Supporting information

Composition and structure of magnetic high-temperature-phase, stable Fe-Au core-shell nanoparticles with zero-valent bcc Fe core

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Table S1: Average Fe content from EDXS measurements of single NPs with standard deviation σ, absolute error Δf, and variance σ².

| at% Au | Au₂₀Fe₈₀ | Au₅₀Fe₅₀ |
|--------|----------|----------|
| average | 22.6 | 50.3 |
| σ      | 2.4    | 6.2     |
| Δf     | 0.5    | 1.8     |
| σ²     | 6.0    | 38.5    |
| Number of NPs | 21 | 12 |

Table S2: quantified EDXS analyses of single NPs (average compositions) for comparison with the subshell approach. The absolute deviation is ±2.3 at% Au on average, calculated from row 4.

| Number of NP | C₁(Subshell approach) Au at% | C₂(Reference) Au at% | absolute Δc Au at% |
|--------------|-------------------------------|----------------------|-------------------|
| 1            | 62                            | 63                   | 0.9               |
| 2            | 52                            | 56                   | 4.0               |
| 3            | 51                            | 53                   | 1.6               |
| 4            | 43                            | 44                   | 1.3               |
| 5            | 52                            | 54                   | 2.0               |
| 6            | 77                            | 78                   | 1.0               |
| 7            | 84                            | 80                   | 4.0               |
| 8            | 83                            | 80                   | 3.0               |
| 9            | 76                            | 78                   | 2.0               |
| 10           | 69                            | 69                   | 0.0               |
| 11           | 71                            | 76                   | 5.0               |
| 12           | 71                            | 74                   | 3.0               |
| 13           | 76                            | 78                   | 2.0               |
Fig. S1: Sketch of the steps of FIB cross-section preparation of NPs. NPs are embedded in C-Matrix before standard lift-out preparation. At the tip of the lamella, a section is extracted from a core-shell (CS) NP.
Fig. S2: (Top row) HAADF-STEM Z-contrast images and (bottom rows) elemental maps for Au (Au-L$_{α1}$ line) and Fe (Fe-K$_{α1}$ line). The overlay of the Fe and Au signals illustrates the of an outermost Fe-containing (presence of a FeO$_x$) deposit on the CS and solid solution NPs, probably stemming from FeO$_x$ by-products present in the liquid before drying.
Fig. S3: EDXS spectrum of the position marked by an asterisk in Fig. 4. Chemical composition is quantified to be 100 at% Fe. Carbon and oxygen signal arises from the carbon matrix, that is needed to stabilize the sample during sample preparation.

Electron beam broadening was calculated by the Goldstein approach using Eq. (1), which yields the broadened beam diameter $d_f$ for an electron beam with an initial probe diameter $d_i$ and energy $E_0$ in keV after passing through a NP characterized by an average atomic number $Z_m$, an average atomic mass $A_m$, an average density $\rho_m$ in g cm$^{-3}$, and a sample thickness (NP diameter) $D$ in nm$^{-1}$. For our transmission electron microscope without aberration corrector, a probe diameter of $d_i=0.4$ nm is reasonable. For electron energy of 200 keV, Eq. (1) yields a broadened beam with $d_f=0.80$ nm for NPs with maximum diameter $D=29$ nm and nominal composition of Au$_{20}$Fe$_{80}$. Beam broadening up to 0.78 nm is expected for NPs with $D=23$ nm, and the average composition of Au$_{50}$Fe$_{50}$. Accordingly, the distance between two adjacent measuring points along EDXS line scans was chosen to be of 1 nm (i.e. larger than $d_f$-values) to avoid overlap of the EDXS signal recorded from two neighbor regions of the NP.
Fig. S4: HAADF-STEM Z-contrast image of the CS NP depicted in Fig. 3 d)-f).

Fig. S5: HRTEM (left) and Fast Fourier Transform (right) of NCS NPs, showing the polycrystalline shell.
Fig. S6: Overview HAADF-STEM Z-contrast image and representative size distribution for Au$_{50}$Fe$_{50}$ solid solution and CS NPs and respective LogNormal fit. Resulting average size ($\langle xc \rangle$) SoSo = 8 nm, CS = 19 nm.
Fig. S7: Overview HAADF-STEM Z-contrast image and representative size distribution of NCS and CS NPs from (Au$_{20}$Fe$_{80}$) and respective LogNormal fit. Resulting average size ($\langle x \rangle$) NCS = 16 nm, CS = 22 nm. Also, the sample contains SoSo NPs that are not shown in this graph.
Fig. S 8: HAADF-STEM Z-contrast image of NCS NPs with fragmented nested cores. Scale bars are 25 nm.

References

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