Electronic Supplementary Information

Structure evolution of nanoparticulate Fe_2O_3

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Melting of α-Fe_2O_3

Figure S1 shows the results of MD simulations for bulk Fe_2O_3 equilibrated at several temperatures between 1800 and 2200 K. After equilibration at 2000 K (Fig. S1a) the structure remains crystalline. In contrast, at 2050 K an amorphous liquid state emerges (Fig. S2b). The phase transition can be seen as a sudden increase of potential energy, ΔE_{pot}, corresponding to the melting point at about 2025 K.

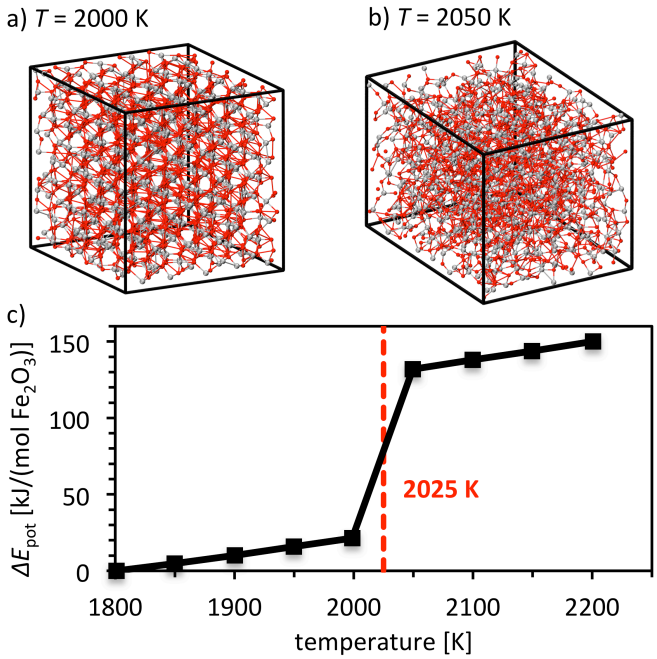

Fig. S1 Simulated melting of bulk α-Fe_2O_3: orthogonal unit cells equilibrated at a) 2000 K, b) 2050 K and c) corresponding potential energy change, ΔE_{pot}, as a function of temperature. Fe: grey, O: red.

Simulated annealing of NP5

Figure S2 shows comparison of the total radial distribution function $G(r_{ij})$ averaged over last 500 ps of equilibration phase at 2000 K for two initial configurations **NP5a** and **NP5b**. The initial structures were created as spherical cutouts from α-Fe_2O_3 (**NP5a**) and γ-Fe_2O_3 (**NP5b**) with diameter of 5 nm. For both **NP5a** and **NP5b** almost identical, amorphous structure of their molten state was obtained. This confirms that the equilibration at 2000 K was sufficient to generate NP models that are independent from their initial configuration.

The most stable structures determined by simulated annealing of both initial NP models are shown in Figure S3 along with histograms of their coordination number (CN) distributions. CN for Fe and O atoms were calculated for the inner NP core with diameters of 4 nm as well as the entire NP. The lowest energy configuration of **NP5b** is only 1.92 kJ/(mol Fe_2O_3) higher in energy than **NP5a**. Both NP show virtually the same structural patterns as well as CN distributions resembling ε-Fe_2O_3. In particular, ε-Fe_2O_3 contains 25 % tetrahedrally and 75 % octahedrally coordinated Fe atoms that are similar to the fractions for both NP cores. The fractions of CN for O atoms in ε-Fe_2O_3 are 0.5, 0.33 and 0.17 for 3-, 4- and 5-fold coordination, respectively. The deviation of the NP structure from the ideal ε-Fe_2O_3 ratios is related to the presence of structural defects within the annealed NP. However, the considerable amount of 5-fold coordinated O atoms and the Fe CN distributions indicate that the structures **NP5a** and **NP5b** are equivalent to ε-Fe_2O_3.

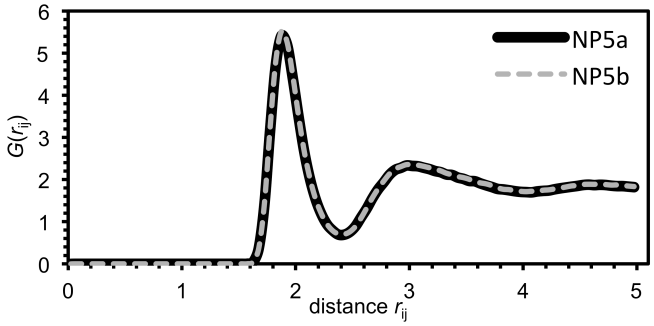

Fig. S2 Total radial distribution function $G(r_{ij})$ for **NP5a** and **NP5b** equilibrated at 2000 K.

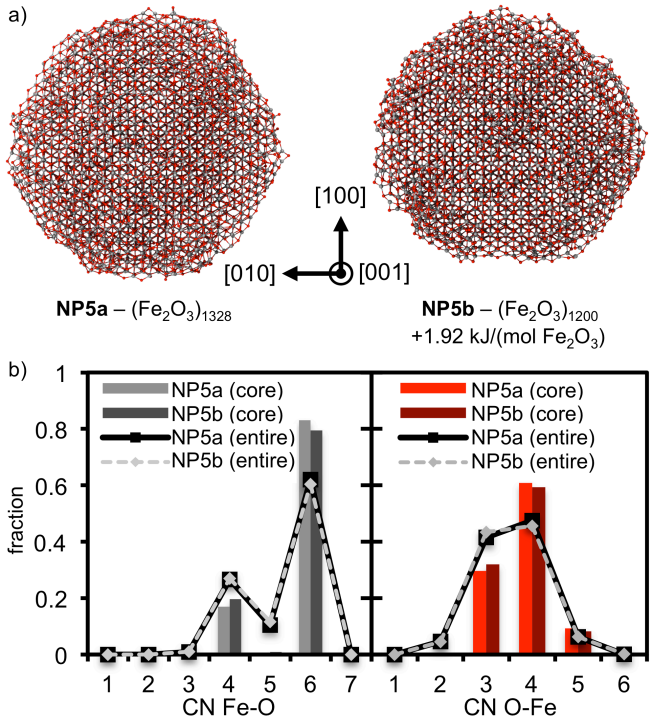

Fig. S3 Comparison of **NP5a** and **NP5b** structures: (a) view onto (001) plane, (b) coordination number (CN) distribution of Fe and O atoms for the NP core (4 nm in diameter) and the entire NP. Fe: grey, O: red.