

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

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**Above 10% efficiency and one-week stability of Si  
photocathodes for water splitting by manipulating the loading of  
Pt catalyst and TiO<sub>2</sub> protective layer**

**Supporting Information**

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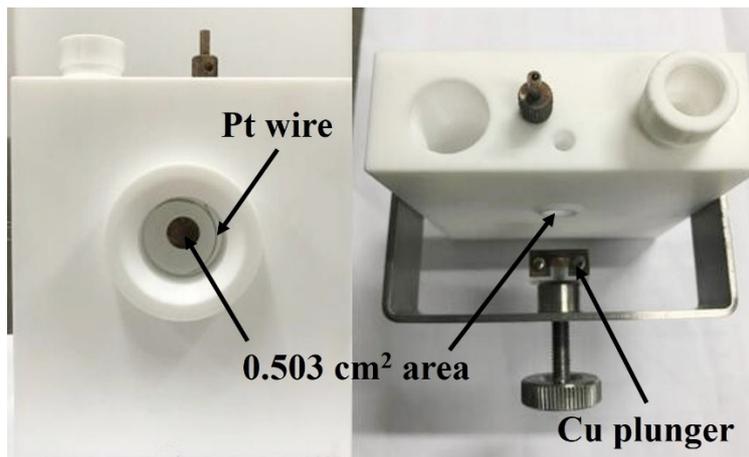


Figure S1. The photograph exhibition of custom-built Teflon electrochemical cell with a size of 96 mm×110 mm×32 mm. The backside of Si photocathode is contacted by a spring-loaded Cu plunger that also serves to press the working electrode against a Teflon gasket so that only the active area contacts the electrolyte. The active area of the Si photocathode is 0.503 cm<sup>2</sup>.

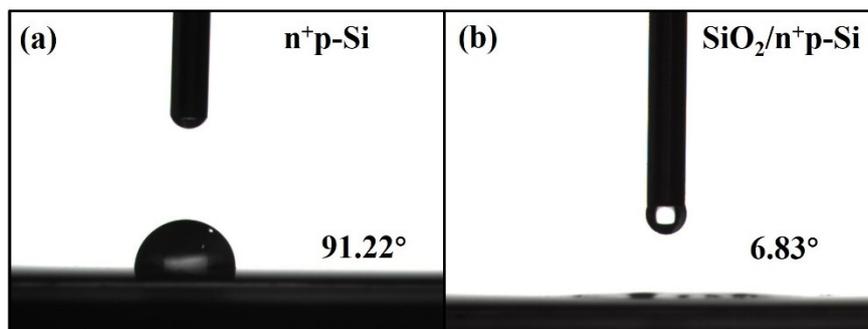


Figure S2. Water wettability of the n<sup>+</sup>p-Si photocathodes (a) with and (b) without the native SiO<sub>2</sub> layer.

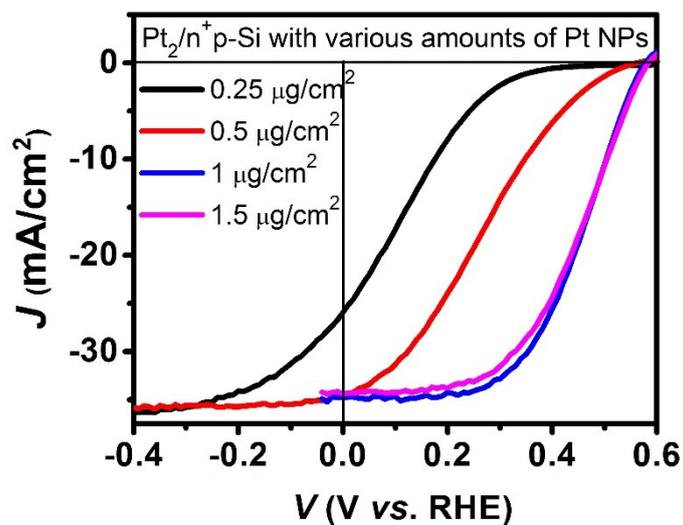


Figure S3. Consecutive LSV measurement for the  $\text{Pt}_2/\text{SiO}_2/\text{n}^+\text{p-Si}$  electrodes decorated with various amounts of Pt NPs.

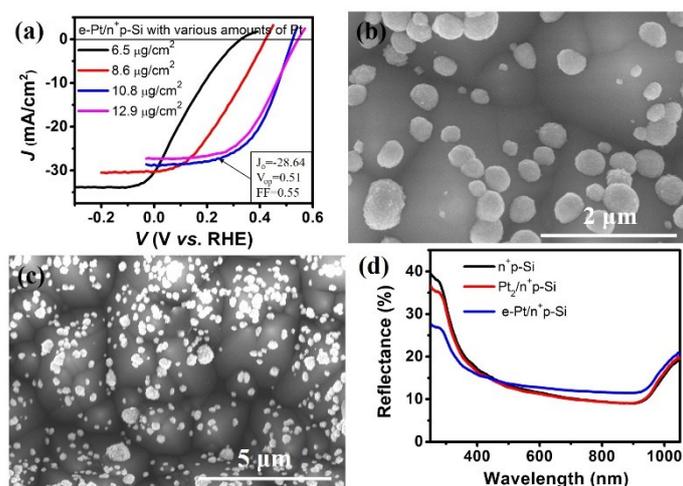


Figure S4. (a) Consecutive LSV measurements for the  $\text{e-Pt}/\text{SiO}_2/\text{n}^+\text{p-Si}$  electrodes decorated with various amounts of e-Pt particles. (b) High-magnification and (c) low-magnification top-down SEM images of the  $\text{e-Pt}/\text{n}^+\text{p-Si}$ . (d) Surface reflectance of bare  $\text{n}^+\text{p-Si}$ ,  $\text{Pt}_2/\text{n}^+\text{p-Si}$  and  $\text{e-Pt}/\text{n}^+\text{p-Si}$  photocathodes.

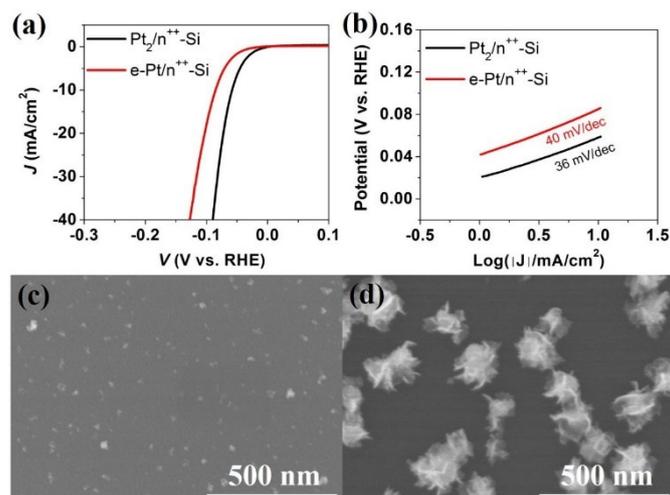


Figure S5. (a), (b) Electrocatalytic HER performance and corresponding Tafel plots of Pt NPs prepared by the electro- and electroless deposition, respectively. We used degenerately doped silicon wafer ( $n^+-Si$ ) as the conductive substrates to replicate the same amount of Pt catalyst. Electrodes were 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.

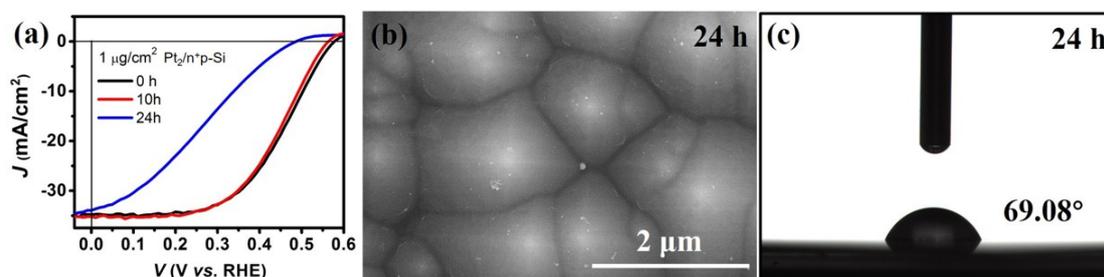


Figure S6. (a) Consecutive LSV measurements of  $Pt_2/n^+p-Si$  during the 10 and 24 h HER test. (b) Top-down SEM image and (c) water wettability of  $1\mu g/cm^2 Pt_2/n^+p-Si$  after a 24 h PEC testing.

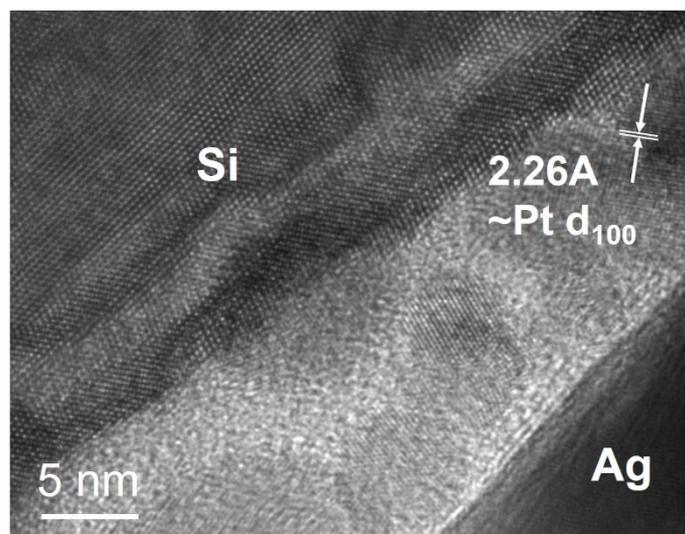


Figure S7. Cross-sectional HRTEM micrograph of Pt<sub>2</sub>/n<sup>+</sup>p-Si surrounded by TiO<sub>2</sub> layer.

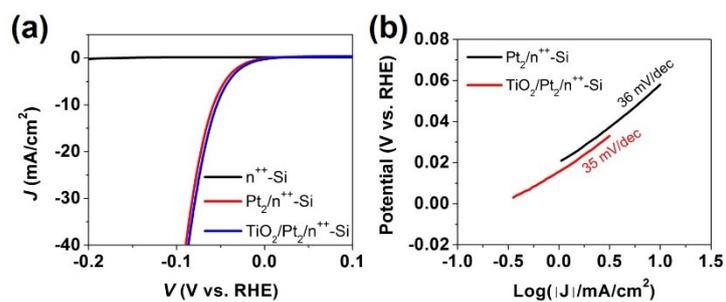


Figure S8. (a), (b) Electrocatalytic HER performance and corresponding Tafel plots of Pt<sub>2</sub>/n<sup>+</sup>-Si with and without the decoration of TiO<sub>2</sub> layer.

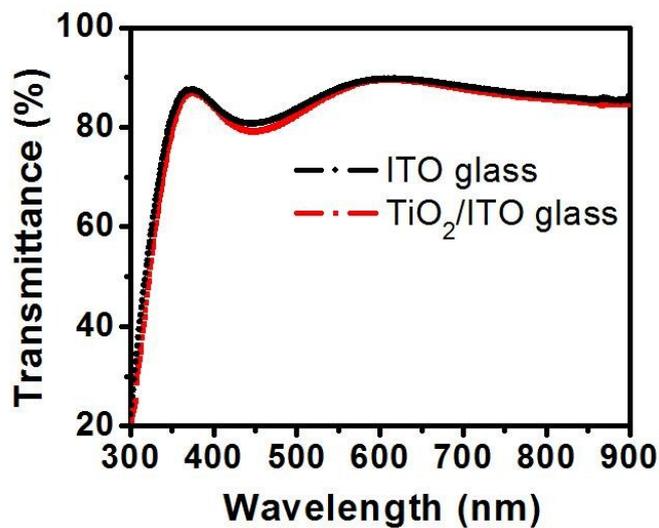


Figure S9. UV-Vis transmittance spectra of ITO glass substrates with and without the decoration of TiO<sub>2</sub> layer.

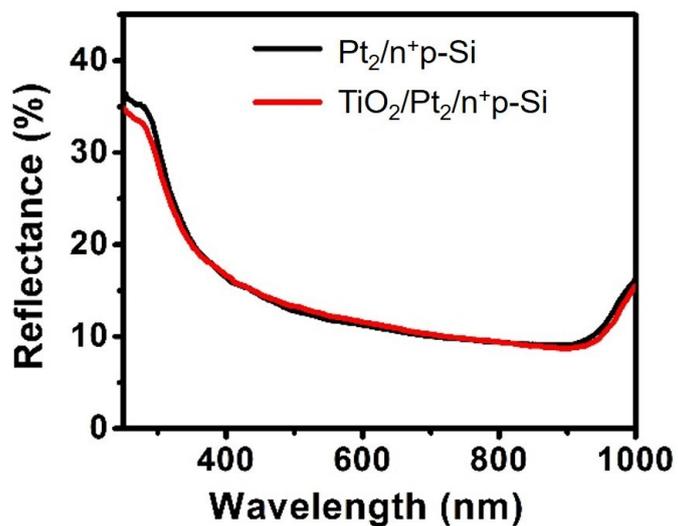


Figure S10. The reflection spectra of the Pt<sub>2</sub>/n<sup>+</sup>p-Si with and without the decoration of TiO<sub>2</sub> layer, measured using a Perkin Elmer Lambda 750 spectrophotometer in a wavelength range of 350–1000 nm, which uses BaSO<sub>4</sub> as a reference. No significant difference is found between them.

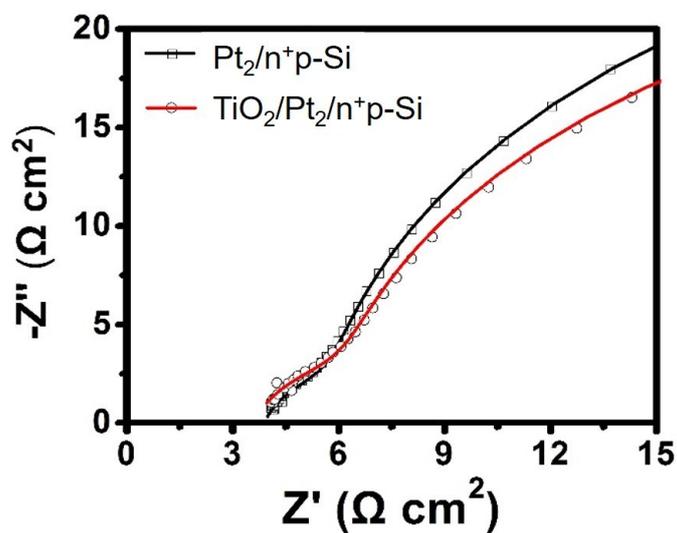
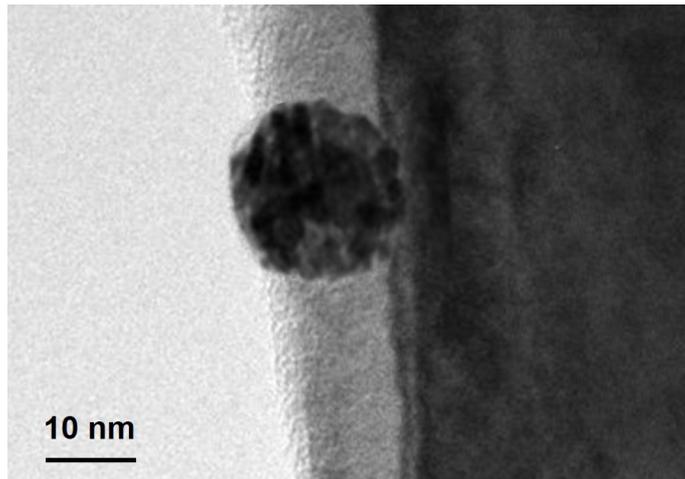
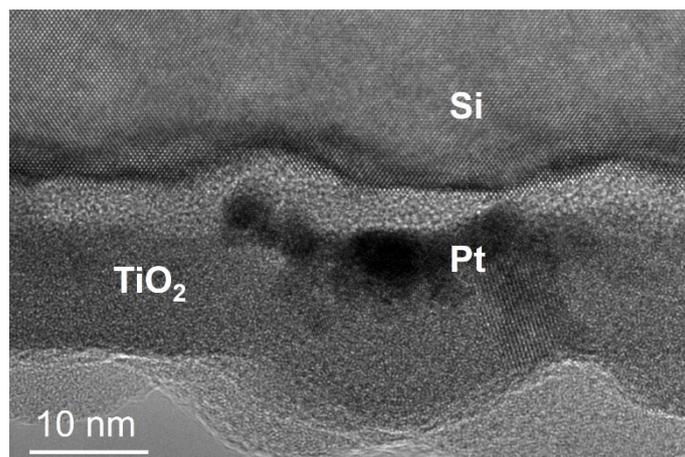


Figure S11. The enlarged photograph of Figure 5b.



[Figure S12. A representative cross-sectional HRTEM micrograph of  \$\text{TiO}\_2/\text{Pt}\_2/\text{n}^+\text{p-Si}\$  sample. The top surface of the Pt NPs with larger size than  \$\sim 15\$  nm is not covered by  \$\text{TiO}\_2\$ .](#)



[Figure S13. TEM measurement for the sample  \$\text{TiO}\_2/\text{Pt}\_2/\text{n}^+\text{p-Si}\$  after the 168-hour electrolysis.](#)

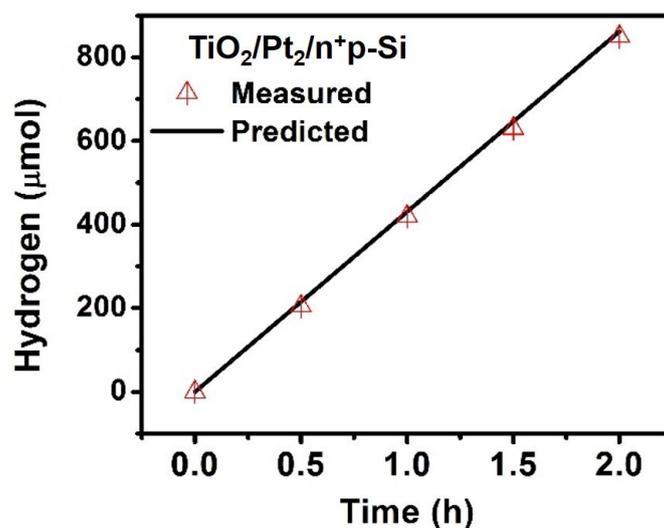


Figure S14. Theoretical calculated and measured  $\text{H}_2$  amount measurements on  $\text{TiO}_2/\text{Pt}_2/\text{n}^+\text{p-Si}$  photocathode under simulated AM 1.5G illumination. These measurements show that this device evolves hydrogen with effectively 96% Faradaic efficiency within the experimental error.

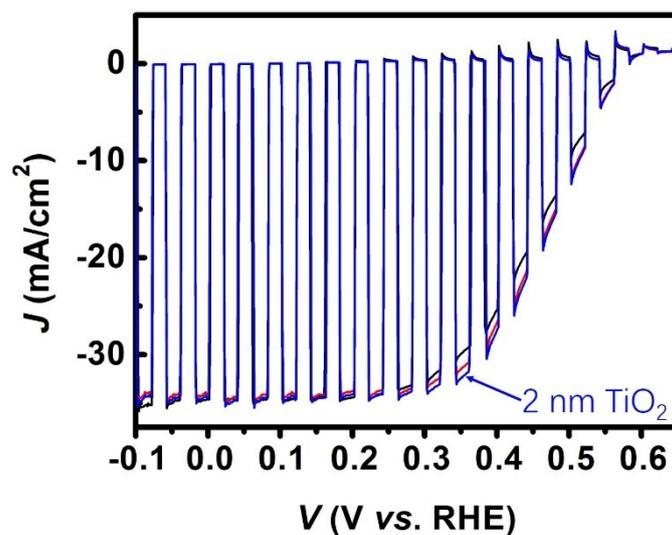


Figure S15. LSV curves under chopped illumination of  $\text{Pt}_2/\text{n}^+\text{p-Si}$  (black), 15 nm  $\text{TiO}_2/\text{Pt}_2/\text{n}^+\text{p-Si}$  (red) and 2 nm  $\text{TiO}_2/\text{Pt}_2/\text{n}^+\text{p-Si}$  (blue) photoelectrodes measured in 1 M  $\text{HClO}_4$  solution under simulated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