Towards the design of contrast-enhanced agents: systematic Ga^{3+} doping on magnetite nanoparticles

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Figure S1. Thermogravimetric curves of the $Fe_{3-x}Ga_xO_4$ ($0.15 \leq x \leq 1.35$) samples at 10 ºC/min.

Figure S2. Rietveld refinements for samples **a)** $Fe_{2.85}Ga_{0.15}O_4$**, b)** $Fe_{2.7}Ga_{0.3}O_4$**, c)** $Fe_{2.55}Ga_{0.45}O_4$**, d)** $Fe_{2.43}Ga_{0.57}O_4$**, e)** $Fe_{1.95}Ga_{1.05}O_4$. The experimental diffractogram is represented with red dots, the calculated one with a black line and the difference between them in blue.

Figure S3. Fit of M(H) curves at R.T. for $Fe_{2.73}Ga_{0.27}O_4$, $Fe_{2.55}Ga_{0.45}O_4$, $Fe_{2.43}Ga_{0.57}O_4$, and $Fe_{1.65}Ga_{1.35}O_4$ samples by the SPM model.

Figure S4. Magnetic susceptibility (ZFC and FC) measured at 10 Oe and derivative $d(\chi_{FC}-\chi_{ZFC})/dT$ of (a) $Fe_{2.86}Ga_{0.14}O_4$, (b) $Fe_{2.73}Ga_{0.27}O_4$, (c)$Fe_{2.42}Ga_{0.54}O_4$, (d) $Fe_{2.43}Ga_{0.57}O_4$, (e) $Fe_{1.95}Ga_{1.05}O_4$ and (f) $Fe_{1.65}Ga_{1.35}O_4$.

Figure S5. Hydrodinamic diameters of (a) $Fe_{2.86}Ga_{0.14}O_4$, (b) $Fe_{2.73}Ga_{0.27}O_4$ and (c)$Fe_{2.42}Ga_{0.54}O_4$ nanoparticle functionalized with PMAO samples measured by DLS in 0.05 mg sample/mL water dispersions.

Table S1. Table S1. Amounts of used reagents, iron(III) acetylacetonate ($Fe(acac)_3$), gallium(III) acetylacetonate ($Ga(acac)_3$), oleic acid, oleylamine, 1,2-hexadecanediol and benzyl solvent volume and poly(maleic anhydride-alt-1-octadecene) (PMAO).

Table S2. Parameters obtained from the deconvolution of (311) and (400) diffraction peaks of Ga doped magnetite and crystallite size using Scherrer equation.

Table S3. Summary of crystallographic data and Rietveld refinement details for samples $Fe_{2.86}Ga_{0.14}O_4$, $Fe_{2.73}Ga_{0.27}O_4$, $Fe_{2.42}Ga_{0.54}O_4$, $Fe_{2.43}Ga_{0.57}O_4$, $Fe_{1.95}Ga_{1.05}O_4$ and $Fe_{1.65}Ga_{1.35}O_4$.

Table S1. Amounts of used reagents, iron(III) acetylacetonate ($Fe(acac)_3$), gallium(III) acetylacetonate ($Ga(acac)_3$), oleic acid, oleylamine, 1,2-hexadecanediol and benzyl solvent volume and poly(maleic anhydride-alt-1-octadecene) (PMAO).

Sample	$Fe(acac)_3$ (mmol)	$Ga(acac)_3$ (mmol)	1,2-Hexadecanediol (mmol)	Oleic acid (mmol)	Oleylamine (mmol)	Benzyl eter (ml)	PMAO (mmol)
$Fe_{2.85}Ga_{0.15}O_4$	1.9	0.1	8	4	4	25	0.081
$Fe_{2.7}Ga_{0.3}O_4$	1.8	0.2	8	4	4	25	0.093
$Fe_{2.55}Ga_{0.45}O_4$	1.8	0.3	8	4	4	25	-
$Fe_{2.43}Ga_{0.57}O_4$	1.6	0.4	8	4	4	25	0.069
$Fe_{1.95}Ga_{1.05}O_4$	1.3	0.7	8	4	4	25	-
$Fe_{1.65}Ga_{1.35}O_4$	1.1	0.9	8	4	4	25	-

Crystalline size of samples using Scherrer equation

The crystalline sizes of $Fe_{3-x}Ga_xO_4$ ($0.15 \leq x \leq 1.35$) samples have been calculated by the deconvolution of the (311) and (400) diffraction peaks of magnetite, using the Scherrer equation (S1):

$$D = \frac{K\lambda}{B_{estruc.}\cos\theta} = \qquad \text{(S1)}$$

Where K is the shape factor (0.85-0.95), $B_{structure} = B_{observed}-B_{instrumental}$ is the full width at half maximum, λ is the X-ray wavelength used (($K\alpha_1+K\alpha_2$)/2=1.5418Å), and θ is the peak position.

Table S2a. Parameters obtained from the deconvolution of (311) of Ga doped magnetite and crystallite size using Scherrer equation.

Sample	Diffraction peak	B obs. (°2θ)	B inst. (°2θ)	B estruc. (°2θ)	Peak pos. (°2θ)	Crystalline size [nm]*
$Fe_{2.86}Ga_{0.14}O_4$	311	1.803	0.100	1.703	43.359	5.0± 0.3
$Fe_{2.73}Ga_{0.27}O_4$	311	1.757	0.100	1.657	35.702	5.0±0.3
$Fe_{2.55}Ga_{0.45}O_4$	311	1.803	0.100	1.703	35.632	4.9±0.3
$Fe_{2.42}Ga_{0.57}O_4$	311	1.336	0.100	1.236	35.686	6.8±0.3
$Fe_{1.95}Ga_{1.05}O_4$	311	1.076	0.100	0.976	35.674	8.6±0.4
$Fe_{1.65}Ga_{1.35}O_4$	311	1.366	0.100	1.266	35.615	6.6±0.4

**The deviation of the size has been obtained using K= 0.85-0.95*

Table S2b. Parameters obtained from the deconvolution of (400) of Ga doped magnetite and crystallite size using Scherrer equation.

Sample	Diffraction peak	B obs. (°2θ)	B inst. (°2θ)	B estruc. (°2θ)	Peak pos. (°2θ)	Crystalline size [nm]*
$Fe_{2.86}Ga_{0.14}O_4$	400	1.745	0.100	1.645	43.242	5.2±0.3
$Fe_{2.73}Ga_{0.27}O_4$	400	1.518	0.100	1.467	43.383	6.0±0.4
$Fe_{2.55}Ga_{0.45}O_4$	400	1.567	0.100	1.418	43.351	5.8±0.4
$Fe_{2.42}Ga_{0.57}O_4$	400	1.209	0.100	1.109	43.359	7.6±0.4
$Fe_{1.95}Ga_{1.05}O_4$	400	1.035	0.100	0.935	43.357	9.1±0.6
$Fe_{1.65}Ga_{1.35}O_4$	400	1.333	0.100	1.233	43.274	7.0±0.4

**The deviation of the size has been obtained using K= 0.85-0.95*

Table S2c. Average crystallite size obtained from deconvolution of (311) and (400) diffraction peaks.

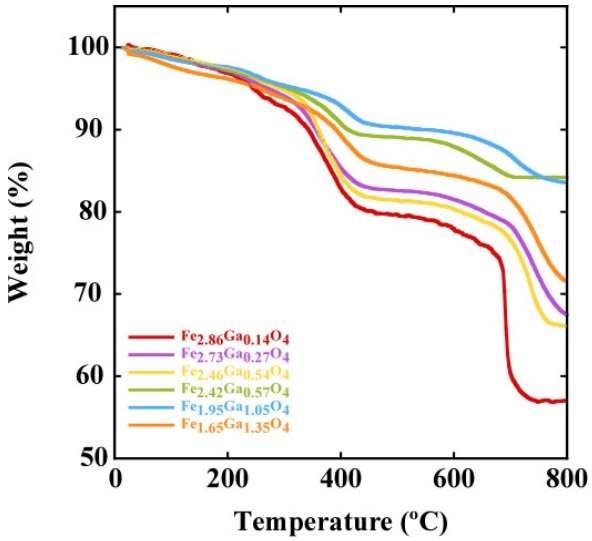
Sample	$Fe_{2.86}Ga_{0.14}O_4$	$Fe_{2.73}Ga_{0.27}O_4$	$Fe_{2.55}Ga_{0.45}O_4$	$Fe_{2.42}Ga_{0.57}O_4$	$Fe_{1.95}Ga_{1.05}O_4$	$Fe_{1.65}Ga_{1.35}O_4$
Average Crystalline size [nm]	5 (1)	6 (1)	6 (1)	7 (1)	9 (1)	7 (1)

Rietveld Refinements

The line shape of the diffraction peaks was generated by a pseudo-Voigt function and the background interpolated between some fixed background points of the diagrams. In the final run the following parameters were refined: unit-cell parameters, zero-point, half-width, symmetry parameters, scale factor, atomic coordinates and thermal isotropic factors.

Table S2. Summary of crystallographic data and Rietveld refinement details for samples $R_p = 100\sum|y_{oi} - y_{ci}|/\sum|y_{oi}|$ the pattern factor R-factor, $R_{wp} = 100\{\sum w_i(y_{oi} - y_{ci})^2/\sum w_i(y_{oi})^2\}^{1/2}$ the weighted pattern R-factor, $R_{exp} = 100\{(N - P + C)^2/\sum w_i(y_{oi})^2\}^{1/2}$ the expected pattern R factor, $R_B = 100\sum|I_{obs} - I_{calc}|/\sum I_{obs}$ Bragg factor, $\chi^2 = 1/N\sum_i(y_{ci} - y_{oi})^2/\sigma^2(y_{oi})^2$ where y_{oi} is the observed intensity at the *i*th step, y_{ci} is the calculated intensity, w_i is the weighting factor, N total number of data points 'observations', P is the number of parameters adjusted and C the number of constraints applied.

	$Fe_{2.86}Ga_{0.14}O_4$	$Fe_{2.73}Ga_{0.27}O_4$	$Fe_{2.55}Ga_{0.45}O_4$	$Fe_{2.42}Ga_{0.57}O_4$	$Fe_{1.95}Ga_{1.05}O_4$	$Fe_{1.95}Ga_{1.05}O_4$
Space Group	F d-3m	F d-3m	F d-3m	F d-3m	F d-3m	F d-3m
a =b= c	8.376(4)	8.379(3)	8.375(3)	8.374(5)	8.358(2)	8.3(2)
V (Å^3)	587.6(4)	588.4(3)	587.5(3)	587.3(3)	583.9(2)	584.4(3)
R_p	57	45.3	34.1	53.2	42.4	51
R_{wp}	51	45.6	34.3	50.6	44.3	46
R_e	35	40.9	35.6	34.9	28	38
χ^2	2.15	1.24	0.93	2.1	2.5	1.4
R_B	18.5	19.4	9.21	13.8	14.5	12.6



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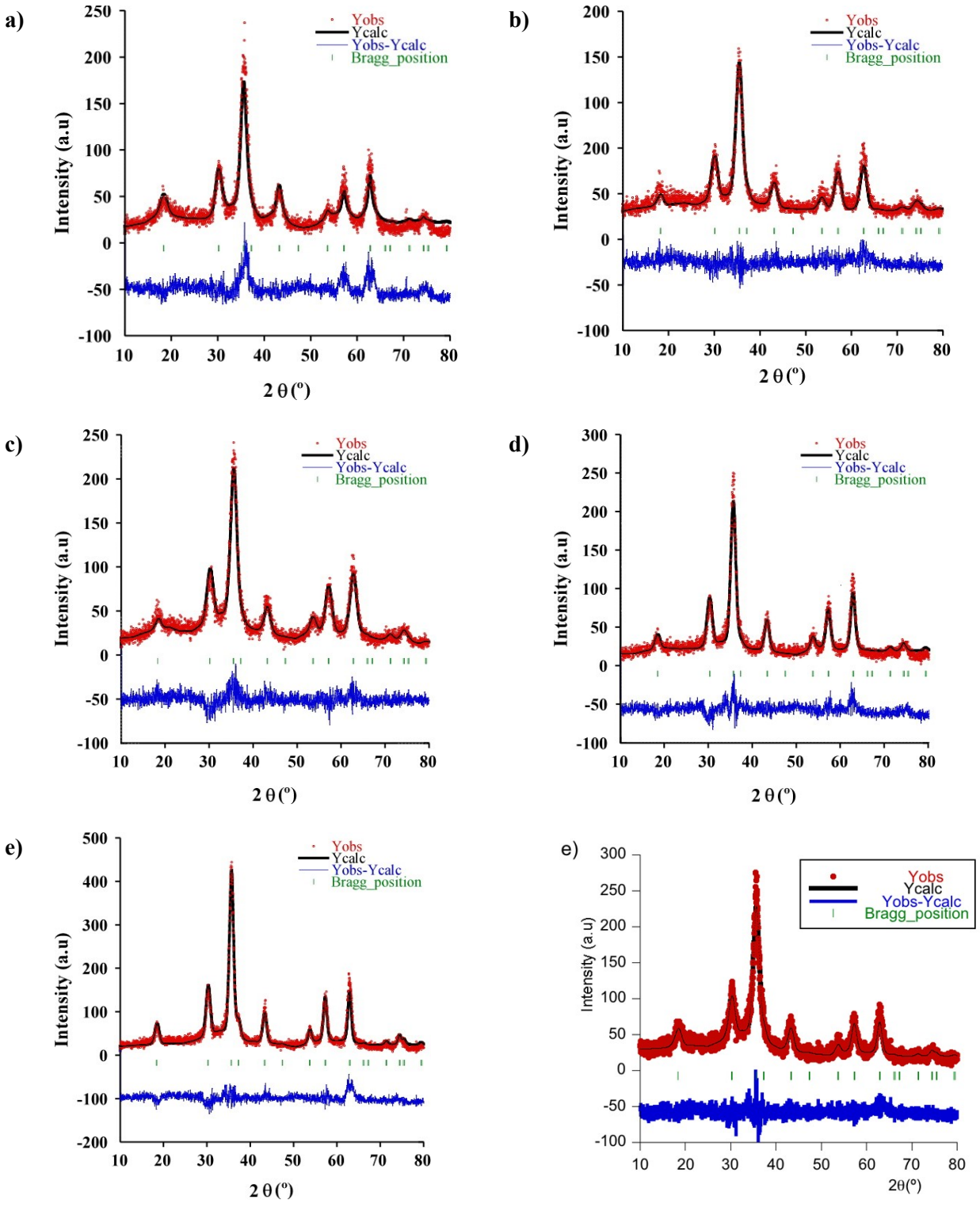

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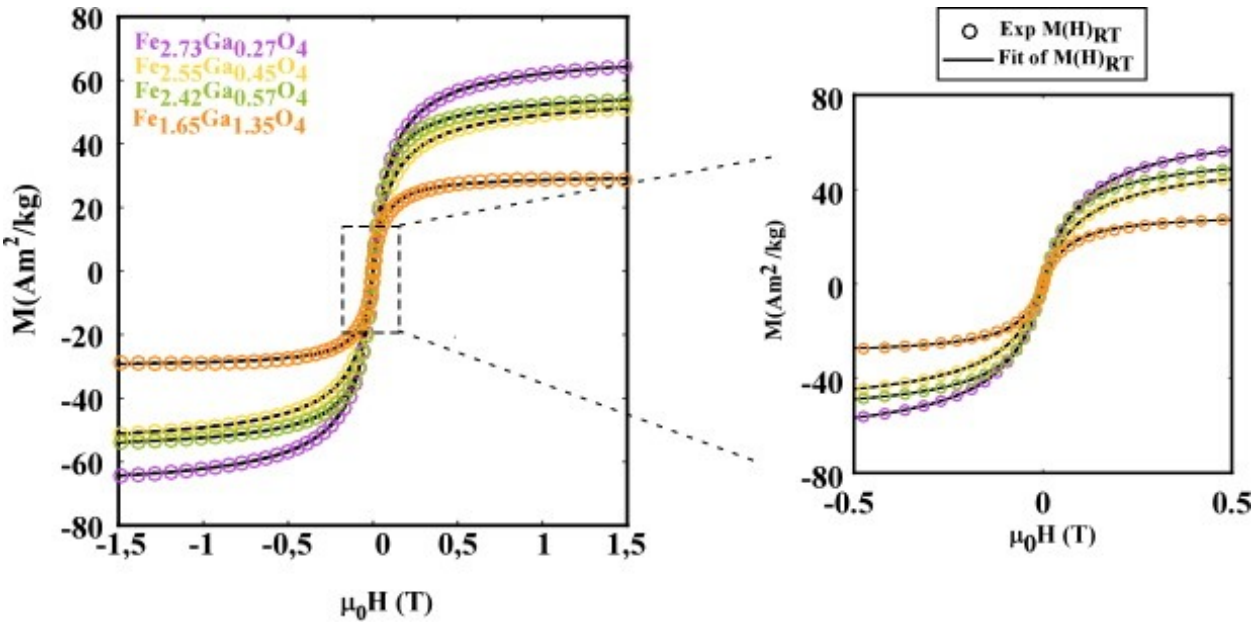

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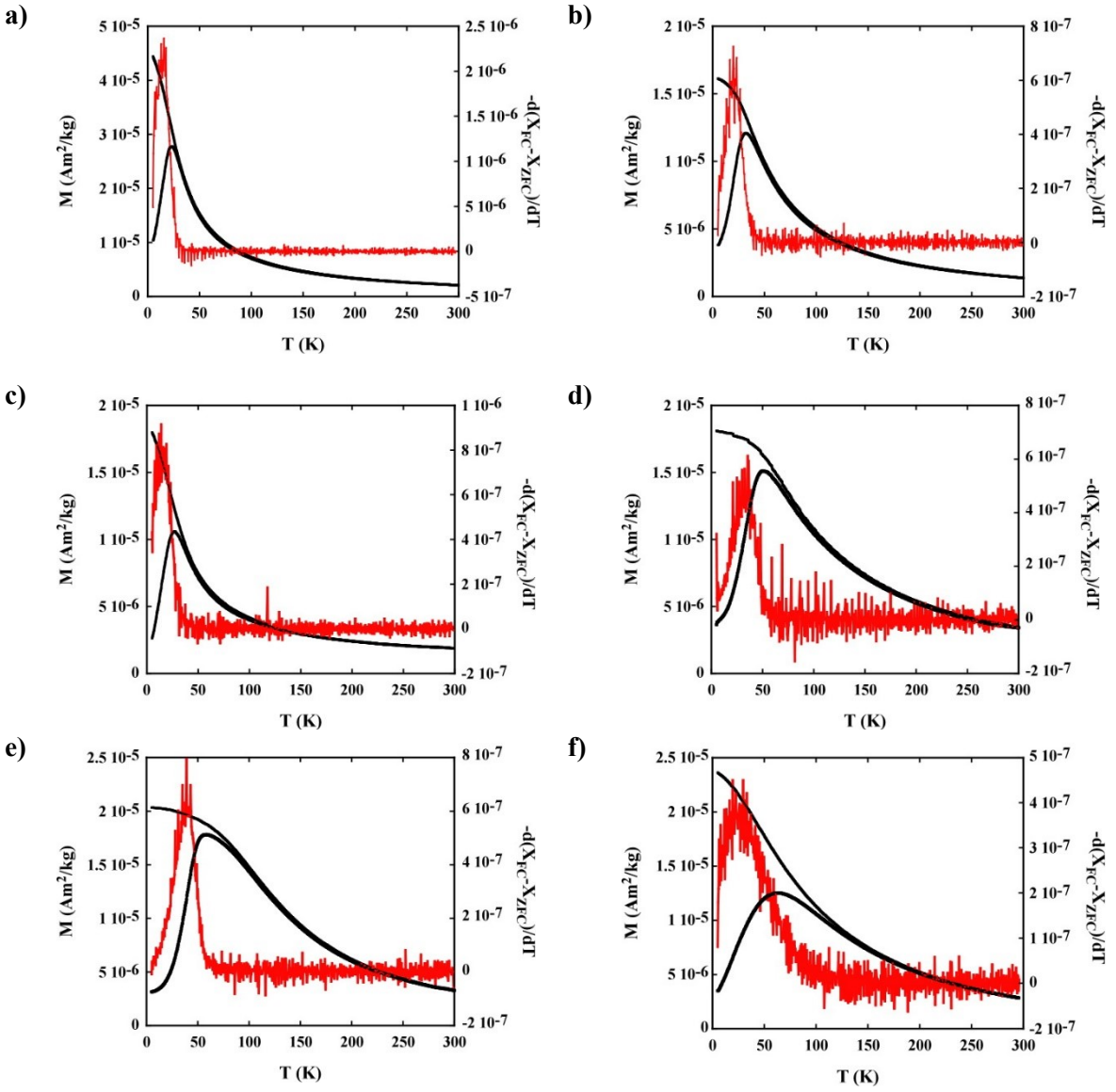

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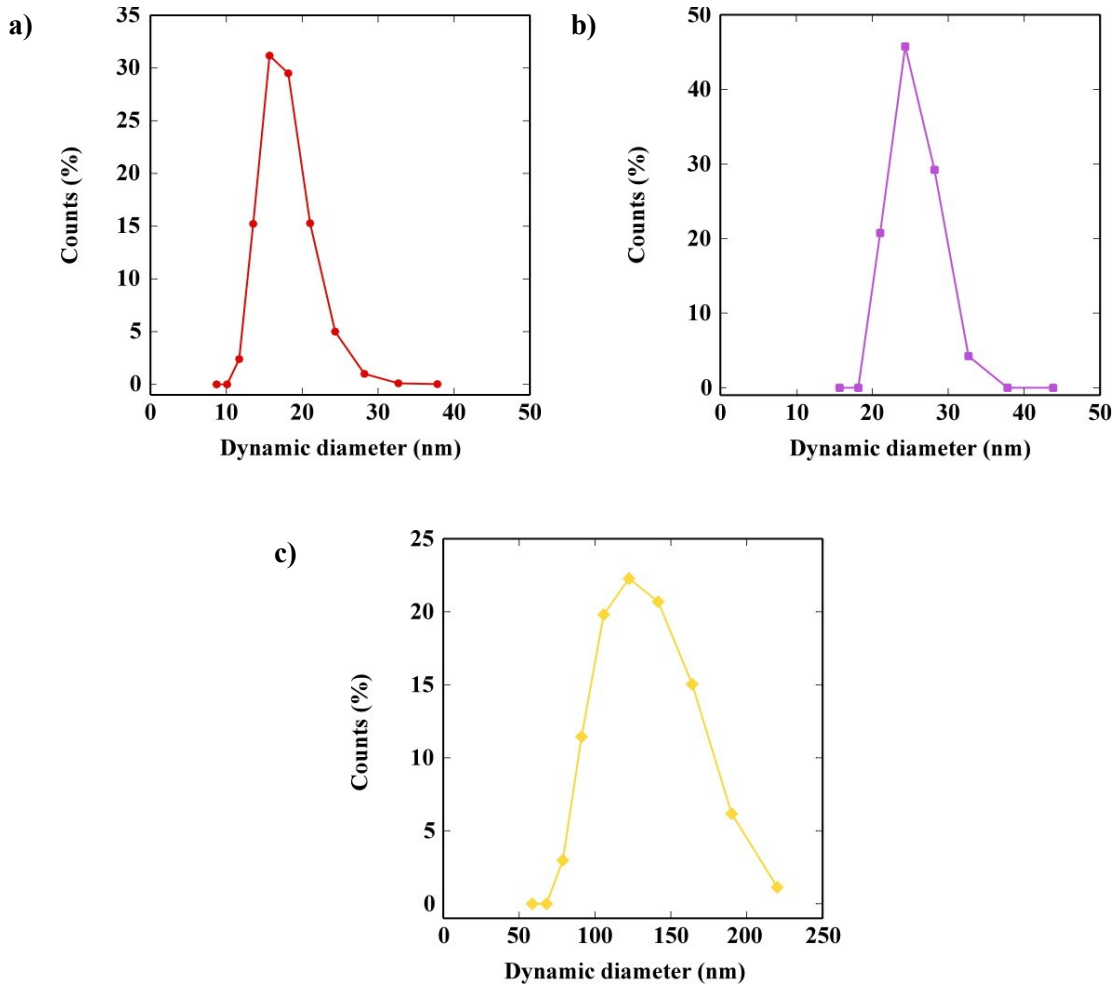

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