Supporting Information

Functional Integration of Catalysts with Si Nanowire Photocathodes for Efficient Utilization of Photogenerated Charge Carriers

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1. EXPERIMENTAL METHODS

1.1 Photoelectrochemical measurements

To generate simulated AM 1.5G irradiation, a 150 W xenon arc lamp was utilized with an air mass filter (1.5 Global), and the intensity was set to 100 mW cm^{-2} by adjusting the distance between the light source and the photoelectrodes. The light intensity was calibrated using a radiometer (Solar Light, PMA-2100) and a pyranometer (Solar Light, PMA-2144). For all the electrochemical experiments, an Ag/AgCl electrode (3 M NaCl, Bioanalytical System) and a coiled Pt wire were employed as the reference and counter electrodes, respectively. The potential from the Ag/AgCl reference electrode was calibrated for conversion to the reversible hydrogen electrode (RHE) scale by measuring the stabilized open-circuit potential versus a commercial RHE electrode (ALS Co.) in an H_2-purged 0.5 M H_2SO_4 electrolyte. The cyclic voltammograms were acquired under forced convective conditions with 300 rpm of stirring.

1.2 Physical characterization

The scanning electron microscope (SEM) was used with a SUPRA 55VP (Carl Zeiss) at 2 kV as an accelerating voltage at the National Instrumentation Center for Environmental Management of Seoul National University (SNU). To observe the cross-sectional view of the SiNW/AgPt by transmission electron microscope (TEM), the sample was prepared by a focused ion beam SMI3050SE (SII Nanotechnology). The TEM analysis was conducted with a JEM-300F (JEOL) at 300 kV at the Research Institute of Advanced Materials in SNU. To quantify the Pt loading by utilizing the inductively coupled plasma-mass spectrometry (ICP-MS, nexION 350D, PerkinElmer Inc.,), the photocathodes were immersed in 5 mL of aqua regia (3:1 $HCl:HNO_3$) for overnight to dissolve Pt and Ag into the solutions. Then, 5 mL of DI water was added and proceeded the analysis at the National Center for Inter-University Research Facility in SNU. The absorption spectra was acquired with a Cary5000 (Agilent) at Yonsei Center for Research Facilities.

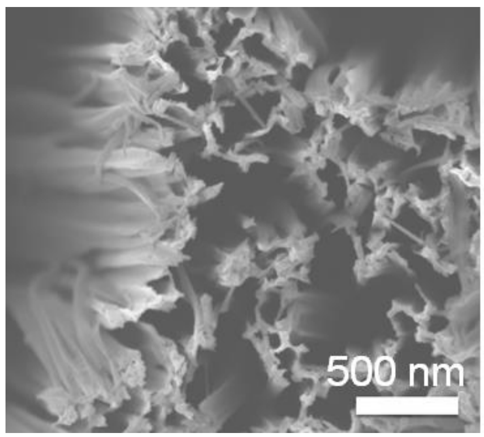

Figure S1. SEM image of bare SiNW.

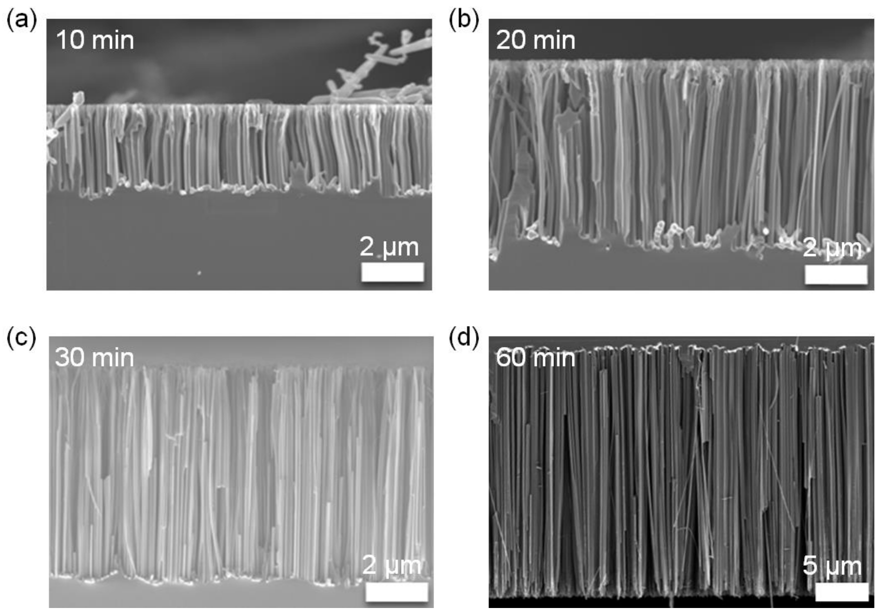

Figure S2. Cross-sectional SEM images of SiNW/AgPt photocathodes with different SiNW lengths fabricated with etching times of (a) 10, (b) 20, (c) 30, and (d) 60 min.

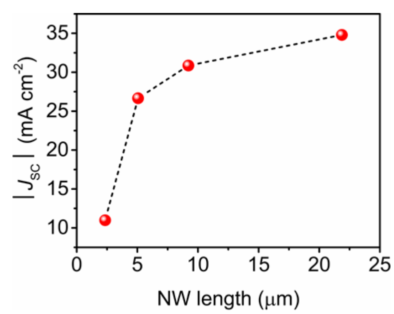

Figure S3. Effect of length of the SiNWs on saturated photocurrent density.

Table S1. Potential for acquiring −10 mA cm^{-2} ($V_{@-10\ mA\ cm^{-2}}$), current density at 0 V_{RHE} ($J_{@0\ V_{RHE}}$), J_{SC}, and V_{OC} in voltammograms for HER of SiNW-based photocathodes under AM 1.5G illumination.

SiNW-based photocathodes	$V_{@-10\ mA\ cm^{-2}}$ (V_{RHE})	$J_{@0\ V_{RHE}}$ (mA cm^{-2})	J_{SC} (mA cm^{-2})	V_{OC}
Pt/C	−0.0179	0	N/A	0
SiNW/Ag	−0.776	−0.0717	N/A	0.336
SiNW/Ag−Pt (10 min etching for NW formation)	−0.298	−4.63	−10.4	0.288
SiNW/Ag−Pt (20 min etching for NW formation)	−0.0169	−8.95	−26.1	0.207
SiNW/Ag−Pt (30 min etching for NW formation)	0.0194	−11.7	−30.6	0.250
SiNW/Ag−Pt (60 min etching for NW formation)	−0.0189	−8.59	−35.0	0.221
Pt_S/SiNW	−0.0166	−9.09	−24.8	0.350
Pt_L/SiNW	0.217	−22.5	−22.8	0.344
Pt_S/SiNW/Ag−Pt	0.182	−22.0	−25.1	0.345