Supporting Information

Self-optimized catalysts: Hot-electron driven photosynthesis of catalytic photocathodes

Evgenia Kontoleta§, Sven H. C. Askes§, and Erik C. Garnett*

Center for Nanophotonics, AMOLF, Science Park 104, 1098 XG Amsterdam, Netherlands.

§E.K. and S.A. contributed equally.

*Corresponding author. Email: E.Garnett@amolf.nl
Supporting Information

**IPCE calculation**

The Incident Photon to Current Efficiency (IPCE) was calculated as follows:

\[
IPCE(\%) = \left( \frac{j_{ph} \left( \frac{mA}{cm^2} \right) \times 1241 \ (V \times nm)}{P \left( \frac{mW}{cm^2} \right) \times \lambda \ (nm)} \right) \times 100
\]

where \( j_{ph} \left( \frac{mA}{cm^2} \right) \) is the average photocurrent retrieved from the Figure S12 for each wavelength, 1241 \((V \times nm)\) represents a multiplication of \( h \) (Planck’s constant) and \( c \) (the speed of light) divided by \( q \) (the electron charge), \( P \left( \frac{mW}{cm^2} \right) \) is the power intensity of each wavelength measured with a Si photodiode power sensor (Thorlabs S120C, see Table S1 for more information, with surface area of the photoelectrode equal to 0.28 cm\(^2\)) and \( \lambda \ (nm) \) is the...
wavelength. The IPCE vs wavelength curve is compared with the absorptance spectrum of the same sample in Figure S14.

Supplementary figures

Figure S1. Photograph of Au nano-islands on glass/ITO.

Figure S2. Photoelectrochemical setup used for deposition of Pt: Teflon cell (1), Au-TiO$_2$ substrate as working electrode (2), conductive aluminum tape (3), potentiostat connections (4), electrolyte (5), reference electrode (6), counter electrode (7), quartz window (8), and laser beam (9).
Figure S3. Optical constants (n,k) of the TiO$_2$ layer on a Si substrate, retrieved by ellipsometry measurements. Reproduced from Kontoleta et al. $^1$ In the public domain.

Figure S4. XRD spectrum of TiO$_2$ layer deposited with ALD on a Si substrate. Dashed lines show the position of the diffraction peaks of the TiO$_2$ anatase phase.$^2$ Reproduced from Kontoleta et al. $^1$ In the public domain.
Figure S5. Maximum height distribution derived from AFM measurements for Au nano-islands covered with TiO$_2$.

Figure S6. a) Secondary, b) backscattered and c) an overlay SEM image of a) and b) depicting the Au nano-islands coated with a TiO$_2$ layer on glass/ITO.
Figure S7. Particle distribution curves derived from SEM image analysis before (blue bottom curve) and after (red top curve) TiO$_2$ deposition.

Figure S8. Absorption spectra of Au nano-islands with (yellow line) and without (blue line) TiO$_2$ and bare TiO$_2$ (red line) on ITO/glass. The absorbance of ITO/glass has been subtracted from the spectra presented here.
Figure S9. Photocurrent density vs applied potential scans of bare TiO₂ (blue solid line), uncoated Au nano-islands (red solid line) and Au nano-islands coated with 18 nm TiO₂ in hexachloroplatinate (pH 3, 0.04 mM, in 0.1 M Na₂SO₄ aqueous solution) under chopped 638 nm illumination (0.5 W/cm²), b) Table of photocurrent and dark-current values, derived from plot (a), at applied potential 0.45 V vs RHE, which is the potential used for the hot-e driven deposition of platinum nanoparticles, c), d) and e) Zoom-in images of plot (a) for Au nano-islands/TiO₂, Au nano-islands and bare TiO₂ respectively.
Figure S10. XPS spectrum of Au/TiO$_2$ nano-islands with photodeposited Pt nanoparticles before photoconditioning at -0.25 V vs RHE. The dashed lines correspond to the 3s, 4f$^{7/2}$ and 4f$^{5/2}$ binding energies of Ti (green color), Pt(II) (black color) and Pt(IV) (red color). The XPS spectrum after photoconditioning can be find in the main text (Figure 3c). In the same figure is clear that most of the Pt oxides were converted to metallic Pt, which allowed for a fair comparison between the samples prepared with hot-electron deposition and electrodeposition of the cocatalyst.
Figure S11. a) and c) SEM images of 2 different regions of the same sample of Au/TiO₂ nano-islands on glass/ITO after an electrical charge of 125 μC/cm² was passed to the sample in presence of hexachloroplatinate (pH 3, 0.04 mM, in 0.1 M Na₂SO₄ aqueous solution) under 638 nm illumination (0.5 W/cm²). b) and d) the EDX measurements of regions a) and c) respectively, where each curve is associated with a number which corresponds to the exact spot investigated and depicted in the SEM images. Solid grey lines correspond to the x-ray emission peaks of Pt, Au and Ti.
Figure S12. Photoconditioning curve (current density vs time) of Au/TiO₂ samples for conversion of the Pt oxides to metallic platinum, in pH 7 phosphate buffer, at -0.25V applied potential, where the first 20 sec the sample was kept in the dark while the following 45 sec the 638 nm laser beam (0.5 W/cm²) hits the sample. The photocurrent is increasing gradually and then remains constant after full conversion of platinum oxides to metallic platinum.

Figure S13. Photocurrent density vs time at different excitation wavelengths of a Au/TiO₂ sample in presence of hexachloroplatinate (pH 3, 0.04 mM, in 0.1 M Na₂SO₄ aqueous solution) at applied potential 0.45 V vs RHE. The width of each of the colored bars corresponds to the time where a different excitation wavelength was used. The respective excitation wavelength (nm) is also depicted on each of the colored bars.
Figure S14. Incident Photon to Current Efficiency (IPCE, blue data points) vs wavelength of Au/TiO₂ photocathode in presence of hexachloroplatinate (pH 3, 0.04 mM, in 0.1 M Na₂SO₄ aqueous solution) and absorptance vs wavelength (red solid line) of the same sample before the IPCE measurement.
Table S1. The different wavelengths (nm) used to excite the Au/TiO$_2$ photocathodes for the IPCE measurements (Figures S11 and S12) and their respective power (μW).

| Wavelength (nm) | Power (μW) |
|-----------------|------------|
| 440             | 22         |
| 460             | 23         |
| 480             | 32         |
| 500             | 47         |
| 520             | 51         |
| 540             | 71         |
| 560             | 105        |
| 580             | 149        |
| 600             | 199        |
| 620             | 203        |
| 640             | 269        |
| 660             | 395        |
| 680             | 492        |
| 700             | 435        |
| 720             | 291        |
| 740             | 171        |
| 760             | 48         |

Figure S15. Photocurrent density vs 638 nm laser intensity of Au/TiO$_2$ in presence of hexachloroplatinate (pH 3, 0.04 mM, in 0.1 M Na$_2$SO$_4$ aqueous solution) in logarithmic (a) and linear (b) scale. Our photodeposition and photocatalysis experiments were conducted at an intensity of 0.5 W/cm$^2$. 
Figure S16. Image from thermal camera from a) the back side of the sample (sample in contact with hexachloroplatinate) and , b) the front side of the sample (the quartz window was removed in this case and the sample was in contact with air).

Figure S17. SEM image of Au nano-islands coated with 18 nm TiO$_2$ on ITO/glass. The sample was immersed in H$_2$PtCl$_6$ solution (pH 3, 0.04 mM, 0.1M Na$_2$SO$_4$) for 20 min, while the solution was heated up to 40°.
Figure S18. FDTD simulations on Au/TiO$_2$ nanoislands for 638 nm excitation. Experimental details given above. a) Schematic 3D representation of the simulation space in Lumerical, with an ITO substrate (white), Au nano-islands (yellow), and a 18 nm conformal TiO$_2$ layer (red transparent). b-d) Cross sections of the absorbed power (in fraction of absorbed power/m$^3$) at 10 nm above the ITO substrate surface for light injection polarized along the x-axis (b) and along the y-axis (c), and a material map (d). e) Cross section of the absorbed power in a single Au/TiO$_2$ nanoisland at 22 nm above the ITO substrate. The corresponding material map is shown in panel (f). Note the lack of absorbed power in the TiO$_2$ shell. g)
Orthogonal projections along the yellow lines for a 500x500 nm absorbed power map at 10 nm above the ITO substrate.

Figure S19. Three-dimensional simulation view of the absorbed power in a section of Au-TiO$_2$ nanoislands (2x2 µm square), made using the Volume Viewer in ImageJ v1.52 in volume mode and with tricubic sharp interpolation. For clarity, the fraction of absorbed power volume (in blue to red color gradient) is overlaid on top of the nanoisland bodies (in grey). The voxel size is 5x5x5 nm. We observe that most of the absorbed power is near the base of structures and that the absorption hotspots are localized all around each particle (i.e. not very well localized).
| Data set #1 (main text Figures 4a and 4b and Figure S20) | Deposited amount (nano grams) | Deposition method |
|--------------------------------------------------------|------------------------------|-------------------|
|                                                        | 19.4                         | Hot-electron assisted (Au/TiO_2/Pt\text{photo}) |
|                                                        | 17.3                         | Electrodeposition (Au/TiO_2/Pt\text{electro}) |
| Data set #2 (Figure S21)                               | 22                           | Hot-electron assisted (Au/TiO_2/Pt\text{photo}) |
|                                                        | 35.8                         | Electrodeposition (Au/TiO_2/Pt\text{electro}) |
| Data set #3 (Figure S22)                               | 25.1                         | Hot-electron assisted (Au/TiO_2/Pt\text{photo}) |
|                                                        | 25.6                         | Electrodeposition (Au/TiO_2/Pt\text{electro}) |

Table S2. The total amount of deposited Pt on glass/Au/TiO_2 samples, in nano grams, retrieved from ICP-MS measurements; Samples prepared with the 2 different methods: hot-electron assisted deposition (photo) and electrodeposition (electro) are compared. Data sets #1, #2 and #3 correspond to 3 different groups of samples, whose photoelectrochemical performance was compared (see Figures 4a & 4b in the main text, Figure S21 and Figure S22 respectively).

Figure S20. XPS spectra of Au/TiO_2/Pt samples presented and compared in Figure 4, prepared with hot-electron driven chemistry (red line) and with electrodeposition (black line).
XPS peak with a binding energy of around 62 eV corresponds to Ti 3s and peaks at 71 eV and 74.3 eV to Pt 4f\(_{7/2}\) and Pt 4f\(_{5/2}\) respectively.

Figure S21. Data set #2 of the photocatalytic performance comparison of two Au/TiO\(_2\)/Pt samples prepared with hot-electron driven chemistry (red line) and electro-deposition (black line), a) current density vs applied potential and b) XPS spectra. XPS peak with a binding energy of around 62 eV corresponds to Ti 3s and peaks at 71 eV and 74.3 eV to Pt 4f\(_{7/2}\) and Pt 4f\(_{5/2}\) respectively. In this data set the deposited amount of Pt is higher on the sample made with electrodeposition (according also to ICP-MS measurements), which could explain why in higher applied potentials the same sample performs better than the sample made with photo-electrodeposition.

Figure S22. Data set #3 of the photocatalytic performance comparison of two Au/TiO\(_2\)/Pt samples prepared with hot-electron driven chemistry (green line) and electro-deposition (black line), a) current density vs applied potential and b) XPS spectra. XPS peak with a
binding energy of around 62 eV corresponds to Ti 3s and peaks at 71 eV and 74.3 eV to Pt 4f_{7/2} and Pt 4f_{5/2} respectively.

References

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