



Progress toward Room-Temperature Synthesis and Functionalization of Iron-Oxide Nanoparticles

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Supplementary Figures

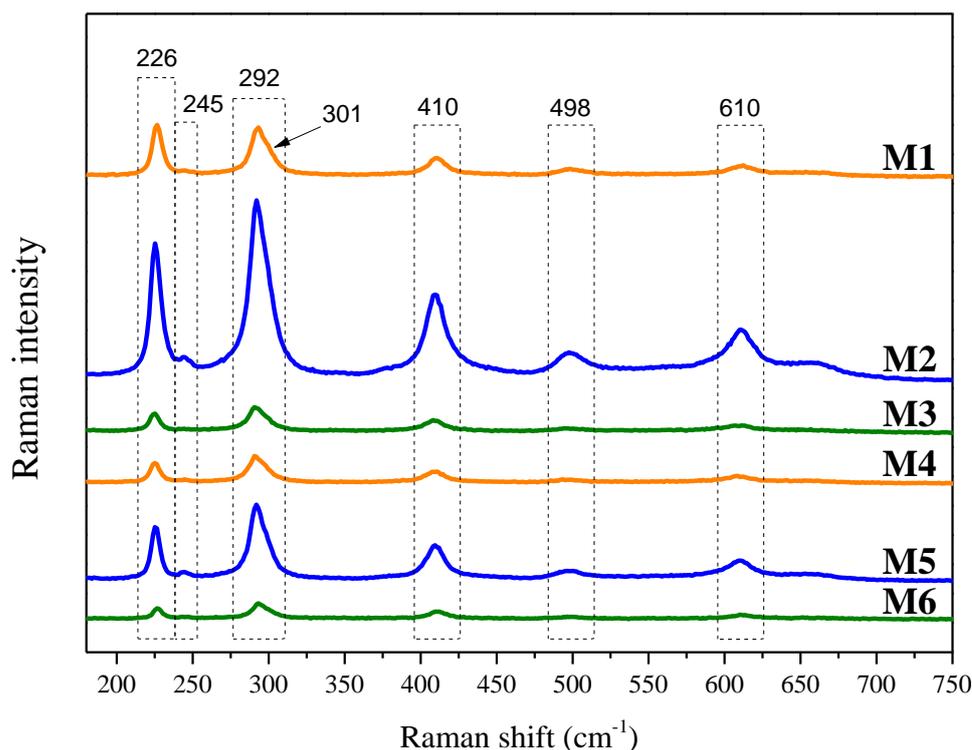


Figure S1. Raman spectra at 8.28 mW after the burning of the M1-M6 samples. The apparent band positions are indicated in cm⁻¹.

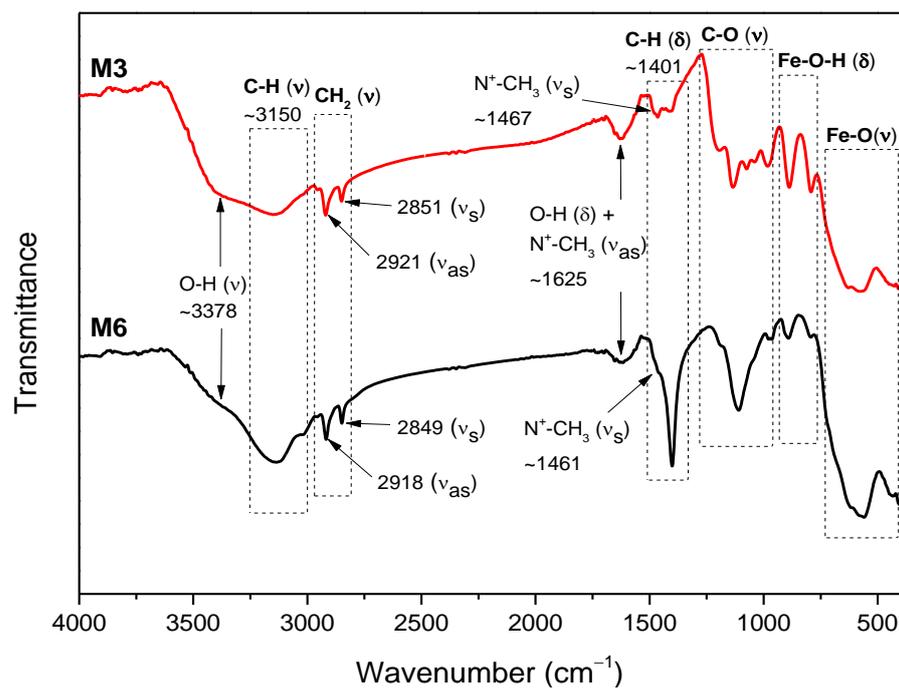


Figure S2. FTIR spectra of the M3 and M6 samples. The peaks positions are indicated in cm^{-1} .

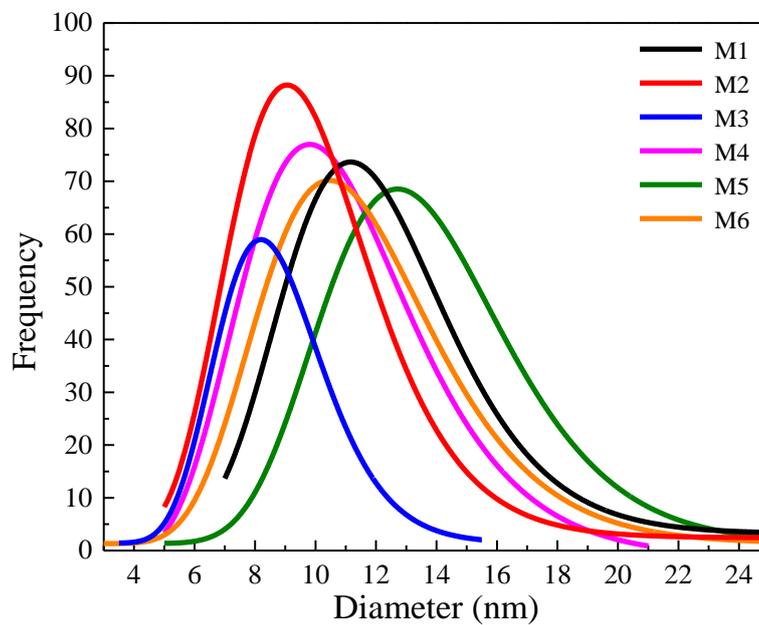


Figure S3. PSD for the M series samples.

Supplementary Tables

Table S1. Refinement and statistical parameters, R_p (%) as profile refinement, R_{wp} (%) (weighted profile residual), R_{exp} (%) as expected profile residual, and Goodness of fit, χ^2 , of the refined samples M1-M6.

Samples	Phases	Cagliotti Parameters			Lattice Parameters (Å)	Statistical Parameters
		U	V	W		
M1	γ -Fe ₂ O ₃	0.83	-0.57	0.36	a = b = c = 8.40 $\alpha = \beta = \gamma = 90^\circ$	$R_p = 73.87$ $R_{wp} = 32.74$
	α -FeOOH	1.08	-1.08	0.21	a = 4.63, b = 10.03 c = 3.04 $\alpha = \beta = \gamma = 90^\circ$	$R_{exp} = 29.34$ $\chi^2 = 1.24$
M2	γ -Fe ₂ O ₃	0.80	-0.80	0.25	a = b = c = 8.41 $\alpha = \beta = \gamma = 90^\circ$	$R_p = 63.81$ $R_{wp} = 30.25$
	α -FeOOH	0.42	-0.07	0.95	a = 4.59, b = 10.00 c = 3.03 $\alpha = \beta = \gamma = 90^\circ$	$R_{exp} = 29.48$ $\chi^2 = 1.05$
M3	γ -Fe ₂ O ₃	0.44	-0.36	0.14	a = b = c = 8.41 $\alpha = \beta = \gamma = 90^\circ$	$R_p = 66.39$ $R_{wp} = 36.72$
	α -FeOOH	0.38	-0.47	0.33	a = 4.65, b = 10.03 c = 3.04 $\alpha = \beta = \gamma = 90^\circ$	$R_{exp} = 36.15$ $\chi^2 = 1.03$
M4	γ -Fe ₂ O ₃	0.13	-0.27	0.17	a = b = c = 8.41 $\alpha = \beta = \gamma = 90^\circ$	$R_p = 99.14$ $R_{wp} = 41.73$
	α -FeOOH	0.24	-0.37	0.17	a = 4.63, b = 10.05 c = 3.04 $\alpha = \beta = \gamma = 90^\circ$	$R_{exp} = 41.69$ $\chi^2 = 1.00$
M5	γ -Fe ₂ O ₃	0.24	-0.37	0.17	a = b = c = 8.40 $\alpha = \beta = \gamma = 90^\circ$	$R_p = 108.75$ $R_{wp} = 47.57$
	α -FeOOH	0.24	-1.71	1.04	a = 4.63, b = 10.05 c = 3.04 $\alpha = \beta = \gamma = 90^\circ$	$R_{exp} = 45.85$ $\chi^2 = 1.08$
M6	γ -Fe ₂ O ₃	0.63	-0.36	0.24	a = b = c = 8.40 $\alpha = \beta = \gamma = 90^\circ$	$R_p = 93.58$ $R_{wp} = 42.42$
	α -FeOOH	1.42	-0.41	0.81	a = 4.59, b = 10.00 c = 3.03 $\alpha = \beta = \gamma = 90^\circ$	$R_{exp} = 38.85$ $\chi^2 = 1.19$

Table S2. Microstructural parameters of the samples M1-M6. D_{XRD} is the mean crystallite diameter.

Samples	Phases	D_{XRD} (nm)	Microstrain (%)	Phase contribution (%)
M1	γ -Fe ₂ O ₃	8.90	42.27	90
	α -FeOOH	14.31	48.23	10
M2	γ -Fe ₂ O ₃	9.67	41.64	95
	α -FeOOH	4.81	78.95	5
M3	γ -Fe ₂ O ₃	7.72	32.75	81
	α -FeOOH	13.91	28.61	19
M4	γ -Fe ₂ O ₃	10.27	16.68	100
M5	γ -Fe ₂ O ₃	12.21	27.66	90
	α -FeOOH	12.33	22.72	10
M6	γ -Fe ₂ O ₃	10.33	48.08	91
	α -FeOOH	10.60	179.86	9

Table S3. Raman shift values of the vibrational modes of each phase of the M1-M6 samples at different laser power values.

Sample	Laser power (mW)	Raman shift (cm ⁻¹)			
		γ -Fe ₂ O ₃	α -FeOOH	α -Fe ₂ O ₃	PSS
M1	4.14	372, 498, 674	244, 299	-	1130
	8.28	365, 491, 690	247, 305	616	1045, 1130
M2	4.14	369, 492, 680	-	-	
	8.28	487, 671	-	217, 281, 391, 601	
M3	0.41	356, 502, 690	308, 384	-	
	0.83	370, 514, 692	250, 304, 389	-	
M4	0.41	366, 503, 681	-	-	1123, 1598
	0.83	350, 500, 690	-	-	1123, 1596
M5	0.83	371, 495, 693	243, 303	-	
	4.14	351, 492, 687	-	220, 288	
M6	0.41	355, 490, 683	255, 300, 385	-	
	0.83	355, 489, 680	250, 302, 385	-	

Table S4. Estimated positions of the observed vibration bands at each type of functionalized nano γ -Fe₂O₃ sample.

Wavenumber (cm ⁻¹)			Assigned bands	References
@PSS	@OA	@CTAB		
3390	3384	3378	O-H stretching vibrations	[33,57,58]
3124	3156	3150	C-H stretching vibrations	[37]
2916	-	2921, 2918	CH ₂ asymmetrical stretch	[31,38,39]
2851	-	2851, 2849	CH ₂ symmetrical stretch	[31,38,39]
-	1661	-	C=O	[33]
1619	1661	1625	O-H bending	[14,34]
		1625	N ⁺ -CH ₃ asymmetrical vibration	[39]
	1568, 1565		COO asymmetrical stretch	[33,34]
		1467	N ⁺ -CH ₃ symmetrical vibration	[39]
	1402, 1413		COO symmetrical stretch	[33,34]
1400	1402, 1413	1401	C-H bending vibration + N bonded ion groups	[40]
1007, 1037, 1124, 1180, 1128	-	-	-SO ₃ stretching vibrations	[30–32]
-	1046, 1126, 1278, 1281	981, 1040, 1075, 1109, 1135, 1193, 1200	C-O stretching vibrations	[14,37,39,42]
795, 890	788, 791, 889	793, 887	Fe-O-H bending vibration	[27–29]
437, 567, 630	438, 565, 630	432, 562, 629	Fe-O stretching vibrations	[25,26]

Table S5. Hyperfine parameters for the M series recorded at RT. RAA: relative spectral absorption area; δ : isomer shift vs Fe at 300K; B_{hf}: Magnetic hyperfine field; Q: quadrupole splitting; σ : width of Gaussian distribution of B_{hf}; log γ_1 , log γ_2 : ¹⁰log of fluctuation rates (see main text); W: Lorentzian width (fixed). Spectra of M4, M5, and M6 reveal an additional doublet component of very fast fluctuating spins.

		RAA (%)	δ (mm/s)	B _{hf} (T)	Q (mm/s)	σ (T)	log γ_1	log γ_2	W (mm/s)
M1	γ -Fe ₂ O ₃ A	15	0.17	48.2	0	1.7			0.24
	γ -Fe ₂ O ₃ B	25	0.40	48.2	0	1.7			0.24

	α -FeOOH	6	0.37	36.0	-0.26	1.5			0.24
	Rel 1	11	0.30	45	0		9.1	7.6	0.24
	Rel 2	42	0.44	44	0.3		8.2	8.0	0.24
M2	γ -Fe ₂ O ₃ A	12	0.17	46.9	0	2.1			0.24
	γ -Fe ₂ O ₃ B	21	0.40	46.9	0	1.9			0.24
	α -FeOOH	5	0.37	34.0	-0.26	4.6			0.24
	Rel 1	14	0.38	45.0	0		9.2	7.9	0.24
	Rel 2	48	0.43	44.0	0.15		8.2	8.0	0.24
M3	Sextet	1	0.40	35	0	1.5			0.24
	Rel 1	20	0.38	48	0		8.4	7.9	0.24
	Rel 2	79	0.29	48	0		8.6	8.4	0.24
M4	γ -Fe ₂ O ₃ A	12	0.17	47.2	0	1.9			0.24
	γ -Fe ₂ O ₃ B	20	0.40	47.2	0	2.6			0.24
	α -FeOOH	2	0.37	38.0	-0.26	0.8			0.24
	Rel 1	11	0.31	45.0	0		9.2	7.8	0.24
	Rel 2	54	0.44	44.0	0.25		8.2	8.0	
	Doublet	2	0.32		0.39				0.21
M5	γ -Fe ₂ O ₃ A	11	0.17	47.4	0	1.9			0.24
	γ -Fe ₂ O ₃ B	19	0.40	47.4	0	2.0			0.24
	α -FeOOH	7	0.37	36.0	-0.26	6.3			0.24
	Rel 1	8	0.31	45.0	0		9.2	7.8	0.24
	Rel 2	54	0.44	44.0	0.15		8.3	8.1	0.24
	Doublet	2	0.32		0.39				
M6	γ -Fe ₂ O ₃ A	14	0.17	48.1	0	1.9			0.24
	γ -Fe ₂ O ₃ B	24	0.40	48.1	0	1.7			0.24
	α -FeOOH	8	0.37	38.0	-0.26	5			0.24
	Rel 1	9	0.31	45.0	0		9.1	7.6	0.24
	Rel 2	44	0.44	44.0	0.15		8.2	8.0	
	Doublet	1	0.32		0.39				0.21
Errors sextets		±3	±0.02	±0.1	±0.02	±0.1	±0.1	±0.1	
Errors doublet		±1	±0.02		±0.02				±0.02

Supplementary References

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- Soares, P.P.; Barcellos, G.S.; Petzhold, C.L.; Lavayen, V. Iron oxide nanoparticles modified with oleic acid: Vibrational and phase determination. *J. Phys. Chem. Solids* **2016**, *99*, 111–118.