Supporting Information

Alkali-Assisted Synthesis of Polymeric Carbon Nitride Photoanodes with Defect and Crystallinity-Mediated Charge Transfer for Efficient Photoelectrochemical Water Splitting

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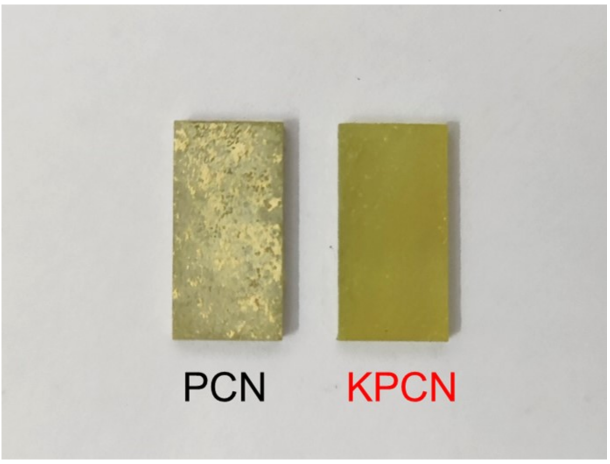

Figure S1. The digital photograph of PCN and KPCN.

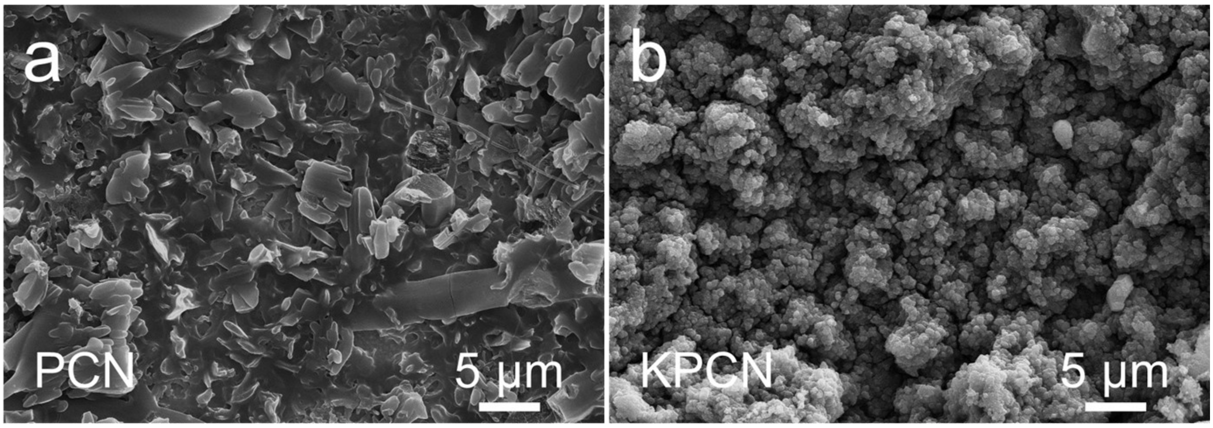

Figure S2. Top view SEM images of (a) PCN and (b) KPCN.

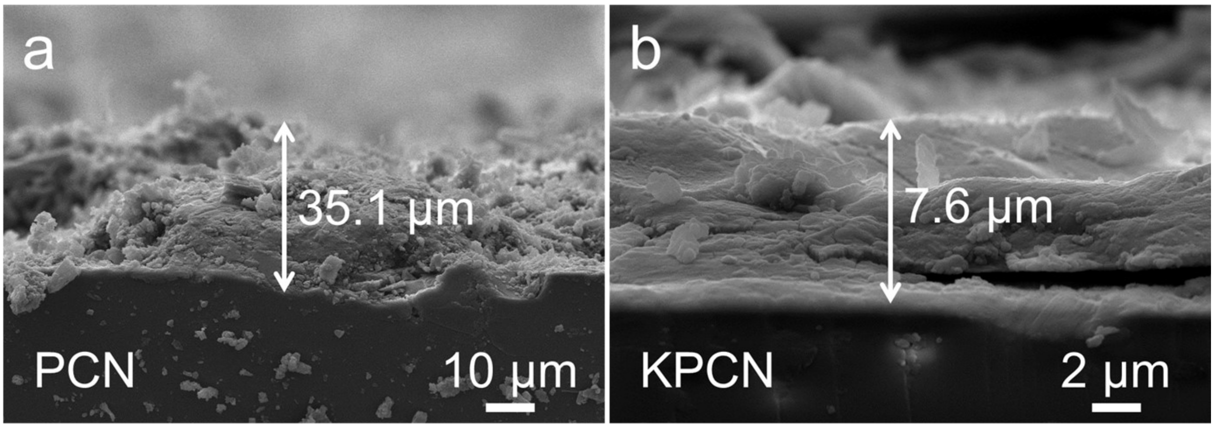

Figure S3. Cross-sectional view SEM images of (a) PCN and (b) KPCN.

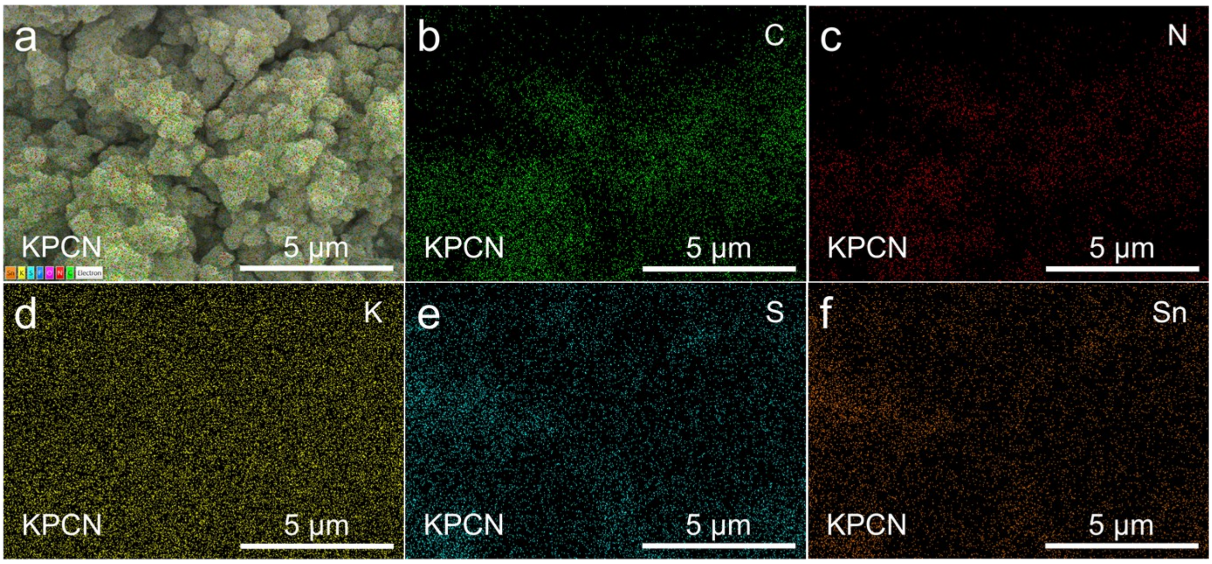

Figure S4. (a) SEM image of the KPCN photoanode surface and the corresponding EDS elemental mapping: (b) C, (c) N, (d) K, (e) S and (f) Sn.

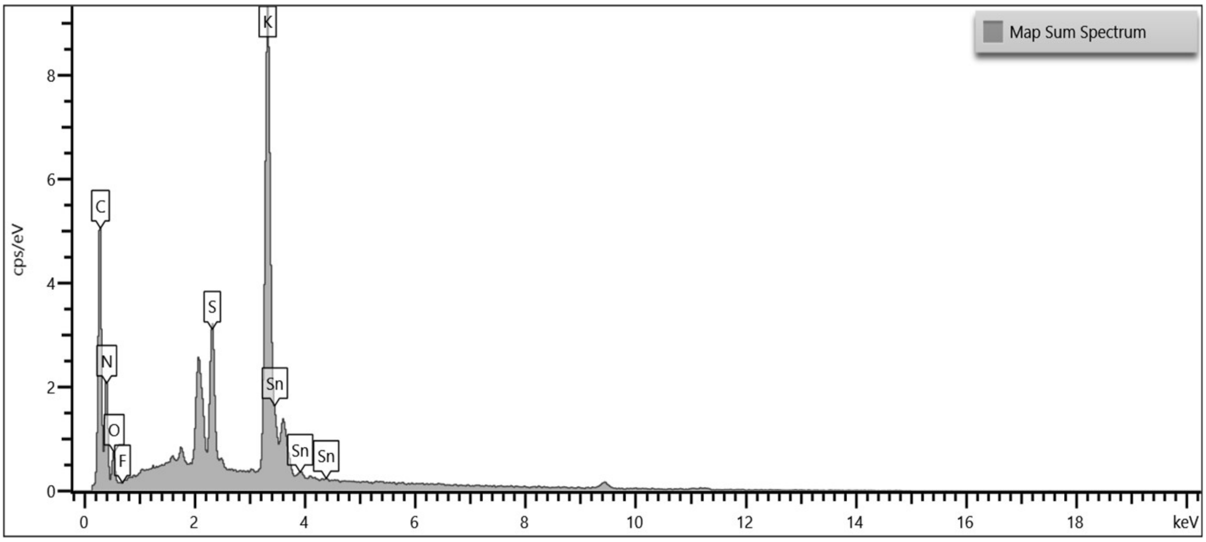

Figure S5. EDS results of the KPCN films.

Table S1. The detail of the elemental analysis of the KPCN films.

Element	Line Type	Apparent Concentration	k Ratio	Wt%	Wt% Sigma	Atomic %	Standard Label	Factory Standard
C	K series	17.49	0.17492	27.23	1.01	39.85	C Vit	Yes
N	K series	29.54	0.05260	32.11	2.16	40.29	BN	Yes
O	K series	2.79	0.00939	5.50	0.34	6.04	SiO2	Yes
F	K series	0.00	0.00000	0.00	0.14	0.00	CaF2	Yes
S	K series	6.30	0.05430	4.56	0.17	2.50	FeS2	Yes
K	K series	30.74	0.26038	22.54	0.75	10.13	KBr	Yes
Sn	L series	7.85	0.07847	8.05	0.43	1.19	Sn	Yes
Total:	-	-	-	100.00	-	100.00	-	-

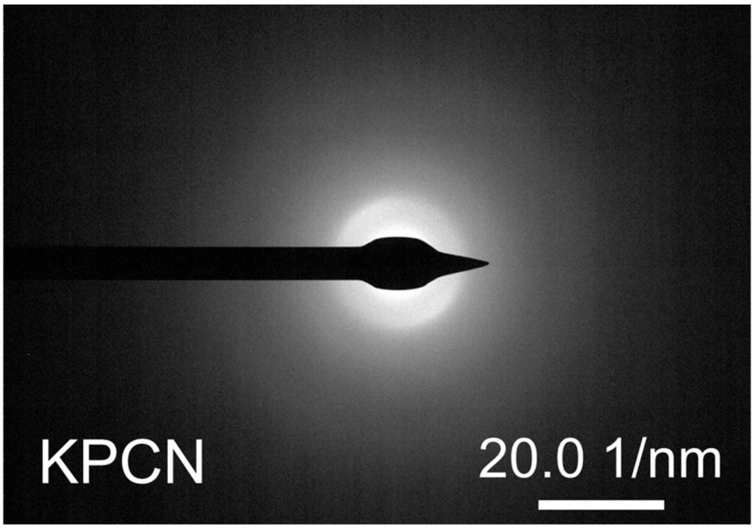

Figure S6. SAED pattern of the KPCN films

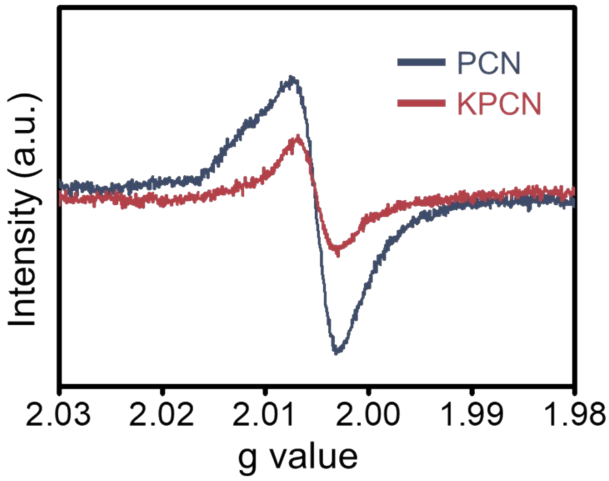

Figure S7. EPR spectra of the powder samples scraped from the PCN and KPCN photoanodes conducted in the dark at room temperature.

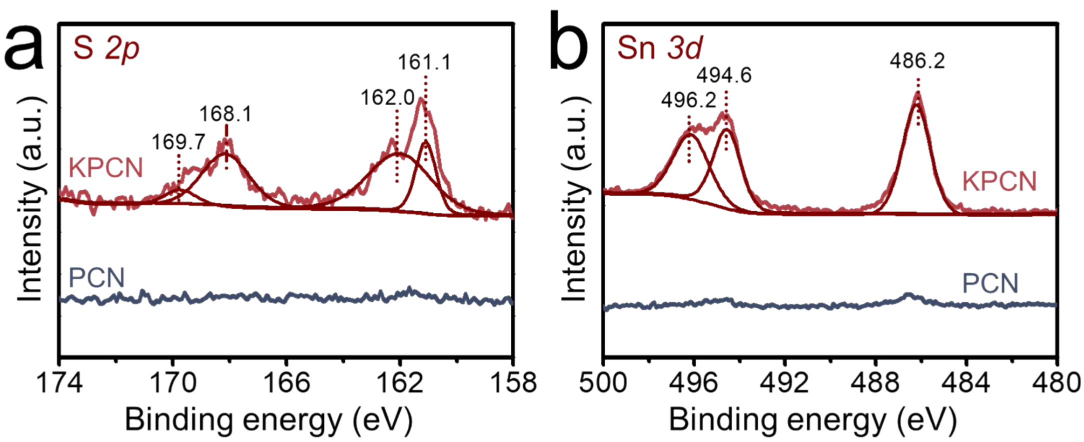

Figure S8. High-resolution XPS spectra of PCN and KPCN: (a) S *2p* and (b) Sn *3d*.

Table S2. Summary of PEC performance of this work and the reported PCN-based photoanodes.

Catalyst	Photocurrent density (μA cm^{-2})	Potential vs RHE (V)	Electrolyte	Light source	Corresponding Author (Ref.)
KPCN photoanode	*ca.* 162	1.23	1.0 M NaOH	300 W Xe lamp, AM 1.5G	This work
K-PHI photoanode	*ca.* 800	1.23	1.0 M NaOH	100 mW cm^{-2}, AM 1.5G (Newport)	[1]
CN-MR/$NiFeO_xH_y$ electrode	472 ± 10	1.23	0.1 M KOH	100 mW cm^{-2}, AM 1.5G (Newport)	[2]
CN_{TM} photoanode	353	1.23	0.1 M KOH	100 mW cm^{-2}, AM 1.5G (Newport)	[3]
CN-$MSG_{0.75}$/M photoanode	270	1.23	0.1 M KOH	100 mW cm^{-2}, AM 1.5G (Newport)	[4]
DPCN photoanode	242	1.23	0.5 M H_2SO_4	150 W Xe lamp, AM 1.5G	[5]
CNP films	230	1.23	0.5 M Na_2SO_4	Xe lamp, AM 1.5G	[6]
CN films	228.2	1.23	0.2 M Na_2SO_4	150 W Xe lamp, AM 1.5G (Newport)	[7]
2CSCN films	200	1.23	1.0 M NaOH	100 mW cm^{-2}, AM 1.5G (Newport)	[8]
P/B-layer-doping C_3N_4 photoanode	150 ± 10	1.23	0.1 M Na_2SO_4	300 W Xe lamp, AM 1.5G	[9]
CN-MeM/$M_{0.20}$	133	1.23	0.1 M KOH	100 mW cm^{-2}, AM 1.5G (Newport)	[10]
In situ grown porous CN/rGO films	124.5	1.23	0.1 M KOH	100 mW cm^{-2}, AM 1.5G (Newport)	[11]
g-CN PNR array photoanode	120.5	1.23	0.1 M Na_2SO_4	500 W Xe lamp, AM 1.5G	[12]
5p-PCN films	ca. 120	1.23	1.0 M NaOH	100 mW cm^{-2}, AM 1.5G (Newport)	[13]
phosphorylated PCN films	ca. 120	1.23	1.0 M NaOH	100 mW cm^{-2}, AM 1.5G	[14]

				(Newport)	
SOCN-75 films	119.2	1.23	0.1 M Na_2SO_4	150 W Xe lamp, AM 1.5G (Newport)	15
CN films	116	1.23	0.1 M KOH	100 mW cm^{-2}, AM 1.5G (Newport)	16
PCN photoanode	ca. 110	1.23	1.0 M NaOH	100 mW cm^{-2}, AM 1.5G (Newport)	17
CN-$U_{10}M_{0.5}$ photoelectrode	ca. 110	1.23	0.1 M KOH	100 mW cm^{-2}, AM 1.5G (Newport)	18
Boron-doped CN films	103.2	1.23	0.1 M Na_2SO_4	150 W Xe lamp, AM 1.5G	19
PCN films	100	1.23	1.0 M NaOH	100 mW cm^{-2}, AM 1.5G (Newport)	20
Thio-CA films	96.2	1.23	0.2 M Na_2SO_4	150 W Xe lamp, AM 1.5G (Newport)	21
CN-$rGO_{0.5}$ films	72	1.23	0.1 M KOH	100 mW cm^{-2}, AM 1.5G (Newport)	22

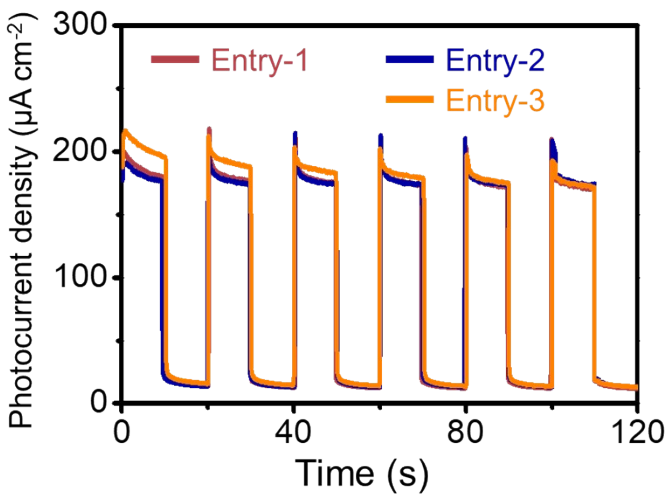

Figure S9. Chronoamperometric measurements of the KPCN photoanodes prepared in three individual synthetic batches in 1.0 M NaOH aqueous solution at 1.23 V *vs.* RHE, on/off cycling of AM 1.5G illumination.

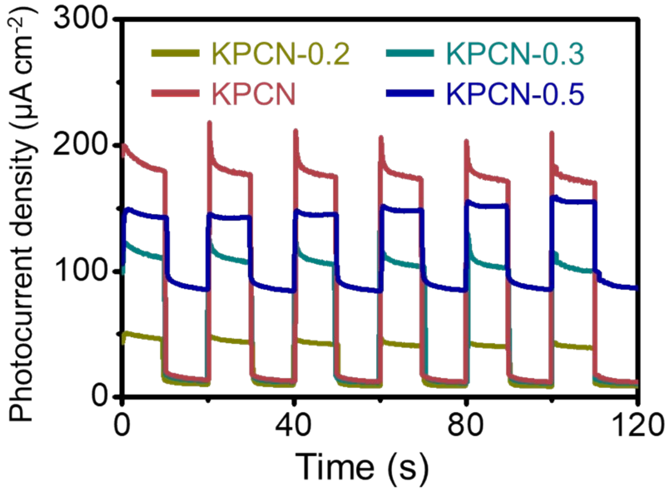

Figure S10. Chronoamperometric measurements of the KPCN photoanodes prepared using the precursor mixture with different KOH amounts in 1.0 M NaOH aqueous solution at 1.23 V *vs.* RHE, on/off cycling of AM 1.5G illumination.

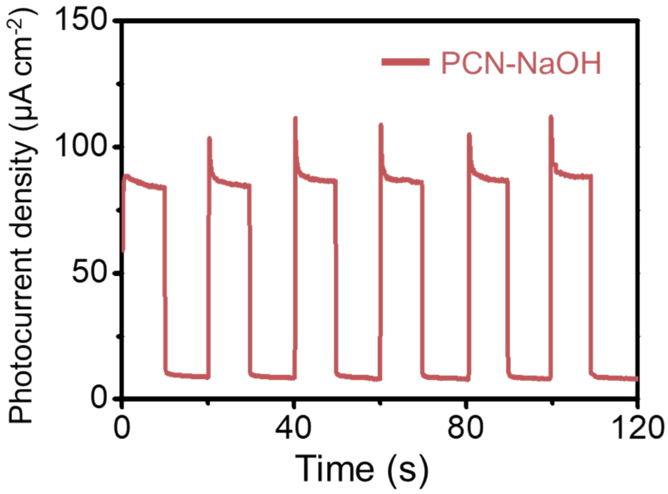

Figure S11. Chronoamperometric measurements of the PCN-NaOH photoanodes prepared using the precursor mixture with 2.5 g NH_4SCN, 0.5 g M400 and 0.4 g NaOH in 1.0 M NaOH aqueous solution at 1.23 V *vs.* RHE, on/off cycling of AM 1.5G illumination.

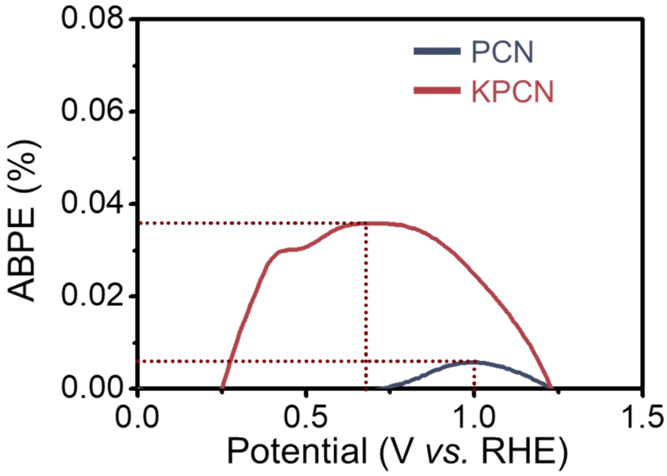

Figure S12. ABPE curves of PCN and KPCN calculated from LSV curves.

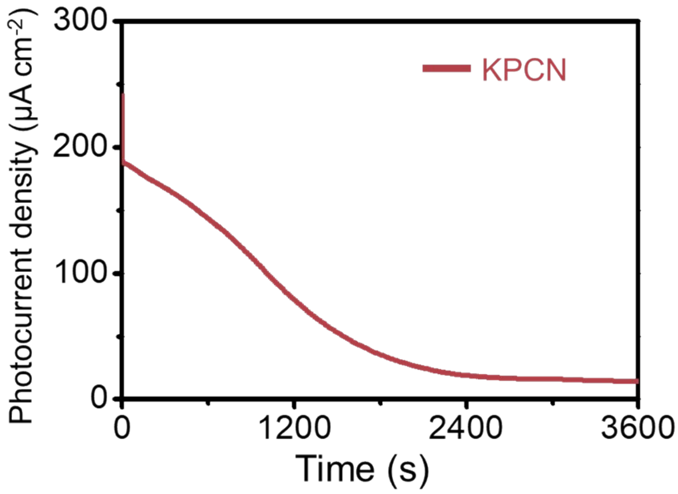

Figure S13. Stability measurements of the KPCN photoanode at 1.23 V *vs.* RHE in 1.0 M NaOH aqueous solution under AM 1.5G illumination.

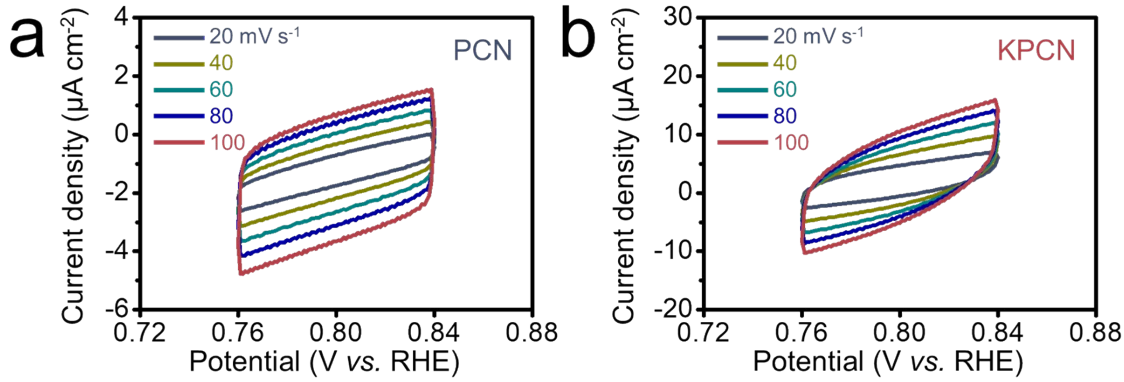

Figure S14. Cyclic voltammetry curves of (a) PCN and (b) KPCN in the region of 0.76~0.84 V *vs.* RHE under dark.

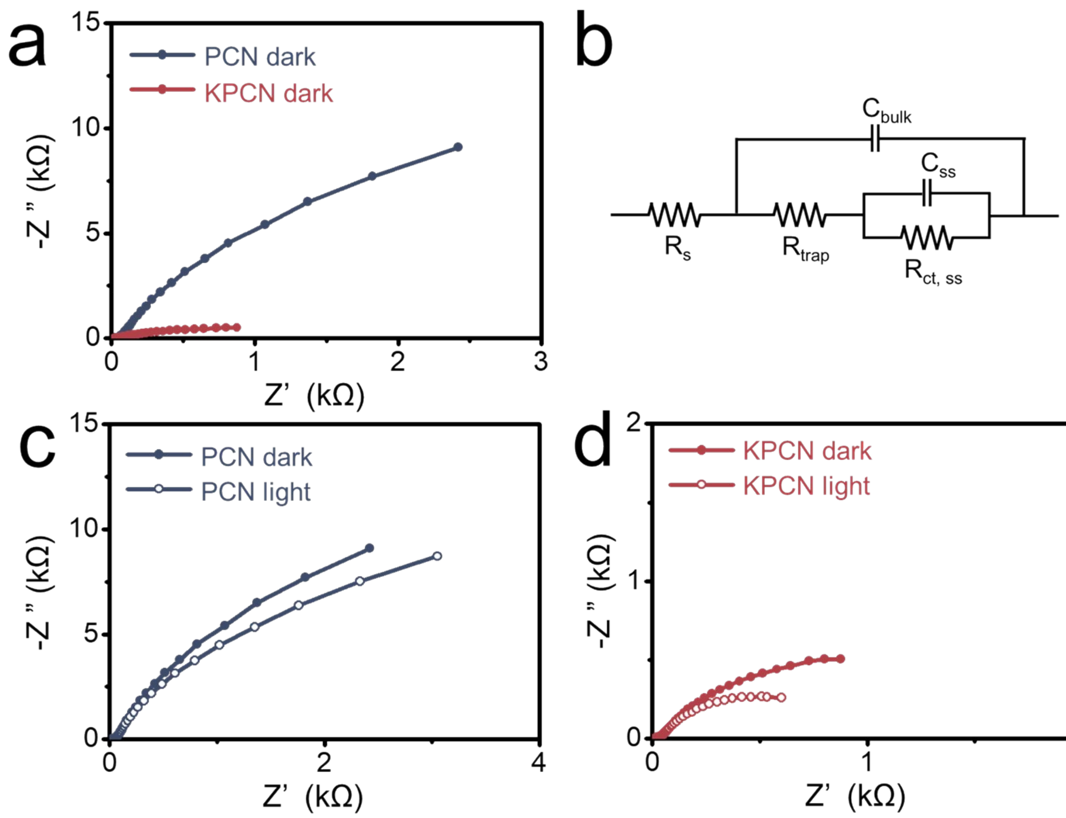

Figure S15. (a) Nyquist plots of PCN and KPCN without illumination. (b) the equivalent circuit, which can be fitted to result series resistance (R_s), the charge transfer resistance from the surface to solution ($R_{ct,\ ss}$), the space charge capacitance (C_{bulk}), the trapping of holes in the surface states (R_{trap}) and steady state concentration of trapped holes (C_{ss}). (c) Nyquist plots of PCN under AM 1.5G illumination and off. (d) Nyquist plots of KPCN under AM 1.5G illumination and off.

Table S3. Fitted parameters for electrochemical impedance spectroscopy results.

Samples	R_s (Ω)	R_{trap} (Ω)	C_{bulk} (F)	$R_{ct, ss}$ (Ω)	C_{ss} (F)
PCN dark	17.46	53.13	12.61×10^{-6}	822850	9.01×10^{-6}
KPCN dark	12.25	41.63	76.39×10^{-6}	1468	98.73×10^{-6}

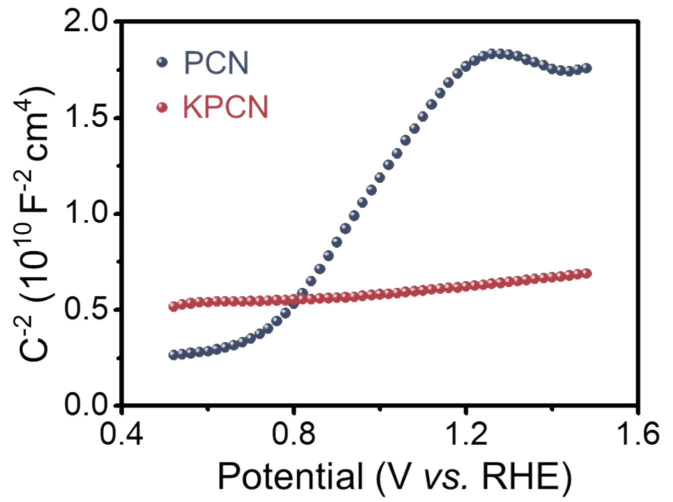

Figure S16. Mott-Schottky plots of PCN and KPCN at 1000 Hz without illumination.

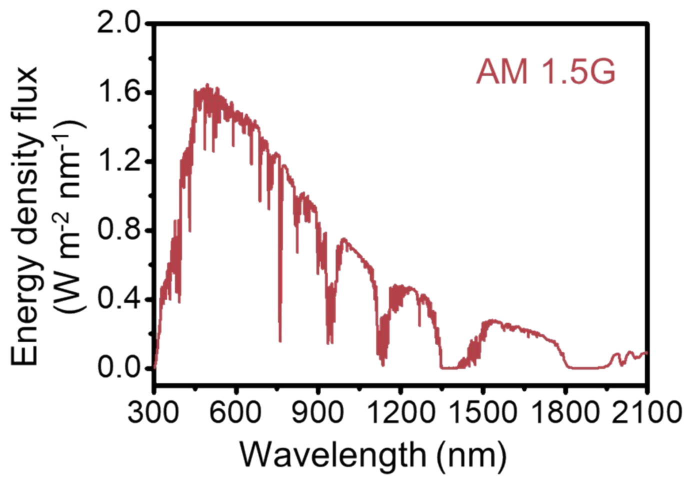

Figure S17. Energy density flux for the standard solar spectrum of AM 1.5G.

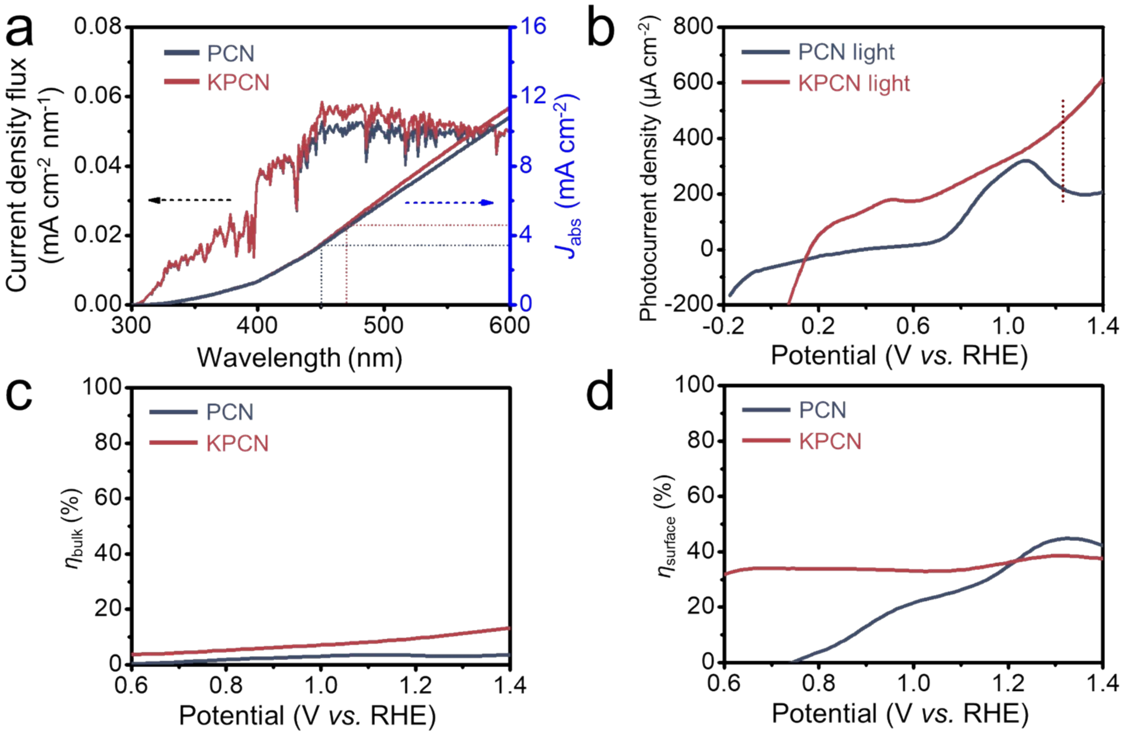

Figure S18. (a) The calculated current density fluxes and the integrated current densities (J_{abs}) of PCN and KPCN. (b) LSV curves of PCN and KPCN measured in the electrolytes of 1.0 M NaOH containing 0.5 M Na_2SO_3 under AM 1.5G illumination. (c) bulk charge separation efficiencies (η_{bulk}) of PCN and KPCN. (d) surface charge injection efficiencies ($\eta_{surface}$) of PCN and KPCN.

Reference

1. X. Li, X. Chen, Y. Fang, W. Lin, Y. Hou, M. Anpo, X. Fu and X. Wang, *Chem. Sci.*, 2022, **13**, 7541-7551.
2. N. Karjule, C. Singh, J. Barrio, J. Tzadikov, I. Liberman, M. Volokh, E. Palomares, I. Hod and M. Shalom, *Adv. Funct. Mater.*, 2021, **31**, 2101724.
3. J. Qin, J. Barrio, G. Peng, J. Tzadikov, L. Abisdris, M. Volokh and M. Shalom, *Nat. Commun.*, 2020, **11**, 4701.
4. N. Karjule, J. Barrio, L. Xing, M. Volokh and M. Shalom, *Nano Lett.*, 2020, **20**, 4618-4624.
5. X. Fan, Z. Wang, T. Lin, D. Du, M. Xiao, P. Chen, S. A. Monny, H. Huang, M. Lyu, M. Lu and L. Wang, *Angew. Chem. Int. Ed.*, 2022, **61**, e202204407.
6. Q. Jia, S. Zhang, Z. Gao, P. Yang and Q. Gu, *Catal. Sci. Technol.*, 2019, **9**, 425-435.
7. W. Xiong, S. Chen, M. Huang, Z. Wang, Z. Lu and R. Q. Zhang, *Chemsuschem*, 2018, **11**, 2497-2501.

8. X. Li, J. Wang, J. Xia, Y. Fang, Y. Hou, X. Fu, M. Shalom and X. Wang, *Chemsuschem*, 2022, **15**, e202200330.
9. P. Luan, Q. Meng, J. Wu, Q. Li, X. Zhang, Y. Zhang, L. A. O'Dell, S. R. Raga, J. Pringle, J. C. Griffith, C. Sun, U. Bach and J. Zhang, *Chemsuschem*, 2020, **13**, 328-333.
10. J. Xia, N. Karjule, L. Abisdris, M. Volokh and M. Shalom, *Chem. Mater.*, 2020, **32**, 5845-5853.
11. G. Peng, J. Qin, M. Volokh, C. Liu and M. Shalom, *J Mater. Chem. A*, 2019, **7**, 11718-11723.
12. B. Guo, L. Tian, W. Xie, A. Batool, G. Xie, Q. Xiang, S. U. Jan, R. Boddula and J. R. Gong, *Nano Lett.*, 2018, **18**, 5954-5960.
13. X. Li, Z. Cheng, Y. Fang, X. Fu and X. Wang, *Sol. RRL*, 2020, **4**, 2000168.
14. Y. Fang, X. Li and X. Wang, *Chemsuschem*, 2019, **12**, 2605-2608.
15. M. Huang, H. Wang, W. Li, Y.-L. Zhao and R.-Q. Zhang, *J Mater. Chem. A*, 2020, **8**, 24005-24012.
16. G. Peng, J. Albero, H. Garcia and M. Shalom, *Angew. Chem. Int. Ed.*, 2018, **57**, 15807-15811.
17. Y. Fang, X. Li, Y. Wang, C. Giordano and X. Wang, *Appl. Catal. B*, 2020, **268**, 118398.
18. A. Tashakory, N. Karjule, L. Abisdris, M. Volokh and M. Shalom, *Adv. Sustain. Syst.*, 2021, **5**, 2100005.
19. Q. Ruan, W. Luo, J. Xie, Y. Wang, X. Liu, Z. Bai, C. J. Carmalt and J. Tang, *Angew. Chem. Int. Ed.*, 2017, **56**, 8221-8225.
20. Y. Fang, X. Li and X. Wang, *ACS Catal.*, 2018, **8**, 8774-8780.
21. W. Xiong, M. Huang, F. Huang and R.-Q. Zhang, *Appl. Surf. Sci.*, 2020, **511**, 145535.
22. G. Peng, M. Volokh, J. Tzadikov, J. Sun and M. Shalom, *Adv. Energy Mater.*, 2018, **8**, 1800566.