rodionov, Baughman, and colleagues, who reported the first multilayer γ -GDY via crystallization-assisted irreversible cross-coupling polymerization. Their method uses the A₃B₃ monomer TBTEB (1,3,5-tribromo-2,4,6-triethynylbenzene) under optimized Sonogashira conditions to achieve exhaustive coupling into an extended graphyne framework. The resulting crystals are semiconducting ($E_g = 0.48$ eV) with a hexagonal lattice ($a = 6.88$ Å) and interlayer spacing of 3.48 Å (Fig. 11b) [95]. The synthesis strategy circumvents the kinetic trap of partially connected intermediates in 2D polymerization by promoting rapid, irreversible multisite coupling. Strained or mismatched sites exhibit enhanced reactivity and are preferentially corrected through further coupling, enabling formation of periodic 2D sheets rather than disordered networks.

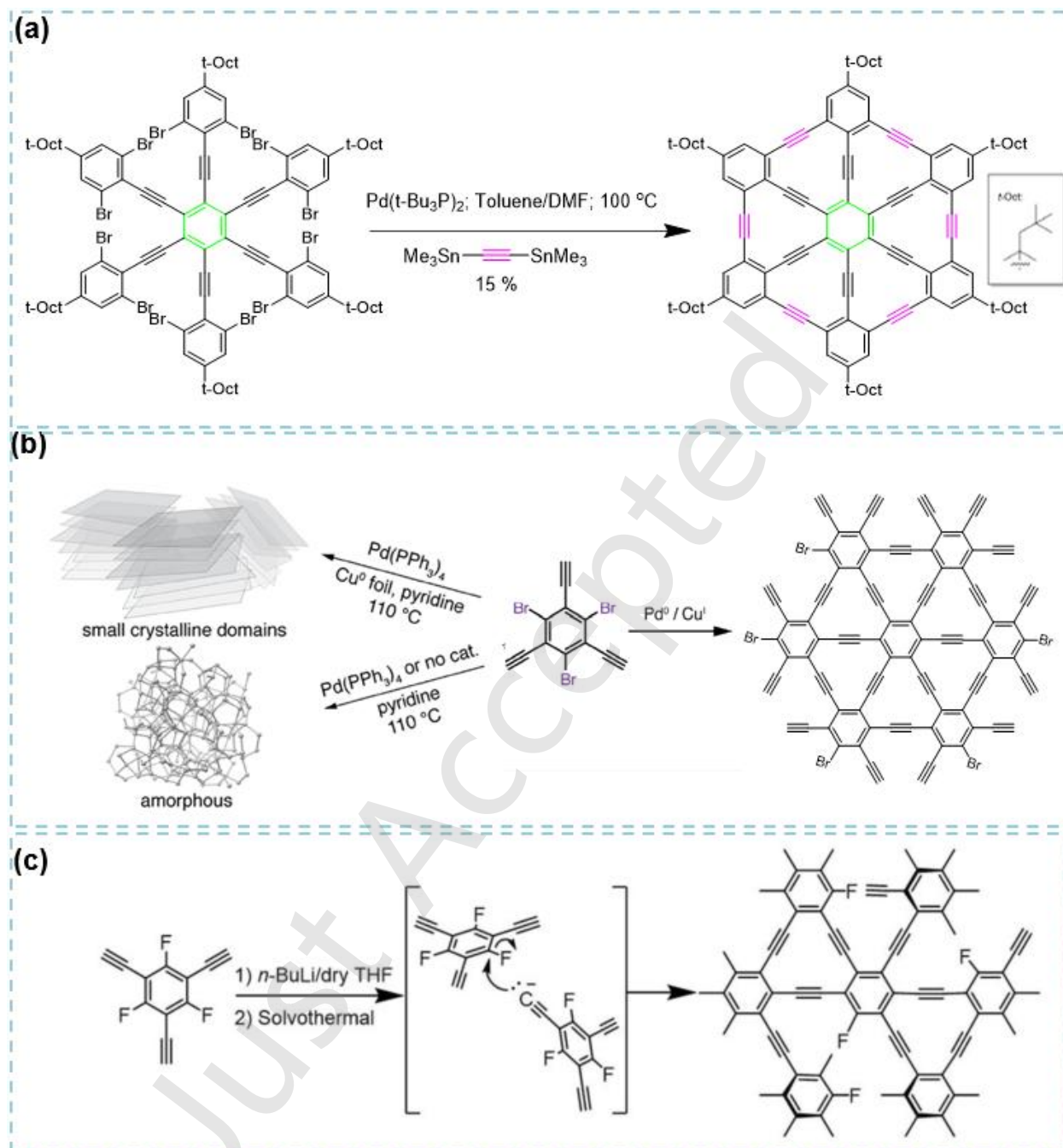


Figure 11 (a) Synthesis of the GY spoke wheel. Reprinted with permission from ref. [94], © 2022 Elsevier Inc. (b) Overview of selected reaction conditions for GY. Reprinted with permission from ref. [95], © 2022 American Chemical Society. (c) The synthetic scheme of γ -G1. Reprinted with permission from ref. [96], © 2021 Wiley-VCH.

These principles extend to fluorinated analogues: electron-withdrawing F activates aryl C–F bonds toward nucleophilic attack, enabling metal-free solvothermal synthesis via aromatic nucleophilic substitution (S_{NAr}) of deprotonated 1,3,5-triethynyl-2,4,6-trifluorobenzene (**Fig. 11c**) [96]. Additionally, unreacted alkynyl groups in the synthesized GY allow post-synthetic functionalization via click chemistry. As a proof of concept, two functional materials (γ -G1-Fc and

γ -G1-TMS) were prepared using 1,2,3-triazole linkages formed from dicyclopentadiazide and trimethylsilyl azide. This approach demonstrates the potential of click chemistry for introducing diverse functionalities onto GY, expanding its application scope.

Large-scale synthesis of GY remains a key challenge. Duan et al. first prepared 1,3,5-triethynylbenzene (and its trifluoro analogue), converted it to carbanions using *n*-butyllithium (**Fig. 12a**) [97], and induced

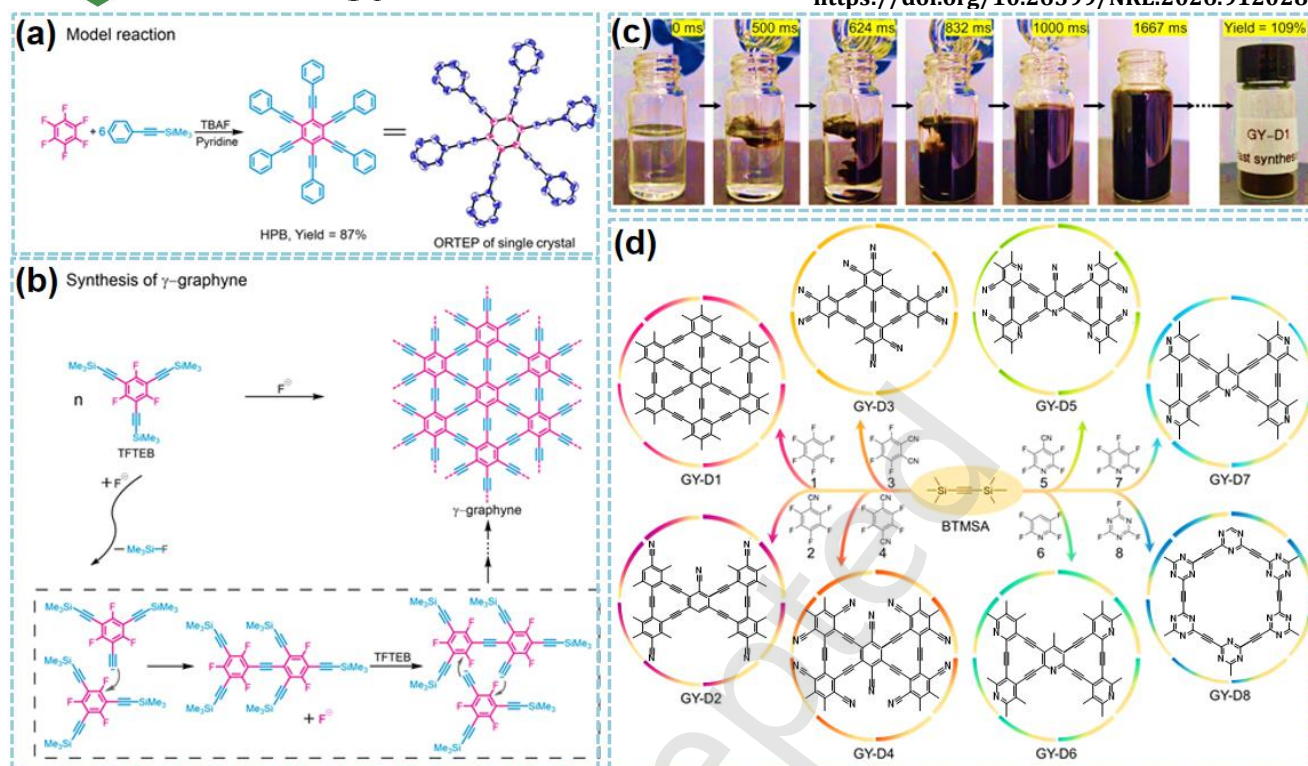


Figure 12 (a) Model reaction scheme for the synthesis of HPB along with its crystal structure. Thermal ellipsoids are set at 75% and all hydrogen atoms are omitted in ORTEP representation; (b) Proposed reaction pathway for the preparation of GY from TFTEB; (c) Rapid synthesis and characterization of GY-D1; (d) Synthesis of GY derivatives. Extension of the nucleophilic crosslinking strategy for the construction of GY derivatives. The structures in the colored circles represent the ideal configurations of GY derivatives. Reprinted with permission from ref. [97], © 2024 The Authors, Wiley-VCH.

nucleophilic substitution via solvothermal treatment to form GY (**Fig. 12b**). An unexpected discovery showed that TMS-protected terminal alkynes, after fluoride-mediated deprotection, could react with fluorobenzene in solution, enabling a wet-chemical, metal-free route to GY via S_{NAr} . To improve structural regularity, the group designed a C_3 -symmetric self-crosslinking monomer, 1,3,5-trifluoro-2,4,6-tri[2-(trimethylsilyl)ethyl]benzene. Optimized polymerization yielded GY with a C/F ratio of 40.00, implying ~ 1 residual F per three benzene rings, preferentially at layer edges. Gram-scale synthesis (up to 16.5 g) confirmed the scalability of this self-crosslinking strategy. Because S_{NAr} is concentration-dependent, rapid synthesis of fluorine-containing amorphous GY derivatives is possible at the expense of structural regularity. Adding a concentrated bis(trimethylsilyl)acetylene/tetra-*n*-butylammonium fluoride (BTMSA/TBAF) pyridine solution triggers nearly instantaneous cross-coupling, as captured within 2 s (**Fig. 12c**). Extending this approach, diverse GY derivatives were prepared directly from commercial fluoro-(hetero)arenes and BTMSA (**Fig. 12d**), enabling facile functionalization and reduced cost. This metal-free, solution-based cross-linking strategy makes GY and its derivatives readily accessible, accelerating their application exploration.

3.2.2 Intermolecular coupling reaction

Another commonly used method for arylene coupling is intermolecular coupling reaction, which involves combining two different functional groups from separate molecules. These reactions are essential for creating complex GY structures because they allow for the incorporation of diverse functional groups. Moreover, intermolecular coupling reactions provide a multitude of possibilities as various combinations of functional groups can be employed. Huang et al. introduced intermolecular coupling reactions at the liquid/liquid interface for the synthesis of DY derivatives, including H-GY, Me-GY, and F-GY (**Fig. 13a**) [98]. The resulting GY products display unique skeletal structures and a gauze-like fibrous morphology at the micrometer scale. Although the synthetic routes for H-GY, Me-GY, and F-GY are closely related, they differ only in the substituents on the starting precursors. Using H-GY as an example, 1,3,5-triacetylenylbenzene is dissolved in CH_2Cl_2 with water forming the aqueous phase. An aqueous solution of $Pd(PPh_3)_2Cl_2$, CuI, and 1,3,5-tribromobenzene is added dropwise, maintaining stability at the H_2O/CH_2Cl_2 interface. Monomers diffuse to the interface and undergo coupling to form H-GY, a benzene network linked by acetylenic bonds, with uniform morphology. Me-GY and

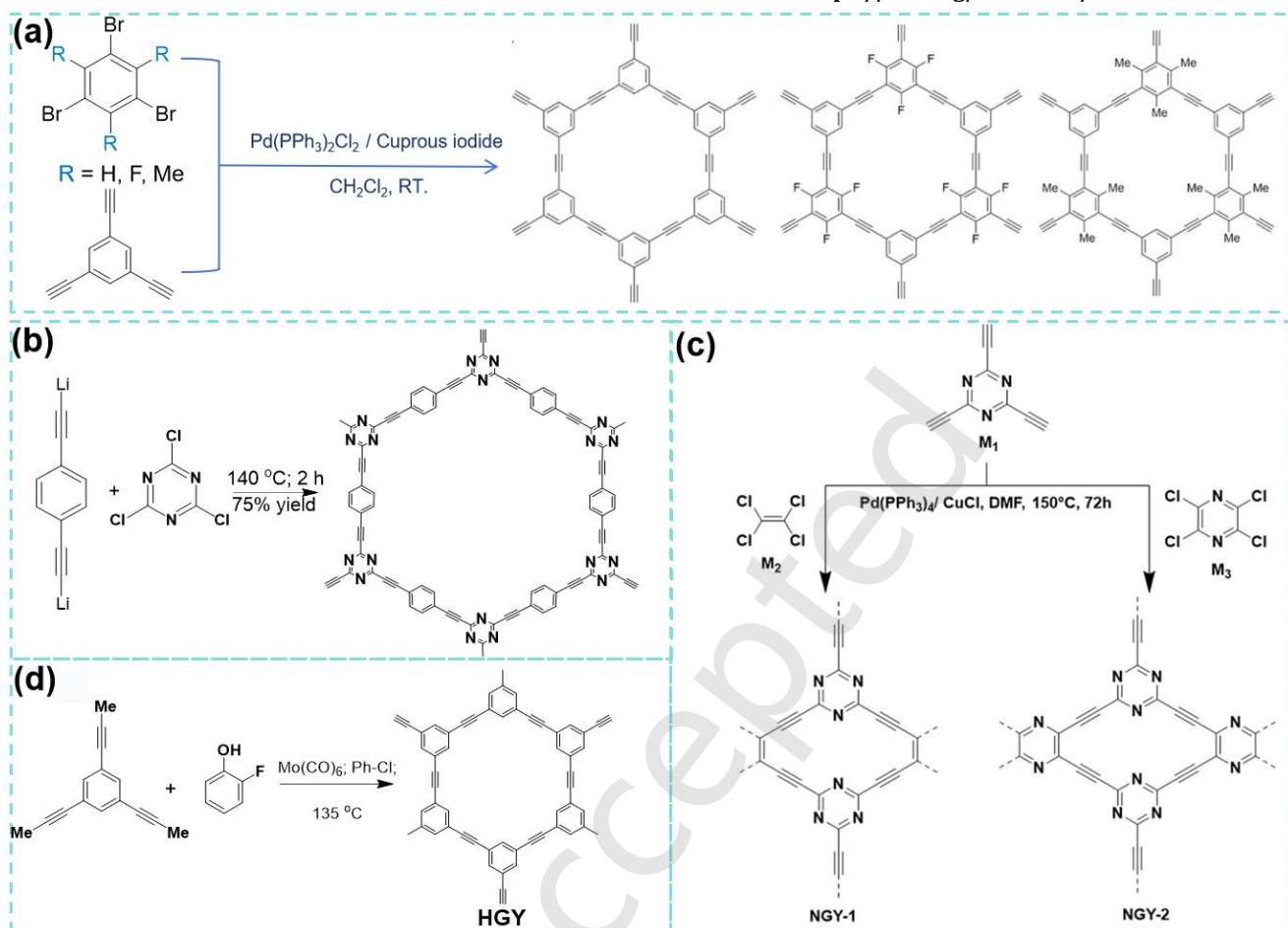


Figure 13 (a) Schematic illustration of the facile interfacial synthetic method. Reprinted with permission from ref. [98] © 2019 Royal Society of Chemistry. (b) Synthesis of TA-BGY. Reprinted with permission from ref. [99], © 2019 Wiley-VCH. (c) Preparation route of N-GY-1 and N-GY-2. Reprinted with permission from ref. [100], © 2022 Elsevier B.V. (d) Schematic illustration of the experimental setup for the HG-Y synthesis through alkyne metathesis reaction. Reprinted with permission from ref. [101], © 2019 WILEY-VCH.

F-GY are prepared analogously using 1,3,5-trimethylbenzene and 1,3,5-trifluorobenzene, respectively. Wen et al. achieved gram-scale synthesis of TA-BGY, a triazine-based GY analogue, via S_{NAr} between cyanuric chloride and the dilithium salt of 1,4-diethynylbenzene in diglyme. A test reaction with phenylethynyl lithium yielded 2,4,6-tris(phenylethynyl)-1,3,5-triazine, validating the approach before scaling to TA-BGY.

Wen et al. also developed a Pd/Cu-catalyzed Sonogashira–Hagihara coupling to construct N-substituted GYs (PY-GY, PM-GY, TA-GY) from halogenated and ethynylated azaarenes (**Fig. 13b**) [99]. By tuning nitrogen content in the precursors, they adjusted the band gaps of the resulting highly π -conjugated frameworks. The catalytic cycle involves oxidative addition of aryl bromide to Pd(0), Cu-mediated alkyne deprotonation, transmetalation, and reductive elimination to form C–C bonds while leaving aromatic C–H bonds intact. Xu, Ren, and colleagues directly synthesized N-doped graphynes (NGY-1 and NGY-2) via cross-coupling

copolymerization of multi-acetylene and polyhalide monomers (**Fig. 13c**) [100]. These N-enriched 2D porous materials, composed of sp^2 C/N and sp -C, are insoluble and chemically robust. Post-synthesis carbonization at 800 °C under N_2 yielded N-GY-1-800 and N-GY-2-800 with enhanced mechanical and thermal stability for energy storage. Overall, arylene cross-coupling offers a versatile route to complex GY architectures with precise structural control.

3.3 Metal-Free Nucleophilic Aromatic Substitution (S_{NAr})

The metal-free nucleophilic aromatic substitution (S_{NAr}) method has recently emerged as a scalable and environmentally benign route to GY and its derivatives. This approach exploits the activation of aryl C–F bonds toward nucleophilic attack by electron-withdrawing substituents (e.g., F, CF_3), enabling coupling without noble-metal catalysts. These principles extend to fluorinated analogues: electron-withdrawing F activates aryl C–F bonds toward nucleophilic attack, enabling metal-free solvothermal synthesis via S_{NAr} of

deprotonated 1,3,5-triethynyl-2,4,6-trifluorobenzene (**Fig. 11c**) [96]. Additionally, unreacted alkynyl groups in the synthesized GY allow post-synthetic functionalization via click chemistry. As a proof of concept, two functional materials (γ -G1-Fc and γ -G1-TMS) were prepared using 1,2,3-triazole linkages formed from dicyclopentadiazide and trimethylsilyl azide. This approach demonstrates the potential of click chemistry for introducing diverse functionalities onto GY, expanding its application scope.

Large-scale synthesis of GY remains a key challenge. Duan et al. first prepared 1,3,5-triethynylbenzene (and its trifluoro analogue), converted it to carbanions using *n*-butyllithium (**Fig. 12a**) [97], and induced intermolecular nucleophilic substitution via solvothermal treatment to form GY (**Fig. 12b**). An unexpected discovery showed that TMS-protected terminal alkynes, after fluoride-mediated deprotection, could react with fluorobenzene in solution, enabling a wet-chemical, metal-free route to GY via S_{NAr} . To improve structural regularity, the group designed a C_3 -symmetric self-crosslinking monomer, 1,3,5-trifluoro-2,4,6-tri[2-(trimethylsilyl)ethyl]benzene. Optimized polymerization yielded GY with a C/F ratio of 40.00, implying ~ 1 residual F per three benzene rings, preferentially at layer edges. Gram-scale synthesis (up to 16.5 g) confirmed the scalability of this self-crosslinking strategy. Because S_{NAr} is concentration-dependent, rapid synthesis of fluorine-containing amorphous GY derivatives is possible at the expense of structural regularity. Adding a concentrated BTMSA/TBAF pyridine solution triggers nearly instantaneous cross-coupling, as captured within 2s (**Fig. 12c**). Extending this approach, diverse GY derivatives were prepared directly from commercial fluoro-(hetero)arenes and BTMSA (**Fig. 12d**), enabling facile functionalization and reduced cost. This metal-free, solution-based cross-linking strategy makes GY and its derivatives readily accessible, accelerating their application exploration.

3.4 Dynamic Alkyne Metathesis (Arylene Exchange)

The arylene exchange method is a process that involves the exchange of arylene units between different precursor molecules, followed by the coupling of reaction units (**Fig. 6c**). This method is particularly useful for the modification or functionalization of pre-existing arylene-containing compounds. By selectively replacing specific arylene units, new molecules with altered properties or functionalities can be obtained. Meanwhile, the arylene exchange method offers a rapid and efficient way to introduce structural diversity into organic compounds. It allows for the introduction of different arylene units, such as electron-rich or electron-deficient substituents, and offers a versatile means of tailoring the optoelectronic properties, chemical reactivity, and supramolecular organization of the target architectures. Harnessing this structure-property relationship, the present protocol has been extended to the rational design of conjugated polymers, pharmacologically active

scaffolds, and solution-processable electronic materials.

Constructing acetylenic linkages in GY synthesis remains challenging. Two main strategies are used: cross-coupling and alkyne metathesis. Cross-coupling enables ethynylene-linked polymers but often suffer from dehalogenation side reactions and Pd contamination. Alkyne metathesis, a reversible $C \equiv C$ bond redistribution process, offers error-correcting polymerization but requires precise design of precursors, catalysts, and ligands to control GY topology and thickness. Hexapropynylbenzene (HPB) is an ideal GY precursor but resists metathesis due to steric congestion from six propynyl groups. Reducing the number of propynyl units alleviates this issue. Zhang et al. synthesized hydrogen-substituted GY (HGY) films at a gas-liquid interface using 1,3,5-tripropynylbenzene (TPB) and an in situ Mo-based catalyst from $Mo(CO)_6$ and 2-fluorophenol (**Fig. 13d**) [101]. Volatile 2-butyne generated during metathesis accumulates less at the interface than in bulk, shifting equilibrium toward polymer growth and confining film formation to the interface. The resulting HGY film features a layered, π -conjugated structure with benzenoid cores linked by acetylenic spacers, making it an effective sulfur host for Li-S batteries via both physical confinement and chemical interaction with polysulfides. HGY@S electrodes show high reversible capacity.

3.5 Summary of Synthetic Methods

GY synthesis has advanced through four main methodologies based on bond-forming chemistry: (1) CaC_2 -mediated nucleophilic/mechanocatalytic routes (e.g., ball-milling aryl halides or aromatics with CaC_2) offer scalable, solvent-free, room-temperature synthesis with heteroatom doping capability but yield defective, irregular products; (2) transition metal-catalyzed cross-coupling polymerization (intramolecular cyclotrimerization and Sonogashira-Hagihara cross-coupling) provides structural precision and access to complex doped frameworks but is limited by multi-step sequences, noble-metal catalysts, side reactions, and low scalability; (3) metal-free S_{NAr} offers gram-scale production under mild conditions with low cost but yields amorphous products; (4) dynamic alkyne metathesis enables self-correcting polymerization and high crystallinity but requires sensitive catalysts, inert conditions, and elevated temperatures, hindering scale-up. Emerging methods offer scalable, mild, and rapid alternatives. Balancing precision, defect control, cost, and scalability remains central, with heteroatom doping serving as a key tool for tuning electronic structure and active sites across all routes.

A comprehensive comparison of these synthetic strategies is provided in **Table 4**, which summarizes precursor, catalyst, solvent, temperature, reaction time, isolated yield, production scale, crystallinity/domain size, defect level, residual metal/impurity content, structural evidence, and major limitations for each method.

Table 4 A comprehensive comparison of these synthetic strategies.

Yield / Scale	Temp.	Solvent / Medium	Catalyst	Precursors	Category (Bond-forming chemistry)
Gram-scale (up to several grams per batch)	Room temp. (ball milling); optional post-annealing at 260 °C under N ₂	Solid-state (dry grinding); or solid-liquid (e.g., benzene/ethanol with CaC ₂)	None (mechanical energy from ball milling or ultrasound)	Aryl halides (e.g., PhBr ₆ , C ₄ Br ₄ S, tetrachloropyridine) or aromatics (benzene, pyrazine) + CaC ₂	CaC ₂ -mediated nucleophilic / mechanochemical routes
Milligram to gram-scale; molecular fragments; mg; extended networks; hundreds of mg	Room temp. to reflux (50–100 °C)	Organic solvents (THF, toluene, Et ₃ N, DMF); or liquid-liquid interfaces (H ₂ O/CH ₂ Cl ₂)	Pd(0)/Pd(II) + CuI (co-catalyst); phosphine ligands (e.g., PPh ₃)	Halogenated arenes (e.g., TBTEB, 1,3,5-tribromobenzene) + terminal alkynes (e.g., triethynylbenzene) or organostannanes; or self-coupling triynes	Transition-metal-catalyzed cross-coupling polymerization
Gram-scale (reported up to 16.5 g per batch)	Room temp. to solvothermal (~150 °C)	Polar aprotic solvents (THF, pyridine, diglyme)	None (base: n-BuLi, TBAF, or K ₂ CO ₃)	Fluoroarenes with electron-withdrawing groups (e.g., 1,3,5-trifluoro-2,4,6-triethynylbenzene)	Metal-free nucleophilic aromatic substitution
Thin films (interface); bulk powder (mg scale); scalable synthesis limited	Room temp. to moderate heating (40–80 °C)	Organic solvents (toluene, CH ₂ Cl ₂); or gas-liquid interfaces	Mo- or W-based catalysts (e.g., Mo(CO) ₆ + 2-fluorophenol, or Schrock-type alkylidyne complexes)	1,3,5-tripropynylbenzene (TPB) or hexapropynylbenzene (HPB) derivatives	Dynamic alkyne metathesis

Cost	Structural evidence	Residual metals	Defect level	Crystallinity
Low (CaC ₂ and halogenated arenes (inexpensive bulk chemicals); post-treatment purification (acid washing))	XRD (broad peaks matching calculated lattice), Raman (sp/sp ² bands), XPS (C-C, C≡C), FTIR (C≡C stretch)	CaBr ₂ / CaCl ₂ by-products; residual unreacted CaC ₂ ; carbonaceous impurities (e.g., amorphous carbon)	High ($I_{10}/I_G = 0.76-1.08$); abundant structural defects, vacancies, and grain boundaries	Low; typically amorphous or poorly ordered; occasional short-range stacking ($d \sim 0.36$ nm)
High (Noble metal catalysts (Pd, typically 0.5–5 wt% residual); CuI co-catalyst; expensive organic solvents; multi-step monomer synthesis)	NMR (¹ H, ¹³ C), MALDI-TOF (fragments), XRD (for stacked layers), TEM/SAED	Residual Pd (typically 0.5–5 wt%) and Cu impurities; ligand residues	Moderate; side reactions (e.g., dehalogenation, Glaser coupling) introduce defects and irregular connections	Moderate to high for molecular fragments (well-defined single-crystal structures); low to moderate for extended networks (polycrystalline or poorly ordered)
Medium low (Fluoroarenes and BTMSA (commercially available); TBAF (catalytic amount); no noble metals)	XRD (broad halo), XPS (C-F, C-C, C≡C), FTIR, solid-state NMR, elemental analysis (C/F ratio)	Residual fluoride / triflate salts; unreacted starting materials; TMS-derived by-products	Moderate to high; incomplete substitution (residual F ~1 per 3 rings at edges); structural irregularities	Low to moderate; predominantly amorphous or glassy; limited long-range order
Very high (Air-/moisture-sensitive Mo/W catalysts (expensive and scarce); stringent inert-atmosphere equipment; complex monomer synthesis; low yield)	SAED (sharp diffraction spots), HRTEM (clear lattice fringes), XRD (sharp peaks), Raman (sharp sp/sp ² bands)	Residual Mo/W metals (typically <1 wt%); catalyst decomposition products; volatile alkyne by-products (2-butyne)	Low (error-correcting polymerization); self-repair of mismatched connections yields fewer defects	High (thermodynamically controlled); well-defined hexagonal lattice ($a = 6.88$ Å); interlayer spacing ~ 3.48 Å

Major limitations	Environmental Impact
Poor structural regularity; difficult to remove impurities; product identity controversial	Low – Solvent- free or minimal solvent; room- temperature operation; no noble metals; byproducts are inorganic salts (CaX ₂)
Multi- step synthesis; expensive noble- metal catalysts; metal contamination; limited scalability; side reactions (dehalogenation, alkyne homo- coupling)	High – Heavy metal (Pd, Cu) contamination; large volumes of organic waste; side reactions reduce atom economy
Amorphous products with limited crystallinity; requires strict exclusion of moisture/oxygen for sensitive bases; structural uniformity difficult to control	Low-Medium – No heavy metals; mild conditions; organic solvents used but in moderate amounts; metal- free process
Air- and moisture- sensitive catalysts; stringent inert- atmosphere conditions; expensive and scarce catalyst metals; limited substrate scope (sterically hindered precursors react poorly); challenging scalability	High – Heavy metal (Mo/W) residues; organic solvents; low atom economy (volatile 2- butyne byproduct); high energy demand

4. Composition Characterization

4.1 Raman spectroscopy

Raman spectroscopy reveals vibrational modes, structural defects, and the presence of alkyne bonds in GY materials [79,102]. This technique has proven particularly useful in studying the phonon behavior and electronic properties of GY materials. **Fig. 14a** shows the original Raman spectrum of GY synthesized by mechanochemistry, smoothed by a Fast Fourier Transform filter, in which two main peaks can be seen [56]. The G-band at approximately 1583 cm⁻¹ is due to the stretching vibration of the C-*sp*² from the benzene rings. The D-band evaluates the defects and disorder in the carbon matrix. Two other weak bands at around 2095 cm⁻¹ and 2250 cm⁻¹ are due to the vibration of C-*sp*. These characteristic peaks help confirm the co-presence of C-*sp* and C-*sp*², further qualitatively identifying the presence of GY. Additionally, the intensity ratio of D and G bands (*I*_D/*I*_G) reflects the graphitization defect of carbon materials in GY. For example, using CaC₂ and C₆Br₆ as raw materials, Cui et al. synthesized GY by sequential ball milling and calcination processes (**Figure 14b**) [103]. The *I*_D/*I*_G ratios of the intermediate products after ball milling and the final samples after calcination are 1.08 and 0.76, respectively. The higher *I*_D/*I*_G ratio provides good evidence that the calcination process has facilitated the self-coupling of the intermediates.

4.2 X-ray photoelectron spectroscopy

XPS characterizes the surface chemistry and elemental composition of GY materials, identifying element types and their chemical states [104,105]. This information is

crucial for understanding the surface reactivity and stability of GY materials. It is usually corrected by the Shirley background and fitted with a combination of Lorentzian and Gaussian functions [106]. From the XPS survey spectrum of GY (**Fig. 14c**) [56], the peak at around 284.8 eV is classified as the C 1s orbital, and the one at around 532.0 eV is classified as the O 1s orbital. The molar ratios of C and O elements were calculated as 87.6% and 12.4%, respectively. Some terminal alkynes are inevitably oxidized due to their porous air adsorption network, which explains why traces of O are found. The core level C 1s peak, which can be divided into four sub-peaks, was then scanned more narrowly to provide further information. The binding energies of 284.2, 284.9, 286.3 and 287.1 eV are labelled C=C (*sp*²), C≡C (*sp*), C–O (*sp*) and C=O (*sp*²), respectively. No C-*sp*³ was observed, indicating that the as-prepared GY consisted only of *sp-sp*² hybridization carbon. Based on peak area fitting, a relative area ratio of *sp/sp*² hybrid carbon atoms of about 1 was calculated. This confirms that a benzene ring carbon network structure is linked by an acetylene group, which is in good agreement with the theoretical structure of GY. In addition, XPS has another important function of characterizing the doping information of heteroatoms in GY. Compared to GY, the survey scanning spectrum of N-doped GY revealed N atoms. **Fig. 14d** shows the high-resolution asymmetric C 1s XPS spectra [86]. They can be classified as C=C (*sp*² hybridized carbon atoms, 284.2 eV), C–C (*sp* hybridized carbon atoms, 285.1 eV), C=N (286 eV), C–O (286.7 eV), and C=O (289.3 eV), respectively. The area ratio of *sp/sp*² carbon atoms is 0.91, which is slightly lower than that of the formal GY of 1.00.

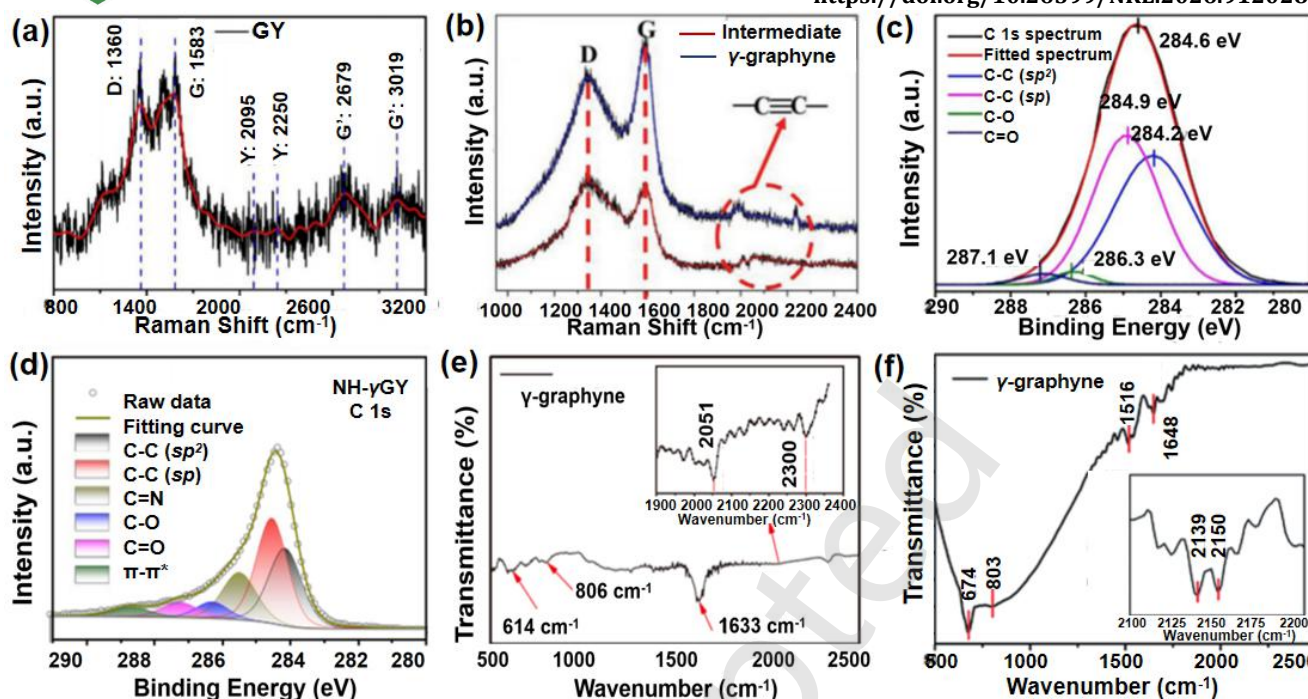


Figure 14 (a) Raman spectrum of the γ -GY. Reprinted with permission from ref. [56], © 2018 Elsevier Ltd.. (b) Raman spectrum of γ -GY. Reprinted with permission from ref. [103], © 2019 WILEY-VCH Verlag GmbH. (c) High-resolution C 1s core-level XPS spectrum of γ -GY. Reprinted with permission from ref. [56], © 2018 Elsevier Ltd.. (d) C 1s core-level high-resolution spectra of dihydrogen-substituted N/H-substituted γ -GY (NH- γ -GY). Reprinted with permission from ref. [86], © 2024 Elsevier B.V. (e) FT-IR spectra of γ -GY. Reprinted with permission from ref. [70], © American Chemical Society. (f) FT-IR spectrum of γ -GY. Reprinted with permission from ref. [88], © 2020 WILEY-VCH Verlag GmbH.

This may be due to the structural defect caused by N doping. Overall, the method of doping with nitrogen heteroatoms influences the distribution of electrons and the adsorption of metals on N-GY.

4.3 Fourier transform infrared spectroscopy

Fourier transform infrared spectroscopy (FTIR) spectroscopy can determine the functional groups of unknown substances, determine chemical structures, observe chemical reaction processes, distinguish isomers, and analyze the purity of substances [107-109]. Sun et al. used an ultrasound-promoted method to fabricate GY using PhBr_6 and CaC_2 as raw materials. In the FTIR spectroscopy of **Fig. 14e**, three primary peaks stand out, situated at around 614 cm^{-1} , 806 cm^{-1} , and 1633 cm^{-1} , respectively [70]. The former pair of peaks are linked to the flexing vibrations of the acetylenyl group and aromatic ring, while the robust peak at 1633 cm^{-1} is a result of the characteristic skeleton vibration of the aromatic ring. The zoomed-in section from 2000 cm^{-1} to 2300 cm^{-1} in the inset of **Fig. 14e** reveals two faint peaks at 2051 cm^{-1} and 2300 cm^{-1} , attributed to the ethynyl stretching vibrations. The ethynyl stretching vibrations in the produced GY seem muffled as a result of the compound's symmetrical molecular arrangement. When the acetylenyl group is symmetrically replaced, it typically does not exhibit strong signals in the FTIR spectra. Cui et al. reported the synthesis of GY using benzene as a precursor through a mechanical ball milling method. The as-prepared GY's

FT-IR spectrum is showcased in **Fig. 14f** [88]. The peaks detected at 674 and 803 cm^{-1} correspond to the flexing movement of ethynyl and the aromatic circle, respectively, which aligns with the findings from the Raman spectrum. While the characteristic skeletal vibrations of the aromatic circle (1516 and 1648 cm^{-1}) were evident, the ethynyl's stretching vibrations (2139 and 2150 cm^{-1}) appeared weak. This potentially indicates the sample's molecular structure possesses strong symmetry properties, as symmetrically substituted ethynyl fails to register a signal in the FTIR spectrum. Overall, the FTIR spectrum of GY is illustrated to offer a rough estimate of the functional groups and bonding situation.

4.4 Nuclear magnetic resonance

NMR spectroscopy has been utilized to investigate the atomic-level structure and dynamics of GY materials. By measuring the interaction between the nuclear spins and an external magnetic field, researchers can obtain valuable information about the chemical bonding, molecular conformation, and surface functionalization of these materials [110-112]. The NMR spectra are powerful tools for analyzing the structural information of different carbon species and verifying the formation of GY. There are two main types of spectra: ^{13}C NMR and ^1H NMR. However, due to the extreme demands placed on the equipment, it is not as widely used as other characterization methods. Four typical ^{13}C NMR peaks can be observed, some of which are weak due to their high

conductivity but can be distinguished [98]. The obvious signals around 140 and 100 ppm are attributed to aromatic carbons and alkyne carbons, respectively. The relatively weak peaks at 20 and 75 ppm come from the residual hexylphenylacetylene end groups. The above results suggest the formation of GY with $sp-sp^2$ hybridized carbon. Cui et al. further used ^1H NMR spectroscopy to investigate the hydrogen content and verify the formation of HGY. The ^1H NMR spectrum shows only one single peak with a chemical shift of 8.88, indicating the presence of only one H chemical environment in HGY [103]. In other words, there is no H on the adjacent carbon atoms of the H-connected carbon atoms, which is consistent with the structural formula of H-substituted graphene. In a nutshell, ^{13}C NMR and ^1H NMR spectra can be used to identify the types of carbon species present in GY materials. It is noted that the NMR signal is weak for conductive GY materials.

4.5 Additional characterizations

In addition to the techniques listed, several other advanced characterization methods provide valuable insights into the structure and properties of GY. Scanning Electron Microscopy (SEM) offers high-resolution images of the surface morphology of GY samples [113]. By scanning the GY sample with a focused electron beam, SEM can provide information on surface topography, particle size, and overall sample uniformity. This technique is essential for evaluating the surface features and dispersion of GY in composite materials or films. Transmission Electron Microscopy (TEM) is a powerful tool for examining the atomic-scale structure of GY [114]. By transmitting electrons through ultra-thin samples, TEM can provide high-resolution images that reveal the detailed arrangement of carbon atoms, interlayer distances, and any structural defects or grain boundaries present in the GY material. This technique is particularly useful for visualizing the lattice structure and confirming the presence of the unique acetylenic linkages characteristic of GY. Thermogravimetric analysis is used to assess the thermal stability and decomposition behavior of GY [115]. By measuring the weight loss of a sample as it is heated, TGA provides information on the thermal degradation temperature and stability under various conditions. This technique helps in understanding the GY material's thermal properties and evaluating its potential applications in high-temperature environments. Electron energy loss spectroscopy (EELS) complements TEM by providing information about the electronic structure of GY [116,117]. By analyzing the energy lost by electrons as they pass through the GY sample, EELS can reveal details about the electronic band structure, bonding characteristics, and elemental composition. This technique is valuable for understanding the electronic and optical properties of GY. Photoelectron spectroscopy (PES) is used to investigate the electronic structure and chemical environment of GY [118]. By measuring the kinetic energy of photoelectrons emitted from the surface

of the GY sample, PES provides information on the binding energies of core-level electrons, which can be used to analyze the electronic states and chemical composition of GY. This technique is particularly useful for studying the interactions between GY and other molecules or functional groups.

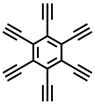
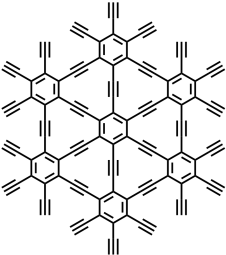
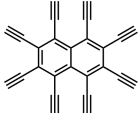
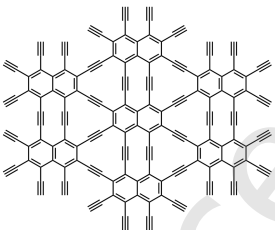
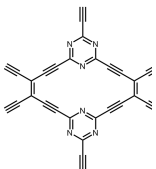
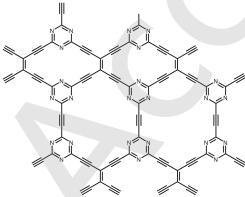
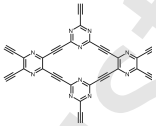
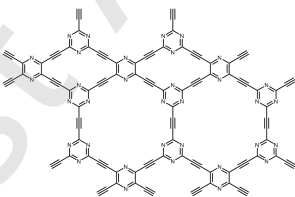
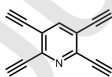
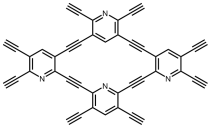
In conclusion, the characterization methods discussed above have greatly contributed to our understanding of the structure-activity relationship of GY materials. These additional techniques offer complementary insights into the structural and chemical properties of GYs, enhancing our understanding of their behavior and potential applications in various fields. By employing these techniques, researchers have been able to gain valuable insights into the crystal structure, surface chemistry, vibrational modes, and mechanical properties of these materials. This knowledge is crucial for optimizing the synthesis methods, tailoring the properties, and exploring the potential applications of GY materials in various fields such as catalysis, energy storage, and biomedical applications.

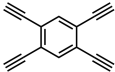
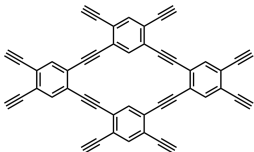
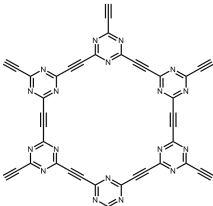
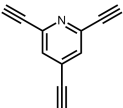
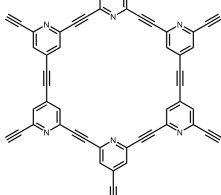
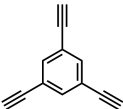
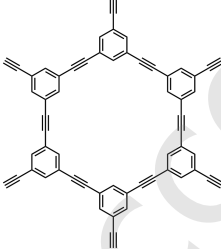
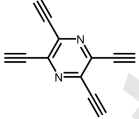
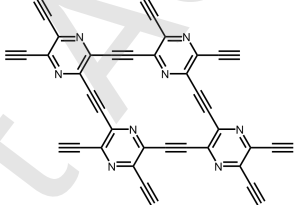
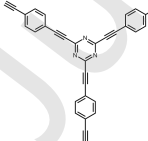
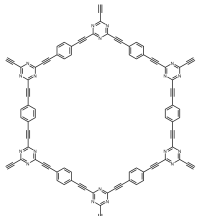
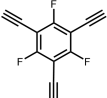
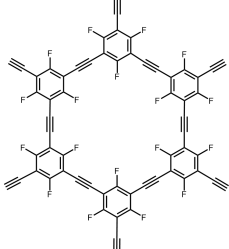
5. Multifunctional applications

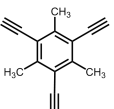
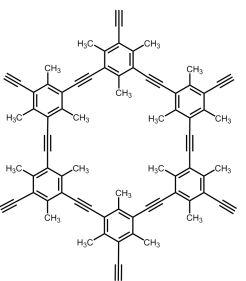
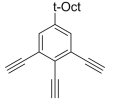
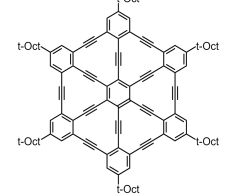
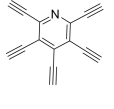
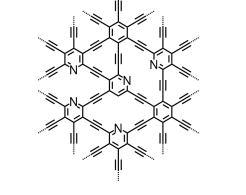
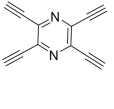
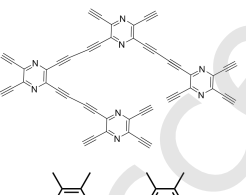
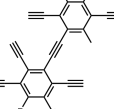
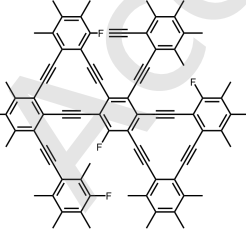
The development of nanostructure with highly tunable band gap nanostructures is of paramount importance for diverse applications. This review meticulously details the extensive research conducted on the applications of γ -GY, with a primary emphasis on environmental remediation, hydrogen production and storage, oxygen evolution reaction (OER) and oxygen reduction reaction (ORR), electrochemical energy storage, biomedicine, and nanoelectronics (Table 5). Compared to other carbon-based nanomaterials, GY has the following structural characteristics: (1) Linked by highly conjugated planar structures, GY possesses the merits of a large surface area and optimized pore structure, providing short diffusion paths and enhanced ion transport; (2) The interlayer distance of GY, measuring at 0.36–0.38 nm, surpasses that of graphite (0.335 nm). The large interlayer spacing of GY (0.35–0.49 nm) is particularly advantageous for fast-charging batteries, as it significantly lowers the energy barrier for metal-ion diffusion. Meanwhile, the acetylenic linkages ($-\text{C}\equiv\text{C}-$) that bridge the benzene rings impart intrinsic semiconducting properties to the GY lattice. The material's high electron density and strong electron-donating character, which have led to its nickname "electron sponge," give rise to both high mobility and a broadly tunable band gap spanning from 0.46 to 2.23 eV; (4) The alkynyl group exhibits higher reactivity compared to the aromatic ring and allows for easier chemical modifications to achieve higher selectivity. Additionally, the tubular distribution of the π electron cloud around the $\text{C}\equiv\text{C}$ bond enables π - π interactions with polycyclic aromatic sulfur heterocycles (PASHs) in various directions, enhancing their overall compatibility. These unique advantages endow GY with tremendous potential for applications in recent years, and

the following chapter of this review will center on its potential usage in the following applications, including (1) supercapacitors, (2) lithium/sodium/potassium-ion batteries, (3) photo-/electro-catalysis, and (4) nonlinear optics.

Table 5 Representative GYs in multifunctional applications

Number	Sample	Monomer	GY structure	Preparation	Application	Reference
1	γ -GY			Arylene mechanical-coupling methods	Supercapacitor	[68]
2	NY			Arylene mechanical-coupling methods	Supercapacitor	[79]
3	NGY-1			Arylene cross-coupling methods Intermolecular-coupling reactions	Supercapacitor	[100]
4	NGY-2			Arylene cross-coupling methods Intermolecular-coupling reactions	Supercapacitor	[100]
5	NH-rGY			Arylene cross-coupling methods	Potassium-ion battery	[86]

6	HH-rGY			Arylene cross-coupling methods	Potassium-ion battery	[83]
7	TA-GY			Arylene mechanical-coupling methods	Lithium-ion battery	[95]
8	PY-GY			Arylene mechanical-coupling methods	Lithium-ion battery	[95]
9	H-GY			Arylene exchange-coupling methods Dynamic alkyne metathesis	Lithium-ion battery	[91]
10	N-GY			Arylene mechanical-coupling methods	Supercapacitor and electrocatalysis	[86]
11	TA-BGY			Arylene exchange-coupling methods	Photocatalysis	[99]
12	F-GY			Arylene exchange-coupling methods Dynamic alkyne metathesis	—	[98]

13	Me-GY			Arylene exchange-coupling methods Dynamic alkyne metathesis	—	[98]
14	A GY spoked wheel			Arylene exchange-coupling methods	—	[94]
15	N1-GDY			Dynamic alkyne metathesis	Photocatalysis	[82]
16	N2-GDY			Dynamic alkyne metathesis	Photocatalysis	[82]
17	γ-G1			Arylene mechanical-coupling methods	—	[82]

5.1 Supercapacitors

Supercapacitors are distinguished by their high-power density and rapid charge-discharge capability [119, 120]. GY, benefiting from its high conductivity, extensive specific surface area, and hierarchical porosity, is an attractive electrode material for electrical double layer capacitance (EDLC) [121]. They are typically manufactured through the electrostatic adsorption of ions onto the surface of active materials, displaying exceptional durability and longevity with millions of recycling cycles. EDLC supercapacitors do not involve any electron exchange or redox reactions, which sets them apart from other types of capacitors [122]. Activated carbon serves as a benchmark material in EDLCs due to its high specific surface area. However, GY offers additional advantages, including intrinsic electrical conductivity and well-defined pore structures for this application. Therefore, the specific surface area directly influences the charge-storage capacity and rate capability of EDLC materials. With its high conductivity, large surface area, thermal stability, and

mesoporous structure, GY stands out as a highly competitive electrode material for supercapacitors. In this section, our main focus will be on GY synthesized through the interaction between PHHCs, polyhalogenated benzene, polyhalogenated naphthalene, N-containing heterocycles, and CaC_2 . These substances exhibit a high specific capacitance within a specific range, making them suitable for use in EDLC supercapacitors.

Li and his research team successfully produced a range of AC materials (ACMs) by utilizing the interfacial mechanochemical reaction between CaC_2 and four commonly found PHHCs, namely CCl_4 (ACM-1), $\text{CCl}_2=\text{CCl}_2$ (ACM-2), C_6Cl_6 (ACM-3), and $\text{C}_6\text{Br}_5\text{CH}_2\text{CH}_2\text{C}_6\text{Br}_5$ (ACM-4) [69]. The four ACMs displayed distinctive characteristics, such as a micro-mesoporous structure, strong graphitization, and prominent presence of *sp*-C. These unique features make them highly suitable for application as active materials in supercapacitors. The CV curves exhibit a near-ideal rectangular shape, signifying

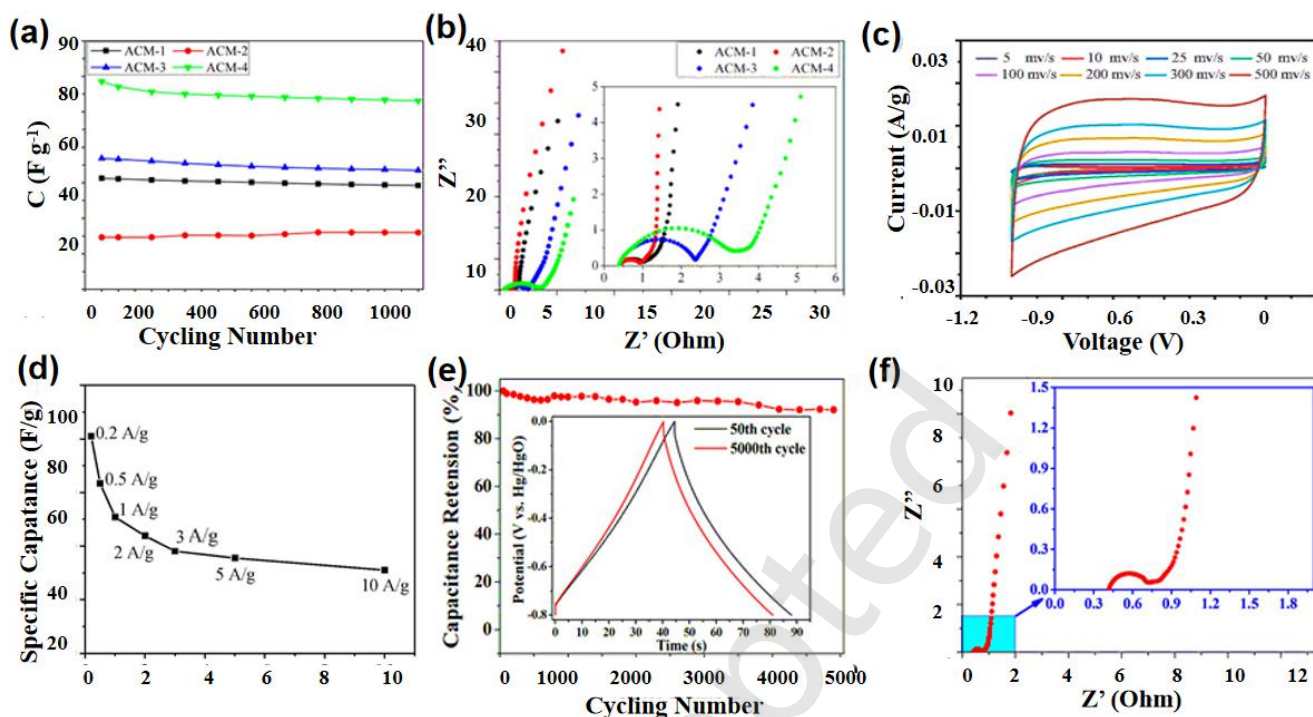


Figure 15 (a) The long-term durability of the ACM electrodes was assessed by galvanostatic cycling at 1 A g⁻¹. (b) The interfacial properties were further investigated by EIS, with the Nyquist plots collected in the frequency interval from 100 kHz to 0.01 Hz under a 5 mV AC voltage. Reprinted with permission from ref. [69], © 2017 American Chemical Society. (c) CV curves recorded over a range of scan rates; and (d) the specific capacitance values of γ-GY measured at current densities from 10 to 0.2 A g⁻¹; the inset shows the capacitance retention at 3 A g⁻¹. Reprinted with permission from ref. [71], © 2018 Elsevier Ltd. (e) Cycling stability of the NY electrode at 2 A g⁻¹, with the inset showing GCD curves at selected cycles. (f) Nyquist plot of the NY electrode acquired from EIS measurements over the frequency range of 100 kHz to 0.01 Hz with an AC amplitude of 5 mV. Reprinted with permission from ref. [79], © 2020 American Chemical Society.

capacitive charge storage with minimal interfacial resistance. Even at a scan rate as high as 30 mV s⁻¹, the electrodes retain a rectangular CV profile, underscoring their outstanding rate performance. The GCD profiles (at 0.1 A g⁻¹) display symmetric triangular shapes, corroborating the capacitive nature of these electrodes. The specific capacitances derived from the GCD curves are 88.7, 56.9, 96.7, and 133.4 F g⁻¹ for ACM-1, ACM-2, ACM-3, and ACM-4, respectively. These results align well with the BET surface area (SBET) values, indicating that the specific surface area plays a crucial role in determining their capacitance performance. Meanwhile, all four ACM electrodes demonstrate remarkable conductivity and CD rates. Particularly, ACM-4 derived from *sp*²-C PHHC exhibits a relatively low equivalent series resistance and a short Warburg region. Additionally, the cyclic stability of the ACM-4 electrode remains excellent, with 93% capacity retained over 1000 cycles at 2 A g⁻¹, as demonstrated in the test results shown in **Fig. 15a**. Moreover, the Nyquist plots of the four ACM electrodes further confirm their outstanding electrochemical performance (**Fig. 15b**). Overall, these four ACM electrodes exhibit high *C_m*, excellent conductivity, impressive rate capability, and cycling stability, making them ideal candidates as active materials for supercapacitors.

Subsequently, Gao and co-workers developed an ultrasound-promoted synthetic route to γ-graphyne using PhBr₆ and CaC₂ as the precursors [71]. The supercapacitor performance characteristics of self-assembled GY were comprehensively investigated through CV and GCD measurements (**Fig. 15c**). Remarkably, the CV curves of GY exhibited a notable absence of redox peaks and polarization phenomena, which provides compelling evidence for the exceptional rate capacity and pseudocapacitive behavior. Even at high scan rates of 300 mV s⁻¹ and 500 mV s⁻¹, GY consistently displayed near-rectangular-shaped CV plots, underscoring its remarkably reversible properties and outstanding rate capabilities. The GCD measurements established the relationship between specific capacitance and discharge current density. GY delivered a maximum specific capacitance of 80 F g⁻¹ at 0.2 A g⁻¹, and retained a capacitance of 31 F g⁻¹ even at a high current density of 10 A g⁻¹ (**Fig. 15d**). Moreover, a capacitance retention of 87.5% was maintained after 5000 charge–discharge cycles at 3 A g⁻¹, with no appreciable morphological degradation. These results collectively confirm the excellent cycling stability of GY as a supercapacitor electrode material.

In addition to the aforementioned two groups of GY,

polyaromatic alkynes introduce a new classification within the alkyne carbon family and hold promising potential as active components in supercapacitors. Li's group achieved the targeted mechanochemical synthesis of naphthalene derivatives from CaC_2 and C_{10}Cl_8 [79]. These derivatives are constructed around a naphthalene core linked through an alkyne-based framework, featuring an extensively conjugated π -system. This unique architecture endows the resulting naphyne (NY) with a high electrical conductivity of 1490 S m^{-1} , making it suitable for high-performance binder-free supercapacitor electrodes. Electrochemical evaluation revealed rectangular CV profiles and symmetric triangular GCD curves, consistent with capacitive charge storage via reversible ion adsorption/desorption. The specific capacitance, determined from GCD measurements at 0.1 A g^{-1} , is 154 F g^{-1} , and remains largely stable with increasing scan rate or current density, confirming the material's superior rate capability. Moreover, after 5000 cycles, the capacitance retention of NY reaches 92.1%, underscoring its exceptional cycling durability and structural integrity (Fig. 15e). The Nyquist curve illustrates that the NY electrode displays near-ideal double-layer capacitance and a low equivalent series resistance (0.42Ω), attributed to the effective electron transfer facilitated by the highly conjugated, well-ordered, and stable carbon framework of NY (Fig. 15f). Collectively, the exceptional electrochemical properties of NY underscore the structural advantages of its alkynyl-linked naphthyl framework and highlight its promise for supercapacitor applications.

5.2 Batteries

GYs represent a family of carbon allotropes distinctive two-dimensional architecture, uniform nanopores, abundant sp -hybridized carbon comprising both sp - and sp^2 -C, and favorable electrochemical properties, GY has emerged as a promising carbon-based material for energy storage applications. Hence, the preparation of GY and its derivatives, exploration of their properties, and development of applications in $\text{Li}^+/\text{Na}^+/\text{K}^+$ batteries hold tremendous potential [122-127]. The extended π - π conjugation within the framework imparts

a highly conjugated skeleton and robust chemical stability. Notably, the large, conjugated rings endow GY with superior Li/Na storage capacity relative to conventional carbon electrodes. Furthermore, the interlayer spacing of GY ($0.36\text{--}0.38 \text{ nm}$) exceeds that of graphite (0.335 nm), facilitating metal-ion diffusion and thereby enhancing battery performance.

5.2.1 Sodium-ion battery

With its plentiful sodium reserves and comparatively wider ion radius (0.102 nm), sodium-ion batteries (SIBs) possess the advantage of not necessitating high energy density [128,129]. This enables the use of low concentration electrolytes and eliminates over-discharge characteristics. Moreover, sodium-ion batteries operate on principles analogous to LIBs, making them well suited for integration into large-scale energy storage devices [130]. Cui and co-workers reported a mechanochemical route to nitrogen-doped graphyne (N-GY) with a distinctive 2D morphology featuring AA stacking mode with an interlayer distance of 0.362 nm (Fig. 16a) [85]. This unique structure, characterized by a multimesoporous architecture and few layers, enhances the electrolyte infiltration of N-GY electrodes, leading to exceptional performance in both LIBs and SIBs (Fig. 16b). As SIBs, the N-GY electrodes demonstrate outstanding rate capability and cycling durability, achieving a high reversible capacity of 570.4 mAh g^{-1} at 100 mA g^{-1} . Remarkably, they maintain a capacity of 180.2 mAh g^{-1} even at a substantially elevated current density of 5 A g^{-1} in sodium-ion batteries, showcasing their impressive rate performance (Fig. 16c). The initial discharge/charge profiles of SIBs reveal a prolonged plateau and a gradual improvement in coulombic efficiency over subsequent cycles. The outstanding Na^+ storage capability of N-GY is attributed to its large and conjugated rings, which act as additional active sites for Na^+ adsorption. Rate tests conducted at varying current densities further confirm the remarkable Na^+ diffusion performance of N-GY, even under high-rate conditions (Fig. 15d).

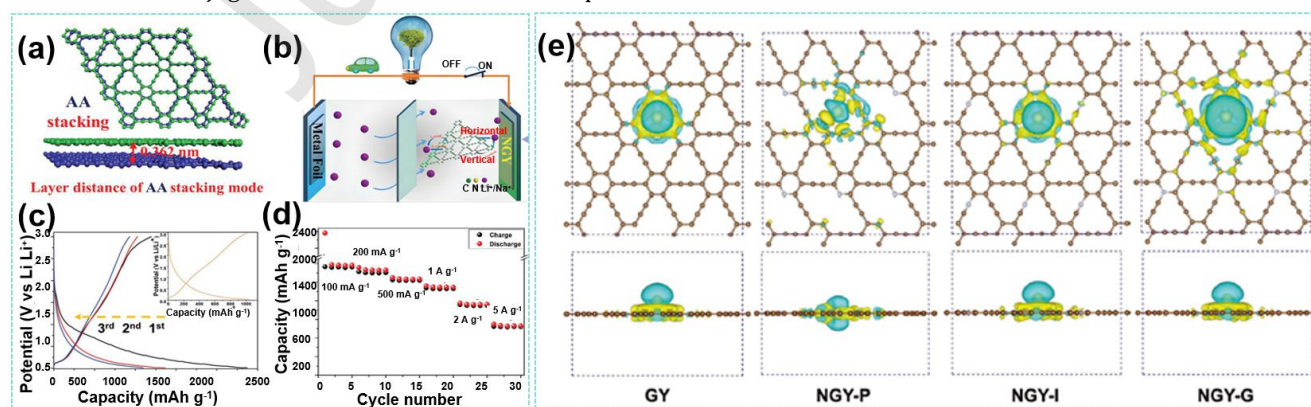


Figure 16 (a) AA stacking modes of γ -GY determined by DFT calculations. (b) Schematic illustration of the preparation of nitrogen doped γ -GY. (c) Galvanostatic charge/discharge profile of N-GY during the initial three cycles (inset shows the profile after 200 cycles). (d) rate capability. (e)

The adsorption abilities of Na atoms in N-GY and the electronic density difference after Na⁺ adsorption. Yellow and blue areas correspond to the increment and reduction of electron density, respectively. Reprinted with permission from ref. [85], © 2020 WILEY-VCH.

Upon returning to a lower current density, the battery maintains a high Na storage capacity, demonstrating its resilience. CV analysis reveals an increase in the contribution of the capacitive-controlled process with increasing scan rates, highlighting the exceptional rate capability of N-GY. Moreover, the battery exhibits excellent cycling stability, maintaining high capacities over extended periods across a broad range of current densities. This superior Na⁺ storage performance can originate from the extended π -conjugation throughout the carbon structure of N-GY and the enhanced electronegativity resulting from nitrogen doping, which facilitates efficient electrode-Na⁺ interactions.

DFT were used to investigate Na sorption-desorption dynamics on N-GY. Due to Na's larger radius, its adsorption pathway differs from Li: Na atoms are first captured in triangular conjugated rings (NaC₂₀ to Na₄C₂₀), then adsorbed between benzene rings (Na₅C₂₀ to Na₆C₂₀), achieving a high capacity of 669.6 mAh g⁻¹. Both Li and Na exhibit minimal migration barriers when traversing triangular rings vertically, highlighting GY's superior ion-channeling capability over conventional carbon electrodes. DFT calculations evaluated Na diffusion barriers across three N-doping configurations: N-GY-P (1.58 eV), N-GY-I (0.46 eV), and N-GY-G (0.55 eV). Nitrogen incorporation redistributes electron density, enhancing alkali metal adsorption and diffusion. Charge transfer analysis shows electrons move from adsorbed Na to surrounding C atoms, with charge accumulation localized at N sites—particularly in N-GY-P and N-GY-I. These configurations (dominated by pyridinic-N and imine-N) improve Na adsorption and electronic structure versus pristine GY, thereby boosting electrochemical performance (Fig. 16e).

5.2.2 Lithium-ion battery

In the early stages, GY was theoretically calculated as a promising candidate for graphene in the next generation of LIBs [131]. On the one hand, GY distinguishes itself as a nanostructured carbon anode material for high-capacity LIBs, owing to its unique large and conjugated rings that afford a high theoretical Li⁺ storage capacity [132]. Its structural robustness, characterized by superior in-plane stiffness and ultimate strength, surpasses that of other GY-based materials [133]. GY variants with shorter acetylenic chains ($n = 1, 2, 3$) are particularly attractive for high-capacity LIBs, benefiting from their conjugated structure and excellent carrier mobility [134, 135]. Mohajeri and co-workers revealed that GY hosts Li⁺ both between the carbon sheets and within its large conjugated rings, yielding a storage capacity that exceeds that of all sp²-carbon materials, including graphite. First-principles calculations by Ghosh and Srinivasu established that a GY monolayer can accommodate four Li atoms per twelve-carbon unit [136], translating to a specific capacity

of 623.4 mAh g⁻¹—nearly double that of graphite (372 mAh g⁻¹). Lee et al. further demonstrated that the Li-intercalated multilayer GY composite C₆Li₃ delivers a capacity of approximately 1000 mAh g⁻¹ [137]. In a recent DFT study, Zhang and colleagues explored the strain-dependent Li⁺ storage and diffusion behavior in GY anodes [138], finding that a 12% strain boosts the maximum capacity to 2233 mAh g⁻¹, twice the value for the unstrained GY (1117 mAh g⁻¹).

Despite the synthetic challenges of pristine GY, innovative routes have enabled the production of heteroatom-doped derivatives with tunable properties. Huang et al. developed a versatile strategy to synthesize N-substituted GYs—pyridine-GY (PY-GY), pyrimidine-GY (PM-GY), and triazine-GY (TA-GY)—by varying the N content in benzene rings [119]. This approach tailors band gaps and lithium storage performance while diversifying the GY family. The resulting N-GYs feature adjacent azaaromatic rings linked by acetylenic bonds. N incorporation modulates charge distribution, band gaps, and conductivity. UV-Vis spectroscopy reveals optical band gaps of 2.28, 2.00, and 1.97 eV for PY-GY, PM-GY, and TA-GY, respectively, indicating potential for electronic applications. As N content increases, total Bader charges rise, electron density increases, and band gaps narrow, enhancing conductivity. Electrochemically, N-GYs—especially TA-GY—exhibit high capacities across current densities and exceptional stability even at 5000 mA g⁻¹. The synergy of microporosity and abundant N sites accelerates Li⁺ migration and diffusion, delivering superior rate performance, high storage capacity, and long cycling durability. These results align with theoretical predictions, underscoring N-GYs as promising candidates for advanced energy storage systems.

5.2.3 Potassium-ion battery

The pursuit of high-energy-density battery systems has directed significant attention toward potassium-ion batteries (PIBs), as the lower standard reduction potential of potassium (−2.93 V vs. E_0) versus sodium (−2.71 V vs. E_0) affords them a superior energy density [138–140]. To advance this field, Cui's team developed a mechanochemical cross-coupling synthetic methodology, employing D_{2h} -symmetric tetrahalogenated organic molecules and alkynyl-containing calcium carbide as precursors to construct ordered rhombic channels in graphyne analogues, specifically dihydrogen- and nitrogen/hydrogen-substituted rhombic graphynes (HH-*r*GY and NH-*r*GY) [84]. The NH-*r*GY electrode delivers a reversible capacity of 230 mAh g⁻¹ after 500 cycles at 50 mA g⁻¹, which represents an impressive capacity retention rate of 90.2%. In contrast, the stable capacities of GY and HH-*r*GY are 172 and 200 mAh g⁻¹, respectively, with capacity retention rates of 73.2% and 72.2%. The superior cycling performance of NH-*r*GY can

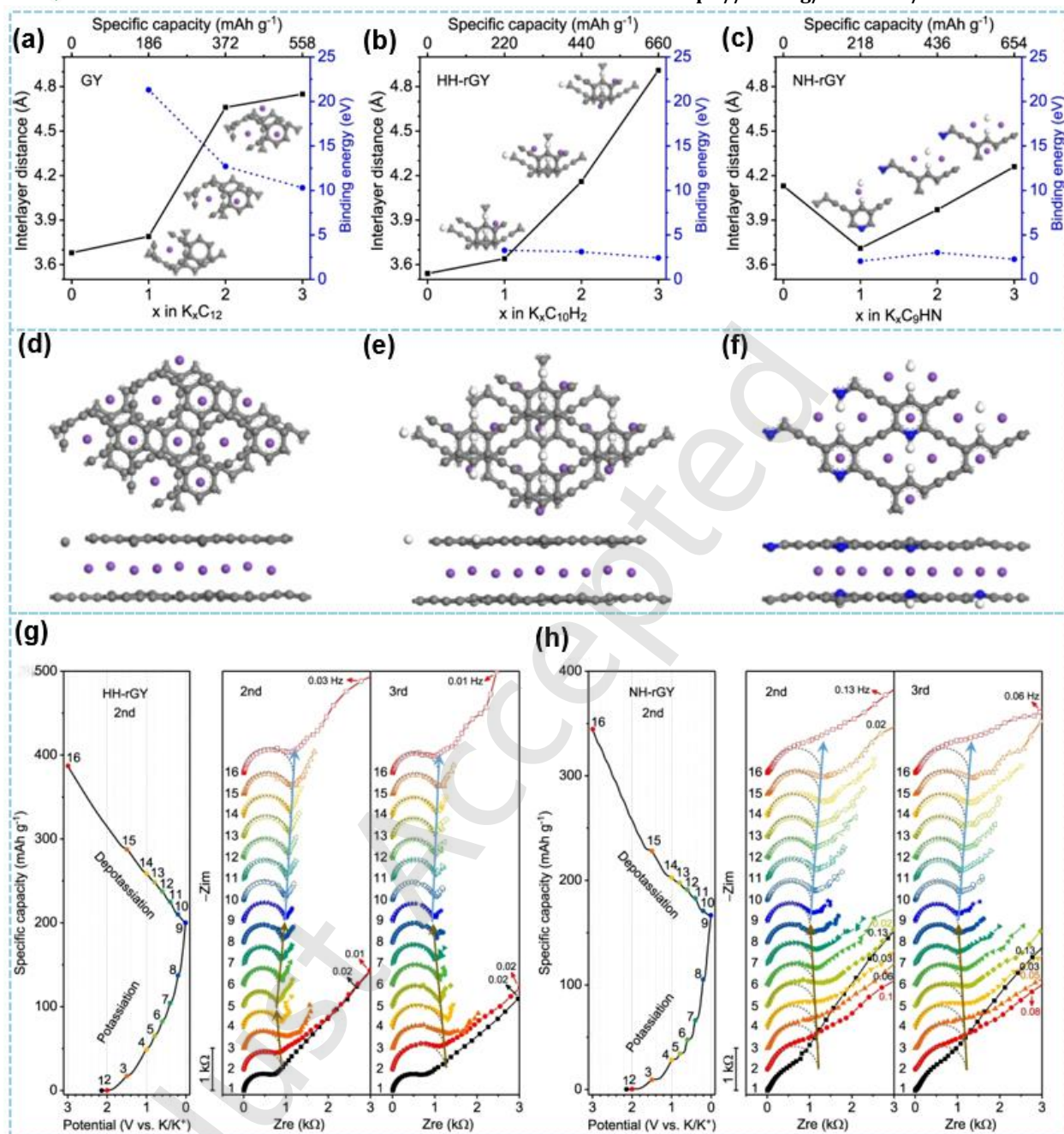


Figure 17 Theoretical calculations of the potassium storage mechanism are presented, encompassing K⁺ adsorption sites, interlayer distance variations, and K⁺ intercalation binding energies for (a) AB-stacked GY, (b) AB-stacked HH-rGY, and (c) AA'-stacked NH-rGY. The top and side views of the fully potassiated configurations—(d) K₃-GY, (e) K₃-HH-rGY, and (f) K₃-NH-rGY—third discharge-charge cycles of (g) HH-rGY and (h) NH-rGY at 50 mA g⁻¹. Reprinted with permission from ref. [84] © 2021 IOP Publishing Limited.

be attributed to the manipulation of electron distribution and structural arrangement by the pyridinic-N atoms, resulting in an ordered vertical rhombic channel configuration known as AA-stacking mode. NH-rGY is distinguished by a 4.1 Å interlayer spacing, 1.16 times broader than HH-rGY, and a near-zero volumetric strain (<3%) upon potassiation, compared with the 29% and 39% expansions estimated for GY and HH-rGY, respectively (Fig. 17a-c). This dimensional stability endows NH-rGY with considerable promise as a

potassium host. Binding energy comparisons reveal that K₃C₁₂ (>10 eV) surpasses K₃C₁₀H₂ (2.42 eV) and K₃C₉HN (2.27 eV) by a factor of approximately five. The thermodynamic limitations of K-ion adsorption in pristine GY are effectively circumvented through the deliberate construction of ordered rhombic channels, which substantially reduce the adsorption energy. The fully potassiated structures (Fig. 17d-f) accommodate three K ions per unit, affording theoretical capacities of 558, 660, and 654 mAh g⁻¹ for GY, HH-rGY, and NH-rGY. GITT

measurements (30 mA g⁻¹, 15 min pulses, 45 min relaxation) yield K⁺ diffusion coefficients on the order of 10⁻¹⁰ cm² s⁻¹, with the diffusion kinetics progressively retarded by the intensified Coulombic repulsion associated with deeper K⁺ intercalation. The de-intercalation sequence proceeds with preferential extraction of K⁺ from the surface-adjacent sites, and the subsequent extraction from the bulk slows down due to the longer pathway. Potential-dependent electrochemical impedance spectroscopy (EIS) measurements were conducted at 50 mA g⁻¹, and the voltage profiles and corresponding Nyquist plots for HH-rGY and NH-rGY are displayed in Fig. 17g and h. The aforementioned kinetics analysis validates that the excellent potassium storage is derived from the storage process dominated by intercalation, fast diffusion throughout the bulk, and the ability for reversible charge transfer at the interface.

5.3 Photo-/Electro-catalysis

5.3.1 Electrocatalysis

Oxygen evolution reaction

Although electrocatalytic water splitting provides a convenient means for hydrogen production, its widespread application is constrained by the oxygen evolution reaction (OER), which suffers from sluggish kinetics and high overpotential. The standard Gibbs free energy for water dissociation is 237.2 kJ mol⁻¹, corresponding to an equilibrium potential of 1.23 V [141-143]. However, in practice, the voltage required for water electrolyzer operation exceeds 1.23 V (often even surpassing 1.4 V per cell). The main obstacles in the water splitting process primarily arise from OER, which serves as the primary hindrance due to its inherent 4-electron transfer mechanism [144, 145]. This process entails uphill intermediate thermodynamic stages, resulting in notably sluggish kinetics and a significant anodic potential requirement [89, 146]. Consequently, the OER becomes both kinetically sluggish and thermodynamically demanding. The reaction can proceed in either acidic or alkaline media, with the mechanistic pathways exhibiting pronounced pH dependence that ultimately yield the same outcome. Considering all these factors, it can be confidently asserted that the development of novel types of OER electrocatalysts represents a highly active research area. GY, characterized by the substitution of diacetylenic linkages with ethynyl linkages, exhibits the most robust framework and displays exceptional semiconductor properties among its counterparts. Theoretical computations have anticipated that GY possesses excellent potential as a superior contender for the OER due to its remarkable carrier mobility. Cui and her colleagues conducted a study that utilized a straightforward mechanochemical technique to produce hydrogen-substituted GY [71]. Departing from traditional routes, this synthetic strategy utilizes CaC₂ as the source of *sp*²-hybridized carbon, with PhBr₃ providing both *sp*²-hybridized carbon and hydrogen atoms. Through the application of ball milling in a vacuum environment, a

cross-coupling reaction was employed to directly synthesize hydrogen-substituted GY. The resulting material exhibited a calculated band gap of 2.30 eV, as determined by UV-Vis DRS spectroscopy. The electrocatalytic performance of the sample was evaluated in a neutral electrolyte (0.5 mol L⁻¹ Na₂SO₄) using a standard three-electrode configuration. The hydrogen evolution reaction exhibited an onset overpotential of -0.17 V; however, the Tafel slope was found to be excessively large. (1088.4 mV dec⁻¹), thus limiting its potential for electrocatalytic hydrogen evolution. Conversely, the OER exhibited a mere 0.04 V overpotential and a Tafel slope of 70.0 mV dec⁻¹, enabling its application in electrocatalytic oxygen evolution. This approach paves the way for the synthesis of GY with excellent electrochemical characteristics through the utilization of easily accessible precursors under gentle conditions, presenting a novel opportunity for advancement.

Cui et al. achieved a breakthrough in GY synthesis using benzene as a precursor via solid-liquid interfacial reaction with CaC₂ [88]. Gram-scale GY exhibited excellent oxygen evolution reaction (OER) performance: at pH = 14, 13, and 12, onset overpotentials were 302, 318, and 308 mV, with Tafel slopes of 64, 72, and 76 mV dec⁻¹, respectively, confirming favorable kinetics. DFT calculations identified *sp*²-hybridized carbon atoms on benzene rings as active sites, with *OOH formation as the rate-determining step. For practical application, GY/Ni foam electrodes were fabricated via hydrothermal coating. At 100 mA cm⁻², the GY/Ni foam electrode achieved an overpotential of 270 mV, significantly outperforming pristine Ni foam (380 mV). Long-term stability tests showed the GY/Ni foam electrode maintained 290 mV over 72 h, whereas Ni foam degraded from 370 to 410 mV. Gas evolution measurements at 100 mA cm⁻² yielded 0.375 mL min⁻¹, with GC analysis confirming a 2:1 H₂:O₂ ratio and 99.1% Faradaic efficiency.

CO₂ photo/electroreduction

Carbon dioxide photo/electroreduction (ECO₂RR) technology, which converts greenhouse gas CO₂ to chemical feedstocks and liquid fuels with renewable electricity, is a promising solution to achieving "Carbon Neutrality" and fulfilling the "Paris Agreement" [147-150]. The reduction products of ECO₂RR range from C1, C2, C3 to H₂ from the competitive HER, which involve different numbers of protons and electrons [151,152]. To this end, the rational design of ECO₂RR is highly desired to controllably tailor reactivity, selectivity and stability, with proficient electrocatalysts at the core of this technology. The scalability of CO₂ electroreduction (CO₂RR) is constrained by the need for high Faradaic efficiency (FE) and stability at elevated current densities—a challenge exacerbated by poor electrochemical stability and competition from the hydrogen evolution reaction (HER) [153-155]. Inspired by mercury's high HER overpotential, Wong et al. synthesized metalloporphyrin-linked

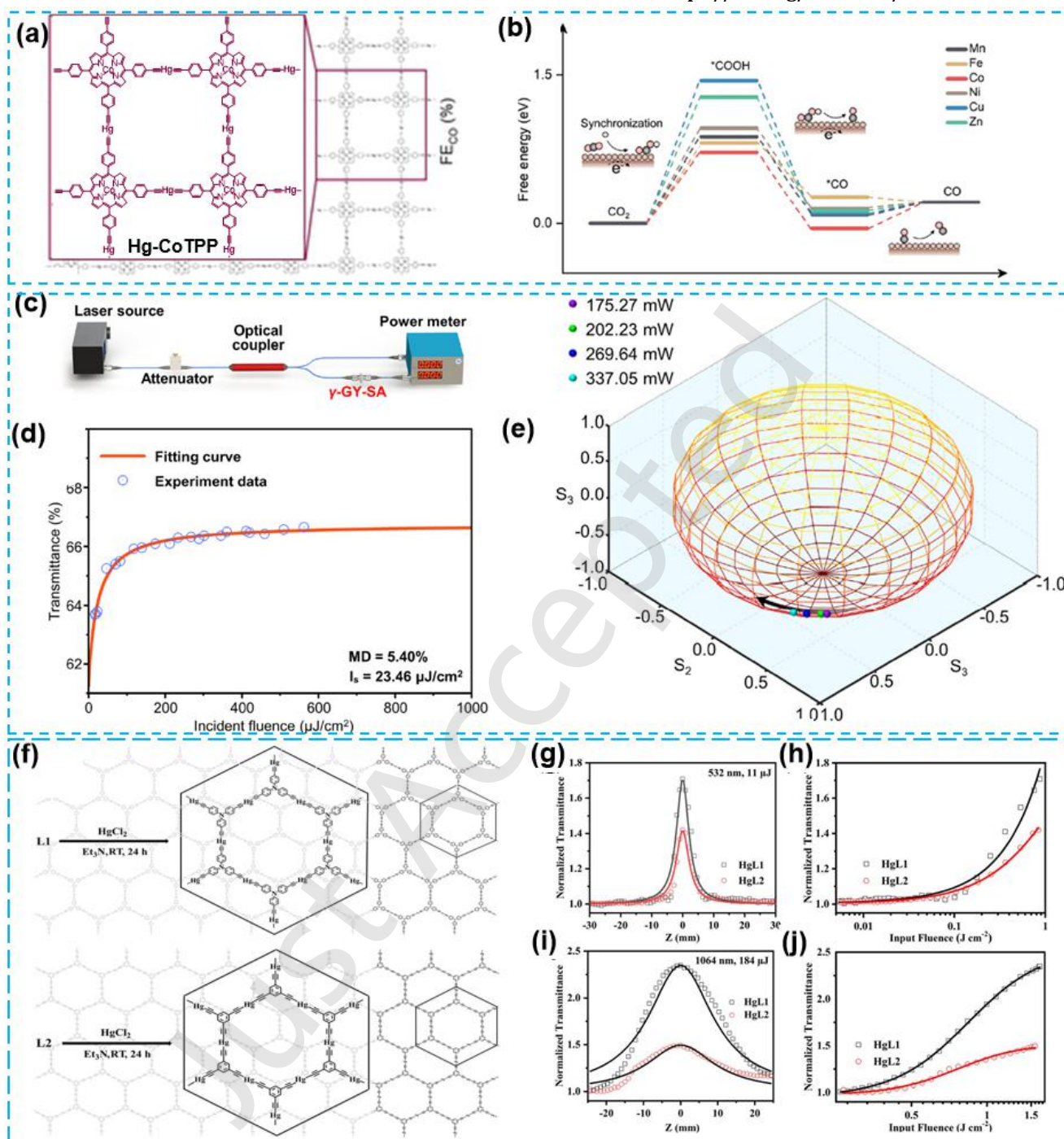


Figure 18 (a) Schematic illustration of the chemical structure of Hg-MTPP (M = Mn, Fe, Co, Ni, Cu, and Zn). (b) Calculated reaction free energy diagram for the electroreduction of CO₂ to CO on Hg-MTPP. Reprinted with permission from ref. [26], © 2021 American Chemical Society. (c) Experimental setup for the balanced twin-detector measurement. (d) Transmittance of the γ -GY-SA versus incident fluence. (e) Evolution of the Stokes parameters on the Poincaré sphere at varying pump powers. Reprinted with permission from ref. [77], © 2023 Royal Society of Chemistry. (f) Chemical structures of the two organic ligands, tris(4-ethynylphenyl)amine (L1) and 1,3,5-triethynylbenzene (L2), and the corresponding mercurated graphyne nanosheets of HgL1 and HgL2. (g) NLO properties of MGONs. Open-aperture Z-scan data and theoretically fitted curves (solid curves) of HgL1-0.75–150 and HgL2-1.0–150 nanosheets at 532 nm with an input energy of 11 mJ; (h) 1064 nm with an input energy of 184 mJ. Theoretically fitted plots of normalized transmittance vs. incident intensity of HgL1-0.75–150 and HgL2-1.0–150 nanosheets at (i) 532 nm with an input energy of 11 mJ; (j) 1064 nm with an input energy of 184 mJ. Reprinted with permission from ref. [24], © 2022 Wiley-VCH.

mercurated graphyne nanosheets (Hg-MTPP, M = Mn, Fe, Co, Ni, Cu, Zn) [26]. Using Hg-CoTPP as an example, nanosheets were prepared via base-catalyzed

dehydrohalogenation between ethynylated CoTPP and HgCl₂ using an interface-assisted method (**Fig. 18a**). DFT simulations indicate tetragonal crystallinity (space group

14/*mmm*) with refined unit cell parameters (~ 24.8 Å in-plane, ~ 3.3 – 3.4 Å out-of-plane). Control Hg-H₂TPP (metal-free porphyrin) shows no CO₂RR activity. In contrast, Hg-CoTPP achieves a peak CO Faradaic efficiency (FE) of 95.6% at -0.76 V vs. RHE in an H-cell, outperforming CoTPP (88.3%) and CoPc (77.0%). Immobilizing Hg-CoTPP on N-doped graphene (NG) via π - π stacking further boosts performance: Hg-CoTPP/NG delivers 98.7% CO FE at -0.65 V and maintains 91.2% at -1.26 V. DFT reveals that the mercuroated graphyne framework raises HER overpotential and modulates the Co d-band center to strengthen COOH binding, while NG shortens Co-N bonds, enhancing electron transfer and lowering the COOH formation barrier (**Fig. 18b**). In a flow cell, Hg-CoTPP/NG achieves nearly 100% CO FE at 1.2 A cm⁻² with exceptional stability (>360 h at ~ 420 mA cm⁻²), highlighting its potential as a highly efficient, scalable CO₂RR electrocatalyst. In Ni(II)-acetylide frameworks (Ni(II)-AFs), the Ni-bis(acetylide) motif serves as an electron-accepting and catalytically active center, while the π -conjugated framework acts as both a charge-transport channel and an electron-donating component [12–14], such frameworks can achieve notable photocatalytic CO₂ reduction activity [156–158].

5.3.2 Photocatalysis

The growing industrial demand for H₂O₂ has driven the development of efficient, sustainable production methods [159–161]. Electrochemical H₂O₂ synthesis—via two-electron oxygen reduction ($2e^-$ ORR) or hydrogen oxidation—offers high selectivity, scalability, and compatibility with renewable energy. Photocatalysis provides economic viability and selectivity, while photoelectrochemical (PEC) systems combine both advantages, enabling solar-driven H₂O₂ production from O₂ and H₂O with minimal back reactions.

In photocatalytic H₂O₂ production, the efficiency is governed by multiple interdependent factors. The charge transfer pathways in N-GY involve photoexcited electron transfer from the conduction band to adsorbed O₂ molecules, initiating the two-electron oxygen reduction reaction ($2e^-$ ORR) [162]. DFT calculations identify pyridinic-N sites as catalytic hotspots that facilitate the rate-limiting proton abstraction step. The band structure engineering achieved through nitrogen doping narrows the optical band gap from 2.58 eV to approximately 2.2 – 2.3 eV, enhancing visible light absorption and improving charge carrier generation. Reactive oxygen species generation primarily proceeds through the superoxide radical pathway, with the electron-rich N sites stabilizing O₂⁻ intermediates and promoting selective H₂O₂ formation. The heterojunction design in the N-GY/TiO₂ photoanode configuration enhances photo-excited carrier separation by creating a built-in electric field at the interface, suppressing charge recombination and H₂O₂ decomposition. The influence of defects and heteroatom doping on photocatalytic activity is critically important [163], pyridinic-N doping

introduces localized electronic states near the Fermi level, acting as active sites for O₂ adsorption and activation, while structural defects (e.g., grain boundaries, vacancies) can serve as additional active centers or charge recombination centers depending on their nature and density.

Wong and his team successfully crafted a free-standing mercuroated GY nanosheet films, named HgL1, distinguished by its ideal band structure and robust light absorption capability [22]. However, its potential in H₂O₂ photoproduction is hindered by its carrier separation efficiency and hydrophobic surface. Carbon dots (CDs), tiny carbon nanoparticles under 10 nm adorned with diverse surface functionalities, excel in optics and electronics, making them a staple in photocatalytic applications. To enhance HgL1's photocatalytic performance, we introduced CDs to form a CDs/HgL1 composite. This hybrid not only accelerated H₂O₂ production by a remarkable 6.4-fold, reaching 800 $\mu\text{mol h}^{-1} \text{g}^{-1}$ compared to pristine HgL1's 125 $\mu\text{mol h}^{-1} \text{g}^{-1}$, but also revealed CDs' multifaceted contributions. Transient photovoltage assessments unveiled a heightened surface effective electron count in CDs/HgL1, a key factor in its enhanced performance. Furthermore, in situ TPV tests confirmed CDs' ability to bolster the ORR activity. Crucially, CDs transformed the catalyst's surface from hydrophobic to hydrophilic, facilitating subsequent reactions. In essence, CDs actively participate throughout the photocatalytic cycle, enhancing HgL1's H₂O₂ yield by expediting electron-hole separation and migration, bolstering redox activity, and altering surface properties. This study delves into the comprehensive functions of CDs within metalated graphyne catalysts for photoinduced H₂O₂ production, deepening our understanding of CDs' pivotal roles.

5.4 Nonlinear optics

Laser technology advancements have heightened the need for effective laser protection devices [164, 165]. Optical limiting (OL) offers superior protection compared to traditional linear methods by restricting transmitted light intensity below damage thresholds while maintaining transparency under low-power irradiation [166]. OL performance relies on third-order nonlinear optical (NLO) effects, providing low limiting thresholds, high damage tolerance, fast response, high transmittance, and broadband protection [167]. Unlike second-order NLO, third-order NLO does not require non-centrosymmetric structures, enabling broader use of 2D materials.

GY excels among NLO materials due to its extensive π -conjugation, uniform pore distribution, and intrinsic band gap, yielding high nonlinear absorption sensitivity, large refractive index, low saturation intensity, and broadband absorption [168]. Zhu et al. fabricated few-layer γ -GY saturable absorbers (SAs) via mechanochemistry and liquid-phase exfoliation, integrating them into passively Q-switched lasers at 639, 1342, and 1932 nm, achieving repetition rates up to 164,

114, and 76 kHz, and pulse energies of 0.49, 1.8, and 4.7 μJ , respectively. Wang et al. reported γ -GY nanosheet thin films as SAs in Q-switched lasers and all-optical switches [169], achieving 241 ns pulses at 1.06 μm (0.76 μJ , 3.15 W peak power) and switch rise/fall times of 1.46/2.13 ms.

Wang et al. synthesized γ -GY nanosheets via improved mechanochemistry and fabricated γ -GY-SAs by laser-induced deposition [77]. As shown in **Fig. 18c–d**, the SA exhibits a saturable fluence of 23.46 $\mu\text{J cm}^{-2}$ and modulation depth of 5.40%. Integrated into an Er^{3+} -doped fiber laser, it enabled stable Q-switched and mode-locked operation, with polarization-locked vector solitons and >97% polarization stability (**Fig. 18e**). Wong et al. synthesized free-standing mercurated graphyne nanosheet films via interface-assisted bottom-up growth (**Fig. 18f**). Hg incorporation yields layered, thickness-controllable structures with enhanced π -conjugation, exhibiting stable broadband saturable absorption at 532 and 1064 nm (**Fig. 18g–j**). The Hg^{II} -polyyne structure induces Pauli blocking, enhancing NLO response via copolymerization of polynes with Hg^{II} . These nanosheets functioned effectively as SAs in Q-switched lasers, highlighting metallated GY's optoelectronic potential. While GY shows promise for visible, near-IR, and mid-IR photonic devices, comprehensive studies of its NLO properties across diverse chemical structures remain an active research frontier [170].

Therefore, the multifunctional capabilities of GY and its derivatives stem from the synergistic interplay of their unique structural features, high specific surface area (theoretical 3440 $\text{m}^2 \text{g}^{-1}$), tunable band gap (0.46–2.23 eV), hierarchical porosity, extended π -conjugation, and facile chemical modifiability, which collectively enable performance across diverse technological domains. In energy storage applications, GY-based supercapacitors deliver specific capacitances of 80–235 F g^{-1} with exceptional cycling stability (>90% retention over 5,000 cycles) and rate capability, while lithium-ion batteries achieve reversible capacities of 623–1003 mAh g^{-1} through intercalation-dominated storage mechanisms

that exploit the material's enlarged interlayer spacing (0.36–0.49 nm) and abundant C_{12} -triangular channels for rapid ion diffusion. The extension to sodium- and potassium-ion batteries further demonstrates the structural advantages of GY, with N-doped variants achieving 570 mAh g^{-1} (sodium) and 230 mAh g^{-1} (potassium) with near-zero volumetric strain (<3% for NH-rGY) compared to 29–39% for pristine GY, highlighting the critical role of heteroatom doping in mitigating volume expansion and enhancing cycle life. In catalysis, GY-based photocatalysts exhibit remarkable activity for H_2O_2 production (800 $\mu\text{mol h}^{-1} \text{g}^{-1}$ with CDs/HgL1 composites), while electrocatalytic applications demonstrate oxygen evolution reaction overpotentials as low as 270 mV at 100 mA cm^{-2} and CO_2 electroreduction Faradaic efficiencies approaching 100% at current densities of 1.2 A cm^{-2} with unprecedented stability exceeding 360 hours. Nonlinear optical applications leverage the electron-rich π -systems and tunable band structures of GY, enabling broadband saturable absorption (532–1064 nm), optical limiting with modulation depths of 5.40%, and polarization-locked vector soliton generation with >97% polarization stability. The integration of metallated GY derivatives expands the functional repertoire through metal-centered electronic modulation, with mercurated graphynes demonstrating enhanced catalytic activity for CO_2RR (Hg-CoTPP: 95.6% FE) and photofunctional properties via Pauli blocking effects and enhanced π -conjugation. Despite these advances, the application landscape reveals critical knowledge gaps: the direct contribution of $\text{C}\equiv\text{C}$ bonds to performance remains largely speculative rather than experimentally verified; systematic structure-activity relationships across different GY allotropes are absent; and standardized benchmarking protocols for property comparison are yet to be established. The emerging applications in gas separation, seawater desalination, and biomedical sensing, while theoretically promising, remain unexplored experimentally, representing substantial opportunities for future investigation.

Table 6 A comprehensive classification of graphyne-based materials.

Category	(i) Theoretically predicted all-carbon GY allotropes	(ii) Experimentally claimed extended GY materials	(iii) Substituted or heteroatom-containing GY analogues	(iv) Finite molecular GY fragments	v) Metal-acetylide or organometallic frameworks
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Key References	Structural Features	Synthesis Status	Crystallinity / Order	Dimensionality	Chemical Composition	Representative Materials
[8], [47–51]	Defined by lattice topology; acetylenic linkages ($-C\equiv C-$) inserted into graphene lattice at specific positions	Predicted only (γ -GY experimentally claimed)	High (ideal periodic lattice)	2D extended networks	Pure carbon ($sp + sp^2$ hybridized)	α -GY, β -GY, γ -GY, δ -GY, 6,6,12-GY
[56], [69], [71], [77], [88], [91], [94]	Hexagonal lattice; defects, finite domain size, and impurities present	Experimentally reported (identity controversial)	Low to moderate (amorphous/polycrystalline); limited long-range order	2D extended networks	Pure carbon ($sp + sp^2$ hybridized)	γ -GY (mechanochemical, interfacial, solution-phase)
[71], [79], [85], [86], [87], [89], [98], [100], [102]	Aromatic rings modified with substituents or heteroatoms; altered electronic structure and active sites	Experimentally synthesized	Low to moderate (amorphous/polycrystalline)	2D extended networks	Carbon with H, N, S, or other heteroatom substituents	H-GY, N-GY, S-GY, N/S-GY, Me-GY, F-GY, PM-GY, PY-GY, TA-GY, r-GY, HH-rGY, NH-rGY
[90], [91], [92]	Finite oligomeric or macrocyclic structures; well-defined molecular weight and structure; serve as model compounds	Experimentally synthesized	High (well-defined by single-crystal X-ray diffraction)	0D/1D discrete molecules	Pure carbon ($sp + sp^2$ hybridized) with organic solubilizing groups	Graphyne spoked wheel, HPB, γ -G1, etc.
[21], [23], [170]	Metal ions coordinated to acetylenic linkages; enhanced optoelectronic and catalytic properties; termed "metallated graphynes" (MGYs)	Experimentally synthesized	Low to moderate (layered, often exfoliable)	2D extended networks (nanosheets)	Carbon with coordinated metal ions (Hg^{2+} , Ni^{2+} , Pt^{2+} , Pd^{2+} , etc.)	Hg-MTPP, HgLL, HgL2, Pd-GY, Ni-GY, Pt-GY, etc.

6. Summary and outlook

GY, a recently developed carbon allotrope, exhibits exceptional sp^2 and sp hybrid electronic structures, coupled with layered 2D flat attributes (Table 6). These distinct characteristics lead to a wealth of chemical bonds, extensive conjugated systems, increased planar spacing, uniformly dispersed pore configurations, modifiable band structures and improved hole/electron mobility. Notably, the extensive π - π conjugation contributed by the alkyne bonds supplies a large electron reservoir to the molecular plane, which in turn bolsters the chemical robustness of GYs. As a result, GY has emerged as an exceptionally promising material with enormous potential in a variety of fields, and there is great anticipation for its rapid development. This review covers advances in GY materials in terms of structural and intrinsic properties, synthesis methods, structure characterization, and potential applications, providing an up-to-date assessment of recent progress. Despite significant progress, the research and practical utilization of GY materials remain in their early stages. Key challenges and future opportunities are outlined below:

(1) Optimized synthesis methods: Exploring large-scale preparation methods for high-quality GY at low cost is critical for advancing its industrial applications. Future studies need to overcome core bottlenecks including limited precursor accessibility, low product yield, uncontrollable structural defects, tedious purification procedures, and poor batch reproducibility, which severely restrict the industrial feasibility of GY. Further efforts are required to lower manufacturing costs, optimize scalable fabrication protocols, and evaluate environmental impacts to break through existing commercialization barriers. In addition, data-driven strategies including high-throughput DFT screening and machine learning-assisted structural prediction and catalyst design are promising avenues to accelerate the discovery of novel high-performance GY structures [171,172]. Notably, relevant computational studies are currently dominated by graphdiyne and its derivatives, whereas AI and theoretical investigations targeting pristine GY remain insufficient, deserving systematic exploration in future research.

(2) Modulated performance methods: One of the most urgent challenges for the future resides in modulating performance via the chemical structure of GY's aromatic rings. Despite the promising characteristics of GY, the impacts of structural alterations on its optoelectronic properties remain largely unexplored. This omission presents a substantial opportunity for research and development. By systematically investigating how changes to the aromatic rings affect the electronic band structure, charge carrier mobility, and optical absorption, we can uncover novel pathways to enhance the functionalities of GY. In parallel, defect engineering, including the precise control of defect types (vacancies, grain boundaries, and topological defects), concentrations, and spatial

distributions, represents a promising yet underexplored strategy for tailoring the electronic structure, mechanical properties, and catalytic activity of GY materials. Systematic investigations into how specific defects influence charge transport, active site density, and stability will be essential for establishing rational design principles and optimizing GY performance across diverse applications.

(3) Expanded application areas: Since the discovery of GY, its wide range of applications has sparked intense discussions in various fields. Despite significant progress in using GY for supercapacitors, lithium/sodium/potassium-ion batteries, photo-/electro-catalysis, and nonlinear optics and photonics, research on GY is still in its early stages, presenting both challenges and promising opportunities in biomedicine, environmental remediation, and smart systems. Its intrinsic uniform pores and functionalizable surface enable targeted drug delivery, bioimaging, and cancer therapy, while serving as molecular-sieving membranes for seawater desalination, water purification, and selective gas separation. The reversible alkyne - alkene conversion imparts GY with smart actuation and self-adaptive sensing capabilities for wearable devices. Although research is nascent, these expanded applications highlight GY's broad potential.

Overall, despite significant progress has been achieved in the synthesis and utilization of GY materials, research and effective utilization of GY are still in the early stages of development and have not yet met our requirement. This review provides insights into the synthesis of GY materials and offers valuable guidance on how to harness the potential of GY materials in various fields. A combined effort from both experimental and theoretical approaches is essential to speed up the advancement of GY research and its applications. By integrating experimental findings with theoretical models, we can unlock new possibilities and applications for GY that were previously unexplored.

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Declaration of conflicting interests

The authors declare no conflicting interests regarding the content of this article.

Data availability

All data needed to support the conclusions in the paper are presented in the manuscript and/or the Supplementary Materials. Additional data related to this paper may be requested from the corresponding author upon request.

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