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## Superflexible C<sub>68</sub>-graphyne as a promising anode material for lithium-ion batteries†

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The breakthrough in the synthesis of graphyne, graphdiyne and graph-4-yne stimulates interest in studying new members of the graphyne family for promising applications. In this work, a new allotrope of graphyne with excellent stability and an ultrahigh specific surface area of  $4255\text{ m}^2\text{ g}^{-1}$ , named C<sub>68</sub>-graphyne, is predicted by first principles calculations. Mechanical tests reveal that C<sub>68</sub>-graphyne exhibits much smaller in-plane tensile stiffness ( $\sim 50.5\text{ N m}^{-1}$ ) and out-of-plane bending stiffness ( $\sim 0.5\text{ eV}$ ) than graphene (in-plane tensile stiffness  $350\text{ N m}^{-1}$  and out-of-plane bending stiffness  $1.4\text{ eV}$ ), suggesting C<sub>68</sub>-graphyne as a superflexible material. Meanwhile, our results show that monolayer C<sub>68</sub>-graphyne is a semiconductor with a direct band gap of  $1.0\text{ eV}$ , which can be tuned by strain-engineering, and the calculated carrier mobility is as high as  $1.81 \times 10^5$  to  $2.97 \times 10^5\text{ cm}^2\text{ V}^{-1}\text{ s}^{-1}$  at  $300\text{ K}$ . Finally, the potential application of C<sub>68</sub>-graphyne as an anode material for lithium-ion batteries is explored and predicted. The calculated results show highly efficient charge transfer from the adsorbed Li ions to C<sub>68</sub>-graphyne yet a low diffusion barrier for Li ions in C<sub>68</sub>-graphyne for fast charge/discharge rates. The storage capacities for Li in monolayer and bilayer C<sub>68</sub>-graphyne are calculated to be as high as  $1954$  and  $1675\text{ mA h g}^{-1}$ , respectively. These features make C<sub>68</sub>-graphyne a promising anode material for lithium-ion batteries with excellent energy storage capacities as well as fast charge/discharge rates.

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## 1. Introduction

Carbon has unique potential for the construction of various architectures. In the past decades, many carbon allotropes such as carbon fullerenes,<sup>1</sup> nanotubes,<sup>2</sup> and graphene<sup>3</sup> have been synthesized and characterized. Over thirty years ago, Baughman and Eckhardt predicted two-dimensional (2D) sheets of carbon, called graphyne (GY), including  $\alpha$ -,  $\beta$ -, and  $\gamma$ -GY.<sup>4</sup> Among them,  $\gamma$ -GY exhibits high stability and semiconductor features.<sup>5</sup> With the increase of acetylenic linkages among adjacent aromatic rings, more members of the GY family, such as graphdiyne (GDY), graph-3-yne, graph-4-yne and graph-5-yne, were obtained.<sup>6</sup>  $\gamma$ -GY consisting of sp and sp<sup>2</sup> carbon atoms can be viewed as resulting from the substitution of the carbon–carbon bonds in graphene by acetylenic ( $-\text{C}\equiv\text{C}-$ ) linkages. The acetylenic linkage is an efficient connecting unit because of the structural linearity without any existing fluctuation arising from *cis*–*trans* isomerization.<sup>7</sup> Therefore, the introduced acetylenic linkages create a planar network of  $\gamma$ -GY with high surface area

and porosity, making its structural, mechanical, thermal, optical and particularly electrical properties quite different from those of graphene or carbon nanotubes.<sup>8–11</sup> For example, the acetylenic linkages in  $\gamma$ -GY and GDY endow them with significant band gaps (0.47 and 0.52 eV, respectively).<sup>6</sup> This is different from graphene, of which the intrinsic zero band gap significantly limits its practical applications in electronic devices and thus considerable efforts such as increasing the thickness,<sup>12,13</sup> introducing a substrate<sup>14</sup>, chemical doping<sup>15</sup> and strain engineering<sup>16</sup> have been made to open the band gap in graphene.

Experimentally, large area GDY was synthesized on the surface of copper *via* a cross-coupling reaction, showing excellent semiconducting properties.<sup>7</sup> Subsequently, GDY nanotube arrays were also synthesized through an anodic aluminum oxide (AAO) template catalyzed with copper foil.<sup>17</sup> The breakthrough in the synthesis of GDY has stimulated great interest in studying new members of the GY family (*i.e.*,  $\gamma$ -GY and graph-4-yne)<sup>18,19</sup> for promising applications such as hydrogen storage<sup>20,21</sup> and lithium-ion batteries (LIBs).<sup>22,23</sup> For instance, it's reported that the maximum capacity of graph-4-yne for Li storage could reach as high as  $947\text{ mA h g}^{-1}$ .<sup>19</sup> It should be noted here that most theoretical studies focus on monolayer materials for use in LIB anodes, which may provide a limited view of the performance as the interlayer chemical interaction of these materials in reality is neglected. The interlayer chemical

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interaction of these materials remains challenging for use in LIB anode materials and thus their effect on the performance needs to be quantitatively evaluated.

In this work, we report a new member of GY with an ultra-high specific surface area of  $4255\text{ m}^2\text{ g}^{-1}$  and direct band gap of 1.00 eV (HSE06), called C<sub>68</sub>-GY. Its stability is carefully checked by both phonon dispersion calculations and *ab initio* molecular dynamics (AIMD). The smaller in-plane tensile stiffness ( $\sim 50.5\text{ N m}^{-1}$ ) and out-of-plane bending stiffness ( $\sim 0.5\text{ eV}$ ) than those of graphene (in-plane tensile stiffness  $350\text{ N m}^{-1}$  and out-of-plane bending stiffness  $1.4\text{ eV}$ ) indicate the exceptional flexibility of C<sub>68</sub>-GY. The calculated highly efficient charge transfer from adsorbed Li ions to C<sub>68</sub>-GY, low diffusion barrier of Li ions in C<sub>68</sub>-GY for fast charge/discharge rates, and ultra-high specific capacity (monolayer:  $1954\text{ mA h g}^{-1}$ , bilayer:  $1675\text{ mA h g}^{-1}$ ) make C<sub>68</sub>-GY an ideal candidate for anode materials of LIBs.

## 2. Computational methods

First principles calculations are carried out in the framework of density functional theory as implemented in the Vienna *ab initio* simulation package (VASP).<sup>24,25</sup> The projector augmented wave method is used to treat the interactions between electrons and ions.<sup>26</sup> General gradient approximation is employed with the Perdew–Burke–Ernzerhof (PBE) functional to describe the exchange and correlation interactions between electrons unless noted otherwise.<sup>27</sup> The energy cutoff is set to 600 eV for all calculations. The *K*-point density used in the calculations is  $>50\text{ \AA}$  based on the Monkhorst–Pack scheme<sup>28</sup>. The cell parameters and ionic positions are fully optimized until the force on each atom is converged below  $0.01\text{ eV \AA}^{-1}$ . In order to avoid interactions between periodic images, a vacuum separation of  $30\text{ \AA}$  is adopted. The electronic properties are calculated by both using

PBE and hybrid functionals (HSE06).<sup>29</sup> Density functional perturbation theory<sup>30</sup> calculations are performed to obtain the phonon dispersion combining VASP and the open source code Phonopy.<sup>31</sup>

## 3. Results and discussion

### 3.1. Structure and chemical analysis

Similar to  $\gamma$ -GY (Fig. S1†), the new form of GY consists of acetylenic linkages and aromatic rings as shown in Fig. 1a. The primitive cell contains 24 carbon atoms (Fig. 1b). The optimized lattice constant ( $10.84\text{ \AA}$ ) is larger than that of  $\gamma$ -GY ( $6.86\text{--}6.89\text{ \AA}$ ), but C<sub>68</sub>-GY has the same hexagonal symmetry ( $P6/mmm$ :  $D_{6h}$ ) as  $\gamma$ -GY.<sup>4,6</sup> From Fig. 1a, it can be observed that two acetylenic linkages concurrently join to the neighboring aromatic rings resulting in an octatomic ring. Besides, the angles between acetylenic linkages and aromatic rings are obtuse ( $\alpha_1 = 125.8^\circ$ ), differing from those in GY ( $60^\circ$ ). According to the previous naming convention of GY,<sup>32</sup> this new GY is named C<sub>68</sub>-GY. As we know, there are three types of C–C bonds in  $\gamma$ -GY (Fig. S1b†):  $sp^2-sp^2$  ( $B_1 = 1.436\text{ \AA}$ ),  $sp^2-sp$  ( $B_2 = 1.408\text{ \AA}$ ) and  $sp-sp$  ( $B_3 = 1.223\text{ \AA}$ ),<sup>5</sup> while there are four types of C–C bonds in C<sub>68</sub>-GY (Fig. 1b): including two types of  $sp^2-sp^2$  ( $B_1 = 1.462\text{ \AA}$  and  $B_2 = 1.397\text{ \AA}$ ),  $sp^2-sp$  ( $B_3 = 1.413\text{ \AA}$ ) and  $sp-sp$  ( $B_4 = 1.227\text{ \AA}$ ). For further insights into the bond characteristics, total electron densities of C<sub>68</sub>-GY are plotted (Fig. 1c). The electron densities of  $sp-sp$  bonds ( $B_4$ ) are obviously higher than those of others, suggesting stronger electron delocalization in the  $sp-sp$  bonds (Fig. 1d). The angles between  $sp^2-sp$  bond ( $B_3$ ) and  $sp-sp$  bond ( $B_4$ ) in the acetylenic linkages of C<sub>68</sub>-GY are of obtuse angle ( $\alpha_2 = 155.8^\circ$ ), which is attributed to the electrostatic repulsive interactions between two adjacent acetylenic linkages in the same octatomic ring. Meanwhile, the interactions further stretch the shared bonds ( $B_1$ ) between octatomic and aromatic

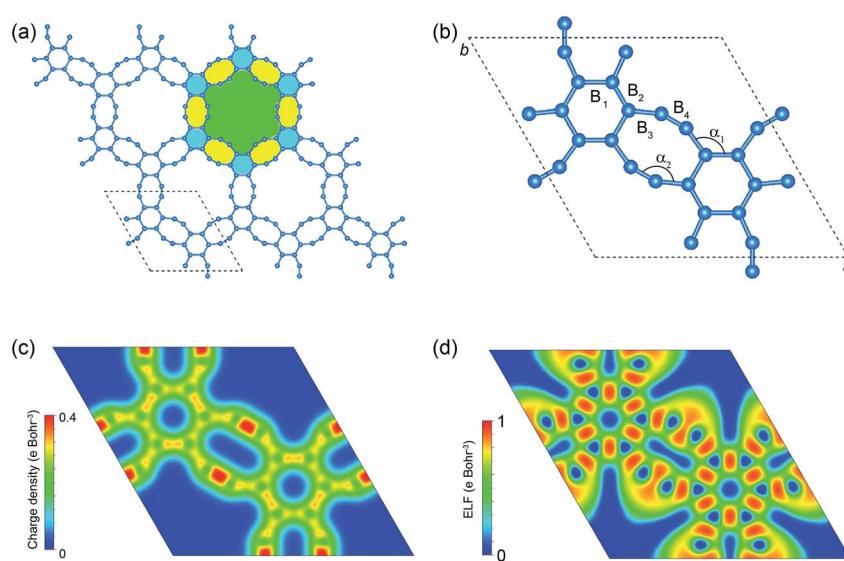


Fig. 1 (a) Schematic diagram of C<sub>68</sub>-GY, and (b) its primitive cell. Color coding is yellow for octatomic rings, cerulean for aromatic rings, and green for the pores. B<sub>1</sub>, B<sub>2</sub>, B<sub>3</sub> and B<sub>4</sub> denote the different bonds, and  $\alpha_1$  and  $\alpha_2$  are two angles. The plotted iso-surfaces of (c) total electron density and (d) electron location function (ELF) are shown in the primitive cell.

rings, thus resulting in the bond  $B_1$  longer than  $B_2$ , which accounts for two types of  $sp^2-sp^2$  bonds in aromatic rings. Meanwhile, the octatomic and aromatic rings together form a pore with a diameter of 8.22 Å (Fig. 1a), much larger than those in graph- $n$ -yne ( $n = 1, 2, 3, 4$  and 5).<sup>33</sup> In particular, the theoretical specific surface area is 4255 m<sup>2</sup> g<sup>-1</sup>, larger than those of activated carbon (~2000 m<sup>2</sup> g<sup>-1</sup>)<sup>34</sup> and graphene (experimental data: ~1500 m<sup>2</sup> g<sup>-1</sup>, theoretical calculation: ~2620 m<sup>2</sup> g<sup>-1</sup>),<sup>35</sup> indicating its potential application for gas adsorption and purification. Besides, two methods are used to determine the van der Waals (vdW) thickness of monolayer C<sub>68</sub>-GY by characterizing the weak interlayer interactions of C<sub>68</sub>-GY. The first one is to calculate the energy curve for two separated C<sub>68</sub>-GY *versus* the different distances (Fig. 2a), from which we find that the equilibrium distance of  $d_{vdw}$  is 3.76 Å with an adhesion energy of 104.3 mJ m<sup>-2</sup>. The other method is to fully optimize the C<sub>68</sub>-GY bilayer with an initial separation of 4 Å. The optimized energy of bilayer C<sub>68</sub>-GY is compared with that of

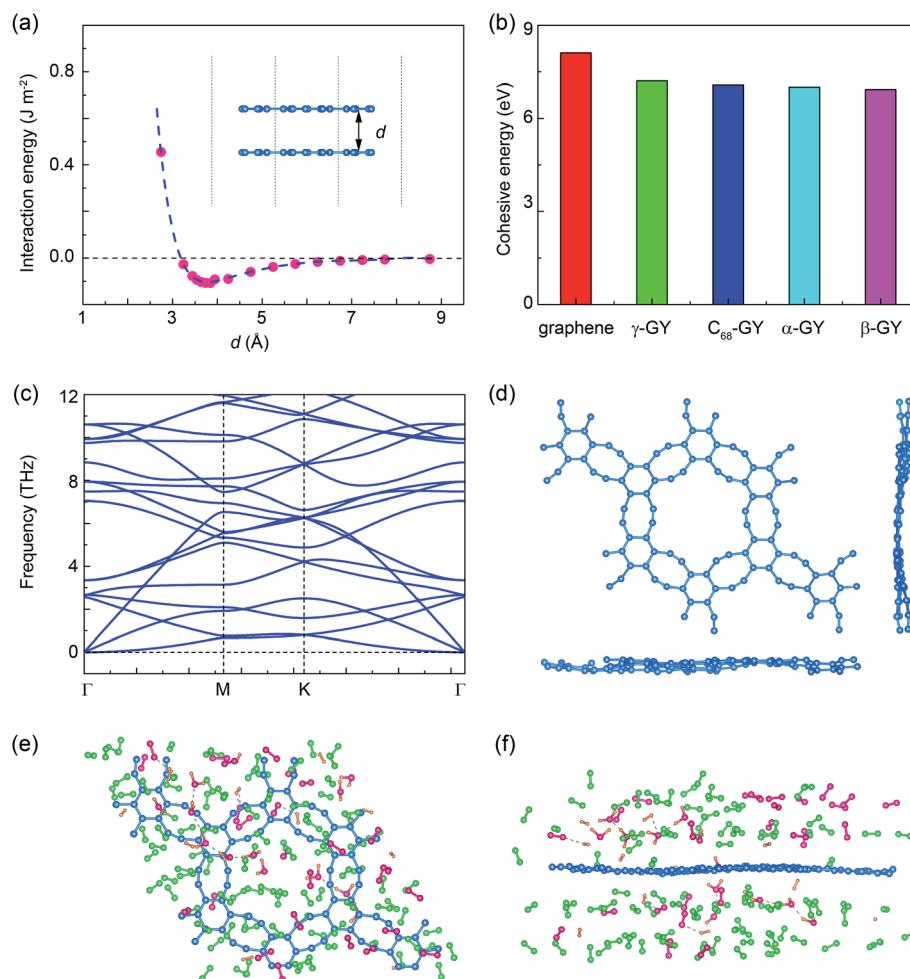
monolayer C<sub>68</sub>-GY to obtain an adhesion energy of 106.6 mJ m<sup>-2</sup>. The smaller adhesion energy of 104.3–106.6 mJ m<sup>-2</sup> found here than that of  $\gamma$ -GY (223.5 mJ m<sup>-2</sup>)<sup>9</sup> is attributed to the sparser distribution of in-plane carbon atoms.

### 3.2. Stability

First, the thermal stability of C<sub>68</sub>-GY with respect to its cohesive energy is evaluated. According to eqn (1), the cohesive energy is determined to be 7.09 eV per atom.

$$E_{coh} = \frac{24E_C - E_{C_{68}-GY}}{24} \quad (1)$$

where  $E_C$  and  $E_{C_{68}-GY}$  denote the energy of the isolated carbon atom and C<sub>68</sub>-GY. Compared with GY and graphene (Fig. 2b), the stability of C<sub>68</sub>-GY closely follows that of  $\gamma$ -GY (7.21 eV)<sup>5</sup> and graphene (8.11 eV).<sup>36</sup> Afterwards, the dynamic stability of C<sub>68</sub>-GY is verified by phonon dispersion calculation, where the absence of imaginary modes<sup>37</sup> indicates the dynamic stability of the C<sub>68</sub>-



**Fig. 2** (a) The interaction energy as a function of various separation  $d$  values, between two layers of C<sub>68</sub>-GY (inset). The blue dashed line denotes the fitting curve for the red points. (b) The comparison of cohesive energies of graphene,  $\alpha$ -,  $\beta$ -, and  $\gamma$ -GY with C<sub>68</sub>-GY. The data for graphene,  $\alpha$ -GY,  $\beta$ -GY and  $\gamma$ -GY are obtained from ref. 5 and 36. (c) The calculated phonon dispersion spectrum of C<sub>68</sub>-GY. (d) The snapshots (top and side views) taken from AIMD simulations of C<sub>68</sub>-GY. (e and f) The snapshots (top and side views) taken from AIMD simulations of C<sub>68</sub>-GY in the atmosphere, where the ratio of the molecular numbers is set to be N<sub>2</sub> : O<sub>2</sub> : H<sub>2</sub>O : H<sub>2</sub> = 22 : 6 : 3 : 3 and the blue, red, green and orange spheres represent C, O, N and H atoms, respectively.

GY monolayer (Fig. 2c). Meanwhile, the thermodynamic stability in a supercell ( $2 \times 2 \times 1$ ) is evaluated by performing AIMD simulations at 300 K for 10 ps. The temperature is controlled by using the Nosé–Hoover thermostat. During the AIMD simulation, C<sub>68</sub>-GY upholds its structural integrity with only slight corrugation because of thermal fluctuations (Fig. 2d). Subsequently, we probe the chemical stability of C<sub>68</sub>-GY under ambient conditions with common molecules in the atmosphere (the molecular ratio is set as N<sub>2</sub> : O<sub>2</sub> : H<sub>2</sub>O : H<sub>2</sub> = 22 : 6 : 3 : 3) for 10 ps in the NPT ensemble with a controlled temperature of 300 K and pressure of 0 bar. A slight fluctuation of lattice constants (Fig. S2a†) and no bonds formed or broken during the whole AIMD simulations (Fig. 2e–f) suggest the great chemical stability of C<sub>68</sub>-GY under ambient conditions. The above results confirm the remarkable energetic, dynamic, thermodynamic and chemical stabilities of C<sub>68</sub>-GY. In addition, recently GDY and graph-4-yne have been successfully synthesized on the surface of copper foil,<sup>7,19</sup> and thus C<sub>68</sub>-GY could be expected to be grown on the copper substrate.

### 3.3. Mechanical properties

To investigate the mechanical properties of C<sub>68</sub>-GY, tensile tests for monolayer C<sub>68</sub>-GY in a rectangle cell are performed (Fig. 3a,b). The uniaxial stress-strain in Fig. 3c shows that the tensile strength ( $\sigma$ ) along  $x$ - and  $y$ -directions is 21.7 N m<sup>-1</sup> (58.0 GPa, using a thickness of 3.74 Å for monolayer C<sub>68</sub>-GY) and 14.7 N m<sup>-1</sup> (39.3 GPa), corresponding to the failure strain of 32% and 20%, respectively. The larger failure strain along the  $x$ -direction is attributed to some acetylenic linkages directly bearing the tensile load. Similar to graphene,<sup>38,39</sup> C<sub>68</sub>-GY has an almost isotropic in-plane elastic response with an in-plane tensile stiffness of ~50.5 N m<sup>-1</sup> (135.0 GPa), which is smaller than those of graphene (350 N m<sup>-1</sup> and 1050 GPa).<sup>39</sup> Note that, as  $\varepsilon_x = 25\%$ , the stress–strain and strain energy–strain

responses abruptly change, implying that the atomic structure of C<sub>68</sub>-GY has a significant transformation. As shown in Fig. 3b, we find that only the acetylenic linkages directly bear load along the  $x$ -direction, and other acetylenic linkages are broken and then reconstructed. In addition to in-plane mechanical behaviors, we also examine its out-of-plane elasticity, *i.e.* bending stiffness  $D$ . Two methods can be used to calculate  $D$ . The first one is to fit the bending energy per unit area  $E_{\text{ben}}$  of a C<sub>68</sub>-GY nanotube as a function of its radius  $R$ , based on the equation  $E_{\text{ben}} = DR^{-2}/2$ .<sup>40</sup> The second one is to fit the phonon dispersions  $\omega(q)$  with the equation  $\omega^2 = (D/\rho)q^4$  according to the quadratic dispersion of the flexural phonon mode ZA,<sup>41</sup> where  $\rho$  is the areal density of C<sub>68</sub>-GY ( $4.70 \times 10^{-7}$  kg m<sup>-2</sup>). Due to the first method requiring high computational costs, the second approach is adopted in this work (Fig. S2b†). The calculated  $D$  values along  $\Gamma$ -M and  $\Gamma$ -K are both  $\sim 0.50$  eV. In the same way, a  $D$  value of 1.43 eV for graphene is calculated (Fig. S2c†), coinciding with previous DFT calculations (1.44 eV).<sup>42</sup> Moreover, the comparison of mechanical properties with those of other typical carbon allotropes is provided in Table S1.† The small in-plane tensile stiffness and out-of-plane bending stiffness make C<sub>68</sub>-GY an atomic membrane with exceptional flexibility.

### 3.4. Electronic properties

The band structure and projected density of states (PDOS) are computed with the PBE functional. Unlike  $\gamma$ -GY (at the M point),<sup>43</sup> the conduction band minimum (CBM) and valence band maximum (VBM) of C<sub>68</sub>-GY are located at the K point in the Brillouin zone. The band gap of 0.51 eV (Fig. 4a) is larger than that of  $\gamma$ -GY (0.46 eV).<sup>5</sup> From the PDOS (Fig. S3a†), only contribution of p<sub>z</sub> orbitals is found around the Fermi level ( $-1.3$  eV to  $2.6$  eV). Therefore, only bands corresponding to  $\pi$  and  $\pi^*$  states are present in this gap. Because the PBE functional tends to underestimate the band gaps of materials,<sup>44</sup>

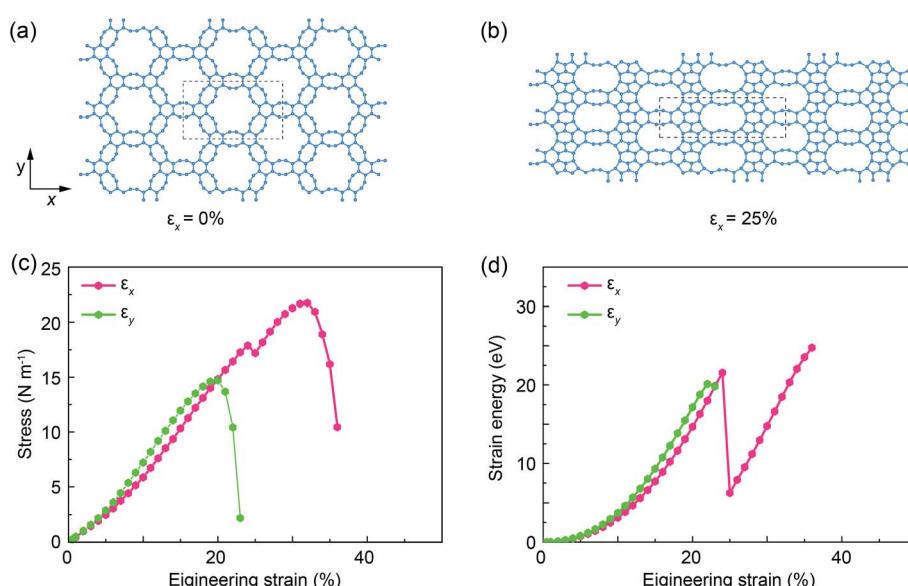
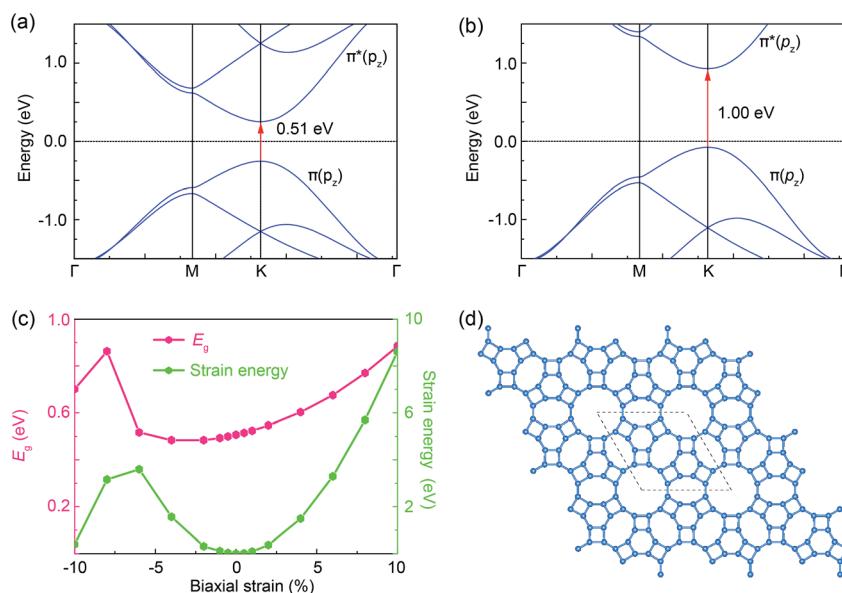


Fig. 3 (a) The schematic diagram of uniaxial tensile tests using a rectangular cell (dashed line); (b) the atomic configuration under a uniaxial tension of  $\varepsilon_x = 25\%$ ; (c) the stress and (d) strain energy responses under the uniaxial tension.



**Fig. 4** Band structures of the C<sub>68</sub>-GY monolayer are calculated by using (a) PBE and (b) HSE06 functionals following the path Γ–M–K–Γ of the first Brillouin zone. (c) The calculated band gap E<sub>g</sub> and strain energy under different biaxial strains. (d) The atomic configuration of C<sub>68</sub>-GY at a biaxial strain of −8%.

a more reliable method with the HSE06 functional is used to recompute the band structure ( $E_g = 1.00$  eV) as depicted in Fig. 4b. Furthermore, we calculate the effective masses utilizing the expression:

$$m^* = \frac{\hbar^2}{\partial^2 E / \partial k^2} \quad (2)$$

The  $|m^*|$  values along the K–M direction are larger than those along the K–Γ direction. Meanwhile, biaxial strain ( $\varepsilon$ ) ranging from −10% to 10% is used to tune the electronic properties of C<sub>68</sub>-GY. The band gap  $E_g$ , strain energy, and the effective masses for electrons and holes are calculated corresponding to the strain (Fig. 4c and Table S2†). The  $E_g$  and  $|m^*|$  both increase with the increase of strain. As  $\varepsilon = 10\%$ ,  $E_g$  increases to be 0.88 eV. During the compression,  $E_g$  first decreases and then increases, whereas the band structures show an indirect feature as C<sub>68</sub>-GY is further compressed to an  $\varepsilon$  of about −8% (Fig. S4†). Meanwhile, the strain energies abnormally decrease at an  $\varepsilon$  of about −8%, implying that the structures substantially change. We checked the structures corresponding to this critical strain and confirmed that a phase transition occurs, in which the original octatomic rings reconstruct to be tetratomic and new octatomic rings (Fig. 4d). Finally, the carrier mobilities of C<sub>68</sub>-GY are given by<sup>45</sup>

$$\mu_{2D} = \frac{e\hbar^3 C_{2D}}{k_B T |m^*| m_d(E_1)} \quad (3)$$

where  $m_d$  is the average effective mass determined by  $\sqrt{m_x^* m_y^*}$ ,  $m_x^*$  and  $m_y^*$  are the effective mass ( $m^*$ ) along the  $x$ - and  $y$ -directions of transport, respectively,  $C_{2D}$  is the elastic constant and  $E_1$  is the DP constant (Fig. S5†).  $C_{2D}$  can be determined by

the calculations of the elastic constant matrix of monolayer C<sub>68</sub>-GY. Hence, the carrier mobilities along  $x$ - and  $y$ -directions are obtained (Table 1). For monolayer C<sub>68</sub>-GY at room temperature (300 K), the carrier mobility is as high as  $1.81 \times 10^5$  to  $2.97 \times 10^5$  cm<sup>2</sup> V<sup>−1</sup> s<sup>−1</sup>, which is much higher compared to those of other 2D materials such as MoS<sub>2</sub> (ref. 46) and black phosphorene.<sup>45</sup> The high carrier mobility mainly originates from the small deformation potential (0.4 eV) that is much smaller than those of graphene (5.0 eV),<sup>47</sup> MoS<sub>2</sub> (3.9 eV)<sup>46</sup> and phosphorene (2.7 eV).<sup>45</sup> The tunable electronic structure and excellent electronic conductance make C<sub>68</sub>-GY a promising candidate for future flexural electronic devices.

### 3.5. The application of C<sub>68</sub>-GY as the anode material for lithium-ion batteries

The promising application of C<sub>68</sub>-GY as the anode material for LIBs is investigated in this part. First, the strongest adsorption site for an isolated Li on the C<sub>68</sub>-GY monolayer (2 × 2 × 1) is determined by evaluating the adsorption energy  $E_{ad}$ :

$$E_{ad} = \frac{E(m@C_{68}\text{-GY}) - E(C_{68}\text{-GY}) - m\mu(\text{Li})}{m} \quad (4)$$

where  $E(C_{68}\text{-GY})$  and  $E(m@C_{68}\text{-GY})$  are the total energies of C<sub>68</sub>-GY before and after adsorption of  $m$  Li ions, respectively, and  $\mu(\text{Li})$  is the chemical potential of Li.<sup>48</sup> Five intercalation positions denoted as S1–S5 are considered (Fig. 5a). The DFT-D3 method of Grimme is employed for the corrections of the van der Waals interactions.<sup>49</sup> The results show that the most favorite site of Li adsorbed on C<sub>68</sub>-GY is S4 with the lowest  $E_{ad}$  of −3.01 eV (Table 2). The absolute values of adsorption energies are all larger than those of graphite (−0.78 eV),<sup>50</sup> suggesting a strong ionic binding between Li ions and the C<sub>68</sub>-GY substrate. The charge density difference is plotted as depicted

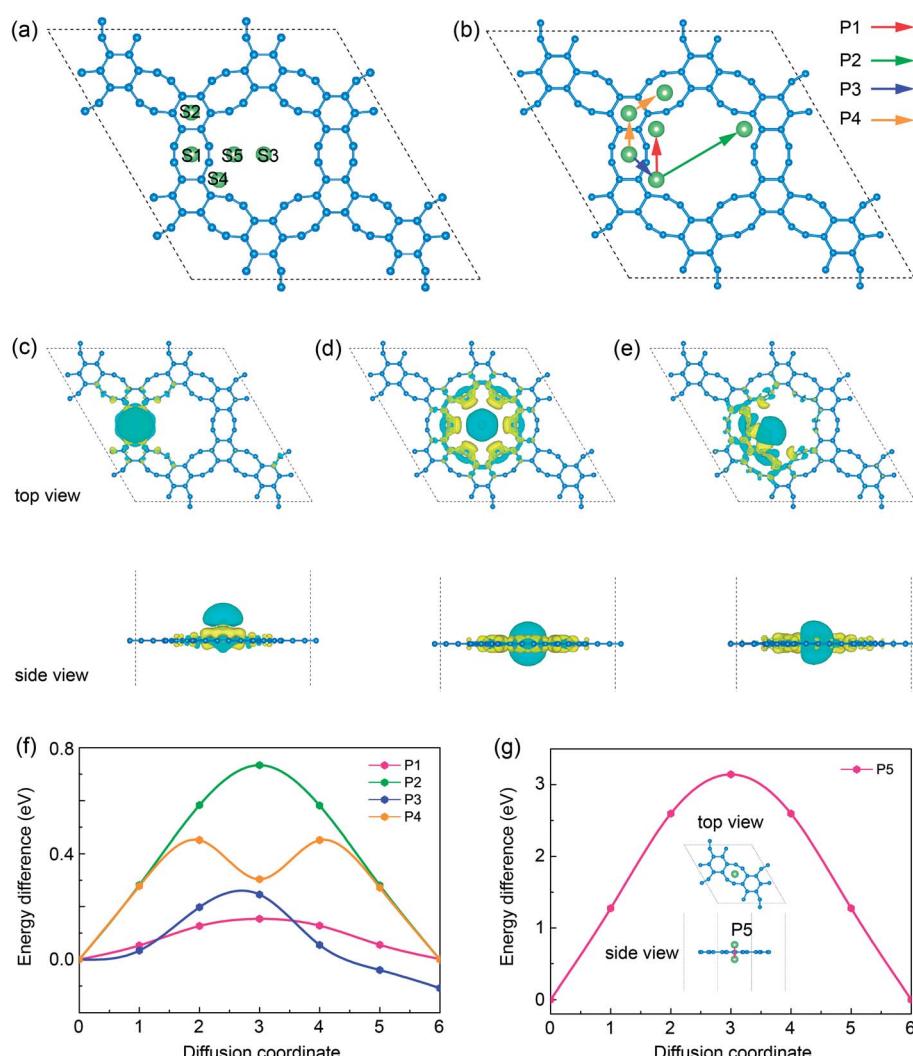
**Table 1** The calculated carrier mobility  $\mu_{2D}$  at 300 K for monolayer C<sub>68</sub>-GY along the x- and y-directions, including the in-plane elastic constants  $C_{2D}$ , DP constant,  $E_1$  and effective mass  $m^*$

Carrier type	$m_x^*/m_0$	$m_y^*/m_0$	$E_{1x}$ (eV)	$E_{1y}$ (eV)	$C_{2D,x}$ (N m <sup>-1</sup> )	$C_{2D,y}$ (N m <sup>-1</sup> )	$\mu_{2D,x}$ ( $10^5$ cm <sup>2</sup> V <sup>-1</sup> s <sup>-1</sup> )	$\mu_{2D,y}$ ( $10^5$ cm <sup>2</sup> V <sup>-1</sup> s <sup>-1</sup> )
Electron	0.214	0.185	0.382	0.406	78.202	78.202	2.681	2.745
Hole	-0.223	-0.193	-0.446	-0.374	78.202	78.202	1.810	2.974

in Fig. 5c–e, showing that Li is ionized as adsorbed on the surface of C<sub>68</sub>-GY. This observation coincides with the Bader charge analysis revealing that Li transfers charges of 0.91e (S1), 0.98e (S3) and 0.92e (S4) to C<sub>68</sub>-GY, respectively, approaching that of MoN<sub>2</sub> (0.89e).<sup>51</sup> These results clearly demonstrate that the Li ion is in the cationic state and is chemically adsorbed on the C<sub>68</sub>-GY monolayer. Moreover, PDOS calculations (Fig. S3b-d†) clearly show the metallic characters of C<sub>68</sub>-GY that adsorbed one Li, arising from p<sub>z</sub> orbitals around the Fermi level to the

left. The excellent electrical conduction is of significance for anode materials.

Besides, the charge/discharge rate is of great importance for the performance of anode materials, which depends upon the mobility of ions. Therefore, we probe the diffusion behaviors of Li ions over and through C<sub>68</sub>-GY using the climbing-image nudged elastic band (CI-NEB) method.<sup>52</sup> For the in-plane diffusion, the diffusion paths P1, P2, P3 and P4 are considered (Fig. 5b). Among them, P1 and P2 are the paths through



**Fig. 5** (a) Five potential different adsorption sites of an intercalated Li ion in the C<sub>68</sub>-GY monolayer, and the blue and green spheres represent C and Li atoms, respectively. (b) Schematics of the diffusion P1 to P4 (top view). Top and side views of the differential charge density of one Li ion adsorbed on (c) S1, (d) S3 and (e) S4 with an isosurface value of 0.0006 e Bohr<sup>-3</sup>. Color coding is yellow for charge gain and green for charge loss. The diffusion barrier profiles of (f) in-plane diffusion (P1–P4) and (g) the out-plane diffusion (P5).

**Table 2** The adsorption energy ( $E_{\text{ad}}$ ) and height ( $h$ ) for the five different adsorption sites in the supercell ( $2 \times 2 \times 1$ ) of monolayer C<sub>68</sub>-GY

Monolayer	Sites	$E_{\text{ad}}$ (eV)	$h$ (Å) <sup>a</sup>
$2 \times 2 \times 1$	S1	-2.90	1.67
	S2	-2.62	1.77
	S3	-2.28	0
	S4	-3.01	0.12
	S5	-2.86	0

<sup>a</sup> The adsorption height  $h$  denotes the vertical distance between Li ions and the C<sub>68</sub>-GY monolayer.

which Li migrates from the most favorite site (S4) to another one. For the out-of-plane diffusion paths, P5 denotes the path passing through S1 (octatomic ring) from one side to another. The diffusion barriers of ions over and through monolayer C<sub>68</sub>-GY are shown in Fig. 5f–g, involving the low diffusion barriers of 0.13 eV, 0.25 eV and 0.45 eV for P1, P3 and P4, respectively. For the out-of-plane diffusion, P5 uncovers the highest diffusion barrier of 3.14 eV. It can be understood that the small pore size of the octatomic ring results in a larger repulsive Coulomb interaction, which significantly enhances the diffusion barrier. These diffusion barriers of in-plane diffusion are smaller than those of the well-studied electrode materials, such as bulk silicon (0.57 eV)<sup>53,54</sup> and TiO<sub>2</sub>-based polymorphs (0.65 eV).<sup>55,56</sup> To further probe the effect of interlayer chemical interaction on the diffusion properties, we calculate the diffusion path P1 (Fig. 5b) for bilayer C<sub>68</sub>-GY (Fig. S6a†) with a barrier of 8.4 meV. From the barrier profile, the state at coordinate 3 is more stable than the initial/final state (Li on S4). Conversely, it can be speculated that the barrier of Li diffusing from coordinate 3 to the transition state (TS) is 57 meV (Fig. S6b†). Compared to the diffusion barriers of Li on the monolayer, the weak interlayer vdW interaction reduces the diffusion barriers and alters the most favorite site where Li is intercalated in C<sub>68</sub>-GY.

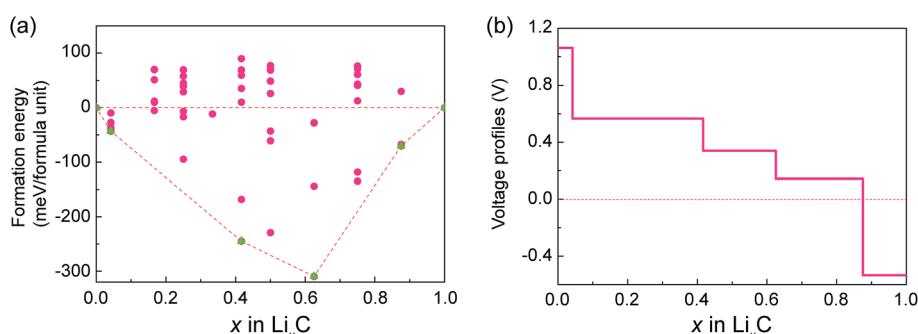
Furthermore, we evaluated the Li concentration intercalated in C<sub>68</sub>-GY to determine the specific capacity for Li storage. The specific capacity is calculated by:

$$C = \frac{xF}{M} \quad (5)$$

where  $x$  is the concentration of Li ions in C<sub>68</sub>-GY (the ratio between intercalated Li ions and carbon atoms in the hybrid system),  $F$  denotes the Faraday constant 26.8 A h mol<sup>-1</sup>, and  $M$  is the mass of carbon atoms. To explore the stabilities of the intermediate product (Li<sub>x</sub>C) with various Li ion concentrations ( $x$ ), the formation energy is calculated to plot the convex hull. There are two methods used to calculate the formation energy:<sup>57–59</sup> The first one is to use metallic Li and non-lithiated C<sub>68</sub>-GY as reference states; the second one is to use non-lithiated C<sub>68</sub>-GY and the fully lithiated C<sub>68</sub>-GY as reference states. Herein the second method is adopted, and the formation energy of Li<sub>x</sub>C is calculated by:

$$E_{\text{form}} = E - x \times E_{\text{LiC}} - (1 - x) \times E_{\text{C}} \quad (6)$$

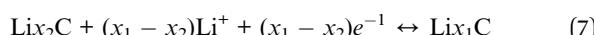
where  $E$  is the total energy of the configuration per Li<sub>x</sub>C formula unit ( $0 < x < 1$ ),  $E_{\text{LiC}}$  is the energy of LiC, and  $E_{\text{C}}$  is the energy of C<sub>68</sub>-GY per carbon atom. Fig. 6a displays the formation energies for Li<sub>x</sub>C with varying Li concentrations for monolayer C<sub>68</sub>-GY. AIMD simulations for the configurations of LiC are performed under the NPT ensemble with a temperature of 300 K and pressure of 0 bar to investigate the thermodynamic stability (Fig. S7a†). After running for 10 ps, LiC still holds the structural integrity but with corrugations leading to lattice contraction within the range of -5% (Fig. S7b†) accompanied by some of the original octatomic rings being reconstructed to be tetratomic and new octatomic rings, indicating a phase transition (Fig. S7c and d†). Besides, the volume expansion or contraction is considered during the adsorption process which is a key parameter controlling whether electrode reactions are reversible. As we know, the volume of 2D materials is not easy to identify. Instead, the in-plane expansion or contraction is considered using the lattice constant ( $a$ ) ratio, which can be calculated using  $a/a_0$ , where  $a_0$  and  $a$  are the lattice constants of C<sub>68</sub>-GY before and after adsorption of Li ions, respectively. Along these structures with the minimum formation energy (Fig. 6a, green points) as depicted in Fig. S8,† the adsorption energy and lattice changes are calculated as shown in Fig. S9a,† The negative adsorption energies demonstrate that these adsorption processes are exoergic without formation of Li clusters. Tiny lattice changes of C<sub>68</sub>-GY manifest that the intercalation of Li ions weakly influences the in-plane



**Fig. 6** (a) Formation energies calculated for different configurations of C<sub>68</sub>-GY intercalated Li ions; (b) the calculated voltage profile along the minimum energy path of formation energies, green points of (a).

expansion or contraction. On the one hand, with the increase of Li ions intercalated in C<sub>68</sub>-GY, the repulsive electrostatic interactions between Li ions will induce in-plane lattice expansion (Fig. S8a and b†). On the other hand, C<sub>68</sub>-GY with weak out-of-plane resistance is apt to be corrugated if Li more ions asymmetrically distribute on C<sub>68</sub>-GY (Fig. S8c and d†), which thus results in the in-plane contraction of the system. These two competitive mechanisms explain the trend of lattice constant changes. For Li intercalated in bilayer C<sub>68</sub>-GY, three configurations with varying Li concentrations (Fig. S8e–g†) are probed with negative adsorption energies (Table 3). Meanwhile, the calculated formation energies further show that the intermediate configurations with Li ions intercalated in bilayer C<sub>68</sub>-GY are also stable.

Afterwards, the OCV profiles are calculated, which is a measurement of the performance of the anode materials of LIBs. The charge/discharge processes of C<sub>68</sub>-GY follow the half-cell reaction vs. Li/Li<sup>+</sup>:



where  $x_1 > x_2$ . Then the voltage is

$$V = -\frac{G(\text{Li}_{x_1}\text{C}) - G(\text{Li}_{x_2}\text{C}) - (x_1 - x_2)G(\text{Li})}{(x_1 - x_2)ze} \quad (8)$$

where  $G$  is the Gibbs free energy of the compound,  $\Delta x = x_1 - x_2$  ( $x_1 > x_2$ ) and  $z$  represents the charge of the metal ion (here  $z = 1$  for Li). Since the contribution of entropy ( $T\Delta S \approx 25$  meV at 300 K) and enthalpy ( $P\Delta V$  in the order of  $1.0^{-5}$  eV) can be neglected,<sup>60</sup> the Gibbs free energy ( $\Delta G = \Delta E + P\Delta V - T\Delta S$ ) can be approximated as the internal energy  $\Delta E$ .<sup>61</sup> Within this approximation, the voltage profiles are calculated along these structures with minimum formation energy (Fig. 6a).<sup>62</sup> From the voltage profile (Fig. 6b), as  $x$  increases to 0.875, corresponding to a specific capacity of 1954 mA h g<sup>-1</sup>, the voltage decreases to 0.14 V. As  $x$  approaches 1.0, the voltage would decrease to −0.54 V, indicating that the lithiation process will stop. Similarly, for Li intercalations in bilayer C<sub>68</sub>-GY, the calculated voltage is 0.37 V when  $x$  increases to 0.75, corresponding to a capacity of 1675 mA h g<sup>-1</sup>. As  $x$  increases to 1.125, the voltage of Li<sub>1.125</sub>C decreases to −0.11 V. Besides, the comparisons of the specific capacities of C<sub>68</sub>-GY with other typical carbon allotropes are shown in Fig. S9b,† indicating that C<sub>68</sub>-GY is an ideal candidate for anode materials of LIBs with high specific capacity.

**Table 3** The adsorption energy  $E_{\text{ad}}$ , formation energy  $E_{\text{form}}$ , and the lattice constant ratios,  $a/a_0$  for Li ions in bilayer C<sub>68</sub>-GY. The formation energy for these bilayer configurations is calculated by using non-lithiated C<sub>68</sub>-GY and the lithiated Li<sub>1.125</sub>C as reference states

Bilayer	Li <sub>0.375</sub> C	Li <sub>0.75</sub> C	Li <sub>1.125</sub> C
$E_{\text{ad}}$ (eV)	−0.44	−0.55	−0.43
$E_{\text{form}}$ (meV per formula unit)	−3.6	−91.8	0
$a/a_0$	0.998	0.991	1.032

## 4. Conclusion

In this work, we predict a novel allotropy of GY using first principles calculations, named C<sub>68</sub>-GY. The remarkable energetic, dynamic, thermodynamic and chemical stabilities of C<sub>68</sub>-GY are confirmed by the first principles calculations. The unique atomic structures endow it with ultrahigh specific surface area (4255 m<sup>2</sup> g<sup>-1</sup>), high ductility (20–32%) and excellent elastic flexibility (in-plane tensile stiffness  $\sim$ 50.5 N m<sup>-1</sup> and out-of-plane bending stiffness  $\sim$ 0.5 eV). The calculated electronic structure shows a direct gap in the band structure (0.51 eV and 1.00 eV at PBE and HSE06 levels, respectively). The tunability of the band structure by strain-engineering is further explored. The band gap is observed to be increasing with increasing strain. The calculated high carrier mobilities of  $1.81 \times 10^5$  to  $2.97 \times 10^5$  cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup> indicate the potential applications of C<sub>68</sub>-GY in electronic devices. Finally, C<sub>68</sub>-GY possesses a low diffusion energy barrier for fast charge/discharge rates as well as high specific capacities (monolayer: 1954 mA h g<sup>-1</sup>, bilayer: 1675 mA h g<sup>-1</sup>). These exceptional electrical conductivity, fast charge/discharge rates and high capacity suggest that C<sub>68</sub>-GY can be utilized as a promising anode material for LIBs with high performance.

## Conflicts of interest

There are no conflicts to declare.

## Acknowledgements

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## References

- H. W. Kroto, J. R. Heath, S. C. O'Brien, R. F. Curl and R. E. Smalley, *Nature*, 1985, **318**, 162–163.
- S. Iijima, *Nature*, 1991, **354**, 56–58.
- K. S. Novoselov, A. K. Geim, S. V. Morozov, D. Jiang, Y. Zhang, S. V. Dubonos, I. V. Grigorieva and A. A. Firsov, *Science*, 2004, **306**, 666–669.
- R. Baughman, H. Eckhardt and M. Kertesz, *J. Chem. Phys.*, 1987, **87**, 6687–6699.
- A. R. Puigdollers, G. Alonso and P. J. C. Gamallo, *Carbon*, 2016, **96**, 879–887.
- N. Narita, S. Nagai, S. Suzuki and K. Nakao, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 1998, **58**, 11009–11014.
- G. Li, Y. Li, H. Liu, Y. Guo, Y. Li and D. Zhu, *Chem. Commun.*, 2010, **46**, 3256–3258.
- Y. Zhang, Q. Pei and C. Wang, *Appl. Phys. Lett.*, 2012, **101**, 081909.

- 9 S. W. Cranford and M. J. Buehler, *Carbon*, 2011, **49**, 4111–4121.
- 10 J. Kang, J. Li, F. Wu, S.-S. Li and J.-B. Xia, *J. Phys. Chem. C*, 2011, **115**, 20466–20470.
- 11 T. Ouyang, Y. Chen, L.-M. Liu, Y. Xie, X. Wei and J. Zhong, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 2012, **85**, 235436.
- 12 Y. Zhang, T.-T. Tang, C. Girit, Z. Hao, M. C. Martin, A. Zettl, M. F. Crommie, Y. R. Shen and F. J. N. Wang, *Nature*, 2009, **459**, 820–823.
- 13 E. V. Castro, K. Novoselov, S. Morozov, N. Peres, J. L. Dos Santos, J. Nilsson, F. Guinea, A. Geim and A. C. J. P. r. l. Neto, *Phys. Rev. Lett.*, 2007, **99**, 216802.
- 14 S. Y. Zhou, G. H. Gweon, A. V. Fedorov, P. N. First, W. A. de Heer, D. H. Lee, F. Guinea, A. H. Castro Neto and A. Lanzara, *Nat. Mater.*, 2007, **6**, 770–775.
- 15 W. Zhang, C.-T. Lin, K.-K. Liu, T. Tite, C.-Y. Su, C.-H. Chang, Y.-H. Lee, C.-W. Chu, K.-H. Wei, J.-L. Kuo and L.-J. Li, *ACS Nano*, 2011, **5**, 7517–7524.
- 16 G. Gui, J. Li and J. J. P. R. B. Zhong, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 2008, **78**, 075435.
- 17 G. Li, Y. Li, X. Qian, H. Liu, H. Lin, N. Chen and Y. Li, *J. Phys. Chem. C*, 2011, **115**, 2611–2615.
- 18 Q. Li, Y. Li, Y. Chen, L. Wu, C. Yang and X. Cui, *Carbon*, 2018, **136**, 248–254.
- 19 J. Gao, J. Li, Y. Chen, Z. Zuo, Y. Li, H. Liu and Y. Li, *Nano Energy*, 2018, **43**, 192–199.
- 20 S. Kumar and Dhilip Kumar Thogluva Janardhanan, *ACS Appl. Mater. Interfaces*, 2017, **9**, 28659–28666.
- 21 H. J. Hwang, Y. Kwon and H. Lee, *J. Phys. Chem. C*, 2012, **116**, 20220–20224.
- 22 H. Zhang, M. Zhao, X. He, Z. Wang, X. Zhang and X. Liu, *J. Phys. Chem. C*, 2011, **115**, 8845–8850.
- 23 H. J. Hwang, J. Koo, M. Park, N. Park, Y. Kwon and H. Lee, *J. Phys. Chem. C*, 2013, **117**, 6919–6923.
- 24 G. Kresse and J. Hafner, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 1994, **49**, 14251–14269.
- 25 G. Kresse and J. Furthmüller, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 1996, **54**, 11169–11186.
- 26 P. E. Blöchl, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 1994, **50**, 17953–17979.
- 27 J. P. Perdew, K. Burke and M. Ernzerhof, *Phys. Rev. Lett.*, 1996, **77**, 3865–3868.
- 28 H. J. Monkhorst and J. D. Pack, *Phys. Rev. B: Solid State*, 1976, **13**, 5188–5192.
- 29 J. Heyd, G. E. Scuseria and M. Ernzerhof, *J. Chem. Phys.*, 2003, **118**, 8207–8215.
- 30 S. Baroni, S. De Gironcoli, A. Dal Corso and P. Giannozzi, *Rev. Mod. Phys.*, 2001, **73**, 515–562.
- 31 A. Togo and I. Tanaka, *Scr. Mater.*, 2015, **108**, 1–5.
- 32 H. Lu and S.-D. Li, *J. Phys. Chem. C*, 2013, **1**, 3677–3680.
- 33 S. Lin and M. J. Buehler, *Nanoscale*, 2013, **5**, 11801–11807.
- 34 S. Y. Lu, M. Jin, Y. Zhang, Y. B. Niu, J. C. Gao and C. M. Li, *Adv. Energy Mater.*, 2018, **8**, 1702545.
- 35 Z.-S. Wu, G. Zhou, L.-C. Yin, W. Ren, F. Li and H.-M. Cheng, *Nano Energy*, 2012, **1**, 107–131.
- 36 V. O. Özçelik and S. Ciraci, *J. Phys. Chem. C*, 2013, **117**, 2175–2182.
- 37 Y. Li, Y. Liao and Z. Chen, *Angew. Chem., Int. Ed.*, 2014, **53**, 7248–7252.
- 38 X. Wei, B. Fragneaud, C. A. Marianetti and J. W. Kysar, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 2009, **80**, 205407.
- 39 F. Liu, P. Ming and J. Li, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 2007, **76**, 064120.
- 40 Z. Zhang, Y. Yang, E. S. Penev and B. I. Yakobson, *Adv. Funct. Mater.*, 2017, **27**, 1605059.
- 41 L. J. Karssemeijer and A. Fasolino, *Surf. Sci.*, 2011, **605**, 1611–1615.
- 42 Y. Wei, B. Wang, J. Wu, R. Yang and M. L. Dunn, *Nano Lett.*, 2013, **13**, 26–30.
- 43 K. Srinivasu and S. K. Ghosh, *J. Phys. Chem. C*, 2012, **116**, 5951–5956.
- 44 C. Filippi, D. J. Singh and C. Umrigar, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 1994, **50**, 14947–14951.
- 45 J. Qiao, X. Kong, Z.-X. Hu, F. Yang and W. Ji, *Nat. Commun.*, 2014, **5**, 4475.
- 46 K. Kaasbjerg, K. S. Thygesen and K. W. Jacobsen, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 2012, **85**, 115317.
- 47 J. Xi, M. Long, L. Tang, D. Wang and Z. Shuai, *Nanoscale*, 2012, **4**, 4348–4369.
- 48 H. Xie, Y. Qie, M. Imran and Q. Sun, *J. Phys. Chem. A*, 2019, **7**, 14253–14259.
- 49 S. Grimme, J. Antony, S. Ehrlich and H. Krieg, *J. Chem. Phys.*, 2010, **132**, 154104.
- 50 J. Liu, S. Wang, Y. Qie, J. Yu and Q. Sun, *Carbon*, 2018, **140**, 680–687.
- 51 X. Zhang, Z. Yu, S.-S. Wang, S. Guan, H. Y. Yang, Y. Yao and S. A. Yang, *J. Phys. Chem. A*, 2016, **4**, 15224–15231.
- 52 G. Henkelman, B. P. Uberuaga and H. Jónsson, *J. Chem. Phys.*, 2000, **113**, 9901–9904.
- 53 I. M. Oleksandr, L. T. Teck and M. Sergei, *Appl. Phys. Express*, 2013, **6**, 027301.
- 54 V. V. Kulish, O. I. Malyi, M.-F. Ng, P. Wu and Z. Chen, *RSC Adv.*, 2013, **3**, 4231–4236.
- 55 M. Wagemaker, R. van de Krol, A. P. M. Kentgens, A. A. van Well and F. M. Mulder, *J. Am. Chem. Soc.*, 2001, **123**, 11454–11461.
- 56 M. V. Koudriachova, N. M. Harrison and S. W. de Leeuw, *Phys. Rev. Lett.*, 2001, **86**, 1275–1278.
- 57 K. Persson, Y. Hinuma, Y. S. Meng, A. Van der Ven and G. Ceder, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 2010, **82**, 125416.
- 58 A. Van der Ven, M. K. Aydinol, G. Ceder, G. Kresse and J. Hafner, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 1998, **58**, 2975–2987.
- 59 M. E. Arroyo y de Dompablo, A. Van der Ven and G. Ceder, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 2002, **66**, 064112.
- 60 M. K. Aydinol, A. F. Kohan, G. Ceder, K. Cho and J. Joannopoulos, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 1997, **56**, 1354–1365.
- 61 D. Çakır, C. Sevik, O. Gülsen and F. M. Peeters, *J. Phys. Chem. A*, 2016, **4**, 6029–6035.
- 62 H. Kim, D. J. Kim, D.-H. Seo, M. S. Yeom, K. Kang, D. K. Kim and Y. Jung, *Chem. Mater.*, 2012, **24**, 1205–1211.

# Supplementary Materials for **Superflexible C<sub>68</sub>-graphyne as promising anode materials for lithium-ion batteries**

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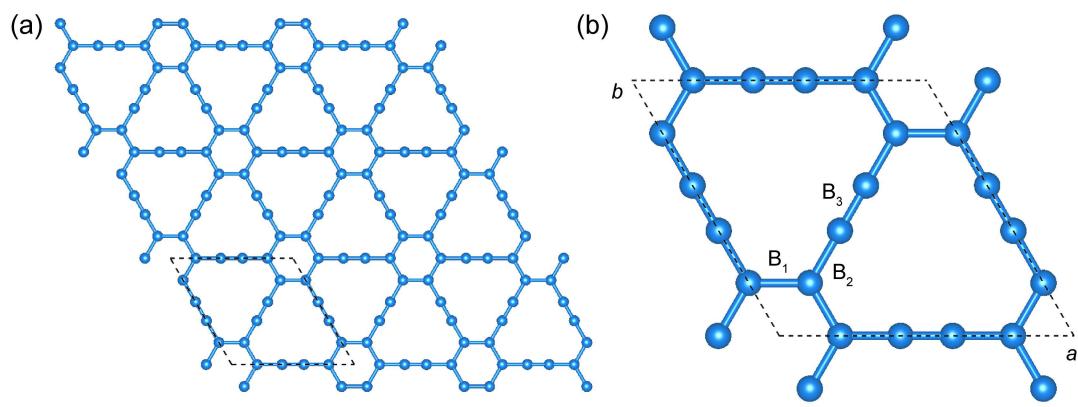
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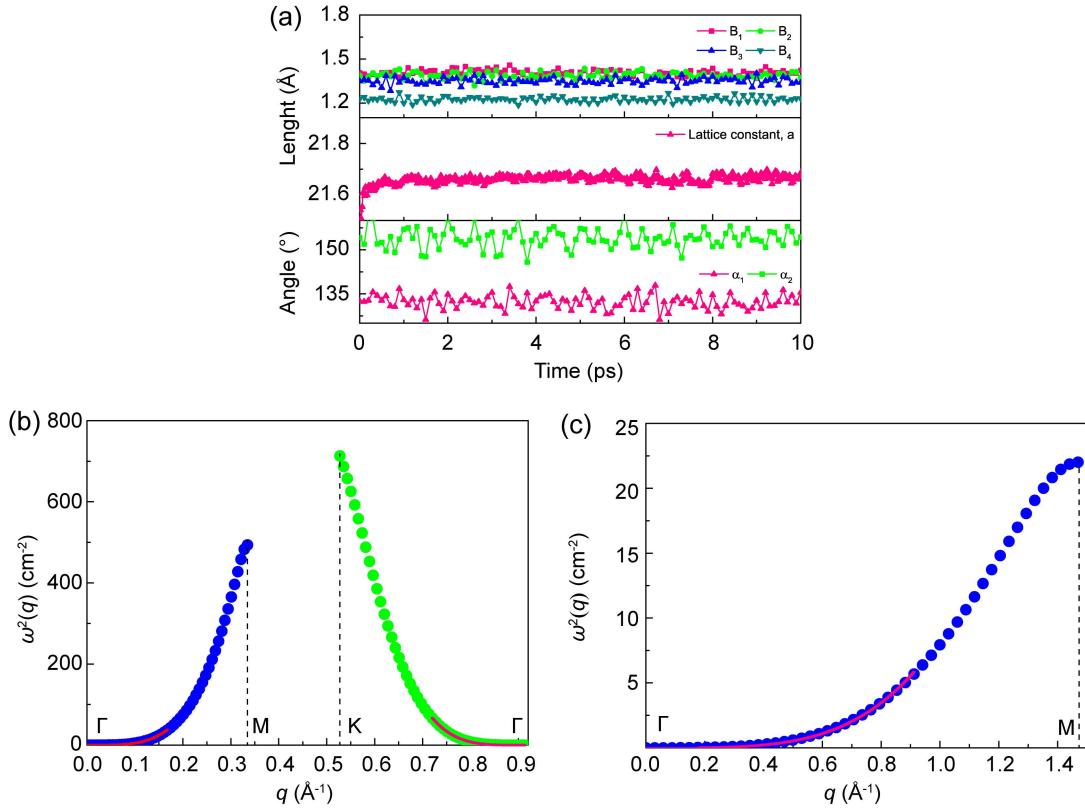
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The Supporting Materials contain

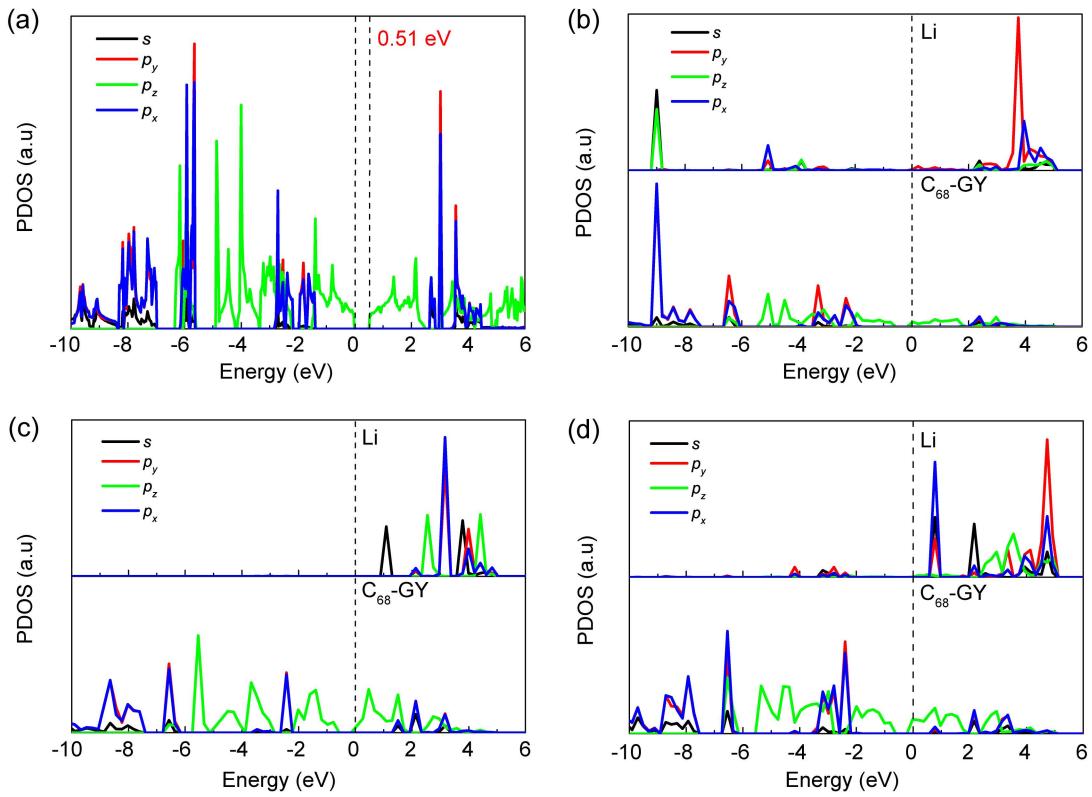
- Supplementary Figures S1-S9.
- Supplementary Tables S1-S2.



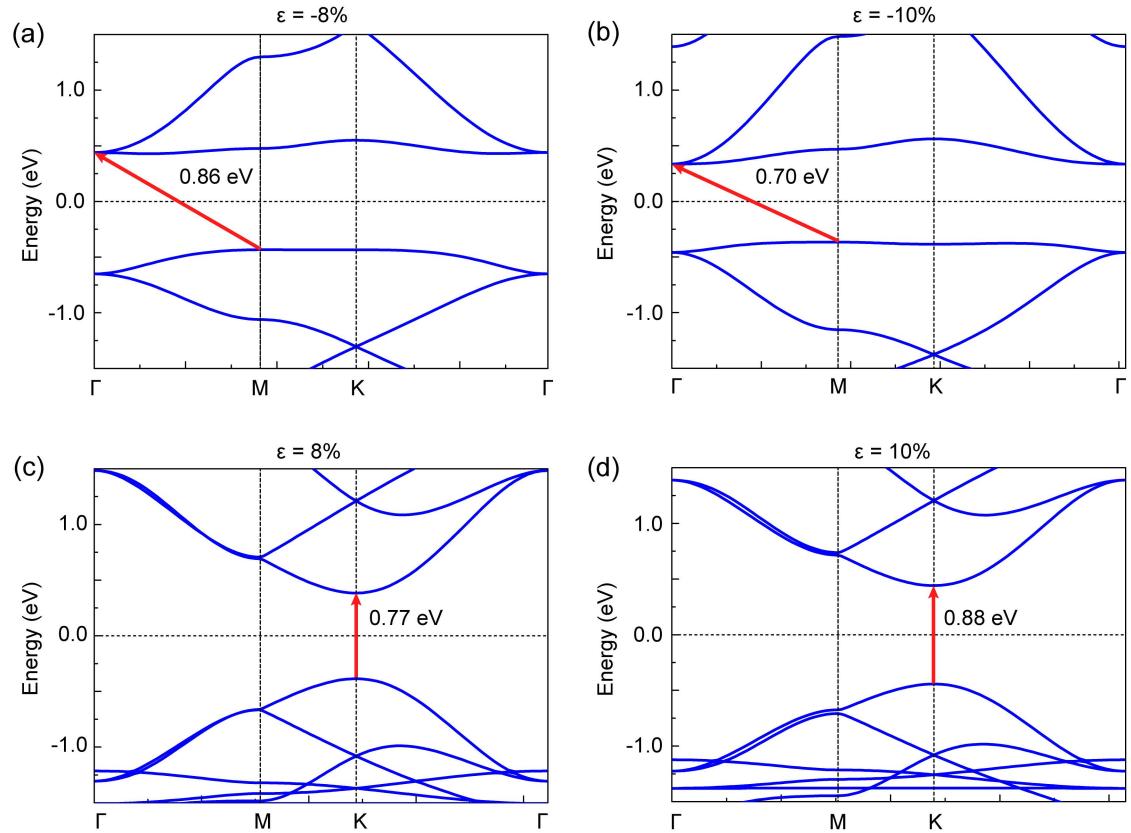
**Fig. S1** (a) Schematic diagram of  $\gamma$ -GY and (b) its primitive cell, different bonds are marked as  $B_{1-3}$ .



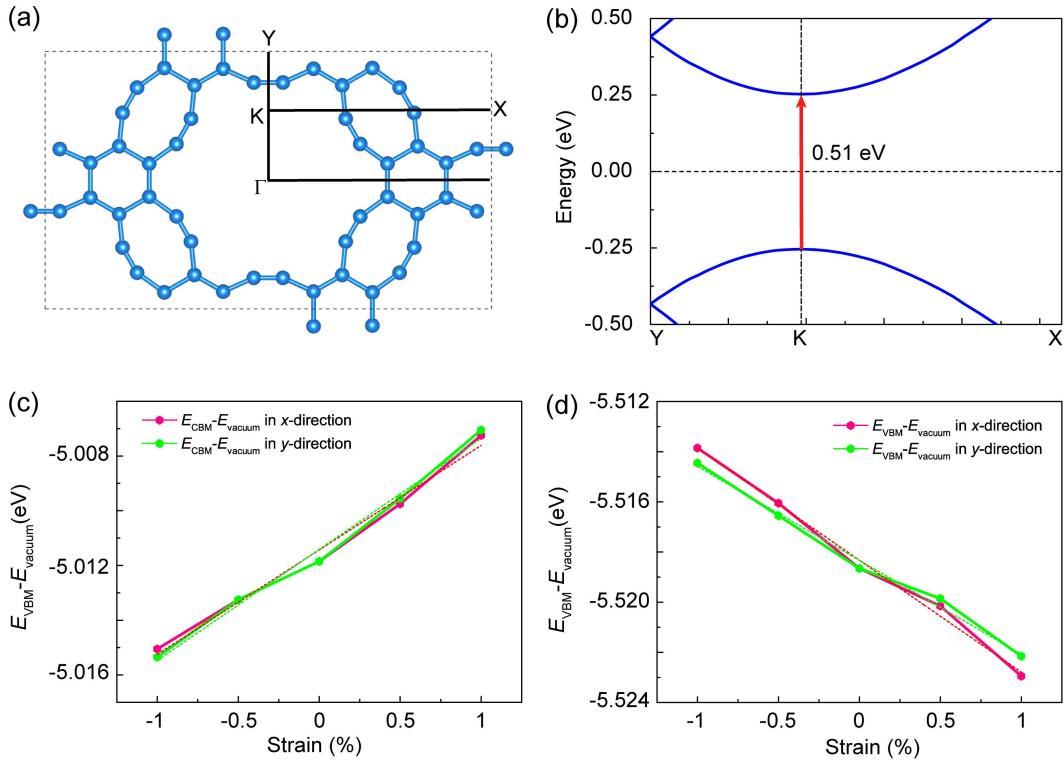
**Fig. S2** (a) The fluctuation of bonds, angles and lattice constant of C<sub>68</sub>-GY during the AIMD simulations. The quadratic dispersion of flexural phonon mode ZA in (b) C<sub>68</sub>-GY and (c) graphene, in which the red lines denote the fitting curves.



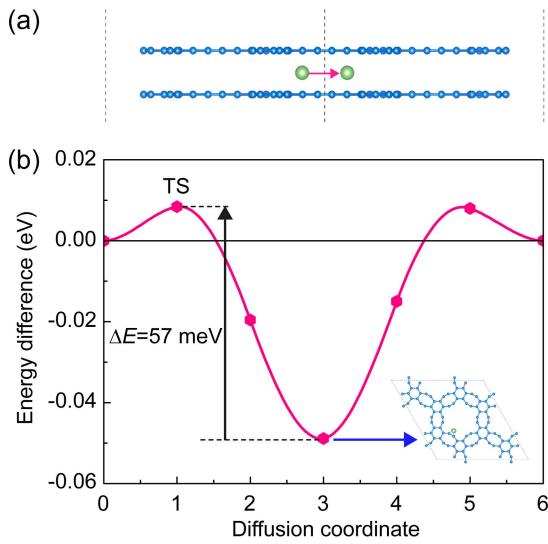
**Fig. S3** Projected density of state (PDOS) of (a) pristine  $C_{68}$ -GY with an adsorbed Li on Site (b) S1, (c) S3 and (d) S4.



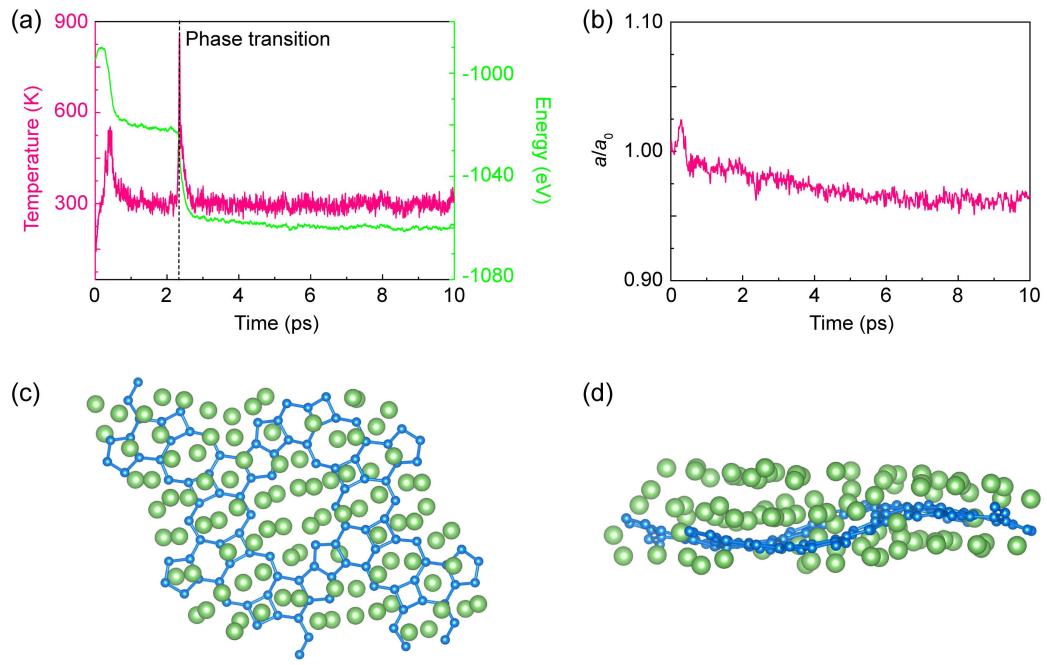
**Fig. S4** Effect of biaxial strain ( $\varepsilon$ ) on the band structures of C<sub>68</sub>-GY.



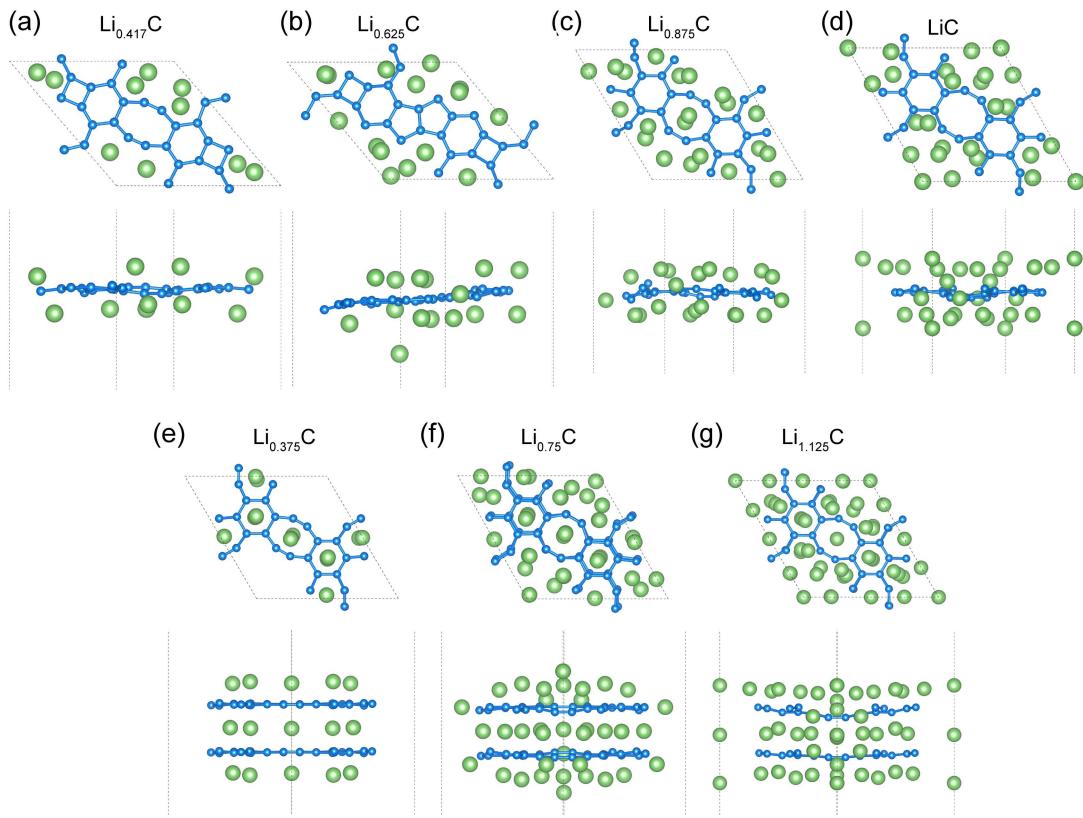
**Fig. S5** (a) The K-path in the Brillouin zone for the calculation of carrier mobilities. (b) The calculated band structure along Y-K-X path at PBE functional level. Band energy shift of (c) CBM and (d) VBM under the strain along  $x$ - and  $y$ -direction. The term  $E_1$  is determined by using  $E_1 = \Delta E/\varepsilon$  to fit the curves in (c) and (d). The dashed lines belong to the fitting lines with respect to  $x$ - and  $y$ -direction, respectively.



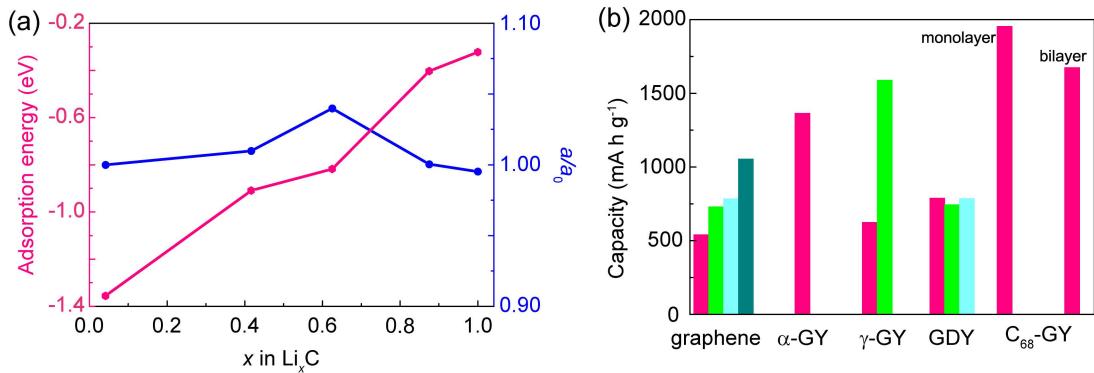
**Fig. S6** (a) Schematics of the diffusion path in bilayer C<sub>68</sub>-graphyne along diffusion path of P1 (side view); (b) the diffusion barrier profile.



**Fig. S7** The fluctuations of (a) temperature and energy in the AIMD simulations of LiC, as well as (b) the lattice changes,  $a/a_0$ ; (c) Top and (d) side views of the snapshots of LiC taken from AIMD simulations. The green and blue spheres represent Li and C atoms, respectively.



**Fig. S8** (a-d) Top and side views of the intermediate configurations with different Li ion concentrations along the minimum formation energy path. (e-g) The considered configurations with varying Li concentrations intercalated in bilayer C<sub>68</sub>-GY.



**Fig. S9** (a) The calculated adsorption energy and lattice change profiles along the minimum energy path of formation energies as shown as green points in **Fig. 6a**; (b) The specific capacity ( $C$ ) of  $\text{C}_{68}$ -GY as anode materials for LIBs, and the comparison with other typical carbon allotropes. The data for graphene,  $\alpha$ -GY,  $\gamma$ -GY and GDY are obtained from **Refs. 1-7**.

**Table S1** The calculated in-plane stiffness  $S$ , Poisson ratio  $\nu$ , tensile strengths  $\sigma_s$  and strain to failure  $\epsilon_s$  of C<sub>68</sub>-GY, and the comparison with other typical carbon allotropes.

Materials	$S$ (N m <sup>-1</sup> )		$\nu$		$\sigma_s$ (N m <sup>-1</sup> )		$\epsilon_s$		$D$ (eV)
	$S_x$	$S_y$	$\nu_x$	$\nu_y$	$\sigma_{sx}$	$\sigma_{sy}$	$\epsilon_{sx}$	$\epsilon_{sy}$	
C <sub>68</sub> -GY	49.4	51.7	0.713	0.714	21.7	14.7	0.32	0.20	0.50
Graphene	350 <sup>8</sup>	350 <sup>8</sup>	0.186 <sup>8</sup>	0.186 <sup>8</sup>	36.7 <sup>8</sup>	40.4 <sup>8</sup>	0.194 <sup>8</sup>	0.266 <sup>8</sup>	1.44~1.46 <sup>9</sup> 10
$\alpha$ -GY	21.98 <sup>11</sup>	21.98 <sup>11</sup>	0.87 <sup>11</sup>	0.87 <sup>11</sup>	12.4 <sup>12</sup>	11.0 <sup>12</sup>	0.178 <sup>12</sup>	0.156 <sup>12</sup>	-
$\beta$ -GY	73.07 <sup>11</sup>	73.07 <sup>11</sup>	0.67 <sup>11</sup>	0.67 <sup>11</sup>	15.7 <sup>12</sup>	12.9 <sup>12</sup>	0.162 <sup>12</sup>	0.130 <sup>12</sup>	-
$\gamma$ -GY	162 <sup>13</sup>	162 <sup>13</sup>	0.429 <sup>13</sup>	0.429 <sup>13</sup>	15.4 <sup>14</sup>	34.4 <sup>14</sup>	0.08 <sup>14</sup>	0.13 <sup>14</sup>	2.69 <sup>14</sup>
GDY	123.1 <sup>15</sup>	123.1 <sup>15</sup>	0.446 <sup>15</sup>	0.446 <sup>15</sup>	-	-	-	-	-
Graph-3-yne	101.8 <sup>15</sup>	101.8 <sup>15</sup>	0.436 <sup>15</sup>	0.436 <sup>15</sup>	-	-	-	-	-
Graph-4-yne	87.7 <sup>15</sup>	87.7 <sup>15</sup>	0.432 <sup>15</sup>	0.432 <sup>15</sup>	-	-	-	-	-

**Table S2** The calculated effective masses for electrons ( $m_e^*$ ) and holes ( $m_h^*$ ) in the direct band structures of C<sub>68</sub>-GY at PBE level with applying various biaxial strain.

Biaxial strain (%)	$m_e^* / m_0$ (K-M)	$m_e^* / m_0$ (K-Γ)	$m_h^* / m_0$ (K-M)	$m_h^* / m_0$ (K-Γ)
-6	0.641	0.298	-0.575	-0.296
-4	0.556	0.278	-0.685	-0.293
-2	0.712	0.271	-0.864	-0.294
-1	0.325	0.199	-0.342	-0.209
-0.5	0.325	0.199	-0.343	-0.210
0	0.326	0.200	-0.345	-0.211
0.5	0.326	0.200	-0.347	-0.212
1	0.327	0.201	-0.350	-0.214
2	0.329	0.203	-0.355	-0.218
4	0.336	0.210	-0.368	-0.228
6	0.347	0.221	-0.386	-0.243
8	0.364	0.238	-0.410	-0.265
10	0.391	0.266	-0.448	-0.300

## References

1. E. Yoo, J. Kim, E. Hosono, H.-s. Zhou, T. Kudo and I. Honma, *Nano letters*, 2008, **8**, 2277-2282.
2. D. Pan, S. Wang, B. Zhao, M. Wu, H. Zhang, Y. Wang and Z. Jiao, *Chemistry of Materials*, 2009, **21**, 3136-3142.
3. H. J. Hwang, J. Koo, M. Park, N. Park, Y. Kwon and H. Lee, *The Journal of Physical Chemistry C*, 2013, **117**, 6919-6923.
4. K. Srinivasu and S. K. Ghosh, *The Journal of Physical Chemistry C*, 2012, **116**, 5951-5956.
5. C. Sun and D. J. Searles, *The Journal of Physical Chemistry C*, 2012, **116**, 26222-26226.
6. H. Zhang, Y. Xia, H. Bu, X. Wang, M. Zhang, Y. Luo and M. Zhao, *Journal of Applied Physics*, 2013, **113**, 044309.
7. S. Zhang, H. Du, J. He, C. Huang, H. Liu, G. Cui, Y. and Y. Li, *ACS Applied Materials & Interfaces*, 2016, **8**, 8467-8473.
8. F. Liu, P. Ming and J. Li, *Physical Review B*, 2007, **76**, 064120.
9. K. N. Kudin, G. E. Scuseria and B. I. Yakobson, *Physical Review B*, 2001, **64**, 235406.
10. Y. Wei, B. Wang, J. Wu, R. Yang and M. L. Dunn, *Nano Letters*, 2013, **13**, 26-30.
11. A. R. Puigdollers, G. Alonso and P. J. C. Gamallo, *Carbon*, 2016, **96**, 879-887.
12. Y. Zhang, Q. Pei and C. Wang, *Applied Physics Letters*, 2012, **101**, 081909.
13. Q. Peng, W. Ji and S. De, *Physical Chemistry Chemical Physics*, 2012, **14**, 13385-13391.
14. S. W. Cranford and M. J. Buehler, *Carbon*, 2011, **49**, 4111-4121.
15. Q. Yue, S. Chang, J. Kang, S. Qin and J. Li, *The Journal of Physical Chemistry C*, 2013, **117**, 14804-14811.