

# Tailoring the Electronic Band Gap of Graphyne

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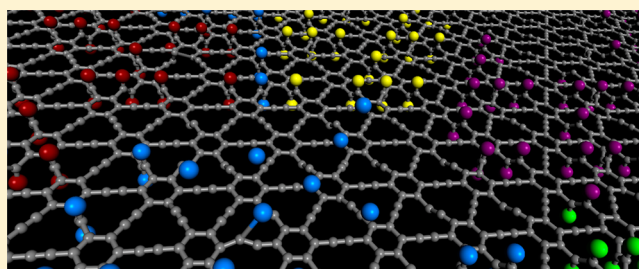
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**ABSTRACT:** We report a first-principles study on tuning the electronic band gap of graphyne, consisting of two-dimensional  $sp-sp^2$  hybrid carbon atoms, by chemical functionalization. Halogen atoms form a  $sp^2$  hybridization with  $sp$ -bonded carbon atoms. This is in sharp contrast to the adsorption of halogen atoms onto graphene: fluorine atoms on graphene form  $sp^3$  bonds, while chlorine, bromine, and iodine atoms do not form any bond to graphene. The band gaps of graphyne increase by  $\sim 3$  eV as the halogen concentration varies, comparable to the  $\sim 3.4$  and  $\sim 2.7$  eV engineered band gaps of graphene by hydrogenation and fluorination, respectively. We also find that the mixture adsorption of hydrogen and halogen atoms is favorable compared with the segregation of the hydrogen-attached phase and the halogen-attached one and that the band gaps are tunable by  $\sim 1.5$  eV as the hydrogen–halogen concentration varies. We also consider  $sp^3$  hybrid bonds by halogenation to  $sp$ -bonded carbon atoms.



## INTRODUCTION

Graphene, a two-dimensional (2D) atomic layer of  $sp^2$ -bonded carbon atoms, has received a great deal of attention because of its unique electronic properties, such as the Dirac cone structure and high electron mobility.<sup>1–3</sup> Because of its metallicity, various methods have been devised for opening the band gap for applications in 2D device materials. For example, hydrogenation and fluorination of graphene were theoretically proposed to modify the band gap up to  $\sim 3.4$  and  $\sim 2.7$  eV, respectively.<sup>4–6</sup> Recent experimental studies confirmed that the band gap of graphene can be opened by hydrogenation<sup>7</sup> or fluorination.<sup>8</sup> However, H or F atoms on graphene tend to aggregate with each other, thereby making it difficult to achieve band gap tuning (or engineering) of graphene by segregation.<sup>9–13</sup>

Graphyne, a carbon allotrope of layered carbon structures consisting of  $sp-sp^2$  hybrid carbon atoms,<sup>14</sup> was predicted to have intriguing electronic properties, such as the coexistence of symmetric and asymmetric Dirac cones.<sup>15–17</sup> The asymmetric Dirac cone can allow electrons to flow in a preferred direction. It was demonstrated theoretically that the energy band gap of graphyne can be opened by an AB sublattice symmetry breaking of the honeycomb lattice.<sup>18</sup> The  $\gamma$ -graphyne is known to have intrinsic band gaps by Kekule distortion.<sup>18</sup> This presents the possibility of applications for new 2D device materials. On the other hand, its porous structure and large surface area may allow for a variety of potential applications in

energy storage, such as hydrogen storage and in lithium-ion batteries.<sup>19–23</sup> There have been experimental efforts to synthesize graphyne flakes<sup>24–26</sup> and graphdiyne films<sup>27</sup> and flakes,<sup>28</sup> providing evidence that the synthesis of graphyne and graphdiyne is possible.

In a previous paper,<sup>29</sup> we studied the attractive geometrical and electrical properties of hydrogenated graphyne and found that no clustering of hydrogen atoms on graphyne took place. This implies that adjustment of the graphyne band gap can be achieved by adsorption of other elements without segregation to disturb the engineering, as in the case of graphene. In this paper, we propose that the electronic properties of graphyne are also adjustable by halogenation, which may be easier to handle. For example,  $XeF_2$  is known to be usable for the fluorination of graphene and to adjust its electronic properties.<sup>8</sup>

Herein, we investigate the band gap tunability of graphyne by halogenation. The halogen atoms preferentially adsorb on the  $sp$ -bonded carbon atoms to form  $sp^2$  bonds, which is in sharp contrast to the adsorption on graphene, where only fluorine atoms attached to graphene form  $sp^3$  hybridized bonds, while chlorine, bromine, and iodine atoms on graphene do not form any hybrid bonds.<sup>30</sup> We also investigate the band gaps of the halogenated graphyne as a function of the concentration of

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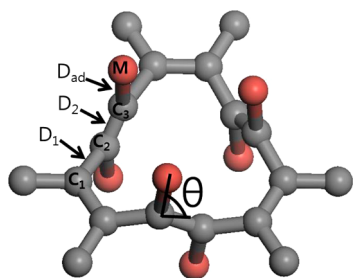
halogen atoms. The band gaps are tunable to  $\sim 3$  eV as the halogen concentration varies, comparable to band gap tuning by  $\sim 3.4$  and  $\sim 2.7$  eV by hydrogenation and fluorination of graphene, that is,  $C_1H_1$  and  $C_1F_1$ , respectively.<sup>4–6</sup> The mixture adsorption of hydrogen and halogen atoms on graphyne is also studied. We find that the mixed adsorption is favorable in comparison to segregation into two phases and that the band gaps are tunable up to  $\sim 1.5$  eV as the halogen–hydrogen concentration varies. Our results provide evidence that the band gap of graphyne can be tailored for new 2D device applications.

## CALCULATION METHODS

Using density functional theory (DFT)<sup>31</sup> and working from first principles, we developed and implemented our calculations in the Vienna Ab Initio Simulation Package (VASP) with a projector-augmented-wave (PAW) method.<sup>32</sup> For the exchange correlation energy functional, the generalized gradient approximation (GGA) was employed in the Perdew–Burke–Ernzerhof (PBE) scheme<sup>33</sup> as well as the Heyd–Scuseria–Ernzerhof (HSE06) scheme,<sup>34</sup> and the kinetic energy cutoff was taken to be 400 eV. For calculations of halogen adsorption, our model of  $\gamma$ -graphyne was a  $1 \times 1$  hexagonal cell containing twelve carbon atoms. Geometrical optimization of the hydrogenated graphyne was carried out until the Hellmann–Feynman force acting on each atom was smaller than 0.01 eV/Å. The first Brillouin zone integration was performed using the Monkhorst–Pack scheme.<sup>35</sup> We utilized  $8 \times 8$   $k$ -point sampling for the  $1 \times 1$  graphyne cell, which is accurate enough based on our test calculations.

## RESULTS AND DISCUSSION

Although graphynes have various types of phases with different local geometries consisting of hexagons, triangles, and tetragons, we chose the most energetically stable phase,  $\gamma$ -graphyne. Here, for ease of use, we denote  $\gamma$ -graphyne as simply “graphyne.” In the halogen family, we chose fluorine (F), chlorine (Cl), bromine (Br), and iodine (I), where the halogen atom is denoted by M. There are two distinct attachment sites on graphyne, that is,  $sp$ -bonded and  $sp^2$ -bonded carbon atom sites. We found that the adsorbate atoms preferentially bind to  $sp$ -bonded carbon atoms rather than to  $sp^2$ -bonded carbon atoms and that in adsorption of an alternative pair one halogen atom is attached above the graphyne plane and the other under the plane, as shown in Figure 1. This alternating pair adsorption



**Figure 1.** Atomic structure of halogen atoms adsorbed on graphyne when pairs of halogens are attached to two adjacent  $sp$ -bonded carbon atoms. The gray-colored and red-colored spheres represent carbon and halogen atoms, respectively.  $D_1$ ,  $D_2$ , and  $D_{ad}$  indicate the  $C_1$ – $C_2$  bond length, the  $C_2$ – $C_3$  bond length, the  $C_3$ –M bond length, and  $\theta$  is the angle between the C–M and the plane of the sheet, respectively.

is the most stable because of reduced repulsive interaction between the halogen atoms compared with the other configurations due to the longer M–M distance in the alternative configuration. This is consistent with the preference for hydrogen attachments on graphyne.<sup>29</sup>

We performed calculations on the adsorption of halogen atoms on the  $sp$ -bonded carbon atoms. In contrast to the hydrogenation of graphyne, where three adsorption geometries of in-plane, oblique-plane, and out-of-plane were found,<sup>29</sup> only out-of-plane adsorption is found to be stable in the halogenation of graphyne. This difference is associated with steric effects in the triangle from the larger ionic radii of halogen atoms; the ionic radii of the F, Cl, Br, and I ions are 1.33, 1.74, 1.96, and 2.20 Å, respectively. The bond length between the C–M atoms is found to increase as the atomic number of the halogen atom increases: the calculated C–M bond lengths are 1.37, 1.74, 1.92, and 2.14 Å for the C–F, C–Cl, C–Br, and C–I bonds, respectively. These lengths are much longer than the C–H bond length (1.1 Å) in hydrogenated graphyne. Two different bond lengths between  $sp$ -bonded carbon atoms were found and the angle between the C–M bond and the plane of the sheet is almost  $90^\circ$ , as listed in Table 1.

**Table 1.** Calculated Bond Lengths ( $D_1$ ,  $D_2$ , and  $D_{ad}$ ) and Angles for Hydrogenated or Halogenated Graphyne<sup>a</sup>

structures	$D_1$ (Å)	$D_2$ (Å)	$D_{ad}$ (Å)	$\theta$ ( $^\circ$ )
$C_1H_{0.5}$ -oblique	1.50	1.36	1.10	44
$C_1F_{0.5}$	1.50	1.34	1.37	83
$C_1Cl_{0.5}$	1.51	1.35	1.74	84
$C_1Br_{0.5}$	1.50	1.34	1.92	84

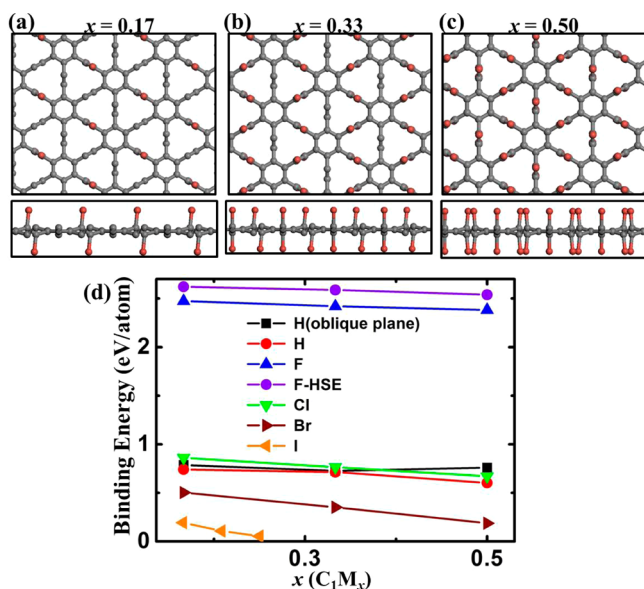
<sup>a</sup> $D_1$ ,  $D_2$ , and  $D_{ad}$  are shown in Figure 1.

We studied how the adsorption of halogen atoms affected the band structure as the concentration increased. The binding energy of the halogen atoms on graphyne was calculated as a function of  $x$ , the concentration in  $C_1M_x$ . The calculated binding energy of the halogen atoms is defined as

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

where  $N$  is the number of attached M atoms per cell for a given  $x$ ,  $E_{C-M}^x$  is the total energy of the halogenated graphyne with an  $x$  concentration of M atoms,  $E_C$  is the total energy of the pristine graphyne, and  $E_M$  is the total energy per M atom of an isolated  $M_2$  molecule in a vacuum. Figure 2 displays the optimized atomic geometries of the out-of-plane halogenated graphyne at  $x = 0.17$ , 0.33, and 0.50, where the atoms are attached to the  $sp$ -bonded carbon atoms. However, iodine atoms were found to continue to attach to graphyne until the concentration reaches 0.25, while the adsorption process above a concentration of 0.25 is endothermic, as shown in Figure 2d. At  $x = 0.50$ , the calculated binding energies are 0.60, 2.38, 0.67, and 0.19 eV/atom for H, F, Cl, and Br atoms, respectively. We found that the changes in binding energies were very small as the concentration varied, indicating that the repulsive interaction between halogen atoms was small. We note that the distance between halogen atoms was greater than  $\sim 3.5$  Å. This leads us to conclude that the clustering of the halogen atoms is not energetically preferable, making band gap tuning possible.

We analyzed the electronic structures of halogenated graphyne. According to our DFT calculations, the energy



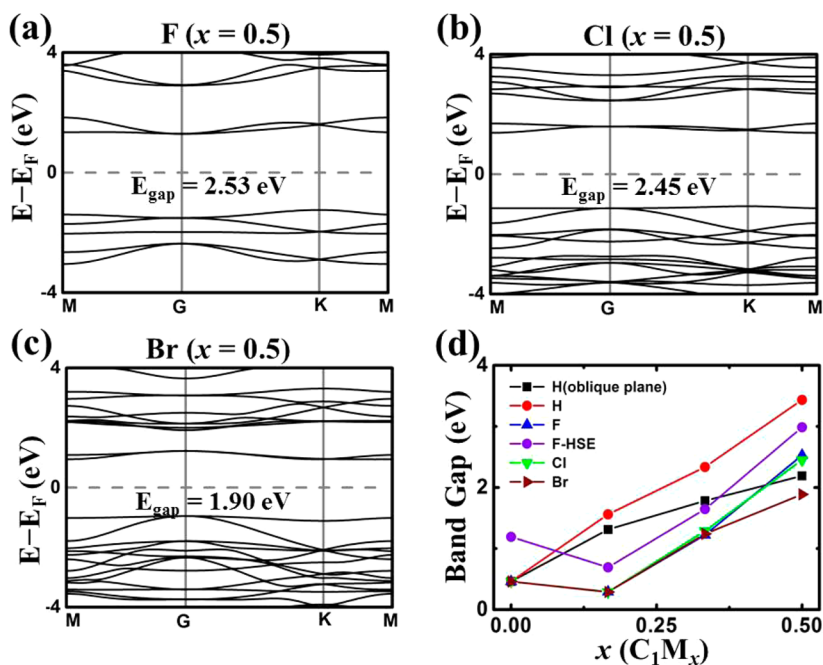
**Figure 2.** Atomic structures of halogen atoms adsorbed on graphyne when pairs of halogens are attached to two adjacent sp-bonded carbon atoms at the concentrations (a)  $x = 0.17$ , (b)  $x = 0.33$ , and (c)  $x = 0.50$ , where  $x$  is defined from  $C_1M_x$  and  $M$  denotes hydrogen or halogen atoms. (d) The calculated binding energies of the attached atoms as a function of the concentration  $x$ .

band gaps of graphyne by adsorption of F, Cl, and Br atoms at an  $x = 0.5$  concentration are 2.53, 2.45, and 1.90 eV, respectively, as shown in Figure 3a–c. The band gap of the hydrogenated graphyne was also computed for comparison. The band gaps depend on whether hydrogen or halogen atoms are bonded to the graphyne because of the difference in the adsorption geometry (whether out-of-plane or oblique-plane). The degree of band gap tuning is  $\sim 1.53$  eV as the type of atoms changes from hydrogen to halogen atoms, and  $\sim 2.5$  eV as the

concentration of halogen atoms increased, as shown in Figure 3d. The band gaps increase as the adsorbate concentration increases, regardless of the type of the adsorbate. However, the band gap tuning is negligible as regards the type of halogen atoms; only hydrogen atoms affect the band gap tuning. Since hybrid functional can give the improved electronic band gaps,<sup>36</sup> we performed hybrid functional calculations using the HSE on the fluorinated graphyne. The band gaps with the HSE are larger than those with the PBE by 0.45 eV at the  $x = 0.5$  concentration as shown in Figure 3d. In addition, the binding energies of the F atoms with the HSE also are slightly larger than those with the PBE by  $\sim 0.15$  eV/F, as shown in Figure 2d. For more accurate energy band gaps, an independent study of many-body effects such as GW will be necessary.

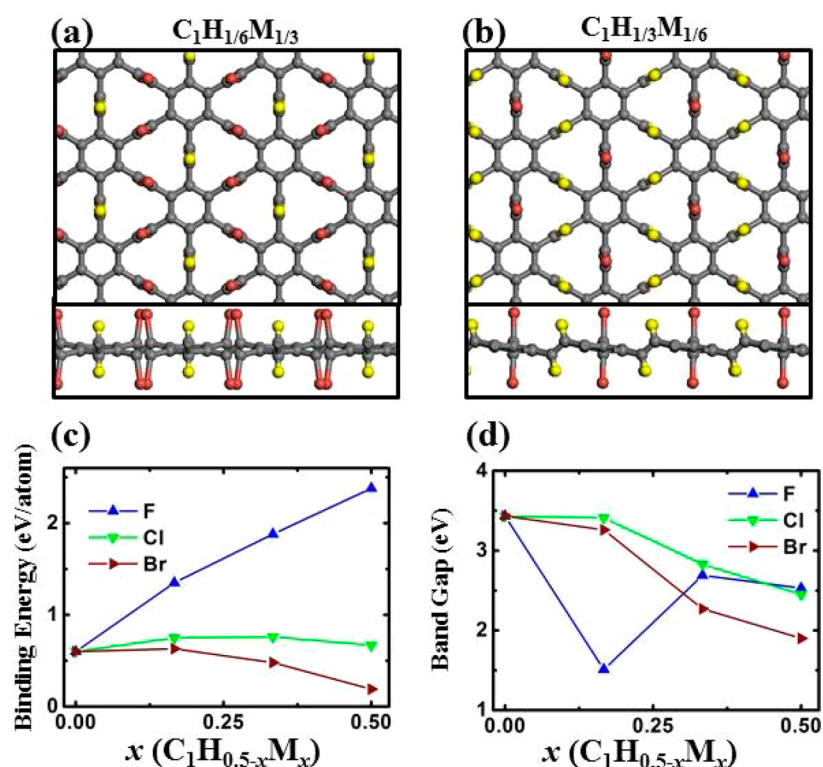
Finally, we examined the mixture adsorption of halogen–hydrogen atoms as the band gap tuning by the mixture is expected to be significant due to large band gap changes between hydrogenated and halogenated graphynes. We found that hydrogen and halogen atoms preferentially attach to adjacent sp-bonded carbon atoms on each side as presented in Figure 4a,b. The calculated binding energies of the adsorbed atoms are 1.88, 0.76, and 0.48 eV/atom for hydrogen and halogen concentrations of  $C_1H_{1/6}F_{1/3}$ ,  $C_1H_{1/6}Cl_{1/3}$ , and  $C_1H_{1/6}Br_{1/3}$ , respectively (Figure 4c). These values are slightly larger than or equal to the 1.86, 0.75, and 0.48 eV/atom values calculated from the binding energies of the structures of  $C_1H_{1/2}$  and  $C_1M_{1/2}$ . This may be attributed to increased distance between the adsorbed atoms. In the case of the H–F combination, the H–F distance is 3.75 Å, while in the pure F case, the F–F distance is 3.55 Å, so that the binding energy of the H–F mixture adsorption increases because of the reduced repulsive interaction between H and F atoms.

The configuration entropy generated from the different H–M geometrical configurations of  $C_1H_{0.5-x}M_x$  is given by  $S = -k_B[x \log x + (1 - x) \log(1 - x)]$ , so that a  $-TS$  term is added to the Helmholtz free energy. Therefore, the mixture

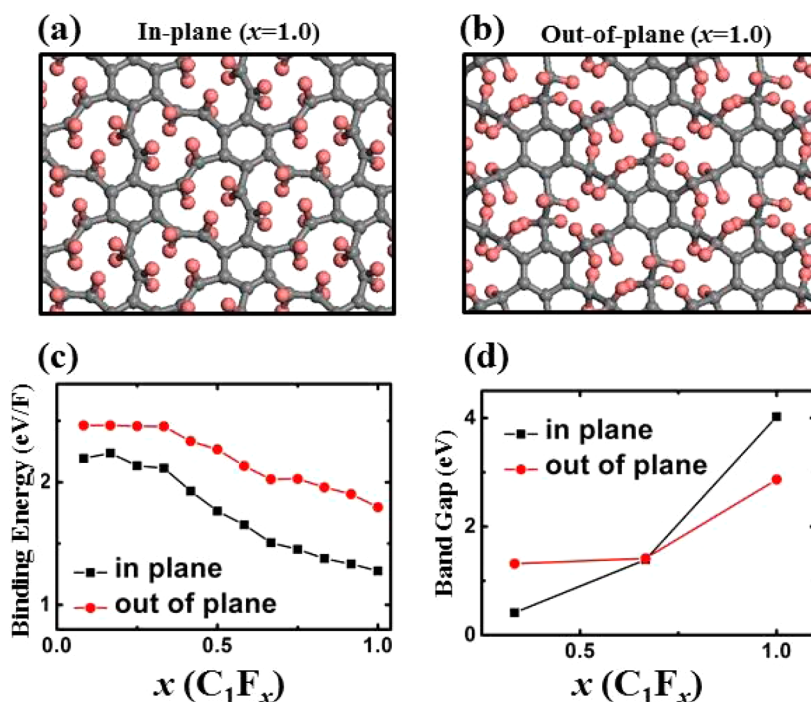


**Figure 3.** Calculated band structures of halogenated graphyne at the  $x = 0.5$  concentration with different halogen elements: (a) F, (b) Cl, and (c) Br. The Fermi energy is set as zero. (d) The calculated band gaps as a function of the concentration  $x$  ( $C_1M_x$ ).





**Figure 4.** Atomic structure of graphyne with adsorbed halogen atoms when pairs of H and F atoms are attached to each sp-bonded carbon atom with two distinct geometries, with a concentration of  $x = 1/3$  (a) and  $x = 1/6$  (b), where  $x$  is defined from  $C_1H_{0.5-x}M_x$ . (c) The calculated binding energy of the attached atoms and (d) the band gaps vs the concentration  $x$  of M.



**Figure 5.** Atomic structure of graphyne with adsorbed halogen atoms when pairs of F atoms are attached to each sp-bonded carbon atom with two distinct geometries, (a) in-plane and (b) out-of-plane, with a concentration of  $x = 0.10$ , where  $x$  is defined from  $C_1F_x$ . (c) The calculated binding energy of the attached atoms and (d) the band gaps vs the concentration  $x$  of F.

adsorption of halogen and hydrogen atoms may be more favorable than separated phases when the contribution of configuration entropy is considered. Another attractive feature of the mixture adsorption is that the band gaps are tunable by

$\sim 1.5$  eV as the concentration of the mixture of hydrogen and halogen atoms increases, as shown in Figure 4d. The singularity at the  $x = 1/6$  concentration of F is related to configuration change of the halogen atoms: The local geometry of the F

atoms is changed to oblique-plane configuration, affected by the H atoms adsorbed with oblique-plane configuration. We believe that the tunable band gaps may originate from a symmetry breaking, such as the mixture of hydrogen and halogens. This result shows that the band gaps of graphyne can be tuned by a mixture of halogen–hydrogen atoms.

We also considered  $sp^3$  hybrid bonds created through halogenation of the  $sp$ -bonded carbon atoms. We found that only fluorine atoms adsorbed on  $sp$ -bonded carbon atoms form  $sp^3$  bonds and that the other types of halogen atoms (Cl, Br, and I) do not form  $sp^3$  hybrid bonds because of steric hindrance in the triangle. The two distinct geometries of the fluorinated graphyne were found to be in-plane and out-of-plane, as shown in Figure 5a and b, respectively. These configurations are defined based on whether the center points of the two adsorbed atoms lie in-plane (Figure 5a) or out-of-plane (Figure 5b). This is consistent with the hydrogenation of graphyne found in our previous study.<sup>29</sup> Unlike  $sp^2$  hybrid bonds created through halogenation to  $sp$ -bonded carbon atoms, the binding energy of the F atoms decreases as the concentration increases, because the repulsive interaction between the F atoms is increased (Figure 5c). The out-of-plane configurations are more stable than the in-plane configurations because the repulsive interaction is smaller. We found that the band gap is widely tunable by  $\sim 4$  eV as the concentration changes, as shown in Figure 5d.

## CONCLUSION

In conclusion, we have conducted density functional calculations of the total energy of halogenated or mixed hydrogenated–halogenated graphyne to investigate its electronic properties. The geometrical and electronic properties of graphyne are distinct from those of hydrogenated graphene. The band gaps were found to be broadly tunable by  $\sim 3$  eV through a local geometrical change of the hydrogenation and by  $\sim 3.5$  eV through a change in the halogen concentration. Changing the degree of hydrogenation and halogenation in the mixed hydrogenated–halogenated graphyne can also be used to tune the band gap. Unlike in graphene, a clustering of halogen atoms on graphyne was not preferred. Therefore, it is feasible to tune the band gap for specific applications. Our results suggest that graphyne can be more advantageous than graphene for tailoring energy band gaps for the applications to nanoelectronics.

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### Notes

The authors declare no competing financial interest.

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