Spinel ferrites MFe_2O_4 (M = Co, Cu, Zn) for photocatalysis: theoretical and experimental insights

Supplementary Information

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1. Normalisation Procedure

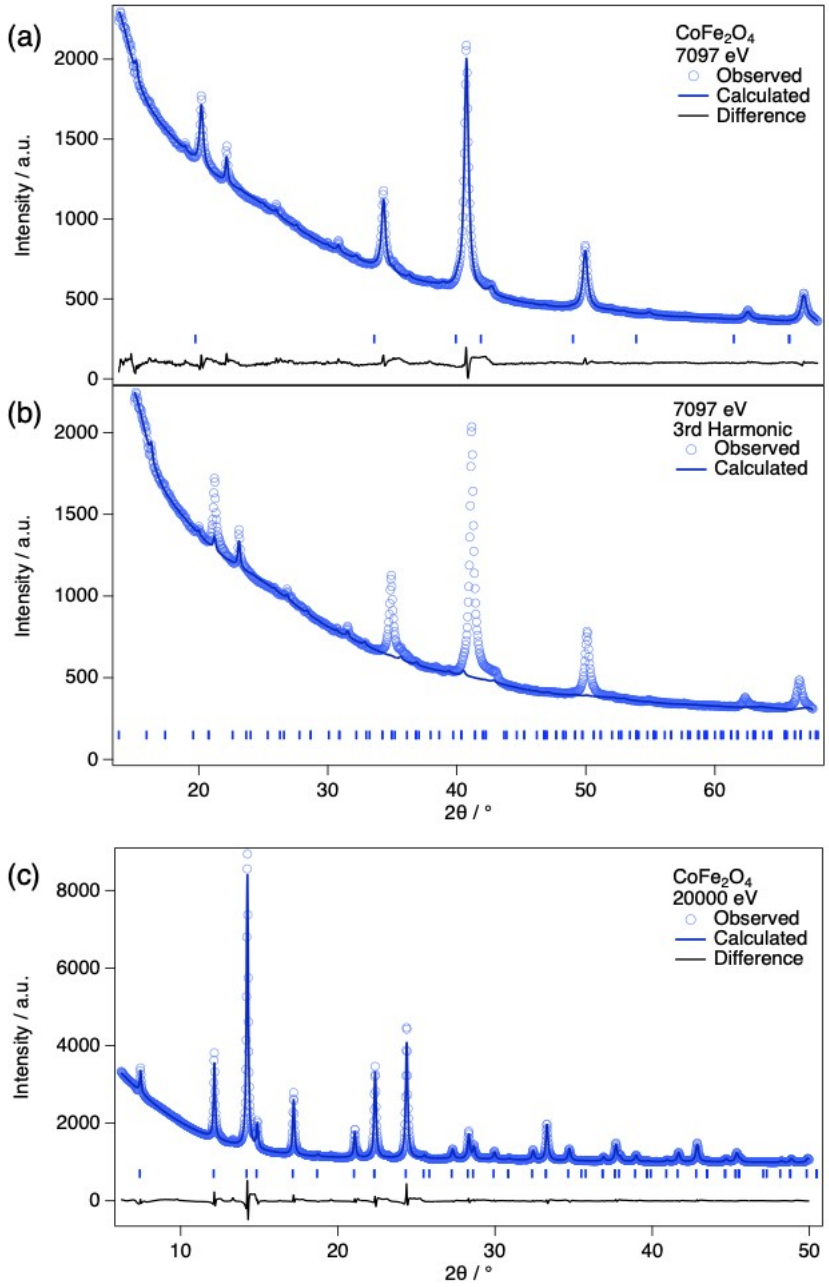
NEXAFS

The spectra were normalised to the beamline transmission by subtracting the I_0 measurement. The background and edge jumps were subtracted with a Fermi-Dirac step function. Two step functions with a width of 7 eV [1] were used with a 2:1 jump ratio for the L_3 and L_2 edges respectively. The edge jump position was shifted by 3 eV with respect to the peak maximum. [2] Finally, the integral of each spectrum was normalised with respect to the average number of holes, 4.8 (20% Fe^{2+} and 80% Fe^{3+} as determined by the XMCD fitting).

XMCD

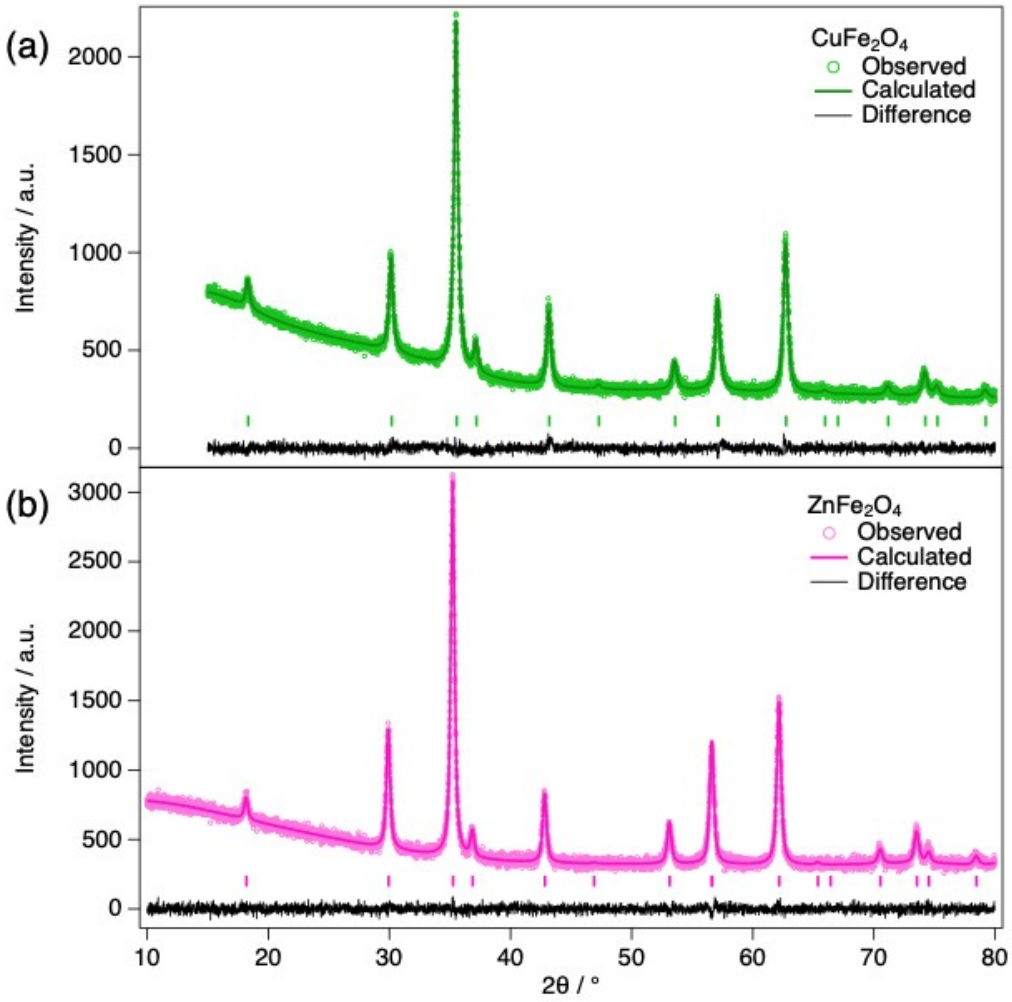
The positive and negative circularly polarised XAS spectra measured were first normalised with respect to the beamline transmission and then normalised to the pre-edge region. The difference in these normalised spectra was taken to obtain the XMCD signals.

2. Anomalous X-Ray Scattering (AXRS) patterns



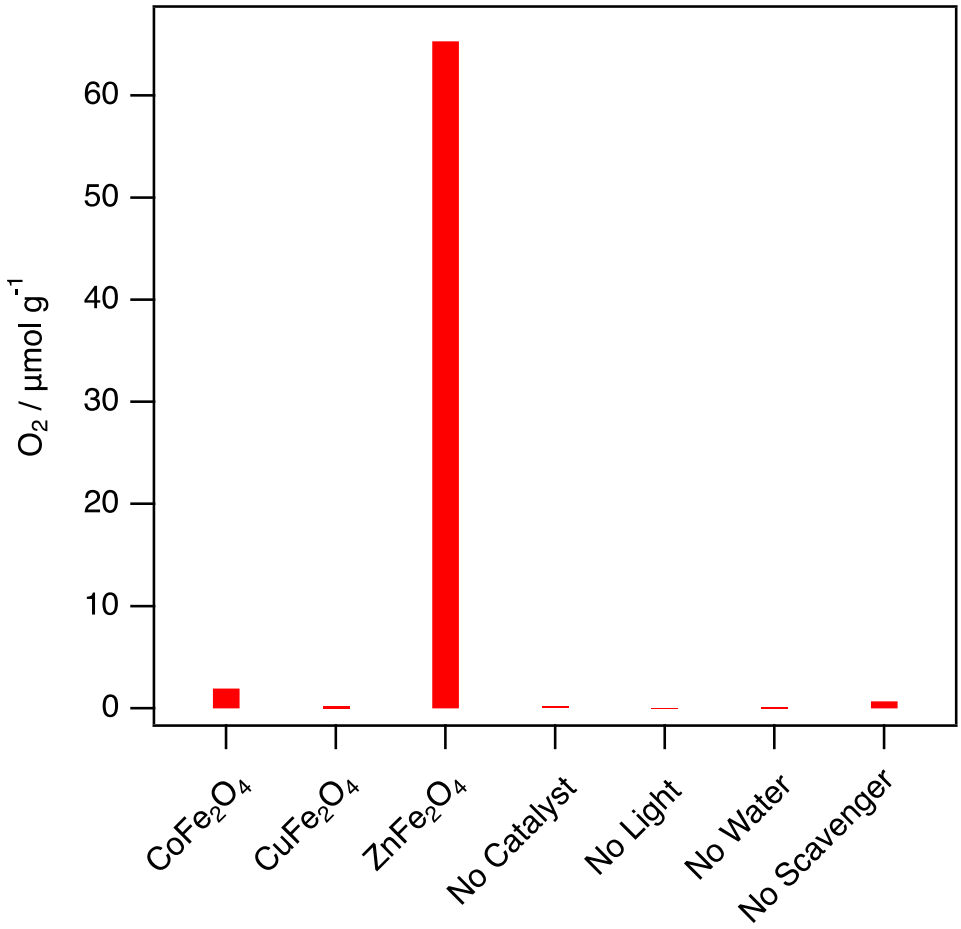
Supplementary Figure 1. AXRS patterns of $CoFe_2O_4$ at 7097 eV (a) and (b) (only 3rd harmonic contribution) and at 2000 eV (c)

3. X-Ray diffraction (XRD) patterns



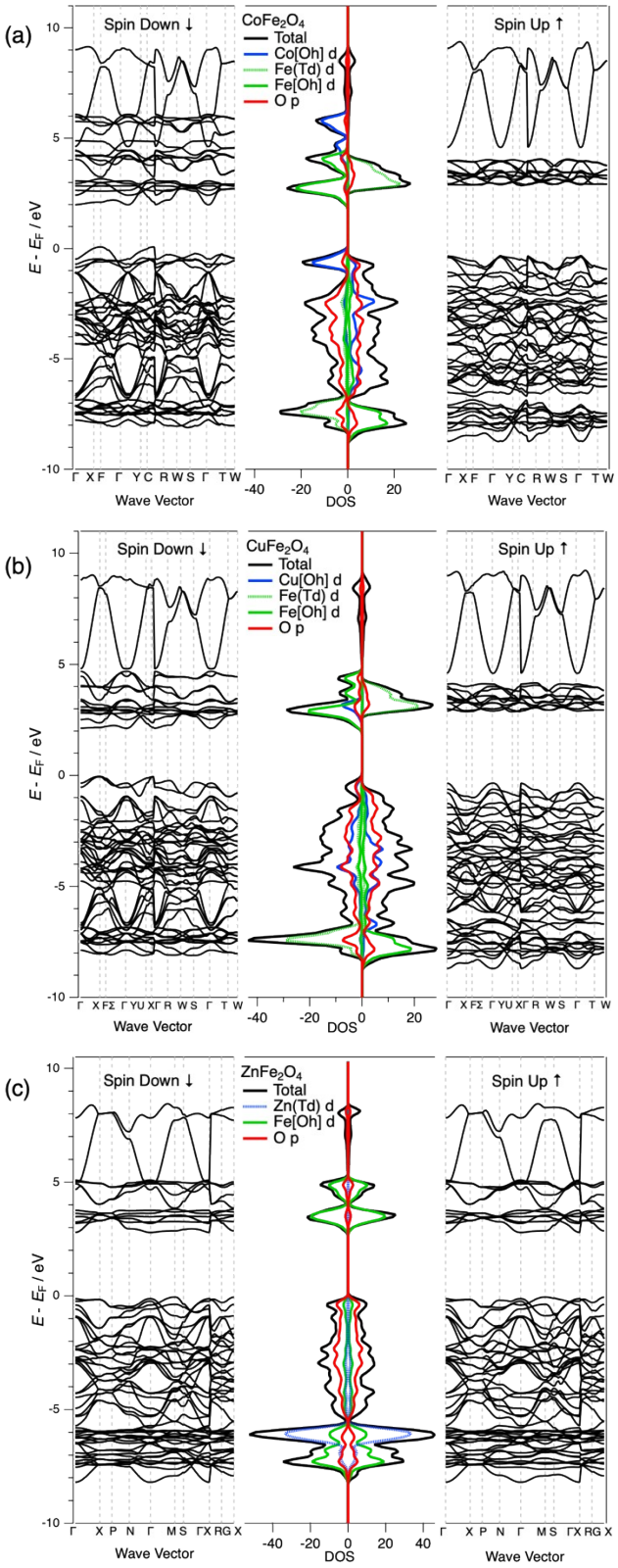
Supplementary Figure 2. XRD of a) $CuFe_2O_4$ and b) $ZnFe_2O_4$

4. Catalytic testing control experiments



Supplementary Figure 3. The amount of oxygen produced by the spinels MFe_2O_4 (M = Co, Cu or Zn) under the photocatalytic conditions outlined in section 2.4 of the article, and the oxygen produced by the control measurements: with no catalyst, or with $ZnFe_2O_4$ catalyst but no UV light, no water or no Ag^+ sacrificial agent (scavenger).

5. Calculated band structure



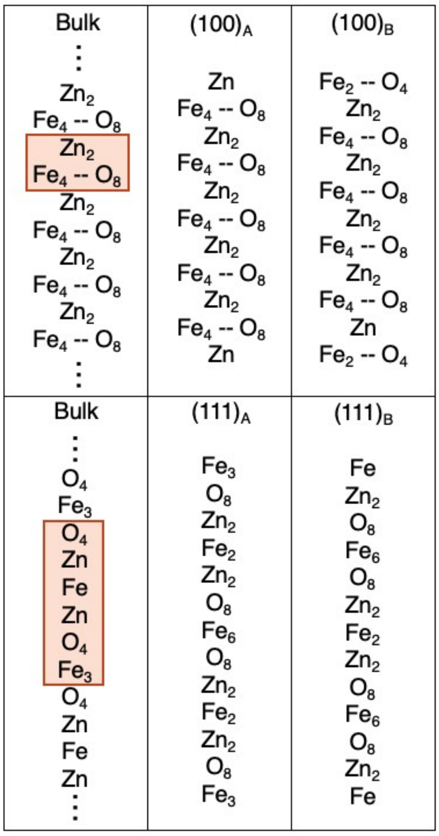
Supplementary Figure 4. Band structure calculated at HSE06 level for a) $CoFe_2O_4$, b) $CuFe_2O_4$ and c) $ZnFe_2O_4$.

6. Details of surface slabs

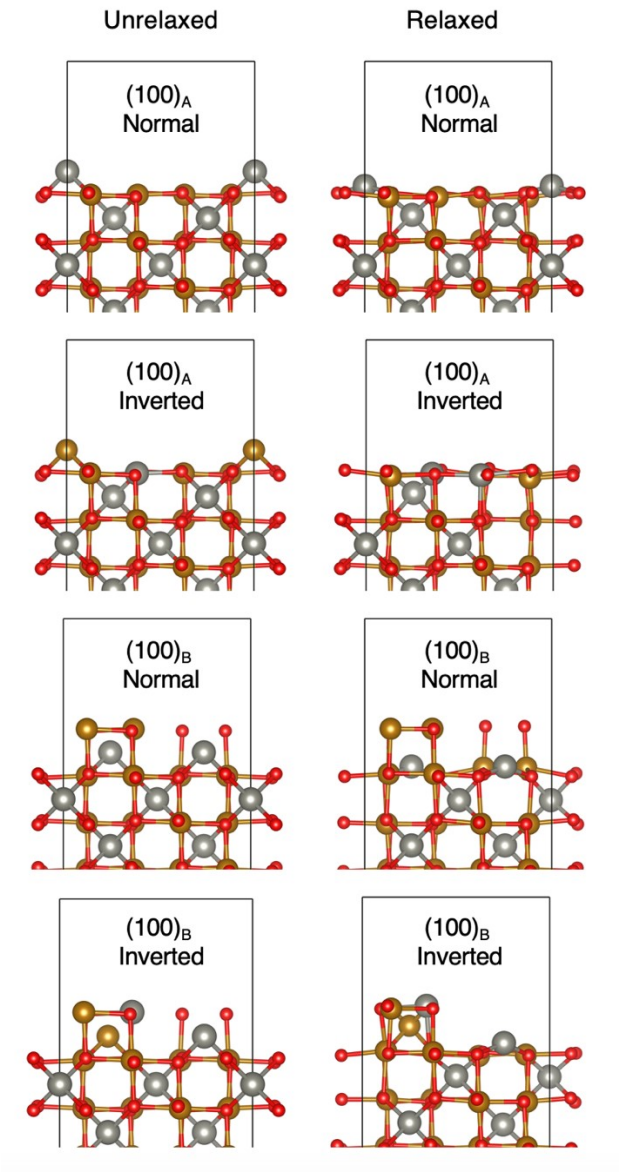
To build stoichiometric and non-polar surface models the surface must be reconstructed. The schematic for how each surface is terminated and their respective notations can be seen in **Supplementary Figure 4**. The opposite surfaces of each slab have the same, symmetric terminations. The notation used for these surfaces follows that used in Ref. [3].

The $(100)_A$ surface is Zn-terminated, whereas the $(100)_B$ surface ends at the Fe-O layer, with half of the layer atoms removed.

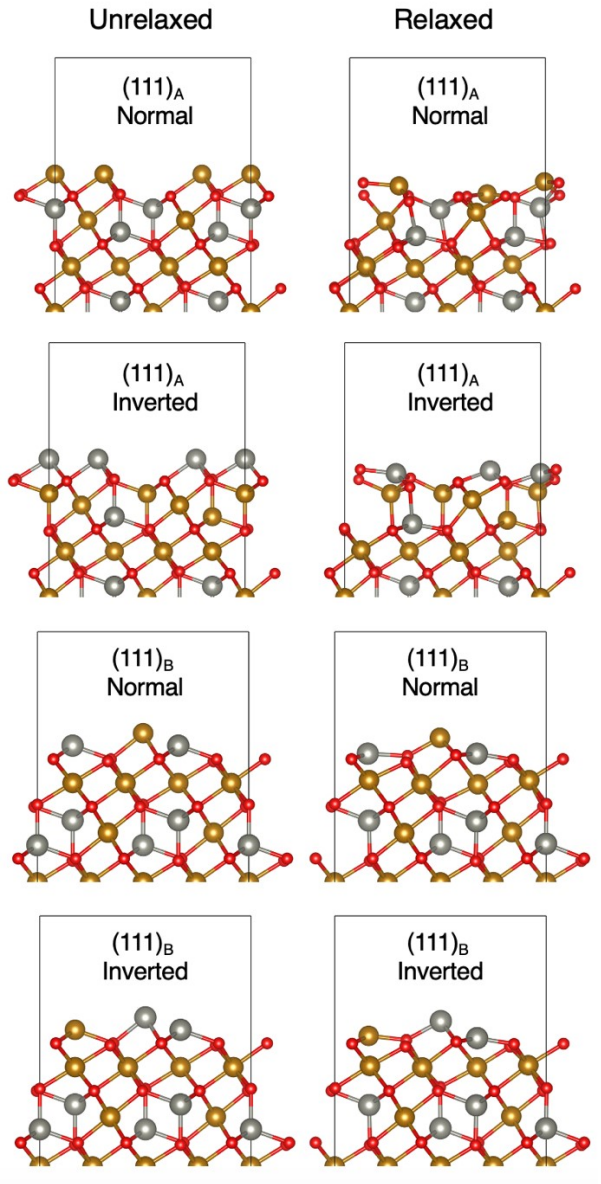
The (111) surfaces are Fe-terminated. Building the (111) surfaces requires the unit cell to be expanded in both lateral directions, which leads to the two different types of bulk Fe layers having six and one Fe atoms per cell, respectively. The $(111)_A$ surface ends at the Fe_6 layer, but half of the surface atoms are removed (Fe_3 termination). The $(111)_B$ surface ends at the Fe_2 layer, and again half of the Fe atoms are removed to maintain the stoichiometry (Fe termination).



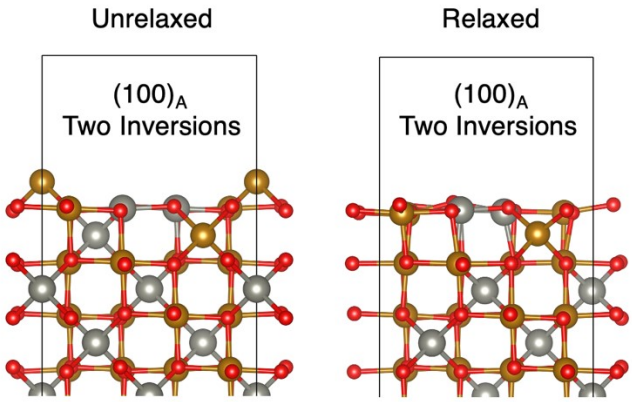
Supplementary Figure 5. Schematic representation of the $ZnFe_2O_4$ (100) and (111) surface reconstructions. The column of the left shows the sequence of layers in the bulk for the given direction; the shaded rectangles in the bulk scheme highlight a stoichiometric unit.



Supplementary Figure 6. $ZnFe_2O_4$ (100) A and B terminated surfaces before and after relaxation. Colour scheme: Zn = silver; Fe = gold; oxygen = red.



Supplementary Figure 7. $ZnFe_2O_4$ (111) A and B terminated surfaces before and after relaxation. Colour scheme: Zn = silver; Fe = gold; oxygen = red.



Supplementary Figure 8. $ZnFe_2O_4$ $(100)_A$ surfaces with two cation pairs inverted before and after relaxation. Colour scheme: Zn = silver; Fe = gold; oxygen = red.

7. Fitted XMCD percentages

Supplementary Table 1. Percentages of Fe cations in different oxidation states (Fe^{2+}/Fe^{3+}) and sites (Oh/Td) at the spinel near-surfaces, as derived from the XMCD fitting.

Sample	Fe^{3+} Oh	Fe^{3+} Td	Fe^{2+} Oh
$CoFe_2O_4$	42.9%	38.1%	19.0%
$CuFe_2O_4$	44.5%	37.2%	18.3%
$ZnFe_2O_4$	46.8%	25.1%	28.1%

References

1. M. Ghiasi, A. Hariki, M. Winder, J. Kuneš, A. Regoutz, T.-L. Lee, Y. Hu, J.-P. Rueff and F. M. F. de Groot, *Physical Review B*, 2019, **100**.
2. G. Van Der Laan, J. Zaanem and G. A. Sawatzky, *Physical Review B*, 1986, **33**, 4253-4263.
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