In this work, we studied the electronic band structure of the halogen (F, Cl, and Br) functionalized graphdiynes (GDYs) by using hybrid density functional theory. The results revealed that the bandgap energies of modified GDYs increase as the number of halogen atoms increases. It is also found that the position of the valence band maximum (VBM) is influenced by the electronegativity of halogen atoms. The higher the electronegativity, the deeper the VBM of the GDYs modified by the same number of halogen atoms. Importantly, our results revealed that the bandgap of GDY could be effectively tuned by mixing types of halogen atoms. The new generated conduction band and valence band edges are properly aligned with the oxidation and reduction potentials of water. Further thermodynamic analysis confirms that some models with mixing types of halogen atoms exhibit higher performance of overall photocatalytic water splitting than non-mixing models. This work provides useful insights for designing efficient photocatalysts that can be used for overall water splitting.

Key words: Graphdiyne, Band structure engineering, Water splitting, Photocatalysis, Density functional theory

I. INTRODUCTION

The combustion of fossil fuels can cause environmental pollution and changes in the global climate. The combustion of fossil fuels also results in the depletion of natural sources of energy. These issues have attracted the attention of people globally [1]. It is important to develop methods that can be used to obtain clean and renewable energy to address these problems. Hydrogen energy is a promising source of clean energy that can replace fossil fuels as carbonaceous species are not emitted during the usage of hydrogen energy. Since the discovery of TiO$_2$ electrodes (that were used by Fujishima and Honda to realize photocatalytic water splitting in 1972 [2]), the method of water splitting, driven by photocatalysis, is considered as one of the most attractive methods that can be used for hydrogen generation [3–8].

An effective photocatalyst that can be efficiently used to realize water splitting should be characterized by a bandgap of >1.23 eV [9] and a suitable band edge alignment (the position of the conduction band minimum (CBM) should be higher than the reduction potential of H$^+$/H$_2$, and the position of the valence band...
maximum (VBM) should be lower than the oxidation potential of \(\text{O}_2/\text{H}_2\text{O}^+\) [10, 11]. The oxygen evolution reaction (OER) is a lower efficiency process than the hydrogen evolution reaction (HER). This is considered the key bottleneck in the path of realizing efficient hydrogen production during the process of water splitting driven by photocatalysis [12]. To date, a large number of photocatalysts have been explored [13–17]. However, most photocatalysts fail to drive HER and OER simultaneously [18]. Thus, it is challenging to design new photocatalysts that can be used to simultaneously drive HER and OER.

It has been recently reported that two-dimensional (2D) carbon-based materials are promising candidates that can be used for overall photocatalytic water splitting. These materials have attracted immense attention as they are cost-efficient, present in abundance in nature, and exhibit desirable structures [19–21]. For example, g-C\(_3\)N\(_4\) material with a bandgap of 2.70 eV was successfully developed by Wang et al. for overall photocatalytic water splitting under visible-light irradiation [22]. They also found that iodine-doped and fluorinated g-C\(_3\)N\(_4\) displayed a narrowed bandgap with an obvious red-shift of absorption band edge, leading to an improvement in HER activity [23, 24]. Huang et al. reported a simple synthesis route for fabricating the BCN photocatalysts which was demonstrated to be active for overall water splitting as well as \(\text{CO}_2\) reduction under visible-light illumination [25]. These results suggested that the engineering of 2D carbon-based materials provides a promising way to achieve efficient photocatalytic water splitting without the use of metals.

Graphdiyne (GDY), a 2D carbon material involving sp- and sp\(^2\)-hybridized carbon atoms, has been successfully synthesized [26]. Results from experiments reveal that the GDY is characterized by a moderate bandgap of 0.81 eV [27]. Unfortunately, such a bandgap is far too narrow for efficiently utilizing visible-light, limiting its application in overall photocatalytic water splitting. Nonetheless, our theoretical studies have demonstrated that the band structure of GDY can be successfully modified by various physical and chemical methods. For example, by density functional theory (DFT), we demonstrate that the bandgap energies of GDY can be tuned to levels (direct bandgaps with energies of \(\pm 3\) eV) appropriate for the absorption of visible-light by B, N-codoping [12]. In addition, the VBM and CBM appropriately match with the oxidation and reduction potentials of water. Subsequently, we proposed that fluorine-passivated graphdiyne nanoribbons via doping with BN pairs possess high catalytic activity for photocatalytic water splitting [28]. In particular, we indicated that fluorine passivation plays an important role in lowering the position of VBM in graphdiyne nanoribbons.

This current work extends our study to the electronic band structures of the halogen atoms (F, Cl, and Br) adsorbed on GDY. Hybrid-DFT calculation results showed that the bandgap increases with an increase in the number of halogen atoms but significant change in the bandgap was not observed when the number of halogen atoms on GDY is greater than six. The degree to which the VBM decreases depends on the electronegativity of the halogen atom. Furthermore, our results revealed that the bandgap could be more effectively tuned by mixing types of halogen atoms. The conduction band and valence band edges are properly aligned with the energies of the primary reactions involved in the water splitting process. The results obtained from this study help to design efficient metal-free photocatalysts that can be used to realize overall water splitting.

II. COMPUTATIONAL METHODS

The calculations were performed using the Vienna \textit{ab initio} Simulation Package (VASP) based on plane-wave basis sets [29]. The projected-augmented wave (PAW) pseudopotentials were used to describe the electron-ion interactions [30, 31]. The energy cutoff was set to 450 eV. The generalized gradient approximation (GGA) method coupled with the Perdew-Burke-Ernzerhof (PBE) functional was used to optimize the structures [32]. The energy convergence precision was \(10^{-4}\) eV, and the force convergence precision was 0.05 eV/Å. A Monkhorst-Pack \(k\)-point mesh of \(5\times5\times1\) was used to sample the Brillouin zone [33] for geometry optimizations. The Heyd-Scuseria-Ernzerhof (HSE06) screened hybrid density functional method [34] was used to determine the electronic band structures and the optical absorption coefficients to avoid the underestimation of the semiconductor bandgap calculated using the pure DFT method. A space vacuum of \(~10\) Å was added in the \(z\)-direction to prevent the spurious interaction between the two periodic layers. The computational details for free energy change are shown in Supplementary materials.
III. RESULTS AND DISCUSSION

A. Structures and electronic properties of functionalized GDY

First, we optimized the structure of the pristine GDY, and the results are shown in FIG. 1(a). All the atoms in GDY are coplanar, and GDY contains three types of C atoms labeled as C\textsubscript{1}, C\textsubscript{2}, and C\textsubscript{3}, respectively. The C\textsubscript{1}–C\textsubscript{2}, C\textsubscript{2}–C\textsubscript{3}, and the C\textsubscript{3}–C\textsubscript{3} bond lengths are 1.38, 1.23, and 1.33 Å, respectively. The optimized lattice constant for stable GDY is 9.37 Å. These results agree well with previously reported results \[12\]. The band structure of GDY is presented in FIG. 1(b), which indicates that pristine GDY functions as a semiconductor with a direct bandgap of 0.81 eV, which agrees well with the experimental observation \[27\]. This value is much smaller than the value (1.23 eV) required for photocatalytic water splitting. Therefore, pristine GDY is unsuitable for overall photocatalytic water splitting.

As shown in FIG. 1, the presence of sp- and sp\textsuperscript{2}-hybridized C atoms can provide abundant adsorption sites for halogen atoms. A previous study indicated that the efficiency of the sp-hybridized C atoms in GDY for adsorbing H, F, O, and other atoms is higher than that of the sp\textsuperscript{2}-hybridized C atoms in the carbon hexagons of GDY \[35\]. Accordingly, we built a series of halogenated GDYs, labeled \(n\)X-GDY (\(n=2, 4, 6, \cdots 12; X=\text{F, Cl, and Br}\) in which the halogen atoms bond to the sp-hybridized C atoms. The corresponding optimized structures are shown in FIG. 2.

In the following, the effects of the type and number of halogen atoms on bandgap energy were studied. For \(n\)F-GDY, \(n\)Cl-GDY and \(n\)Br-GDY, when \(n\) increases from two to six, the bandgap increases sharply from 0.90 eV to 3.06, 3.51, 3.33 eV, respectively. While for the number of halogen atoms larger than six, the change in bandgap energy is very small. For example, for \(n\)F-GDY, the bandgap is calculated to be 2.98, 2.92 and 3.03 eV when \(n\) is equal to 8, 10 and 12, respectively. More importantly, we observed that the position of VBM of GDY is influenced by the electronegativity of halogen atoms. This phenomenon was also found in our previous DFT study on fluorine-passivated graphdiyne nanoribbons \[28\]. As shown in FIG. 3, it is clear to see that the higher the electronegativity, the deeper the VBM position of the GDYs modified by the same number of halogen atoms. For example, for 6F-GDY, the VBM is calculated to be 7.22 eV while for 6Cl-GDY and 6Br-GDY, the VBM energies are much higher with the values of 6.67 and 6.60 eV, respectively. For 12F-GDY, the position (–7.56 eV) of VBM in energy is the deepest while for 12Br-GDY, the VBM has the highest energy of –6.21 eV. This trend is consistent with the electron-withdrawing ability order: F > Cl > Br \[36\]. Therefore, it is concluded that the functionalization of halogen atoms can effectively tune the bandgap as well as the position of VBM in GDY.

It is noted that although the position of VBM in \(n\)F-GDY is sharply reduced to the lowest among all the halogen-functionalized GDY materials, the CBM energy in \(n\)F-GDY is simultaneously lowered, which might cause the decrease of driving force for HER. For example, for 12F-GDY, the position of CBM is over-reduced to –4.53 eV, which is below the hydrogen reduction potential. Under the circumstances, 12F-GDY cannot be used for overall photocatalytic water splitting. It is natural and interesting to ask whether the mixing types of halogen atoms can lead to the VBM and CBM properly matching the oxidation and reduction potential of water.

DOI:10.1063/1674-0068/cjcp2110195 ©2021 Chinese Physical Society
FIG. 2 Top and side views of the optimized structures of halogens adsorbed on GDY (nX-GDY). The number of atoms \(n=2, 4, 6, 8, 10, 12\) for i, ii, iii, iv, v, vi, respectively. (a) F adsorption, (b) Cl adsorption, and (c) Br adsorption. The grey, blue, green, and red spheres represent C, F, Cl, and Br, respectively.

FIG. 3 Bandgap and band-edge positions for \(nX\)-GDY based on the functionalized scheme illustrated in FIG. 2. The reduction potential of \(H^+/H_2\) and the oxidation potential of \(O_2/H_2O\) at pH=0 are marked by the dashed lines. The band edges associated with the conduction band minimum (CBM) and the valence band maximum (VBM) for each \(nX\)-GDY system are labeled using short black and red lines, respectively. The corresponding values of CBM and VBM are marked using black and red numbers, respectively. The purple number in the middle represents the bandgap energy.

Based on these results, we studied the effect of mixing types of halogen atoms on the efficiency of GDY. The structure of the system characterized by the mixed adsorption of halogen atoms is expressed as \(n_1X_1+n_2X_2+n_3X_3\)-GDY, where \(n_1\), \(n_2\), and \(n_3\) represent the number of different halogen atoms, and \(X_1\), \(X_2\), and \(X_3\) represent the corresponding halogen atoms. The optimized structures are displayed in FIG. 4 and FIG. S1 in Supplementary materials. Herein, we have two main objectives: (i) the decrease in the VBM energy was not accompanied by a significant decrease in the CBM energy. (ii) The number of halogen atoms adsorbed on GDYs should be in the range of 6–10 to ensure that the bandgap is smaller than 3 eV and suitable active sites are available for overall photocatalytic water splitting.

Next, the electronic band structures of \(n_1X_1+n_2X_2+n_3X_3\)-GDY were investigated. FIG. 5 and DOI:10.1063/1674-0068/cjcp2110195 ©2021 Chinese Physical Society
FIG. 4 Optimized structures of GDYs with mixed types of halogen atoms. The total number of halogen atoms is six (a-i: 4F+2Br-GDY, a-ii: 4F+2Cl-GDY), eight (b-i: 6F+2Br-GDY, b-ii: 6F+2Cl-GDY) and ten (c-i: 6F+4Br-GDY, c-ii: 6F+2Br+2Cl-GDY, c-iii: 6F+4Cl-GDY, c-iv: 8F+2Br-GDY, and c-v: 8F+2Cl-GDY). The grey, blue, green, and red spheres represent the C, F, Cl, and Br atoms, respectively.

FIG. 5 Bandgap and band-edge energies for $n_1X_1+n_2X_2+n_3X_3$-GDY. Horizontal dashed lines represent the redox potentials of water at pH=0. The numbers in white (6, 8, and 10) represent the total number of halogen atoms adsorbed on GDY. All $n_1X_1+n_2X_2+n_3X_3$-GDYs exhibit semiconductor-like properties, and the electronic bandgap ranges from 2.79 eV to 3.23 eV. In addition, it is found that the bandgap energy and the position of the band edges could be effectively tuned by a mixture of different halogen atoms. Under the circumstances, the CBM positions are higher than the reduction potential of the proton ($H^+/H_2$) and the VBM positions are lower than the oxidation potential of water ($O_2/H_2O$). We observed that most of the structures follow a trend, that is, when the total number of halogen atoms is the same, the greater the electronegativity of the total halogen atoms, the deeper the valence band position is. For example, 6F+2Cl+2Br-GDY has a deeper VBM ($-6.86$ eV) position than that ($-6.79$ eV) of 6F+4Br-GDY because the electronegativity of Cl is larger than Br. Another example is that the VBM position ($-7.15$ eV) in 8F+2Cl-GDY is much deeper than that ($-6.94$ eV) in 6F+4Cl-GDY due to the fact that F has stronger electronegativity than Cl. This finding agrees well with the result mentioned earlier.

FIG. S2 in Supplementary materials display the band alignments of CBM and VBM (for $n_1X_1+n_2X_2+n_3X_3$-GDY), as well as the redox potential of water at pH=0. All $n_1X_1+n_2X_2+n_3X_3$-GDYs exhibit semiconductor-like properties, and the electronic bandgap ranges from 2.79 eV to 3.23 eV. In addition, it is found that the bandgap energy and the position of the band edges could be effectively tuned by a mixture of different halogen atoms. Under the circumstances, the CBM positions are higher than the reduction potential of the proton ($H^+/H_2$) and the VBM positions are lower than the oxidation potential of water ($O_2/H_2O$). We observed that most of the structures follow a trend, that is, when the total number of halogen atoms is the same, the greater the electronegativity of the total halogen atoms, the deeper the valence band position is. For example, 6F+2Cl+2Br-GDY has a deeper VBM ($-6.86$ eV) position than that ($-6.79$ eV) of 6F+4Br-GDY because the electronegativity of Cl is larger than Br. Another example is that the VBM position ($-7.15$ eV) in 8F+2Cl-GDY is much deeper than that ($-6.94$ eV) in 6F+4Cl-GDY due to the fact that F has stronger electronegativity than Cl. This finding agrees well with the result mentioned earlier.

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FIG. 6 (a) Proposed photocatalytic pathways for the OER. The calculated Gibbs free energy changes at pH=7 during OER in the presence of (b) 4F+2Cl-GDY, (c) 6F+2Br-GDY, and (d) 6F+2Cl-GDY.

by studying GDY modified with the same halogen atoms. Among all the configurations, we can see that 4F+2Cl-GDY, 6F+2Br-GDY, and 6F+2Cl-GDY are characterized by deep-seated VBM in energy, which can potentially provide sufficient driving force for the OER. Although 8F+2Br-GDY and 8F+2Cl-GDY have low position of VBM, their CBM is relatively deep, which might cause low activity for the HER.

B. OER and HER performance

It is known that for a photocatalytic water splitting reaction, the photogenerated holes and electrons must provide sufficient driving force to promote HER and OER under conditions of visible-light irradiation. In the following, we aim to evaluate the performance of 4F+2Cl-GDY, 6F+2Br-GDY, and 6F+2Cl-GDY in overall photocatalytic water splitting by thermodynamic analysis. The possible active sites for the OER and HER are shown in FIG. S3 in Supplementary materials.

FIG. 6(a) illustrates the four elementary steps involved in the four-electron OER process. We calculated the change in the Gibbs free energy change ($\Delta G$) of the intermediates produced during the OER process when 4F+2Cl-GDY, 6F+2Br-GDY, or 6F+2Cl-GDY was used as the catalysts. Analysis of the results reveals that the third step involving the formation of the OOH$^*$ species ($^*O+H_2O\rightarrow OOH+H^++e^-$) is the rate-determining step. On all the three catalysts, $C_3$ is found to be the most favorable active site for the OER as the rate-determining step is characterized by the lowest $\Delta G$ value (2.07, 2.09, and 2.05 eV for 4F+2Cl-GDY, 6F+2Br-GDY, and 6F+2Cl-GDY, respectively), as shown in Table S1 in Supplementary materials. The optimized structures of the three intermediates produced at the $C_3$ positions of 4F+2Cl-GDY, 6F+2Br-GDY, and 6F+2Cl-GDY during OER are shown in FIG. S4 in Supplementary materials and the corresponding free energy profiles are presented in FIG. 6(b–d).

In the absence of light-induced bias potential [7] ($U=0$) at pH=7, the calculated energy pathways (black lines in FIG. 6(b–d)) show that the OER cannot proceed efficiently on the surface of the 4F+2Cl-GDY, 6F+2Br-GDY, and 6F+2Cl-GDY monolayers as the reaction process is energetically unfavorable (all the reaction steps are uphill in energy). When the sam-
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FIG. 7 Calculated Gibbs free energy changes for the intermediate states involved in the HER processes on (a) 4F+2Cl-GDY, (b) 6F+2Br-GDY, and (c) 6F+2Cl-GDY at pH=7.

ple is irradiated with light, the photogenerated holes provide a bias potential \( U_h \), which is defined as the difference in energy between VBM and the hydrogen reduction potential, it was determined to be 2.54, 2.56, and 2.63 V for 4F+2Cl-GDY, 6F+2Br-GDY, and 6F+2Cl-GDY, respectively, at pH=0. As the \( U_h \) values are relative to the standard hydrogen electrode (SHE), the \( U_h \) values change with pH according to \( U_h = 2.54 - 0.059 \times pH, U_h = 2.56 - 0.059 \times pH, \) and \( U_h = 2.63 - 0.059 \times pH \) for 4F+2Cl-GDY, 6F+2Br-GDY, and 6F+2Cl-GDY monolayers, respectively [6]. The results reveal that the \( U_h \) values for the irradiation-induced holes are 2.13, 2.15, and 2.22 V for 4F+2Cl-GDY, 6F+2Br-GDY, and 6F+2Cl-GDY, respectively, at pH=7. The red lines in FIG. 6(b–d) indicate that all the reaction steps in the 4F+2Cl-GDY, 6F+2Br-GDY, and 6F+2Cl-GDY monolayers are downhill in terms of energy when the irradiation-induced external bias potential \( U_h \) is applied. This indicates that 4F+2Cl-GDY, 6F+2Br-GDY, and 6F+2Cl-GDY can be used to realize photocatalytic OER.

Next, we calculated the \( \Delta G \) of the intermediates produced during the HER process which contains two elementary steps \( (\text{H}^+ + e^- \rightarrow \text{H} \) and \( \text{H}^+ + \text{H}^- \rightarrow \text{H}_2 \)). Unlike the OER process happening at C3, the active sites for the HER are C2, C1, and C1 on the 4F+2Cl-GDY, 6F+2Br-GDY, and 6F+2Cl-GDY monolayers, respectively. FIG. S5 in Supplementary materials presents the configurations of \( \text{H}^+ \) adsorption at different active carbon sites. The rate-determining step on 4F+2Cl-GDY is the desorption of \( \text{H}_2 \), while it turns to \( \text{H}^+ \) adsorption on 6F+2Br-GDY and 6F+2Cl-GDY. The corresponding \( \Delta G \) values for the rate-determining step are 0.61, 0.67, and 0.73 eV, respectively. FIG. 7(a–c) illustrates the elementary steps involved in HER and the corresponding free energy change profiles at pH=7 in the presence and absence of light-induced bias potential for 4F+2Cl-GDY, 6F+2Br-GDY, and 6F+2Cl-GDY. In the absence of light-induced bias potential, the HER process is thermodynamically unfavorable because the reaction steps are endothermic. When the sample is irradiated with light, the photogenerated electrons provide a bias potential \( U_e \), which is defined as the energy difference between the hydrogen reduction potential and CBM at pH=0. \( U_e \) also varies with pH, calculated in the same way as \( U_h \), except that 0.059 \times pH is added to \( U_e \). The results show that the values of the light-induced external bias potential \( U_e \) provided by electrons are 0.83 V, 0.80 V, and 0.76 V for 4F+2Cl-GDY, 6F+2Br-GDY, and 6F+2Cl-GDY, respectively, implying that the HER is spontaneous when the sample is irradiated under visible-light.

Finally, we compare the catalytic performance between the mixed and non-mixed models with same number of halogen atoms. As shown in FIG. 3, although 6F-GDY has deeper VBM position (~7.22 eV) than that (~6.98 eV) of 4F+2Cl-GDY, its bandgap is larger than 3 eV, which might not be suitable for water splitting under visible-light illumination. Compared with 6F+2Br-GDY and 6F+2Cl-GDY, 8F-GDY has a very similar bandgap (2.98 eV) and has a much deeper VBM position (~7.28 eV) that can facilitate the OER process (FIG. S6 in Supplementary materials). However, its energy of CBM is too low to sufficiently drive the HER half-reaction. Further thermodynamic calculations demonstrate that not all steps of HER on the 6F+2Br-GDY and 6F+2Cl-GDY monolayers are downhill in terms of energy when the irradiation-induced external bias potential \( U_e \) is applied (FIG. S6 in Sup-
FIG. 8 Optical absorption spectra for the 4F+2Cl-GDY, 6F+2Br-GDY, and 6F+2Cl-GDY monolayers.

The above results highlight the importance of mixing types of halogen atoms in functionalizing GDYs for efficient photocatalysis.

C. Optical properties

An effective photocatalyst should be characterized by appropriate bandgap and suitable band edge positions. It should also be able to absorb most of the sunlight. The optical absorbance $\alpha(\omega)$ exhibited by the 4F+2Cl-GDY, 6F+2Br-GDY, and 6F+2Cl-GDY monolayers was studied using the following formula [28]:

$$\alpha(\omega) = \sqrt{2\omega} \sqrt{\varepsilon_1(\omega) + \varepsilon_2^2(\omega)}$$  

where $\varepsilon_1$ and $\varepsilon_2$ are the real and imaginary parts of the dielectric function, respectively. FIG. 8 shows the absorption spectral profiles for the 4F+2Cl-GDY, 6F+2Br-GDY, and 6F+2Cl-GDY configurations. It is noteworthy that the 4F+2Cl-GDY, 6F+2Br-GDY, and 6F+2Cl-GDY monolayers exhibit excellent optical absorption in the visible region, indicating that this photocatalyst can effectively utilize sunlight.

IV. CONCLUSION

In summary, we studied the electronic properties of halogenated GDY systems by extensive hybrid-DFT calculations. Our results show that the bandgap of GDY increases significantly with an increase in the number of halogen (F, Cl, and Br) atoms. The position of the valence band is influenced by the electronegativity of halogen atoms. The higher the electronegativity, the deeper the valence band of the GDYs modified by the same number of halogen atoms. Then, we investigated the electronic band structures of GDYs functionalized by mixing types of halogen atoms. It is found that 4F+2Cl-GDY, 6F+2Br-GDY, and 6F+2Cl-GDY have bandgaps of 2.96, 2.95 and 2.98 eV, respectively, corresponding to visible-light response. In addition, their valence and conduction band edges are found to perfectly match the oxidation and reduction potential of water, respectively. Further thermodynamic analysis demonstrates that they can effectively catalyze the decomposition of water into H$_2$ and O$_2$ under visible-light irradiation. This work highlights the important role of halogenation in opening the bandgap of 2D GDY material for overall photocatalytic water splitting. More importantly, it helps the rational design of a new and more effective photocatalyst that avoids the use of metals.

Supplementary materials: Computational details for the Gibbs free energy change, the optimized configurations with corresponding edge positions of other halogen-modified GDY mentioned in this work, and the optimized intermediate configurations involved in photocatalytic water splitting are available.

V. ACKNOWLEDGMENTS

This work was funded by the National Natural Science Foundation of China (No.21973013 and No.21673040), the Natural Science Foundation of Fujian Province of China (No.2020J02025) and “Chuying Program” for the Top Young Talents of Fujian Province.
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