Onion-like Fe_3O_4/MgO/$CoFe_2O_4$ magnetic nanoparticles: new ways to control magnetic coupling between soft/hard magnetic phases

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Figure S1 shows the energy loss near edge structure (ELNES) analysis of the O-K core-loss edge of the Fe_3O_4/MgO/$CoFe_2O_4$ onion-like nanoparticles. The analysis was performed at 80 keV electron energy and with a collection angle of 68 mrad. Figure S1-b) and d) compares the O-K edge at 530 eV corresponding to the core, core-shell and core-shell-shell areas of a NP as indicated in Fig. S1-c. This figure also includes the spectra of the Fe_3O_4 magnetite and a MgO as reference. From this figure is clearly observed a pre-peak located at 530 eV, which is strong in the core region and the outer shell, while shows a decreased intensity in the inner shell. These results support the Fe_3O_4/MgO/$CoFe_2O_4$ core/shell/shell structure, as the magnetite shows a prominent pre-peak, while it is completely absent for MgO. The fact that the electron beam passes through both shells also in the core regions explains the difference between spectra of the core region and the magnetite reference and similarly for the MgO shell. Also the intensity of the pre-peak diminished in the outer shell which is consistent with the doping of the cobalt ferrite with Mg that is expected to alter the O-K edge as well.

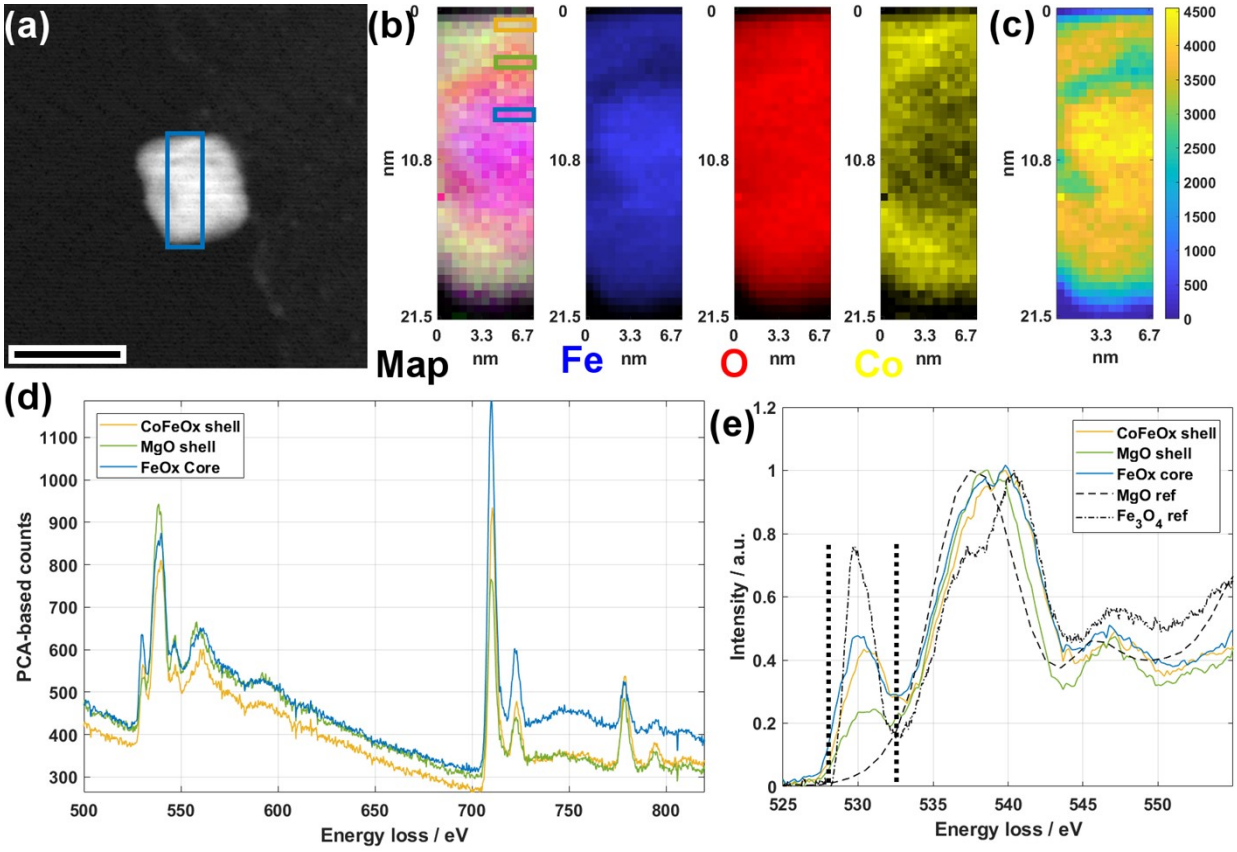

Figure S1: EELS analysis of O-K, Fe-L and Co-L core-loss edges of a core-shell-shell NP. (a) Survey image with the NP attached to the supporting C film. (b) Chemical distribution maps of Fe (blue), O (red) and Co (yellow, green in the map) with core and shells clearly visible. As Mg is not mapped in the EELS analysis, the MgO shell manifests itself in a depletion in Fe and Co while O intensity remains largely similar throughout the NP. (c) Map of integrated intensity in pre-peak of O-K edge between 528 and 532.5 eV as marked by vertical dashed lines in (e). The map clearly reveals the difference between core (bright yellow), incomplete MgO shell (light blue) and CoFeO shell (darker yellow) due to the different intensity in the pre-peak. (d) PCA-filtered EEL spectra of core (blue), core-shell (green) and core-shell-shell (yellow) regions as marked in chemical map in (b). (e) Comparison of background-subtracted O-K edge for the same regions in comparison with Fe_3O_4 magnetite and MgO reference.