Electronic Supplementary Material (ESI) for Energy & Environmental Science

Supporting Materials

Hierarchical TiO_2/Si Nanowire Architecture with Photoelectrochemical Activity under Visible Light Illumination

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Materials and Methods

Nanowire growth. High-density ~20 μm-long Si NW arrays were prepared by a wet-chemical etching method from highly-doped Si substrate (0.001 ~ 0.005 Ω·cm), in which 0.02 M $AgNO_3$ and 5 M HF served as the etching chemicals. After etching for 5 hours, 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. Each Si NW substrate was 1 cm wide and 10 cm long.

A homemade ALD system was applied to perform SPCVD growth of TiO_2 NWs. Si NW substrate was loaded in the tube chamber with its front side 2.5 cm away from the precursor nozzles. The chamber temperature was then ramped into 600 ^oC quickly with 40 sccm constant flow of carrier gas N_2. DI water and $TiCl_4$ were introduced as growth precursors sequentially with pulsing and purging durations of 2 s and 60 s, respectively. The chamber pressure variance before and after $TiCl_4$ pulsing stage was controlled to be 20 miliTorr by adjusting the temperature of $TiCl_4$ reservoir. After 400-cycle SPCVD growth, the reaction chamber was cooled down to room temperature naturally and the 3D hierarchical TiO_2/Si NW architecture was obtained.

PEC anode preparation and characterization. Before the PEC anode fabrication, the native oxide layer (SiO_2) formed during the TiO_2 NW growth was removed by immersing the TiO_2/Si NW architecture in 1:50 HF (48% wt):H_2O solution for 30 minutes. A 10 - 25 nm ALD overcoating layer of anatase TiO_2 polycrystalline thin film was then deposited at 300 ^oC on the as-rinsed NW architecture to completely cover the Si surfaces to isolate Si from the electrolyte. The growth conditions of overcoating were 500 ms H_2O pulsing + 60 s purging + 500 ms $TiCl_4$ pulsing + 60 s purging.

A Solartron potentiostatn (SI 1287) system was used for *J-E* measurement. Prior to potentiodynamic testing, back side of the sample was covered by epoxy to prevent the contact between Si surface and electrolyte. On the front side, half sample surface was scratched by blade to remove semiconducting TiO_2 and the other half surface was partially covered by epoxy. To test the sample, the scratched sample surface was clamped to the measurement system. The region that was covered by epoxy was immersed in the electrolyte with the exposed surface facing the incident light.

Typical three-electrode system was utilized for testing the PEC anode, in which Pt served as counter electrode and a saturated calomel electrode (SCE) as reference electrode. All the electrodes were immersed in a Teflon cell with PEC anode facing onto a quartz window through which illumination was applied. Constant flow of N_2 gas was delivered into the electrolyte (1 M KOH in water) to bubble away the instantaneously produced O_2 in the NW anode and H_2 in the Pt cathode. Illumination source was from a 500 W Hg (Xe) arc lamp (Oriel, 66142) with or without UV filter or green light filter. A liquid water filter (Oriel, 6123NS) was always applied in the measurements to eliminate the IR heating effect on electrolyte.

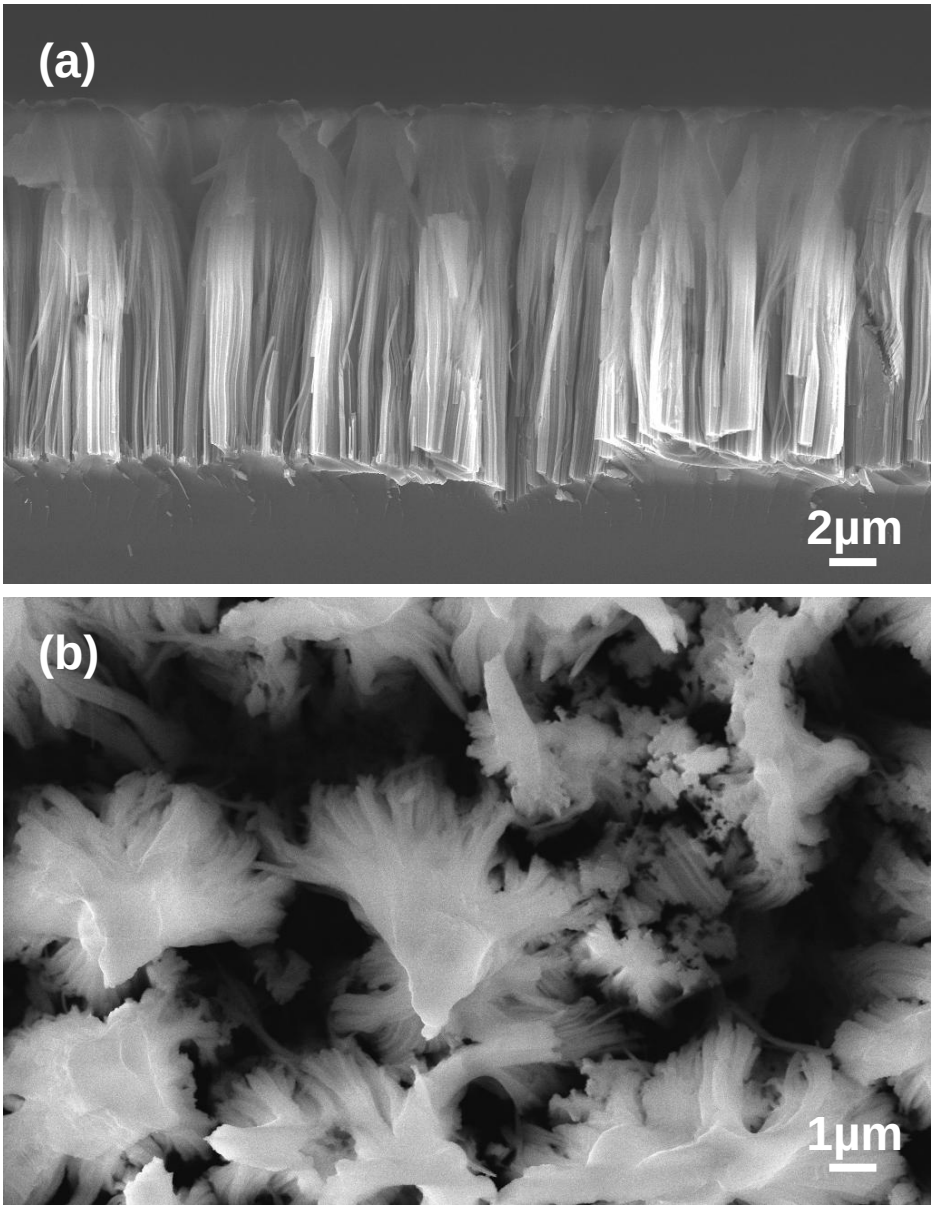

Figure S1. Wet-etched Si NWs. (a) Cross section view of the as-etched Si NWs shows the densely packed NW arrays and very narrow spaces among adjacent NWs. (b) Planar view of Si NWs showing the tip of Si NWs were bundled together.

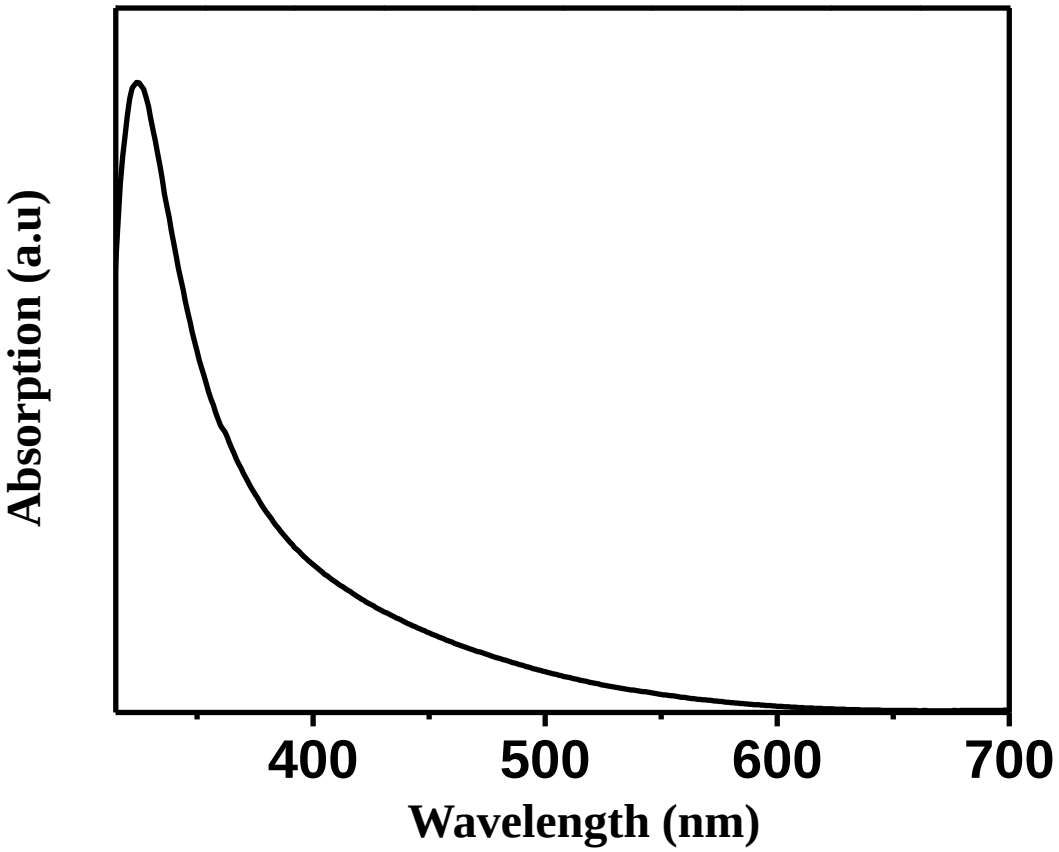

Figure S2. UV-Vis absorption spectrum of TiO_2 nanowires grown on FTO substrate with the absorption edge locating at ~600 nm.

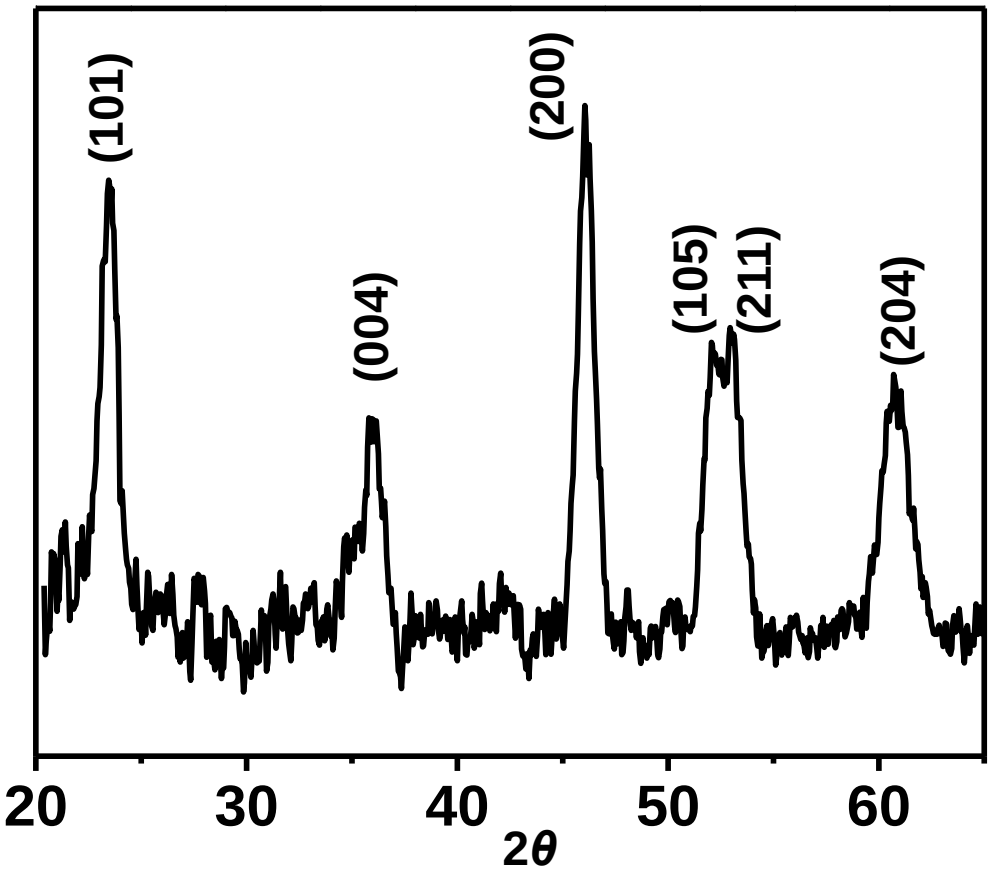

Figure S3. XRD spectrum of TiO_2 NWs with all peaks assigned to typical anatase phase.

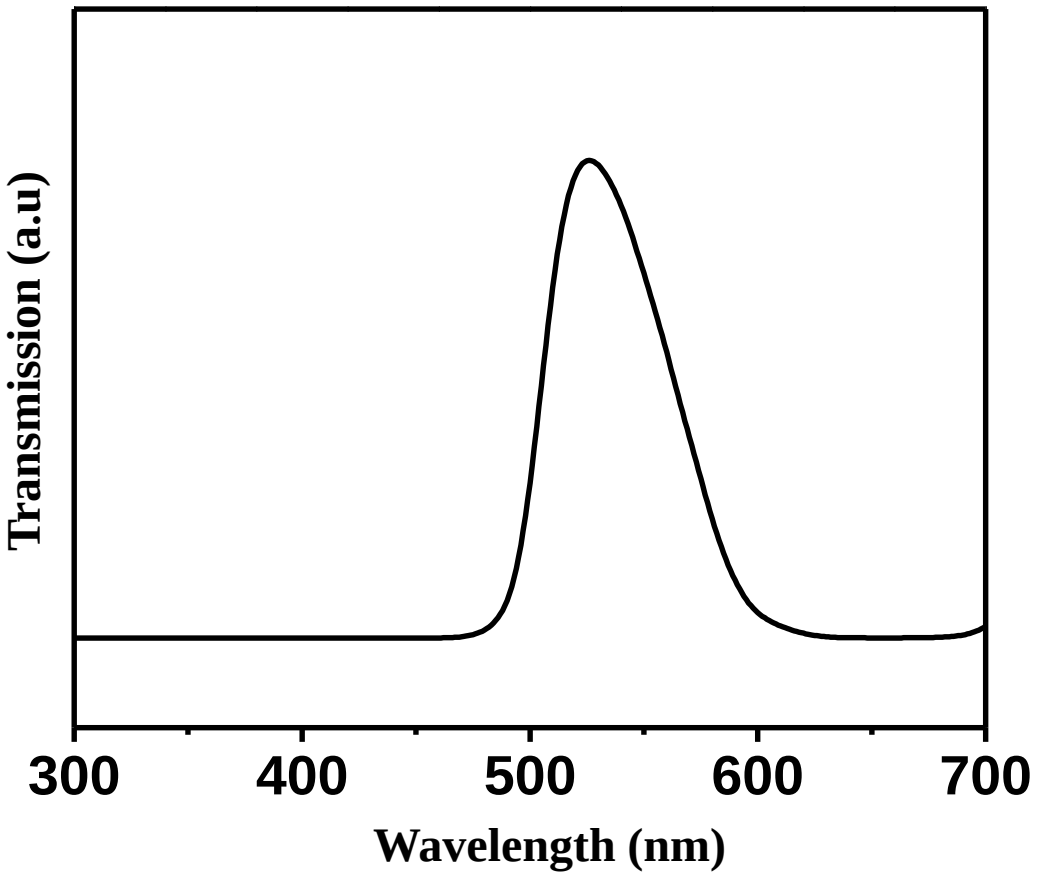

Figure S4. Transmittance spectrum of the green light filter that only allows light with wavelength between 500 and 600 nm to pass through.

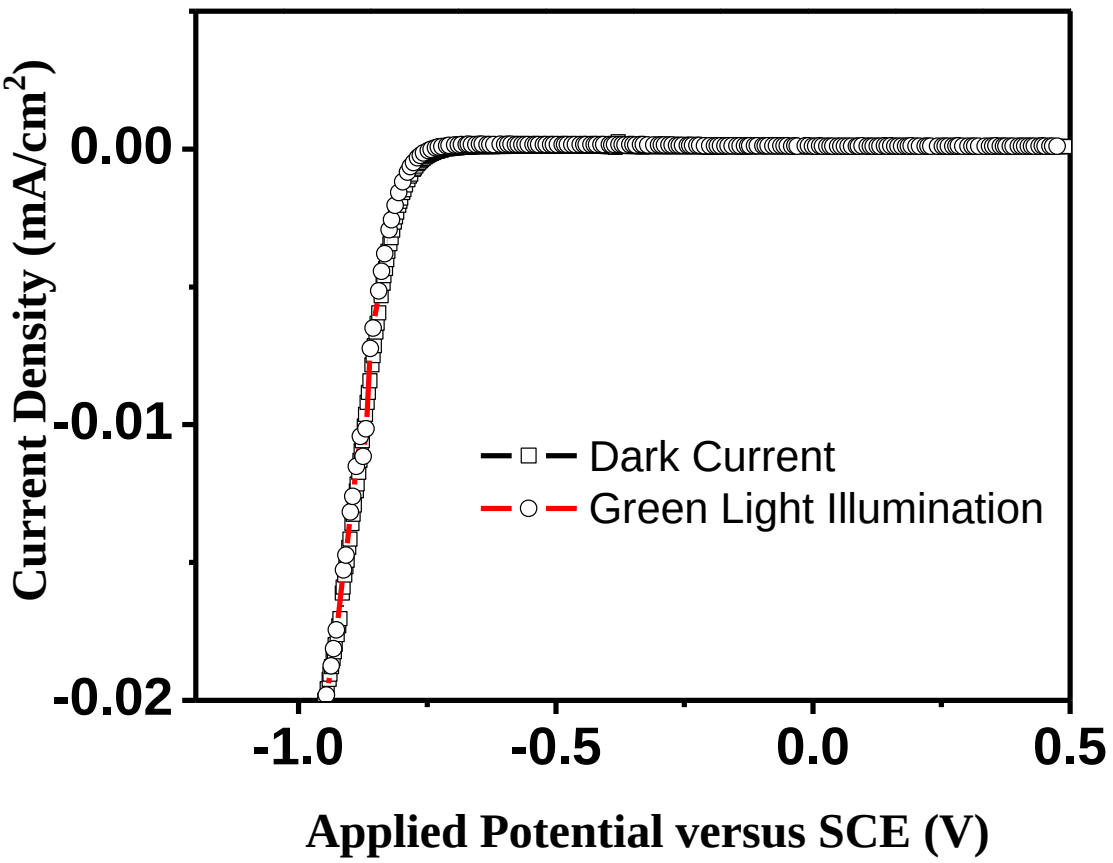

Figure S5. Photoactivity of Si nanowires coated with 25 nm thick ALD TiO_2 layer. There is no photocurrent observed under green light illumination, indicating that Si is not photoactive in our 3D TiO_2-nanowire-Si-nanowire architecture. Intensity of green light is 33 mW/cm^2.