Electronic Supplementary Material (ESI) for Green Chemistry.

Electronic Supplementary Information

Fully Solution-Processable Cu_2O-$BiVO_4$ Photoelectrochemical Cells for Bias-Free Solar Water Splitting

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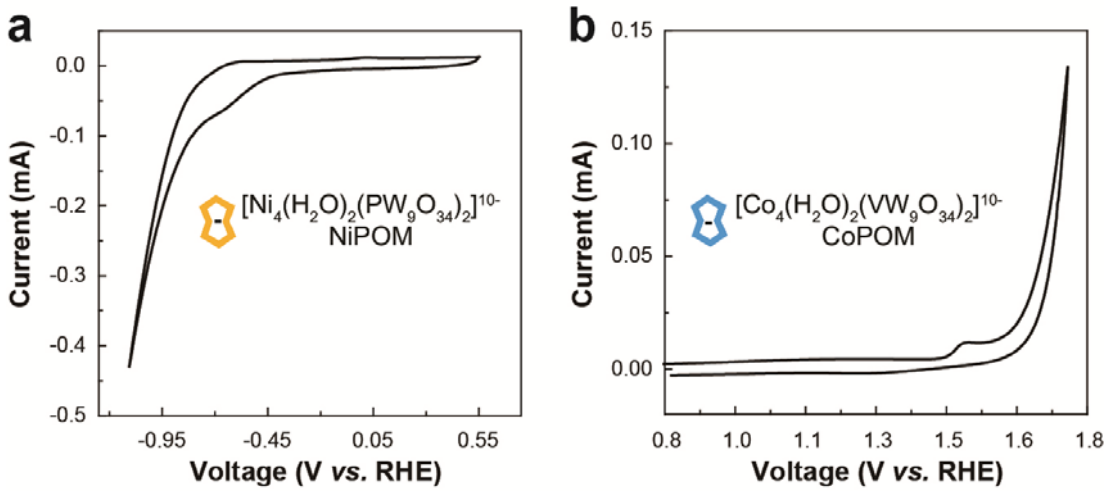

Fig. S1 Cyclic voltammograms showing the HER and OER catalytic activity of NiPOM and CoPOM, respectively.

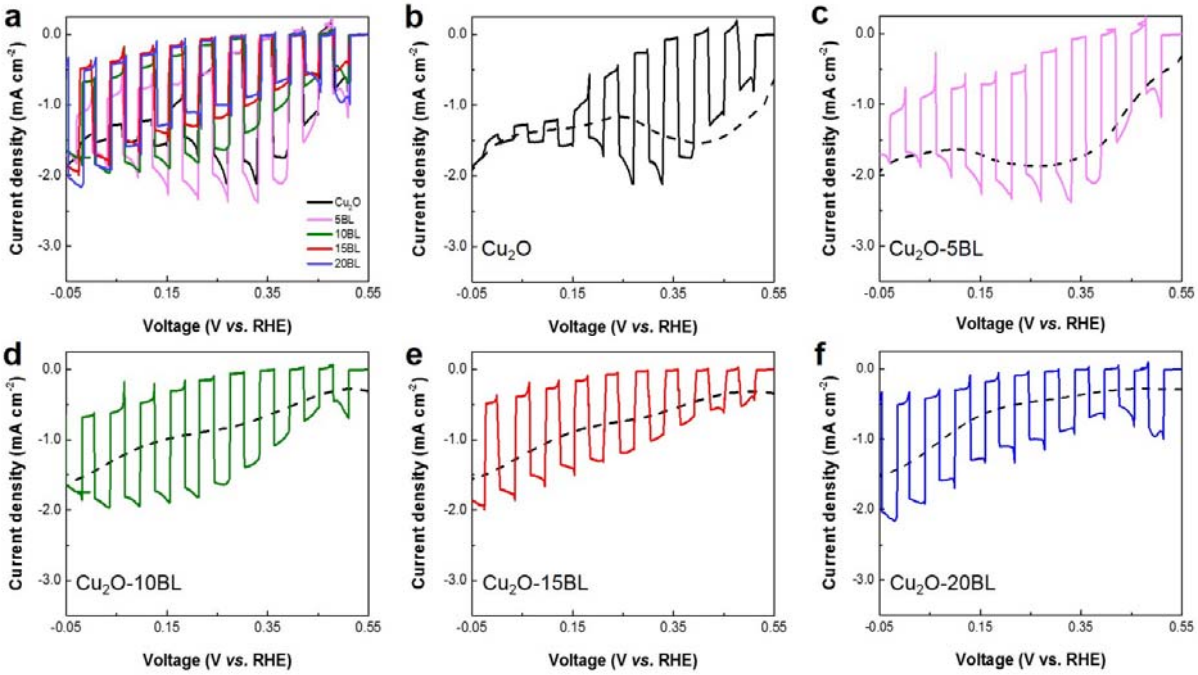

Fig. S2 LSV curves showing the effect of the number of HER BLs on the performance and stability of the Cu_2O photocathode. LSV curves were measured under periodic and continuous illumination.

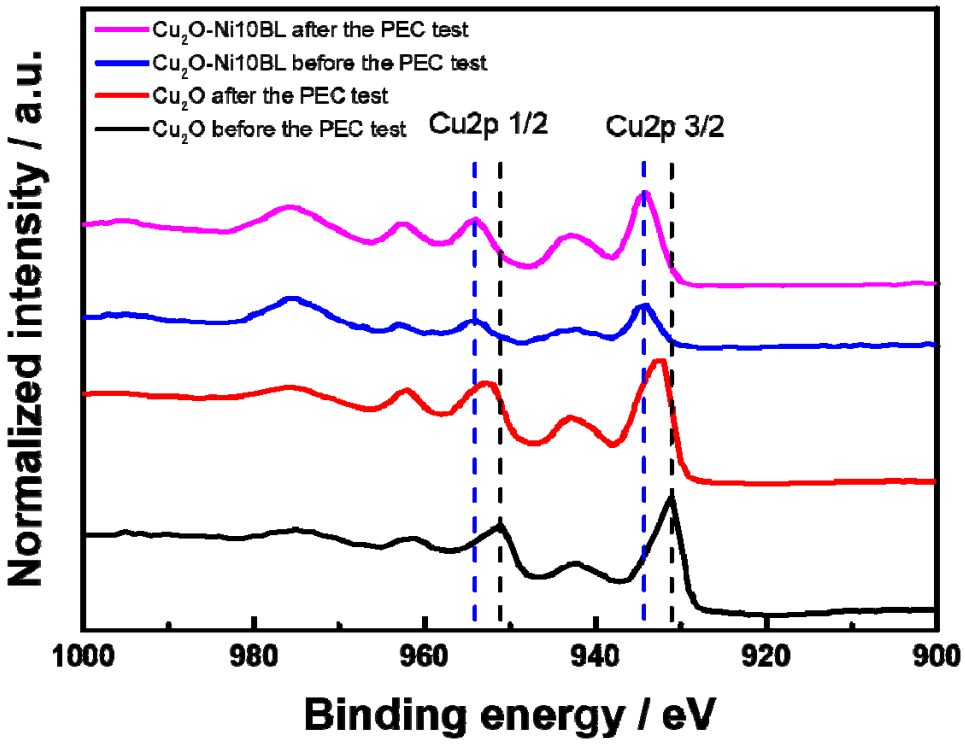

Fig. S3 *Ex situ* XPS spectra of the bare Cu_2O and the Cu_2O with 10 BL of the HER CMs before and after the PEC hydrogen evolution test at an applied bias of 0.35V *vs.* RHE for 1h. (Black dotted line for Cu_2O, Blue dotted line for Cu_2O-Ni10BL)

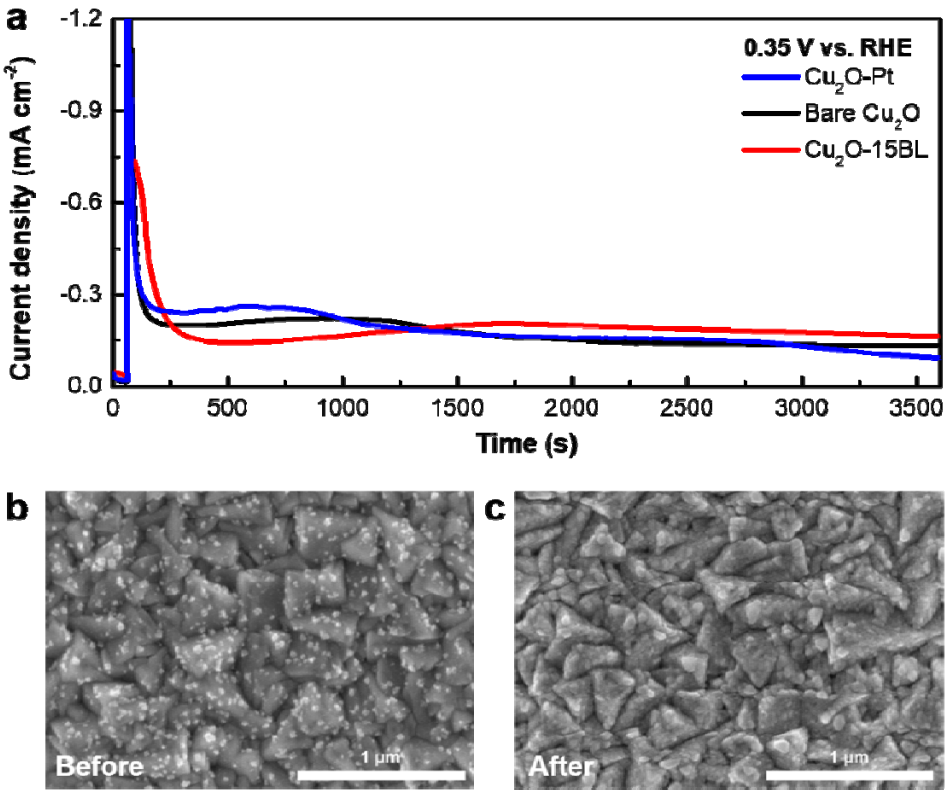

Fig. S4 Performance of Cu_2O photocathodes modified with Pt nanoparticles (Cu_2O-Pt). (a) Chronoamperograms of various Cu_2O photocathodes—the bare Cu_2O, Cu_2O with Pt nanoparticles, and Cu_2O with the HER CMs—are shown for comparison. (b, c) SEM images of the Cu_2O-Pt photocathode before and after the PEC test at an applied bias of 0.35 V vs. RHE for 1h.

Table S1. The fitting results for the EIS spectra (Fig. 4a) of the Cu_2O photocathode with and without 15 BL of the HER CMs.

R (Ω)	R_S	R_1	R_2
Cu_2O	30.26	79.5	992.3
Cu_2O-15BL	32.73	38.25	589.3

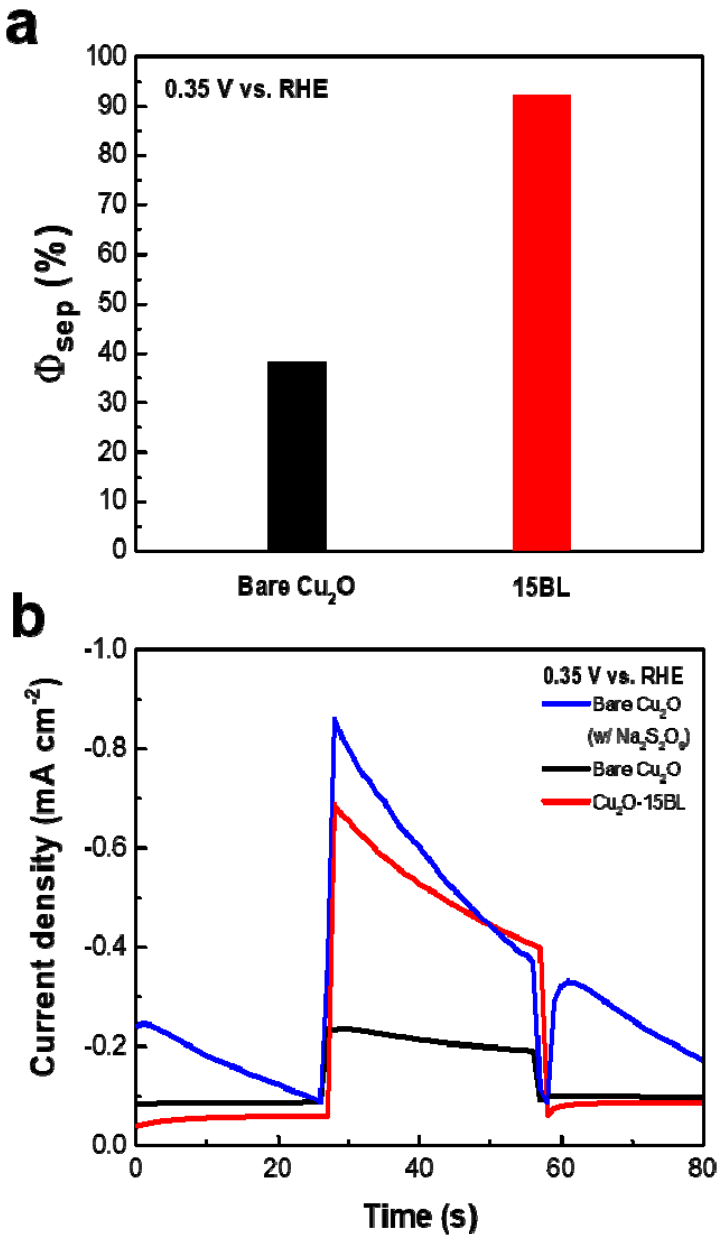

Fig. S5 (a) Comparison between the charge separation efficiency for the bare Cu_2O and the Cu_2O with 15 BL of the HER CMs. (b) Chronoamperograms measured for the calculation of the charge separation efficiency. 0.1 M sodium persulfate ($Na_2S_2O_8$) was used as an electron scavenger.

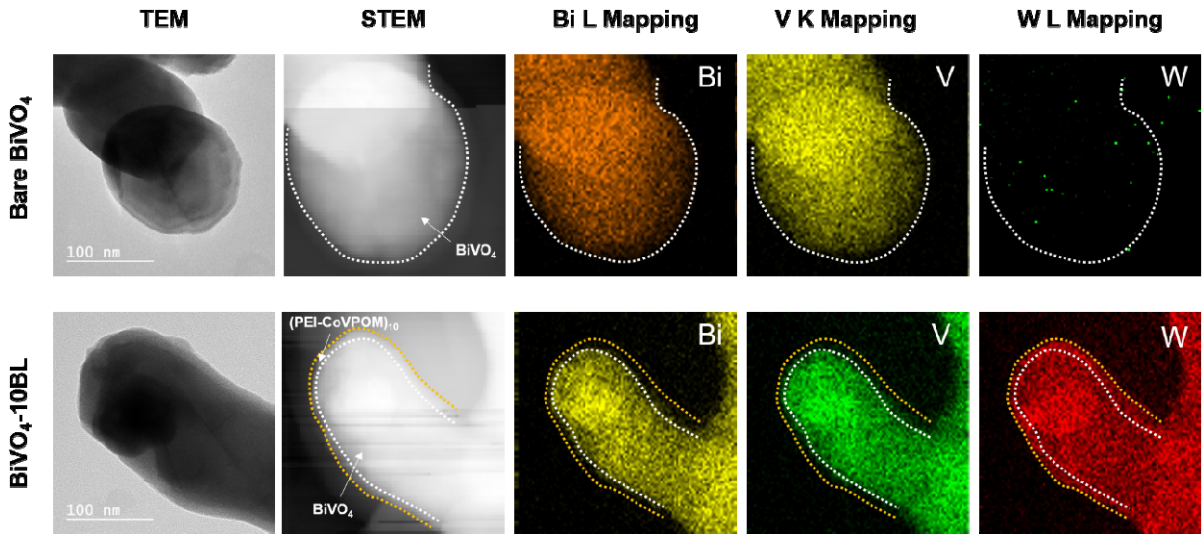

Fig. S6 TEM, STEM and elemental mapping analyses of $BiVO_4$ photoanodes before and after the modification with 10 BLs of the OER CMs.

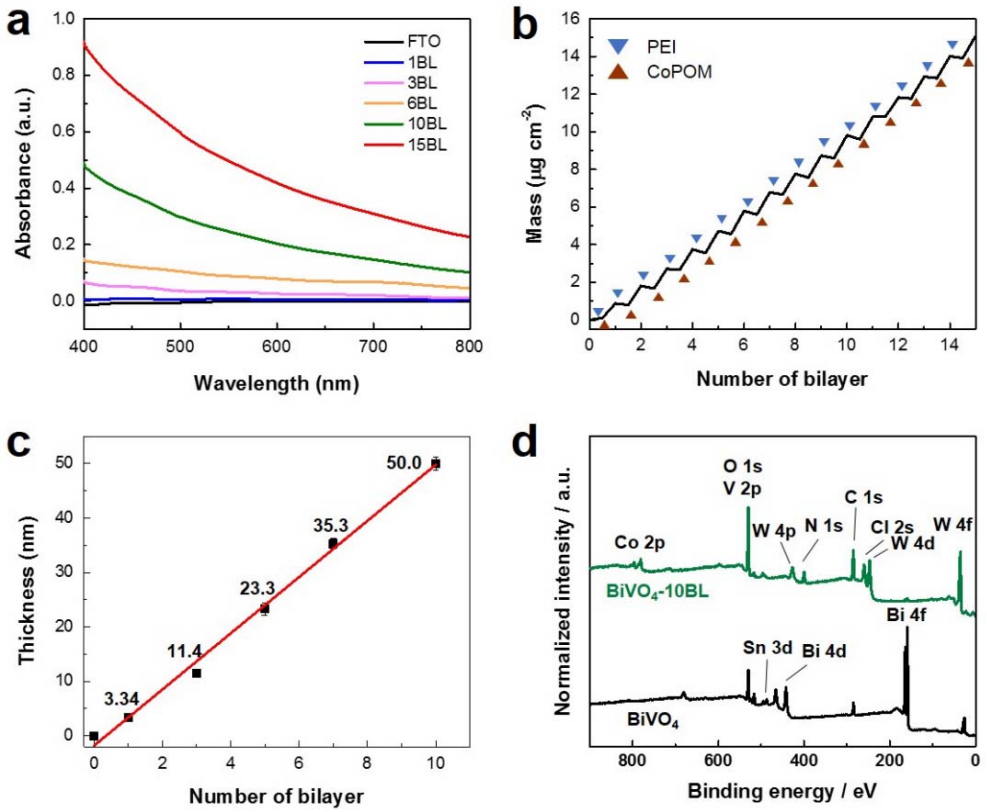

Fig. S7 Formation of the OER CMs was investigated with (a) UV-vis absorption spectroscopy, (b) QCM analysis, (c) ellipsometry, and (d) XPS.

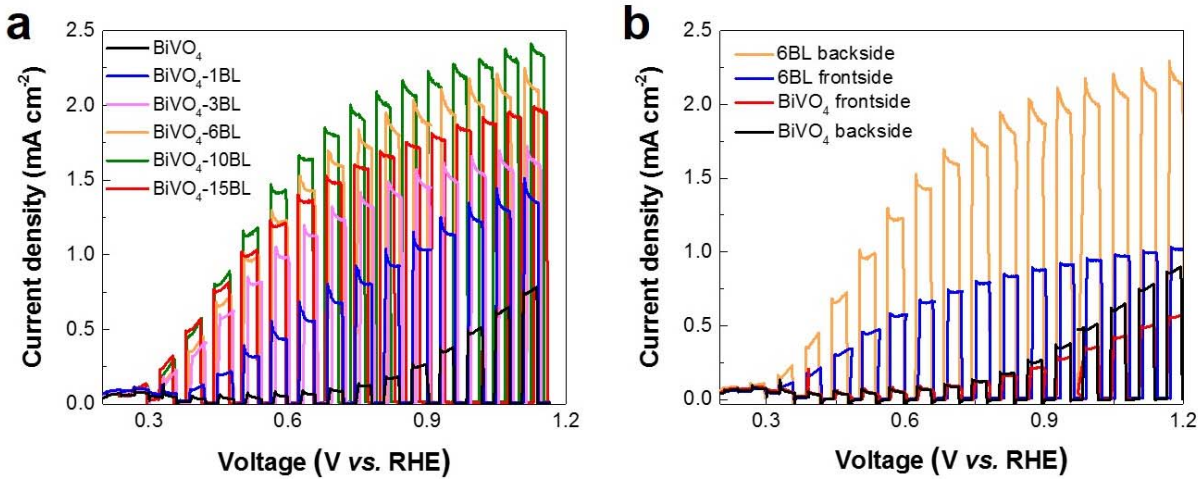

Fig. S8 LSV curves showing the effect of (a) the number of OER BL and (b) illumination-direction on the performance of the $BiVO_4$ photoanode.

Table S2. The fitting results for the EIS spectra (Fig. 5e) of the $BiVO_4$ photoanode with and without OER CMs.

	R_S (Ω)	R_1 (Ω)	*CPE1* (F)	R_2 (Ω)	*CPE2* (F)
$BiVO_4$	26.51	360.3	7.66×10^{-5}	2.00×10^{5}	7.95×10^{-5}
$BiVO_4$-5BL	31.95	173.3	4.58×10^{-5}	988.4	1.75×10^{-4}
$BiVO_4$-10BL	21.58	123.2	4.00×10^{-5}	727.6	4.39×10^{-4}
$BiVO_4$-15BL	24.42	134.2	6.90×10^{-5}	832.4	3.25×10^{-4}

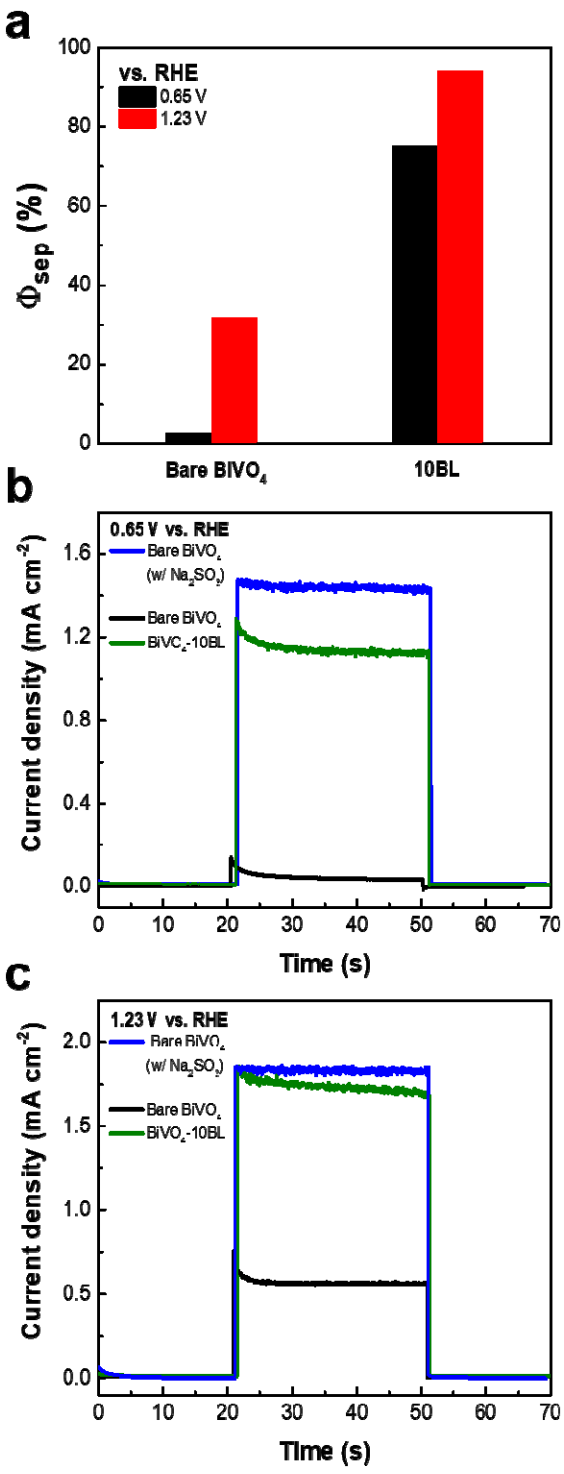

Figure S9. (a) Comparison between the charge separation efficiency for the bare $BiVO_4$ and the $BiVO_4$ with 10 BL of the OER CMs. (b, c) Chronoamperograms measured for the calculation of the charge separation efficiency. 0.5 M sodium sulfite (Na_2SO_3) was used as a hole scavenger.