Oxygen Vacancies Engineering of Iron Oxides Films for Solar Water Splitting

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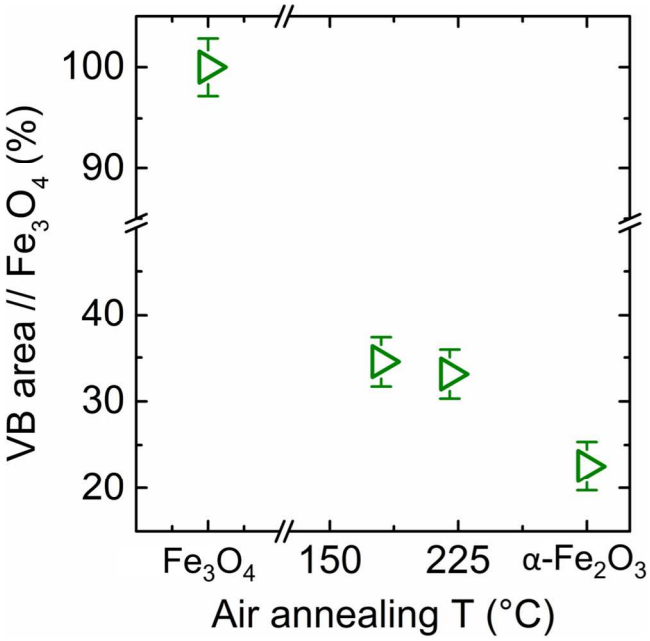

Figure S1: Area of the valence band region in the [-2; 1.65] eV binding energy range, with respect to the value for an as-grown Fe_3O_4 film, for air-annealed Fe_3O_4 films (as-grown Fe_3O_4, 180-air and 220-air samples) and a reference α-Fe_2O_3 film.

The bottom limit of the binding energy range was taken at -2 eV because the photoemission signal for the Fe_3O_4 film vanishes below this value (*cf.* figure 3.b). The upper limit of the binding energy range (1.65 eV) corresponds to the inflexion point of the valence band cut-off for the α-Fe_2O_3 film and the 180-air and 220-air samples. In the end, the integration window is close to the one of the grey area highlighted on figure 3.b.

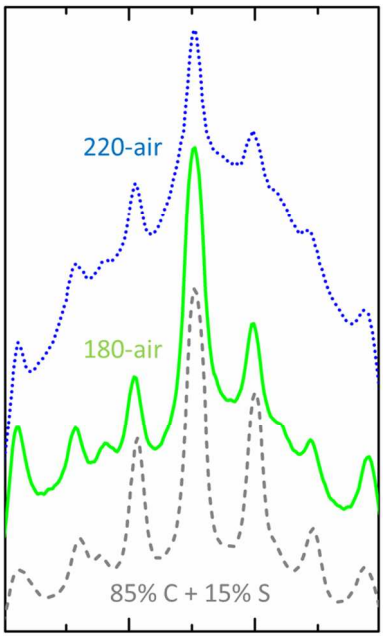

Figure S2: Comparison of the profiles obtained by integrating the RHEED patterns along the streak direction using the integration box highlighted with red dashes on figure 2.a bottom. From bottom to top: linear combination of the profiles for a reference α-Fe_2O_3 (85%) and Fe_3O_4 (15%) films (grey dashed line, C stands for corundum and S for spinel), 180-air (green solid line) and 220-air (blue dotted line) samples.

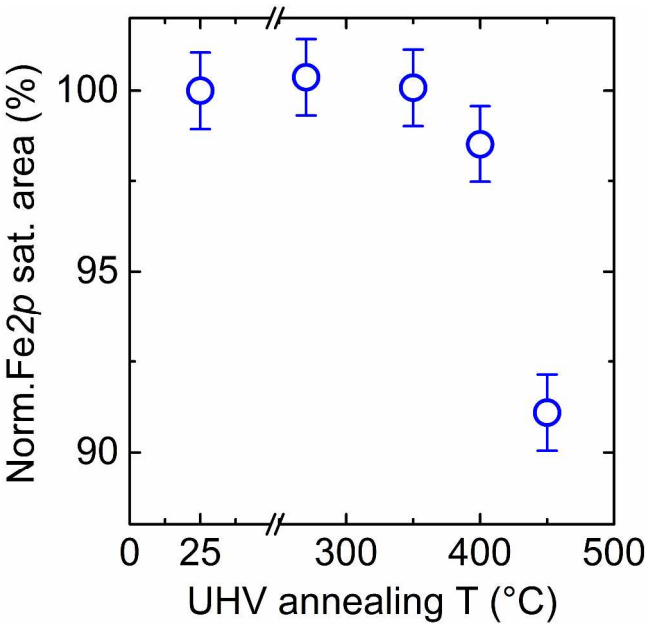

Figure S3. Fe$2p_{3/2}$ satellite area (normalized to the value for pure α-Fe_2O_3) as a function of the UHV annealing temperature for vac-annealed samples.

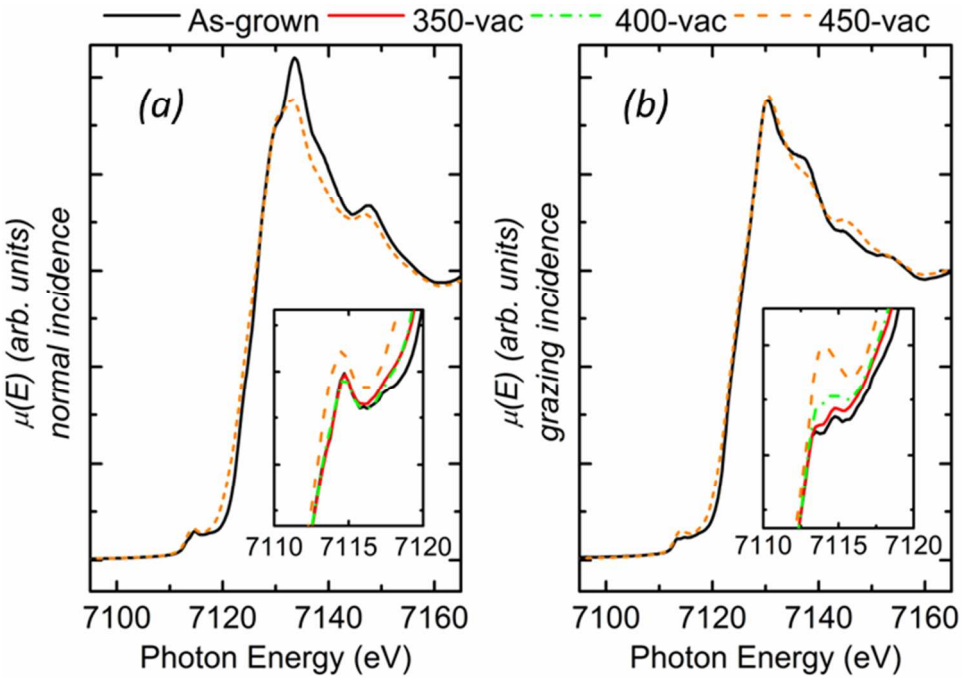

Figure S4: *In situ* experimental XANES spectra in (a) normal and (b) grazing incidences for 15 nm thick as-grown (black solid line) and 450-vac (orange dashed line) hematite films. Insets show a zoom of the pre-edge region where the data for the 350-vac (green solid line) and 400-vac (blue dash-dotted line) samples were added. The data for the 270-vac sample are not shown for the sake of clarity and because their relevance for this figure was limited.

Firstly, the overall XANES shapes are different, meaning that a 450°C annealing in UHV modifies the iron oxide structure and the overall iron valence state. Indeed the spectra recorded in normal and grazing incidences are very different for the as-grown sample, accounting for a strong anisotropic structure (expected for hematite), whereas for the 450-vac sample differences are lighter, accounting for a less anisotropic structure with respect to the as-grown structure. Secondly, we can see a slight shift of the XANES spectra toward lower photons energies for the 450-vac sample with respect to the as-grown one, meaning that the valence state of iron is not

only Fe^{3+}, but a mix of Fe^{2+} and Fe^{3+}, [S1] which is consistent with the XPS observations. On the pre-edge region, the data recorded in normal incidence are almost equivalent for all samples (except for the 450-vac sample), whereas in grazing incidence, significant changes are seen for the 400-vac and 450-vac sample, accounting for iron reduction in these samples with respect to the as-grown sample[S1]. The 270-vac samples featured shapes similar to the as-grown sample.

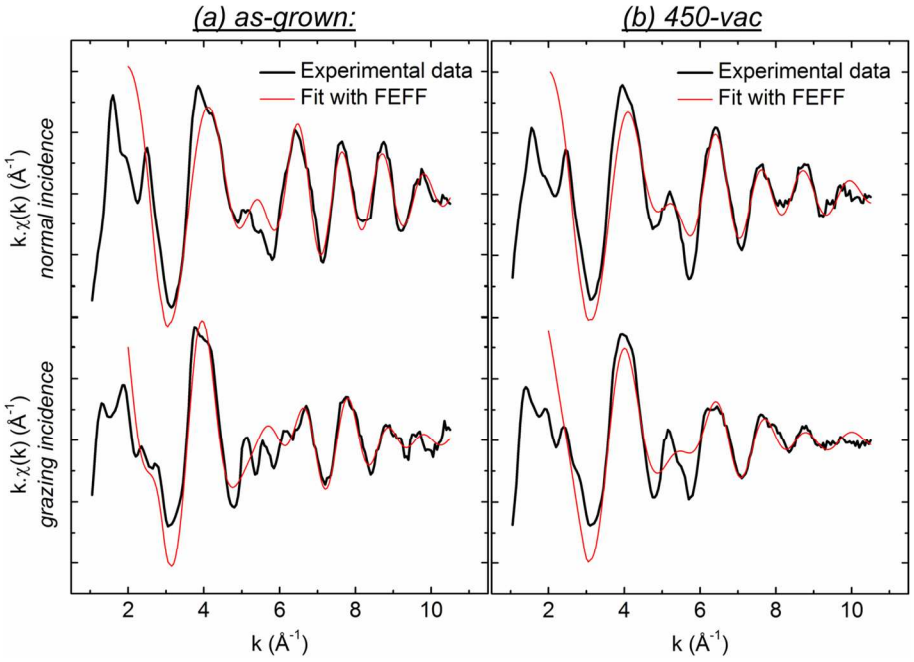

Figure S5: Experimental (black thick line) kχ(k) EXAFS oscillations and fit (red thin line) by FEFF calculations (assuming a corundum structure) obtained in normal (upper curves) and grazing (lower curves) incidences. Samples: (a) as-grown and (b) 450-vac 15 nm thick α-Fe_2O_3 / Pt (111).

Table S1. Structural parameters (interatomic distances (R) and DW factors (DW)) obtained by EXAFS simulations at the Fe K edge for as-grown and UHV-annealed 15 nm thick hematite films. The interatomic distances (resp. DW factors) are given in Å (resp. Å-2), the error bar is ± 0.03 Å (resp. ± 10%). The simulated structure was hematite. Structural parameters for bulk hematite (resp. magnetite) for the two first (resp. first) neighbor shells of an absorbing Fe atom (in O_h site) obtained from FEFF calculations are also shown.

Sample	Fe-O1 (Å)		Fe-O2 (Å)		Fe-Fe1 (Å)		Fe-Fe2 (Å)	
	R	DW	R	DW	R	DW	R	DW
pure α-Fe_2O_3 (FEFF)	1.945		2.11		2.90		2.97	
As-grown	1.95	0.004	2.10	0.005	2.90	0.005	2.99	0.006
200-vac	1.95	0.003	2.10	0.007	2.91	0.003	2.98	0.001
270-vac	1.95	0.006	2.11	0.010	2.91	0.003	2.98	0.004
350-vac	1.95	0.002	2.11	0.005	2.91	0.004	2.98	0.004
400-vac	1.96	0.003	2.08	0.008	2.92	0.006	2.99	0.003
450-vac	1.96	0.007	2.07	0.007	2.97	0.007	2.99	0.005
Fe in O_h site in pure Fe_3O_4 (FEFF)	2.06		2.06		2.97		2.97	

REFERENCES

(S1) Berry, A. J.; O'Neill, H. St.C.; Jayasuriya, K. D.; Campbell, S. J.; Foran, G. J. XANES Calibrations for the Oxidation State of Iron in a Silicate Glass. *American Mineralogist* **2003**, *88*, 967-977.