

Figure S1. XRD patterns of the as-prepared metal dicyanamides.

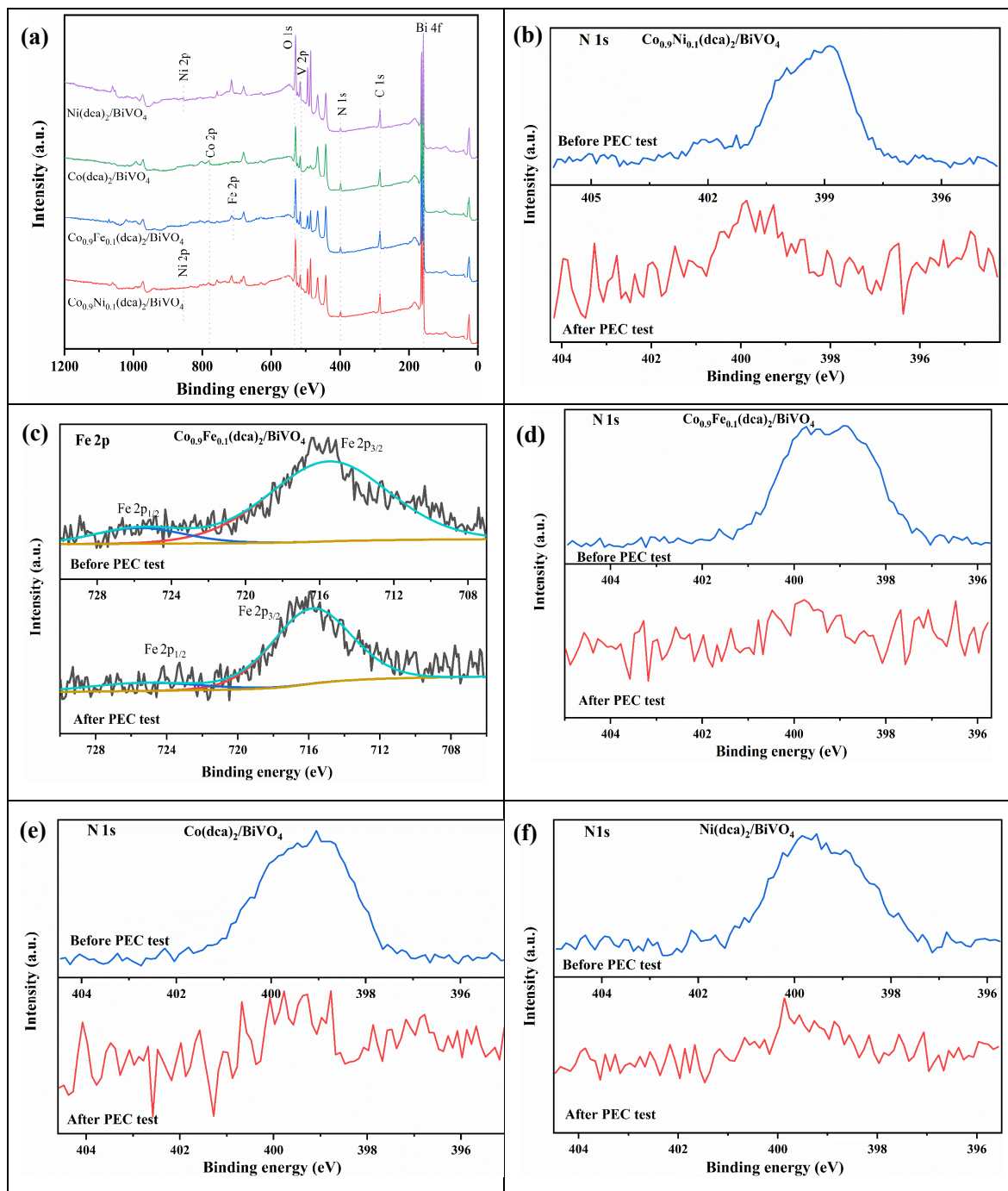


Figure S2. (a) XPS survey spectra of $M(dca)_2/BiVO_4$ photoanodes, (b) XPS N 1s spectra of $Co_{0.9}Ni_{0.1}(dca)_2/BiVO_4$, (c) XPS Fe 2p spectra of $Co_{0.9}Fe_{0.1}(dca)_2/BiVO_4$, (d) XPS N 1s spectra of $Co_{0.9}Fe_{0.1}(dca)_2/BiVO_4$, (e) XPS N 1s spectra of $Co(dca)_2/BiVO_4$, (f) XPS N 1s spectra of $Ni(dca)_2/BiVO_4$ before and after PEC tests.

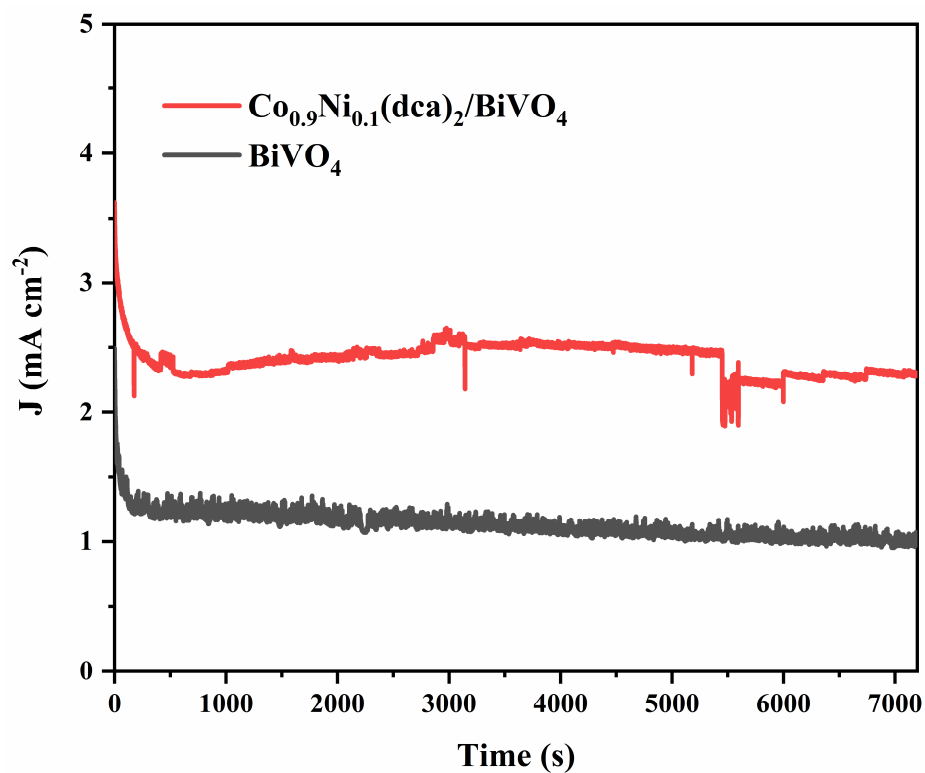


Figure S3. Stability I-t curves of $\text{Co}_{0.9}\text{Ni}_{0.1}(\text{dca})_2/\text{BiVO}_4$ and bare BiVO_4 photoanodes measured at 1.23 V vs. RHE in 0.5 M Na_2SO_4 aqueous solution under AM 1.5G illumination.

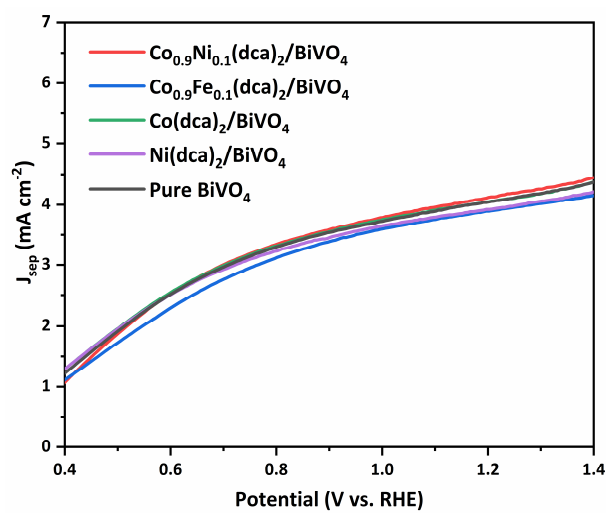


Figure S4. Photocurrent densities for BiVO_4 and $\text{M}(\text{dca})_2/\text{BiVO}_4$ photoanodes in 0.1 M Na_2SO_3 aqueous solution under AM 1.5G illumination.

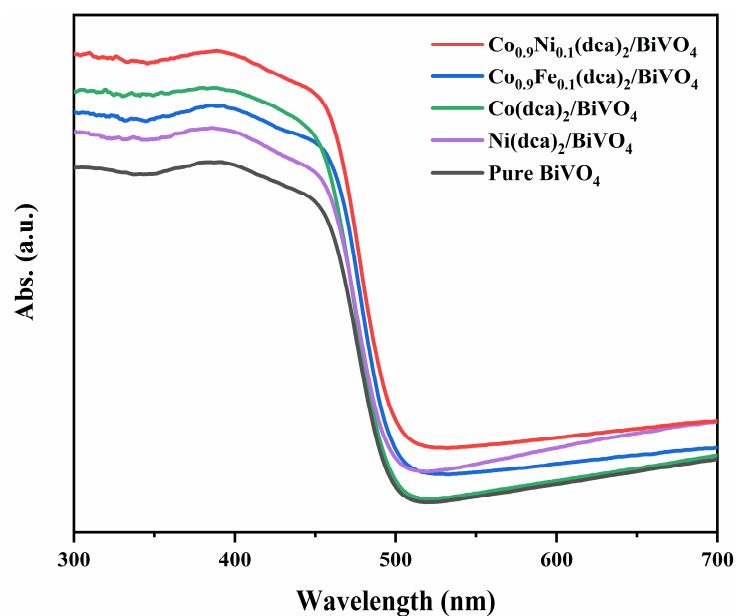


Figure S5. UV-Vis spectra of BiVO₄ and M(dca)₂/BiVO₄ photoanodes.

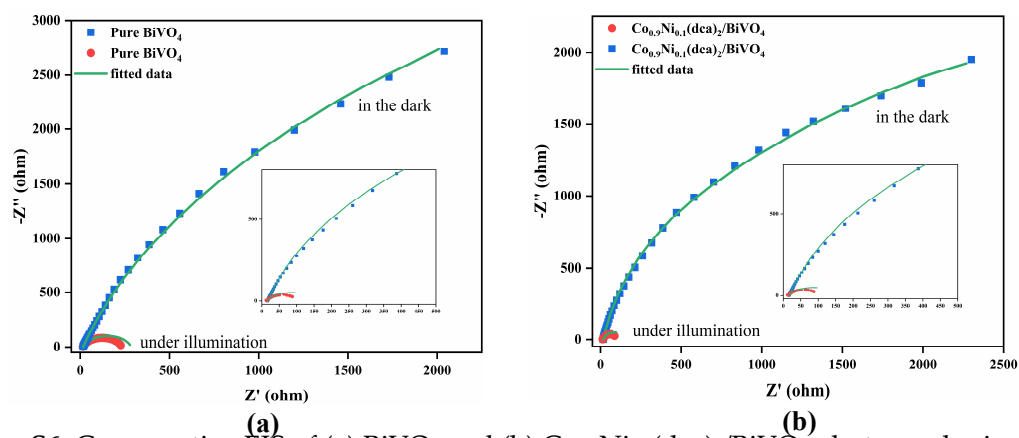


Figure S6. Comparative EIS of (a) BiVO₄ and (b) Co_{0.9}Ni_{0.1}(dca)₂/BiVO₄ photoanodes in the dark and under illumination.

Table S1. EIS-fitted values and flat-band potentials of BiVO₄ and M(dca)₂/BiVO₄ photoanodes in the equivalent circuit for PEC water oxidation.

	Co _{0.9} Ni _{0.1} (dca) ₂ /BiVO ₄	Co _{0.9} Fe _{0.1} (dca) ₂ /BiVO ₄	Co(dca) ₂ /BiVO ₄	Ni(dca) ₂ /BiVO ₄	BiVO ₄
Flat band potential (mV vs. RHE)	5.16	18.8	39.8	42.5	46.9
R _{CT} (Ω)	96.02	135.7	180.2	216.6	269.2
R _{SC} (Ω)	14.29	17.55	19.98	16.35	21.4
R _S (Ω)	21.55	21.86	21.68	24.19	21.7
Q _H	4.56×10 ⁻⁴	4.49×10 ⁻⁴	3.41×10 ⁻⁴	2.61×10 ⁻⁴	3.14×10 ⁻⁴
Q _{SC}	6.03×10 ⁻⁷	1.53×10 ⁻⁷	5.47×10 ⁻⁸	1.76×10 ⁻⁷	8.59×10 ⁻⁸