Double-differential pair distribution function analysis to study hydration shells around iron oxide nanoparticles

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Interfaces between iron oxide nanoparticles (IONP) and water are of great importance in various fields spanning biomedicine, waste water treatment and catalysis. Recently we showed [1], that facetted magnetic IONPs of 7 and 15 nm in size, freshly redispersed after purification, with particle concentrations of about 0.5 wt%, exhibit a strong interfacial signal in perfect agreement with restructured water ordering at planar bulk iron oxide surfaces [2]. Meanwhile the synthesis strategy was improved [3] and we can now obtain nanopowders, which can be readily redispersed in water with a concentration up to 10 wt% after freeze drying. For those dispersions, we acquired a total scattering signal for the interfacial water around the IONPs, which is significantly different from the previous one.

Here we present a high energy X-ray total scattering study of aqueous IONP dispersions of 7 and 15 nm in diameter. Pushing the boundaries of detection efficiencies for diminutive signals from weak scatterers (sub 1% of total scattered intensity), hydration shell signals are retrieved by careful double-difference pair distribution function (dd-PDF) analysis of the total scattering data from the dispersion minus bulk water minus the IONP powder. Thereby, sharp distance correlations within the water layer directly adsorbed to the IONP surfaces below 5 Å, as well as, broader features up to about 15 Å beyond, correlating to looser bound hydration layers, are resolved.
We disentangle the effect of size, ligand decoration and, small remaining residuals of organic solvents from purification onto the hydration shell signal. We conjecture that, when about 3 vol% of organic solvent from purification remain in the aqueous dispersions a solvent-rich layer stabilizing the particles is built at the interface. This way even particles with no capping agent, but only little residual amounts of diethylene glycol from synthesis on the surface, can be dispersed and are stable over months.
Further, the X-ray dd-PDF study is correlated with results from a neutron (dd-)PDF study of wet IONP powders with varying amounts of water layers and IONP dispersions in heavy water highlighting the contribution of surface-OH (-OD) groups to the interfacial signal.

[1] Thomä, S. L. J.; et al., Atomic Insight into Hydration Shells around Iron Oxide Nanoparticles, Nature Communications, 10 (2019)
[2] Spagnoli, D. ; et al., Predicitions on the effect of size and morphology on the structure of water around hematite nanoparticles, Geochim Cosmochim Acta ,73 (2009)
[3] Eckardt, M., et al., Long Term Stable Aqueous Dispersion of < 5 nm Spinel Ferrite Nanoparticles, Chemistry Open, 9 (2020)