Electronic Supplementary Material (ESI) for Nanoscale.

Supporting Information

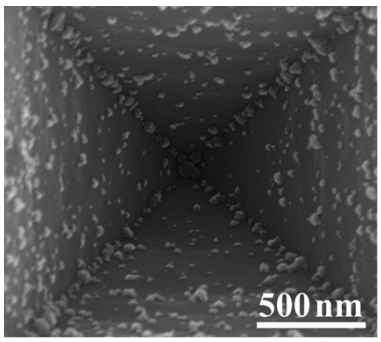

Figure S1. Microscopy for Cu NPs-coated sidewalls of SiIP wafers etched with Cu^{2+} (18 mM)-contained etchant.

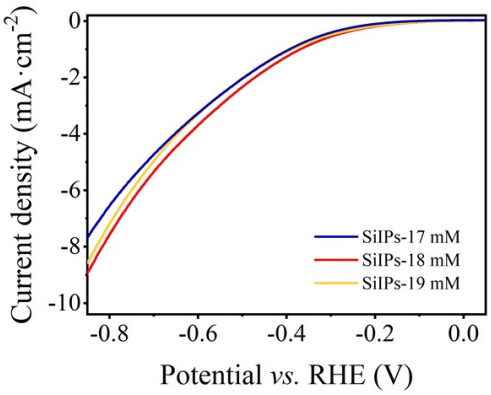

Figure S2. *J-V* curves for pristine SiIP photocathodes (under one sun illumination).

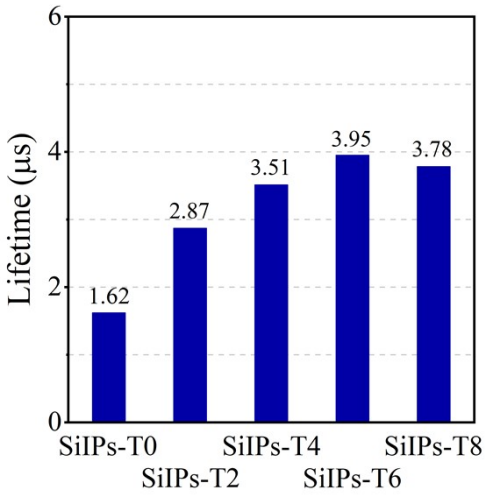

Figure S3. Minority carrier lifetime results for various TiO_2/SiIPs/TiO_2 wafers.

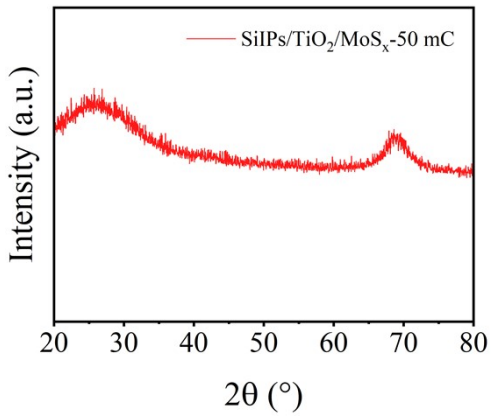

Figure S4. XRD patterns of SiIPs-T2/TiO_2/MoS_x-50 mC photocathodes.

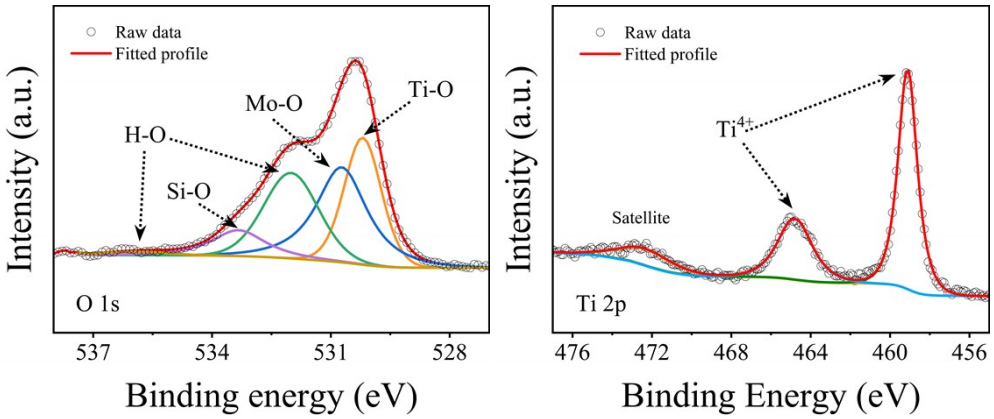

Figure S5. XPS spectra of SiIPs-T2/TiO_2/MoS_x-50 mC photocathodes in O 1s and Ti 2p regions.

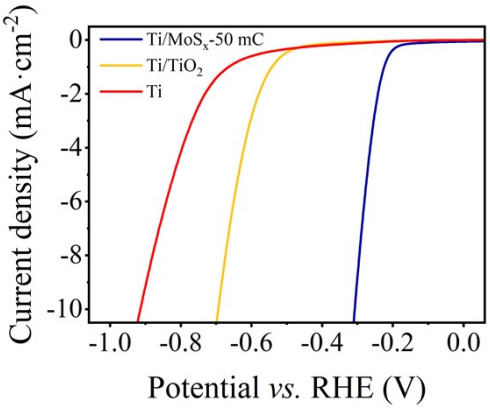

Figure S6. *J-V* curves for cocatalysts-coated Ti electrodes (in the dark).

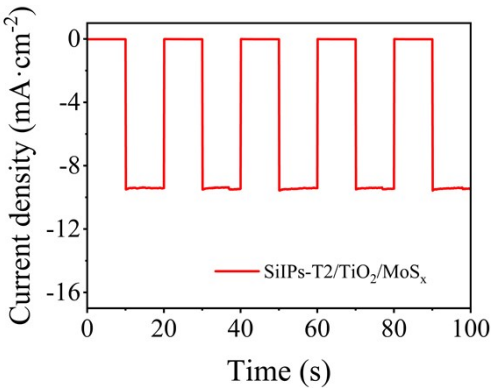

Figure S7. *J-t* curve for SiIPs-T2/TiO_2/MoS_x-50 mC photocathode (under chopped one sun illumination).

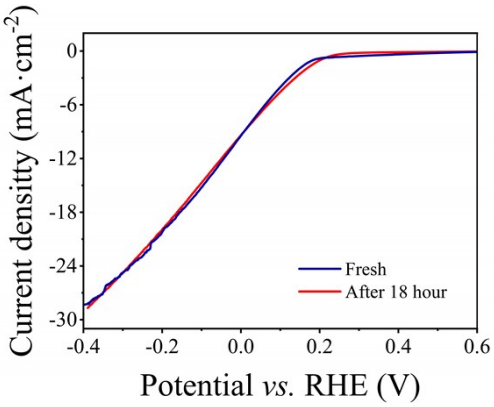

Figure S8. *J-V* curves comparisons for SiIPs-T2/TiO_2/MoS_x-50 mC cathode test before and after 18 h-long PEC catalysis.

Table S1. Mean reflectivity results of various (TiO_2-coated) SiIP photocathodes.

TiO_2 deposition	SiIPs-T0	SiIPs-T2	SiIPs-T4	SiIPs-T6	SiIPs-T8	Planar Si
w/o TiO_2 layer	5.87%	9.59%	13.58%	13.99%	15.44%	38.74%
w TiO_2 layer	3.90%	6.60%	9.00%	10.38%	12.18%	29.69%

Table S2. Fitting results of EIS data for various SiIP electrodes.

Photocathode	R_s (Ω cm^2)	R_{ct1} (Ω cm^2)	R_{ct2} (Ω cm^2)	R_{ct3} (Ω cm^2)
SiIPs-T2	27.69	N/A	N/A	3109.4
SiIPs-T2/TiO_2	17.56	5.76	15.37	57.36
SiIPs-T2/TiO_2/Mo-S	17.9	6.15	10.72	16.33

EIS data are fitted using an equivalent circuit with three constant phase elements (CPEs) and four resistive components, as shown in the inset of Fig. 7b. Among them, R_s represents electrolyte resistance. R_{ct1} is interfacial charge transfer resistance at Si/TiO_2 interface, while R_{ct2} means the charge diffusion resistance within TiO_2 layer. Besides, R_{ct3} indicates interfacial charge transfer resistance at electrode/electrolyte interface, reflecting total charge transfer capability and hydrogen evolution kinetics of Si-based electrodes.

Table S3. Onset potential and current density data for various SiIP electrodes.

Photocathode	Onset potential (V *vs.* RHE)	Current density ($mA \cdot cm^{-2}$ @0 V *vs.* RHE)
SiIPs-T0	-0.37	0.01
SiIPs-T2	-0.35	0.03
SiIPs-T4	-0.36	0.03
SiIPs-T6	-0.40	0.03
SiIPs-T8	-0.40	0.03
SiIPs-T0/TiO_2	0.09	2.08
SiIPs-T2/TiO_2	0.10	2.42
SiIPs-T4/TiO_2	0.12	2.57
SiIPs-T6/TiO_2	0.09	2.01
SiIPs-T8/TiO_2	0.07	1.75
SiIPs-T2/TiO_2/MoS_x-10 mC	0.18	7.53
SiIPs-T2/TiO_2/MoS_x-50 mC	0.18	9.45
SiIPs-T2/TiO_2/MoS_x-100 mC	0.19	7.35
SiIPs-T2/TiO_2/MoS_x-200 mC	0.19	6.41

Note that we define onset potential as the specific RHE potential at which the photocurrent density reaches up to 1 $mA \cdot cm^{-2}$.