Electronic Supplementary Information

Conformal $BiVO_4$-Layer/WO_3-Nanoplate-Array Heterojunction Photoanode Modified with Cobalt Phosphate Cocatalyst for Significantly Enhanced Photoelectrochemical Performances

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S1. Sample Preparation

WO_3 NPAs were prepared by a modified facile hydrothermal method previously reported.[37] Typically, 0.23 g of sodium tungsten ($Na_2WO_4•2H_2O$) was dissolved in 30 mL of deionized water under constant stirring at room temperature, then 6mL of 3 M hydrochloric acid (HCl) was added drop wise to obtain light yellow precipitate. The suspension became transparent after several minutes of stirring by adding 0.2 g ammonium oxalate ($(NH_4)_2C_2O_4$). The as-prepared precursor was transferred into a 50 mL Teflon-lined stainless steel autoclave, which contained a piece of FTO glass substrate leaning against the wall of Teflon vessel with the conducting side facing down. The FTO was ultrasonically cleaned in advance by alcohol, acetone, and alcohol in sequence and dried in a high-pressure nitrogen stream. The autoclave was sealed and placed in an oven, the hydrothermal reaction was carried out at 120 °C for 12 h. After the autoclave was cooled naturally to room temperature, the FTO with a yellow film was taken out and washed by deionized water several times and dried at 60 °C in ambient air overnight. Finally, the as-prepared sample was further heated to 500 °C at a heating rate of 2 °C/min for 1 h in air.

The thin conformal $BiVO_4$ layer was deposited on WO_3 NPAs by a stepwise spin-coating process. In detail, a solution containing 50 mM bismuth and 46.5 mM vanadium were first prepared by dissolving 0.12 g bismuth nitrate pentahydrate ($BiNO_3•5H_2O$) and 0.08 g vanadyl acetylacetonate ($VO(C_5H_7O_2)_2$) in 5 mL mixed solution containing acetic acid and acetyl acetone with volume ratio of 20:1, which was then dropped on the WO_3 NPAs by stepwise spin-coating method. For each coating, 10 μL of precursor solution was dropped on the sample, which was allowed to dry at room temperature and then briefly annealed in a preheated furnace at 450 °C for 5 min. The four kinds of samples were denoted as $BiVO_4$-x/WO_3 (x: the amount of $BiVO_4$ precursor). For example, the $BiVO_4$-20/WO_3 film was prepared by repeating above-mentioned process twice, 20 μL of

$BiVO_4$ precursor solution was used in total. After all the coating steps the samples were annealed at 550 °C in a box furnace for 2 h to yield a conformal $BiVO_4$ shell, which densely coated on the surface of WO_3 NPAs.

Co-Pi OEC was photodeposited on $BiVO_4/WO_3$ heterojunction as described previously.[38, 39] A three-electrode configuration was employed with the as-prepared films as the working electrode, a Ag/AgCl/3MKCl as the reference electrode and a platinum wire as counter electrode. The electrolyte solution was prepared by dissolving 0.5mM cobalt nitrate hexahydrate in 50 mL 0.1 M potassium phosphate buffer solution adjusted to pH = 7. The deposition was carried out at 1.2 V_{RHE} applied potential by an electrochemical workstation (CHI 660E Instruments) under illumination from a 500 W Xe lamp coupled with an AM1.5G filter, with typical photocurrent density of ~0.5–1 mA/cm^2 during deposition. The deposition time was controlled to 100 seconds for optimized thick Co-Pi overlayer.

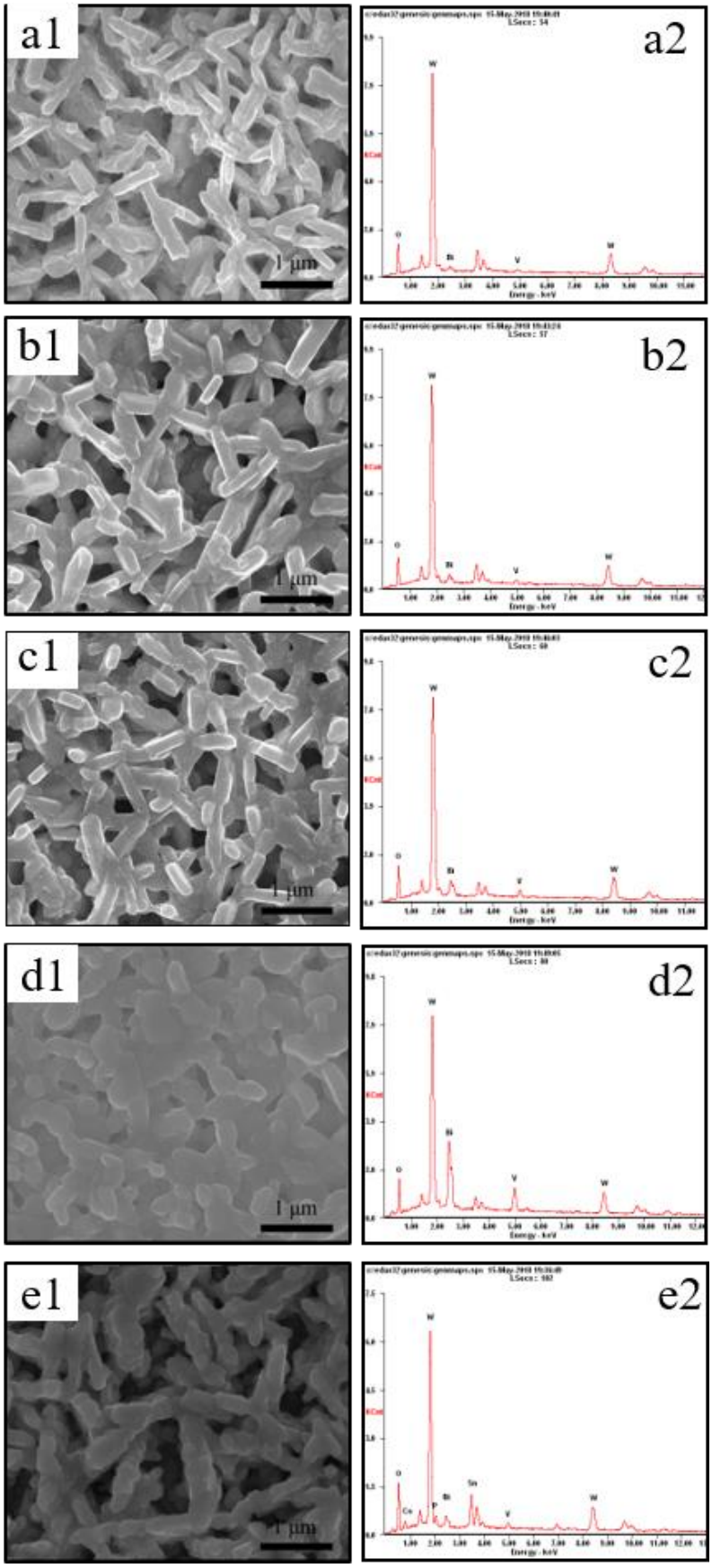

Fig. S1 SEM images and corresponding EDX analysis of $BiVO_4$-x/$WO_3$with different $BiVO_4$ content (a1 and a2 for $BiVO_4$-10/WO_3, b1 and b2 for $BiVO_4$-20/WO_3, c1 and c2 for $BiVO_4$-30/WO_3, d1 and d2 for $BiVO_4$-40/WO_3, and e1 and e2 for Co-Pi@$BiVO_4$-10/WO_3.)

Table S1 Atomic ratios of $BiVO_4$-x/WO_3 heterojunction film and Co-Pi@$BiVO_4$-20/WO_3 measured by SEM-EDX

Samples	W	Bi	V	O	Co
$BiVO_4$-10/WO_3	37.01	1.50	1.55	59.94	—
$BiVO_4$-20/WO_3	35.67	2.89	2.88	58.55	—
$BiVO_4$-30/WO_3	32.94	4.98	4.50	57.58	—
$BiVO_4$-40/WO_3	25.48	13.55	11.04	49.93	
Co-Pi@ $BiVO_4$-20/WO_3	28.01	2.13	2.79	58.68	8.39

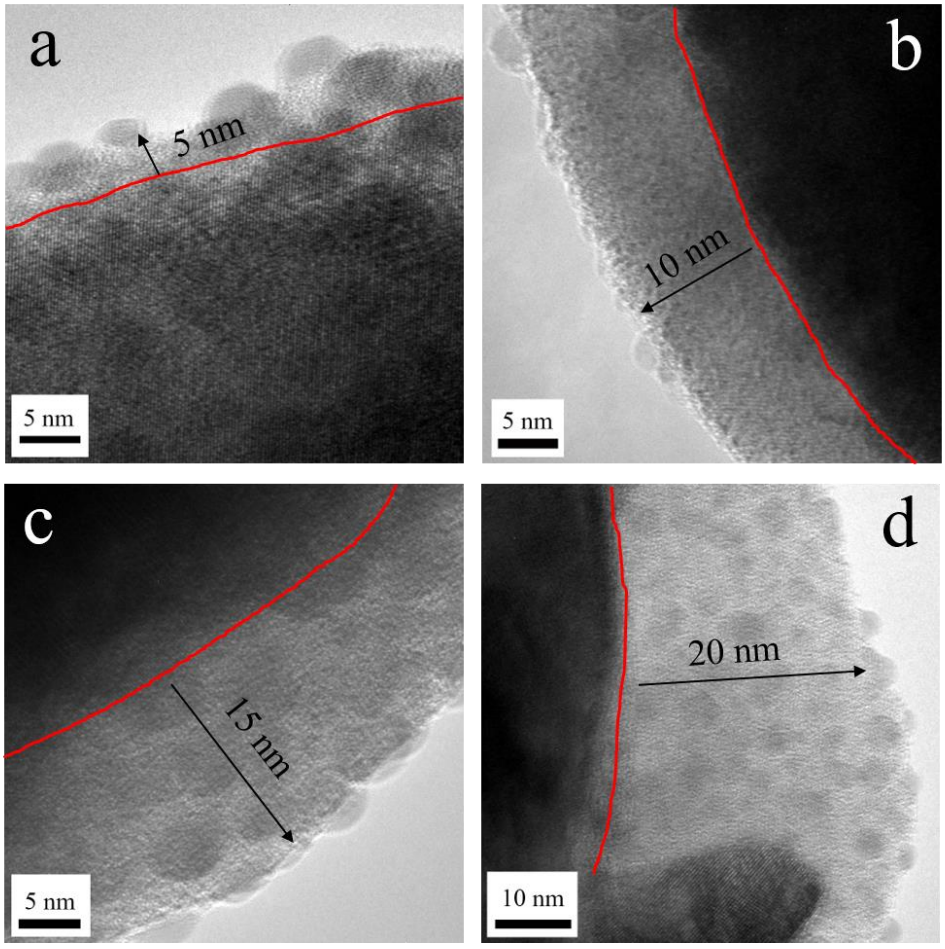

Fig. S2 HR-TEM images of $BiVO_4$-x/WO_3 heterojunction with different $BiVO_4$ content (a, b, c, and d correspond to $BiVO_4$-10/WO_3, $BiVO_4$-20/WO_3, $BiVO_4$-30/WO_3, $BiVO_4$-40/WO_3, respectively), showing different thicknesses of $BiVO_4$ layer.

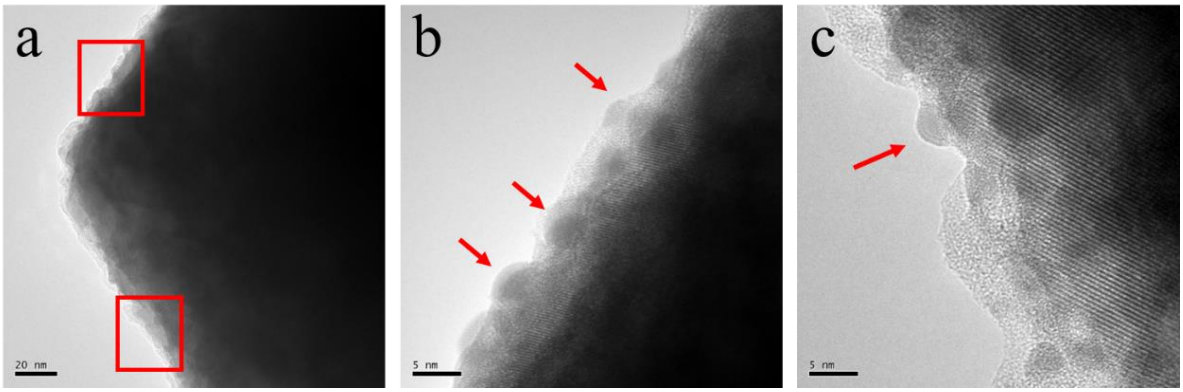

Fig. S3 TEM image (a) and HRTEM image (b) and (c) of $BiVO_4$-20/WO_3, The nano-dots point out by red arrows were element bismuth segregated from $BiVO_4$ due to the irradiation of high intensity current electron beam for long duration.

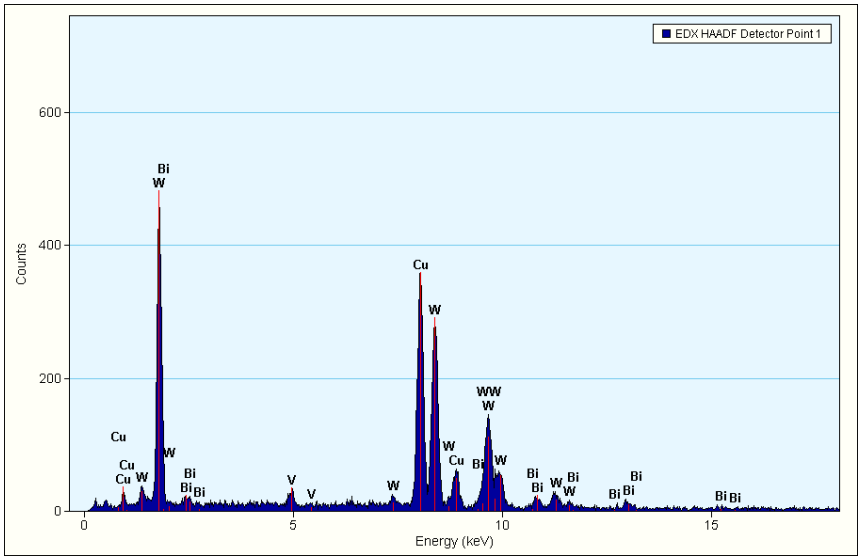

Fig. S4 TEM-EDX survey spectrum of $BiVO_4$-20/WO_3.

Table S2 Weight and atomic ratios of Bi:V:W in $BiVO_4$-20/WO_3 measured by TEM-EDX

Element	Weight %	Atom %
Bi(L)	5.029	4.310
V(K)	1.246	4.384
W(L)	93.724	91.305

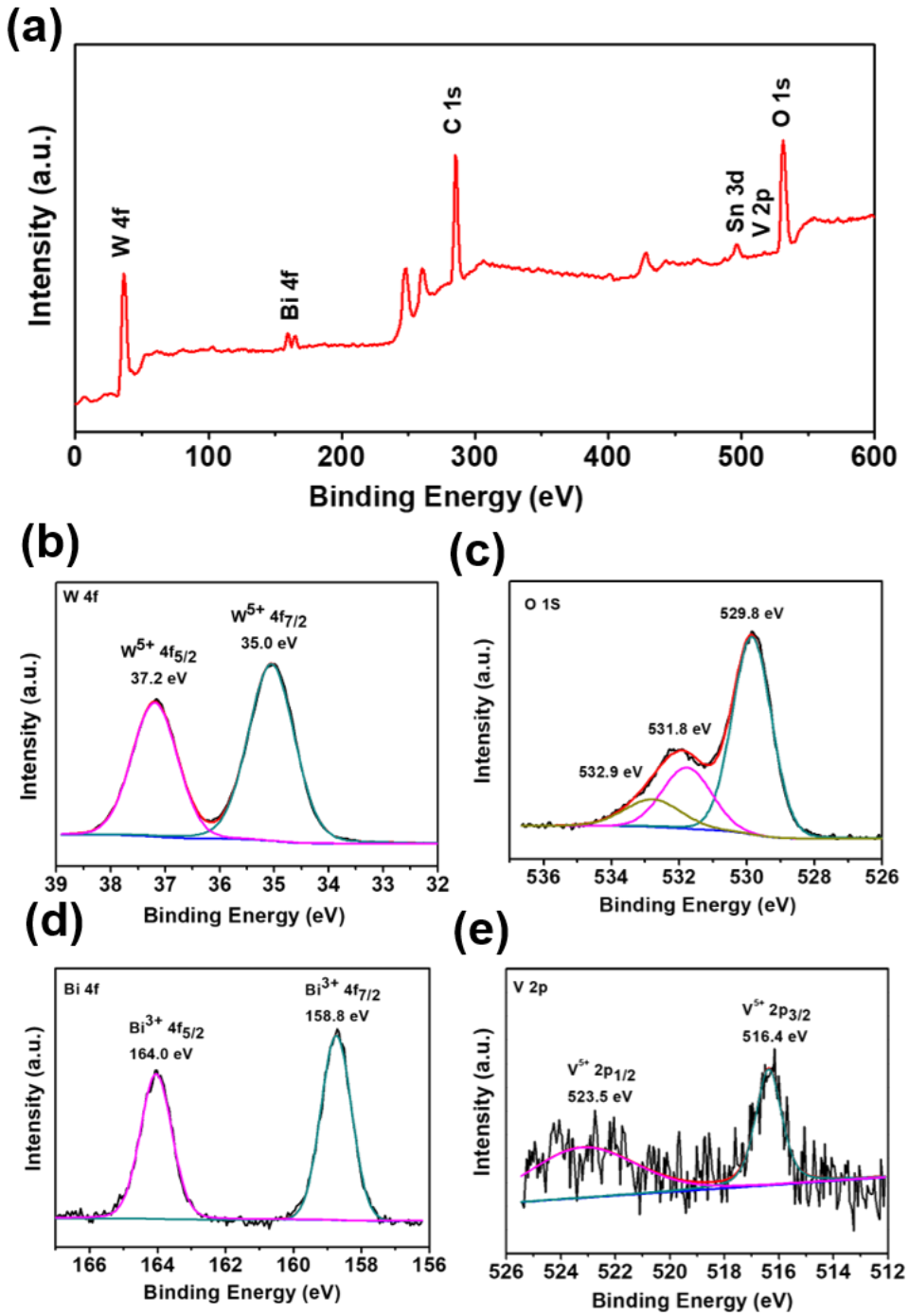

Fig. S5 XPS spectra of $BiVO_2$-20/WO_3: the survey spectrum (a) and high resolution XPS spectrum of W 4f (b), O 1s (c), Bi 4f (d) and V 2p (e).

Table S3 Atomic ratio of $BiVO_4$-20/WO_3 heterojunction film calculated from XPS measurement

Sample	W	Bi	V	O
$BiVO_4$-20/WO_3	22.76	1.76	1.36	74.13

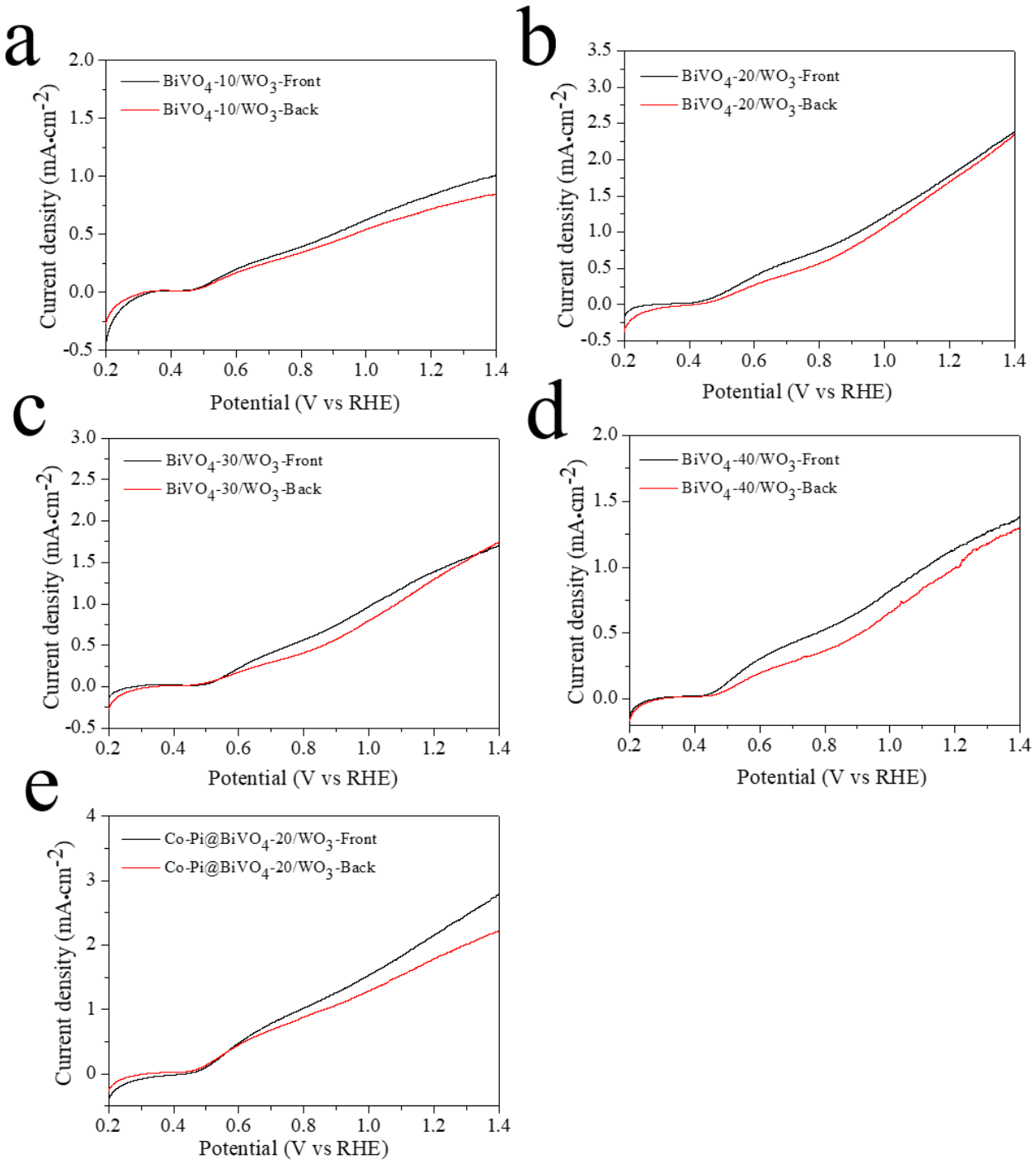

Fig. S6 J-V curves of (a) $BiVO_4$-10/WO_3, (b) and $BiVO_4$-20/WO_3, (c) $BiVO_4$-30/WO_3, (d) $BiVO_4$-40/WO_3, and (e) Co-Pi@$BiVO_4$-20/WO_3 measured in 0.1M phosphate buffer (pH = 7) under front (black line) and back (red line) illuminations.

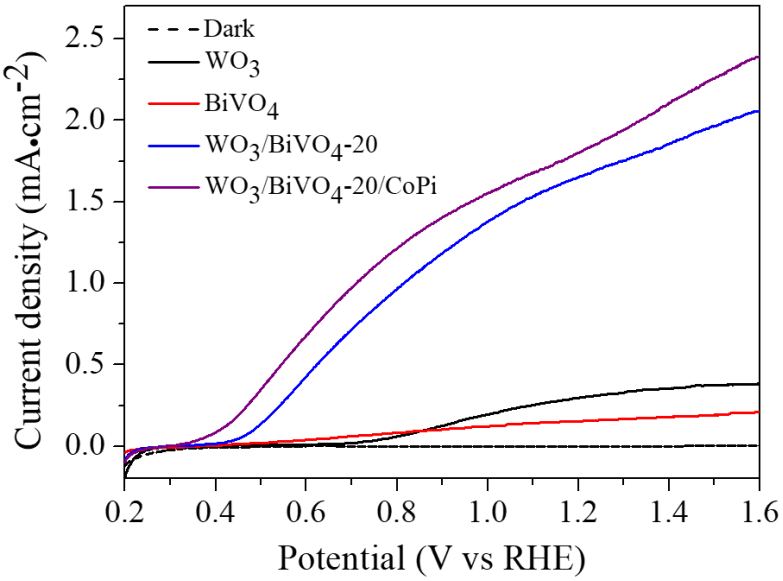

Fig. S7 J-V curves of WO_3 NPAs, $BiVO_4$, $BiVO_4$-20/WO_3 and Co-Pi@$BiVO_4$-20/WO_3 measured in 0.1 M phosphate buffer (pH=7) under AM1.5G illumination.

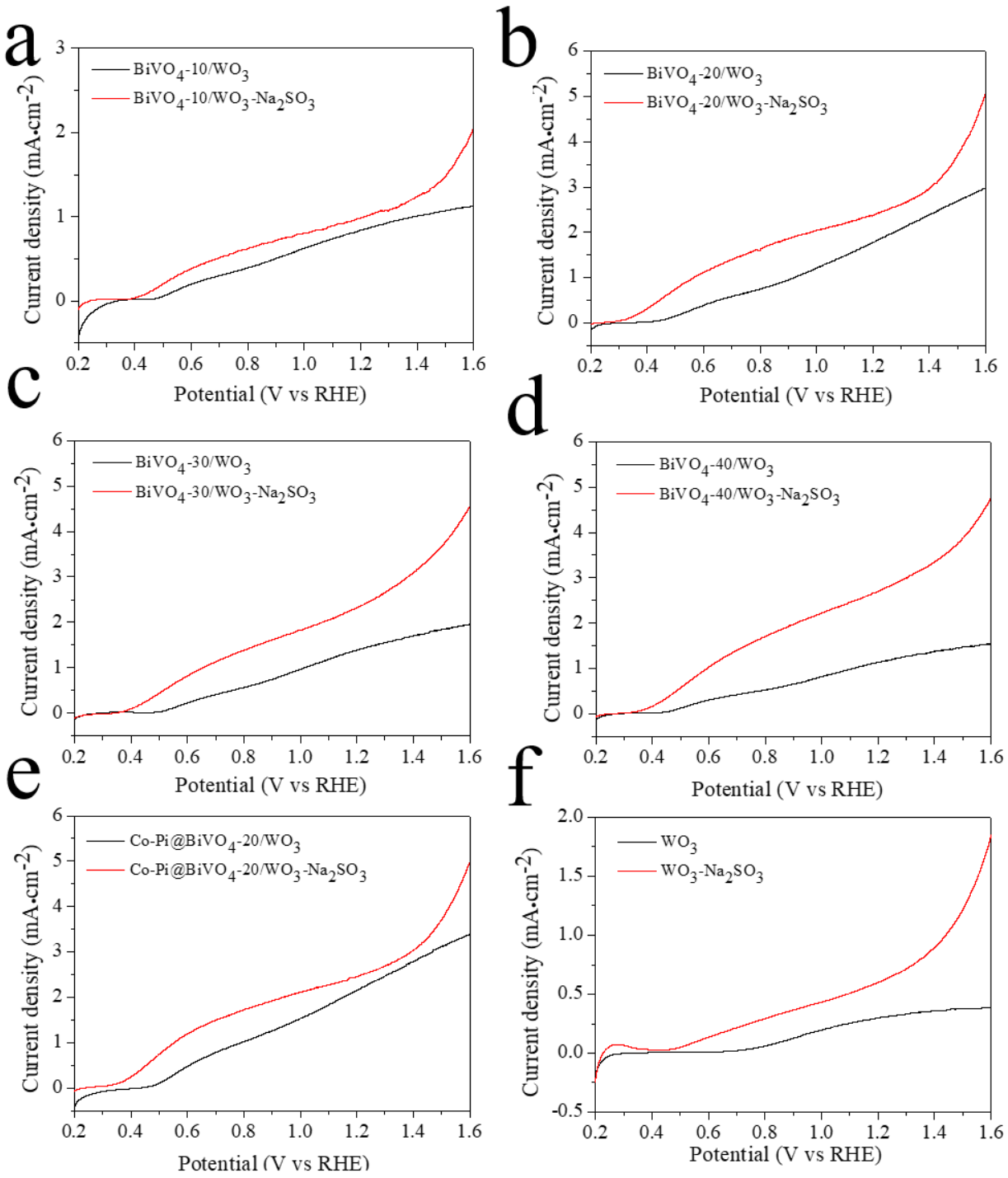

Fig. S8 LSV curves of $BiVO_4$-x/WO_3 heterojunction with different $BiVO_4$ content and Co-Pi@$BiVO_4$-20/WO_3 under AM 1.5G illumination in the potassium phosphate electrolyte with (red line) and without (black line) Na_2SO_3 hole scavenger. (a, b, c, d, e and f correspond to $BiVO_4$-10/WO_3, $BiVO_4$-20/WO_3, $BiVO_4$-30/WO_3, $BiVO_4$-40/WO_3, Co-Pi@ $BiVO_4$-20/WO_3, and WO_3, respectively)

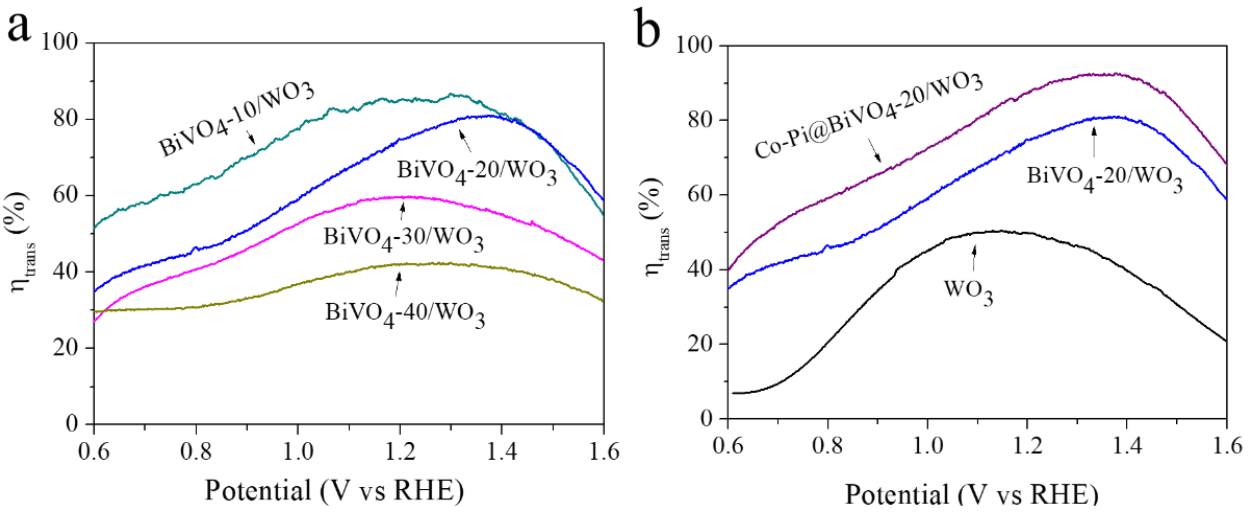

Fig. S9 Surface charge separation efficiency of (a) $BiVO_4$-x/WO_3 heterojunction, and (b) WO_3, $BiVO_4$-20/WO_3, and Co-Pi@$BiVO_4$-20/WO_3 for water oxidation.

Table S4. The fitted equivalent circuit and simulated electrochemical parameters of as-prepared photoanodes.

Samples	R_s	R_{sc}	C_{sc}	R_{ct}	C_H
WO_3	5.774	50.46	3.579E-8	2781	3.705E-5
$BiVO_4$	6.036	58.1	2.823E-8	1880	5.135E-6
$BiVO_4$-10/WO_3	6.773	57.77	1.653E-8	946.6	2.843E-5
$BiVO_4$-20/WO_3	4.577	58.46	1.603E-7	266.2	2.31E-5
$BiVO_4$-30/WO_3	8.818	61.6	1.37E-8	327.9	6.261E-5
$BiVO_4$-40/WO_3	7.921	59.09	1.448E-8	476.1	6.957E-5
Co-Pi@$BiVO_4$-20/WO_3	1.834	22.75	8.352E-6	124.3	4.198E-5

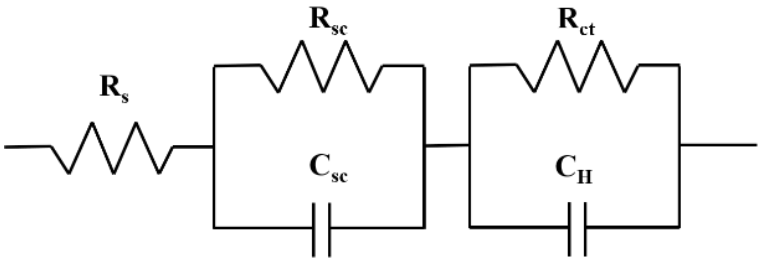

Table S5 Comparation of calculated lifetime of electron for bare WO_3, bare $BiVO_4$, and $BiVO_4$-20/WO_3 heterojunction film.

Photoanodes	**f_{max}(Hz)**	**τ_n(s)**
WO_3	318324	5.00E-07
$BiVO_4$	384240	4.14E-07
$BiVO_4$-20/WO_3	68325	2.33E-06
Co-Pi@$BiVO_4$-20/WO_3	2150	7.41E-05