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Enhanced Catalytic Hydrogen Evolution Reaction in Phosphorene Nanosheet via Cobalt Intercalation

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Searching alternatives to Pt-based catalyst for producing hydrogen via water splitting has gathered enormous attention to develop renewable energy. Phosphorene has been investigated widely for its large surface area, low cost, and high carrier mobility, however, the poor activity in hydrogen evolution reaction (HER) and low conductivity limit its practical application. Herein, on the basis of first-principles calculations, we demonstrate that the catalytic HER in phosphorene can be enhanced significantly with cobalt intercalations. The Co-intercalated phosphorene is metallic with charge transfer from Co atoms to phosphorene, which could enhance the catalytic activity of phosphorene. In addition, the calculated Gibbs free energy of hydrogen adsorption on Co-intercalated phosphorene bilayer is comparable to that on Pt(111) surface, independent of the degree of hydrogen coverage. Our study implies that the Co intercalation provides an effective approach to enhance the catalytic HER in phosphorene.

Key words: Phosphorene, Cobalt intercalation, Hydrogen evolution reaction, Charge transfer

I. INTRODUCTION

Electrochemical water splitting is an important technology to produce hydrogen, which is a renewable clean energy to replace traditional fossil fuels [1–5]. In order to realize scalable commercial production of hydrogen via electrochemical water splitting, developing low-cost and high-efficiency catalyst is of particular importance. Till now, noble metals, such as Pt and Pt-based materials, are the most efficient catalysts toward the hydrogen evolution reaction (HER) in electrochemical water splitting [6]. However, the high cost and low abundance of Pt in nature limit their wide application in industrial hydrogen production. Developing low-cost and high-efficiency novel catalyst is highly desired for practical implementation in electrochemical hydrogen production [7–12].

Phosphorene, a single layer of black phosphorus (BP), has been investigated recently as a potential electrocatalyst for HER due to its large surface area, high carrier mobility, long carrier diffusion distance, and lone pair electrons in phosphorous atom [13–19]. For example, Pumera’s group reported that BP nanoparticles possess weak catalytic activity in \( \text{H}_2\text{SO}_4 \) solution, generating a current density of \(-10\ \text{mA/cm}^2\) at \(-0.81\ \text{V} \) [20]. Pan and co-workers demonstrated a low HER overpotential for a \( \text{Ni}_2\text{PCBP} \) hybrid material in acidic electrolyte [21]. Yu’s group indicated that an in-plane heterostructure of \( \text{BP}/\text{Co}_2\text{P} \) could exhibit stable and excellent HER activity in both \( \text{H}_2\text{SO}_4 \) and \( \text{NaOH} \) solution [22]. However, the HER activity in either bulk or nanostructure pristine BP is generally lower than that of other common electrocatalysts, which is possibly caused by the relative weak adsorption of hydrogen or limited electrical conductivity.

Intercalation of metal into layered materials has been proven to be an efficient way to enhance the electrochemical hydrogen evolution reaction in them [23–25]. Among various metals, cobalt has attracted great research interest due to its catalytic power toward water splitting, and considerable efforts have been devoted to developing cobalt based catalysts for HER [26–29]. In this work, herein, the HER performance of Co-intercalated phosphorene bilayer (Co-BP) is investigated by using first-principles calculations. Our results demonstrate that Co atoms bond strongly with phosphorene and Co intercalated phosphorene bilayer could maintain its structure. In addition, the catalytic HER can be significantly enhanced in phosphorene via Co...
intercalation, where the Gibbs free energy of hydrogen adsorption is comparable with that of Pt(111) surface. The promotional effect is ascribed to the charge transfer from Co atoms to phosphorene. Electronic structure reveals that phosphorene undergoes a transition from semiconductor to conductor with the conductivity of phosphorene being promoted greatly.

II. COMPUTATIONAL METHODS

All first-principles calculations were performed by using density functional theory (DFT) method implemented in the Vienna ab initio Simulation Package (VASP) package [30, 31]. Electronic exchange and correlation effects were described within the generalized gradient approximation (GGA) of Perdew-Burke-Ernzerhof (PBE) functional [32]. Projector augmented wave method was used for the self-consistent total energy calculations and geometry optimization [33, 34]. The plane-wave kinetic energy cutoff was set to 500 eV. Account for the van der Waals interactions between two layers of phosphorene, the dispersion correction of Grimme DFT-D3 method was used [35].

For the geometry optimization, 9×9×1 Monkhorst-Pack k-meshes were adopted for the bilayer phosphorene [36]. A vacuum spacing of 20 Å was used so that the interaction between adjacent bilayers can be neglected. During the geometric optimization, both lattice constants and atomic positions were relaxed until the interaction between adjacent bilayers can be neglected. The plane-wave kinetic energy cutoff was set to 500 eV. Account for the van der Waals interactions between two layers of phosphorene, the dispersion correction of Grimme DFT-D3 method was used [35].

The intercalation energy ∆E_{inter} per Co atom is calculated by

$$\Delta E_{inter} = \frac{E_{Co-BP} - E_{BP} - nE_{Co}}{n} \quad (1)$$

where $E_{Co-BP}$ and $E_{BP}$ represent the total energy of the Co intercalated BP and pristine BP, respectively. $E_{Co}$ is the energy of Co atom calculated from its bulk cohesive energy and $n$ is the number of intercalated Co atoms in super cell. So a negative and positive value of the intercalation energy indicates the Co intercalation in BP is exothermic and endothermic, respectively.

The HER performance can be estimated by the Gibbs free energy of hydrogen adsorption $\Delta G_H$ [37, 38], which can be calculated from the following equation:

$$\Delta G_H = \Delta E_H + \Delta E_{ZPE} - T \Delta S_H \quad (2)$$

where $\Delta E_H$ is the hydrogen chemisorption energy and defined as:

$$\Delta E_H = E_{sub + nH} - E_{sub + (n-1)H} - \frac{1}{2}E(H_2) \quad (3)$$

where $E_{sub + nH}$ and $E_{sub}$ are total energies of Co intercalated phosphorene with and without hydrogen atoms adsorbed on surface, respectively. $n$ is the number of H atoms adsorbed on the surface of phosphorene.

FIG. 1 Top view and side view of phosphorene bilayers with (a) AA, (b) AB, and (c) AC-stacking orders are displayed.

$E(H_2)$ is the energy of the hydrogen molecule in gas phase, $\Delta E_{ZPE}$ is the difference in zero point energy between the adsorbed and the gas phase, and $\Delta S_H$ is the entropy difference in the adsorbed state and gas phase of $H_2$. The vibrational entropy is small (nearly zero) in the adsorbed state and thus $\Delta S_H$ will be approximately equal to $1/2\Delta S_{H_2}$ where $1/2\Delta S_{H_2}$ denotes the entropy of $H_2$ in the gas phase [39–41]. The free energy corresponding to hydrogen adsorption can be written as $\Delta G_H = \Delta E_H + 0.24 eV$, and $\Delta G_H$ should be close to zero for a good HER catalyst [42, 43].

We studied the charge transfer between Co atoms and phosphorene by analysing the charge density difference ρ_{diff}, which is defined as

$$\rho_{diff} = \rho_{Co-BP} - \rho_{BP} - \rho_{Co} \quad (4)$$

where $\rho_{Co-BP}$, $\rho_{BP}$, and $\rho_{Co}$ correspond to the total charge densities of the hybrid Co-BP systems, pure bilayer phosphorene and Co, respectively. The negative and positive values of $\rho_{diff}$ present the charge depletion and accumulation, respectively. And the amount of charge transfer is estimated from the Bader charge analysis [44].

III. RESULTS AND DISCUSSION

At first, three configurations of phosphorene bilayers with AA-, AB- and AC-stacking orders are considered to determine the most stable structure, as shown in FIG. 1. The optimized nearest distance between the top and bottom layer ($d_{int}$) varies from 3.19 Å (AB-stacking) to 3.72 Å (AC-stacking). The calculated energy indicates that the AB-stacking phosphorene bilayer is the most energetic favorable, which is 9 and 16 meV/atom lower than that of AA- and AC-stacking,
respectively, as summarized in Table S1 (see supplementary materials). Therefore, the following investigation is based on the phosphorene bilayer with AB-stacking configuration.

It is well known that the large interspace together with weak van der Waals interactions in graphene-like 2D material could allow foreign atoms to insert into its interlayer [45]. As shown in FIG. 2(a), four high-symmetry sites between two phosphorene layers were considered in order to determine the most stable adsorption site for Co atom, including two hollow sites (H1 and H2), one top site (T), and one bridge site (B). A supercell of 3×3 unitcells of phosphorene is adopted to investigate the most stable adsorption site for a single Co atom intercalated in phosphorene bilayer with AB-stacking configuration. As summarized in Table S2 (see supplementary materials), the calculated intercalation energies of Co atom in phosphorene bilayer are $-1.29, -0.65, -0.92, \text{and} -1.02 \text{eV per Co atom for } H_1, H_2, B, \text{and } T \text{ sites, respectively, implying that the } H_1 \text{ position is the most favorable adsorption site for the adsorption of Co atom in phosphorene bilayer with AB-stacking configuration (FIG. 2(b)).}$ The interlayer distance in phosphorene bilayer with the intercalation of Co atom is about 3.15 Å, almost identical to the value of phosphorene bilayer without Co, i.e. 3.19 Å. The average bond length is about 2.24 Å between Co and the six nearest P atoms. This value is very close to the Co–P bond length in bulk CoP (2.27 Å) and Co$_2$P (2.16 Å) [46, 47], implying strong bonding interaction between Co and P atoms.

Next, we investigate the effect of the concentration of Co atoms on the structures and intercalation energy. The Co-intercalated phosphorene bilayer with different concentrations of Co atoms is abbreviated as $n_1$Co-$n_2$×$n_3$BP, where $n_1$ is the number of intercalated Co atoms per super cell, and $n_2$×$n_3$ represents that the size of super cell is $n_2$×$n_3$ of unit cell of BP. The optimized configurations of Co intercalated BP with different concentrations are displayed in FIG. S1 (see supplementary materials). The structural information and intercalated energies are summarized in Table I. Except 3Co-2×2BP with Co atoms occupied T sites, all Co atoms in other models occupy the H site of phosphorene bilayer. With different intercalation concentrations, the interlayer distance in phosphorene bilayer varies from 3.06 Å to 3.16 Å, and the Co–P bond lengths range from 2.24 Å to 2.35 Å. In addition, the deformation in the z-direction of P atoms in phosphorene implies that the Co intercalation weakens the flatness of phosphorene. The calculated intercalation energies are negative, implying that the intercalation of Co atom inside phosphorene bilayer is exothermic, which increases slightly with the increasing concentration of Co atoms.

Then, the adsorption of hydrogen on the Co-intercalated phosphorene bilayer is studied. The Gibbs free energy $\Delta G_H$ is calculated to evaluate the HER activity of Co-intercalated phosphorene bilayer [48, 49]. Several possible hydrogen adsorption sites are considered to determine the most stable configuration, as shown in FIG. S2 (supplementary materials). The corresponding hydrogen adsorption energies are listed in Table S3 (supplementary materials). The calculated $\Delta G_H$ values of the most stable adsorption sites with different concentrations of Co atoms are shown in FIG. 3(a). The results indicate a relative poor activity of pure phosphorene for HER because the hydrogen adsorption is endothermic and the $\Delta G_H$ value is as high as 1.16 eV, agreeing with previous reports [50, 51]. As the concentration of Co increases, the value of $\Delta G_H$ decreases significantly from 1.16 eV to $-0.09 \text{ eV}$, suggesting that the existence of Co atoms strengthens the binding strength of the H atoms with the surface P atoms. In particular,

![FIG. 2](a) Four possible adsorption sites of Co atom intercalated in phosphorene bilayer are labelled with H1, H2, T, and B, respectively; (b) the most favorable adsorption site for Co intercalation.

**TABLE I** The calculated intercalation energy ($\Delta E_{\text{inter}}$), the interlayer distance ($d_{\text{int}}$), average Co–P bond length ($d_{\text{Co–P}}$) and the deformation of phosphorene in the direction perpendicular to the surface ($\Delta Z_{\max}$) at the most favourable adsorption sites.

<table>
<thead>
<tr>
<th>Site</th>
<th>$\Delta E_{\text{inter}}$/eV</th>
<th>$d_{\text{int}}$/Å</th>
<th>$d_{\text{Co–P}}$/Å</th>
<th>$\Delta Z_{\max}$/Å</th>
</tr>
</thead>
<tbody>
<tr>
<td>1Co-3×3BP H1</td>
<td>$-1.29$</td>
<td>3.16</td>
<td>2.31</td>
<td>0.11</td>
</tr>
<tr>
<td>1Co-2×2BP H1</td>
<td>$-0.98$</td>
<td>3.10</td>
<td>2.24</td>
<td>0.42</td>
</tr>
<tr>
<td>2Co-2×2BP H1</td>
<td>$-1.11$</td>
<td>3.06</td>
<td>2.33</td>
<td>0.19</td>
</tr>
<tr>
<td>3Co-2×2BP T</td>
<td>$-1.19$</td>
<td>3.12</td>
<td>2.35</td>
<td>0.31</td>
</tr>
<tr>
<td>4Co-2×2BP H1</td>
<td>$-1.27$</td>
<td>3.15</td>
<td>2.27</td>
<td>0.37</td>
</tr>
</tbody>
</table>
FIG. 3 (a) The calculated Gibbs free energy diagram of HER at the equilibrium potential on Co-intercalated phosphorene bilayer with different Co concentrations. (b) The $\Delta G_H$ values as a function of hydrogen coverage $\theta_H$ (ranging from 0 to 1) on the surface of the Co-intercalated phosphorene bilayer are displayed.

FIG. 4 (a) The calculated electronic band structures of bilayer phosphorene. (b) The electronic band structure and PDOS of 4Co-2BP. The Fermi energy is set to zero.

the calculated Gibbs free energy of hydrogen atom on 4Co-2BP is $-0.09$ eV, which is comparable to previously reported theoretical value on Pt(111) surface ($-0.09$ eV) [52, 53]. In addition, the effect of hydrogen coverage ($\theta_H$) on the value of $\Delta G_H$ is also investigated. Here, $\theta_H$ is defined as $n/N$, where $n$ is the number of the adsorbed H atoms on the surface and $N$ is the number of surface P atoms in the supercell. As illustrated in FIG. 3(b), with the increase of $\theta_H$ from 0 to 1, the values of $\Delta G_H$ increase slightly. In particular, on 4Co-2BP, the value of $\Delta G_H$ lies in the range from $-0.09$ eV to 0.15 eV, indicating that it could preserve high HER catalytic activity over a wide range of hydrogen coverage. In contrary, the value of $\Delta G_H$ on pure phosphorene ranges from 1.14 eV to 1.32 eV when $\theta_H$ increases from 0 to 1, confirming again the inert HER activity on pure phosphorene.

Except the $\Delta G_H$ value, the electrical conductivity of catalyst is another important indicator to evaluate their electrocatalytic performance. Note that high electrical conductivity represents good charge transfer in catalysts for HER [54, 55]. Here, we calculated the electronic band structures and density of states (DOS) of pure phosphorene and 4Co-2BP. The density of states of other Co-intercalated bilayer phosphorene are displayed in FIG. S3 (see supplementary materials). As displayed in FIG. 4(a), the pure phosphorene bilayer is a semiconductor with a band gap of 0.46 eV, which is
in accordance with a previous report [56]. Differently, there are energy bands crossing the Fermi level in Co-intercalated phosphorene bilayer, implying metallic behavior of them, as shown in FIG. 4(b). The calculated projected density of states (PDOS) on atomic orbital indicate that there is strong hybridization between Co’s 3d and P’s 2p orbitals, confirming the strong Co–P bonding in Co-intercalated phosphorene bilayer. The transition from semiconductor to metal intercalation is induced by Co atoms intercalation in phosphorene bilayer, and thus increases its electrical conductivity for electrocatalysis.

Previous studies have shown that the carrier doping can modify the hydrogen adsorption and improve the HER performance of phosphorene [57]. Here, to understand the enhanced catalytic activity of phosphorene with the intercalation of Co, the charge transfer between Co atoms and phosphorene is studied by analysis of charge density differences $\rho_{\text{diff}}$ (see FIG. S4 in supplementary materials). The Bader charge analysis results (Table S4 in supplementary materials) indicate that charge is transferred from Co atoms to P atoms. With the increase of the concentration of Co atoms, more electrons are transferred from Co atoms to the neighboring P atoms. As indicated in FIG. 5, the charge depletion locates on Co atoms, while the charge accumulates between the Co and neighboring P atoms in 4Co-2×2BP, which is consistent with the Bader charge analysis results and confirms the strong bonding characteristics between Co and P atoms. The charge transfer from Co to phosphorene strengthens the adsorption of H atoms on phosphorene, and thus enhances the catalytic HER activity of phosphorene bilayer.

At last, a detailed analysis of DOS combined with the molecular orbital theory is performed to understand the enhancement of hydrogen adsorption on the Co-intercalated phosphorene bilayer. The formation of H–P bonds results in a fully filled bonding orbital ($\sigma$) and a partially filled anti-bonding orbital ($\sigma^*$), which are formed by the linear combination of H’s 1s and P’s 2p orbitals. FIG. 6 displays the PDOS of hydrogen adsorbed phosphorene bilayer intercalated with Co atoms. It is clear that the splitting of the bonding and anti-bonding states contributed by H’s 1s and P’s 2p orbitals increases when the concentration of intercalated Co atoms increases, implying that the energy benefiting from the adsorption of hydrogen on phosphorene surface increases and leads to strong adsorption of hydrogen atom. This behavior is consistent with the calculated Gibbs free energy with different concentration of Co atoms in phosphorene bilayer.

IV. CONCLUSION

In summary, we study the HER performance of phosphorene bilayer with and without the intercalation of Co atoms by using first principles calculations. Our calculations show that pure phosphorene is not an ideal catalyst for HER, while its catalytic performance can be engineered by introducing Co atoms. The intercalation of Co atoms in phosphorene bilayer induces a transition from semiconductor to metal, and thus increases its electrical conductivity. Meanwhile, the intercalation of Co atoms strengthens the adsorption of hydrogen atom on phosphorene, which is dependent on the concentration of Co atoms. In particular, the value of $\Delta G_H$ on 4Co-2×2BP is about $-0.09$ eV, which is comparable to that on Pt(111) surface. With the increase of hydrogen coverage, the absolute values of $\Delta G_H$ on 4Co-2×2BP vary from $0.05$ eV to $0.16$ eV, implying the HER performance of the Co-intercalated phosphorene bilayer is stable. This study presents a pathway to engineering the catalytic HER on phosphorene by being intercalated with transitional metal.

Supplementary materials: Tables of three different stacking orders, calculated intercalation energies, H adsorption energies at different positions and charge transfer are available. Illustrations of Co-intercalated bilayer phosphorene structures, considered H adsorption sites, PDOS of pure phosphorene and Co-intercalated phosphorene and charge density difference of Co-intercalated phosphorene are also given.
FIG. 6 PDOS plots of Co intercalated phosphorene projected onto the P atom bonded to hydrogen atom before (black solid line) and after (red solid line) hydrogen adsorption. PDOSs of H 1s (blue solid line) are scaled up by a factor of five for better visualization.

V. ACKNOWLEDGMENTS

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