Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.
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Supporting Information

# Wafer-scale antireflective protection layer of solution-processed $TiO_2$ nanorods for high performance silicon-based water splitting photocathodes

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The length and diameter of the $TiO_2$ NRs was highly dependent on the synthesis time, temperature and cooling condition of the autoclave that contained the samples. When the temperature was fixed at 180°C, the synthesis time at 30 to 120 min and the autoclave cooled to 100°C naturally and subsequently to room temperature by dousing with water, the heights of the synthesized NRs increased. For example, the heights of the $TiO_2$ NRs at 180°C and 30" were ~100 nm, (Figure S1 a,b), whereas using a similar temperature with synthesis times of 1 and 2 h, the heights of $TiO_2$ NRs were 1 and 2 μm, respectively (Figure S1 e-h). Using similar synthesis conditions, at 180°C and 1 h, with the exception of autoclave cooling, when synthesis was complete the autoclave was removed from the oven and cooled to room temperature by dousing with water. The length of $TiO_2$NRs was ~350 nm, (Figure S1 c-d). When the temperature was changed to 220°C from 180°C, with synthesis for 2 h and the

autoclave cooled to room temperature similar to the same described for (g-h), the height and diameter of the resulting $TiO_2$ NRs decreased to 1 μm and ~32 nm, respectively, compared to their counterpart samples (g-h). In contrast, the diameter of the $TiO_2$ NRs decreased with increasing reaction time and temperature.

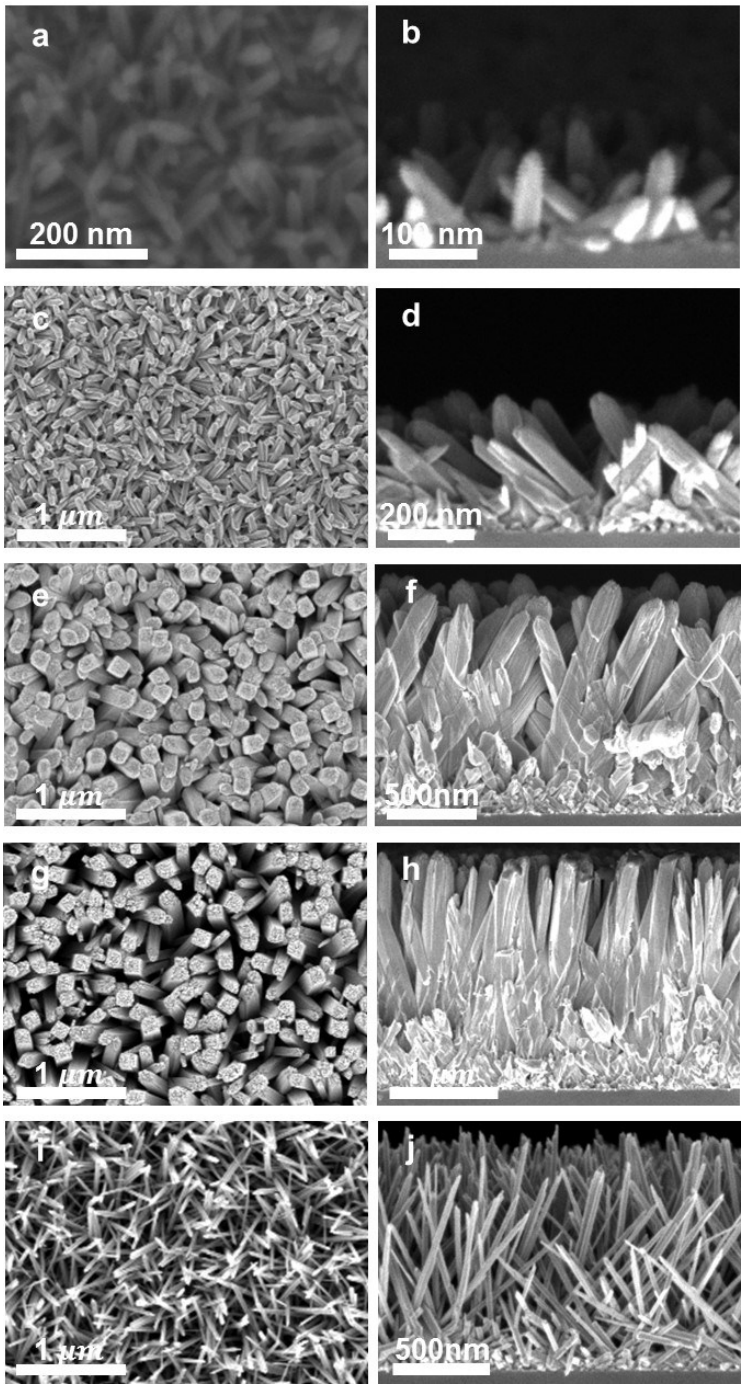


**Figure S1. FSEM images of hydrothermally grown $TiO_2$ NRs/*p*-Si with controlled height and diameter. a-b,** ~100 nm high, **c-d,** ~ 350 nm high, **e-f, i-j,** ~ 1 μm high **g-h,** ~ 2 μm high and their diameters is ~ 120 nm- 160nm for sample (a-h) and ~ 32 nm for i,j samples.

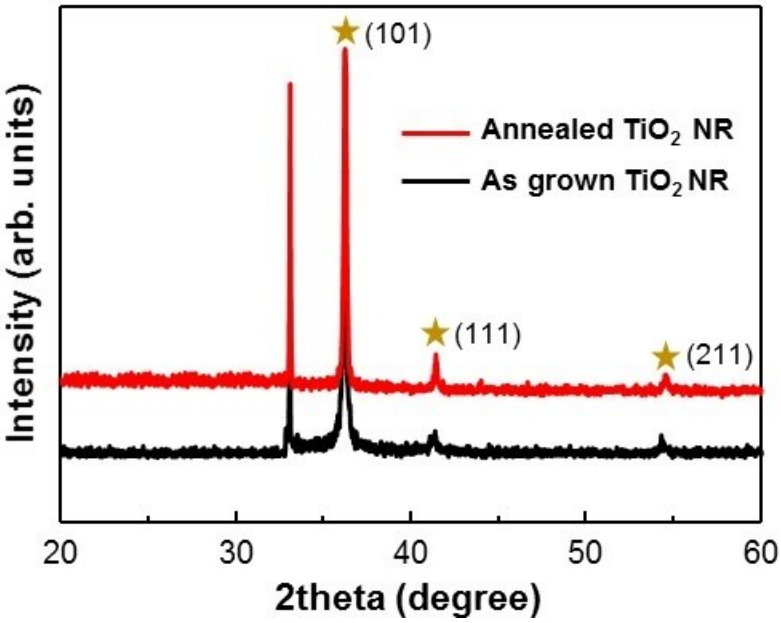


**Figure S2**. XRD spectra of hydrothermally grown $TiO_2$ NRs.

Both annealed and as grown $TiO_2$ NRs are Rutile as shown in figure S2. It is also revealed their difference in crystallinity between as grown and annealed sample.

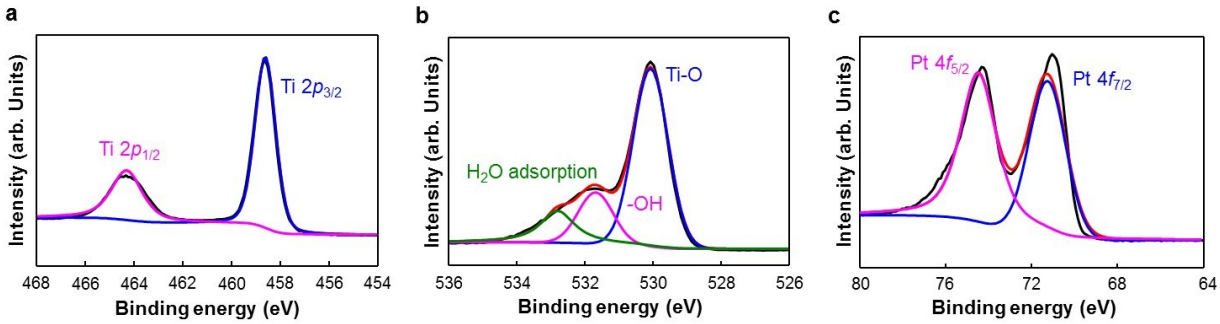


**Figure S3**. **a-c,** High resolution X-ray photoelectron spectra of hydrothermally grown $TiO_2$ NRs with the electron beam deposited Pt nanoparticle (diameter 1- 2.5 nm) on the $TiO_2$ NRs.

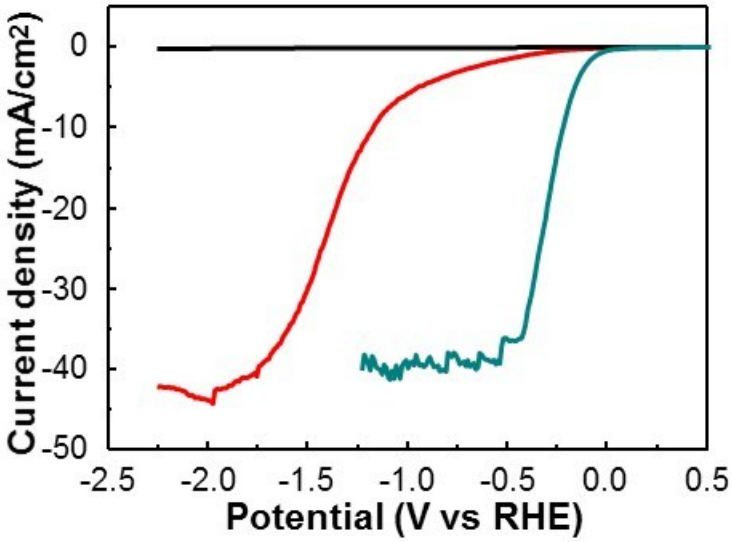


**Figure S4**. LSV of $TiO_2$ NRs/*p*-Si annealed at 500°C for an hour (red curve) and as grown $TiO_2$ NRs/*p*-Si (green curve).

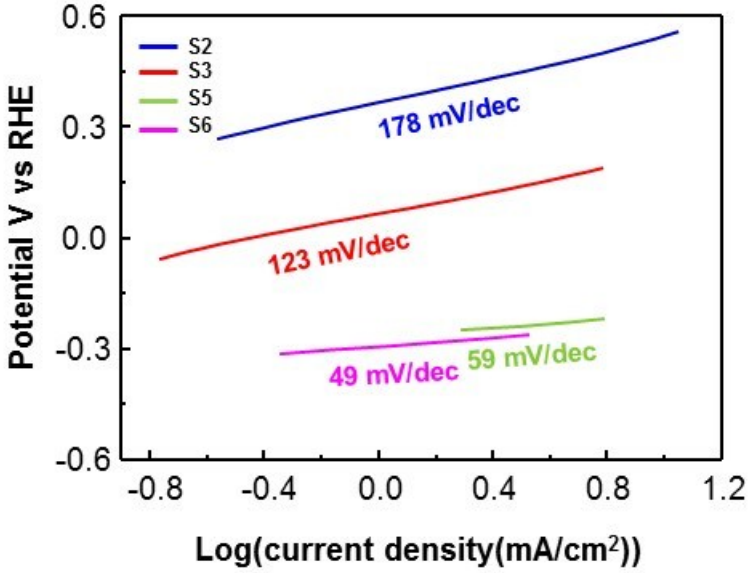


**Figure S5.** Tafel slopes of $TiO_2$ seed layer, $TiO_2$ NRs, Pt/$TiO_2$ seed layer/*p*-Si and Pt/$TiO_2$ NRs samples plotted as log (j) against potential vs. RHE.

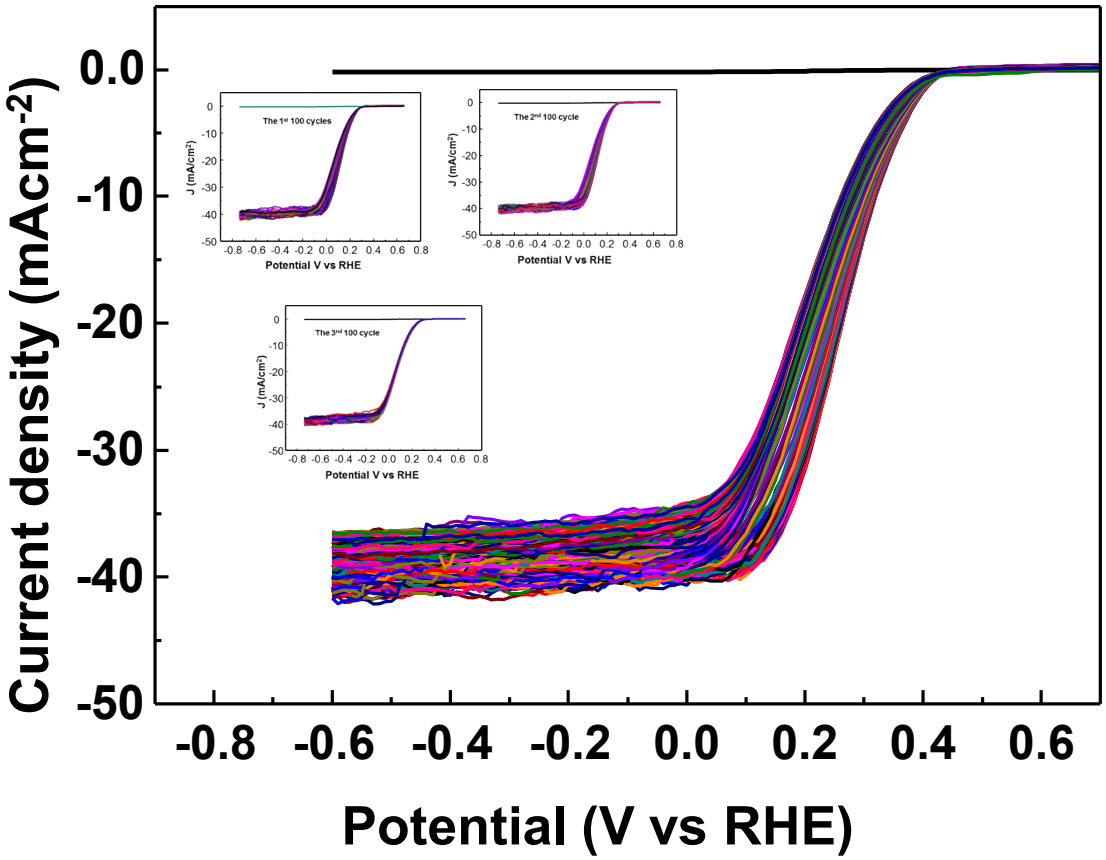


**Figure S6.** 300 cycles of LSV of the S6 photocathode measured after a week. The insets are LSV curves after each 100 cycles, the 1st, 2nd and 3rd hundreds cycles.

**Video S1. Video for Hydrogen bubbling off.** The spillover of $H_2$ from the S1, S2 and S3 photocathodes at the applied bias voltage between -0.4 V to -0.6 V.

**Video S2. Video for Hydrogen bubbling off .**The spillover of $H_2$ from the S4, S5 and S6 photocathodes at the applied bias voltage between 0.1 V to -0.1 V.