Supplementary Information

Unraveling of cocatalysts photodeposited selectively on facets of BiVO₄ to boost solar water splitting

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Supplementary Figures

Supplementary Fig. 1 Typical FESEM images of the BiVO$_4$ loaded with different cocatalysts. (a) Ir/BiVO$_4$, (b) CoO$_x$/BiVO$_4$. The Ir nanoparticles are deposited on the \{010\} facet of BiVO$_4$ and the CoO$_x$ is deposited on the \{110\} facet of BiVO$_4$.

Supplementary Fig. 2 UV-vis DRS of the BiVO$_4$ and Ir-FeCoO$_x$/BiVO$_4$. The long wavelength absorption increases after loading the dual-cocatalysts, indicating the successful deposition of the dual-cocatalysts.
Supplementary Fig. 3 The XANES spectroscopy of Ir element of on the \( \text{Ir-FeCoO}_x/\text{BiVO}_4 \). The deposited Ir species are verified to exist as metallic Ir after comparing with the Ir foil as the reference.

Supplementary Fig. 4 The Representative HRTEM image of \( \text{Ir-FeCoO}_x/\text{BiVO}_4 \). The lattice spacing of 0.230 nm is attributed to Ir and the nanoparticle size is about 2~3 nm.
Supplementary Fig. 5 Elemental mappings of FeCoO$_x$/BiVO$_4$. (a) STEM image, (b) Bi element, (c) V element, (d) O element, (e) Fe element, (f) Co element, (g) simulated dispersion of Co and Fe element and (h) simulated dispersion of Bi, V and O element. The Fe, Co and O species are similarly located and dispersed, demonstrating that Co and Fe combine together in the form of oxidation state.

Supplementary Fig. 6 Confirmation of Fe and Co elements. (a) STEM image of FeCoO$_x$/BiVO$_4$ and (b) EELS spectra of the beam place. Both Fe and Co are simultaneously detected in the beam area.
Supplementary Fig. 7 Radial distance $\chi(R)$ space spectra of FeCoO$_x$/BiVO$_4$. Fe K-edge and Fe foil as reference, Co K-edge and Co foil as reference. There is no Fe-Fe and Co-Co bond in the FeCoO$_x$/BiVO$_4$ sample.
Supplementary Fig. 8 Comparison of fingerprint features of typical samples. (a,b) Radial distance $\chi(R)$ space spectra of FeCoO$_x$/BiVO$_4$: Fe K-edge and FeOOH, Fe$_2$O$_3$ as reference (a), Co K-edge and CoOOH, Co$_2$O$_3$ as reference (b); (c,d) The first derivative of Normalized XANES $\mu(E)$ spectra of FeCoO$_x$/BiVO$_4$: Fe K-edge and FeOOH, Fe$_2$O$_3$ as reference (c), Co K-edge and CoOOH, Co$_2$O$_3$ as reference (d). The FeCoO$_x$ is a homogeneous phase of bimetallic hydroxide, not the single-phase Fe or Co hydroxides.

Supplementary Fig. 9 $k^2\chi(k)$ space spectra fitting curves of FeCoO$_x$/BiVO$_4$. (a) Fe K-edge; (b) Co K-edge. The fitting of $\chi(k)$ space spectra is good.
Supplementary Fig. 10 3D contour Wavelet of reference samples. The extended X-ray absorption fine structure (WTEXAFS) map with 2D projection of Fe K-edge of Fe foil (a) and FeOOH (b), Co K-edge of Co foil (c) and CoOOH (d), respectively. There are no Fe-Fe, Co-Co, Fe-O-Fe and Co-O-Co bonds in the FeCoO₅/BiVO₄ sample after comparing with the references.
Supplementary Fig. 11 Photoelectrochemical performance and analysis of FeCoOₓ/BiVO₄ and CoOₓ/BiVO₄. (a) The photocurrent-voltage (J-V) curves of FeCoOₓ/BiVO₄ and CoOₓ/BiVO₄ in the electrolyte containing 1 M potassium borate (KBi, pH 9) and 0.2 M Na₂SO₃. (b) The integrated maximum photocurrent (j_{abs}) of BiVO₄ photoanodes based on the UV-vis DRS spectra. (c) Charge injection efficiencies of CoOₓ/BiVO₄ and FeCoOₓ/BiVO₄ at different bias voltages. (d) Charge separation efficiencies of CoOₓ/BiVO₄ and FeCoOₓ/BiVO₄ at different bias voltages.
The J-V curves of the typical photoanodes in the presence of 0.2 M Na$_2$SO$_3$ (hole scavenger, $j_{\text{sulfite}}$) are given in Supplementary Fig. 11a. According to the equations: $\eta_{\text{inj}} = j_{\text{water}}/j_{\text{sulfite}}$ and $\eta_{\text{sep}} = j_{\text{sulfite}}/j_{\text{abs}}$, where $j_{\text{abs}}$ is the maximum photocurrent density that a photoanode can achieve ($j_{\text{abs}} = 5.7$ mA/cm$^2$ determined by the light absorption of BiVO$_4$, Supplementary Fig. 11b).

Supplementary Fig. 12 Schematic of the whole OER mechanism on the FeCoO$_x$/BiVO$_4$ and CoO$_x$/BiVO$_4$. (a1) to (a4) denote $^\ast$, O$H$\,$^\ast$, O$^\ast$, OOH$^\ast$ of Co site of FeCoO$_x$/BiVO$_4$. (b1) to (b4) denote $^\ast$, O$H$\,$^\ast$, O$^\ast$, OOH$^\ast$ of Fe site of FeCoO$_x$/BiVO$_4$. (c1) to (c4) denote $^\ast$, O$H$\,$^\ast$, O$^\ast$, OOH$^\ast$ of Co site of CoO$_x$/BiVO$_4$, respectively.
**Supplementary Fig. 13** Bird view of the interface structures for DFT calculations. (a) BiVO$_4$ {110} surface, (b) FeCoO$_x$/BiVO$_4$ {110} interface and (c) CoO$_x$/BiVO$_4$ {110} interface.

**Supplementary Fig. 14** Structural characterizations of typical samples. The Co K-edge XANES $\mu$(E) spectra of the CoO$_x$/BiVO$_4$ and FeCoO$_x$/BiVO$_4$. The valence state of Co in FeCoO$_x$/BiVO$_4$ is higher that of CoO$_x$/BiVO$_4$, which is consistent with the changing trend of bader charge from the DFT calculations.
Supplementary Fig. 15 **Comparison of d-band center (Ed) of active sites.** The Ed value of Co sites in FeCoOₓ/BiVO₄ and CoOₓ/BiVO₄. The d-band center (Ed) value of Co active sites in FeCoOₓ/BiVO₄ is calculated as -1.63 eV, and the Co active sites in CoOₓ/BiVO₄ is -2.56 eV.

Supplementary Fig. 16 **Structure characterization of the HEP and OEP.** The XRD patterns of MgTa₂O₆₋ₓNₓ/TaON, ZrO₂/TaON and BiVO₄. The synthesized MgTa₂O₆₋ₓNₓ/TaON, ZrO₂/TaON and BiVO₄ all well with their respective PDF cards.
Supplementary Fig. 17 Typical FESEM images of the HEP and OEP. (a) ZrO$_2$/TaON, (b) MgTa$_2$O$_{6-x}$N$_y$/TaON and (c) BiVO$_4$. The surface of ZrO$_2$/TaON is rough and porous, while the surface of MgTa$_2$O$_{6-x}$N$_y$ is smooth. The BiVO$_4$ is a decahedron structure with exposed $\{010\}$ and $\{110\}$ facets.

Supplementary Fig. 18 The rates of O$_2$ evolution on the Ir/BiVO$_4$ as a function of Ir content. The optimal loading content of Ir is 0.8 wt%.

**Reaction conditions:** 20 mg photocatalyst; 20 mL 50 mM sodium phosphate buffer solution (pH 6.0) containing K$_3$[Fe(CN)$_6$] (5 mM); 300 W xenon lamp ($\lambda \geq 420$ nm), 0.5 h top-irradiation.
Supplementary Fig. 19 Optimization of the Co loading amounts with regard to photocatalytic O$_2$-evolving rates. The optimal content of Co is 0.2 wt%.

**Reaction conditions:** 20 mg BiVO$_4$ (0.8 wt% Ir fixed); 20 mL 50 mM sodium phosphate buffer solution (pH 6.0) containing K$_3$[Fe(CN)$_6$] (5 mM); 300 W xenon lamp ($\lambda \geq 420$ nm), 0.5 h top-irradiation.

Supplementary Fig. 20 Comparison of the Z-scheme OWS performances using BiVO$_4$ without and with dual-cocatalysts loaded by different methods. When using the Ir-CoO$_x$(Imp.)/BiVO$_4$ with Ir and Co randomly dispersion or BiVO$_4$ as the OEP, the OWS will not be achieved.

**Reaction conditions:** 50 mg BiVO$_4$ with dual-cocatalysts loaded using different methods, 50 mg HEP (ZrO$_2$/TaON, 1.0 wt% Rh, 1.5 wt% Cr), 100 mL 25 mM sodium phosphate buffer solution (pH 6.0) containing K$_4$[Fe(CN)$_6$] (10 mM), 300 W xenon lamp ($\lambda \geq 420$ nm), temperature: 298 K, Pyrex top-irradiation type.
Supplementary Fig. 21 Multiple cycles of Z-scheme overall water splitting using Ir-FeCoOₓ/BiVO₄ as the OEP and RhₓCr₂₋ₓO₃-ZrO₂/TaON as the HEP via [Fe(CN)₆]³⁻/⁴⁻ redox mediator. After the vacuum treatment, the activity does not decrease, indicating the good photostability.

**Reaction conditions:** 50 mg OEP (0.8 wt% Ir; 0.2 wt% Co), 50 mg HEP (1.0 wt% Rh, 1.5 wt% Cr), 100 mL 25 mM sodium phosphate buffer solution (PBS pH = 6.0) containing K₄[Fe(CN)₆] (10 mM), 300 W xenon lamp (λ ≥ 420 nm), temperature: 288 K, Pyrex top-irradiation type.

Supplementary Fig. 22 Multiple cycles of curve of Z-scheme OWS under illumination of the standard solar simulator (AM 1.5G, 100 mW cm⁻²). The activity maintains well after long time irradiation, indicating the good photostability of the system.

**Reaction conditions:** 50 mg OEP (0.8 wt% Ir; 0.2 wt% Co), 50 mg HEP (ZrO₂/TaON, 1.0 wt% Rh, 1.5 wt% Cr), 100 mL 25 mM sodium phosphate buffer solution (pH 6.0) containing K₄[Fe(CN)₆] (10 mM), temperature: 288 K, Pyrex top-irradiation type.
Supplementary Fig. 23 Dependence curve of AQE value as a function of irradiation wavelength and UV-vis DRS of the HEP and OEP. The AQE value of OWS is in good accordance with the UV-vis DRS of MgTa$_2$O$_{6-x}$N$_y$/TaON and BiVO$_4$ as a function of absorption wavelength.

**Reaction conditions:** 75 mg OEP (Ir-FeCoO$_x$/BiVO$_4$, 0.8 wt% Ir; 0.2 wt% Co), 150 mg HEP (MgTa$_2$O$_{6-x}$N$_y$/TaON, 2.5 wt% Rh, 3.75 wt% Cr), 150 mL 25 mM sodium phosphate buffer solution (pH 6.0) containing K$_4[Fe(CN)_6]$ (10 mM), 300 W xenon lamp, temperature: 298 K, Pyrex top-irradiation type.
### Supplementary Tables

**Supplementary Table 1** Structural parameters extracted from the K-edge Fe and Co $\chi(R)$ space spectra fitting of FeCoO$_x$/BiVO$_4$

|                | Reduced Chi-square ($\chi^2$) | R-factor (%) |
|----------------|-----------------------------|-------------|
| Fe K-edge      | 9831.42                     | 0.0524      |
| FeCoO$_x$/BiVO$_4$ |                             |             |

| amp/ $S_0^c$ | $N_{(Fe-O\text{ path})}$ | $R_{(Fe-O\text{ path})}$ (Å) | $\sigma^2_{(Fe-O\text{ path})}$ ($10^{-3}$ Å$^2$) | $\Delta E_0$ (eV) |
|--------------|--------------------------|-------------------------------|---------------------------------|-----------------|
| 0.96+/−0.16  | 4.5                      | 1.884 ± 0.064                | 4.9+/−1.8                       | 5.08+/−2.49     |
| amp/ $S_0^c$ | $N_{(Fe-O-Co\text{ path})}$ | $R_{(Fe-O-Co\text{ path})}$ (Å) | $\sigma^2_{(Fe-O-Co\text{ path})}$ ($10^{-3}$ Å$^2$) | $\Delta E_0$ (eV) |
| 1.06+/−0.12  | 2                        | 2.745 ± 0.103                | 6.2+/−2.5                       | 6.30+/−2.78     |

|                | Reduced Chi-square ($\chi^2$) | R-factor (%) |
|----------------|-----------------------------|-------------|
| Co K-edge      | 4604.98                     | 0.0290      |
| FeCoO$_x$/BiVO$_4$ |                             |             |

| amp/ $S_0^c$ | $N_{(Co-O\text{ path})}$ | $R_{(Co-O\text{ path})}$ (Å) | $\sigma^2_{(Co-O\text{ path})}$ ($10^{-3}$ Å$^2$) | $\Delta E_0$ (eV) |
|--------------|--------------------------|-------------------------------|---------------------------------|-----------------|
| 0.94+/−0.12  | 3.5                      | 1.756 ± 0.023                | 4.9+/−1.8                       | 3.41+/−1.72     |
| amp/ $S_0^c$ | $N_{(Co-O-Fe\text{ path})}$ | $R_{(Co-O-Fe\text{ path})}$ (Å) | $\sigma^2_{(Co-O-Fe\text{ path})}$ ($10^{-3}$ Å$^2$) | $\Delta E_0$ (eV) |
| 0.98+/−0.13  | 2                        | 2.761 ± 0.037                | 6.2+/−2.5                       | 5.55+/−2.44     |
Supplementary Table 2 Values of $R_s$ and $R_{ct}$ of various BiVO$_4$-based electrodes loaded with different reduction cocatalysts

| Entry | Photocatalysts           | $R_s$ (Ohm) | $R_{ct}$ (Ohm) |
|-------|--------------------------|-------------|----------------|
| 1     | BiVO$_4$/FTO             | 38.7        | 5156           |
| 2     | Au/BiVO$_4$/FTO          | 58.9        | 1123           |
| 3     | Ir/BiVO$_4$/FTO          | 32.9        | 473            |

Supplementary Table 3 Values of $R_s$ and $R_{ct}$ of various BiVO$_4$-based electrodes loaded with different oxidation cocatalysts

| Entry | Photocatalysts           | $R_s$ (Ohm) | $R_{ct}$ (Ohm) |
|-------|--------------------------|-------------|----------------|
| 1     | BiVO$_4$/FTO             | 49.2        | 3976           |
| 2     | CoO$_x$/BiVO$_4$/FTO     | 48.4        | 2552           |
| 3     | FeCoO$_x$/BiVO$_4$/FTO   | 45.1        | 1878           |

Supplementary Table 4 Calculated Bader charge for Fe, Co within the CoO$_x$/BiVO$_4$ and FeCoO$_x$/BiVO$_4$

|                | Co in CoO$_x$/BiVO$_4$ | Co in FeCoO$_x$/BiVO$_4$ | Fe in FeCoO$_x$/BiVO$_4$ |
|----------------|------------------------|--------------------------|--------------------------|
| Bader charge   | 1.2 a.u.               | 1.3 a.u.                 | 1.6 a.u.                 |
**Supplementary Table 5** Free energy corrections for species.

| Species | ZPE  | TΔS  |
|---------|------|------|
| H₂O     | 0.573| 0.67 (0.035 bar) |
| H₂      | 0.284| 0.403 |
| O*      | 0.066| 0.092 |
| OH*     | 0.359| 0.110 |
| OOH*    | 0.427| 0.168 |

**Supplementary Table 6** Comparison of details of $\Delta G_1$, $\Delta G_2$, $\Delta G_3$, $\Delta G_4$, and overpotential of water oxidation on the FeCoO$_x$/BiVO$_4$ and CoO$_x$/BiVO$_4$.

| Index             | $\Delta G_1$ | $\Delta G_2$ | $\Delta G_3$ | $\Delta G_4$ | $\eta$ |
|-------------------|--------------|--------------|--------------|--------------|--------|
| FeCoO$_x$/BiVO$_4$ Co site | 0.304 | 1.413 | 1.657 | 1.546 | 0.427 |
| FeCoO$_x$/BiVO$_4$ Fe site  | -0.071 | 1.445 | 2.079 | 1.467 | 0.849 |
| CoO$_x$/BiVO$_4$          | 1.083 | 1.074 | 1.789 | 0.974 | 0.559 |
Supplementary Methods

Materials and reagents

For the preparation of ZrO$_2$-modified TaON, MgTa$_2$O$_6$-$x$N$_y$/TaON composite and BiVO$_4$ samples, Ta$_2$O$_5$ (99.9%, High Purity Chemicals), ZrO(NO$_3$)$_2$·2H$_2$O (ZrO$_2$ 45.0%, Guangfu Chemical Reagent), MgSO$_4$ (99.5%, Alfa Aesar), Bi(NO$_3$)$_3$·5H$_2$O (99.0%, Sinopharm Chemical), NH$_4$VO$_3$ (99.0%, Sinopharm Chemical) and polyvinyl alcohol (PVA, Sigma-Aldrich, 99%) were used. Na$_3$RhCl$_6$·12H$_2$O (Rh 17.1%, Alfa Aesar), K$_2$CrO$_4$ (99.5% Kermal Chemical Reagent), K$_2$IrCl$_6$ (Ir: 39% Alfa Aesar) and CoSO$_4$·7H$_2$O (99.5%, Sinopharm Chemical) were employed as the precursors of cocatalysts. Methanol (99.5%, Sinopharm Chemical) and K$_4$[Fe(CN)$_6$]·3H$_2$O (99.5%, Sinopharm Chemical) were used as hole acceptors. K$_3$[Fe(CN)$_6$] (99.5%, Sinopharm Chemical) and NaIO$_3$ (99.8%, Guangfu Chemical Reagent) were used as electron scavengers. All chemicals were used as-purchased without further purification.

Preparation of Ir-CoO$_x$(Imp.)/BiVO$_4$

Typically, 0.2 g BiVO$_4$ sample was immersed in a calculated K$_2$IrCl$_6$ (0.8 wt%) and CoSO$_4$ (0.2 wt%) aqueous solution with ultrasonic agitation for ca. 5 min. After the solution was completely evaporated in a water bath at 353 K, the impregnated powder was collected and calcinated at 673 K for 1 h under air. Afterwards, it was reduced at 573 K for 1 h under a flow of 5% H$_2$/Ar (200 mL min$^{-1}$).

Characterizations of photocatalysts

X-ray diffraction (XRD) measurement was carried out on a Rigaku D/Max-2500/PC powder diffractometer (Cu K$_\alpha$ radiation) with an operating voltage of 40 kV and an operating current of 200 mA. The scan rate applied was 5° min$^{-1}$ with a step size of 0.02° in the experimental range. UV-Vis diffuse reflectance spectra (DRS) was recorded on a UV-Vis spectrophotometer (JASCO
V-550) equipped with an integrating sphere, and BaSO$_4$ powder was used as the reference for baseline correction. The morphologies and particle sizes were examined by field emission scanning electron microscopy (FESEM; S-5500, Hitachi) taken with a Quanta 200 FEG scanning electron microscope. High-resolution transmission electron microscopy (HRTEM), scanning transmission electron microscopy (STEM), electron energy loss spectroscopy (EELS) analysis and element mapping were performed on a JEOL JEM-ARM200F microscope operating at 200 kV with an electron energy filter (Gif Quantum ER) as well as the X-ray electron energy dispersive spectrometer (EDS, JEOL Co.,). The lock-in-based surface photovoltage (SPV) spectroscopic measurement system consisted of a 500 W xenon lamp (LSH-X500, Zolix), a grating monochromator (Omni-5007, Zolix), a lock-in amplifier (SR830-DSP, Stanford) with a light chopper (SR540, Stanford), a photovoltaic cell, and a computer. Monochromatic light was provided by passing light from a 500 W xenon lamp through the grating monochromator. A low chopping frequency of 23 Hz was used in the conventional testing. And the measurements were carried out in air atmosphere at room temperature.

**Photocatalytic reactions**

The photocatalytic reactions were carried out in a Pyrex top irradiation-type reaction vessel connected to a closed gas circulation system. Before reactions, the mixed solution containing catalysts was evacuated and then irradiated using a 300 W Xenon lamp with a cut-off filter (Hoya, L-42; $\lambda \geq 420$ nm). A flow of cooling water was used to maintain the reaction system at 288 K. The gases evolved were analyzed by gas chromatography (Agilent; GC-7890A, MS-5A column, TCD, Ar carrier).

**X-ray absorption fine structure (XAFS) measurements**

The XAFS spectra of Fe K-edge were collected at BL14W1 beamline of Shanghai Synchrotron Radiation Facility (SSRF) while Co K-edge were collected at 1W1B beamline of Beijing
Synchrotron Radiation Facility (BSRF). The data were collected in fluorescence mode using a Lytle detector while the corresponding reference samples were collected in transmission mode. The samples were grinded and uniformly daubed on the special adhesive tape.

**XAFS analysis and results**

The acquired EXAFS data were processed according to the standard procedures using the ATHENA module of Demeter software packages.

The extended X-ray absorption fine structure (EXAFS) spectra were obtained by subtracting the post-edge background from the overall absorption and then normalizing it with respect to the edge-jump step. Subsequently, the \( \chi(k) \) data were Fourier transformed to real (R) space using a hanning windows (\( dk=1.0 \ \text{Å}\-1 \)) to separate the EXAFS contribution from different coordination shells. To obtain the quantitative structural parameters around central atoms, least-squares curve parameter fitting was performed using the ARTEMIS module of Demeter software packages.

The following EXAFS equation was used:

\[
\chi(k) = \sum_j \frac{N_j S_0^2 F_j(k)}{kR_j^2} \cdot \exp[-2k^2\sigma_j^2] \cdot \exp[-\frac{2R_j}{\lambda(k)}] \cdot \sin[2kR_j + \phi_j(k)]
\]

the theoretical scattering amplitudes, phase shifts and the photoelectron mean free path for all paths calculated. \( S_0^2 \) is the amplitude reduction factor, \( F_j(k) \) is the effective curved-wave backscattering amplitude, \( N_j \) is the number of neighbors in the \( j^{\text{th}} \) atomic shell, \( R_j \) is the distance between the X-ray absorbing central atom and the atoms in the \( j^{\text{th}} \) atomic shell (backscatterer), \( \lambda \) is the mean free path in \( \text{Å} \), \( \phi_j(k) \) is the phase shift (including the phase shift for each shell and the total central atom phase shift), \( \sigma_j \) is the Debye-Waller parameter of the \( j^{\text{th}} \) atomic shell (variation of distances around the average \( R_j \)). The functions \( F_j(k), \lambda \) and \( \phi_j(k) \) were calculated with the ab initio code FEFF9. The additional details for EXAFS simulations are given below.

All fits were performed in the \( R \) space with \( k \)-weight of 2 while phase correction was also
applied in the first coordination shell to make R value close to the physical interatomic distance between the absorber and shell scatterer. The coordination numbers of model samples were fixed as the nominal values. The obtained $S_0^2$ was fixed in the subsequent fitting. While the internal atomic distances R, Debye-Waller factor $\sigma^2$, and the edge-energy shift $\Delta$ were allowed to run freely.

**Computational details**

The density-functional theory (DFT)$^{1,2}$ calculations with the Hubbard U (DFT+U) corrections were performed with the Vienna Ab-initio Simulation Package (VASP)$^3$ codes 5.4. The PAW$^{4,5}$ pseudo-potentials, as well as the Perdew-Burke-Ernzerhof$^6$ exchange-correlation functional, and a plane wave cutoff of 500 eV have been used in the calculations. For a better description of the 3d electrons, the hybrid HF-DFT PBE0 functional is employed in our calculations$^7$. All periodic slab calculations were carried out using a vacuum spacing of at least 12 Ang. All surface structural models had a minimum 7 Ang thickness with 2 Ang thickness are fixed. 2x2x1 Monkhorst-Pack k-point mesh is sampled in the calculations. Spin-polarized calculations were identified for all surfaces, and the convergence of energy and force was set to $10^{-5}$ eV and 0.03 eV/angstrom. The DFT-D3 method$^{8,9}$ was adopted to consider van der Waals correction.

**Theoretical Evaluation of Activity**

The theoretical overpotentials for FeCoO$_x$/BiVO$_4$ and CoO$_x$/BiVO$_4$ interfaces were determined, assuming the conventional oxygen evolution reaction (OER) mechanism$^{10}$. The computational hydrogen electrode model$^{11}$ was used for the expression of the chemical potentials of protons and electrons at any given pH and applied potential as in previous OER works$^{12,13}$. The elementary steps by which the OER occurs are believed to involve adsorbed OH, O and OOH species on the surface ($^*$) according to the following equations:

$$\text{OH}^* + e^- \rightarrow \text{OH}^* + e^- \quad (1)$$

$$\text{OH}^* + \text{OH}^- \rightarrow \text{O}^* + \text{H}_2\text{O} + e^- \quad (2)$$
\[ O^* + OH^- \rightarrow OOH^* + e^- \quad (3) \]

\[ OOH^* + OH^- \rightarrow *O_2 + H_2O + e^- \quad (4) \]

To model the thermochemistry of the OER, it is more convenient to work at acidic condition, where steps 1, 2, 3, and 4 are modified as:

\[ H_2O + * \rightarrow OH^* + H^+ + e^- \quad (5) \]

\[ OH^* + H_2O \rightarrow O^* + H_2O + H^+ + e^- \quad (6) \]

\[ O^* + H_2O \rightarrow OOH^* + H^+ + e^- \quad (7) \]

\[ OOH^* + H_2O \rightarrow *O_2 + H_2O + H^+ + e^- \quad (8) \]

Thus, the Gibbs free energy change for steps 5 to 8 can be expressed as:

\[ \Delta G_1 = \Delta G_{OH} - eU + \Delta G_{H^+}(pH) \quad (9) \]

\[ \Delta G_2 = \Delta G_{O} - \Delta G_{OH} - eU + \Delta G_{H^+}(pH) \quad (10) \]

\[ \Delta G_3 = \Delta G_{OOH} - \Delta G_{O} - eU + \Delta G_{H^+}(pH) \quad (11) \]

\[ \Delta G_4 = 4.92 eV - \Delta G_{OOH} - eU + \Delta G_{H^+}(pH) \quad (12) \]

Here, -eU accounts for the applied external bias U; \( \Delta G_{H^+}(pH) = -kBT\ln(10)\times pH \) is the free energy change due to a nonzero pH value; The sum of \( \Delta G_{1\text{to}4} \) is fixed to the negative of experimental Gibbs free energy of formation of two H_2O molecules 4.92 eV in order to avoid the calculation of the O_2 bond energy, which is difficult to accurately determine within DFT calculations. The Gibbs free energy differences of these intermediates include zero-point energy (ZPE) and entropy corrections. Specifically, the entropic contributions from H_2 and H_2O molecules are taken from the experimental results and the contributions from absorbed species on the surface are all listed in Supplementary Table 5. The theoretical overpotential is then be defined as: \( \eta = \max(\Delta G_1, \Delta G_2, \Delta G_3, \Delta G_4)/e - 1.23 eV \) (13). The comparison of details of \( \Delta G_1, \Delta G_2, \Delta G_3, \Delta G_4, \) and overpotential of FeCoO\( _x \)/BiVO\(_4\) and CoO\(_x\)/BiVO\(_4\) are listed in Supplementary Table 6.
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