## **Supporting Information**

# Direct observation of the electronic states of photoexcited hematite with ultrafast 2p3d x-ray absorption spectroscopy and resonant inelastic x-ray scattering

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#### Hematite Thin Film Fabrication and Characterization

50nm hematite thin film sample was deposited on indium tin oxide (ITO)/fused silicon dioxide substrate by pulsed laser deposition. The thin film surface morphology was studied with scanning electron microscopy (SEM) using FEI Helios Nanolab G3 at 5 kV acceleration voltage (Fig. S1 (a)). Different spots in the samples were investigated to ensure the surface homogeneity. To confirm the iron oxidation state, X-ray photoelectron spectroscopy (XPS, Fig. S1 (b)) and full X-ray absorption spectroscopy (XAS, Fig. S1 (c)) scan was measured in SPring-8 BL07LSU. The spectral features of both measurements confirm the presence of iron 3+ sites in hematite. The electronic transitions and band gaps of the sample were studied using a UV-VIS-NIR spectrometer (Fig. S1 (d)). Both transmittance and absorption spectra were recorded from 800 nm to 350 nm using a UV-vis-NIR Cary 500 (Varian) spectrophotometer.



**Figure S1**: The basic characterizations of the prepared hematite sample: (a) SEM image (b) Fe 2p XPS spectrum, (c) Fe 2p XAS spectrum and (d) a UV-Vis spectrum

#### The evaluated parameters from the fittings (Fig. 3)

The kinetic parameters estimated from the results of PAL-XFEL are listed below. The kinetic traces were supposed to be an exponential function ( $y = A^* \exp(-t/k) + B$ ).

	1/k [ps]	А	В
Fig. 3 (a)	$0.20 \pm 0.1$	$0.008 \pm 0.002$	0.0093
Fig. 3 (b)	6 ± 7	$0.008 \pm 0.003$	$0.006 \pm 0.004$

TABLE S.1 Estimated parameters for kinetic traces in Fig. 3

#### The kinetic trace at longer delay times

The kinetic trace around 709 eV were measured in the longer delay times at BL07LSU in SPring-8<sup>1</sup>. As shown in Fig. 3, the kinetic trace around 709 eV rose within 0.2 ps, which corresponds to the time resolution in PAL-XFEL. The time resolution in the beamline was estimated as less than 50 ps. <sup>1</sup> It should be expected that the time resolution can be estimated from the kinetic trace around 709 eV. As shown in Fig. S2, the convolution function between a step function and a gaussian function with FWHM = 80 ps reproduced well the rising of the transient signals around a delay time of 0 ps. The estimated time resolution was longer than the value estimated before<sup>1</sup> because of the difference of the operation modes. The observed transient signals seems to be stable by 200 ps and then gradually decreases. Considering the kinetic traces in the faster delay times, the decay process of photoexcited hematite should be as follows:

- $1. \sim 1$  ps: photoexcitation and the relaxation of hot carriers.
- 2. < 10 ps: the fast carrier recombination process
- 3. > 200 ps: another charge recombination process



Figure S2: The kinetic trace around 709 eV in the longer delay times

### References

(1) Takubo, K.; Yamamoto, K.; Hirata, Y.; Yokoyama, Y.; Kubota, Y.; Yamamoto, S.; Yamamoto, S.; Matsuda, I.; Shin, S.; Seki, T.; Takanashi, K.; Wadati, H. Capturing ultrafast magnetic dynamics by time-resolved soft x-ray magnetic circular dichroism. Appl. Phys. Lett. 2017, 110, 162401.