Electronic Supplementary Material (ESI) for Sustainable Energy & Fuels.

A highly enhanced photoelectrochemical performance of $BiVO_4$ photoanodes modified with CoPi groups by increasing energy band bending, accelerating hole separation and improving water oxidation kinetics

Wanqing Fang, [a] Ai Qin, [a] Yimin Lin, [a] Rongzi Xv, [a] and Li Fu [*a]

[a] Fujian Provincial Key Laboratory of Advanced Materials Oriented Chemical Engineering, Fujian Provincial Key Laboratory of Polymer Materials, Colloge of Chemistry and Material Science, Fujian Normal University, Cangshan Campus, No.8 Shangsan Road, Fuzhou, Fujian 350007, China.

***Corresponding author**

E-mail address: wodimeige@163.com

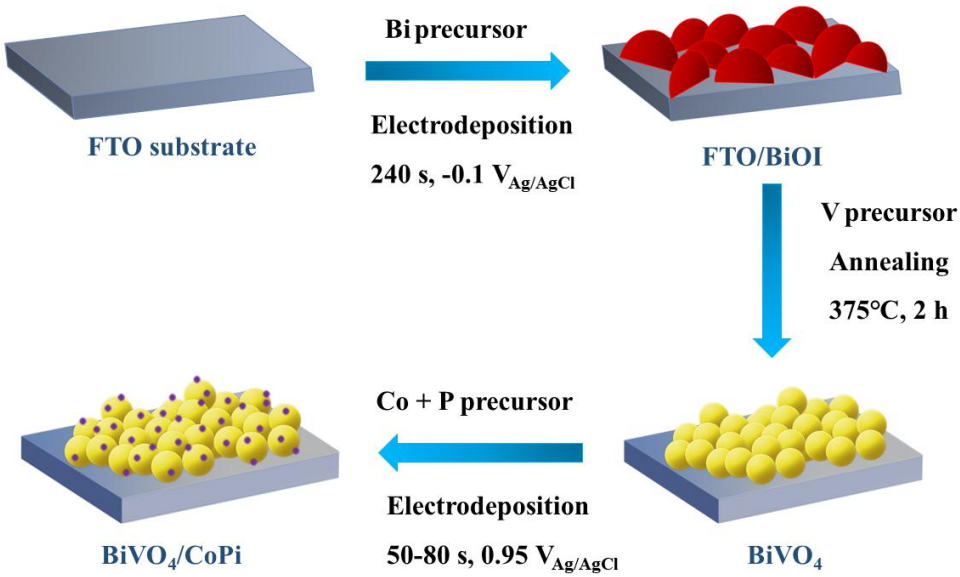

Figure S1 Synthetic process of bare $BiVO_4$ and $BiVO_4$/CoPi photoanodes.

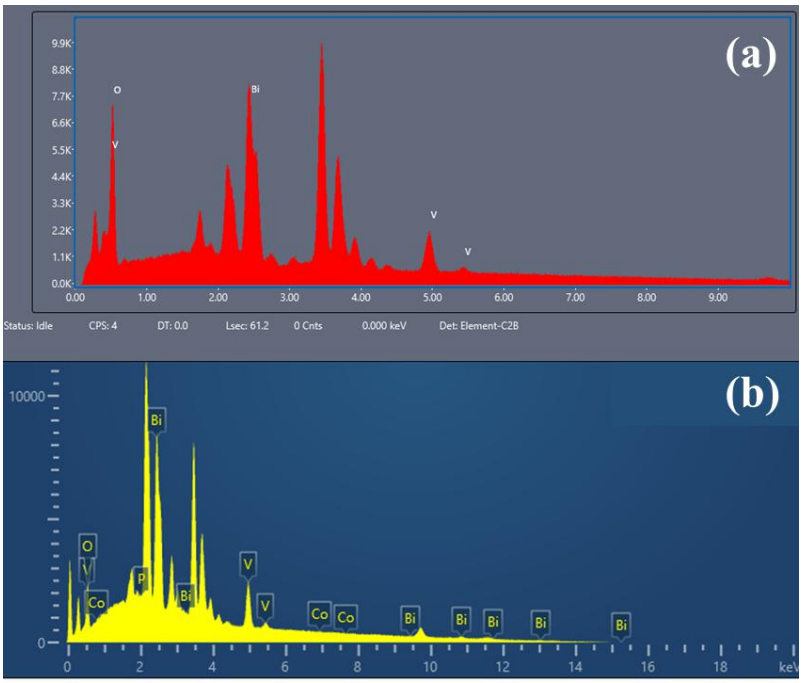

Figure S2 EDX scanning spectra of (a) $BiVO_4$ and (b) $BiVO_4$/CoPi.

Table S1 The content of the corresponding elements in $BiVO_4$ and $BiVO_4$/CoPi from the EDX scanning spectra.

Element	wt%		at%	
	$BiVO_4$	$BiVO_4$/CoPi	$BiVO_4$	$BiVO_4$/CoPi
Bi	62.86	71.92	16.82	23.94
V	19.44	14.98	21.33	20.46
O	17.70	12.67	61.85	55.10
Co	0	0.43	0	0.50

Table S2 The content of each element in $BiVO_4$ and $BiVO_4$/CoPi from the XPS spectra of overall survey.

Sample	$BiVO_4$	$BiVO_4$/CoPi
Name	**Atomic %**	**Atomic %**
Bi 4f	16.62	13.58
V 2p	25.13	23.23
O 1s	59.25	54.75
Co 2p	0	2.98
P 2p	0	5.45

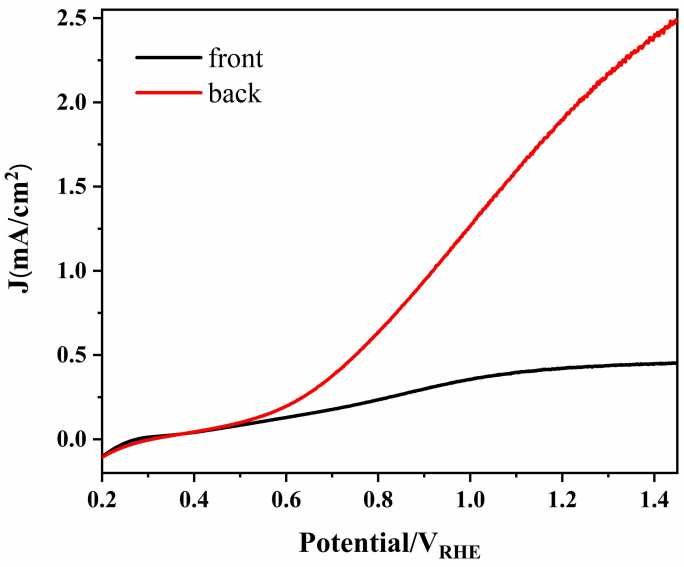

Figure S3 LSV curves of $BiVO_4$ photoanode front and back irradiation.

Table S3 Comparisons of photoelectrochemical performance of reported previously $BiVO_4$-based photoanode with our results.

Photoelectrode	**Fabrication process**	**Test condition**	**Bias**	**Photocurrent density(mA/cm²)**			**Ref.**
				bare	**Treated**	**Fold**	
$BiVO_4$/CoPi	electrodeposition process	2 M NaBi	1.23 V	1.81	5.87	3.24	This work
Co:$BiVO_4$	spin coating	0.5 M Na_2SO_4	1.23 V	0.22	0.46	2.09	[1]
$BiVO_4$/$Co(CO_3)_xOH_y$	hydrothermal process	1 M NaOH	1.23 V	2.20	5.00	2.27	[2]
WO_3/$BiVO_4$	sol – gel process	0.1 M KPi	1.23 V	0.53	2.50	4.72	[3]
Li:$BiVO_4$	pulsed laser deposition	0.1 M PBS (pH=7)	1.23 V	0.74	0.87	1.18	[4]
Au:$BiVO_4$	solution drop casting	0.1 M KOH	1.23 V	0.07	0.24	3.43	[5]
$BiVO_4$/Co(OH)F	solution drop casting	0.5 M KPi	1.23 V	1.45	3.40	2.40	[6]
SnO_2@$BiVO_4$/Co-	electrodeposition process	0.1 M PBS	1.23 V	0.40	2.63	6.58	[7]

Pi		(pH=7)					
Mo:$BiVO_4$	hydrothermal process	0.1 M Na_2SO_4	1.23 V	1.25	1.70	1.36	[8]
MCo_2O_4(M=Mn, Zn)/$BiVO_4$	spin coating	0.5 M KPi	1.23 V	0.80	2.80	3.5	[9]
Mo,W:$BiVO_4$/PC	solution drop casting	0.1 M Na_2SO_4	1.23 V	0.4	2.50	6.25	[10]
α -Fe_2O_3							
$BiVO_4$/CoSi	PEPD	0.5 M $K_2B_4O_7$ (pH=9.5)	1.23 V	1.7	5.0	2.9	[11]
F-$BiVO_4$@NiFe-LDH	electrodeposition process	0.1 M PBS (pH=7)	1.23 V	0.45	2.67	6.0	[12]
CoPi/PANI/ $BiVO_4$	PEPD	0.5 M KH_2PO_4	1.23 V	0.98	4.05	4.13	[13]
$BiVO_4$-N/C-CoPOM	dipping process	0.5 M PBS	1.23 V	0.61	3.30	5.4	[14]
CoFeOH/Cu_2S/ $BiVO_4$	SILAR	0.5 M PBS	1.23 V	2.03	3.07	1.51	[15]
$BiVO_4$/WO_3 NRs	hydrothermal process	0.5 M KPi	1.23 V	0.40	0.64	1.60	[16]
$BiVO_4$/WO_3/ITO	pulsed laser deposition	0.5 M Na_2SO_4	1.23 V	0.35	0.86	2.46	[17]
N-$BiVO_4$	solution drop casting	0.1 M KPi	1.23 V	1.6	3.3	2.1	[18]
CoP/$BiVO_4$	solution drop casting	KBi (pH=9)	1.23 V	2.0	4.1	2.05	[19]
R-$BiVO_4$	dipping process	0.2M KPi	1.23 V	2.24	3.18	2.21	[20]
Mo：$BiVO_4$/	spin coating	0.1 M PBS	1.23 V	0.03	1.1	36.7	[21]

CoOOH							
$BiVO_4$/Co-$LaFeO_3$	electrodeposition process	0.5 M KPi	1.23 V	0.85	3.40	4	[22]
CuTCPP/GO/ $BiVO_4$	dipping process	0.5 M PBS (pH=9)	1.23 V	1.25	5.0	4	[23]
FeOOH/Au/ $BiVO_4$	electrodeposition process	0.1 M Na_2SO_4	1.23 V	1.19	4.64	3.74	[24]
Co-Ci/Mo: $BiVO_4$	PEPD	0.5 M Na_2SO_4	1.23 V	0.82	3.95	4.8	[25]

Unless otherwise specified, all photoelectrochemical tests were carried out under simulated 1 sun (AM 1.5 G, 100mW $\cdot$ cm^{-2}) illumination and all biases were converted to RHE (V_{RHE}). The fabrication process represents the modification way of bare $BiVO_4$.

Involved abbreviations: PC, partically covered; PEPD, photoelectrophoretic deposition; PBS, phosphate butter saline; PANI, polyaniline; SILAR, successive ionic layer adsorption; NRs, nanorods; R-$BiVO_4$,the photoassisted self-reduction of the $BiVO_4$; Co-Ci, carbon-based cobalt.

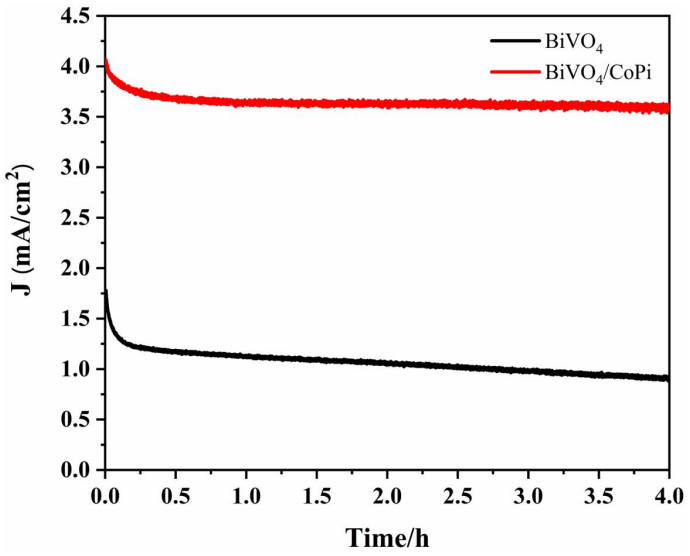

Figure S4 Stability test of 4 h for $BiVO_4$ and $BiVO_4$/CoPi films at 1.23 V_{RHE} under AM 1.5G (100 mW cm^{-2}) illumination in borate buffer.

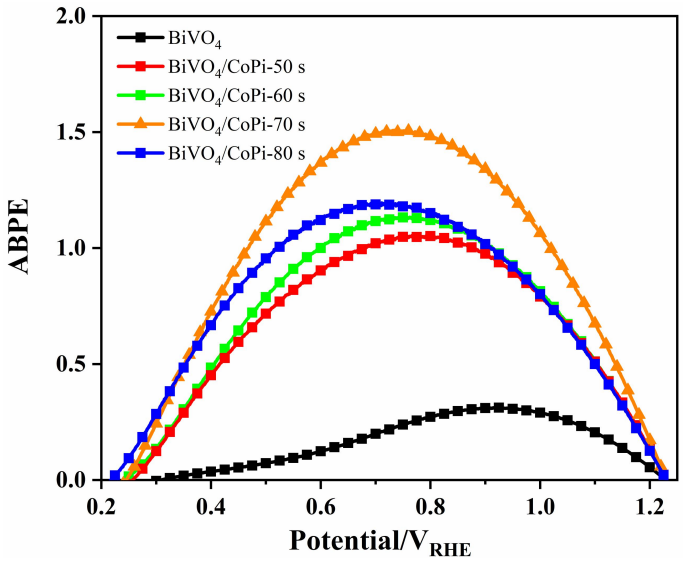

Figure S5 ABPE of $BiVO_4$ and various deposition times (50-80 s) of $BiVO_4$/CoPi films with a voltage in the range of 0.2~1.23 V_{RHE}.

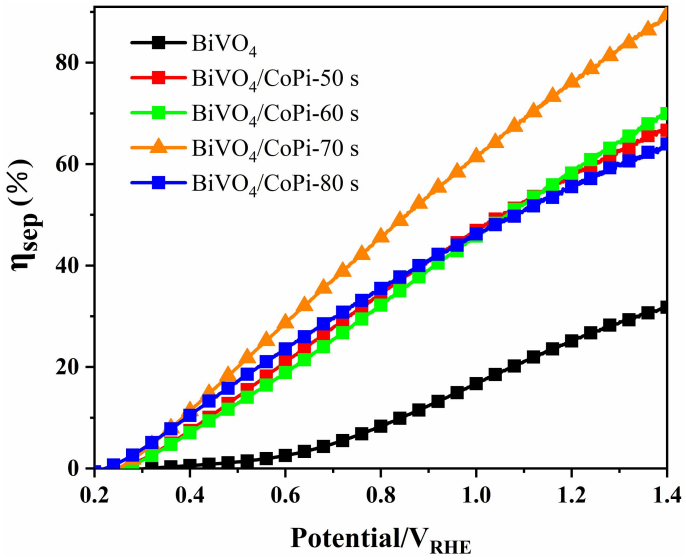

Figure S6 η_{sep} of $BiVO_4$ and various deposition times (50-80 s) of $BiVO_4$/CoPi films with a voltage in the range of 0.2~1.4 V_{RHE}.

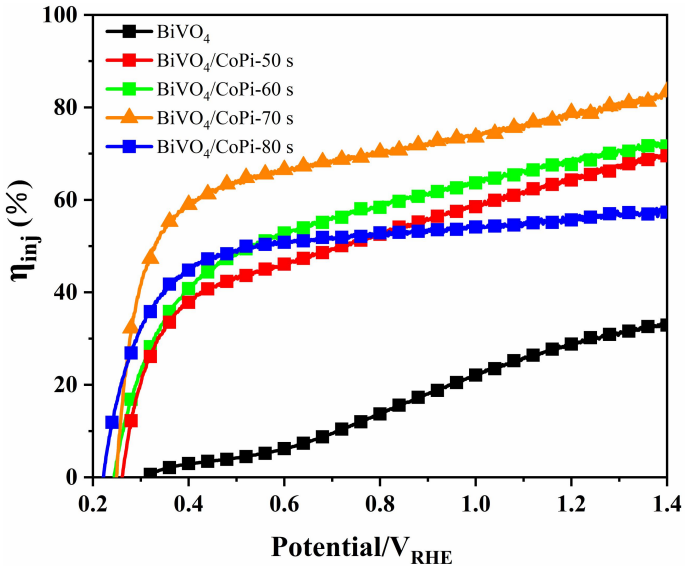

Figure S7 η_{inj} of $BiVO_4$ and various deposition times (50-80 s) of $BiVO_4$/CoPi films with a voltage in the range of 0.2~1.4 V_{RHE}.

Table S4 Values of the elements in equivalent circuit fitted in the Nyquist plots of Fig. 8a.

sample	Rs/Ω (error/%)	Rct/Ω (error/%)	CPE/F (error/%)
$BiVO_4$	58.65 (0.78)	194.6 (1.11)	7.49×10^{-5} (5.16)
$BiVO_4$/CoPi	51.44 (1.27)	122.0 (3.12)	16.32×10^{-5} (3.76)

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