

## Article

# Structural, Electronic and Photocatalytic Properties of P-Doped g-C<sub>3</sub>N<sub>4</sub>: A DFT Analysis

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## Abstract

Solar-driven photocatalytic water splitting is a promising approach for green hydrogen production. Despite the great potential of g-C<sub>3</sub>N<sub>4</sub> photocatalysts, non-metal doping studies currently suffer from conflicting results and unclear doping configurations. Herein, first-principles calculations were adopted to compare P-, O-, and S-doped g-C<sub>3</sub>N<sub>4</sub>. P-g-C<sub>3</sub>N<sub>4</sub> with P substituting N shows the best stability, a narrower band gap, and enhanced visible light absorption. It achieves high carrier mobility and suitable band edges for overall water splitting, with a maximum STH efficiency of 15.8%. This work clarifies doping mechanisms and offers solid theoretical support for developing high-performance g-C<sub>3</sub>N<sub>4</sub>-based photocatalysts.

**Keywords:** P-g-C<sub>3</sub>N<sub>4</sub>; HER; DFT

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## 1. Introduction

Hydrogen energy plays a pivotal role in advancing the global energy transition. Photocatalytic water splitting, which drives both the hydrogen evolution reaction (HER) and oxygen evolution reaction (OER), has emerged as a leading route to sustainable green hydrogen production [1]. Boasting zero carbon emissions, high energy density, and excellent long-duration storage capacity, hydrogen is an ideal clean energy carrier [2]. By drawing on the principles of natural photosynthesis, this technique harvests solar energy to split water and generate hydrogen. Since it merely relies on sunlight, water, and functional photocatalysts, the approach features low inherent costs and is expected to become a cost-effective solution for green hydrogen synthesis.

Traditional three-dimensional (3D) photocatalysts, represented by TiO<sub>2</sub> [3], are plagued by multiple technical bottlenecks. Their band gaps exceed 3 eV, which restricts light capture capability. The 3D architecture also causes intense light scattering, lowering photon transmission efficiency and resulting in quantum yields far below theoretical values [2]. Additionally, these catalysts involve complicated synthesis procedures and are hard to recover; their intricate structures also impede uniform coating during large-scale manufacturing [4]. Therefore, exploring new photocatalytic materials that combine high

quantum efficiency, low manufacturing cost, and robust structural stability has become a key research focus for water-splitting hydrogen production.

In studies of photocatalytic HER, two-dimensional (2D) materials have emerged as highly competitive candidates against conventional photocatalysts by virtue of their large specific surface area, abundant reactive sites, shortened carrier migration distances, and outstanding optical properties [5]. As one representative material in this category, graphitic carbon nitride (g-C<sub>3</sub>N<sub>4</sub>) draws extensive research attention for its inexpensive precursors, facile synthesis, non-toxic nature, and environmental compatibility. Even so, this material still has inherent drawbacks, including restricted light absorption, rapid charge carrier recombination, unsatisfactory electrical conductivity, and slow surface reaction kinetics [6].

Numerous theoretical and experimental works have proven that nonmetal doping can effectively improve the photocatalytic activity of g-C<sub>3</sub>N<sub>4</sub>, with O [7], S [8], and P [9] widely adopted as dopants in relevant investigations. For example, Lv et al. [10] synthesized P-doped hollow g-C<sub>3</sub>N<sub>4</sub> photocatalysts with an ultrathin shell (thickness < 25 nm) via a P vapor-assisted method. The as-obtained P-doped ultrathin hollow g-C<sub>3</sub>N<sub>4</sub> spheres (P/UH-CNS) exhibited enlarged surface area and wider light absorption range. Meanwhile, the modified structure restrained charge recombination and alleviated carrier self-trapping, thereby boosting charge transport capability. Benefiting from these improvements, the sample delivered a prominent hydrogen evolution rate of 9653  $\mu\text{mol}\cdot\text{h}^{-1}\cdot\text{g}^{-1}$  under photocatalytic reactions.

Current academic studies regarding the modification and photocatalytic performance optimization of g-C<sub>3</sub>N<sub>4</sub> via elemental doping still present several unresolved deficiencies and inconsistent conclusions, which restrict the in-depth development of related research. At present, there are still several issues regarding research on element doping of g-C<sub>3</sub>N<sub>4</sub>. First, diverse non-metal doping elements exert disparate modification effects on the photocatalytic properties of g-C<sub>3</sub>N<sub>4</sub>, and conflicting findings exist across the relevant literature. In comparative studies on four common non-metal dopants (B, O, P, and S), Arumugam et al. [11] verified that S doping delivers the most prominent improvement in the electron transfer efficiency and photocatalytic CO<sub>2</sub> reduction performance of porous g-C<sub>3</sub>N<sub>4</sub>. In contrast, the theoretical calculation results from Ghashghaee et al. [12] indicated that among the four dopants (B, O, S, P), O doping triggers the most substantial modulation of the HOMO-LUMO band gap in g-C<sub>3</sub>N<sub>4</sub> quantum dots, implying a more significant regulatory effect on the electronic structure of the catalyst. Such divergent outcomes fail to form a unified consensus on the optimal non-metal doping scheme for g-C<sub>3</sub>N<sub>4</sub> modification. Second, the microscopic existing form of doped atoms in modified g-C<sub>3</sub>N<sub>4</sub> materials has not been explicitly and quantitatively identified. Researchers have not yet reached a consistent conclusion on whether doped atoms are anchored on the material's surface via grafting or embedded into the intrinsic crystal lattice of g-C<sub>3</sub>N<sub>4</sub>. Focusing on O doping modification, Zhao et al. [13] demonstrated that O atoms tend to substitute nitrogen lattice sites within the g-C<sub>3</sub>N<sub>4</sub> framework under UV-induced doping conditions, which eliminates deep electron trapping centers and improves CO<sub>2</sub> photoreduction capacity. Nevertheless, Sun et al. [7] proposed a dual existing form of doped O atoms, stating that O can not only replace framework N sites but also bond with surface N atoms to form stable N–O bonds. Third, for dopants embedded in the g-C<sub>3</sub>N<sub>4</sub> crystal lattice, accurate verification of their specific substitution positions remains a technical challenge, i.e., did the dopants replace C atoms or N atoms in g-C<sub>3</sub>N<sub>4</sub>? Relevant research on S-doped g-C<sub>3</sub>N<sub>4</sub> has revealed obvious discrepancies. Zhou et al. [14] confirmed that doped S atoms can simultaneously replace C and N sites, forming C–S and N–S covalent bonds. On the contrary, Guan et al. [15] concluded that S atoms only selectively substitute N sites in the g-C<sub>3</sub>N<sub>4</sub> framework, with no C-site substitution observed in the synthetic system.

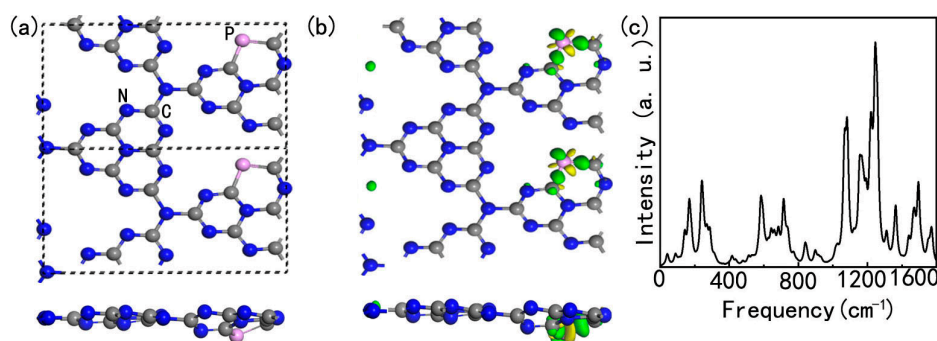
To address the aforementioned issues, this work systematically explores the binding energy characteristics and optical performance of g-C<sub>3</sub>N<sub>4</sub> modified with three typical non-metal dopants, namely P, O, and S. We adopt VASP for DFT simulations owing to its unique merits over Quantum ESPRESSO, CP2K, and CASTEP for 2D doped g-C<sub>3</sub>N<sub>4</sub>. Its PAW potentials precisely describe diffuse p-orbitals and local lattice distortion induced by heteroatom substitution, more accurate than ultrasoft pseudopotentials. Built-in DFT-D3 corrections natively handle van der Waals forces in layered monolayers without extra plug-ins. VASP delivers efficient parallel computation for our large doping supercells and fully supports HSE06-based band, optical, mechanical, and reaction free-energy calculations. Moreover, massive validated precedents in carbon nitride photocatalysis guarantee reliable, comparable results for binding energy, carrier mobility, and STH efficiency. The computational and analytical results demonstrate that P-doped g-C<sub>3</sub>N<sub>4</sub> (P-g-C<sub>3</sub>N<sub>4</sub>) outperforms its O-doped and S-doped counterparts in terms of binding energy. Structural stability analysis verifies that the substitution of lattice N atoms by P heteroatoms delivers the most stable configuration of the doped system. Moreover, P-g-C<sub>3</sub>N<sub>4</sub> presents a well-matched band gap and favorable band edge alignment relative to the redox potentials of water splitting. This unique electronic structure enables spontaneous HER at C and OER at P active sites. The optimized P-g-C<sub>3</sub>N<sub>4</sub> photocatalyst achieves a solar-to-hydrogen (STH) conversion efficiency of up to 15.8%. Collectively, these results confirm that P-g-C<sub>3</sub>N<sub>4</sub> serves as a promising and efficient photocatalytic material for water-splitting-driven hydrogen production.

## 2. Results and Discussion

The optimized lattice constant of pristine g-C<sub>3</sub>N<sub>4</sub> was calculated to be 7.13 Å, which closely matches the experimental and computational results reported in previous studies [16]. To systematically explore the substitution behaviors of P, O, and S heteroatoms at carbon or nitrogen lattice sites, as well as their surface adsorption characteristics on g-C<sub>3</sub>N<sub>4</sub>, a  $\sqrt{2} \times \sqrt{2}$  supercell model was constructed for all subsequent computational simulations, as visualized in Figure S1 (Supplementary Information). For each dopant A (A = P, O, or S), multiple computational models were established to cover substitution at diverse lattice positions and adsorption on different surface sites of g-C<sub>3</sub>N<sub>4</sub>. Binding energy ( $E_b$ ) analysis serves as a reliable indicator for evaluating the structural stability of modified systems, and the calculation results reveal that heteroatom doping yields far more stable g-C<sub>3</sub>N<sub>4</sub> configurations than surface adsorption: the  $E_b$  values of doped structures are over 1.5 eV higher than those of adsorption-modified structures with identical dopants.

Among all constructed doping models, the configuration where P atoms substitute N<sub>2</sub> lattice sites (see Figure S1) presents the maximal binding energy of 8.762 eV. According to the definition of  $E_b$  in the Supplementary Information (Formula S1), a larger positive  $E_b$  value indicates that the material is more stable. This value is at least 0.12 eV larger than those of other P doping sites and all tested O- and S-doped g-C<sub>3</sub>N<sub>4</sub> systems, demonstrating its energy superiority. The optimal P doping site determined in this work is consistent with the findings reported by Srinivasu et al. [17] and Liu et al. [18]. Collectively, these results verify that lattice doping delivers higher structural stability than surface adsorption, and P doping endows g-C<sub>3</sub>N<sub>4</sub> with the most stable structure among the three non-metal modification strategies. Accordingly, subsequent discussions in this study primarily focus on the optimized P-g-C<sub>3</sub>N<sub>4</sub> system. The geometric structure of the most stable P-g-C<sub>3</sub>N<sub>4</sub> model is displayed in Figure 1a, in which N, C, and P atoms are represented by blue, gray, and pale purple spheres, respectively. Owing to the larger covalent radius of P (1.233 Å) relative to N (0.741 Å), the newly formed P–C bonds exhibit an average bond

length of 1.800 Å, distinctly longer than the intrinsic C–N bond length of approximately 1.360 Å in pristine g-C<sub>3</sub>N<sub>4</sub>. Meanwhile, the local structural distortion induced by P substitution reduces the original C–N–C bond angle of nearly 120° to 97.909° for the C–P–C linkage in the optimized doped structure.



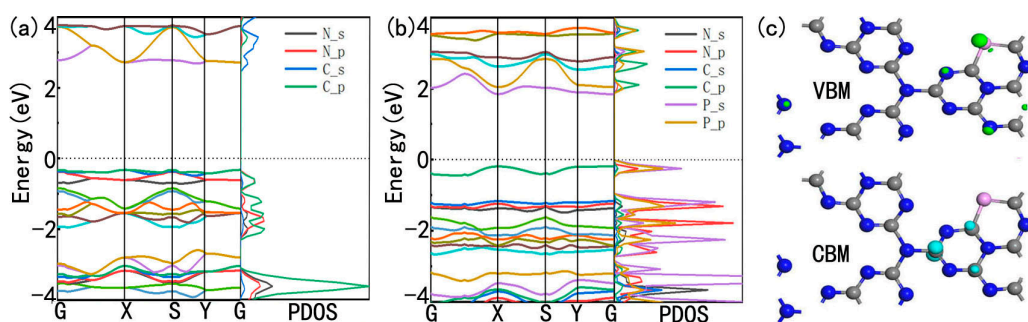
**Figure 1.** (a) Top and side views (the dashed box indicates the unit cell), (b) CDD, (c) Raman spectrum of monolayer P–g-C<sub>3</sub>N<sub>4</sub>.

Charge density difference (CDD) calculations were performed to elucidate the charge transfer behavior between doped P atoms and the g-C<sub>3</sub>N<sub>4</sub> substrate framework. As illustrated in Figure 1b, electron migration occurs from the P p-orbitals to the surrounding P–C bonding regions within the optimized structure. In the CDD cloud diagram, yellow domains correspond to electron depletion areas, whereas green domains denote electron accumulation regions. Complementary Mulliken charge analysis further validates the charge distribution characteristics observed from CDD results. Quantitative calculation data show that the P atom loses 0.58 valence electrons in the optimized P-g-C<sub>3</sub>N<sub>4</sub> system, which can be fundamentally explained by its lower electronegativity (2.19) relative to C atoms (2.55). To provide theoretical references for subsequent experimental characterization of the synthesized P-g-C<sub>3</sub>N<sub>4</sub> monolayer, simulated Raman spectra of the optimized structure were acquired and displayed in Figure 1c.

First-principles calculations were implemented to examine the mechanical properties of the P-g-C<sub>3</sub>N<sub>4</sub> monolayer through systematic evaluation of its elastic stiffness coefficients. The elastic constants of the optimized structure were quantified in units of N m<sup>−1</sup>, yielding the following values: C<sub>11</sub> = 76.7, C<sub>22</sub> = 99.5, C<sub>12</sub> = C<sub>21</sub> = 4.6, and C<sub>44</sub> = 50.3. Structural mechanical stability was further verified in accordance with classic Born stability criteria, which require satisfaction of the inequalities C<sub>11</sub>C<sub>22</sub> − C<sub>12</sub><sup>2</sup> > 0 and C<sub>44</sub> > 0 [19]. The calculated in-plane Young's moduli of P-g-C<sub>3</sub>N<sub>4</sub> are Y<sub>x</sub> = 76.5 N m<sup>−1</sup> and Y<sub>y</sub> = 99.2 N m<sup>−1</sup>, which agree with the parameter range of 90–110 N m<sup>−1</sup> reported in previous studies on P-g-C<sub>3</sub>N<sub>4</sub> [20]. Comparative analysis reveals that the Young's moduli of P-g-C<sub>3</sub>N<sub>4</sub> are substantially lower than those of pristine g-C<sub>3</sub>N<sub>4</sub> (approximately 187 N m<sup>−1</sup>) [21], as well as C-doped (175–185 N m<sup>−1</sup>) and B-doped g-C<sub>3</sub>N<sub>4</sub> systems (155–165 N m<sup>−1</sup>) [20]. Additionally, the P-g-C<sub>3</sub>N<sub>4</sub> monolayer exhibits extremely low Poisson's ratios of ν<sub>x</sub> = 0.05 and ν<sub>y</sub> = 0.06. Such low values indicate negligible lateral shrinkage when the material undergoes axial tensile deformation. This unique mechanical characteristic endows P-g-C<sub>3</sub>N<sub>4</sub> with excellent structural stability under external mechanical loading, broadening its potential applicability in photocatalytic device systems.

Figure 2a presents the electronic band structure of the pristine g-C<sub>3</sub>N<sub>4</sub> monolayer. The material is confirmed to be an indirect-bandgap semiconductor. Calculations using the HSE06 functional yield a bandgap of 2.79 eV, which is consistent with previously reported theoretical results [22]. Figure 2b displays the band structure of P-g-C<sub>3</sub>N<sub>4</sub>. In contrast, the P-doped sample exhibits a direct bandgap of 2.03 eV, which is close to that

reported for the P-doped system [23]. A comparative analysis reveals that P doping narrows the bandgap by 0.76 eV, a variation that greatly facilitates the photocatalytic HER. Both the valence band maximum (VBM) and conduction band minimum (CBM) are situated at the X point within the first Brillouin zone. The partial density of states (PDOS) of P-g-C<sub>3</sub>N<sub>4</sub> demonstrates that the VBM originates from the hybridization of P<sub>p</sub> and P<sub>s</sub> orbitals, while the CBM is predominantly contributed by C<sub>p</sub> orbitals. Furthermore, the electron density distribution of the P-g-C<sub>3</sub>N<sub>4</sub> monolayer (Figure 2c) indicates that the VBM is localized mainly around P atoms, whereas the CBM is distributed over C atoms. These observations agree well with the PDOS analysis. Spatial separation of photogenerated charge carriers can effectively suppress carrier recombination throughout the photocatalytic redox reaction process, serving as a pivotal prerequisite for high-efficiency photocatalysis. Such favorable separation behavior substantially prolongs the lifespan of electrons located at the CBM and greatly mitigates the recombination of internal charge carriers. The exposed C atoms with partial negative charges can act as efficient active sites, enabling the favorable adsorption of positively charged H protons during HER. In addition, the bandgap value of P-g-C<sub>3</sub>N<sub>4</sub> is highly consistent with the optimal theoretical bandgap of around 2.20 eV reported in previous studies [24]. This unique bandgap characteristic endows the modified material with excellent catalytic potential for both HER and OER.



**Figure 2.** Computed HSE06 band structure and PDOS of g-C<sub>3</sub>N<sub>4</sub> (a) and P-g-C<sub>3</sub>N<sub>4</sub> (b) nanosheets. The Fermi level is set to zero. Partial charge densities of VBM and CBM (c) of the P-g-C<sub>3</sub>N<sub>4</sub> nanosheet. The isosurface value is taken as 0.10 e Å<sup>-3</sup>.

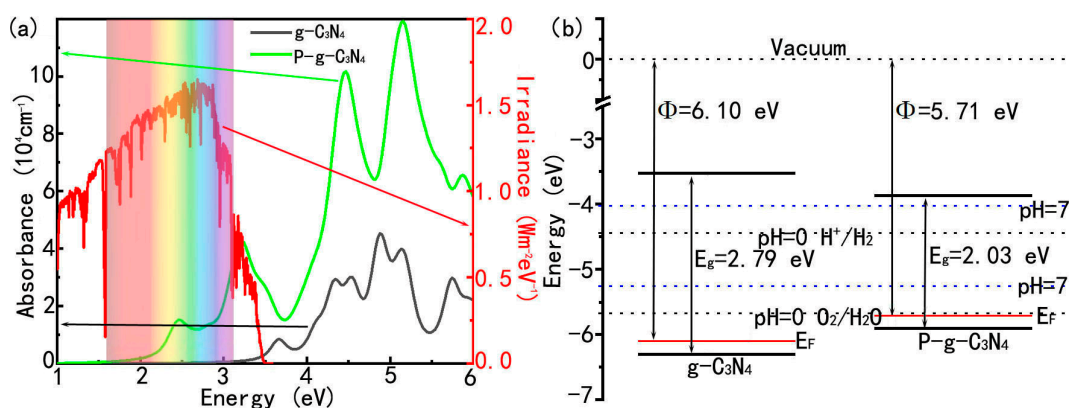
Carrier mobility determines the overall working efficiency of optoelectronic devices. Table 1 lists the critical parameters of the P-g-C<sub>3</sub>N<sub>4</sub> monolayer investigated in this work. The effective mass ( $m^*$ ) of charge carriers exhibits obvious anisotropic characteristics, which originate from the asymmetric atomic configuration of the material along the x and y directions (Figure 1a). As summarized in Table 1, the hole effective mass along the x-axis is nearly four-fold greater than that of the electron. This phenomenon aligns well with the electronic band features presented in Figure 2a, where the valence band displays a flat profile while the conduction band shows prominent dispersion. Generally, smaller  $m^*$  values enable faster carrier migration to catalytic active sites, which is beneficial to photocatalytic reaction kinetics. The energy-strain relationship was further analyzed to calculate the in-plane 2D elastic moduli ( $C_{2D}$ ) of the material, which were measured as 71.22 N·m<sup>-1</sup> and 87.15 N·m<sup>-1</sup>, respectively. Deformation potential ( $E_{DP}$ ) calculations also revealed distinct directional differences: the absolute value for holes along the y-direction reaches 9.52 eV, far exceeding that for electrons (5.93 eV). Combined with the calculated  $m^*$ ,  $C_{2D}$ , and  $E_{DP}$ , the carrier mobility at 300 K was quantitatively evaluated. The results show that the electron mobility ( $\mu_e$ ) along the x-direction is 246.83 cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup>, roughly four times higher than the y-direction hole mobility ( $\mu_h$ , 47.26 cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup>). A comparison with the existing literature demonstrates that the  $\mu_e$  value of P-g-C<sub>3</sub>N<sub>4</sub> is superior to that of pristine g-C<sub>3</sub>N<sub>4</sub> monolayer (127.39 cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup>) [17] and 10% P-g-C<sub>3</sub>N<sub>4</sub>/SWCNT composites (6.12

$\text{cm}^2 \text{V}^{-1} \text{s}^{-1}$ ) [25]. The remarkable improvement in carrier mobility allows photogenerated electrons and holes to migrate along different directions, which effectively restrains the recombination of electron–hole pairs.

**Table 1.** Calculated effective mass  $m^*$  ( $m_e$ ), elastic modulus  $C_{2D}$  ( $\text{N m}^{-1}$ ), absolute value of the deformation potential constant  $E_{DP}$  (eV), and carrier mobility  $\mu$  ( $\text{cm}^2 \text{V}^{-1} \text{s}^{-1}$ ) along the x and y directions for P-g- $\text{C}_3\text{N}_4$  monolayer at 300 K.  $m_e$  is the electron rest mass.

| Carrier Type | Direction | $m^*$ | $C_{2D}$ | $E_{DP}$ | $\mu$  |
|--------------|-----------|-------|----------|----------|--------|
| e            | x         | 0.50  | 71.22    | 5.93     | 246.83 |
|              | y         | 0.24  | 87.15    | 15.62    | 90.73  |
| h            | x         | 1.913 | 71.22    | 7.36     | 11.60  |
|              | y         | 0.914 | 87.15    | 5.71     | 47.26  |

A photocatalyst's light-harvesting ability is a decisive factor that affects the overall water splitting efficiency. The optical absorption behaviors of pristine g- $\text{C}_3\text{N}_4$  and P-g- $\text{C}_3\text{N}_4$  monolayers were simulated using the HSE06 hybrid exchange–correlation functional, and the calculated spectral profiles are presented in Figure 3a. Consistent with earlier results [26], pure g- $\text{C}_3\text{N}_4$  only generates noticeable optical absorption when the photon energy exceeds 3.5 eV, which restricts its usability within the solar spectrum. In contrast, P doping greatly boosts the light absorption capability of g- $\text{C}_3\text{N}_4$  and shifts the absorption edge downward to 2.10 eV. Such a prominent red shift originates from the introduction of P impurity states within the band gap, which optimizes the material's optical response range. For the P-g- $\text{C}_3\text{N}_4$  monolayer, two distinct absorption bands arise in the visible region. The first absorption peak occurs at 2.45 eV (507 nm) and the second at 3.20 eV (388 nm), both with absorption coefficients above  $10^4 \text{ cm}^{-1}$  and in the visible light band. A stronger absorption signal is also captured in the deep ultraviolet region at 4.36 eV (285 nm), with absorption intensity approaching  $1 \times 10^5 \text{ cm}^{-1}$ . Quantitative analysis of reflectivity and electron energy-loss spectra (EELS, Figure S2) reveals weak optical attenuation and minor plasmonic energy loss over the calculated energy window; these two optical observables collectively indicate limited energy dissipation of the monolayer. These optical characteristics confirm that P doping endows g- $\text{C}_3\text{N}_4$  with broad and strong light absorption spanning visible and ultraviolet regions, making the modified material a promising candidate for practical visible-light-triggered overall water splitting.



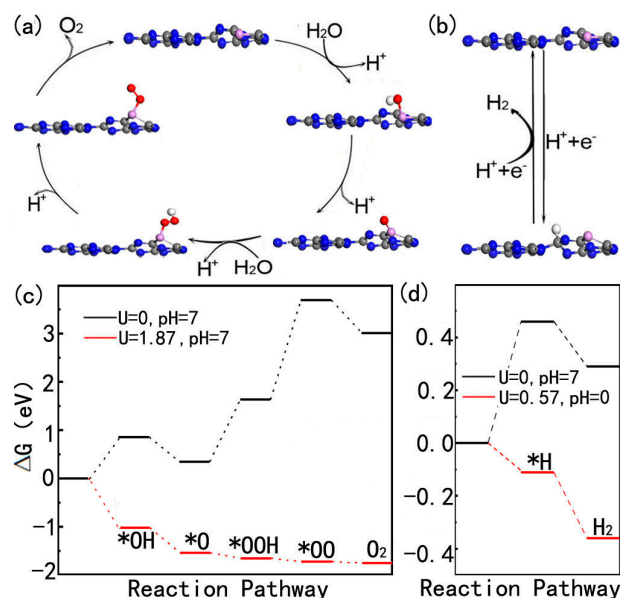
**Figure 3.** (a) Optical absorption coefficients of the g- $\text{C}_3\text{N}_4$  and P-g- $\text{C}_3\text{N}_4$  monolayers at the HSE06 level and solar radiation data of AM 1.5 G. (b) HSE06 level band edge positions compared with water redox potentials of  $\text{H}^+/\text{H}_2$  and  $\text{H}_2\text{O}/\text{O}_2$  at both neutral (pH = 7) and acidic (pH = 0) conditions. The vacuum energy level is set to 0.

Suitable band edge alignment is a fundamental thermodynamic requirement for photocatalysts applied in overall water splitting. Specifically, the CBM must lie above the hydrogen reduction potential ( $E_{H^+/H_2} = -4.44$  eV vs. vacuum), while the VBM needs to be positioned below the water oxidation potential ( $E_{O_2/H_2O} = -5.67$  eV vs. vacuum). These criteria ensure that both the HER and OER proceed spontaneously. As illustrated in Figure 3b, the P-g-C<sub>3</sub>N<sub>4</sub> monolayer exhibits a CBM potential of  $-3.87$  eV and a VBM potential of  $-5.90$  eV, which fully meets the band edge criteria for simultaneous water reduction and oxidation at pH = 0. Valid band edge configurations can also be maintained under neutral conditions (pH = 7). Although pristine g-C<sub>3</sub>N<sub>4</sub> also satisfies the thermodynamic requirements for water splitting, with a CBM of  $-3.51$  eV and a VBM of  $-6.30$  eV, its intrinsically wider band gap severely limits solar light absorption capacity (Figure 3a).

Figure 4 displays the geometric structures of the P-g-C<sub>3</sub>N<sub>4</sub> monolayer with adsorbed intermediates throughout the OER and HER processes, alongside the corresponding Gibbs free energy evolution profiles. Figure 4a depicts the conventional four-electron transfer mechanism for OER [27], which involves four key reaction intermediates, namely \*OH, \*O, \*OOH, and \*OO. The calculated Gibbs free energy changes ( $\Delta G$ ) for the OER half-reaction in neutral aqueous solution are presented in Figure 4c, with black and red curves representing the reaction states without and with external applied potential ( $U$ ), respectively. Under dark and neutral conditions, thermodynamic analysis reveals that only the second and the fifth reaction steps proceed spontaneously among the entire OER pathway. The initial step corresponds to the conversion of adsorbed water molecules into \*OH intermediates, which requires an energy input of  $0.86$  eV. The subsequent transformation from \*OH to \*O is an exergonic process with a  $\Delta G$  value of  $-0.52$  eV, which benefits from the strong adsorption affinity of the P-g-C<sub>3</sub>N<sub>4</sub> surface toward oxygen species. In the third step, the generated \*O reacts with free water molecules to form \*OOH intermediates anchored at P sites, consuming a free energy of  $1.30$  eV. The fourth step for \*OO formation acts as the rate-determining step, possessing the maximum energy barrier of  $2.01$  eV. By contrast, the final oxygen desorption step occurs spontaneously with a negative free energy change of  $-0.69$  eV. These computational results demonstrate that the P-g-C<sub>3</sub>N<sub>4</sub> monolayer requires an overpotential of  $2.01$  V to complete the full OER catalytic cycle under neutral dark conditions, which is lower than the overpotential of pristine g-C<sub>3</sub>N<sub>4</sub> ( $2.28$  V) [28]. This indicates that the OER process on P-g-C<sub>3</sub>N<sub>4</sub> cannot occur spontaneously in neutral dark environments. Notably, photoexcitation effectively addresses this thermodynamic limitation. Photogenerated holes endow the catalyst with an additional external potential of  $1.87$  V, which activates the OER catalytic reaction. Under light irradiation, all elementary reaction steps deliver negative  $\Delta G$  values of  $-1.01$ ,  $-0.52$ ,  $-0.12$ ,  $-0.08$ , and  $-0.03$  eV in turn, verifying the thermodynamic spontaneity of water oxidation into oxygen in neutral aqueous solution. Such photovoltage-driven catalytic behavior enables efficient and sustainable OER conversion without external energy input under light illumination.

Further investigations were carried out for elementary HER pathways of the P-g-C<sub>3</sub>N<sub>4</sub> monolayer under neutral pH conditions, with Gibbs free energy profiles for both dark and illuminated states summarized in Figure 4b,d. Under dark environments ( $U = 0$  V), the adsorption process of hydrogen atoms to form \*H intermediates on the P-g-C<sub>3</sub>N<sub>4</sub> surface is thermodynamically unfavorable, with a free energy barrier of  $0.46$  eV. The subsequent desorption process of \*H to generate H<sub>2</sub> molecules presents a negative free energy change of  $0.17$  eV, indicating sluggish HER kinetics without light excitation. Conversely, solar irradiation triggers the generation of photocarriers, providing a stable applied bias of  $U = 0.57$  eV (in an acidic environment, pH = 0) to drive the HER process. This photoinduced potential completely modulates the thermodynamic properties of the reaction

pathway, making both hydrogen adsorption and H<sub>2</sub> desorption steps spontaneous. The corresponding free energy changes decrease to −0.11 eV and −0.25 eV, respectively, suggesting a substantial reduction in reaction energy barriers. The above thermodynamic analyses of HER and OER, combined with the band structure characteristics and mobilities of P- g-C<sub>3</sub>N<sub>4</sub>, collectively demonstrate that P doping endows the g-C<sub>3</sub>N<sub>4</sub> monolayer with optimized electronic structures, favorable photoelectric transport performance, and superior photocatalytic reaction thermodynamics.



**Figure 4.** Pathways of water oxidation (a) and hydrogen reduction (b) half-reactions on the P-g-C<sub>3</sub>N<sub>4</sub> monolayer with the adsorbed intermediates ( $*OH$ ,  $*O$ ,  $*OOH$ ,  $*OO$ , and  $*H$ ). The red (white) ball is an O (H) atom. Gibbs free energy diagrams of OER (c) and HER (d) on P-g-C<sub>3</sub>N<sub>4</sub> monolayer under different conditions.

Energy conversion efficiency is a core evaluation index for quantifying the practical performance of photocatalysts in water splitting systems. On the basis of band alignment calculations, the energy conversion performance of the P-g-C<sub>3</sub>N<sub>4</sub> monolayer was evaluated under the assumption of 100% catalytic reaction yield [29]. Key efficiency parameters including light absorption efficiency ( $\eta_{abs}$ ), carrier utilization efficiency ( $\eta_{cu}$ ), and solar-to-hydrogen conversion efficiency ( $\eta_{STH}$ ) are summarized in Table S2. The P-g-C<sub>3</sub>N<sub>4</sub> monolayer achieves a  $\eta_{abs}$  value of 34.3% and a  $\eta_{cu}$  exceeding 30%, which is attributed to its favorable  $\chi$  (H<sub>2</sub>) and  $\chi$  (O<sub>2</sub>) across a wide pH range of 0 to 7. Remarkably, the P-g-C<sub>3</sub>N<sub>4</sub> monolayer delivers a maximum  $\eta_{STH}$  of 15.8% at pH = 7, which benefits from the synergistic effect of its excellent  $\eta_{abs}$  and  $\eta_{cu}$  (Table S2). The high STH efficiency originates from separated charge carriers, reduced bandgap, strong visible absorption, and fast electron transport. Its performance can be further promoted by optimizing P doping dosage, loading HER/OER co-catalysts, or constructing 2D heterojunctions to suppress recombination and lower Gibbs free energy barriers of surface redox steps. This value is far higher than the  $\eta_{STH}$  of pristine g-C<sub>3</sub>N<sub>4</sub> (~2.2%) [30] and is close to the classic theoretical limit of around 18% [29]. Furthermore, the  $\eta_{STH}$  of P-g-C<sub>3</sub>N<sub>4</sub> surpasses the 10% threshold, which is recognized as the minimum efficiency standard for economically feasible photocatalytic hydrogen production [31].

### 3. Computational Methods

All structural optimizations, total energy calculations, and photocatalytic property evaluations in this study were implemented via VASP [32,33]. The projector augmented wave (PAW) approach [34] was adopted to characterize the interactive behaviors between electrons and ions within the simulated systems. For exchange–correlation energy processing, the Perdew–Burke–Ernzerhof (PBE) functional [35] based on the generalized gradient approximation (GGA) was applied throughout geometric optimization and energy computation processes. Grimme’s DFT-D3 semiempirical correction method [36] was further introduced to accurately capture van der Waals (vdW) interactions in all computational cases. To acquire more reliable electronic structure data and precise optical absorption spectral analysis, the HSE06 hybrid functional [37] was adopted for subsequent electronic and optical property calculations. Partial first-principles calculation outputs were post-processed using the VASPKIT program [38] for further data sorting and analysis. Detailed computational principles and parameter settings for electronic characteristics, optical behaviors, and photocatalytic performance simulations are provided in the Supporting Information (SI).

### 4. Conclusions

This work systematically explored the structural stability, electronic properties, and optical characteristics of three non-metal atoms (P, O, and S) doped or adsorbed onto g-C<sub>3</sub>N<sub>4</sub> via DFT calculations, aiming to screen out optimal heteroatom dopants for boosting its photocatalytic water splitting performance. Computational results demonstrate that P doping endows the g-C<sub>3</sub>N<sub>4</sub> monolayer with the strongest binding energy among all modified systems, which guarantees robust structural stability for long-term photocatalytic reactions. In addition, the optimized P-g-C<sub>3</sub>N<sub>4</sub> material delivers a well-matched band gap and favorable band edge alignment that fully covers the redox potential window of water splitting. Benefiting from P atom modulation, the modified catalyst exhibits enhanced visible-light absorption capacity and superior electron migration efficiency. Thermodynamic analysis further confirms that P-g-C<sub>3</sub>N<sub>4</sub> can simultaneously drive spontaneous HER and OER under solar irradiation. More importantly, the calculated solar-to-hydrogen conversion efficiency of P-g-C<sub>3</sub>N<sub>4</sub> exceeds the 10% threshold for commercial hydrogen production, achieving a technically and economically viable performance level. Collectively, this theoretical evidence proves that P-g-C<sub>3</sub>N<sub>4</sub> serves as a competitive photocatalyst for large-scale solar-driven hydrogen generation.

**Supplementary Materials:** The following supporting information can be downloaded at <https://www.mdpi.com/article/10.3390/catal16080743/s1>. Computational details: Figure S1: Different doping (a) and adsorption (b) sites of P, S, and O atoms in/on g-C<sub>3</sub>N<sub>4</sub>. The notations C1, etc., represent different doping sites in (a), while T1, etc., denote various adsorption sites in (b). Figure S2: The electron energy loss spectra (EELS) and reflectivity of g-C<sub>3</sub>N<sub>4</sub> (a) and P-g-C<sub>3</sub>N<sub>4</sub> (b) monolayers; Free energy difference ( $\Delta G$ ). Table S1: Zero-point energy correction (EZPE), entropy contribution (TS, T = 298.15K), total energy (E), and the Gibbs free energy (G) of molecules and intermediate products adsorbed on the P-g-C<sub>3</sub>N<sub>4</sub> monolayer; the Solar-to-hydrogen (STH) efficiency. Table S2: Calculated overpotentials for HER  $\chi$  (H<sub>2</sub>) and OER  $\chi$  (O<sub>2</sub>), the energy of photons of P-g-C<sub>3</sub>N<sub>4</sub> monolayer, as a function of pH ( $E_{\text{pH}}$ ), and the energy conversion efficiency of light absorption ( $\eta_{\text{abs}}$ ), carrier utilization ( $\eta_{\text{cu}}$ ), and STH ( $\eta_{\text{STH}}$ ). References [39–42].

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## References

1. Dharmarajan, N.P.; Vidyasagar, D.; Yang, J.-H.; Talapaneni, S.N.; Lee, J.; Ramadass, K.; Singh, G.; Fawaz, M.; Kumar, P.; Vinu, A. Bio-Inspired Supramolecular Self-Assembled Carbon Nitride Nanostructures for Photocatalytic Water Splitting. *Adv. Mater.* **2024**, *36*, 2306895.
2. Ma, D.D.; Chen, J.T.; Li, J.; Ji, X.; Shi, J.-W. A review on passivation engineering for improving photocatalytic hydrogen evolution performance. *J. Mater. Chem. A* **2024**, *12*, 12293–12324.
3. Rosa, D.; Palma, L.D. Advanced solar photocatalysis in continuous mode: H<sub>2</sub>O<sub>2</sub>-enhanced removal of organic contaminants in simulated and real wastewater. *J. Water Process Eng.* **2025**, *80*, 109114.
4. Chu, X.Z.; Sathish, C.I.; Yang, J.-H.; Guan, X.W.; Zhang, X.W.; Qiao, L.; Domen, K.; Wang, S.B.; Vinu, A.; Yi, J.B. Strategies for Improving the Photocatalytic Hydrogen Evolution Reaction of Carbon Nitride-Based Catalysts. *Small* **2023**, *19*, 2302875.
5. Guo, R.-T.; Zhang, Z.-R.; Xia, C.; Li, C.-F.; Pan, W.-G. Recent progress of cocatalysts loaded on carbon nitride for selective photoreduction of CO<sub>2</sub> to CH<sub>4</sub>. *Nanoscale* **2023**, *15*, 8548–8577.
6. Lv, S.J.; Wu, C.X.; Ng, Y.H.; Zhang, Y.F.; Peng, J.H.; Liu, Y.X.; Zhang, Q.C.; Li, S.; Sun, Y.J.; Jing, L.; et al. Phosphorus-containing g-C<sub>3</sub>N<sub>4</sub> photocatalysts for hydrogen evolution: A review. *Int. J. Hydrogen Energy* **2022**, *47*, 42136–42149.
7. Sun, S.; Li, J.; Gou, X.; Cui, J.; Yang, Q.; Liang, S.; Yang, Z.; Zhang, J. Constructing oxygen-doped g-C<sub>3</sub>N<sub>4</sub> nanosheet with enlarged conductive band edge for enhanced visible-light-driven hydrogen evolution. *Inorg. Chem. Front.* **2018**, *5*, 1721–1727.
8. Zhang, Z.F.; Song, C.H.; Fan, J.P.; Fang, Z.J.; Wang, H.T.; Zou, J. Morphology and doping engineering of sulfur-doped g-C<sub>3</sub>N<sub>4</sub> hollow nanovesicles for boosting photocatalytic hydrogen production. *J. Mater. Chem. A* **2025**, *13*, 6385–6396.
9. Li, C.H.; Yang, Q.Y.; Song, T.; Xie, C.; Shi, W.B.; Yang, P. P/S-g-C<sub>3</sub>N<sub>4</sub> nanosheet composites with enhanced photocatalytic water splitting and dye degradation. *J. Alloys Compd.* **2024**, *973*, 172962.
10. Lv, S.J.; Ng, Y.H.; Zhu, R.X.; Li, S.; Wu, C.X.; Liu, Y.X.; Zhang, Y.F.; Jing, L.; Deng, J.G.; Dai, H.X. Phosphorus vapor assisted preparation of P-doped ultrathin hollow g-C<sub>3</sub>N<sub>4</sub> sphere for efficient solar-to-hydrogen conversion. *Appl. Catal. B Environ.* **2021**, *297*, 120438.
11. Arumugam, M.; Tahir, M.; Praserttham, P. Effect of nonmetals (B, O, P, and S) doped with porous g-C<sub>3</sub>N<sub>4</sub> for improved electron transfer towards photocatalytic CO<sub>2</sub> reduction with water into CH<sub>4</sub>. *Chemosphere* **2022**, *286*, 131765.
12. Ghashghaee, M.; Azizi, Z.; Ghambarian, M. Conductivity tuning of charged triazine and heptazine graphitic carbon nitride (g-C<sub>3</sub>N<sub>4</sub>) quantum dots via nonmetal (B, O, S, P) doping: DFT calculations. *J. Phys. Chem. Solids* **2020**, *141*, 109422.
13. Zhao, X.L.; Yi, X.P.; Pan, W.D.; Wang, Y.F.; Luo, S.J.; Zhang, Y.G.; Xie, R.J.; Leung, D.Y.C. UV light-induced oxygen doping in graphitic carbon nitride with suppressed deep trapping for enhancement in CO<sub>2</sub> photoreduction activity. *J. Mater. Sci. Technol.* **2023**, *133*, 135–144.
14. Zhou, Y.; Lv, W.; Zhu, B.; Tong, F.; Pan, J.; Bai, J.; Zhou, Q.; Qin, H. Template-free one-step synthesis of g-C<sub>3</sub>N<sub>4</sub> nanosheets with simultaneous porous network and S-doping for remarkable visible-light-driven hydrogen evolution. *ACS Sustain. Chem. Eng.* **2019**, *7*, 5801–5807.
15. Guan, K.; Li, J.; Lei, W.; Wang, H.; Zhang, S. Synthesis of sulfur doped g-C<sub>3</sub>N<sub>4</sub> with enhanced photocatalytic activity in molten salt. *J. Mater. Chem.* **2021**, *7*, 1131–1142.
16. Wang, X.; Maeda, K.; Thomas, A.; Takanabe, K.; Xin, G.; Carlsson, J.; Domen, K.; Antonietti, M. A metal-free polymeric photocatalyst for hydrogen production from water under visible light. *Nat. Mater.* **2009**, *8*, 76–80.
17. Srinivasu, K.; Modak, B.; Ghosh, S.K. Porous Graphitic Carbon Nitride: A Possible Metal-free Photocatalyst for Water Splitting. *J. Phys. Chem. C* **2014**, *118*, 26479–26484.

18. Liu, J.J. Effect of phosphorus doping on electronic structure and photocatalytic performance of g-C<sub>3</sub>N<sub>4</sub>: Insights from hybrid density functional calculation. *J. Alloys Compd.* **2016**, *672*, 271–276.
19. Ding, Y.; Wang, Y.L. Density Functional Theory Study of the Silicene-like SiX and XSi<sub>3</sub> (X = B, C, N, Al, P) Honeycomb Lattices: The Various Buckled Structures and Versatile Electronic Properties. *J. Phys. Chem. C* **2013**, *117*, 18266–18278.
20. Ruan, L.W.; Zhu, Y.J.; Qiu, L.G.; Lu, Y.X. Mechanical properties of doped g-C<sub>3</sub>N<sub>4</sub>—A first-principle study. *Vacuum* **2014**, *106*, 79–85.
21. Qu, L.H.; Deng, Z.Y.; Yu, J.; Lu, X.K.; Zhong, C.G.; Zhou, P.X.; Lu, T.S.; Zhang, J.M.; Fu, X.L. Mechanical and electronic properties of graphitic carbon nitride (g-C<sub>3</sub>N<sub>4</sub>) under biaxial strain. *Vacuum* **2020**, *176*, 109358.
22. Wang, J.; Guan, Z.; Huang, J.; Li, Q.; Yang, J. Enhanced photocatalytic mechanism for the hybrid g-C<sub>3</sub>N<sub>4</sub>/MoS<sub>2</sub> nanocomposite. *J. Mater. Chem.* **2014**, *2*, 7960–7966.
23. Zhou, X.F.; Wang, P.; Li, M.; Wu, M.F.; Jin, B.; Luo, J.; Chen, M.F.; Zhou, X.Q.; Zhang, Y.N.; Zhou, X.S. Synergistic effect of phosphorus doping and MoS<sub>2</sub> co-catalysts on g-C<sub>3</sub>N<sub>4</sub> photocatalysts for enhanced solar water splitting. *J. Mater. Sci. Technol.* **2023**, *158*, 171–179.
24. Meng, X.Y.; Wang, L.; Liu, D.Y.; Wen, X.; Zhu, Q.; Goddard Iii, W.A.; An, Q. Discovery of Fe<sub>2</sub>P-Type Ti(Zr/Hf)<sub>2</sub>O<sub>6</sub> Photocatalysts toward Water Splitting. *Chem. Mater.* **2016**, *28*, 1335–1342.
25. Ma, X.L.; Li, Y.; Jiang, C.; Chen, S.; Liu, H.; Zhang, Y.F.; Zhang, Q.; Du, F.P. Elements Doping Strategy for Improving the Thermoelectric Properties of g-C<sub>3</sub>N<sub>4</sub>/SWCNT Composite Films. *ACS Appl. Mater. Interfaces* **2025**, *17*, 14510–14519.
26. Ran, J.R.; Ma, T.Y.; Gao, G.P.; Duc, X.W.; Qiao, S.; Z. Porous P-doped graphitic carbon nitride nanosheets for synergistically enhanced visible-light photocatalytic H<sub>2</sub> production. *Energy Environ. Sci.* **2015**, *8*, 3708–3717.
27. Wang, J.J.; Tian, J.F.; Han, P.; Song, L.X.; Wang, W.; Lin, K.Y.; Feng, D.; Ma, B.J. Enhanced Photocatalytic Hydrogen Production Activity Driven by TiO<sub>2</sub>/(MoP/CdS): Insights from Powder Particles to Thin Films. *Langmuir* **2024**, *40*, 21161–21170.
28. Zhang, Y.; Antonietti, M. Photocurrent Generation by Polymeric Carbon Nitride Solids: An Initial Step towards a Novel Photo-voltaic System. *Chem. — Asian J.* **2010**, *5*, 1307–1311.
29. Fu, C.-F.; Sun, J.; Luo, Q.; Li, X.; Hu, W.; Yang, J. Intrinsic Electric Fields in Two-dimensional Materials Boost the Solar-to-Hydrogen Efficiency for Photocatalytic Water Splitting. *Nano Lett.* **2018**, *18*, 6312–6317.
30. Wang, Y.; Brocks, G.; Er, S. Data-Driven Discovery of Intrinsic Direct-Gap 2D Materials as Potential Photocatalysts for Efficient Water Splitting. *ACS Catal.* **2024**, *14*, 1336–1350.
31. Yang, H.; Ma, Y.; Zhang, S.; Jin, H.; Huang, B.; Dai, Y. GeSe@SnS: Stacked Janus Structures for Overall Water Splitting. *J. Mater. Chem. A* **2019**, *7*, 12060–12067.
32. Kresse, G.; Hafner, J. Ab initio molecular dynamics for liquid metals. *Phys. Rev. B* **1993**, *47*, 558.
33. Kresse, G.; Furthmüller, J. Efficient iterative schemes for ab initio total-energy calculations using a plane-wave basis set. *Phys. Rev. B* **1996**, *54*, 11169.
34. Blöchl, P.E. Projector augmented-wave method. *Phys. Rev. B* **1994**, *50*, 17953–17979.
35. Perdew, J.P.; Burke, K.; Ernzerhof, M. Generalized gradient approximation made simple. *Phys. Rev. Lett.* **1996**, *78*, 1396.
36. Grimme, S.; Antony, J.; Ehrlich, S.; Krieg, H. A consistent and accurate ab initio parametrization of density functional dispersion correction (DFT-D) for the 94 elements H–Pu. *J. Chem. Phys.* **2010**, *132*, 154104.
37. Heyd, J.; Scuseria, G.E.; Ernzerhof, M. Hybrid functionals based on a screened coulomb potential. *J. Chem. Phys.* **2003**, *118*, 8207–8215.
38. Wang, V.; Xu, N.; Liu, J.-C.; Tang, G.; Geng, W.-T. VASPKIT: A User-Friendly Interface Facilitating High-Throughput Computing and Analysis Using VASP Code. *Comput. Phys. Commun.* **2021**, *267*, 108033.
39. Bardeen, J.; Shockley, W. Deformation Potentials and Mobilities in Non-Polar Crystals. *Phys. Rev.*, **1950**, *80*, 72–80.
40. Chakrapani, V.; Angus, J. C.; Anderson, A. B.; Wolter, S. D.; Stonera, B. R.; Sumanasekera, G. U. Charge Transfer Equilibria Between Diamond and an Aqueous Oxygen Electrochemical Redox Couple. *Science*, **2007**, *318*, 1424–1430.
41. Nørskov, J. K.; Rossmeisl, J.; Logadottir, A.; Lindqvist, L.; Kitchin, J. R.; Bligaard, T.; Jónsson, H. Origin of the Overpotential for Oxygen Reduction at a Fuel-Cell Cathode. *J. Phys. Chem. B*, **2004**, *108*, 17886–17892.
42. Gueymard, C. A. The sun’s total and spectral irradiance for solar energy applications and solar radiation models. *Sol. Energy*, **2004**, *76*, 423–453.

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