Electronic Supplementary Information for

Silicon Nanowire Arrays Coupled with Cobalt Phosphide Spheres as a Low-Cost Photocathode for Efficient Solar Hydrogen Evolution

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Experimental details:

Fabrication of SiNW arrays: A 6-inch p-type Si (100) wafer (B-doped, 8 – 30 Ω cm, LG Siltron) was cleaned by ultrasonication in acetone for 5 min, rinsed sequentially by isopropanol and deionized (DI) water (≥ 18 MΩ cm), and then dried in a nitrogen (N_2) flow. Next, a 300-nm aluminum (Al) layer was sputtered on the backside of the wafer (Singulus FTM magnetron sputtering tool). The wafer was subsequently cut into small pieces with an area of 2.7 × 2.7 cm^2 using a dicing saw (DISCO DAD 3350). The actual area exposed to the electrolyte and to light during the PEC test is 2.5 cm^2 (1.8 cm in diameter), which is defined by the PEC test cell we used (PECC2, Zahner). Prior to etching, the Al layer was protected by an HF-resistant tape. Afterwards, the Si wafer was immersed into a mixture of 4 mM $AgNO_3$ + 2 M HF for 4 min to deposit a catalyst layer of Ag nanoparticles (AgNPs). The wafer was then rinsed with DI water and dried in a N_2 flow. The vertically aligned SiNW array was formed when soaking the AgNPs-coated Si wafer in a mixed aqueous solution of 0.5 M H_2O_2 and 9 M HF for 1 min. To remove the AgNPs, the sample was immersed into a diluted HNO_3 solution for 30 min, and then was rinsed with copious DI water and dried in N_2. After that, the protective tape was peeled off from the Si wafer. The Si wafer was subsequently fast-annealed in high-purity N_2 (99.999%) at 400 °C for 1 min to form a Si/Al ohmic contact.

Fabrication of SiNW/Co-P and SiNW/PtNPs electrodes: Co-P hollow spheres were decorated on the SiNW arrays by photo-assisted electrodeposition of Co nanoparticles (CoNPs), followed by phosphorization treatment at a high temperature. The deposition of CoNPs was carried out in 0.5 M $CoCl_2$ (Sigma, buffered at pH =1) in a three-electrode configuration, using the SiNW array as the working electrode, a Pt coil as the counter electrode, and a Hg/Hg_2SO_4 electrode (MSE,

saturated K_2SO_4) as the reference. The deposition was conducted in galvanostatic mode at 1 mA cm^{-2} under a constant illumination of 100 mW cm^{-2} (tungsten lamp WOW01, Zahner) for 5min. After electrodeposition, the SiNW/CoNPs electrode was carefully cleaned with DI water and then dried in a N_2 flow. The phosphorization treatment was performed in a tube furnace (Carbonite) at 400, 500 or 600 °C for 6 h by flowing phosphoric vapor over the SiNW/CoNPs electrode, using high-purity N_2 (99.999%) as the carrier gas. The red phosphorus (Sigma-Aldrich) and the SiNW/CoNPs electrode were placed in the same ceramic boat and separated by a distance of ca. 1 cm. The N_2 flow was set at ca. 800 SCCM and monitored by a flow meter. The loading mass of Co-P catalysts on SiNW arrays was determined by measuring the mass difference of the electrode before Co NPs loading and after the phosphorization treatment, using a high-precision microbalance (Sartorius MCM36). 17.1, 17.7, and 18.3 μg cm^{-2} catalysts were loaded on SiNW/Co-P-400, SiNW/Co-P-500, and SiNW/Co-P-600 photocathodes, respectively.

In order to compare the electrocatalytic performance of Co-P catalysts with that of the benchmark Pt nanoparticles (PtNPs), SiNW array electrodes decorated with PtNPs were fabricated according to the following procedure: firstly, the Si wafer on which the SiNW array was formed, was immersed into a 2.5 wt% HF solution for 5 min to remove the native oxide layer. The Al layer on the backside of the wafer was masked with an HF-resistant tape during this process. Subsequently, PtNPs were impregnated onto the surface of SiNWs by soaking the wafer in a solution of 0.4 M HF (Sigma) and 1 mM K_2PtCl_6 (Sigma-Aldrich) for 3 min. Afterwards, the sample was rinsed with DI water and then dried in a N_2 flow. This impregnation process was repeated 5 times, resulting in a Pt loading of 3.9 μg cm^{-2}. Finally, the protective tape was removed from the backside of the wafer.

Structural characterization: The morphology and microstructure of the samples were examined by scanning electron microscopy (SEM, FEI Quanta FEG 650) and aberration-corrected transmission electron microscopy (TEM, FEI Titan ChemiSTEM 80-200, operating at 200 keV). For TEM investigation, the Co-P hollow spheres and SiNWs were scratched off the Si substrate and directly dispersed on a carbon-coated copper grid. The grid was then heated in a vacuum oven at 110 °C for 2 h before being mounted on the TEM sample stage. The crystal phase of the samples was investigated by X-ray diffractometry (XRD, PANalytical X'pertPro) with Cu $K\alpha$ radiation (λ=1.541874 Å) and a PIXcel detector. Data were collected at 45 kV and 40 mA using the Bragg-Brentano configuration in the 2θ range of 30 – 80°. Si was used as an internal calibration standard. The XRD patterns were indexed according to the International Centre for Diffraction Data (ICDD) PDF-4+ database using a HighScore software package (PANalytical).

Photoelectrochemical (PEC) tests: The PEC tests were carried out in a commercially available thin Teflon cell (PECC2, Zahner). A Pt coil and a MSE electrode were used as counter and reference electrodes, respectively. The SiNW array photocathode was exposed to an electrolyte consisting of 0.5 M K_2SO_4 (≥ 99%, Sigma-Aldrich) buffered at pH = 1 using sulfuric acid (95-98%, Sigma-Aldrich). A calibrated tungsten lamp (WOW01, Zahner) with adjustable intensities was used as the light source and controlled by an external potentiostat (Zahner PP211). A photo-sensor (EPIGAP EPD-470-5-0.5 based on GaP doping) and a feedback loop circuit were employed to detect and tune the light intensity (Zahner). The *J-U*, EIS, and *J-t* curves were recorded by a Zennium electrochemical workstation (Zahner). The *J-U* curves were recorded by sweeping the potential at 20 mV s^{-1} toward the cathodic direction. The EIS measurements were performed in the frequency range of 0.1 Hz – 100 kHz at a fixed potential of 0 V vs. RHE under nominal

illumination of 100 mW cm^{-2} (with an actual intensity of 60 mW cm^{-2}, see below the description), with an AC voltage amplitude of 10 mV. Prior to each measurement, high-purity N_2 gas (99.999%) was flowed through the cell for 5 min. The sample's temperature was maintained at 23±1 °C during the test through a home-made cooling unit connected to a refrigerated chiller (HAAKE Phoenix II, Thermo Scientific). For each measurement, the tungsten lamp was first calibrated at 100 mW cm^{-2} and then an IR filter (Newport, 20HMS-O hot mirror) was placed perpendicularly to the light path. The irradiance spectra of the tungsten lamp recorded without and with the IR filter are shown in **Fig. S9**. The intensity of the incident light hitting on the photocathode (i.e., IR filtered) is calculated to be 60 mW cm^{-2} (actual light intensity) by integration.

Unless otherwise stated, all potentials were reported versus reversible hydrogen electrode (RHE) by converting the potentials measured versus MSE through the following equation:

$$V_{RHE} = V_{MSE} + 0.654 + 0.059\ pH \qquad (S1)$$

Supplementary Figures:

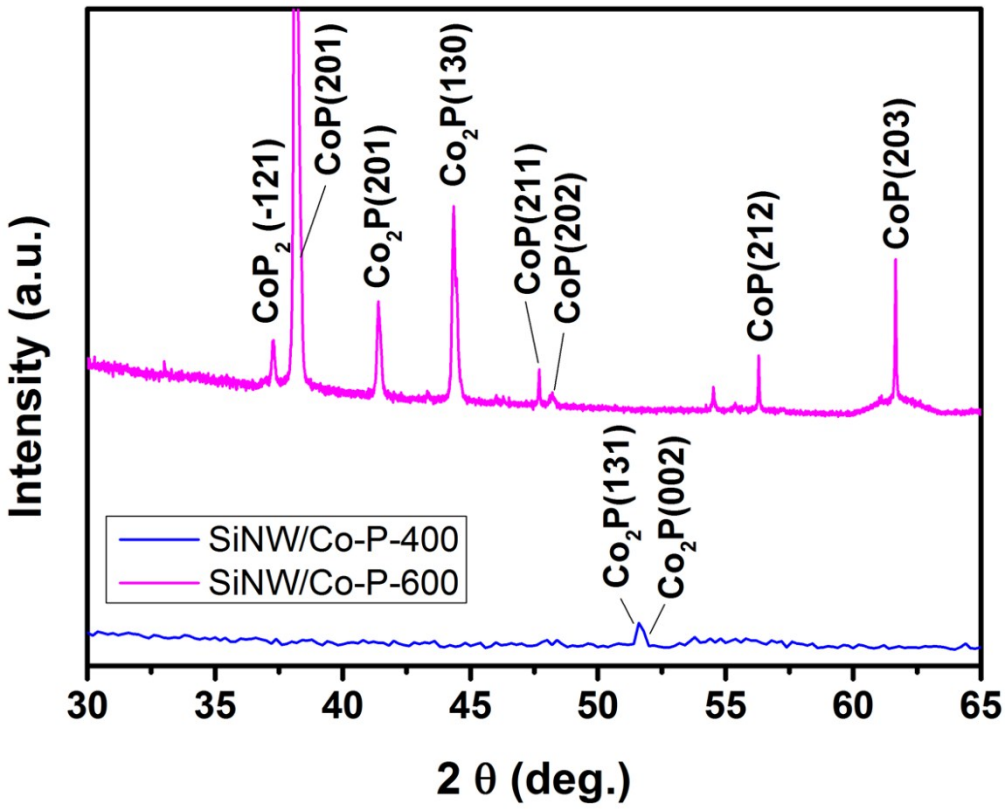

Figure S1. XRD patterns of SiNW/Co-P-400 and SiNW/Co-P-600 photocathodes that were fabricated by phosphorizing the SiNW/CoNPs electrode at 400 and 600 °C, respectively. For the SiNW/Co-P-400, only a wide, weak diffraction peak is observed, which can be indexed to the diffraction from Co_2P (131) or Co_2P (002) (ICDD No. 32-0306). This indicates that the crystallinity of the Co-P catalysts is very poor. For the SiNW/Co-P-600, while few peaks from the Co_2P phase still remain, the major diffraction peaks can be assigned to the diffractions from the orthorhombic CoP (ICDD No. 29-0497). Besides, a peak from the P-rich CoP_2 phase (monoclinic, ICDD No. 026-0481) is also observed.

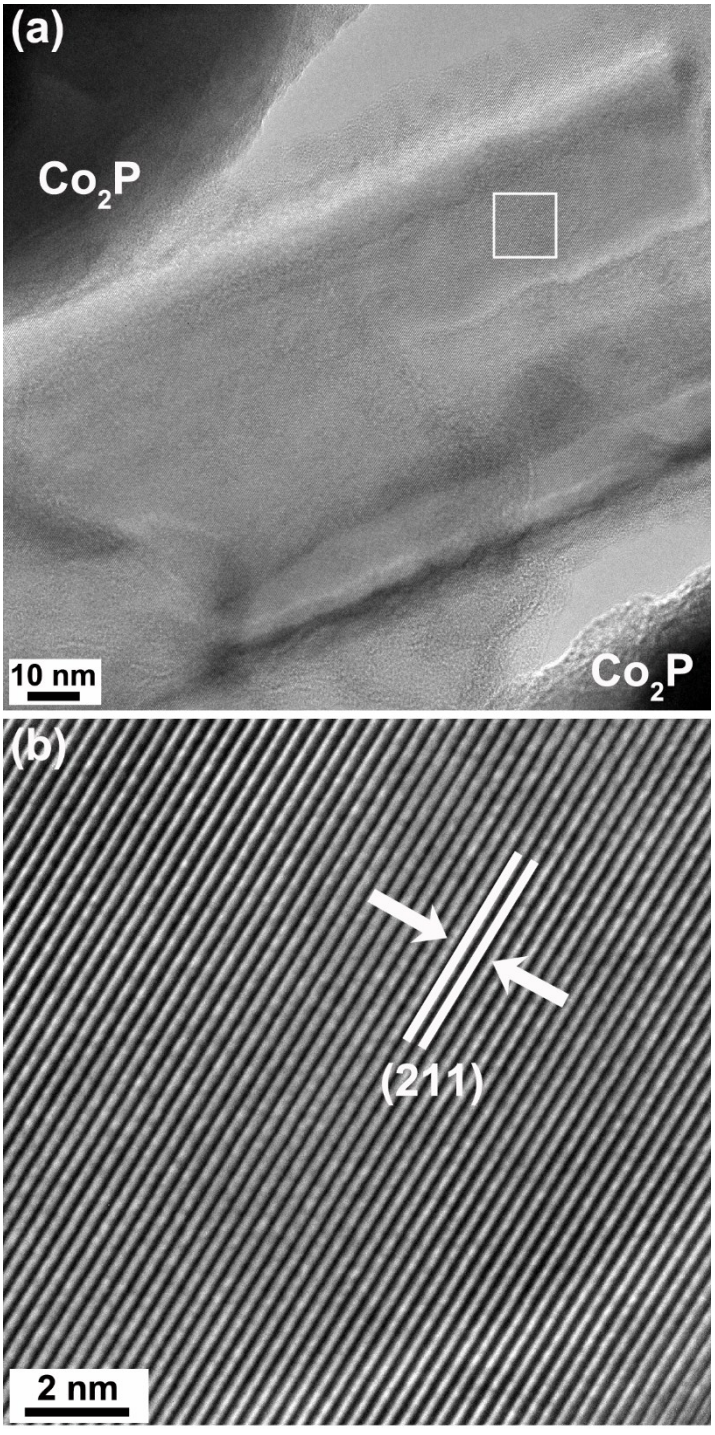

Figure S2. (a) TEM image of the SiNWs fabricated by MACE. (b) HRTEM image of the square-marked area in (a).

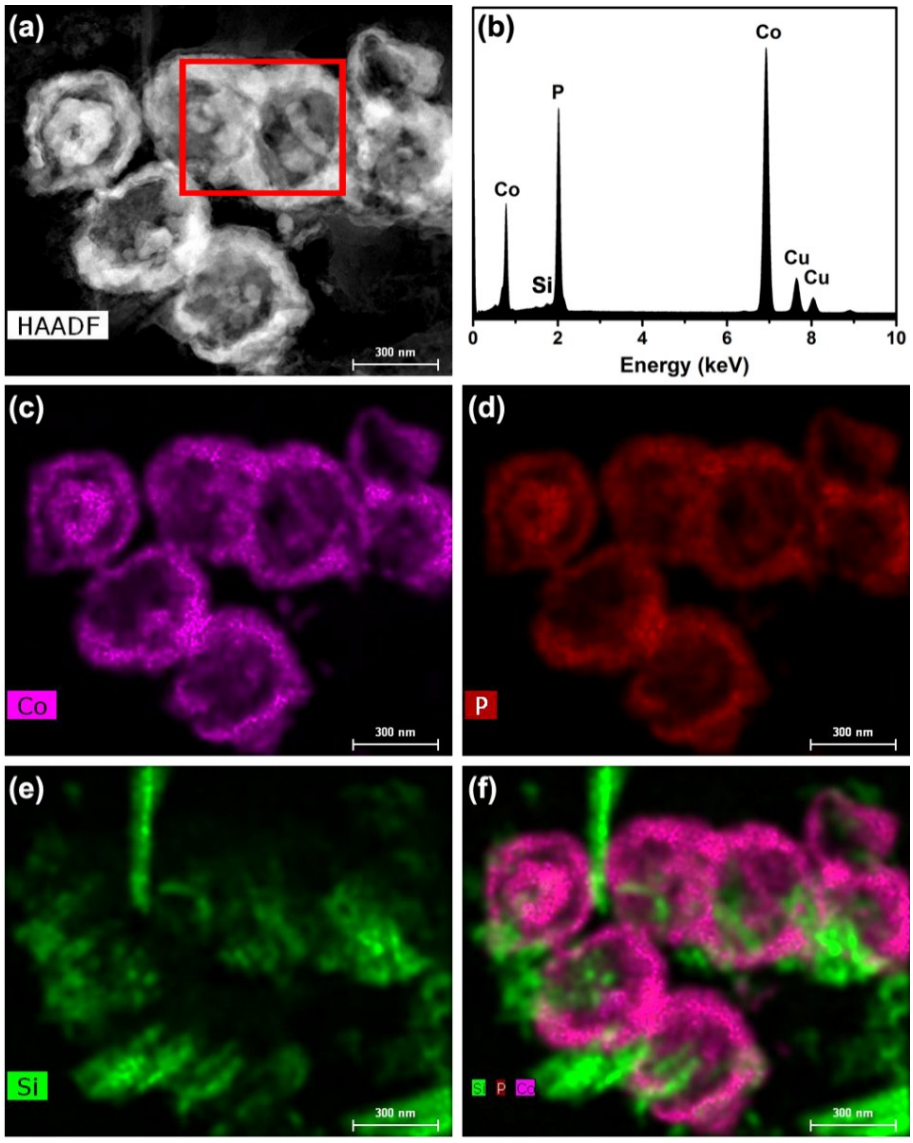

Figure S3. (a) HAADF-STEM image of Co-P hollow spheres obtained by a phosphorization treatment at 500 °C; (b) EDX spectrum taken in the selected area in (a). Elemental maps of (c) Co, (d) P, (e) Si, and (f) their overlap.

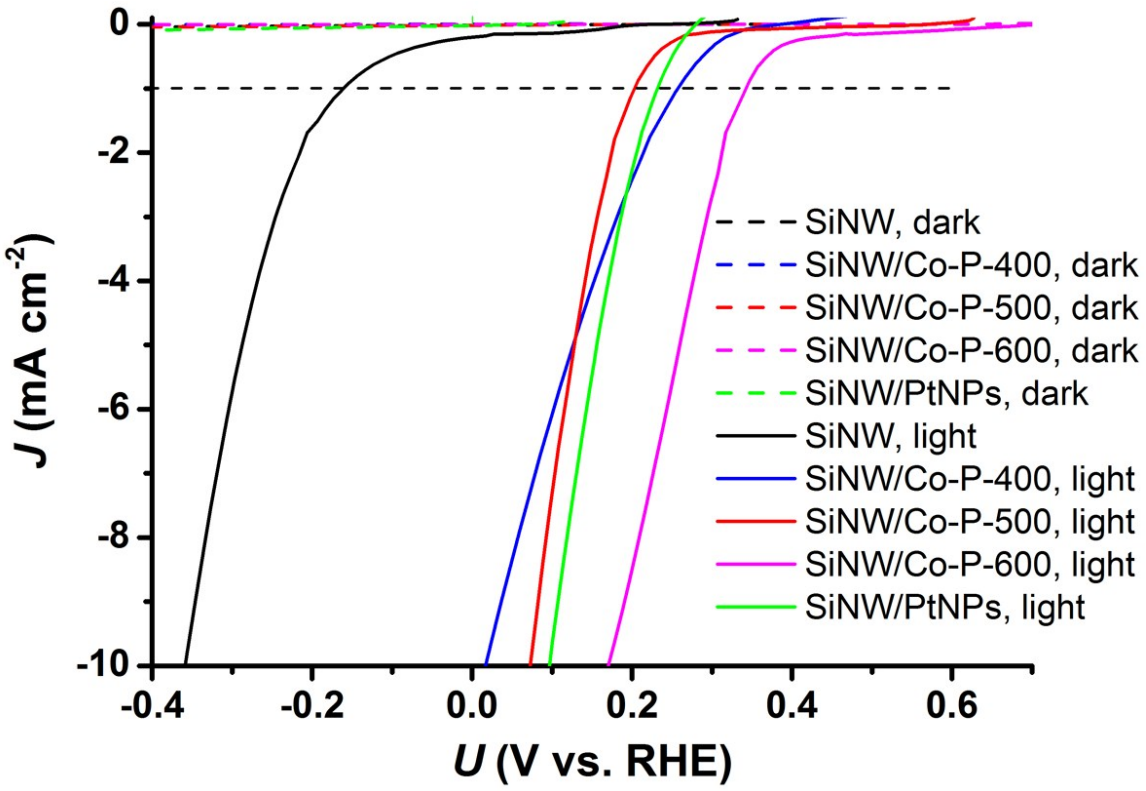

Figure S4. Zoomed view of **Figure 4a**, which shows that the HER onset potential of the SiNW/Co-P electrodes is > 0.35 V positive compared to that of the bare SiNW electrodes. The onset potential is defined as the potential at which the photocurrent is −1 mA cm^{-2}.

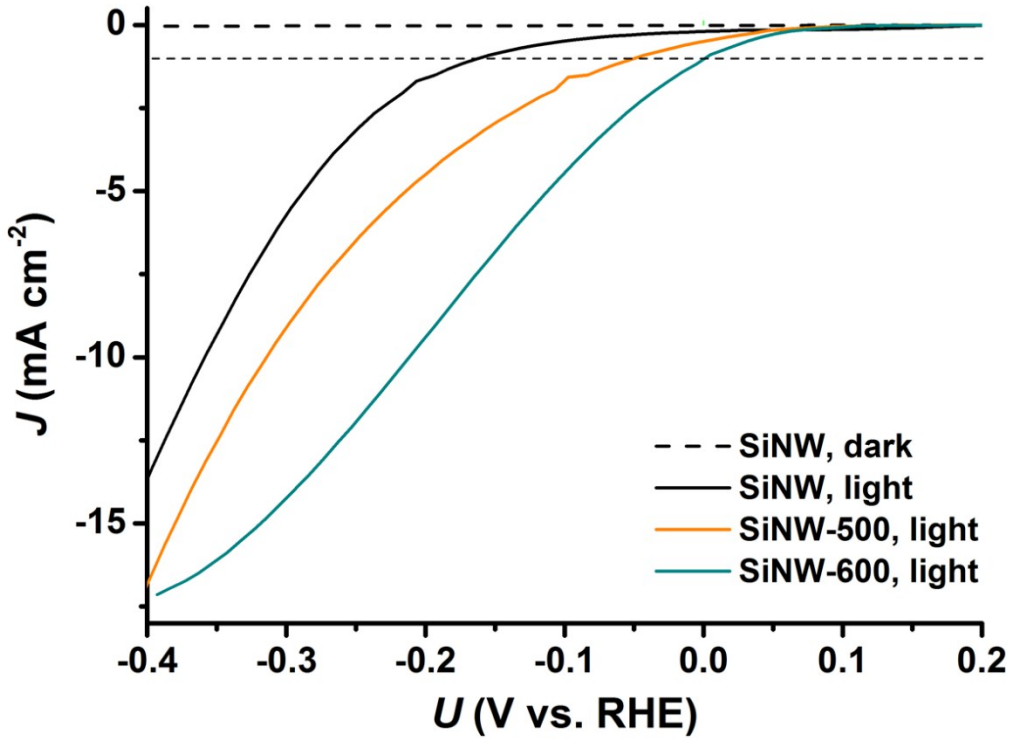

Figure S5. Effect of phosphorization on the PEC performance of bare SiNW arrays. $V_{onset,SiNW}$ = -0.162 V; $V_{onset,SiNW-500}$ = -0.049 V; $V_{onset,SiNW-600}$ = 0.002 V.

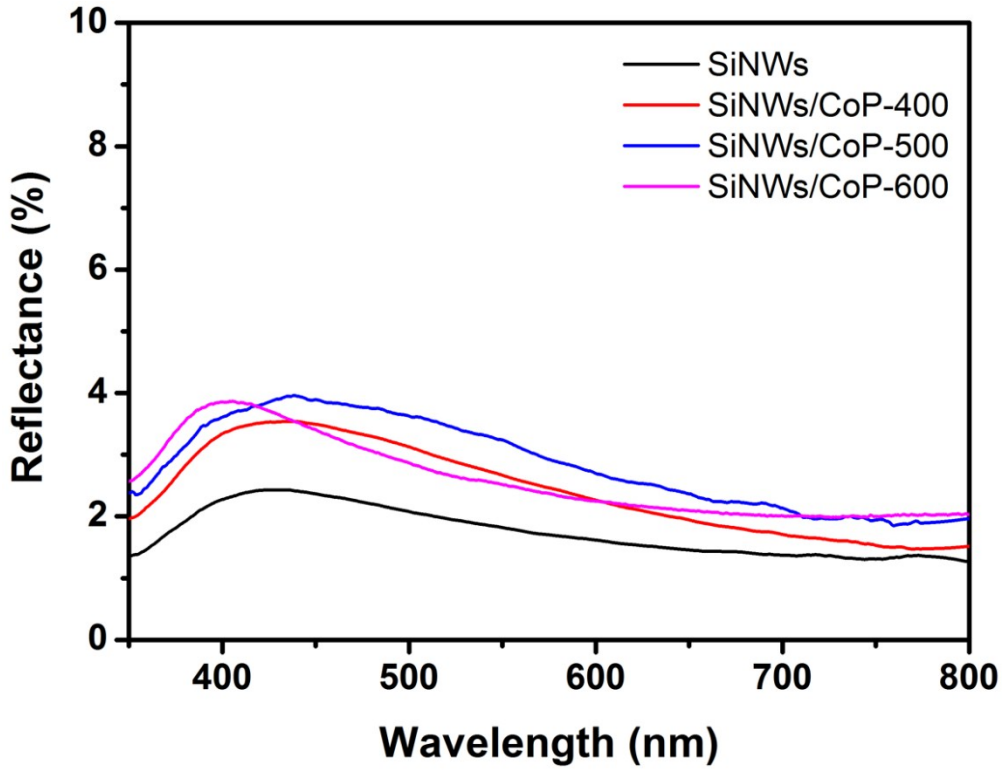

Figure S6. UV-Vis spectra of the SiNW/Co-P-400, -500 and -600. The spectrum of bare SiNW arrays is also given for comparison.

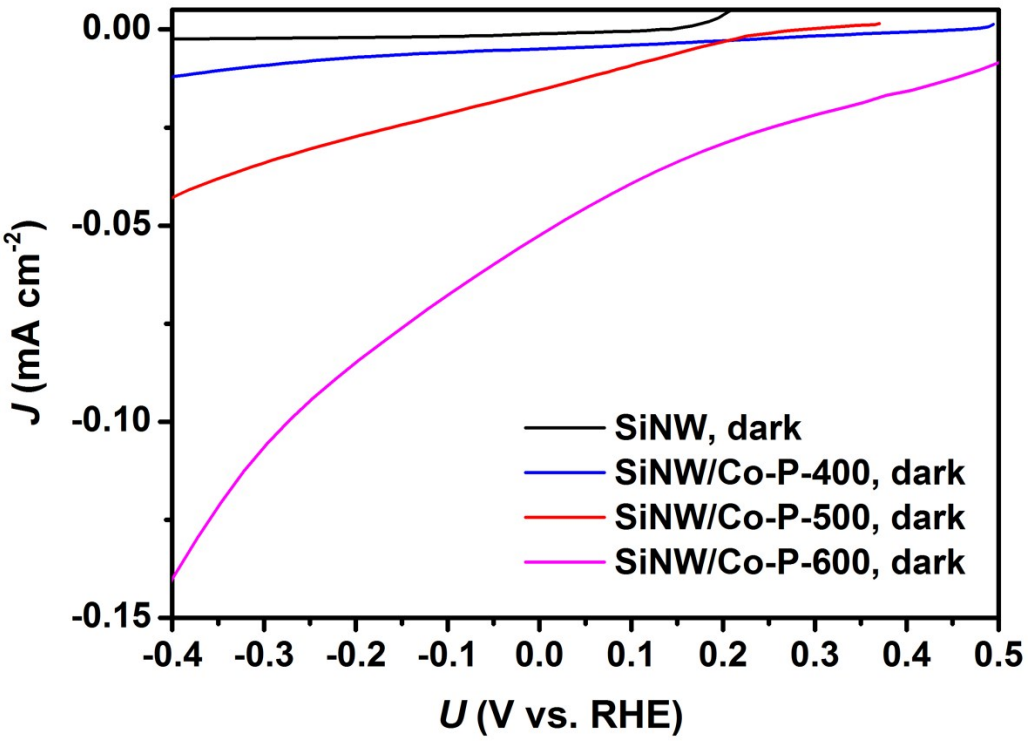

Figure S7. *J-U* profiles of the bare SiNW arrays, SiNW/Co-P-400, -500, and -600 recorded in 0.5 M K_2SO_4 solution (pH = 1) in the dark.

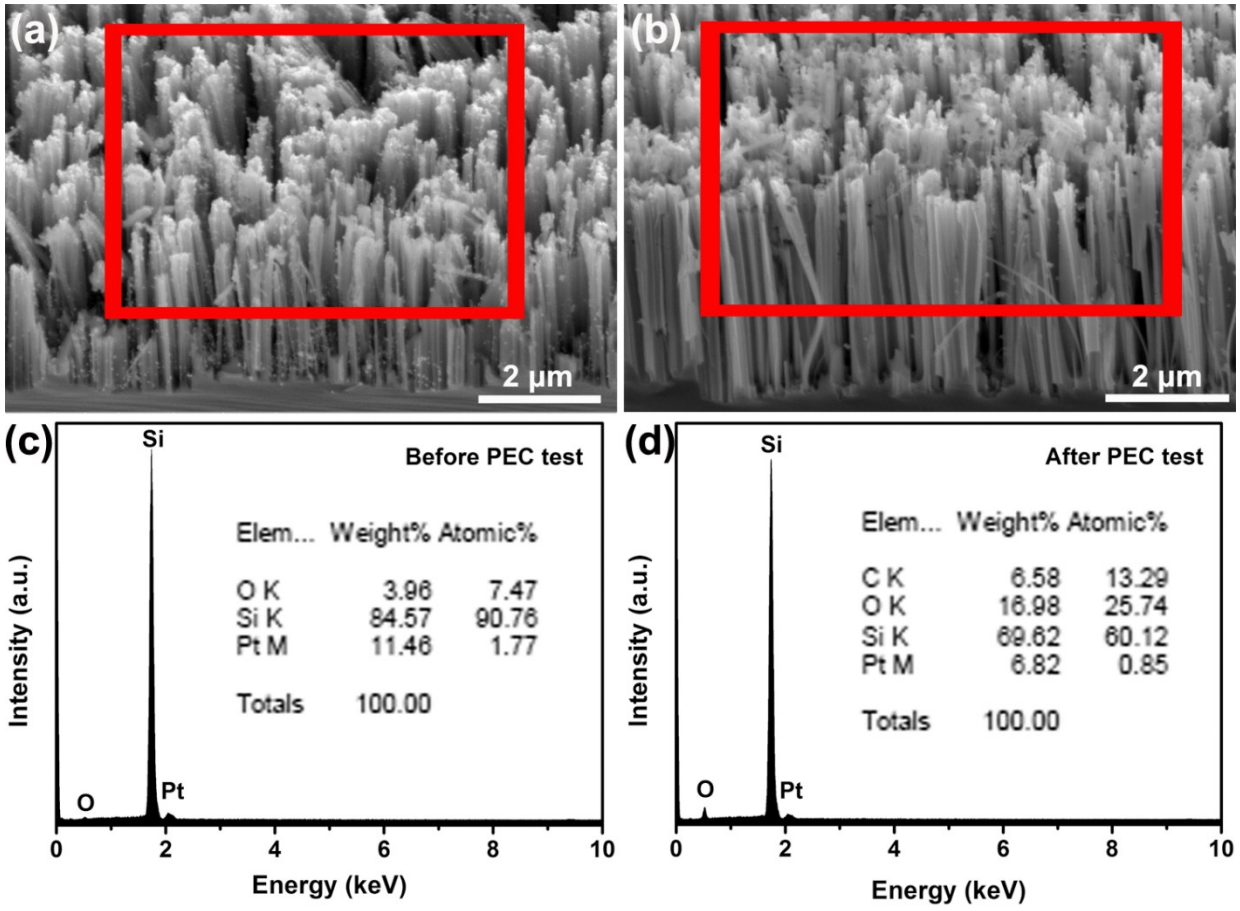

Figure 8. Morphology and EDX spectrum of the SiNW/PtNPs electrodes (a, c) before and (b, d) after the *J-t* tests in 0.5 K_2SO_4 (pH = 1) under nominal illumination of 100 mW cm^{-2}.

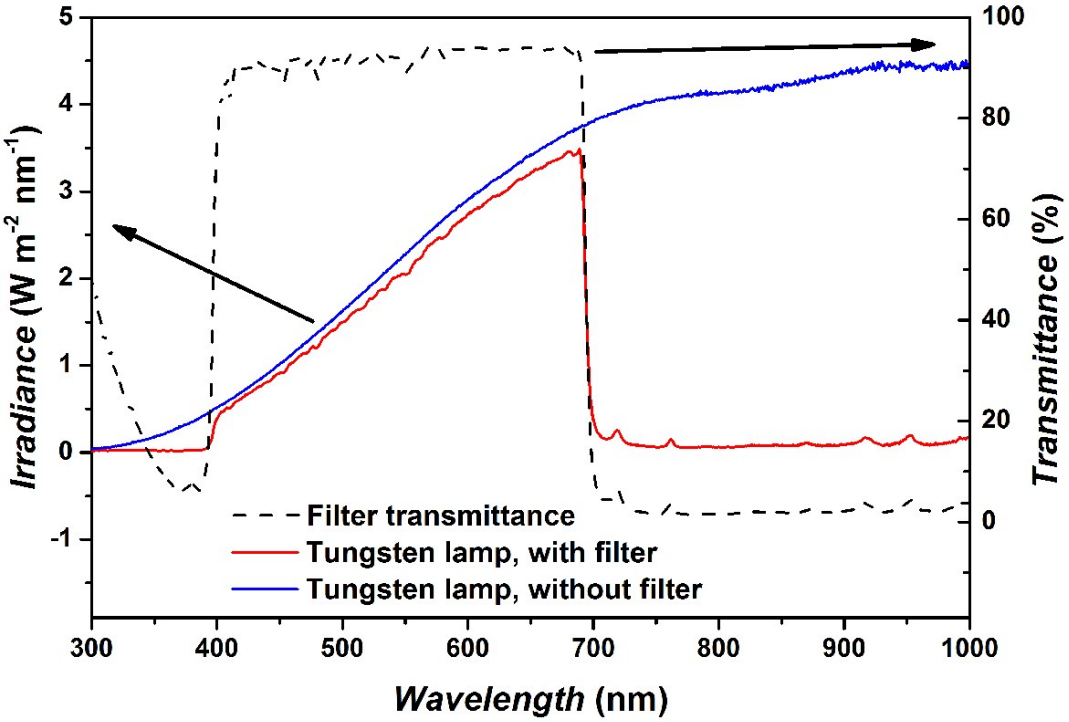

Figure S9. Spectra of the light source (Tungsten lamp WOW01, Zahner) measured with and without an IR filter (Newport, 20HMS-O hot mirror). The dotted line is a transmittance spectrum of the IR filter.

Table S1. Comparison of the PEC performance of the SiNW/Co-P photocathodes with that of PtNPs-decorated SiMW/SiNW arrays reported in the literature.

Samples	V_{OC} (mV)	J_{SC} (mA cm^{-2})	FF	η
n$^+$p-SiMW(60-100 μm)/PtNPs[S1]	440±14	13.2±5.8	0.47±0.08	2.7±1.3
n$^+$p-SiMW(40-60 μm)/PtNPs[S2]	540±10	15±2	0.71±0.02	5.8±0.5
SiNW (20 μm)/PtNPs[6b]	442	18.0	/	/
SiNW (15 μm)/PtNPs (ALD)[8b]	310	9.0	0.55	1.53
SiNW (15 μm)/PtNPs (ELD)[8b]	280	23	0.28	1.80
SiNW(29.3 μm)/PtNPs[S3*]	480	12.81	/	1.20
SiNW (2 μm)/PtNPs (this work)	280	19.6	0.17	1.60
SiNW (2 μm)/Co-P-400 (this work)	379	10.8	0.15	1.05
SiNW (2 μm)/Co-P-500 (this work)	399	18.2	0.10	1.24
SiNW (2 μm)/Co-P-600 (this work)	407	15.6	0.27	2.86

* The PEC performance of more Pt-decorated planar Si and SiMW/NW arrays is listed and compared in **Table S2** in the reference S3.

ALD – Atomic Layer Deposition

ELD – Electroless Deposition

Table S2. Fitting parameters obtained by fitting the Nyquist plots presented in **Figure 4c** with the equivalent circuit model shown in the inset.

Samples	R_e (Ω)	R_{ct} (Ω)	C_2 (μF)	R_1 (Ω)	C_1 (μF)	m
SiNWs	1.66	145.40	308.0	–	–	–
SiNW/PtNPs	1.02	0.73	201.2	0.94	19.3	0.12
SiNW/Co-P-400	1.96	3.42	222.5	1.78	303.9	0.54
SiNW/Co-P-500	2.03	1.02	661.5	0.60	325.8	0.96
SiNW/Co-P-600	1.69	1.52	491.5	3.35	290.3	0.38

References:

S1. E.L. Warren, J. R. McKone, H.A. Atwater, H.B. Gray, N.S. Lewis, *Energy Environ. Sci.* 2012, **5**, 9653-9661.

S2. S.W. Boettcher, E.L. Warren, M.C. Putnam, E.A. Santori, D. Turner-Evans, M.D. Kelzenberg, M.G. Walter, J.R. McKone, B.S. Brunschwig, H.A. Atwater, *J. Am. Chem. Soc.* 2011 **133**, 1216-1219.

S3. U. Sim, H.Y. Jeong, T.Y. Yang, K.T. Nam, *J. Mater. Chem. A* 2013, **1**, 5414-5422.