Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.

Electronic Supporting Information

Demonstration of thermally assisted diffusion in aged organic solar cells by a combination of electronic and mechanical characterisation techniques

by

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Table S1: Initial device parameter values (PCE, J_{SC}, V_{OC}, and FF) for the inverted PCDTBT:$PC_{71}BM$ OPV devices. Uncertainties represent one standard deviation across 12 devices.

HTL/Metal	PCE	J_{SC} (mA cm^{-2})	V_{OC} (mV)	Fill factor
MoO_3/Al	5.16±0.13%	10.34±0.14	0.889±0.005	0.56±0.01
MoO_3/Ag	5.02±0.09%	9.70±0.17	0.890±0.004	0.58±0.01

Table S2: The optimised device parameter values (PCE, J_{SC}, V_{OC}, and FF) for OPV devices fabricated in Greenbank, et al., Appl. Phys. Lett.*, 2015, **107**, 263301. Note that the samples containing WO_3 HTLs required one hour of thermal annealing (1h at 85°C) in order to reach optimal performance. Uncertainties represent one standard deviation across 16 devices.*

HTL/Metal	PCE	J_{SC} (mA cm^{-2})	V_{OC} (mV)	Fill factor	*J_{SC} extracted from EQE* (mA cm^{-2})
MoO_3/Al	3.21±0.13%	11.77±0.45	0. 504±0.006	0.54±0.01	**10.1**
WO_3/Al	3.54±0.09%	10.43±0.33	0.530±0.005	0.64±0.01	**9.1**
MoO_3/Ag	3.18±0.14%	11.62±0.41	0.509±0.004	0.54±0.01	**10.4**
WO_3/Ag	3.32±0.11%	10.40±0.37	0.534±0.005	0.60±0.01	**9.0**

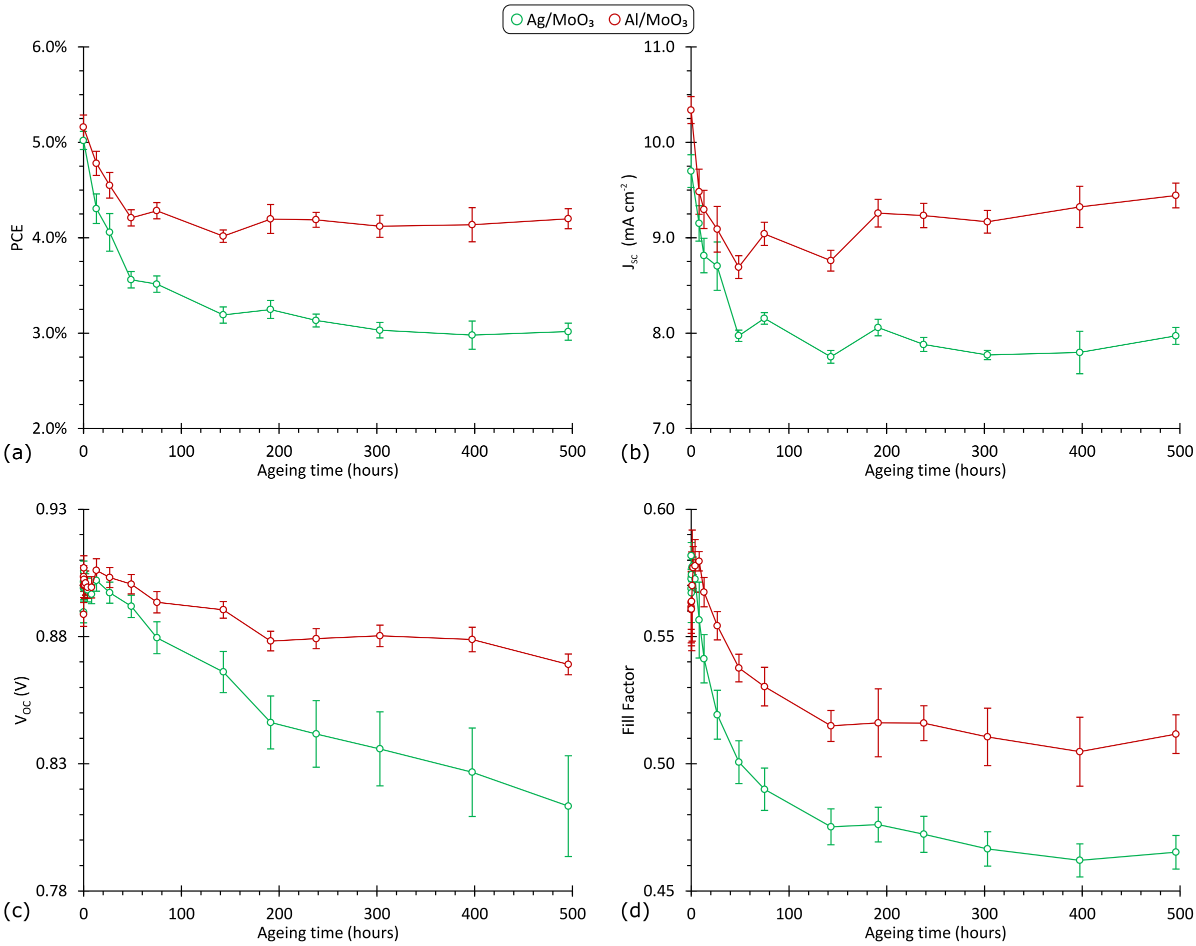

Figure S1: The evolution of the PCE (a), J_{SC} (b), the V_{OC} (c), and the fill factor (d) of the PCDTBT:PC_{71}BM inverted OPV devices with thermal ageing in the dark in an inert atmosphere. The devices have MoO_3 HTLs and either aluminium or silver top electrodes. The uncertainties represent one standard deviation when averaged across 12 devices.

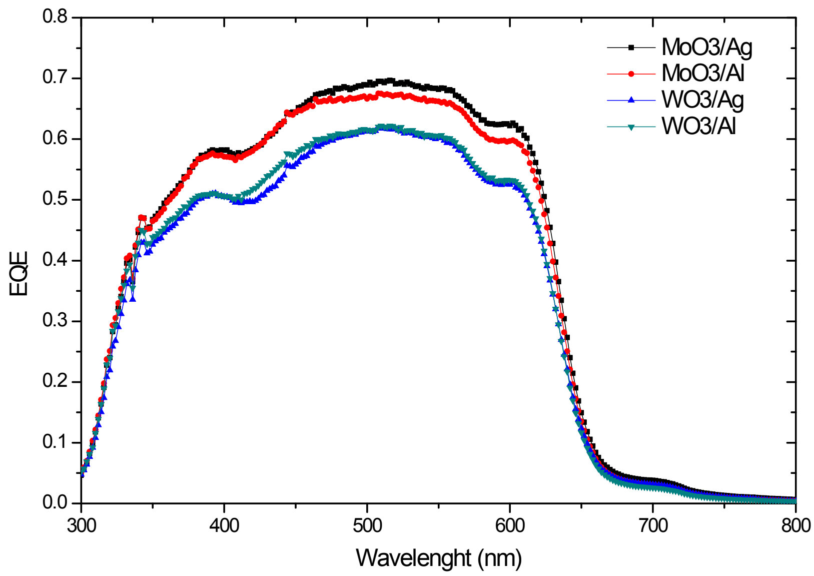

Figure S2: EQE spectra of P3HT:PCBM organic solar cells with different combination of top electrode (MoO_3/Ag, MoO_3/Al, WO_3/Ag and WO_3/Al).

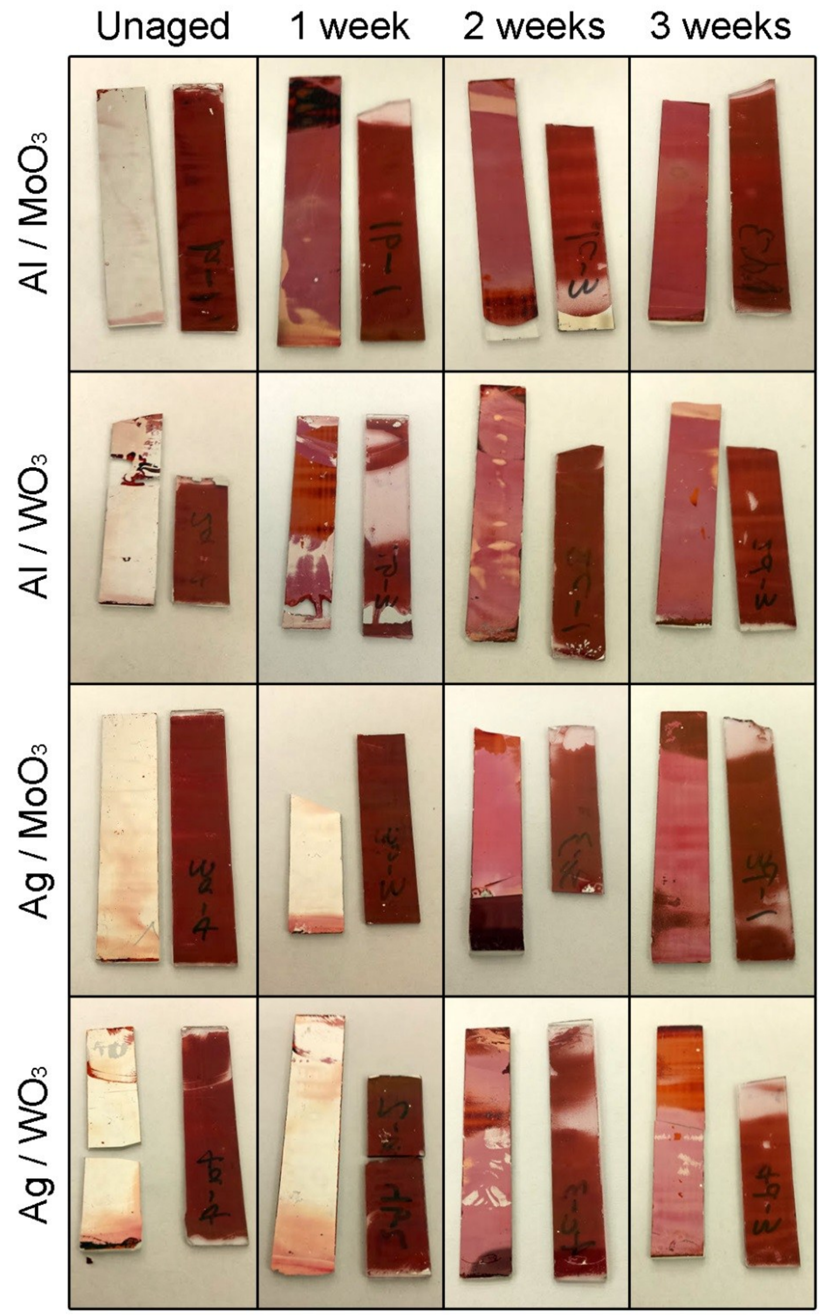

Figure S3: Photographs of fractured samples from each top electrode/HTL material combination that have been thermally aged for between 0 and 3 weeks at 85°C in the dark under an inert atmosphere. In each image, the "metal side" fractured half is shown on the left, and the "ZnO side" half on the right. A sample that fractures in the BHJ exhibits purple colouration of both halves, while those that fracture at the HTL/BHJ interface only exhibit purple colouration on the ZnO side.

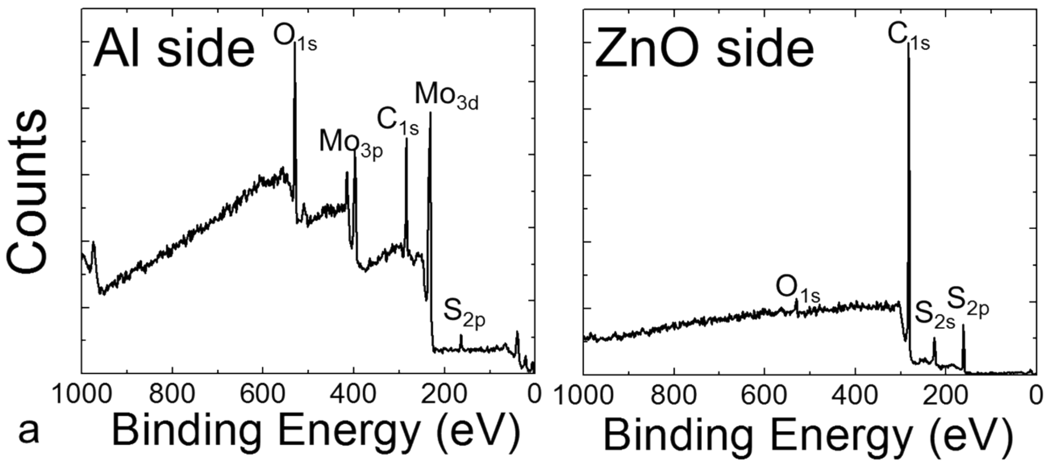

Figure S4: The XPS survey scans measured from the fractured unaged Al/MoO_3 sample. The metal side is shown on the left and the ZnO side on the right.

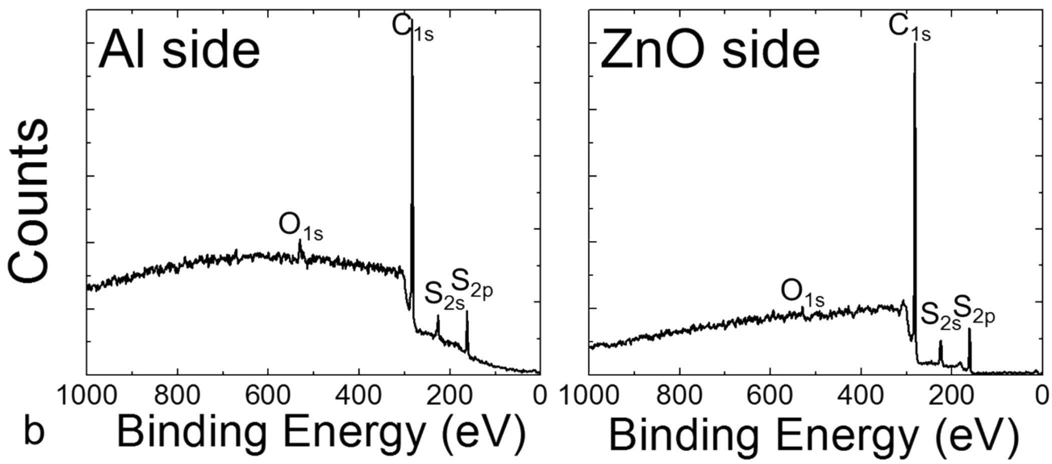

Figure S5: The XPS survey scans measured from the fractured unaged Al/WO_3 sample. The metal side is shown on the left and the ZnO side on the right.

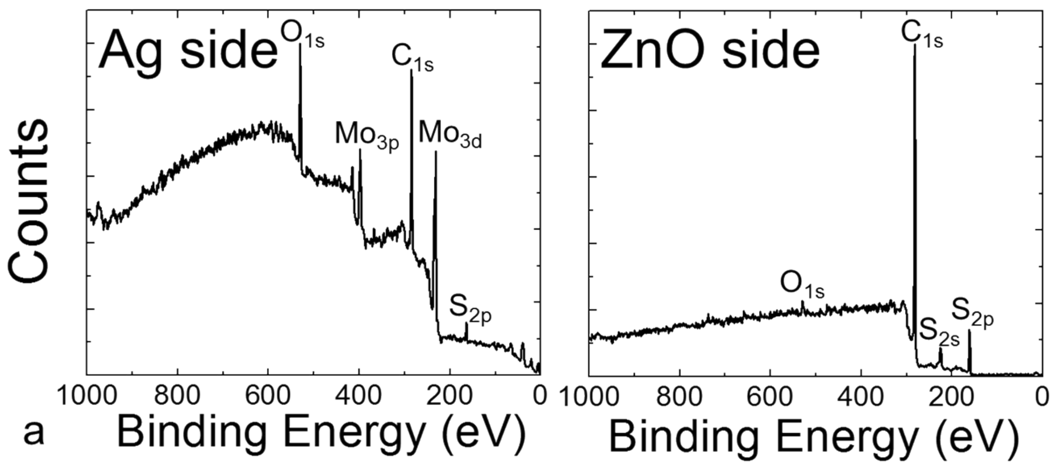

Figure S6: The XPS survey scans measured from the fractured unaged Ag/MoO_3 sample. The metal side is shown on the left and the ZnO side on the right.

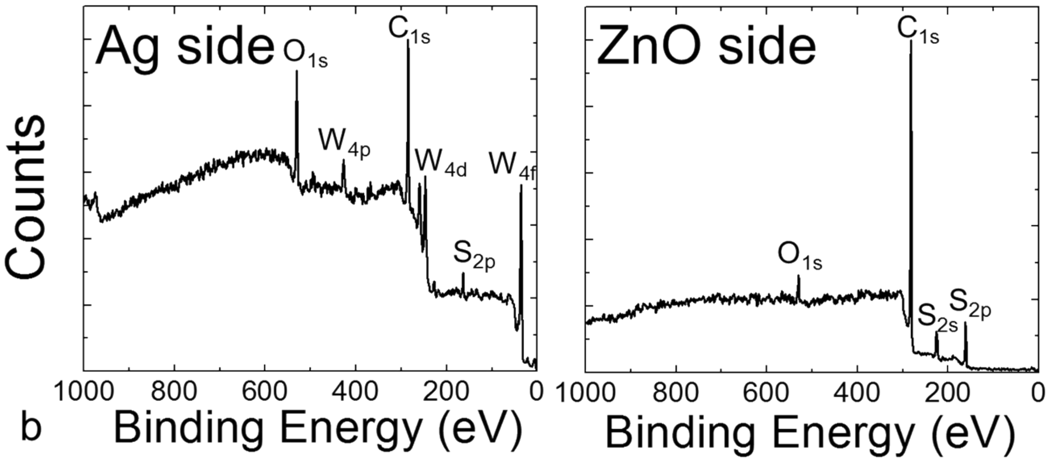

Figure S7: The XPS survey scans measured from the fractured unaged Ag/WO_3 sample. The metal side is shown on the left and the ZnO side on the right.

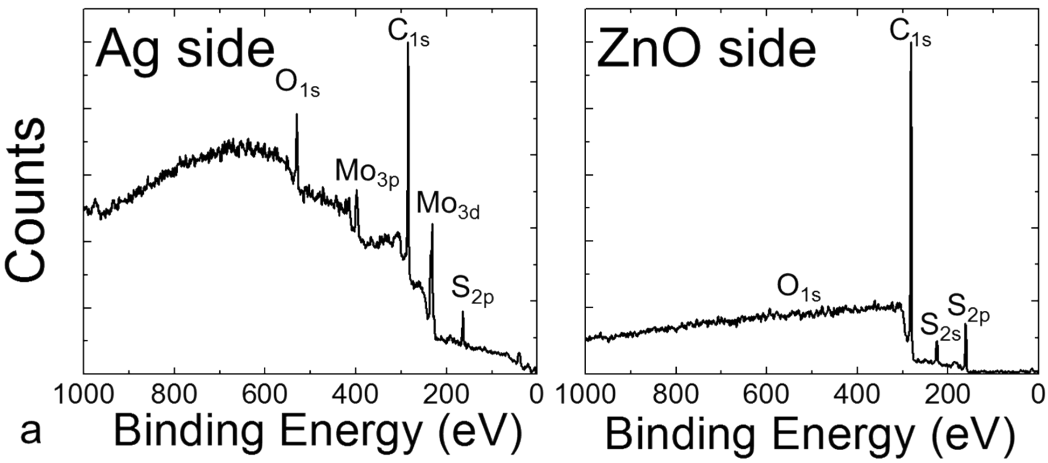

Figure S8: The XPS survey scans measured from the fractured Ag/MoO_3 sample that was aged one week. The metal side is shown on the left and the ZnO side on the right.

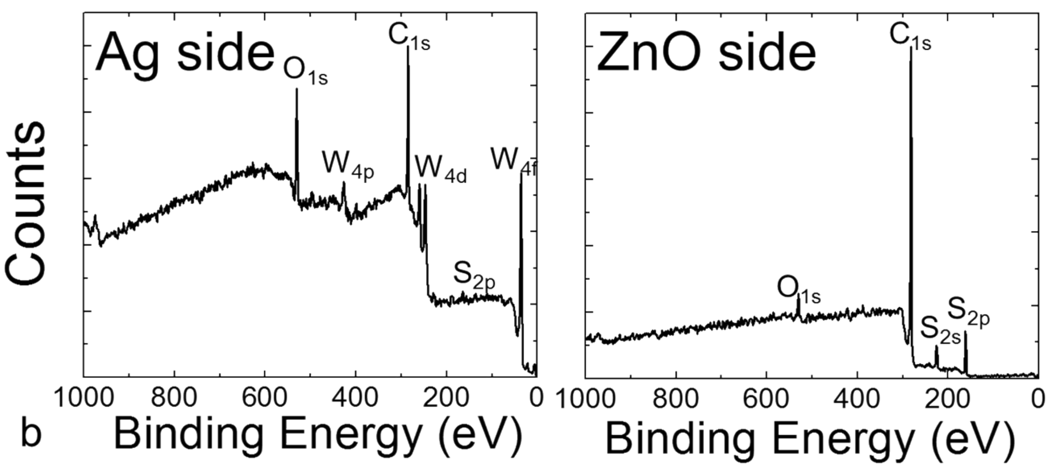

Figure S9: The XPS survey scans measured from the fractured Ag/WO_3 sample that was aged one week. The metal side is shown on the left and the ZnO side on the right.

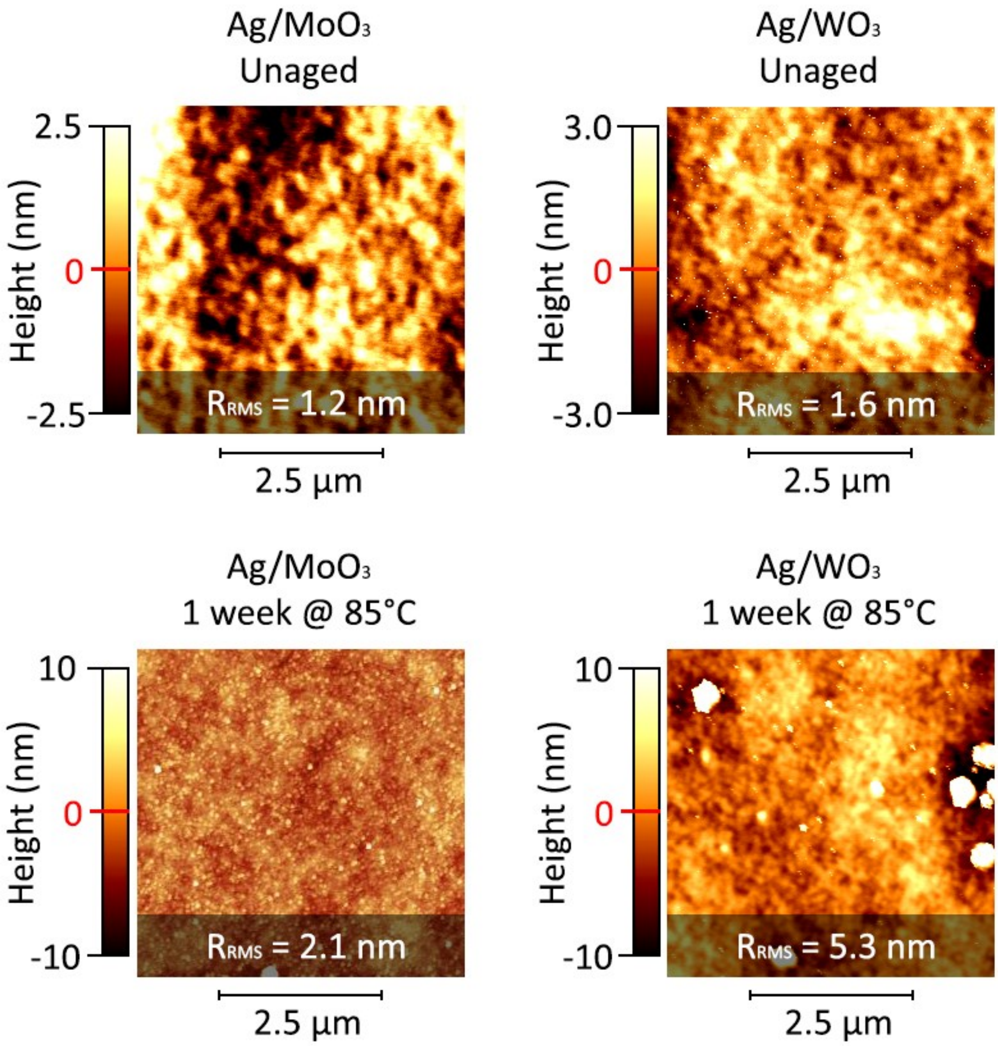

Figure S10: AFM topography data obtained from the fractured silver-containing samples that underwent XPS depth profiling. The RMS roughness (R_{RMS}) values are superimposed on the micrographs, indicating only minor changes in roughness occur with thermal ageing.