

Supporting Information

ALD Pt Nanoparticles and Thin-Film Coatings Enhancing the Stability and Performance of Silicon Photocathodes for Solar Water Splitting

*Christos Trompoukis**, *Ji-Yu Feng*, *Tom Bosserez*, *Jan Rongé*, *Jolien Dendooven*, *Christophe Detavernier*, *Roel Baets*, *Johan A. Martens*

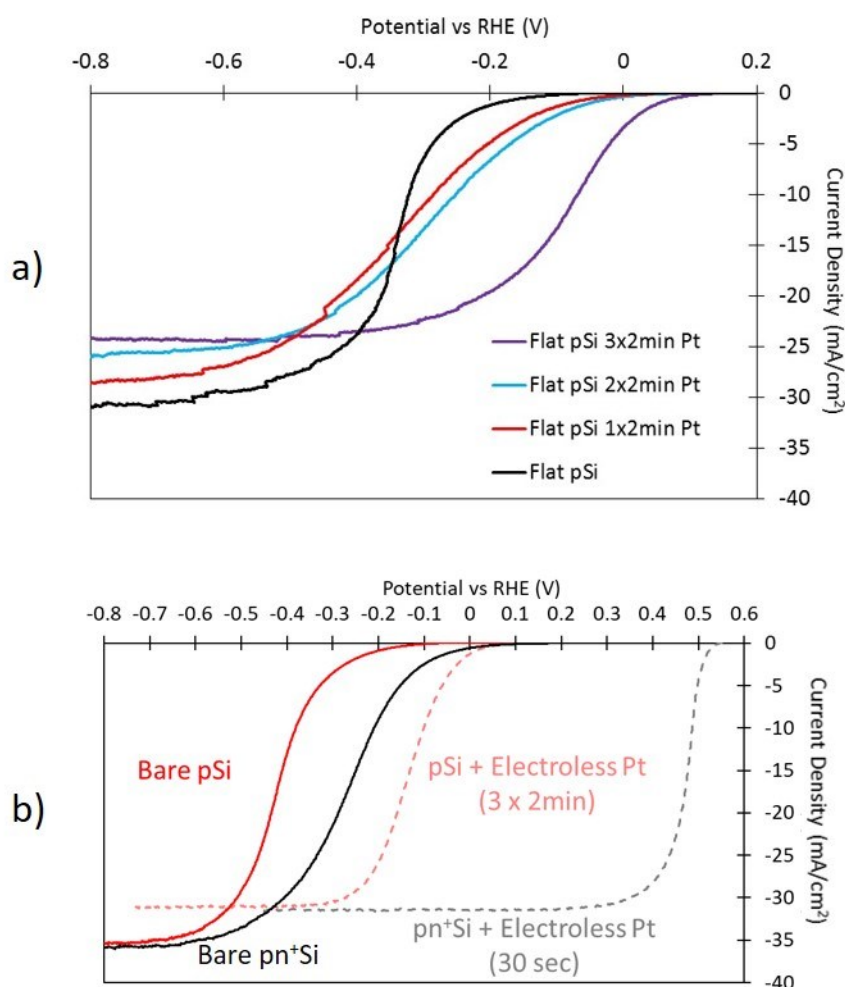


Figure S1. a) Optimising the Pt loadings from electroless deposition: PEC performance of flat p-type silicon photoelectrodes with various electroless depositions times. For the case of the pn⁺Si photocathodes, the optimal electroless deposition time was found to be 30 seconds. b) Semiconductor/liquid junction versus solid state junction: PEC performance of random

pyramid textured pSi (i.e. semiconductor/liquid junction, red curves) versus random pyramid textured pn⁺Si (i.e. solid state junction, black curves) with (faded dashed curves) and without (bold continuous curves) Pt nanoparticles deposited by electroless deposition.

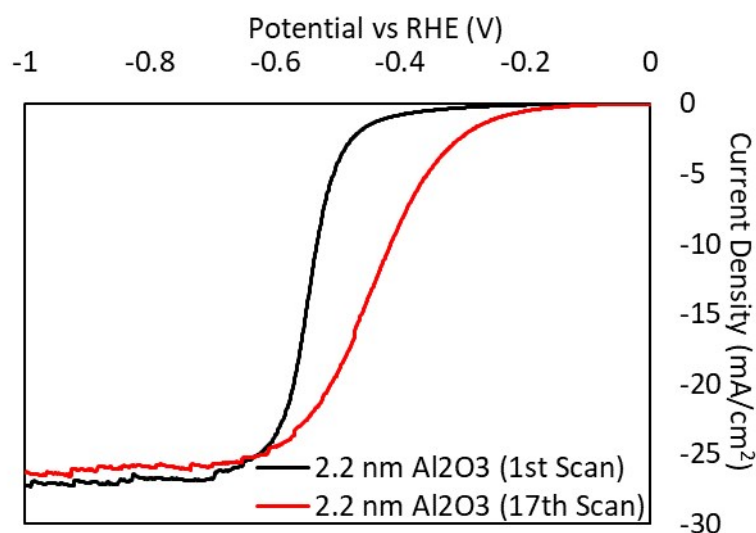


Figure S2. Current density – voltage characteristics of 2.2 nm thin Al₂O₃ ALD coating on flat p-type Si photocathodes during the 1st and the 17th scan, highlighting the instability of Al₂O₃ in contact with acidic electrolytes.

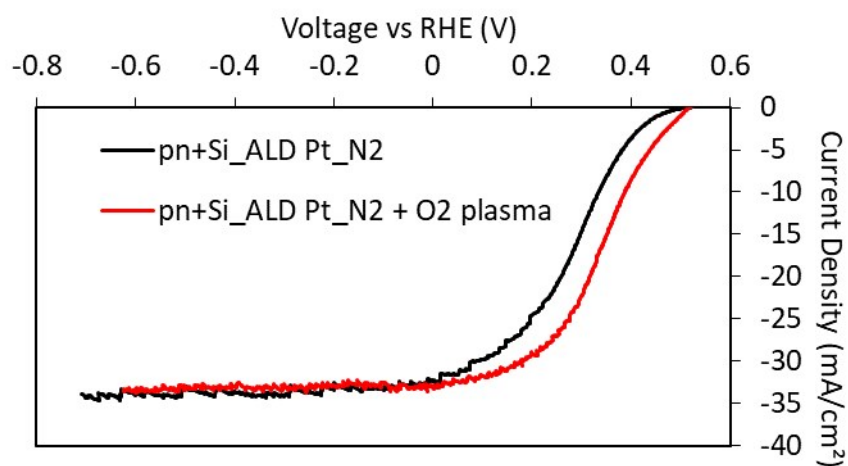


Figure S3. Current density – voltage (JV) characteristics of random pyramid textured pn⁺Si photocathodes coated by ALD Pt-N₂ nanoparticles with (red) and without (black) an O₂ plasma treatment highlighting the impact of the O₂ plasma on the performance of the photocathode.

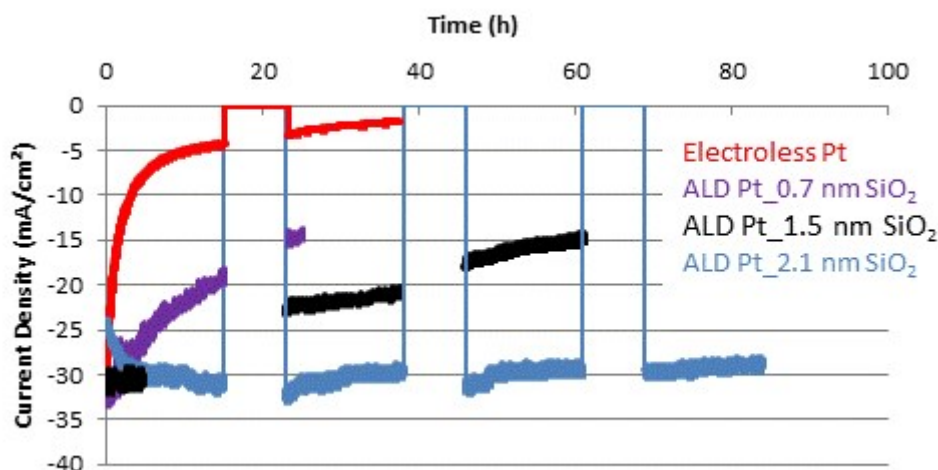


Figure S4. A comparative summary of the day/night operation for random pyramid textured pn^+Si photocathodes coated by electroless Pt nanoparticles (red curve), ALD Pt nanoparticles and 0.7 nm SiO_2 overcoating (purple), ALD Pt nanoparticles and 1.5 nm SiO_2 overcoating (black) and ALD Pt nanoparticles and 2.1 nm SiO_2 overcoating (blue). The data missing between the 6th and the 15th hour of operation from the case of the 1.5 nm coating (black curve) is due to a lost communication between the potentiostat and the computer during that measurement. However, we consider it makes sense to include this data set in the supporting information since this case correlates well with the overall trend of increased stability for thicker SiO_2 coatings.

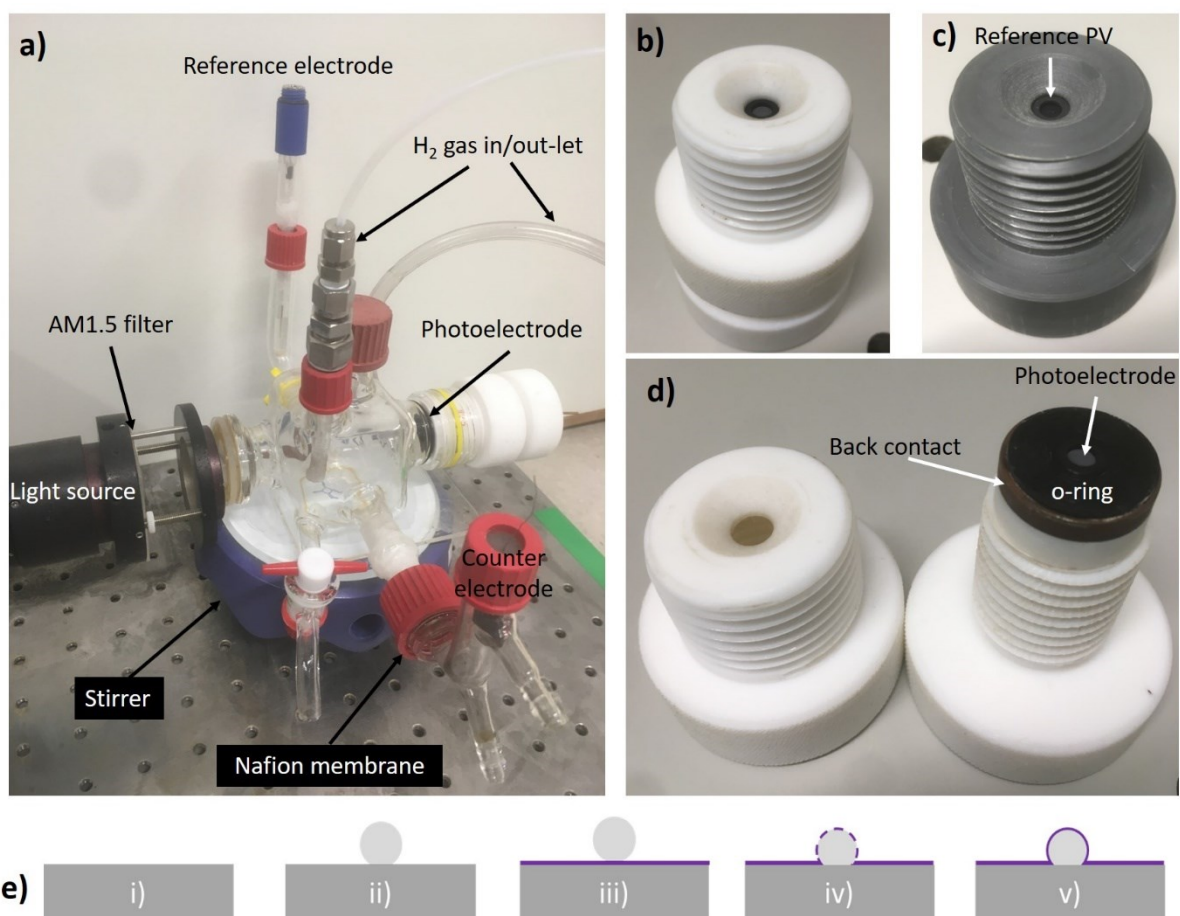


Figure S5. a) PEC cell used during the experiments for the CV and CA scans, b) sample holder for the photoelectrode, c) holder for the solar cell used for the calibration of the light source, placed in exactly the same position as the photoelectrode, d) interior of the sample holder and e) simplified schematic cross section of the various cases of photocathodes: i) bare Si, ii) ALD Pt_{N2} nanoparticle on Si, iii) ALD Pt_{O2} nanoparticle on Si where a thin SiO₂ grows at the interface, iv) ALD Pt_{N2} nanoparticle on Si coated by thin ALD SiO₂ and v) ALD Pt_{N2} nanoparticle on Si coated by thicker ALD SiO₂.

Table S1. Current density (J_{sc}), onset potential (V_{on}), current density at maximum power point (J_{mpp}), voltage at maximum power point (V_{mpp}) and fill factor (FF) of the curves shown in Figure 3.

Sample	J_{sc} (mA/cm²)	V_{on} @ 0.1 mA/cm² (V)	J_{mpp} (mA/cm²)	V_{mpp} (V)	FF (%)
Electroless	31.6	528	26.2	352	55
No overcoat	34.7	505	22	240	30
Pt_N ₂ and 0.7 nm overcoat	34	525	24.3	352	48
Pt_N ₂ and 1.5 nm overcoat	33.1	525	23.2	355	47
Pt_N ₂ and 2.1 nm overcoat	33.9	485	14.7	371	33
Pt_N ₂ and 3.5 nm overcoat	33.6	426	12.9	98	9
Pt_N ₂ and 5 nm overcoat	34	68	0.01	169	0.01