Electronic Supplementary Information

Characterisation of Co@Fe_3O_4 core@shell nanoparticles using advanced electron microscopy

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Bright Field TEM

Detailed analysis of particle morphology was performed using Digital Micrograph 3.6.5. The values of average *d*-spacing were obtained from Fourier transforms of high magnification images (x800k, x1m, x1.2m). The average *d*-spacing was further verified using the profile tool in Digital Micrograph by averaging over 10 *d*-spacings. To determine the error in the value of *d*-spacing thus obtained, detailed TEM examination of CeO_2 and Au nanoparticles was undertaken. The relationship between the diameter of the FT rings and the DV value (a measure of the objective lens focusing voltage) was established for DV values between –6 and +6 and the value of standard deviation in *d*-spacing was established to be 10% when compared to literature values.

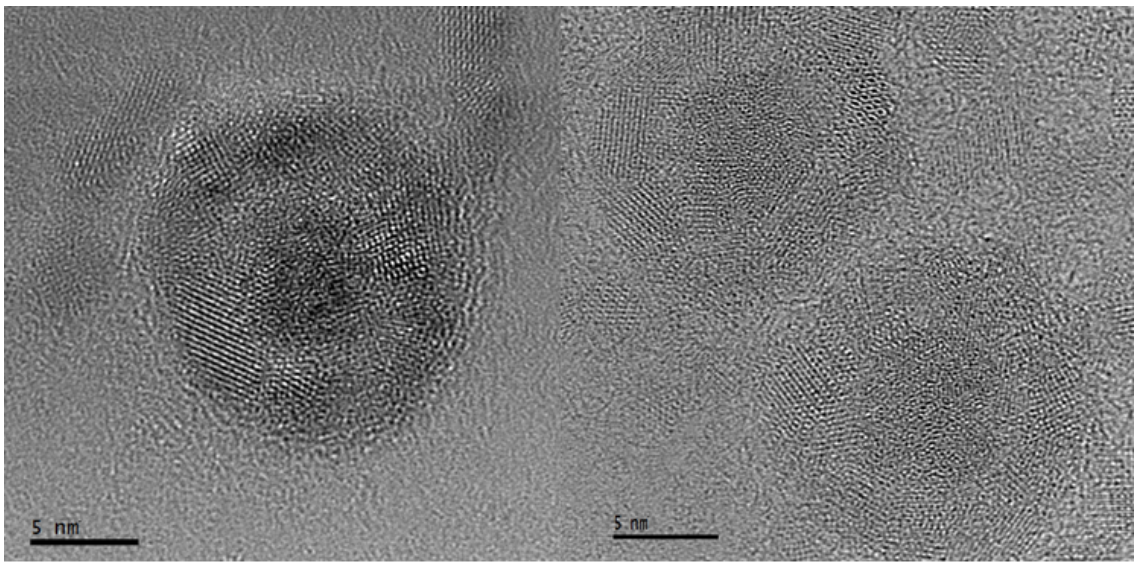

Figure S1 – TEM micrographs of Co@Fe_3O_4 NPs obtained on an FEI Titan in Karlsruhe at magnifications of x670k and x620k respectively.

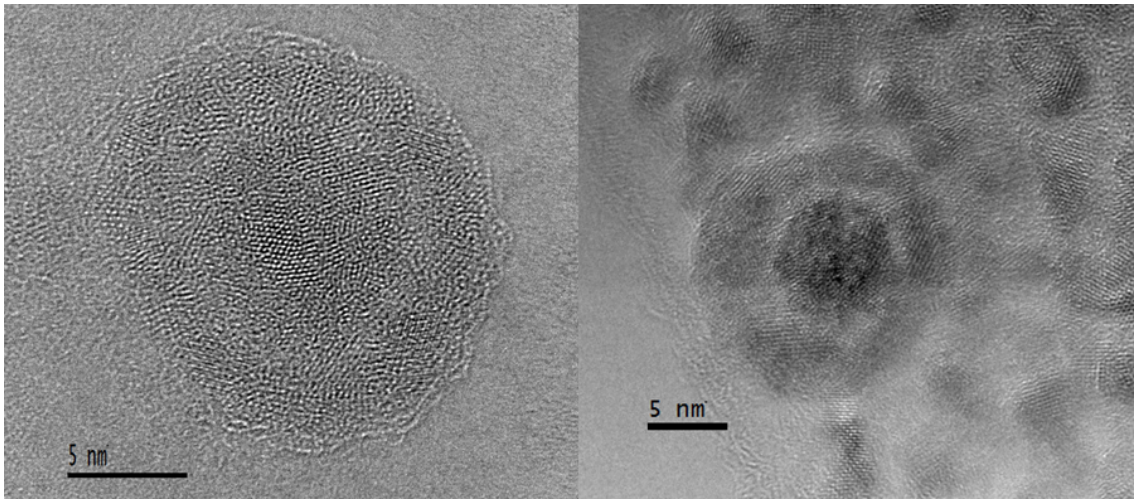

Figure S2 - TEM micrographs of Co@Fe_3O_4 NPs obtained on an FEI Titan in Karlsruhe at magnifications of x620k and x370k respectively.

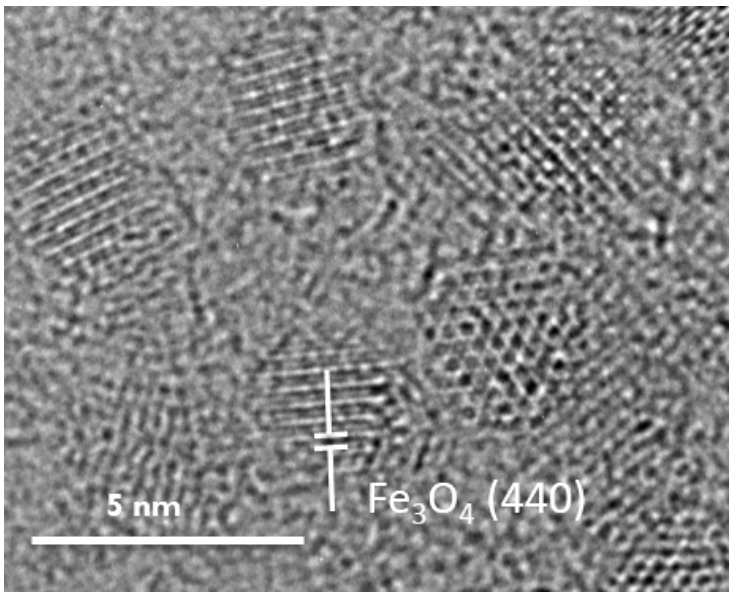

Figure S3 – Fringes in the smaller (~2 nm) particles suggesting that their composition is the same as that of the shell of the larger core@shell particles (see also EELS data in Figure S9).

EDS

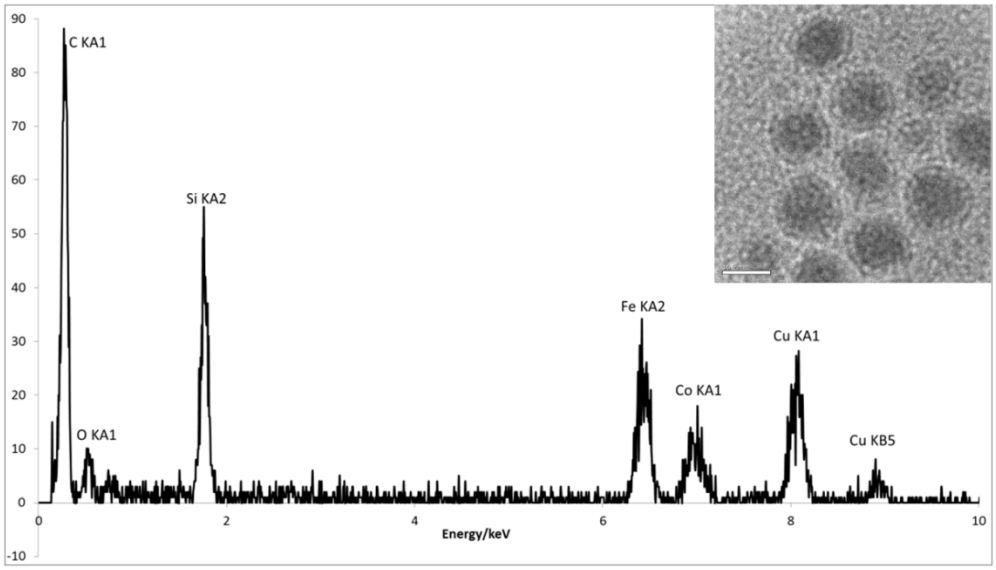

Figure S4 - EDS of Co@Fe_3O_4 at x300k magnification with a spot size of approximately 50 nm in diameter. Insert: TEM image of the region analysed using EDS (scale bar = 10 nm). The carbon and copper peaks are caused by the support (Cu grid, holey carbon film, 300 mesh, Agar Scientific), while the silicon peak is likely due to the detector window.

EFTEM

A series of EFTEM images of the fresh NPs were taken using electrons from a 10 eV window. The images corresponding to the core losses of Co (779 eV), Fe (708 eV) and O (532 eV) were then selected, producing dark field TEM images mapping the presence of Co, Fe and O in individual particles and giving preliminary indications of particle structure as a function of elemental composition. Figure S5 shows Co (top left), Fe (top right) and O (bottom left) maps. Particle shells are highlighted in Figure S5b and c, suggesting these to be Fe- and O-rich. In contrast, the Co map highlights particle cores. Figure S5 also shows a coloured overlay of the Fe and Co maps, in which Co-rich cores (green) surrounded by Fe-rich shells (pink) are clearly visible.

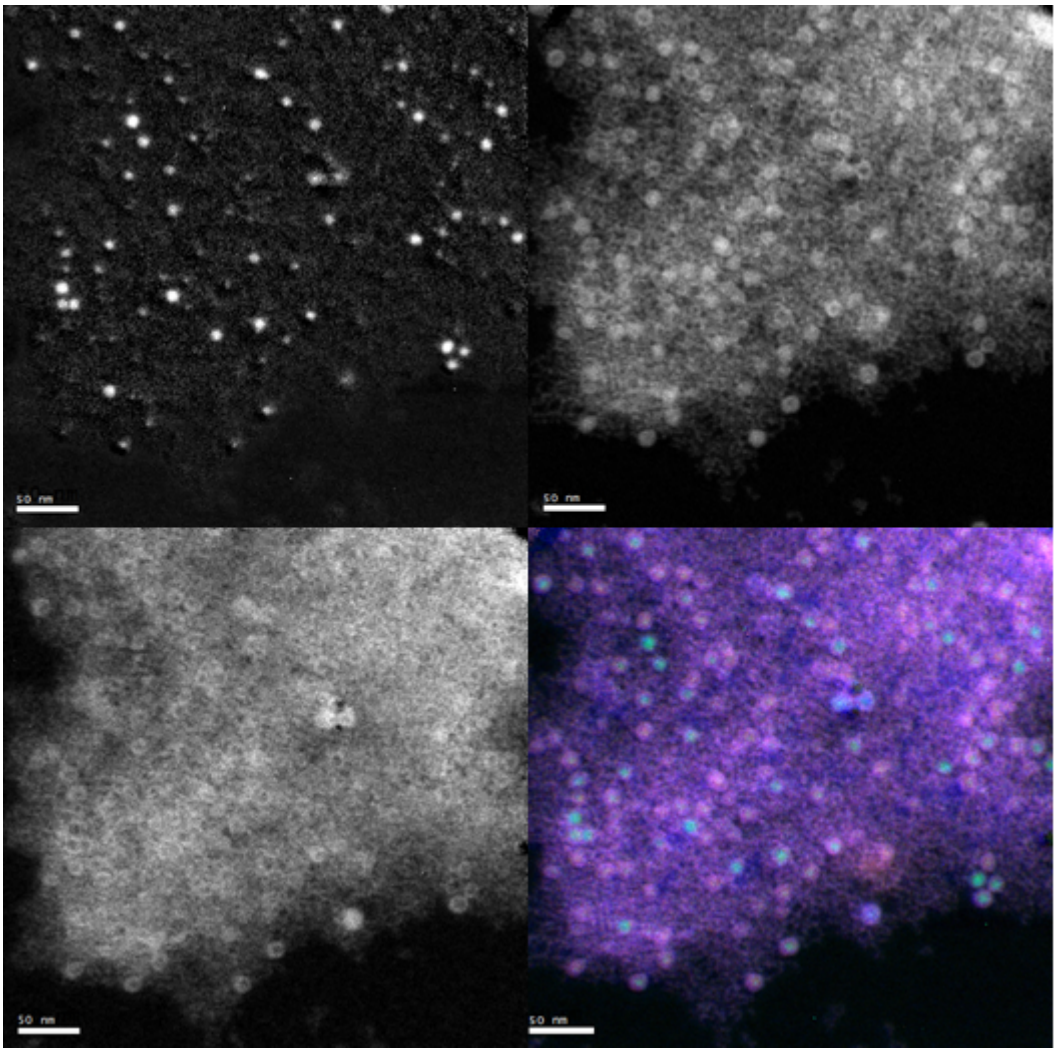

Figure S5 – A lower magnification version of Figure 5 (in the paper), showing Co, Fe and O maps as well as a composite image. Scale bars are 50 nm.

Line Profile Analysis

EELS

Paper Figure 10

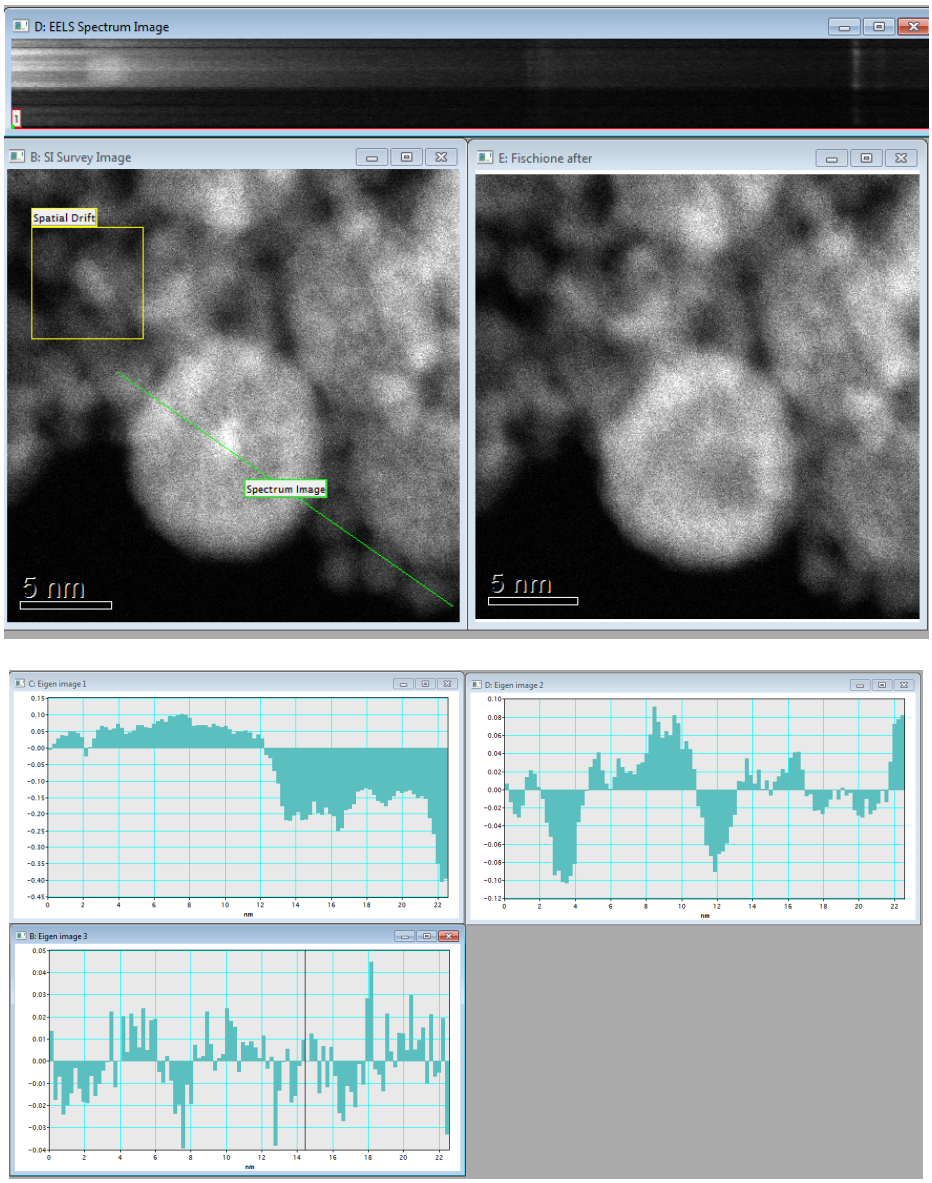

Figure S6 - Images of a particle (middle) before and after a line scan (Figure 10 in the paper) shown with the EELS spectrum image (top), and the eigenvalues (bottom) used in the MSA of the data.

Paper Figure 7

Figure S7 - Representations of the eigenvalues used in the MSA for Figure 7 in the paper.

EDS Mapping

EDS maps were acquired in STEM mode, recording a separate spectrum for each point/pixel scanned. These pixel scans could be summed to elucidate the elemental composition of a given region of the image. An EDS map recorded from an individual core@shell nanoparticle can be seen in Figure S8. The separate elemental maps are shown for O K, Fe K_α and Co K_α (Figure S8b, c and d, respectively). Figure S8 clearly shows a shell structure comprised of iron oxide, with an O-deficient region in the centre matching the strong Co signal observable in Figure S8d.

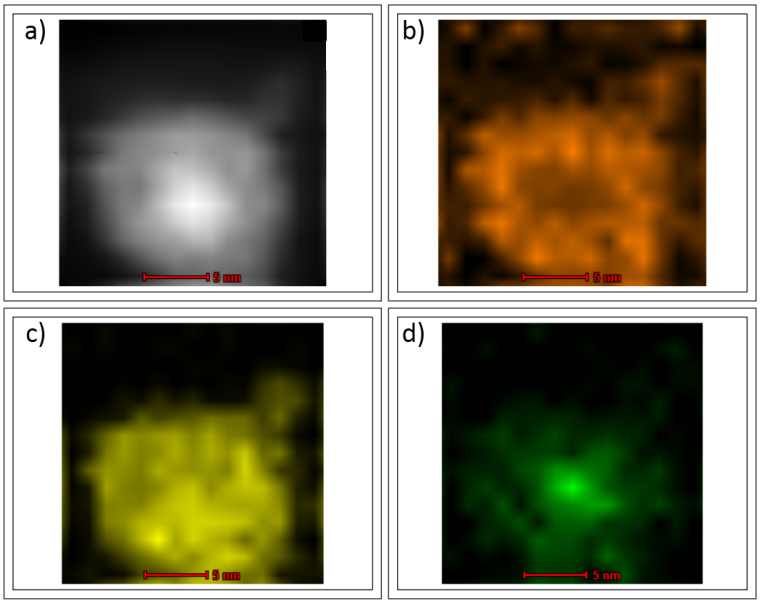

Figure S8. EDS map from the FEI Titan of an individual core@shell particle. a) STEM HAADF image; b) oxygen K map; c) Fe K_α map; d) Co K_α map. Scale bars are 5 nm.

EELS Point Scans

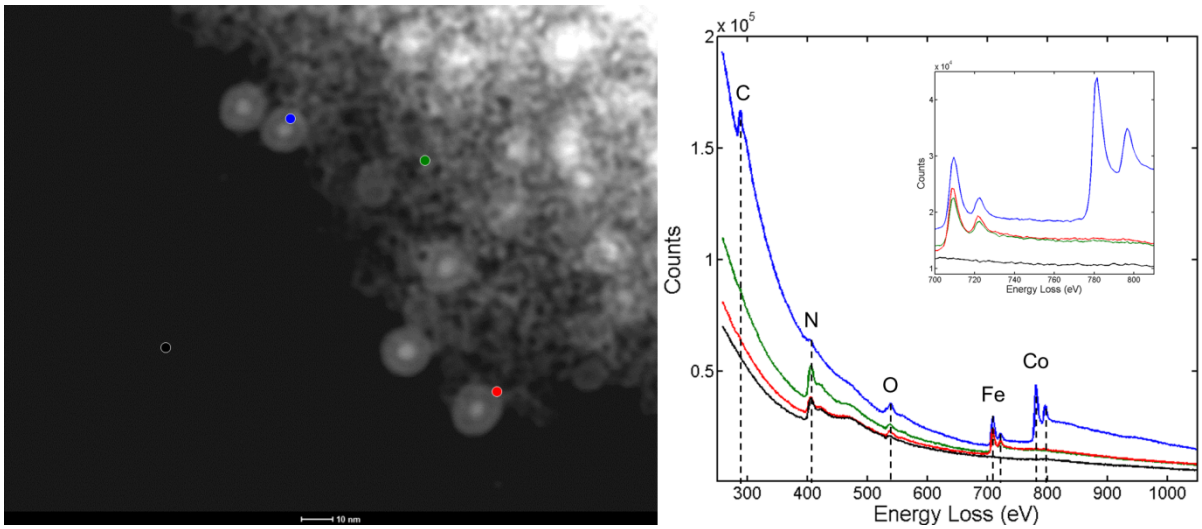

Figure S9 - EELS point scans showing that the composition of the small 2nm particles is identical to the shell of the core@shell particles, with the Fe $L_{2,3}$ edges indicating the Fe_3O_4 phase.