Structural Origin for Efficient Photoelectrochemical Water Splitting over Fe-Modified BiVO₄

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1. INTRODUCTION

Photoelectrochemical (PEC) water splitting in neutral pH offers an attractive solution for producing H₂ fuel in an economic and environmentally friendly way.¹⁻³ For BiVO₄, a non-toxic, low-cost, and visible-light-absorbing semiconductor, the PEC oxygen evolution reaction (OER) is only ~1.8 mA/cm² (with reference to the activity at 1.23 V vs reversible hydrogen electrode (RHE) under Air Mass (AM) 1.5 G illumination hereafter) due to the sluggish OER kinetics and low efficiency of photogenerated charge migration.⁴ Much effort has been devoted to improving the activity via BiVO₄-based composite materials to enhance the charge transfer and improve the OER kinetics.⁵⁻⁷ Among BiVO₄-based binary materials working in the neutral environment, such as C₃N₆/BiVO₄,¹⁵ TiO₂/BiVO₄,¹⁶ and Fe(Ni)Oₓ/BiVO₄, the Fe(Ni) modifier not only achieves the top activity, e.g. 4.3–4.5 mA/cm²,⁷ but also has the advantage of the simple fabrication procedure and the crustal abundance of Fe and Ni. To date, the origin of the high activity of the Fe-modified composite material remains elusive due to the lack of atomic-level understanding on the catalyst structure.

The FeOₓ/BiVO₄ composite catalyst, usually synthesized by depositing Fe ions on pre-synthesized monoclinic clinobisvanite (no. 15, I/b) BiVO₄ crystals, is named after the α-FeOOH phase detected by X-ray diffraction (XRD) when the Fe-containing component has large particles. However, such catalysts with large FeOOH particles are rather poor in activity (below 2.7 mA/cm²),⁸ and the true active site of the Fe-containing component is thus still a mystery. This might not be surprising as FeOOH has rich phases under ambient conditions,¹⁷ from amorphous to different crystalline forms (α-, β-, γ-, and ε-FeOOH).

Indeed, the performance of the FeOₓ/BiVO₄ catalyst was found to be very sensitive to the synthetic conditions and methods, which may affect the Fe component structure (e.g. particle size, the phase and interface with BiVO₄ surfaces). The active catalyst generally has a low amount of Fe content (Fe/BiOₓ ratio < 8 wt%) with non-detectable Fe crystal phases, as shown by XRD. Different active Fe phases were suggested in literature. By using the photoelectrodeposition method to grow Fe on BiVO₄, Kim and Choi⁵ suggested that the Fe-containing
phase is amorphous according to the transmission electron microscopy (TEM) image. Their catalyst has a PEC current density of ∼4 mA/cm² in neutral electrolyte. On the other hand, Zhang et al. managed to identify tiny peaks in XRD patterns at 2θ = 18 and 27° in the chemical bath-synthesized sample and thus suggested that β-FeOOH might be the active phase.

Herein, we utilize combined theoretical and experimental techniques to determine what the active Fe component is and where the nanostructures grow on BiVO₄ surfaces. The recently developed machine learning interface (ML-interface) method is first utilized to find the coherent FeOOH/BiVO₄ interface from thousands of likely interface candidates, which shows that the ε-FeOOH(011)/BiVO₄(001) interface is the most stable. The subsequent density functional theory (DFT) calculations and orthogonal PEC experiments then confirm the high catalytic activity of the ε-FeOOH(011)/BiVO₄(001) interface. Importantly, the best conditions to synthesize the active ε-FeOOH(011)/BiVO₄(001) interface is identified, which leads to the high activity of 5.4 mA/cm², ~0.9 mV/cm² higher compared to the previous experiment.

2. METHODS

2.1. ML-Interface Search. Our ML-interface approach was developed to search for the composite junctions and has been utilized to identify GaP/TiO₂, Ru/RuO₂, and more recently Si/SiO₂ interfaces. The central part of the ML-interface method is the stochastic surface walking (SSW) global structure search based on a global neural network (GNN) potential (SSW-NN), which is guided by the phenomenological theory of martensitic crystallography (PTMC) to identify the likely coherent interface. The PTMC effectively reduces the computational loading of SSW-NN and speed up the search for the atomically coherent interface. These two parts are briefly described below.

2.1.1. SSW-NN Global Optimization. The SSW potential method was utilized for the global potential energy surface (PES) exploration of bulk and surfaces. The SSW-NN method is implemented in large-scale atomic simulations using the neural network potential code LASP (www.lasphub.com). In this work, a Bi−V−O−Fe−H five-element GNN potential is first generated by an iterative learning DFT dataset using the PES structures sampled from the SSW global PES exploration. The final data set contains 36,442 structures containing different bulk, surface, and interface structures with different Bi, V, O, Fe, and H compositions. The Bi−V−O−Fe−H five-element GNN potential has 448 power-type structure descriptors (PTSDs) for each element (215 two-body, 173 three-body, and 30 four-body PTSDs), achieving the accuracy of the root-mean-square for energy and force of 7.729 meV/atom and 0.208 eV/Å (Table S1), respectively, which is enough to distinguish the low-energy minima FeOOH₄ phases on BiVO₄ (the benchmark of GNN calculations against DFT results is tabulated in Table S2). The GNN calculations achieve more than 4 orders of magnitude speedup compared to DFT calculations, allowing efficient global PES sampling to identify low-energy interface structures. All low-energy structures obtained from SSW-NN were further verified using DFT calculations (see Section 2.2), and all energetics reported in this work without explicit mentioning are from DFT.

2.1.2. Modified PTMC Method. The modified PTMC method was utilized to find the lattice-matched orientation relation (OR) between two bulk structures in forming interfaces. The PTMC is based on the martensitic phase transformation of a solid material and has recently been extended to identify the interface between two different solid bulk structures which is required to achieve the best lattice match. To be specific, in order to determine the low-strain interfaces, a large quantity of ORs and lattice correspondences will be enumerated by joining two transformed bulk lattices, and the strain of the obtained interface is evaluated according to the interface lattice parameters. The lattice transformation is carried out by multiplying the conventional lattice by a random transformation metric, where the matrix elements are integers randomly selected from −6 to 6.

2.2. DFT Calculations and Models. All energies reported in this work are from DFT calculations using the plane-wave Vienna ab initio simulation package (VASP). The electron–ion interaction is represented by the projector-augmented wave potential, and the kinetic cutoff was set as 450 eV. The first Brillouin zone k-points were sampled using the Monkhorst−Pack scheme with an automated mesh determined by 25 times reciprocal lattice vectors. The exchange−correlation potential employed was generalized gradient approximation with Perdew−Burke−Ernzerhof (GGA−PBE) with Hubbard terms for 3 d metals (PBE + U), in most calculations without explicitly mentioning (U−J = 3.5 and 3.1 eV for Fe and V, respectively), and the hybrid DFT calculations with the HSE06 functional were also utilized to better describe the band structure. The van der Waals corrections at the level of PBE-D3 were utilized, which is found to be important to yield the correct ground state for the FeOOH phase (Figure S1 and Table S3). It should be mentioned that spin polarization was explicitly considered for all Fe-containing systems, and the ferromagnetic and antiferromagnetic solutions were compared for the key bulk and interface structures. The lowest energy FeOOH phase was found to be anti-ferromagnetic with alternating spins (+5 or −5) on Fe atoms, although the energy ordering among low-energy FeOOH phases is little affected by the spin ordering.

The interface slab model is based on the p(1 × 2) model of BiVO₄(001), which contains four BiVO₄ layers. To measure the relative stability of the FeOOH overlayer structures on different BiVO₄ surfaces, we utilize eq 1 to compute the formation energy ΔEf:

$$\Delta E_f = \frac{1}{A} \left( E_{\text{int}} - n_1 E_{\text{bulk,FeOOH}} - n_2 E_{\text{bulk,Fe(OH)}_2} - m E_{\text{bulk,BiVO}_4} - \gamma_{\text{BiVO}_4} \right)$$  \hspace{1cm} (1)$$

where γBiVO₄ represents the surface energy of the BiVO₄ surface, the prefactor A is the interface area, Ebulk,X represents the bulk energy of ε-FeOOH (the GM of FeOOH) and BiVO₄, and Eint is the total energy of the interface structure. ΔEf thus measures the energy gain/cost during the deposition of FeOOH on a BiVO₄ surface, which creates an interface between FeOOH/BiVO₄, terminates the original BiVO₄ surface, and exposes a new FeOOH surface. Under synthetic conditions, FeOOH could be in the redox equilibrium with FeOOH₁₋ₓ and Fe(OH)₂. Using the chemical reaction FeOOH + H⁺ + e⁻ = Fe(OH)₂, we can relate Ebulk,Fe(OH)₂ to Ebulk,FeOOH (eq 1) at a given potential U by exploiting the standard hydrogen electrode equilibrium (1/2H₂ = H⁺ + e⁻). In this
work, $U = +0.5$ V, as computed from the work function of BiVO$_4$ surface in aqueous solution, see Supporting Information Figure S3. Under OER conditions, the $U$ value is set as +1.3 V to evaluate the stability of the FeOOH film, which shows that FeOOH structures with all Fe(III) are favored thermodynamically (see Section 3.2).

In computing the OER energy profile, the Gibbs free energy is referred to the ambient conditions (298.15 K and 101.3 kPa). The solvation effect in the presence of aqueous solution is taken into account using the periodic continuum solvation model with a modified Poisson–Boltzmann equation.$^{39}$ All transition states (TS) search was performed using the double-ended surface walking,$^{40}$ as implemented in the LASP code.

### 2.3. FeOOH/BiVO$_4$ Photoanode Synthesis

The BiVO$_4$ photoanodes were synthesized by an electrodeposition method as reported previously$^5$ and also described in Supporting Information Section S1.2. FeOOH was deposited on BiVO$_4$ using the in situ chemical bath method,$^7$ in which the BiVO$_4$ photoanode was stewed in 5 mM Fe salt solution ($\text{FeCl}_3$, $\text{Fe(NO}_3)_3$, $\text{FeSO}_4$, and $\text{FeCl}_2$) for 2 to 12 h under 20 to 60 °C.

## 3. RESULTS AND DISCUSSION

It is well established that for any photocatalysts the photogenerated carriers need to survive during their migration from the photoactive bulk material to the catalyst surface across the phase junctions or composite interfaces, if present.
As the large structural distortions and the presence of defects often lead to charge trapping, the interface as a charge valve should be thermodynamically stable and defect-free.\textsuperscript{18,41}

Our investigation starts from the search of the likely interface between BiVO\textsubscript{4} and FeOOH phases by using our recently-developed ML-interface method, as illustrated in Figure 1. Our aim is to identify a coherent and thermodynamically favorable interface, which could maximally prevent the carrier trapping during their migration across the interface.\textsuperscript{52}

The ML-interface simulations, as shown in Figure 1, first utilizes monoclinic BiVO\textsubscript{4} and different FeOOH bulk phases as the input to construct the initial interface model, and each low strain interface from the PTMC screening is then explored by SSW-NN global structure optimization to identify the best interface atomic structure.

Specifically, all likely interfaces between two most stable BiVO\textsubscript{4} surface namely (001) and (101), and more than 1500 different surfaces from different FeOOH bulk phases, including α-(no P$\beta$ma, 62), β-(no I$\beta$m, 12), γ-(no Cm$\beta$2$_{1}$, 36) and ε-phase (no P$\beta$2$_{1}$/m, 31), were enumerated, which yields more than 10,000 possible ORs. The two stable surfaces of BiVO\textsubscript{4} were identified via a thorough examination of low \{hkl\} Miller-index \((l,h,k,l \leq 3)\) surfaces as listed in Supporting Information Table S4. After PTMC fast screening, only 6 pairs of ORs (Table S5) survive to have both the low lattice strain <5% and relatively small lattice parameters (either \(a\) or \(b < 1.5\) nm).

Next, SSW-NN simulation was performed for these six candidates to search for thermodynamically feasible interface structures, in which the slab models containing BiVO\textsubscript{4} and FeOOH phases were utilized with varied FeOOH thicknesses (1–4 layers). In SSW-NN simulations, over 100,000 minima were visited, from which the most stable interface is finally identified according to the calculated FeOOH/BiVO\textsubscript{4} interface formation energy \(\Delta E_{f}\) in aqueous solution (calculated by eq 1 in Section 2.2). With the most stable interface identified, we then performed SSW-NN simulations by adding H atoms from the most stable interface to further evaluate the stability of FeOOH\textsubscript{1.5} and FeOOH\textsubscript{2} overlayers.

3.1. FeOOH\textsubscript{x}/BiVO\textsubscript{4}(001) Interface Structure. The most stable interface identified has the OR of ε-FeOOH\textsubscript{x}//BiVO\textsubscript{4}(001) and ε-FeOOH\textsubscript{1.5}//BiVO\textsubscript{4}(100). Figure 2a shows the energy profile for this FeOOH\textsubscript{x}//BiVO\textsubscript{4}(001) interface at different thicknesses (layers) and different numbers of H (\(x = 1, 1.5\) and 2, corresponding to the pure Fe(III) overlayer, mixed Fe(III)/Fe(II) overlayer and pure Fe(OH)$_{2}$ overlayer, respectively). One layer of FeOOH\textsubscript{x} is ~0.3 nm thick where the Fe atoms are about the same height with respect to BiVO\textsubscript{4} surface. The y axis of Figure 2a is the FeOOH\textsubscript{x} layer formation energy, \(\Delta E_{f}\) (see eq 1) with \(U = +0.5\) V, and the x axis indicates the number of FeOOH\textsubscript{x} overlayer on BiVO\textsubscript{4} surface. The color ribbons show the energy spectra of distinct minima identified by SSW-NN at different layer thicknesses of FeOOH\textsubscript{x}//BiVO\textsubscript{4} from which the energy gap between the GM and the less stable minima can be identified. It should be mentioned that the structure for \(x = 1\) and 1.5, i.e. FeOOH and FeOOH\textsubscript{1.5}, the interface structure share the same skeleton of ε-FeOOH\textsubscript{x} phase, but when \(x = 2\), i.e. Fe(OH)$_{2}$, the ε-FeOOH\textsubscript{2} skeleton is no longer stable and the interface adopts the Fe(OH)$_{2}$ phase structure, being Fe(OH)$_{2}$(011)//BiVO\textsubscript{4}(001) (more details are shown in Figure S5). Two major findings on the stability of the FeOOH overlayers are outlined as follows.

First, the overlayer structure at the integer layer number (1-layer, 2-layer, etc.) prefers the crystalline structure, manifested by the large energy gap between the GM and the second lowest energy minimum (SLM). For instance, at the 2-layer FeOOH, the GM is more than 0.2 eV per (1 × 2) supercell more stable than the SLM. On the other hand, the non-integer overlayer structures are much less stable and amorphous, where many likely conformations are energetically degenerate. Since these amorphous non-integer overlayer structures are always less stable than their neighboring integer overlayer minima, we can conclude that the crystallization of FeOOH on the BiVO\textsubscript{4}(001) surface is thermodynamically more favorable.

Second, the stability decreases with the increase of FeOOH layer thickness. This is apparently due to the strain (4%) of the interface, where the thicker FeOOH layers incur a larger energy cost due to the lattice expansion. For example, \(\Delta E_{f}\) of 3-layer FeOOH/BiVO\textsubscript{4} is 0.2 J/m$^{2}$ higher than the 2-layer and 0.1 J/m$^{2}$ higher than the 1-layer.

The FeOOH overlayer can be partially reduced to FeOOH\textsubscript{1.5} and then fully reduced to Fe(OH)$_{2}$ overlayers. These reduced layers are generally more stable than the FeOOH overlayer under synthetic conditions (\(U = +0.5\) V). In particular, for the 2-layer FeOOH, the partial reduction from Fe(III) to Fe(II) leads to the decrease of \(\Delta E_{f}\) by nearly 0.4 J/m$^{2}$. This suggests the as-synthesized FeOOH/BiVO\textsubscript{4} under the ambient conditions should in fact be FeOOH\textsubscript{1.5}/BiVO\textsubscript{4} with mixed Fe(II) and Fe(III) cations, and the overlayer can be re-oxidized to the fully oxidized FeOOH under OER conditions. When the FeOOH\textsubscript{x} layers are thick (>3 layers), the Fe(OH)$_{2}$/BiVO\textsubscript{4} has the highest stability, suggesting the destroy of the ε-FeOOH skeleton and thus it is necessary to control the growth of FeOOH.

Now we focus on the integer overlayers that are crystalline and thermodynamically more stable. For the 1-layer FeOOH, it is basically the epitaxial layer of BiVO\textsubscript{4} with the lattice Bi and V replaced by Fe atoms (four Fe cations per BiVO\textsubscript{4}(001) \(p(1 \times 2)\) supercell, equivalent to the number of exposed cations (Bi and V) atoms of the BiVO\textsubscript{4} substrate). Each Fe is 4 to 6 coordinated with Fe−O distances being ~2.2 Å. By performing DFT calculations, the band structure for the 1-layer FeOOH/BiVO\textsubscript{4} composite is obtained and the wavefunctions for the valence band maximum (VBM) and the conduction band minimum (CBM) are plotted in Figure 2b. As shown, the VBM and CBM are overlapped in space, delocalizing both at the FeOOH overlayer and the BiVO\textsubscript{4} bulk. The density of states (DOS) plot is shown in Supporting Information Figure S7, which shows that the 1-layer of FeOOH does not perturb much the BiVO\textsubscript{4} band structure, neither forming a new VBM edge nor a new CBM edge.

The FeOOH overlayers above two layers adopt the structure of ε-FeOOH phase. In the structure all Fe atoms are six coordinated with Fe−O bond length 2.0 ± 0.1 Å, which is close to the bulk structure. The interface has a low strain, less than 4%, as calculated from minimum matched supercell BiVO\textsubscript{4} (001) \(p(1 \times 2)\) 5.16 Å × 10.32 Å and ε-FeOOH(001) \(p(1 \times 2)\) 4.93 Å × 10.70 Å.

The band structure for the 2-layer FeOOH/BiVO\textsubscript{4} composite is also calculated by DFT with the total and partial DOS shown in Figure 2c and the wavefunctions for the VBM and CBM shown in Figure 2d. It can be seen that the presence of 2-layer FeOOH narrows the band gap from 2.4 eV of the original BiVO\textsubscript{4} to the 1.6 eV of the composite. This gap value is consistent with that derived from the computed optical
absorption spectra shown in Figure S8, wherein the onset energy value of BiVO$_4$ and FeOOH/BiVO$_4$ are $\sim$2.1 and $\sim$1.7 eV respectively. Importantly, the composite offers a type-II band structure where the VBM and CBM are spatially separated and localized at the FeOOH side (blue in Figure 2d) and BiVO$_4$ side (red), respectively. It is noted that the H$_2$O/O$_2$ redox potential lies in the band gap, indicating the ability to trigger OER and an appropriate photogenerated voltage of 0.9 V (potential difference between the edge of VBM and H$_2$O/O$_2$ potential) can be exploited to enhance the PEC water splitting.

Our results indicate that FeOOH$_{1.5}$ thin films with one- or two-layer thickness, where the $\Delta E_f$ is less than 0.75 J/m$^2$ is the most favorable overlayer grown on BiVO$_4$. Under the OER reaction condition, where the high electrochemical voltage is applied during PEC OER, these thin FeOOH$_i$ overlayers can be further oxidized to all-Fe(III) FeOOH overlayer. Since only the 2-layer FeOOH$_2$/BiVO$_4$ has the desired type II band structure qualified for PEC catalysis, the theoretical results imply that the deposited FeOOH in the experiment should not be too thin (1-layer) and cannot be too thick (above 2-layers).

3.2. OER Mechanism. DFT calculations was then performed to verify the catalytic activity of the two-layer FeOOH$_{1.5}$/BiVO$_4$ composite that has the desirable electronic band structure. Under oxidative OER conditions (>1.23 V), FeOOH$_{1.5}$ is oxidized to FeOOH as determined by thermodynamics (Figure S4), and thus our OER pathway exploration utilizes the two-layer FeOOH/BiVO$_4$ as the catalyst surface. Three likely reaction pathways as mentioned in literatures were investigated, namely the adsorbate evolution mechanism (AEM), the lattice peroxide mechanism (LPM), and the oxide mechanism, which differs in how the O–O bond is formed. The two with the low Gibbs free energy profiles at 1.3 V vs RHE are shown in Figure 3, where the AEM features the direct O–O coupling and the LPM experiences a water-assisted O + H$_2$O coupling step to form an OOH intermediate. The oxide mechanism with the highest reaction barrier is shown in Figure S9.

Both AEM and LPM pathways start from the same initial state (IS) structure where the $\varepsilon$-FeOOH surface has a pre-adsorbed 0.5 ML each H$_2$O and OH on the exposed Fe sites, which makes all surface Fe cations six coordinated. The adsorbed OH can first lose its H, a proton-coupled electron transfer (PCET) step, to the aqueous solution, forming an adsorbed O atom stabilized by nearby H$_2$O with only 0.47 eV in free energy. In the AEM pathway, which has the lowest energy profile, the nascent O reacts with a nearby water molecule and the reacting H$_2$O simultaneously loses its H to the neighboring OH, leading to a TS, only 0.64 eV higher than the IS. The newly-formed OOH product can further pass the H to the solution via PCET and release an oxygen molecule which is strongly exothermic by over 2 eV. As for the less favored LPM, the reaction features the adsorbed O directly coupling with the lattice bridging O, giving an OO peroxide in the lattice. The reaction barrier is 1.04, 0.4 eV higher than that in the AEM pathway. The OO peroxide can then desorb to the gas phase and leaves a surface O vacancy, which can be healed rapidly by the nearby *OH adsorbate, leaving a coordinated unsaturated Fe site. The surface is recovered after a PCET step of the lattice OH to lose H and a H$_2$O adsorption on the exposed Fe site. Our DFT results demonstrate that the FeOOH/BiVO$_4$ composite is catalytically active under ambient conditions above 1.3 V, where the OER reaction can follow an AEM pathway with only 0.64 eV barrier.

3.3. PEC Activity Test Experiments. To confirm our theoretical findings on the interface structure, we performed PEC experiments using the previously-reported chemical bath synthetic method to prepare the FeOOH/BiVO$_4$ composite. All PEC activity tests were performed under the standard AM 1.5 G illumination and neutral 0.2 M Na$_2$SO$_4$ electrolyte. As shown in Figure 4a, three key conditions in catalyst synthesis, including the Fe salt precursor, the deposition time, and the temperature, are varied to optimize the catalytic performance since our theoretical results indicate the overlayer thickness and the Fe oxidation states as two critical factors to determine the stability of the FeOOH overlayer. In Figure 4a the activity of photoanodes is distinguished by the color bar and the x/y/z axis represents the salt/temperature/time conditions in synthesis (detailed data listed in Table S7). Indeed, our experimental data indicate that the catalytic activity is very sensitive to the three synthetic conditions. The sample prepared using FeSO$_4$ solution with the deposition temperature 40 °C and time 4 h achieves the best performance of 5.4 mA/cm$^2$, which is even higher than the top activity (4.3 mA/cm$^2$) reported in the previous experiment using 0.5 M FeCl$_3$, depositing for 10 h and under room temperature conditions.

Figure 4b presents the photocurrent–voltage ($J$–$V$) curves of the best FeOOH/BiVO$_4$ photoanodes corresponding to different Fe salts at the optimal synthetic conditions, as labeled by Fe-salt/BiVO$_4$, e.g., FeSO$_4$/BiVO$_4$. The photocurrent at 1.23 V is 5.4 (FeSO$_4$ 4 h, 40 °C), 4.5 (FeCl$_3$, 10 h, 20 °C), 4.2 (FeCl$_3$, 10 h, 20 °C) and 3.0 (Fe(NO$_3$)$_3$, 8 h, 20 °C) mA/cm$^2$ for these four different photoanodes (Table S7, data in red), which are all much higher than the pure BiVO$_4$ photoanode. In addition, the two most active FeSO$_4$ and FeCl$_3$ photoanodes shift the onset potential of BiVO$_4$ from ~0.40 V (vs RHE) to ~0.25 V, while the other two do not have obvious improvement. Similarly, these four samples exhibit the same activity order in applied biased photo-to-current efficiency (ABPE) curves, shown in Figure S11. The FeSO$_4$ sample has the highest ABPE peak of 1.46% at ~0.82 V (vs RHE), followed by FeCl$_3$, 1.22% at 0.90 V, FeCl$_3$ 0.85% at 0.91 V, Fe(NO$_3$)$_3$, 0.68% at 0.93 V, which are much higher than the pure BiVO$_4$ that achieves only 0.22% at 0.90 V. This same activity order is also reflected in the electrochemistry impedance spectroscopy measurement (Figure S12 and Table S8), where FeSO$_4$/BiVO$_4$ has the smallest charge transfer resistance ($R_t$ $\sim$ 121.8 Ω).

Figure 3. OER mechanism. Gibbs free energy profile at $U$ = 1.3 V and the reaction snapshots during OER from DFT calculations. AEM: red; LPM: blue.
BiVO with different deposition times. Dark in (b,c) represents the curve of the optimal FeSO_{4}/BiVO light absorbance ability of FeSO_{4}/BiVO for achieving the best catalytic performance. Could be explained by the critical thickness (2-layer) of short deposition time will deteriorate the performance. This h, deposition yields the highest activity. A too-long or too-

Figure 4. Experimental results for FeOOH/BiVO. (a) PEC catalysts' activity of different photoanodes. (b) J–V curves of the optimal photoanodes with different Fe sources. (c) J–V curves of FeSO_{4}/BiVO with different deposition times. Dark in (b,c) represents the J–V curve of the optimal FeSO_{4}/BiVO recorded without illumination.

Figure 4c further compares the J–V curves of FeSO_{4} samples at different deposition times (0 to 8 h) at the same deposition temperature (40 °C). Obviously, a medium-time, 4 h, deposition yields the highest activity. A too-long or too-short deposition time will deteriorate the performance. This could be explained by the critical thickness (2-layer) of FeOOH for achieving the best catalytic performance.

By using UV–vis spectra (Figure S13), we compared the light absorbance ability of FeSO_{4}/BiVO and pure BiVO photoanodes. The bandgap deduced from the spectra is ~2.36 eV for FeSO_{4}/BiVO and ~2.47 for pure BiVO. This bandgap reduction (0.11 eV) is smaller, although in the same trend, than the calculated value from the 2-layer FeOOH/BiVO model (~0.4 eV from Figure S8). This suggests the FeSO_{4}/BiVO photoanode in experiment should not be 100% 2-layer FeOOH/BiVO, but a mixture of FeOOH overlayers with different thicknesses.

To understand the catalytic role of interface, we performed the activity test with extra sacrificial agent (SA) (0.2 M Na_{2}SO_{3}, hole scavenger) and the results are shown in Supporting Information Figure S14 which compares the J–V curves for pure BiVO and Fe-modified BiVO with and without SA. This hole scavenger SA is able to accept surface-reaching holes immediately (much faster than water oxidation), and thus enables the examination of the PEC properties of the samples independently of OER kinetics. We found that the photocurrent without SA is indeed smaller than that with SA at low potentials. With SA the onset potential of BiVO shifts downward from ~+0.40 to ~+0.11 V, suggesting the photogenerated holes suffer from recombination due to the slow OER kinetics on BiVO (Figure S14a). By contrast, FeSO_{4}/BiVO with SA has the onset potential at ~+0.12 V, very close to that of BiVO, indicating that the oxidation of photogenerated holes is barely diminished by recombination and impeded in the presence of FeOOH overlayer and thus confirming the separation of electron–hole and the good hole migration efficiency across the FeOOH_{4}/BiVO interface in the FeSO_{4}/BiVO sample. Indeed, by comparing the J–V curves for different Fe–BiVO photoanodes (Figure S14b), we note that the onset potential increases in the order of FeSO_{4}/BiVO (0.12 V), FeCl_{3}/BiVO (0.23 V), FeCl_{2}/BiVO (0.22 V) and Fe(NO_{3})_{3} (0.31 V), which is consistent with the activity order mentioned above (Figure 4b)—the spatial separation of electron–hole and the efficiency of the interface for conducting holes dictates the activity sequence.

Finally, the stability test of the catalyst are carried out and the results are provided in Supporting Information Figure S15. FeSO_{4}/BiVO manages to be active with >3.0 mA/cm^2 after 4 h illumination, which is better than other photoanodes.

3.4. Structure Characterization. The structures of FeOOH/BiVO catalysts were characterized by SEM, XPS, and TEM techniques. For the catalyst morphology in SEM, different catalysts prepared with a long-deposition time (>8 h) reveal the structural difference between samples. Figure 5a–e plots the SEM pattern for pure BiVO_{4} and long-deposition-time FeSO_{4}/BiVO (8 h, 40 °C), FeCl_{3}/BiVO (12 h, 20 °C), FeCl_{2}/BiVO (12 h, 20 °C), and Fe(NO_{3})_{3}/BiVO (10 h, 20 °C). FeSO_{4}/BiVO exhibits clear grass-like crystalline materials, attributed to FeOOH overlayers, grown on worm-like BiVO_{4} (Figure 5a). The grass-like overlayers are, however, barely visible in the FeCl_{3}/BiVO sample, but the surface of BiVO_{4} is roughened by the overlayer (Figure 5c). For the FeCl_{2} sample, FeOOH additive poorly adheres to the BiVO_{4} surface with separated crystalline sheets surrounding the BiVO_{4} worm (Figure 5c). On the other hand, FeOOH forms large amorphous chunks on BiVO_{4} in the Fe(NO_{3})_{3} sample, which is distinct from the grass feature in the FeSO_{4} sample. We emphasize that all these long-deposition samples are catalytically less active (Figure 4a), and the morphology shown in Figure 5 only reflects the adherence and crystallization abilities between different Fe salts and BiVO_{4} substrates. These pictures imply that FeSO_{4} can facilitate the formation of the FeOOH overlayer with a good crystalline structure.

Subsequently, we performed XPS to measure the Fe(II)/Fe(III) ratio for different photoanodes. The high-resolution Fe 2p XPS spectra of optimal photoanodes with different Fe salts are plotted in Figures S5 and S16, where the characteristic peaks of Fe 2p_{3/2} and 2p_{1/2} (~712 eV for Fe(III) and ~710 eV for Fe(II)) are identified. Through peak area analysis, we found that the Fe(II)/Fe(III) ratio in the FeSO_{4}/BiVO anode is 0.9, much higher than that (0.5) in FeCl_{2}/BiVO (Figure S5) and also higher than the other two less active catalysts, FeCl_{3}/BiVO (0.7) and Fe(NO_{3})_{3}/BiVO (0.5) (Figure S16). Not
surprisingly, the Fe(II) salt as the Fe source can lead to a higher Fe(II)/Fe(III) ratio in the catalyst. Additionally, the measured Fe(II)/Fe(III) ratio of these photoanodes with varied deposition times (optimal time, ± 2 h) as tabulated in Table S9 can reflect the ratio change with respect to the change of salt type and the deposition time. In Fe$^{2+}$ salt...
solution (FeSO$_4$ and FeCl$_3$), the Fe(II)/Fe(III) ratio decreases as the time extends and finally reaches around 1.0 after ~6 h (FeSO$_4$) or 10 h (FeCl$_3$). On the other hand, the ratio is below 0.7 in Fe$^{3+}$ salt solution.

It might be mentioned that the Bi 4f high-resolution XPS spectra of optimal photoanodes shown in Figure 5g also suggest the same trend: FeSO$_4$/BiVO$_4$ has the highest Fe(II) content since it leads to the smallest binding energy shift of the Bi 4f peak,$^{43}$ and the peak shift then increases in the order of FeCl$_3$/BiVO, Fe(NO$_3$)$_3$/BiVO, and FeCl$_3$/BiVO. The strong influence of the Fe cation on the Bi electronic structure also supports the significance of the FeOOH/BiVO$_4$ interface to the high PEC catalytic activity.

To reveal the atomic structure details of FeOOH/BiVO$_4$, we then utilized HRTEM to film the grass-like structures. When the deposition time was short, samples, such as the FeSO$_4$/BiVO anode synthesized under optimal conditions, do not display a clear lattice structure of FeOOH, as seen from the HRTEM image (Supporting Information Figure S21). FeOOH grown on the substrate BiVO$_4$ is less than 2 nm thick, and the characteristic lattice patterns cannot be observed. For the long-deposition-time samples, consistent with the SEM observations, the grass-like overlayer is particularly abundant on the most active catalyst FeSO$_4$/BiVO, as seen from the HRTEM image in Figure 6a,b (in the rectangle), which becomes much less visible on the less active FeCl$_3$/BiVO and FeCl$_3$/BiVO catalyst samples, Figures 6c and S18, and appears to be totally diminished in Fe(NO$_3$)$_3$/BiVO, Figure S19. By zooming into these FeOOH grasses, we can identify the clear lattice stripes of FeOOH, where a characteristic pattern is highlighted in Figures 6c and S18 that has a large spacing stripe, ~0.5 nm, and is about 64° with respect to another ~0.19 nm stripe. By constructing a number of likely atomic models and comparing their simulated HRTEM pattern with the experiment, we finally obtained a matched picture of $\varepsilon$-FeOOH, whose (111) surface is 65° with respect to the (100) surface, Figure 5d. It should be mentioned that the XRD of all these catalysts do not exhibit the crystalline peaks of FeOOH (Figure S20), even though with a long deposition time, which is due to the low concentration of the FeOOH overlayer.

Finally, we can rationalize how FeOOH$_x$ grows on the BiVO$_4$(001) surface as summarized by Figure 6e. Starting from Fe(II) ions in solutions, these Fe species adsorb selectively on the BiVO$_4$(001) surface to fill the surface cationic (Bi/V) sites, which is driven by the thermodynamics. This adsorption is accompanied by the Fe(II) oxidation to Fe(III), and the subsequent deposition leads to the formation of $\varepsilon$-FeOOH(011) [the (011) plane is ~30° with respect to $\varepsilon$-FeOOH(111)]. Further epitaxial growth of $\varepsilon$-FeOOH is, however, thermodynamically hindered since Fe(OH)$_2$ becomes more stable (Figure 2a) and the surface layer will gradually be dominated by Fe(OH)$_2$. The growth of the $\varepsilon$-FeOOH overlayer is terminated once the surface is fully covered by Fe(OH)$_2$.

4. CONCLUSIONS

This work via combined theoretical and experimental methods reveals a highly active Fe–BiVO$_4$ anode for PEC water splitting to produce O$_2$ that achieves 5.4 mA/cm$^2$ activity and provides the atomic level understanding of its high activity. The key step of our investigation is the fast screening of more than ten-thousands of likely interface structures, which leads to the finding of only one coherent interface, $\varepsilon$-FeOOH$_{1.5}$(011)/BiVO$_4$(001), which has a mixed-valence Fe(II)/Fe(III) and high stability (0.7 J/m$^2$ formation energy and less than 4% strain). The catalyst properties and activity are determined by DFT calculations, and the optimum synthetic conditions are identified by designed orthogonal experiments. DFT calculations prove that the two-layer $\varepsilon$-FeOOH/BiVO$_4$ has the type-II band structure with a desirable band gap (~1.6 eV) and high OER activity. The orthogonal experiments show that the Fe(II) salt (FeSO$_4$) with 4~6 h of deposition time in chemical bath synthesis can produce the most active anode catalyst. The high activity of the catalyst is attributed to the presence of a high concentration of the mixed-valence FeOOH$_{1.5}$ crystalline structures as thin overlayers grown on BiVO$_4$.

### ASSOCIATED CONTENT

#### Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acscatal.3c02504.

Experimental details; G-NN potential training data; benchmark of G-NN calculations against DFT; structural information on FeOOH and BiVO$_4$; OR information; FeOOH/BiVO$_4$ structural information; OER mechanism; detailed data of orthogonal experiments; PEC testing results; and characterization results (PDF)

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#### Author Contributions

Z.P.L. conceived the project and guided the research. Y.F.H. designed and performed the experiments. Y.F.L. wrote the code of ML-interface method. All authors discussed the manuscript and agreed with the content.

#### Notes

The authors declare no competing financial interest.
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