

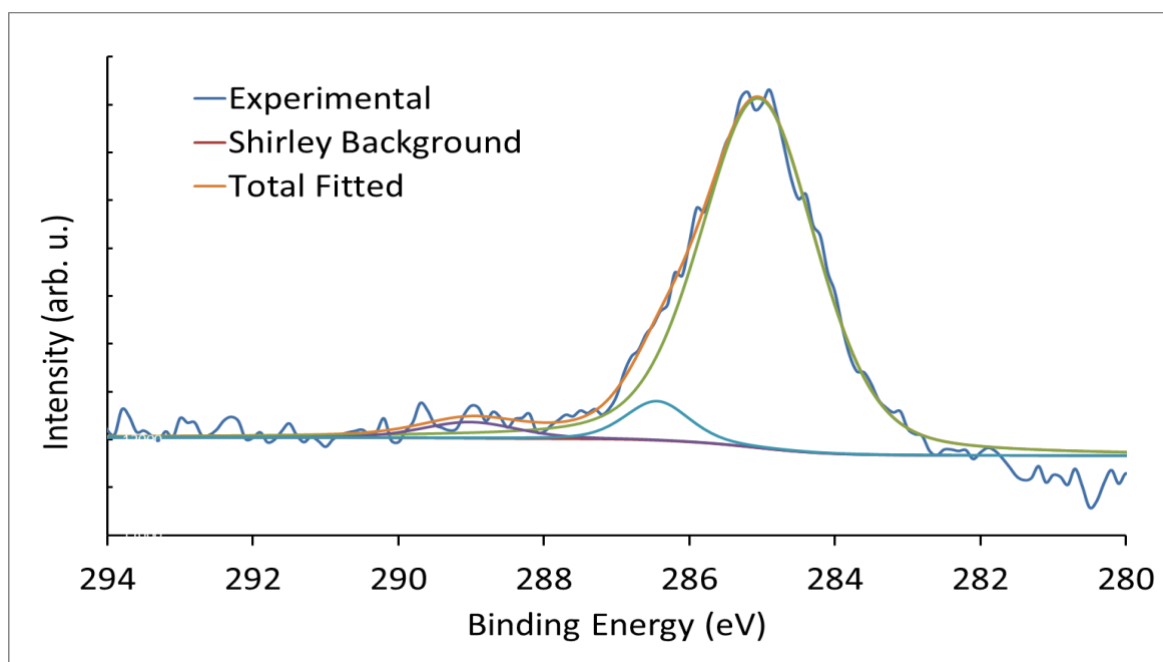
## Chapter 3

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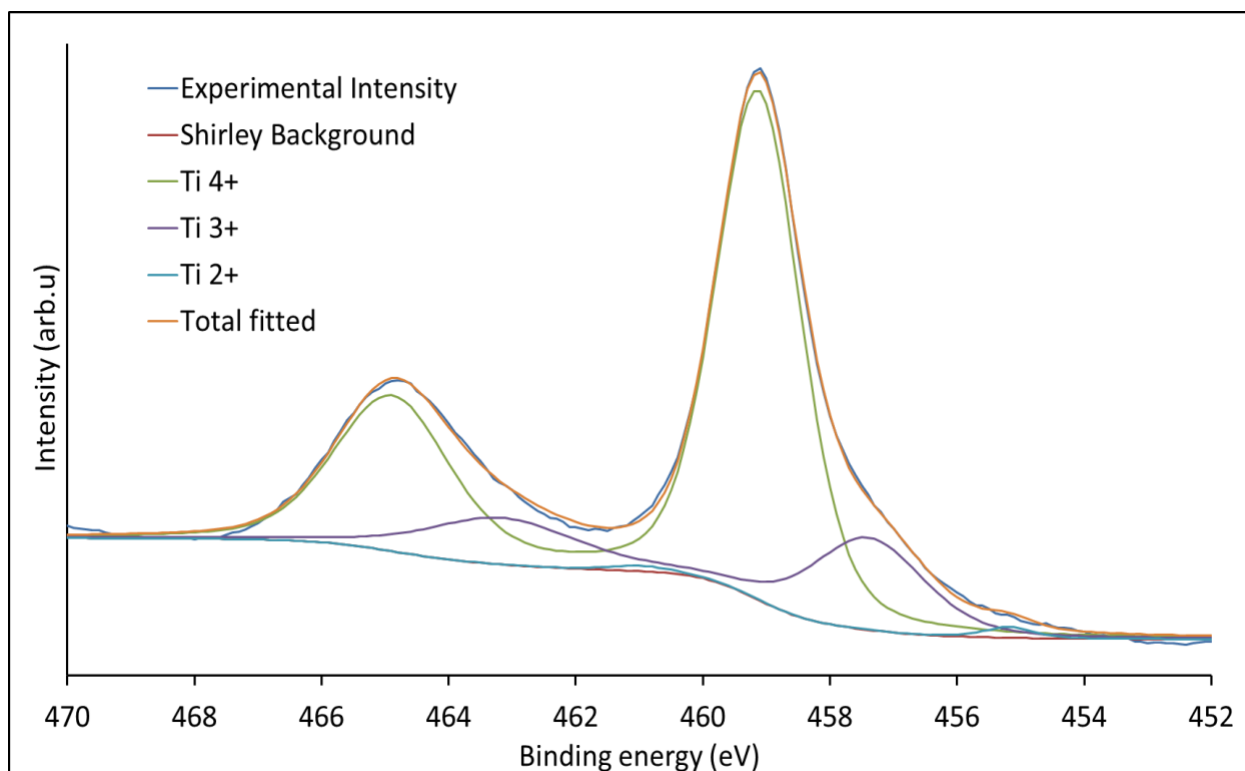
# Investigation of Ligand Stabilized Gold Clusters on Defect Rich Titania

## Supporting Information

Further details XPS data



*Figure S1 The fitting of the XPS C peak with the Shirley background. The peak at binding energy 285eV is used as the calibration for all other XP spectra.*



*Figure S2: Ti XP spectra fitted with the Shirley background and showing the amount of defect sites ( $Ti^{3+}$  and  $Ti^{2+}$ ) after sputtering (exposed to air) and before the gold deposition. The sample was heated and sputtered in the same way as the sample for which Ti 2p XP spectra are shown in Figure 2.*

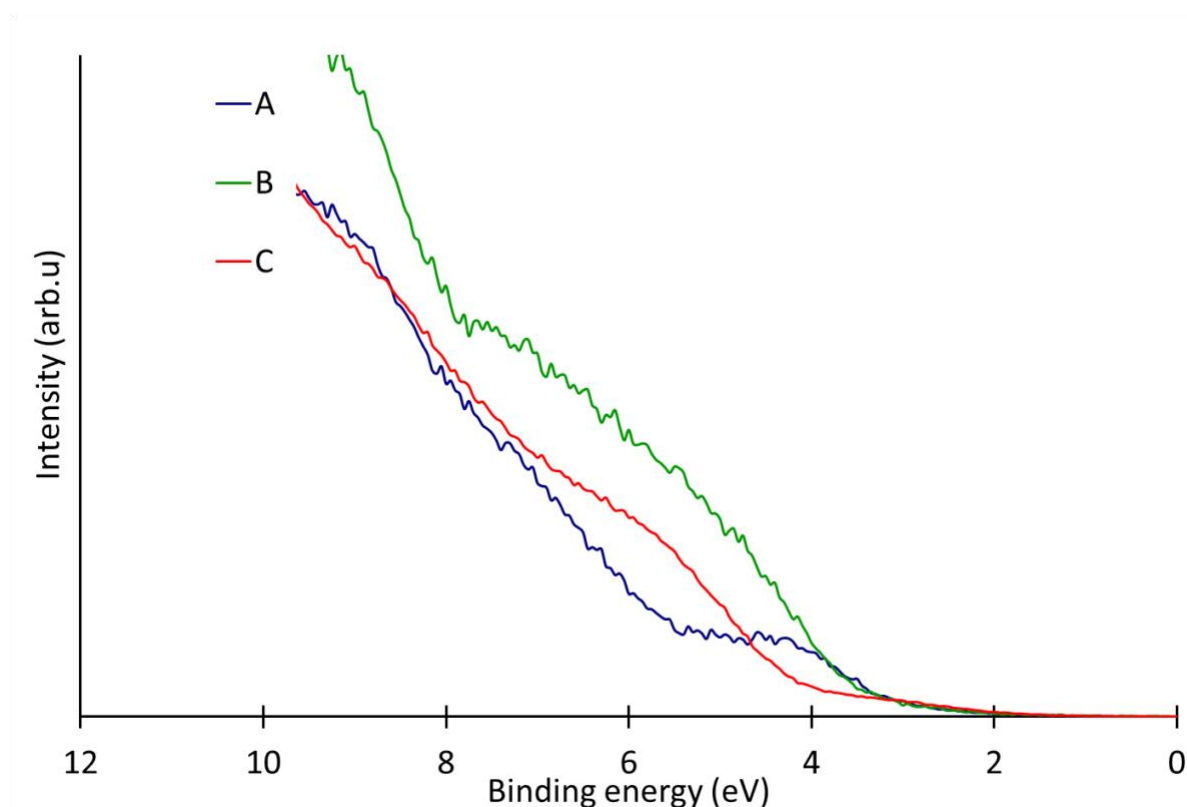
Table S1 Peak position, FWHM and intensity of various concentrations of Au.

Au	After deposition			After heating		
Concentration	Peak position (eV)	FWHM (eV)	Intensity (cps)	Peak position (eV)	FWHM (eV)	Intensity (cps)
0.06	85.4 ± 0.1	1.5 ± 0.1	0.27 ± 0.01	84.7 ± 0.1	1.5 ± 0.1	0.23 ± 0.01
0.03	85.1 ± 0.1	1.5 ± 0.1	0.40 ± 0.02	84.5 ± 0.1	1.4 ± 0.1	0.33 ± 0.01
0.01	85.3 ± 0.1	1.4 ± 0.1	0.14 ± 0.01	84.6 ± 0.1	1.4 ± 0.1	0.11 ± 0.01
0.006	85.4 ± 0.1	1.3 ± 0.1	0.08 ± 0.01	84.8 ± 0.1	1.5 ± 0.1	0.08 ± 0.01
0.003	85.2 ± 0.1	1.2 ± 0.1	0.07 ± 0.01	84.6 ± 0.1	1.3 ± 0.1	0.07 ± 0.01
0.001	85.3 ± 0.1	1.6 ± 0.1	0.09 ± 0.01	84.7 ± 0.1	1.5 ± 0.1	0.08 ± 0.01
0.0006	85.4 ± 0.1	1.2 ± 0.1	0.04 ± 0.01	84.5 ± 0.1	1.3 ± 0.1	0.06 ± 0.01
0.0003	85.3 ± 0.1	1.3 ± 0.1	0.06 ± 0.01	84.6 ± 0.1	1.4 ± 0.1	0.09 ± 0.01
0.0001	85.5 ± 0.1	1.5 ± 0.1	0.01 ± 0.01	85.1 ± 0.3	1.4 ± 0.1	0.01 ± 0.01

Table S2 Peak position, FWHM and intensity of P with various concentrations of Au.

Au	After deposition			After heating		
Concentration	Peak position (eV)	FWHM (eV)	Intensity (cps)	Peak position (eV)	FWHM (eV)	Intensity (cps)
0.06	131.9 ± 0.1	0.8 ± 0.1	0.19 ± 0.01	133.7 ± 0.1	1.1 ± 0.4	0.08 ± 0.01
0.03	131.7 ± 0.1	1.6 ± 0.1	0.47 ± 0.03	134.1 ± 0.1	2.1 ± 0.4	0.15 ± 0.01
0.01	132.1 ± 0.1	1.0 ± 0.1	0.12 ± 0.01	133.5 ± 0.1	1.6 ± 0.4	0.09 ± 0.01
0.006	132.2 ± 0.1	1.1 ± 0.1	0.12 ± 0.01	134 ± 0.1	1.9 ± 0.4	0.09 ± 0.01
0.003	131.9 ± 0.1	1.1 ± 0.1	0.11 ± 0.01	133.7 ± 0.1	1.2 ± 0.4	0.04 ± 0.01
0.001	132.1 ± 0.1	1.3 ± 0.1	0.01 ± 0.01	-	-	-
0.0006	132.5 ± 0.1	1.8 ± 0.1	0.12 ± 0.01	133.4 ± 0.1	1.6 ± 0.4	0.11 ± 0.01
0.0003	131.8 ± 0.1	1.8 ± 0.1	0.11 ± 0.01	132.8 ± 0.1	0.9 ± 0.4	0.06 ± 0.01
0.0001	132.9 ± 0.1	3.0 ± 0.1	0.01 ± 0.01	-	-	-

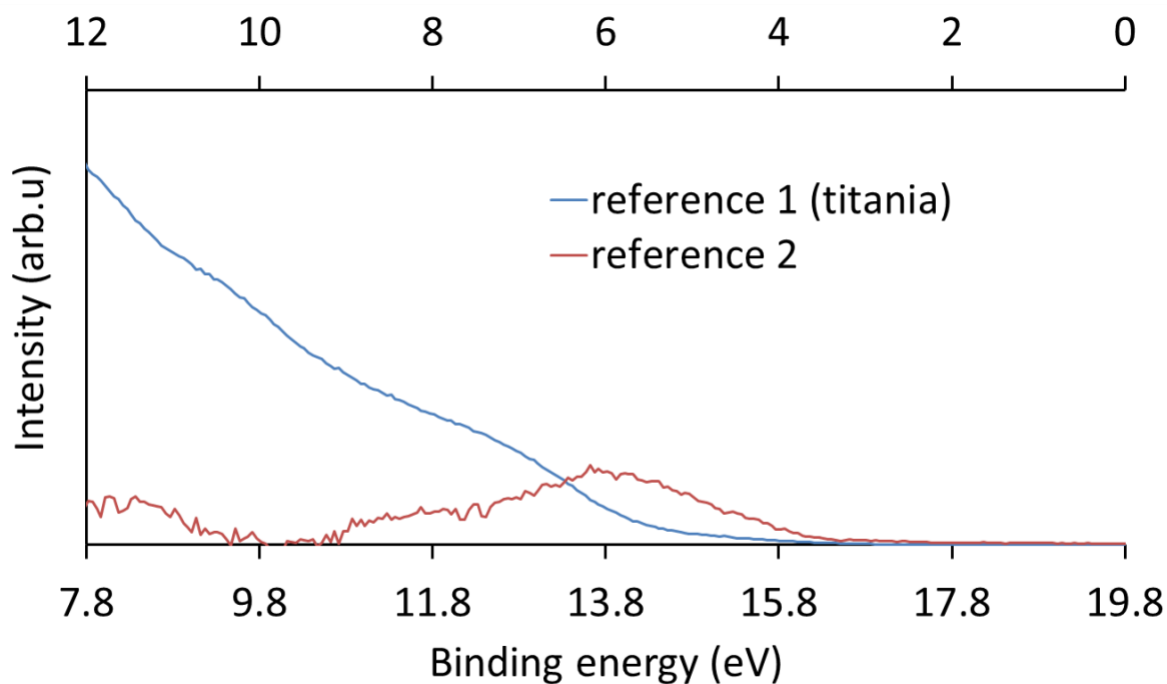
## MIES results with all spectra of the first series of measurements.



*Figure S3: The MIES reference spectrum from the SVD algorithm after post heat treatment with 10 inputs.*

The SVD algorithm procedure resulted in 3 base spectra for MIES with the 10 inputs. The figure shows the three reference spectra from the 10 input samples in which one of them labelled as B seem to be different compared to other ones.

The SVD algorithm for 10 input samples including blank ALD titania results in 3 base spectra. It was found that the 0.06 mM spectrum was different compared to the spectra of the samples with the other Au concentrations. When removing the 0.06 mM sample from the series the SVD analysis results in only 2 reference spectra which are shown in Figure 6b. The 0.06 sample was removed from the series and MIE spectra was taken for the sample with the same concentration plus a few more concentrations. The resulting reference spectra are shown Figure S3 and have the same features but differ slightly in shape from those shown in the main manuscript. The difference is mainly in the shape of the secondary electron background and in the shape of the features with a slight change of position relative to the reference spectrum 2 shown in Figure 6b. The change in shape of the secondary electron background is irrelevant for the interpretation of the spectra.



*Figure S4: The resulting MIES reference spectra with the re-measured samples after post-treatment. The difference is mainly in the shape of the secondary electron background and in the shape of the features.*

Figure S shows the resulting reference spectrum from the SVD algorithm of the re-measured samples. The number of base spectra required to fit the re-measured samples is 2 as a result of SVD algorithm. The procedure for determining the meaningful reference spectra is the same as outlined earlier and results in two reference spectra. The pre-treated blank ALD titania is considered as one of the reference spectra. The second reference spectra resulted in the same features which has same density of states at lower binding energies except they differ from the secondary electron contribution. The second reference spectra shown in Figure S4 sets on around 3.5 eV and has prominent features at binding energies 6 eV, 8.7 eV and 11 eV.

## UPS results

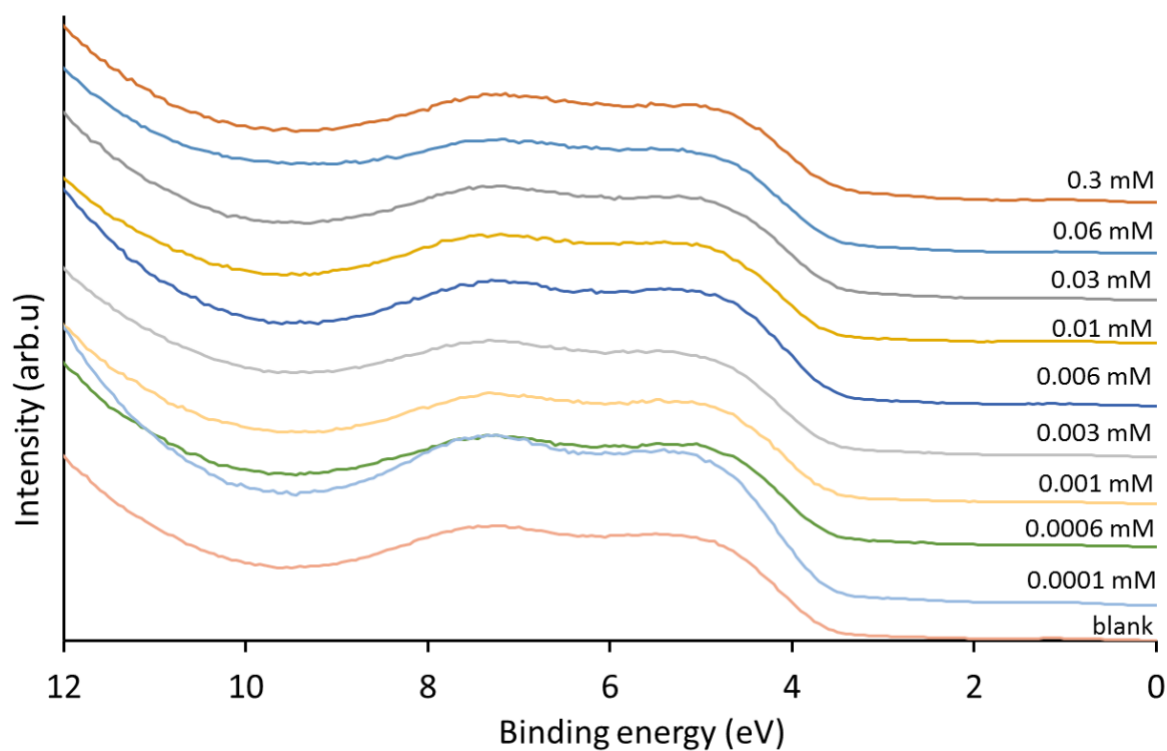


Figure S5: UPS spectra of various Au concentrations after heating.

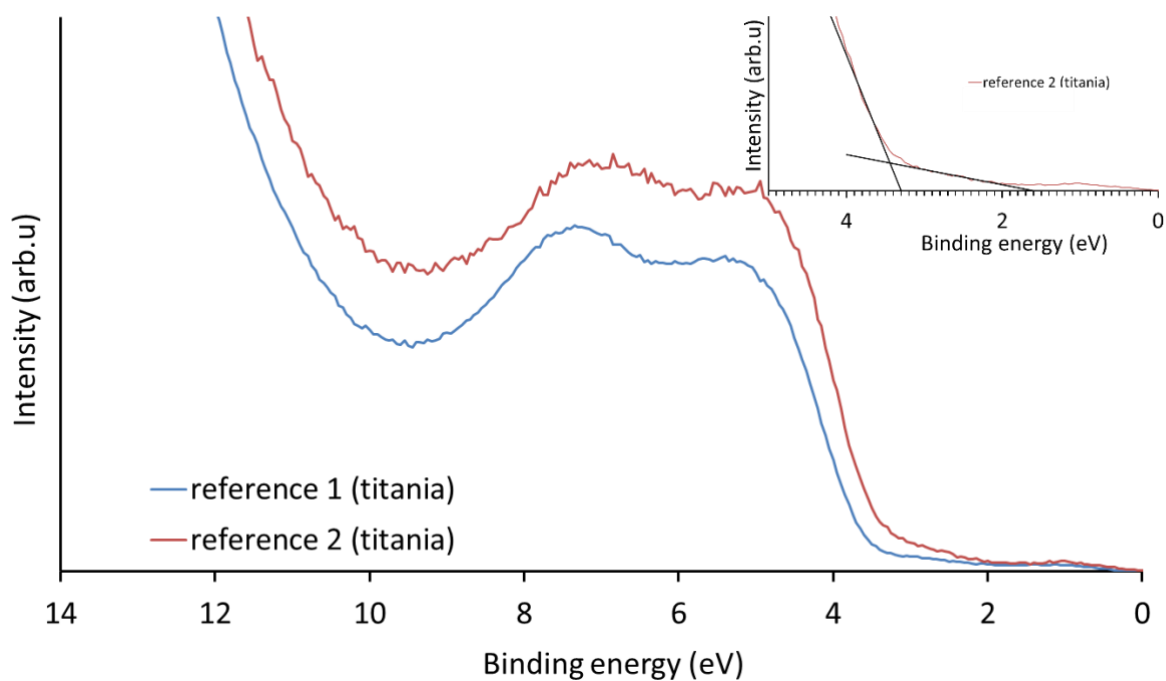
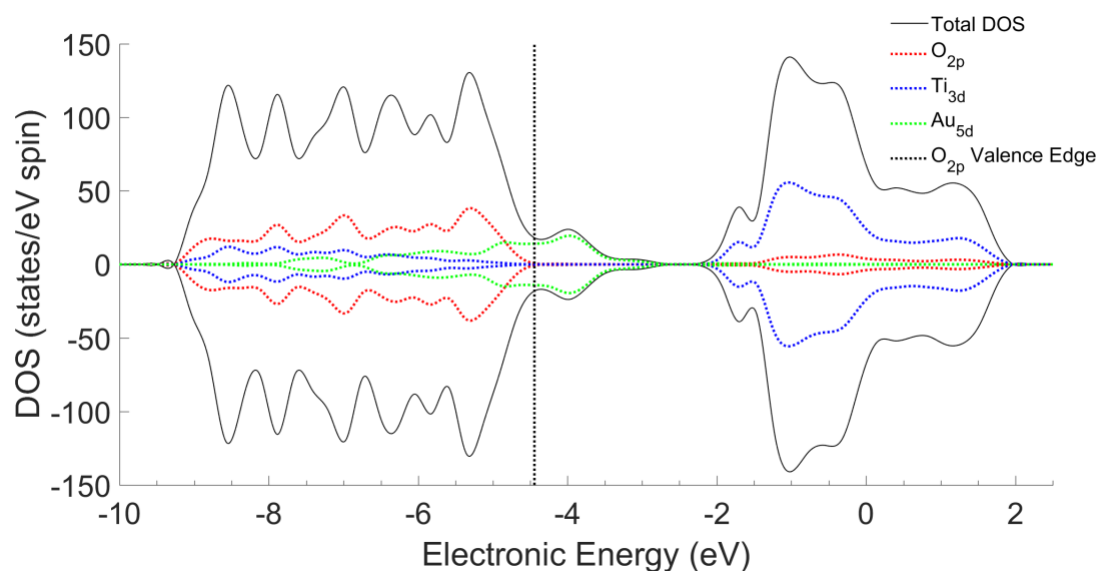


Figure S6: UPS reference spectra after heating from SVD algorithm. The inset displays an enlargement of the binding energy between 0 – 5 eV and showing an extrapolation yielding the position of the valence band edge at 3.4 eV.

## Results DFT calculations

The SVD algorithm from UPS results in two reference spectra. The first and second reference spectrum from UPS represents the titania shifted relative to each other. The reason is unclear but potentially the spectra could represent two different crystal faces. The feature at binding energy 1.1 eV represent the  $\text{Ti}^{3+}$  states. The density of states at 4.5 – 7.5 eV result from the O 2p contribution. Note that no features from Au or P are detected because of their very small concentrations which are only on the surface (unlike MIES, which is surface sensitive). The work function calculation was done for all concentrations of Au, which results in the range of 4.5 – 4.6 eV. The valence band cut-off is found by approximating the spectra around the valence band cut-off with straight lines and is estimated to be at  $3.4 \pm 0.1$  eV.



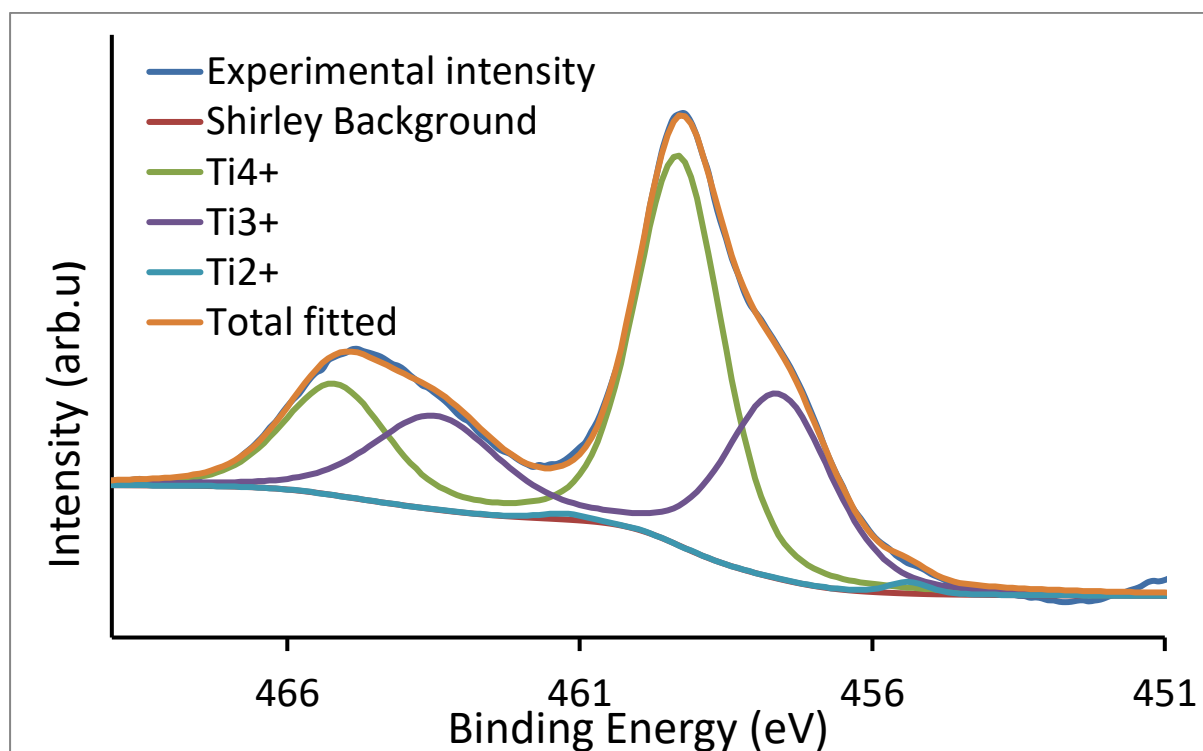
*Figure S8: Plot of the O 2p and Ti 3d LPDOS, as well as the total DOS (i.e. bulk), calculated for the optimized Au<sub>9</sub>/TiO<sub>2</sub> (101) structure. The dotted vertical line indicates the onset of the O 2p valence edge. The Fermi level is not shown but is calculated to be at  $-2.15$  eV.*



## Chapter 4

# Investigation of Phosphine ligand protected Gold [Au<sub>13</sub>(PPh<sub>3</sub>)<sub>8</sub>(NO<sub>3</sub>)<sub>3</sub>] on defect rich ALD titania using electron spectroscopies

## Supporting Information



*Figure S1: Peak position of titania defect sites (Ti<sup>3+</sup> and Ti<sup>2+</sup>) found after heating and subsequent sputtering.*

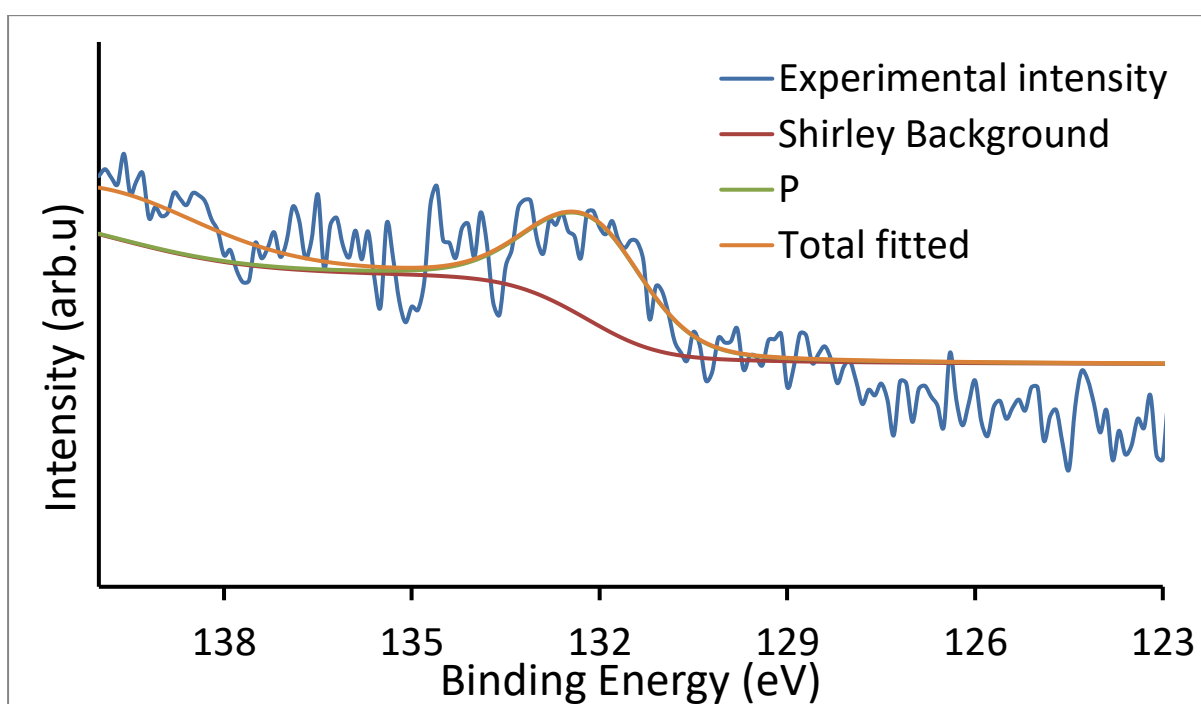
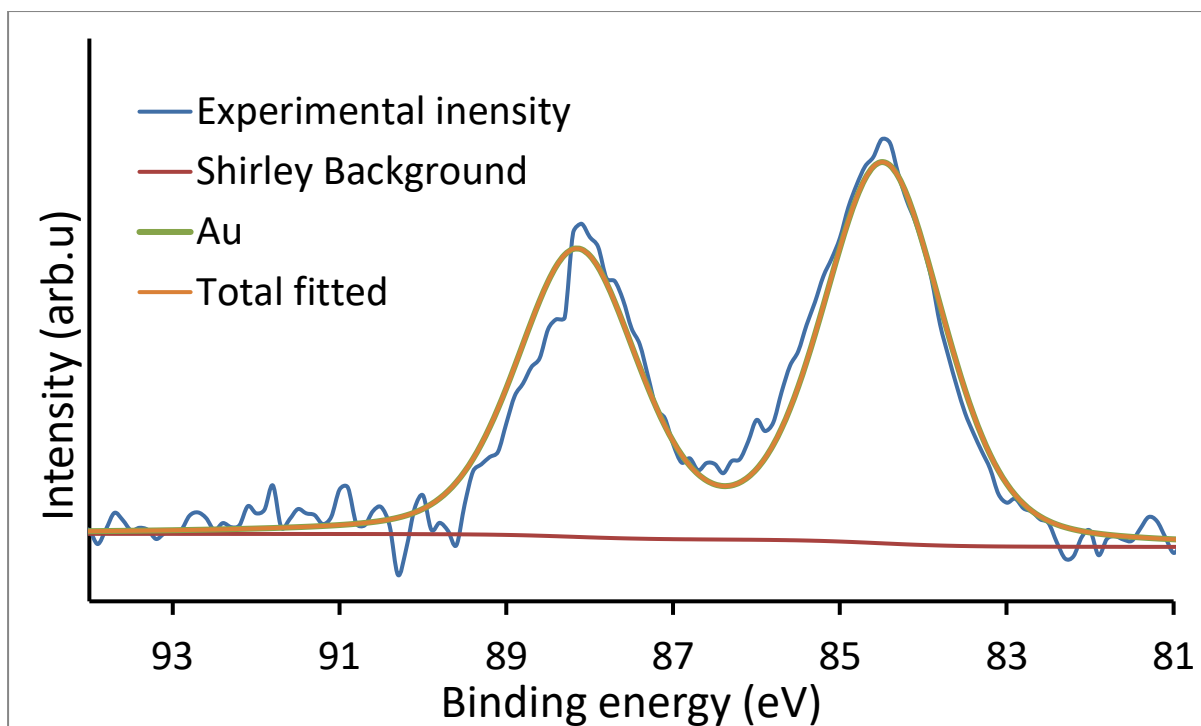
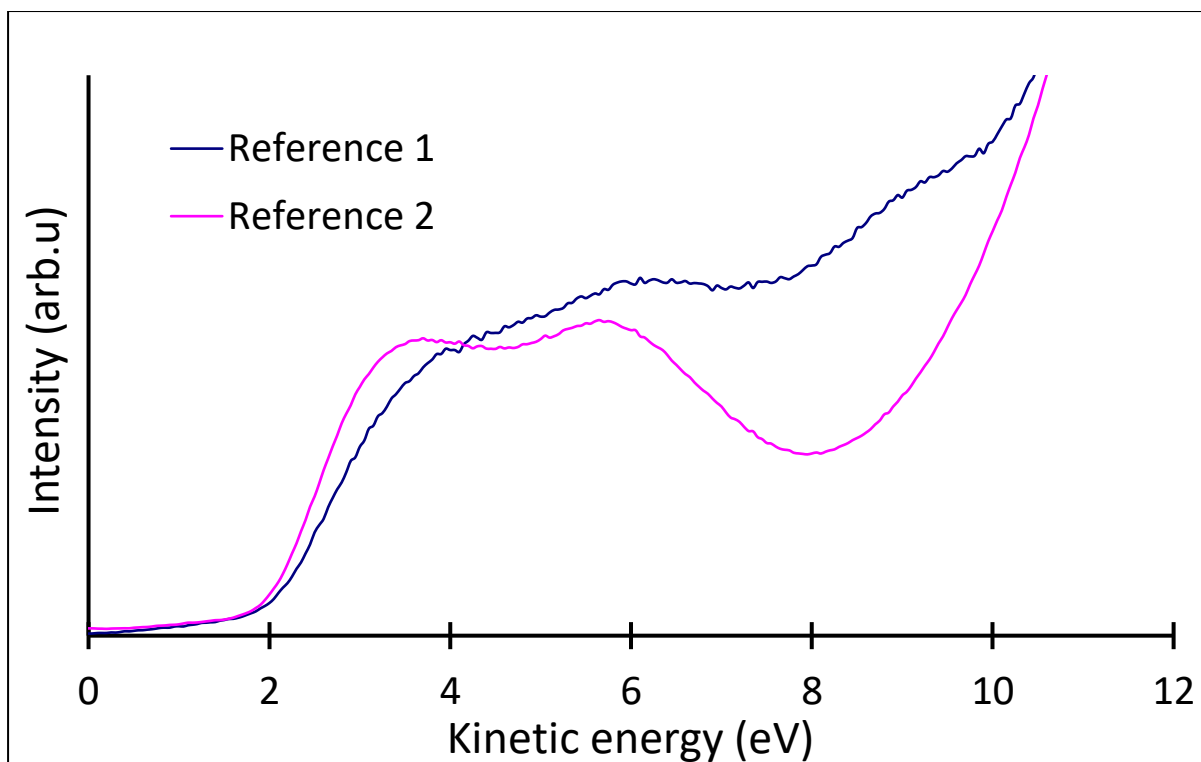


Figure S2: XPS peak fitting with the Shirley background after post heat treatment for a) gold peak (0.06mM) b) phosphorous peak (0.06mM).



*Figure S3: UPS reference spectra as a result of SVD algorithm.*