

Recent advances in nitrogen-doped graphdiyne and polyoxometalate–graphdiyne interfaces for energy conversion and storage

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Received: 1 July 2026; Revised: 24 September 2026; Accepted: 1 October 2026

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Cite This: *Polyoxometalates*, 2027, 6, 9140165



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ABSTRACT: Graphdiyne (GDY) is a two-dimensional carbon allotrope constructed from both sp- and sp²-hybridized carbon atoms. Its π -conjugated framework connected by butadiyne linkages combines regular nanopores, tunable electronic structures, and abundant chemically modifiable sites. Compared with pristine GDY, nitrogen-containing graphdiyne (N-GDY) provides diverse nitrogen configurations and, in metal-containing derivatives, metal–N coordination motifs; these features can redistribute local charge density, tune intermediate adsorption, and facilitate charge transport. Related composites combining polyoxometalates (POMs), molecular metal–oxo clusters with rich redox chemistry, and graphdiyne supports have been reported, whereas structurally defined POM/N-GDY interfaces remain less established. This review systematically summarizes the recent progress in N-GDY and POM/graphdiyne interfacial systems, covering bottom-up monomer design, post-doping/functionalization strategies, and structural characterization. The applications of these materials in electrocatalysis (ORR, OER, HER, CO₂RR, NRR), energy storage, photocatalysis, sensing, and interfacial engineering are discussed. In N-GDY systems, the role of nitrogen is better understood in terms of site chemistry rather than overall doping level. Different N configurations, including pyridinic, imine-type, sp-N, sp²-N and metal-N coordination sites, can polarize adjacent sp/sp² carbon atoms, regulate intermediate adsorption, and alter interfacial charge-transfer pathways. For reported POM/graphdiyne hybrids and proposed POM/N-GDY interfaces, these effects may couple with POM–carbon interactions and thereby influence cluster retention, redox behavior, and catalytic stability. Finally, the remaining challenges related to precise nitrogen-site and POM-interface construction, scalable synthesis, in situ characterization, identification of true active sites, and device-level validation are discussed, together with possible future directions.

KEYWORDS: graphdiyne; polyoxometalates; electrocatalysis; interfacial engineering

1 Introduction

Carbon-based materials continue to provide an essential materials foundation for mechanical engineering, electronic information technologies, metallurgy and chemical manufacturing. The evolution from conventional carbon forms, such as graphite, diamond, carbon black, porous carbon and activated carbon, to low-dimensional allotropes has reshaped the structure-property landscape of carbon materials [1]. Since the beginning of the twenty-first century, fullerenes, carbon nanotubes and graphene have successively expanded the boundaries of carbon science and have stimulated intensive research into low-dimensional carbon systems with unusual electronic structures and physicochemical properties [2–4].

Graphdiyne (GDY), a two-dimensional carbon network composed of both sp- and sp²-hybridized carbon atoms, has attracted particular attention among emerging carbon allotropes. In contrast to graphene, which is built exclusively from sp² carbon atoms, GDY consists of benzene rings connected by butadiyne

linkages ($\text{--C}\equiv\text{C--C}\equiv\text{C--}$), giving rise to an extended conjugated framework with intrinsic nanopores [5, 6]. This bonding topology endows GDY with a delocalized π -conjugated network, a tunable band structure, potentially high carrier mobility and chemically addressable acetylenic sites [7, 8]. Its ordered porosity also benefits ion transport and molecular adsorption, making GDY attractive for energy storage, catalysis and separation-related applications [9].

Compared with N-doped graphene and carbon nanotubes, whose continuous sp² networks favor rapid electron transport, N-GDY provides a distinct rather than universally superior platform [4, 10]. Its mixed sp/sp² skeleton introduces chemically addressable acetylenic linkages and intrinsic pores, enabling local charge polarization, tunable adsorption/coordination sites, and more traceable nitrogen configurations through precursor design [5, 6, 11, 12]. These features can benefit intermediate adsorption and provide candidate coordination or confinement sites for molecular species; however, the roles established in N-GDY electrocatalysis cannot be directly transferred to POM

immobilization, and direct evidence for enhanced POM retention on site-defined N-GDY remains limited [12–16]. In addition, GDY still faces limitations in conductivity, synthesis complexity, and structural disorder; therefore, its advantages depend on effective framework and interface control [6, 11, 13].

The concept of graphdiyne-type carbon materials originated from theoretical predictions. Baughman and co-workers proposed planar carbon networks containing both sp^2 and sp carbon atoms and discussed their possible stability and structural characteristics [5]. Experimental progress was delayed for a long period because of synthetic challenges. In 2010, Li and co-workers reported the preparation of graphdiyne films through the coupling of hexaethynylbenzene on copper substrates, marking a decisive transition of GDY from a theoretical structure to an experimentally accessible carbon material [6]. Since then, substantial efforts have been devoted to structural regulation, property optimization and application-oriented development of GDY, with reported potential in electrocatalysis, energy storage and conversion, water treatment and gas separation [9, 11, 17].

Despite these advantages, pristine GDY is not yet ideal for many practical electrochemical applications. Its intrinsic catalytic activity and electrical conductivity often require further improvement [13]. Rational structural modification is therefore central to the development of high-performance GDY-based materials. Heteroatom engineering is one of the most effective strategies because it can tune the electronic structure, surface chemistry and local reaction microenvironment of the carbon framework [13,14]. Introducing nitrogen, boron, sulfur or phosphorus into the GDY lattice can redistribute charge density, modulate the band structure and increase the number of catalytically accessible sites [18]. These effects can enhance ion adsorption, accelerate charge transfer and improve interfacial reaction kinetics [19, 20]. Among different dopants, nitrogen is especially important because it can polarize neighboring carbon atoms and activate adjacent sp -carbon sites for reactions such as the oxygen reduction reaction (ORR) [12].

Heteroatoms can be incorporated into GDY mainly through two conceptual routes. The first is a bottom-up precursor-design strategy, in which heteroatom-containing molecular monomers are coupled during framework formation. This route offers relatively high structural traceability because the dopant position and local coordination environment are partly predetermined by the monomer. The second is a top-down post-modification strategy, in which a preformed GDY framework is treated with reactive nitrogen sources, atmospheres or functional molecules [13,16]. Post-modification is experimentally convenient but usually leads to broad distributions of nitrogen species and dopant depths. Bottom-up synthesis is more demanding at the monomer and interface-control levels, but it is more suitable for establishing clear structure-performance relationships at the atomic or molecular scale.

Simultaneously, polyoxometalates (POMs)—a vast class of discrete, anionic transition metal-oxide clusters—have emerged as important molecular components in the fields of catalysis, energy storage, and optoelectronics. Representative POM architectures include Keggin, Wells–Dawson, Anderson–Evans, Lindqvist, and high-nuclearity polyoxovanadate structures. Their redox potentials, proton-coupled electron-transfer behavior, solubility, and interfacial reactivity can be regulated through the

addenda and heteroatom composition, substituted metal centers, protonation state, counterions, and organic functionalization. POMs are generally constructed from high-valent transition metals such as Mo, W, V, and Nb and can participate in reversible multielectron redox processes. However, retention of the original molecular cluster is not universal and depends on the POM composition, protonation state, pH, electrolyte, and applied potential; dissolution, hydrolysis, or potential-induced reconstruction may occur under operating conditions. These properties have enabled POM-based molecular and hybrid materials to be widely investigated in batteries, solar-energy-related devices, photothermal conversion, and other energy storage and conversion technologies [21–23]. In particular, high-nuclearity polyoxovanadates have been developed as multielectron active hosts for aqueous zinc-ion batteries, while hybridization and interfacial regulation can alleviate POM dissolution and stabilize electrode/electrolyte interfaces [24–26]. Reported $Co_{5.7}Ni_{2.3}$ -POM@FGDY and $Co_4(PW_9)_2$ @GDY systems demonstrate that graphdiyne-type frameworks can provide conductive networks, interfacial contact, and structural protection for POM-containing phases, while Co_4 -POM@Co-PGDY represents a related POM/N-containing graphdiyne-type system. For site-defined N-GDY, selected nitrogen environments may offer additional attachment or charge-transfer pathways, but direct evidence for defined POM–N coordination and improved resistance to POM leaching remains limited [14–16, 27].

This review connects two related research directions: nitrogen-site engineering in graphdiyne and the development of POM/graphdiyne interfaces for energy conversion and storage. We first summarize synthetic routes and nitrogen-site characterization and then discuss energy-related applications and representative POM@GDY, POM@FGDY, and POM/N-containing graphdiyne systems. Throughout the review, experimentally demonstrated support effects are distinguished from proposed POM/N-GDY coordination and charge-transfer mechanisms. A central theme of this review is that functional performance cannot be explained by total nitrogen content alone, but must be considered in relation to nitrogen configuration and local site chemistry. Electrocatalysis and energy storage constitute the main application focus, whereas photocatalytic, sensing, and separation studies are considered as related examples of transferable design principles.

2 Synthetic Strategies for Nitrogen-Containing Graphdiyne

2.1 Monomer Design and Bottom-Up Framework Construction

In situ synthesis of N-GDY generally relies on embedding nitrogen atoms into rationally designed heteroaromatic ethynyl monomers before polymerization. Subsequent coupling reactions directly generate nitrogen-containing acetylenic aromatic networks. The major advantage of this strategy is structural traceability: the nitrogen position, dopant type and framework composition are partially encoded in the monomer structure. Nevertheless, a well-defined monomer does not guarantee a completely ordered two-dimensional product. Polymerization

defects, edge sites, incomplete coupling and interlayer stacking may still appear during material growth. Thus, bottom-up synthesis should be regarded as a route that improves structural predictability rather than a method that removes all structural uncertainty. Kan et al. reported an early interfacial synthesis of two-dimensional N-graphdiyne films using triazine-based and pyrazine-based ethynyl monomers through Glaser-type coupling at liquid/liquid and gas/liquid interfaces. The gas/liquid interfacial route produced thinner films with improved crystallinity, and the minimum thickness reached about 4 nm. This work was important because it experimentally demonstrated that nitrogen-containing heteroaromatic units do not have to be introduced only by post-treatment; instead, they can be directly written into an extended acetylenic carbon network through bottom-up monomer coupling [28].

Pan et al. further extended this concept by using pyridine-, pyrazine- and triazine-derived monomers to prepare N1-GDY, N2-GDY and N3-GDY nanosheets at a liquid/liquid interface [29]. As shown in Fig. 1(a,b), this work connected molecular monomer design with the formation of two-dimensional N-GDY sheets and confirmed the morphology by structural models, TEM, SEM and

AFM. Increasing the number of nitrogen atoms in the monomer enhanced surface hydrophilicity and improved Rh-mediated photocatalytic NADH regeneration from N1-GDY to N3-GDY. These results associate monomer design with changes in framework composition, wettability, band structure, and photocatalytic behavior; because these factors vary together, the activity trend cannot be assigned to nitrogen content alone.

After interfacial N-GDY synthesis became feasible, research attention shifted toward the programmed incorporation of specific nitrogen-containing building units. Triazine-graphdiyne (TA-GDY) reported by Yang et al. showed that triazine units could act as well-defined structural nodes within the graphdiyne network, creating a nitrogen-containing carbon skeleton with a designed heterocyclic composition [30]. In a subsequent study, the same group proposed atomically precise nitrogen sites in graphdiyne for efficient Li^+ anchoring, illustrating that monomer engineering can introduce defined nitrogen environments with relatively high structural certainty [31]. These studies transformed in situ N-GDY synthesis from a simple dopant-introduction strategy into a more precise approach for regulating nitrogen type, position and local electronic structure.

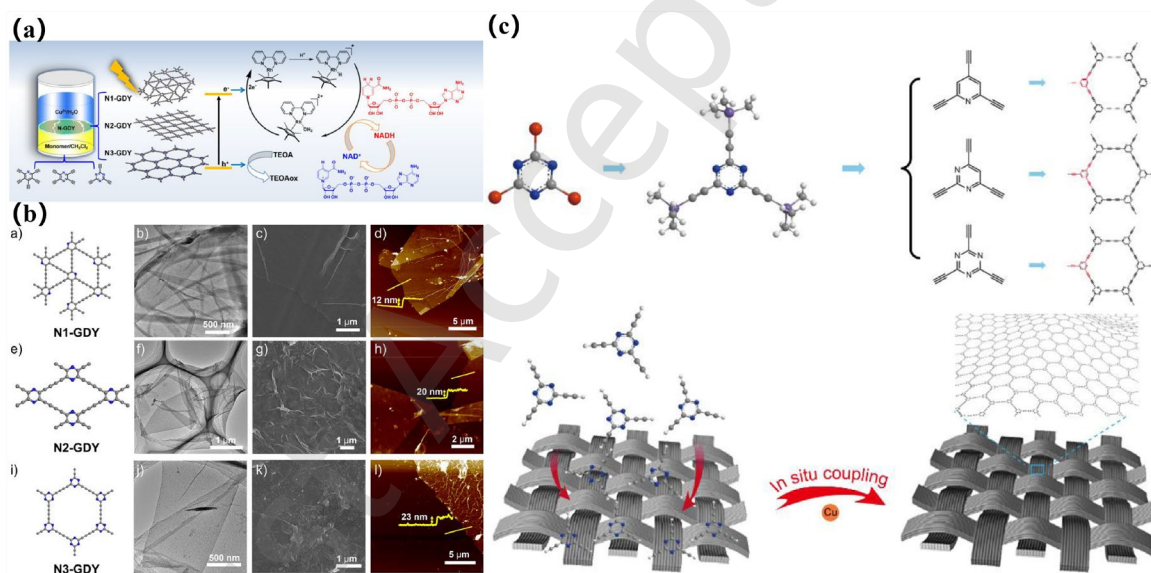


Figure 1 Bottom-up synthesis and monomer-directed construction of N-GDY. (a) Liquid/liquid interfacial synthesis of N1-GDY, N2-GDY and N3-GDY from nitrogen-containing ethynyl monomers, followed by Rh-mediated photocatalytic NADH regeneration. Adapted with permission from Ref. [29], © American Chemical Society 2018. (b) Proposed structures and representative TEM, SEM and AFM images of N1-GDY, N2-GDY and N3-GDY, showing two-dimensional nanosheet morphologies associated with the proposed nitrogen-containing frameworks. Adapted with permission from Ref. [29], © American Chemical Society 2018. (c) Monomer-directed in situ coupling strategy for constructing 1NGDY, 2NGDY and 3NGDY with tunable $\text{sp}^2\text{-N}$ configurations. Adapted with permission from Ref. [32], © The Authors 2025.

Recent bottom-up studies have moved from simple N-heteroarenes to larger π -conjugated and nitrogen-rich monomers. Gao et al. constructed high-quality pyrazinoquinoxaline-based graphdiyne, showing that extended fused N-heteroaromatic units can also be integrated into graphdiyne frameworks [33]. Hou et al. reported hexaazatrinaphthylene-containing HATN-GDY, further expanding the structural diversity of nitrogen-rich graphdiyne materials [34]. In 2025, Wang et al. prepared metal-free graphdiyne with precisely modulated $\text{sp}^2\text{-N}$ configurations by a bottom-up route and applied it to OER optimization [32]. As illustrated in Fig. 1(c), this work directly linked monomer structure, $\text{sp}^2\text{-N}$ configuration and catalytic-site regulation,

indicating that bottom-up N-GDY chemistry has evolved from framework synthesis toward catalytic site engineering.

Overall, bottom-up synthesis based on nitrogen-containing ethynyl monomers has become a central route for preparing N-GDY-related materials. The strategy preinstalls nitrogen-containing units at the molecular level and then converts them into extended two-dimensional conjugated networks through interfacial or solution-phase coupling [28–34]. Remaining challenges include the multistep synthesis and limited stability of nitrogen-containing ethynyl monomers, low interfacial polymerization yields, difficulties in simultaneously controlling film thickness and crystallinity, and the lack of mature large-area or scalable production methods. Future work should therefore

focus on robust monomer design, reaction-kinetic control at interfaces, improved film quality and scalable fabrication protocols.

2.2 Post-Doping and Post-Synthetic Introduction of Nitrogen

In contrast to bottom-up construction, post-doping introduces nitrogen after the GDY skeleton has already formed. Representative post-synthetic strategies include NH_3 annealing, adsorption/annealing treatments using nitrogen-containing molecules, and reactions with thermally generated nitrogen-containing fragments. These methods differ substantially in nitrogen-source chemistry, site selectivity and structural side effects. Therefore, post-doping should not be treated as a single uniform route, but should be classified according to how nitrogen is introduced into the preformed GDY framework. The development of this approach has moved from simple thermal

ammoniation toward multistep cooperative modification and, more recently, toward more site-directed nitrogen configuration control. In an early representative study, Liu et al. treated GDY powders under an NH_3/Ar atmosphere and obtained nitrogen-doped GDY samples at different temperatures [13]. The incorporated nitrogen was mainly assigned to imine-type species accompanied by a small amount of pyridinic nitrogen. The sample treated at 550 °C exhibited the best ORR activity, indicating that imine-like nitrogen associated with sp-carbon sites can be an effective dopant configuration in post-treated GDY. Zhang et al. later applied NH_3 thermal treatment to GDY films and distinguished possible imine1N, imine2N and pyridinic-N species by XPS analysis [18]. Their results suggested that nitrogen introduction partially weakens the acetylenic signatures, increases defect density and creates additional electrochemically active sites. This confirms that thermal ammoniation is applicable not only to powders but also to GDY films.

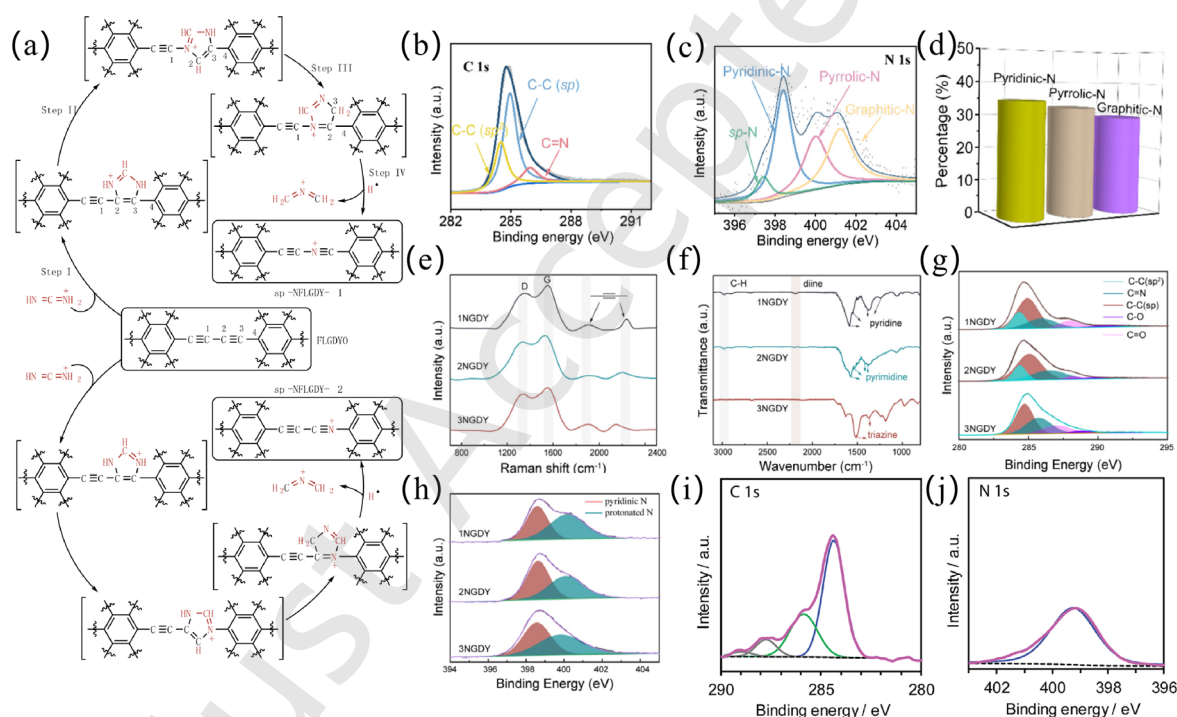


Figure 2 Representative N-site configurations and structural verification of N-GDY obtained by post-doping and bottom-up strategies. (a) Proposed pathway for introducing sp-N into few-layer graphdiyne oxide using melamine-derived fragments. Adapted with permission from Ref. [12], © Springer Nature Limited 2018. (b–d) High-resolution C 1s and N 1s XPS spectra and relative N-species distribution of porous ZnT-N-GDY, showing the coexistence of sp-N, pyridinic-N, pyrrolic-N and graphitic-N. Adapted with permission from Ref. [35] under CC BY 4.0. (e–h) Raman, FTIR, C 1s and N 1s spectra of 1NGDY, 2NGDY and 3NGDY, supporting the preservation of diyne linkages and the formation of sp²-N-containing frameworks through bottom-up monomer design. Adapted with permission from Ref. [32], © The Authors 2025. (i, j) C 1s and N 1s spectra of PR-GDY, in which the N 1s signal is mainly assigned to pyridinic nitrogen. Adapted with permission from Ref. [36], © The Royal Society of Chemistry 2018. Overall, bottom-up monomer design affords more structurally traceable sp²-N-containing frameworks, whereas post-synthetic modification more often produces porous or defect-rich structures with multiple coexisting N species, although site-directed sp-N formation is also achievable.

Lv et al. developed a sequential post-treatment process involving pyridine preadsorption, high-temperature annealing and secondary NH_3 treatment. In this strategy, GDY first adsorbed a small amount of pyridine and was then annealed at 700–1000 °C to generate N-GDY; further NH_3 treatment of N-GDY-900 produced N/N-GDY. This method increased the nitrogen content, enlarged the specific surface area and generated a richer porous structure, thereby combining faster mass transfer with more exposed active sites. XPS fitting and DFT calculations

suggested that imineN-2, imineN-2,2 and partly pyridinic nitrogen might be responsible for the improved ORR activity. The focus of post-doping research therefore shifted from whether nitrogen was introduced to where nitrogen resides and what configuration it adopts [19]. A more site-directed example was provided by Zhao et al., who introduced sp-hybridized nitrogen at acetylenic sites through a pericyclic substitution reaction between few-layer graphdiyne oxide and melamine-derived active nitrogen fragment. The sp-N content could be tuned by the annealing

temperature and melamine/FLGDYO mass ratio, and ORR activity increased with the sp²-N proportion. This study demonstrates that post-doping does not necessarily generate only random nitrogen defects; with a suitable reaction design, identifiable and tunable nitrogen configurations can also be obtained [12].

These studies indicate that post-synthetic nitrogen introduction should be differentiated according to the nitrogen source and reaction pathway. Direct NH₃ annealing is simple and applicable to GDY powders or films, but it usually gives mixed imine-type and pyridinic-N species and may introduce additional defects [13, 18]. Pyridine-assisted annealing followed by secondary NH₃ treatment can increase nitrogen content and porosity, making it useful for ORR-oriented activity enhancement, although the effects of N configuration and pore evolution are difficult to separate [19]. By contrast, melamine-mediated modification provides a more traceable route for constructing sp²-N at acetylenic sites, but it requires specific GDY-derived precursors and careful thermal control [12]. Therefore, NH₃ annealing is more suitable for general modification, molecule-assisted treatment for coupling N doping with morphology/porosity regulation, and melamine-mediated chemistry for site-defined mechanistic studies.

Fig. 2 compares structural evidence for nitrogen-site identification in post-doped and bottom-up N-GDY systems. Fig. 2(a) shows the sp²-N introduction mechanism proposed by Zhao et al., in which melamine-derived fragments react with acetylenic sites in few-layer graphdiyne oxide [12]. Fig. 2(b,c) present the high-resolution C 1s and N 1s spectra of ZnT-N-GDY, while Fig. 2(d) summarizes the relative distribution of nitrogen species. The coexistence of sp²-N, pyridinic-N, pyrrolic-N and graphitic-N suggests that real post-treated samples often contain multiple nitrogen configurations, making it risky to assign catalytic enhancement to a single N species [35]. By comparison, Raman and FTIR spectra of 1NGDY, 2NGDY and 3NGDY in Fig. 2(e,f) verify the preservation of diyne linkages and nitrogen-containing heteroaromatic units after polymerization, and the C 1s/N 1s spectra in Fig. 2(g,h) further support the formation of sp²-N-containing frameworks [32]. Fig. 2(i,j) show C 1s and N 1s spectra of PR-GDY, where the N 1s signal is mainly attributed to pyridinic nitrogen [36]. These examples illustrate that the key issue is not merely whether nitrogen has been introduced, but what chemical state it adopts and whether that state participates in the catalytic reaction. Post-doping is flexible because it does not require the redesign of nitrogen-containing monomers. It can regulate electronic structures, defect distributions and pore environments on an existing GDY skeleton. However, conventional thermal routes still suffer from broad dopant distributions, multiple coexisting nitrogen configurations, limited quantitative accuracy and poor control over dopant depth. Future post-doping studies should therefore emphasize selective site chemistry, combined in situ spectroscopy and theoretical modeling, and the coupling between nitrogen configuration, interlayer structure and porosity.

2.3 Structural Characterization and Identification of Nitrogen Configurations

Nitrogen labels used in this review describe different structural attributes and are not necessarily mutually exclusive. The terms sp²-N and sp³-N refer mainly to hybridization-related structural assignments, whereas pyridinic, pyrazinic, triazinic, imine-type, and metal-coordinated N describe local bonding or coordination environments. Reliable identification of nitrogen configurations in N-GDY requires a combination of spectroscopic and microscopic evidence rather than a single characterization method. XPS is the most commonly used technique for distinguishing nitrogen chemical states. In N 1s spectra, pyridinic-N, imine-type N, pyrrolic-N, graphitic-N and sp²-N-related species are generally assigned according to their binding-energy differences, while C 1s spectra provide complementary information on C=C, C≡C, C-N and C=N bonding environments. However, because the binding energies of different N species may partially overlap, XPS peak fitting should be interpreted together with framework-preservation and morphology evidence. Across the cited studies, sp²-N-related components are generally reported at lower N 1s binding energies (approximately 396–397 eV), pyridinic or imine-type components mainly around 398–400 eV, pyrrolic or protonated N around 400–401 eV, and graphitic N at higher binding energies (approximately 401–402 eV). Because these ranges can overlap and vary with local bonding and energy calibration, assignments should be cross-validated using C 1s, Raman/FTIR, and structural evidence.

Raman and FTIR spectroscopy are particularly important for judging whether the acetylenic carbon skeleton is retained after nitrogen incorporation. Raman spectra provide information on carbon disorder through D/G-band features and can also reflect changes in graphdiyne-related acetylenic structures. FTIR spectra are useful for identifying C≡C stretching and C–N/C=N vibrations, thereby helping to verify whether diyne linkages and nitrogen-containing heteroaromatic units are preserved after bottom-up polymerization or post-synthetic treatment. Microscopic techniques such as TEM, SEM and AFM further reveal whether the obtained materials exist as nanosheets, nanofilms, nanotubes or porous frameworks. For POM/N-GDY-related hybrids, XAS/EXAFS, Raman/FTIR and quasi-in situ XPS are also valuable for probing metal-N coordination, POM metal-oxo integrity and interfacial charge redistribution. Therefore, the assignment of nitrogen configurations should be based on a combined evidence chain involving XPS, Raman, FTIR and morphology characterization, rather than on N 1s fitting alone.

Overall, Fig. 1 and Fig. 2 distinguish two major synthetic logics: bottom-up synthesis uses predefined heteroaromatic monomers to improve nitrogen-site traceability, whereas post-doping introduces nitrogen into preformed GDY and often produces mixed N species together with defect, porosity and morphology changes.

As summarized in Table 1, the major nitrogen configurations reported in N-containing graphdiyne materials differ in their preparation routes, electronic effects, and catalytic relevance. This comparison underscores the importance of the local nitrogen environment in interpreting their electrocatalytic behavior.

Table 1 Comparison of nitrogen configurations in N-containing graphdiyne materials, including their typical preparation routes, main

electronic effects, and reported catalytic relevance.

N configuration	Typical preparation route	Main electronic effect	Reported catalytic relevance	Ref.
sp-N	Site-directed substitution at acetylenic sites using melamine-derived N fragments	Redistributes local charge and regulates intermediate adsorption	ORR; OER/HER in S- or B-codoped systems	[12, 20, 37, 38]
Pyridinic-N	Bottom-up coupling of pentaethynylpyridine or NH ₃ treatment of HsGDY	Polarizes neighbouring carbon atoms and promotes interfacial electron transfer	ORR and Zn-air batteries; reaction pathway depends on the local framework	[39–41]
Pyrrolic-N	High-temperature treatment of porous N-GDY, usually with other N species	Individual electronic effect remains unresolved	No independent catalytic preference established	[35]
Imine-type N	NH ₃ /Ar annealing or sequential pyridine/NH ₃ treatment	Modifies C=N-related charge distribution; structural assignment remains model-dependent	Associated with ORR in mixed-N systems	[13, 19]
Graphitic-N	High-temperature treatment or heteroatom codoping	Modifies the π -electron distribution, but its individual effect has not been isolated	No independent catalytic preference established	[20, 35]
Pyrazinic-/triazinic-N	Bottom-up coupling of ethynyl pyrazine/triazine monomers	Regulates electron-withdrawing strength, band structure and charge transfer	Oxygen redox reactions, OER and HER; activity is motif-dependent	[28, 32, 36, 39]
Metal-coordinated N	Incorporation of metal centers into N-containing GDY or formation of M–N _x motifs	Modifies the local coordination and electronic structure of metal sites and may stabilize isolated metal centers	ORR/HER in Co–N–GDY and CO ₂ RR in Cu–N ₂ –GDY; effects depend on the metal and coordination	[42, 43]

Note: These categories are not necessarily mutually exclusive. Their reported catalytic relevance depends on the local framework, metal center, reaction, and test conditions and should not be interpreted as a universal activity or POM-binding ranking.

3 Properties and Applications of Nitrogen-Containing Graphdiyne

3.1 Electrocatalytic Reactions

3.1.1 Oxygen Reduction Reaction

The oxygen reduction reaction is a kinetically sluggish cathodic process and a major cathodic bottleneck in fuel cells and metal–air batteries. Since the discovery of nitrogen-doped carbon nanotube arrays as metal-free ORR catalysts, nitrogen-containing carbon materials have been widely studied as alternatives to Pt-based catalysts [10]. GDY provides a distinct platform for ORR catalyst design because it combines an sp/sp²-conjugated skeleton, charge redistribution induced by acetylenic linkages, intrinsic pores and tunable dopant sites. In N-GDY systems, Liu et al. first demonstrated that NH₃-treated N-GDY exhibited ORR activity in alkaline media comparable to commercial Pt/C, together with better stability and methanol tolerance [13]. Zhang et al. subsequently proposed heteroatom-doped GDY as an efficient metal-free ORR catalyst and showed that dopant-induced electronic modulation can improve the adsorption behavior of

oxygen-containing intermediates [44].

The research focus has gradually shifted from whether nitrogen doping is effective to which nitrogen configuration is most active. Lv et al. reported porous nitrogen-doped GDY prepared by a dual nitrogen-source strategy involving pyridine and ammonia. The resulting N/N-GDY displayed an onset potential of 0.98 V, a limiting current density of 5.1 mA cm^{−2}, an electron-transfer number above 3.84 and a H₂O₂ yield below 8% in 0.1 M KOH, indicating a dominant four-electron pathway [19]. Zhao et al. introduced sp-N into ultrathin GDY at acetylenic sites through a pericyclic reaction and demonstrated enhanced O₂ adsorption and charge transfer. The catalyst performed comparably to Pt/C in alkaline media and outperformed many metal-free carbon catalysts in acidic electrolytes [12]. In parallel, Lv et al. designed hydrogen-substituted GDY as an in-plane edge-like model and selectively introduced pyridinic nitrogen, showing that pyridinic-N can also generate efficient active centers within graphdiyne-like frameworks [41]. These studies collectively show that ORR activity is controlled more by nitrogen configuration, site location and neighboring carbon polarization than by total nitrogen content alone.

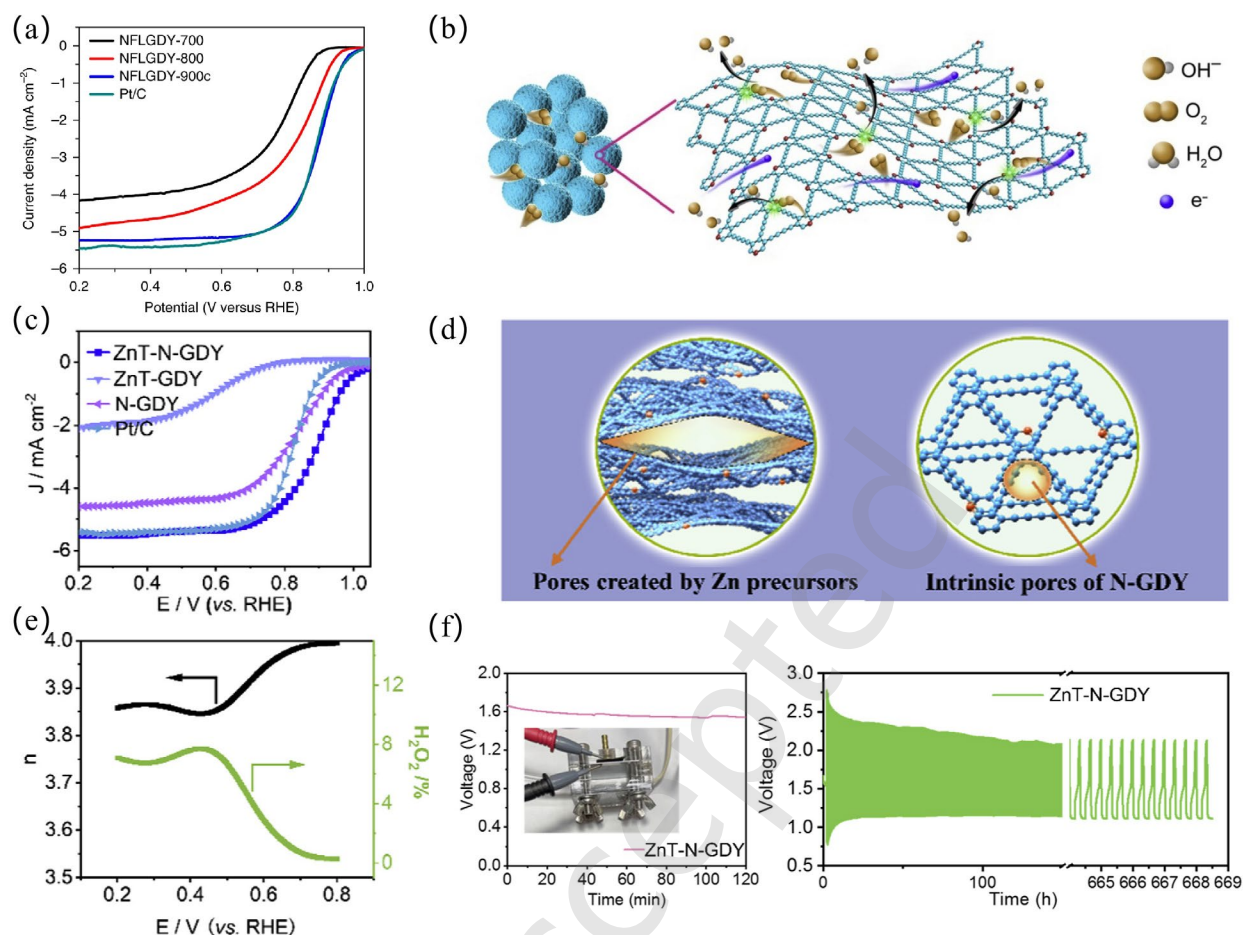


Figure 3 ORR structure-activity relationship and Zn-air battery validation of N-GDY-based catalysts. (a) ORR polarization curves of sp-N-doped few-layer GDY. Adapted with permission from Ref. [12], © Springer Nature Limited 2018. (b) Schematic ORR process on a pyridinic-N-rich GDY-like framework. Adapted with permission from Ref. [40], © Elsevier B.V. 2019. (c) ORR polarization curves of ZnT-N-GDY and reference catalysts. (d) Pores generated by Zn precursors and intrinsic pores of N-GDY. (e) Electron-transfer number and H₂O₂ yield of ZnT-N-GDY. (f) Open-circuit voltage and long-term cycling stability of a ZnT-N-GDY-based Zn-air battery. Adapted with permission from Ref. [35] under CC BY 4.0.

Theoretical work has refined the mechanistic understanding of ORR on N-GDY. Chen et al. suggested that N atoms are not necessarily the direct O₂ adsorption sites; instead, they tune the adsorption free energies of *OOH, *O and *OH by redistributing charge on adjacent carbon atoms. Among the investigated structures, the sp-N (II) configuration gave the most favorable increase in onset potential [37]. Kang et al. further argued that the high ORR activity of graphdiyne cannot be ascribed exclusively to sp-N. Rather, a synergistic effect between sp-N and sp²-N configurations can modulate *OOH/*OH adsorption and lower the theoretical overpotential to a level close to Pt-based catalysts [45]. More recently, Sun et al. used monomer engineering to construct graphdiyne models containing triazinic-N, pyrazinic-N or pyridinic-N, and found that these nitrogen types can markedly change the electron-transfer number and reaction pathway: tz-GDY, pz-GDY, and py-GDY exhibited electron-transfer numbers of 3.21, 2.45, and 2.20, respectively, indicating a greater contribution from the four-electron pathway in tz-GDY under the reported conditions [39]. Together with the other pyridinic- and sp-N-containing systems discussed above, this comparison shows that an N-site label alone does not determine ORR selectivity; the surrounding framework, adjacent carbon sites, and experimental conditions must also be considered.

In addition to nitrogen configuration, pore and morphology

engineering strongly affect the apparent ORR performance. Liu et al. showed that GDY/NGDY nanotubes can increase the reaction interface and reduce charge-transfer resistance, leading to a higher half-wave potential than undoped GDY nanotubes [46]. Si et al. used zinc acetylacetonate as a sacrificial template and porogen to construct porous ZnT-N-GDY. The catalyst exposed more nitrogen sites, especially pyridinic-N species, and exhibited ORR activity superior to Pt/C together with promising Zn-air battery durability [35]. As shown in Fig. 3(a), the ORR polarization curves of sp-N-doped few-layer GDY demonstrate that introducing sp-N sites at acetylenic positions markedly enhances oxygen reduction activity. This improvement indicated that N-site-induced electronic restructuring of neighboring sp/sp² carbon atoms is favorable for O₂ adsorption and interfacial electron transfer [12]. Fig. 3(b) further illustrates the proposed reaction process, showing that the heteroaromatic N sites and adjacent carbon atoms in the pyridinic-N-rich GDY-like framework may cooperatively participate in O₂ activation, electron transfer, and OH⁻ desorption [40]. For porous ZnT-N-GDY, Fig. 3(c) shows that its ORR polarization curve outperforms those of the control samples, including N-GDY, ZnT-GDY, and Pt/C. Fig. 3(d) further indicates that the pore structure generated by the Zn precursor and the intrinsic channels of N-GDY can synergistically increase active-site exposure and facilitate mass

transport. Moreover, the electron transfer number close to 4 and the low H_2O_2 yield shown in Fig. 3(e) suggest that ZnT-N-GDY predominantly follows a four-electron ORR pathway. The open-circuit voltage and long-term cycling performance of the Zn-air battery in Fig. 3(f) further demonstrate its potential to advance from three-electrode half-cell evaluation toward practical air-cathode device validation [35]. Overall, N-GDY ORR design follows two complementary principles: the intrinsic activity can be optimized by precise nitrogen-site engineering, whereas the electrochemical response can be amplified by hierarchical porosity, nanomorphology and mass-transfer control. Further advances require quantitative active-site identification, improved acid stability and long-term device validation beyond half-cell tests [12, 19, 35, 37, 39, 41, 45, 46].

3.1.2 Oxygen Evolution Reaction

N-GDY research in the oxygen evolution reaction has moved from empirical doping toward programmable site regulation. The essential idea is to reconstruct the local charge density and spin state of the GDY skeleton through nitrogen incorporation, thereby optimizing the adsorption/desorption of key oxygen-containing intermediates such as $\ast\text{OH}$, $\ast\text{O}$ and $\ast\text{OOH}$. Early studies on nitrogen-containing graphyne-like acetylenic carbon materials, although not always typical GDY frameworks, provided useful evidence that nitrogen defects can improve electrochemically active surface area, charge transport and OER kinetics [47]. Theoretical calculations by Gu et al. further indicated that heteroatom configuration strongly affects ORR/OER activity in graphdiyne-type materials, and that selected sp-N configurations can improve the free-energy profile of OER intermediates [48]. Experimentally, Zhao et al. achieved stereodefined codoping of sp-N and S atoms in few-layer graphdiyne and significantly improved OER activity by jointly tuning the local electronic structure and reactive sites [20]. As shown in Fig. 4(a, b), the N 1s and S 2p spectra of NSFLGDY-900 reveal distinguishable sp-N, pyridinic-N, graphitic-N and S-C/S=C environments, supporting the presence of distinct nitrogen- and sulfur-containing chemical environments. The OER polarization curve in Fig. 4(c) shifts positively relative to FLGDY-900 and approaches or surpasses RuO_2 , confirming that sp-N/S codoping can improve oxygen-intermediate adsorption and interfacial charge-transfer kinetics. Zheng et al. further extended metal-free graphdiyne systems to acidic OER and demonstrated that electronic-structure modulation can still

optimize intermediate adsorption under more demanding electrolyte conditions [49]. In a recent bottom-up study, Wang et al. prepared 1NGDY, 2NGDY and 3NGDY with different numbers of $\text{sp}^2\text{-N}$ sites and showed experimentally and theoretically that 3NGDY gives the best OER performance. The overpotential at 10 mA cm^{-2} in 1 M KOH was about 310 mV, and theoretical free-energy analysis indicated that increasing the number of $\text{sp}^2\text{-N}$ units lowers the barrier of the key $\ast\text{O}$ to $\ast\text{OOH}$ conversion step [32]. Fig. 4(d-g) summarize the Tafel behavior and OER free-energy diagrams of these materials. These results support the view that OER enhancement in N-GDY depends on local electronic reconstruction induced by defined sp-N/S codoping or $\text{sp}^2\text{-N}$ modulation rather than on nitrogen content alone. From the perspective of POM functionalization, POM/GDY systems provide a related structural reference for prospective N-GDY interfacial OER design. Iron-cubane-containing POMs have been used for visible-light-driven water oxidation, showing the advantages of structurally defined metal-oxo clusters in water-oxidation catalysis [50]. Luo et al. deposited Dexter-Silverton-type NiCo-POM microcrystals on nickel foam and achieved sustained OER at pH 13, with an overpotential of 360 mV at 10 mA cm^{-2} and about 96% Faradaic efficiency [27]. Sun et al. then combined $\text{Co}_{5.7}\text{Ni}_{2.3}\text{W}_{12}\text{O}_{42}(\text{OH})_4$ with fluorographdiyne to form $\text{Co}_{5.7}\text{Ni}_{2.3}\text{-POM@FGDY}$, where the three-dimensional porous FGDY framework and conjugated conductive network alleviated the low conductivity of the POM component [14]. $\text{Co}_4(\text{PW}_9)_2\text{@GDY}$ core-shell hybrids further showed that the GDY shell can enhance POM conductivity, pore transport and stability while inducing local charge redistribution through interactions between terminal POM oxygen atoms and GDY [15]. The corresponding POM@FGDY and POM@GDY structures are shown in Fig. 8(a-c).

These POM/graphdiyne systems should be viewed as structural references rather than direct POM/N-GDY examples. In $\text{Co}_{5.7}\text{Ni}_{2.3}\text{-POM@FGDY}$ and $\text{Co}_4(\text{PW}_9)_2\text{@GDY}$, the graphdiyne type shell mainly improves POM-based OER through enhanced conductivity, pore-assisted mass transfer, structural protection and interfacial electron transfer. In particular, $\text{Co}_4(\text{PW}_9)_2\text{@GDY}$ was proposed to involve interfacial effects between terminal POM oxygen atoms and the GDY shell. These findings motivate the hypothesis that selected nitrogen environments in N-GDY could provide additional attachment or charge-transfer pathways for POM species. However, stronger POM binding or more efficient charge redistribution cannot be assumed without direct comparison among GDY, FGDY, and site-defined N-GDY supports under otherwise consistent conditions.

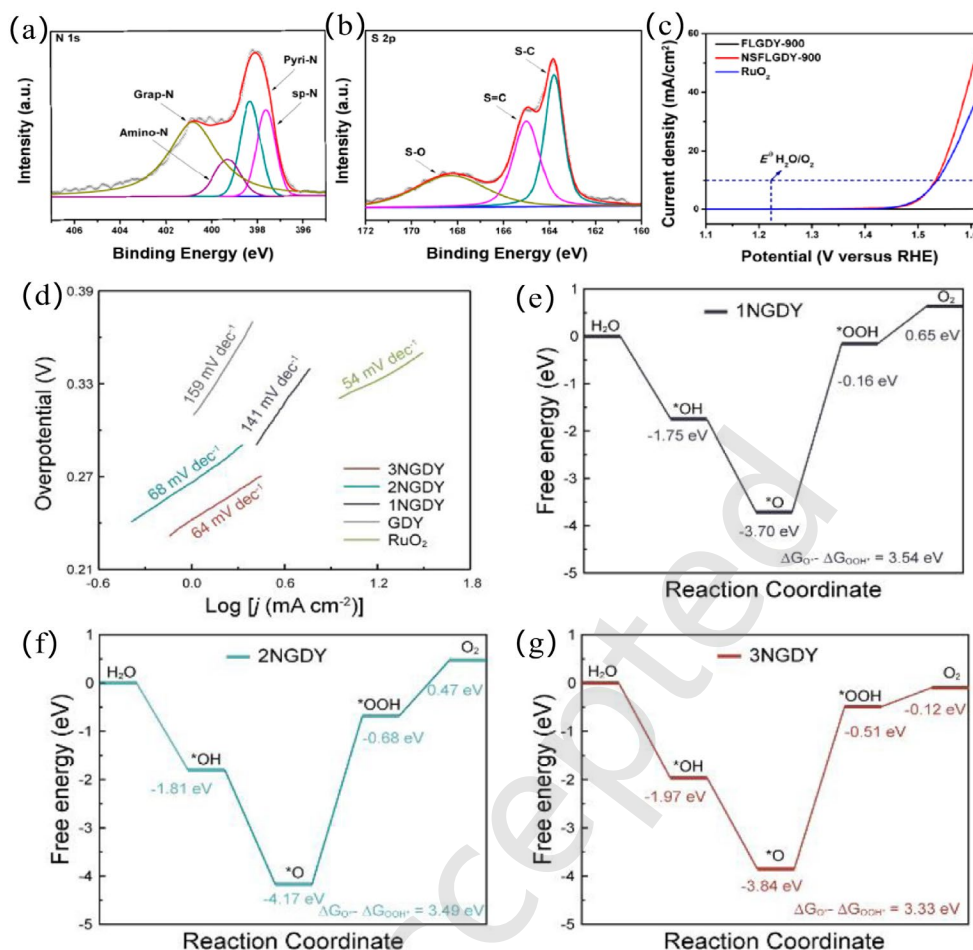


Figure 4 N-site engineering of GDY-based materials for OER. (a, b) High-resolution N 1s and S 2p XPS spectra of NSFLGDY-900, showing fitted components assigned to sp-N/S-codoped species. (c) OER polarization curves of NSFLGDY-900, FLGDY-900 and RuO₂. Adapted with permission from Ref. [20], © American Chemical Society 2019. (d) Tafel plots of 1NGDY, 2NGDY, 3NGDY, GDY and RuO₂. (e–g) OER free-energy diagrams of 1NGDY, 2NGDY and 3NGDY, showing the effect of sp²-N modulation on oxygen-intermediate conversion. Adapted with permission from Ref. [32], © The Authors 2025.

3.1.3 Hydrogen Evolution Reaction

Compared with ORR, the hydrogen evolution reaction on N-GDY emphasizes the relationship among nitrogen configuration, local electronic structure and H⁺ adsorption free energy. Current evidence suggests that HER activity is not governed simply by nitrogen loading; it depends primarily on the bonding mode, location and electronic influence of nitrogen atoms on neighboring sp²/sp³ carbon sites. Sakamoto et al. constructed a pyrazine-incorporated graphdiyne nanofilm (PR-GDY) and showed that embedding N-heteroaromatic units into the graphdiyne skeleton can activate intrinsic metal-free HER activity [36]. He et al. later reported amino-graphdiyne, demonstrating that nitrogen-containing functional groups can facilitate interfacial charge transfer, proton transport and acidic HER stability [51]. In configuration engineering, Zhao et al. reported B,N-codoped few-layer GDY and identified sp-N as an important nitrogen species for reducing HER overpotential, while B introduction further optimized the electronic structure through cooperative coupling. The optimized N,BFLGDY-900 required only 84 mV to reach 10 mA cm⁻² in 1.0 M KOH, with a Tafel slope of 89 mV dec⁻¹, and retained about 93% of its initial current after 10,000 s [38].

As shown in Fig. 5, PR-GDY and N,BFLGDY represent two typical HER optimization strategies: activation of the nitrogen-containing heteroaromatic framework and synergistic regulation by dual heteroatom doping, respectively. Fig. 5(a,b) present the HER polarization curves and Tafel plots of PR-GDY. Compared with pristine GDY, PR-GDY exhibits a lower hydrogen evolution overpotential and a smaller Tafel slope, indicating that the incorporation of pyrazine/pyridinic-N units into the GDY framework can effectively accelerate HER kinetics in metal-free catalytic systems [36]. Fig. 5(c,d) further compare the HER polarization curves and Tafel slopes of N,BFLGDY-900, B,NFLGDY-900, BFLGDY-900, and Pt/C. The results show that N,BFLGDY-900 exhibits a lower overpotential and faster reaction kinetics among the non-noble-metal samples, indicating that the doping sequence of sp-N and B and their local electronic coupling play important roles in regulating H⁺ adsorption and interfacial charge transfer. Fig. 5(e) compares the overpotentials of different N/B-codoped samples at 10 mA cm⁻², further confirming that N,BFLGDY-900 is the most active catalyst in this series. The stability test in Fig. 5(f) shows that N,BFLGDY-900 retained approximately 93% of its initial current during a 10,000 s (≈2.8 h) chronoamperometric test. This result indicates short-duration operational stability, while substantially longer testing is required to establish long-term durability [38].

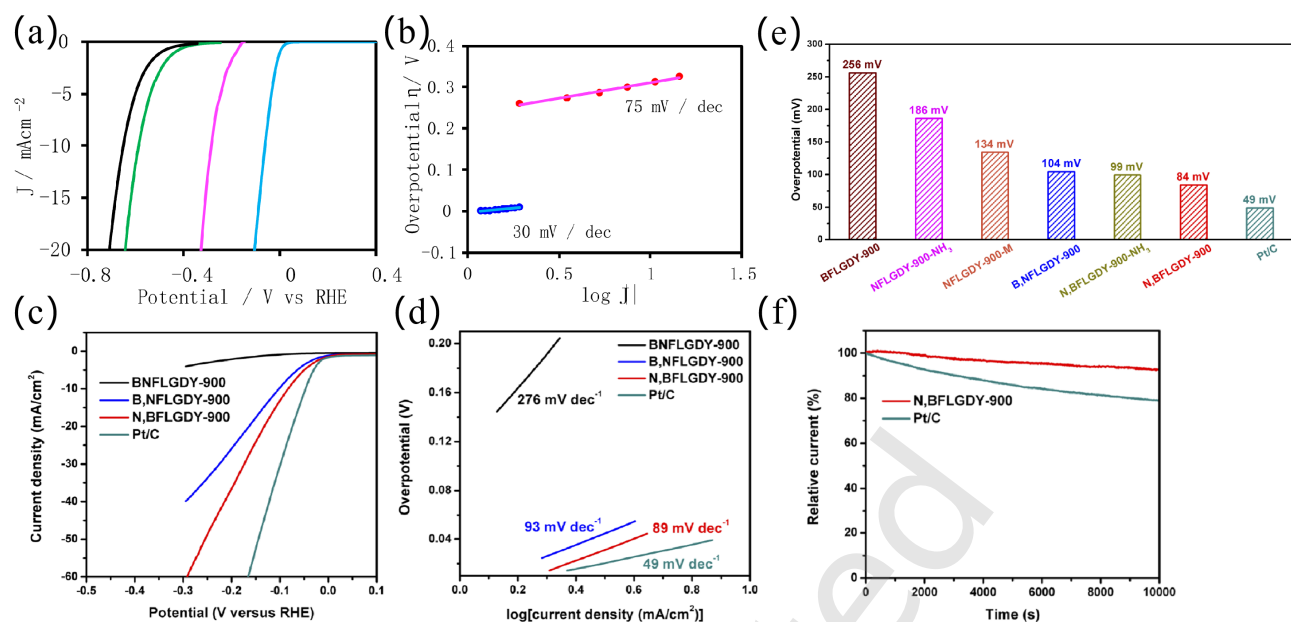


Figure 5 HER performance and configuration modulation of N-GDY-based materials. (a, b) HER polarization curves and Tafel plots of PR-GDY, showing the promoted hydrogen evolution kinetics after incorporation of pyrazine/pyridinic N units. Adapted with permission from Ref. [36], © The Royal Society of Chemistry 2018. (c, d) HER polarization curves and Tafel plots of N,BFLGDY-900 and control samples. (e) Overpotential comparison of different N/B-codoped FLGDY samples at 10 mA cm^{-2} . (f) Stability test of N,BFLGDY-900 and Pt/C. Adapted from Ref. [38] under CC BY 4.0.

N-GDY can also act as a coordination and electronic-regulation platform for metal-containing active centers. Wang et al. prepared Co-N-GDY and showed that N-doped GDY can stabilize cobalt sites and accelerate interfacial electron transfer; the optimized 1% Co-N-GDY exhibited an onset overpotential of 97 mV and a Tafel slope of 132 mV dec^{-1} in 1 M KOH, while maintaining stability for 20 h [42]. Yu et al. grew MoS_2 nanosheets on two-dimensional N-doped GDY nanolayers, illustrating that N-GDY can serve as an interfacial coupling support for water reduction [52]. Theoretical work by Lv et al. highlighted the significance of edge effects: beta-N1-type $\text{sp}^2\text{-N}$ and $\text{sp}^2\text{-N}$ near edges can improve HER by optimizing the local electronic states and ΔG_{H} [53]. Therefore, current research on N-GDY for HER has gradually evolved from empirical optimization based on increasing nitrogen content toward rational design centered on precise regulation of active nitrogen configurations and interfacial synergy. In future studies, in situ spectroscopy, quantitative site characterization, and theoretical calculations should be combined to further clarify the actual contributions of $\text{sp}^2\text{-N}$, pyridinic N, amino N, and edge N under different electrolyte conditions, thereby establishing a unified structure–activity relationship for efficient hydrogen evolution [36, 38, 51, 42, 52, 53].

POM-containing N-graphdiyne-like hybrids further broaden the HER design space. POM-derived hierarchical bimetallic electrocatalysts demonstrate that POMs can act not only as intact metal-oxo clusters but also as metal sources or structural precursors for water-reduction catalysts [54]. Ping et al. constructed Keggin-type $\text{Co}_4\text{-POM@Co-PGDY}$, in which Co-PGDY is a cobalt-porphyrin-linked graphdiyne containing pyridinic N, metal-coordinated N, graphitic N and Co-N_4 sites. In this structure, the $\text{Co}_4\text{-POM}$ core provides metal-oxo cluster activity, while Co-PGDY functions as a conductive shell, a Co-N_4 coactive platform and a protective layer in seawater. The hybrid required 99 mV at 10 mA cm^{-2} in 1 M KOH and 301 mV at 10 mA cm^{-2} in seawater, with good stability over 50 h. In situ Raman/SR-FTIR observations of H_3O^+ intermediates suggested that the POM/N-containing graphdiyne interface may promote water dissociation and proton transfer [16]. Mechanistically, $\text{Co}_4\text{-POM@Co-PGDY}$ is more accurately described as a POM/N-containing graphdiyne interfacial catalyst rather than a conventional N-doped GDY material. The $\text{Co}_4\text{-POM}$ core provides redox-active metal-oxo clusters, whereas Co-PGDY contributes a conductive acetylenic shell, porphyrinic Co-N_4 sites, pyridinic/metal-coordinated/graphitic N species and seawater-protective confinement. The lower charge-transfer resistance and the observation of H_3O^+ intermediates by Raman/SR-FTIR indicate that the POM/Co-PGDY interface can accelerate electron transfer and promote water dissociation/proton-transfer steps. However, the current evidence supports interfacial electronic cooperation rather than proving a specific covalent POM–N bonding mode. This system provides a related structural reference for designing future POM/N-GDY interfaces.

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3.1.4 Carbon Dioxide Electroreduction Reaction

In the electrochemical CO_2 reduction reaction (CO_2RR), nitrogen-containing graphdiyne and its derivative systems have shown distinct advantages in site-specific electronic-structure regulation. In general, the incorporation of nitrogen can increase the density of states near the Fermi level of the GDY framework and strengthen the adsorption of key intermediates such as $^*\text{COOH}$ and $^*\text{CHO}$. In addition, the construction of N-coordinated single-atom centers can modulate the d-electron distribution of metal sites, thereby lowering the energy barriers for initial CO_2 activation and subsequent deep hydrogenation [55–57]. Liu et al. showed by DFT calculations that the intrinsic $\text{sp}^2\text{-sp}^2$ hybridized sites in GDY already exhibit higher CO_2RR

activity than purely sp^2 carbon frameworks. After N doping, the formation barrier of $^*COOH$ is further reduced and shows pronounced site dependence: the N1 site is more favorable for CH_4 formation, the N3 site tends to promote the CO pathway, whereas the N6/N7 sites are more conducive to CH_3OH production. In particular, the limiting potential for CH_3OH formation at the N6 site can be as low as -0.46 V. These results indicate that N doping not only enhances CO_2 activation but also provides tunable control over product selectivity [55]. Furthermore, Feng et al. found that after single Cu atoms were anchored on N-doped GDY, Cu@N-doped GDY exhibited more favorable spontaneous CO_2 adsorption and charge-transfer behavior than Cu@B-doped GDY. Among the investigated models, Cu@Nb-GDY showed a common limiting potential of -0.65 V for the $HCOOH$, CO, OCH_2 , CH_3OH , and CH_4 pathways, while CO_2RR was thermodynamically preferred over the competing HER. These results suggest that the N-coordination environment can effectively optimize the electronic structure of Cu centers and broaden the reaction window for multiple C1 products [56]. In terms of heterostructure design, Yang et al. proposed Co- N_4 @GRA/GDY, in which d- π coupling weakens the adsorption scaling relationship among key intermediates. This system shows a limiting potential of -0.567 V for the CH_4 pathway. After charged interfaces and continuum solvation effects were considered, the potential-determining step could be further lowered to 0.366 eV, highlighting the potential of the metal- N_x

site-GDY conductive framework synergy for regulating multi-electron deep reduction processes [57]. As shown in Fig. 6, the theoretical model proposed by Yang et al. further elucidates the role of the GDY/GRA heterostructure in single-atom catalysis for CO_2RR . Fig. 6(a) presents the structural model of TM- N_4 @GRA/GDY, in which the metal center is coordinated by an N_4 moiety and embedded within the conjugated GDY/GRA heterostructure. This result indicates that GDY serves not only as a conductive support, but also as an active electronic regulator of the metal center through its acetylenic π -conjugated framework. In Fig. 6(b), the band structure of Co- N_4 @GRA/GDY reveals pronounced coupling among the Co, N, and C orbitals near the Fermi level, providing an electronic-structure basis for the multielectron transfer process in CO_2RR . Furthermore, Fig. 6(c) distinguishes the selective pathways toward CO and $HCOOH$ by comparing the adsorption free energies of $^*COOH$ and $^*OCHO$, whereas Fig. 6(d) correlates the adsorption of CO_2RR intermediates with that of $^*H$ to evaluate the selectivity difference between CO_2RR and the competing HER. These results suggest that the activity and product selectivity of TM- N_4 sites supported on GDY/GRA heterostructures do not depend solely on the metal center itself, but are jointly governed by the synergistic interplay among the metal- N_4 coordination environment, the conjugated GDY/GRA framework, and the adsorption behavior of key intermediates.

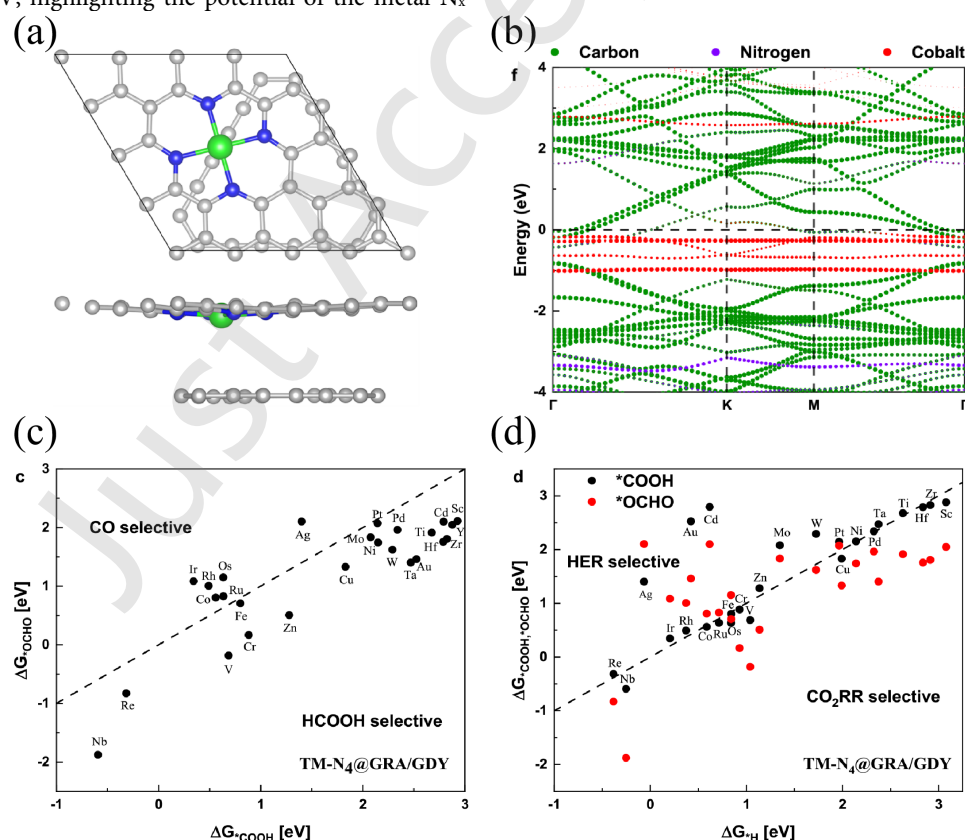


Figure 6 Theoretical screening of TM- N_4 single-atom sites supported on GRA/GDY heterostructures for CO_2RR . (a) Structural model of TM- N_4 @GRA/GDY. (b) Band structure of Co- N_4 @GRA/GDY with orbital contributions from C, N and Co atoms. (c) Product-selectivity descriptor based on the adsorption free energies of $^*COOH$ and $^*OCHO$ for distinguishing CO and $HCOOH$ pathways. (d) CO_2RR /HER selectivity descriptor for evaluating the competition between CO_2 reduction and hydrogen evolution. Adapted with permission from Ref. [57], © American Chemical Society 2022.

Related experimental studies further illustrate the importance

of nitrogen coordination in graphdiyne-supported metal catalysts.

Dai et al. reported Cu_{1.0}/N₂-GDY, in which under-coordinated Cu-N₂ single-atom centers were constructed on uniform N₂ bidentate sites within the nitrogen-containing GDY framework. This catalyst delivered a CH₄ Faradaic efficiency of 80.6% and a CH₄ partial current density of 160 mA cm⁻² at -0.96 V vs. RHE. More importantly, CH₄ selectivity remained above 70% over a wide total current density range of 100-300 mA cm⁻². These results provide experimental evidence that coupling a nitrogen-containing graphdiyne scaffold with under-coordinated Cu single atoms is an effective strategy for promoting the eight-electron deep reduction of CO₂ to CH₄ [43].

In a related non-GDY system, Keggin-type XW₁₁Co polyoxoanions (X = Si, P, or Co) confined within ZIF-8 cavities showed that the central heteroatom can influence CO₂ to CO electrocatalytic performance [58]. In parallel, Gu et al. demonstrated that a GDY/graphene heterostructure can serve as an efficient scaffold for immobilizing cobalt phthalocyanine (CoPc) molecules. The resulting catalyst achieved a FE_{CO} of 96% with a CO partial current density of 12 mA cm⁻² in an H-cell, and further delivered a FE_{CO} of 97% at 100 mA cm⁻² in a flow cell with stable operation for more than 24 h. This work suggests that GDY is not limited to acting as an electronic regulator for N-coordinated or single-atom active sites; it can also function as a robust anchoring platform for molecular catalytic centers [59]. Beyond conventional N-GDY systems, related nitrogen-containing graphdiyne analogues also offer useful insights into CO₂RR selectivity. Masaud et al. constructed a Cu single-atom catalyst with dual active sites on a crystalline graphdiyne porphyrin analogue, which achieved a total Faradaic efficiency of 70% and a C₂-product Faradaic efficiency exceeding 45%. This result indicates that nitrogen-containing graphdiyne-like conjugated frameworks may not only facilitate deep reduction toward C1 products, but also provide a structural basis for promoting C-C coupling [60]. Studies based on GDY-anchored Fe models with precisely controlled atomic numbers further suggest that the coupling between metal-center configuration and the GDY framework plays a decisive role in governing intermediate adsorption and product distribution [61]. From a broader CO₂RR perspective, however, multi-electron deep reduction and C-C coupling remain key kinetic challenges for achieving highly selective CH₄ and C₂⁺ production [62]. Future studies on nitrogen-containing GDY systems for CO₂RR should therefore move beyond simply correlating activity with nitrogen content. A key priority is to disentangle the respective roles of different N configurations, including pyridinic N, pyrrolic N, graphitic N, and N₂/N₄ coordination motifs, in *COOH formation, deep hydrogenation of *CO, and HER suppression. Combining in situ spectroscopy with high-current-density device testing will be essential for establishing a more reliable structure-activity relationship based on the coupled N site-metal center-acetylenic

carbon motif.

3.1.5 Nitrogen Reduction Reaction: Theoretical Potential and Experimental Bottlenecks

Compared with ORR, OER and CO₂RR, N-GDY-based nitrogen reduction reaction (NRR) studies remain limited and are mainly theoretical. Available calculations suggest that nitrogen doping can promote N₂ adsorption and activation by redistributing charge density on neighboring carbon atoms. Among substitutional models, the sp-N-2 configuration shows relatively favorable NRR activity, while pyridinic-N-related sites may further reduce the reaction barrier through a Mars-van Krevelen-like mechanism coupled with defects [63]. The potential NRR activity of N-GDY therefore arises from the combined effects of nitrogen configuration, local electronic regulation and defect chemistry. However, direct experimental evidence for N-GDY-catalyzed N₂ to NH₃ conversion is still scarce, mainly because N₂ activation is intrinsically difficult, HER competition is severe in aqueous electrolytes, and low NH₃ yields are highly sensitive to possible nitrogen-containing contaminants. Because experimental evidence is still insufficient, this section should be treated as a forward-looking discussion. Future work should prioritize the controllable preparation of specific nitrogen configurations, the suppression of the competing HER, and rigorous experimental validation using Ar/N₂ controls, purified N₂ feed gas, contamination analysis, and ¹⁵N₂ isotope-labeling experiments [64, 65]. A recent experimental study reported Ru single atoms supported on crystalline GDY-like frameworks, achieving an NH₃ yield rate of 188.7 ± 1.6 µg h⁻¹ mg⁻¹ and a Faradaic efficiency of 37.4 ± 0.6% [66]. However, these frameworks possess pure-carbon skeletons and should therefore be regarded as related GDY evidence rather than direct N-GDY examples. Nitrogen-containing surface species and impurities in commercial ¹⁵N₂ gas may also generate misleading NH₃ signals, further emphasizing the need for rigorous blank and isotope-labeling controls.

To provide a clearer comparison of the electrocatalytic performance discussed above, representative N-GDY, N-containing graphdiyne and POM/graphdiyne-based catalysts are summarized in Table 2. Only experimentally reported parameters are included in the main table, whereas purely theoretical limiting potentials are retained in the corresponding discussion sections.

As summarized in Table 2, the relevant performance descriptors vary with the reaction type. ORR activity is mainly evaluated by *E*_{onset}, *E*_{1/2}, electron-transfer number and H₂O₂ yield, whereas OER and HER are commonly compared by η₁₀, Tafel slope and the reported durability metric and test duration. For CO₂RR, product selectivity, partial current density and mass activity are more informative than overpotential alone. Across these systems, the catalytic performance is closely associated with nitrogen-site chemistry, metal-N coordination, pore-assisted mass transport and POM/graphdiyne interfacial electron transfer.

Table 2 Electrocatalytic performance of representative N-GDY, N-containing graphdiyne and POM/graphdiyne-based catalysts.

Catalyst	Design strategy / active site	Reaction/condition	Representative performance and durability	Ref.
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N/N-GDY	Porous N-GDY with imine-type and pyridinic-N-related sites	ORR, 0.1 M KOH	$E_{\text{onset}} = 0.98 \text{ V}$; limiting current density = 5.1 mA cm^{-2} ; $n > 3.84$; H_2O_2 yield < 8%; $E_{1/2}$ shift of 19 mV after 5,000 CV cycles	[19]
NFLGDY-900c	sp-N-doped few-layer GDY at acetylenic sites	ORR; 0.1 M KOH and 0.1 M HClO_4	$E_{1/2} = 0.87 \text{ V}$; $n \approx 3.9$; Tafel slope = 60 mV dec^{-1} ; retained 92% current in 0.1 M KOH and 85% in 0.1 M HClO_4 after 10,000 s	[12]
ZnT-N-GDY	Porous N-GDY templated from zinc acetylacetonate	ORR; Zn-air battery	$E_{1/2} = 0.879 \text{ V}$; $E_{\text{onset}} = 1.04 \text{ V}$; $n = 3.82\text{-}3.89$; H_2O_2 yield < 7.70%; Zn-air battery OCV = 1.55 V and stable operation up to 670 h / 2,000 cycles	[35]
NSFLGDY-900	Stereodefined sp-N/S-codoped few-layer GDY	OER; 1.0 M KOH	$\eta_{10} = 299 \text{ mV}$; current density = 47.2 mA cm^{-2} at 1.6 V vs. RHE; retained 95% current after 20,000 s	[20]
3NGDY	Bottom-up sp^2 -N-modified GDY with three sp^2 -N atoms in each repeating unit	OER; 1.0 M KOH	$\eta_{10} = 310 \text{ mV}$; Tafel slope = 68 mV dec^{-1} ; retained 96% activity after 10 h; negligible degradation after 1,000 cycles	[32]
$\text{Co}_{5.7}\text{Ni}_{2.3}$ -POM@FGDY	Dexter-Silverton-type POM coupled with porous fluorographdiyne	OER; 1.0 M KOH	$E = 1.57$ and 1.71 V vs. RHE at 10 and 300 mA cm^{-2} ; Tafel slope = 76 mV dec^{-1} ; stable for 20 h	[14]
$\text{Co}_4(\text{PW}_9)_2$ @GDY	POM/GDY core-shell composite cluster	OER; 1.0 M KOH	$E_{10} = 1.52 \text{ V}$ vs. RHE; Tafel slope = 80 mV dec^{-1} ; TOF = 0.86 s^{-1} ; stable for 30 h	[15]
N,BFLGDY-900	Sequential sp-N/B-codoped few-layer GDY	HER; 1.0 M KOH	$\eta_{10} = 84 \text{ mV}$; Tafel slope = 89 mV dec^{-1} ; retained 93% initial current after 10,000 s	[38]
1% Co-N-GDY	Co/N-codoped GDY with Co-N-related active sites	ORR, 0.1 M KOH; HER, 1.0 M KOH	ORR: $E_{\text{onset}} = 0.92 \text{ V}$, $E_{1/2} = 0.81 \text{ V}$; HER: onset overpotential = 97 mV, Tafel slope = 132 mV dec^{-1} ; stable HER operation for 20 h	[42]
Co_4 -POM@Co-PGDY	Keggin-type Co_4 -POM coupled with cobalt-porphyrin-linked graphdiyne	HER; 1.0 M KOH and seawater	$\eta_{10} = 99 \text{ mV}$ in 1.0 M KOH and 301 mV in seawater; Tafel slopes = $131 / 175 \text{ mV dec}^{-1}$; stable for 50 h in seawater	[16]
$\text{Cu}_{1.0}/\text{N}_2$ -GDY	Undercoordinated Cu-N ₂ single-atom sites on nitrogen-containing GDY	CO_2RR to CH_4 , flow cell, 1.0 M KOH	$\text{FE}_{\text{CH}_4} = 80.6\%$ at -0.96 V vs. RHE; $j_{\text{CH}_4} = 160 \text{ mA cm}^{-2}$; CH_4 selectivity > 70% at 100-300 mA cm^{-2} ; isolated Cu sites retained after electrolysis	[43]

The reported values were obtained under different electrolytes, catalyst loadings, electrode configurations, iR-correction protocols, and durability tests and therefore should not be interpreted as a direct activity ranking. Potentials are reported versus RHE unless otherwise stated.

3.2 Energy Storage Applications

Beyond electrocatalysis, N-GDY has important potential as an energy-storage electrode material. Nitrogen incorporation can increase the adsorption and anchoring ability toward carrier ions such as Li^+ by modulating local charge density and spin density. At the same time, the two-dimensional π -conjugated skeleton and ordered pores of GDY can facilitate electronic conduction and ion diffusion. N-doped GDY has been shown to improve reversible capacity, rate capability and cycling stability in lithium-ion storage. As shown in Fig. 7(a-c), NH_3 -treated N-GDY exhibits lower charge-transfer resistance and better rate performance than pristine GDY, indicating that nitrogen doping enhances lithium-storage kinetics through electronic and interfacial regulation [18]. Atomically precise nitrogen sites in graphdiyne further improve Li^+ anchoring behavior [31]. Pyrazinoquinoxaline-based graphdiyne films enable efficient gradient Li-ion storage [33], and nitrogen-rich HATN-GDY combines a two-dimensional conjugated framework with in-plane nitrogen-rich cavities, giving a high capacity of up to 2139 mA h g^{-1} and good long-term stability [34]. Beyond battery systems, nitrogen-containing graphdiyne also shows clear potential for supercapacitor applications, where controllable nitrogen configurations and porous architectures can work together to improve specific capacitance and energy density [67]. Nanoporous triazine-based graphdiyne has also been explored for supercapacitive energy storage, further indicating that nitrogen-containing graphdiyne frameworks have

considerable adaptability across both battery-type and capacitive energy-storage systems [68]. The fundamental value of N-GDY in energy storage lies in the synergy between nitrogen-site chemistry and a conjugated porous carbon skeleton, which together support high capacity, fast kinetics and structural stability. However, nitrogen chemistry, pore structure, disorder, and electrode morphology vary simultaneously across these materials. Current comparisons therefore do not isolate a universal effect of a single nitrogen configuration on capacity, rate performance, or cycling stability.

3.3 Photoelectric and Sensing Applications

As a secondary application area, photoelectronic and sensing studies are discussed here to illustrate how nitrogen-site, pore, and interfacial regulation can affect charge transfer and molecular recognition beyond the central energy-conversion and storage focus. Research on nitrogen-containing graphdiyne in photoelectronic and sensing applications is largely enabled by its tunable band structure, high specific surface area, abundant edge/defect sites, and nitrogen-induced interfacial charge redistribution. Previous studies have shown that N-graphdiyne nanosheets prepared at liquid/liquid interfaces can regulate surface wettability and photoinduced carrier behavior by varying the nitrogen content, and can serve as metal-free light-harvesting components in Rh-mediated photocatalytic NADH regeneration.

As shown in Fig. 7(d), the NADH regeneration efficiency increases progressively from N1-GDY to N2-GDY and N3-GDY, with N3-GDY displaying the highest activity. This trend suggests that N-site engineering not only modifies surface wettability, but also affects the transfer of photogenerated electrons to the Rh mediator, thereby influencing the photocatalytic reduction of NAD^+ to NADH [29]. However, nitrogen content, framework electronic structure, wettability, and interaction with the Rh mediator vary together in this series; the activity trend therefore does not isolate the contribution of a single nitrogen configuration. These findings indicate that nitrogen-containing graphdiyne is not merely a conductive scaffold, but can also actively participate in photoinduced electron-transfer processes. In the sensing field, nitrogen-containing graphdiyne and its quantum-dot derivatives have shown promising performance in optical and electrochemical sensing. Owing to their defect-rich structures and improved conductivity, N-doped graphdiyne quantum dots enable highly sensitive optical-electrochemical detection of dopamine [69]. Studies using N-doped graphdiyne directly as an electroactive electrode interface have further shown that abundant sp-N interaction sites, an enlarged electrochemically active surface area, and accelerated interfacial charge transfer are beneficial for anti-interference dopamine detection in complex biofluids. The sensor exhibited a linear response range of 1–550 μM and a detection limit of 0.46 μM [70]. Beyond dopamine detection, N-doped graphdiyne has also been developed as a robust electrochemical biosensing platform for the ultrasensitive monitoring of environmental pollutants [71]. Similarly, graphdiyne quantum-dot-based sensing systems have been used for the electrochemical quantification of chloramphenicol in water samples [72]. These studies show that sensitivity may benefit from accessible surface area and faster electron transfer, whereas selectivity and anti-interference performance require evidence of differential analyte interactions and tests in relevant sample matrices. Because these contributions are not separated consistently across the reported systems, improved sensing performance should not be attributed to a single nitrogen configuration alone.

3.4 Interfacial Modification and POM/Graphdiyne Interfaces

Interfacial modification is an increasingly important application direction for N-GDY. Compared with many conventional carbon supports, N-GDY combines a conductive conjugated carbon skeleton with Lewis-basic or coordinative nitrogen sites. It can therefore passivate defects, regulate energy-level alignment and facilitate carrier extraction at various heterogeneous interfaces. In perovskite solar cells, triazine-based graphdiyne has been used for grain-boundary passivation to suppress interfacial recombination and hysteresis [73]. A 2024 study further showed that a buried interfacial electron-collection center based on triazine graphdiyne can passivate undercoordinated Sn sites at the SnO_2 /perovskite interface, reduce trap density, promote more uniform perovskite grain

growth and increase device efficiency to 24.83% [74]. Polyoxovanadate-modified SnO_2 electron-transport layers have also improved perovskite photodetectors, illustrating that POM units can regulate oxide/semiconductor interfacial charge transport [75]. In membrane interfaces, ultrathin nitrogen-rich graphdiyne films introduced onto Nafion membranes can suppress methanol crossover in direct methanol fuel cells. Single-layer and bilayer films reduced crossover by about 43% and 69%, respectively, improving output performance and long-term stability [76]. Thus, the interfacial role of N-GDY is not a simple coating effect; it arises from the combined action of nitrogen-site interactions, continuous two-dimensional conductive networks and tunable surface energy.

POM functionalization represents an important extension of graphdiyne-based interfacial chemistry. Compared with conventional inorganic nanoparticles, POMs possess structurally defined metal-oxo clusters, tunable redox states and molecular-level electron-storage capability. For interfacial design, the POM architecture, metal composition, protonation state, overall charge, and counterions can influence binding geometry, electron-transfer direction, solubility, and structural stability. Consequently, the behavior observed for one POM/graphdiyne combination should not be generalized to other cluster families without direct structural and electrochemical evidence. Existing $\text{Co}_{5.7}\text{Ni}_{2.3}\text{-POM@FGDY}$, $\text{Co}_4(\text{PW}_9)_2\text{@GDY}$ and $\text{Co}_4\text{-POM@Co-PGDY}$ systems show that graphdiyne-type frameworks can improve POM-based catalysis through conductive carbon networks, pore confinement, interfacial contact and structural protection [14–16]. These systems should therefore be distinguished as POM/FGDY, POM/GDY, and POM/N-containing graphdiyne composites rather than treated as equivalent site-defined POM/N-GDY hybrids.

$\text{Co}_4\text{-POM@Co-PGDY}$ provides an experimental example of combining a POM-containing phase with an N-containing cobalt-porphyrin-linked graphdiyne support. However, the N 1s components assigned to pyridinic, metal-coordinated, and graphitic N characterize nitrogen environments within the support and do not by themselves demonstrate a POM–N bond across the interface. Possible interfacial coupling could influence electron transport, POM retention, and the electron density of terminal or bridging M–O units involved in catalytic redox processes; however, the magnitude of these effects has not yet been quantitatively established. Nevertheless, direct POM–N coordination and molecular-orbital coupling in ideal POM/N-GDY hybrids remain insufficiently verified, and should be further clarified by operando XAS, in situ Raman/FTIR, quasi-in situ XPS and realistic theoretical models.

At the orbital level, donor states associated with pyridinic or imine-type N sites and the conjugated N-GDY π network may interact with low-lying metal-centered d or metal-oxo frontier states of POMs. Depending on the POM composition, protonation state and binding geometry, such coupling may redistribute interfacial charge and modify the electron density and reactivity of terminal or bridging M–O units involved in catalytic redox processes. Because direct spectroscopic evidence for a defined POM–N bond remains scarce, this interpretation is presented as a testable hypothesis requiring PDOS/COHP calculations, charge-density and Bader analyses, and operando spectroscopic verification.

Accordingly, the current evidence should be separated into three levels: direct experimental evidence for composite formation and catalytic performance in the reported systems [14–16], system-specific spectroscopic or theoretical evidence for electronic interaction, and hypotheses concerning site-defined POM/N-GDY interfaces. Accessible pyridinic or imine-type N may act as candidate donors only when a POM contains a coordinatively available metal site, whereas protonated N may contribute to electrostatic association; metal-coordinated N is not

equivalent to an unoccupied donor site. For sp³-N-containing motifs, changes in the electronic structure of adjacent acetylenic carbon sites should be distinguished from direct coordination of nitrogen to a POM metal center. Likewise, sp²-N is too broad a descriptor to predict POM binding without specifying the local bonding environment, protonation state, and accessibility of the nitrogen site. The studies reviewed here do not establish a universal ranking of nitrogen configurations for POM immobilization or catalytic enhancement.

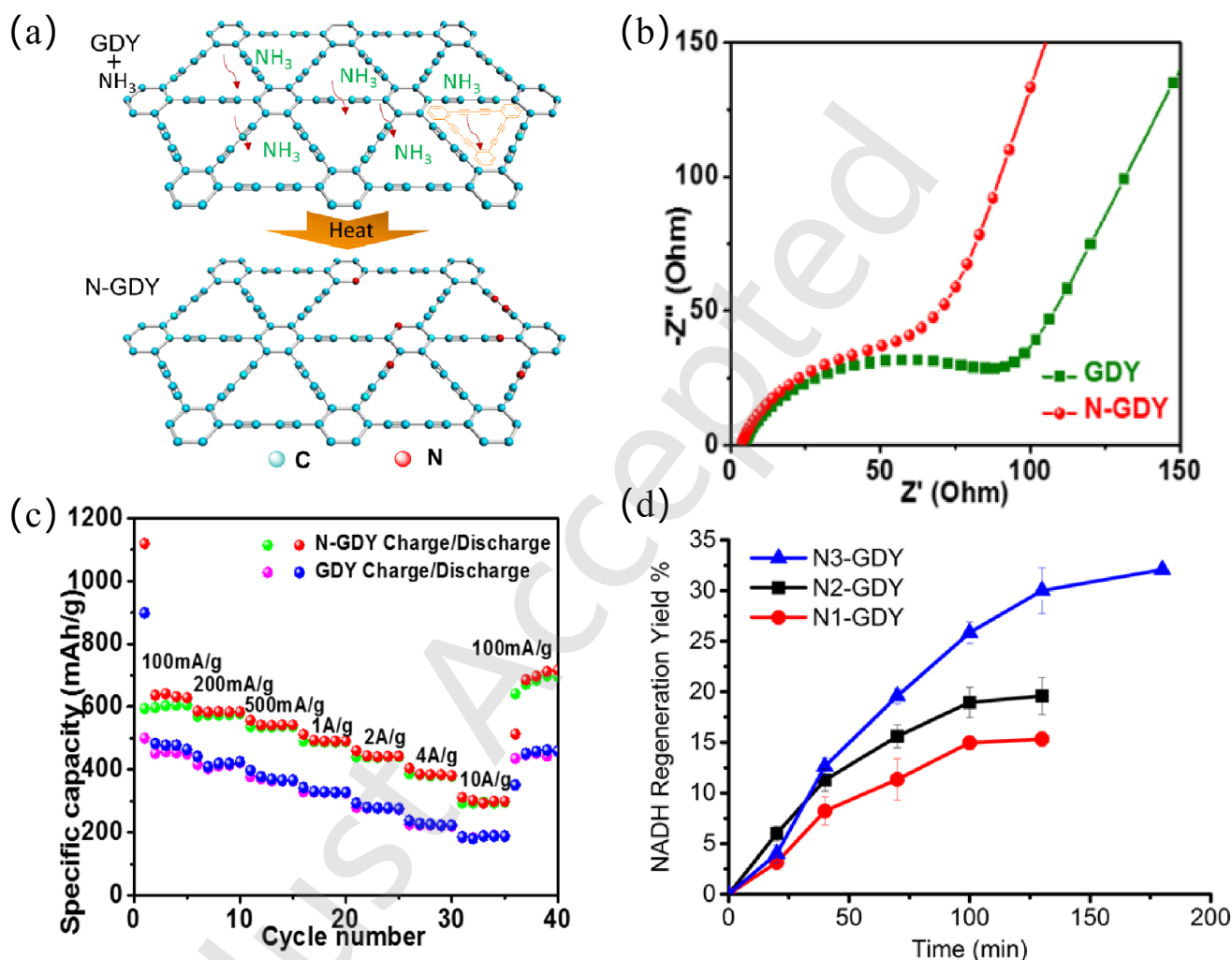


Figure 7 Representative applications of N-GDY in energy storage and photocatalysis. (a) Schematic illustration of N-GDY preparation via NH₃ treatment. (b) Electrochemical impedance spectra of GDY and N-GDY electrodes. (c) Rate performance of GDY and N-GDY at different current densities. Adapted with permission from Ref. [18], © American Chemical Society 2016. (d) Photocatalytic NADH regeneration yields of N1-GDY, N2-GDY and N3-GDY. Adapted with permission from Ref. [29], © American Chemical Society 2018.

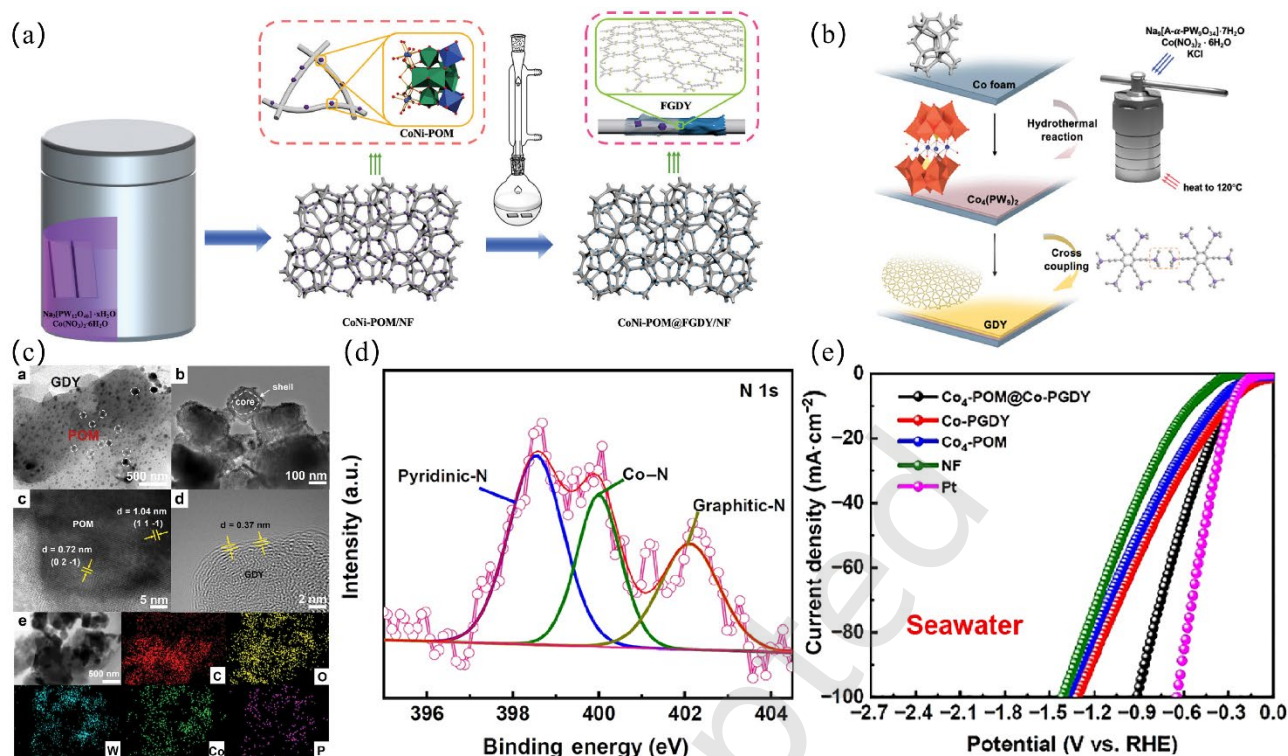


Figure 8 Representative POM-functionalized graphdiyne and N-containing graphdiyne hybrid electrocatalysts. (a) Synthetic strategy of Co_{5.7}Ni_{2.3}-POM@FGDY. Adapted with permission from Ref. [14], © the Partner Organisations 2021. (b, c) Construction and structural characterization of Co₄(PW₉)₂@GDY core-shell hybrids. Adapted with permission from Ref. [15], © The Royal Society of Chemistry 2022. (d) N 1s XPS spectrum of Co₄-POM@Co-PGDY, showing fitted components assigned to pyridinic N, Co-N, and graphitic N species. (e) Seawater HER polarization curves of Co₄-POM@Co-PGDY and control samples. Adapted with permission from Ref. [16], © Tsinghua University Press 2023.

3.5 Other Applications

N-GDY also shows promise in gas separation and flexible microelectronics, although these applications remain at the theoretical or proof-of-concept stage. For gas separation, calculations suggest that nitrogen-functionalized graphdiyne can lower the diffusion barrier of H₂ while increasing the permeation barriers of CO and CH₄, making it promising for hydrogen purification [77]. Nitrogen doping therefore changes not only pore-size effects but also the electronic environment at pore edges. From an intrinsic-property perspective, N-graphdiyne is a two-dimensional semiconductor with a tunable band gap of approximately 0.98-3.33 eV, visible-to-infrared absorption, low thermal conductivity and high stretchability [78]. These features indicate that N-GDY could be extended from electrochemical materials to flexible optoelectronic devices, low-dimensional electronics and selective separation membranes. Compared with electrocatalysis and energy storage, however, these applications still require advances in controllable synthesis, large-area integration and stability under realistic operating conditions.

4 Challenges and Outlook

Although nitrogen-containing graphdiyne and POM/graphdiyne materials have independently demonstrated promising energy-related functions, the construction of structurally defined POM/N-GDY interfaces remains at an early stage. To establish predictive and scalable design rules for these promising hybrid systems, several key challenges must be

addressed in future research.

First, precision synthesis and controlled interfacial assembly in POM/graphdiyne systems, especially site-defined POM/N-GDY interfaces, remain major challenges. While bottom-up monomer pre-design offers structural traceability, actual polymerization often generates edge defects and stacking disorder, whereas post-doping leads to heterogeneous nitrogen configurations. More importantly, uncontrolled physical mixing may lead to nonuniform POM loading, aggregation, and electrolyte-dependent leaching, and therefore requires comparison with more clearly defined interfacial assembly strategies. Future research should focus on developing milder, highly controllable coupling reactions to yield N-GDY with well-defined nitrogen configurations. Simultaneously, candidate anchoring strategies include nitrogen-metal coordination, electrostatic assembly, and the copolymerization of organically modified POMs with ethynyl monomers. These candidate immobilization strategies should be evaluated by quantifying POM loading, dispersion, and retention rather than being assumed to produce atomically defined or leakage-free interfaces. In addition, the resistance to leaching of these hybrids should be evaluated by combining long-term electrolysis with post-reaction ICP-MS analysis of the electrolyte, UV-vis monitoring of dissolved POM species, and post-catalysis structural characterization of the solid catalyst.

Second, deciphering the interfacial charge transfer and synergistic mechanisms requires deeper theoretical and physical insights. Orbital coupling between POM states and the conjugated electronic structure of N-GDY has been proposed as a possible contributor to interfacial behavior, but its magnitude and catalytic relevance have not yet been established experimentally. Models of isolated components or idealized single-layer supports may omit

interfacial bonding, stacking, defects, and electrolyte effects relevant to the experimental system. Quantitative DFT evaluation should combine interfacial binding energy and charge-density-difference/Bader analyses to determine binding stability and charge-transfer direction, together with PDOS or COHP/ICOHP analysis to assess orbital coupling. Adsorption modulation should be evaluated using consistently defined adsorption energies and electrochemical Gibbs free energies corrected for zero-point energy, entropy, solvation, and electrode potential. Because these values depend on the interface model and computational parameters, only results obtained under comparable settings should be directly compared. Calculations performed separately for an isolated POM or an isolated N-GDY model should therefore not be treated as direct evidence for an explicit POM/N-GDY interface.

Third, tracking the dynamic structural evolution and identifying the true active sites under working conditions is essential. Under harsh electrochemical potentials or corrosive electrolytes, both POMs and N-GDY can undergo structural reconstruction. A critical question in POM chemistry is whether the molecular metal-oxo clusters maintain their structural integrity during catalysis, or undergo *in situ* transformation into amorphous metal oxides, oxyhydroxides, or sub-nanometer metal clusters. Standard *ex situ* characterizations are insufficient to capture these transient states. Accordingly, *operando* XAS can track the average oxidation state and local coordination of POM metal centers, while *in situ* Raman/FTIR can monitor POM metal-oxo vibrations and N-GDY acetylenic linkages. Quasi-*in situ* XPS provides potential-dependent snapshots of nitrogen coordination and interfacial charge redistribution, whereas electrochemical online ICP-MS reveals metal release but cannot distinguish intact POMs from fragments. Major limitations include weak ensemble-averaged signals caused by low interfacial loading, spectral overlap, beam-induced perturbations under intense irradiation, insufficient temporal and spatial resolution for rapid or heterogeneous reconstruction, and differences between spectroelectrochemical cells and practical operating conditions. Therefore, reliable identification of the active phase requires cross-validation using complementary *operando* measurements, electrochemical data, dissolution analysis, and post-reaction characterization.

Fourth, overcoming the stability bottleneck and demonstrating device-level viability are key to practical energy applications. The solubility and structural stability of POMs vary with their composition, counterions, electrolyte, and operating potential and can contribute to performance degradation through dissolution, redistribution, or reconstruction. Furthermore, because many molecular POMs exhibit low bulk electronic conductivity, future work must optimize the loading mass of POMs on N-GDY to maximize active site density without compromising overall electrical conductivity. One possible strategy is to combine controlled POM loading with candidate coordination-assisted or electrostatic attachment sites and larger hierarchical pores or interlayer spaces, while maintaining electron transport and electrolyte accessibility. Crucially, evaluation of these hybrids must extend beyond laboratory-scale half-cell testing to practical configurations, such as proton exchange membrane (PEM) electrolyzers, zinc-air batteries, gas-diffusion electrodes, and redox flow batteries, under realistic current

densities and long-term operating conditions.

5 Conclusions

In summary, studies of nitrogen-containing graphdiyne show that catalytic and energy-storage behavior depends on the combined effects of nitrogen configuration, local carbon structure, porosity, and operating conditions rather than on total nitrogen content alone. Reported POM/graphdiyne composites extend this design space by coupling molecular metal-oxo components with acetylenic carbon supports, but the existing systems differ in support structure and should not be treated as equivalent POM/N-GDY hybrids. Direct relationships among specific nitrogen configurations, POM binding geometry, active-phase evolution, and device performance remain insufficiently established. Progress will depend on matched support comparisons, quantitative evaluation of POM retention and charge transfer, identification of the working active phase, and durability testing under device-relevant conditions.

Acknowledgements

Thanks for the support from the Analysis & Testing Center of Beijing Institute of Technology.

Declaration of competing interest

There is no conflict of interest

Use of AI statement

None.

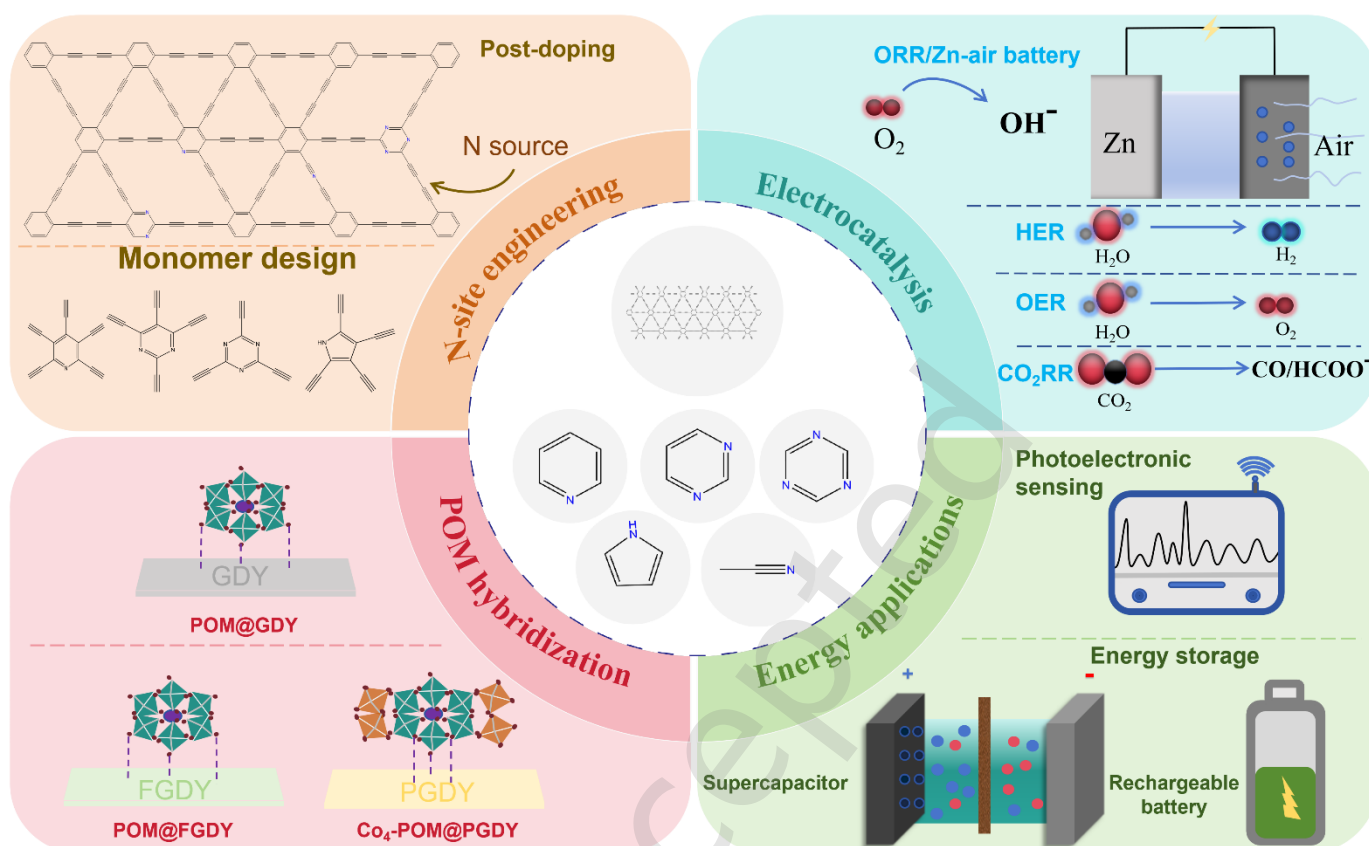
References

- [1] Dresselhaus, M. S.; Dresselhaus, G. Intercalation compounds of graphite. *Adv. Phys.* 2002, *51*, 1–186.
- [2] Iijima, S. Helical microtubules of graphitic carbon. *Nature* 1991, *354*, 56–58.
- [3] Kroto, H. W.; Heath, J. R.; O'Brien, S. C.; Curl, R. F.; Smalley, R. E. C60: Buckminsterfullerene. *Nature* 1985, *318*, 162–163.
- [4] Novoselov, K. S.; Geim, A. K.; Morozov, S. V.; Jiang, D.; Zhang, Y.; Dubonos, S. V.; et al. Electric Field Effect in Atomically Thin Carbon Films. *Science* 2004, *306*, 666–669.
- [5] Baughman, R. H.; Eckhardt, H.; Kertesz, M. Structure-property predictions for new planar forms of carbon: Layered phases containing sp² and sp atoms. *J. Chem. Phys.* 1987, *87*, 6687–6699.
- [6] Li, G.; Li, Y.; Liu, H.; Guo, Y.; Li, Y.; Zhu, D. Architecture of graphdiyne nanoscale films. *Chem. Commun.* 2010, *46*, 3256–3258.
- [7] Malko, D.; Neiss, C.; Viñes, F.; Görling, A. Competition for Graphene: Graphynes with Direction-Dependent Dirac Cones. *Phys. Rev. Lett.* 2012, *108*, 086804.
- [8] Narita, N.; Nagai, S.; Suzuki, S.; Nakao, K. Optimized geometries and electronic structures of graphyne and its family. *Phys. Rev. B* 1998, *58*, 11009–11014.
- [9] Zou, X.; Zhang, Y. Noble metal-free hydrogen evolution catalysts for water splitting. *Chem. Soc. Rev.* 2015, *44*, 5148–5180.
- [10] Gong, K.; Du, F.; Xia, Z.; Durstock, M.; Dai, L. Nitrogen-

- Doped Carbon Nanotube Arrays with High Electrocatalytic Activity for Oxygen Reduction. *Science* 2009, 323, 760–764.
- [11] Li, Y.; Xu, L.; Liu, H.; Li, Y. Graphdiyne and graphyne: from theoretical predictions to practical construction. *Chem. Soc. Rev.* 2014, 43, 2572–2586.
 - [12] Zhao, Y.; Wan, J.; Yao, H.; Zhang, L.; Lin, K.; Wang, L.; et al. Few-layer graphdiyne doped with sp-hybridized nitrogen atoms at acetylenic sites for oxygen reduction electrocatalysis. *Nat. Chem.* 2018, 10, 924–931.
 - [13] Liu, R.; Liu, H.; Li, Y.; Yi, Y.; Shang, X.; Zhang, S.; et al. Nitrogen-doped graphdiyne as a metal-free catalyst for high-performance oxygen reduction reactions. *Nanoscale* 2014, 6, 11336–11343.
 - [14] Sun, H.; Xu, X.; Jing, C.; Shang, W.; Wang, Y.; Zeng, M.; et al. Composite clusters: Co_{5.7}Ni_{2.3}W₁₂O₄₂(OH)₄@fluoro-graphdiyne as a stable electrode for sustained electrochemical oxygen evolution under high current conditions. *Mater. Chem. Front.* 2021, 5, 7666–7674.
 - [15] Sun, H.; Jing, C.; Shang, W.; Wang, F.; Zeng, M.; Ju, S.; et al. Polyoxometalate-based composite cluster with core-shell structure: Co₄(PW₉)₂@graphdiyne as stable electrocatalyst for oxygen evolution and its mechanism research. *New J. Chem.* 2022, 46, 11553–11561.
 - [16] Ping, J.; He, D.; Wang, F.; Wang, N.; Fu, Y.; Xing, Z.; et al. Nanocomposite: Keggin-type Co₄-polyoxometalate@cobalt-porphyrin linked graphdiyne for hydrogen evolution in seawater. *Nano Res.* 2024, 17, 1281–1287.
 - [17] Qian, X.; Ning, Z.; Li, Y.; Liu, H.; Ouyang, C.; Chen, Q.; et al. Construction of graphdiyne nanowires with high-conductivity and mobility. *Dalton Trans* 2012, 41, 730–733.
 - [18] Zhang, S.; Du, H.; He, J.; Huang, C.; Liu, H.; Cui, G.; et al. Nitrogen-Doped Graphdiyne Applied for Lithium-Ion Storage. *ACS Appl. Mater. Interfaces* 2016, 8, 8467–8473.
 - [19] Lv, Q.; Si, W.; Yang, Z.; Wang, N.; Tu, Z.; Yi, Y.; et al. Nitrogen-Doped Porous Graphdiyne: A Highly Efficient Metal-Free Electrocatalyst for Oxygen Reduction Reaction. *ACS Appl. Mater. Interfaces* 2017, 9, 29744–29752.
 - [20] Zhao, Y.; Yang, N.; Yao, H.; Liu, D.; Song, L.; Zhu, J.; et al. Stereodefined Codoping of sp-N and S Atoms in Few-Layer Graphdiyne for Oxygen Evolution Reaction. *J. Am. Chem. Soc.* 2019, 141, 7240–7244.
 - [21] Zhang, Y.; Zhang, Y.; Liu, J. The controllable preparation of polyoxometalate-based sub-1 nm materials and their applications in energy storage and conversion. *Polyoxometalates* 2026, 5, 9140114.
 - [22] Zhang, S.; Liu, R.; Streb, C.; Zhang, G. Design and synthesis of novel polyoxometalate-based binary and ternary nanohybrids for energy conversion and storage. *Polyoxometalates* 2023, 2, 9140037.
 - [23] Hu, Y.; Wang, Y.; Zhao, J.; Chen, L. Recent advances of polyoxometalate-based materials applied for electron-related devices. *Coord. Chem. Rev.* 2024, 506, 215724.
 - [24] Yang, K.; Hu, Y.; Li, L.; Cui, L.; He, L.; Wang, S.; et al. First high-nuclearity mixed-valence polyoxometalate with hierarchical interconnected Zn²⁺ migration channels as an advanced cathode material in aqueous zinc-ion battery. *Nano Energy* 2020, 74, 104851.
 - [25] Yang, K.; Ying, Y.; Cui, L.; Sun, J.; Luo, H.; Hu, Y.; et al. Stable aqueous Zn–Ag and Zn–polyoxometalate hybrid battery driven by successive Ag⁺ cation and polyoxoanion redox reactions. *Energy Storage Mater.* 2021, 34, 203–210.
 - [26] Yang, K.; Hu, Y.; Zhang, T.; Wang, B.; Qin, J.; Li, N.; et al. Triple-Functional Polyoxovanadate Cluster in Regulating Cathode, Anode, and Electrolyte for Tough Aqueous Zinc-Ion Battery. *Adv. Energy Mater.* 2022, 12, 2202671.
 - [27] Luo, W.; Hu, J.; Diao, H.; Schwarz, B.; Streb, C.; Song, Y.-F. Robust Polyoxometalate/Nickel Foam Composite Electrodes for Sustained Electrochemical Oxygen Evolution at High pH. *Angew. Chem. Int. Ed.* 2017, 56, 4941–4944.
 - [28] Kan, X.; Ban, Y.; Wu, C.; Pan, Q.; Liu, H.; Song, J.; et al. Interfacial Synthesis of Conjugated Two-Dimensional N-Graphdiyne. *ACS Appl. Mater. Interfaces* 2018, 10, 53–58.
 - [29] Pan, Q.; Liu, H.; Zhao, Y.; Chen, S.; Xue, B.; Kan, X.; et al. Preparation of N-Graphdiyne Nanosheets at Liquid/Liquid Interface for Photocatalytic NADH Regeneration. *ACS Appl. Mater. Interfaces* 2019, 11, 2740–2744.
 - [30] Yang, Z.; Liu, R.; Wang, N.; He, J.; Wang, K.; Li, X.; et al. Triazine-graphdiyne: A new nitrogen-carbonous material and its application as an advanced rechargeable battery anode. *Carbon* 2018, 137, 442–450.
 - [31] Yang, Z.; Shen, X.; Wang, N.; He, J.; Li, X.; Wang, X.; et al. Graphdiyne Containing Atomically Precise N Atoms for Efficient Anchoring of Lithium Ion. *ACS Appl. Mater. Interfaces* 2019, 11, 2608–2617.
 - [32] Wang, M.; Fu, X.; Lu, M.; Shi, G.; Liu, X.; Yuan, M. Modulation of electronic structure of metal-free graphdiyne via precise nitrogen modification for oxygen evolution reaction. *ChemPhysMater* 2025, 4, 289–295.
 - [33] Gao, L.; Ge, X.; Zuo, Z.; Wang, F.; Liu, X.; Lv, M.; et al. High Quality Pyrazinoquinoxaline-Based Graphdiyne for Efficient Gradient Storage of Lithium Ions. *Nano Lett.* 2020, 20, 7333–7341.
 - [34] Hou, J.; Wang, D.; Chao, M.; Zhang, L.; Liu, H.; Zhao, Y. A nitrogen-rich graphdiyne containing hexaazatrinaphthylene for high-performance lithium-ion batteries. *Chem. Commun.* 2024, 60, 1908–1911.
 - [35] Si, W.; Li, M.; Yan, X.; Lv, Q.; Huang, C. Porous nitrogen-doped graphdiyne templated from zinc acetylacetonate for enhanced oxygen reduction reaction. *ChemPhysMater* 2025, 4, 274–279.
 - [36] Sakamoto, R.; Shiotsuki, R.; Wada, K.; Fukui, N.; Maeda, H.; Komeda, J.; et al. A pyrazine-incorporated graphdiyne nanofilm as a metal-free electrocatalyst for the hydrogen evolution reaction. *J. Mater. Chem. A* 2018, 6, 22189–22194.
 - [37] Chen, X.; Ong, W.-J.; Kong, Z.; Zhao, X.; Li, N. Probing the active sites of site-specific nitrogen doping in metal-free

- graphdiyne for electrochemical oxygen reduction reactions. *Sci. Bull.* 2020, 65, 45–54.
- [38] Zhao, Y.; Yang, N.; Wang, C.; Song, L.; Yu, R.; Wang, D. Boosting hydrogen evolution reaction on few-layer graphdiyne by sp-N and B co-doping. *APL Mater.* 2021, 9, 071102.
- [39] Sun, H.; Huang, Y.; Su, W.; Gao, J.; Chen, Z.; Zhoumei, W.; et al. Regulating Electron Transfer Number and Catalytic Activity via Nitrogen-Doping in Graphdiyne for Electrochemical Oxygen Redox Reactions. *ACS Appl. Mater. Interfaces* 2026, 18, 19101–19113.
- [40] Lv, Q.; Wang, N.; Si, W.; Hou, Z.; Li, X.; Wang, X.; et al. Pyridinic nitrogen exclusively doped carbon materials as efficient oxygen reduction electrocatalysts for Zn-air batteries. *Appl. Catal. B Environ.* 2020, 261, 118234.
- [41] Lv, Q.; Si, W.; He, J.; Sun, L.; Zhang, C.; Wang, N.; et al. Selectively nitrogen-doped carbon materials as superior metal-free catalysts for oxygen reduction. *Nat. Commun.* 2018, 9, 3376.
- [42] Wang, X.; Yang, Z.; Si, W.; Shen, X.; Li, X.; Li, R.; et al. Cobalt-nitrogen-doped graphdiyne as an efficient bifunctional catalyst for oxygen reduction and hydrogen evolution reactions. *Carbon* 2019, 147, 9–18.
- [43] Dai, H.; Song, T.; Yue, X.; Wei, S.; Li, F.; Xu, Y.; et al. Cu single-atom electrocatalyst on nitrogen-containing graphdiyne for CO₂ electroreduction to CH₄. *Chin. J. Catal.* 2024, 64, 123–132.
- [44] Zhang, S.; Cai, Y.; He, H.; Zhang, Y.; Liu, R.; Cao, H.; et al. Heteroatom doped graphdiyne as efficient metal-free electrocatalyst for oxygen reduction reaction in alkaline medium. *J. Mater. Chem. A* 2016, 4, 4738–4744.
- [45] Kang, B.; Wu, S.; Ma, J.; Ai, H.; Lee, J. Y. Synergy of sp-N and sp²-N codoping endows graphdiyne with comparable oxygen reduction reaction performance to Pt. *Nanoscale* 2019, 11, 16599–16605.
- [46] Liu, T.; Hao, X.; Liu, J.; Zhang, P.; Chang, J.; Shang, H.; et al. Graphdiyne and Nitrogen-Doped Graphdiyne Nanotubes as Highly Efficient Electrocatalysts for Oxygen Reduction Reaction. *Int. J. Mol. Sci.* 2023, 24, 16813.
- [47] Ding, W.; Sun, M.; Gao, B.; Liu, W.; Ding, Z.; Anandan, S. A ball-milling synthesis of N-graphyne with controllable nitrogen doping sites for efficient electrocatalytic oxygen evolution and supercapacitors. *Dalton Trans.* 2020, 49, 10958–10969.
- [48] Gu, J.; Magagula, S.; Zhao, J.; Chen, Z. Boosting ORR/OER Activity of Graphdiyne by Simple Heteroatom Doping. *Small Methods* 2019, 3, 1800550.
- [49] Zheng, Z.; Xue, Y.; Gao, Y.; Wang, Z.; Zhao, S.; Luan, X.; et al. Electronic structure modulation of metal-free graphdiyne for acidic oxygen evolution reaction. *2D Mater.* 2022, 9, 014008.
- [50] Hasnain, K.; Feng, Y.; Song, B.; Li, B.; Umer, K.; Chen, M.; et al. Water oxidation catalyzed by polyoxometalate containing iron cubane structure under visible light. *Polyoxometalates* 2025, 4, 9140094.
- [51] He, F.; Xing, C.; Xue, Y. Metal-free amino-graphdiyne for applications in electrocatalytic hydrogen evolution. *J. Catal.* 2021, 395, 129–135.
- [52] Yu, H.; Xue, Y.; Hui, L.; Zhang, C.; Zhao, Y.; Li, Z.; et al. Controlled Growth of MoS₂ Nanosheets on 2D N-Doped Graphdiyne Nanolayers for Highly Associated Effects on Water Reduction. *Adv. Funct. Mater.* 2018, 28, 1707564.
- [53] Lv, Y.; Kang, B.; Chen, G.; Yuan, Y.; Ren, J.; Lee, J. Y. Revisiting the origin of ORR and HER activities of N-doped γ -graphdiyne from the perspective of edge effects. *Appl. Surf. Sci.* 2023, 613, 156084.
- [54] Liu, S.; Zhang, Y.; Pan, Q. Q.; Li, J.; Li, X.; Su, Z. Hierarchical bimetallic electrocatalysts derived from polyoxometalate for hydrogen evolution reaction. *Polyoxometalates* 2025, 4, 9140105.
- [55] Liu, T.; Wang, Q.; Wang, G.; Bao, X. Electrochemical CO₂ reduction on graphdiyne: a DFT study. *Green Chem.* 2021, 23, 1212–1219.
- [56] Feng, Z.; Tang, Y.; Ma, Y.; Li, Y.; Dai, Y.; Ding, H.; et al. Theoretical investigation of CO₂ electroreduction on N (B)-doped graphdiyne monolayer supported single copper atom. *Appl. Surf. Sci.* 2021, 538, 148145.
- [57] Yang, Y.; Yang, Z.; Zhang, C.; Zhou, J.; Liu, S.; Cao, Q. Single-Atom Catalysts Supported on the Graphene/Graphdiyne Heterostructure for Effective CO₂ Electroreduction. *Inorg. Chem.* 2022, 61, 12012–12022.
- [58] Li, C.; Zhang, Y.; Shu, L.; Teng, Y.-L.; Wang, Y.-R.; Dong, B.-X. Boosting electrochemical reduction of CO₂ to CO via fixation Keggin-type polyoxoanions XW₁₁Co (X = Si, P, Co) into ZIF-8 cavities: Pivotal role of central atoms in catalytic performance. *Polyoxometalates* 2025, 4, 9140097.
- [59] Gu, H.; Zhong, L.; Shi, G.; Li, J.; Yu, K.; Li, J.; et al. Graphdiyne/Graphene Heterostructure: A Universal 2D Scaffold Anchoring Monodispersed Transition-Metal Phthalocyanines for Selective and Durable CO₂ Electroreduction. *J. Am. Chem. Soc.* 2021, 143, 8679–8688.
- [60] Masaud, Z.; Gustavsen, K. R.; Huang, H.; Booth, A. M.; Roseng, L. E.; Wang, K. Cu single atoms supported on crystalline graphdiyne porphyrin analogs with dual active sites for enhanced C₂ product formation. *J. CO₂ Util.* 2025, 95, 103067.
- [61] He, T.; Zhang, L.; Kour, G.; Du, A. Electrochemical reduction of carbon dioxide on precise number of Fe atoms anchored graphdiyne. *J. CO₂ Util.* 2020, 37, 272–277.
- [62] Nitopi, S.; Bertheussen, E.; Scott, S. B.; Liu, X.; Engstfeld, A. K.; Horch, S.; et al. Progress and Perspectives of Electrochemical CO₂ Reduction on Copper in Aqueous Electrolyte. *Chem. Rev.* 2019, 119, 7610–7672.
- [63] Wang, G.; Cai, W.; Fan, T.; Ji, Y. Nitrogen-doped graphdiyne for efficient electrocatalytic N₂ reduction: A first-principles study. *Appl. Surf. Sci.* 2021, 570, 151109.
- [64] Maldonado-Lopez, D.; Huang, P.-W.; Sanchez-Lievanos, K. R.; Jana, G.; Mendoza-Cortes, J. L.; Knowles, K. E.; et al. Nitrogen-Containing Surface Ligands Lead to False Positives for Photofixation of N₂ on Metal Oxide

- Nanocrystals: An Experimental and Theoretical Study. *Adv. Funct. Mater.* 2025, 35, 2413319.
- [65] Tang, S.; Mao, C.; Zhao, G.; Ye, J.; Qu, W.; Wu, L.; et al. Fact or fiction: What is in your 15N₂ and 15NH₃ cylinders for sustainable ammonia and urea research? *iScience* 2025, 28, 112072.
- [66] Feng, B.; Zhang, D.; Han, Z.; Shi, P.; Yan, P.; Zhao, J.; et al. Rational Synthesis of Isomeric Graphdiyne Frameworks toward Single-Ruthenium Catalysts and High-Performance Nitrogen Reduction. *Adv. Mater.* 2025, 37, 2502980.
- [67] Shang, H.; Zuo, Z.; Zheng, H.; Li, K.; Tu, Z.; Yi, Y.; et al. N-doped graphdiyne for high-performance electrochemical electrodes. *Nano Energy* 2018, 44, 144–154.
- [68] Yue, Y.; Xu, Y.; Kong, F.; Li, Q.; Ren, S. Bulk-synthesis and supercapacitive energy storage applications of nanoporous triazine-based graphdiyne. *Carbon* 2020, 167, 202–208.
- [69] Bai, Q.; Luo, H.; Yi, X.; Shi, S.; Wang, L.; Liu, M.; et al. Nitrogen-Doped Graphdiyne Quantum-dots as an Optical-Electrochemical sensor for sensitive detection of dopamine. *Microchem. J.* 2022, 179, 107521.
- [70] Cui, M.; Xin, P.; Che, Z.; Zou, M.; Zhang, M.; Sun, X.; et al. Highly anti-interference electrocatalytic sensing for dopamine with nitrogen-doped graphdiyne directly in biofluids. *Chem. Eng. J.* 2023, 464, 142629.
- [71] Niu, K.; Gao, J.; Wu, L.; Lu, X.; Chen, J. Nitrogen-Doped Graphdiyne as a Robust Electrochemical Biosensing Platform for Ultrasensitive Detection of Environmental Pollutants. *Anal. Chem.* 2021, 93, 8656–8662.
- [72] Gu, Q.; Wang, Z.; Qiao, L.; Fan, J.; Pan, Y.; Wu, P.; et al. Nitrogen-Doped Graphdiyne Quantum Dots for Electrochemical Chloramphenicol Quantification in Water. *ACS Appl. Nano Mater.* 2021, 4, 12755–12765.
- [73] Chen, S.; Pan, Q.; Li, J.; Zhao, C.; Guo, X.; Zhao, Y.; et al. Grain boundary passivation with triazine-graphdiyne to improve perovskite solar cell performance. *Sci. China Mater.* 2020, 63, 2465–2476.
- [74] Bai, L.; Yu, Z.; Liu, L.; Chang, Y.; Ma, Z.; Jiu, T. Construction of homogeneous electron collection center at buried interface based on triazine-based graphdiyne for efficient perovskite solar cells. *Nano Energy* 2024, 131, 110310.
- [75] Liu, Z.; Hao, Y.; Zhang, J.; He, Y.; Chen, W. Polyoxovanadate-modified SnO₂ electron transport layer for perovskite photodetectors. *Polyoxometalates* 2025, 4, 9140076.
- [76] Li, L.; Zuo, Z.; He, F.; Jiang, Z.; Li, Y. Nitrogen-rich Graphdiyne Film for Efficiently Suppressing the Methanol Crossover in Direct Methanol Fuel Cells. *Chem. Res. Chin. Univ.* 2021, 37, 1275–1282.
- [77] Jiao, Y.; Du, A.; Smith, S. C.; Zhu, Z.; Qiao, S. Z. H₂ purification by functionalized graphdiyne – role of nitrogen doping. *J. Mater. Chem. A* 2015, 3, 6767–6771.
- [78] Mortazavi, B.; Makaremi, M.; Shahrokhi, M.; Fan, Z.; Rabczuk, T. N-graphdiyne two-dimensional nanomaterials: Semiconductors with low thermal conductivity and high stretchability. *Carbon* 2018, 137, 57–67.



Nitrogen-containing graphdiyne and related polyoxometalate/graphdiyne interfaces provide complementary platforms for linking molecular-level structure with energy-related performance. This review highlights nitrogen configurations, reported POM/graphdiyne interfacial behavior, and the evidence needed to evaluate prospective POM/N-GDY systems.