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SUPPLEMENTARY INFORMATION

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A silicon-based photocathode for water reduction with an epitaxial $SrTiO_3$ protection layer and a nanostructured catalyst

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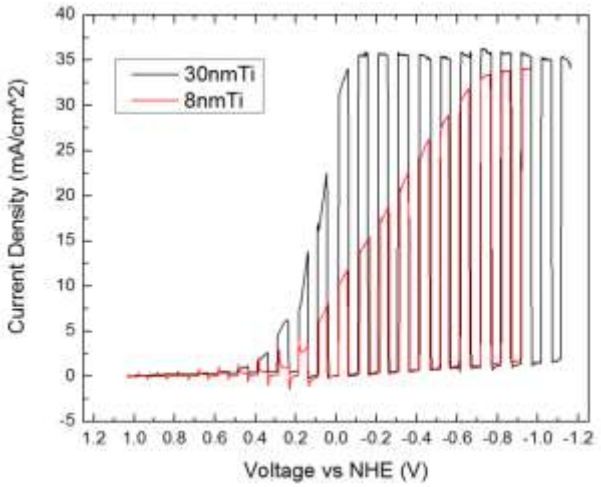

Supplementary Figure 1 | Linear sweep voltammetry (LSV) results for 30nm Pt/Ti/4 unit-cell STO/p-Si with 8nm and 30nm Ti. The illumination was chopped during the measurement. 0.5M H_2SO_4 was used as electrolyte.

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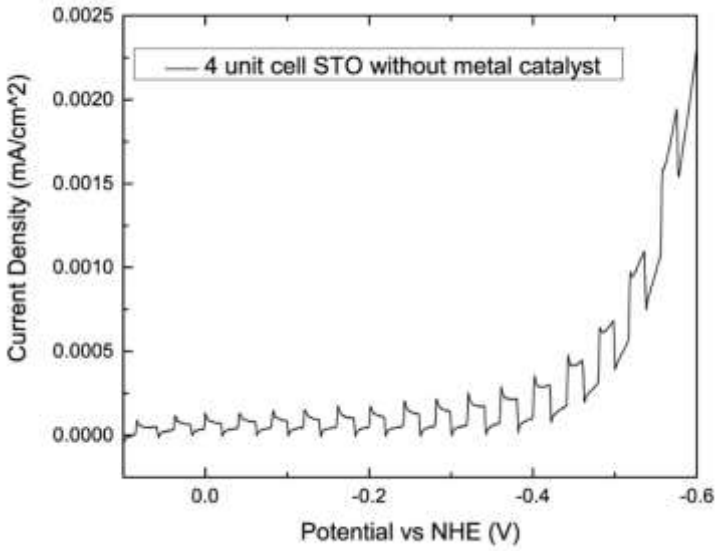
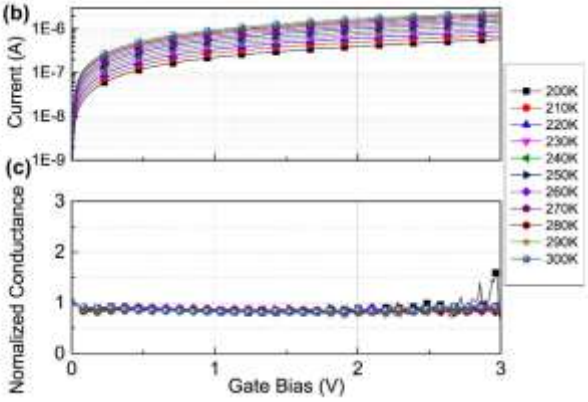


Supplementary Figure 2 | LSV results for 4 u.c. STO/pSi without any metal catalyst. The illumination was chopped during the measurement. 0.5M H_2SO_4 was used as electrolyte.

(a)

Transport Mechanism	Current Density	Normalized Conductance
Poole-Frenkel	$J \propto AV_{ox}e^{\left(\frac{B\sqrt{V_{ox}}}{kT}\right)}$	$1+\frac{B\sqrt{V_{ox}}}{2}$
Fowler-Nordheim Tunneling	$J \propto AV_{ox}^2 e^{\left(-\frac{B}{V_{ox}}\right)}$	$2+\frac{B}{V_{ox}}$
Schottky	$J \propto AT^2 e^{\left(\frac{B\sqrt{V_{ox}}}{kT}\right)}$	$\frac{B\sqrt{V_{ox}}}{2}$
Hopping	$J \propto AV_{ox}e^{(BV_{ox})}$	$1+BV_{ox}$
Ohmic	$J \propto AV_{ox}e^{\left(-\frac{B}{kT}\right)}$	1

J = current density. Vox = voltage drop over the oxide layer.
A, B = constant. k = the Boltzmann constant. T = temperature.



Supplementary Figure 3 | (a) Figure S3 (**new**). (a) Table of transport mechanisms (b) I-V measurements and (b) normalized conductance Gn=(dI/dV)/(I/V) in rough vaccum under various temperatures. The voltage is applied to the top metal contact. The electrical measurements is conducted by Agilent B1500A Semiconductor Device Analyzer.

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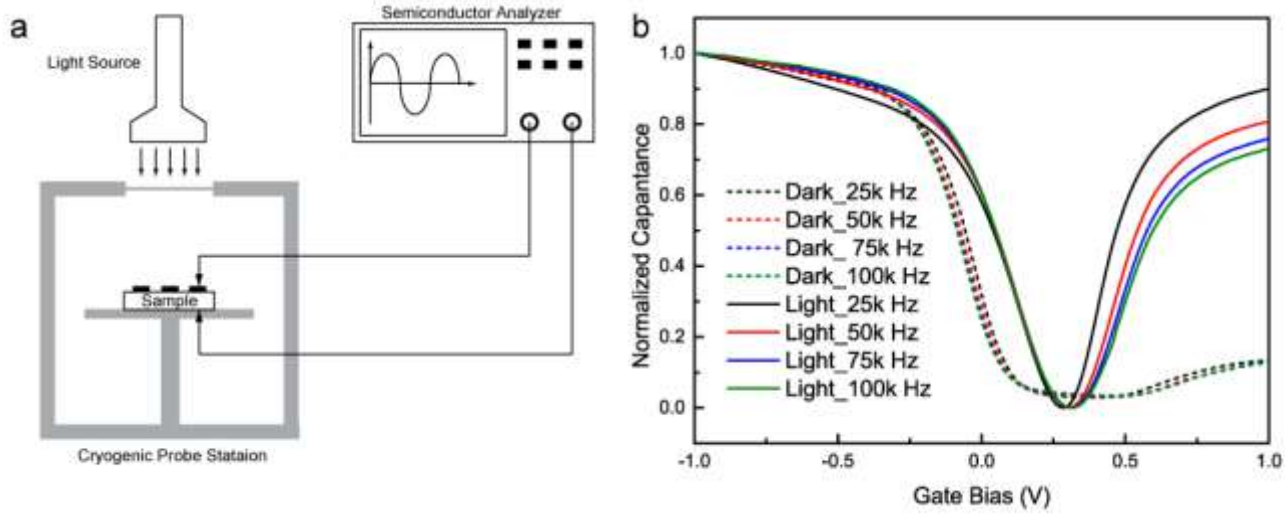
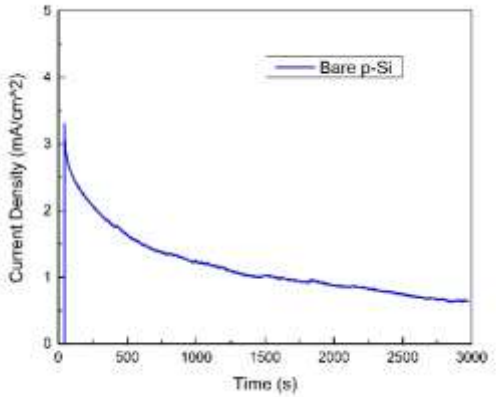


Supplementary Figure 4 | (a) Schematic of the measurement apparatus and configuration. (b) Normalized capacitance for 4 unit-cell STO sample with 400 μm diameter metal dots as the top contact under dark and light conditions. The voltage is applied to the gate (top contact). In dark, it is normal high-frequency response for MOS capacitor. At room temperature, the minority carrier response is much slower and not instantaneous over the frequency range from 25k ~ 100k Hz. So at positive bias, the capacitance is low. However, when illuminated, the capacitance increased rapidly to a value greater than the thermal equilibrium value in the dark by increasing steady-state carrier concentration generated by the light. The gate electrode is sufficiently thick and opaque and has no scratches or pinholes. The minority carriers generated within a diffusion length of the gate will form an inversion layer under the gate.



Supplementary Figure 5 | Stability test for bare p-Si wafer in 0.5M H_2SO_4 under -0.2V bias vs NHE. These results agree well with previous work[1].

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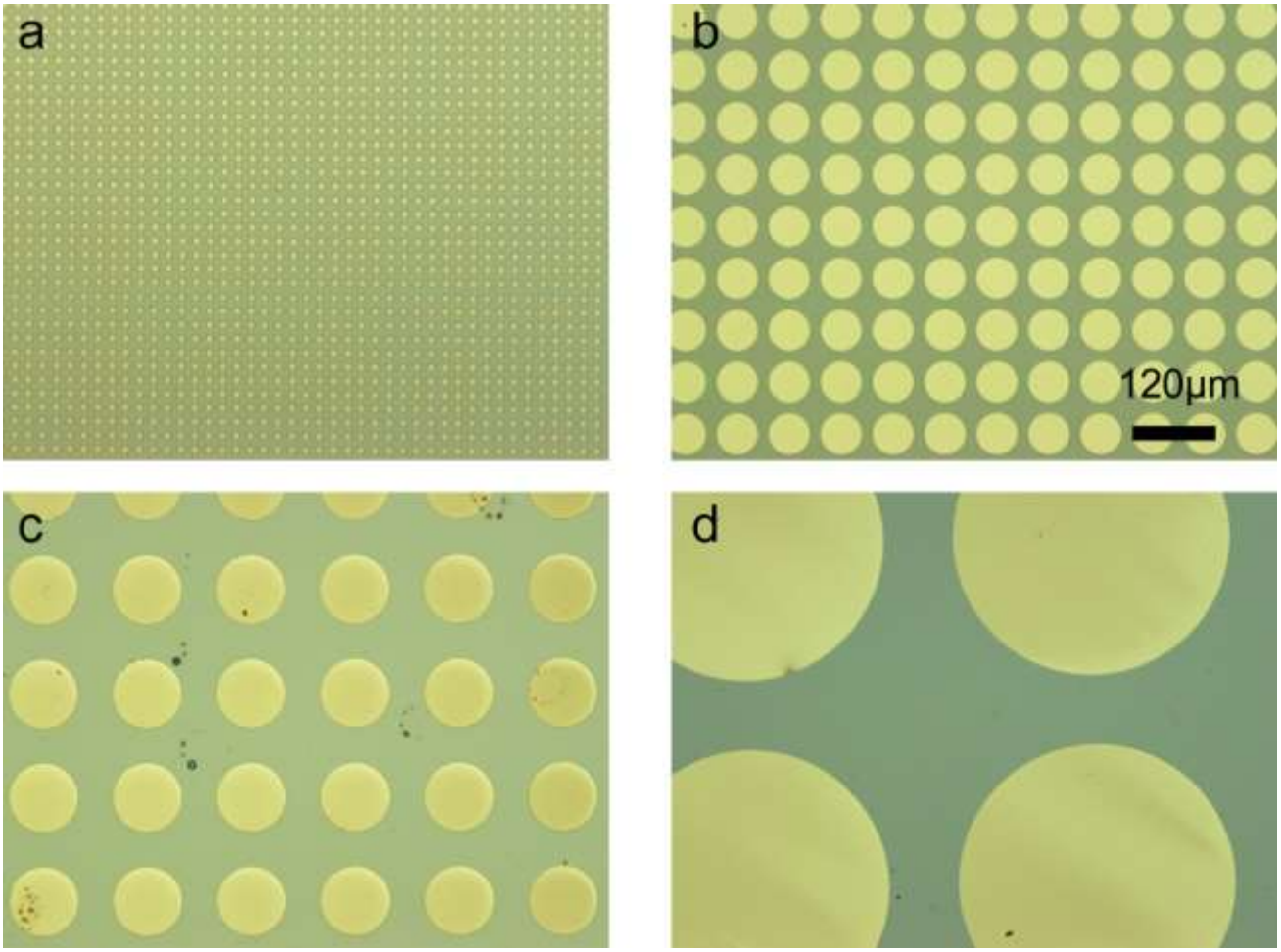
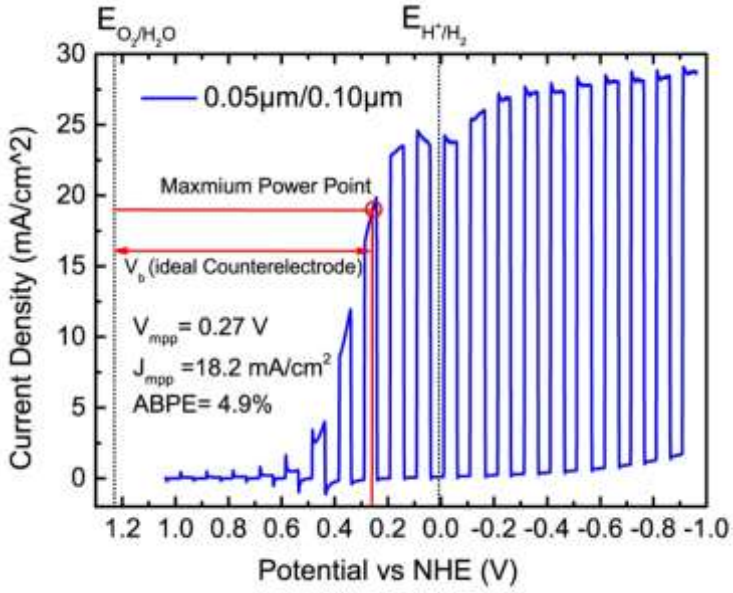


Supplementary Figure 6 | Optical Microscopy image of Ti/Pt bilayer metal catalyst with various diameter/spacing fabricated by photolithography. (a) 1μm/2μm. (b) 60μm/75μm. (c) 100μm/125μm. (d) 400μm/500μm.



Supplementary Figure 7 | LSV results of 20nmPt/30nmTi/4 u.c. STO/pSi sample with 0.05μm/0.1μm via nanosphere lithography and corresponding ABPE calculation. The illumination was chopped during the measurement. 0.5M H_2SO_4 was used as the electrolyte.

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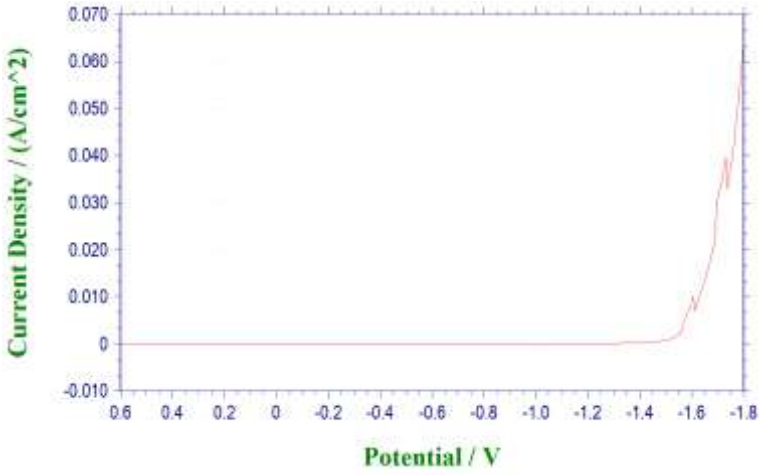

Supplementary Figure 8 | LSV results for p-Si wafer we used as substrate in this work. No HF treatment was applied. The illumination was chopped during the measurement. 0.5M H_2SO_4 was used as the electrolyte.

References

1. Sim U, *et al.* N-doped monolayer graphene catalyst on silicon photocathode for hydrogen production. *Energ Environ Sci* **6**, 3658-3664 (2013).