

Supporting Information

Molecular species forming at the α -Fe₂O₃ nanoparticle – aqueous solution interface

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Additional Information on: Lattice-oxygen O 1s absorption spectra from Fe₂O₃ NP (aq)

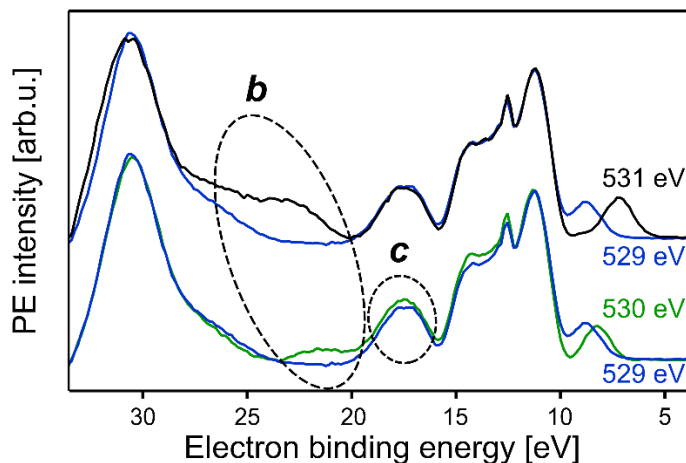


Figure SI-1 Selected RPE spectra from 5 wt% NP / 0.1 M HNO₃ aqueous solution which are taken from Figure 2A for photon energies 530.0 eV (*c* resonance) and 531.0 eV (energy between *c* and *b* resonances). Each spectrum is presented together with the off-resonant valence PE spectrum measured at 529.0 eV. Important to notice is the slightly larger intensity in the 530-eV spectrum at 17.5 eV BE (bottom tier), which disappears shortly above the resonance (top tier). This is the same contribution that gives rise to the weak signal enhancement, labeled *c*, in Figure 2C. All peaks appearing in the < 10 eV BE region result from water O 1s ionization by the second-order light (2x hv) which is not blocked at the beamline.

Additional Information on: Nitrate and hydroxide O 1s absorption spectra from Fe₂O₃ NP aqueous solutions

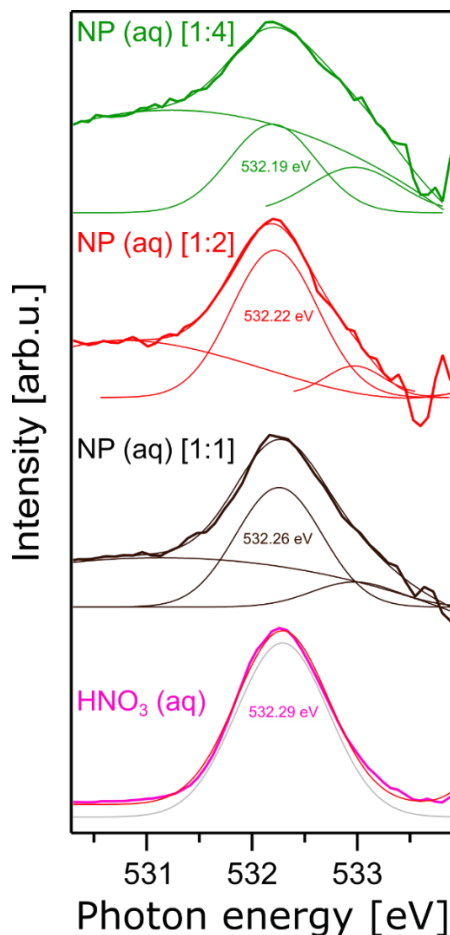


Figure SI-2 PEY-XA spectra from 0.5 M HNO₃ aqueous solution and from three NP solutions, 5 wt% NP / 0.1 M HNO₃, 10 wt% NP / 0.1 M HNO₃, and 10 wt% NP / 0.05 M HNO₃. The presented photon energy region 531-534 eV corresponds to absorption α in Figure 2B. Spectra were generated by integration of the respective RPE spectral intensities as a function of photon energy as explained for Figure 2 in the main text. In Figure SI-2 the spectra from different solutions were energy-calibrated and intensity-normalized at the O 1s liquid water pre-peak at 535.0 eV photon energy, after subtraction of the water-vapor absorption spectrum; compare Figure 3A in the manuscript. For the 5 wt% solution the ratio of available NO₃⁻ molecules to adsorption sites at the NP (6 nm diameter) surface is approximately 1:1. That is, the surface of the NPs is expected to be fully covered by adsorbed nitrate, and the concentration of aqueous-phase NO₃⁻ (aq) should be very low. Then, at 10 wt% NP concentration in 0.1 M HNO₃ and in 0.05 M HNO₃, the nitrate-to-surface site ratio decreases to 1:2 and 1:4, implying that H₂O molecules can now interact directly with the NP surface, forming OH interfacial species. Above ratios are a coarse estimate based on the total surface of the NPs in a given volume, and assuming a density of adsorption sites of 5.6 nm⁻² which is the value reported for crystalline hematite. [E. McCafferty and A. C. Zettlemoyer, Discuss. Faraday Soc., 1971, 239.] Smaller ratios were not investigated as to avoid agglomeration of the NPs; all measurements presented here were performed from freshly prepared NP solutions.

Additional Information on: Adsorbed nitrate and hydroxide on the NP surface observed in the O 1s RPE spectra from Fe₂O₃ NP aqueous solutions

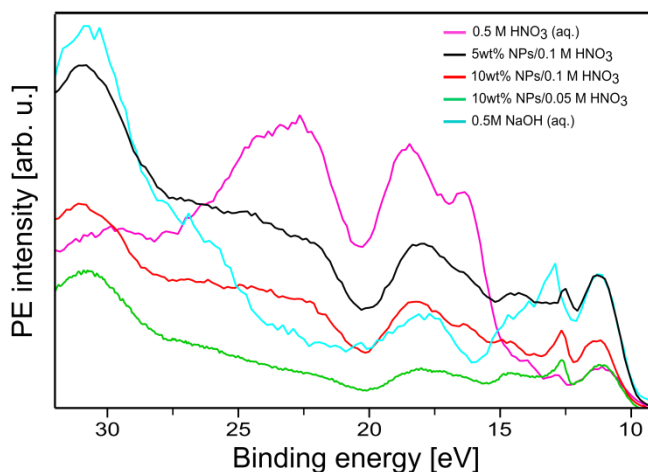


Figure SI-3 Photoelectron spectra at resonance *a* (532.2 eV) for the same three α -Fe₂O₃ NPs aqueous solutions considered in Figure SI-2. In addition, spectra from 0.5 M HNO₃ and 0.5 M NaOH (measured at near *a*) aqueous solution, are shown. Unlike in Figure 4 of the manuscript spectra are shown as measured without the off-resonant photoelectron spectrum subtracted. Otherwise Figure SI-3 and Figure 4 are identical.

Additional Information on: Valence photoelectron spectra from 1 M HNO₃ aqueous solution

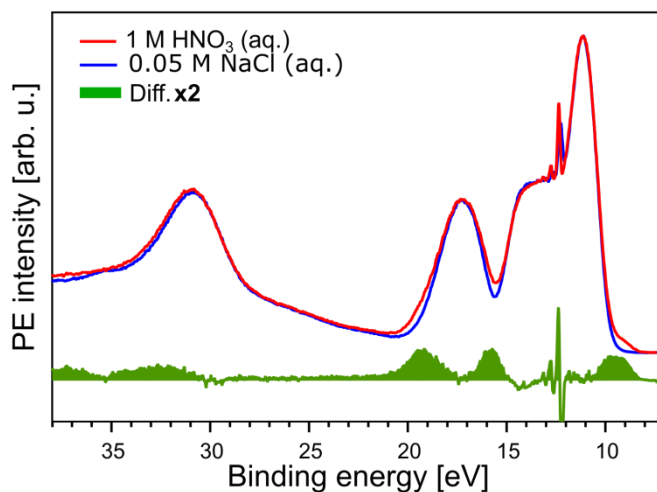


Figure SI-4 Valence photoelectron spectra from 1 M HNO₃ and from 0.05 M NaCl (which is essentially the spectrum from neat liquid water) aqueous solutions measured at 200 eV photon energy. The green curve is the difference spectrum, HNO₃ minus NaCl, and highlights the signal contributions from ionization of NO₃⁻ (aq). Peaks occur at 9.5, 16.0, 19.5 eV binding energy; these energies are in good agreement with computed energies. [R. D. Poshusta, D. C. Tseng, A. C. Hess and M. I. McCarthy, *J. Phys. Chem.*, 1993, **97**, 7295-7303]

Additional Information on: O 1s photoelectron spectra from Fe₂O₃ NP aqueous solution

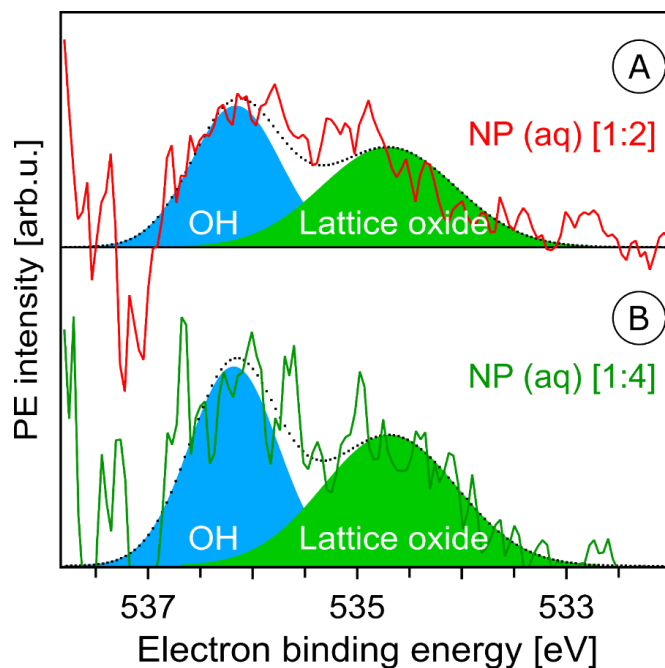


Figure SI-5 Oxygen 1s photoelectron spectra from the 10 wt% hematite NPs in 0.1 M HNO₃ aqueous solution showing the 538-532 eV binding energy region which covers the O 1s photoelectron spectra from OH⁻ (536.1 eV) and lattice oxide (534.7 eV). Ionization photon energy was 1200 eV. In this figure we present the raw data, whereas in Figures 5B and 5C we show the same data for 5-point binning. Each contribution is presented by a Gaussian, and the total fit is shown by the dotted curve. (A) shows results for the 10 wt% hematite NPs / 0.1 M HNO₃ aqueous solution (corresponding to [1:2]), and (B) for 10 wt% hematite NPs / 0.05 M HNO₃ aqueous solution (corresponding to [1:4]) after subtraction of the 0.05 M NaCl aqueous solution spectrum.

The table below presents the positions and areas of both the hydroxide and lattice-oxide O1s photoelectron peaks along with the respective error bars of the raw data.

NPs in 0.1 M HNO ₃ aq solution	Peak [eV]	Area [arb. u.]
Lattice Oxide	534.8 ± 0.2	114.4 ± 32
OH ⁻	536.2 ± 0.1	91.2 ± 29

NPs in 0.05M HNO ₃ aq solution	Peak [eV]	Area [arb. u.]
Lattice Oxide	534.7 ± 0.2	139.2 ± 31
OH ⁻	536.2 ± 0.1	140.2 ± 30