Supporting Information for

Femtosecond $M_{2,3}$-Edge Spectroscopy of Transition Metal Oxides: Photoinduced Oxidation State Change in α-Fe_2O_3

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Contents:

1) Fabrication and Electron Diffraction of α-Fe_2O_3 films

Films were fabricated by e-beam deposition of 9.3 nm Fe, followed by oxidation in an O_2 furnace at 500°C for 5 hours. The α-Fe_2O_3 film was confirmed to be phase-pure hematite by electron diffraction, according to the following procedure: The combined iron oxide/silicon nitride thin film was transferred to an amorphous carbon TEM grid. Electron diffraction in a

Tecnai G2 Super-Twin TEM with a LaB_6 thermionic emission filament at 200kV was conducted at 5 spots widely spaced across the thin film to ensure sample homogeneity. Electron diffraction patterns were radially integrated, their intensities normalized, and the background was subtracted using a single exponential. The diffraction axis was converted to Cu $K\alpha_1$-equivalent. As shown in Figure S1, the location of the peaks in the observed diffractogram matches those of the standard JCPDS file 01-089-0597 for α-Fe_2O_3. The black stems' heights are proportional to their standard intensity in the JCPDS. The high background from 25-40 degrees is due to an additional signal from the amorphous carbon grid that is not removed by the single-exponential background subtraction.

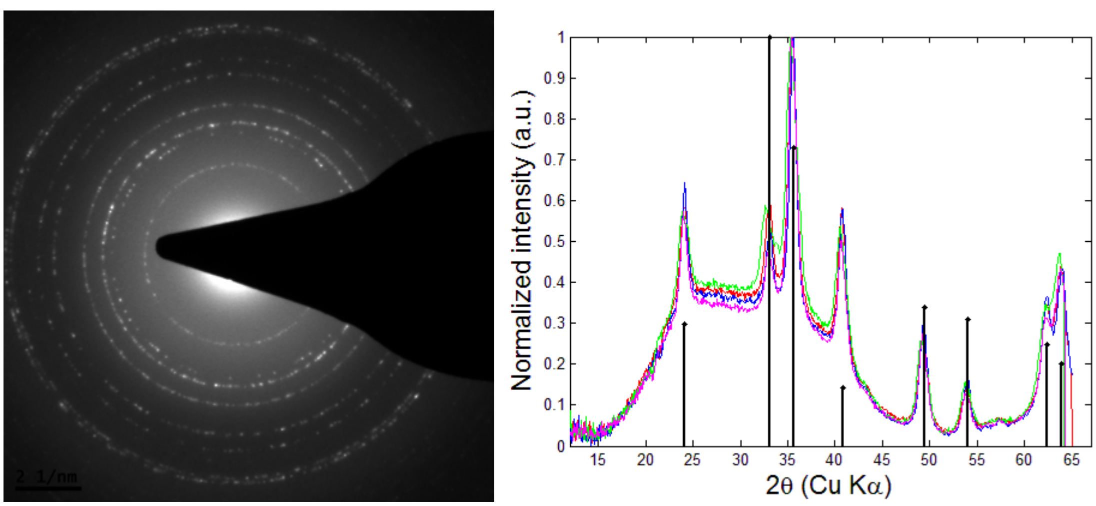

Figure S1: Left: Electron diffraction image from α-Fe_2O_3 film. **Right:** Diffractogram of five different spots of the sample, overlaid with expected peaks for α-Fe_2O_3 (black stems). The heights of the stems are proportional to their standard intensity in the JCPDS.

2) UV-Vis spectrum of α-Fe_2O_3

The UV-Vis spectrum of α-Fe_2O_3 on a glass slide is shown in Figure S2 (the small size and fragility of the 3x3 mm Si_3N_4 samples precluded their use in a standard UV-Vis spectrometer). Note that this sample is slightly thicker than the ones used in the transient absorption experiment, which had an absorption of 0.5 at 400 nm as measured by the transmission and reflection of the pump beam.

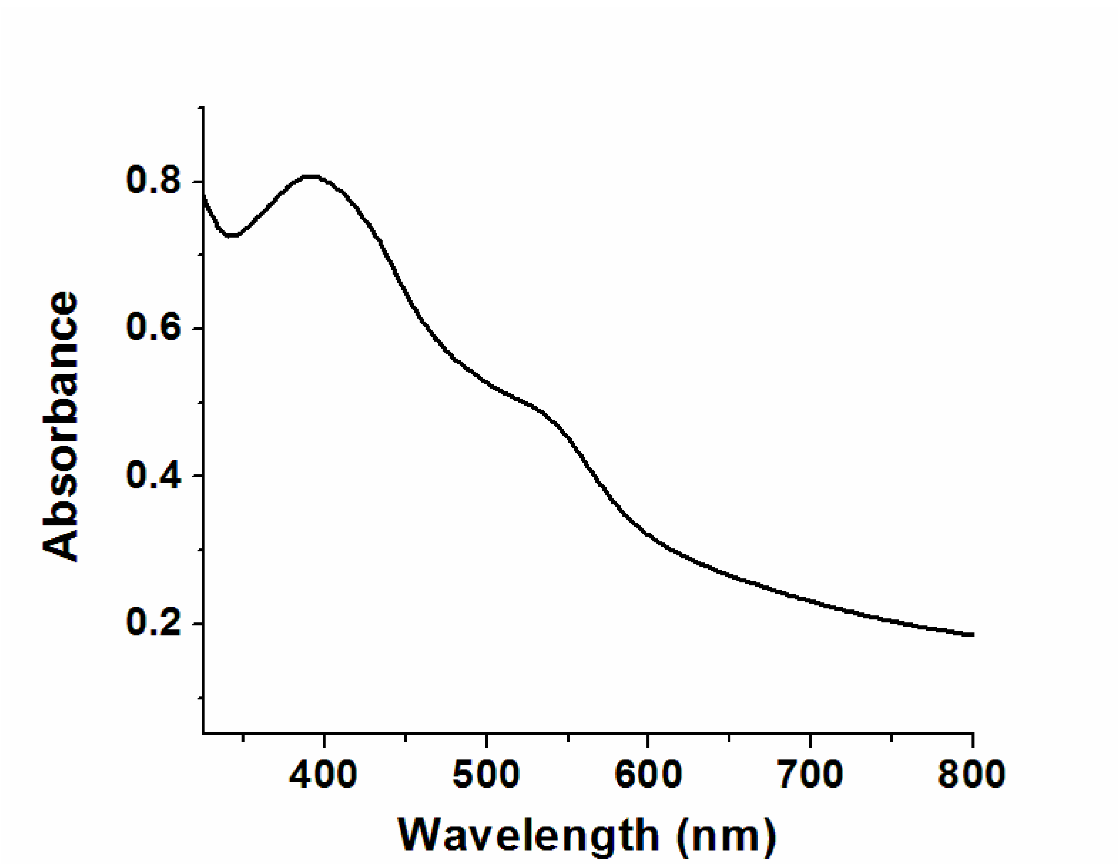

Figure S2: UV-Vis spectrum of α-Fe_2O_3

3) Linewidths of simulated spectra

Following Berlasso et al (Ref 27 in the body of the article), the calculated stick spectrum is broadened with a Lorentzian linewidth parameter Γ increasing linearly from 0.1 at 52 eV to 1.5 eV at 56.5 eV and higher. This variable broadening accounts for the Auger lifetimes of the core-hole excited states, which are shorter for higher-energy states due to an increase in the number of decay channels.[1] A Fano asymmetry parameter of 3.5 is applied to the spectrum, explained briefly as follows:[2,3] photoelectrons can be produced either by directly photoionizing a 3d electron (e.g. $3p^6 3d^5 \rightarrow 3p^6 3d^4 \epsilon f$) , or by 3p→3d excitation followed by Auger decay that ejects a 3d electron (e.g. $3p^6 3d^5 \rightarrow 3p^5 3d^6 \rightarrow 3p^6 3d^4 \epsilon f$). Because these two pathways share the same initial and final states, they interfere and produce the observed Fano lineshape.[4] Finally, the spectrum is convoluted with a Gaussian function with $\sigma = 0.2$ eV to account for the instrument energy resolution.

4) Additional References for Supporting Information

(1) Taguchi, M.; Uozumi, T.; Kotani, A. Theory of X-ray Photoemission and X-ray Emission Spectra in Mn Compounds, *J. Phys. Soc. Jpn.* **1997**, *66*, 247-256.

(2) Shin, S.; Suga, S.; Kanzaki, H.; Shibuya, S.; Yamaguchi, T. Multiplet Structures of the Inner Core Absorption-Spectra of $KMnF_3$ and $KCoF_3$ Measured by Synchrotron Radiation. *Solid State Commun.* **1981**, *38*, 1281-1284.

(3) Davis, L.C.; Feldkamp, L.A. $M_{2,3}$ spectrum of atomic Mn. *Phys. Rev. A.* **1978**, *17*, 2012-2022.

(4) Fano, U. Effects of Configuration Interaction on Intensities and Phase Shifts. *Phys. Rev*. **1961**, *124*, 1866-1878.