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Exotic Geometrical and Electronic Properties in Hydrogenated Graphyne

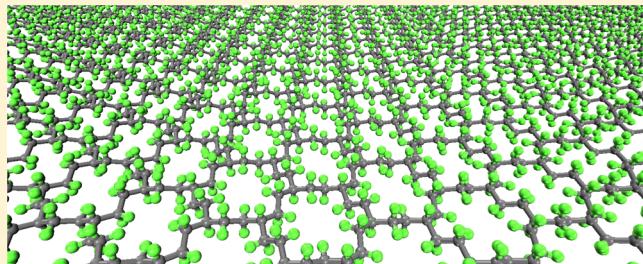
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ABSTRACT: On the basis of first-principles calculations, we present exotic geometrical and electronic properties in hydrogenated graphyne, a 2D material of sp-sp² hybrid carbon networks. Hydrogen atoms adsorbed onto sp-bonded carbon atoms can form both sp²- and sp³-hybridized bonds and can exist in three different geometries: in-plane, out-of-plane, and oblique-plane; this is in sharp contrast to hydrogenated graphene, which has only one hydrogenation geometry. The band gaps of hydrogenated graphyne can vary by ~3 eV as the geometry changes. We also find that change in the hydrogen concentration allows a large band-gap tuning of ~5 eV. Unlike hydrogenated graphene, in which H atoms show a tendency to cluster, H atoms tend to be dispersed in graphyne, making band-gap tuning feasible. These exotic properties in hydrogenated graphyne indicate that the band gap of hydrogenated graphyne can be tailored for new device applications. Furthermore, the composite of fully hydrogenated graphyne is C₁H_{1.75}, which has a hydrogen-to-carbon ratio greater than that of graphane (C₁H₁). This large hydrogen capacity (~13 wt % H) suggests that graphyne also can be used as a high-capacity hydrogen storage material.



INTRODUCTION

Graphene, a two-dimensional (2D) layer of sp²-bonded carbon atoms, has received tremendous attention in recent years because its unique physical properties are suitable for various device-related and energy-related applications.^{1–3} The physical properties of semimetallic graphene can be further extended through chemical functionalization. For example, the hydrogenation of graphene leads to the formation of graphane, a 2D layer of sp³-bonded carbon atoms, in which each carbon atom accommodates a hydrogen atom, forming C₁H₁.⁴ The process of hydrogenation of graphene can be used to tune its electronic band gap for optoelectronic applications.^{5–7} It can also be used as a method of hydrogen storage in the context of the development of hydrogen fuel-cell vehicles due to its large surface area.⁸ In fact, recent experimental and theoretical studies have shown that the band gap of graphene can be tuned through hydrogenation from 0 to ~3.7 eV.^{9–11} However, the H atoms in graphene always tend to form clusters and an inhomogeneous phase generally exists in hydrogenated graphene systems, which may largely downgrade the performance of hydrogenated graphene.¹² On the other hand, it has also been shown that metal-decorated graphitic materials are capable of hydrogen storage when subjected to hydrogen spillover with catalysts.^{13,14}

Graphynes, which consist of 2D sp-sp² hybrid carbon networks,¹⁵ are another type of layered carbon structures that

have recently been predicted to possess unusual electronics properties, for example, coexistence of symmetric and asymmetric Dirac cones.^{16–20} The presence of an asymmetric Dirac cone can lead to electron collimation transport, such as that observed in graphene superlattices.^{21,22} A recent density functional theory (DFT) tight-binding (TB) study¹⁹ showed that the energy band gap of α -graphyne can be opened by AB sublattice symmetry breaking of the honeycomb lattice, in a mechanism similar to that of band-gap opening in graphene. Some graphynes are known to be semiconducting via Kekulé distortion.¹⁹ Because of these unusual physical properties, there are currently increased efforts toward synthesizing graphyne flakes^{23–25} and graphdiyne films²⁶ and flakes,²⁷ thereby providing evidence that the synthesis of graphynes and graphdiyne is possible in the near future. Here, graphdiyne is a 2D material of sp-sp² hybrid carbon networks of benzene rings linked by diacetylene ($-\text{C}\equiv\text{C}-\text{C}\equiv\text{C}-$), similar to graphyne. Another attractive feature of graphynes is that they are sheets of 1D carbon chain networks with the area of the hexagon being considerably larger than that of graphene, thereby providing a larger surface area than graphene. From the application point of view, this low surface density could allow a variety of potential applications for energy storage, such as hydrogen storage and in lithium-ion batteries.^{28–32} For

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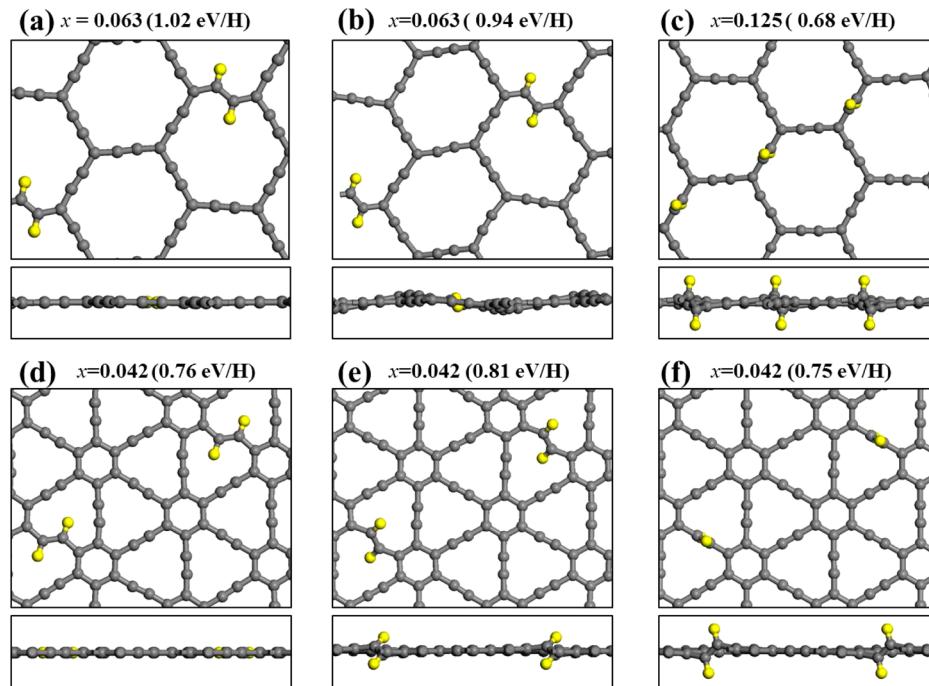


Figure 1. Atomic structures of hydrogenated α -graphyne [γ -graphyne] when a few pairs of H atoms are attached to two adjacent sp-bonded carbon atoms. At the concentration x (C_1H_x), three different adsorption geometries were observed: (a) [(d)] in-plane geometry, (b) [(e)] oblique-plane geometry, and (c) [(f)] out-of-plane geometry.

instance, calcium-decorated graphynes in which calcium atoms act as H_2 attractors can be used as high-capacity hydrogen storage materials due to the high calcium coverage provided by the large surface area of graphyne.²⁸ Furthermore, it has been theoretically demonstrated that multilayer graphynes can be used as high-capacity lithium-ion battery anodes due to the high Li diffusion rate and increased electrical conductivity caused by the metallicity of graphyne.^{31,32}

Since the electronic structure of graphynes has been studied previously, in this study, we focused on the difference between graphene and graphynes and the advantages of utilizing graphynes for specific applications. For example, are graphynes more suitable than graphene for hydrogen storage? For tuning the band gap, can the hybrid sp-sp² bond prevent the hydrogen clustering observed in hydrogenated graphene such that the band-gap tuning can be made more efficient? In this study, we investigated the geometrical and electronic properties of hydrogenated graphynes using first-principles DFT calculations. We found that hydrogen atoms prefer to attach to sp-bonded carbon atom sites, forming sp²-bonded carbon atoms. Hydrogen adsorption in graphyne can exhibit three different geometries: in-plane, out-of-plane, and oblique-plane. This is in sharp contrast to hydrogenated graphene that has only one hydrogenation geometry. The band gaps can vary by ~ 3 eV as the geometry changes. Band-gap tuning by as much as 5 eV is also possible by changing the hydrogen concentration. Additional hydrogenation to sp²-bonded carbon atoms can also occur. Unlike in graphene, where hydrogen atoms prefer to form clusters, hydrogen atoms show a tendency to be dispersed in graphyne, enabling an increased degree of band-gap tuning. These findings demonstrate that the electronic properties of hydrogenated graphyne can be controlled as a function of the hydrogenation geometries and the hydrogen concentration, which can be used for tailoring band gaps for new device applications. Furthermore, the composite of fully hydrogenated

graphyne is $C_1H_{1.75}$, and therefore, the ratio of hydrogen atoms to carbon atoms is greater than that of graphene (C_1H_1). The hydrogen capacity can reach ~ 13 wt % H, thereby surpassing the target of 9 wt % H set by the U.S. Department of the Energy. This indicates that graphynes could be used as high-capacity hydrogen storage materials.

■ CALCULATION METHODS

All of our calculations were performed using the first-principles density functional theory³³ as implemented in the Vienna Ab-initio Simulation Package (VASP) with a projector-augmented-wave (PAW) method.³⁴ The generalized gradient approximation (GGA) in the Perdew–Burke–Ernzerhof scheme³⁵ was used for the exchange-correlation energy functional, and the kinetic energy cutoff was taken to be 400 eV. For calculations of hydrogen adsorption, our model α (γ)-graphyne system was a 2×2 hexagonal supercell containing 32 (48) C atoms. The geometrical optimization of the hydrogenated graphyne was carried out until the Hellmann–Feynman force acting on each atom was less than 0.01 eV/Å. The first Brillouin zone integration was carried out using the Monkhorst–Pack scheme.³⁶ The 4×4 k -point sampling was used for the 2×2 graphyne supercells.

■ RESULTS AND DISCUSSION

To investigate the hydrogenation properties of graphynes, α - and γ -graphynes consisting of hexagonal and triangular lattice units of sp- and sp²-bonded carbon atoms are chosen as representatives because these structures can be used to describe the general tendency of hydrogenation. There are two distinct hydrogenation sites in graphynes, that is, sp-bonded and sp²-bonded carbon atom sites. We find that hydrogen atoms tend to be adsorbed onto sp-bonded carbon atoms rather than onto sp²-bonded carbon atoms. The hydrogenation properties, such as the adsorption geometry and the binding energy, depend

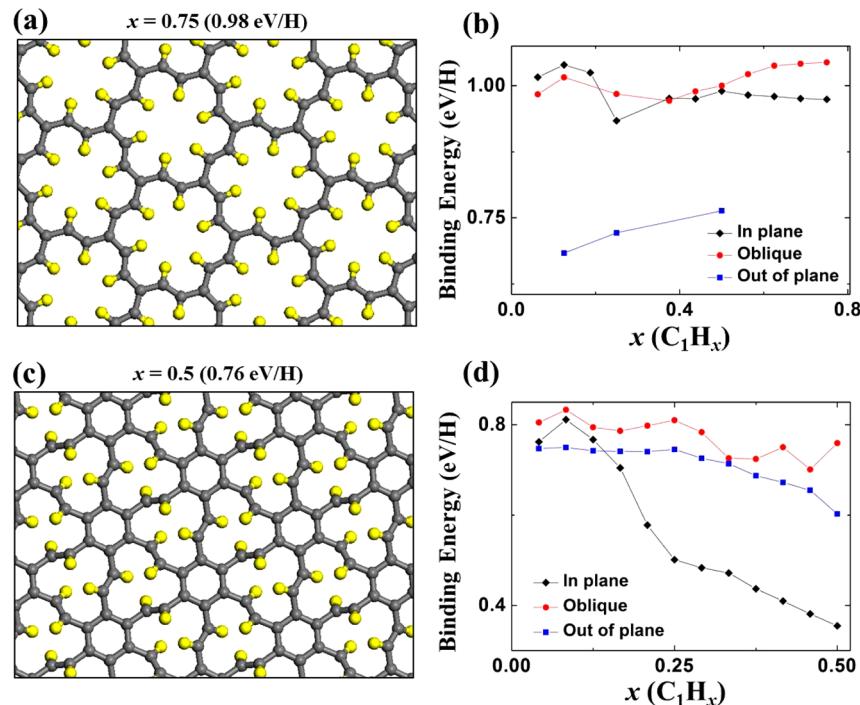


Figure 2. [(a)] Shows the atomic structures of hydrogenated α -graphyne [γ -graphyne] with $x = 0.75$ [$x = 0.5$] for (C_1H_x) when an sp-bonded carbon atom accommodates one H atom. (b) [(d)] Shows the corresponding calculated binding energies (eV/H) of the H atoms as a function of the concentration x . The gray-colored and yellow-colored dots indicate carbon atoms and hydrogen atoms, respectively.

mainly on whether H is adsorbed onto sp-bonded carbon atoms or onto sp^2 -bonded ones, though graphynes exhibit various kinds of phases with different local geometries consisting of hexagons, triangles, and tetragons. We calculated the binding energy of H atoms on a 2×2 graphyne sheet as a function of the H concentration x , where x denotes the concentration in C_1H_x . The calculated binding energy of H atoms is given as

$$E_{\text{bind}}^x(\text{H}) = (E_{\text{C}} + N \cdot E_{\text{H}} - E_{\text{C-H}}^x)/N \quad (1)$$

Here, N denotes the number of attached H atoms per cell for a given value of x , $E_{\text{C-H}}^x$ denotes the total energy of the hydrogenated graphyne with a H-atom concentration of x , E_{C} denotes the total energy of the pristine graphyne, and E_{H} denotes the total energy per H atom of an isolated H_2 molecule in vacuum. For the 2×2 γ -graphyne sheet, $N = 48x$ so that C_{48}H_N can be written as C_1H_x .

We first consider the attachment of a H atom to an sp-bonded carbon atom of α - and γ -graphynes, forming sp^2 hybrid bonds. We denote this hydrogenation as sp^2 -hydrogenation. When a pair of H atoms is attached to two adjacent sp-bonded carbon atoms, the pair of hydrogens prefer to position themselves on opposite sides of the plane, similar to that observed in hydrogenated graphene.¹⁰ However, we found that, unlike in hydrogenated graphene, which exhibits only one local hydrogenation geometry, due to the increased space available in graphynes, there are three possible local hydrogenation geometries in both α -graphyne and γ -graphyne: in-plane, oblique-plane, and out-of-plane. Figure 1 shows the optimized local structures of the three distinct hydrogenation geometries and their relative stabilities. The structures in which each sp-bonded carbon atom accommodates one H atom are somewhat distorted to form an sp^2 -hybridized bond, as shown in Figure 1.

Hydrogenation to γ -graphyne occurs at a more oblique angle from the plane compared to that of α -graphyne (Figure 1b,e).

Next, we investigate the sp^2 -hydrogenation of α - and γ -graphynes as a function of the concentration x , which is the H versus C ratio in C_1H_x . Figure 2 shows the atomic geometries of fully sp^2 -hydrogenated α - and γ -graphynes, where each sp-bonded carbon atom accommodates a H atom, along with the calculated binding energy of the H atoms obtained using eq 1. The composite of the in-plane fully hydrogenated α -graphyne as shown in Figure 2a is $\text{C}_1\text{H}_{0.75}$. For α -graphyne, the oblique-plane hydrogenation configuration was found to be most stable, whereas the out-of-plane adsorption configuration was the least stable. Figure 2c depicts the optimized geometry of the oblique-plane hydrogenated γ -graphyne when the composite is $\text{C}_1\text{H}_{0.5}$. For γ -graphyne, hydrogenation in the oblique plane was found to be most stable, whereas the in-plane adsorption configuration exhibited the least stability. The binding energy of H atoms in the oblique-plane hydrogenation configuration remains somewhat constant over varying values of the concentration x (Figure 2b,d). This may be attributed to the fact that the repulsive interaction between neighboring H atoms in the oblique-plane hydrogenation configuration is reduced compared with the corresponding interaction in the in-plane hydrogenation configuration. For in-plane hydrogenation, we find that the binding energy of H atoms to γ -graphyne decreases as the concentration x increases, whereas it remains constant for α -graphyne. This can be attributed to the fact that the interaction between adsorbed H atoms is repulsive in the case of γ -graphyne, whereas the H–H interaction is very mildly repulsive in α -graphyne, whose hexagon has a significantly larger area than the triangle of γ -graphyne. Whether in the case of α -graphyne or in the case of γ -graphyne, the H binding energy is smaller than that in the case of oblique-plane hydrogenation for all the hydrogen concentrations considered;

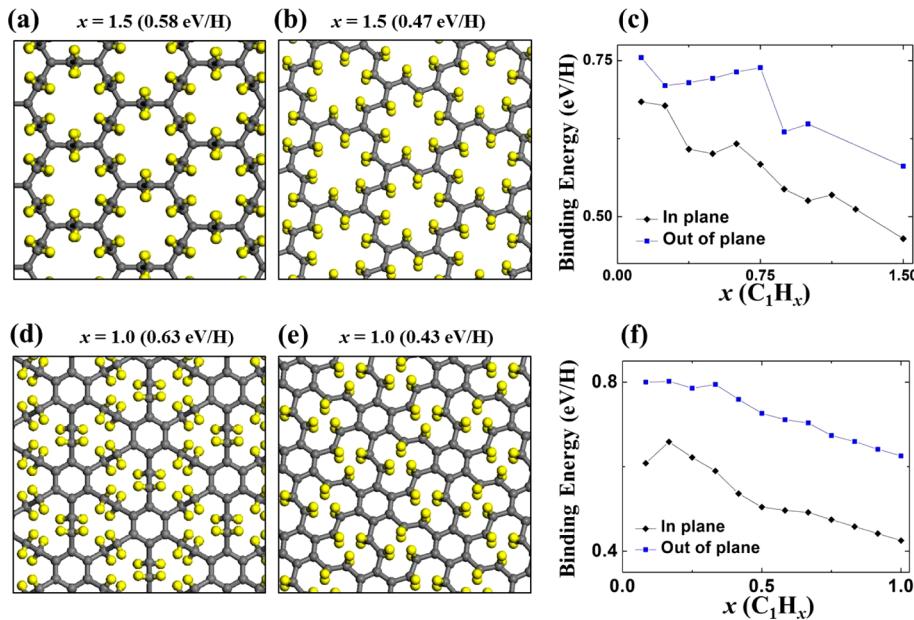


Figure 3. Atomic structures of hydrogenated α -graphyne [γ -graphyne] with a concentration of $x = 1.5$ [$x = 1.0$] when each sp-bonded carbon atom accommodates two H atoms in the (a) [(d)] out-of-plane configuration and (b) [(e)] in-plane configuration. (c) [(f)] Shows the corresponding calculated binding energies of the H atoms (eV/H).

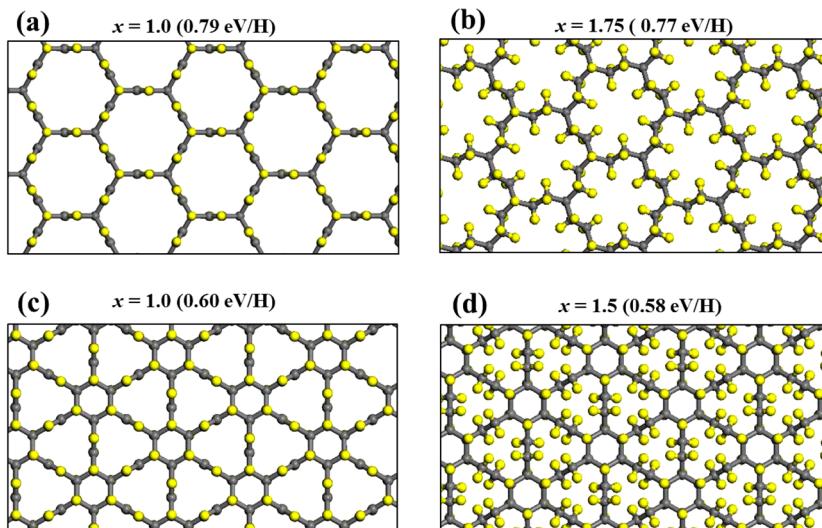


Figure 4. (a) [(c)] Shows the atomic structures of hydrogenated α -graphyne [γ -graphyne] with a concentration of $x = 1.0$ when each carbon atom binds one H atom. (b) [(d)] Shows atomic structures of hydrogenated α -graphyne [γ -graphyne] with a concentration of $x = 1.75$ [$x = 1.5$] when each sp- and sp^2 -bonded carbon atom binds two H atoms and one H atom, respectively.

this is attributed to reduced p_z-p_z hybridization in the out-of-plane configuration (p_z orbitals indicate p orbitals aligned vertically with respect to the graphyne sheet). Another interesting feature is that out-of-plane hydrogenation occurred at higher concentrations only in γ -graphyne, but not in α -graphyne (Figure 2b,d). This indicates that, at higher concentrations, the configurations are unstable in α -graphyne because sp^2 -bonded carbon p_z orbitals do not bond at all. However, at low concentrations, the out-of-plane configuration becomes stable because the p_z orbitals of the sp^2 -bonded carbon atoms can hybridize with the p_z orbitals of the neighboring sp-bonded carbon atoms to which H atoms are not attached. In contrast, the out-of-plane configurations of γ -graphyne are stable regardless of the concentration x because the p_z orbital of an sp^2 -bonded carbon atom can hybridize with

those of the neighboring sp^2 -bonded carbon atoms, thereby satisfying Huckel's rule.

Next, we consider another type of hydrogenation, the attachment of two H atoms to an sp-bonded carbon atom of graphynes, which is denoted as sp^3 -hydrogenation. As in the case of sp^2 -hybridization, pairs of H atoms adsorbed onto two adjacent sp-bonded carbon atoms are energetically preferred. There are two distinct configurations for the sp^3 -hydrogenations: in-plane and out-of-plane hydrogenations. Figure 3 shows the optimized out-of-plane and in-plane geometries of sp^3 -hydrogenated graphynes when maximally hydrogenated, along with the calculated binding energy of H atoms as a function of the concentration $x (\text{C}_1\text{H}_x)$. The out-of-plane hydrogenated configurations are found to be more stable than the in-plane hydrogenated configurations for both α - and γ -

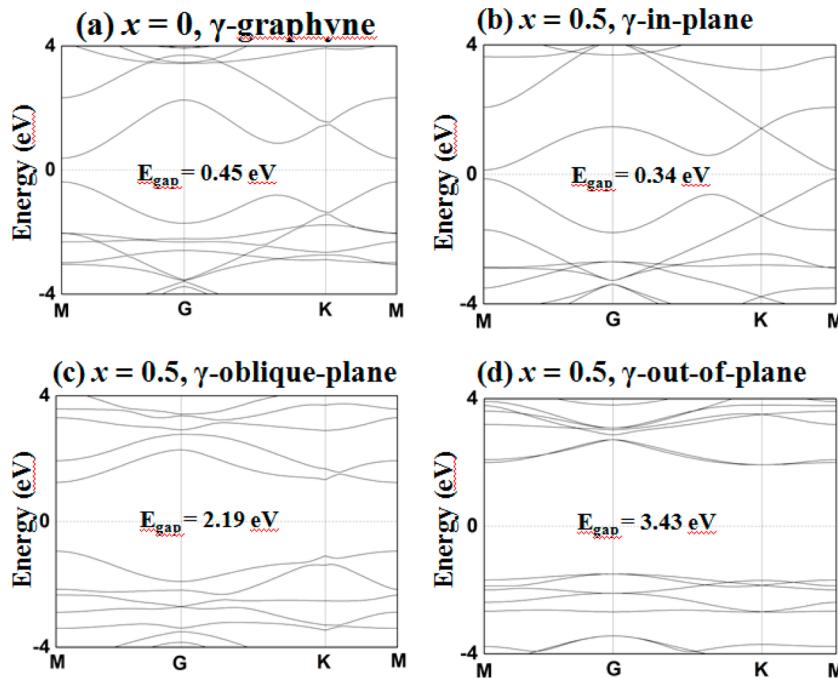


Figure 5. Calculated band structures of sp^2 -hydrogenated γ -graphyne with different hydrogenation geometries: (a) γ -graphyne at $x = 0$, (b) in-plane at $x = 0.5$, (c) oblique-plane at $x = 0.5$, and (d) out-of-plane at $x = 0.5$. The Fermi level is set to zero.

graphynes. For α - and γ -graphynes, sp^3 -hydrogenation of the originally sp -bonded carbon atoms causes distortion of the sp^3 -hybridized bonds, as shown in Figure 3. The composites of fully sp^3 -hydrogenated α - and γ -graphynes are $\text{C}_1\text{H}_{1.5}$ and $\text{C}_1\text{H}_{1.0}$, respectively. We found that, unlike in the case of γ -graphyne, the lattice constant of α -graphyne is decreased by 10% upon sp^3 -hydrogenation. The nearest C–H distance in both sp^2 - and sp^3 -hybridized bonds is 1.1 Å, and the angle of H–C–H is about 103°, which corresponds to the formation of typical sp^3 bonds. The binding energy of H atoms in the case of sp^2 -hydrogenation in α -graphyne is larger than that in the case of sp^3 -hydrogenation. The binding energy of H atoms in sp^3 -hydrogenation of both α - and γ -graphynes decreases as the concentration x increases because the interaction between the adsorbed H atoms is repulsive. In contrast, the H binding energy of sp^3 -hydrogenated γ -graphyne is comparable to that of sp^2 -hydrogenated γ -graphyne.

We also investigated the additional possible hydrogenation of sp^2 -bonded carbon atoms to form sp^3 -hybridized bonds even though hydrogenation to sp -bonded carbon atoms is the general tendency. There is one (six) sp^2 -bonded carbon atom present per hexagon in α -graphyne (γ -graphyne). We explored various configurations of H atoms attached to the sp^2 -bonded carbon atoms, and we found that there is only one stable configuration in which each sp^2 -bonded carbon atom accommodates one H atom on opposite sides of the graphyne sheet in an alternating arrangement. All other configurations or partial hydrogenation of the sp^2 -bonded carbon atoms were found to be unstable; this result is consistent with that observed in the case of hydrogenated graphene (graphane).¹⁰ Figure 4 shows the optimized geometries of hydrogenated α - and γ -graphynes when each of the sp^2 -bonded carbon atoms binds one additional H atom in an alternating order. When additional H atoms are attached to the sp^2 -bonded carbon atoms of the hydrogenated α - and γ -graphynes, $\text{C}_1\text{H}_{1.5}$ and $\text{C}_1\text{H}_{1.0}$, the calculated additional (average) H binding energies of $\text{C}_1\text{H}_{1.5}$

and $\text{C}_1\text{H}_{1.5}$ are 1.91 (0.77) and 0.48 (0.58) eV/H, respectively. Therefore, the composite of fully hydrogenated α - and γ -graphynes can form $\text{C}_1\text{H}_{1.75}$ and $\text{C}_1\text{H}_{1.5}$, respectively, and the ratio of hydrogen to carbon is considerably higher than that of fully hydrogenated graphene (C_1H_1).

For further investigation of the stability of the hydrogenated graphynes, we next compute the formation energy defined by

$$F(x) = E_{\text{C}-\text{H}}^x - E_{\text{C}} - N \cdot E_{\text{H}} - N \mu_{\text{H}} \quad (2)$$

Here, μ_{H} denotes the chemical potential (per H) of H_2 gas. Combined with the definition of the binding energy of H atoms in eq 1, the expression for the formation energy can be reduced to $F(x) = -N(E_{\text{bind}}^x + \mu_{\text{H}})$. When the energy of H atoms in the hydrogenated graphynes is less than the chemical potential of H_2 gas ($-E_{\text{bind}}^x < \mu_{\text{H}}$), the formation energy becomes negative and the hydrogenated graphynes rather than graphynes and H_2 gas are stable at a given temperature and pressure. We note that the binding energy plus the chemical potential is positive at room temperature and ambient pressure ($-E_{\text{bind}}^x < -0.4$ eV and $\mu_{\text{H}} \sim -0.16$ eV³⁷). This indicates that the formation energy is negative, and thus, we conclude that hydrogenation of graphynes occurs. To see whether the hydrogenated graphynes remain stable or transform into a hydrocarbon, we also compared the energy of the structure of the hydrogenated γ -graphyne ($\text{C}_1\text{H}_{1.5}$) with the energy of the structure of benzene (C_6H_6)–acetylene (C_2H_2)–hydrogen (H_2). We confirmed that the structure of the hydrogenated graphyne $\text{C}_1\text{H}_{1.5}$ is energetically lower than the structures of benzene, acetylene, and H_2 molecules by ~0.31 eV/atom. This result shows that hydrogenated graphynes are stable. In addition, we did not find any stress of the hydrogenated graphyne.

Next, we investigate the electronic structure of hydrogenated graphynes as function of different hydrogenation geometries and H concentrations. Figure 5 shows the band structures of γ -graphyne with different H-adsorption geometries at $x = 0.5$. We find that the band gaps of hydrogenated graphynes strongly

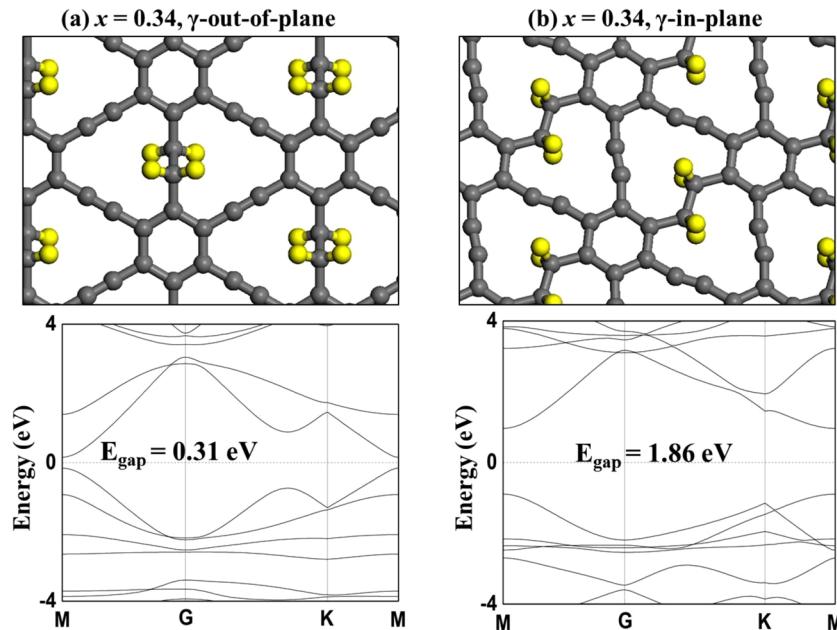


Figure 6. Calculated band structures of sp^3 -hydrogenated γ -graphyne with different hydrogenation geometries: (a) out-of-plane at $x = 0.34$ and (b) in-plane at $x = 0.34$. The Fermi level is set to zero.

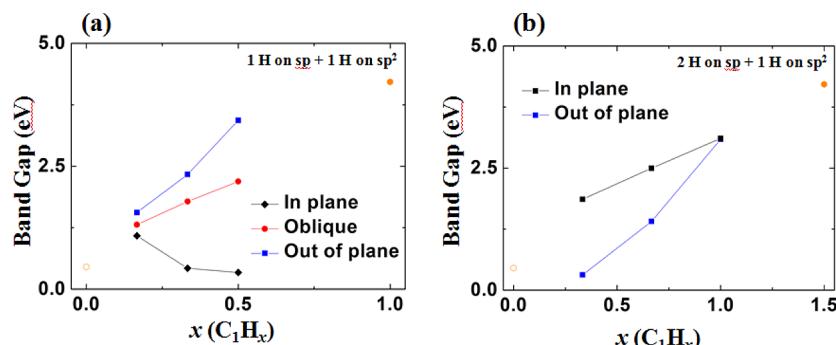


Figure 7. Calculated band gaps (eV) of (a) sp^2 -hydrogenation and (b) sp^3 -hydrogenation to sp-bonded carbon atoms of γ -graphyne as a function of the concentration x . The solid (orange) dot in (a) and (b) indicates band gaps of the structures of additional hydrogenation to sp^2 -bonded carbon atoms.

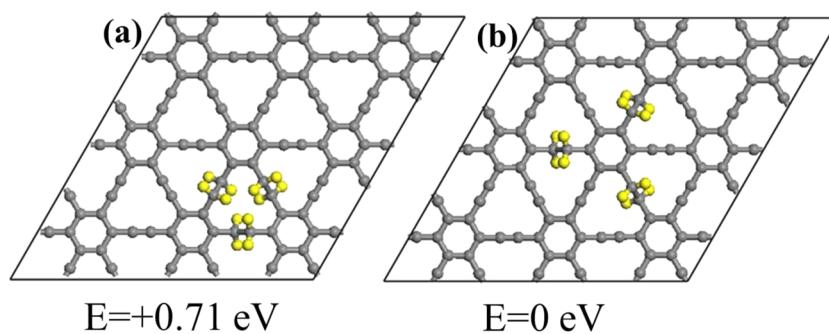


Figure 8. Optimized geometries of γ -graphyne with (a) aggregated H atoms and (b) dispersed H atoms. Aggregated hydrogenated graphyne has an energy higher than that of dispersed hydrogenated graphyne by $0.71 \text{ eV}/12\text{H}$.

depend on the H geometries and concentrations. For sp^2 -hydrogenation, the band gap in hydrogenated γ -graphyne can differ by ~ 3 eV when the geometry changes. The magnitude of the band gaps increases from in-plane to oblique-plane to out-of-plane geometries. Another point of interest is that the band gap of in-plane hydrogenated γ -graphyne at a concentration of $x = 0.5$ is decreased to 0.34 eV from the value of 0.45 eV for

pristine γ -graphyne (see Figure 5a,b). For sp^3 -hydrogenation, the band gap in γ -graphyne at $x = 0.34$ is also tunable by as much as 1.55 eV between the configurations of in-plane and out-of-plane hydrogenation (see Figure 6a,b). The band gap tuning is generated from the distortion of sp-bonded carbon atoms along the in-plane direction via in-plane hydrogenation,

whereas no distortion occurs due to out-of-plane hydrogenation, as shown in Figure 6b.

Figure 7 shows the calculated band gap of hydrogenated γ -graphyne as function of the H concentration as well as the geometry. Using this data, we propose two novel methods to tune the band gap. One method involves controlling the hydrogenation geometry in sp^2 -hydrogenation; the band gap is tunable from 0 to ~ 3 eV as the local geometry changes from the in-plane structure to the oblique-plane and further to the out-of-plane one, as shown in Figure 7a. The tunability of the band gap is due to the degree of p_z-p_z hybridization. This hybridization is reduced as the angle of the attached H atoms with respect to graphyne increases, thereby leading to an increase in the band gap. The other method involves controlling the hydrogenation concentration in sp^3 -hydrogenation, as shown in Figure 7b. The calculated energy band gap of fully hydrogenated γ -graphyne ($C_1H_{1.5}$) is as large as 4.9 eV, which indicates that the band gap of graphyne can be tuned by ~ 4.5 eV as the concentration varies because of the removal of p_z orbitals. This is the same mechanism that operates as regards band gap tunability in hydrogenated graphene.⁹ However, H atoms tend to cluster in graphene,^{11,12} and this can cause difficulties in tuning the band gap under practical conditions. In contrast, H atoms tend to disperse in graphynes (as shown in Figure 8) because the H atoms repel each other (the H binding energy decreases as the concentration increases, as shown in Figure 3c,f). Thus, a broad and reliable tuning of the energy band gap for device applications can be achieved via the hydrogenation of graphyne. For tuning the band gap via the geometry method, the transformation of the H geometry from the oblique-plane structure to the in-plane one is potentially achievable. The geometry transformation may be achieved by applying perturbations, such as uniaxial or biaxial strains, to graphynes. In this light, further studies on band-gap tuning by mechanical deformations will be necessary.

Another possible application of graphyne is high-capacity hydrogen storage. The gravimetric capacity of fully hydrogenated α -graphyne ($C_1H_{1.75}$) and γ -graphyne ($C_1H_{1.5}$) can reach 12.8 and 11.2 wt %, respectively; these values are considerably larger than the target (9 wt %) set by the U.S. Department of Energy as regards the development of hydrogen fuel cells. In addition, the hydrogen surface density for the configurations of $C_1H_{1.75}$ for α -graphyne and $C_1H_{1.5}$ for γ -graphyne is estimated to be 3.3×10^{15} and $3.8 \times 10^{15} \text{ cm}^{-2}$, respectively; these values are comparable to the hydrogen surface density value of $3.8 \times 10^{15} \text{ cm}^{-2}$ for graphane (C_1H_1). In our study, we also considered the possibility of hydrogen spillover in graphynes using Pt catalysts. A recent study⁸ on hydrogen spillover in graphene using Pt catalysts provides the thermodynamic requirements for hydrogen spillover; the energy of H atoms attached to graphene should be less than their energy of attachment to Pt catalysts, which, in turn, is less than the chemical potential of H_2 gas. Since the energy of H atoms in a Pt_4 cluster ranges from ~ -0.6 to ~ -0.1 eV/H and the chemical potential of H_2 gas is ~ -0.16 eV/H at room temperature, the binding energy of H atoms attached to graphyne is suitable for hydrogen storage via the process of hydrogen spillover using Pt catalysts. Therefore, we believe that hydrogen spillover in graphynes is possible. However, since Pt clusters are expected to be strongly attached to graphyne, in realistic applications, the hydrogen storage capacity of ~ 13 wt % could be slightly smaller than that we estimated.

Finally, we discuss a recent DFT study³⁸ carried out by Psolfiannakis et al. on the hydrogenation of graphdiyne. The symmetry of graphdiyne is the same as that of γ -graphyne. Psolfiannakis et al. found that the stable geometries of hydrogenated graphdiyne are graphdiene (each sp -bonded carbon atom accommodates one H atom) and graphbutane (each sp -bonded carbon atom accommodates two H atoms). The local formation of hydrogenated graphdiyne (i.e., graphiene) is similar to that of the oblique-plane (out-of-plane) hydrogenated γ -graphyne. However, Psolfiannakis et al. did not consider additional hydrogenation to sp^2 -bonded carbon atoms that appear in graphynes. We believe that hydrogenation to sp^2 -bonded carbon atoms can occur in graphdiyne also, and further, the hydrogenated configuration may be thermodynamically stable. In another DFT study,³⁹ Tan et al. performed hydrogenation to γ -graphyne and estimated the composite of C_1H_1 . Basically, Tan et al. only considered the attachment of a single H atom per carbon atom of γ -graphyne. The estimated composite of hydrogenated γ -graphyne was C_1H_1 , which is lower by 50% than that ($C_1H_{1.5}$) of our calculations because Tan et al. did not consider the sp^3 -hydrogenation to sp -bonded carbon atoms. Furthermore, band-gap tuning was only considered by the change of the H concentration and the H clustering issue was not treated.

CONCLUSION

In conclusion, we performed the first-principles DFT calculations on hydrogenated graphynes to investigate their geometrical and electronic properties. The geometrical and electronic properties of hydrogenated graphynes are in sharp contrast to those of hydrogenated graphene. Band gaps were found to be broadly tunable by ~ 3 eV through the local geometrical change of the hydrogenation and by ~ 5 eV through changes in the H concentration. Because, unlike graphene, clustering of hydrogen on graphyne is not favorable, band-gap tuning for specific device applications is feasible. In addition, the stable composite of fully hydrogenated graphyne was $C_1H_{1.75}$, corresponding to ~ 13 wt % H. The H binding energy value can facilitate hydrogen storage by spillover using Pt catalysts. Our results suggest that, for tailoring energy band gaps for device applications and for high-capacity hydrogen storage, the use of graphyne could prove more advantageous than graphene.

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Notes

The authors declare no competing financial interest.

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