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Supporting Information

Photoelectrochemical H_2 Evolution on $WO_3/BiVO_4$ Enabled by Single Crystalline TiO_2 Overlayer-Modulations

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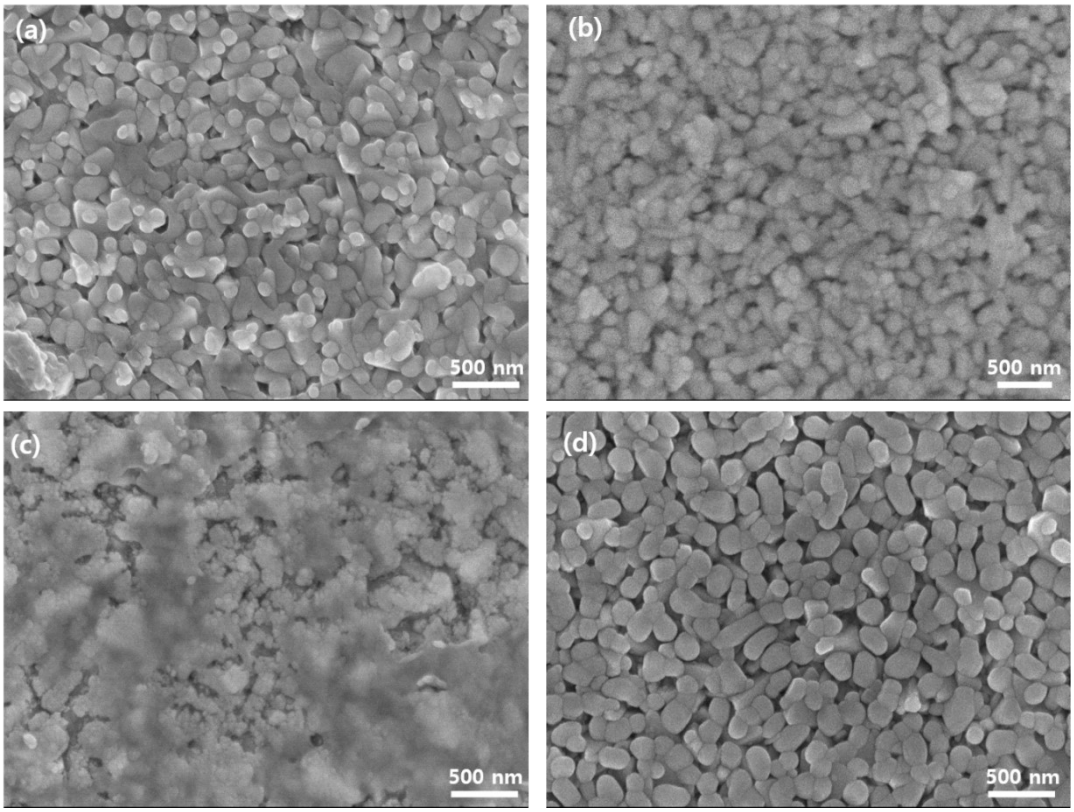

Figure S1. FE-SEM images of the $WO_3/BiVO_4$ heterostructure prepared at different cycling steps (a) 20 cycles, (b) 30 cycles, (c) 40 cycles, (d) 20 cycles with prior air annealing at 100°C for 5 min after 10 cycles.

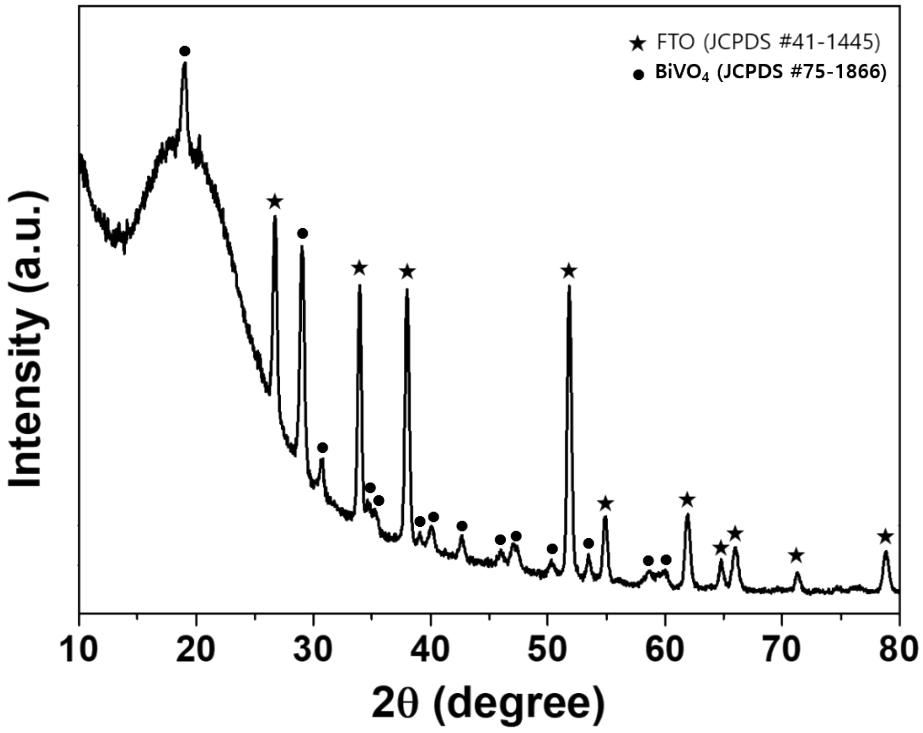

Figure S2. XRD pattern of pristine $BiVO_4$.

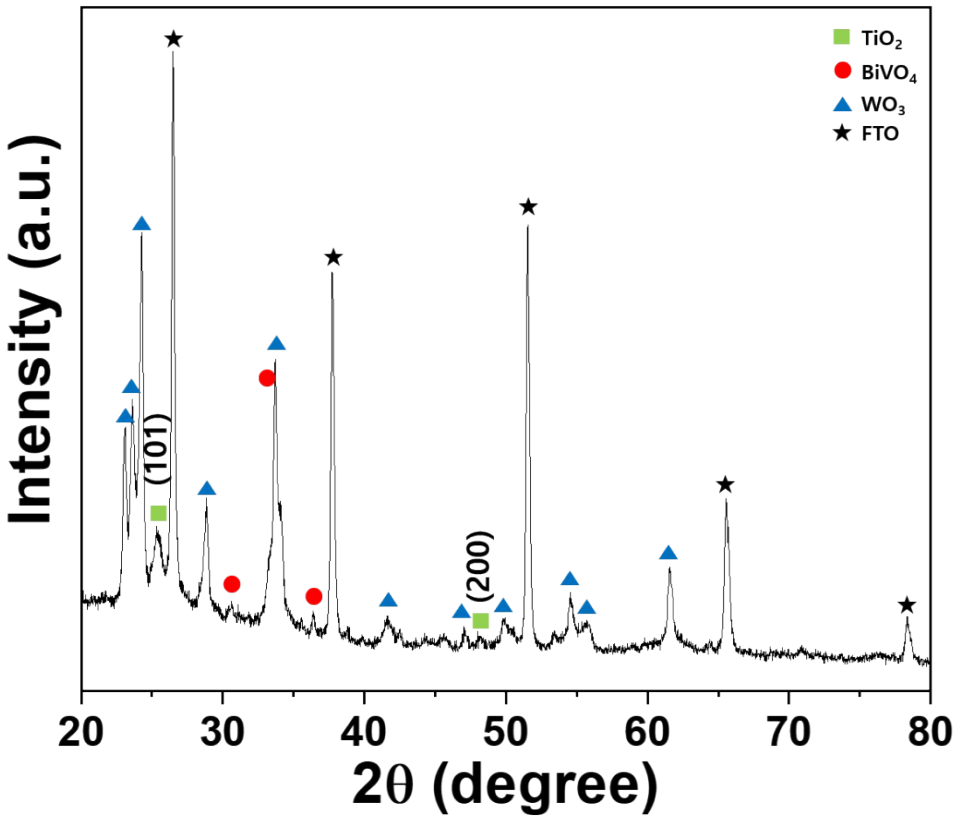

Figure S3. XRD pattern of five-cycle spin-coated TiO_2 on $WO_3/BiVO_4$.

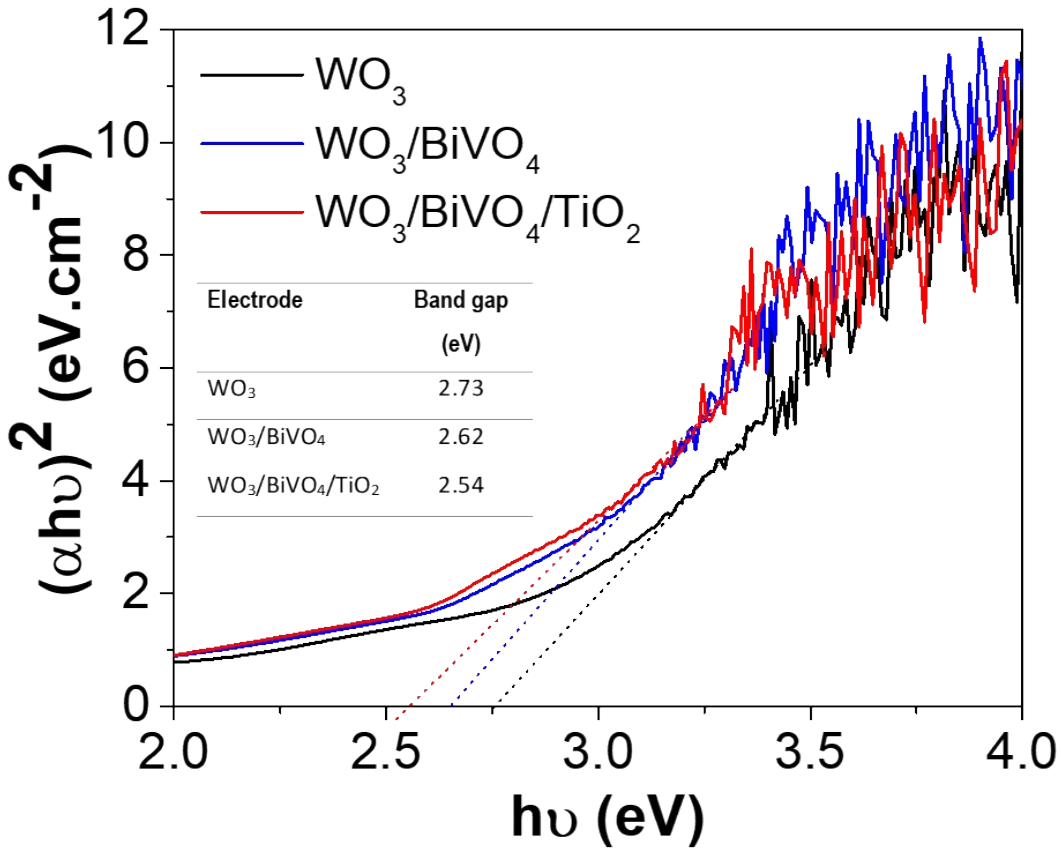

Figure S4. Tauc plot of WO_3, $WO_3/BiVO_4$ and $WO_3/BiVO_4/TiO_2$ photoelectrodes.

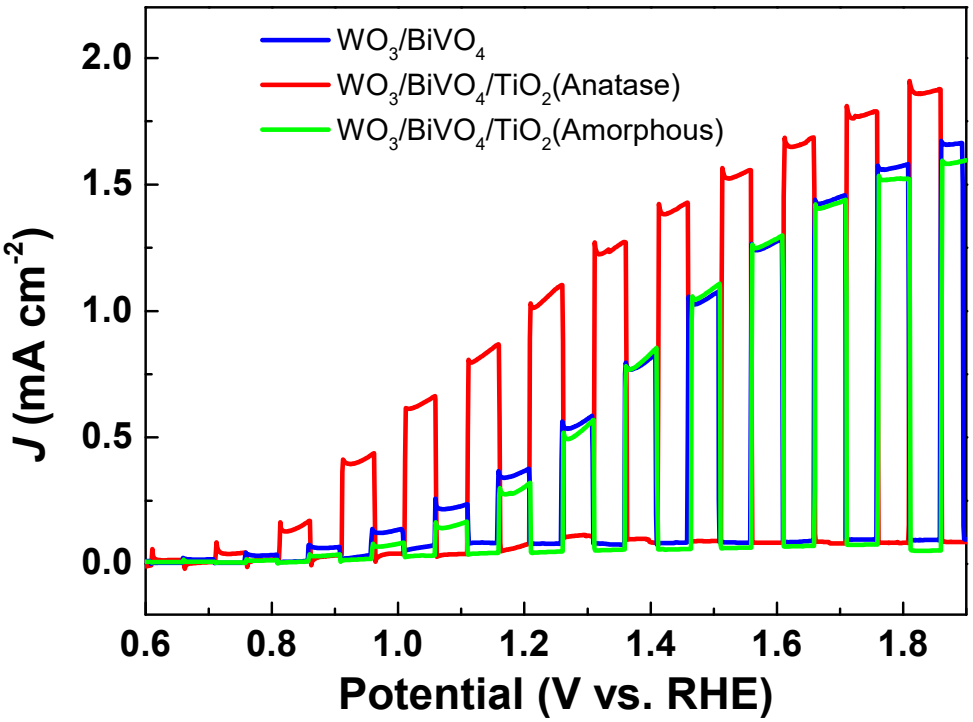

Figure S5. Linear sweep voltammetry curves of $WO_3/BiVO_4$, $WO_3/BiVO_4/TiO_2$ (anatase), and $WO_3/BiVO_4/TiO_2$ (amorphous) photoelectrodes.

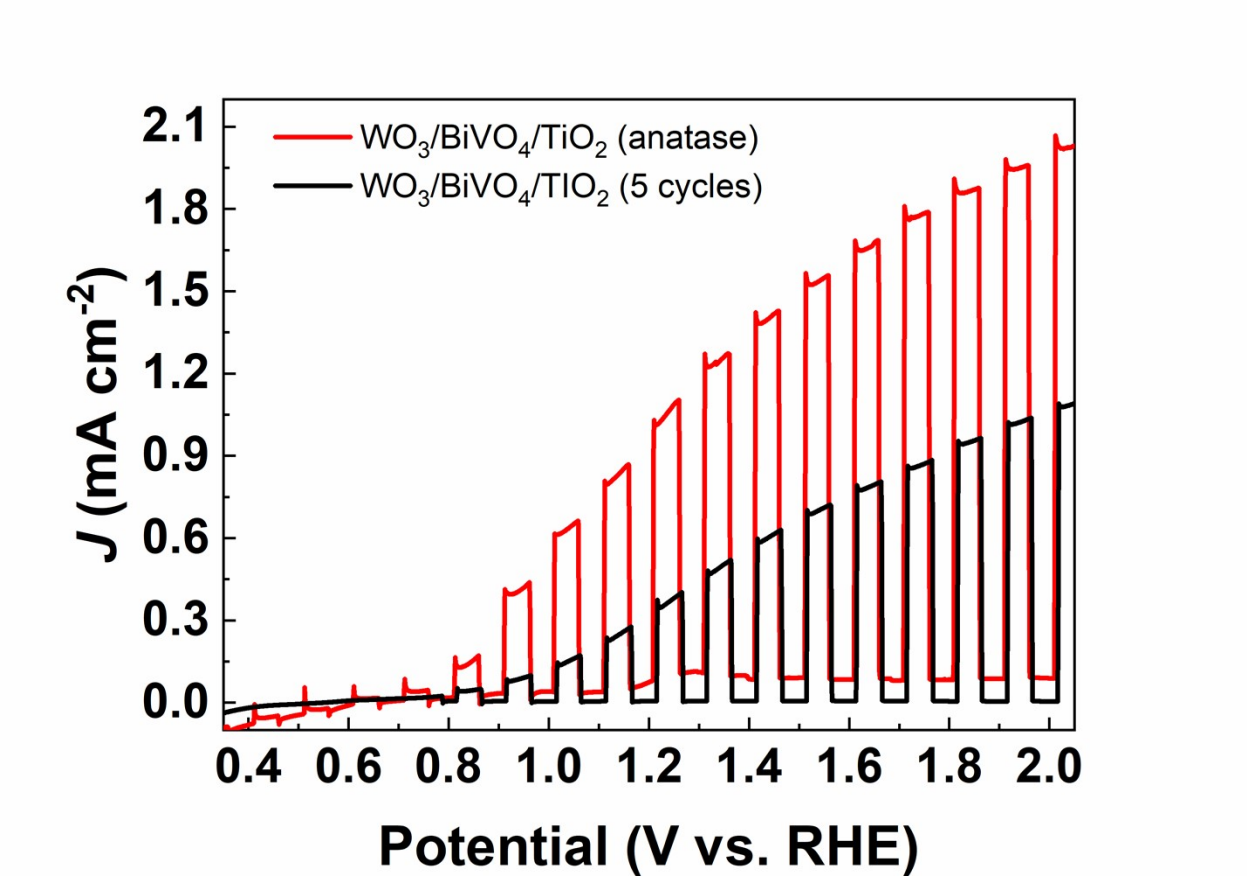

Figure S6. Linear sweep voltammetry curves of $WO_3/BiVO_4/TiO_2$ (anatase) and $WO_3/BiVO_4/TiO_2$ (five cycles) photoelectrodes.

Table S1. Summary of photostability parameter comparison with state-of-the-art $WO_3/BiVO_4$-related photoelectrodes

Electrode	Synthesis method	Initial *J* (mA/cm^2)	Final *J* (mA/cm^2)	Time	Electrolyte	Applied potential	Ref.
$WO_3/BiVO_4$	WO_3: Spray coating $BiVO_4$: ED	1.1	0.6	2 h	0.1 M phosphate buffer with 1 M Na_2SO_4	1.23 V vs. RHE	[1]
$SnO_2/BiVO_4/TiO_2$	SnO_2, $BiVO_4$, TiO_2: Spin-coating	1.1	0.6	5 h	0.5 M phosphate buffer with H_2O_2	1 V vs. Pt	[2]
$SnO_2/WO_3/BiVO_4$	SnO_2, WO_3: Electron-beam deposition $BiVO_4$: Drop casting	1.9	1.5	5 h	Phosphate buffer with 0.5 M Na_2SO_3	1.23 V vs. RHE	[3]
$WO_3/BiVO_4/ZnO$	WO_3: Hydrothermal $BiVO_4$: Spin-coating ZnO: ALD	2.9	2.6	6 h	0.5 M Na_2SO_4	1.23 V vs. RHE	[4]
$TiO_2/WO_3/BiVO_4$	TiO_2: ALD WO_3, $BiVO_4$: ED	3.1	2.4	5 h	0.5 M Na_2SO_4 with 0.1M Na_2SO_3	-	[5]
$WO_3/BiVO_4/BiFeO_3$	WO_3, $BiVO_4$, $BiFeO_3$: Spin-coating	1.6	1.1	50 min	0.5 M Na_2SO_4	1.5 V vs. RHE	[6]
$WO_3/BiVO_4$/(FeOOH/NiOOH)	WO_3: Hydro-deposition $BiVO_4$: Drop-casting FeOOH/NiOOH: Photodeposition	4.8	4.5	30 min	0.5 M Na_2SO_4	1.23 V vs. RHE	[7]

SnO_2/$BiVO_4$/Co-Pi	SnO_2: CVD $BiVO_4$, Co-Pi: ED	0.9	0.8	1 h	0.1M phosphate buffer	1.23 V vs. RHE	[8]

ED = Electrodeposition; ALD = Atomic layer deposition; CVD = Chemical vapor deposition

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