Effects of Fluorination and Molybdenum Codoping on Monoclinic BiVO₄ Photocatalyst by HSE Calculations

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ABSTRACT: Monoclinic phase bismuth vanadate (BiVO₄) is one of the most promising photoelectrochemical materials used in water-splitting photoelectrochemical cells. It could be even better if its band gap and charge transport characteristics were optimized. Although codoping of BiVO₄ has proven to be an effective strategy, its effects are remarkably poorly understood. Using the Heyd–Scuseria–Ernzerhof (HSE) hybrid functional, we estimate the formation energy, electronic properties, and photocatalytic activities of F and Mo codoped BiVO₄. We find that Mo atoms prefer to replace V atoms, whereas F atoms prefer to replace O atoms (F₀Mo₄-doped BiVO₄) under oxygen-poor conditions according to calculated formation energies. BiVO₄ doped with F₀Mo₄ is found to be shallow-level doped, occurring with some continuum states above the conduction band edge, which is advantageous for photochemical catalysis. Moreover, F₀Mo₄-doped BiVO₄ shows absorption stronger than that of pure BiVO₄ in the visible spectrum. Based on the band-edge calculation, BiVO₄ doped with F₀Mo₄ still retains a high oxidizing capacity. It has been shown that F₀Mo₄-doped BiVO₄ exhibits a very high photocatalytic activity under visible light.

1. INTRODUCTION

In 1999, Kudo et al.¹ reported monoclinic phase bismuth vanadate (BiVO₄) as a photocatalyst to achieve water oxidation. They used Ag⁺ ions as an electron scavenger under visible light irradiation. Since then, BiVO₄ has gradually been a hot research topic because of its great potential in energy conversion and the environmental field. However, the wide application of BiVO₄ is still limited. This is due to its low electron transfer efficiency, slow water oxidation kinetics, poor charge carrier mobility, and weak surface adsorption capacity. Therefore, various modification strategies have enhanced photocatalytic performance in the past few years. These strategies included morphological modification, crystal facet control, semiconductor coupling, deposition of cocatalysts, element doping, and defect formation. Among the above strategies, the doping of pure BiVO₄ with either anions or cations remains one of the most common methods used to increase carrier density and reduce charge transfer resistance. For cation doping, notably, Mo doping could effectively modulate the electronic structure of BiVO₄, leading to both increased carrier concentration and improved optical absorption. For example, Yang et al. synthesized a high-quality Mo-doped BiVO₄ photoanode using a simple drop-casting method. The results revealed that Mo-doped BiVO₄ produced a much higher photocurrent than undoped BiVO₄ under AM 1.5G illumination for water oxidation. For anion doping, it has been widely adopted to improve the electrochemical properties of BiVO₄. Experimentally, a F-doped BiVO₄ photocatalyst is synthesized by a simple two-step hydrothermal process. It is found that the substitution of O by F could result in the decrease of the BiVO₄ lattice parameters, influence the chemical environment surrounding the Bi, V, and O elements, cause the red-shift of the adsorption edge, and modify the absorption abilities in the visible light region. More importantly, the anion–cation codoping has been an effective method to improve the photocatalytic effect. For instance, Rohloff et al. fabricated a F/Mo:BiVO₄ thin film photoanode via soft fluorination. They demonstrated that anion and cation doping in BiVO₄ allows combining the PEC-relevant benefits associated with each type of dopant, the increased conductivity and charge separation due to Mo doping, and the increased water oxidation catalysis efficiency introduced by fluorination. However, it is still unclear what exactly these promoting effects are. The F/Mo codoping effects on BiVO₄’s photocatalytic activity are still not entirely understood.
Theoretically, F- or Mo-doped BiVO₄ has been calculated with the generalized gradient approximation (GGA)¹⁷ of the Perdew–Burke–Ernzerhof (PBE)¹⁸ method (GGA-PBE) and GGA+U method. Ding et al.¹⁹ calculated the band structure and density of states of F-doped BiVO₄. It was discovered that the doped F would act as electron capture traps that would benefit the separation of the photoinduced carriers and improve the photocatalytic performance of BiVO₄. Because of the difference in valence electrons between the F and O atoms, the F atom has one more. The substitution of an F atom for an O atom in BiVO₄ will increase the Fermi level by one electron. Our previous GGA+U study²⁰ for Mo-doped BiVO₄ indicated that the Mo 4d impurity states would be observed in the band gap when Mo is doped on the Bi lattice site. It is important to note that these impurities can easily trap carriers and lower carrier mobility, which can harm the application of Mo-doped BiVO₄ in the photoelectrochemical conversion of solar energy. There is no impurity state in the band gap while Mo is doping on the V lattice site. The band gap is smaller in this case, resulting in higher optical absorption. These results are the same as the other GGA method.²¹ However, it is known that the GGA-PBE usually suffers from band gap underestimation.²² Furthermore, the GGA+U correction was only applied to the d electrons of V and Mo, while the other components were treated within GGA. Thus, quantitatively more accurate calculations are necessary.

In this paper, based on the Heyd–Scuseria–Ernzerhof (HSE) hybrid functional, we calculate the formation energy, electronic properties, and photocatalytic activity of F and Mo codoped BiVO₄. According to calculated formation energies, Mo atoms prefer to replace V atoms, whereas F atoms prefer to replace O atoms (F₃MoO₄-doped BiVO₄) under oxygen-poor conditions. BiVO₄ doped with F₃MoO₄ is found to be shallower in band gap, with some continuum states occurring above the conduction band edge. Moreover, F₃MoO₄-doped BiVO₄ shows absorption stronger than that of pure BiVO₄ in the visible spectrum. Based on the band-edge calculation, BiVO₄ doped with F₃MoO₄ still retains a high oxidizing capacity. Thus, F₃MoO₄-doped BiVO₄ is particularly suitable for visible light photocatalysis. Our results provide more general design guidelines for the preparation of codoped BiVO₄ with the promise of further performance improvements.

### 2. Computational Details

A plane-wave projector-augmented wave (PAW) method²² is used to perform all density functional theory calculations using the Vienna Ab initio Simulation Package (VASP).²³,²⁴ A kinetic-energy cutoff of 500 eV is tested to be sufficient for plane-wave expansion to achieve good convergence. Electronic self-consistent interaction convergence is considered sufficient for a total energy difference of less than 10⁻⁵ eV, and the forces on each ion converged were less than 0.03 eV/Å. The positions of all atoms in the system are allowed to relax. The PAW potentials with the valence electrons 6s⁶6p⁶ for Bi, 3d⁶⁴s² for V, 2s²2p⁶ for O, 2s²2p⁵ for F, and 4d³5s² for Mo have been employed. We used the PBE exchange-correlation functional within the GGA for geometry optimizations. Doping defect calculations are performed in a 2 × 2 × 1 supercell. For these systems, we used 3 × 3 × 3 Monkhorst–Pack k-point meshes,²⁵ which are found to be sufficient to reach convergence for bulk calculations and used for geometry optimization and electronic property calculations. It is well-known that the PBE typically suffers from the underestimation of the band gap.²⁶,²⁷ The HSE functional can now provide more accurate band gap measurements than the GGA methods. Therefore, this paper obtains the electronic structures, the optical absorption coefficient, and electrostatic potential energy using the HSE functional. For the HSE hybrid functional, the screening parameter is set to 0.2 Å⁻¹, the Hartree–Fock mixing parameter is α = 0.15. Using these HSE parameters, we calculated the band gap of pure BiVO₄ to be 2.4 eV, which is consistent with experiment (2.5 eV) and the previous theoretical study (2.45 eV³⁸ and 2.58 eV).²⁹

The defect formation energy is an essential measure of the stability for the F and/or Mo defects in BiVO₄, which is defined as

\[
e_{\text{form}} = E_{\text{def}} - E_{\text{pure}} + \sum_{i} \mu_i
\]

In the formula, \(E_{\text{def}}\) and \(E_{\text{pure}}\) are the total energies of supercells with a defect and a perfect supercell, respectively. \(\mu_i\) is the chemical potential of chemical species \(i (i = \text{Bi, V, O, F, Mo})\). For Bi, V, and O in BiVO₄ chemical potentials are not arbitrary but are influenced by thermodynamic constraints that can represent experimental conditions. In our previous work, we calculated the phase diagram of BiVO₄ as a two-dimensional panel with three independent variables \(\Delta \mu_{\text{Bi}V}, \Delta \mu_{\text{F}V}\), and \(\Delta \mu_{\text{O}}\) by the HSE functional.¹² Thus, as shown in Figure S3 of ref 12, in this paper, we use representative chemical potential point \(A_{\text{HSE}} (\Delta \mu_{\text{Bi}V}, \Delta \mu_{\text{F}V}, \Delta \mu_{\text{O}}) = (-3.69, -8.27, 0)\) for the O-rich growth condition and \(D_{\text{HSE}} (\Delta \mu_{\text{Bi}V}, \Delta \mu_{\text{F}V}, \Delta \mu_{\text{O}}) = (0, -2.12, -2.46)\) for the O-poor growth condition. Due to \(\mu_{\text{Bi}} = E_{\text{Bi}} + \mu_{\text{BiV}}\), \(\mu_{\text{V}} = \mu_{\text{V}F}\), \(\mu_{\text{O}} = \mu_{\text{OF}}\), the corresponding chemical potential \(\mu\) limits for \(A_{\text{HSE}} (\mu_{\text{Bi}}, \mu_{\text{V}}, \mu_{\text{O}}) = (-7.98, -18.0, -6.16)\) and \(D_{\text{HSE}} (\mu_{\text{Bi}}, \mu_{\text{V}}, \mu_{\text{O}}) = (-4.29, -11.85, -8.62)\).

In order to avoid the formation of phases containing impurities, the chemical potential of the impurities must meet the constraints. For Mo and F doping, the chemical potential of Mo and F is constrained by

\[
\Delta \mu_{\text{F}} < 0, \quad \Delta \mu_{\text{Mo}O} < 0
\]

\[
\Delta \mu_{\text{Mo}O} < 3 \Delta \mu_{\text{O}} < \Delta H_{\text{f}}(\text{MoO}_3)
\]

\[
\Delta \mu_{\text{Mo}O} < 6 \Delta \mu_{\text{F}} < \Delta H_{\text{f}}(\text{MoF}_6)
\]

\[
\Delta \mu_{\text{Bi}} < 3 \Delta \mu_{\text{O}} < \Delta H_{\text{f}}(\text{BiF}_3)
\]

\[
\Delta \mu_{\text{V}} + 2 \Delta \mu_{\text{F}} < \Delta H_{\text{f}}(\text{VF}_5)
\]

\[
\Delta \mu_{\text{V}} + 5 \Delta \mu_{\text{F}} < \Delta H_{\text{f}}(\text{VF}_5)
\]

### Table 1. Formation Enthalpy (eV/formula unit) Calculated by HSE Functional Compared to Experimental Values³³

| Material            | HSE    | Experiment |
|---------------------|--------|------------|
| \(\Delta H_{\text{f}}(\text{MoO}_3)\) | -6.80  | -7.76      |
| \(\Delta H_{\text{f}}(\text{MoF}_6)\) | -16.58 | -17.65     |
| \(\Delta H_{\text{f}}(\text{BiF}_3)\) | -9.90  | -9.41      |
| \(\Delta H_{\text{f}}(\text{VF}_5)\) | -6.95  | -8.72      |
| \(\Delta H_{\text{f}}(\text{VF}_5)\) | -16.23 | -14.60     |
HSE calculations produce similar results, and the calculated values agree with the experimental values. HSE total energy calculations are performed using experimental lattice constants for MoO₃, MoF₆, BiF₃, VF₂, and VF₅. Table 2 lists these lattice constants. The following calculations use maximum Mo and F chemical potential that satisfies these inequations. Under the O-rich growth condition, Mo and F chemical potentials are −18.86 and −4.71 eV, respectively, whereas under the O-poor growth condition, Mo and F chemical potentials are −11.48 and −5.94 eV, respectively. We use these chemical potentials to calculate formation energy for Mo- and F-related defects.

### Table 2. Experimental Lattice Constants of MoO₃, MoF₆, BiF₃, VF₂, and VF₅ Used for the HSE Functional Total Energy Calculations

| Material    | k-points | space group | experiment          |
|-------------|----------|-------------|---------------------|
| MoO₃        | 8 × 3 × 10 | Pbnm         | a = 3.964, b = 13.863, c = 3.699; α = 90, β = 90, γ = 90°        |
| MoF₆        | 3 × 4 × 6  | Pmma         | a = 9.480, b = 8.600, c = 4.993; α = 90, β = 90, γ = 90°        |
| BiF₃        | 5 × 5 × 5  | Pmnm         | a = 5.861, b = 5.861, c = 5.861; α = 90, β = 90, γ = 90°        |
| VF₂         | 6 × 6 × 9  | P4/mn        | a = 4.804, b = 4.804, c = 3.236; α = 90, β = 90, γ = 90°        |
| VF₅         | 6 × 2 × 4  | Pmcn         | a = 5.4, b = 16.72, c = 7.53; α = 90, β = 90, γ = 90°         |

Values a, b, and c are in angstroms, and the values α, β, and γ are in degrees.

### 3. RESULTS AND DISCUSSION

#### 3.1. Doped Configuration and Formation Energies

Because the I2/b space group is easily related to the tetragonal scheelite structure for pure BiVO₄, we chose to use it. We used two BiVO₄ units (primitive units) to determine the structure through careful optimization of volume and relaxation of atomic positions. The optimization parameters are as follows: a = 5.1556 Å, b = 5.0958 Å, c = 11.6067 Å, and γ = 90.2416°. There is good agreement between these lattice parameters and experimental values. The results indicate that our calculation methods are accurate, while the calculated results are legitimate. In order to dope the structures, we used the 2 × 2 × 1 supercell of monoclinic BiVO₄ (Figure 1a), which contains 64 oxygen atoms and 16 bismuth atoms. The doping concentration is about 1–2 atom %, consistent with the experimental results.

In order to introduce impurity atoms into the supercell, we use the modes FO (F atoms substituting for O atoms in the lattice, Figure 1b), MoBi (Mo atoms substituting for the Bi atoms in the lattice, Figure 1c), and MoV (Mo atoms substituting for V atoms in the lattice, Figure 1d), resulting in two different modes of F/Mo codoped monoclinic BiVO₄ models F₀MoBi-BiVO₄ (Figure 1e) and F₀MoV-BiVO₄ (Figure 1f).

Table 3 lists the formation energies for F and Mo monodoped and F/Mo codoped BiVO₄ under O-poor and O-rich growth conditions. It can be seen from Table 3 that the formation energies under the oxygen-poor condition are smaller than those of the oxygen-rich condition, which is consistent with the previous theoretical calculation. This result implies that the oxygen-poor condition should always be used, whether cation site doping or anion site doping. Under the O-poor growth condition, the formation energy of FO is 0.75 eV, which is close to 0 eV. This result suggests that the F doping on the O site in BiVO₄ is realized experimentally.

#### Table 3. Formation Energies (eV) for F and Mo Monodoped and F/Mo Codoped BiVO₄

| doped BiVO₄ | O-poor | O-rich |
|-------------|--------|--------|
| FO          | 0.75   | 1.98   |
| MoBi        | 1.77   | 5.46   |
| MoV         | 0.22   | 1.45   |
| F₀MoBi      | 2.19   | 7.11   |
| F₀MoV       | 0.75   | 3.21   |

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Under the O-poor and O-rich growth conditions, the
formation energies of MoV are smaller than those of MoBi. This means the Mo atom prefers to substitute the V atom, consistent with the experimental\textsuperscript{43} and theoretical\textsuperscript{11,31} results. This has resulted in the formation energies of FOMoV being smaller than those of FOMoBi. This result suggests that the F/Mo codoped BiVO\textsubscript{4} is much easier to form FOMoV-BiVO\textsubscript{4}\textsuperscript{16} and FOMoBi-BiVO\textsubscript{4} is generally hard to obtain experimentally.

3.2. Electronic Structures. Figure 2 shows the total density of states (TDOS) and partial density of states (PDOS) of FO, MoBi, MoV, FOMoBi, and FOMoV-doped BiVO\textsubscript{4} between −5 and 2 eV based on the HSE function. Additionally, the electronic properties of pure BiVO\textsubscript{4} are also calculated in order to compare the F/Mo codoped BiVO\textsubscript{4} is much easier to form FOMoV-BiVO\textsubscript{4}\textsuperscript{16} and FOMoBi-BiVO\textsubscript{4} is generally hard to obtain experimentally.

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Figure 2. Total density of states and partial density of states for (a) bulk BiVO\textsubscript{4} and (b) FO, (c) MoBi, (d) MoV, (e) FOMoBi, and (f) FOMoV-doped BiVO\textsubscript{4}. The red dot-dash lines denote the Fermi level.
For FOMoBi-doped BiVO$_4$, as shown in Figure 2e, the impurity state appears near the bottom of the conduction band edge and would also behave as a donor. A significant reduction in band gap from 2.4 to 2.05 eV is observed. The partial charge density at the CBM (Figure 3d) shows that the wave function is delocalized, implying shallow-level doping. However, as shown in Table 3, the formation energy of FOMoBi-doped BiVO$_4$ is the highest under O-poor and O-rich conditions. They are unlikely to form. This indicates that the FOMoBi defect in BiVO$_4$ is challenging to form.

Finally, for FOMoV-doped BiVO$_4$, as shown in Figure 2f, similar to that of FOMoBi-doped BiVO$_4$, the impurity state appears near the bottom of the conduction band edge and would also behave as a donor. Its band gap is 2.25 eV, smaller than that of bulk BiVO$_4$ (2.4 eV). This suggests that visible light absorptions with red shifts of the optical band gap transition are expected compared with undoped BiVO$_4$, which will be discussed in section 3.3. The partial charge density at the CBM (Figure 3e) shows that the wave function is delocalized, mainly over the V atoms and the Mo atom, which implies shallow-level doping. Thus, this shallow level doping state can promote the charge carrier mobility and photocatalytic activity of FOMoV-doped BiVO$_4$ instead of the deep-level state. More importantly, under O-poor conditions, the formation energy of FOMoV-doped BiVO$_4$ is the lowest (energetically favorable). This means that shallow-level doping and the lowest formation energy can explain the experimental observation of the FOMoV-doped BiVO$_4$ enhanced photocatalytic efficiency.

3.3. Optical Properties. In general, the optical absorption properties of photocatalytic semiconductor materials are closely related to their electronic band structure. It is a significant factor affecting the photocatalytic activity. Due to their large formation energies, the optical absorption properties of MoBi and FOMoBi are not discussed in this paper. The frequency-dependent absorption coefficients of the FOMoV-doped BiVO$_4$ can be obtained from the frequency-dependent complex dielectric function:

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where \( e_1(\omega) \) and \( e_2(\omega) \) are the real and imaginary parts of the dielectric function, respectively, and \( \omega \) is the photon energy. The imaginary part \( e_2(\omega) \) of the dielectric function \( e(\omega) \) is calculated using the standard formulation: \(^{18}\)

\[
e_2(\omega) = \frac{Vc^2}{2\pi \hbar^2 \omega^2} \int d^3k \sum_{n_k} |(nklpnlk')|^2 f_{nk'} (1 - f_{nk})
\]

where \( V \) is the cell volume, \( \hbar \omega \) is the incident photon’s energy, \( p \) is the momentum operator, \( lnk \) denotes the electronic state \( k \) in band \( n \), and \( f_{nk} \) is the Fermi occupation function. The real part \( e_1(\omega) \) is related to \( e_2(\omega) \) by the Kramer–Kronig transformation. The absorption coefficient \( \alpha(\omega) \) can be derived from \( e_1(\omega) \) and \( e_2(\omega) \) as follows:\(^{9,11,36}\)

\[
\alpha(\omega) = \frac{\sqrt{2} \omega}{c} \sqrt{\left( e_1^2(\omega) + e_2^2(\omega) \right) - e_1^2(\omega)} \right)^{1/2} \quad (10)
\]

The frequency-dependent absorption coefficients along the [100], [010], and [001] directions between 1.5 and 3.5 eV are shown in Figure 4 using the HSE method. It is shown that the doping effect on optical absorption coefficients along the [001] (Figure 4c) is larger than that along [100] and [010] directions (Figure 4a,b). Therefore, we focus on the optical absorption coefficients of the FO-, MoBi-, MoV-, and FOMoV-doped BiVO 4 along the [001] direction. In Figure 4c, it can be seen that the optical absorption coefficients of the FO-doped BiVO 4 exhibit one main peak at 2.15 eV. This is due to a transition between nodes occupying the O 2p valence band and states occupying the V 3d and Mo 4d states. Among the main peaks, this one exhibits the most optical absorption (FO-, MoBi-, and FOMoV). The results are also consistent with the aforementioned electronic properties. When the energy is greater than 2.4 eV, the optical absorption coefficient for the Mo-doped BiVO 4 is significantly higher than the FOMoV-doped BiVO 4. Further, this result shows that the Mo-doped BiVO 4 highly effectively improves optical absorption in the visible region. This agrees with the experimental\(^{11,12}\) and theoretical results. \(^{11}\)

### 3.4. Band-Edge Potential

In general, the edge potentials of the conduction band (CB) and valence band (VB) significantly impact photocatalysis. The Mulliken electronegativity theory\(^{20}\) can predict the CB and VB potentials of bulk BiVO 4 and FO-, MoBi-, MoV- and FOMoV-doped BiVO 4: \( E_{CB} = \chi - E_g - 0.5E_g \) (or \( E_{VB} = \chi - E_g + 0.5E_g \)), where \( E_{CB} \) (or \( E_{VB} \)) is the conduction (valence) band potential, \( \chi \) is the absolute electronegativity of bulk BiVO 4, and \( F_{05}, M_{05}, M_{02}, F_{05}, M_{05}, M_{02}, \) and \( F_{05}, M_{05}, M_{02} \)-doped BiVO 4. The band position and photoelectric thresholds for several compounds have been calculated \(^{9,11,13,52}\).

Using the calculation method based on our previous literature,\(^{52}\) we obtained the Mulliken electronegativity (\( \chi \)) of Bi, V, O, F, and Mo from these data, which are 4.12, 3.60, 7.54, 10.40, and 4.05 eV, respectively.\(^{33,54}\) The \( \chi \) value for BiVO 4 is 6.04 eV. Therefore, the \( E_{CB} \) value of BiVO 4 was calculated to be +0.33 eV, and the \( E_{VB} \) value was estimated to be +2.73 eV, which agrees well with our previous calculation.\(^9\)

The band-edge positions for bulk BiVO 4 and FO-, MoBi-, MoV-, FOMoBi-, and FOMoV-doped BiVO 4 are presented in Table 3. The calculated band gaps and band edge positions of bulk BiVO 4 and FO-, MoBi-, MoV-, FOMoBi-, and FOMoV-doped BiVO 4 are shown in Figure 4 using the HSE method. It is shown that the band gap is 2.05 eV, which is the reason. Furthermore, for FOMoV-doped BiVO 4, the CBM is shifted by 0.10 eV toward positive potential. The VBM is lowered by 0.05 eV, leading to a slight decrease in the oxidizing capacity of the VB and the reducing capacity of the CB. Under visible light irradiation, it exhibits high photocatalytic efficiency and a wide light response range. Its shallow-level doping leads to a small intrinsic band gap and the lowest formation energy.

### 4. CONCLUSION

This study calculates the formation energy, electronic properties, and photocatalytic activity of FOMoV codoped BiVO 4 based on the HSE hybrid functional. From the calculated formation energies, we find that Mo atoms prefer to replace V atoms, whereas F atoms prefer to replace O atoms under oxygen-poor conditions. More importantly, BiVO 4 doped with FOMoV is found to be shallow-level doped, with the occurrence of some continuum states above the conduction band edge. Moreover, FOMoV-doped BiVO 4 shows absorption stronger than that of pure BiVO 4 in the visible spectrum. Finally, based on the band-edge calculation, BiVO 4 doped with FOMoV retains a high oxidizing capacity. The present results show consistency with the relevant experimental observations.
Complete contact information is available at: https://pubs.acs.org/10.1021/acsomega.2c00382

Author Contributions

X.C. and Y.W. contributed equally to this paper.

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