# Supporting information for: Photoelectrochemical hydrogen evolution of

## tapered silicon nanowires improved by chemically modulated surface

#### **Experimental section**

### A. SiNW fabrication and post KOH etching

The SiNW fabrication followed two-step metal assisted chemical etching (MaCE). Prior to the etching, Czochralski-grown single side polished p-type (100) Si with resistivity 1-10  $\Omega$  cm were cleaned in a Piranha (98% H<sub>2</sub>SO<sub>4</sub>/ 30% H<sub>2</sub>O<sub>2</sub> = 3:1, (v/v)) solution for 15 min and then rinsed by DI water. Clean Si wafers were then cut into pieces of suitable size and dipped into 5% HF solution for 3 min to remove the native oxide. Subsequently, the MaCE was carried out by immersing Si samples into 5 M HF and 10 mM AgNO<sub>3</sub> solution for deposition of Ag nanoparticles (AgNPs) and then etched in an aqueous etchant containing 5 M HF and 0.3 M H<sub>2</sub>O<sub>2</sub>. After etching, the Si samples were dipped into highly concentrated HNO<sub>3</sub> to remove the AgNPs.

For post KOH etching, Si samples were firstly dipping into 5 % HF solution and then were rinsed by DI water and dried by N<sub>2</sub> gas blowing. Afterwards Si samples were immediately transferred into 1 wt% KOH solution for etching. All experiments were performed at room temperature inside a fume hood.

### **B.** Optical characterization and PEC setup

Optical reflection measurements have been performed over 300–2200 nm wavelengths using a UV–Vis/NIR spectrophotometer (Lambda 750, Perkin Elmer) in which a 60 mm integrating sphere (Labsphere) is equipped to account for total light reflected from the samples.

A Si sample was mounted at the backside of a Teflon photoelectrochemical cell by screws. An ohmic contact was formed by smearing In-Ga eutectic on the backside of Si sample. The PEC measurements were conducted using an IVIUM potentiostat in a three electrode configuration. An Ag/AgCl (Saturated KCl) acted as the reference electrode and platinum wire was used as counter electrode. The electrolyte was 0.5 M H<sub>2</sub>SO<sub>4</sub>. Prior to the PEC measurements, the native oxide on the Si photo-electrodes was removed by a 3-minute-dip in a 5% HF solution. The light source used was a 150 W Xe arc lamp with AM 1.5 G filters a light source shining at the top of PEC cell. The incident flux was measured using a calibrated power meter, double-checked also by the NREL-calibrated solar cell (PV Measurements, Inc.). The photo-electrochemical J-V curves were ramped from – 1.6 V to 0.2 V (vs. Ag/AgCl electrode, 3M KCl) at a rate of 50 mV/s.



**Figure S1.** Tilted-SEM views of SiNWs with different post-KOH etching times (a) 0 s (b) 30 s (c) 60 s (d) 90 s.



Figure S2. Cross sectional SEM view of SiNWs with different etching time (a) 1min and (b) 5

min. Tiny pores are visible at the top of SiNWs.



Figure S3. TEM images of SiNWs fabricated by MaCE. There are tiny pores located at the top

of SiNWs.



Figure S4. Lifetime versus exposing time in air after HF dipping. Planar EG-Si(100) wafer

(Black square), EG-SiNW etched for 5 min (Red circle) and 60 min (Blue triangle).

## Simulation details:

A three dimensional finite element method (FEM) simulation is performed using a commercially available FEM package (COMSOL Multiphysics 4.2a). Truncated cones are periodically distributed in a square lattice. The period, bottom diameter and height of the truncated cones are fixed to be p=200 nm, d=150 nm and h =600 nm, which are chosen to be similar to our experimental data. In our modeling, the top diameter (t) is varied to form different geometries. When t approaches 0, we have an explicit nano-cone array; when t equals to d = 150 nm, we have a Si nano-wire array; when 0<t<d, it is a nano-frustum array. The schematics are shown in Fig. S3.



Figure S5. Schematic representing Si nanowire, nanofrustrum and nanocone.

In the simulation, only one unit cell is considered in which only one nanocone is included. The incident light is set to be x-polarized propagating along the -z axis.Boundary conditions of perfect magnetic conductors (PMCs) were used for y=-p/2 and y=p/2 planes, and perfect electric conductors (PECs) conditions were used for the other two planes, x=-p/2 and x=p/2. Perfect matched layers (PMLs) were used at the top and bottom of the unit cell and ended with the scattering boundaries. The reflectance is determined by:

$$R = 1 - \frac{\iint P_z dx dy}{E_{in}}$$

in which Pz is the is the the averaged power flow in a probe plane in front of the cell and Ein is the total energy of the incident light in each cell. The electron generated rate is calculated using the following spectral weighted integration

$$EGR = \int \frac{\varepsilon'' |E|^2}{2h} \Gamma_{solar} (\lambda) d\lambda$$

in which  $\varepsilon$ " is the imaginary part of permittivity, E is the calculated electric field, and  $\Gamma_{solar}(\lambda)$  is the AM1.5 solar irradiance spectrum. The EGR reveals the number of electrons that are generated in a specific position per second.