

## Supporting Information

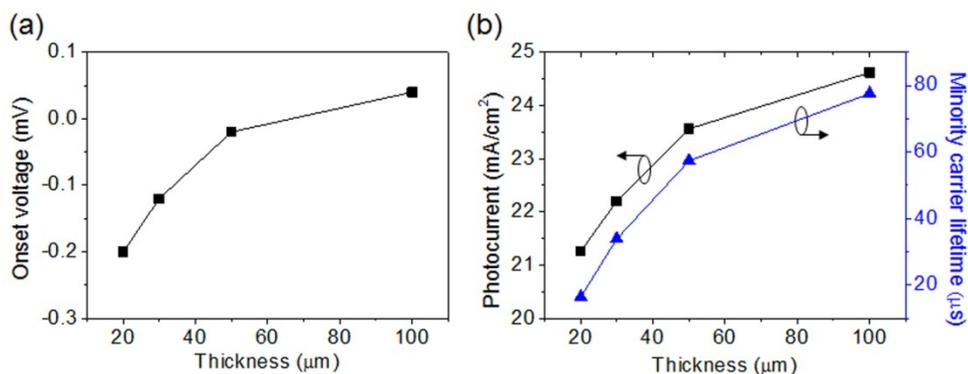
# High Performance H<sub>2</sub> Evolution Realized in 20- $\mu$ m-thin Silicon Nanostructured Photocathode

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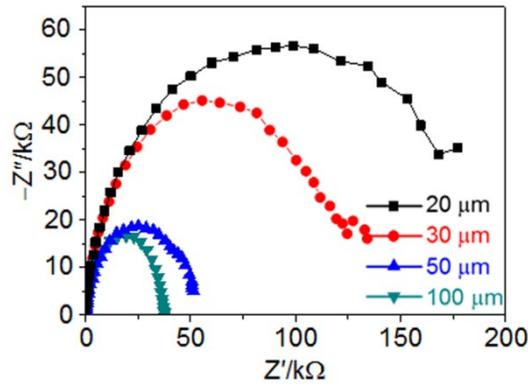
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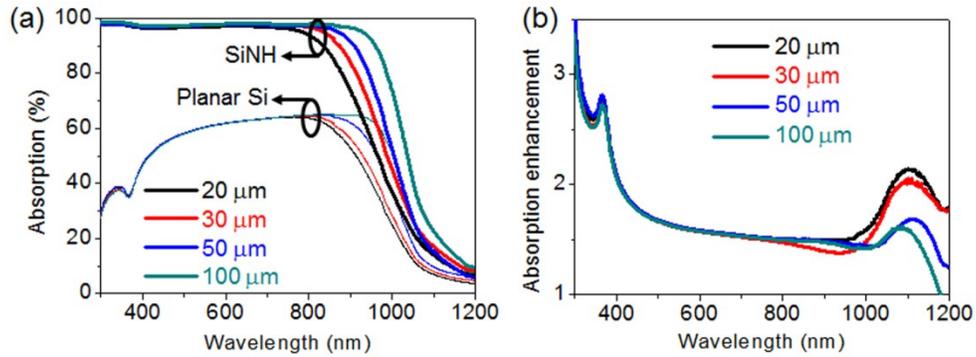


**Figure S1.** (a) Onset voltage ( $V_{ph}$ ) for planar Si as a function of substrate thickness ( $W$ ). (b) Saturated photocurrent density ( $J_{ph}$ ) and effective minority carrier lifetime ( $\tau_{eff}$ ). Generally,  $\tau_{eff}$  is expressed as follows:  $1/\tau_{eff} = 1/\tau_{bulk} + 1/\tau_{surf}$ , where  $\tau_{bulk}$  is the bulk minority carrier lifetime.

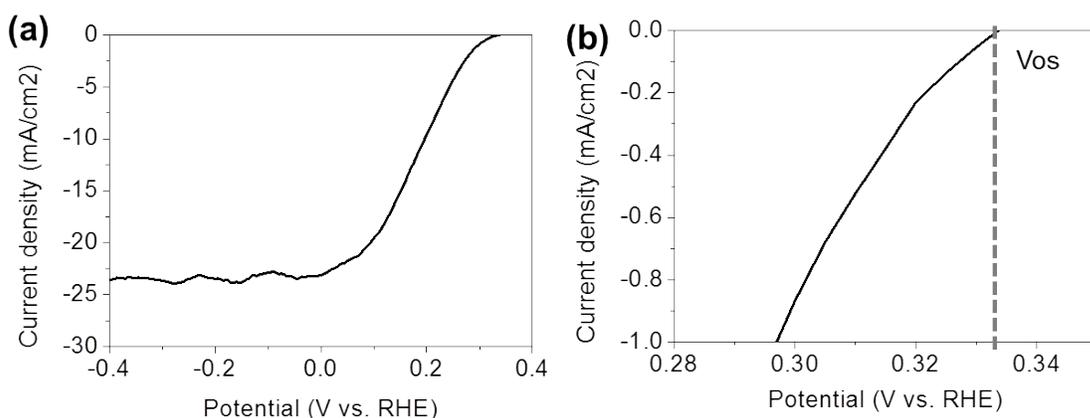
Assuming that the  $\tau_{bulk}$  value ( $\sim 1$  ms for our silicon wafers) is negligible,  $\tau_{eff}$  can be approximated as  $\tau_{surf}$ , i.e.,  $\tau_{eff} \approx \tau_{surf}$ .



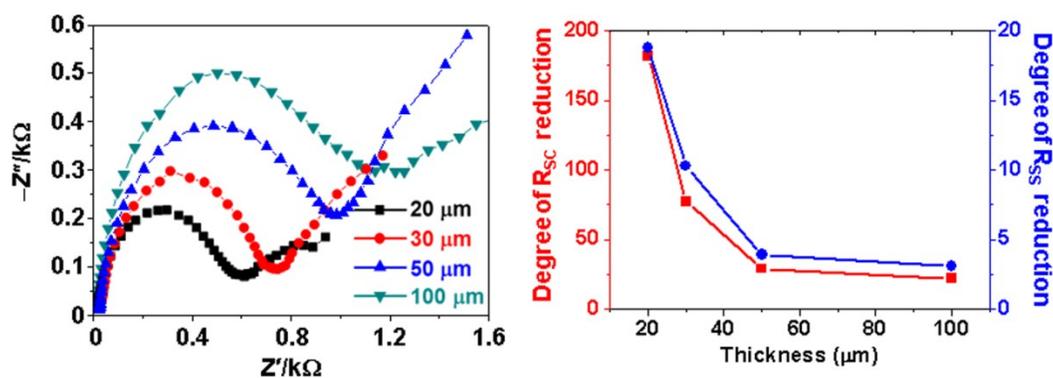
**Figure S2.** Nyquist plot of impedance spectroscopy data for planar Si as a function of thickness ( $W$ ) at  $20 \mu\text{m}$  (black),  $30 \mu\text{m}$  (red), and  $50 \mu\text{m}$  (blue), and  $100 \mu\text{m}$  (cyan).



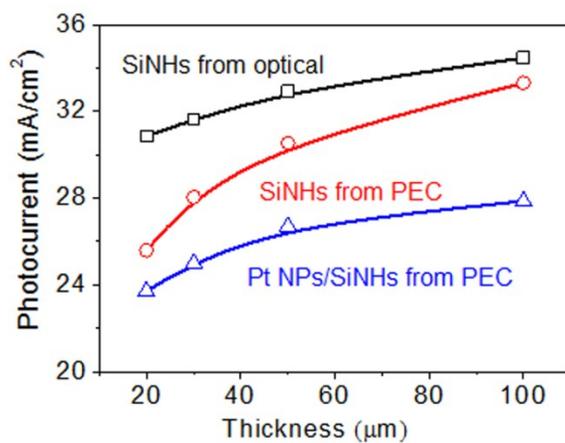
**Figure S3.** (a) Light absorption spectra and of Si NH (thick lines) and planar Si (thin lines) for various  $W$  values of  $20, 30, 50,$  and  $100 \mu\text{m}$ . (b) The absorption enhancement spectra of tapered SiNH with varying  $W$ . Tapered Si NH structures exhibit a gradual change of effective refractive indexes, which act as antireflective dielectric multilayers delivering superior broadband anti-reflectance.



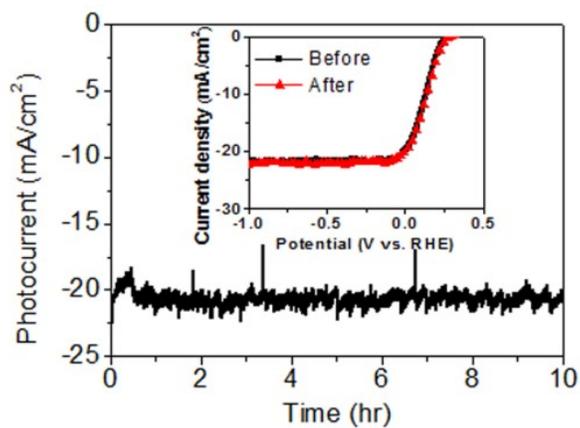
**Figure S4.** (a) J-V curve of Pt NPs/Si NHs photocathodes (20 μm-thick) and (b) magnification of J-V curve around the 0-1 mA/cm<sup>2</sup> photocurrent.



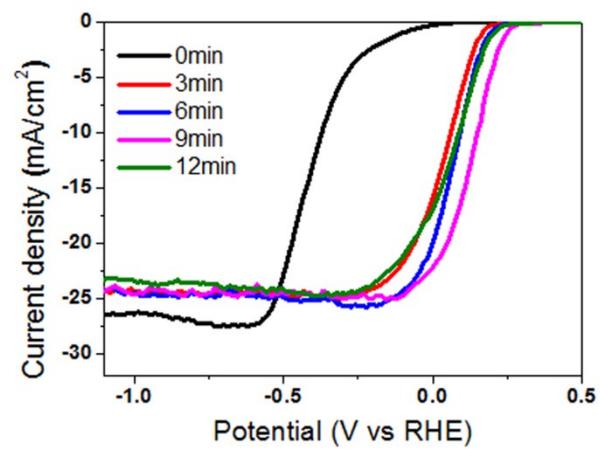
**Figure S5.** (a) Nyquist plots of impedance spectroscopy data for Pt NPs-planar Si as a function of W. (b) The overall amount of R<sub>sc</sub> and R<sub>ss</sub> reduction for planar Si after coating Pt NPs. The greatest reduction in charge transfer resistance was observed for the thinnest planar Si.



**Figure S6.** Saturated photocurrent values measured as a function of wafer thickness in the saturated region (1.5 V vs. RHE) of SiNHs and Pt NPs/SiNHs.



**Figure S7.** Long-term stability test of 20- $\mu$ m-thin Si photocathode employing Pt/Si NHs at 0 V vs. RHE. Insets show J-V curves before and after the 10 hr stability test.



**Figure S8.** J-V curve of SiNH photocathode as a function of Pt deposition time.