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Supporting Information

The development of cobalt phosphide co-catalyst on $BiVO_4$ photoanode to improve H_2O_2 production

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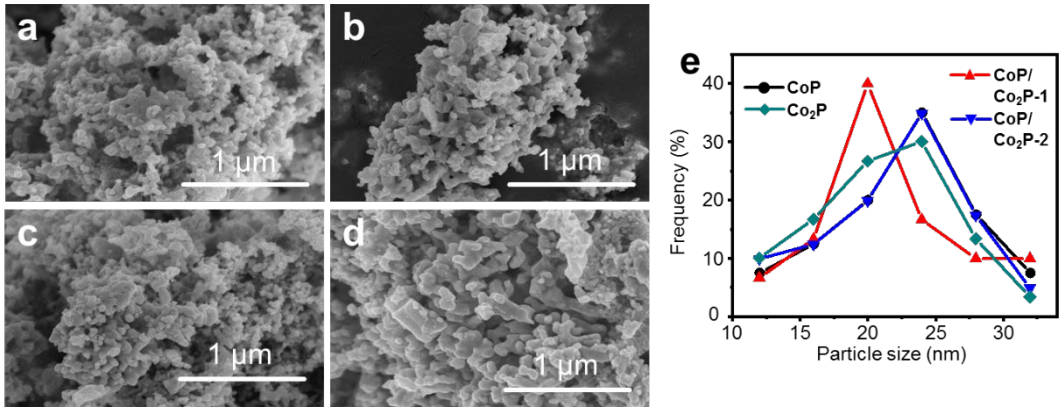


Figure S1. SEM images of (a) CoP, (b) CoP/Co_2P-1, (c) CoP/Co_2P-2 and (d) Co_2P. (e) Particle size distribution of CoP, CoP/Co_2P-1, CoP/Co_2P-2 and Co_2P.

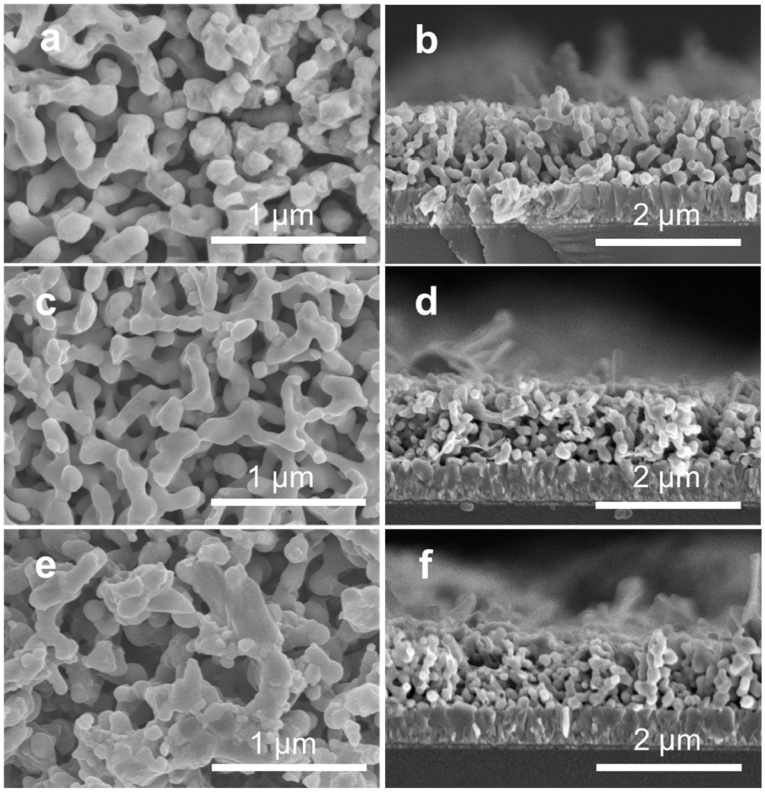


Figure S2. Top view and cross section view SEM images of (a)-(b) CPB-1, (c)-(d) CPB-2 and (e)-(f) CPB-3.

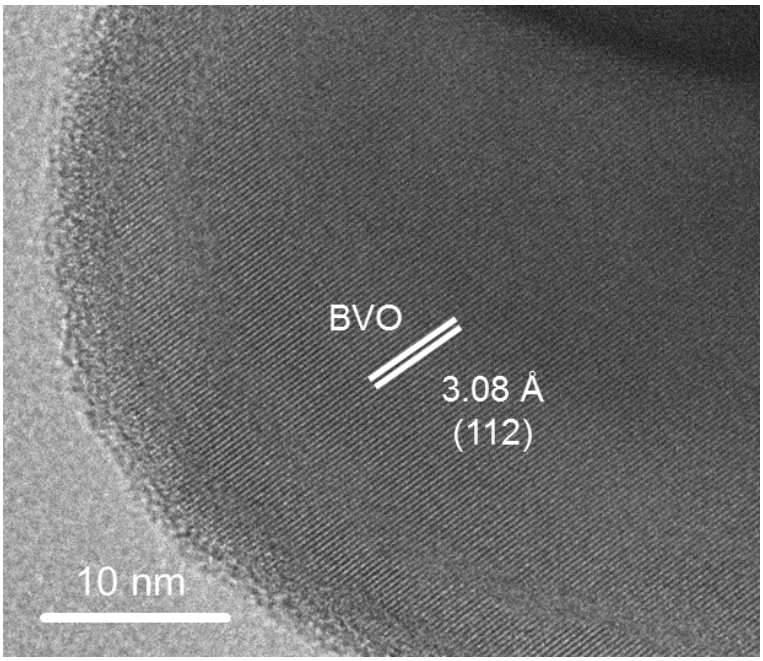


Figure S3. HR-TEM images of pristine BVO photoanode.

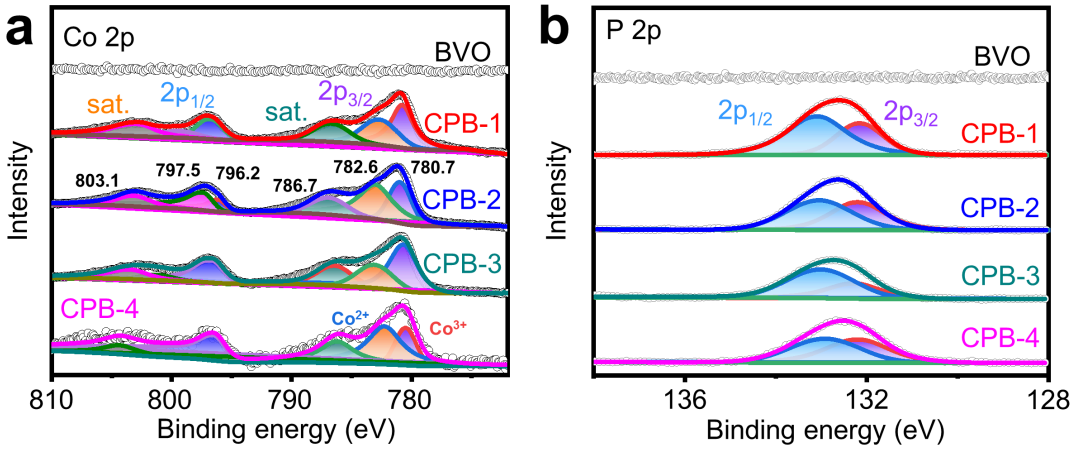


Figure S4. High resolution XPS spectra of (a) Co 2p and (b) P 2p of BVO and CPB photoanodes.

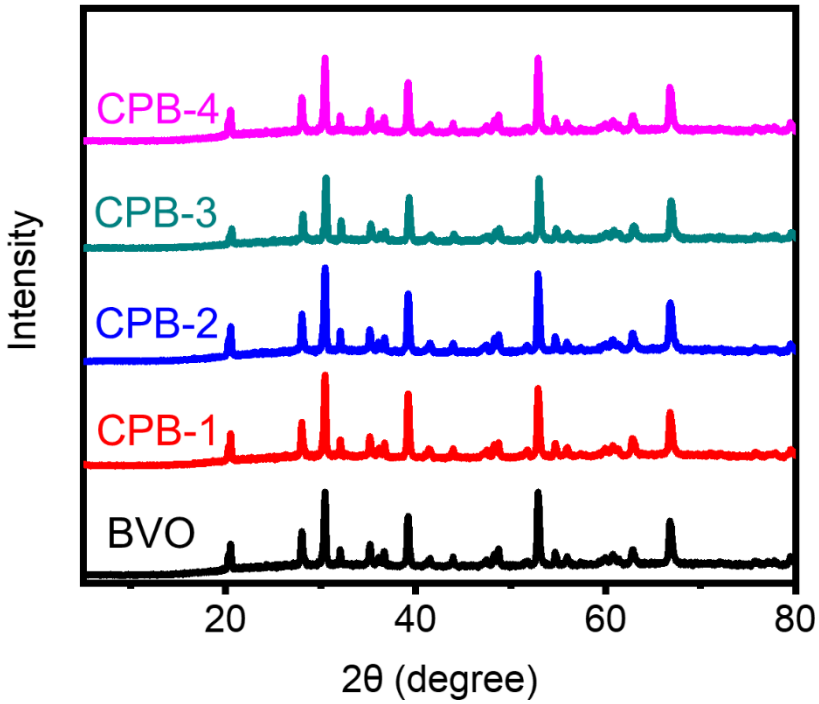


Figure S5. XRD patterns of BVO and CPB photoanodes.

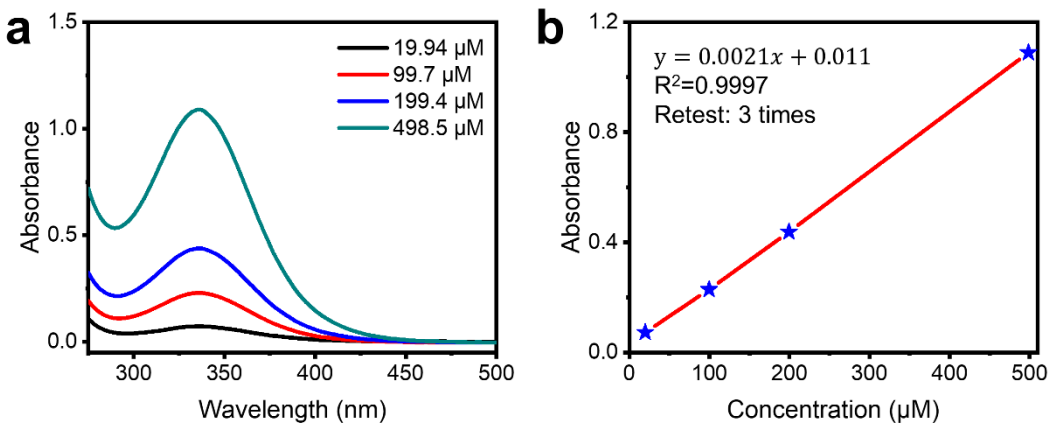


Figure S6. (a) Absorbance curve of standard concentration obtained by UV-Vis-NIR spectrophotometer, (b) the standard curve.

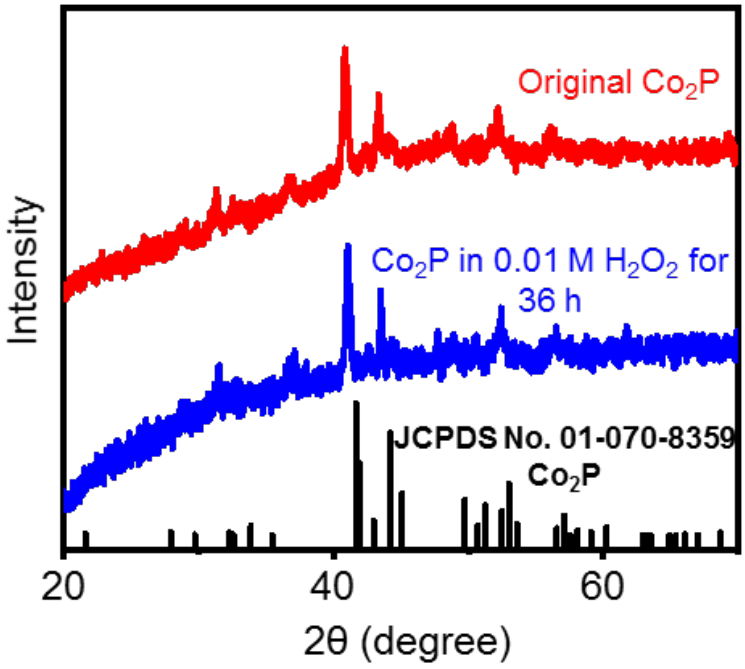


Figure S7. XRD spectra of origin Co_2P and the Co_2P that soaked in 0.01 M H_2O_2 solution for 36 h.

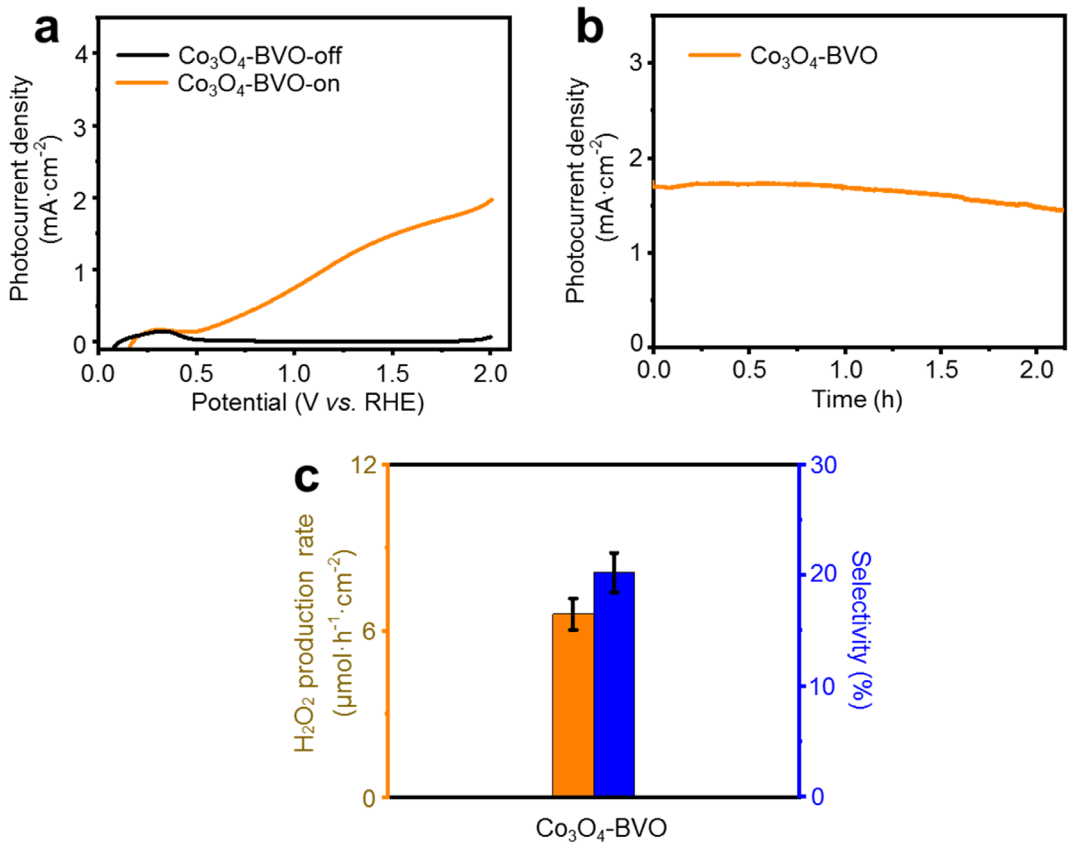


Figure S8. (a) Photocurrent density of the Co_3O_4-BVO photoanode for H_2O_2 production under AM 1.5 G illumination. (b) CA curve of the Co_3O_4-BVO photoanode for H_2O_2 production with the applied voltage of 1.7 V_{RHE}. (c) The H_2O_2 production and selectivity of the Co_3O_4-BVO photoanode for H_2O_2 production with three times of independent repeated experiments.

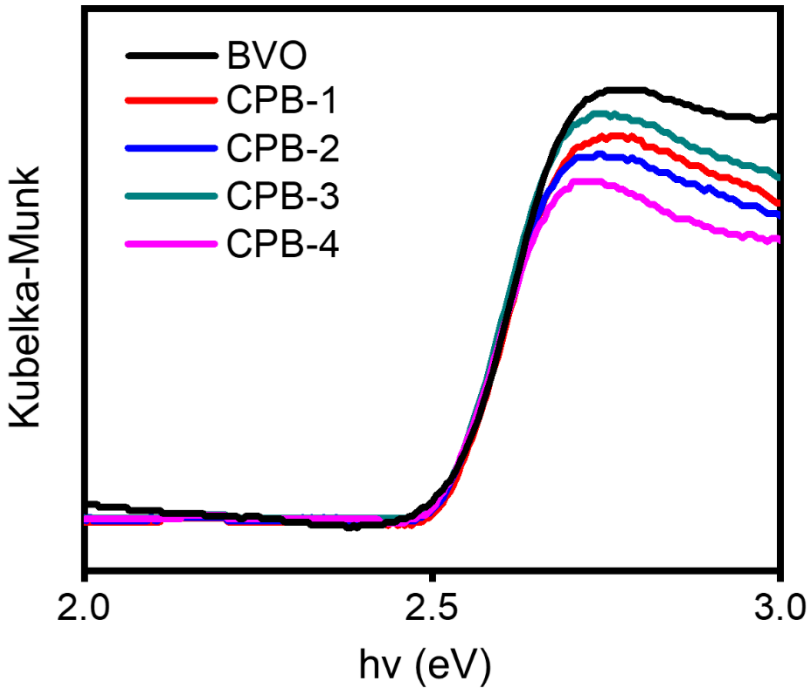


Figure S9. UV-Vis DRS spectra of BVO and CPB photoanodes of Kubelka-Munk spectra.

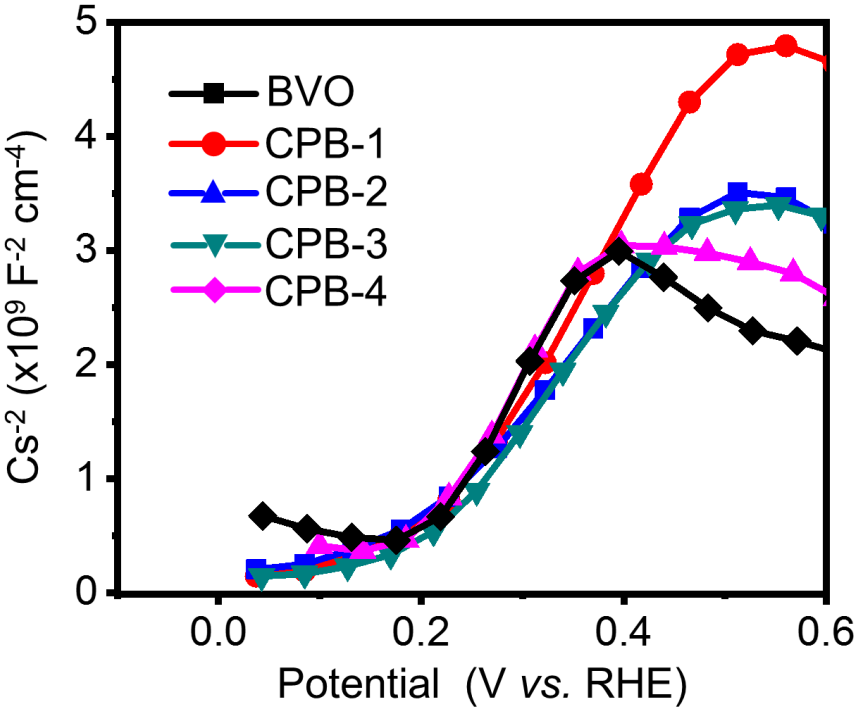


Figure S10. The Mott-Schottky plots to measure the flat-band potentials of BVO photoanode and CPB samples.

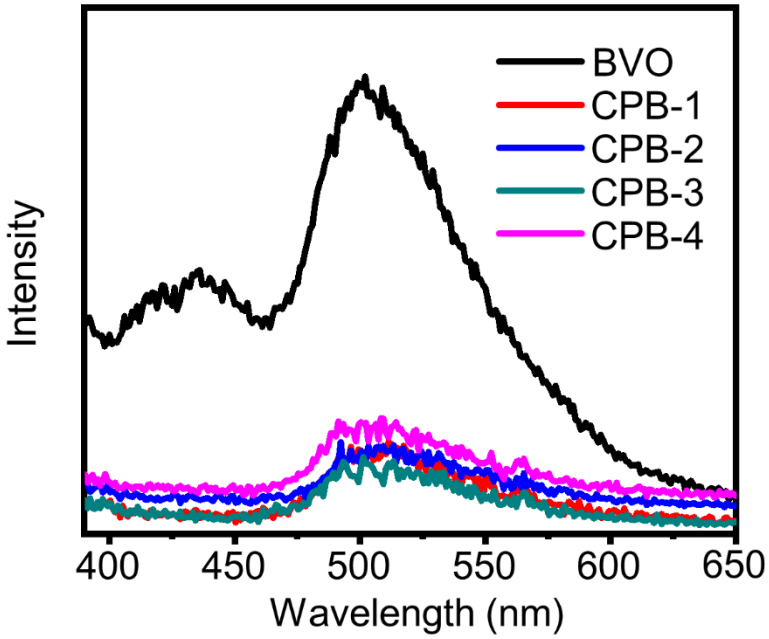
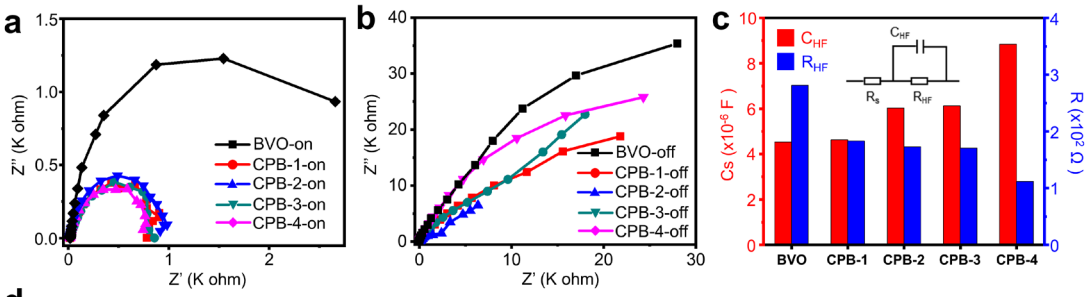


Figure S11. Fluorescence intensity spectra of BVO photoanode and CPB samples.



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Samples	R_s (Ω)	R_{LF} (Ω)	C_{HF} (F)	R_{HF} (Ω)	C_{LF} (F)
BVO	17.11	2850	4.54×10^{-6}	281.2	2.02×10^{-6}
CPB-1	16.56	703	4.62×10^{-6}	183.4	3.48×10^{-6}
CPB-2	17.18	743.1	6.04×10^{-6}	172.9	6.55×10^{-6}
CPB-3	17.26	650.4	6.13×10^{-6}	170.5	7.82×10^{-6}
CPB-4	16.88	587.6	8.84×10^{-6}	112.1	1.70×10^{-5}

Figure S12. The Nyquist plots of EIS measurements of BVO and CPB photoanodes of (a) under illumination, (b) in the dark, with (c) the fitting of the impedance spectrum of R_{HF} and C_{HF}.

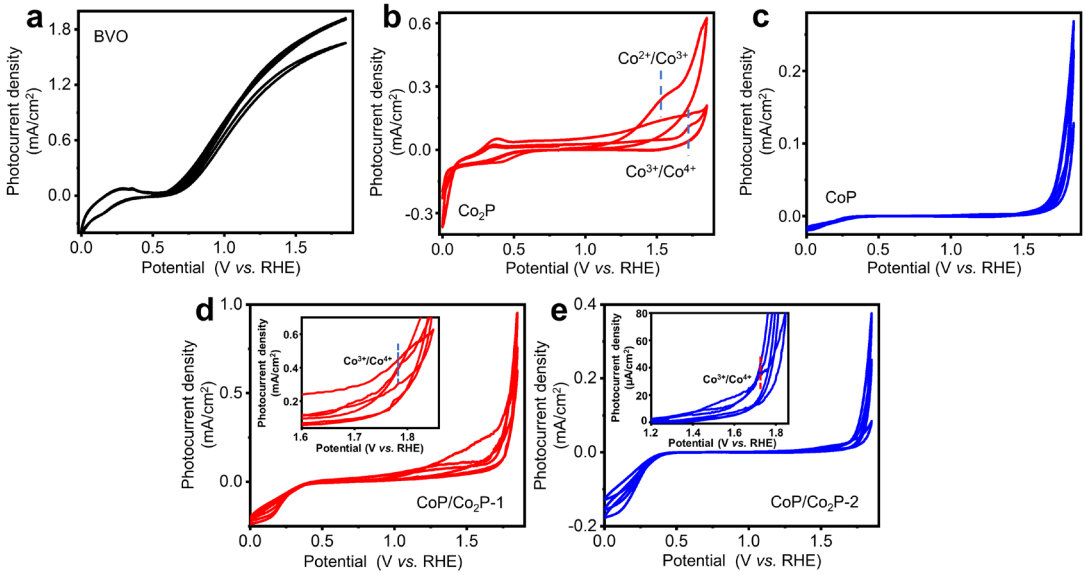

Figure S13. CV curves of (a) BVO, (b) Co_2P, (c) CoP, (d) CoP/Co_2P-1 and (e) CoP/Co_2P-2.

In **Figure S13a**, no apparent peaks can be observed for BVO photoanode at 1.0 to 1.9 V *vs.* RHE. In **Figure S13d** and **13e**, CoP/Co_2P-1 and CoP/Co_2P-2 presented peaks at 1.53 and 1.75 V_{RHE}, which are known as Co^{2+} to Co^{3+} and peaks of Co^{3+} to Co^{4+}.

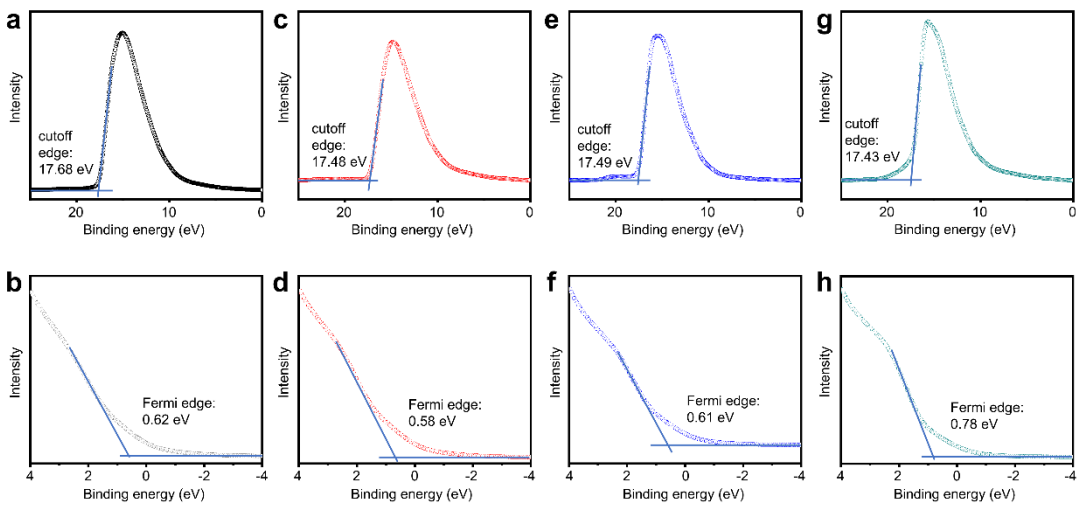

Figure S14. UPS spectra that show the cutoff edge and fermi edge of (a)-(b) CPB-1, (c)-(d) CPB-2, (e)-(f) CPB-3 and (g)-(h) CPB-4.

The cutoff edge of CPB-1, CPB-2, CPB-3 and CPB-4 are 17.68, 17.48, 17.49 and 17.43 eV (**Figure S14a, S14c, S14e,** and **S14g**). The fermi level of CPB-1, CPB-2, CPB-3 and CPB-4 are 0.62, 0.58, 0.61 and 0.78 eV (**Figure S14b, S14d, S14f,** and **S14h**).

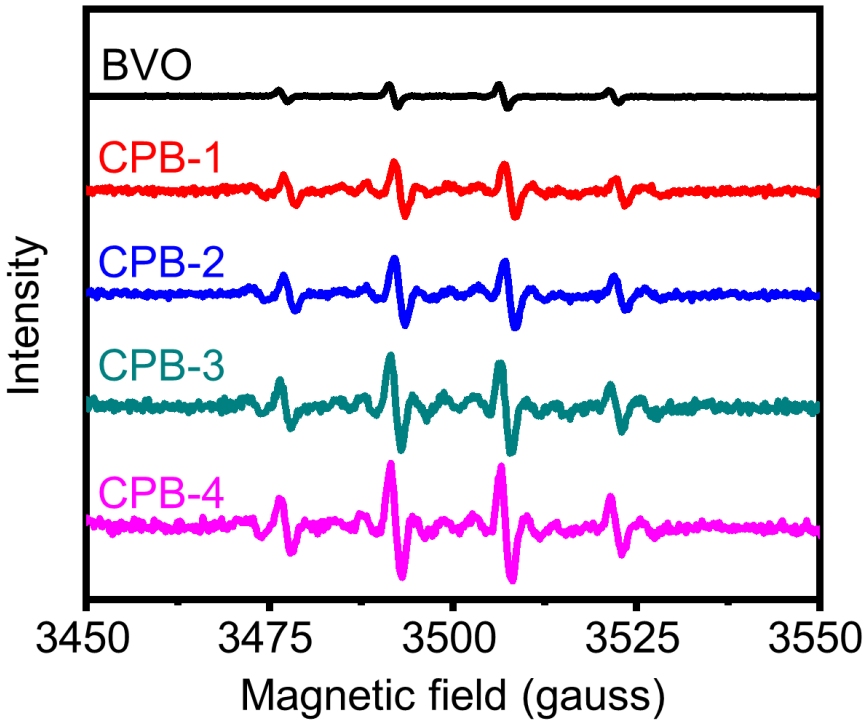

Figure S15. EPR spectra of BVO and CPB photoanodes.

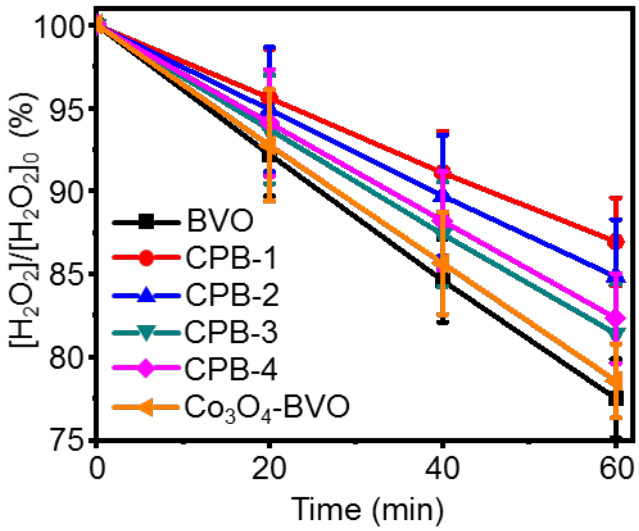

Figure S16. H_2O_2 desorption curves of BVO, CPB and Co_3O_4-BVO photoanodes with three times of independent experiments.

photoanodes for photoanodic H_2O_2 production			
photoanodes	**Electrolyte**	**Production rate (μmol min^{-1} cm^{-2})**	**References**
Co_3O_4/TiO_2	0.5 M $KHCO_3$	0.021 (1 mA at 0.4-1.2 V)	[1]
$WO_3/BiVO_4$	2 M $KHCO_3$	0.022 at 1.5 V *vs.* RHE	[2]
$WO_3/BiVO_4$	2 M $KHCO_3$	0.066 at 1.23 V *vs.* RHE	[3]
$BiVO_4$-Air/V	1 M $NaHCO_3$	0.092 at 1.23 V *vs.* RHE	[4]
CPB	1 M $KHCO_3$	0.16 at 1.7 V *vs.* RHE	This work

Table S1. Summary of reported photoanodes and this work for photoanodic H_2O_2 production.

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