Graphdiyne: synthesis, properties, and applications

Xin Gao,† Huibiao Liu,‡ Dan Wang§ and Jin Zhang*†

Graphdiyne (GDY), a new two-dimensional (2D) carbon allotrope, has been receiving increased attention. Its unique sp–sp² carbon atoms, uniform pores, and highly π-conjugated structure provide promising potential in practical applications, such as gas separation, catalysis, water remediation, humidity sensor, and energy-related fields. In the recent years, considerable efforts have been expended toward the development of well-defined GDY. However, GDY materials still face numerous challenges, including the need for a more thorough understanding of the growth mechanism, strategies for synthesizing one- or few-layer single-crystalline GDY films, characterization of basic physicochemical properties, and achievement of promising applications. This review aims at providing a comprehensive update on the synthesis of GDY and GDY-based materials, as well as their properties, including structural, electronic, mechanical, and spectral properties, and their applications in nanotechnology.

1. Introduction

Designing and synthesizing new low-dimensional carbon materials is one of the hot topics that researchers are concerned about in the recent years. Graphynes are a series of new two-dimensional (2D) carbon materials formed by the combination of sp- and sp²-hybridized carbon atoms according to a certain periodic rule.1,2 Due to the presence of sp-hybridized carbon atoms, graphynes have completely different structures and properties when compared with other carbon allotropes, which only comprise sp²-hybridized carbon atoms (e.g., carbon nanotubes (CNTs))3,4 and graphene (GR)).6 For example, graphynes have well-distributed pore structures and large π-conjugated systems, endowing them with potential applications in gas separation,7,8 catalysis,9–11 and energy-related fields.12–17

The first structural model of graphynes was proposed by R. H. Baughman et al. in 1987.1 Owing to the high formation energy and flexibility of sp bonds, the first graphyne film (defined as γ-graphdiyne, GDY) was not prepared until 2010 via an in situ Glaser coupling reaction of...
hexaethylbenzene (HEB) monomers on a copper (Cu) substrate by Prof. Yuliang Li’s group. Since then, graphynes have been fervently discussed over nearly ten years, as shown in Fig. 1. Significantly, among all the graphyne-related articles, more than half of them discuss GDY-related topics. In this review, we will focus on GDY.

GDY is a 2D planar network structure formed by inserting diacetylenic linkage between two benzene rings in a GR structure. It is the most stable non-natural carbon allotrope containing diacetylene bonds and has a direct bandgap (0.46 eV) and high carrier mobility at room temperature ($10^4$–$10^5$ cm$^2$ V$^{-1}$ s$^{-1}$), making it promising for future nanoelectronics. Since the first experimental synthesis of GDY in 2010, the annual number of GDY-related journal publications has grown exponentially in the past few years. GDY materials with different morphologies (e.g., films, powders, and nanowalls) have been prepared by various synthesis methods (dry and wet methods) and applied in worthwhile fields (catalysis, energy storage, and water remediation) (Fig. 1). Despite the huge advance in pursuing the fabrication of high-quality GDY and endowing it with unique properties to make it suitable for practical applications, there is still a sizeable gap between idealism and reality. The ideal GDY has a perfect single-crystal structure consisting of sp- and sp$^2$-hybridized carbon with thickness of only one atom, while the as-prepared GDY is almost polycrystalline or amorphous and the thickness is difficult to control. Therefore, the exhibited properties of the as-prepared GDY are not as good as the theoretical prediction results.

In this review, we will introduce the basic properties of GDY, namely, stability, electrical properties, mechanical properties, and Raman spectroscopy, both from the viewpoints of experimental and theoretical aspects. More importantly, we will focus on the feasibility of various synthesis strategies, delineating an architectural blueprint toward the design and synthesis of high-quality GDY in which it retains its “2D characteristic.” At last, the review concludes by summarizing the current potential applications of the prepared GDY.

2. Nomenclature, structure, and stability

2.1 Nomenclature

Graphynes are a series of new 2D carbon allotropes composed of sp- and sp$^2$-hybridized carbon atoms. Their structural models were first proposed by R. H. Baughman et al. They have a 2D structure reminiscent of graphite and contain acetylenic linkages (sp components), simply named as graphyne. Evidently, sp- and sp$^2$-hybridized carbon atoms can be interconnected by covalent bonds according to a certain rule, yielding a variety of 2D structures. Therefore, “graphynes” is a generic name given to a class of structures, where two adjacent sp$^2$-hybridized carbon atoms are connected by $n$ “–C≡C–” linkages. We can simply classify this class of materials based on the number of “–C≡C–” linkages that connect two adjacent sp$^2$-hybridized carbon atoms. As shown in Fig. 2a, they are called graphyne, graphdiyne, and graphyne-$n$.

Moreover, there are two main methods for the naming of graphynes, i.e., system nomenclature and custom nomenclature. The former names graphynes based on the number of carbon atoms in the ring of graphynes. According to this method, graphynes can be named as $\alpha$, $\beta$, and $\gamma$-graphyne, where $\alpha$ and $\beta$
represent the number of carbon atoms in the smallest ring of the graphynes (\(a\) ring) and number of carbon atoms in the adjacent smallest ring of the graphynes (\(b\) ring), respectively. Among them, the \(a\) and \(b\) rings are connected by C(sp\(^2\))C(sp). The index \(g\) is the number of carbon atoms in the third ring of graphynes, which is connected to the \(b\) ring by C(sp\(^2\))C(sp)C(sp)C(sp\(^2\)). According to this nomenclature, graphyne in Fig. 2c can be named as 12,12,12-graphyne. Similarly, the graphyne in Fig. 2e can be named as 6,6,12-graphyne.

In addition, for convenience, several graphynes are popularly named via greek letters, which can be termed as customary nomenclature. Using such customary nomenclature, we can name 12,12,12-graphyne as \(\alpha\)-graphyne. Fig. 2 shows several graphynes, which are named according to the customary nomenclature: \(\alpha\)-graphyne (Fig. 2b), \(\beta\)-graphyne (Fig. 2c), \(\gamma\)-graphyne (Fig. 2d), \(\beta\)-graphdiyne (Fig. 2f), and GDY (Fig. 2g). Using both the aforementioned nomenclatures, most of the graphynes can be named, but the naming systems of graphynes have their own limitations and still need to be further improved. For example, the systemic nomenclature is complicated and confusing, while customary nomenclature has limitations and cannot represent all kinds of graphynes.

### 2.2 Structure and stability of graphynes

The different arrangement rule of sp- and sp\(^2\)-hybridized carbon atoms in graphynes determines their different structural characteristics. For example, different kinds of single-layer graphynes have different crystal structures and symmetries (Fig. 2 and Table 1). Most of the graphynes have hexagonal symmetry like GR, except for 6,6,12-graphyne that has rectangular symmetry and the original cell has a rectangular shape with in-plane anisotropy. Table 1 lists the optimal lattice constants and the percentage of the acetylenic linkages of different kinds of graphynes. In order to facilitate a comparative analysis, the basic parameters of GR are also listed in the table as a reference (the percentage of acetylenic linkages in GR is defined as 0). Among them, \(\alpha\)-graphyne can be fabricated by replacing all the carbon–carbon bonds in GR using acetylenic (–C–C–) linkages. \(\beta\)-graphyne results from the replacement of two-third carbon–carbon bonds in GR by acetylenic linkages, and \(\gamma\)-graphyne results from the replacement of one-third carbon–carbon bonds in GR by acetylenic linkages. It is distinctly clear that \(\alpha\)-graphyne has the highest

### Table 1 Basic structural parameters of graphynes

<table>
<thead>
<tr>
<th>Carbon allotropes</th>
<th>Lattice constant (Å)</th>
<th>Percentage of the acetylenic linkages (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\alpha)-Graphyne</td>
<td>6.9812(^{38})</td>
<td>100(^{34})</td>
</tr>
<tr>
<td>(\beta)-Graphyne</td>
<td>9.3004(^{36})</td>
<td>66.67(^{31,36})</td>
</tr>
<tr>
<td>(\gamma)-Graphyne</td>
<td>6.8826(^{35})</td>
<td>33.33(^{31,36})</td>
</tr>
<tr>
<td>6,6,12-Graphyne</td>
<td>(a = 9.44)</td>
<td>41.67(^{31,36})</td>
</tr>
<tr>
<td></td>
<td>(b = 6.90)</td>
<td>50(^{20})</td>
</tr>
<tr>
<td>(\gamma)-Graphdiyne</td>
<td>9.48(^{39})</td>
<td>0(^{20})</td>
</tr>
<tr>
<td>Graphene</td>
<td>2.47(^{22})</td>
<td>0(^{20})</td>
</tr>
</tbody>
</table>
percentage of acetylenic linkages (100%). For β-graphyne, γ-graphyne, 6,6,12-graphyne, and GDY, the percentage of acetylenic linkages is 66.67%, 33.33%, 41.67% and 50%, respectively.

Among them, GDY was predicted to be the most stable carbon allotrope containing “–C≡C–C≡C–” linkages with heat formation of 18.3 kcal per g-atom C.19 Besides, the stability of several abovementioned graphynes was also examined by calculating the differences in the total energies between the examined graphyne and pristine GR, as shown in Fig. 3.32

2.3 Structural parameters and selected area electron diffraction (SAED) patterns of one- and few-layer GDY

In the following, we will focus on the structural characteristics of one- and few-layer GDY and analyze their corresponding SAED patterns. Prof. Zhigang Shuai et al.30 first calculated the structure of GDY nanosheets by using the molecular dynamics simulation (VASP) method and obtained an optimized lattice parameter of 9.48 Å. Similar to GR, single-layer GDY belongs to the hexagonal system and belongs to the P6/mmm space group. Formula 1 is the calculation formula of d-spacing in the hexagonal system. For GDY, the d-spacings of the (100) and (110) planes are 0.821 nm and 0.474 nm, respectively.

\[
\frac{1}{d^2} = \frac{4}{3} \left( \frac{h^2 + hk + k^2}{a^2} \right) + \frac{\rho^2}{c^2}
\]  

(1)

Moreover, there are three different stacking modes of few-layer GDY with high symmetry (defined as AA-, AB-, and ABC-stacking modes), as shown in Fig. 4a–c. AA-, AB-, and ABC-stacked GDY structural models belong to the P6/mmm, P63/mmc, and R3m symmetries, respectively. Nishihara et al. first simulated the SAED pattern of GDY with AA-, AB-, and ABC-stacking modes.33 Among all the stacking modes of GDY structures having high symmetry, the (100) reflections of the ABC-stacked GDY are absent, which corresponds to the systematic extinction of rhombohedral (R)-centering (Fig. 4d–f). Experimentally, Luo and Lu et al. obtained the SAED pattern and high-resolution TEM (HRTEM) image of a six-layer GDY sheet (Fig. 4g–i).34 Recently, Zhang and Liu et al. further obtained the SAED pattern and HRTEM image of a trilayer ABC-stacked GDY film, which provides strong evidence toward the existence of few-layer GDY films.35

3. Properties

3.1 Mechanical properties

The excellent mechanical properties of carbon materials such as GR and CNTs are well known. Investigating the mechanical properties of graphynes is also worthwhile because of their unique pore structures. In 2012, Wang et al. used the molecular dynamics method to study this aspect. They compared fracture stresses, strains, and Young’s moduli of GR with different types of graphynes and found that the existence of acetylenic linkages had a significant effect on the mechanical properties of graphynes. The corresponding results are shown in Table 2.36 As the percentage of acetylenic linkages increases, the fracture stress and Young’s modulus of graphynes decrease owing to the decrease in the atomic density and weak carbon–carbon single bonds from the acetylenic linkages. GR possesses the highest fracture stress and Young’s modulus, followed by γ-, 6,6,12-, β-, and α-graphynes. In particular, 6,6,12-graphyne exhibits directional anisotropy in its mechanical properties, e.g., the Young’s modulus of 0.445 TPa and 0.35 TPa in the x (zigzag) and y (armchair) directions, respectively. In contrast, the acetylenic linkages in graphynes induces flexibility, thereby enhancing the fracture strain accordingly, as shown in Table 2.

In 2013, Li et al. used the first-principles method to perform additional in-depth theoretical calculations on the electrical and mechanical properties of graphynes.37 For the first time, they calculated the change in the bandgap of graphynes with different applied tensile stresses. Further, similar conclusions
were obtained with Wang et al. As the number of acetylenic linkages increases (obviously, the number of carbon–carbon single bonds increases as the number of acetylenic linkages increases), the in-plane intensity of graphyne decreases. The intensity of stiffness $C$ is a function of the number of acetylenic linkages $n$, and all of them are smaller than GR, without exceptions. For the band structure, they found that different strain forms have different bandgap changes; at the same time, the band structures of graphyne, graphyne-3, GDY, and graphyne-4 have different responses to strain. These results are shown in Fig. 5.

When comparing $d$ and $f$, it is evident that graphyne-3 has a direct bandgap at the $M$ or $S$ point of the Brillouin zone at different strains, and the change in bandgap will be different due to the different strain forms, that is, the bandgap will increase under homogeneous tensile stretching, but will decrease under uniaxial tensile stretching. Similar changes have been seen in graphyne-4. However, the difference is that the direct gap point always appears at the $\Gamma$ point of the Brillouin zone. The energy state near the Fermi level moves under strain, which results in a change in the band structure. This work further explored the mechanical properties of graphynes and yielded a semi-empirical mathematical model. More importantly, the possibility of stressing graphyne to qualitatively or even quantitatively regulate the energy band structure was computationally verified. This reveals the potential applications of graphyne in strained nanoelectronics and optoelectronics.

### Table 2  Fracture stresses, strains, and Young’s moduli of graphynes and graphene

<table>
<thead>
<tr>
<th>Model</th>
<th>Atom density (atoms per nm$^2$)</th>
<th>Stress (GPa)</th>
<th>Difference in stresses (%)</th>
<th>Strain</th>
<th>Difference in strains (%)</th>
<th>Young’s modulus (TPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\alpha$-Graphyne</td>
<td>18.92</td>
<td>36.36</td>
<td>10.69</td>
<td>0.178</td>
<td>12.37</td>
<td>0.12</td>
</tr>
<tr>
<td>$\beta$-Graphyne</td>
<td>23.13</td>
<td>46.26</td>
<td>17.72</td>
<td>0.162</td>
<td>19.54</td>
<td>0.261</td>
</tr>
<tr>
<td>6,6,12-Graphyne</td>
<td>28.02</td>
<td>61.62</td>
<td>36.61</td>
<td>0.147</td>
<td>21.54</td>
<td>0.445</td>
</tr>
<tr>
<td>$\gamma$-Graphyne</td>
<td>29.61</td>
<td>63.77</td>
<td>21.20</td>
<td>0.148</td>
<td>24.09</td>
<td>0.505</td>
</tr>
<tr>
<td>Graphene</td>
<td>39.95</td>
<td>125.2</td>
<td>17.27</td>
<td>0.191</td>
<td>29.93</td>
<td>0.995</td>
</tr>
</tbody>
</table>

3.2 Electronic properties

#### 3.2.1 Electronic properties of single-layer graphynes

GR is a zero bandgap semiconductor material with a Dirac cone. GDY is the first carbon allotrope material that has been chemically synthesized after GR, which has attracted increased attention. Theoretical predictions have indicated that graphyne may exceed GR with regard to electrical properties. The intrinsic bandgap of graphyne is always closed at the $\Gamma$ point of the Brillouin zone. The energy state near the Fermi level moves under strain, which results in a change in the band structure. This work further explored the mechanical properties of graphynes and yielded a semi-empirical mathematical model. More importantly, the possibility of stressing graphyne to qualitatively or even quantitatively regulate the energy band structure was computationally verified. This reveals the potential applications of graphyne in strained nanoelectronics and optoelectronics.
Graphene 3.316, 31 a

The bandgap was 0.46 eV at the semiconductor material, GDY has an intrinsic electron mobility of semiconductor materials in the field of electronics. As a novel conductor materials, and it also determines the applications of parameter that characterizes the electrical properties of semiconductor materials in the field of electronics. As a novel semiconductor material, GDY has an intrinsic electron mobility of \(10^3\) cm² V⁻¹ s⁻¹ at room temperature, and the hole mobility is one order of magnitude lower than the electron mobility.

In Table 3, we counted the theoretical calculation results of the bandgap and room temperature mobility of several common single-layer graphynes containing GDY. For comparison, the related results for GR are also listed. In this table, it is worth noting that 6,6,12-graphyne does not have hexagonal symmetry in its structure and has two Dirac cones with different mobility values in both a and b directions, exhibiting anisotropy. As a result, the mobility in a particular direction is significantly higher than that of GR, and therefore, graphene may exhibit more excellent electronic properties than GR.

Electronic properties of GDY with different layers and stacking models. Different layers and different stacking methods also affect the electronic properties of the layered material. Jing Lu et al. used the density functional method to study the different stacking behaviors and related electronic properties (bandgap and mobility) of GDY. The results showed that the stacking of the benzene ring in the Bernal mode (shown in Fig. 6b and c) is the most stable stacking mode for bilayer and trilayer GDY. The bandgap of the most stable structure of the bilayer GDY is 0.35 eV and that of trilayer GDY is 0.33 eV, both of which are smaller than the intrinsic bandgap of the single-layer GDY. Notably, when the bilayer and trilayer GDY materials display AA- and AAA-stacking modes, respectively, they exhibit metallic characteristics. Hiroshi Nishihara33 and Jin Zhang’s group35 proposed another stacking model of GDY, as shown in Fig. 4a–c. Furthermore, they used the hybrid functional HSE06 to predict their band structures and bandgaps \(E_g\) for single-layer, bilayer (AB-stacking), and trilayer (ABC-stacking) GDY. As the number of GDY layers increases, the bandgap of the GDY is reduced, but the direct bandgap is retained. Experimentally, they measured the photoluminescence (PL) spectrum of the trilayer GDY with ABC stacking. A single emission peak with a maximum at the photon energy of 1.79 eV was observed, which is close to the predicted bandgap of trilayer GDY.35

### Optical properties

#### 3.3.1 Optical absorption.

Optical absorption is one of the most fundamental optical properties of materials. The optical absorption spectrum of GDY was calculated and measured by Lu et al.33,45 As-grown GDY according to Li’s method18 was transferred onto a quartz glass substrate for the measurement of ultraviolet-visible-near-infrared (UV-vis-NIR) spectrum. A typical absorption spectrum of a GDY film is shown in Fig. 7a (blue line), where the red line is the background. After subtracting the background, the absorbance of the GDY film in the NIR to UV range is shown in Fig. 7b, which was then compared with the theoretical results at the random-phase approximation (GW+RPA) and Bethe–Salpeter equation (BSE) levels. When compared with GW+RPA, the experimental results (three absorption peaks at 0.56, 0.89, and 1.79 eV) were more consistent with the BSE calculation results (three absorption peaks at 0.75, 1.00, and 1.82 eV). The first peak resulted from transitions around the bandgap, and the others were from the transitions around the

![Fig. 6](image_url) (a) Band structure of single-layer GDY; reprinted with permission from ref. 20. Copyright 2011 American Chemical Society. (b) Most stable conformation, AB (B), of the bilayer GDY and its energy band structure. (c) Most stable conformation, ABA, of the trilayer GDY (\(\gamma\)) and its band structure. Reprinted with permission from ref. 44. Copyright 2012 The Royal Society of Chemistry.

#### Table 3 Intrinsic hole and electron mobilities (300 K) and bandgap of single-layer graphene material obtained by different calculation methods

<table>
<thead>
<tr>
<th>Carbon allotropes</th>
<th>Hole mobility (\mu^h) (\left(10^4\ \text{cm}^2\ \text{V}^{-1}\ \text{s}^{-1}\right))</th>
<th>Electron mobility (\mu^e) (\left(10^4\ \text{cm}^2\ \text{V}^{-1}\ \text{s}^{-1}\right))</th>
<th>Bandgap (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\alpha)-Graphyne</td>
<td>3.316, 31a 2.960, 31a 0.96, 31a</td>
<td>3.327, 31a 2.716, 31a 1.03, 31a</td>
<td>0, 31</td>
</tr>
<tr>
<td>(\beta)-Graphyne</td>
<td>1.076, 31a 0.856, 31a</td>
<td>0.892, 31a 0.798, 31a</td>
<td>0, 31</td>
</tr>
<tr>
<td>(\gamma)-Graphyne</td>
<td>0.35, 31g</td>
<td>1.62, 31g</td>
<td>0, 31</td>
</tr>
<tr>
<td>6,6,12-Graphyne</td>
<td>42.92, 31a 14.59, 31a</td>
<td>54.10, 31a 24.58, 31a</td>
<td>1.82, 31</td>
</tr>
<tr>
<td>(\gamma)-Graphdiyne</td>
<td>1.97, 31a 1.91, 31a</td>
<td>20.81, 31a 17.22, 31b</td>
<td>2, 31</td>
</tr>
<tr>
<td>Graphene</td>
<td>32.17, 31a 35.12, 31a 23.49, 31a</td>
<td>33.89, 31a 32.02, 31a 20.05, 31a</td>
<td>1.82, 31</td>
</tr>
</tbody>
</table>

a Zigzag direction, b Armchair direction.
Van Hove singularities. In addition, Liu and Zhang et al. also obtained a similar UV-vis spectrum as that of the as-grown GDY nanowalls.46 When compared with a monomer, there was an obvious bathochromic shift in the UV-vis spectrum (Fig. 7c), which may result from the enhanced electron delocalization through the extended conjugated π-system.

3.3.2 Raman spectroscopy of GDY. Raman scattering can reflect the structural information of GDY, particularly for Raman-active diyne linkers arranged in the specific topology of GDY. Liu and Zhang et al.47 studied the Raman spectrum of GDY using group theory and first-principles calculations. When compared with GR, GDY exhibited additional complicated vibrational modes because of the presence of acetylenic linkages and more atoms in a primitive cell. As shown in Fig. 7d and h, GDY exhibits six kinds of vibrational modes, which correspond to six peaks in the Raman spectrum. Two typical Raman peaks, Y and Y′ (Fig. 7d), originated from synchronous and out-of-phase stretching/contracting modes of alkyne triple bonds, respectively. GDY also has a G peak similar to that of GR, which is attributed to the stretching of aromatic bonds. However, the G peak in GDY has a bathochromic shift when compared with that in GR, which is a general feature of alkyne-rich 2D aromatic systems.

Although the typical Raman spectrum of GDY was systematically studied by Liu et al., experimentally, the reported Raman spectra18,33,46 cannot always be in good agreement with the predicted spectral features of GDY, showing poorly resolved and broadened bands (e.g., Fig. 7e), which may result from the poor crystallinity and/or highly defective structure. More recently, Zhang and Liu et al. produced a trilayer single-crystalline GDY film via the solution-phase van der Waals epitaxy method, where GR was used as the substrate for GDY growth.35 Owing to the perfect structure of the as-grown GDY and the Raman enhancement effect from GR, they received the perfect Raman spectrum, which could effectively match with the predicted spectral features of GDY, as shown in Fig. 7f. Furthermore, Liu et al. studied the in situ Raman spectra of GDY under different pressures. A pressure-induced interlayer crosslinking of sp-hybridized carbon atoms began to occur at a
pressure of 5.2 GPa and a three-dimensional (3D) sp$^2$ structure was formed under higher pressures.$^{48}$

3.3.3 X-ray absorption (XAS). Wang et al. used XAS to characterize the electronic structure of GDY powders and compared it with the corresponding XAS spectra of CNTs and graphene oxide (GO),$^{49}$ as shown in Fig. 7i. The K-edge absorption spectrum of carbon was analyzed. The A peak was considered to be from the 1s-π* absorption peak of sp$^2$ carbon and peak C came from 1s-σ*. The B peak was the characteristic absorption of sp$^2$ carbon with oxygen (O)-containing functional groups. When compared with the XAS spectrum of CNTs, GDY exhibits a distinct shoulder near the A peak [higher than the A peak by 0.3 eV], called A', which can be attributed to the 1s-π* transition of sp carbon. Wang et al. further determined that the GDY sample contains a few functional groups such as O and N, and the K-edge absorption spectra of O and nitrogen (N) were also analyzed. Some N-containing functional groups mainly exist on the surface of GDY and could be removed by annealing at 800 °C, but a small amount of O-containing functional groups were retained. In addition, the XAS spectrum of GDY placed in air for three months was measured in order to study the stability of GDY, as shown by the blue line in Fig. 7i. A new peak named A' appeared, and the authors explained that it was from the transition of the carbon–carbon triple bond to the carbon–carbon double bond at the defect site. Moreover, owing to the sp carbon atoms in the specific topology, GDY exhibits a high-resolution asymmetric C 1s X-ray photoelectron spectroscopy (XPS) spectrum, as shown in Fig. 7j, which is different from those of CNTs and GR, showing a unique sub-peak from C–C (sp).$^{18}$

3.4 Magnetic properties

The intrinsic magnetism of low-dimensional carbon martials has attracted much attention in recent years due to their promising potential in spintronics. Generally speaking, vacancy and sp$^3$-type defects in 2D carbon materials are considered to be the main cause of inducing magnetism, which will break the delocalized π electronic system and prevent the clustering of sp$^3$-type functional groups.

GDY is a narrow bandgap semiconductor material and consists of sp- and sp$^3$-hybridized carbon atoms. Its unique structural features offer the opportunity to prevent sp$^3$-type functional group clustering. Tang and Liu et al. first investigated the intrinsic magnetism of GDY.$^{50}$ It exhibits spin-half paramagnetism. The generated magnetism of the as-prepared GDY was further studied by using density functional theory (DFT). The results indicated that hydroxyl groups on GDY were the major magnetic source. The hydroxyl groups on GDY had higher migrating barrier energy than GR, which prevents their clustering. GDY became antiferromagnetic after annealing at 600 °C. Moreover, the paramagnetism of GDY can be enhanced by doping with N. Huang et al. annealed GDY under an ammonia atmosphere and observed a twofold enhancement in the saturation moment of GDY at 2 K.$^{51}$

3.5 Properties of functional GDY

In 2012, Sun et al. used DFT to study the electronic and magnetic properties of single 3d transition metal (TM) atoms (V, Cr, Mn, Fe, Co, and Ni) adsorbed on γ-graphyne (GY) and GDY.$^{40}$ They found that the electronic structures of TM-GY/GDY were sensitive to the value of the onsite Coulomb energy for the TM 3d orbital. The adsorption of TM atoms can efficiently modulate the electronic structures of the GY/GDY system and can also induce excellent magnetic properties, such as those of spin-polarized half-semiconductors. There is charge transfer between the TM-adsorbed atoms and GY/GDY film, and the electrons of the s, p, and d orbitals in the TM atom are redistributed, thereby inducing this phenomenon.

Fig. 8 shows the magnetic and electronic properties of TM-GY/GDY systems, which are summarized as follows: (i) the adsorption of a single TM atom does not necessarily induce magnetism, such as Ni-GY and Ni-GDY. The order of the magnetic moments from low to high is as follows: Cr > V > Mn > Fe > Co for TM-GY and Cr > Mn > V > Fe > Co for TM-GDY. In fact, there is an energy difference (spin-polarized energy, $\Delta E_{\text{spin}}$) between the nonmagnetic and magnetic states, and the size sequence is the same as the magnetic moment. (ii) The adsorption of single TM atom can also effectively regulate the band structure of GY and GDY. V, Mn, Co-GY, and Co-GDY behave as spin-polarized half-semiconductors. Cr, Fe-GY, V, Cr, Mn, and Fe-GDY behave as metals. The most interesting is Ni-GY/GDY, showing nonmagnetic semiconductor characteristics.

The above results show that the adsorption of a single TM atom can effectively modulate the electrical and magnetic properties of GDY.
GY and GDY. This modulation is mainly due to the electron transfer between the single TM atom and GY/GDY and the electron transfer between the single TM atom’s internal atomic orbitals. The latter is caused by the strong coupling between the single TM atom and GY/GDY. The aforementioned TM-GY/GDY systems exhibit promising potential in spintronics applications.

4. Synthesis

GDY, with outstanding physical and chemical properties, has already become famous in the field of carbon materials. To date, several attempts have been made to fabricate GDY with controlled architectures and extended GDY structures. An exhaustive overview of the typical synthesis technology of GDY is shown in Fig. 9, including dry chemistry and wet chemistry. Moreover, the synthesis process of functionalized GDY and other GDY-based materials will also be discussed in this section.

4.1 GDY

4.1.1 Dry chemistry. There are three primary ways to synthesize GDY via the dry chemical route: on-surface synthesis in scanning tunneling microscopy (STM)/chemical vapor deposition (CVD) systems, explosion method, and top-down method.

4.1.1.1 On-surface synthesis. The on-surface reaction process is a method to construct covalently bonded molecular structures on metal surfaces using designed precursors. This process could appear both in STM systems under ultrahigh vacuum (UHV) conditions and in chemical vapor deposition (CVD) systems under a certain atmosphere. The former was regarded as an effective way to produce and in situ observe GDY-based substructures, which could facilitate the monitoring of the coupling process, intermediates, and byproducts in real time. Fig. 10b and c show two typical alkyne coupling reactions on noble metal surfaces in STM systems. One work reported by Florian Klappenberger et al. shows a terminal alkyne coupling reaction on the surface of Ag(111) using 1,3,5-triacetylenylbenzene (4) and 1,3,5-tri-(4-ethynylphenyl)benzene (5) as precursors, where surface-assisted alkyne coupling reactions took place with hydrogen (H₂) as the only byproduct, forming an ordered alkyne-rich macrocycle fragment (Fig. 10b and i). They further exploited the high-index step surface of Ag(877) as a synthetic template to improve the chemoselectivity of the coupling process. Using the linear diethylthyl-terphenyl precursor (6) combined with the templating effect, extended-GDY wires with lengths reaching 30 nm along the vicinal Ag(877) surface could be produced (Fig. 10k). Moreover, the cyanonitride (CN) functionalization terminal alkyne precursors were also used to synthesize functionalized GDY nanowires via surface-assisted reactions under UHV conditions. CN functionalization could enable higher selective alkyne homocoupling reactions producing polymer wires when compared with the original linear precursor (6).

Wei Xu et al. designed specific precursors (7–9) with terminal alkynyl bromide, which could couple with each other on the Au(111) surface through the dehalogenative homocoupling reaction. Owing to the lower bonding energy of the C–Br bond than the C–H bond, this method could yield higher selectivity and fewer byproducts, thereby producing an ordered 2D porous network with acetylenic linkages, as shown in Fig. 10g. Recently, Harald Fuchs et al. reported a σ-bond metathesis reaction on the metal surface using hexakis[(trimethylsilyl)ethynyl]benzene (TMS-HEB,1) as the precursor (Fig. 10a). After annealing for a long time at room temperature, TMS-HEB molecules could...
remove their trimethylsilyl protecting groups on the Ag(111) surface, which formed an ordered self-assembled structure of HEB molecules (Fig. 10d). Using the same method, they also fabricated σ-bond metathesis products 2 and 3. Notably, Glaser polymers could be clearly formed (Fig. 10f) through σ-bond metathesis (Fig. 10e) followed by Glaser coupling reaction of 3 at 170 °C on the Au(111) surface. However, this work does not further report the synthesis of GDY via the Glaser coupling reaction of self-assembled HEB, which may result from the poor stability of HEB and side reactions of HEB coupling on the metal surface. Other than the Ag and Au surfaces, Cu(111) surface was also used to construct molecular wires incorporated by −C≡C− bonds by Pei-Nian Liu et al. They fabricated a −C≡C− bond on Cu(111) by using the coupling of two −CCl3 groups of 1,4-bis(trichloromethyl)benzene (BTCMB) under UHV conditions.63 In addition, Liu and Zhang et al. synthesized a GDY-contained monolayer on Ag foil through the on-surface synthesis method in a CVD system.52 HEB precursors were transferred by Ar gas and deposited on the Ag foil surface, where Glaser coupling took place (Fig. 11a). The AFM result shows that a uniform carbon film was synthesized, the thickness of which was only 0.6 nm (Fig. 11b), indicating a self-limited growth process. After overlaying the as-grown film layer by a layer for ten times on the Ag surface, an obvious Raman peak attributed to the conjugated diyne links was observed (Fig. 11d). X-ray photoelectron spectroscopy (XPS) reveals the chemical state of C existing within the as-grown film (284.5, 285.3, and 286.3 eV assigned to the orbital of C−C (sp²), C−C (sp), and C≡O) (Fig. 11e). Unfortunately, the SAED pattern reveals that the as-grown film was amorphous (Fig. 11c).

Up to now, considerable progress has been made in the on-surface synthesis of carbon-based nanomaterials using terminal alkynes. However, due to the inevitable side reactions on the metal surface (e.g., cis/trans hydrogenations, multiple insertion reactions, and cyclotrimerization) and the instability of the monomers with alkynyl groups, most of the methods can only yield certain GDY-like oligomers.

### 4.1.1.2 Top-down method

Top-down approaches such as micromechanical exfoliation and exfoliation of layered bulk materials in solvents have been widely used in the preparation of one- or few-layer GR, transition metal disulfides (TMDs), and other 2D materials.64–67 Alternatively, the top-down strategy was also used to synthesize a GDY thin film. Li et al. used as-synthesized bulk GDY powder as the source to synthesize GDY thin films on ZnO nanorod arrays through a combination of reduction and self-catalyzed vapor–liquid–solid (VLS) growth process (Fig. 11f).53 The as-grown GDY films revealed a layered structure with a thickness of 22 nm (Fig. 11g and h).

### 4.1.1.3 Explosion method

The explosion method proposed by Yuliang Li et al. provides a scalable way to synthesize GDY.55
By the simple heating of HEB monomers in N or air under the
given conditions, the homocoupling reaction of HEB took place
in the gas phase without requiring any additional metal catalyst
(Fig. 12a). Through the simple adjustment of the heat treatment
process (atmosphere and heating rate), the micro-morphology of
the GDY powders could be effectively controlled. As a result, GDY
powders with different morphologies (e.g., GDY nanoribbon, 3D
GDY framework, and GDY nanochain) were synthesized. For
example, if HEB monomers were gradually heated (10 \( ^{10} \text{C m}^{-1}/\text{C} 0^1 \))
to 120 \( ^{10} \text{C} \) in N, it would change from light yellow to black without
any volume expansion. A GDY nanobelt powder was obtained
(Fig. 12b) under this condition. However, if the same HEB
monomers were heated to 120 \( ^{10} \text{C} \) in air, the reaction activity
would be significantly enhanced, and 3D frameworks of GDY
were synthesized (Fig. 12d). The volume of the product was
significantly expanded as compared to the reactants. In particular,
a more violent explosion was immediately initiated, when the
monomer powder was quickly added to a preheated flask (120 \( ^{10} \text{C} \))
in air. A microscopic structure of the powder obtained after the
reaction was like a nanochain (Fig. 12c). The Raman spectra of the
as-grown nanostructures reveal the corresponding characteristic
peaks of GDY, indicating the successful coupling of HEB (Fig. 12e).
The new method is characterized by the synthesis of an all-carbon
material without any additional metal catalyst, providing an effective
way to scale-up GDY production. However, the as-grown GDY
powders are inferior in crystallinity when compared with the GDY
films prepared by the surface/interface synthesis method (which will
be introduced in the wet chemical section). In addition, the same
group can load the monomers on various substrates such as Cu
foam, nickel foam, and silica. Under the same conditions (120 \( ^{10} \text{C} \), air), GDY on those substrates can be produced via “explosion.”54

4.1.2 Wet chemistry. When compared with the aforementioned dry chemistry methods, the wet chemical route provides a
more effective approach to prepare large-area GDY films suitable for
practical applications. There are three primary ways to synthesize
GDY via the wet chemical route (shown in Fig. 9): Cu-surface-
mediated synthesis, interface-assisted synthesis, and solution-
phase van der Waals epitaxy. Some potential precursors and
synthetic approaches to graphynes are shown in Fig. 13.68–70

4.1.2.1 State-of-the-art acetylenic coupling in solution. Currently,
studies involving the synthesis of GDY via the solution-phase
method focused mainly on the design of homocoupling reactions and the reaction substrate for GDY growth. GDY could be produced by using the acetylenic coupling of HEB monomers on specific substrates. There are two categories of acetylenic coupling reactions applied in GDY growth, as shown in Fig. 14.71 One type is the Cu-catalyzed terminal alkyne coupling reaction. A typical reaction of this type is the Glaser coupling reaction, developed by Glaser in 1869,72 which involves the synthesis of symmetric or cyclic bisacetylenes via the coupling reaction of terminal alkynes. Terminal alkynes yield diyne compounds under the action of cuprous salts, alkalis, and oxidants. Glaser coupling has high selectivity because of which the conversion of phenylacetylene, as reported in the literature, can reach more than 90%.73 Later, it was developed into the Hay condition,74 where an organic base (e.g., pyridine and N,N,N′,N′-tetramethylethylenediamine, TMEDA) was added instead of hydroxylamine. In Glaser coupling, catalytic Cu(I) was used, which is reoxidized in the catalytic cycle by O2 in the reaction medium.75 The Eglinton reaction was developed on the basis of Glaser coupling, using Cu(II) acetate instead of cuprous chloride as the catalyst.76 The Eglinton coupling reaction uses pyridine as an organic base ligand and methanol as the solvent, which can be carried out at room temperature. The Eglinton reaction is also an oxidative coupling reaction of the terminal alkyne. The difference is that the Eglinton reaction passes through the free-radical intermediate and Cu(II) salt acts as an oxidant. The two mechanisms of Glaser–Hay and Eglinton coupling are shown in Fig. 15. The reaction process of Eglinton is relatively simple, wherein the acid–base reaction between pyridine and terminal alkyne in the first step is the decisive step in the entire reaction cycle.76 In contrast, the Glaser–Hay reaction undergoes a more complex reaction process where the catalytic cycle of Cu(i)/Cu(II)/Cu(i) occurs. Cu acetylide can be oxidized by molecular O2 and a dicopper–dioxo complex with [Cu2(μ-O2)]2+ core can be obtained.77 This step has been proven to be the critical step in the reaction mechanism. When compared with the classic Glaser coupling reaction, Eglinton
coupling reaction is more efficient and the reaction conditions are milder and more controllable.

Another type is the coupling reaction of alkynylsilanes mediated by a Cu(i) salt (Fig. 14b, Hiyama coupling). The relatively stable terminal alkyne with the trimethylsilyl (TMS) protecting group can be used as the monomer and cuprous chloride as the catalyst in a polar organic solvent, e.g., N,N′-dimethylformamide (DMF) and dimethyl sulfoxide (DMSO). In 2000, Nishihara et al. developed a coupling reaction of the terminal alkyne with a trimethylsilyl alkyne protecting group, which was catalyzed by Cu(i) salt and achieved a reaction yield of greater than 99%, as shown in Fig. 14b. The TMS-protected terminal alkyne can directly yield the alkynyl coupling product and the deprotecting step is not required. However, the coupling efficiency of TMS-HEB via this route is low, and therefore, more byproducts are generated in the reaction system.

Using the abovementioned coupling reaction, in 2010, Li et al. first prepared large-area GDY films on the surface of Cu foils. In this reaction, the precursor, HEB, was first adsorbed on the Cu surface, after which it polymerized into a large all-carbon film via the in situ homocoupling reaction with the catalysis of Cu. Since then, other coupling reactions have also been introduced into such surface-assisted liquid-phase synthesis systems. GDY films with different morphologies and qualities have been synthesized via the solid–liquid or liquid–liquid reaction processes by using different surfaces/interfaces and precursor solution concentrations. Notably, combined with the solution-phase van der Waals epitaxial method, highly crystalline ultrathin GDY films can be obtained on GR by the Eglinton coupling reaction. The detailed processes are introduced in the next section.

4.1.2.2 Cu-surface-mediated synthesis

Synthesis of GDY on Cu-based substrates. Synthesizing GDY by a Cu-surface-mediated method was first realized by Li’s group in 2010. Using designed HEB monomers, they synthesized GDY by using an in situ Glaser coupling reaction on a Cu foil, wherein the Cu foil served as both reservoir of the catalyst and planar template catering for the conformal growth of GDY (Fig. 16a). In this process, pyridine acted as both ligand and solvent, which can dissolve Cu ions from the surface of the Cu foil. Cu ions could act as a catalyst, where the Glaser coupling reaction of HEB monomers occurs. Through this method, GDY films (~1 μm) were obtained on the surface of the Cu foil, with a conductivity of $2.516 \times 10^{-4}$ S m$^{-1}$ (Fig. 16b–d). The catalyst was limited by the substrate, thereby realizing the solid–liquid interface growth of the GDY. However, since the catalyst ions generated on the surface of the Cu foil may diffuse in the solution due to the concentration gradient, the catalyst had not completely retained on the surface of the substrate. Therefore, the bulk polymerization of the monomers inevitably occurs for this method. Further, it cannot yield the ideal 2D material.

On the basis of this method, Liu and Zhang et al. further optimized the reaction conditions and proposed a modified Glaser–Hay coupling method for fabricating GDY nanowalls on the Cu foil. The method used acetone instead of pyridine as the reaction solvent. By adjusting the addition amount of the organic base (pyridine and TMEDA), the concentration of the catalyst ions was controlled, thereby achieving control over the reactive sites. At the initial stage of the reaction, only a few Cu ions get dissolved on the Cu foil, and the coupling reaction first occurs at these active sites to form isolated GDY
nanosheets. As the reaction progresses, more and more Cu ions are dissolved, and the active sites gradually spread over the entire surface of the Cu foil. The nanosheets formed at the active sites overlap each other to form an ordered 3D honeycomb structure, called GDY nanowalls. The height of the as-synthesized nanowalls is about 1 μm (Fig. 16e). The thickness of each nanosheet is about 10 nm (Fig. 16f). The HRTEM results reveal a larger d-spacing of 0.466 nm, which can be indexed to the (110) reflections of GDY (Fig. 16g), further confirming the successful fabrication of GDY. During the experiment, the authors found that a low monomer concentration was also a necessary condition for the synthesis of GDY nanowalls. As the monomer concentration increased, the morphology of the as-synthesized GDY films tended toward being disordered.

The aforementioned methods are generic methods for realizing GDY growth on Cu-based substrates. In addition to 2D Cu foils, GDY was also synthesized on other Cu-based substrates, such as 1D Cu wires, 3D Cu mesh, and Cu foam by similar in situ coupling of HEB. Notably, ordered GDY striped arrays were also synthesized on Cu through a wettability-facilitated method. In this system, the reaction process of HEB coupling only took place in confined microscale reaction channels, fabricated by a micro-grooved super-lyophilic template with a Cu foil cap.

Synthesis of GDY on arbitrary substrates. The realization of the synthesis of GDY films with specific aggregation morphology on specific substrates (e.g., insulating substrate and functional semiconductor) is one of the key problems that needs to be resolved in the field of GDY synthesis. One work reported by Li et al. shows the synthesis of GDY nanotubes via an aluminum oxide (AAO) template for highly efficient field emission. In this work, the authors fixed a Cu foil as the catalyst source at the bottom of the AAO template, thereby realizing the in situ growth of GDY on the AAO template. Zhang and Liu et al. developed a simple method to synthesize GDY nanowalls on arbitrary substrates, which is called the “Cu envelope” synthesis method. The target substrate for the growth of GDY was placed in an envelope folded from a Cu foil and the envelope was put into a mixed solution of HEB, acetone, pyridine, and TMEDA. Under alkaline conditions, a sufficient concentration of the catalyst could diffuse into the interface between the solution of HEB monomers and target substrate, where the Glaser–Hay coupling reaction of HEB monomers took place (Fig. 17a). GDY was grown in situ on the target substrate. Through the Cu-envelope-assisted synthesis strategy, the structure-controlled growth of GDY films on 1D, 2D, and 3D substrates was achieved (Fig. 17c–e), providing several potential applications for GDY. As an application example, the authors grew GDY in situ on a bismuth vanadate (BiVO₄) electrode and applied this composite into a photoelectrochemical (PEC) water splitting cell, showing good performance. More recently, Huang et al. developed a controlled-release method to synthesize GDY on arbitrary substrates. They used a polyvinylpyrrolidone (average mol wt: 40 000)/Cu(II)–acetate composite film instead of a Cu envelope as the catalyst reservoir (Fig. 17b). Cu(II) ions could escape from the catalyst reservoir onto the surface of the target substrates (e.g., SiO₂, ZnO, Al, etc.), where the acetylenic coupling reaction would take place, thereby inducing GDY growth.

**Fig. 17** Synthesis of GDY on arbitrary substrates via (a) a Cu envelop catalysis strategy or (b) a controlled-release method. SEM images of typical substrates after the growth of GDY nanowalls via the Cu envelop catalysis method. (c) 1D silicon nanowires, (d) 2D Au foil, and (e) 3D graphene foam. Reprinted with permission from ref. 81. Copyright 2017 Wiley-VCH. Reprinted with permission from ref. 82. Copyright 2018 The Royal Society of Chemistry.
4.1.2.3 Interface-assisted synthesis. Recently, Hiroshi Nishihara et al. proposed a feasible method for the synthesis of GDY at the liquid–liquid or liquid–vapor interfaces. They dissolved the monomer (HEB) and the catalyst (Cu(OAc)$_2$) into two kinds of insoluble solvents, respectively, such as dichloromethane and water. With the extremely low monomer concentration, a GDY thin film (thickness: 24 nm) was obtained by the Eglinton coupling reaction at the liquid–liquid interface (Fig. 18c). The schematic diagram and photograph of the liquid–liquid-interface-assisted method are shown in Fig. 18a and b. The results of the electron diffraction indicated that the as-grown GDY film exhibited high crystallinity (Fig. 18d). Combined with theoretical simulation analysis, this proves that few-layer GDY exhibits the ABC-stacking mode. Furthermore, the HEB coupling reaction was confined to the liquid–vapor interface by spraying a small amount of HEB solution (monomer) above the Cu acetate aqueous solution (catalyst), as shown in Fig. 18e. As a result, crystalline hexagonal GDY nanosheets with an average thickness of 3 nm and average size of 1.5 μm were obtained at the liquid–vapor interface (Fig. 18f and g). High-quality GDY films and nanosheets were realized by the aforementioned interface-assisted synthesis method, providing the basis to study the intrinsic properties of GDY.

4.1.2.4 Solution-phase van der Waals epitaxy. Although researchers have made considerable progress in the synthesis of high-quality GDY films in recent years, most of the reported methods still cannot achieve the fabrication of large-area one- or few-layer GDY films, which are sufficiently thin to retain their “2D characteristic.”

More recently, Zhang and Liu et al. achieved the synthesis of trilayer single-crystal GDY films via the solution-phase van der Waals epitaxial method. To fabricate high-quality GDY thin films, three key factors were considered in their experiment: monomer design, coupling reaction, and confining the coupling reaction in a 2D plane. Firstly, HEB molecules with higher symmetry were selected as the monomers. In order to maintain the stability of the monomers during the reaction, the adopted concentration of the monomer solution (0.04 mM) was kept very low. Next, to fabricate GDY using HEB monomers, a terminal alkyne coupling reaction (Eglinton coupling reaction) was applied using which the acetylenic bonds in HEB could be interlinked, and the as-grown film efficiently grows slowly at room temperature even under a lower monomer concentration. At last, GR was used as the epitaxial substrate to confine the free rotation around the alkyne–aryl single bonds in monomers when the coupling reaction took place. The weak interaction ($\pi-\pi$ and van der Waals) between the monomer and GR confined the growth of GDY in the 2D GR plane. In addition, the monomers have a weaker interaction with GDY on the epitaxial layer than GR on the substrate, which can effectively weaken the Ehlrich–Schwoebel (ES) diffusion barrier of the monomers and benefit from the growth of the thin film. As a result, a trilayer GDY film on GR was successfully fabricated via the solution-phase van der Waals epitaxy. The structure and properties of the as-synthesized film were characterized, as shown in Fig. 19.

Moreover, Liu and Zhang et al. directly used TMS-HEB as the monomer to process the Hiyama coupling for the synthesis of GDY. Without the deprotection process, this monomer becomes more stable than HEB, which can deter the oxidation and self-polymerization of the monomers in long reaction periods. Through the surface template method, a continuous graphdiyne film with a thickness less than 3 nm can be obtained.

4.2 Functionalization and beyond

Annealing. Comprehensive studies on the preparation of GDY doping with heteroatoms have recently been reported. N-Doped GDY has been synthesized by annealing as-grown GDY under ammonia at 400–600 °C and was used as a metal-free catalyst for efficient O reduction reaction (ORR). Li et al. further developed this method and reported the co-doping of GDY with two heteroatoms by annealing GDY with mixed precursors (NH$_3$ and NH$_4$F for N and F; NH$_3$ and thiourea for N and S; NH$_3$ and B$_2$O$_3$ for N and B) at 700 °C (Fig. 20a). The morphology of GDY before and after doping is shown in Fig. 20b–d. The EDS elemental mapping results showed that the N and F elements were homogeneously distributed in the GDY structure (Fig. 20e). In addition to N-doped GDY, Mao et al. reported the synthesis of GDY oxide (GDYO) by the acid-oxidation treatment method. The as-grown GDY was oxidized into GDYO in a concentrated H$_2$SO$_4$/HNO$_3$ mixture (3:1, volume ratio) with KMnO$_4$. Using a similar acid-oxidation treatment method,
Wang et al. obtained GDYO by treating GDY with HNO₃ at 80 °C for 5 h in an oil bath with constant vigorous stirring. The formation process of GDYO is shown in Fig. 20f. By annealing as-grown GDYO with melamine, a new N-doped GDY was produced in a tubular furnace at 700–1000 °C. Notably, the as-synthesized N-doped GDY has site-specific sp-N atoms, which could not be introduced in GR or CNTs, but it could only be achieved in the GDY system. This new doped type of N exhibits high performance for O reduction electrocatalysis, which is comparable with commercial Pt/C.

In situ Glaser coupling method. Some molecules containing terminal alkynyl groups were designed and synthesized to directly fabricate a new type of GDY and their derivatives by the in situ Glaser coupling method. The chemical structures of these molecules and as-grown GDY derivatives are shown in Fig. 21. Tetraethynylethylene (TEE) molecule was applied to fabricate β-GDY films. In addition, using the same TEE monomers, Li’s research group also prepared a similar enriched film by the Glaser coupling reaction on Cu foils, the corresponding GDY derivatives including H₂-substituted GDY (H-GDY), chlorine-substituted GDY (Cl-GDY), boron-substituted GDY (B-GDY), N-substituted GDY (N-GDY), and fluorine-substituted GDY (F-GDY) were produced and applied to energy-related fields (Fig. 21b–d and g).

Other methods. Li et al. synthesized a series of N-containing derivatives of HEB (e.g., Fig. 21g) to produce N-GDY powders with different N contents through the aforementioned explosion method. Furthermore, Li and Liu et al. dissolved designed N-rich precursors into CH₂Cl₂, while Cu(OAc)₂ (catalyst) was dissolved into H₂O. After the confined Eglinton coupling of monomers, well-defined 2D N-GDY nanosheets were produced and applied to energy-related fields (Fig. 21b–d and g).

In addition, Huang et al. fabricated a series of specific monomers to prepare various GDY derivatives. By in situ Glaser coupling reaction on Cu foils, the corresponding GDY derivatives including H₂-substituted GDY (H-GDY), chlorine-substituted GDY (Cl-GDY), boron-substituted GDY (B-GDY), N-substituted GDY (N-GDY), and fluorine-substituted GDY (F-GDY) were produced and applied to energy-related fields (Fig. 21b–d and g).
argon atmosphere. A porous graphyne-like carbon-rich network was prepared, showing the selective absorption of CO₂ over N₂.⁹⁹

These works indicated that 2D acetylenic carbon allotropes with different degrees of sp and sp² hybridizations could be designed by simply using monomers with diverse structures.

5. Applications

5.1 Gas separation

GDY is a 2D porous framework and exhibits promising potential in the separation of mixed gases. Different numbers of acetylenic linkages determine the pore size of triangular pores, allowing the selective permeation of molecules with different sizes. Heteroatom-substituted GDY also has different pore sizes; because the electronic structure changes, the source of selectivity is more diverse. Further, there is certain selectivity for molecules of a similar size. Under the guidance of this idea, people have made several attempts, as shown in Fig. 22.

In 2011, Sean C. Smith et al. explored the potential of GDY to separate H₂ from methane (CH₄) and carbon monoxide (CO) from a theoretical calculation point of view (Fig. 22a).⁷ They calculated and found that the energy of the near-central adsorption-diffusion process of H₂ is the smallest, and therefore, exhibits the best permeability. According to the Arrhenius equation, they estimate that GDY exhibits a H₂ permeation rate that is 10⁴ times faster than that of a porous GR structure.

One year later, in 2012, Markus J. Buehler et al. used molecular dynamics to investigate this issue in more detail.⁸ Based on comprehensive molecular dynamics simulations, they determined the selective diffusion properties of GDY to H₂, CH₄, and CO gas mixtures (syngas), as shown in Fig. 21b. They found that...
gas through the filter requires a certain pressure. Out of the three gases, H₂ requires the lowest air pressure; near atmospheric pressure, only H₂ can penetrate the GDY film.

In 2017, Guo et al. studied the selective separation of CO₂/N₂/CH₄ by substituting GDY (H-GDY, O-GDY, and F-GDY) through DFT and molecular dynamics simulations (Fig. 21c). They found that F-GDYF and O-GDY films can effectively separate N₂ and CH₄ over a wide temperature range. In addition, O-GDY can effectively separate CO₂/N₂ gas mixture at temperatures below 300 K. This work theoretically studied the application prospects of GR-like acetylene films in gas separation, and it is very instructive for subsequent works.

5.2 Graphdiyne derivatives (composites) as catalysts

The photodegradation of organic pollutants and utilizing solar illumination for H₂ evolution and O evolution are two of the most potential approaches for fighting the current energy and environmental crises. Several semiconductor-based heterogeneous photocatalytic systems have been designed since the last two decades. As a new type of carbon allotrope, GDY comprising sp–sp² carbon atoms contains hexagonal benzene rings and diacetylenic linkages. Its high carrier mobility, natural moderate bandgap, highly conjugated structure, and uniformly distributed pores facilitate its application as an ideal candidate for photocatalysis and photoelectrocatalysis.

**Photocatalyst.** Wang Dan et al. synthesized a titania nanoparticles (P25)/GDY hybrid composite by a hydrothermal method and reported its excellent photocatalytic performance. As shown in Fig. 23a, the impurity bands of carbon p orbitals from GDY could insert into the bandgap of TiO₂, thereby facilitating the migration of electrons from the valence band (VB) to the conduction band (CB) with the help of the impurity band. As compared to P25/CNTs and P25/GR composites, P25/GDY showed the best photocatalytic degradation rates for methylene blue (Fig. 23b). FTIR spectroscopy detected the formation of Ti–O–C between P25 and GDY, which played a crucial role in the photocatalysis process.

In addition, to further understand the charge transfer mechanism at the interface of GDY and TiO₂, they calculated the chemical structure and electronic properties of TiO₂/GR.

![Photocatalysis and photoelectrocatalysis](image-url)

**Fig. 23** Photocatalysis and photoelectrocatalysis. (a) Schematic drawing of the photocatalytic degradation of methylene blue (MB) via P25/GDY as the catalyst. (b) Photodegradation plot of MB via P25, P25/CNTs, P25/GR, and P25/GDY under visible-light irradiation. (c) Fabrication process and catalytic mechanism of GDY-based photocathodes for PEC water splitting cells. (d) Linear sweep voltammetry (LSV) scanning for GDY-based photocathodes. Scanning from 0.3 to −0.4 V at 2 mV s⁻¹ in 0.1 M Na₂SO₄ aqueous solution. Light off (black line); light on (red line). (e) Controlled potential electrolysis of the as-prepared GDY-based photocathodes during testing for 12 h. Reprinted with permission from ref. 101. Copyright 2012 Wiley-VCH. Reprinted with permission from ref. 104. Copyright 2016 American Chemical Society.
and TiO$_2$/GDY composite with different TiO$_2$ facets. The first-principles DFT calculations show that TiO$_2$(001)/GDY composite has a more positive Mulliken charge than TiO$_2$(001)/GR, leading to the easier capture of electrons and stronger photocatalytic oxidation. In experiments, TiO$_2$(001)/GDY composite was synthesized, which exhibited outstanding performance in photocatalysis, which further confirmed the theoretical predictions. Recently, Liu and Zhang et al. prepared a β-GDY film on Cu foils by using the Glaser–Hay coupling reaction. The as-prepared β-GDY film exhibited conductivity of $3.47 \times 10^{-6}$ S m$^{-1}$. The work function was 5.22 eV. As compared to GDY, β-GDY has a larger ring and more acetylenic bonds (twice that of γ-GDY), which could provide more binding points for Ti atoms to form additional Ti–C bonds, thereby leading to better photocatalytic activity. Moreover, ZnO/GDY photocatalyst was designed by additional Ti–C bonds, thereby leading to better photocatalytic performance resulting from the electron transfer property of GDY, which is similar to that of the aforementioned TiO$_2$/GDY system.

**Photoelectrochemical (PEC) water splitting.** Wu and Zhang et al. attempted to use GDY as the hole-transfer layer to fabricate quantum dots (QDs)-sensitized photocathodes for PEC water splitting (Fig. 23c). In their work, 4-mercaptopyridine surface-functionalized CdSe QDs were synthesized and assembled on the surface of GDY nanowalls through π–π stacking, which was evidenced by the ultraviolet photoelectron spectroscopy and Raman spectroscopy. Under irradiation by a Xe lamp, the integrated photocathode achieved a current density of $-70 \mu$A cm$^{-2}$ at 0 V vs. NHE in 0.1 M Na$_2$SO$_4$ which was much higher than that of bare GDY or CdSe QDs. In addition, the photocathode could retain a constant current density for 12 h and nearly 90 ± 5% faradic efficiency for H$_2$ production. This work indicated that GDY was a promising hole-transfer material to fabricate PEC cells. Therefore, they applied GDY in the fabrication of BiVO$_4$ photoanodes to facilitate the separation of the photogenerated carriers. The GDY/BiVO$_4$ hybrid photocathode exhibited much higher activity toward O evolution. At 1.23 V vs. RHE, the hole-injection efficiency of GDY/BiVO$_4$ could reach 60%, twice as much as that of bare BiVO$_4$. Owing to the fast extraction of the photogenerated holes, the GDY/BiVO$_4$ photocathode maintained a relatively constant current density during testing for 4 h, deterring the oxidation of BiVO$_4$ itself. Recently, Lu et al. constructed a metal-free graphitic carbon nitride (g-C$_3$N$_4$)/GDY heterojunction for PEC H$_2$ evolution. As compared to bare g-C$_3$N$_4$, the g-C$_3$N$_4$/GDY photocathode showed a nearly threefold increase in the photocurrent density at 0 V vs. NHE. The Bode phase plots indicated that the electron lifetime of g-C$_3$N$_4$/GDY photocathode was $\approx 610 \mu$s, which is much longer than that of bare g-C$_3$N$_4$ (88 μs). This can be ascribed to the excellent hole-transfer ability of GDY. More recently, GDY nanowalls were introduced into a Si heterojunction (Si/HJ)-based PEC water splitting cells by Zhang et al. GDY nanowalls significantly enhanced the PEC performance of original Si-based systems. With further modification of NiO$_x$, the optimized SiHJ/GDY/NiO$_x$-10 nm exhibited a saturated photocurrent density reaching up to 39.1 mA cm$^{-2}$.

**GDY-based electrolyzer.** Apart from fabricating a PEC cell, GDY has also been used to fabricate electrolyzers. The first electrolyzer of GDY was constructed by Li et al. In this contribution, core–shell nanowire arrays (Cu nanowires as the core and GDY films as the shell) on Cu foam were employed as high-efficiency H$_2$ evolution reaction (HER) catalysts. Under potential cycling treatment in 0.5 M H$_2$SO$_4$, the electrode displayed high catalytic activity for HER with an onset over-potential of 52 mV and a Tafel slope of 69 mV dec$^{-1}$. The synergetic interaction between GDY and Cu may be crucial for the catalytic performance of the electrode. Subsequently, they reported GDY-supported cobalt (Co) NPs wrapped by N-doped carbon layer (CoNC/GDY) electrocatalyst for efficient HER (Fig. 24a). The onset potential of CoNC/GDY (about 170 mV) electrode was lower than those of Co/GDY (260 mV), NC/GDY (300 mV), and pristine GDY (700 mV). Notably, the recorded polarization curve of the as-prepared CoNC/GDY electrode was almost identical to its initial curve, even after 36 000 cyclic voltammetry (CV) scanning cycles. In contrast, with regard to commercial Pt/C (10 wt%), an obvious loss of activity was observed in the low current density range after only 8000 cycles. Herein, the durability of CoNC/GDY was apparently much greater than that of Pt/C for long-term electrochemical HER processing in alkaline electrolytes. These results reveal that GDY was stable for all the pH values.

At the same time, Wu and Zhang et al. reported GDY-supported cobalt nanoparticle electrocatalyst for O evolution reaction (OER). In this work, the loading of Co NPs on the GDY substrate was simply undertaken by the facile chemical reduction of Co$^{2+}$ salt precursor in an aqueous solution due to the close interaction between the metal ions and alkylene-rich π-conjugated networks (Fig. 24b). The size of the particles absorbed onto the GDY surface is nearly 4 nm, which ensures the sufficient exposure of the catalytically active sites. The as-prepared Co NPs/GDY electrode exhibited high OER electrocatalytic activity with a small overpotential of nearly 0.3 V and a large unit mass activity of 413 A g$^{-1}$ at 1.60 V vs. RHE. The electrode could maintain a constant current density during electrolysis for 4 h, indicating that GDY was a promising catalyst support to stabilize metal nanoparticles for OER.

In addition, GDY were recently reported as an efficient support material for bifunctional electrocatalysts with enhanced catalytic activity and stability for overall water splitting. NiCo$_2$S$_4$ nanowires were synthesized in situ as building blocks on 3D GDY foam. The as-fabricated bifunctional electrode (NiCo$_2$S$_4$/3DGDF) showed excellent catalytic activity and long-term stability for both HER and OER, as well as the overall water splitting process, in 1.0 M KOH. The corresponding two-electrode alkaline water electrolyzer needs low cell voltages of only 1.53 and 1.56 V to achieve outputs of 10 and 20 mA cm$^{-2}$, respectively. The stability could reach over 140 h under continuous electrolysis operation at 20 mA cm$^{-2}$, indicating that GDY could be employed as a bifunctional carbon support in electrocatalytic water splitting. Recently, Li’s group reported the fabrication of
GDY-supported single-atom Ni(0) and Fe(0) by the electrochemical reduction of Ni^{2+} and Fe^{3+} on GDY.\textsuperscript{24} The hybrid composites exhibit excellent activity and long-term stability for HER, which is much better than that of state-of-the-art catalysts. Such outstanding activity was ascribed to the synergetic effects between single-atom Ni/Fe and GDY, which achieved a fast charge transfer between the catalytic active sites and GDY. In summary, as a new carbon allotrope, GDY already possesses an attractive structure and properties, which has ensured its promising applications in water splitting. The high hole-transfer ability enables its use as a hole-transfer layer in PEC cells. The excellent electronic property enables its use as a catalyst support in an electrolyzer, including HER, OER, and bifunctional catalyst support.

ORR is important for energy-related applications. Doping carbon materials with heteroatoms improves catalytic activity and can be used as a promising metal-free catalyst for ORR. Among all the reported doping carbon materials, GDY was more interesting as it could provide more heteroatom-doped forms (Fig. 24c). For example, GDY doped with imine N atoms was produced by treating GDY with NH\textsubscript{3} or pyridine.\textsuperscript{111} As-prepared N-doped GDY exhibits high catalytic activity for ORR. More recently, the formation of sp-N forms in N-doped GDY was reported by Wang \textit{et al.}\textsuperscript{88} When compared with other N-doped forms (imine N, amino N, pyridinic N, graphitic N, pyrrolic N, nitrile N, and oxidized N), the sp-N atom is the most beneficial for O\textsubscript{2} adsorption. As a result, this kind of sp-N-doped GDY exhibits a smaller Tafel slope (60 mV dec\textsuperscript{−1}) than other N-doped GDY forms that are even smaller than that of Pt/C (76 mV dec\textsuperscript{−1}), as shown in Fig. 24d.

Mao \textit{et al}. tried to use GDY as a reducing agent and stabilizer for the electroless deposition of Pd.\textsuperscript{87} Due to the lower reduction potential, GDY can easily reduce Pd in [PdCl\textsubscript{4}]\textsuperscript{2−} to the elemental state and eventually deposit onto GDY in the form of clusters. Notably, they were pleasantly surprised to find that GDYO has more excellent capabilities in this regard and can yield smaller-sized clusters. After the Pd/GDYO nanocomposite was obtained, the author used it to catalyze the reaction of sodium borohydride (NaBH\textsubscript{4}) to reduce 4-nitrophenol (4-NP), yielding better catalytic performance.

5.3 Energy storage and conversion

LIBs based on GDY. GDY has both the characteristics of 2D materials and porous materials, with excellent electron transport properties. Its large surface area and porous channels can accommodate metal ions such as lithium ions; therefore, it can be used in energy storage devices. Chandra Shekar \textit{et al.}\textsuperscript{112} and Sun \textit{et al.}\textsuperscript{113} used DFT calculations to determine that due to the presence of acetylenic bonds, the density of atoms decreased; therefore, GDY can form LiC\textsubscript{3} by the surface adsorption of lithium, and its theoretical specific capacity can be about 744 mA h g\textsuperscript{−1}, which is as much as twice the theoretical capacity of graphite.\textsuperscript{114,115} The large triangular pores of GDY can also allow lithium ions to cross between the layers of GDY, forming out-of-plane diffusion, and the energy barrier for diffusion is only 0.18–0.84 eV. Luo’s group\textsuperscript{13} studied the energy and kinetics of lithium in single-layer GDY using the first-principles calculations and found that lithium is in the three possible storage sites of GDY (Fig. 25a). In GDY, the diffusion
direction of lithium will not be limited to the interlayer plane parallel to the GDY layer. It can also rapidly diffuse between the layers in three dimensions. Therefore, GDY could be used as the anode material for LIBs with high capacity and rate capability.\textsuperscript{116}

Li et al. first demonstrated the application of GDY grown on Cu as the working electrode for the fabrication of high-performance LIBs (Fig. 25b).\textsuperscript{117} The as-prepared GDY-based battery showed a reversible capacity of up to 520 mA h g\textsuperscript{−1} after 400 cycles at a current density of 500 mA g\textsuperscript{−1} (Fig. 25c). At a higher current density of 2 A g\textsuperscript{−1}, such a GDY-based battery retained its high specific capacity at 420 mA h g\textsuperscript{−1} after 1000 cycles. This shows that GDY-based LIBs had excellent electrochemical performance, such as outstanding rate performances, high specific capacities, and good cycle stability. By comparing the theoretical mass density of GDY with the experimental data, it was confirmed that lithium storage was mainly a process of intercalation and adsorption, which is consistent with the theoretical calculation results. GDY powder was also applied as the negative electrode material for LIBs.\textsuperscript{118} These as-prepared LIBs exhibit high capacity, good cycling stability, and high Coulombic efficiency. A reversible capacity of 552 mA h g\textsuperscript{−1} was obtained at a current density of 50 mA g\textsuperscript{−1} for 200 cycles due to the high specific surface area and good chemical stability of GDY. The porous structure and low lithium-ion diffusion resistance of GDY are favorable for the rapid transmission of ions and electrons on the surface of GDY, thereby facilitating the suitability of GDY in Li storage even at high charge–discharge rates.

As shown in Fig. 25d, Li et al. developed a new carbon ene–yne (CEY) as a high-performance carbon-based anode for LIBs.\textsuperscript{16} CEY was predicted to be a semiconductor with the smallest bandgap of 0.05 eV at the \textit{Γ}-point. The band structures of CEY is shown in Fig. 25e. The assembled CEY-based LIBs exhibit a high reversible specific capacity up to 1326 mA h g\textsuperscript{−1}, which is triple than that of commercial graphite. Even after long-term cycling at a high current density of 748 mA g\textsuperscript{−1}, the as-prepared CEY-based LIBs still maintained considerably higher and reversible capacities of up to 410 mA h g\textsuperscript{−1}. Its enlarged structural parameters and high conjugation degrees endowed the CEY film electrode with excellent rate performance and long-term stability.
Several subsequent efforts have been sought to create GDY-based LIBs with higher energy density and specific capacity. N doping was an effective route to enhance the performance of GDY-based electrode materials. Li et al. prepared N-GDY films by annealing GDY under a NH₃ atmosphere and applied them as the electrode material of LIBs to evaluate the properties of Li storage (Fig. 25f). They found that N atoms in N-GDY offered more heteroatom defects and active sites. Therefore, the improved electrochemical performances (reversible capacity, rate performance, and cycling stability) were achieved. The N-GDY electrode showed a reversible capacity as high as 785 mA h g⁻¹ after 200 cycles at a current density of 200 mA g⁻¹. At a higher current density of 2 A g⁻¹, these N-GDY-based electrodes still exhibited a reversible capacity of 510 mA h g⁻¹ after 1000 cycles (Fig. 25g).

Other than N-GDY, there are many derivatives of GDY that can be used for LIBs. Cl-GDY was prepared by using the in situ Glaser–Hay coupling reaction on a Cu foil. The 2D structure of Cl-GDY has more transfer tunnels for Li ions along the perpendicular direction of the molecule plane and more Li storage sites (Fig. 26a). A remarkable charge capacity of 1150 mA h g⁻¹ at a current density of 50 mA g⁻¹ and stable specific capacity of 500 mA h g⁻¹ for 200 cycles at a current density as high as 2 A g⁻¹ were obtained, exhibiting excellent rate performances and cycling stability (Fig. 26b and c). By simple changing the monomers, H-GDY (Fig. 26d) and B-GDY (Fig. 26g) have been prepared via the Hay–Glaser coupling reaction. The as-prepared H-GDY film could act as a free-standing flexible electrode for both LIBs and sodium-ion batteries (SIBs), exhibiting outstanding electrochemical performance. For LIBs, the reversible capacity of H-GDY electrode was up to 1050 mA h g⁻¹ at the current density of 0.1 A g⁻¹, while a reversible capacity of 650 mA h g⁻¹ at the current density of 0.1 A g⁻¹ was achieved for SIBs (Fig. 26e and f). Moreover, the H-GDY electrode exhibited excellent cycle performance and superior rate capability. As compared to the abovementioned, B-GDY exhibits excellent conductivity, proper bandgap and packing mode of the molecular plane, and expanded molecular pore size, which facilitate the transfer of metal ions along the perpendicular direction, and therefore, more stable storage sites for the Na atom and larger transfer tunnels for Na ions can be obtained. Such B-GDY films exhibited superior capacity retention ability at different current densities. A good reversible capacity of 600 mA h g⁻¹ at 50 mA g⁻¹ and a stable specific capacity of about 220 mA h g⁻¹ for 2000 cycles at a current density as high as 2 A g⁻¹ were realized in Na ion half-cells (Fig. 26h). The coulombic efficiency was approximately 98% on average at different current densities.
In summary, the unique structure of GDY and its derivatives endow LIBs and SIBs with high performance due to the high charge mobility and high capacity of Li and Na. GDY-based materials are promising for use in both LIBs and SIBs, yielding excellent specific capacity, rate capacity, and electrochemical stability. The overview of the batteries based on these GDY-based materials is summarized in Table 4.

**Electrochemical actuator.** Wei Chen *et al.* reported a molecular-scale active GDY-based electrochemical actuator with a high electromechanical transduction efficiency of up to 6.03% and energy density of 11.5 kJ m$^{-3}$ (Fig. 27).** Meanwhile, the actuator has negligible degradation after 100 000 cycles at 1 Hz under 2.5 V. They found that the surrounding ions absorbed onto graphdiyne under electric stimulus can change the bond length of graphdiyne, which bends the actuator under electric stimulus. They believe that the surrounding ions coordinated with alkyne bonds and because of their unoccupied orbitals, alkyne bonds would transform into alkene bonds accompanied with variations in the bond length. This bond length variation of alkene–alkyne complex transitions ultimately leads

### Table 4 Comprehensive overview of GDY-based anode materials in LIBs and SIBs

<table>
<thead>
<tr>
<th>2D material</th>
<th>Electrodes</th>
<th>Potential range applied (vs. Li$^+/$/Li) (V)</th>
<th>Discharge rate</th>
<th>Specific capacity</th>
<th>Cycle number</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>GDY</td>
<td>GDY film grown on the copper foil</td>
<td>0.005–3</td>
<td>500 mA g$^{-1}$</td>
<td>520 mA h g$^{-1}$</td>
<td>400</td>
<td>117</td>
</tr>
<tr>
<td></td>
<td>GDY powder</td>
<td>0.005–3</td>
<td>50 mA g$^{-1}$</td>
<td>552 mA h g$^{-1}$</td>
<td>200</td>
<td>118</td>
</tr>
<tr>
<td></td>
<td>3D GDY</td>
<td>0.01–3</td>
<td>50 mA g$^{-1}$</td>
<td>610 mA h g$^{-1}$</td>
<td>200</td>
<td>145</td>
</tr>
<tr>
<td>SinPs/GDY</td>
<td>SinPs/GDY</td>
<td>0.005–2</td>
<td>1 A g$^{-1}$</td>
<td>1250 mA h g$^{-1}$</td>
<td>200</td>
<td>26</td>
</tr>
<tr>
<td>Cu/GDY</td>
<td>Cu/GDY</td>
<td>0.005–3</td>
<td>5 A g$^{-1}$</td>
<td>1043 mA h g$^{-1}$</td>
<td>500</td>
<td>146</td>
</tr>
<tr>
<td>CEY (β-GDY)</td>
<td>CEY film grown on the copper foil</td>
<td>0.005–3</td>
<td>748 mA g$^{-1}$</td>
<td>410 mA h g$^{-1}$</td>
<td>120</td>
<td>16</td>
</tr>
<tr>
<td>N-GDY</td>
<td>N-GDY film</td>
<td>0.005–3</td>
<td>785 mA h g$^{-1}$</td>
<td>200</td>
<td>119</td>
<td></td>
</tr>
<tr>
<td>Cl-GDY</td>
<td>Cl-GDY film grown on the copper foil</td>
<td>0.005–3</td>
<td>1150 mA h g$^{-1}$</td>
<td>100</td>
<td>92</td>
<td></td>
</tr>
<tr>
<td>hsGDY</td>
<td>Free-standing HsGDY film</td>
<td>0.005–3</td>
<td>1050 mA h g$^{-1}$</td>
<td>100</td>
<td>91</td>
<td></td>
</tr>
<tr>
<td>F-GDY</td>
<td>Free-standing F-GDY film</td>
<td>0.005–3</td>
<td>650 mA h g$^{-1}$ for SIBs</td>
<td>100</td>
<td>91</td>
<td></td>
</tr>
<tr>
<td>BGDY</td>
<td>BGDY film grown on the copper foil</td>
<td>0.005–3</td>
<td>2 A g$^{-1}$</td>
<td>350 mA h g$^{-1}$</td>
<td>9000</td>
<td>95</td>
</tr>
</tbody>
</table>

Fig. 27 (a) Assembly process of GDY-based actuators. Cross-sectional view of a GDY-based actuator, showing fine interfacial adhesion. Scale bar: 10 μm. (b) Attenuation strain of as-prepared GDY-based actuators with increasing frequency. (c) Schematic diagram of the actuation mechanism of the actuator. Optical images show the bent actuator under 2.5 V at 0.1 Hz. (d) Actuation strain of GDY with encountering electric stimulus. Reprinted with permission from ref. 25. Copyright 2018 Nature Publishing Group.
to a dimensional change in the covalent bond network in the graphdiyne structure. Meanwhile, the transition process is reversible and controlled by external electric fields.

Solar cell. Li and Meng et al. introduced GDY as a dopant of the hole-transporting material layer (P3HT) into CH$_3$NH$_3$PbI$_3$ perovskite solar cells. Spectroscopy results indicated that a strong $\pi-\pi$ interaction existed between GDY and P3HT, which facilitates hole transportation, thereby realizing a higher light-to-electricity conversion efficiency of 14.58%. Following this work, planar-heterojunction perovskite solar cells were fabricated using GDY-doped phenyl-C61-butyric acid methyl ester (PCBM) as the electron-transport layer. GDY as a dopant improved the conductivity and interfacial coverage of the original PCBM film. As a result, GDY-doped PCBM-based solar cells achieved 28.7% enhancement in power conversion efficiency (PCE) as compared to that of pure PCBM-based solar cells. These results indicated that GDY was promising for solar cells, which could act as the dopant in the hole- or electron-transfer layers.

5.4 Water remediation

Superhydrophobic materials are widely used in self-cleaning, anti-fog, oil-water separation, and energy-related fields. In recent years, increased attention has been paid to the exploration and design of such materials. By combining highly rough surface structures with low-surface-energy coatings, a large number of superhydrophobic materials have been designed and constructed.

GDY, a new member of the 2D carbon family, exhibits excellent physical and chemical properties and has been widely used in several fields. In particular, GDY with ordered porous structures could be prepared by a wet chemical method on Cu substrates. Inspired by this, Zhang's group constructed a robust superhydrophobic foam material by the in situ synthesis of 3D honeycomb-like GDY on rigid Cu foam. The as-prepared GDY-based hierarchical structure has both ordered porous nanostructures and a robust 3D porous framework (Fig. 28a). After coating a low-surface-energy PDMS layer, the as-prepared GDY-based foam exhibits superhydrophobicity (static contact angle: $\sim 160.1^\circ$) and achieves the efficient separation of various oil–water mixtures. In addition, GDY-based foam was utilized to decontaminate lead-ion-polluted water, as shown in Fig. 28b and c. Benefiting from the strong interaction of acetylenic links in GDY with metal ions, the as-prepared GDY filter could efficiently adsorb lead ions from water with a removal efficiency of 99.6%.

5.5 Humidity sensor

More recently, Mao et al. made progress in the topic of GDYO. They found that if the alkyne bond in GDY is partially oxidized to form O-containing functional groups, the resulting material, i.e., GDYO, will have an unprecedented response speed, namely, only $\sim$ 7 ms. This corresponding speed is three times faster than that using GO with the same thickness and O/C ratio. A more in-depth understanding is that GDYO contains more acetylenic bonds than GO's ethylenic bonds, and therefore, can bind water molecules faster. Their work demonstrated the GDYO's powerful moderate sensing capabilities and bright application prospects, which provided new insights into further understanding the structure–activity relationship of 2D carbon materials.

6. Conclusions and future prospects

As a new member of the carbon family, GDY exhibits linear acetylenic linkages (–C≡C–), uniform pores, and highly conjugated structures, in which sp- and sp$^2$-hybridized carbon atoms are topologically ordered in a planar polymeric network with atomic-scale thickness. The unique chemical structure endows it with extraordinary physical and chemical properties. GDY is the most stable carbon phase with diacetylenic linkages. The bandgap of GDY was predicted between 0.44–1.47 eV and with a high charge carrier mobility of $\sim 10^5$ cm$^2$ V$^{-1}$ s$^{-1}$ at room temperature. These excellent electronic properties facilitate it to become a replacement for silicon semiconductors in nanoelectronics. Moreover, benefiting from the high-energy sp-hybridized carbon atoms, it is possible to fabricate chemically doped GDY (e.g., introduction of sp-N), which provides a new way for the design of nonmetallic catalysts in HER.

In spite of this, the requirements of high formation energy and flexibility of sp bonds complicate the synthesis process. There are two targets for the synthesis of such a new material, namely, GDY (Fig. 29). One is the structure-controlled synthesis (e.g., monolayer, single-crystals) for understanding the intrinsic properties. For this purpose, traditional high-temperature synthesis cannot be employed (e.g., CVD methods) owing to the inevitable side reactions that occur at higher temperatures. In contrast, the intermolecular terminal alkyne coupling of HEB monomers in solution was considered to be
the ideal route. To further achieve structural control, a Cu foil and GR were applied as the template for confined growth. GDY films were first synthesized by a wet method. Li’s group synthesized GDY using the \textit{in situ} Glaser coupling on Cu foils, where a Cu foil acted as both substrate and catalyst. Thereafter, some advances were also reported in the synthesis of GDY with higher quality. The classical interface-assisted method has also been introduced into the GDY fabrication. As a result, the thickness of as-prepared GDY could be controlled; even a trilayer single-crystalline GDY film was produced on GR via the solution-phase van der Waals epitaxy process.

Another target for the synthesis of GDY is the scale-up synthesis for practical applications. The explosion method by Li’s group achieved the scalable synthesis of GDY,\textsuperscript{55} but this method failed to produce high-quality layered crystal samples due to the free rotation around the alkyne–aryl single bonds in the monomers. Moreover, the poor stability of HEB monomers in air or in highly concentrated solutions results in the formation of amorphous samples. Therefore, the design of a feasible reaction route for confining HEB coupling onto the 2D plane and to ensure the stability of HEB molecules in the process of GDY growth hold the key toward synthesizing large-scale high-quality GDY materials.

**Future prospects**

Although the synthesis and applications of GDY have undergone several progresses, such as electronics, energy storage, catalysis, and sensors, the research on GDY is still in its infancy, and the following problems need to be resolved. First of all, the development of simpler and more efficient preparation methods is crucial for such new materials. To date, several feasible pathways have been established. In this review, the authors have summarized the current advances in GDY growth processes. For example, Zhang \textit{et al.} developed a solution-phase van der Waals epitaxial method to fabricate GDY using GR as the template, producing a trilayer single-crystal GDY film on GR.\textsuperscript{35} However, this method confines GDY on specific growth substrates (e.g., GR), which limits the determination of its intrinsic physical properties. More importantly, the properties of 2D materials are often affected by their interlayer stacking. For example, a single layer of molybdenum disulfide is a direct bandgap semiconductor, and bilayer molybdenum disulfide is an indirect bandgap semiconductor.\textsuperscript{137,138} Therefore, in order to achieve the basic physical property measurement of a new material such as GDY, a single-layer single-crystalline sample is required. Therefore, developing an effective method to produce high-quality single-layer GDY is crucial. For example, investigating reversible synthesis reactions, such as metathesis of alkynes instead of the original terminal alkyne coupling reaction, may be a possible way\textsuperscript{139} using which the as-prepared GDY can self-repair during the formation process. In addition, developing suitable methods to exfoliate the as-prepared GDY powders is also an effective way to obtain one- or few-layer GDY materials.
Secondly, developing clean transfer technology for GDY is urgent. Although the PMMA-assisted transfer method\textsuperscript{1,40,141} can guarantee the integrity of the film to a certain extent, it often introduces the residue of amorphous impurities,\textsuperscript{142} which affects the high-resolution electron microscopy characterization of GDY to a large extent. In addition, hydrofluoric acid was used during the transfer process. Although the Raman results show that hydrofluoric acid does not have any influence on the structure of GDY, it decreases the intensity of the Raman peak. Moreover, it cannot be guaranteed that hydrofluoric acid does not have any influence on the structure of GDY. Therefore, determining a nondestructive and clean transfer method for GDY fabrication is crucial toward the development of this field. Of course, another way to resolve this problem is to grow \textit{in situ}, but the \textit{in situ} growth process in the solution phase often causes damage to the Cu grid for TEM characterization, and the grid is also prone to damage during complex post-treatment cleaning processes. In spite of these issues, the method of \textit{in situ} growth on a Cu grid for structure characterization is still worthwhile.

Thirdly, it is particularly important to find a simple and versatile method to quickly judge the quality and structure of graphyne. At present, the main methods used to characterize graphyne are traditional 2D material characterization methods, which lack their own characteristics. Raman spectroscopy was used to demonstrate the existence of acetylenic linkages in GDY, but this method fails to analyze the percentage of carbon–carbon triple bonds, which is important for judging the structure of graphyne (different kinds of graphynes often have different percentages of acetylenic linkages). In addition, different growth methods often yield samples with different qualities. Therefore, it is necessary to develop an effective way to accurately determine the polymerization degree of GDY samples.

Again, let us explore the key issues in the applications of GDY. Since the initial synthesis of GDY films, the application of GDY in different fields has been a fervently discussed topic. Unfortunately, there are few applications to explore the direct use of carbon–carbon triple bonds and insufficient direct evidence to prove the crucial role of carbon–carbon triple bonds in such applications. Therefore, the characterization and utilization of carbon–carbon triple bonds is the goal for the future. Another feature of GDY is that it has a uniform pore structure. There are many theoretical predictions for the application of pore structures, and it is predicted to have prospective applications in the fields of gas separation and seawater desalination.\textsuperscript{5,143} However, current experiments in this area are still not worthwhile. The important limiting factor is the quality of the as-prepared samples. The coupling in the 3D direction leads to the low crystallinity of the sample, which limits its performance in practical applications. The preparation determines the applications, and the application determines the future of GDY, which reverts to the question of developing the preparation method.

Finally, the author wants to state that graphyne is not one material, but a class of materials. More importantly, in this series of materials, each different material has its own unique properties. Therefore, our work should not be limited to GDY. Developing new members of the graphyne family is also an important topic. This review is devoted to comprehensively reviewing the basic properties and synthesis methods of GDY, as well as its applications in specific fields. We hope that this review can provide a new perspective for the preparation of GDY materials, and useful guidance for the application design of GDY materials in related fields.

**Conflicts of interest**

There are no conflicts to declare.

**Acknowledgements**

This work was supported by the Ministry of Science and Technology of China (2016YFA02000101 and 2016YFA0200104), the National Natural Science Foundation of China (Grant No. 51432002, 51720150503 and 21790052), and the Beijing Municipal Science and Technology Project (Grant No. Z161100002116026).

**Notes and references**


