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\textsubscript{2} NRs/p-Si annealed at 500°C for an hour (red curve) and as grown TiO\textsubscript{2} NRs/p-Si (green curve).

Figure S5. Tafel slopes of TiO\textsubscript{2} seed layer, TiO\textsubscript{2} NRs, Pt/TiO\textsubscript{2} seed layer/p-Si and Pt/TiO\textsubscript{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 1\textsuperscript{st}, 2\textsuperscript{nd} and 3\textsuperscript{rd} hundreds cycles.

Video S1. Video for Hydrogen bubbling off. The spillover of H\textsubscript{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\textsubscript{2} from the S4, S5 and S6 photocathodes at the applied bias voltage between 0.1 V to -0.1 V.