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Supporting information

Boosting the performance of a silicon photocathode for photoelectrochemical hydrogen production by immobilization of a cobalt tetraazamacrocyclic catalyst

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Experimental details

Materials and instruments

Silver nitrate (99%), pyruvic acid (99%), ammonium persulfate (99%), cobalt(II) bromide (99%), 4-bromopyridine hydrochloride (98%), methyl isonicotinate (> 98%), diethyl phosphite (99%), tetrakis(triphenylphosphine)palladium (99%), and bromotrimethylsilane (98%) were purchased from Aladdin®. 3,3'-Diaminodipropylamine (98%) was purchased from Energy Chemical. Silicon wafers (10–20 Ω·cm) were purchased from Hangzhou Bojing Science and Technology Limited Company, and titanium oxide paste (TiO_2 nanoparticles, 18–20 nm, anatase, hydrophilicity) was purchased from Heptachroma company in Dalian, China. All reagents were used as received without further purification.

^{1}H NMR spectra were measured on a Bruker Avance II 500 instrument at 298 K. Mass spectra were obtained on an MALDI Micro MX and LTQ Orbitrap XL instrument. The attenuated total reflectance fourier-transform infrared (ATR-FTIR) spectra were recorded on a Thermo Fisher Nicolet iN10 spectrometer. Field-emission scanning electron microscope (SEM) images were recorded on a Nova NanoSEM 450 instrument. X-ray photoelectron spectroscopy (XPS) spectra were obtained on an ESCALAB 250Xi (Thermo Scientific). The loading amount of the cobalt catalyst on Si/TiO_2 electrode was determined by inductively coupled plasma-optical emission spectrometry (ICP-OES) (PerkinElmer 2000 DV).

Preparation of complex Co(CR-DCP)

The 2,6-dicarboxypyridin-4-yl (DCP)-functionalized tetraazamacrocyclic cobalt(III) complex [Co(CR-DCP)Br_2]Br was prepared as the procedure described in our previous report.[S1] Complex Co(CR-DCP) was obtained in a yield of 80–85%. MS (ESI) calcd for $[M–Br]^+$ ($C_{22}H_{25}Br_2CoN_5O_4$): $m/z = 641.96$, found: 642.01. ^1H NMR (500 MHz, DMSO-d_6): δ 13.83 (br s, 2H), 9.21 (s, 2H), 9.02 (s, 2H), 6.74 (t, J = 9.5 Hz, 1H), 4.24 (d, J = 10.8 Hz, 2H), 3.62–3.55 (m, 4H), 3.25 (t, J = 9.5 Hz, 2H), 3.08 (s, 6H), 2.29 (d, J = 12.8 Hz, 2H), 2.11 (m, 2H). ^{13}C NMR (125.8 MHz, CD_3OD): δ 180.20, 166.98, 159.68, 151.27, 150.75, 148.26, 127.61, 127.23, 52.93, 51.94, 27.56, 17.99.

Fabrication of the Si/TiO_2/Co(CR-DCP) hybrid photocathode

The Si/TiO_2 electrode was fabricated referring to the literature procedure.[S2] The TiO_2 film was coated on the surface of the freshly treated p-Si wafer by doctor-blading of a paste of TiO_2 nanoparticles (18–20 nm), and then Si/TiO_2 was annealed following a reported controlled sintering procedure up to 450 °C under atmospheric conditions.[S2] Then the DCP-functionalized cobalt tetraazamacrocyclic catalyst was immobilized on the Si/TiO_2 electrode by immersing the electrode in the MeOH solution of the cobalt catalyst (1.0 mM) for 16 h in the dark. Afterward, the electrode was thoroughly rinsed with MeOH to remove the nonbonded catalyst molecules on the surface of the electrode. In addition, the Si/$TiO_{2(5\ nm,ALD)}$/Co(CR-DCP) electrode with a 5 nm TiO_2 film deposited by using an ALD system (YUANTEC, Ensure Scientific Group) was also fabricated with an essentially identical procedure. The amount of immobilized cobalt catalyst on Si/TiO_2 electrode was determined by ICP-OES analysis. The following manufacturing process for encapsulating the hybrid electrode was identical to that as described in our previous report.[S3]

Photoelectrochemical measurements

All photoelectrochemical measurements were performed in a three-electrode cell under Ar at 25 °C using an electrochemical workstation (CHI 650E) with the as-fabricated Si/TiO_2/Co(CR-DCP) photocathode as the working electrode (geometric area 1 cm^{-2}), a Ag/AgCl electrode as the reference electrode, and a Pt foil (1 cm^2) as the counter electrode. A 300 W Xenon arc lamp (100 mW cm^{-2}, AM 1.5G) with an optical filter (λ > 400 nm) was employed as the light source. All experimentally measured potentials were converted to the ones versus RHE by using the following equation: $E(\mathrm{RHE}) = E(\mathrm{Ag/AgCl}) + E^{\Theta}(\mathrm{Ag/AgCl}) + 0.059\mathrm{pH}$ V ($E^{\Theta}(\mathrm{Ag/AgCl}) = 0.197$ V at 25 °C).

The LSVs of Si/TiO_2/Co(CR-DCP) and bare Si/TiO_2 were measured in 0.1 M acetate buffer at pH 4.5, or 0.1 M phosphate buffer at pH 7, or 0.1 M borate buffer at pH 9 under continuous or chopped illumination at a scan rate of 10 mV s^{-1}. The controlled potential photoelectrolysis (CPP) experiments of Si/TiO_2/Co(CR-DCP) and Si/TiO_2 electrodes were conducted at 0 V vs RHE in 0.1 M acetate buffer at pH 4.5 with 2 min dark chop every hour of illumination. The amount of evolved H_2 in the headspace of the sealed gas-tight cell was analyzed by a gas chromatograph (GC, Ceaulight GC-7920) equipped with a 5 Å molecular sieve column (2 mm × 2 m) during CPP experiments. The faradaic efficiencies were determined from the CPP experiments at 0 V over 2 h of illumination. The IPCE values of Si/TiO_2/Co(CR-DCP) were measured on a Zahner photoelectrochemical workstation (CIMPS-2) under illumination from a LED lamp (TLS03) with a wavelength scan range from 365 to 1020 nm.

The electrochemical impedance spectra (EIS) were measured at zero bias in 0.1 M acetate buffer at pH 4.5 under illumination with the sweeping frequency from 100 kHz to 0.1 Hz and a 5 mV amplitude using a potentiostat (CHI650E). The intensity modulated photocurrent spectra (IMPS) were conducted on a Zahner photoelectrochemical workstation (CIMPS-2). Intensity-modulated light was provided by a white light-emitting diode with an intensity of 100 mW cm^{-2}.

The superimposition of sinusoidal modulation of light-emitting diode was 10% and the modulation amplitude voltage was 2 mV. IMPS data was collected over the 10 kHz to 0.1 Hz frequency range at different applied potentials.

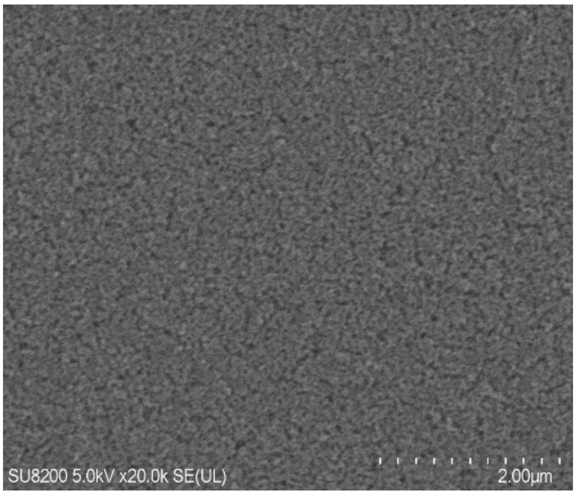

Fig. S1 Top-view SEM image of the Si/TiO_2 electrode.

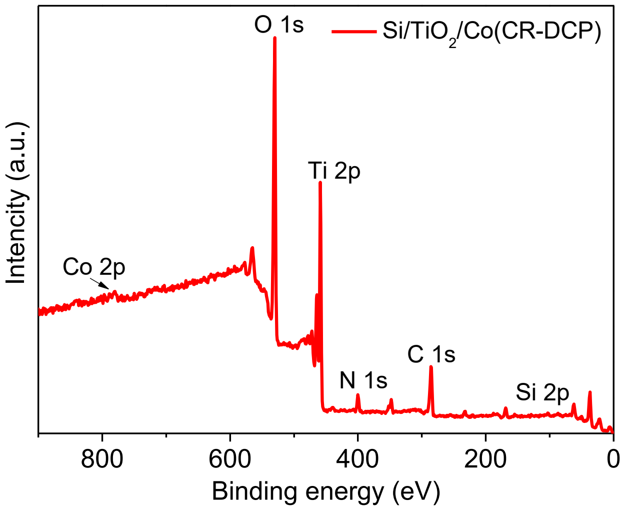

Fig. S2 X-ray photoelectron spectroscopy (XPS) survey of the as-prepared Si/TiO_2/Co(CR-DCP) electrode.

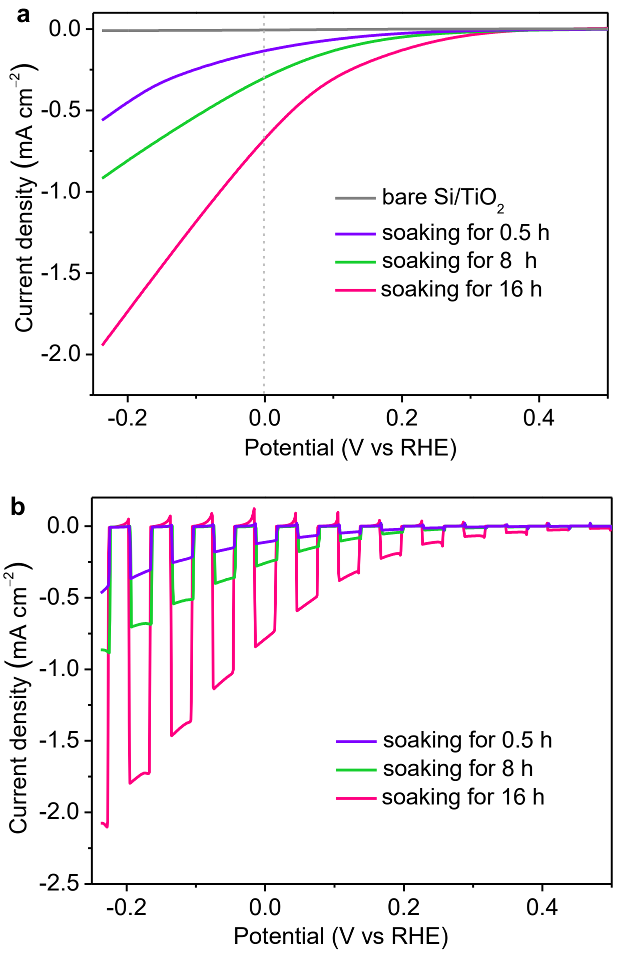

Fig. S3 LSVs of the Si/TiO_2/Co(CR-DCP) photocathodes prepared with varying soaking time and bare Si/TiO_2 in 0.1 M acetate buffer at pH 4.5 under (a) continuous and (b) chopped illumination, at a scan rate of 10 mV s^{-1}.

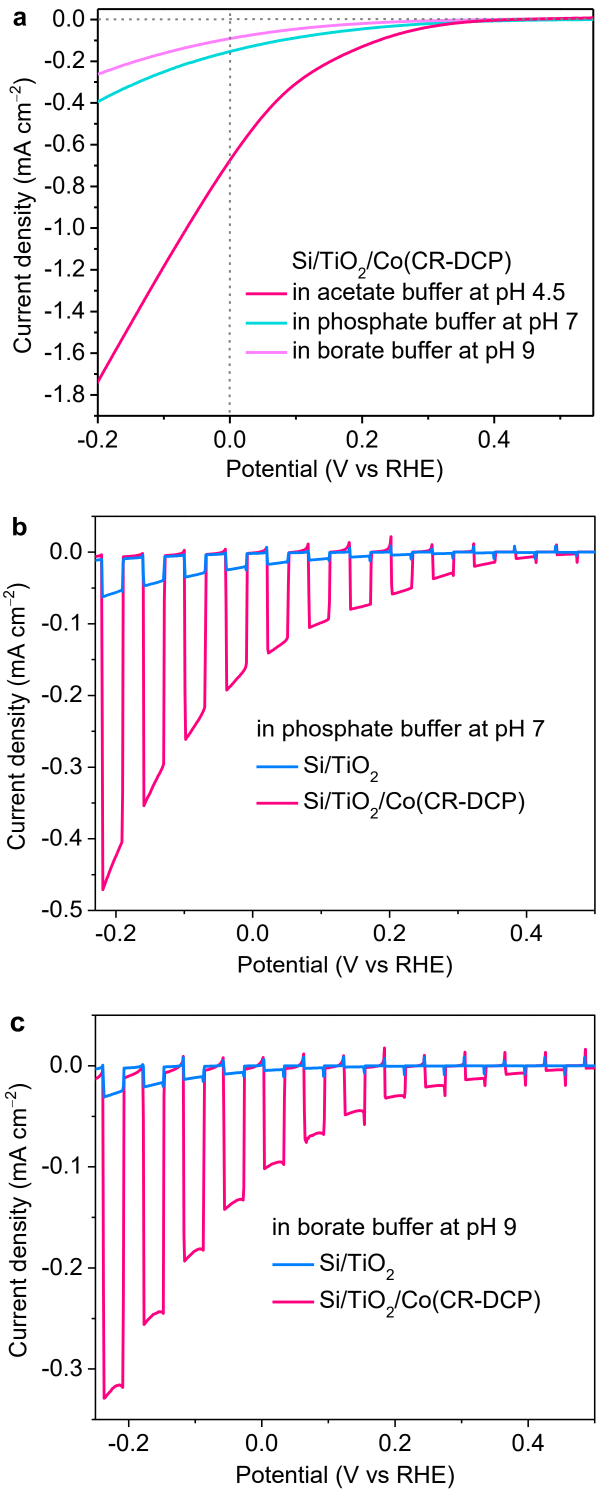

Fig. S4 (a) LSVs of Si/TiO$_2$/Co(CR-DCP) in different buffers (0.1 M) at pH 4.5, 7, and 9. LSVs of Si/TiO$_2$/Co(CR-DCP) and bare Si/TiO$_2$ (b) in phosphate buffer at pH 7 and (c) in borate buffer at pH 9 under chopped illumination at a scan rate of 10 mV s^{-1}.

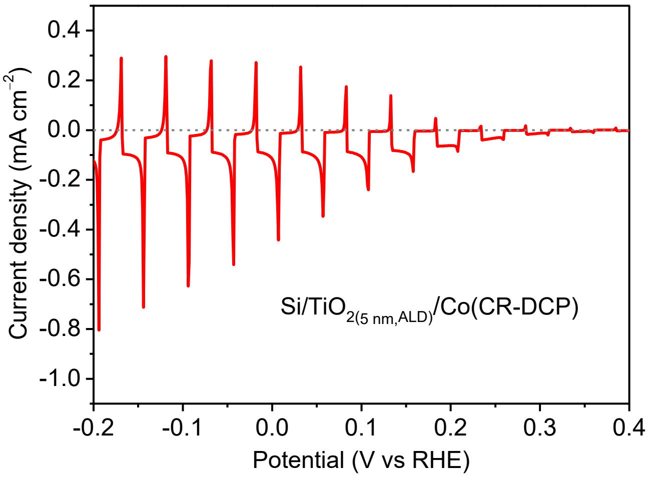

Fig. S5 *J*-*V* curve of Si/TiO$_{2(5\ \mathrm{nm,ALD})}$/Co(CR-DCP) under chopped illumination at 10 mV s^{-1}.

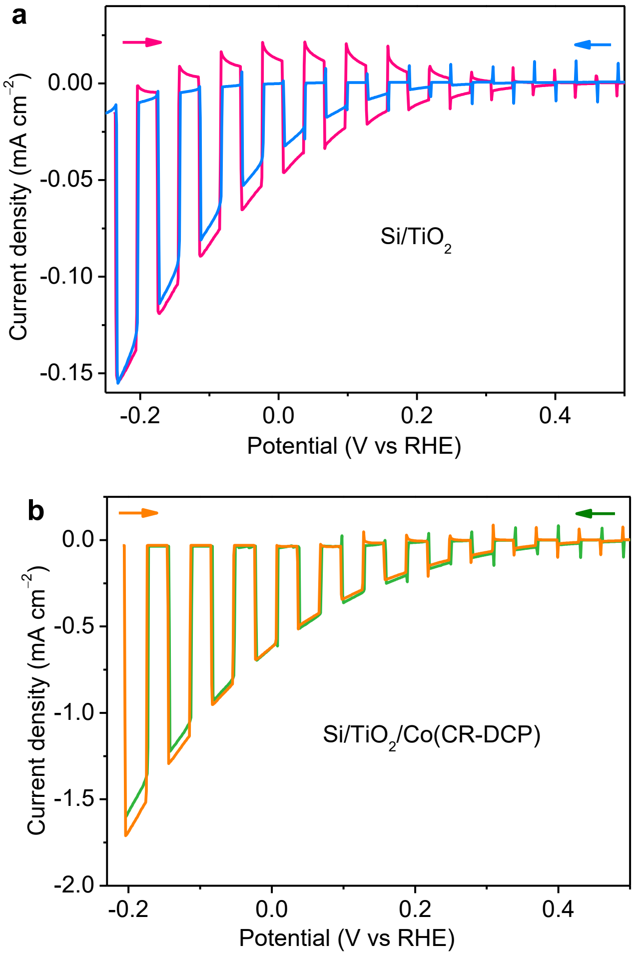

Fig. S6 *J*-*V* curves of (a) bare Si/TiO_2 and (b) Si/TiO_2/Co(CR-DCP) with a 5 μm, porous TiO_2 film, scanning first in cathodic direction and then in anodic direction under chopped illumination at 10 mV s^{-1}.

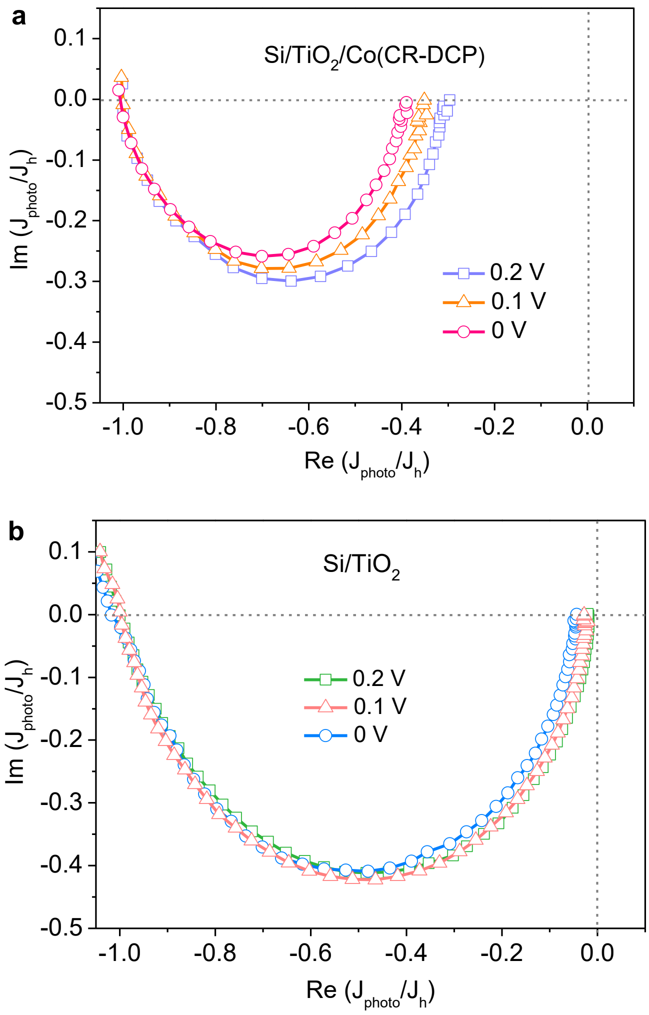

Fig. S7 Normalized IMPS responses of (a) Si/TiO$_2$/Co(CR-DCP) and (b) bare Si/TiO$_2$ at applied potentials of 0.2, 0.1, and 0 V.

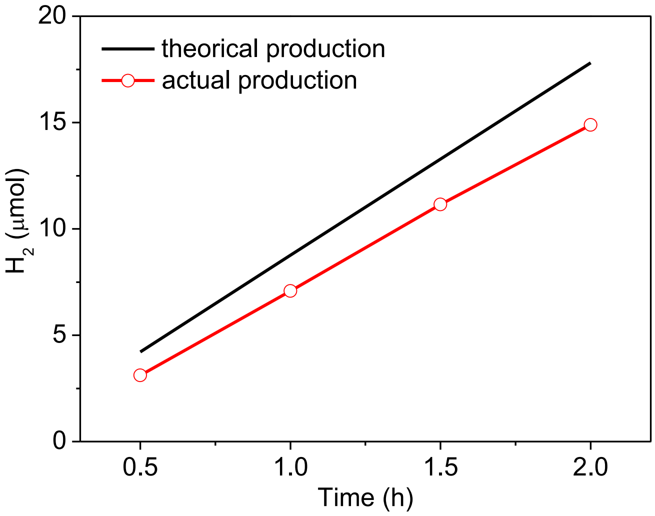

Fig. S8 Current efficiency of Si/TiO_2/Co(CR-DCP) for PEC H_2 production in 0.1 acetate buffer at pH 4.5 under 100 mW cm^{-2} illumination over 2 h (a geometrical surface area of about 1 cm^{-2} for the working electrode).

Table S1 Previously reported non-sensitized planar semiconductor/molecular catalyst photocathodes for PEC H_2 production in water[a]

Photocathode	Anchor	Electrolyte (pH)	$J_{(0\ \mathrm{V})}$[b] (mA cm^{-2})	E_{on}[c] (V)	Stability[d] (loss % of photocurrent)	Ref.
$InGaP_2/TiO_2$/cobaloxime/TiO_2	Carboxylate	0.1 M NaOH (pH 13)	−9	0.7	5% @ 0 V after 20 min	S3
Si/TiO_2/cobaloxime	Hydroxamate	0.1 M borate (pH 9)	−0.32	0.32	2.9% @ 0 V after 6 h	S4
GaP-PVP/cobaloxime	PVP polymer grafting[e]	1 M phosphate (pH 7)	−2.7	0.76	17% @ 0.17 V after 5 min	S5
GaP-PVP/cobaloxime	PVP polymer grafting	0.1 M phosphate (pH 7)	−1.3	0.61	27% @ 0 V after 60 min	S6
GaP-PVP/cobaloxime	PVP polymer grafting	0.1 M phosphate (pH 7)	−0.92	0.72	~10% @ 0.17 V after 5 min	S7
GaP(100)-PVI/cobaloxime	PVI polymer grafting[f]	0.1 M phosphate (pH 7)	−1.2	0.58	n/a	S8
GaP(111)-PVI/cobaloxime	PVI polymer grafting	0.1 M phosphate (pH 7)	−0.89	0.65	13% @ 0 V after 55 min	S8
GaP/cobalt porphyrin	Carbon chain	0.1 M phosphate (pH 7)	−1.31	0.55	< 10% @ 0 V after 4 h	S9
Au/InP/$Fe_2S_2(CO)_6$[g]	Direct S coordination	0.1 M $NaBF_4$ (pH 7)	-4.5×10^{4}	0.51	n/a	S10
Si/ALD-TiO_2/SC-TiO_2/$CoC_{11}P$/ALD-TiO_2	Phosphonate	1 M phosphate (pH 7)	−1.25	0.47	24% @ 0 V after 1 h	S11
Si/ALD-TiO_2/SC-TiO_2/$CoC_{11}P$	Phosphonate	1 M phosphate (pH 7)	−0.5	0.09	rapid decrease @ 0 V in 2 h	S11
$CuFe_xO_y$/cobaloxime	DCP	0.2 M phosphate (pH 6.7)	–	0.86	rapid decrease @ 0.4 V in 8 min	S12
GaP-PVP/cobaloxime	PVP polymer grafting	0.1 M acetate (pH 4.5)	−1.10	0.5	18 @ −0.12 V after 15 min	S13
Si/mesoTiO_2/DuBois' Ni catalyst	Phosphonate	0.1 M acetate (pH 4.5)	−0.34	0.4	50 @ 0 V after 8 h	S2
Si/mesoTiO_2/cobaloxime	Phosphonate	0.1 M acetate (pH 4.5)	−0.33	~ 0.36	100 @ 0 V after 0.5 h	S2
Si/mesoTiO_2/Pt	–	0.1 M acetate (pH 4.5)	−0.43	~ 0.4	Steady @ 0 V over 24 h	S2
P3HT:PCBM/cobaloxime	By click reaction	0.1 M acetate (pH 4.5)	−0.002	n/a	n/a	S14
Si/TiO_2/Co(CR-DCP)	DCP	0.1 M acetate (pH 4.5)	−0.682	0.37	Steady @ 0 V over 10 h	This work

[a] Illumination intensity: 100 mW cm^{-2}. [b] LSV measurements. [c] All potentials are versus RHE. [d] Chronoamperometry measurements. [e] PVP = polyvinylpyridine. [f] PVI = polyvinylimidazole. [g] Under illumination of 395 nm LED.

Table S2 Kinetic data obtained from IMPS responses of photoelectrodes

Photocathode	Potential (V)	k_{trans} (s^{-1})	k_{rec} (s^{-1})	$k_{trans}/(k_{trans} + k_{rec})$ (%)
Si/TiO_2/Co(CR-DCP)	0	1293	2022	39
	0.1	1194	2121	36
	0.2	1160	2154	35
Si/TiO_2	0	125	4644	2.6
	0.1	69	4859	1.7
	0.2	45	4918	0.9

Table S3 Quantitative data obtained from ICP-OES analysis for the amounts of the immobilized catalyst on the surface of Si/TiO_2 electrodes and the Co^{n+} species in the electrolytes before and after 10 h CPP experiments

Photocathode	Amount of immobilized catalyst on electrode surface (nmol cm^{-2})	Amount of Co^{n+} species in electrolyte (nmol mL^{-1})
Si/TiO_2/Co(CR-DCP) before used	37.8 ± 5.8	0.12 ± 0.02
Si/TiO_2/Co(CR-DCP) after used	27.4 ± 6.4	0.26 ± 0.01

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