

SUPPORTING INFORMATION FOR:

Structure and Reactivity of a Model Oxide Supported Silver Nanocluster Catalyst Studied by Near Ambient Pressure X-ray Photoelectron Spectroscopy

Michael Wagstaffe,[†] Hadeel Hussain,^{‡@} Matthew Acres,[‡] Rosemary Jones,[§] Karen

L. Syres,^{*¶} and Andrew G. Thomas^{*‡§}

[†] School of Physics and Astronomy, The University of Manchester, Oxford Road, M13 9PL, UK.

[‡] School of Materials, The Mill, The University of Manchester, Sackville Street, Manchester, M13 9PL, UK.

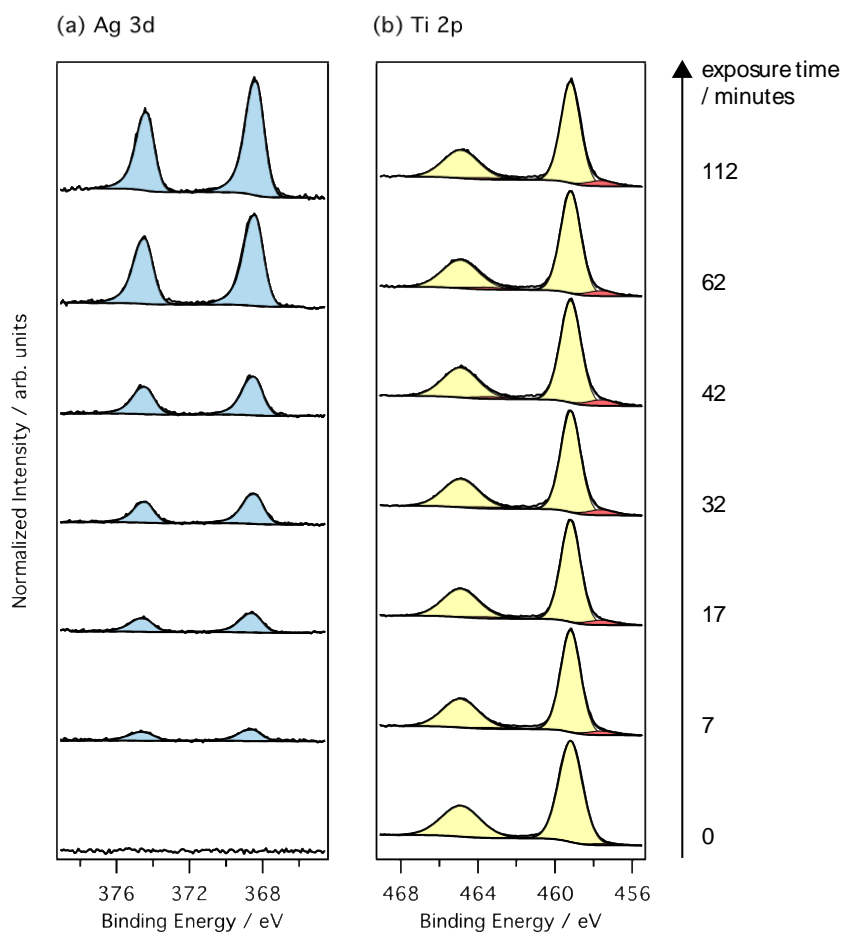
[§] Photon Science Institute, The University of Manchester, Oxford Road, Manchester, M13 9PL, UK .

[¶] Jeremiah Horrocks Institute, The University of Central Lancashire, Fylde Road, Preston, PR1 2HE, UK.

@Current address: Diamond Light Source, Harwell Science and Innovation Campus, Didcot, Oxfordshire, OX11 0DE, UK.

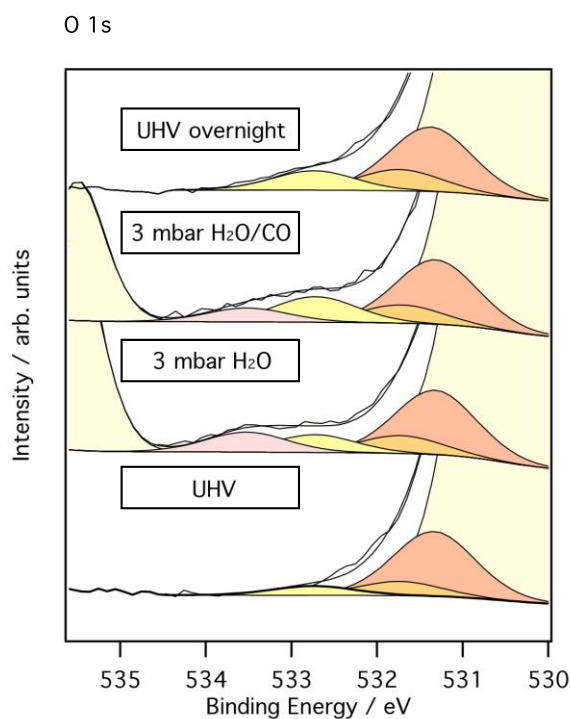
E-mail: andrew.g.thomas@manchester.ac.uk

Figure S1. Core level photoelectron spectra for (a) Ag 3d and (b) Ti 2p



Complete set of Ag 3d XPS core-level spectra (a) with the corresponding Ti 2p core-level spectra (b) ($h\nu = 1$ keV) showing, from bottom to top, an increasing Ag coverage. The spectra are normalized to the intensity of the Ti 2p $\text{Ti}^{4+}_{3/2}$ peak at 459.2 eV.

Figure S2. Enlarged Core level NAP-XPS spectra for O 1s showing components due to H₂O and CO exposure in more detail.



O 1s core- level NAP-XPS spectra recorded at UHV, under exposure to 3 mbar H₂O, under exposure to 3mbar H₂O/CO and at UHV the following day. The O 1s spectra highlight the high binding energy shoulder shown in Figure 4 of the main manuscript for clarity.

The assignment of the fitted peaks for the O 1s, Ti 2p and Ag 3d is given below in Table S1. The gas phase O 1s peaks are not included in the table. These occur at 535.5 eV (H₂O) and 538.2 eV (CO).

Table S1. Binding energy and assignment of Ti 2p, O 1s and Ag 3d XPS core-level peaks.

		UHV		3 mbar H ₂ O		3 mbar H ₂ O/CO		UHV-next day	
Species	Assignment	BE / eV ± 0.1 eV	% ±1%	BE \ eV ± 0.1 eV	% ±1 %	BE / eV ± 0.1 eV	% ±1 %	BE \ eV ± 0.1 eV	% ±1 %
Ti 2p _{3/2}	Ti ³⁺	457.7	7.3	457.7	6.3	457.7	6.7	457.7	5.2
	Ti ⁴⁺	459.2	92.7	459.2	93.7	459.2	93.3	459.2	94.8
O 1s	TiO ₂	530.4	88.0	530.4	84.3	530.4	84.1	530.4	86.2
	O _{intrinsic} ¹	531.4	8.8	531.3	8.4	531.3	8.4	531.3	8.6
	O _{defect} /OH _{ads}	531.8	1.9	531.7	2.3	531.7	2.4	531.7	2.6
	O _{defect} /CO _{ads} /OH _{ads}	532.7	1.2	532.7	2.0	532.7	3.3	532.7	2.1
	H ₂ O	-	0	533.5	2.6	533.5	1.8	-	0
Ag 3d _{5/2}	Ag ^{δ+} /Ag(III)	-	0	-	-	367.6	5.5	367.6	0
	Ag(0)	368.4	100	368.4	100	368.4	89.0	368.4	100
	Ag(III) _{satellite}	-	0	-	0	371.4	5.5	371.4	0

- (1) Jackman, M. J.; Thomas, A. G.; Murny, C. Photoelectron Spectroscopy Study of Stoichiometric and Reduced Anatase TiO₂(101) Surfaces: The Effect of Subsurface Defects on Water Adsorption at Near-Ambient Pressures. *J. Phys. Chem. C* **2015**, *119*, 13682–13690.