Electronic Supplementary Information for

Diameter-Dependent Photoelectrochemical Performance of Silicon Nanowires

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Experimental Methods

Synthesis of SiNWs. Ultra-long SiNWs were synthesized by thermally evaporating SiO power in a high-temperature tube furnace with the length of 1.2 m and the inner diameter of 39 mm. A 5-cm long alumina boat loaded with 4 g of SiO (Aldrich, 325 mesh, 99.9%) was placed in the high-temperature tube center. Another 15-cm long alumina boat loaded with 10 g of Sn was placed 8 cm away from the high-temperature center. The tube was first pumped to 1000 Pa and sealed. Then the high-temperature center was heated from room temperature to 1330 ^{o}C at a ramping rate of 15 ^{o}C min^{-1}. After keeping the high-temperature center at 1330 ^{o}C for 6 h, a dark yellow product was obtained. After treated with hydrofluoric (HF) acid solution (5%, mass fraction), bare silicon nanowires are obtained and their morphologies were studied with SEM (S-4300, Hitachi).

Fabrication of single SiNW photoelectrode. As shown in **Fig. 1a**, a single SiNW was first treated by HF solution (5 %, mass fraction) to remove the outer oxide layer and then transferred to a glass substrate. After conducted with silver paste on one end, the photoelectrode was partially capsulated with silicone rubber, leaving a 1-mm long SiNW area exposed along the wire axis.

Photoelectrochemical measurement. Current density versus voltage (*J*-*V*) measurements were performed in a two-electrode configuration with a single SiNW photoelectrode as the work electrode and a 1 cm*1 cm Pt slice as the counter electrode under an inert atmosphere. The electrolyte solution consisted of 200 mM dimethylferrocene (Me_2Fc), 0.5 mM Me_2FcBF_4, 1 M $LiClO_4$ in methanol solvent. The cell was illuminated perpendicular to the photoelectrode substrate with a solar simulator (Oriel Solar 3A, Newport) and electrical data were recorded with an electrochemical workstation (CHI660E, CH Instruments, Inc.).

The plots of the relationship between the diameter of SiNWs and PEC parameters including V_{oc}, J_{sc} and η, were obtained by measuring 80 samples. SiNWs with the diameter distribution within 50 nm were taken as a group. Diameters and PEC parameters from each group of SiNWs were averaged as one single data point.

The relationship between the diameter of SiNWs and fill factors were obtained by *I-V* measurement of the photoelectrodes made from different segments of a single nanowire. In other words, a single ultra-long SiNW was cut into several segments and every segment was integrated into a photoelectrode. Symbols and the line with the same color in **Fig. 5** are the experimental data and the corresponding fitting line from different segments of a single nanowire, respectively.

Monochromatic incident photon-to-electron conversion efficiency (IPCE) measurement was conducted by using a 500 W xenon lamp as the light source and a monochromator to produce monochromatic light, whose intensity was tested with a power meter (PM100D&S120VC, Thorlabs).

Supplementary information 1 The morphology and structure of the SiNWs

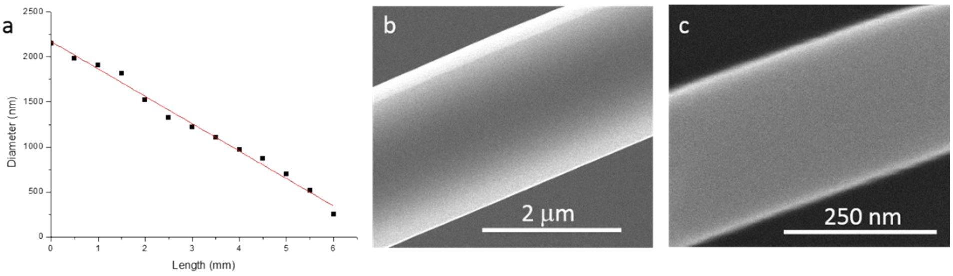

Fig. S1 *(a) Plot of diameter versus length from a single SiNW after treated with a 5% HF solution. (b) SEM image of the thick end of the single SiNW. (c) SEM image of the thin end of the single SiNW.*

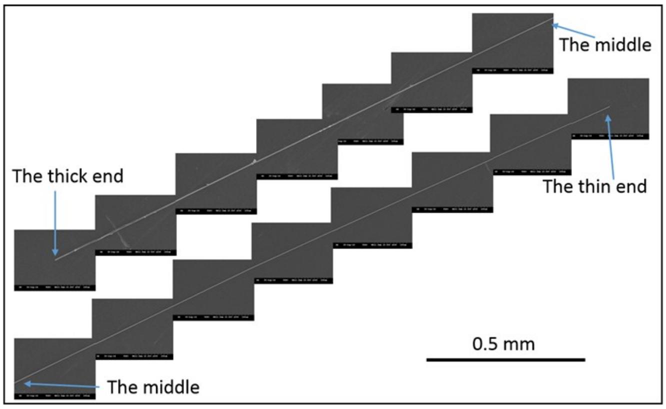

Fig. S2 Integrated SEM images show a 3.8 mm segment of SiNW with the diameter smoothly changing from 2.62 μm to 1.44 μm.

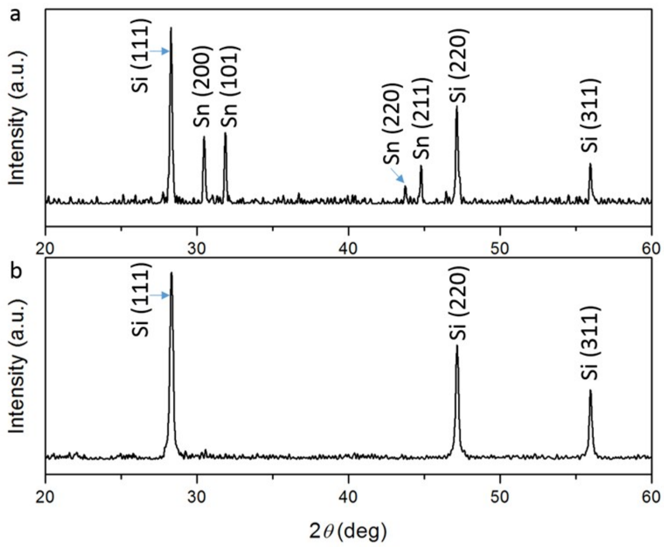

Fig. S3 XRD patterns of the as-synthesized (a) and HF-treated (b) silicon nanowires, respectively.

The SiNWs are usually 5-8 mm in length with a linearly changing diameter along the axis from about 200 nm to more than 2000 nm (Fig. S1, ESI†). It is pointed out that this diameter variation could be noted only because the product has such an ultra-long feature. For SiNWs used in the PEC measurement, the rate of change is roughly 31 nm in diameter per 100 μm in length (i.e. 0.031%), which is so small that could be neglected in ordinary nanostructure with the length of hundreds of micrometers. We take the arithmetical mean of the largest and smallest diameters of every sample as the diameter of the sampled value. We believe the smooth change in diameter along the longitudinal direction implies that the single nanowire samples are suitable to be used to investigate the structure-property relationships of SiNWs:

i) The light absorption area could be correctly calculated by $d*l$ with the average diameter d in consideration of the linearly changing diameter.

ii) In consideration of the absorption peaks' gradual and continuous changes with diameter, the absorption spectrum from the single nanowire sample could possess basically the same peaks as that from the SiNW with the average diameter.

iii) We measured the resistivity of the samples using four probe measurement (Fig. S6, ESI) and it shows the diameter change has ignorable effect on the resistivity.

More importantly, the sampling method is set the same for each sample, so the systematical deviation arising from the diameter variation might be ignorable on the view of the whole experiment. On these basis, it is believed the measured relationships between photoelectrochemical performance and the diameter are reasonable.

Supplementary information 2

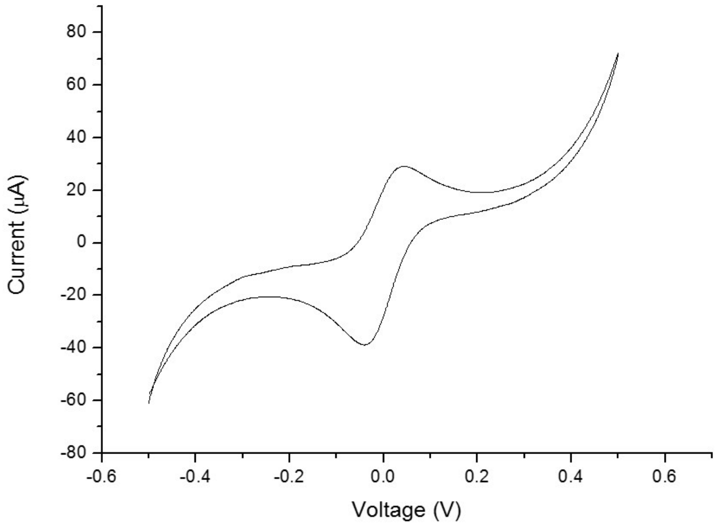

Fig. S4 *Cyclic voltammetry curve of the electrolyte solution with two 1 cm*1 cm Pt slices as electrodes.*

Cyclic voltammetry measurement was tested in two electrodes configuration with two 1 cm*1 cm Pt slices as electrodes in the same electrolyte solution for the PEC testing. The current is in the magnitude of 10^{-5} A in this test, which is at least two orders of magnitude larger than the current (no more than 10^{-7} A) in the single nanowire PEC test. Considering that the only difference between the two tests is the different work electrodes, this result suggests that the electrochemical reaction on Pt slice electrode occurs much easier than that on single nanowire photoelectrode. Hence，the current-voltage data from the single SiNW PEC system mainly depend on the property of single SiNW photoelectrode and thus the two-electrodes PEC configuration used in the main text could be an effective setup for investigating the PEC performance of single SiNWs.

Supplementary information 3

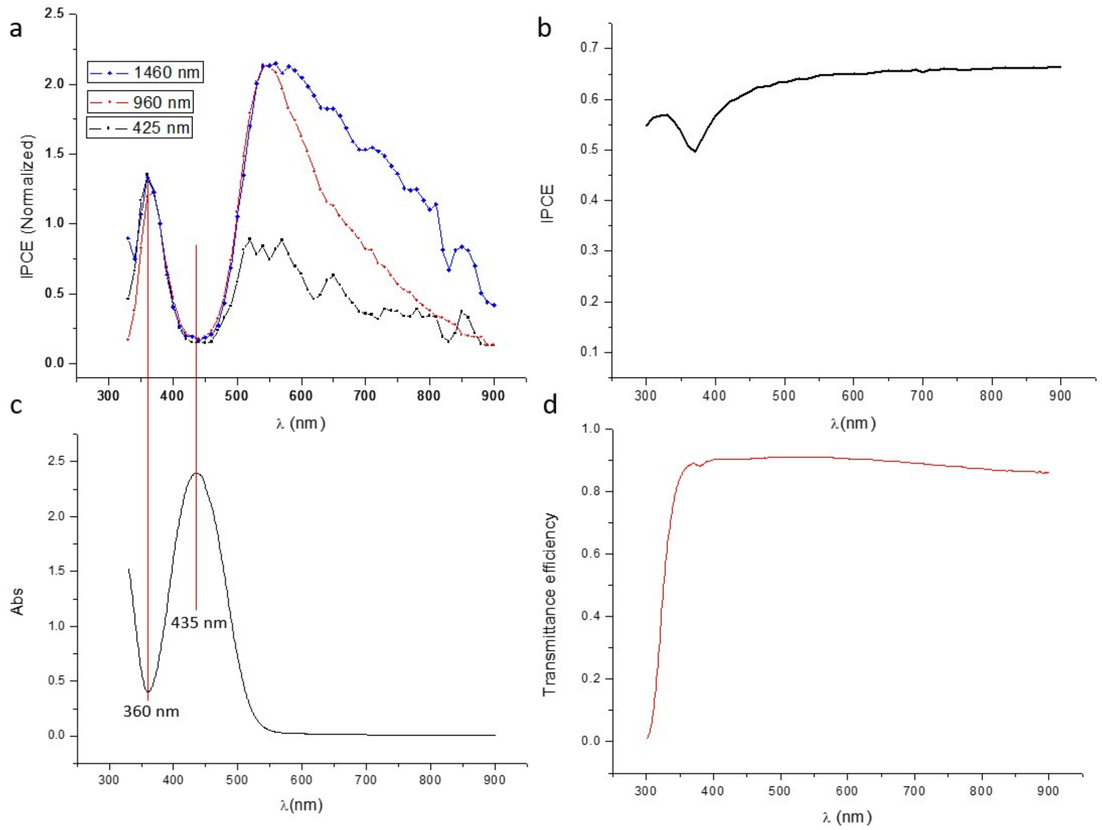

Fig. S5 *(a) the original data (normalized with the value at wavelength of 380 nm) of the monochromatic incident photon-to-electron conversion efficiency (IPCE) from single SiNW photoelectrodes with nanowire diameters of 425 nm, 960 nm, and 1460 nm, respectively; (b) the IPCE of standard silicon cell (Newport Oriel instrument); (c) the absorbance of the electrolyte solution with the thickness of 1 mm; (d) the transmittance efficiency of the glass substrate for single nanowire photoelectrode.*

IPCE is defined as the ratio of the number of electrons generated in the circuit in unit time to the number of incident monochromatic photons in unit time.

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where e is the elementary charge, $1.6*10^{-19}$ Coulomb; I_{sc} is the short current; P_{in} is the power density of incident monochromatic light; S is the light collection cross-sectional area; h is Planck constant; c is the light velocity; λ is the wavelength of the incident monochromatic light. When the units of I_{sc}, S, P_{in}, and λ are respectively μA,

cm^2, W/m^2 and nm, IPCE could be obtained by

In the single nanowire PEC configuration, light has to pass through the electrolyte solution of about 0.4 mm thick and a glass substrate before reaching the nanowire. Thus the data in **Fig. S5a** need to be corrected according to the following method in order to show the real IPCE of single nanowires.

According to the Lambert-Beer law, $A = -\lg\left({}^{I}/_{I_0}\right) = klc$, in which A is the absorbance of the solution; I is the intensity of transmission monochromatic light; I_0 is the intensity of incident monochromatic light; ${}^{I}/_{I_0}$ is the transmittance efficiency of monochromatic light; k is the molar absorptivity; l is the optical path in the solution; c is the molar concentration of the solution. And thus the transmittance efficiency of 0.4 mm thick solution $({}^{I}/_{I_0})_{0.4}$ could be calculated from the absorbance of the electrolyte solution of 1 mm thick ($A_{1.0}$) in **Fig. S5c** as follows.

$$({}^{I}/_{I_0})_{0.4} = 10^{-0.4A_{1.0}}$$

In consideration of , corrected IPCE value equals to the measured IPCE in **Fig. S5a** divided by the transmittance efficiency of 0.4-mm thick solution $({}^{I}/_{I_0})_{0.4}$ and the transmittance efficiency of the glass substrate $({}^{I}/_{I_0})_{glass}$ (**Fig. S5d**),

$$IPCE_{corrected} = \frac{IPCE_{measure}}{({}^{I}/_{I_0})_{0.4} * ({}^{I}/_{I_0})_{glass}}$$

And then the resulted IPCE is further normalized on the basis of value at wavelength of 380 nm, which is shown in **Fig. 3** in the main text.

Supplementary information 4

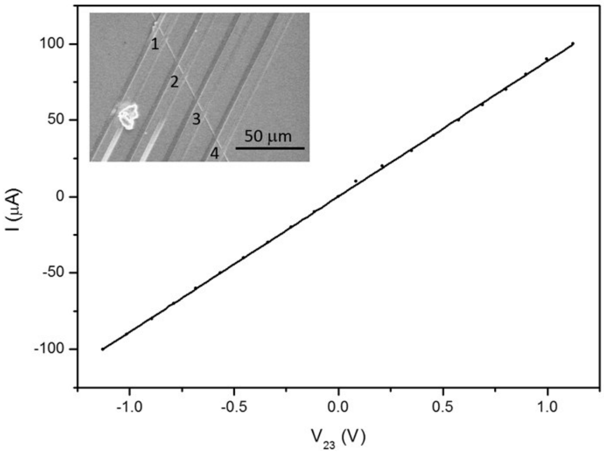

Fig. S6 *Plot of current versus voltage from a single SiNW with the four-probe method. The inset SEM image shows the tested part of the single SiNW and the four-probe electrodes.*

The resistivity and doping level of the SiNWs were evaluated using the four-probe method and a typical *I-V* plot is shown in **Fig. S6**. The average resistivity of the SiNWs is $5*10^{-3}$ Ω cm and the doping level calculated from the resistivity is $1.22*10^{19}$ cm^{-3} (SEMI, MF723-99).

The electrical resistance of a single SiNW of 1000 nm in width and 1 mm in length in this work is calculated to be about 64,000 Ω.

Supplementary information 5

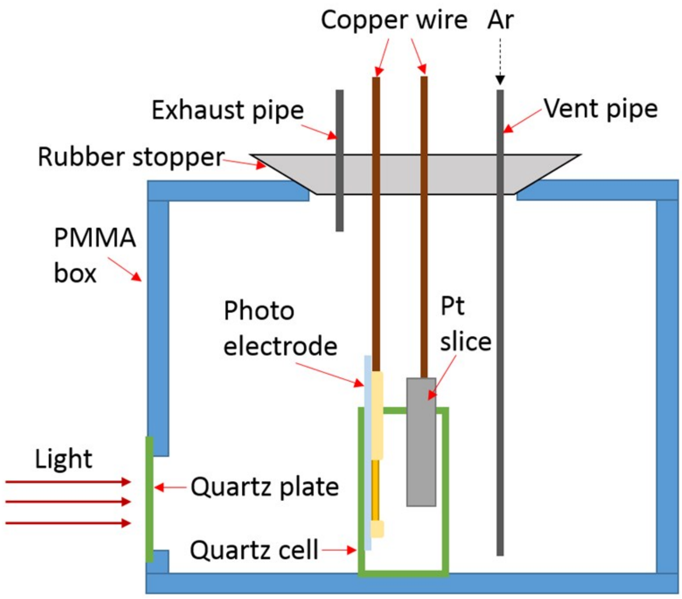

Fig. S7 Schematic picture of the photoelectrochemical cell. The only difference in PEC (J-V) test and IPCE test is the different light sources. A solar simulator was used to provide simulated AM 1.5G solar illumination in the PEC (i.e. J-V) test, while a combination of a 500 W xenon lamp and a monochromator to produce monochromatic light in the IPCE test.