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Multiscale simulations of the hydration shells surrounding spherical Fe_3O_4 nanoparticles and effect on magnetic properties

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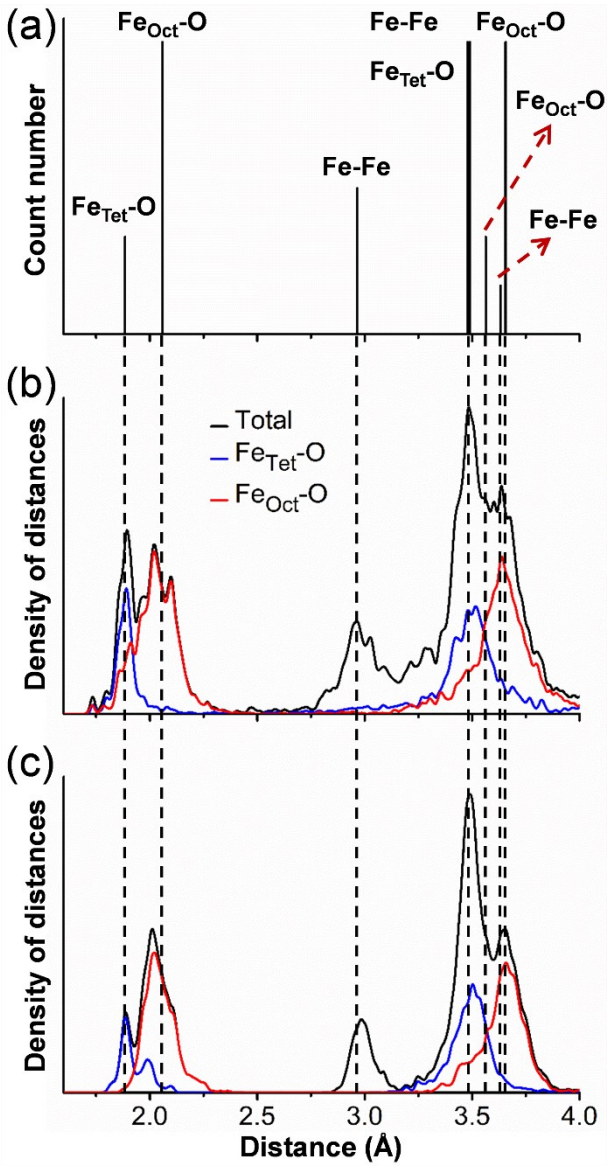

Figure S1. Simulated extended X-ray adsorption fine structure (EXAFS) spectra for (a) the Fe_3O_4 bulk, (b) nanoparticle (NP) in vacuum and (c) NP with a water monolayer adsorbed. (Data are obtained by HSE06 calculations.)

The real space EXAFS was simulated by calculating the density of distances for each Fe ions with other (Fe or O) ions and projecting them on octahedral and tetrahedral Fe ions with O. In general, the range of Fe_{Tet}-O and Fe_{Oct}-O bond lengths is broadened in the case of nanoparticles with respect to bulk magnetite because of the structural distortions and low coordination near the surface. The broader the peaks, the worse the crystallinity of the nanoparticles. Peaks in simulated EXAFS spectra become sharper when the NP is covered by a water monolayer, as compared with the one in vacuum. For example, the peak for FeOct-O centered around 2.0 Å, ranging from 1.70 to 2.30 Å in vacuum, shrinks from 1.89 to 2.27 Å when covered with a water monolayer. Similarly, peaks centered around 3.50 Å and 3.65 Å also become sharper upon the coverage of a water monolayer. Therefore, we can conclude that water adsorption improves the degree of crystallinity of the NP.

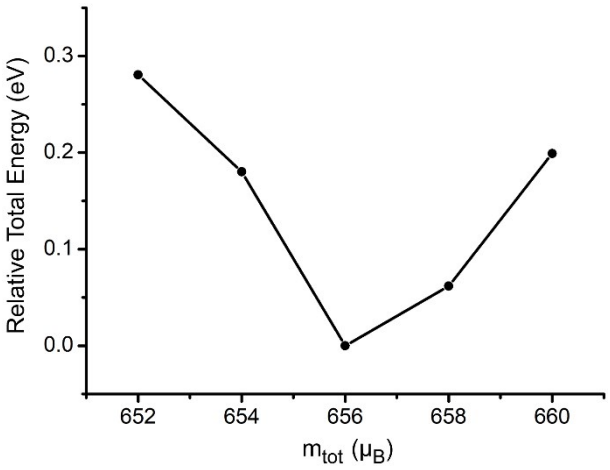

Figure S2. The relative total energy as a function of the total magnetic moment (m_{tot}) for the hydrated Fe_3O_4 nanosphere. With each m_{tot} the nanosphere is fully relaxed with HSE06 method.

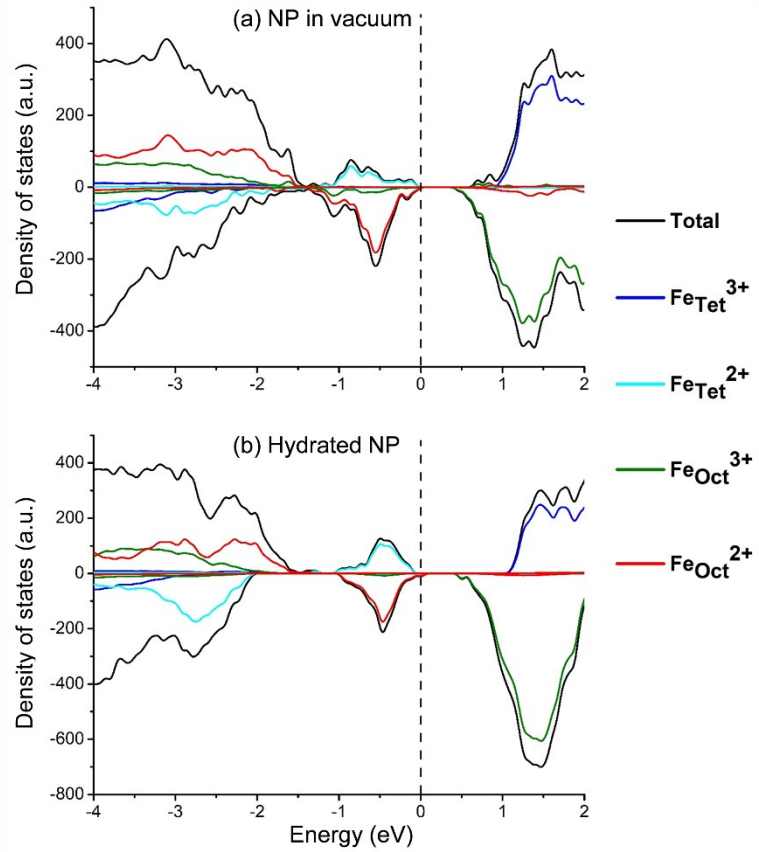

Figure S3. Partial density of states (PDOS) on the d orbits of different Fe ions in the Fe_3O_4 NP. (a) NP in vacuum. (b) Hydrated NP. Legend of colors is on the right. The Fermi level is scaled to zero as indicated by the dashed black lines.