Supplementary Information File

Details of preparation conditions

The samples were prepared by thermal decomposition of the iron oleate or Fe(acac)₃ (acac = acetyl acetonate) precursors in the presence of the high boiling solvent (1-octadecene) and the oleic acid or oleylamine acting as stabilizers. The reaction was carried out under nitrogen atmosphere (argon atmosphere in case of the NP13 sample) in a round-bottomed flask of 0.5 L, equipped with a mechanical stirrer (PTFE centrifugal stirrer shaft, $\emptyset = 75$ mm) thermometer, entry for nitrogen flow and reflux condenser. The details of reaction conditions, namely the relative ratio of the concentration precursors and stabilizers, the heating rate and the stirring process are clearly summarized in Table S1. The NPs were coated with the dimercaptosuccinic acid (DMSA) by a ligand exchange process in order to obtain hydrophilic NPs.

Sample	Precursor	Stabilizers	1- octadecene (mL)	Stirring process	Temperature conditions
NP6, NP7	20 mmol of Fe(acac)3	60 mmol oleic acid; 60 mmol oleylamine; 100 mmol 1,2-dodecanediol	200	All time	1.5 °C/min to 200 °C (2 h), then 1°C/min to reflux at 265 °C (30 min)
NP15	15 mmol of Fe(acac) ₃	45 mmol oleic acid; 30 mmol 1,2-dodecanediol	150	All time	10 °C/min 30 min at 220 °C, then 1 °C/min to reflux at 280 °C (2 h)
NP13*, NP14	5 mmol of Fe(oleate) ₃	2.5 mmol oleic acid	50	Stopped at 50 °C	3 °C/min Refluxed at 315 °C (1 h)
NP18	5 mmol of Fe(oleate) ₃	2.5 mmol oleic acid	50	Stopped at 60 °C	1°C/min to 200 °C, then 4 °C/min until reflux at 315 °C (2 h)
NP10	5 mmol of Fe(oleate) ₃	2.5 mmol oleic acid	50	Stopped at 60 °C	1.5 °C/min to 200 °C (2 h), then 10°C/min to eflux at 300 °C (1 h)

Table S1: The preparation conditions of samples prepared by thermal decomposition:

*The NP13 sample was prepared under argon atmosphere, the other samples were prepared under nitrogen.

Characterization of the samples

= 18.2 nm dTEM N = 6.2 **NP18** NP6 TEM N 20 25 30 10 8 d (nm) d (nm) 13.0 nm 100 nm 40 nm 50 nm 12 14 d (nm)

Figure S1: The TEM images of selected samples, the histograms fitted with the number-weighted log-normal distribution in the insets.

Log-normal distribution function used for the refinement of the histograms of the TEM diameters has a form:

$$f_{\log-norm}(x) = \frac{1}{\sqrt{2\pi}x\sigma} \exp\left(-\frac{\ln^2\left(\frac{x}{x_0}\right)}{2\sigma^2}\right), x_m = x_0 \exp\frac{\sigma^2}{2}$$
(S1),

where *x* is the particle diameter in our case and σ is the distribution width, *x*₀ is the median diameter and *x*_m is the mean diameter.

Variance of log-normal function is then calculated as variance = $x^2_m(\exp \sigma^2 - 1)$ (S2).

Standard deviation SD of the log-normal distribution, the square root of the variance is:

$$SD = x_m \sqrt{(\exp \sigma^2 - 1)}$$
(S3)

SD is the error value for the x_m in the manuscript body.

For the PDI index calculation in the manuscript body, we used arithmetic SD as the standard deviation (SD_dTEM_N) and x_m as the mean particle diameter:

$$SD_{dTEM_N} = \sqrt{\sum_{i=1..N} p_i (x_i - x_m)^2}$$
 (S4),

where x_m is the mean diameter, x_i are individual NP diameters within the set and p_i is their 'probability of occurrence' in the log normal distribution of particle diameters

$$PDI = \left(\frac{SD_{dTEM}N}{x_m}\right)^2$$
(S5).

TEM

Mössbauer spectroscopy – hyperfine parameters

Table S2: The hyperfine parameters of the samples prepared by thermal decomposition determined at room temperature: the isomer shift, δ (range of error ~ 0.1 mm.s⁻¹); quadrupolar shift/splitting, $2\varepsilon/\Delta E_Q$ (range of error ~ 0.02 mm.s⁻¹); hyperfine field, B_{hf} , the full width at half maximum of the absorption peaks, *FWHM*, the distribution of the B_{hf} , $\sigma(B_{hf})$ and the relative areas together with the interpretation of the individual spectra.

	δ	$2\epsilon/AE_0$	$B_{ m hf}$	$FWHM/\sigma(B_{\rm bf})$	Area
	$(mm.s^{-1})$	(mm.s^{-1})	(T)		(%)
NP6	, , , , , , , , , , , , , , , , , , ,	· · · ·			
Para Fe ³⁺	0.35	-	-	2.92 ± 0.05	91±5
Fe^{3+} near T_B	0.35	-0.02	43.8 ± 0.2	0.35 ± 0.02	9±5
				$/10 \pm 1.0$	
NP7					
Fe^{3+} near T_B	0.34	-	-	2.48	-
NP10					
γ -Fe ₂ O ₃ $O_{\rm h}$	0.31	-0.05	44.7 ± 0.4	0.65 ± 0.02	35 ± 10
γ -Fe ₂ O ₃ T_{d}	0.41	0.0	36.7 ± 0.6	0.85 ± 0.10	61 ± 20
Fe^{3+} near T_B	0.33	-	-	11.30 ± 0.50	-
Para Fe ³⁺	0.41	0.70	-	0.40 ± 0.02	4 ± 5
NP13					
Fe^{3+} near T_B	0.36	-	-	10.95 ± 0.50	80 ± 15
Fe^{3+} near T_B	0.35	-0.02	40.0 ± 0.4	0.99 ± 0.10	20 ± 15
				$/10.7\pm0.6$	
NP14					
Fe^{3+} near T_B	0.45	-	-	13.48 ± 0.80	-
γ-Fe ₂ O ₃	0.42	-0.04	41.4 ± 0.6	0.50 ± 0.10	-
				$/8.5 \pm 1.0$	
NP15					
$Fe_3O_4 T_d$	0.33	-0.03	47.7 ± 0.2	0.44 ± 0.01	27 ± 10
Fe ₃ O ₄ O _h	0.52	0.01	44.4 ± 0.3	0.87 ± 0.03	53 ± 15
γ-Fe ₂ O ₃	0.31	0.00	49.1 ± 0.2	0.41 ± 0.01	20 ± 10
NP18					
$Fe_3O_4 T_d$	0.34	-0.01	46.2 ± 0.2	0.54 ± 0.02	22 ± 10
Fe ₃ O ₄ O _h	0.48	-0.02	42.6 ± 0.3	0.59 ± 0.03	43 ± 20
				$/4.2 \pm 0.5$	
γ-Fe ₂ O ₃	0.32	-0.02	48.3 ± 0.2	0.50 ± 0.02	35 ± 10
Fe^{3+} near T_B	0.36	-	-	6.30 ± 0.50	-

Comments: *FWHM* expressed in mm.s⁻¹, $\sigma(B_{hf})$ = distribution of B_{hf} expressed in T.

PXRD – strain analysis

Refinement of the microstrain peak broadening, represented by the pseudo-Voight function, is included in the full profile refinement within the Mstruct software, as is mentioned in the manuscript body. Hence it is refined simultaneously with other profile parameters. However; to demonstrate explicitly the level of microstrain ε present in the selected samples, we plotted Williamson-Hall plots of selected samples (Figure S2), assuming peak broadening due to the strain, β_{ε} is related to θ as $\beta_{\varepsilon} = C\varepsilon \tan\theta$.



Figure S2. Williamson-Hall plots of selected sample(s).



Figure S3: The ZFC-FC curves of selected samples performed at 10 mT.

Determination of the magnetic size, d_{mag}

For the real system of the superparamagnetic NPs with a size distribution, the magnetization, M of the NPs in the magnetic field, H can be written as a weighted sum of the Langevin functions [Ferrari1997]:

$$M(H,T) = \int_{0}^{\infty} \mu L\left(\frac{\mu H}{k_{\rm B}T}\right) f(\mu) d\mu + \chi_{\rm linear} H$$
(S6)

where $f(\mu)$ correspond to the unimodal log-normal distribution of the magnetic moments, μ expressed as:

$$f(\mu) = \frac{1}{\sqrt{2\pi}\mu\sigma} \exp\left(-\frac{\ln^2\left(\frac{\mu}{\mu_0}\right)}{2\sigma^2}\right), \quad \mu_m = \mu_0 \exp\frac{\sigma^2}{2}$$
(S7)

where σ is the distribution width, μ_0 and μ_m are the median and mean magnetic moment, respectively. The second term in the equation (S6) corresponds to additional linear contribution to the magnetization, which can originate from some diamagnetic or paramagnetic components of the sample (usually from the disordered parts of NPs). The parameters of $f(\mu)$ were obtained from the refinement of the magnetization isotherm measured above T_B in the Matlab/Octave software using equation (S6).

The median magnetic size, d_{mag} of the particle was calculated from the μ_0 using the expression:

$$d_{\rm mag} = \sqrt[3]{\frac{6\mu_0 a^3}{\mu_{\rm uc}\pi}}$$
(S8)

where *a* and μ_{uc} is the lattice parameter and the magnetic moment of the unit cell of the maghemite phase, respectively.

3D correlation plots

To show correlation of the particle diameters d_{TEM} and d_{XRD} with M_{s} , we constructed correlation plot for the data presented in the manuscript body. Simultaneous visualization of _{mag} shows that for the samples with $d_{\text{TEM}} \sim d_{\text{XRD}}$ and low M_{s} , d_{mag} is also lower than d_{TEM} or d_{XRD} . Importance of $d_{\text{TEM}}(d_{\text{XRD}})$ cross-correlation in magnetic response of samples is universal, as can be seen creating the correlation plot for old, already published data [Bittova2012, Pacakova2016]. See Figure S4.



Figure S4. 3D correlation plot of the data from the manuscript body (black dots as data and grey dots as projections into individual planes) together with the already published data on spinels - six CoFe₂O₄ NP samples [Bittova2012, Pacakova2016], nine γ -Fe₂O₃ NP samples [Repko2013, Bittova_Nano2012, Roca2009, Wortmann2014] and one MgFe₂O₄ NP sample [Holec2009] (blue dots representing data and yellow dots as projections into individual planes).

Simple model of effective anisotropy, K_{eff} for the core-shell particle.

In general, single particle energy barrier to rotation [1] is described by the anisotropy energy, $E_{\mathbf{A}}$ and is defined as:

$$E_{\rm A} = K_{\rm eff} V_{\rm NP},\tag{S9}$$

where K_{eff} is the particle effective anisotropy and V_{NP} is the particle volume. K_{eff} includes many contributions, such as the magneto-crystalline anisotropy, K_{C} , shape anisotropy and surface anisotropy, K_{S} . K_{eff} of the NP is size dependent and increases with increasing diameter, following the phenomenological formula (so-called finite size effect) for the spherical NPs:

$$K_{\rm eff} = K_{\rm C} + \frac{6K_{\rm S}}{d_{\rm NP}},\tag{S10}$$

where d_{NP} is the NP diameter.

For a core-shell NP (as is presented in the manuscript body), the single particle anisotropy energy E_A can be viewed as the sum of anisotropy energy of ordered core, E_A^{core} and disordered shell, E_A^{shell} :

$$E_{\mathbf{A}} = E_{\mathbf{A}}^{\text{core}} + E_{\mathbf{A}}^{\text{shell}}.$$
(S11)

Then individual energies of anisotropy can be written as:

$$E_{\rm A}^{\rm core} = (K_{\rm C}^{\rm core} + \frac{6K_{\rm S}^{\rm core}}{d_{\rm core}}) \times V_{\rm core},\tag{S12}$$

$$E_{\rm A}^{\rm shell} = \left(K_{\rm C}^{\rm shell} + \frac{6K_{\rm S}^{\rm shell}}{d_{\rm NP}}\right) \times V_{\rm NP} - \left(K_{\rm C}^{\rm shell} + \frac{6K_{\rm S}^{\rm shell}}{d_{\rm core}}\right) \times V_{\rm core}.$$
 (S13)

Putting equations S10, S11, S12 and S13 together, we get formula for the K_{eff} of single particle:

$$K_{\rm eff} = \frac{K_{\rm C}^{\rm core} V_{\rm core} + K_{\rm C}^{\rm shell} V_{\rm shell} + K_{\rm S}^{\rm core} S_{\rm core} + K_{\rm S}^{\rm shell} (S_{\rm NP} - S_{\rm core})}{V_{\rm NP}},$$
 (S14)

where V_{shell} is the shell volume, $V_{\text{shell}} = V_{\text{NP}} - V_{\text{core}}$, S_{core} and S_{NP} is the surface of the NP core or NP itself.



Figure S5: Evolution of the K_{eff} with increasing NP core.

Using the diameter of whole NP and core, we finally get relation:

$$K_{\rm eff} = K_{\rm C}^{\rm core} \frac{d_{\rm core}^3}{d_{\rm NP}^3} + K_{\rm C}^{\rm shell} \frac{(d_{\rm NP}^3 - d_{\rm core}^3)}{d_{\rm NP}^3} + 6K_{\rm S}^{\rm core} \frac{d_{\rm core}^2}{d_{\rm NP}^3} + 6K_{\rm S}^{\rm shell} \frac{1}{d_{\rm NP}} - 6K_{\rm S}^{\rm shell} \frac{d_{\rm core}^2}{d_{\rm NP}^3}.$$
 (S15)

To be consistent with the core-shell model and introduced disorder parameter, magnetic diameter d_{MAG} represents magnetically perfectly aligned core, hence $d_{\text{core}} = d_{\text{MAG}}$ and $d_{\text{TEM}} = d_{\text{NP}}$. $K_{\text{eff}}(d_{\text{MAG}}/d_{\text{TEM}})$ dependence scaled as $K_{\text{eff}}(1) = 1$ is plotted in the manuscript body (Figure 6).

Example for the real core-shell particle with $K_{\rm C}^{\rm core} = 2.7 \times 10^5 \,{\rm J/m^{-3}}$ and $K_{\rm S}^{\rm core} = 6.5 \times 10^{-3} \,{\rm J/m^{-2}}$ is depicted in Figure S8. Particle shell is viewed as the completely disordered, hence $K_{\rm C}^{\rm shell} = K_{\rm S}^{\rm shell} = 0$.

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