Above 10% efficiency and one-week stability of Si photocathodes for water splitting by manipulating the loading of Pt catalyst and TiO$_2$ protective layer

Supporting Information

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Figure S1. The photograph exhibition of custom-built Teflon electrochemical cell with a size of 96 mm×110 mm×32 mm. The backside of Si photocathode is contacted by a spring-loaded Cu plunger that also serves to press the working electrode against a Teflon gasket so that only the active area contacts the electrolyte. The active area of the Si photocathode is 0.503 cm².

Figure S2. Water wettability of the n⁺p-Si photocathodes (a) with and (b) without the native SiO₂ layer.
Figure S3. Consecutive LSV measurement for the Pt$_2$/SiO$_2$/n$^+$p-Si electrodes decorated with various amounts of Pt NPs.

Figure S4. (a) Consecutive LSV measurements for the e-Pt/SiO$_2$/n$^+$p-Si electrodes decorated with various amounts of e-Pt particles. (b) High-magnification and (c) low-magnification top-down SEM images of the e-Pt/n$^+$p-Si. (d) Surface reflectance of bare n$^+$p-Si, Pt$_2$/n$^+$p-Si and e-Pt/n$^+$p-Si photocathodes.
Figure S5. (a), (b) Electrocatalytic HER performance and corresponding Tafel plots of Pt NPs prepared by the electro- and electroless deposition, respectively. We used degenerately doped silicon wafer (n$^{++}$-Si) as the conductive substrates to replicate the same amount of Pt catalyst. Electrodes were then measured using a typical three electrode system in 1 M HClO$_4$ aqueous solution. (c), (d) The surface morphology of Pt NPs prepared by the electroless and electro- deposition on n$^{++}$-Si, respectively.

Figure S6. (a) Consecutive LSV measurements of Pt$_2$/n$^+$-p-Si during the 10 and 24 h HER test. (b) Top-down SEM image and (c) water wettability of 1μg/cm$^2$ Pt$_2$/n$^+$-p-Si after a 24 h PEC testing.
Figure S7. Cross-sectional HRTEM micrograph of Pt$_2$/n$^+$-p-Si surrounded by TiO$_2$ layer.

Figure S8. (a), (b) Electrocatalytic HER performance and corresponding Tafel plots of Pt$_2$/n$^+$-Si with and without the decoration of TiO$_2$ layer.
Figure S9. UV-Vis transmittance spectra of ITO glass substrates with and without the decoration of TiO$_2$ layer.

Figure S10. The reflection spectra of the Pt$_x$/n$^+$p-Si with and without the decoration of TiO$_2$ layer, measured using a Perkin Elmer Lambda 750 spectrophotometer in a wavelength range of 350–1000 nm, which uses BaSO$_4$ as a reference. No significant difference is found between them.

Figure S11. The enlarged photograph of Figure 5b.
**Figure S12.** A representative cross-sectional HRTEM micrograph of TiO$_2$/Pt$_2$/n$^+$p-Si sample. The top surface of the Pt NPs with larger size than ~15 nm is not covered by TiO$_2$.

**Figure S13.** TEM measurement for the sample TiO$_2$/Pt$_2$/n$^+$p-Si after the 168-hour electrolysis.
Figure S14. Theoretical calculated and measured H$_2$ amount measurements on TiO$_2$/Pt$_2$/n$^+$p-Si photocathode under simulated AM 1.5G illumination. These measurements show that this device evolves hydrogen with effectively 96% Faradaic efficiency within the experimental error.

Figure S15. LSV curves under chopped illumination of Pt$_2$/n$^+$p-Si (black), 15 nm TiO$_2$/Pt$_2$/n$^+$p-Si (red) and 2 nm TiO$_2$/Pt$_2$/n$^+$p-Si (blue) photoelectrodes measured in 1 M HClO$_4$ solution under simulated AM 1.5G illumination.