Supplementary information

High-efficiency unbiased water splitting with photoanodes harnessing polycarbazole hole transport layers

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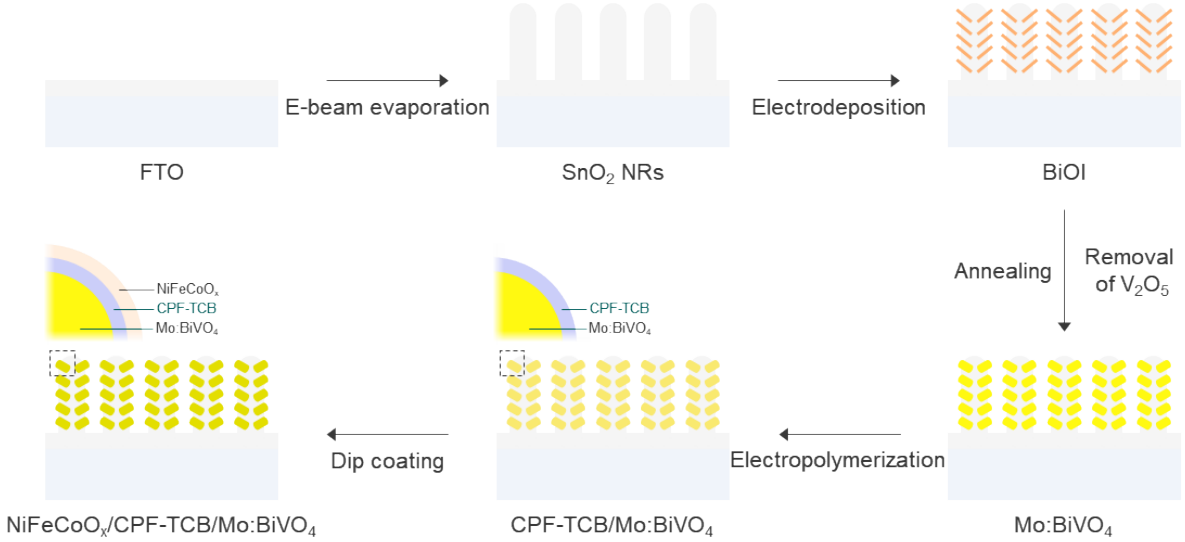

Fig. S1 Schematic illustration of $NiFeCoO_x$/CPF-TCB/Mo:$BiVO_4$ photoanode fabrication process.

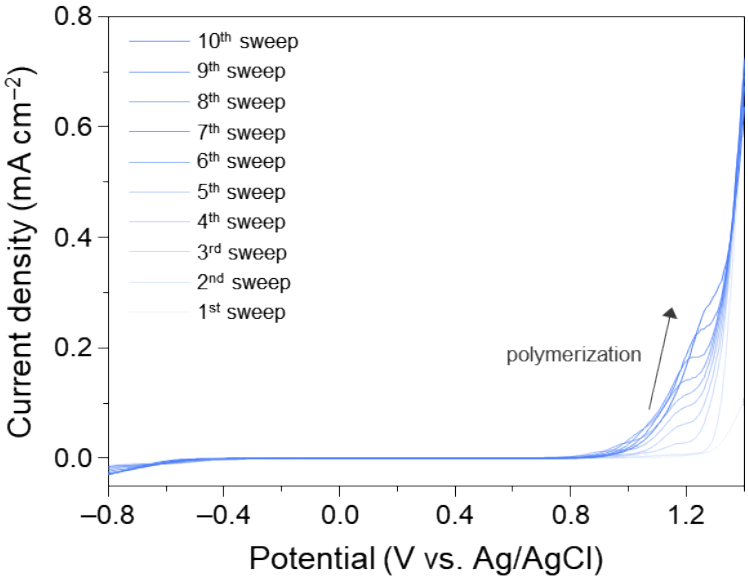

Fig. S2 *J-V* curves for electropolymerization of CPF-TCB on Mo:$BiVO_4$.

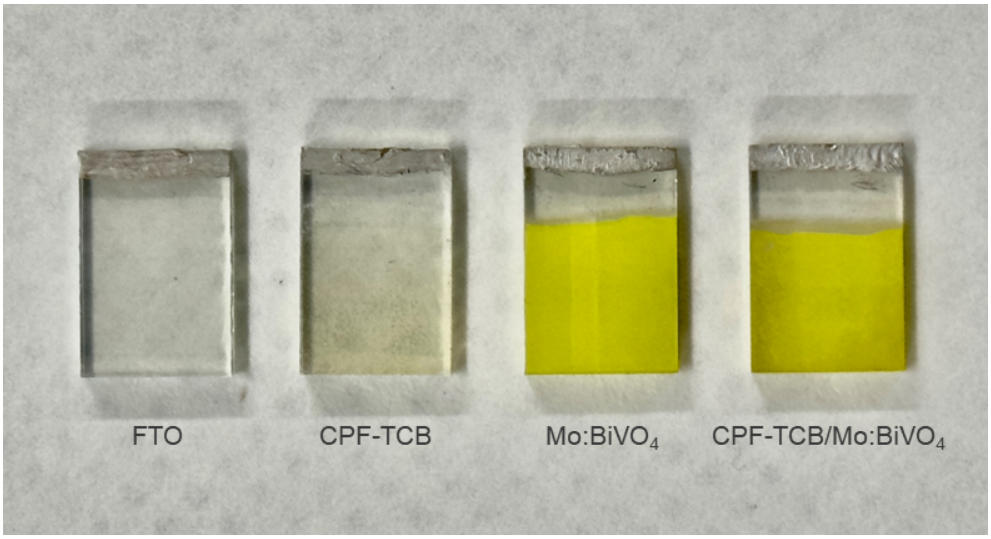

Fig. S3 Photographs of fabricated samples.

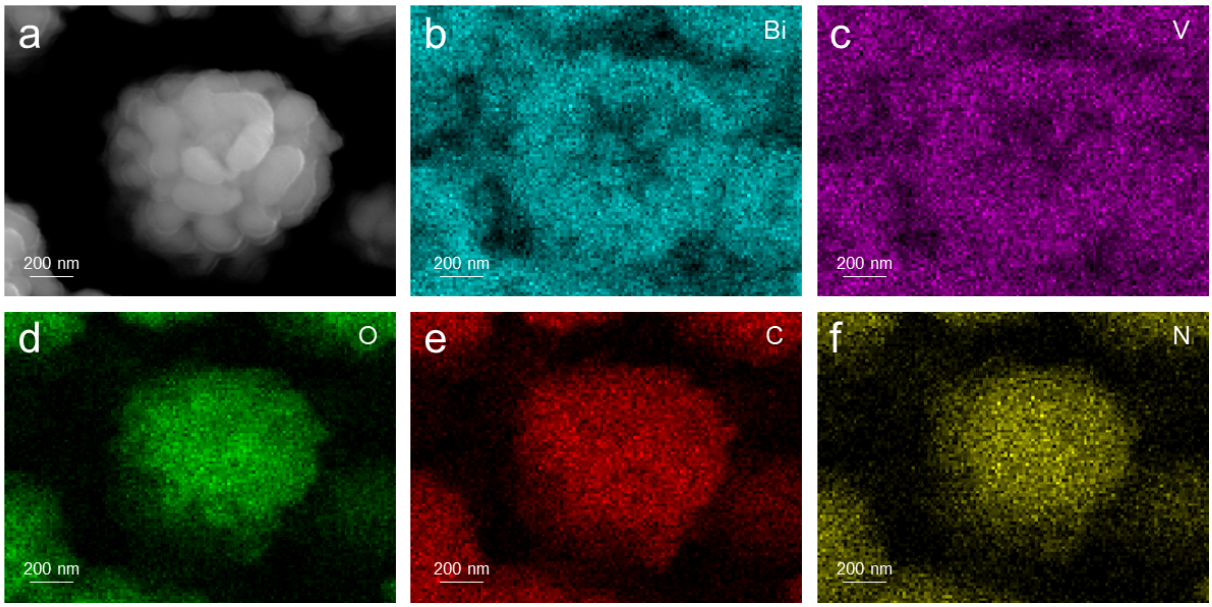

Fig. S4 (a) Top SEM image of CPF-TCB/Mo:$BiVO_4$ and EDX mapping of (b) Bi, (c) V, (d) O, (e) C, and (f) N.

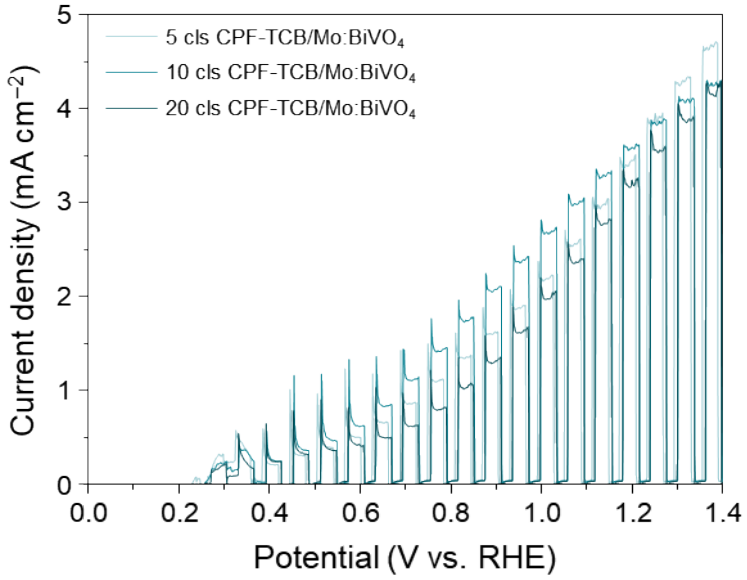

Fig. S5 *J-V* curves of CPF-TCB/Mo:$BiVO_4$ with different thicknesses of CPF-TCB in K-B_i buffer (pH 9.5).

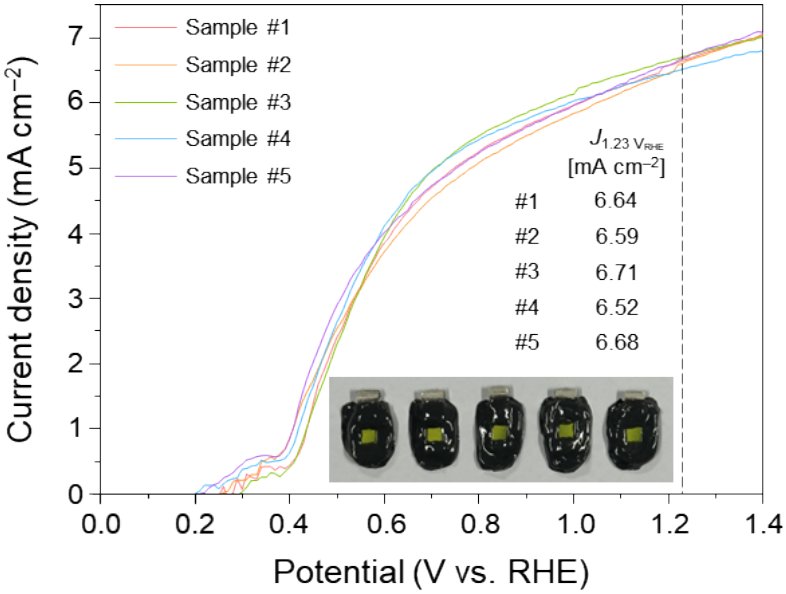

Fig. S6 *J-V* curves of different $NiFeCoO_x$/CPF-TCB/Mo:$BiVO_4$ photoanodes manufactured with the same process.

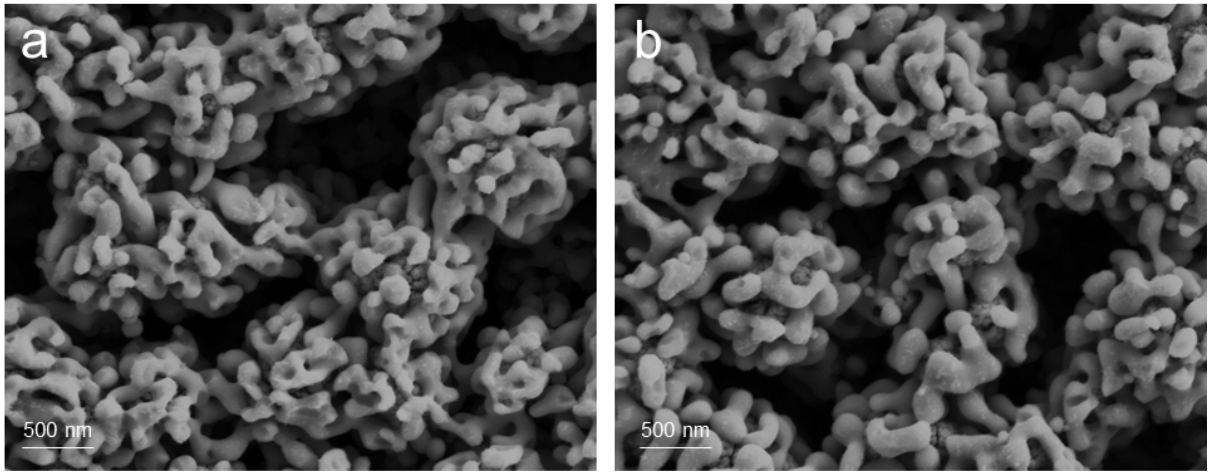

Fig. S7 Top SEM images of $NiFeCoO_x$/CPF-TCB/Mo:$BiVO_4$ (a) before and (b) after the LSV measurement.

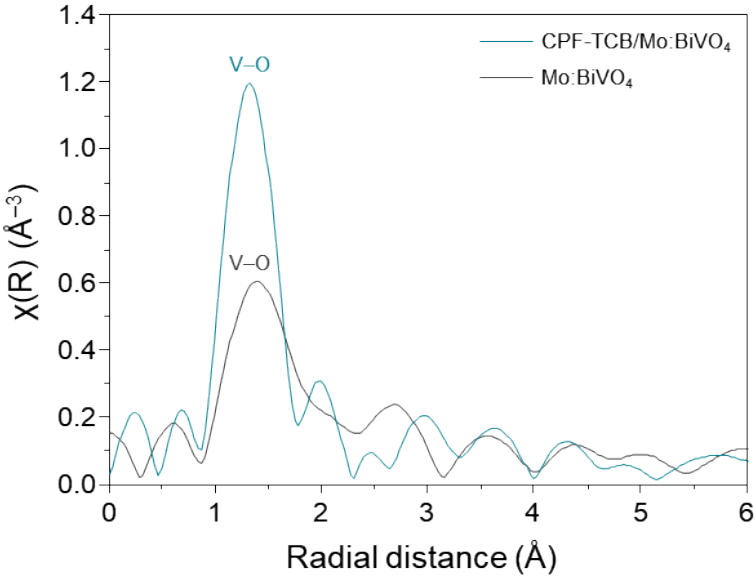

Fig. S8 Fourier transformed V *K*-edge EXAFS spectra of Mo:$BiVO_4$ and CPF-TCB/Mo:$BiVO_4$.

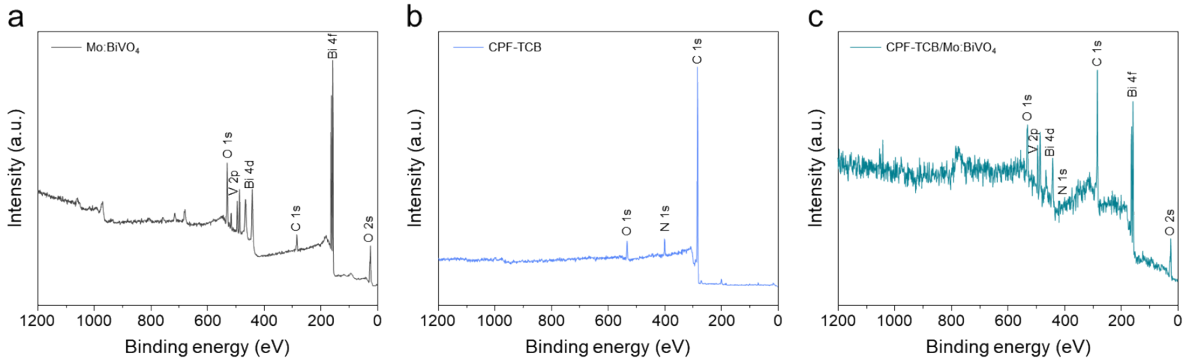

Fig. S9 XPS wide spectra of (a) Mo:$BiVO_4$, (b) CPF-TCB, and (c) CPF-TCB/Mo:$BiVO_4$.

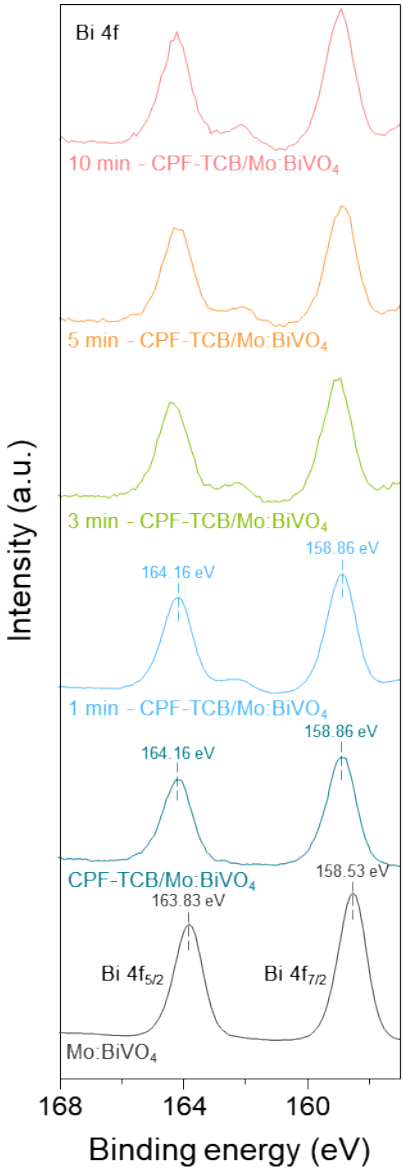

Fig. S10 Bi 4f XPS spectra of Mo:$BiVO_4$ and CPF-TCB/Mo:$BiVO_4$ with different Ar plasma etching times.

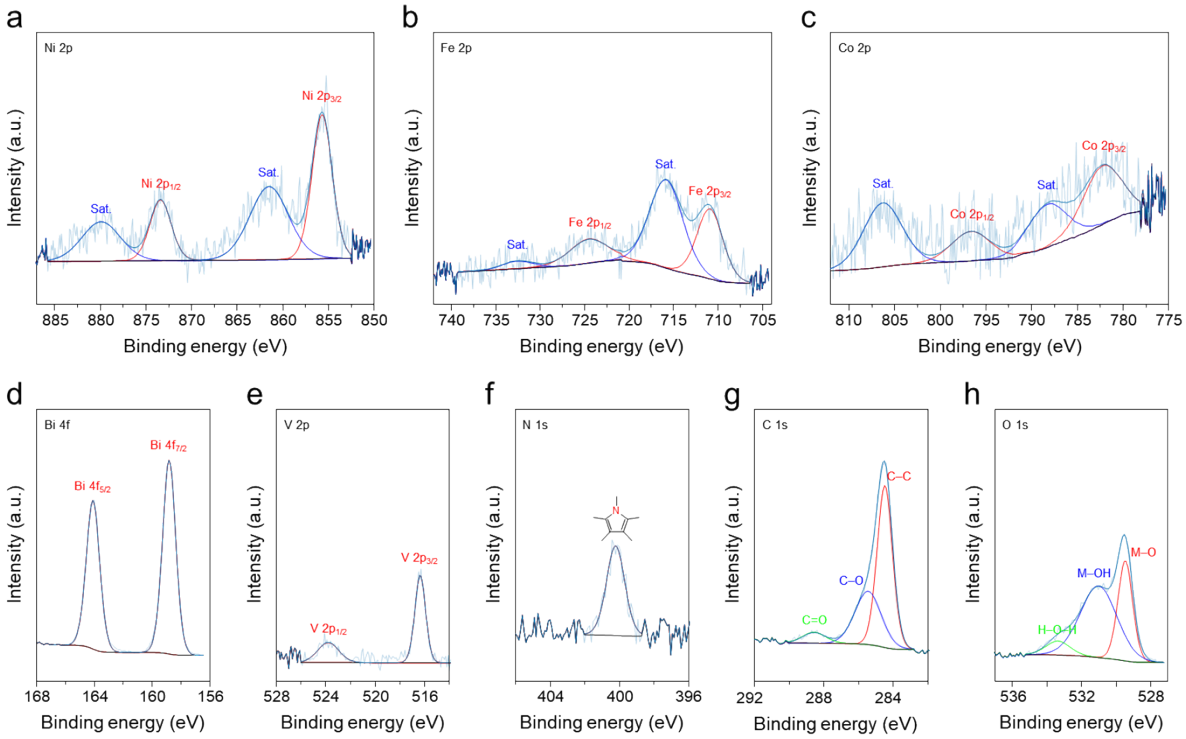

Fig. S11 a) Ni 2p, (b) Fe 2p, (c) Co 2p, (d) Bi 4f, (e) V 2p, (f) N 1s, (g) C 1s, and (h) O 1s XPS spectra of $NiFeCoO_x$/CPF-TCB/Mo:$BiVO_4$.

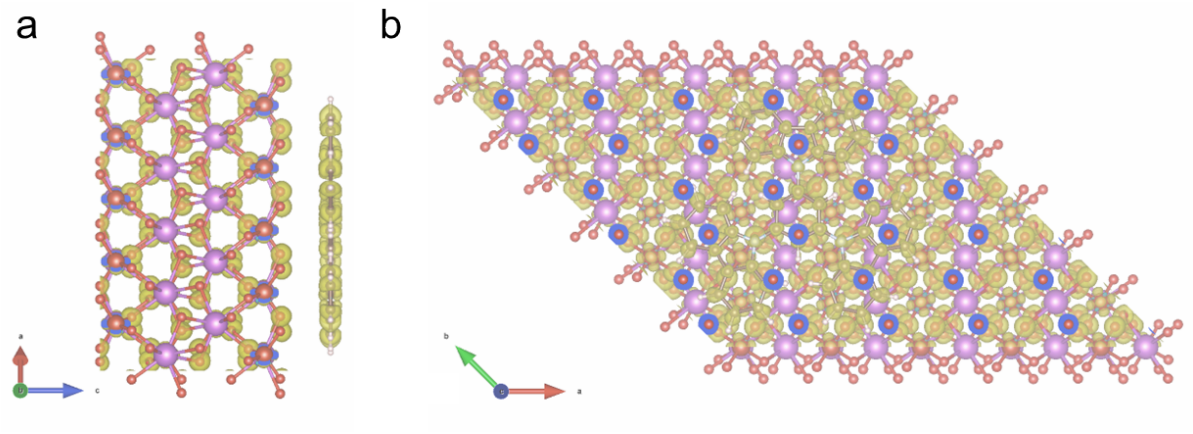

Fig. S12 Optimized structures of CPF-TCB/$BiVO_4$ in (a) side and (b) top view for DFT calculations.

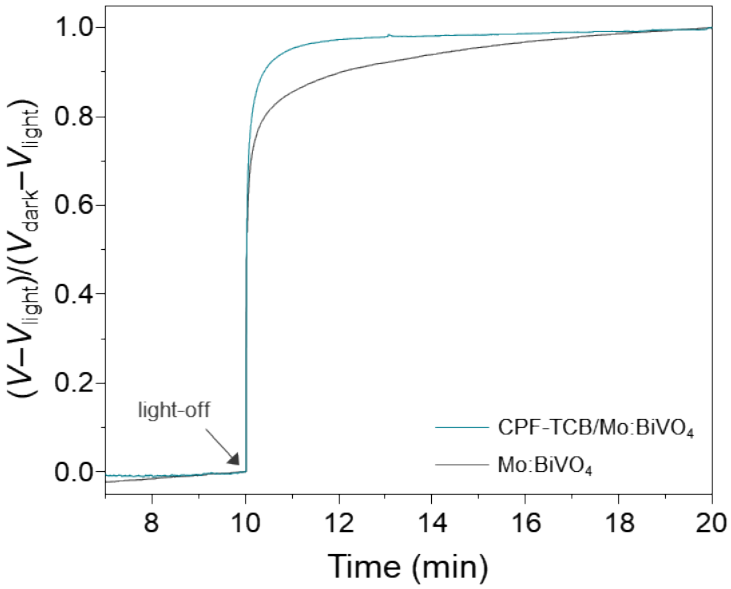

Fig. S13 Normalized OCP decay profiles of Mo:$BiVO_4$ and CPF-TCB/Mo:$BiVO_4$.

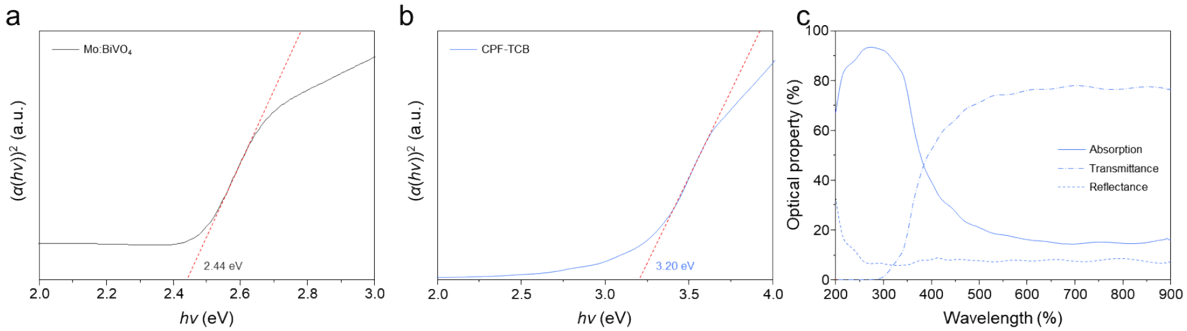

Fig. S14 UV-vis Tauc plots and optical band gaps of (a) Mo:$BiVO_4$ and (b) CPF-TCB. (c) UV-vis spectra of CPF-TCB.

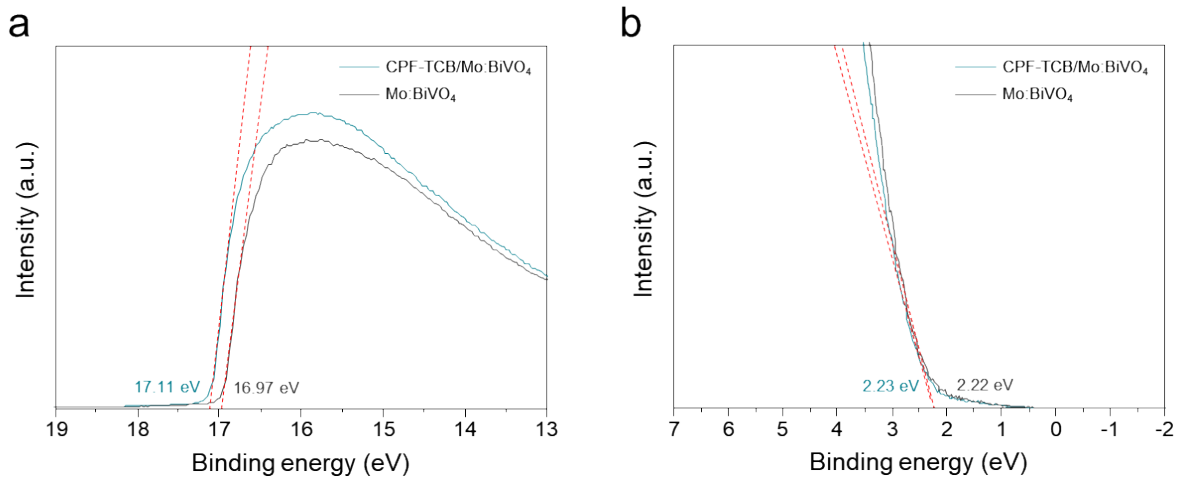

Fig. S15 UPS (a) SEE spectra and (b) VB spectra of Mo:$BiVO_4$ and CPF-TCB/Mo:$BiVO_4$.

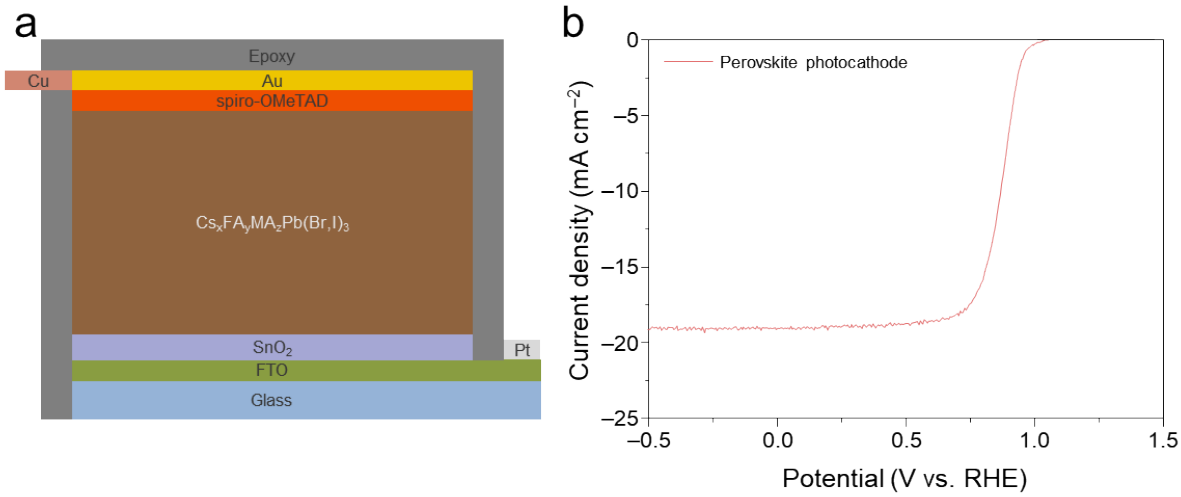

Fig. S16 (a) Schematic illustration and (b) 3 electrode *J*-*V* curves of the perovskite photocathode in K-P_i buffer (pH 7).

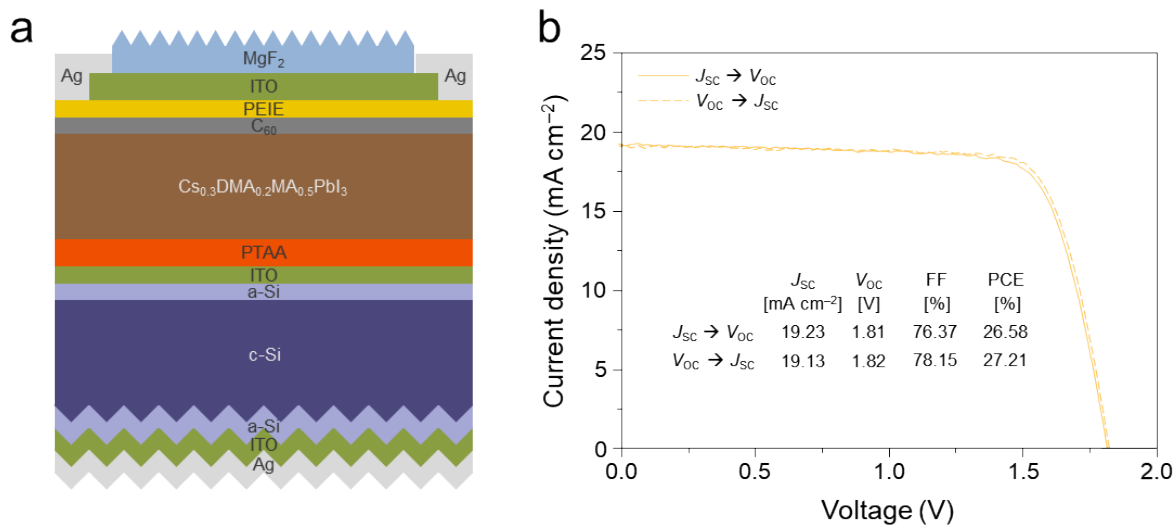

Fig. S17 (a) Schematic illustration and (b) 2 electrode *J*-*V* curves of the perovskite/Si tandem solar cell.

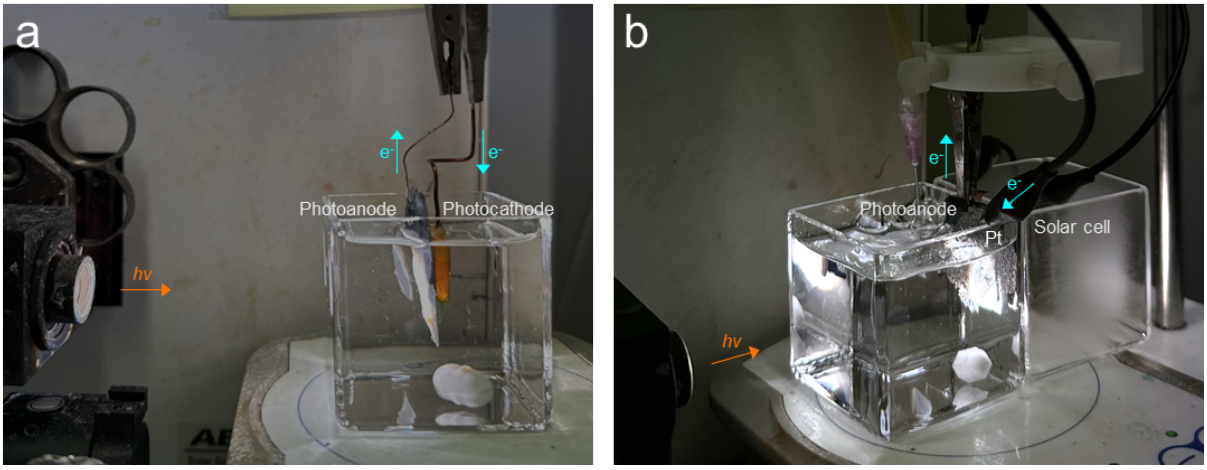

Fig. S18 Photographs of (a) PA-PC and (b) PV-PA tandem devices.

Table S1. Series resistances (R_s), charge transport resistances (R_{sc}), charge transfer resistances (R_{ct}), and chi-squared (X^2) values fitted from EIS curves.

Photoanodes	R_s [Ω cm^2]	R_{sc} [Ω cm^2]	R_{ct} [Ω cm^2]	X^2 [10^{-3}]
$NiFeCoO_x$/CPF-TCB/Mo:$BiVO_4$	4.192	5.525	41.45	6.118
$NiFeCoO_x$/Mo:$BiVO_4$	4.233	36.13	42.65	6.051

Table S2. Donor densities (N_D) of photoanodes calculated by M-S plots

Photoanodes	N_D **[10^{20} cm^{-3}]**
CPF-TCB/Mo:$BiVO_4$	2.125
Mo:$BiVO_4$	1.438

Table S3. Fitting parameters and chi-squared (X^2) values of the TRPL.

Photoanodes	A_1 **[%]**	τ_1 **[ns]**	A_2 **[%]**	τ_2 **[ns]**	τ_{avg} **[ns]**	X^2
CPF-TCB/Mo:$BiVO_4$	30.32	1.750	69.68	0.2058	0.6740	1.499
Mo:$BiVO_4$	44.89	3.899	55.11	0.1455	1.830	2.082

Table S4. STH conversion efficiency benchmarks of PA-PC tandem devices in mode T.

Year	Photoanode	Photocathode	STH [%]	Ref
this work	**$NiFeCoO_x$/CPF-TCB/Mo:$BiVO_4$/SnO_2**	**Pt/ITO/SnO_2/Perovskite/spiro-OMeTAD/Au**	**6.75**	
2022	NiCoFe-B_i/CPF-TCzB/Sb_2S_3	Pt/TiO_2/p-Si/SLG	5.21	1
2022	RuO_2/PDDA/Sb_2S_3/TiO_2	Pt/TiO_2/p-Si	4.92	2
2021	Co_4O_4/pGO/$BiVO_4$/SnO_x	Pt/TiO_x/PIP/CuO_x	4.30	3
2018	$NiFeO_x$-B_i/$BiVO_4$	Pt/CdS/$CuIn_{0.5}Ga_{0.5}Se_2$/Mo	3.70	4
2021	$NiFeO_x$/CTF-BTh/Mo:$BiVO_4$	MoS_x/CTF-BTh/Cu_2O/Au	3.24	5
2021	$NiFeO_x$-B_i/$BiVO_4$	Pt/HfO_2/CdS/HfO_2/Cu_2ZnSnS_4/Mo	3.17	6
2018	$NiFeO_x$/Mo:$BiVO_4$	RuO_x/TiO_2/Ga_2O_3/Cu_2O/Au	3.00	7
2023	NiFe/Mo:$BiVO_4$/SnO_2	Pt/TiO_2/CdS/Bi_2S_3/Cu_3BiS_3/Au	2.33	8
2018	NiOOH/FeOOH/Mo:$BiVO_4$	NiMo/SiO_2/n^+p-Si	2.10	9
2021	Co-P_i/$BiVO_4$	Pt/TiO_2/CdS/Cu_3BiS_3/Mo	2.04	10
2020	NiOOH/FeOOH/$BiVO_4$	Pt/TiO_2/n-Si/TiO_2/Ni	1.90	11
2021	NiFe/Mo:$BiVO_4$/SnO_2	Pt/Ga_2O_3/CdS/SnS/Au	1.70	12

Table S5. STH conversion efficiency benchmarks of PV-PA tandem devices in mode T.

Year	Photoanode	Solar cell	STH [%]	Ref
this work	**$NiFeCoO_x$/CPF-TCB/Mo:$BiVO_4$/SnO_2**	**Perovskite/Si**	**9.0**	
2015	Co-P_i/$BiVO_4$/WO_3	GaAs/InGaAsP	8.1	[13]
2019	NiOOH/FeOOH/$BaSnO_{3-x}$	Perovskite	7.9	[14]
2016	NiOOH/FeOOH/$BiVO_4$ // Ni_2FeO_x/Fe_2O_3 (dual PA)	2jn c-Si	7.7	[15]
2021	NiFe/$BiVO_4$/SnO_2	Perovskite/Si	7.3	[16]
2016	NiOOH/FeOOH/W,Mo:$BiVO_4$/WO_3	Dye-sensitized	7.1	[17]
2023	$BiVO_4$/SnO_2	Perovskite	7.0	[18]
2018	2 × NiOOH/FeOOH/$BiVO_4$ (dual PA)	Perovskite	6.5	[19]
2017	NiOOH/FeOOH/Mo:$BiVO_4$/SnO_2	Perovskite	6.3	[20]
2016	$Ni(OH)_2$/$Fe(OH)_2$/Mo:$BiVO_4$/SnO_2	Perovskite	6.2	[21]
2023	$NiFeO_x$/$BiVO_4$/In_2O_3	Perovskite/Si	6.1	[22]
2015	NiOOH/FeOOH/W,Mo:$BiVO_4$/WO_3	Dye-sensitized	5.7	[23]
2013	Co-P_i/W:$BiVO_4$	2jn a-Si	4.9	[24]

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