Supporting Information for

"Three-dimensional ZnO/Si broom-like nanowire heterostructures as photoelectrochemical anodes for solar energy conversion"

[Phys. Status Solidi A, **DOI** 10.1002/pssa.201329214 (2013)]

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Received 31 March 2013, revised 20 June 2013, accepted 23 July 2013
Published online August 2013

Keywords solar energy conversion, water splitting, photoelectrochemical cells, water oxidation, nanowires, heterostructures, ZnO, silicon

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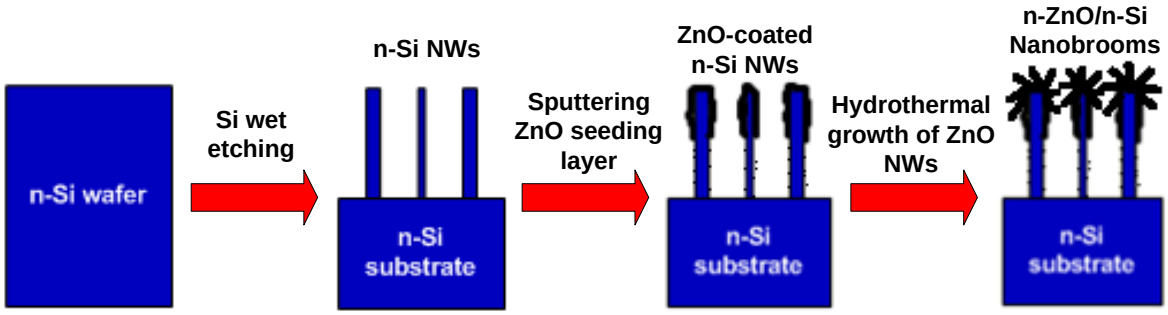

Figure S1 Fabrication procedure for the 3D n-ZnO/n-Si nanobrooms. The coating of ZnO seeding layer is not uniform with larger thickness at the top part of Si NWs than other parts of NWs. This non-uniform ZnO coating can also be seen in SEM images in Fig. 1 in the main text.

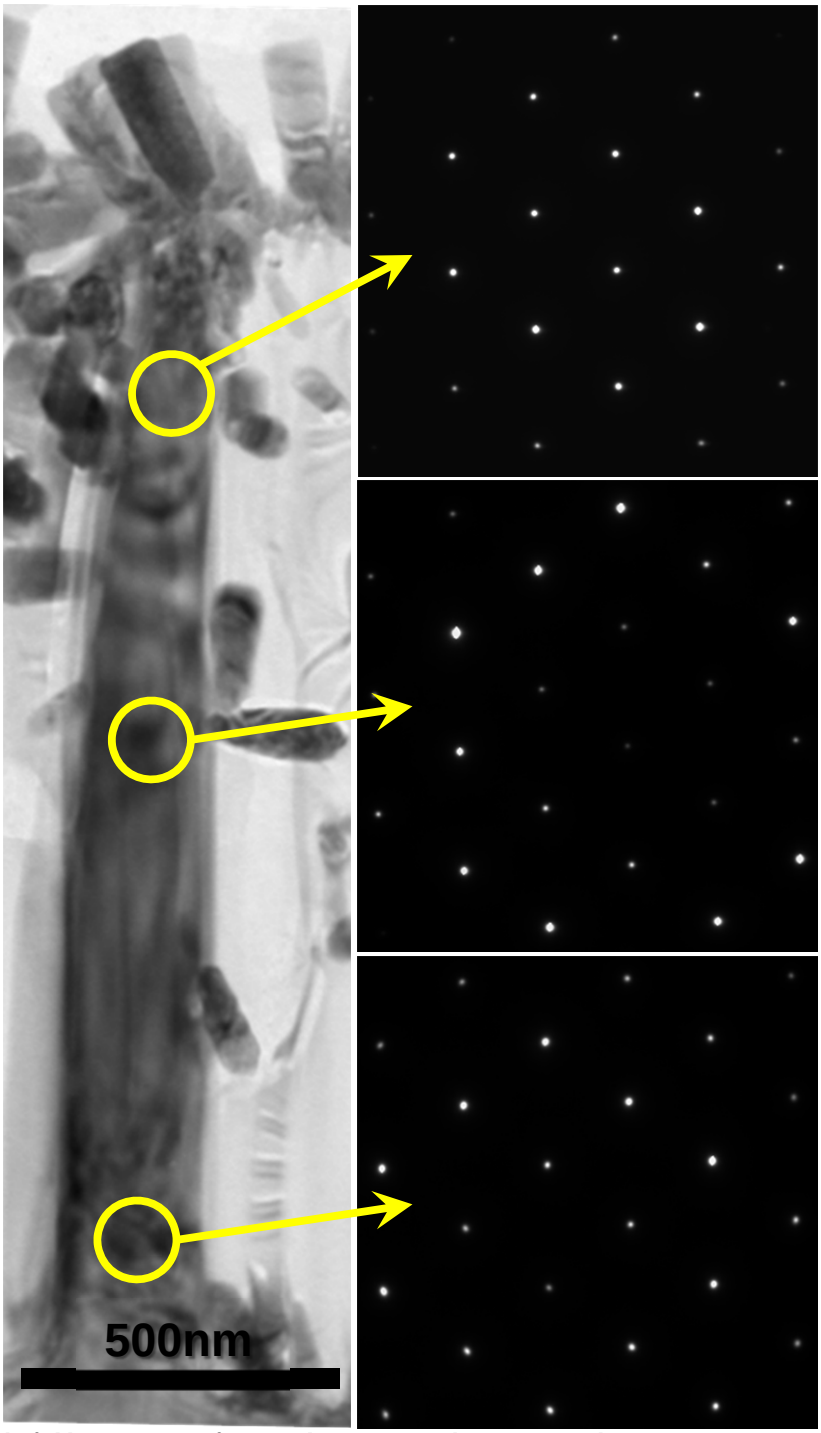

Figure S2 Bright field TEM image of one single ZnO/Si nanobroom on Si substrate (10 min Si NW backbones with 10 min ZnO NW stalls) with corresponding diffraction patterns along the Si NW backbone revealing the single crystallinity with symmetric patterns.

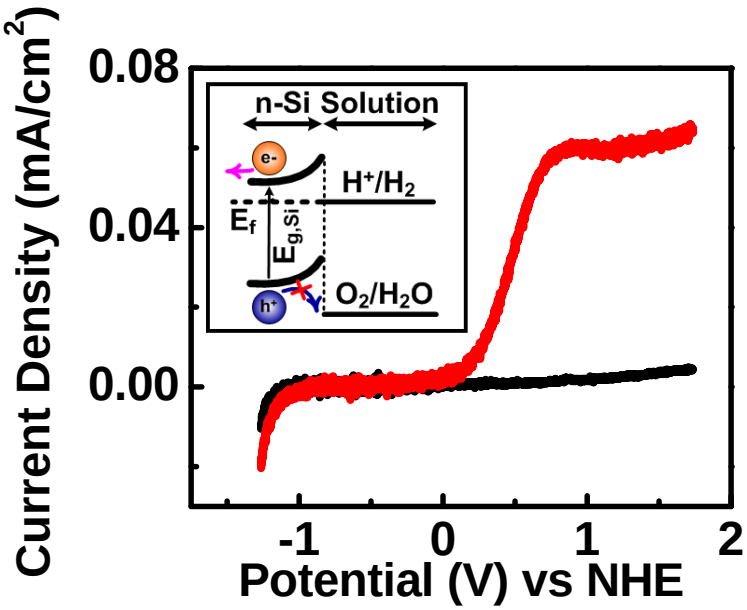

Figure S3 Current density versus applied potential for 5 min etched n-Si NW array (bare sample) in neutral solution (pH = 7.25). The red and black curves indicate the current density under illumination and at dark, respectively. Scan rates were 5 mV/s and the scans direction was from reversed to forward biases (from -1.264 V to 1.736 V versus NHE). The inset shows the approximate energy band diagram of n-Si NW in contact with electrolyte under thermal equilibrium and illuminated with solar light.

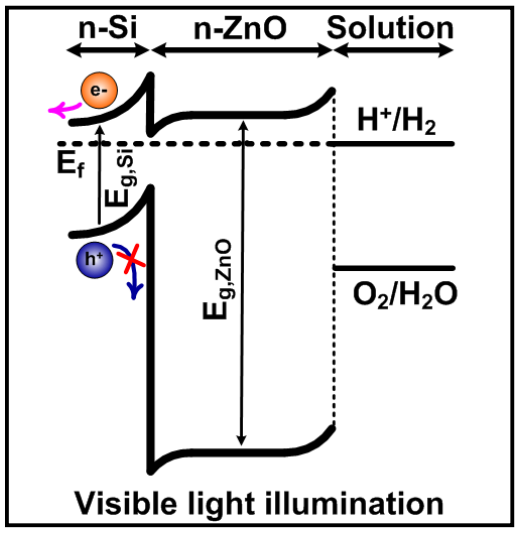

Figure S4 Proposed (approximate) energy band diagram of n-ZnO/n-Si NW heterojunction in contact with electrolyte under thermal equilibrium and illuminated with visible light.

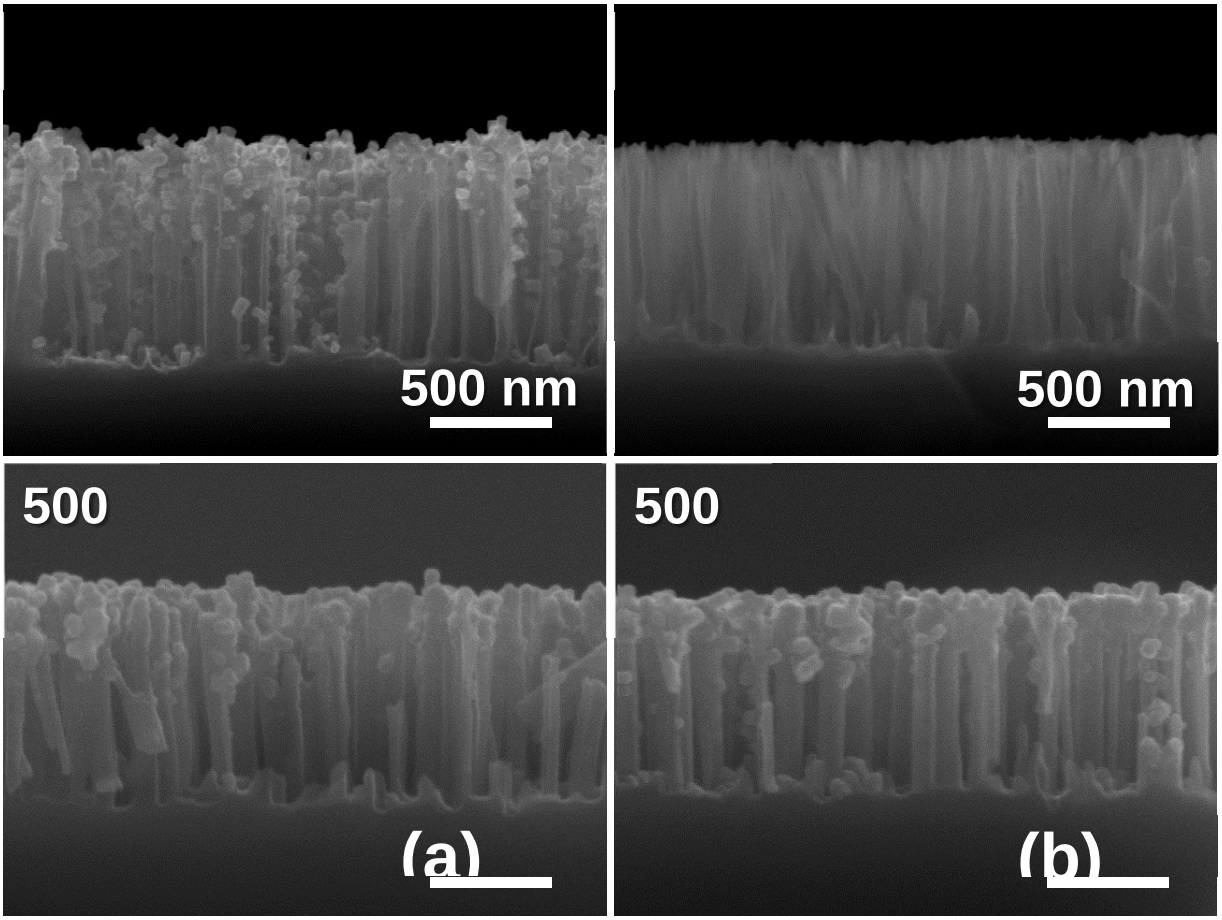

Figure S5 High-magnification cross-sectional SEM images of bare and TiO_2-coated nanobrooms for before and after PEC and stability tests. Bare nanobrooms (a) before any PEC and stability tests (as-grown sample) and (b) after PEC tests and long-term stability test. TiO_2-coated nanobrooms (c) before any PEC and stability tests and (d) after PEC tests and long-term stability test. The thickness of TiO_2 was 10 nm. Nanobrooms in (a)-(d) are from 5min n-Si NW backbones with 5min ZnO NWs. These SEM images are for the samples shown in Fig. 7 in the main text.

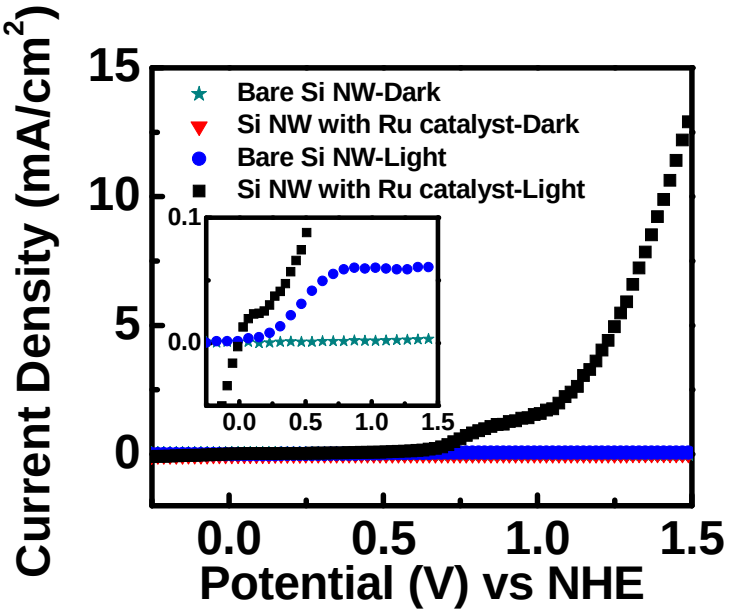

Figure S6 Current density versus applied potential for 5 min etched n-Si NWs with and without Ru catalyst in neutral solution (pH = 7.25). “Light” and “Dark” indicate the current density under illumination and at dark, respectively. The inset is the zoomed curves to show the level of current densities for the bare n-Si NW array in comparison to the light current of n-Si NW array with Ru catalyst. Scan rates were 5 mV/s and the scans direction was from reversed to forward biases (from -0.25 V to 1.5 V versus NHE).