Defect and Doping Engineered Penta-graphene for Catalysis of Hydrogen Evolution Reaction

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Abstract

Water electrolysis is a sustainable and clean method to produce hydrogen fuel via hydrogen evolution reaction (HER). Using stable, effective and low-cost electrocatalysts for HER to substitute expensive noble metals is highly desired. In this paper, by using first-principles calculation, we designed a defect and N-, S-, P-doped penta-graphene (PG) as a two-dimensional (2D) electrocatalyst for HER, and its stability, electronic properties and catalytic performance were investigated. The Gibbs free energy (Δ\(G_H\)), which is the best descriptor for the HER, is calculated and optimized, the calculation results show that the Δ\(G_H\) can be 0 eV with C2 vacancies and P doping at C1 active sites, which should be the optimal performance for a HER catalyst. Moreover, we reveal that the larger charge transfer from PG to H, the closer Δ\(G_H\) is to zero according to the calculation of the electron charge density differences and Bader charges analysis. Ulteriorly, we demonstrated that the HER performance prefers the Volmer–Heyrovsky mechanism in this study.

Keywords: Penta-graphene, Hydrogen evolution reaction, Electrocatalysis, First-principles calculation

Background

Because of the climate change and environmental pollution caused by fossil fuels usage, exploitation and utilization of clean and renewable energy are the mean way after nowadays [1–4]. As a clean, renewable and environmentally friendly energy source, hydrogen (H2) has been attracting considerable attention to fulfill human future energy needs [5, 6]. Water electrolysis is a sustainable and clean method to produce H2, and electrocatalysts can enhance the efficiency of water splitting observably [7, 8]. For hydrogen evolution reaction (HER), platinum-based nanomaterials are considered as the best electrocatalysts because of a small Tafel slope, a low overpotential, a slightly negative Gibbs free energy (Δ\(G_H\)) and a high exchange current density [9, 10], but the scarcity and high cost hamper their industrial scale applications [11]. Therefore, developing effective, earth-abundant and low-cost electrocatalysts is essential for HER [12–14].

In fact, a wide range of earth-abundant electrocatalysts have been studied and designed for HER [15–17]. Among these materials, two-dimensional (2D) nanomaterials provide new opportunities for HER because of the compelling structural and electronic properties. To date, the transition metal dichalcogenides (TMDs) and the graphene-based materials are the biggest and most intensively studied groups of 2D electrocatalysts for HER [18–23]. The TMDs HER catalysts have low overpotential and small Tafel slope, unusual electronic properties and high air stability, exhibit high HER performance, and different methods were taken for enhancing their catalytic performance [24, 25]. The graphene-based HER catalysts have attracted considerable attention and persistent studying because of their...
distinctive structural merits, such as high electrical conductivity, large surface area and good chemical stability [26, 27]. Many methods were taken for enhancing the catalytic activity, such as heteroatom doping and defection engineering [28, 29]. Meanwhile, the intensive research on other new 2D carbon allotropes have also been developed, such as graphdiyne [30] and penta-graphene (PG) [31]. As a 2D carbon allotrope, PG is composed of only carbon pentagons and inherits many exceptional properties of 2D materials, such as finite electronic band gap, abundant active sites and large surface area, so it is anticipated to be a versatile material for lots of potential applications like other 2D graphene-based materials [32–35]. Since there are only applications in gas adsorption [36–38], H2 storage [39, 40], anode materials at present [41, 42], no report has ever been found on the application in HER. Therefore, research on HER by PG is of great significance and cannot only fill such a gap but also broaden the scope of graphene-based HER catalysts. However, the pristine PG is found to be inert for the HER with a relatively large ΔG1H, which means that hydrogen adsorption is difficult and inhibits the HER. This is similar to the problems encountered by pristine graphene (ΔG1H = 1.85 eV [43]). Heteroatom doping into graphene-based materials could adjust their electronic and catalytic properties, which makes them prospective catalysts for the practical applications [3]. Therefore, we managed to tailor the catalytic activity of PG by heteroatom doping [44–46] and defection engineering [47, 48].

In this paper, by using first-principles calculation, we designed and demonstrated a defect and N-, S-, P-doped PG and investigated their stability and electronic properties and evaluated their performance as HER electrocatalysts. Our results reveal that the defect and doped PG can obviously enhance the catalytic activity toward HER, compared with the pristine PG. It is also shown that the ΔG1H can be 0 eV with C2 vacancies and P doping at C1 active sites, which should be the optimal performance for a HER catalyst, so P-doped PG has the optimal ΔG1H and activation energy barrier for the rate-determining step among the three counterparts, and it exhibits more favorable performance. We further show that the catalytic activity arises from the incorporated doping atoms, which can provide efficient pathway for charge transport during the electrolysis, resulting in the reduction in ΔG1H. We also demonstrate that the Volmer–Heyrovsky mechanism is more preferred for HER on defect and doped PG. We compared our results with that of other researchers on graphene, and it can be found that the defection and doping engineering are more effective for PG in catalysis of HER. Thus, our effort on defect and doped PG makes it a high promising electrocatalyst for HER, and our findings provide a deep understanding in designing efficient and durable electrocatalysts. This method can be also applied to other graphene-based materials.

**Computational Methods**

Our first-principles calculations were performed using the Vienna Ab initio Simulation Package (VASP) [49]. The projected augmented wave (PAW) potentials were used to analyze the interactions between core electrons and valence electrons [50–52]. The electron exchange–correlation interactions were described by using the Perdew–Burke–Ernzerhof (PBE) functional within the generalized gradient approximation (GGA) [53]. The DFT-D3 exchange–correlation functional was introduced in structural optimization to take the van der Waals interaction into account. The vacuum space along the z-direction was set to 20 Å in order to eliminate the interactions between PG and its periodic images.

The plane-wave energy cutoff was set to 500 eV. The convergence criterion was set as 10−5 eV for a total energy. All the atomic positions and lattice structures were fully relaxed with the threshold of a maximum force of 0.02 eV Å−1. In order to ensure the accuracy and efficiency of the calculation, a Gamma-centered k-point mesh with a Monkhorst–Pack method 5 × 5 × 1 was employed for all considered structures after convergence test [54]. The amount of the charge transfer between the C atoms and H atoms was calculated using Bader code [55]. We also calculated H* adsorption energy barriers using the climbing image-nudged elastic band (CI-NEB) method [56, 57]. The CI-NEB is an efficient method to determine the minimum energy path and saddle points between a given initial and final position [58–60], and in our CI-NEB calculations, the initial and the final structures were fully optimized.

The adsorption energy (ΔE1H) is defined as

\[ \Delta E_{1H} = E(\ast H) - E(\ast) - \frac{1}{2} E(H_2) \]

where \( E(\ast H) \) and \( E(\ast) \) are the total energy of structures with and without hydrogen adsorption, respectively, and \( E(H_2) \) is the total energy of a H2 molecule.

The Gibbs free energy (ΔG1H) is defined as:

\[ \Delta G_{1H} = \Delta E_{1H} + \Delta E_{ZPE} - T \Delta S_{1H} \]

where ΔE1H is the adsorption energy, ΔE_{ZPE} is the difference in zero-point energy, \( T \) is the temperature (298.15 K) and \( \Delta S_{1H} \) is the entropy difference of H adsorbed and H in the gas phase. We approximated the entropy of hydrogen adsorption as \( \Delta S_{1H} \approx \frac{1}{2} \Delta S_{H^2} \), where \( \Delta S_{H^2} \) is the entropy of gas phase H2 at standard conditions, \( T \Delta S_{H^2} \) was set to be −0.202 eV after calculation in this study.
Results and Discussion
Structure and Catalytic Activity of Defect and Doped PG

The optimized structure of PG is shown in Fig. 1. For convenience of discussion, we hereafter group the \( sp^3 \) and \( sp^2 \) hybridized C atoms as C1 and C2, respectively. The distance between the C1 and C2 is 1.55 Å, and the C2–C2 bond length is 1.34 Å, which is consistent with the experimental result [31].

At the beginning, we first investigated the sites C1 and C2 in the basal plane of pristine PG for HER, the calculated \( \Delta G_H \) values are 2.43 eV and 2.72 eV, respectively. So our calculations show that the pristine PG is found to be inert for the HER with a relatively large \( \Delta G_H \) of H, which means that hydrogen adsorption is difficult and HER is inhibited. Therefore, we managed to use some methods to tailor the catalytic activity of PG. We researched the possible active sites for doping and we also investigated the active sites for C1 and C2 with N, S, P doping, respectively. The calculation results show that no obvious improvement of HER can be obtained if only doping engineering was introduced. In the case of the P-doped structure, the calculated \( \Delta G_H \) values of C1 and C2 sites are 1.24 eV and 1.40 eV, respectively. Ulteriorly, we investigated the defect PG with C vacancy sites. The calculation results reveal that C1 vacancy structure cannot improve the HER performance but C2 vacancy structure can decrease \( \Delta G_H \) obviously, so we use C2 vacancy structure in this study. The calculation results show that C1 vacancy structure cannot improve the HER performance but C2 vacancy structure can decrease \( \Delta G_H \) obviously, so we use C2 vacancy structure in this study. The optimized structures with \( V_{C\text{-UP}} \) and \( V_{C\text{-DOWN}} \) C2 vacancies sites are shown in Fig. 2, the vacancy defects are built by removing C2 atoms from C2-UP or C2-DOWN site in a 24-atom supercell. The calculated \( \Delta G_H \) values are shown in Table 1, where C1 and C2 are the active sites for hydrogen adsorption.

![Fig. 1](image1.png)  
**Fig. 1** a Top and b side views of the optimized structure of PG. The black dashed rectangle indicate unit cell, the blue dashed circles indicate two C vacancy sites, the red dashed circles indicate doping sites used in this paper

![Fig. 2](image2.png)  
**Fig. 2** The optimized structures of PG with two different C2 vacancy sites: a \( V_{C\text{-UP}} \) C2 vacancy site, b \( V_{C\text{-DOWN}} \) C2 vacancy site

Though it is confirmed by our calculations that C2 vacancies are efficient to enhance the HER activity, PG with C2 vacancy structure is not yet optimal for a HER catalyst. Thus, we further investigated the defect and doped PG for HER. We used PG with C2 vacancy as initial structure, which is shown in Fig. 2 and then investigated all the different possible active sites with N, S, P doping, including C1, C2-UP and C2-DOWN sites. As a result, we found that better HER performance could be achieved with a combination of C2 vacancy and heteroatom doping. We investigated all the possible structures, and the results showed that there are two structures that can achieve better HER performance, one structure is a combination of the C2-UP vacancy and heteroatom doping in the C2-DOWN site, and the other is a combination of the C2-DOWN vacancy and heteroatom doping in the C2-UP site. So we focused on these two structures and found that they can shift the \( \Delta G_H \) values closer to zero. The optimized structures are shown in Fig. 3, and the calculated bond lengths are summarized in Table 2.

![Table 1](image3.png)  
**Table 1** Calculated \( \Delta G_H \) values for different possible active sites

| Structure | Site     | \( \Delta G_H \) (eV) |
|-----------|----------|------------------------|
| Pristine  | C1       | 2.43                   |
|           | C2       | 2.72                   |
| N-doped   | C1       | 1.48                   |
|           | C2       | 1.99                   |
| S-doped   | C1       | 1.53                   |
|           | C2       | 1.65                   |
| P-doped   | C1       | 1.24                   |
|           | C2       | 1.40                   |
|           | VC-UP    | 0.24                   |
|           | C1       | 0.23                   |
|           | C2       | 0.24                   |
|           | VC-DOWN  | 0.24                   |
of pristine PG. Because of the large radius of S and P atoms, these two structures undergo much more distortion, but they can both maintain the structure of PG.

To investigate the stability of PG with C2 vacancy and heteroatom doping, we calculated the formation energy, which is defined as

\[
E_f = \left( E_t - E_V + E_C - E_d - \frac{1}{2} \mu_H \right)
\]

where \( E_t \) is the total energy of the defect and doped system, and \( E_V \) is the energy of C2 vacancy PG, \( E_C \) is the average energy per C atom of the pristine PG, \( E_d \) is the energy of doping atoms, \( \mu_H \) is taken from the total energy of the H\(_2\) molecule, respectively. One of our calculation results about the formation energies of preceding two structures with C1 active sites for HER is shown in Fig. 4. We can see that negative formation energies indicate energetically favorable and feasible defect and S-, P-doped PG. Similarly, \( E_f \) values of N-doped structures with active sites for HER are all positive. We investigated all the possible active sites and got the similar results as shown in Fig. 4, so we will investigate only the S- and P-doped PG. According to the definition, a more negative \( E_f \) value indicates higher stability of the structure, so P-doped PG has excellent stability, as well as good HER performance.

**Origin of the HER Catalytic Activity**

**DOS and Band Structures**

To achieve an in-depth understanding of the nature of C2 vacancy and doping engineering in the HER activity, we investigated the total and projected DOS, electronic band structure of the defect and S-, P-doped PG. Figure 5 is one of our calculation results about electronic band structures, total and projected DOS of pristine PG, \( V_{C-UP} \), \( V_{C-UPS} \)-doped and \( V_{C-UPP} \)-doped PG.

From the figure, we can see that when C2 vacancy is introduced, some new defect states highlighted by red curves appear in the forbidden band near the Fermi level. Obviously, these new states arise from the C2 vacancy. Furthermore, when S, P heteroatom doping is
introduced, the band gap gets narrower (from 2.22 eV [31] to 0.37 eV) and the number of new defect states near the Fermi level increases, which can possibly improve the H* adsorption strength.

However, we found that the DOS of VC-UP near the Fermi level is much larger than that of pristine PG. In addition, the electron density near the Fermi level of C2 vacancy and S-, P-doped PG is further increased relative to pristine PG. We also found that the S 3p and P 3p orbitals undergo significant hybridization with the C1 and C2 states, leading to strong interactions between the heteroatoms and C, and the formation of S–C and P–C bonds. These results demonstrate that combination of the C2 vacancy and S, P heteroatoms doping may be a better engineering for improving HER activity.

Electron Density Difference and Charge Transfer
Moreover, to study the binding interaction between the H atom and PG, we calculated the electron charge density differences for defect and S-, P-doped PG with different active sites for hydrogen evolution. One of our calculation results about the electron charge density difference and Bader charges analysis for a C2-DOWN vacancy and P-doped PG with H* adsorbed at the different active sites for hydrogen adsorption is shown in Fig. 6. The yellow and blue colors represent charge accumulation and reduction, respectively.
noticed that H* is absorbed onto C instead of P, indicating that the increased charge density can contribute to the electrocatalyst on H atom. So our calculations show that P doping into the PG can lead to enhanced adsorption of H* on C atoms. As mentioned above, the DFT calculations also suggested that the P doping into PG could much more efficiently enhance the HER activity than that of S-doping.

**Activity of Defect and Doped PG Toward HER**

**Gibbs Free Energies of HER**

The $\Delta G_H$ is the vital descriptor of the HER for a variety of electrocatalysts, the optimal $\Delta G_H$ value for a electrocatalyst is zero, so the H* adsorption and desorption can occur spontaneously without activation energy barrier [61, 62]. To evaluate the HER activity of the PG and investigate the defection and doping engineering, we calculated the $\Delta G_H$ of HER. One of our calculation results about $\Delta G_H$ versus reaction coordinate of the HER for PG is shown in Fig. 8, where C1 and C2 inside the brackets are active sites for hydrogen adsorption.

Our calculations show that the pristine PG is found to be inert for the HER with a relatively large Gibbs free energy of H* ($\Delta G_H = 2.72$ eV(C2), $\Delta G_H = 2.43$ eV(C1)). When vacancies are introduced, there are two different C vacancy sites, C1 vacancy site and C2 vacancy site. We calculated the $\Delta G_H$ on the two sites and found that C2 vacancy can notably decrease $\Delta G_H$ ($\Delta G_H = 0.24$ eV), which indicates that H* preferentially adsorbs on C2 vacancy structures. The optimized structures with C2 vacancy sites ($V_{C\text{-UP}}$ and $V_{C\text{-DOWN}}$) are shown in Fig. 2. Though C2 vacancies show significant improvement over the pristine PG, they are still not the optimal for the hydrogen adsorption, so doping engineering is explored to improve the HER performance. We show our effects of C2 vacancies and S, P heteroatom doping on the HER activity and optimize the HER performance. The $\Delta G_H$ values are summarized in Table 3, and the active sites for hydrogen evolution are shown in Fig. 3.

The calculation results reveal that $\Delta G_H$ decreases significantly, demonstrating that the defection and doping engineering are very effective in reducing $\Delta G_H$. Remarkably, we found that the $\Delta G_H$ values of active sites C1, C$_{2\text{-UP}}$ and C$_{2\text{-UP(n)}}$ for $V_{C\text{-UP}}$, active sites C1, C$_{2\text{-DOWN}}$ and C$_{2\text{-DOWN(n)}}$ for $V_{C\text{-DOWN}}$ are very close to zero, especially for two C1 sites, signifying the optimal conditions can be achieved, which are significantly superior to pristine PG. And we compared our results with previous work from other researchers on graphene, for instance, graphene with C vacancy ($\Delta G_H = -2.108$ eV) [28], graphene with N-doped ($\Delta G_H = -0.693$ eV) [28], graphene with C vacancy and N-doped ($\Delta G_H = -0.595$ eV) [28], graphene

### Table 3 Calculated $\Delta G_H$ values of C2 vacancies and S-, P-doped PG

| Structure        | Site     | $\Delta G_H$ (eV) |
|------------------|----------|-------------------|
| $V_{C\text{-UP}}$S-doped | C1       | -0.007            |
|                  | C$_{2\text{UP}}$ | -0.30            |
|                  | C$_{2\text{UP(n)}}$ | -0.071          |
|                  | C$_{2\text{DOWN}}$ | -0.240         |
| $V_{C\text{-UP}}$P-doped | C1       | 0.005             |
|                  | C$_{2\text{UP}}$ | 0.030            |
|                  | C$_{2\text{UP(n)}}$ | 0.090          |
|                  | C$_{2\text{DOWN}}$ | 0.130           |
| $V_{C\text{-DOWN}}$S-doped | C1       | -0.016            |
|                  | C$_{2\text{UP}}$ | -0.030           |
|                  | C$_{2\text{DOWN}}$ | -0.060         |
|                  | C$_{2\text{DOWN(n)}}$ | -0.240       |
| $V_{C\text{-DOWN}}$P-doped | C1       | -0.002            |
|                  | C$_{2\text{DOWN}}$ | 0.025            |
|                  | C$_{2\text{DOWN(n)}}$ | 0.087          |
|                  | C$_{2\text{UP}}$ | -0.130           |
with S-doped ($\Delta G_{\text{H}} = -0.30 \text{ eV}$) [29] and graphene with N/S co-doped ($\Delta G_{\text{H}} = -0.12 \text{ eV}$) [29]. We can find that the defection and doping engineering are more effective for PG. Thus, our results clearly suggest that the $\Delta G_{\text{H}}$ of PG can be manipulated by applying defection and doping engineering to achieve the optimal HER activity.

**The Reaction Pathways of Defect and Doped PG**

The HER proceeds in a multistep electrochemical process, via one of two pathways which are known as the Volmer–Tafel and the Volmer–Heyrovsky mechanisms. The first step of HER is the $\text{H}^*$ adsorption on the electrocatalyst surface (i.e., Volmer reaction), which is described by $\text{H}^++e^-\rightarrow\text{H}^*$. Then, $\text{H}^*$ combines with $\text{H}^+$ and an electron ($e^-$) to form a $\text{H}_2$ molecule, known as the Heyrovsky step, which is described by $\text{H}^*+\text{H}^++e^-\rightarrow\text{H}_2$. Alternatively, $\text{H}_2$ molecule can be formed via the Tafel step, i.e., the combination of two $\text{H}^*$ on the electrocatalyst surface, which is described by $2\text{H}^*\rightarrow\text{H}_2$ [63].

To investigate the defection and doping engineering effects on PG and further understand the mechanism of superior HER activity, the energy barriers of Tafel and Heyrovsky reactions with $C_{2\text{-UP}}$ and $C_{2\text{-DOWN}}$ vacancies, S-, P-doped PG for C1 site were calculated. The initial state (IS), the final state (FS) and the transition state (TS) are displayed in Fig. 9 with the corresponding energy barriers. For the Tafel reaction, the recombination of $2\text{H}^*$ shows energy barriers of 1.51 eV (S-doped), 1.32 eV (P-doped), respectively. Whereas the release of a $\text{H}_2$ molecule in the Heyrovsky reaction involved in a proton reacting with an adsorbed $\text{H}^*$ needs to overcome the energy barriers of 1.01 eV (S-doped), 0.99 eV (P-doped), respectively. The results reveal that the energy barriers of Tafel reaction are significantly higher than that of the Heyrovsky reaction. So the HER on defect and doped PG prefers the Volmer–Heyrovsky mechanism.

**Conclusions**

We theoretically designed a C vacancy and N-, S-, P-doped PG and investigated their stability and unique role of electrocatalyst toward HER systematically. We find that defection and doping engineering possess a superior HER performance over the pristine PG. Importantly, the optimal HER activity can be achieved with C2 vacancies and S, P heteroatoms doping, which indicates that the catalytic properties of the defect and doped PG can be tuned easily and effectively. Our calculations reveal that $\Delta G_{\text{H}}$ decreases significantly with C2 vacancies and S, P heteroatom doping, and the optimal conditions can be achieved with P doping at C1 active sites, for which defection or doping engineering alone cannot achieve the optimal conditions. The electronic structure analysis shows that when C2 vacancy and S, P heteroatom doping are introduced, several new defection states move closer to the Fermi level, leading to the narrower band gap and an improvement of the hydrogen adsorption strength. We also find the charge transfer from PG to $\text{H}^*$ by calculating the electron charge density differences, the larger charge transfer to $\text{H}^*$, the closer $\Delta G_{\text{H}}$ values to zero by using Bader charges analysis, which indicates the optimal performance for a HER catalyst. And we further demonstrate
the HER on defect and doped PG prefers the Volmer–Heyrovsky mechanism. So our study shows that the designed defect and doped PG is highly activated toward HER electrocatalyst, the optimal HER activity can be achieved, and abundant catalytic activity sites are provided. It is expected that the strategies developed in this paper may be applied for designing 2D graphene-based electrocatalysts for low-cost and high-performance HER applications.

Abbreviations
HER: Hydrogen evolution reaction; PG: Penta-graphene; 2D: Two dimensional; ΔG0: The Gibbs free energy; TMDs: The transition metal dichalcogenides; VASP: Vienna Ab initio Simulation Package; PAW: Projected augmented wave; PBE: The Perdew–Burke–Ernzerhof; GGA: The generalized gradient approximation; CI-NEB: The climbing image-nudged elastic band; IS: Initial state; FS: The final state; TS: The transition state.

Authors’ contributions
XHZ and DL conceived and designed the study. JBH, FW and LL performed the calculations and analyzed the result data; JBH and CLZ wrote the manuscript. XGM and PFL participated in the discussions and edited the manuscript. All authors read and approved the final manuscript.

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Availability of data and materials
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Declarations
Competing interests
The authors declare that they have no competing interests.

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