REVIEW ARTICLE

Graphdiyne based catalysts for energy applications

Tong Wu[1], Mingzi Sun[1], Bolong Huang[1]*

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Demands of clean and sustainable energy have promoted the rapid development of novel materials for various new energy applications. Graphdiyne (GDY), a carbon allotrope with unique carbon hybridization states, electronic structure and physical properties, has raised tremendous research interest after the first successful synthesis in 2010. Ever since then, GDY has become one of the most attractive carbon materials in different applications. In recent years, the intriguing properties of GDY have been extensively investigated by both theoretical calculations and experiments, which make GDY a promising candidate to be exploited in many different energy applications. Therefore, in this review, we will first introduce the fundamental lattice and electronic structures of GDY. Then, the recent advances of GDY-based materials for efficient electrocatalysts and energy storage materials have been provided. In the end, for the future research, we have supplied a section of conclusion and outlook perspectives to summarize the current developments of GDY-based materials and their potential developments. This review will inspire more research attention in GDY-based materials for broad applications in the future.

Introduction

The current global energy and environmental crisis demand clean and renewable energy conversion technologies. Novel energy applications such as fuel cells, water splitting, and carbon/nitrogen fixation have demonstrated the potential to address this challenge and received extensive research interests. Nonetheless, the sluggish kinetics of these reactions require effective and robust catalysts to boost the performance for practical applications. Currently, noble metals have demonstrated their dominant status as the electrocatalysts for renewable energy conversion technologies. However, their scarcity and relatively low stability limit the large-scale applications in practical. Therefore, searching for non-noble metal or metal-free catalysts as alternatives has become the research focus in recent years. Among different materials, carbon materials stand out as the promising substitutes for noble-metal catalysts in many fields, particularly for their robustness, durability and low cost.[1-4] To fully utilize their potentials, more in-depth understandings of catalytic mechanisms as well as how to scale up the production are needed.[5-7]

Carbon allotropes could be generally categorized by the different hybridization states of carbon atoms, such as diamond (sp^3), fullerenes (sp^2), carbon nanotubes (sp^2), and graphene (sp^2).[8] The mechanical and electronic properties of these allotropes vary from soft to hard and from insulative to conductive, respectively. Notably, the unique properties of these carbon materials originate from the same hybridization of carbon atoms. Although 2D carbon materials composed of sp- and sp^2-hybridized carbons have been theoretically predicted, little was known about their properties due to the difficulties in facile synthesis.[9] In 2010, Li *et al.* reported a methodology for mild condition synthesis of graphdiyne (GDY), which is an atom-thick sp- and sp^2-hybridized 2D carbon material.[10] The sp-acetylene linkages in hexagonal directions of benzene rings form cavities, which endows the conjugated GDY with a nonuniform electronic structure. The butadiyne carbon units have two perpendicular π orbitals, one is in-plane and the other one is out-of-plane. These extra out-of-plane electrons bring more possibilities in charge transfer and bonding chances when compared to the all sp^2-C_6 composed graphene. The special bonding patterns and hybridizations of carbon atoms in GDY lead to the porous structure, nonuniform electronic distributions and controllable all-carbon framework.[11] These unique properties endow GDY to be a promising candidate in many fields, including solar cells, electrochemical actuators, radiation protection, solar steam generation, batteries and catalysis.[12-20] Meanwhile, GDY-based materials also supplies a good platform for the biochemical sensing devices.[21] GDY not only is able to catalyze reactions independently as a metal-free catalyst but also is also easy to modulate their catalytic performances by doping with other element atoms.[22] Due to the cavity-rich structure and the uneven electron distributions, GDY has been reported to be a promising substrate for the synthesis of the novel single atom catalysts (SAC) or dual atom catalysts (DAC).[23-26] The enormous potential of GDY remains to be discovered for a variety of applications.

In the following sections, we will briefly introduce the properties of GDY and summarize the recent progress on the applications of GDY in energy conversion and storage (**Scheme 1**). The advanced techniques for the synthesis of GDY and derivatives will also be covered. This work not only highlights the achievements of the investigations and applications of GDY but also provides new insight into the modifications of GDY to address the challenges in current energy devices.

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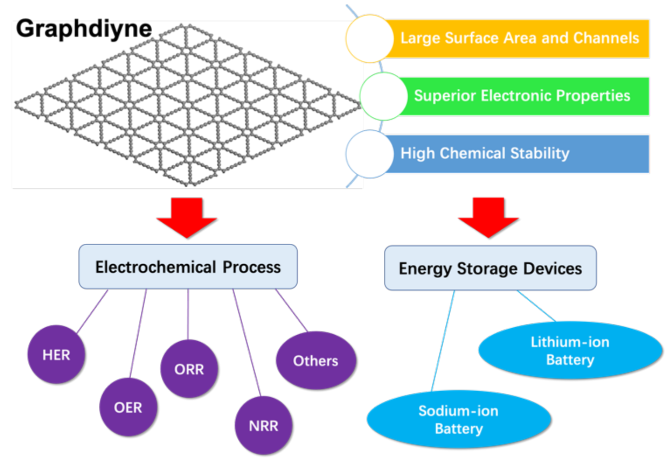
[a] *Department of Applied Biology and Chemical Technology, The Hong Kong Polytechnic University, Hung Hom, Kowloon, Hong Kong SAR, China*
**Correspondence Author: bhuang@polyu.edu.hk*



Scheme 1. Overview of topics in this review.

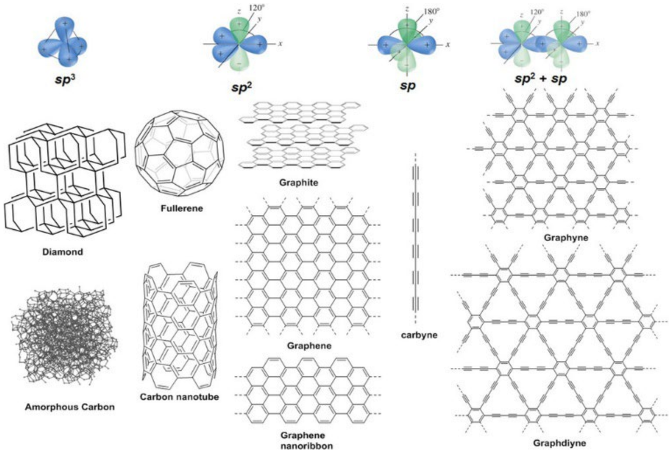


Figure 1. Variety of carbon allotropes with different hybridized carbon. Reprinted with permission from Annalen der Physik, 2017, 529, 1700056. Copyright 2017, WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.[8]

Unique properties of GDY

GDY stands out from other carbon allotropes with its mixed sp- and sp^2-hybridization states of carbon atoms (**Figure 1**). The sp^2-hybridized carbon atoms in benzene rings and sp-hybridized carbon atoms in acetylene linkages provide more possible reactive sites and naturally uniform porous structure enables more efficient mass transfer. GDY is typically synthesized through a highly efficient acetylene coupling reaction under mild conditions.[10] Compared with the chemical vapor deposition method for carbon nanotubes and graphene, this strategy for GDY is feasible for in situ productions. Moreover, it also enables accurate control of the final structure via modification of the monomer. Introduction of additional sp-hybridized carbon and associated free electrons in all conjugated carbon structures are favorable for practical applications, especially in electrochemical catalysis and energy storage batteries.[22] The conductive and electron-rich layered structure with adjustable cavities allow GDY to store Li^+ and Na^+ in the batteries.[27] The electron-rich diacetylene units provide additional coordination sites with metal atoms or the intermediate units of a reaction and catalyze the process of chemical reactions.[28, 29] GDY shows unique potential for interfacial applications in many electrochemical devices because the activity of the carbon-carbon triple bonds would be activated under the external stimulus.[22] With these advantages, GDY is regarded as a valuable material for various energy-based applications, especially electrochemical catalysis and energy storage.

Electrochemical applications of GDY

Hydrogen evolution reaction (HER)

Hydrogen is clean and sustainable energy to address the global energy and environmental crisis from the rapid consumption of fossil fuels. Electrochemical water splitting is a promising, efficacious, and benign tactic for hydrogen evolution.[30, 31] Hydrogen evolution reaction (HER) occurs at the negative electrode in the electrocatalytic hydrolysis process, which take the advantage of the abundant water resource to be the promising and reliable hydrogen source. Nonetheless, the sluggish HER kinetics make effective catalysts essential to the practical uses of HER. Although noble metal-based catalysts have been recognized as state-of-the-art HER catalysts, their scarcity and expensive cost arouse the search and development of efficacious non-noble metal-based alternatives. GDY, a novel carbon allotrope that features unique electronic structures and physical properties, has been reported to be a promising substrate material for non-noble metal-based HER catalysts.

The applications of GDY for HER can be categorized by the compositions and characteristic bonding systems. In the following section, we will introduce the GDY-based HER catalysts according to their structural and composition features to provide a comprehensive overview.

Heterostructure GDY-based HER catalysts. Transition metal dichalcogenides (TMDs), e.g., MoS_2 and WS_2, have been found to be promising non-noble metal catalysts candidates for electrochemical water splitting. However, their intrinsic catalytic activities are not sufficiently high to meet the demand for practical uses. Notably, it is reported that the combination of TMDs and GDY could effectively boost the HER activity of TMDs to be comparable to the state-of-the-art noble metal-based catalysts.[32, 33] In 2018, Li's group reported the synthesis of 2D N-doped GDY nanolayer/MoS_2 nanosheets and 3D flexible GDY/MoS_2 heterojunction materials, revealing the significant catalytic activity enhancement for TMDs brought by GDY.[32, 33] They studied the structural effect of GDY and its derivatives on HER catalytic performance by comparing the pristine GDY/MoS_2, N-doped GDY (NGDY)/MoS_2 and GDY oxide (GDYO)/MoS_2 powders coated on the glass carbon electrode (GCE) surface. Results showed that NGDY/MoS_2 possesses the best catalytic activity (186 mV at 10 mA cm^{-2} and Tafel slope of 63 mV dec^{-1}) and stability that higher than all reported MoS_2 and even that of commercial Pt (≈15200 cycles) (**Figure 2A**).[32] The extraordinary catalytic activity was a result of the strong interactions between NGDY and MoS_2, which effectively facilitate the charge transfer and improvement of the HER kinetics. Li also activated WS_2 with GDY by constructing a layered 2D-nanohybrid (GD-WS_2 2D-NH), which owned abundant active sites and large surface area.[34] The synergistic effect between the electric field of GDY and WS_2 produced an enhanced charge transfer, which activated the originally inert basal plane of WS_2 for efficient HER. As

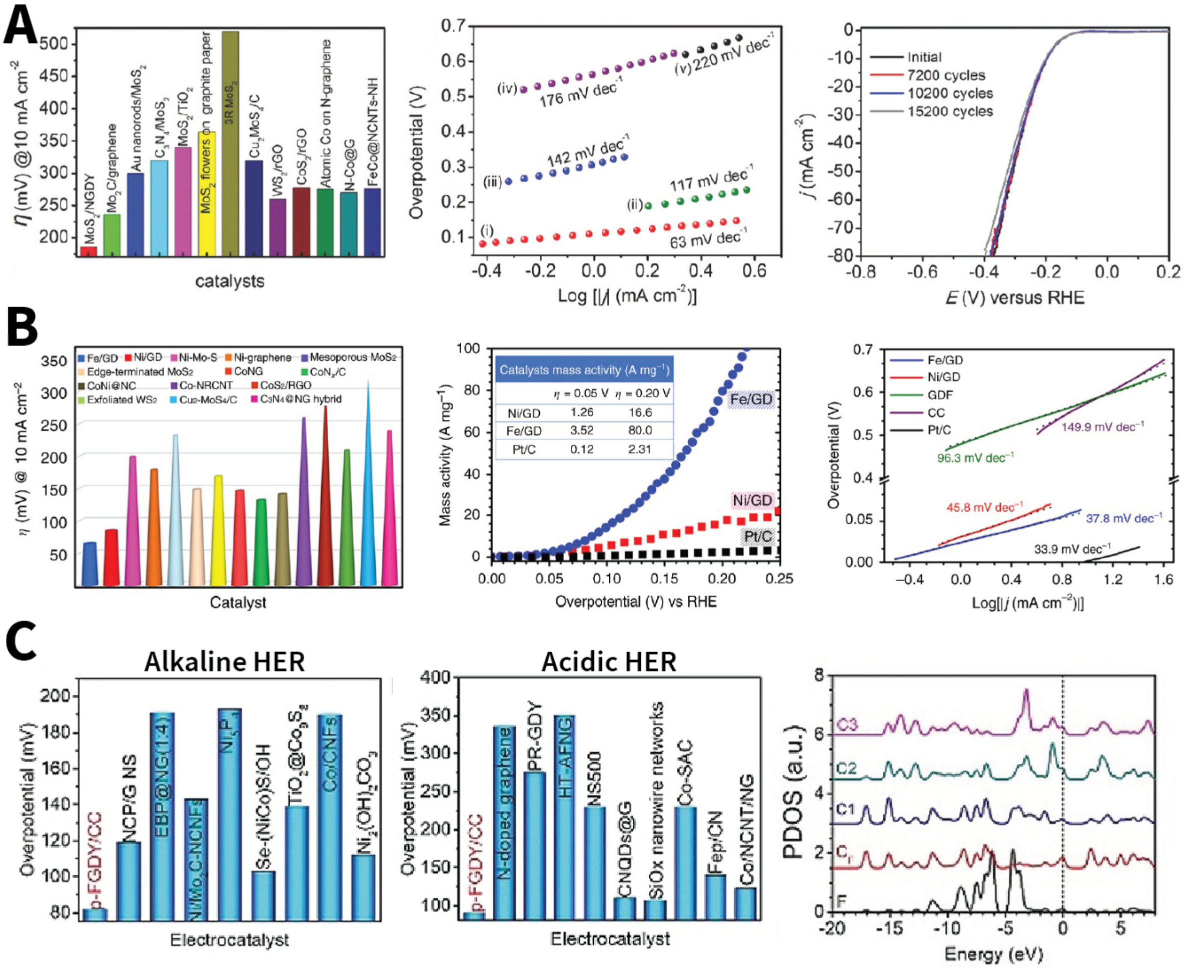


Figure 2. **A**: left: Comparison of overpotentials of MoS_2/NGDY to other catalysts at 10 mA cm^{-2}; center: Tafel slopes; right: LSV curves of cycling tests. Reprinted with permission from Advanced Functional Materials, 2018, 28, 1707564. Copyright 2018 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.[32] **B**: left: Comparison of overpotentials of Fe/GD and Ni/GD to other catalysts at 10 mA cm^{-2}; center: Mass activities of Ni/GD, Fe/GD, and Pt/C; right: Tafel slopes plot. Reprinted with permission from Nature Communications, 2018, 9, 1460. Copyright 2018, The Author(s) (Yurui Xue et al).[23] **C**: left: Comparison of overpotential of p-FGDY/CC to other catalysts in alkaline HER; center: Comparison of overpotential of p-FGDY/CC to other catalysts in acidic HER; right: Individual site-dependent PDOSs of C1, C2 and C3 sites, as well as the C site bonded to F (C_F). Reprinted with permission from Angewandte Chemie International Edition, 2019, 58, 13897-13903. Copyright 2019, WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.[48]

a result, the GD-WS_2 2D-NH presented a reduced HER onset potential of 140 mV and superior Tafel slope as low as 54 mV dec^{-1} in acidic media. Compared with 2D GDY materials, 3D GDY materials are supposed to provide more electrochemical active sites and diffusion channels for faster mass/ions transport, which contribute to better electrocatalytic performance.[35] Li's group subsequently reported the synthesis of a 3D self-supported, seamlessly GDY/MoS_2 HER cathode through seamless growth of MoS_2 nanosheet arrays directly on GDY foam.[33] The electron rich GDY (eGDY) acts as the host for the MoS_2 catalytic center. The GDY/MoS_2 demonstrated greatly enhanced catalytic activities and durable stabilities in both acidic and alkaline conditions. The electronic structure analysis revealed that the combination of two semiconductor materials of GDY and MoS_2 reaches the metallic property, which has not been observed for other carbon materials. The electronic interactions at the interface between the eGDY and MoS_2 were predicted by DFT calculations and confirmed by experimental results. This synergistic effect led to the small overpotentials (128 mV@10 mA cm^{-2} in 0.5 M H_2SO_4;99 mV@10 mA cm^{-2} in 1.0 M KOH) and Tafel slopes (46 mV dec^{-1} in 0.5 M H_2SO_4; 89 mV dec^{-1} in 1.0 M KOH) in both acidic and alkaline medias with long-term stability. Notably, the alkaline HER catalytic activity of eGDY/MoS_2 surpassed that of commercial Pt/C. Additionally, a great enhancement in photocurrent density was also observed.

In 2016, Li's group developed a self-supported 3D Cu@GDY core-shell (Cu as the core and GDY as the shell) nanowire arrays on Cu foam (denoted as Cu@GDY NA/CF), which was the first GDY based 3D carbon nanoarchitecture as HER catalyst.[36] It featured small overpotentials (onset potential of 52 mV, 79 mV at 10 mA cm^{-2}) and a small Tafel slope (69 mV dec^{-1}) in acidic condition. The synergistic interactions between Cu and GDY were the origin of the enhanced HER catalytic activity and were proven by both experimental results and DFT calculations. In general, the HER is coupled with oxygen evolution reaction (OER) in the water splitting process. Since the best OER catalysts only work under neutral or alkaline conditions, the HER catalysts should also adapt to a broader pH range. Following this principle, Li's group prepared a GDY nanosheet-supported cobalt nanoparticles wrapped by N-doped carbon (CoNC/GDY) with pH universal HER catalytic activity.[37] The durability of the CoNC/GDY structure was evidenced by the stable HER activity after long-term stability tests under basic, acidic and neutral conditions, which all exceed the performance of commercial Pt/C under the same conditions. The composite of GDY nanosheet and CoNC particles exhibited improved physical/chemical properties, facilitating electron transfer and excellent HER activity. Recently, Li's group further fabricated a new type of HER electrocatalyst based on loading the OsO_x quantum dot on 3D flexible GDY (OsO_x QDs/GDY), where the heterostructure not only increases the hole transport but also the number of active sites.[38] Owing to the photocurrent performance and photo/electrocatalytic activity of the QDs and GDY, the overpotential of HER has been significantly decreased to 42 mV at 100 mA^{-2}.

These heterostructure HER catalysts demonstrate the capability of GDY in promoting the catalytic performance of pristine catalysts. Beyond the TMDs, GDY also has great synergies with other catalytic materials, leaving enormous possibilities to be discovered in the future.

GDY-based atom catalysts for HER. Atom catalysts have been the research front in the field of catalysis.[39-42] The concept of atom catalyst originates from the observation that downsizing the particle sizes will expose more active sites. When the size of the catalyst is regulated to atomic levels, the exposure of active sites reaches maximum.[43] However, decreasing particle size inevitably leads to the high surface energy of the single atoms, which destabilizes the single atoms and makes them prone to aggregate during the fabrication and catalytic process.[44] Therefore, the substrates can form strong metal-support interaction with the single atoms are essential to guarantee the durability of atom catalysts.[44] Moreover, the substrate should also have high electroconductivity, abundant loading of metal atom sites to facilitate the catalytic performance. GDY has been considered as a suitable atom catalyst substrate due to its unique sp- and sp^2-hybridizations of carbon atoms, the evenly distributed pores and the regular structure. The sp- and sp^2 hybridization in GDY reveals that the $\boldsymbol{\pi/\pi^*}$ orbitals can rotate in any direction perpendicular to the $-\boldsymbol{C}\equiv\boldsymbol{C}-$ bonds, creating suitable anchoring environments for the single atoms.[45, 46] This unique nature leads to high-speed charge migration between single atoms and GDY.[47]

Owing to the unique electronic properties and porous regular structure, GDY has been regarded as a promising substrate for the fabrication of single atom catalysts. In traditional SACs, the valence states of metal atoms are usually hard to determine or not an integer-valence state. The previously reported single atom catalysts in other support generally have positive valence states or mixed valence states. The preparation of zero-valence state SACs and subsequent investigations of properties and applications are therefore highly expected. With the appearance of GDY, zero valence single atom catalysts have been successfully synthesized, which is regarded as a great breakthrough in the field of catalysis.[47] In 2018, Li and coworkers successfully anchored zero-valence Ni and Fe atoms on GDY.[23] The zero-valence Ni/GDY and Fe/GDY realized the high dispersion of active centers, and address the issues on traditional SACs such as easy migration, aggregation tendency, unstable charge transfer, etc. The long-term stabilities of these two SACs were experimentally evidenced during the cycling operation, in which no aggregation of metal atoms was observed. The Fe/GDY and Ni/GDY demonstrated superior HER catalytic activities to most of the state-of-the-art HER catalysts. They presented very small Tafel slopes of 37.8 and 45.8 mV dec^{-1}, respectively, which are only slightly larger than that of Pt/C (33.9 mV dec^{-1}) (**Figure 2B**). The overpotentials at 10 mA cm^{-2} were 66 mV for Fe/GDY and 88 mV for Ni/GDY, which are significantly smaller than most non-noble-metal HER catalysts and comparable to the noble-metal-based catalysts.[23] Due to the intrinsic low metal loading of SAC, they demonstrated remarkable mass activity toward HER than commercial Pt/C, which were as high as 34.6 (Fe/GDY) and 7.19 (Ni/GDY) times greater than Pt/C (**Figure 2B**). The outstanding HER performances originated from the strong chemical interactions and electronic coupling between the single Ni/Fe atoms and GDY. The zero-valence state is the evidence of the strong electron transfer between the GDY and Ni/Fe atoms, which facilitates the charge exchange and adsorption for HER. In addition to the excellent HER catalytic activity and long-term stability, the synthesis method for Ni/GDY and Fe/GDY is also facile, which is highly favorable for large-scale practical uses. In 2019, Li and coworkers developed another zero-valence atom catalyst, Mo^0/GDY, which is a highly efficient and selective catalyst for both nitrogen reduction reaction (NRR) and HER.[24] Notably, this is the first bifunctional atom catalyst for NRR and HER in aqueous solutions at room temperature and pressure. It shows a higher HER activity with the smaller overpotential of 48 mV at 10 mA cm^{-2} than 20 wt % Pt/C (59 mV) and other conventional single atom catalysts. At the overpotential of 0.2 V, the Mo^0/GDY exhibited an approximately 2.6 times larger mass activity compared with that of commercial Pt/C (5.89 A mg_{metal}^{-1}). The successful synthesis of these three zero-valence SACs will pave a path for the development of GDY-based practical commercial HER catalysts.

Metal-free GDY-based HER catalysts. From noble-metal-based to non-noble-metal-based materials, the search for cost-effective and efficient HER catalysts have taken a great leap in recent years. As mentioned above, there have been a number of non-noble-metal-based catalysts showing comparable or even superior HER activity to that of commercial Pt/C catalysts. Nevertheless, the metal-based catalysts still suffer from inherent corrosion susceptibility to acidic electrolytes. Developing an efficient and stable HER catalyst is still a long-standing challenge to the development of water-splitting based energy conversion systems. Since metals have intrinsic stability issues in the working condition of water-splitting, it is natural to consider exploring the possibilities of using metal-free catalysts with high HER activity and durability. Metal-free carbon materials become the promising candidates owing to their abundance, tunable chemical/electronic structures and high tolerance to acidic/alkaline conditions.[48, 49] However, the traditional carbon materials, e.g., graphene-based materials, carbon nanotubes and their N-doped derivatives, suffer from complicated synthesis and unsatisfying stability in HER working conditions. The emergence of GDY opens a new path for carbon-based catalyst materials.

In 2019, Li's group reported the first GDY-based metal-free bifunctional catalyst for both HER and OER and the overall water-splitting (OWS) process in both acidic and alkaline conditions.[48] It was a 3D porous fluorographdiyne nanostructures on carbon cloth (p-FGDY/CC) with maximized active surface area and active sites. The unique chemical and electronic structures of FGDY and the constructed 3D hierarchical porous structure resulted in the

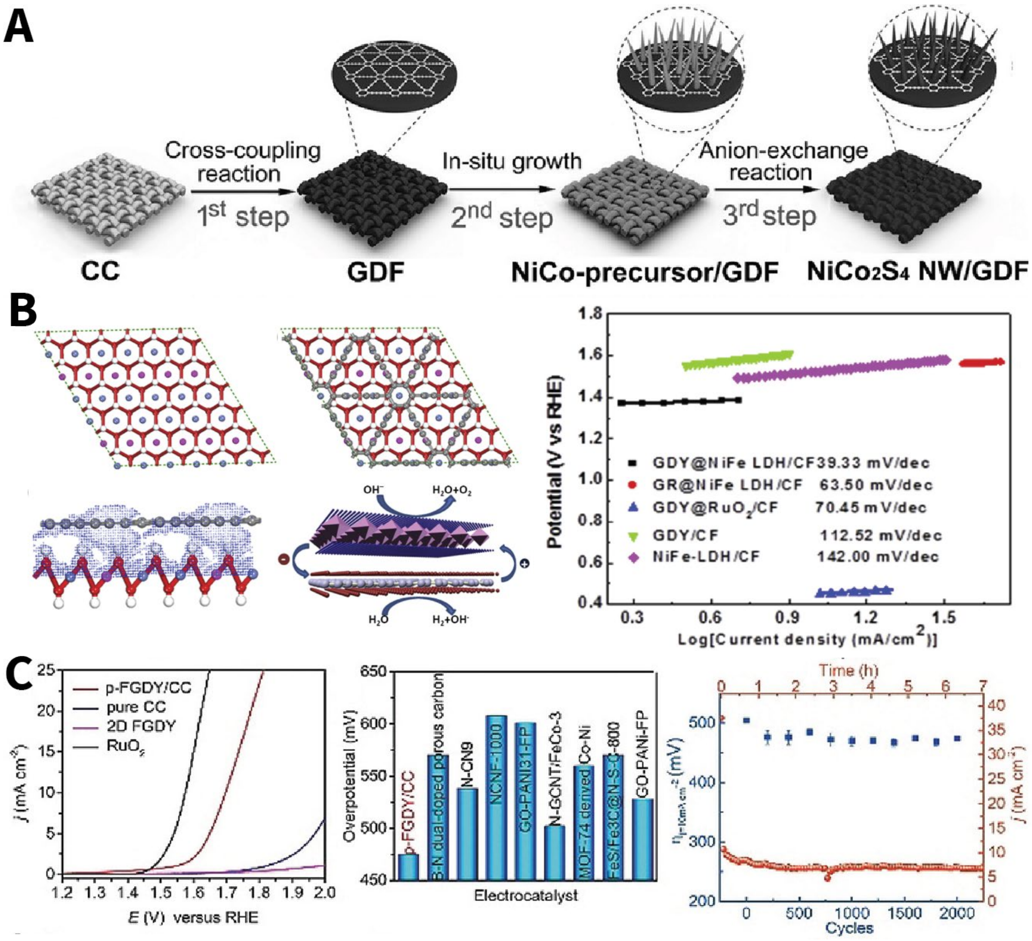


Figure 3. A: Schematic illustration of synthesis process of $NiCo_2S_4$ NW/GDF and scanning microscope (SEM) images of samples. Reprinted with permission from Small 2017, 13, 1700936. Copyright 2017, WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.[55] **B**: left: DFT calculation studies of GDY@NiFe LDH and schematic of the probable HER and OER reaction mechanism of GDY@NiFe LDH; right: Tafel slopes comparison of GDY@NiFe LDH to other related catalysts. Reprinted with permission from Journal of Alloys and Compounds 2019, 794, 261-267. Copyright 2019, Elsevier B.V.[57] **C**: left: Polarization curves of catalysts for OER in 1.0 M KOH; center: Comparison of OER overpotentials between p-FGDY/CC and other catalysts; right: Long-term stability tests of p-FGDY/CC in 1.0 M KOH during the OER process. Reprinted with permission from Angewandte Chemie International Edition, 2019, 58, 13897-13903. Copyright 2019 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.[48]

outstanding catalytic activity to HER, OER and OWS together with excellent long-term stability. The onset potential of HER was as low as 82 mV at 10 mA cm^{-2} in 1.0 M KOH, which exceeded all other metal-free catalysts reported before and even comparable to metal-based catalysts (**Figure 2C**).[48] In the strongly acidic condition, the overpotential was 92 mV at 10 mA cm^{-2}, which still exceeds other reference catalysts (**Figure 2C**). Theoretical calculations revealed that the strong F-C bonding modified the electronic orbital filling via the local p-p coupling, leading to the enhancement of electron-rich character at the C2 site of FGDY (**Figure 2C**).

Besides, several other metal-free catalysts have been reported. Wang et al. have reported tetraphenylmethane-graphdiyne (TPM-GDY) and triphenylamine-graphdiyne (TPN-GDY) through the bottom-to-up cross-coupling strategy.[50] These two kinds of materials have modified the morphology, surface area, and pore distribution, where the active sites have determined the HER performances. He et al. have successfully synthesized the 1,2,4-triamino-graphdiyne (TAGDY).[51] For the acidic HER, the adsorption of proton pair (H^++e^-) on the alkyne bonds has led to the bond transition phenomenon towards -C=C- bonds, which is accompanied by the migration of H^+ intermediates to promote the HER process. These works have offered new ideas for designing GDY-based catalysts.

Oxygen evolution reaction (OER)

OER is regarded as the key step of a variety of electrochemical energy-related applications, including water-splitting, metal-air battery, and regenerative fuel cell.[52-54] The kinetics of OER are sluggish, and the reaction mechanism is complicated since it involves multistep proton-coupled electron transfer processes. In recent years, efficient and durable catalysts for OER are under extensive research. Non-noble-metal-based OER catalysts and metal-free OER catalysts are expected to replace the current noble-metal-based catalysts in the future for practical applications in energy conversion and storage. Research on electrocatalysts for HER and OER has made enormous progress in recent years. However, the catalytic activities of these catalysts are generally pH-dependent. Therefore, integrating different catalysts for the water-splitting process will increase the operation cost and complexity with poor catalytic efficiency. Developing low-cost and efficient bifunctional catalysts is a promising path to solve this challenge.

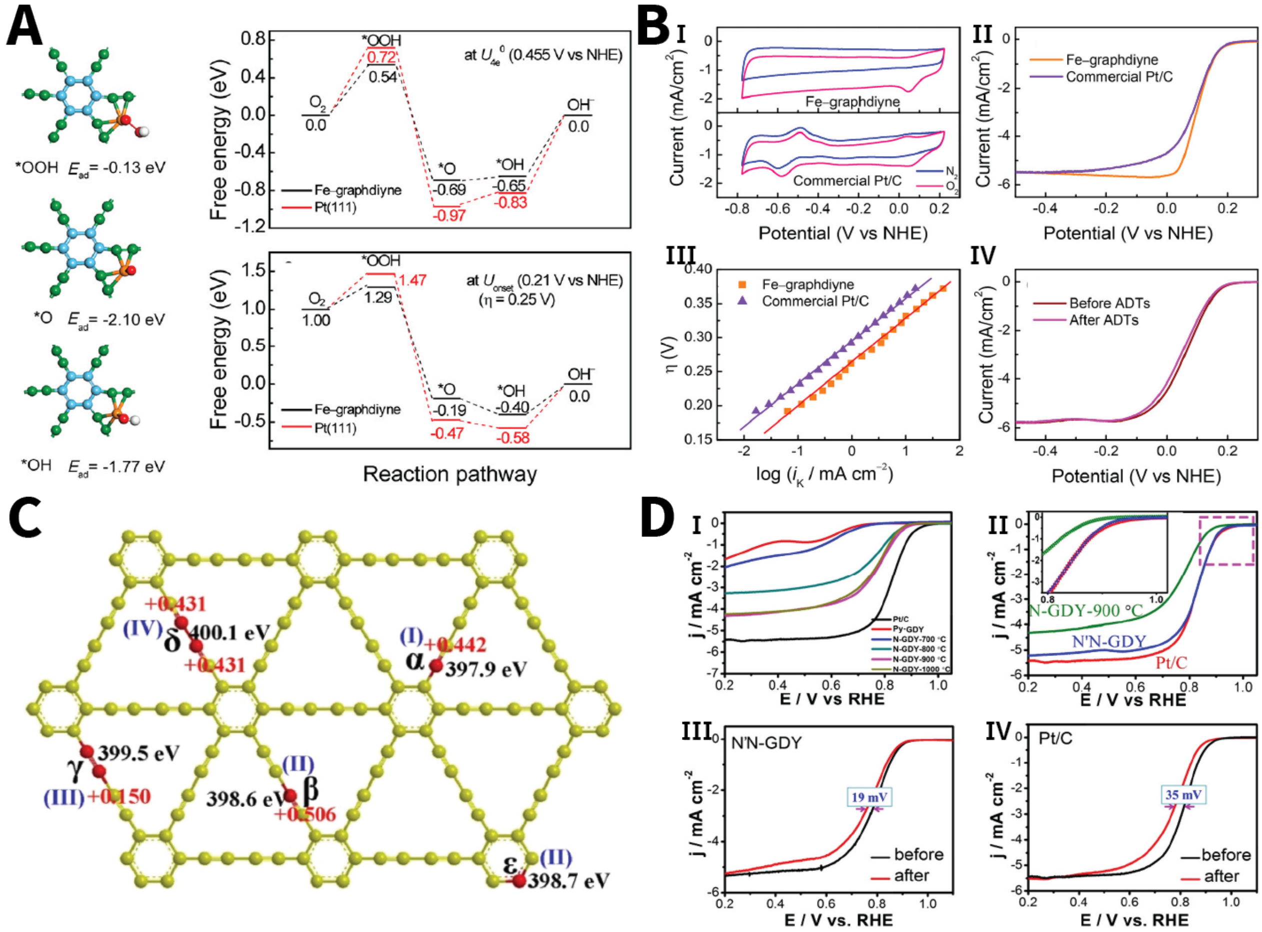


Figure 4. A: Atomic configurations of adsorbed *OOH, *O, and *OH on Fe-GDY surface, and calculated free energy diagrams of 4e$^-$ pathways of ORR at Fe-GDY and Pt (111). **B**: I: CV responses of Fe-GDY and commercial Pt/C in N_2- and O_2-saturated 0.1 M KOH solution. II: RDE measurements in O_2-saturated 0.1 M KOH solution. III: Tafel plots of ORR. IV: Stability test of Fe-GDY to ORR. Reprinted with permission from ACS Catalysis, 2018, 8, 10364-10374. Copyright 2018, American Chemical Society.[63] **C**: Schematic representation of the possible doping position of N atoms in the N-GDY. **D**: I: LSV curves of commercial Pt/C, Py-GDY and all N-GDY at 1600 rpm in O_2-saturated 0.1 M KOH. II: LSV curves of N-GDY-900 °C, N'N-GDY and commercial Pt/C at 1600 rpm in O_2-saturated 0.1 M KOH. Durability test of III: N'N-GDY and IV: commercial Pt/C for 5000 CV cycles in O_2-saturated 0.1 M KOH. Reprinted with permission from ACS Applied Materials & Interfaces, 2017, 9, 29744-29752.. Copyright 2017, American Chemical Society.[68]

Due to its intriguing electronic properties and structural features, GDY has been considered to be an excellent substrate to boost the catalytic activity of anchored metals and increase the durability of the catalyst.[55, 56] $NiCo_2S_4$ nanowires were synthesized in situ as building blocks on 3D GDY foam ($NiCo_2S_4$/3DGDF) (**Figure 3A**).[55] The $NiCo_2S_4$/3DGDF electrode exhibits excellent catalytic activity and extraordinary long-term stability for both the HER and OER, as well as overall water-splitting in 1.0 M KOH. The overpotentials at 10 and 20 mA cm^{-2} are 1.53 and 1.56 V, respectively. At 20 mA cm^{-2}, the catalytic performance remains intact for at least 140 h. Hui *et al.* designed and synthesized an HER/OER bifunctional catalyst, the ultrathin graphdiyne-wrapped iron carbonate hydroxide nanosheets array on Ni foam (FeCH@GDY/NF).[56] In a basic medium of 1.0 M KOH, FeCH@GDY/NF can deliver 10 mA cm^{-2} at an overpotential of 260 mV for OER and 148 mV for HER and remarkable durability (at least 10000 cycles for OER and 9000 for HER). When used as a two-electrode electrolyzer, FeCH@GDY/NF drives 10 and 100 mA cm^{-2} at 1.49 and 1.53 V, respectively. Experimental results indicated that the introduction of GDY endows the catalysts with high ECSA, improved charge transports, facilitated kinetics and extraordinary long-term stability. Last but not least, the 3D morphology of FeCH@GDY/NF effectively promotes the gas evolution and release from the architecture, which also contributes to durability. Si *et al.* synthesized a 3D hierarchical graphdiyne (GDY)@NiFe layered double hydroxide (LDH) heterostructured catalyst toward overall water-splitting (**Figure 3B**).[57] The catalyst exhibits bifunctional catalytic activity for OER and HER with overpotentials of 220 mV and 163 mV at a current density of 10 mA cm^{-2}, respectively. The Tafel slope for OER is 39.33 mV dec^{-1}, which is much lower than that of pure NiFeLDH/CF (copper foam) with a value of 112 mV dec^{-1} (**Figure 3B**). Compared with the HER and OER activities of the pristine catalysts, the GDY@NiFe LDH achieves significant improvements in both reactions. DFT calculations reveal that the electron density accumulates at the GDY, and subsequently produce holes that accumulate on the NiFe LDH side, promoting the HER and OER catalytic performance, respectively. It is noteworthy that metal-free carbon bifunctional catalyst for HER and OER has been designed and synthesized with the use of fluorographdiyne (FGDY).[48] The 3D porous fluorographdiyne nanostructures on carbon cloth (p-FGDY/CC) demonstrate robust and efficient catalytic performance for HER and OER. In 1.0 M KOH, the p-FGDY/CC exhibits a low onset potential of 1.54 V (vs. RHE) and reaches 10 mA cm^{-2} at the potential of 1.69 V (vs. RHE). These values are lower than most of the reported benchmark metal-free catalysts (**Figure 3C**). The OER activity of p-FGDY/CC could be maintained after 2000 continuous cycles and a 9-hour electrolysis test (**Figure 3C**). Experiments and theoretical calculations reveal that the enhancement of catalytic activity and durability are ascribed to the intrinsic properties of FGDY, such as the high electron-transfer ability, high conductivity, and edge/defect-rich structure. Moreover, Wang et al. have reported the co-doping strategy in GDY by sp-N and S atoms to improve the OER performances based on a site-controlled method.[58] The obtained sample has displayed an overpotential of 299 mV and a current density of 7.2 mA/cm^2, which is superior to the benchmark electrocatalyst RuO_2.

Oxygen reduction reaction (ORR)

Fuel cell is regarded as one of the most promising clean and sustainable energy devices. Compared with fossil fuels, it has several advantages such as high energy density, sufficient energy conversion efficiency, low to zero pollution emission, and high reliability.[59] Fuel cell is expected to be applied in residential applications, vehicles and stationary power systems.[60] However, the intrinsically sluggish kinetics of the cathode reaction, ORR, and the reliance on the expensive and scarce noble-metal-based catalyst, severely hinder the practical applications of the fuel cell at the current stage. In consideration of cost and durability, enormous efforts have been devoted to the development of non-noble-metal-based catalysts and metal-free catalysts for ORR. Since the successful synthesis of GDY in 2010, GDY has shown significant potential in electrocatalysis because of its unique electronic and physical properties. In particular, researchers of electrochemistry have also explored the possibility of developing high-performance and durable ORR catalysts based on GDY.

GDY-based atom catalysts for ORR. In GDY, the charge distributions at each carbon atom are not uniform, indicating the existence of positively charged carbon atoms, which are favorable to the adsorption of O_2 and OOH^+ molecules.[61] The porous structure of GDY also contributes to the O_2 adsorption, as the size of the pores is ≈ 2.5 Å.[62] These intrinsic advantages of GDY facilitate the ORR catalytic performance. Gao *et al.* utilized GDY as the Fe SAC support, achieving a high catalytic activity towards ORR similar to or even better than the benchmark commercial Pt/C (20 wt%).[63] It is highlighted that this catalyst was first predicted by DFT calculations, and then the activity was experimentally validated. DFT calculations predicted that an O_2 molecule could bind with a Fe atom, and the $4e^-$ ORR process would be favorable with high selectivity. Moreover, the energy pathway constructed for alkaline $4e^-$ ORR on this Fe/GDY SAC had a lower energy level of rate-determining step (RDS) than that of Pt (111), suggesting better catalytic activity than the commercial Pt/C (**Figure 4A**). The predicted excellent ORR catalytic activity was verified with electrochemical experiments (**Figure 4B**, I-IV). In the alkaline condition, the onset potential was 0.21 V (vs. NHE), which was almost identical to the 0.20 V of Pt/C. The cathodic peak potential of Fe/GDY was observed at ~53 mV (vs. NHE), and the peak current was ~0.42 mA/cm^2. Compared to the benchmark Pt/C catalyst, the peak potential of Fe/GDY was at the same level (~56 mV vs. NHE for Pt/C) while the peak current was slightly higher than the 0.25 mA/cm^2 of Pt/C. The Fe/GDY has better durability in alkaline conditions due to the highly dispersed Fe atoms anchored on GDY.

Metal-free GDY-based ORR catalysts. Metal-free ORR catalysts are also receiving huge research interest for their potentially higher cost-efficiency. Doping carbon materials with heteroatoms improves catalytic activity, which is a promising method to design ORR metal-free catalysts.[64-66] In 2014, Zhang's group successfully prepared the N-doped GDY (NGDY) as a metal-free ORR catalyst in alkaline conditions.[64] The NGDY exhibits comparable ORR catalytic activity to commercial Pt/C and better stability and increased tolerance to the cross-over effect. They further explored more types of heteroatom doping on GDY for alkaline ORR catalysts, including sulfur (SGDY), boron (BGDY), fluorine (FGDY) and the above ones co-doped with nitrogen (NSGDY, BNGDY and NFGDY, respectively).[67] The as-prepared NFGDY demonstrated high selectivity for the four-electron ORR pathway, complete tolerance for CO and methanol. Moreover, the NFGDY exhibited comparable performance to the state-of-the-art Pt/C catalyst in the homemade primary Zn-air battery. Lv *et al.* proposed that based on previous studies on the effect of doped N-atoms on ORR, the ORR activities of NGDY could be further improved by choosing proper doping positions on GDY.[68] Accordingly, they explored a new heteroatom-doping style of GDY, that substituting sp-hybridized carbon atoms with N atoms from pyridine and NH_3 as N sources (N'N-GDY) (**Figure 4C**).[68] The catalytic activity of N'N-GDY was further enhanced compared to the N-GDY calcinated at different temperatures from 700 to 900 °C (**Figure 4D** I, II). The onset potential of N'N-GDY was 0.98 V and the limited current density increased to 5.1 mA cm^{-2}, which were both comparable to those of commercial Pt/C. The accelerated aging tests demonstrated that the N'N-GDY was more stable than Pt/C by the less shift of the half-wave potential (**Figure 4D** III, IV). DFT calculations and experimental results reveal that the high catalytic activity originates from the sp orbitals of the N dopant, which facilitates O_2 adsorption and surface electron transfer. Later, Wang and Li's groups have reported the few-layered N-doping GDY, where the -sp-hybridized nitrogen (sp-N) atoms have been introduced to replace the acetylene groups.[69] In particular, the peak potential, half-wave potential and current density have shown highly remarkable performances, exceeding other non-metal electrocatalysts. The introduction of sp-N has significantly improved the O_2 adsorption as well as the electron transfer, which guarantees the fast kinetic of ORR. This work has introduced a new strategy to enhance the electrocatalytic performances of GDY.

Nitrogen reduction reaction (NRR)

Ammonia is one of the most essential chemicals in modern life.[70, 71] It is an important raw material in agriculture, medicaments and chemical industry for the synthesis of nitrogen products. Moreover, it is also a promising green energy carrier for its high energy density and convenience in storage and transport.[72, 73] Direct synthesis of NH_3 is therefore of great significance. Nonetheless, the chemical inertness of the N_2 triple bond makes it hard to reduce N_2 to NH_3. Currently, the industrial NH_3 direct synthesis method is Haber-Bosch process, which requires high temperatures and pressures (300-500 °C and 150-300 atm) to break the bond and accelerate the reduction process.[74] It is necessary to develop efficient and sustainable N_2

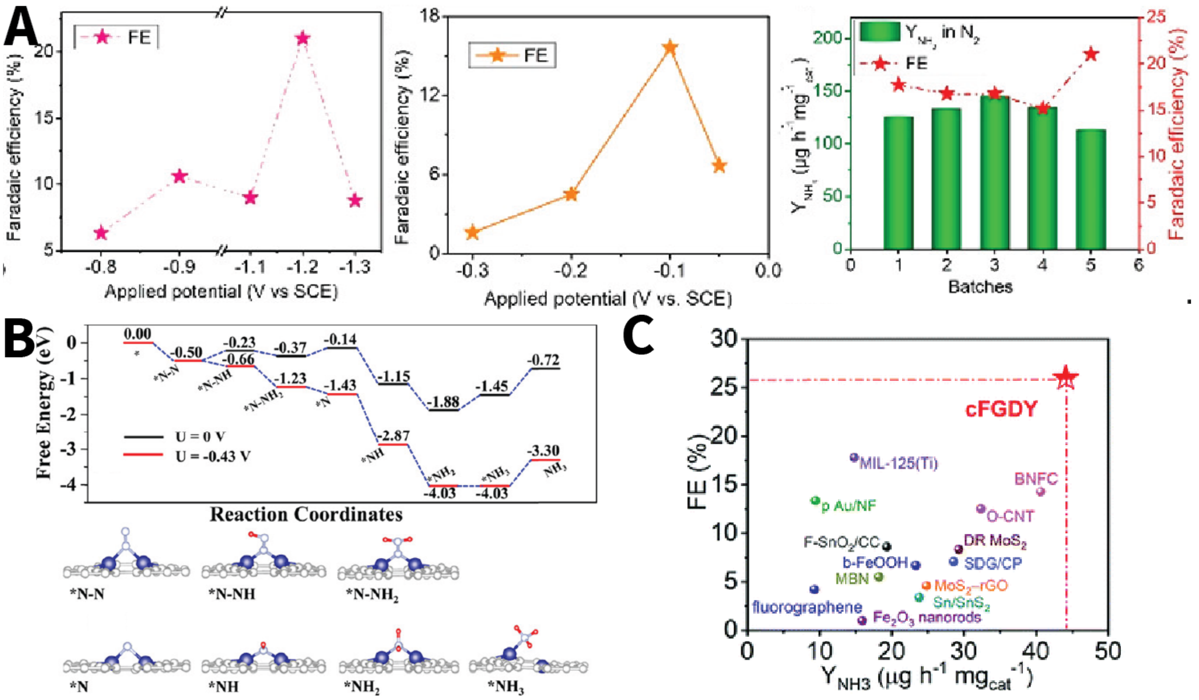


Figure 5. A: left: Faradaic efficiencies (FEs) at different potentials in 0.1 M Na_2SO_4; center: FEs at different potentials in 0.1 M HCl; right: NH_3 yield and FEs of NH_3 production of different batches of Mo^0/GDY samples. Reprinted with permission from Journal of the American Chemical Society, 2019, 141, 10677-10683. Copyright 2019, American Chemical Society.[75] **B**: (a) Free energy diagrams for NRR on Co_2@GDY through distal mechanism and (b) corresponding structures of intermediates. Red spheres indicate H atoms. Reprinted with permission from The Journal of Physical Chemistry C, 2019, 123, 19066-19076. Copyright 2019, American Chemical Society.[83] **C**: Comparison of NH_3 yield and FEs of cFGDY with reported metal-free and metal-based catalysts. Reprinted with permission from Nanoscale Horizons, 2020,5, 1274-1278. Copyright 2020, The Royal Society of Chemistry.[87]

fixation methods to relieve the energy consumption and emission of greenhouse gases in the Haber-Bosch process. Currently, the electrochemical NRR process catalyzed by heterogeneous catalysts has been regarded as a promising way for sustainable N_2 fixation at ambient conditions.[75] In recent years, some progress towards efficient electrochemical N_2 reduction has been made by applying transition metal nanomaterials. However, most NRR electrocatalysts suffer from the low faradaic efficiency due to the competing HER on the surface, which has a similar onset potential of NRR.[76, 77]

GDY-based atom catalysts for NRR. Among the recent novel explorations of electrochemical NRR catalysts, atom catalyst is one of the most promising strategies. The atom catalysts combine the advantages of homogeneous catalysts and heterogeneous catalysts, offering enhanced catalytic activity, higher selectivity and faradaic efficiency, and longer durability.[44, 78] Consequently, characterizations on atom catalysts have been carried out to identify their performances in NRR.[44, 78] Nonetheless, atom catalysts need to resolve the high aggregation tendency owing to the extremely small particle size. Substrates that have strong interactions with atoms are demanded the synthesis and long-term practice of atom catalysts. GDY is expected to be an excellent substrate material for atom catalysts to anchor transition metal atoms due to the sp- and sp^2-hybridized carbon atoms and uneven charge distribution on the GDY surface.[75] Many research groups have conducted theoretical calculation screenings of the proper transition metal atoms or even rare-earth metal atoms to be anchored on GDY to function as NRR electrocatalysts.[25, 75, 79, 80] Besides the noble metals (e.g. Au[81], Pd[82] and Rh[80]), non-noble metal elements also demonstrate excellent NRR activity when integrated with GDY to form atom catalysts. Accordingly, Mo-,[24, 75, 79] V-,[80] Co-GDY[83] atomic catalysts exhibit outstanding NRR activity when anchored on the GDY monolayer. Zhai *et al.* conducted a computational study, predicting the Mo@GDY with an ultra-low onset potential of -0.33 V would be an efficient NRR electrocatalyst.[75] The DFT calculations revealed that the strong metal-support interaction of GDY could stabilize the embedded Mo atoms and facilitates the N_2 adsorption. Moreover, given the more positive adsorption energy of H (-0.45 eV vs. -0.93 eV of N_2), it is expected that HER would be suppressed on Mo@GDY, resulting in much improved faradaic efficiency. In 2019, Hui *et al.* synthesized an atom catalyst with zerovalent Mo atoms on GDY (Mo^0/GDY) with a high mass content of Mo atoms (up to 7.5 wt %) via a facile and scalable process.[24] DFT calculations revealed that the strong electron-rich GDY environment preserves Mo^0 by a strong p-d coupling. Interestingly, the Mo^0/GDY demonstrates bifunctional catalytic activity to both NRR and HER, depending on the N_2 saturation in solutions. At room temperature and pressure, Mo^0/GDY shows excellent selectivity and NH_3 yield rates in both neutral and acidic electrolytes saturated with N_2 (**Figure 5A**). For example, in 0.1 M Na_2SO_4, the NH_3 yield rate and faradaic efficiency reach 145.4 μg h^{-1} $mg_{cat.}^{-1}$ and > 21 %, respectively. In 0.5 M H_2SO_4 non-N_2-saturated solutions, Mo^0/GDY exhibits higher HER activity than that of the commercial 20 wt % Pt/C and conventional electrocatalysts.

Recently, the concept of atom catalyst is not limited to single atom catalyst (SAC) but has been developed into double atom catalyst (DAC) and triple atom catalyst (TAC). The inspiration of these new atom catalysts is that the single atomic site might not offer the optimal adsorption configuration for the adsorbates. Introducing well dispersed but neighboring double or triple atoms as a unit can significantly resolve this issue. It has been revealed that DACs are better than the corresponding SACs for NRR.[83, 84] However, due to the repulsion forces between the metal atoms, DACs and TACs are harder to synthesize compared to SACs. In this case, GDY again becomes a promising substrate for the fabrication of stable DACs and TACs due to the unique electronic distribution and naturally uniform pores.[25] Ma and coworkers conducted a computational evaluation of electrochemical NRR on TM SAC, DAC and TAC (TM = Mn, Fe, Co, Ni) based on GDY monolayers.[83] The analysis unveiled that the Co_2@GDY would exhibit the best NRR catalytic activity with the onset potential of -0.43 V and suppress the HER (**Figure 5B**). The high NRR catalytic activity of Co_2@GDY was attributed to the strong electron-donating ability of the GDY monolayer. Nonetheless, the successful synthesis of GDY-based DACs and TACs for NRR are still rare, which should be a major challenge to address in the future.

Other GDY-based NRR catalysts. Besides atom catalysts, there are other types of GDY-based electrocatalysts for NRR. For instance, the 3D GDY-cobalt nitride (GDY/Co_2N) functions as an NRR catalyst at the interface region, reported by Fang *et al*.[85] Under ambient pressure and temperature, GDY/Co_2N created a record-high NH_3 yield rate and faradaic efficiency of 219.72 μg h^{-1} $mg_{cat.}^{-1}$ and 58.60 %, respectively, in acidic conditions. DFT calculations reveal that the interface-bonded GDY optimally modifies the Co-N surface bonding by contributing the unique p-electronic character, and hence generates the superior NRR catalytic activity at the interface. Metal-free GDY catalysts for NRR are also under active exploration. Feng and coworkers investigated heteroatom-doped GDY for NRR catalysis with DFT calculations and identified that O-doped GDY would be a metal-free NRR catalyst.[86] The reaction mechanism and effect of tensile strain were also discussed. Zeng's group probed into the synergistic effect of B-N doped defective GDY (BN@GDY) for NRR catalysis, which suggested that the NRR catalytic activity and selectivity would be boosted on the BN@GDY.[87] In 2020, Xing *et al.* reported a new 3D metal-free NRR electrocatalyst based on crystalline fluorographdiyne film grown on the surface of carbon fibers (cFGDY).[28] The cFGDY demonstrated good stability at different potentials and the highest NH_3 yield rate of 44.14±4.54 μg h^{-1} mg_{cat}^{-1} at -1.2 V vs SCE, which surpassed many reported metal-free electrocatalysts and even higher than metal-based ones (**Figure 5C**). It also showed the largest faradaic efficiency of 25.95±2.6 % at -1.2 V vs SCE among the reported metal-free electrocatalysts.

Other Chemical Reactions

Besides the common electrocatalysis of energy generation, GDY-based catalysts have also shown great potential in lots of other chemical reactions such as the methanol electrooxidation reaction (MOR) and the Suzuki-Miyaura coupling reactions. For the MOR process, Li et al. have demonstrated the anchoring of PdCu nanoparticles on the inner wall of the freestanding GDY structures.[88] Depending on the highly ordered nanochannels in the electrocatalysts, the MOR process has been confined in the structure with effective suppressions of the methanol crossover. Based on such an anodic electrode material, the constructed direct methanol fuel cell (DMFC) has shown a remarkable performance, which reaches a power density of 90 mW cm^{-2} at 80 degrees. The operation of the DMFC also maintains stable for over 500 hours with only 19% loss of the original power density. This work has indicated the great potential of GDY-based catalysts for broad applications. Suzuki-Miyaura coupling reaction is typical as a cross-coupling reaction to link boronic acid and an organohalide, which usually uses Pd(0) as the electrocatalyst. Shen et al. have anchored Pd, Pt, Ni and Cu nanoparticles on the N-doped GDY (NGDY), displaying evident charge transfer between the substrate and the supported metals.[89] In particular, the Pd-NGDY has shown a great potential for the Suzuki-Miyaura reactions, which have been proved by both experiments and DFT calculations. The TOF value of the Suzuki-Miayaura coupling reactions reaches 1287 h^{-1} confirm the strong reactivity of Pd-NGDY, which further extends the applications of GDY-based catalysts in broad chemical reactions.

Energy storage applications of GDY

Lithium ion batteries

Rechargeable lithium ion batteries (LIBs) have drawn much research interest because they have led to the evolutions in electric vehicles and portable electronics. The further improvements on the performance of LIBs have gradually become the bottleneck of the development for these applications. Currently, it is still challenging for LIBs to reach a better rate performance, higher capacity and stability, and longer cycling life.[90] Graphite is the most commonly used anode material in commercialized batteries, which consists of all sp^2-hybridized carbon atoms.[91] Although other carbon allotropes such as fullerenes, carbon nanotubes and graphene have been studied as alternatives as graphite, their hybridization states are the same as graphite. Hence, despite the increased Li capacity, the nature of Li-intercalated layer does not change significantly.[27] GDY has been predicted to be a promising Li storage material owing to its high capacity and rate capability, and its intriguing sp- and sp^2-hybridization states of carbon.[27, 92] Through the combination with other materials, GDY-based composite materials also display high performances in lithium-ion batteries. GDY is able to form the seamless coating on metal oxide to stabilize the structure and interface, which prevents the degradations of metal oxide as LIB anodes.[93] The Nafion@graphdiyne core-shell nanostructure has been reported, which can effectively store the sulfur species and promote the cathodic reactions through the sp-hybridized carbons.[94] Based on this, the Li-S battery has reached the volume capacity of 1832 Ah L^{-1} and high stability for over 800 cycles.

In addition, Huang *et al.* reported that GDY films exhibited a high specific Li capacity, long cycle life and high stability as electrode materials in Li-ion batteries (**Figure 6A**).[27] The GDY films were deposited on Cu foils and used as the working electrode. The tested battery with the GDY electrode featured a reversible capacity of up to 520 mAh g^{-1} after 400 cycles at a current density of 500 mA g^{-1}. At a higher current density of 2 A g^{-1}, a specific capacity of 420 mAh g^{-1} was retained after 1000 cycles. In accordance with the theoretical analysis, this excellent performance was ascribed to the numerous Li storage sites and rapid transport of electrons and ions. In subsequent works, bulk GDY powders with a porous structure were successfully synthesized and applied as electrode materials for lithium storage.[95] The assembled GDY powder-based LIBs exhibited a highly stable specific capacity of 552 mA h g^{-1} for 200 cycles and outstanding rate performance.

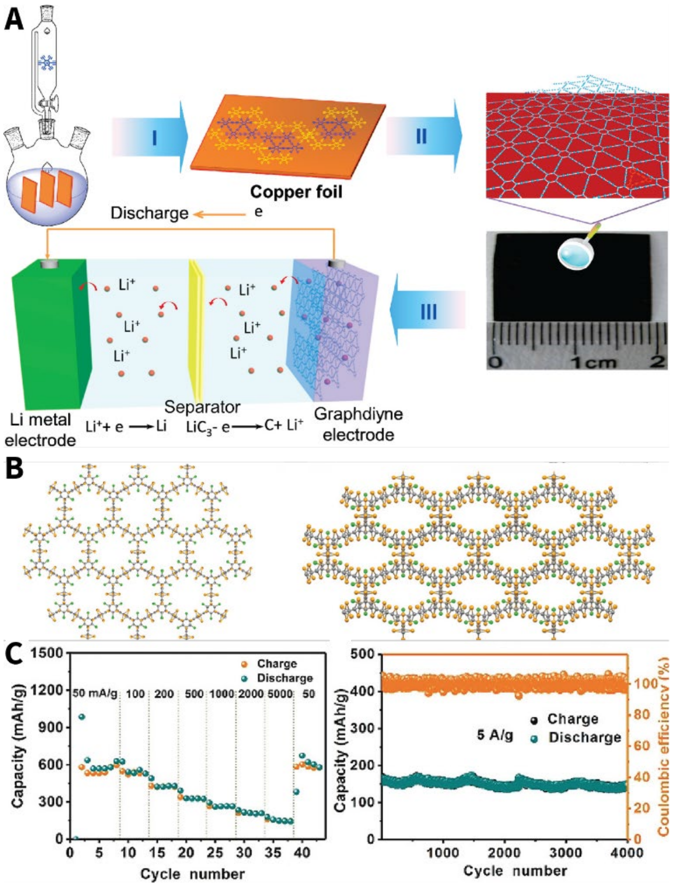


Figure 6. **A**: Schematic of GDY synthesis and Li-ion batteries preparation process. Reprinted with permission from Nano Energy 2015, 11, 481-489. Copyright 2014, Elsevier Ltd.[27] **B**: The possible Li storage sites in Cl-GDY and the function of chlorine. C gray, Cl green, Li orange. Reprinted with permission from Angewandte Chemie International Edition 2017, 56, 10740-10745. Copyright 2017, WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.[97] **C**: The rate performance (left) and the cycle performance at 5 A g^{-1}(right) of the BGDY electrode for NIBs. Reprinted with permission from Angewandte Chemie International Edition 2018, 57, 3968-3973. Copyright 2018, WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.[102]

Recently, halogen functionalization of carbon materials has drawn much attention, as it provides opportunities to optimize the conductivity, bandgap, and morphology properties owing to the different electronegativity and atom size of the halogen atoms.[96] Li's group reported the chlorine-substituted GDY (Cl-GDY) for lithium ion storage (**Figure 6B**).[97] The chlorine atoms are homogeneously distributed in the two-dimensional molecular plane, which would stabilize the intercalated Li atoms and generate more storage sites. Meanwhile, the substitution of chlorine on the carbon framework expanded the pore size of GDY, which would be favorable for the perpendicular lithium ion diffusion. The Cl-GDY film on copper foil was implemented as practical LIBs and achieved a highly improved reversible capacity of 1150 mAh g^{-1} at a current density of 50 mA g^{-1}. The durability was also greatly improved as it showed a stable specific capacity around 500 mAh g^{-1} for 500 cycles at the current density of 2 A g^{-1} in lithium-ion half-cells. Li's group subsequently synthesized fluorine-substituted GDY (F-GDY) as a free-standing electrode for LIBs.[98] The structure of F-GDY was similar to Cl-GDY. In particular, F-GDY exhibited excellent compatibility with non-aqueous electrolytes and a stable SEI film was established on the interface to minimize the side reaction. F-GDY achieved a highly improved reversible capacity of 1700 mAh g^{-1} at a current rate of 50 mA g^{-1}, and a specific capacity of around 350 mAh g^{-1} for 9000 cycles at a current density of 2 A g^{-1}. The C-F bond in F-GDY could transition from covalent to ionic bonds reversibly, which was confirmed by the ex-situ XPS spectra and endowed it the durability at different current densities.

Sodium ion batteries

Although the most common commercial-scale rechargeable battery is lithium-ion battery (LIBs), concerns on the supplies of lithium have raised research interest in alternatives of LIBs.[99, 100] Sodium ion batteries (NIBs) has been considered to be the promising candidate to replace current LIBs. Following the previous theoretical and experimental works of GDY as LIBs anode materials, researchers started to investigate the possibility of using GDY for NIBs systems. Xu *et al.* provided important information on the binding of Na on single and bulk GDY, and diffusion on a single GDY sheet.[101]Afterwards, Searles's group presented DFT calculations about the Na capacity and transitions on GDY.[99] Analysis results suggested that Na on GDY would be a potentially suitable anode for rechargeable batteries. The maximum capacity of Na in GDY could reach 497 mAh g^{-1}. DFT calculations showed that the Na transition energy barriers would be either lower or similar to those observed for Li on graphene. Prof. Li's group reported the synthesis of Boron-graphdiyne (BGDY) and its application in sodium ion batteries (**Figure 6C**).[102] The unique all sp-hybridized carbon and evenly distributed boron in the BGDY framework endowed BGDY with excellent electronic structure and good conducting properties. The BGDY based electrode showed an excellent rate performance and reversible capacity in a long cycle, which could maintain at 180 mAh g^{-1} after even 4000 cycles at a current density of 5 A g^{-1}. Compared to the GDY, the prominent performance of BGDY might be ascribed to the proper electronegativity and size of the decorated molecular pores of BGDY.

Conclusion and perspectives

In this work, we summarized and reviewed the recent advances in energy-based application of GDY. The GDY-based catalysts for various fundamental electrochemical reactions are reviewed by their structural features, such as heteroatom-doping, atom catalysts and metal-free GDY catalysts. Since the initial synthesis in 2010 by Li's group, theoretical and experimental investigations about the GDY properties and applications have been thriving.[10] The excellent physical and chemical properties of GDY endow it the sufficient durability and catalytic activity for electrochemical reaction catalysis. The sp-hybridized carbon atoms in GDY provide firm bindings with metal atoms, and hence it has been widely applied to design and synthesize novel atom electrocatalysts. The all-conjugated carbon frameworks of GDY also guarantee its electronic conductivity, making it a suitable substrate to combine with heterostructures and metals to boost the activity of the pristine catalyst units. Besides electrocatalysis, GDY has also been considered as a promising anode material for LIBs and NIBs owing to its capability of storing these two ions in uniform pores on the molecular plane.

The possibilities of applications of GDY are still under exploration. While there have been many theoretical studies that predict a variety of GDY-based materials with great potentials in electrocatalysts and energy storage materials, the advances in synthesis techniques limit the experimental verification of them. It is expected that more accurate control of the composition, structure and morphology of GDY materials should be achieved to fully excavate their untapped potentials. In the meantime, GDY mainly acts as the auxiliary role to the chemically active component. For instance, single atom catalysts utilized the strong interactions between metal and GDY to enhance the activity of the transition metal atom sites and the stability of the anchored isolated atoms. However, there are few applications to explore the direct use of carbon-carbon triple bonds. In addition, solid evidence to prove the crucial role of carbon-carbon triple bonds is still insufficient, which requires more research attention. The metal-free GDY catalysts for energy-related electrochemical reactions are also demanding more research attentions for the merit of lower cost and less pollution issues. It is also expected that a more novel design of catalysts could be inspired by the various binding sites in GDY. The exploration of DAC, TAC and even single cluster catalyst (SCC) on GDY is a promising direction for future research.[79, 103] We believe the potential of GDY is enormous, and GDY will participate in more energy-related applications in the future.

Conflicts of interest

There are no conflicts to declare.

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