Supporting Information

3D High-Density Hierarchical Nanowire Architectures for High-Performance Photoelectrochemical Electrodes

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Experimental details

(1) Experimental setup and procedures for TiO_2 NR growth.
Surface-reaction-limited pulsed chemical vapor deposition (SPCVD) process was used to grow TiO_2 NRs from a home-made atomic layer deposition (ALD) facility. Separated exposures of gaseous $TiCl_4$ and H_2O vapors were controlled by solenoid valves and adjusted by fine tuning the precursor tank temperature. In details, substrates were placed at the center of the stainless steel-made ALD chamber and 10 cm downstream away from the precursor inlet nozzle. During the growth, a constant flow of 40 sccm N_2 was applied into the chamber as the carrier gas, which provided a background pressure of 2.7 Torr. The chamber temperature was maintained at 600 ^oC. In a typical TiO_2 NRs growth process, $TiCl_4$ and H_2O vapor precursors were pulsed into the chamber for 500 ms each and separated by purging N_2 for 60 s. Thus, one growth cycle includes 500 ms of H_2O pulsing + 60 s of N_2 purging + 500 ms of $TiCl_4$ pulsing + 60 s of N_2 purging. After growth, the chamber cooled down to room temperature naturally under N_2 flow.

(2) Fabrication of patterned Si NW arrays by dry etching
Patterned and vertically aligned Si NWs were fabricated by deep reactive ion etching (RIE) method using mono-dispersed silica spheres as mask. First, n-type

Si (100) wafer (resistant = 0.001~0.005 Ωcm) was cleaned by acetone, ethanol and DI water and then dried by N_2. Second, a monolayer of silica spheres (498 nm, 3×10^8 particles/mL, Fisher Scientific) was self-assembled on the Si wafer surface by rolling rod method.[1] This method provide a uniformly distributed SiO_2 sphere monolayer covering the entire Si wafer surface with closely-packed domain sizes ranging from ~20-100 μm. Third, Surface Technologies Systems (STS) silicon etching facility was applied with alternating etching (3.5 s pulse SF_6) and sidewall passivation (2.5 s pulse C_4F_8) steps using a 13.56 MHz plasma to etch high-aspect ratio Si NWs. 30 minute etch led to 10 μm long NWs. Finally, the silica spheres left on top of Si NWs were washed away by immersing the sample in an HF solution for 5 minutes.

(3) Fabrication of Si NW arrays by wet etching

Highly orientated Si NWs arrays were fabricated by the metal assisted electroless etching method. The same n-type Si wafer as those used in dry etching experiments was selected and cleaned following the same procedure. The etchant solution was a 40 mL mixture of 0.02 M $AgNO_3$ and 5 M HF. The Si wafer was then immersed in the etchant solution at room temperature for different periods of time. Typically, 30-minute etching yielded 1.5 μm long NWs; 7, and 20 hour etching yielded 10, and 20 μm long NWs, respectively. After etching, the substrates were cleaned by DI water and then immersed in HNO_3 to remove the Ag residual. Finally, the Si substrates were rinsed by DI water again and dried by N_2 gas.

(4) TiO_2 Overcoating

After the growth of TiO_2 NRs on either dry-etched Si NWs or wet-etched Si NWs, the substrates were immersed in 40 mL HF (1:50) for 10 minutes and then 40 mL HCl (10%) for 5 minutes to remove possible oxidized Si and contamination. Then the samples were loaded in the deposition chamber for TiO_2 ALD overcoating. The growth conditions were 500 ms H_2O pulsing + 60 s purging + 500 ms $TiCl_4$ pulsing + 60 s purging at 300 ^oC. Other deposition conditions were identical to SPCVD. After overcoating, the chamber was cooled down to room temperature naturally under N_2 flow.

References:

[1] S. Jeong, L. Hu, H. R. Lee, E. Garnett, J. W. Choi and Y. Cui, "Fast and Scalable Printing of Large Area Monolayer Nanoparticles for Nanotexturing Applications," *Nano Letters*, 10, 2989-2994(2010).

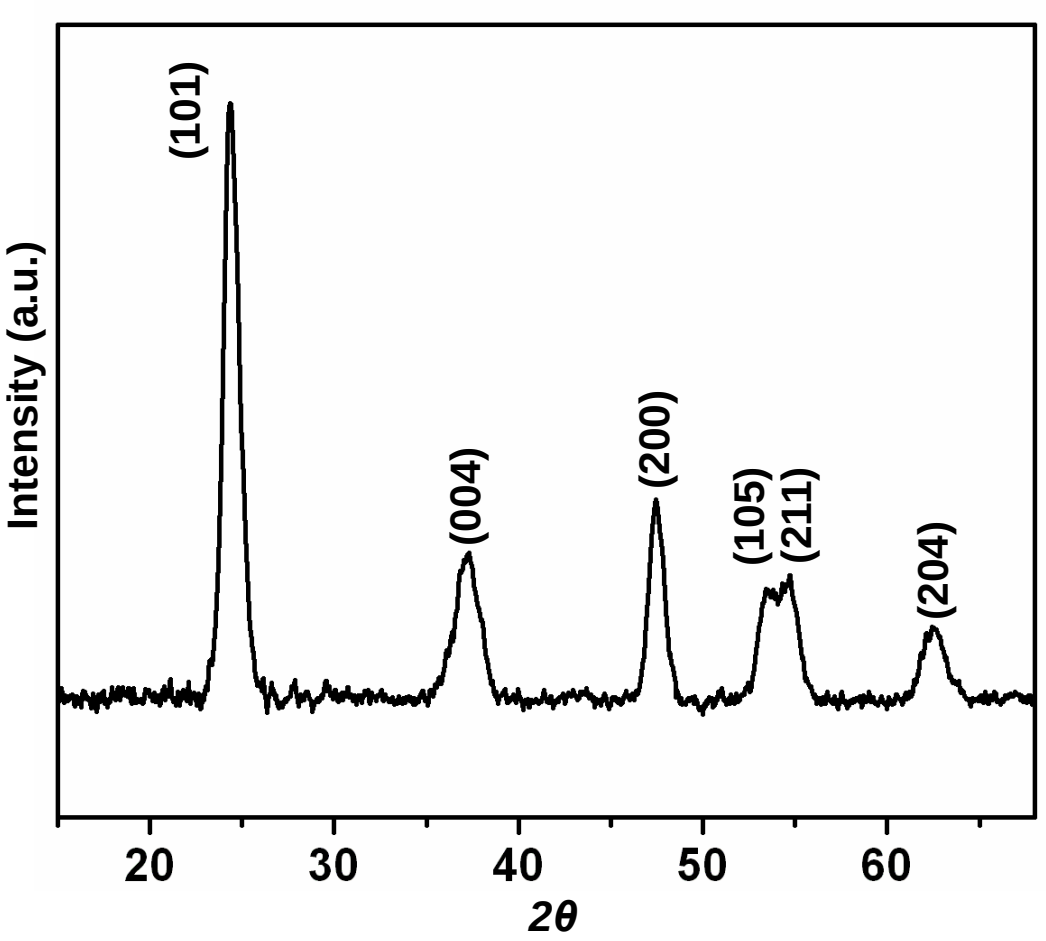

Figure S1. X-ray diffraction pattern (XRD) of as-grown TiO_2 NRs identifying the pure anatase phase.

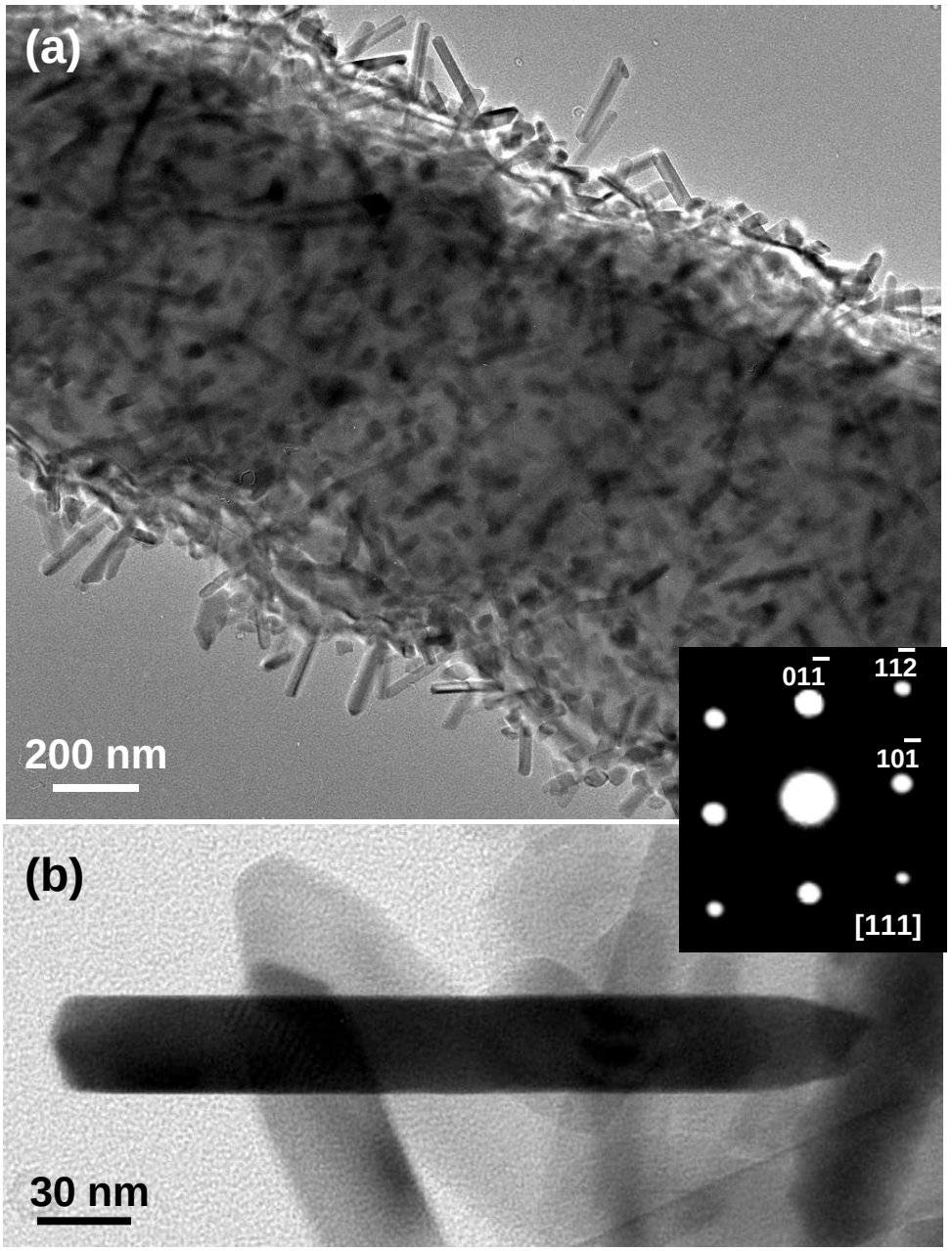

Figure S2. (a) TEM image of TiO_2 NRs grown on a big Si wire showing a dense and uniform coverage of TiO_2 NRs on Si surfaces. (b) Higher resolution TEM image of a single TiO_2 NR showing the uniform thickness and well faceted surfaces. Inset is the corresponding selective area diffraction pattern confirms the anatase phase.

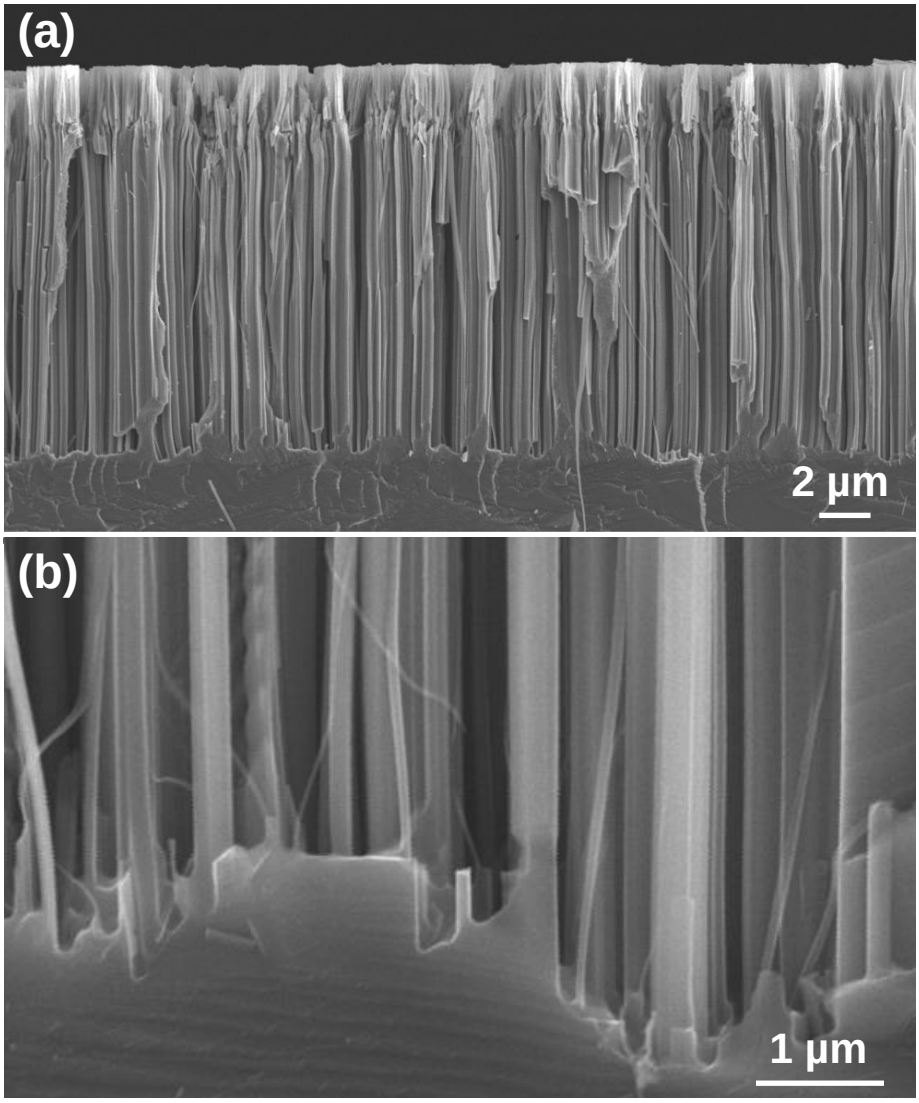

Figure S3. (a) An SEM image of as-fabricated Si NWs by metal assisted electroless wet etching method. With a length of ~20 μm, all the Si NWs were straight and perpendicular to the substrate surface. The top 2-3 μm were bundled together. **(b)** A magnified SEM image of the root region showing a wide size variation of the NW thickness. In average, ~200-300 nm open spaces were left between Si NWs.

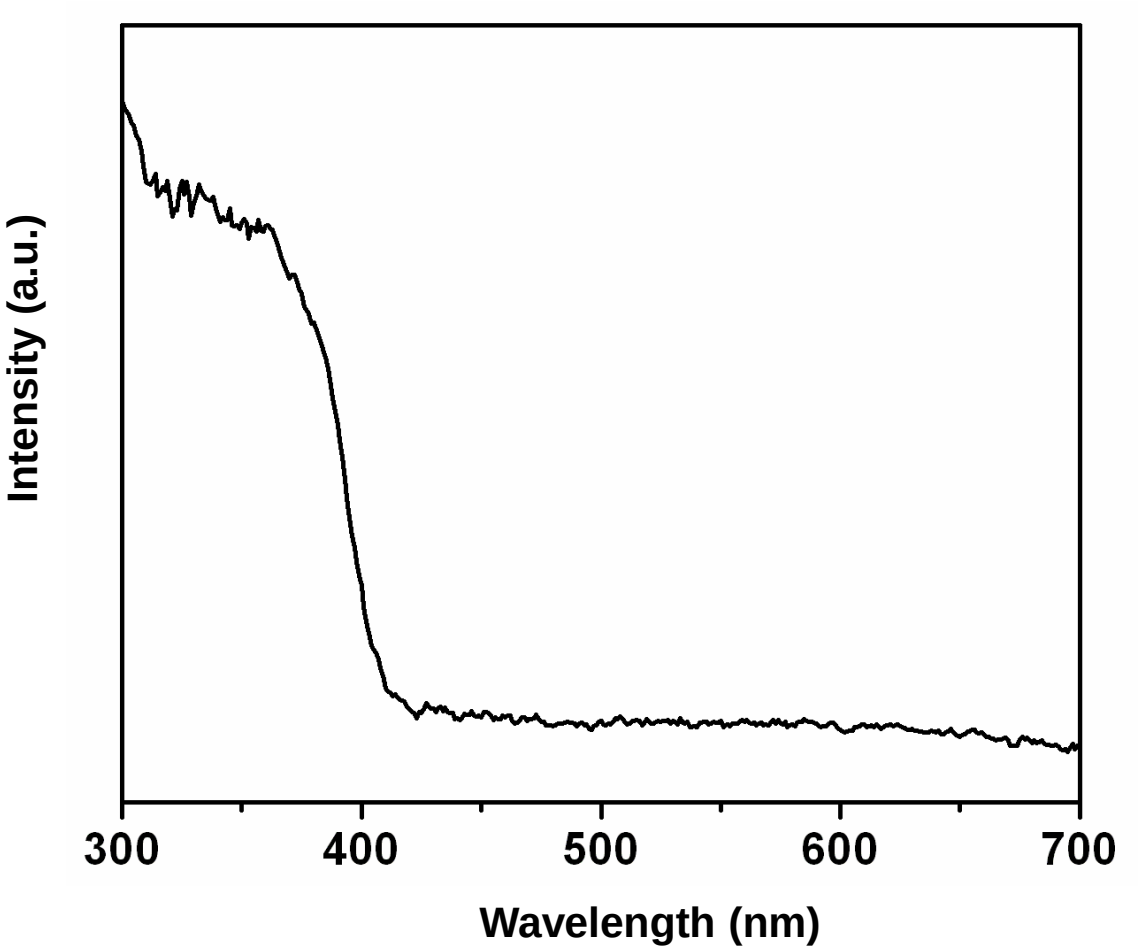

Figure S4. UV-Vis absorption spectrum of 600 cycles-TiO_2 NRs grown on alumina substrate.

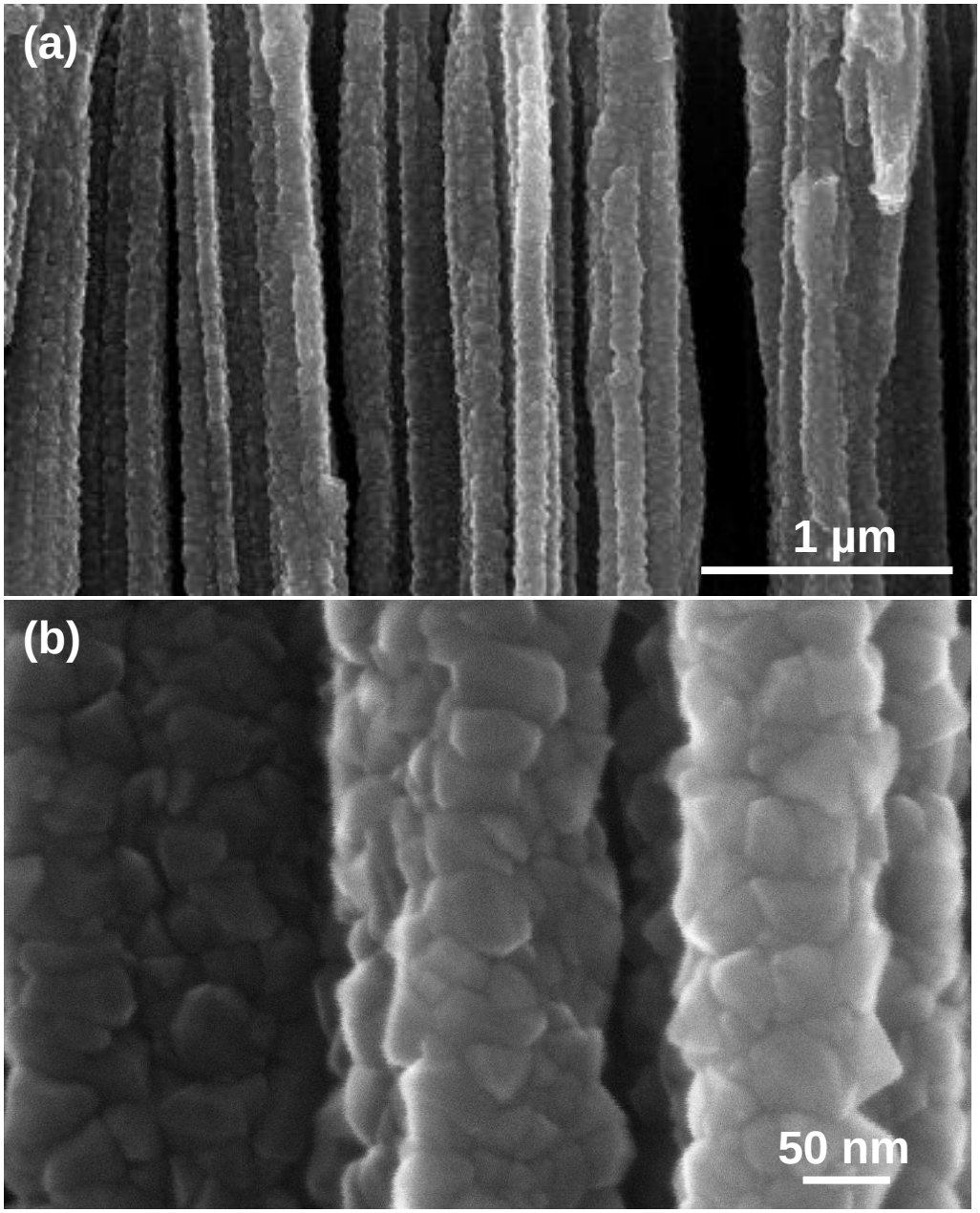

Figure S5. (a) SEM image TiO_2 film-coated Si NWs. The TiO_2 film was deposited by 375 cycles of ALD at 300 °C. All the Si NWs were covered uniformly. **(b)** Magnified image showing the polycrystalline feature of TiO_2 film and the grain size varied from ~10 to 50 nm.

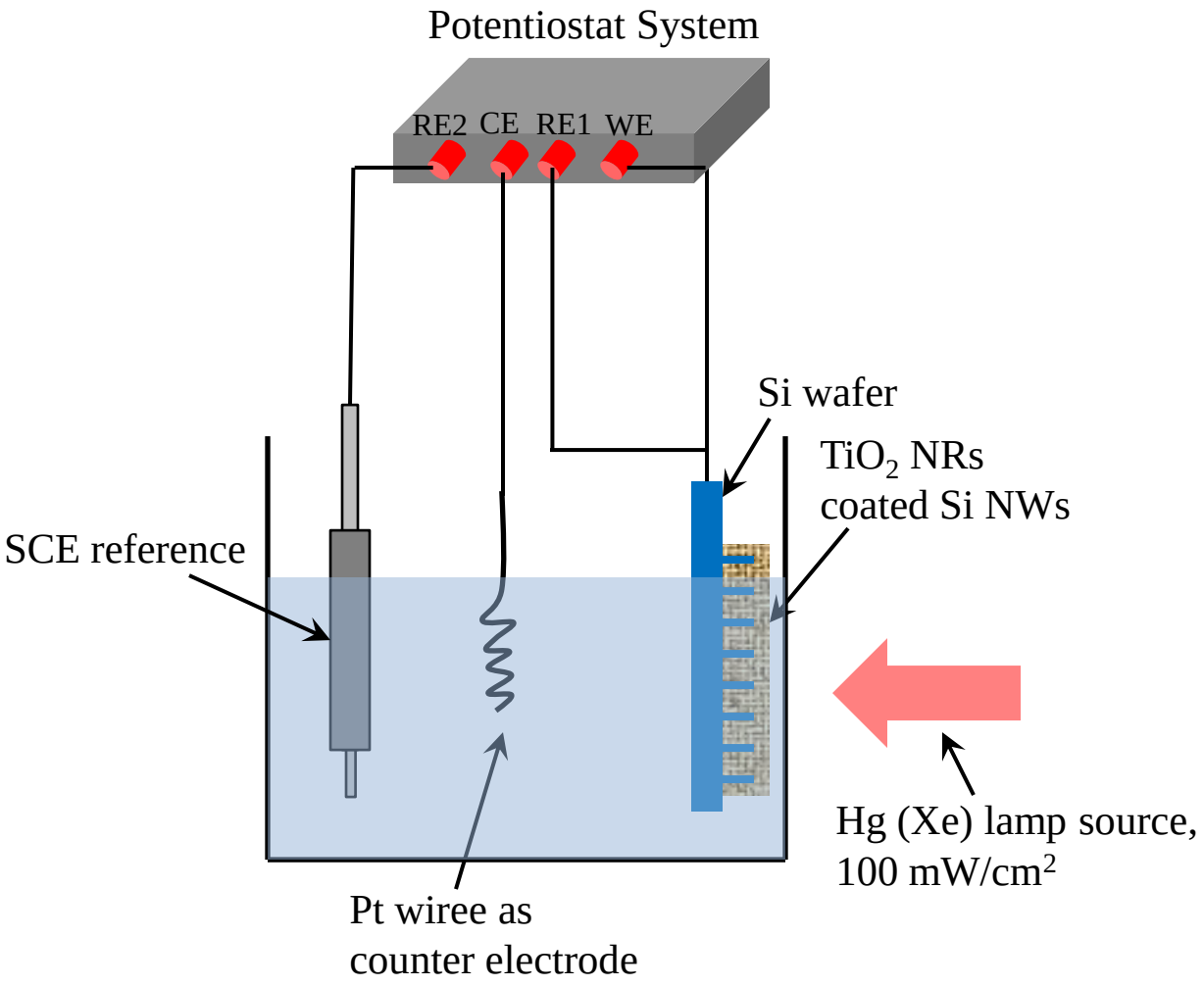

Figure S6. Schematic of PEC measurement system. A Solartron potentiostatn (SI 1287) system was used for *J-E* measurement. Prior to potentiodynamic testing, back side of a 3 cm × 1 cm sample was covered by epoxy to prevent the contact between Si surface and electrolyte. On the front side, half sample surface was scratched by razor to remove TiO_2 and the other half surface was partially covered by epoxy. The exposed sample region was usually a few millimeter square to a few tens of millimeter square. To test the sample, the scratched sample surface was connected to the measurement circuit. The epoxy covered region was immersed in the electrolyte with the exposed surface facing the incident light.

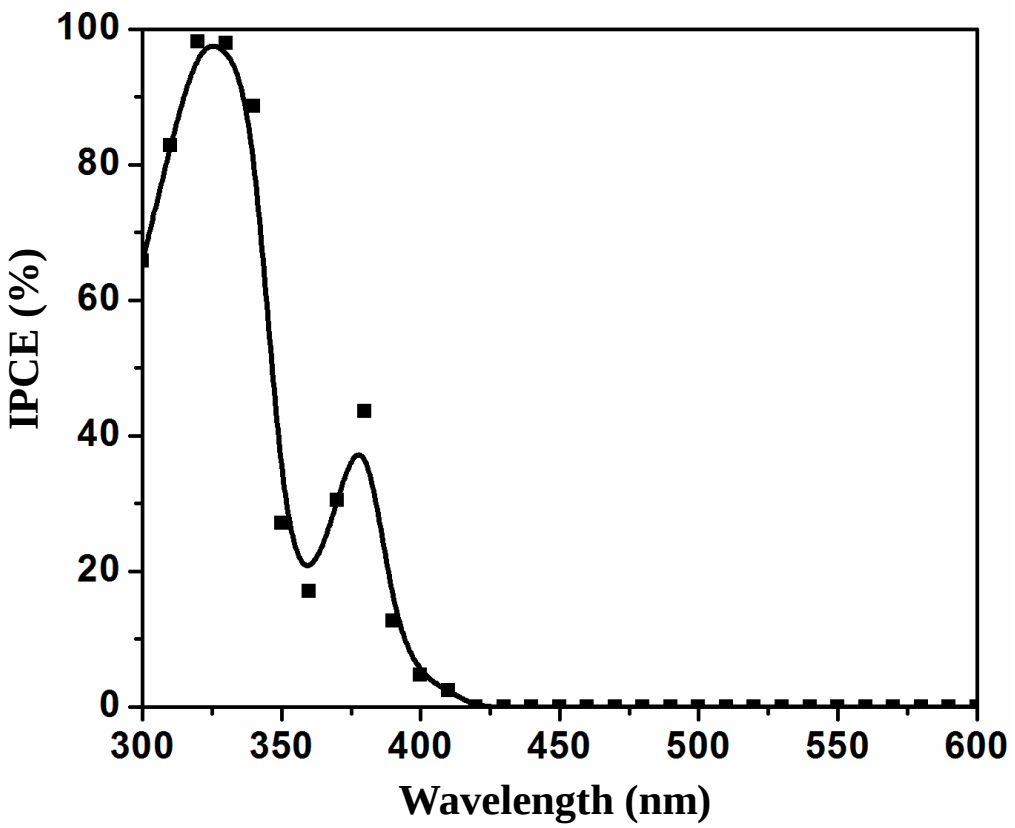

Figure S7. Incident photon to charge carrier efficiency (IPCE) measured on 10 μm-long wet-etched Si NW arrays covered with TiO_2 NRs and 250-cycle overcoating. The measurement was conducted at a constant bias potential of -0.64 V vs. SCE. IPCE measured from other TiO_2 NR-Si NW configurations showed similar curves. All cut-off wavelengths were observed at ~420 nm, which was well aligned with the absorption peak (Fig. S4).

The peak of ~50% near the absorption edge evidences the proposed charge transport scheme of the TiO_2-Si heterojunction structure (Fig. 5a). When the electron energy is low (near the absorption edge), additional e-h pairs in Si would be necessary for electron conduction through the anode. Thus, absorption of two photons may be required for the completion of one redox reaction. For high-energy electrons (generated by photons with shorter wavelength), the barrier between TiO_2 and Si becomes negligible and a nearly 100% IPCE could be obtained.

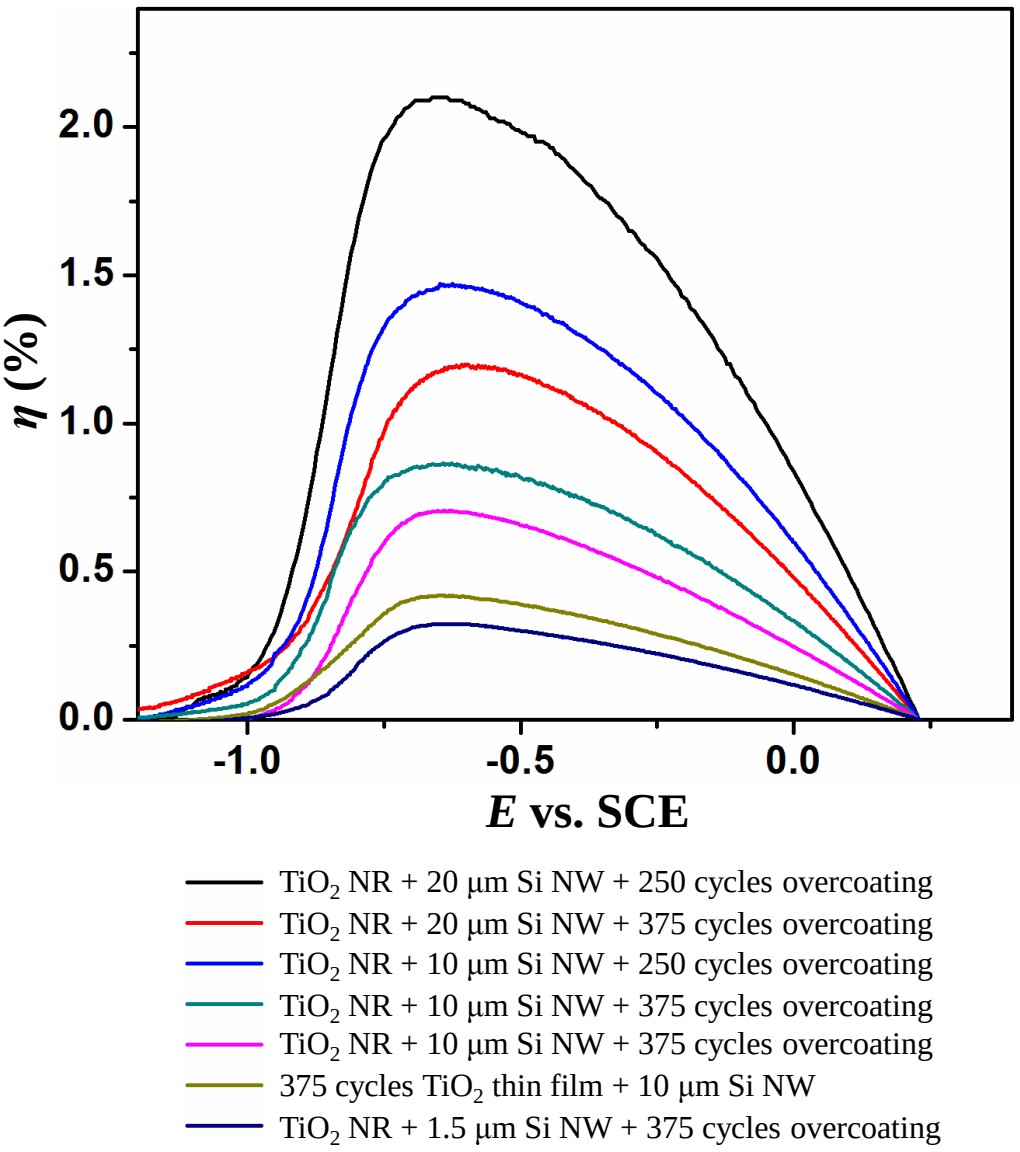

Figure S8. Efficiency vs. bias potential of different TiO_2 NR-Si NW configurations calculated using equation presented in the main content.