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Non-Metal Doping as a First-Principles Study for Promoting the Hydrogen Evolution of Two-Dimensional Electride Y₂C Electrocatalysts

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Abstract: The two-dimensional electrochemical Y₂C's low work function and strong charge transfer qualities limit its applicability in catalysis due to its poor catalytic activity. In this paper, based on density functional theory calculations, we use two techniques to increase the HER catalytic activity of the Y₂C monolayer: substitution doping (X_C) and adsorption doping (X_T) of non-metal (X = N, P, O, S, and F). The results showed that the absolute values of hydrogen free energies (ΔG_{H^*}) of the substitutional dopants of P_C, S_C and adsorptive dopants of N_T, O_T, S_T, and P_T had increased catalytic activity compared with those of the pristine Y₂C monolayer (−0.673 eV). It was highlighted that the adsorption doping of P_T can further reduce the adsorption free energy of the pristine Y₂C monolayer to −0.19 eV, which is close to the optimal zero value, and the binding energy of the hydrogen atoms on the Y₂C surface significantly increased from −0.913 to −0.438 eV, which is more favorable for the desorption of hydrogen atoms. These results demonstrate that the doping of non-metals activates the adsorption of hydrogen atoms on monolayer Y₂C and provides a feasible method for hydrogen generation.

Keywords: two-dimensional electride; Y₂C; hydrogen evolution reaction; non-metal doping; first-principles



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1. Introduction

Global demand for all types of energy is rising in tandem with the growing population. Expert predictions state that over the course of the 28-year period from 2012 to 2040, there will be a significant increase in the total global demand for energy in its most basic form, or primary energy, which includes both renewable and conventional fossil fuels like coal and non-renewable energy sources like solar and wind power, oil, and natural gas [1,2]. Approximately 80% of this demand for energy will still come from traditional fossil fuels, and the extensive use of these fuels can result in serious environmental issues [3]. It is critical to locate clean, plentiful, and renewable energy sources in order to reduce environmental pollution and solve the world's energy dilemma [4–9]. Hydrogen's zero-pollution characteristic has made it a potential substitute for fossil fuels [9–12]. Electrochemical water decomposition (EWD) is a green alternative for the efficient synthesis of high-quality hydrogen [13,14]. Many investigations and theories have revealed that the Gibbs free energy of hydrogen adsorbed on the electrode surface is the primary component in influencing the hydrogen precipitation reaction activity [15]. Platinum is currently the best HER catalyst material [16,17]. However, its high cost and unavailability have substantially limited its wide application in reality [18–22]. In order to achieve the large-scale and sustainable production of H₂, researchers need to identify new materials or adapt existing materials to increase HER performance given their limited

economic efficiency and storage capacity. In the past few years, 2D materials have been proposed as effective HER catalysts due to their large specific surface area, abundant active sites, tunable electronic properties, and good electrocatalytic performance, such as transition metal carbon/oxygen/phosphorus/sulfides [23–27], graphene-like carbon nitrides (g-C₃N₄) [28,29], layered double hydroxides (LDHs) [30], monoatomic catalysts (SACs) [31], and two-dimensional electronic compounds (2D-electrides) [32].

In recent years, two-dimensional electrides (2D-electrides) as new two-dimensional (2D) materials have been exploited in catalysis because to their high electron transport capacity, low work function, and excellent catalytic activity [33–35]. For example, the electride [Ca₂₄Al₂₈O₆₄]⁴⁺·4e[−] (commonly abbreviated as C12A7: e[−]) has a low figure of merit and good electron transfer ability and is employed in the synthesis of ammonia-catalyzed organics, light-emitting diodes, and other materials [36]. Ru-loaded Y₅Si₃ (Ru/Y₅Si₃) is a very efficient catalyst for ammonia synthesis because of its excellent electron transfer capacity, which can minimize the activation energy of the ammonia synthesis reaction [37]. The Cu-based intermetallic electride LaCu_{0.67}Si_{1.33} has high carrier densities and low work functions, which can effectively reduce the activation energy of chemical reactions and exhibit excellent catalytic activity in various hydrogenation reactions [38]. Recently, a layered electride material, yttriumized, with dicarbon-containing 2D anionic electrons has been disclosed. This multilayer electride (Y₂C) has been proposed as a candidate for prospective HER catalysts due to its low work function (2.7 eV) and efficient charge-transfer characteristics, broad pH application, and good stability [39–42]. However, its weak catalytic activity ($\Delta G_{H^*} = -0.673$ eV) limits its application in catalysis. Catalyst modification via elemental doping is widely used to enhance HER performance. According to Shi et al., P doping at a concentration of 2.85 weight percent significantly increased the catalytic activity of Mo₂C because of the increased electron density close to the Fermi level of the compound. This led to a decrease in Mo-H bonding and a faster rate of HER kinetics [43]. Wu et al., doped non-metal oxygen (O) elements into Co₂P to increase the HER activity of Co₂P in alkaline media [44]. Sun et al., inserted N dopants into WC with a considerable rise in the (H-atom) hydrogen-atom binding energy from −1.05 eV to −0.72 eV on the surface of WC (001), which is more favorable for hydrogen atoms desorption [45]. Therefore, elemental doping is a powerful technique for altering the electronic structure and optimizing the physical properties of a compound, therefore dramatically enhancing the HER performance of the compound.

In this work, we examine the hydrogen (H) adsorption on the structure of the two-dimensional electrochemical Y₂C monolayer using first-principles density-functional theory (DFT) computations. A non-metal doping technique is suggested to raise Y₂C monolayers' HER catalytic activity. The outcomes demonstrate that this technique can raise the HER catalytic activity of Y₂C monolayers to a better level with Gibbs free energy $|\Delta G_{H^*}| < 0.2$ eV.

2. Computational Methods

In this investigation, density functional theory (DFT) calculations were conducted with the MedeA platform and based on the Vienna ab initio simulation package (MedeA-VASP) [46–48]. The projected augmented wave (PAW) [49] generalized gradient approximation of Perdew–Burke–Ernzerhof (GGA-PBE) [50,51] pseudopotential was applied to represent the electron exchange correlation energy. The cutoff energy was set to 500 eV. $4 \times 4 \times 1$ supercell of the Y₂C monolayer and 15 Å vacuum perpendicular to the 2D plane were employed to prevent the interactions from the periodic boundary condition. The electronic characteristics and structural optimizations were estimated, with the force converged to 0.01 eV/Å and the energy converged to 1.0×10^{-5} eV/atom. Furthermore, a denser $5 \times 5 \times 1$ k-point grid was used for density of states (DOS) calculations, a $3 \times 3 \times 1$ k-point grid for static self-consistent calculations, and a $1 \times 1 \times 1$ k-point grid for structural optimizations were used to sample the first Brillouin zones. Ab initio molecular dynamics (AIMD) [52] simulations utilizing the Nose–Hoover thermostat (NVT) ensemble were run for 10 ps at 300 K with a time step of 2.0 fs in order to verify the thermal stability. The

formation energy of non-metal ($X_C = N, P, O, S, F$) dopants embedded in the C vacancy was calculated according to:

$$E_f(X_C@Y_2C) = E(X_C@Y_2C) - E(Y_2C) - E(X_C) + E(C) \quad (1)$$

The formation energy of non-metal ($X_T = N, P, O, S, F$) dopants adsorbed above the three Y vacancies was calculated according to:

$$E_f(X_T@Y_2C) = E(X_T@Y_2C) - E(Y_2C) - E(X_T) \quad (2)$$

where $E_f(X_C@Y_2C)$ and $E_f(X_T@Y_2C)$ signify the total Y_2C energies for the substitution of C atoms by non-metallic X atoms and for the adsorption of non-metallic X atoms onto the hollow sites of the three Y, respectively. $E(Y_2C)$ and $E(C)$ signify the energies of the monolayer of Y_2C and the energies of the graphitic carbon, respectively. For the non-metallic elements, a portion of the chemical potential originates from their solid state; the P and S atoms' chemical potentials are calculated from their orthorhombic phase, while the C atoms' chemical potential is derived from graphene. The energies of an atom in F_2 , O_2 , and N_2 are the chemical potentials of the F, O, and N atoms, respectively. The second component originates from the gas phase. The hydrogen evolution reaction (HER) mechanism under standard conditions is:



The Gibbs free energy is formulated as:

$$\Delta G_{H^*} = \Delta E_{H^*} + \Delta E_{ZPE} - T\Delta S_{H^*} \quad (5)$$

where ΔE_{ZPE} and ΔS_{H^*} are the variations in the zero-point energy and entropy between the adsorbed and gas phase hydrogen and ΔE_{H^*} is the hydrogen adsorption energy. In this case, the acidic HER process is considered at standard conditions ($p = 1$ bar, $pH = 0$, and $T = 298.15$ K), and based on the calculations of Nørskov et al. [53,54]. We rewrote the equation as $\Delta G_{H^*} = \Delta E_{H^*} + 0.24$ eV.

3. Results and Discussion

3.1. Catalytic Properties of Pristine Y_2C

The Y_2C monolayer with space group R-3m has a two-dimensional crystal structure made up of two Y layers sandwiched between a C layer. Each surface Y atom is coordinated to three C atoms, while each C atom is covalently bound to six Y atoms. The Y-C bond length is 2.482 Å, and the optimized Y_2C monolayer lattice parameter is $a = b = 3.62$ Å. This result is consistent with the literature [39–42]. Long-term operation of the two-dimensional structural framework requires stability. Consequently, by using ab initio arithmetic molecular dynamics (AIMD) simulations with the Nose–Hoover thermal bath technique, the thermal stability of the Y_2C monolayer structure was assessed. After 10 ps simulation, the Y_2C monolayer structure remained intact at 300 K. Figure 1 shows the final structure and energy distribution during the AIMD simulation, and the Y_2C monolayer structure did not undergo deformation, indicating its good thermal stability at room temperature.

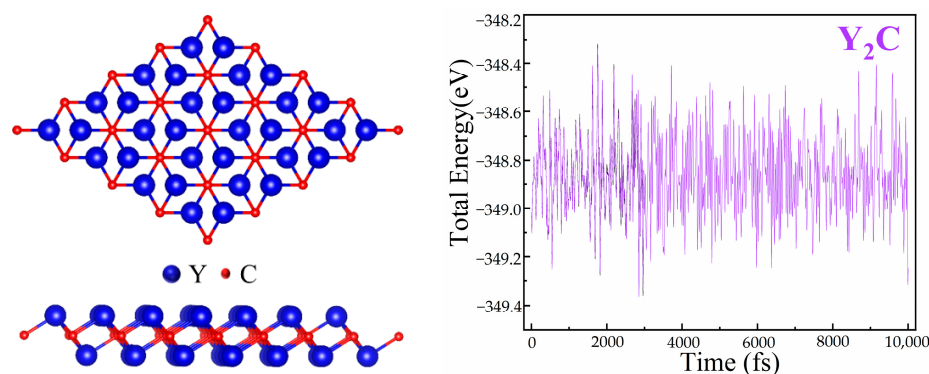


Figure 1. Final structures after molecular dynamics simulation for 10 ps (**left panel**) and the corresponding energy profiles (**right panel**).

The catalytic activity of HER is frequently characterized by the Gibbs free energy of hydrogen adsorption (ΔG_{H^*}). To guarantee the highest catalytic activity, the value of ΔG_{H^*} on the catalyst should be very near zero. The adsorption behavior of hydrogen atoms on the surface of the Y_2C monolayer was first computed to identify the most advantageous adsorption sites in order to investigate the HER catalytic activity of Y_2C . On top of three Y atoms on the surface lies the best active site for H adsorption, as shown in Figure 2. There are three basic reactions for HER, which are the Vollmer reaction, the Tafel reaction, and the Helovsky reaction. The Volmer reaction, or electrochemical adsorption ($H^+ + e^- \rightarrow H^*$), is the initial stage. Hydrogen atoms are adsorbed onto the catalyst's active sites during this process. In the subsequent phase, known as desorption, the adsorbed H^* atoms undergo reduction to generate H_2 molecules through either the Tafel reaction ($H^+ + e^- + H^* \rightarrow H_2$) or the Heyrovsky reaction ($H^* + H^* \rightarrow H_2$). However, the values of Y_2C adsorption and desorption processes are close to 1 eV, which suggests that hydrogen atoms are difficult to desorb from the catalyst surface. Our DFT calculations confirm the low HER catalytic activity of the pristine Y_2C monolayer, which is reflected by the corresponding ΔG_{H^*} value (−0.673 eV).

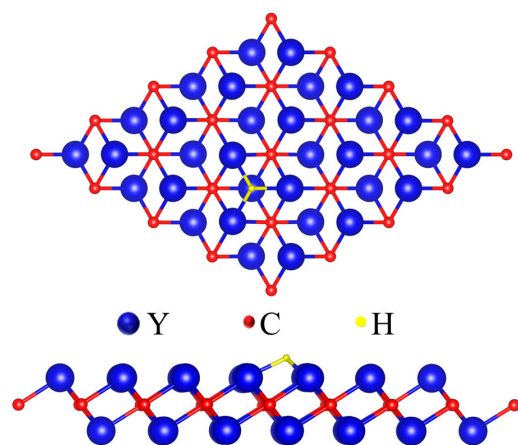


Figure 2. Top and side views of the considered H adsorption sites for Y_2C .

3.2. Catalytic Properties of Y_2C Doped with Non-Metallic Atoms

Therefore, to further tune the ΔG_{H^*} value to zero, we explored the doping of Y_2C monolayers with simple atoms N, P, O, S, and F. The doping of Y_2C monolayers with simple atoms N, P, O, S, and F was also explored. In two-dimensional transition metal carbides, the true active site is generally dominated by cations, and the surrounding anionic environment generally modulates the cations and enhances activity. Due to the strong or weak binding to the reaction intermediates, the doped metal elements lead to the complexity of the active metal sites; therefore, we influenced the electronic structure of the metal ions by substituting

the original anions of the compounds with non-metal atoms ($X = N, P, O, S$, and F) and influence the interactions of the active sites with the reactants, intermediary adsorption, and the final products during the reaction process, which modulates the intrinsic activity, to further improve catalytic performance. For the doping of non-metallic atom X , two doping configurations were considered: (a) one non-metal X atom replacing one C atom, X_C , and (b) non-metal X adsorbing on the top of the hollow site of three Y center, X_T , as shown in Figure 3.

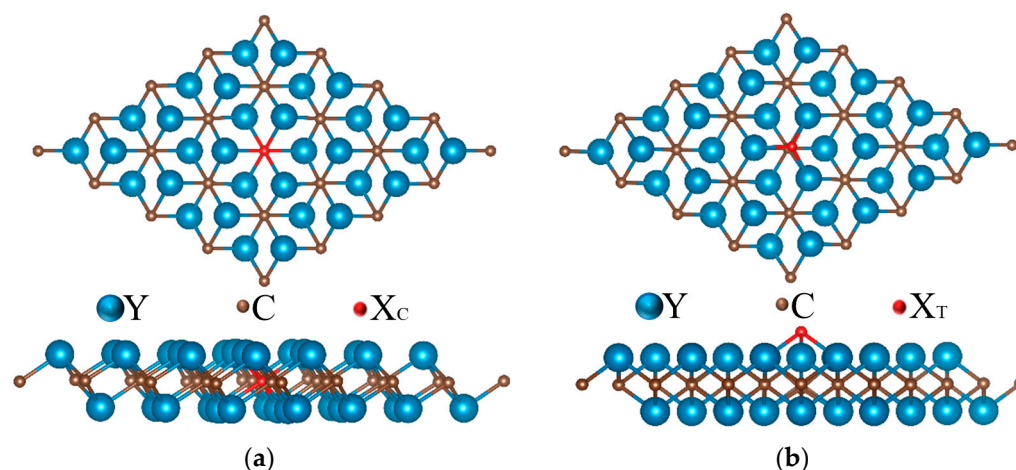


Figure 3. Top view and side view of (a) $X_C @Y_2C$ and (b) $X_T @Y_2C$ after doping.

The formation energies (E_f) of $X_C @Y_2C$ and $X_T @Y_2C$ doping can be used to estimate the likelihood of a doping reaction occurring based on the E_f values: a negative value indicates that the doping reaction proceeds spontaneously, and a positive value indicates that additional energy is required to overcome the energy barrier when dopant atoms are introduced into the host structure, which is calculated as shown in Table 1. For non-metallic substitutional doping, the formation energies of N_C , O_C , S_C , and F_C are all negative, except for P_C , which has a positive formation energy of 1.215 eV, indicating that the formation process of N_C , O_C , S_C , and F_C is exothermic and the formation reaction of P_C is heat-absorbing. Interestingly, the formation energies of all X_T are negative, indicating that non-metallic elements are readily adsorbed on Y_2C . In addition, the formation energy of the F atom is the largest, confirming the strong adsorption of non-metallic elements on Y_2C .

Table 1. The formation energy E_f (eV) for N , P , O , S , and F dopants.

Dopant	X_C	X_T
N	−0.417	−1.874
P	1.215	−0.835
O	−2.646	−5.677
S	−0.797	−3.848
F	−1.444	−6.028

In order to evaluate the catalytic activity of the Y_2C monolayer surface after doping with non-metal atoms, the optimal adsorption sites on the $4 \times 4 \times 1$ supercell model were first investigated, and since hydrogen adsorption can take place at all possible positions on all surfaces, it was necessary to find the most energetically favorable configuration with different adsorption sites of H , as shown in Figure 4. A suitable value of ΔE_{H^*} is necessary in the HER reaction to enhance desorption, as illustrated in Table 2. In this regard, $N_T @Y_2C$ (0.1 eV), $P_T @Y_2C$ (−0.438), and $O_T @Y_2C$ (−0.492 eV) exhibit ΔE_{H^*} close to half of that of Y_2C (−0.913 eV), showing equilibrium ΔE_{H^*} values relative to Y_2C throughout adsorption and desorption.

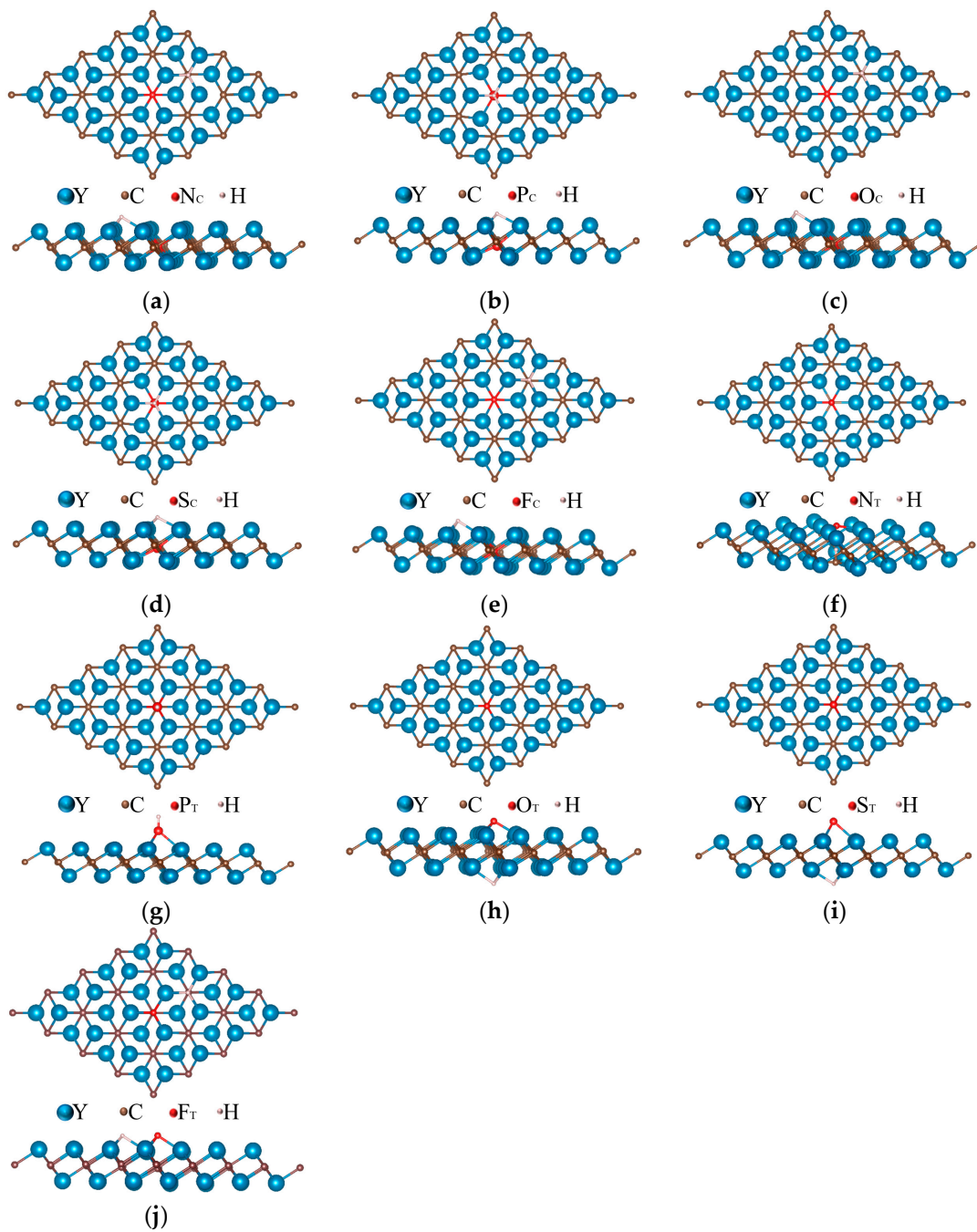


Figure 4. Top and side views of the considered H adsorption sites for (a) $\text{N}_\text{C}@\text{Y}_2\text{C}$, (b) $\text{P}_\text{C}@\text{Y}_2\text{C}$, (c) $\text{O}_\text{C}@\text{Y}_2\text{C}$, (d) $\text{S}_\text{C}@\text{Y}_2\text{C}$, (e) $\text{F}_\text{C}@\text{Y}_2\text{C}$, (f) $\text{N}_\text{T}@\text{Y}_2\text{C}$, (g) $\text{P}_\text{T}@\text{Y}_2\text{C}$, (h) $\text{O}_\text{T}@\text{Y}_2\text{C}$, (i) $\text{S}_\text{T}@\text{Y}_2\text{C}$, and (j) $\text{F}_\text{T}@\text{Y}_2\text{C}$.

Table 2. Calculated adsorption energies ΔE_{H^*} (eV) for N, P, O, S, and F dopants.

Dopant	X_C	X_T
N	−0.910	0.101
P	−0.737	−0.438
O	−0.876	−0.492
S	−0.714	−0.719
F	−0.914	−0.907

Table 3 and Figure 5 show the ΔG_{H^*} of N, P, O, S, and F doping on the monolayer Y_2C surface. On the fully mono-doped surface, the catalytic hydrogenolysis ability of monolayer Y_2C doped with non-metallic N_C , O_C , F_C , and F_T is comparable to that of the pristine Y_2C monolayer, which is unsuitable for HER. The ΔG_{H^*} values of P_C , S_C , N_T , O_T and S_T doped on the monolayer Y_2C surface are in the range of $-0.25 \sim -0.5$ eV, and compared to pure transition metallizers (Table 4), the introduction of surface heteroatom (non-metallic atom) dopants in MXenes can activate their surfaces and further increase the number of active sites, thus improving catalytic activity, which are significantly lower in number compared to those of pristine Y_2C , indicating an increase in its HER activity. Notably, compared to the Gibbs free energy of H adsorption (ΔG_{H^*}) of the above five doped configurations, only P_T doped on the monolayer Y_2C surface has $|\Delta G_{H^*}|$ less than 0.2 eV, indicating the highest catalytic activity. This is consistent with the results analyzed later that P atoms have the least electronegativity and that doping increases the charge density of the space charge layer in this region, increasing the catalytic activity of its surface. In addition, charge transfer is another indicator used to characterize the adsorption strength of the Y_2C substrate with H atoms. The less charge transfer, the weaker the interaction between the substrate and H atoms. As shown in Figure 6, the Bader charge analysis reveals that the ΔG_{H^*} of non-metal substitution and adsorption doping in monolayer Y_2C is negatively and linearly correlated with the transferred charge.

Table 3. Hydrogen adsorption free energies ΔG_{H^*} (eV) for N, P, O, S, and F dopants.

Dopant	X_C	X_T
N	−0.670	0.341
P	−0.50	−0.192
O	−0.636	−0.252
S	−0.474	−0.478
F	−0.680	−0.652

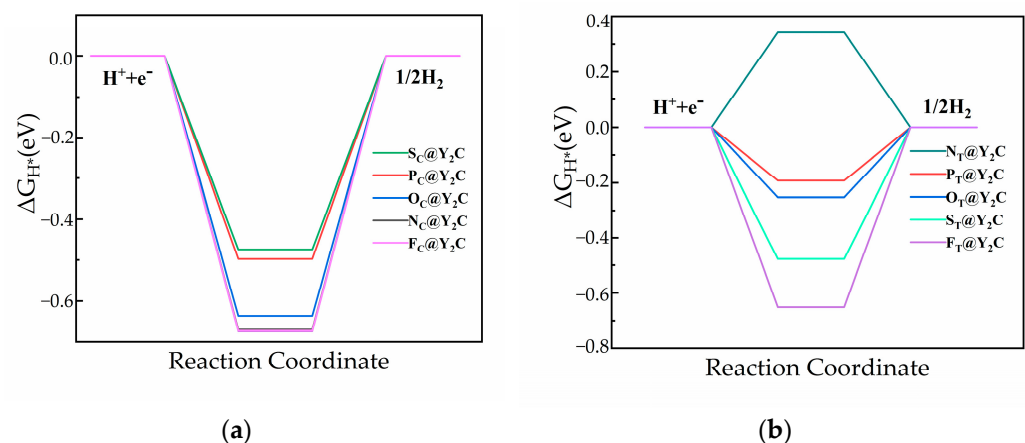


Figure 5. Gibbs free energy diagram at 1/16 hydrogen coverage: (a) ΔG_{H^*} ($X_C@Y_2C$) and (b) ΔG_{H^*} ($X_T@Y_2C$).

Table 4. Hydrogen adsorption free energies ΔG_{H^*} (eV) for transition metal compounds.

	ΔG_{H^*} (eV)	Refs.
Ca_2N	−0.599	[55]
Mo_2C	−0.73	[56]
WC	−0.56	[57]
Y_2C	−0.673	This work

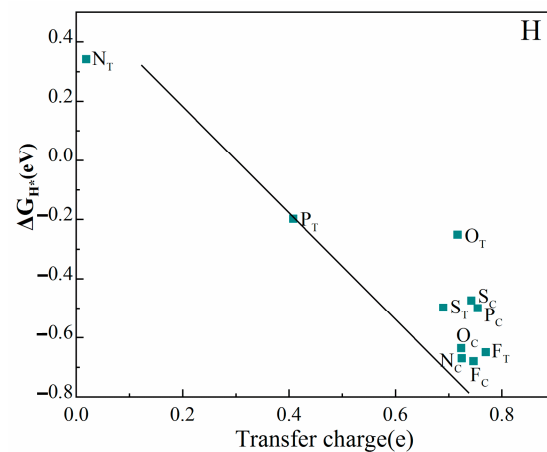


Figure 6. ΔG_{H^*} as function of the Bader transfer charge of H atoms.

To determine the explanation for the increased HER performance, we studied the electronic structure of Y_2C . As shown in Figure 7, we calculated the total and projected DOS of the Y_2C structure without H. By examining the density of states, we showed that the electronic density of states at the Fermi energy level is not zero after doping with N, P, O, S, and F. This implies that the two-dimensional electrode monolayer Y_2C is still a conductor after doping with non-metallic materials. This implies that the two-dimensional electrode monolayer Y_2C remains a conductor despite doping with non-metallic elements, indicating metallic conductivity. To further illustrate the charge transfer capabilities of monolayer Y_2C , Figure 8 illustrates the varied charge densities of monolayers $X_C@Y_2C$ and $X_T@Y_2C$ without H adsorption. As can be observed from the figure, the electronic state of Y_2C can be regulated due to the varied electronegativity of the non-metal, in which the Y-X bonding interaction reduces the electron density surrounding the C atom, thus weakening the Y-C bond. Compared with pure Y_2C , the inclusion of non-metallic atoms generates more electrons on the X- Y_2C surface, lowers the number of C-H interactions, accelerates the detachment of H^* from the surface, and favors the production of H_2 . Therefore, it is conceivable to participate and contribute to the HER process by introducing new non-metallic elements to control the transition metal ions or activate their own anions to attain the perfect H adsorption energy (near to zero) and thereby improve HER efficiency.

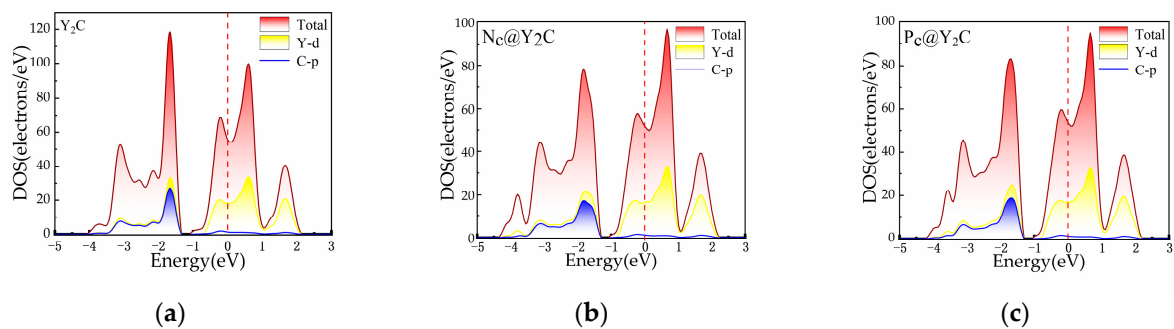


Figure 7. Cont.

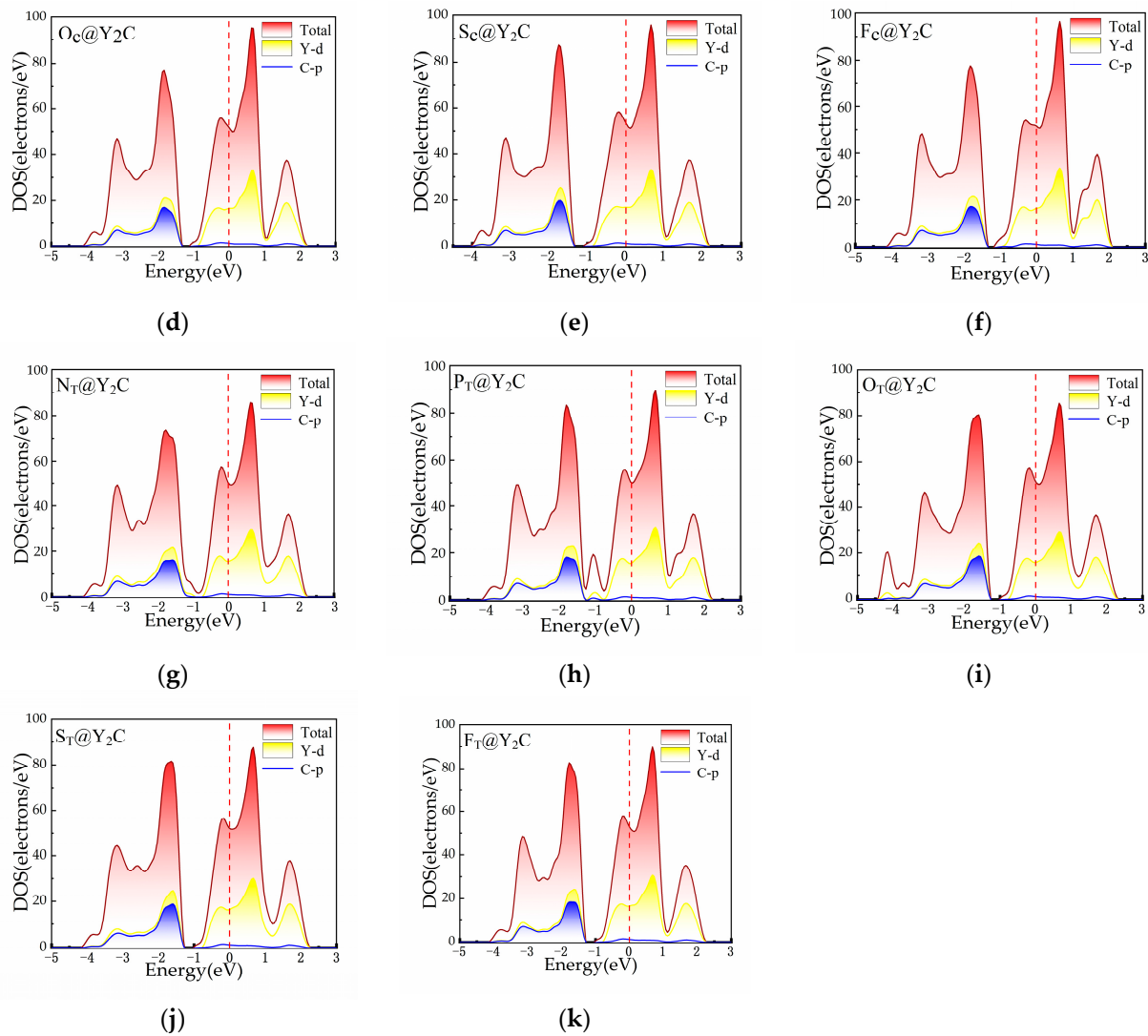


Figure 7. The total and projected density of states (PDOS): (a) Y₂C, (b) N_C@Y₂C, (c) P_C@Y₂C, (d) O_C@Y₂C, (e) S_C@Y₂C, (f) F_C@Y₂C, (g) N_T@Y₂C, (h) P_T@Y₂C, (i) O_T@Y₂C, (j) S_T@Y₂C, and (k) F_T@Y₂C.

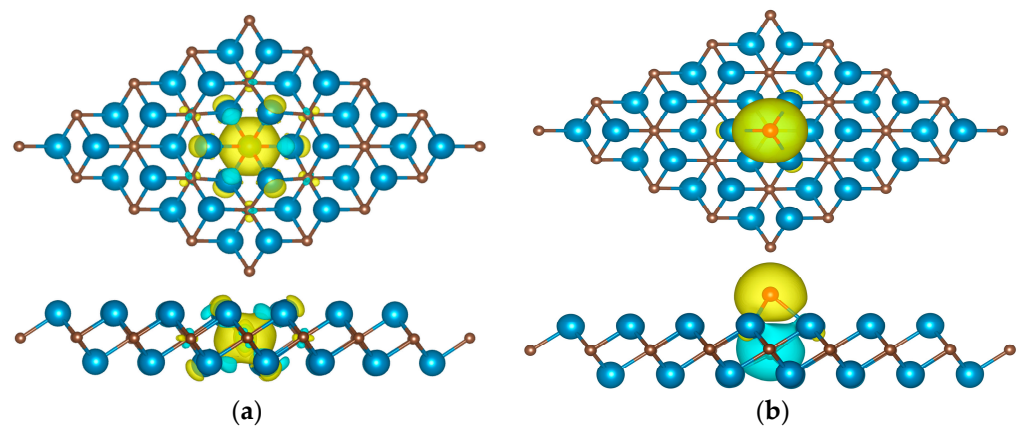


Figure 8. The charge density difference of (a) X_C@Y₂C and (b) X_T@Y₂C, where the yellow and blue regions indicate the charge density accumulation and depletion, respectively. The isosurface is set to 0.005 e/bohr³.

4. Conclusions

In this paper, the effect of surface doping on the catalytic performance of two-dimensional material Y_2C monolayers in a hydrogen precipitation reaction (HER) is systematically investigated by using density functional theory (DFT). Substitution and adsorption doping effects including nitrogen (N), phosphorus (P), oxygen (O), sulfur (S), and fluorine (F) elements were considered. The thermodynamic stability of each doped surface was confirmed by calculating the formation energy. Hydrogen adsorption free energy calculations were used to assess the HER catalytic activity of the doped Y_2C monolayers. The results show that compared to pristine Y_2C , $P_C@Y_2C$ ($\Delta G_{H^*} = -0.50$ eV), $S_C@Y_2C$ ($\Delta G_{H^*} = -0.474$ eV), $N_T@Y_2C$ ($\Delta G_{H^*} = 0.341$ eV), $O_T@Y_2C$ ($\Delta G_{H^*} = -0.252$ eV), and $S_T@Y_2C$ ($\Delta G_{H^*} = -0.478$ eV) all enhance the catalytic activity of Y_2C . In particular, $P_T@Y_2C$ ($\Delta G_{H^*} = -0.192$ eV) showed the most excellent HER catalytic activity and its active site was easy to form. P doping leads to a new density of states peak in Y_2C around the Fermi energy level, which can further improve the electrical conductivity of the material. In addition, P doping made the P site a new active site and reduced the free energy of hydrogen adsorption at the C site in Y_2C . This study not only gives an in-depth explanation and prediction of the hydrogen uptake catalytic activity of non-metal doped Y_2C monolayers but also provides essential theoretical advice for the design of efficient and stable two-dimensional material-based catalysts.

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