Supplementary Information

Unravelling the charge transfer and kinetics of $BiVO_4$ by Co dopant and $NiFeO_x$ co-catalyst for efficient photoelectrochemical water splitting

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Experimental section

1.1. Materials

Fluorine-doped tin oxide (FTO) glass with the model OPV-FTO022-15, imported from Pilkington (NSG Group) in the United States. That possessed a light transmittance of 84 %, a sheet resistance of 13-14 ohms per square, and a thickness of 2.2 mm. Bismuth nitrate pentahydrate [Bi(NO₃)₃ 5H₂O, 99.0 %], p-benzoquinone (C₆H₄O₂, 99.0 %), and vanadyl acetylacetonate (C₁₀H₁₄O₅V, 98 %) were purchased from Shanghai Aladdin Biochemical Technology Co., Ltd. Potassium iodide (KI, 99.0 %) was supplied by Xilong Scientific Co., Ltd. Cobalt (II) acetylacetonate (C₁₀H₁₄O₄Co, 97 %) was provided by Shanghai Macklin Biochemical Co., Ltd. Iron (II) sulfate heptahydrate (FeSO₄ 7H₂O, 99.0 %), nickel (II) sulfate hexahydrate (NiSO₄ 6H₂O, 98.5 %), boric acid (H₃BO₃, 99.5 %), sodium tetraborate decahydrate (Na₂B₄O₇ ·10H₂O, 99.5 %), sodium sulfite (Na₂SO₃, 97 %), dimethyl sulfoxide (C₂H₆OS, 99.5 %), ethanol (C₂H₆O, 99.7 %), and acetone (C₃H₆O, 99.5 %) were obtained from Sinopharm Chemical Reagent Co., Ltd. In the experimental process, all chemical reagents were used directly without further purification.

1.2. Synthesis of Co-BiVO₄/NiFeO_x photoanode

1.2.1. Synthesis of BiVO₄ photoanode

The preparation of BiVO₄ photoanode was based on the methods previously reported by others.¹ For solution A, 0.97 g Bi(NO₃) $5H_2O$ and 3.32 g KI were dissolved in 50 mL deionized water with vigorously stirring for 20 min, and then adjusting the pH to approximately 1.70 by dropwise addition of HNO₃. The configuration of Solution B was obtained by dissolving 0.497 g of p-benzoquinone in 20 mL anhydrous ethanol after that intensely stirring for 30 min. The preparation of the Bi precursor solution was acquired by

slowly adding solution B to solution A, and continuing to stir vigorously for 30 min. The V precursor solution was prepared by dissolving 0.265 g Vanadyl acetylacetonate in 5 mL dimethyl sulfoxide. In a typical three-electrode system, FTO is used as the working electrode, Ag/AgCl electrode is the reference electrode, and Pt electrode is the counter electrode. The BiOI was electrodeposited under i-t with a constant voltage of -0.1 $V_{Ag/AgCl}$. The optimal time for deposition was selected for 150 s. The fabricated samples was rinsed with deionized water and then placed in a ventilated drying oven at 60 °C to dry overnight. Subsequently, 70 µL of the V precursor solution was slowly dropped onto the BiOI film. Afterwards, it was annealed at 400 °C for 2 h with a heating rate of 2 °C min⁻¹ to obtain the BiVO₄ photoanode. The samples were immersed in 1 M KOH for 30 min to remove excess V₂O₅ on the surface of photoanode. Finally, the BiVO₄ photoanodes were rinsed with deionized water and then placed in a oven at 60 °C for drying.

1.2.2. Synthesis of Co-BiVO₄ photoanode

Firstly, the BiOI precursor films were prepared by the experimental method described in 1.2.1. Secondly, 0.265 g of $C_{10}H_{14}O_5V$ and 0.002 g (1.5 mM) of $C_{10}H_{14}O_4Co$ were dissolved in 5 mL of dimethyl sulfoxide to prepare the precursor solution for V and Co, which was stirred for 30 min. Then, 70 µL of the V and Co precursor solution was slowly dropped onto the BiOI film, and it was subsequently placed in a tubular furnace at 400 °C for annealing with 2 h, with a heating rate of 2 °C min⁻¹, to obtain the Co-BiVO₄ photoanode. The BiVO₄ photoanode was soaked in a 1 M KOH for 10 min to remove excess V₂O₅ from the electrode surface. Finally, the Co-BiVO₄ photoanode was rinsed with deionized water and placed in a drying oven at 60 °C for drying.

1.2.3. Synthesis of Co-BiVO₄/NiFeO_x photoanode

Under AM 1.5 G illumination with a light intensity set at 100 mW cm⁻². The NiFeO_x catalysts were prepared using a photo-assisted electrodeposition method. Initially, 30.51 g of Na₂B₄O₇ 10H₂O and 4.95 g of H₃BO₃ were dissolved in deionized water and made up to volume with a 500 mL volumetric flask to prepare a 0.8 M NaBi buffer solution (pH \approx 9). Subsequently, 0.05 g of FeSO₄ 7H₂O and 0.025 g of NiSO₄ 6H₂O were dissolved in 40 mL of the NaBi buffer solution and stirred for 10 min. Then, in a typical three-electrode system, Co-BiVO₄ photoanode served as the working electrode with its front side exposed to light, Ag/AgCl electrode as the reference electrode, and Pt electrode as the counter electrode. The Co-BiVO₄/NiFeO_x photoanode was obtained by photo-assisted electrodeposition which was carried out at an external bias of 0.6 V_{Ag/AgCl} for 600 s. Finally, Co-BiVO₄/NiFeO_x photoanode was rinsed with deionized water and placed in a oven at 60 °C for drying.

1.3. Characterization

The phase and crystal structure of samples were analyzed using an X-ray diffractometer (XRD, Ultima IV, Japan). That operated at a test voltage of 40 kV, a test current of 40 mA, and a Cu Kα radiation source. The scanning angle range was from 10 ° to 80 °. The surface and cross-sectional morphology and size of samples were characterized using a scanning electron microscope (SEM, ZEISS GeminiSEM 300, Germany). The morphology, size, and lattice fringes of samples were further characterized using a transmission electron microscope (TEM, JEOL JEM F200, Japan). The sample powder was dispersed in ethanol and sonicated for 5 min before being placed on a copper mesh for testing. The surface chemical state, elemental valence, and composition of samples were characterized using an X-ray photoelectron spectrometer (XPS, Thermo Scientific K-Alpha+, the United States). All spectral peaks were charge-calibrated using the C-C peak binding energy (284.8 eV) obtained

after deconvolution of C 1s orbital peak. The emission spectra of samples were tested using a fluorescence spectrometer (FS5, Edinburgh Instruments in the UK). That operated at the excitation wavelength set at 390 nm and the test wavelength range from 410 to 810 nm. The optical properties of samples were analyzed using a UV-Vis-NIR spectrophotometer (LAMBDA750S, the United States) with the wavelength scanning range from 200 to 800 nm in an integrating sphere mode.

1.4. Photoelectrochemical (PEC) measurements

All PEC performance tests were conducted on the same electrochemical workstation (CHI750E, Shanghai). In a typical three-electrode system, Pt electrode served as the counter electrode, Ag/AgCl electrode as the reference electrode, and the prepared BiVO₄-based photoanode as the working electrode. The illumination source used for the tests was a xenon lamp (PLS-FX300C, Beijing Perfectlight) equipped with an AM 1.5 G filter, set to a light intensity of 100 mW cm⁻². All tests were carried out in 0.8 M NaBi buffer solution (pH \approx 9).

Relevant calculation equations.

Determine the linear sweep voltammetry (LSV) characteristics by performing tests in a three-electrode system with a scanning potential range of -0.8 to 0.8 V (versus Ag/AgCl) and a scan rate of 10 mV s⁻¹. Convert the applied potentials (versus Ag/AgCl) to potentials versus the reversible hydrogen electrode (versus RHE) using the Nernst **Eq. S1**.

$$E_{RHE} = E_{Ag/AgCl} + 0.059 \times pH + E_{Ag/AgCl}^0 \tag{S1}$$

Where, E_{RHE} is the potentials versus the reversible hydrogen electrode, $E_{Ag/AgCl}$ represents the potential set by the Ag/AgCl reference electrode, pH is the pH value of the buffer solution, the value of $E_{Ag/AgCl}^{0}$ is 0.1976 at a temperature of 25 °C.

Calculate the applied bias photon-to-current efficiency (ABPE) based on a 100 % faradaic efficiency according to the **Eq. S2**.

ABPE(%) =
$$\frac{J_{H_2O} \times (1.23 - V_{app})}{P_{light}} \times 100\%$$
 (S2)

Where, J_{H_2O} is the photocurrent density for water oxidation, V_{app} represents applied external bias, P_{light} is the intensity of illumination (100 mW cm⁻²).

Using 0.5 M Na₂SO₃ as a hole sacrificial agent, the charge separation efficiency η_{sep} and charge transfer efficiency $\eta_{transfer}$ are calculated using Eq. S3-4.

$$\eta_{sep} = \frac{J_{Na_2SO_3}}{J_{abs}} \times 100\% \tag{S3}$$

$$\eta_{transfer} = \frac{J_{\rm H_2O}}{J_{Na_2SO_3}} \times 100\%$$
(S4)

Where, J_{H_2O} and $J_{Na_2SO_3}$ represent the photocurrent densities for water oxidation and sulfite oxidation, respectively. J_{abs} is the theoretical photocurrent density where all absorbed photons are fully converted into electric current. This can be obtained by estimating the overlap between the sample of ultraviolet-visible absorption spectrum and the solar spectrum, with a value of 7.5 mA cm⁻².

Under dark conditions, the range of applied bias is -0.8 to 0.8 V (versus Ag/AgCl), with a test frequency set at 1000 Hz. The carrier density (N_d) is calculated using the Mott-Schottky **Eq. S5-6**.

$$\frac{1}{C^2} = \left(\frac{2}{q\epsilon\epsilon_0 A^2 N_d}\right) \left[V - V_{FB} - \frac{kT}{q} \right]$$
(S5)

$$N_d = \frac{2}{q\varepsilon\varepsilon_0} \times \left(\frac{d(1/C^2)}{dV}\right)^{-1} \tag{S6}$$

Where, C represents the capacitance of the space charge layer (F), q is the elementary charge $(1.602 \times 10^{-19} \text{ C})$, ε is the dielectric constant of the semiconductor (BiVO₄ is 68), ε_0 is the vacuum permittivity of the semiconductor (8.854 × 10⁻¹⁴ F cm⁻¹), A is the surface area of the photoanode (cm²), N_d is the carrier density of the photoanode, V is the applied potential, V_{FB} is the flat-band potential of the photoanode, k is the Boltzmann constant (1.38 × 10⁻²³ J K⁻¹), T

is the temperature in Kelvin (298 K), and $d(1/C^2)/dV$ is the slope of the Mott-Schottky (M-S) plot.

The ECSA of the photoanodes was qualitatively analyzed based on the following Eq. S7.

$$ECSA = \frac{C_{dl}}{C_s}$$
(S7)

Where, C_{dl} is the electrochemical double-layer capacitance of the photoanode, and C_s represents the specific capacitance corresponding to a smooth surface sample.

The light harvesting efficiency (LHE) of the photoanode is calculated using **Eq. S8**, which takes into account the light absorption rate obtained from the ultraviolet-visible absorption spectrum.

$$LHE = 1 - 10^{-A(\lambda)} \tag{S8}$$

Where, $A(\lambda)$ is the light absorption rate of the sample at a wavelength of λ .



Scheme S1. Schematic illustration of preparation of Co-BiVO₄/NiFeO_x photoanodes.



Fig. S1. SEM images of (a-b) $BiVO_4$, (c-d) Co- $BiVO_4$ and (e-f) Co- $BiVO_4$ /NiFeO_x photoanodes at different magnification rates (500 nm and 100 nm).



Fig. S2. SEM image of the cross-section of Co-BiVO₄/NiFeO_x photoanode.



Fig. S3. (a-h) SEM-EDS elemental mappings of the cross-section of Co-BiVO₄/NiFeO_x photoanode.



Fig. S4. SEM-EDS spectra of Co-BiVO₄/NiFeO_x photoanode.



Fig. S5. TEM images of (a-b) Co-BiVO₄ and (c-d) Co-BiVO₄/NiFeO_x photoanodes.



Fig. S6. (a) The XRD patterns, (b-d) the fitting data plats of (110) and (011) crystal facets of $BiVO_4$, Co- $BiVO_4$ and Co- $BiVO_4$ /NiFeO_x photoanodes.

 Table S1. Summary of geometric parameters obtained from gaussian fitting and subsequent calculations of

 XRD data of BiVO₄, Co-BiVO₄, and Co-BiVO₄/NiFeO_x photoanodes.

Samples	Crystal plane	2θ(°)	β(°)	D(nm)	$\delta(10^{-3} \text{ nm}^{-2})$	ε(10 ⁻³)	d _{hkl} (nm)
BiVO ₄	(121)	28.83	0.269	30.14	1.10	4.57	0.3093
Co-BiVO ₄	(121)	28.84	0.279	29.06	1.18	4.73	0.3092
$Co-BiVO_4/NiFeO_x$	(121)	28.84	0.288	28.15	1.26	4.89	0.3092
BiVO ₄	(110)	18.63	0.225	111.11	0.08	1.91	0.4757
Co-BiVO ₄	(110)	18.66	0.249	100.41	0.10	2.10	0.4749
$Co-BiVO_4/NiFeO_x$	(110)	18.67	0.253	98.82	0.10	2.14	0.4747
$BiVO_4$	(011)	18.85	0.214	116.86	0.07	1.79	0.4702
Co-BiVO ₄	(011)	18.90	0.225	111.16	0.08	1.88	0.4689
Co-BiVO ₄ /NiFeO _x	(011)	18.88	0.227	110.17	0.08	1.90	0.4694

The grain size (D) which was perpendicular to the crystal plane corresponding to the

diffraction peak was calculated using the Debye-Scherrer formula.²

$$D = \frac{K\lambda}{\beta\cos\theta}$$
(S9)

Where, λ represents the wavelength of the X-ray (0.154 nm), β is the full width at half maximum (FWHM) in radians, K is the Scherrer constant (When β is the integrated height width, the value is 1; When β is the half-peak height width, the value is 0.89.), and θ is the bragg diffraction angle (taken as half the angle corresponding to the diffraction peak).

The calculation formula for dislocation density (δ , nm⁻²) is as follows:

$$\delta = \frac{1}{D^2} \tag{S10}$$

The calculation formula for microstrain (ϵ) is as follows:

$$\varepsilon = \frac{\beta}{4\tan\theta} \tag{S11}$$

The calculation formula for interplanar spacing d_{hkl} :

$$2d_{hkl}\sin\theta = n\lambda$$
 (S12)

Where, d_{hkl} represents the interplanar spacing of the (hkl), n is the order of diffraction, θ is half of the bragg diffraction angle corresponding to the (hkl), and λ is the wavelength of the X-ray.³⁻⁵



Fig. S7. XPS spectra of BiVO₄, Co-BiVO₄ and Co-BiVO₄/NiFeO_x photoanodes.

Table S2. Summary of XPS fitting parameters for the strongest photoelectron binding energy (BE/eV) of BiVO₄, Co-BiVO₄, and Co-BiVO₄/NiFeO_x photoanodes.

			BiVO ₄	Co-BiVO ₄	Co-BiVO ₄ /NiFeO _x
			BE/eV	BE/eV	BE/eV
D; 1f	Bi 4f _{5/2}	1	164.2	164.3	164.1
DI 41	Bi 4f _{7/2}	/	158.9	159.0	158.8
V 2n	V 2p _{1/2}	/	523.9	524.0	523.9
v 2p	V 2p _{3/2}	7	516.5	516.6	516.5
O 1s /		O_L	529.6	529.6	529.7
	/	O_V	531.3	531.2	531.3
		O_A	532.2	532.4	532.6
		Co ³⁺		795.4	795.0
Co	$C_0 2n_{1/2}$	Co ²⁺		797.3	796.8
	CO 2 P1/2	Sat.		801.9	802.1
Co 2p		Sat.	/	805.8	806.2
F		Co ³⁺		780.1	780.0
	Co 2p _{3/2}	Co ²⁺		781.7	781.6
		Sat.		785.7	784.5
		Sat.		788.8	789.5
		Fe ³⁺			725.7
	Fe 2n	Fe ²⁺			723.4
	$1 c 2 p_{1/2}$	Sat.			733.2
		Sat.			728.7
Fe 2p		Fe ³⁺	/	/	712.1
		Fe ²⁺			710.6
	Fe 2p _{3/2}	Sat.			719.0
		Sat.			715.3
		Ni ³⁺			874.5
	Ni 2p _{1/2}	Ni ²⁺			872.9
		Sat.			879.7
Ni 2p		Ni ³⁺	/	/	856.6
	Ni 2p _{3/2}	Ni ²⁺			855.6
	r 5/2	Sat.			861.5



Fig. S8. The pie chart of lattice oxygen (O_L), oxygen vacancy (O_V) and adsorbed oxygen (O_A) of (a) BiVO₄,
(b) Co-BiVO₄ and (c) Co-BiVO₄/NiFeO_x photoanodes.



Fig. S9. C1s spectra of BiVO₄, Co-BiVO₄ and Co-BiVO₄/NiFeO_x photoanodes.



Fig. S10. Photoelectrochemical water oxidation. (a) J-V curves, (b) chopping J-t curves, (c) Mott-Schottky plots, and (d) EIS curves of bare BiVO₄ with various deposition times (120, 150, 180, 210 and 240 s). All measurements were conducted in 0.8 M NaBi buffer (pH \approx 9).

Photoanodes	J[mA cm ⁻²] at 1.23 V _{RHE}	$N_d[10^{21}cm^{-3}]$	$R_s[\Omega cm^2]$	$R_{sc}[\Omega \ cm^2]$	$R_{ct}[\Omega cm^2]$
BiVO ₄ -120 s	2.03	2.53	13.80	64.49	213.90
BiVO ₄ -150 s	2.22	2.03	13.97	67.92	181.00
BiVO ₄ -180 s	2.01	1.40	13.14	67.82	267.60
BiVO ₄ -210 s	1.83	1.38	17.07	64.63	375.60
BiVO ₄ -240 s	1.72	1.71	16.49	65.13	467.90

Table S3. Photocurrent density at 1.23 V_{RHE} (Fig. S10a), N_d (Fig. S10c), and fitting results of the EIS curves (Fig. S10d) of bare BiVO₄ with various deposition times (120, 150, 180, 210 and 240 s).

In a typical three-electrode system, FTO (F-doped tin oxide) is used as the working electrode, Ag/AgCl electrode is the reference electrode, and Pt electrode is the counter electrode. The BiOI was electrodeposited under i-t with a constant voltage of -0.1 $V_{Ag/AgCl}$. The thickness of the BiOI precursor film was determined by controlling the deposition time.

After the addition of equal and appropriate vanadium source, temperature was increased to 400 °C at a rate of 2 °C/min for 2 h of calcination. As shown in Fig. S10a, the photocurrent density of the bare BiVO₄ initially increases and then decreases as the deposition time increases. The maximum photocurrent density was 2.22 mA/cm² at 1.23 V_{RHE} when the deposition time was 150 s. BiVO₄-150 s possesses the highest transient photoelectric response in Fig. S10b. It could be seen from Fig. S10c that all of the curves have positive slope indicating that the photoanodes fabricated were n-type semiconductors. The N_d of the bare BiVO₄ photoanodes at each deposition time was calculated by the slope of the Mott-schottky curve using the Eq. S5-6, BiVO₄-150 s possess relatively high carrier concentration (Table S3). Electrochemical impedance spectroscopy (EIS) at 1.23 V_{RHE} shown in Fig. S10d, the curve in the high frequency area (> 10^3 Hz) and low frequency area (< 10^3 Hz) consists of a semicircular arc, respectively. This manifest that the photoanode fabricated existed two capacitances. R_s represent the series resistance of the circuit, R_{sc} denote the charge transfer resistance in the $BiVO_4$, R_{ct} serves as charge transfer resistance at the photoanode/electrolyte interface, the CPEsc and CPEct refer to space charge capacitance and trap-state capacitance, respectively.^{6, 7} Fitting results of the EIS curves on BiVO₄ with various deposition times according to the equivalent circuit diagram from Fig. S10d, their values are tabulated in Table S3. It could be noted that the R_{ct} of BiVO₄-150 s endowed with the minimum value (181.00 Ω cm^2). These results suggest that the optimal deposition time of the BiOI was 150 s.



Fig. S11. Photoelectrochemical water oxidation. (a) J-V curves, (b) chopping J-t curves, (c) Mott-Schottky plots, and (d) EIS curves of bare BiVO₄ with different calcination temperatures (350, 375, 400, 425 and 450 °C). All measurements were conducted in 0.8 M NaBi buffer (pH \approx 9).

Photoanodes	J[mA cm ⁻²] at 1.23 V _{RHE}	$N_d[10^{21}cm^{-3}]$	$R_s[\Omega cm^2]$	$R_{sc}[\Omega \ cm^2]$	$R_{ct}[\Omega \ cm^2]$
BiVO ₄ -350 °C	0.95	1.48	22.95	46.29	1329.00
BiVO ₄ -375 °C	1.33	1.29	17.73	53.54	698.40
BiVO ₄ -400 °C	2.22	2.03	13.97	67.92	181.00
BiVO ₄ -425 °C	1.29	0.97	19.61	59.81	454.30
BiVO ₄ -450 °C	0.77	0.83	19.34	58.61	991.70

Table S4. Photocurrent density at 1.23 V_{RHE} (Fig. S11a), N_d (Fig. S11c), and fitting results of the EIS curves (Fig. S11d) of bare BiVO₄ with different calcination temperatures (350, 375, 400, 425 and 450 °C).

It could be seen from **Fig. S11a** that the photocurrent density of the bare BiVO₄ first increases and then decreases with the increase in calcination temperature. The maximum photocurrent density was 2.22 mA/cm² at 1.23 V_{RHE} when the calcination temperature was 400 °C. BiVO₄-400 °C endowed with the highest transient photoelectric response as

illustrated in **Fig. S11b**. As shown in **Fig. S11c**, BiVO₄-400 °C have the lowest slope of the Mott-schottky curve, indicating that possess the highest carrier concentration depicted in **Table S4**. The Nyquist plots were fitted with the equivalent circuit (**Fig. S11d**), it is apparent that BiVO₄-400 °C have the smallest R_{ct} value in **Table S4**. These results demonstrated that the optimal calcination temperature of the BiVO₄ was 400 °C.



Fig. S12. Photoelectrochemical water oxidation. (a) chopping J-V curves, (b) photocurrent density at 0.6 V_{RHE} and 1.23 V_{RHE} of all BiVO₄ samples with optimal preparation conditions. All measurements were conducted in 0.8 M NaBi buffer (pH \approx 9).



Fig. S13. Photoelectrochemical water oxidation. (a) J-V curves, (b) chopping J-t curves, (c) Mott-Schottky plots, and (d) EIS curves of BiVO₄ doped with different contents of Co (0.5, 1.0, 1.5 and 2.0 mM). All measurements were conducted in 0.8 M NaBi buffer (pH \approx 9).

Table S5. Photocurrent density at 1.23 V_{RHE} (Fig. S13a), N_d (Fig. S13c), and fitting results of the EIS curves (Fig. S13d) of BiVO₄ doped with different contents of Co (0.5, 1.0, 1.5 and 2.0 mM).

Photospodes	J[mA/cm ²]	N_{10}^{21} cm ⁻³	$\mathbf{R} \left[\mathbf{O} \mathrm{cm}^2 \right]$	$\mathbf{R} [\mathbf{O} \ \mathrm{cm}^2]$	$\mathbf{R} [\mathbf{O} \mathrm{cm}^2]$	
Thotoanoucs	at 1.23 V_{RHE}			R _{sc[22} cm]		
0.5 mM Co-BiVO ₄	3.32	1.41	15.35	49.67	183.3	
1.0 mM Co-BiVO ₄	4.05	1.84	15.85	42.60	153.3	
1.5 mM Co-BiVO ₄	4.56	1.97	16.50	41.96	85.79	
2.0 mM Co-BiVO ₄	2.95	1.46	16.07	42.06	130.9	

In this paper, the doping of Co elements is achieved by adding varying amounts of acetylacetonate Co to the V precursor solutio. As shown in **Fig. S13a**, the photocurrent density of the photoanode first increases and then decreases with the increase in Co content. The maximum photocurrent density was 4.56 mA/cm^2 at 1.23 V_{RHE} when the Co content was 1.5 mM. 1.5 mM Co-BiVO₄ possesses the highest transient photoelectric response in **Fig. S13b**. As shown in **Fig. S13c**, 1.5 mM Co-BiVO₄ have the lowest slope of the Mott-schottky curve,

indicating that possess the highest carrier concentration depicted in **Table S5**. The Nyquist plots were fitted with the equivalent circuit (**Fig. S13d**), it is apparent that 1.5 mM Co-BiVO₄ have the smallest R_{ct} value in **Table S5**. These results illustrated that the optimum Co content was 1.5 mM.



Fig. S14. Photoelectrochemical water oxidation. (a) chopping J-V curves, (b) photocurrent density at 0.6 V_{RHE} and 1.23 V_{RHE} of all Co-BiVO₄ samples with optimal doping conditions. All measurements were conducted in 0.8 M NaBi buffer (pH \approx 9).



Fig. S15. Photoelectrochemical water oxidation. (a) J-V curves of Co-BiVO₄ with various deposition times of NiFeO_x (300, 600, 900 and 1200 s). All measurements were conducted in 0.8 M NaBi buffer (pH \approx 9).



Fig. S16. A comparison bar chart of the progress in PEC performance of $BiVO_4$ -based photoanodes over the past five years.

Photoanode	Electrolyte	$\begin{array}{c} J(mA~cm^{-2}) @ 1.23~V_{RHE} \\ \\ before modification \\ (bare BiVO_4) \end{array}$	J(mA cm ⁻²)@1.23 V _{RHE} after modification	Reference
				Applied Catalysis B:
NiCo-LDH/BiVO ₄	0.5 M Na ₂ SO ₄	1.1	3.4	Environmental 263
				(2020) 118280 ⁸
				Applied Catalysis B:
CoNi-MOFs/BiVO ₄	0.5 M Na ₂ SO ₄	1.2	3.2	Environmental 266
				(2020) 118513 ⁹
	05 MV DO			NATURE
BiVO ₄ /N:NiFeO _x	$0.5 \text{ M } \text{K}_3 \text{B} \text{O}_3$	2.1	6.4	COMMUNICATIONS
	(pH = 9.5)			(2021) 12:6969 ¹⁰
NiOOH/	0.5 M KPi	1.2	6.24	Adv. Mater. 2021, 33,
FeOOH/Co ₃ O ₄ /BiVO ₄	(pH =7)	1.2	6.34	200440611
	0.5 M K ₃ BO ₃	1 (1	6 72	Energy Environ. Sci.,
$FeNiPO_x/BiVO_4$	(pH = 9.5)	1.61	6./3	2022, 15, 2867–2873 ¹²
				Chemical Engineering
NiFe-MOFs/BiVO ₄	(pH = 9.5)	1.46	4.61	Journal 433 (2022)
				133592 ¹³
			6.40	Applied Catalysis B:
NiFeO _x /BVO/BiVO ₄	0.5 M borate buffer (pH = 9.5)	1.37		Environmental 334
				(2023) 122865 ¹⁴
N'OON/G O D'NO	1 M KBi		<i>.</i> .	ACS Catal. 2023, 13,
$N_1OOH/Co_3O_4/B_1VO_4$	(pH = 9.5)	1.45	6.4	5938-5948 ¹⁵
	0.5 M K ₃ BO ₃		- 10	J. Mater. Chem. A, 2023,
N-B1VO ₄ /N1FeO _x	(pH = 9.3)	1.31	5.40	11, 1756–1765 ¹⁶
				Journal of Colloid And
BiVO ₄ /CuSCN/NiFeO _x	0.5 M KBi	0.95	5.6	Interface Science 666
	(pH = 9.3)			(2024) 57–65 ¹⁷
				Applied Catalysis B:
NiFeO _x /CoMoP/BiVO ₄	0.5 M KBi	1.3	5.82	Environment and Energy
	(pH = 9.5)			358 (2024) 124375 ¹⁸
NiFeCoO _x /	1 M K–Bi buffer			Energy Environ. Sci.,
CPF-TCB/Mo:BiVO ₄	(pH = 9.5)	3.30 (Mo:BiVO ₄)	6.66	2024, 17, 2541–2553 ⁶
				Chemical Engineering
BiVO ₄ /Co ₃ O ₄	$0.5 \text{ M} \text{ Na}_2 \text{SO}_4$	1.13	4.66	Journal 483 (2024)
				149104 ¹⁹
Co-BiVO ₄ /NiFeO _x	0.8 M NaBi (pH = 9)	2.22	6.42	This work

Table S6. Summary of progress in $BiVO_4$ -based photoanodes over the past five years.



Fig. S17. The onset potential diagram of BiVO₄, Co-BiVO₄ and Co-BiVO₄/NiFeO_x photoanodes.



Fig. S18. The chopping J-V curves of of $BiVO_4$, Co- $BiVO_4$ and Co- $BiVO_4$ /NiFeO_x in the low bias range of 0.4-0.6 V_{RHE}.



Fig. S19. LSV curves of (a) BiVO₄, (b) Co-BiVO₄ and (c) Co-BiVO₄/NiFeO_x photoanodes under conditions with and without sacrificial agents. The bar charts of charge separation efficiency (η_{sep}) and charge transfer efficiency ($\eta_{transfer}$) for the BiVO₄, Co-BiVO₄ and Co-BiVO₄/NiFeO_x photoanodes at 1.23 V_{RHE}.



Fig. S20. The FF diagram of the BiVO₄, Co-BiVO₄ and Co-BiVO₄/NiFeO_x photoanodes.

The calculation formula for the fill factor is as follows:

To assess the performance of the photoanode, the fill factor (FF) was calculated using the rectangular area of the maximum power point and the following formula⁶.

$$FF(\%) = \frac{J_{MP}(1.23 - V_{MP})}{J_{SC}(1.23 - V_{ON})} \times 100\%$$
(S13)

Where, J_{MP} and V_{MP} represent the photocurrent density and the applied bias (vs. RHE) at the maximum power point, respectively. J_{SC} is the photocurrent density of the photoanode at1.23 V_{RHE} , and V_{ON} is the initial potential at which the photocurrent begins to appear. Through calculations, the fill factor (FF) of the BiVO₄, Co-BiVO₄ and Co-BiVO₄/NiFeO_x photoanodes were 13.9 %, 21.6 % and 22.0 %, respectively.



Fig. S21. The long-term stability test of $BiVO_4$, Co- $BiVO_4$ and Co- $BiVO_4$ /NiFeO_x at 1.1 V_{RHE}.



Fig. S22. The statistical chart of the I_{st}/I_{in} ratio for the BiVO₄, Co-BiVO₄ and Co-BiVO₄/NiFeO_x photoanodes in chopped chronoamperometry tests at 1.23 V_{RHE}.



Fig. S23. The delay of the cathodic photocurrent curves under AM 1.5 G illumination at different potentials (0.4, 0.5, 0.6, 0.7, 0.8, 0.9, 1.0, 1.1 and 1.2 V_{RHE}) of (a) BiVO₄, (b) Co-BiVO₄ and (c) Co-BiVO₄/NiFeO_x.



Fig. S24. (a) OCP decay curves and (b) the values of $\triangle OCP$ for BiVO₄, Co-BiVO₄ and Co-BiVO₄/NiFeO_x.



Fig. S25. The fitting circuit diagram.

 R_s represent the series resistance of the circuit, R_{sc} denote the charge transfer resistance in the BiVO₄, R_{ct} serves as charge transfer resistance at the photoanode/electrolyte interface, the CPE_{sc} and CPE_{ct} refer to space charge capacitance and trap-state capacitance, respectively.^{6,7}

Potential	R _s	R _{sc}	R _{ct}	CPE _{sc} -T/	CPE _{sc} -P	CPE_{ct} -T/10 ⁻³	CPE _{ct} -P
(V _{RHE})	$(\Omega \text{ cm}^2)$	$(\Omega \text{ cm}^2)$	$(\Omega \text{ cm}^2)$	10 ⁻⁷			
0.4	14.69	64.53	4379	1.4737	0.91353	1.2487	0.61691
0.5	14.69	62.13	1345	1.2005	0.92619	1.598	0.5171
0.6	14.64	62.11	341.9	1.1697	0.92683	1.1028	0.54742
0.7	15.69	60.57	201.8	0.6774	0.97466	0.63766	0.64379
0.8	14.42	63.58	174.7	1.1186	0.93203	0.4459	0.7269
0.9	16.53	61.33	157.8	0.83507	0.95959	0.34714	0.73903
1.0	14.82	64.20	163.1	1.3962	0.91445	0.20747	0.77896
1.1	15.16	64.35	190.2	1.2873	0.92455	0.14783	0.80551
1.2	15.10	63.99	338.4	1.0073	0.94342	0.14691	0.78618

Table S7. The fitting results of the EIS curves of bare $BiVO_4$ with various potentials (0.4, 0.5, 0.6, 0.7, 0.8, 0.9, 1.0, 1.1 and 1.2 V_{RHE}).

Potential	R _s	R _{sc}	R _{ct}	CPE _{sc} -T/	CPE _{sc} -P	CPE_{ct} -T/10 ⁻³	CPE _{ct} -P
(V _{RHE})	$(\Omega \text{ cm}^2)$	$(\Omega \text{ cm}^2)$	$(\Omega \text{ cm}^2)$	10 ⁻⁷			
0.4	14.64	58.03	55	0.63297	0.9797	1.0115	0.57659
0.5	14.45	59.79	45.6	0.89073	0.95367	0.3237	0.73275
0.6	13.81	60.27	53.72	0.89636	0.95179	0.30026	0.73307
0.7	14.45	59.67	71.82	0.65287	0.98078	0.30917	0.72705
0.8	13.92	61.20	90.1	0.7925	0.96416	0.22862	0.78764
0.9	14.23	60.72	129.7	0.71631	0.97335	0.26893	0.79024
1.0	14.20	61.60	185.7	0.90847	0.95419	0.28508	0.80716
1.1	14.04	61.72	287.7	0.87562	0.95676	0.28442	0.75994
1.2	13.61	61.75	354.5	0.80373	0.96261	0.19045	0.76843

Table S8. The fitting results of the EIS curves of Co-BiVO₄ with various potentials (0.4, 0.5, 0.6, 0.7, 0.8, 0.9, 1.0, 1.1 and 1.2 V_{RHE}).

Potential	R _s	R _{sc}	R _{ct}	CPE _{sc} - T /10 ⁻⁷	CPE _{sc} -P	CPE_{ct} -T/10 ⁻³	CPE _{ct} -P
(V _{RHE})	$(\Omega \text{ cm}^2)$	$(\Omega \text{ cm}^2)$	$(\Omega \text{ cm}^2)$				
0.4	17.83	56.53	46.27	0.78556	0.96843	0.66934	0.6411
0.5	17.34	57.67	43.79	0.955292	0.952	0.39669	0.70714
0.6	17.49	57.63	48.92	0.99983	0.94885	0.30601	0.73149
0.7	17.4	57.62	66.65	0.6852	0.9905	0.31817	0.72253
0.8	17.45	57.7	86	0.1572	0.97759	0.28448	0.75098
0.9	17.08	58.61	113.5	0.87634	0.9603	0.29362	0.77316
1.0	16.91	58.67	146.7	0.87275	0.96018	0.36237	0.75953
1.1	16.75	58.93	228.7	0.89596	0.95773	0.39615	0.73178
1.2	17.35	58.69	255	0.93035	0.95607	0.31092	0.73493

Table S9. The fitting results of the EIS curves of Co-BiVO₄/NiFeO_x with various potentials (0.4, 0.5, 0.6,

0.7, 0.8, 0.9, 1.0, 1.1 and 1.2 $V_{\text{RHE}}).$



Fig. S26. Bode phase plots of the BiVO₄, Co-BiVO₄ and Co-BiVO₄/NiFeO_x photoanodes.



Fig. S27. Cyclic voltammetry characteristic curves of (a) $BiVO_4$, (b) Co- $BiVO_4$ and (c) Co- $BiVO_4$ /NiFeO_x photoanodes at various scan rates (10, 20, 40, 60, 80 and 100 mV/s).



Fig. S28. (a) UV visible absorption spectra, (b) Tauc plots, and (c) light harvesting efficiency (LHE) plots for $BiVO_4$, Co- $BiVO_4$ and Co- $BiVO_4$ /NiFeO_x.

Table S10. Theory calculations of formation energy of the occupancy of Co ions at the Bi and V sites in

 Co-BiVO₄.

	Edoped	E _{pure}	$\mu_{impurity}$	μ_{host}	E _{form}
Bi	-178.3396029	-177.646353	-2.13666595	-1.30974505	0.13367101
V	-169.2183867	-177.646353	-2.13666595	-3.54423579	7.02039646

	E_{total}/eV	E_{slab}/eV	Eadsorbent(OH)/eV	∆E/eV
Ni	-1175.895566	-1167.140897	-7.12853264	-1.62613624
Fe	-1177.9806	-1167.140897	-7.12853264	-3.71117024
Со	-1174.623147	-1167.140897	-7.12853264	-0.35371695

Table S11. Theory calculations of adsorption energies of OH⁻ on metal elements (Ni, Fe, and Co).



Fig. S29. The Ea plots of BiVO₄, Co-BiVO₄ and Co-BiVO₄/NiFeO_x.

Based on the relationship between photocurrent density and oxygen evolution activity, and in accordance with the law of energy conservation, we have qualitatively derived the activation energy for the OER on the $BiVO_4$ -based photoanodes.²⁰

$$E_{g} \ge E^{\theta} + E_{a} \tag{S14}$$

$$E_{g} + E_{v} \ge E^{\theta} + E_{AOP} \tag{S15}$$

Arrhenius equation:
$$k = A \times exp(-\frac{E_{AOP}}{RT})$$
 (S16)

where, E_g represents the band gap energy of the BiVO₄ photoanode, E^{θ} is the chemical potential for OER at 1.23 V_{RHE}, E_a is the activation energy, E_v is the electrochemical energy applied at the onset potential, E_{AOP} is the activation energy for the OER, and AOP is the activation overpotential.

Since the activation energy for hydrogen evolution in PEC water splitting was relatively low, the focus here was primarily on the activation energy for the OER. As shown in **Fig. S17**, the LSV of $BiVO_4$ -based photoanodes revealed onset potentials of 0.62, 0.38, and 0.35 V for BiVO₄, Co-BiVO₄, and Co-BiVO₄/NiFeO_x, respectively. The lowest E_v is observed for Co-BiVO₄/NiFeO_x. We could qualitatively deduce that Co doping and the NiFeO_x cocatalyst reduced the E_{AOP} of BiVO₄ by using **Eq. S15-16**, thereby significantly enhancing the overall OER kinetics of BiVO₄.

DFT calculations

The density functional theory (DFT) calculations were carried out with the VASP code.²¹ The Perdew–Burke–Ernzerhof (PBE) functional within generalized gradient approximation (GGA) was used to process the exchange–correlation,²² while the projectoraugmented-wave pseudopotential (PAW) was applied with a kinetic energy cut-off of 500 eV,²³ which was utilized to describe the expansion of the electronic eigenfunctions. The vacuum thickness was set to be 20 Å to minimize interlayer interactions. The Brillouin-zone integration was sampled by a Γ -centered 7 × 7× 1 Monkhorst–Pack k-point. All atomic positions were fully relaxed until energy and force reached a tolerance of 1 × 10⁻⁶ eV and 0.01 eV/Å, respectively. The dispersion corrected DFT-D method was employed to consider the long-range interactions.²⁴

The Gibbs free energy change (ΔG) was calculated by computational hydrogen electrode (CHE) model as follows:

$$\Delta G = \Delta E + \Delta Z P E - T \Delta S \quad (S21)$$

where ΔE is the reaction energy obtained by the total energy difference between the reactant and product molecules absorbed on the catalyst surface and ΔS is the change in entropy for each reaction, ΔZPE is the zero-point energy correction to the Gibbs free energy.

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