Electronic Supplementary Material (ESI) for Nanoscale Advances.

Supporting Information for:

Determination of the valence band edge of Fe oxide nanoparticles dispersed in aqueous solution through resonant photoelectron spectroscopy from a liquid microjet

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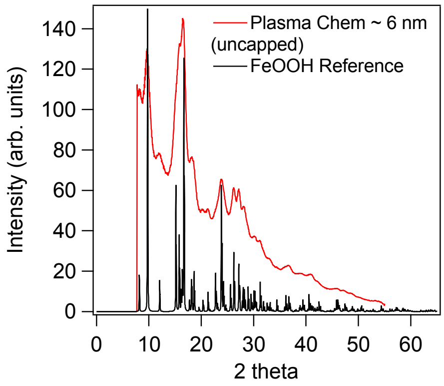

Figure S1. X-ray diffraction measurement of the iron oxide nanoparticles purchased from PlasmaChem (red line) compared to the XRD reference for goethite (FeOOH).

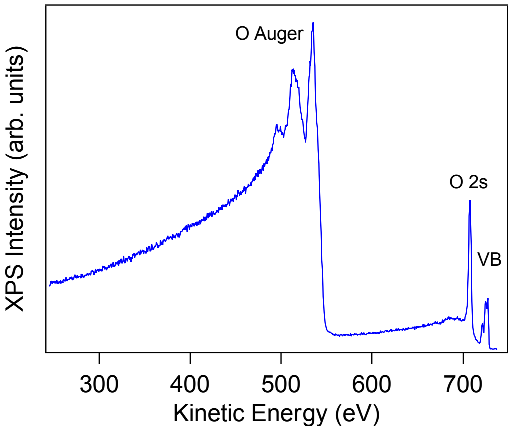

Figure S2. XPS survey of 2 wt% FeOOH nanoparticles dispersed in water taken with a photon energy of 708 eV. No detectable carbon signature expected at about 415 – 425 eV kinetic energy range is present indicating that the nanoparticles are ligand free as declared by the producing company (PlasmaChem).

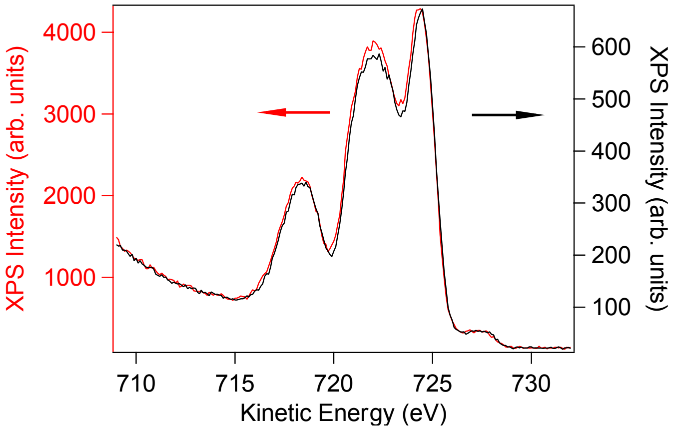

Figure S3. On-resonance valence band spectra for a solution of 2 wt% FeOOH nanoparticles dispersed in water measured with different photon fluxes. The optimized photon flux was reduced by closing the beamline exit slits to measure the spectrum shown in black. Each spectrum has been normalized to the number of the sweeps. No charging effects, such as peak shifting and/or broadening was observed.

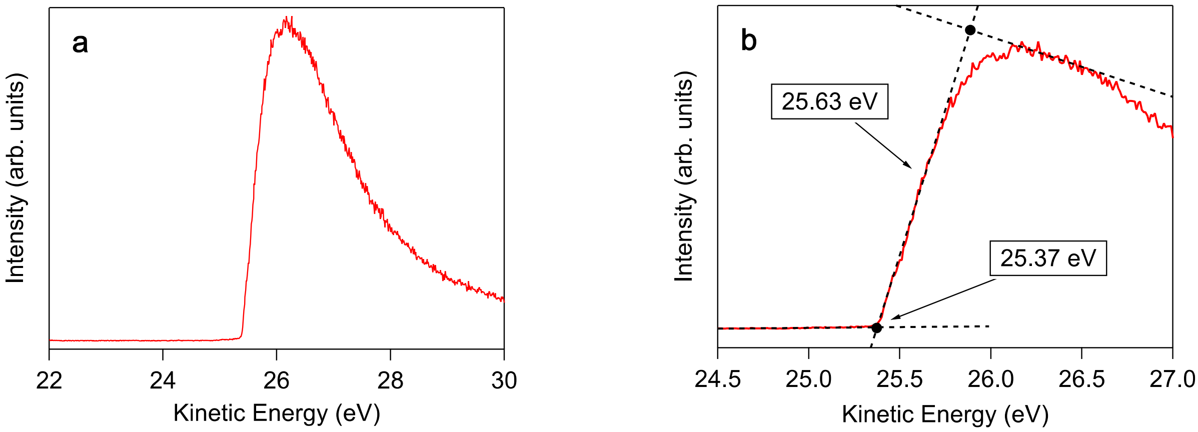

Figure S4. a) Secondary electron energy distribution curve (SEEDC) from a solution of 2 wt% FeOOH nanoparticles dispersed in water under an applied bias of -25 V. b) Extrapolation of the cut-off energy which is found at 25.63(± 0.08) eV.

Energy level correction for the photoemission spectra from a liquid microjet

In a photoemission experiment from a liquid microjet the ionization energy is measured with respect to the vacuum level of the analyzer similarly to the XPS from the gas phase. Since the aqueous solution is in electrical contact with the analyzer, it follows that their Fermi levels are aligned while their respective vacuum levels are misaligned. Therefore, if we want to know the *real* value of the ionization energy of the species in aqueous solution, we need to correct for this vacuum level offset and refer the ionization energies to the vacuum level of the liquid instead than to that of the analyzer. It can be noted that this vacuum level offset is equal to the difference between the work function of the liquid (ϕ_{liq}) and the analyzer (ϕ_{ana}) and therefore the real ionization energy for the species in aqueous solution can be written as:

$$IE_{liq} = h\nu - KE + (\phi_{liq} - \phi_{ana})$$

where $h\nu$ is the calibrated photon energy and KE is the kinetic energy of the photoelectron.
Measuring directly the workfunction of the aqueous solution is not trivial because the Fermi level of an aqueous solution is not evident in the spectra. However, the secondary electron distribution curve (SEEDC) provide a direct measure of the difference between the two vacuum levels as evidenced in the following equation:

$$\phi_{liq} - \phi_{ana} = KE_{cutoff} + e \cdot V_{applied}$$

where KE_{cutoff} is the kinetic energy of the cutoff of the SEEDC under an applied bias $V_{applied}$ and e is the elementary charge. We have measured the SEEDC for our solution of FeOOH nanoparticles dispersed in water while applying a bias of -25 V (Fig. S4 a). In order to extract the energy of the cutoff, we have fitted a line between 1/3 and 2/3 of the maximum value of the SEEDC and looked for intersection with the fitted background and the “right tail” of the cut-off (Fig. S4 b). The cut-off energy, measured as the half-point between these two intersections, is equal to 25.63(±0.08) eV and therefore the vacuum level offset for our solution is 0.63(±0.08) eV.

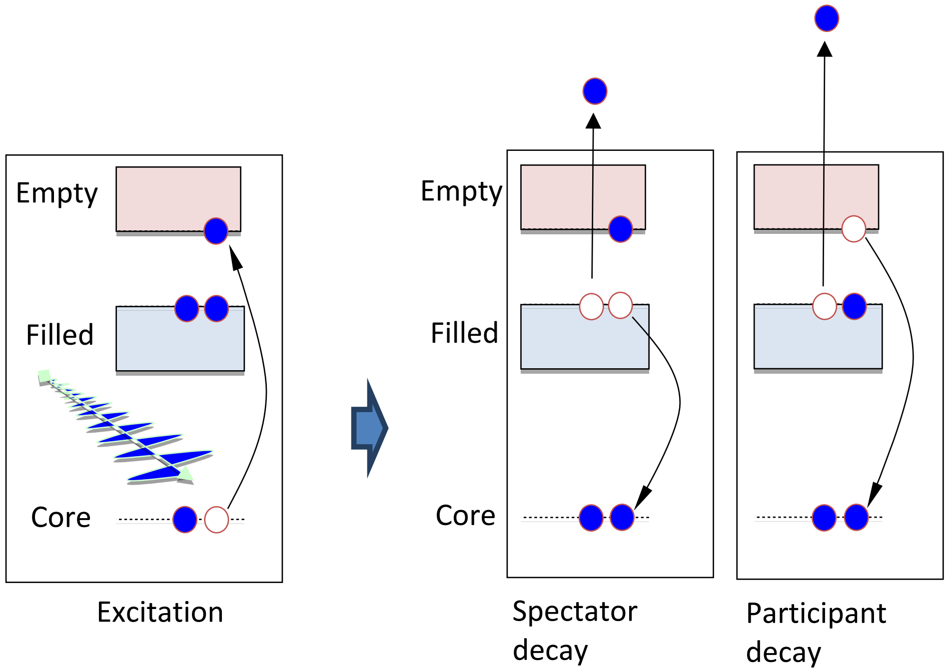

Figure S5. Schematic energy level diagram in Resonant photoemission. a) schematics of core electron excitation to empty state, followed by b) decay of the core hole in which the excited electron spectates the emission of Auger electron and c) core hole decay in which the excited electron participates in de-excitation and Auger electron emission. The Auger electron kinetic energy of c is lower (inelastic) than that of b (elastic).

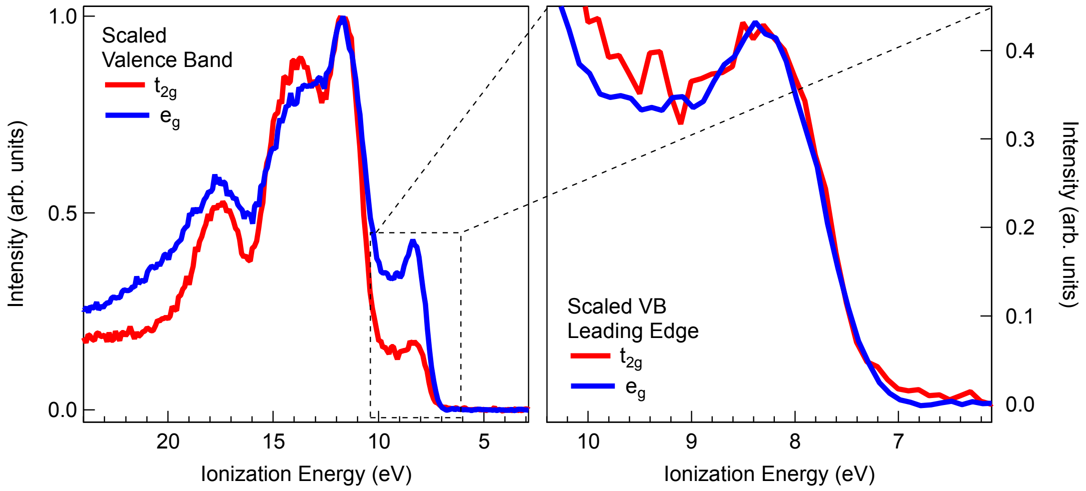

Figure S6. Left side: RPES spectra across the Fe L_3 absorption edge at the t_{2g} (red) and e_g (blue) resonances taken in a dispersion with a substantially higher concentration of FeOOH NPs in the probed volume (caused by a surfactant that encapsulates the NPs and makes them more hydrophobic) that ensured sufficient spectral intensity for the comparison. The two spectra have been normalized to the peak intensity of the highest resonance for comparison. On the right side a close-up view of the VB leading edge, normalized to the peak intensity of the first participant resonance of both spectra is shown. Both spectra evidence the same position of the VBM edge which is resonantly enhanced by participant decay. The position of the VB leading edge matches nicely for both spectra indicating no dependence of the VBM on the photon energy excitation. It also confirms that VBM belongs to the FeOOH NPs.