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Supporting Information

Photoelectrochemical hydrogen production on silicon microwire arrays overlaid with ultrathin titanium nitride

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Table S1. Morphological information of as-fabricated p-Si substrates (projected area: 0.3 cm^2).

p-Si	Diameter (μm)	Interval (μm)	Length (μm)	Density (10^5 wires/cm^2)	Geometric surface area (cm^2)*
Planar					0.30
Wire	1.6	2.5	19.9	59.5	2.08
	4.8	4.8	18.6	10.9	1.21
	9.5	10.6	25	2.5	0.85
	14.6	15.2	22	1.1	0.64

*The surface area calculated by using the measured parameters (diameter, interval, length).

Table S2. PL lifetimes of p-Si wire arrays overlaid with 10 nm-thick TiN layers.

Diameter of Wire/TiN (μm)	Lifetime* (ns)		Average lifetime (ns)
	τ_1	τ_2	τ
1.6	1.500(33.10%)	0.137(66.90%)	1.29
4.8	2.584(35.55%)	0.440(64.45%)	2.08
9.5	2.489(25.02%)	0.380(74.98%)	1.92
14.6	2.357(35.12%)	0.387(64.88%)	1.90

*Lifetimes were estimated by the following equation: $I(t) = A_1\exp(-t/\tau_1) + A_2\exp(-t/\tau_2)$.

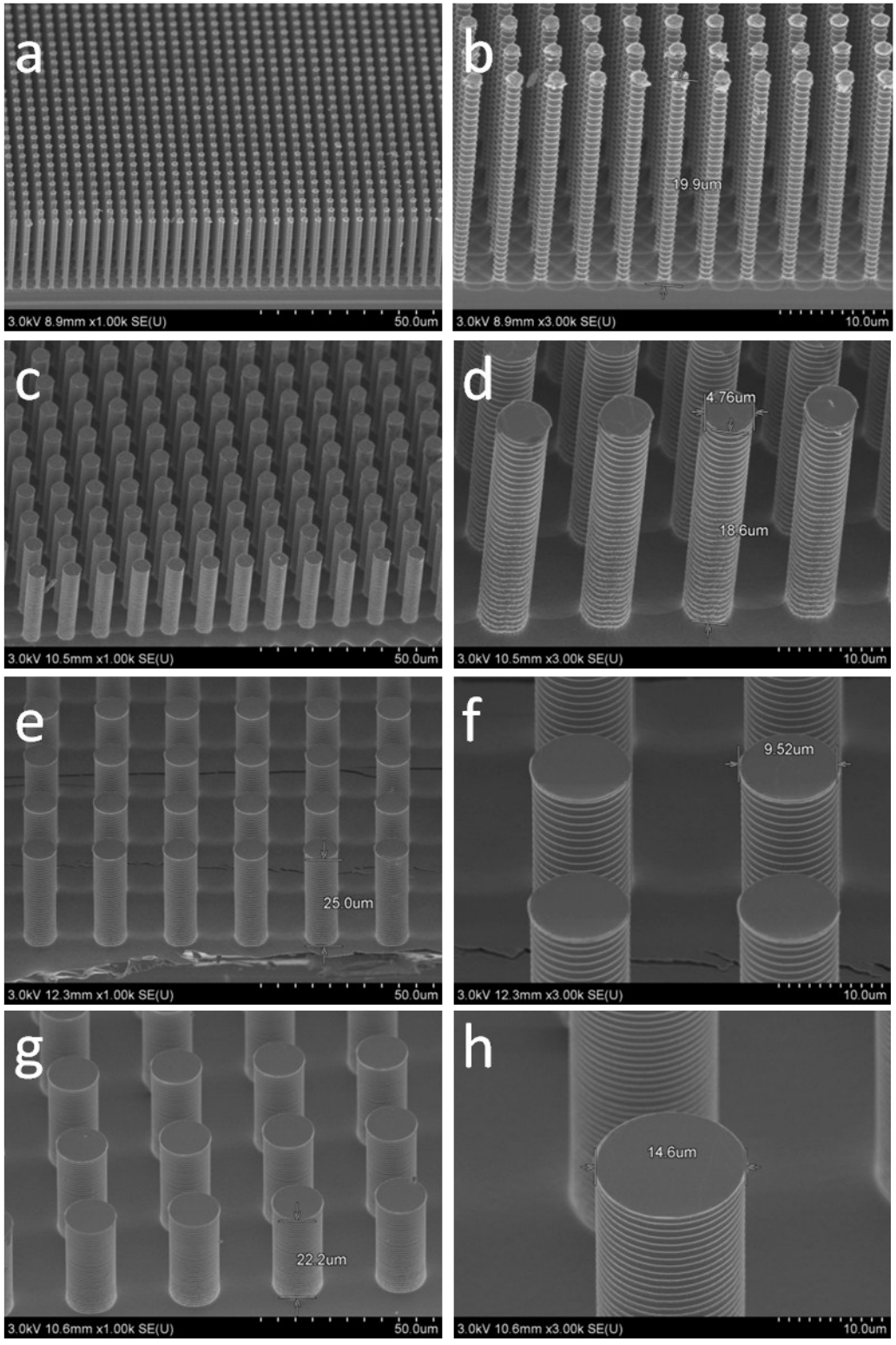

Fig. S1. SEM images of Si wire arrays with varying wire diameters of (a, b) 1.6, (c, d) 4.8, (e, f) 9.5, and (g, h) 15 μm.

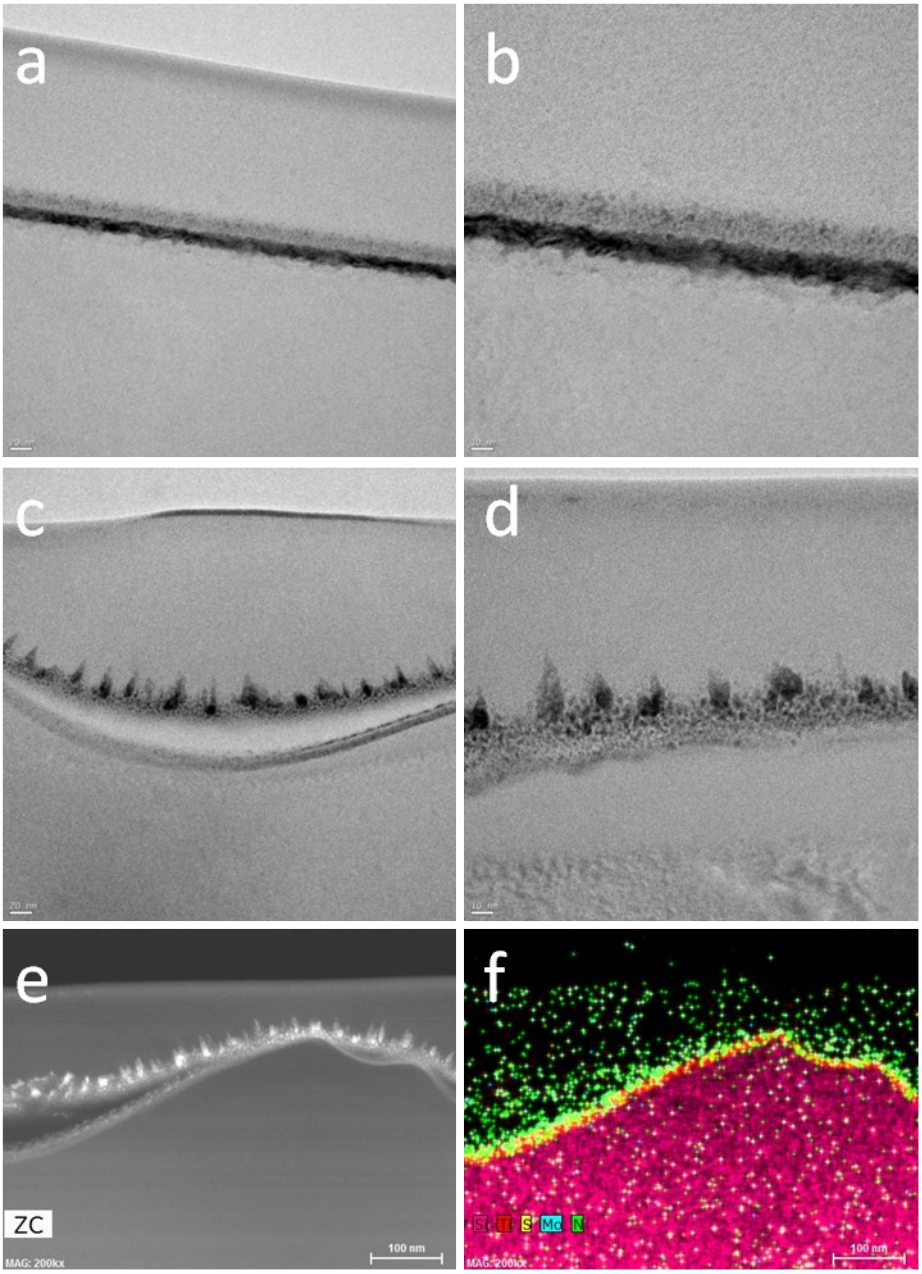

Fig. S2. (a – e) Cross-sectional TEM images of a single Si wire (15 μm in diameter) overlaid with 10 nm-thick TiN layer: (a, b) head and (c – e) body. (f) EDX elemental mapping of the surface (e) in terms of elements (Si, Ti, and N).

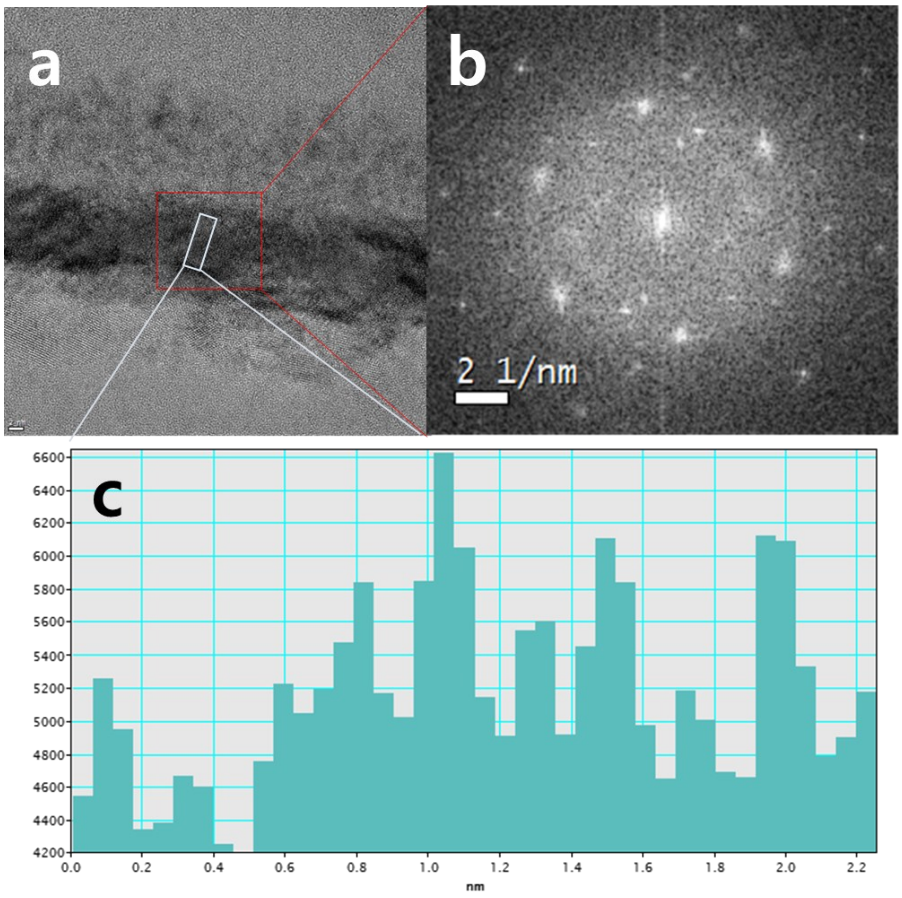

Fig. S3. (a) HR-TEM images of a single Si wire overlaid with 10 nm-thick TiN layer, (b) SAED pattern of the TiN layer marked with a red square, (c) lattice space of TiN.

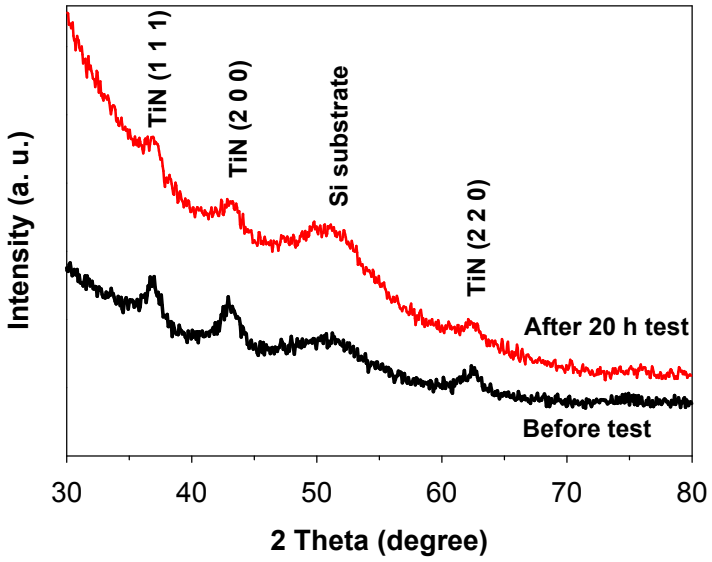

Fig. S4. X-ray diffraction analysis of TiN/planar Si as synthesized and run for 20 h test (see Fig. 3b). The thickness of TiN was 10 nm.

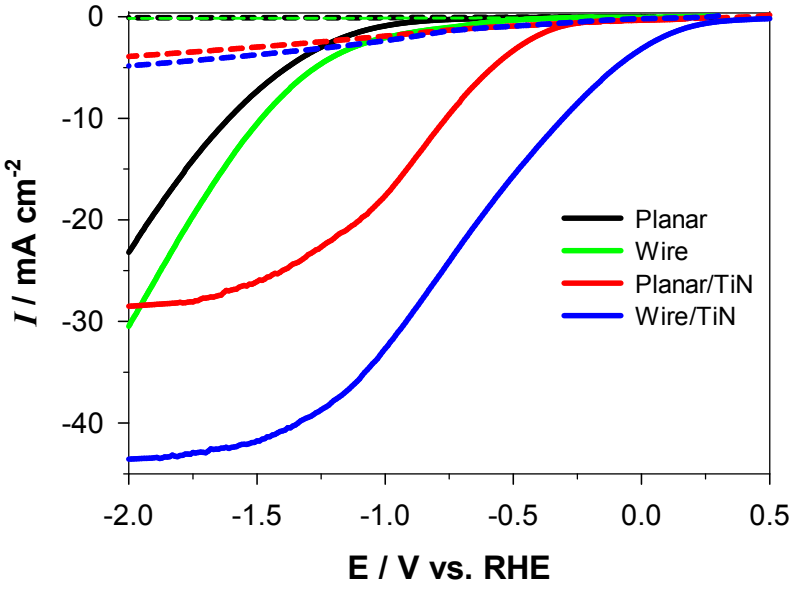

Fig. S5. Linear sweep voltammograms (LSVs) of planar and wire-arrayed p-Si electrodes with and without the 10-nm thick TiN layer (dashed lines: dark, solid lines: irradiated). The wire diameter was fixed at 1.6 μm.

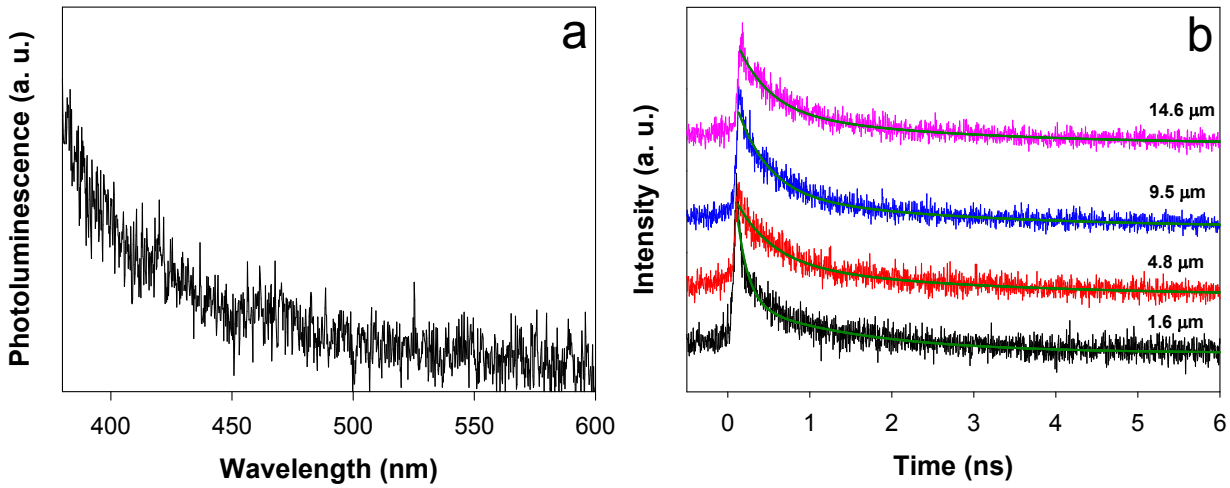

Fig. S6. (a) Photoluminescence emission spectrum of p-Si wire arrays (1.6 μm diameter) overlaid with 10 nm-thick TiN layer at room temperature (b) Time-resolved photoluminescence (TRP) decays of p-Si wire arrays (1.6–14.6 μm in diameters) overlaid with 10 nm-thick TiN layers.

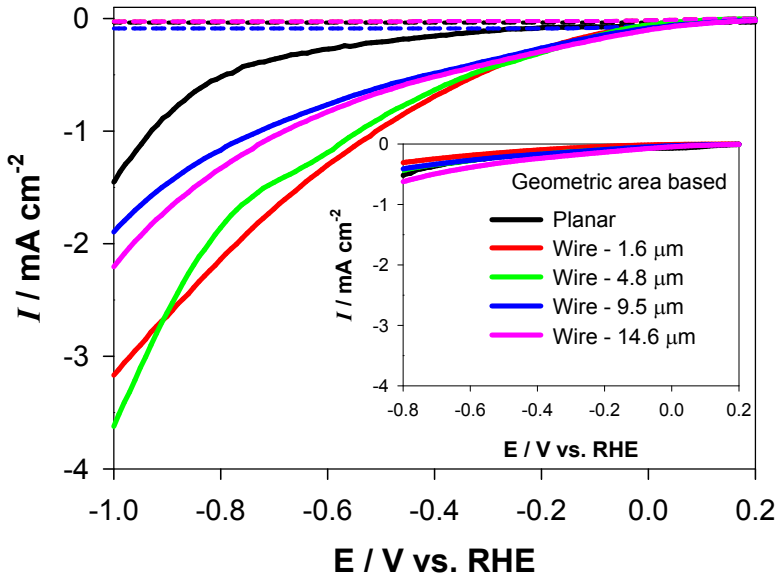

Fig. S7. Linear sweep voltammograms of a planar p-Si electrode and wire-arrayed p-Si electrodes with varying wire diameters (broken lines: dark, solid lines: irradiated) in H_2SO_4 and Na_2SO_4 mixed aqueous solution (each 0.1 M) at pH 1. Irradiation: AM 1.5G (100 mW·cm^{-2}). Inset shows the LSVs of the electrodes with photocurrent densities normalized to their geometric areas (photocurrents divided by geometric areas. See Table S1).

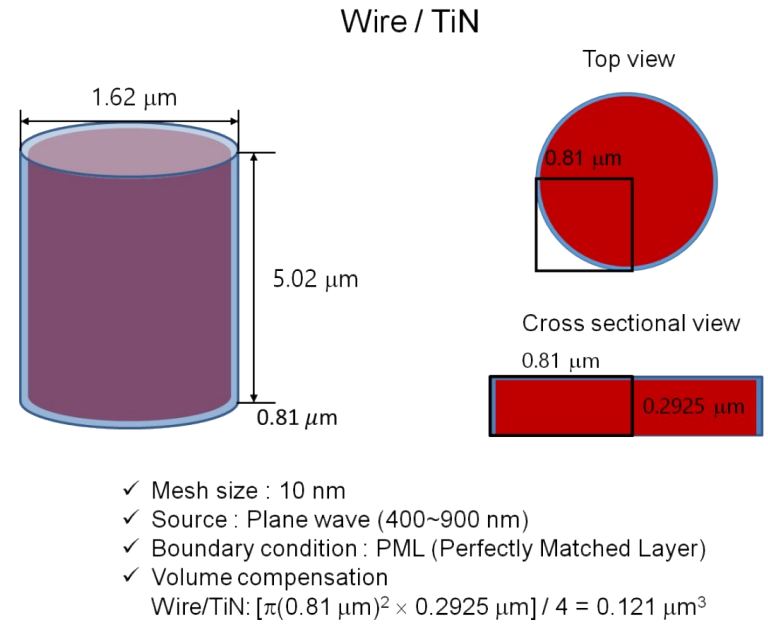

Fig. S8. FDTD simulation parameters

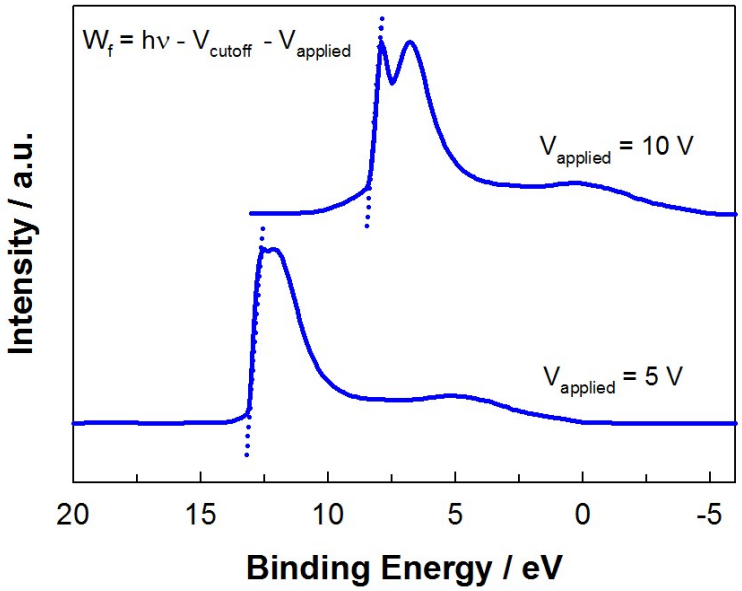

Fig. S9. Ultraviolet photoelectron spectra (UPS) for the 10 nm-thick TiN films (deposited onto planar Si substrate) (hν = 21.2 eV).

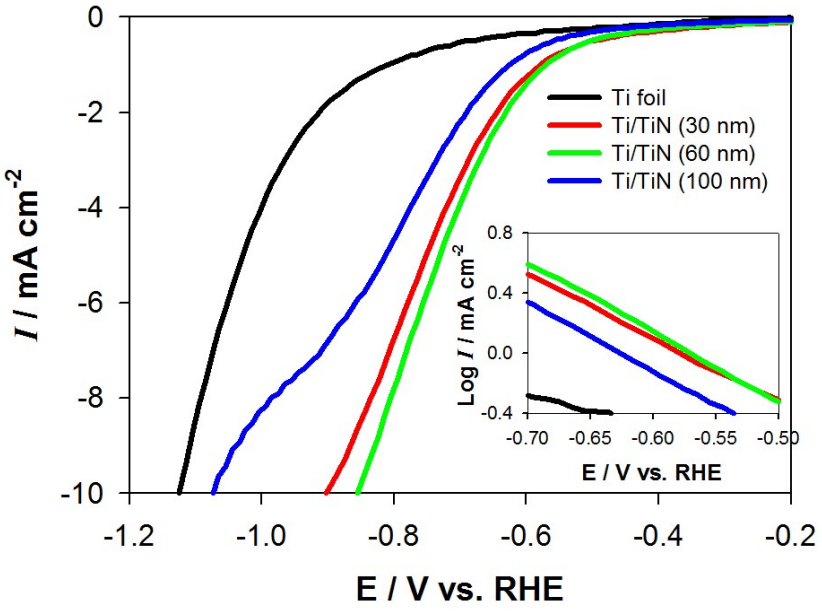

Fig. S10. Linear sweep voltammograms of TiN (deposited on Ti) with varying thickness in H_2SO_4 and Na_2SO_4 mixed aqueous solution (each 0.1 M) at pH 1. Inset shows the Tafel plots derived from the voltammograms.

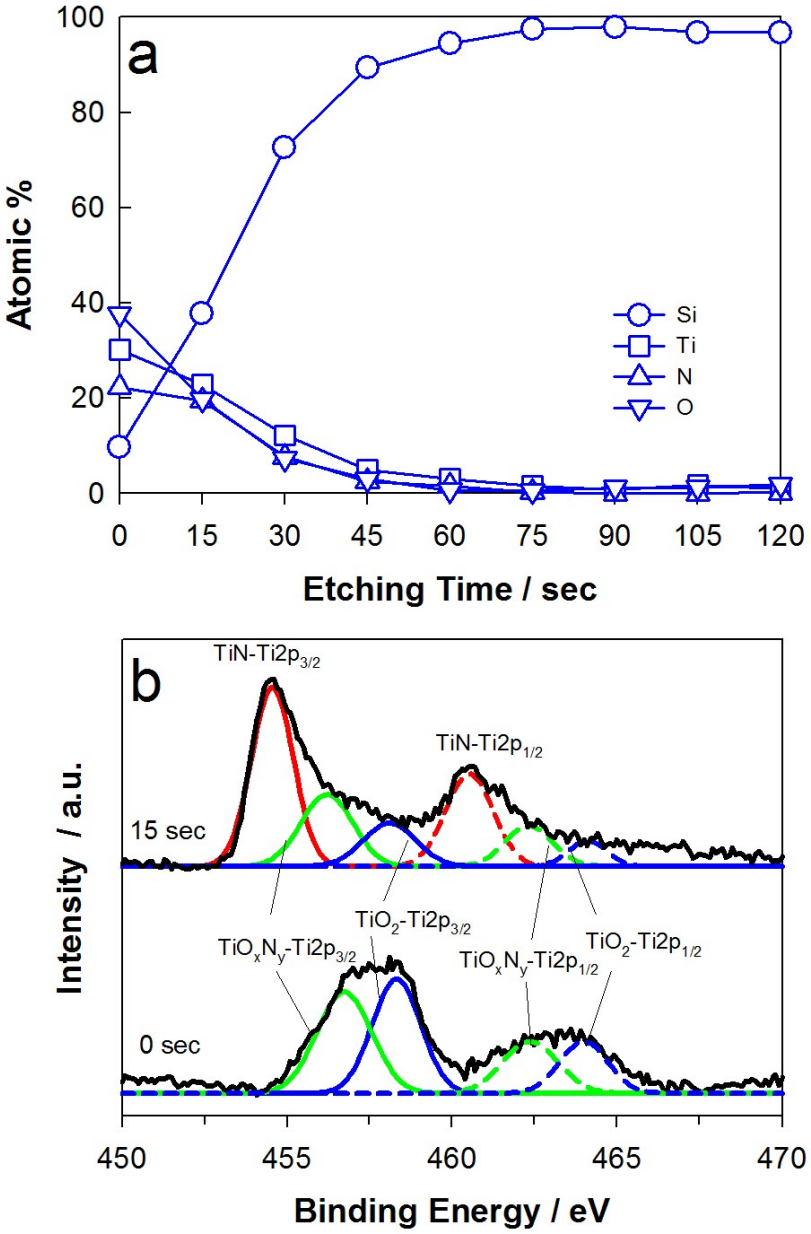

Fig. S11. (a) XPS depth profiling of planar Si deposited with 10 nm-thick TiN layer after 100 times-potential sweeps under irradiation (identical to those of Fig. S8). (b) Ti 2p spectra (original and resolved) of the electrodes at etching times of 0 and 15 seconds.