



## Stable configurations and electronic structures of hydrogenated graphyne



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### ABSTRACT

First-principles calculations are performed to investigate dynamical stability of hydrogenated graphyne and its electronic structures. We find that the zero point energy (ZPE) is important in evaluating the stability of hydrogenated graphyne. Based on the results of formation enthalpy, the hydrogenated configuration with only  $sp^3$  carbon atoms (eHH) is more stable than that with each carbon atom passivated by single hydrogen atom (eH). However, the Helmholtz free energy as functions of temperature indicates that eH is more favorable than eHH below 670 K. Based on DFT-based phonon spectrum calculations, the dynamical stability of eHH and eH is confirmed. Of particular interest is that the band-gap feature of graphyne undergoes direct–indirect–direct transition with the increase in the concentration of hydrogen. The results indicate that eHH is favorable for the applications in the field of deep ultraviolet light-emitting devices.

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### 1. Introduction

Carbon never stops inspiring the enthusiasm and imagination of research due to its various allotropes from one to three dimensions. New carbon allotropes, such as fullerene [1], nanotube [2], and graphene [3], have been successfully synthesized and applied in nano-electronics, gas-storage, and materials science. Graphyne, a two dimensional (2D) carbon allotrope with the same symmetry to graphene, is firstly predicted by Baughman et al. [4] in 1987. Graphyne is made up of hexagonal carbon rings and acetylene linkages, i.e., the  $sp^2$ -hybridized C atoms forming hexagons which are joined together by acetylene linkages ( $-C\equiv C-$ ). In graphyne family, new carbon allotropes can be achieved by increasing the alkyne linkages between the hexagon rings. Graphdiyne is the one with butadiene linkages between the hexagon rings. So far, considerable experimental efforts have been devoted to synthesize these unusual materials with the aim at the applications of them in nano-electronic and optoelectronic devices [5–8]. Intriguingly, graphdiyne has been grown on the surface of copper via a cross-coupling reaction using hexaethynylbenzene [9]. Consequently, we can expect the preparation of graphyne because theoretical work has shown that graphyne is energetically more favorable than graphdiyne [10].

Graphyne, analog to graphene, possesses excellent properties, such as small carrier effective mass [10,11], advanced hydrogen storage capacity [12–14], and high carrier mobility at room temperature [15]. In addition, the outstanding mechanical properties [16–18] of the graphyne family guarantee their functional applications. DFT calculations show that the graphyne is semiconductor with direct band gap of 0.52 eV [10], which makes it suitable for preparation of room temperature field effect transistors (FET). To expand the application of graphyne in nanoelectronics and optoelectronics, modulation of its electronic properties is essential. Recent studies have indicated that similar to that of graphene, strain, patterning, and doping are all in force for modulating the electronic properties of graphyne. For instance, the band gap of graphyne can be continuously tuned under uniform strain [11]. When the graphdiyne is doped by BN unit, the band gap can be effectively modulated but the direct-band gap feature of graphdiyne is intact regardless the doping rate [19]. Such characteristics are hoping to be achieved in graphyne. The electronic properties of graphyne can also be tailored by patterning them into nanoribbons. Pan et al. [20] found that both graphyne and graphdiyne nanoribbons are semiconductor and their band gaps decrease with the increase in the width of nanoribbon.

Previous work has shown that hydrogenation is an effective approach to modulate the band gap of graphene [21,22] and even induce its ferromagnetism [23–26]. The graphane, fully hydrogenated graphene, has been successfully synthesized in experiment [27], which manifested that hydrogenation is a practical route for tailoring the electronic and magnetic properties of graphene [28].

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Comparing with graphene, the  $sp$ – $sp^2$  hybridized carbon network of graphyne offers more freedom for hydrogen adsorption. In analogy to the hydrogenated graphene, the hydrogenation should be an effective approach to modulate the electronic properties of graphyne. Using first-principles method, several hydrogenated configurations of graphyne and its family were investigated. Psogiannakis and Froudakis [29] suggested that the “graphbutane” whose carbon atoms are in  $sp^2$  hybridized form in the hexagon rings but in  $sp^3$  hybridized form in the acetylene chains is thermodynamically favorable up to very high temperature through the calculations of free energy by adding  $H_2$  to graphdiyne. Tan et al. [30] found that at low coverage the hydrogen atoms prefer to chemically adsorb on the acetylene carbon atoms. Moreover, the band gap of hydrogenated graphyne is tunable in a wide range from 0.45 eV to 4.43 eV with the change of hydrogen coverage. They also reported that the stable configuration of hydrogenated graphyne is that each carbon atom passivated by single hydrogen atom, they named it graphine [30]; here we named it eH for short. Recently, the counterpart of graphane for hydrogenated graphyne whose carbon atoms in hexagon rings are passivated with single H and those in acetylene chains are passivated by two H atoms is reported by Koo et al. [31]. Such configuration shows only  $sp^3$  hybridized carbon atoms, we named it eHH for short. With the aim to open up the possibility of modulating the electronic structures of graphyne via hydrogenation, it is significant to compare the relative dynamical stability between eH and eHH and study their band structures.

To this end, we performed first-principles calculations to study the dynamical stability of eH and eHH and their electronic structures. The phonon calculations confirm the dynamical stability of the both configurations. On the basis of formation enthalpy, the results show that eHH is more stable than eH. However, the relative stability between eH and eHH is reversed when taking account of zero point energy (ZPE). Furthermore, our band structure calculations reveal that the feature of the band-gap of graphyne undergoes a direct–indirect–direct transition as the increase in the hydrogen coverage, which paves the way for their applications in the field of deep ultraviolet light-emitting devices similar to the case of hexagonal boron nitride (h-BN) [32–34].

## 2. Method and calculation details

We performed first-principles calculations with density functional theory (DFT) implemented in the Vienna Ab Initio Simulation Package (VASP) [35,36]. The projector-augmented wave (PAW) [37,38] method was used for describing interaction between valence electrons and core, and the electron–electron interaction was treated with a generalized gradient approximation (GGA) proposed by Perdew, Burke, and Ernzerhof (PBE) [39]. A kinetic-energy cutoff of 400 eV was selected for the plane wave basis set and a vacuum space of 15 Å was set to avoid the interaction between neighboring images. In the calculations, Gamma centered k-point mesh generated by the Monkhorst–Pack scheme was used for numerical integrations over the Brillouin zone. The k-point was set to  $7 \times 7 \times 1$ ,  $9 \times 9 \times 1$ , and  $11 \times 11 \times 1$  for structure optimizing, total energy, and density of states (DOS) calculations, respectively. All systems were fully relaxed that the energy converges to  $10^{-7}$  eV and the force on each atoms converges to be less than 0.01 eV/Å. The dipole correction [40] was considered to deal with the impact of the variety of potential distribution introduced by the adsorption of hydrogen atom. All parameters adopted to perform calculations were fully optimized.

To measure the dynamic stability of hydrogenated forms of graphyne, we calculate their phonon band structures using the Phonon [41] package applying forces from VASP calculations.

Because the cohesive energy per atom does not provide a suitable measure for evaluating the relative stability between systems with different compositions, we adopt the formation enthalpy [42,43]  $\Delta G$  to qualitatively evaluate the relative stability of the systems studied in present work as,

$$\Delta G = E_{tot} - \sum \chi_i \mu_i. \quad (1)$$

The term  $E_{tot}$  is the cohesive energy per atom of the hydrogenated systems considered here,  $\chi_i$  ( $i$  denote H, C) is the molar fraction of the atoms in the structures and they obey the rule of  $\sum \chi_i = 1$ .  $\mu_i$  is the chemical potential of the constituents at a given state. We choose  $\mu_C$  as the cohesive energy per atom of pristine graphene and  $\mu_H$  is taken as the binding energy per atom of  $H_2$  molecule. Furthermore, we also calculated the Helmholtz free energies as a function of temperature based on the calculated phonon dispersion. The details will be discussed below.

## 3. Results and discussion

### 3.1. Stability of hydrogenated graphyne

The unit cell of graphyne as shown in Fig. 1(a) is adopted as basic model to investigate the properties of hydrogenated systems. Before investigating the hydrogenated systems, we firstly optimized the pristine graphyne. The optimized lattice constants of graphyne is 6.89 Å. The bond length in carbon hexagons is 1.43 Å and the bond lengths along the acetylene chains are 1.41 Å, 1.22 Å and 1.41 Å. On the basis of the symmetry and the bond length, three types of C–C bonds can be significantly found in graphyne: (i) bond AB, as shown in Fig. 1(a), C=C bond joining two adjacent  $sp^2$  hybridized C atoms around carbon hexagon; (ii) bond BC, connecting a  $sp$  hybridized C atom and a  $sp^2$  hybridized C atom; (iii) bond CD, C≡C bond connecting two  $sp$  hybridized C atoms. All the above results are in good agreement with previous reports [10,19,30,29], which also confirms the accuracy of our calculation. The variety of C–C bonds, in particular, the C≡C which contributes to both the perpendicular  $p_z$  and in-planar  $p_x - p_y$   $\pi$  electrons [11], offers more freedoms for the adsorption of hydrogen in graphyne than that in graphene.

Tan et al. [30] reported that the stable configuration of hydrogenated graphyne is the one with one hydrogen atom adsorbing on each carbon atom in an alternate way at two sides of graphyne as displayed in Fig. 1(b), they named it graphine, here, we named it eH for short. They found the lattice constants of eH is 6.91 Å, which is in good agreement with our result 6.85 Å. Our calculations show that the bond length of C–H bond in hexagons is 1.107 Å, which is slightly longer than that in acetylene chains. The carbon atoms passivated by hydrogen atoms move upward or downward perpendicular to the plane of graphyne forming a zigzag structure. There are still C=C bonds in acetylene chains for eH configuration. Very recently, Koo et al. [31] reported a completely hydrogenated form of graphyne, which we named eHH for short as shown in Fig. 1(c). We can obtain eHH configuration by adsorbing single hydrogen to each carbon atom in the hexagons with  $sp^2$  hybridization in alternate way at two sides of the graphyne plane; and binding double hydrogen to each carbon atom in acetylene chains. After optimization, we find that the angle direction of HCH formed at adjacent carbon atoms in acetylene chains are against each other and point to opposite sides of the graphyne plane. In each unit cell of eHH as shown in Fig. 1(c), the angles of HCH formed at the adjacent two carbon atoms in the acetylene chain are equivalent, named as angle 1. In Table 1, we listed the bond lengths of C–H bonds in eHH and the value of angle 1. The value of angle 1 in eHH is 104.652°. The bond lengths of C–H in the hexagons are longer than that in acetylene chains suggesting that the interaction

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