

Supplement to: Optimised Photocatalytic Hydrogen Production Using Core-Shell AuPd Promoters with Controlled Shell Thickness

Wilm Jones,^{ab} Ren Su,^{c*} Peter P. Wells,^{ad} Yanbin Shen,^{ce} Nikolaos Dimitratos,^{ab} Mike Bowker,^{ab} David Morgan,^b Bo B. Iversen,^{ce} Arunabhiram Chutia,^{ad} Flemming Besenbacher,^c and Graham Hutchings^{ab*}

Microscopic images

Figure S1 shows the additional scanning transmission electron microscope (STEM) images of the 2ML Pd(PD) catalyst, taken with a Jeol JEM-2100 LaB6 TEM operating at 200 KeV fitted with dark field detector. The sample was prepared for STEM characterisation by dispersing the catalyst powder in high purity ethanol, followed by sonication for 10 minutes. A drop of this suspension was then evaporated on a holey carbon film supported by a 300 mesh copper TEM grid. The visible bright areas on the image (~4 nm) indicate the presence of AuPd NPs, which were immobilised on the TiO₂ support. Energy-dispersive X-ray (EDX) spectra were recorded on individual NPs indicated in electron images 1-4. Using L α lines the presence of Au and Pd in individual NPs was established.

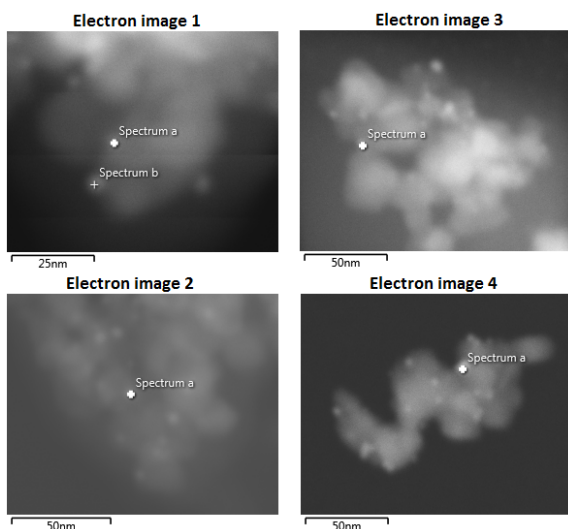


Fig. S1. STEM images of 2ML Pd(PD) NPs supported on TiO₂. Electron images 1-4 show various regions of the 2ML Pd(PD) catalyst with point and id quantification was performed on the NPs indicated by EDX analysis.

Table S1 depicts the EDX weight % (wt%) quantification of the NPs imaged by STEM in Fig. S1 of electron images 1-4. As Au and Pd were the elements of interest for this analysis, all other elements were excluded. Accurate quantification was difficult to establish by EDX at this scale. However it can be seen that Au and Pd were presented together in the NPs scanned here, supporting results from the XAFS analysis of the association of Au and Pd.

Table S1. EDX results of 2ML Pd(PD) NPs supported on TiO₂. The wt% was calculated by EDX analysis using the L α lines only of Au and Pd. Spectra used for the quantification analysis were taken on the spots indicated on electron images 1-4 from Fig. S1.

Electron image 1	Element	wt%	wt% Sigma
Spectrum a	Pd	16.9	17.4
Spectrum a	Au	83.1	17.4
Spectrum b	Pd	19.1	20.3
Spectrum b	Au	80.9	20.3
Electron image 2	Element	wt%	wt% Sigma
Spectrum a	Pd	20.9	24.1
Spectrum a	Au	79.1	24.1
Electron image 3	Element	wt%	wt% Sigma
Spectrum a	Pd	6.1	6.7
Spectrum a	Au	93.9	6.7
Electron image 4	Element	wt%	wt% Sigma
Spectrum a	Pd	5.1	19.3
Spectrum a	Au	94.9	19.3

Figure S2(a) presents the Kubelka-Munk transformed diffuse reflectance spectra (DRS) of all samples measured using a Shimadzu UV-2600 spectrometer. The major absorption of light was observed in the UV region (WL < 380 nm) that originated from the TiO₂ support. Only the Au/TiO₂ sample showed a considerable light absorption in the 450 – 650 nm wavelength range compared to the rest of the samples, which originated from the Au surface plasmon. The spectra indicate that no visible light absorption ($\lambda > 400$ nm) was observed any other samples except Au/TiO₂.

Figure S2(b) shows the emission spectra of the UV LED (365 nm, Optimax 365) that was used in all photocatalysis experiments. The light source was characterised by a peak emission at 365 nm with a full-width-at-half-maximum (FWHM) of 10 nm, which eliminated the possibility of visible light photoreactivity of the Au/TiO₂ sample (if any) and allowed for direct comparison with the other samples.

The average photon flux of the light source was measured using a standard ferrioxalate actinometry method,¹ as demonstrated in Fig. S3(a)-(c). The photon flux was determined to be $\sim 4 \times 10^{17}$ photons·s⁻¹. Details of the methodology can be found elsewhere^{1,2}.

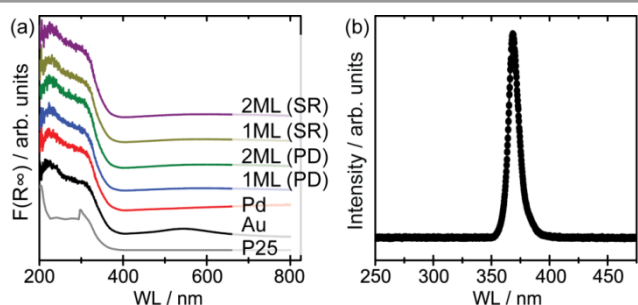


Fig. S2. (a) Kubelka-Munk transformed DRS of all samples. A pristine P25 was also measured for comparison. The spectra were stacked for comparison. (b) Emission spectra of the UV LED light source used for photocatalytic H₂ evolution.

The glass-reactor ($d = 4$ cm) contains 25 mL of $1 \text{ g}\cdot\text{L}^{-1}$ TiO₂ suspension, therefore the depth of the suspension is 2.6 cm. Since the absorption coefficient (α) of bulk TiO₂ at 365 nm is $4.89 \times 10^4 \text{ cm}^{-1}$, α is 11.6 cm^{-1} for the $1 \text{ g}\cdot\text{L}^{-1}$ suspension. Therefore, a full absorption ($> 99\%$) of the light requires a depth of ~ 0.4 cm of the $1 \text{ g}\cdot\text{L}^{-1}$ suspension. Since the TiO₂ suspension scatters the light dramatically, the attenuation coefficients of the suspensions should be larger than the ideal absorption coefficient. By assuming that the number of scattered photons is equal to that of the absorbed photons (attenuation coefficients = 2α), the minimum full absorption length will be ~ 0.2 cm for the $1 \text{ g}\cdot\text{L}^{-1}$ suspension. Thus in all of our photocatalytic reactions, the catalyst suspensions are sufficient to absorb all incident photons.

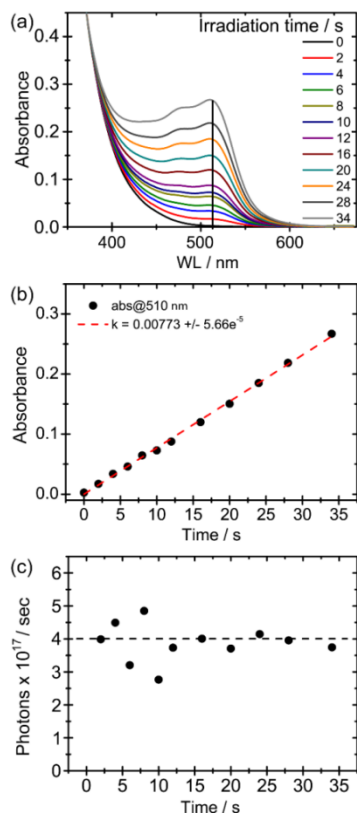


Fig. S3. (a) Ferrioxalate solution absorption spectrum under irradiation; (b) The absorbance of the solution at 510 nm as a function of irradiation time; (c) Photon flux of the light source calculated from ferrioxalate actinometry analysis.²

Figure S4 depicts the O 1s spectra and the deconvolution of all samples. The spectra of all samples can be fitted using three peaks, which correspond to the Ti-O (529.4 eV), H-O (531.5 eV), and C-O (533.2 eV) bonding, respectively. The H-O and C-O peaks may originate from the PVA protecting ligands used during the deposition of Au on TiO₂ via sol-immobilisation, or possibly the consequence of surface adsorbed contamination during sample transportation.

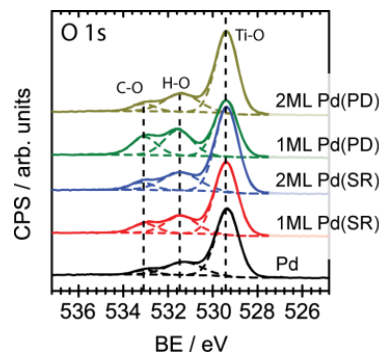


Fig. S4. High resolution XPS spectra of O 1s. The dashed lines are fitting results of the raw data. All catalysts have a metal loading of 1 wt%.

Figure S5 depicts the normalised first derivative of the XANES spectra for the Pd foil as well as the core-shell promoters. XANES spectra of a Pd foil exhibited two peaks in the 1st derivative spectrum, due to 1s to 4d (these are hybridised p and d orbitals with a high degree of d character) and 1s to 5d transitions. For the core-shell samples reported here, the positions of these peaks were shifted upon alloying, however, the centroid position of both features was the same for all samples. This indicates that the Pd in the AuPd NPs was primarily in its metallic form and there was a lack of any significant quantities of PdO in the samples.

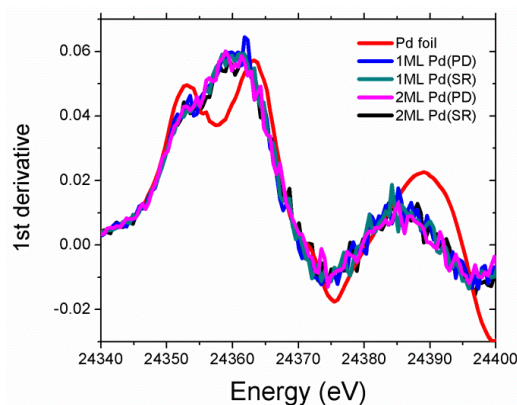


Fig. S5. Normalised first derivative of the XANES spectra.

Figure S6(a-h) depicts the k^2 weighted experimental data and fit for the range of AuPd NPs from the Au and Pd edge. The range extended to $12 \text{ K}\cdot\text{\AA}^{-1}$ to allow sufficient data for an accurate fit shell fit.

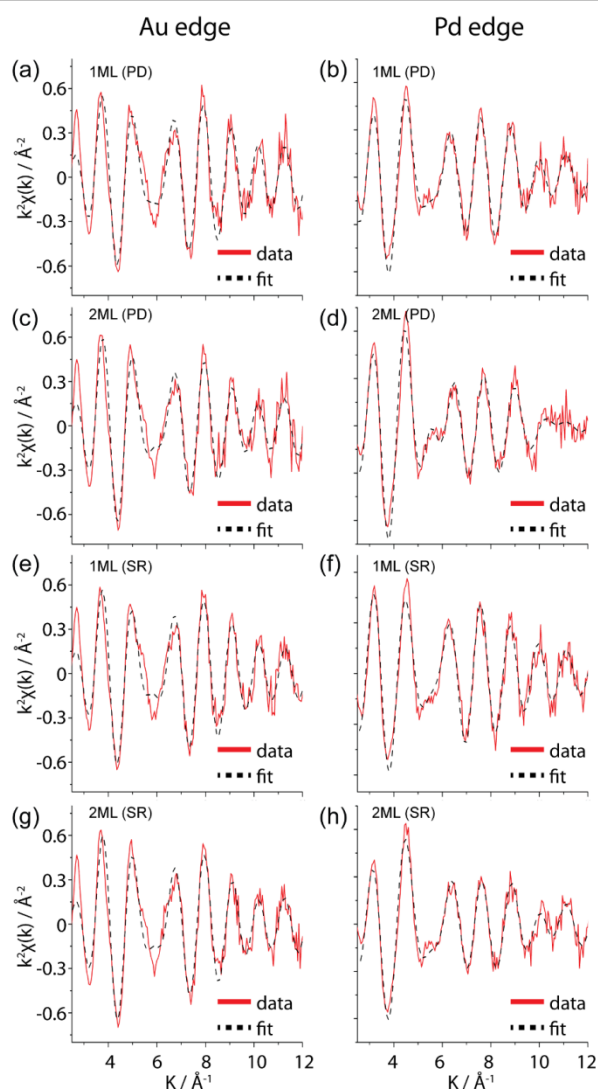


Figure S6(a), (c), (e), and (g): Au edge of k^2 weighted experimental data and fit for 1ML (PD), 2ML (PD), 1ML (SR), and 2ML (SR), respectively. (b), (d), (f), and (h): Pd edge of k^2 weighted experimental data and fit for 1ML (PD), 2ML (PD), 1ML (SR), and 2ML (SR), respectively.

H. H. Jensen, S. Wendt, C. R. A. Catlow, C. J. Kiely, G. J. Hutchings and F. Besenbacher, *ACS Nano*, 2014, 8, 3490-3497.

Notes and references

^a The UK Catalysis Hub, Research Complex at Harwell, Rutherford Appleton Laboratory, Oxfordshire, OX11 0FA, UK

^b Cardiff Catalysis Institute, School of Chemistry, Cardiff University, Cardiff, CF10 3AT, UK Email: Hutch@cardiff.ac.uk

^c Interdisciplinary Nanoscience Center (iNANO) and Department of Physics and Astronomy, Aarhus University, Gustav Wieds Vej 14, DK-8000 Aarhus C, Denmark Email: rensu@inano.au.dk

^d University College London, Kathleen Lonsdale Materials, Department of Chemistry, Gordon Street, London, WC1H 0AJ, UK

^e Department of Chemistry, Aarhus University, Langelandsgade 140, DK-8000 Aarhus C, Denmark

1. H. J. Kuhn, S. E. Braslavsky, R. Schmidt, *Pure Appl. Chem.* 2004, 76, 2105-2146.
2. R. Su, R. Tiruvalam, A. J. Logsdail, Q. He, C. A. Downing, M. T. Jensen, N. Dimitratos, L. Kesavan, P. P. Wells, R. Bechstein,