Supplementary Materials: On the Laser Fragmentation for the Synthesis of Ligand-Free Ultra-Small Iron Nanoparticles in Various Liquid Environments

Ondřej Havelka [1], Martin Cvek [2], Michal Urbánek [2], Dariusz Łukowiec [3], Darina Jašíková [1], Michal Kotek [1], Miroslav Černík [1], Vincenzo Amendola[3] and Rafael Torres-Mendieta [1,*]

- Estimation of laser fluence, roughly considering a beam's free propagation, and calculation of the full evaporation fluence threshold.
- Supporting DLS graphs of supernatant and sediment for all the samples.
- SAED diffraction data displaying the crystallographic families corresponding to the specific type of Fe-based crystals.
- Supporting figure displaying the TEM images of all the samples on a bigger scale than the one reported in the main text, and supporting EDX line scanning graphs of the individual nanoparticles in different solvents.
- The raw ICP-OES data confirming the presence of iron.

The calculation of the laser fluence was determined according to the following set of standard formulas:

$$P = 7.0\,W\,(measured\ average\ power) \tag{1}$$

$$N = 2000\,(number\,of\ pulses) \tag{2}$$

$$E = \frac{P}{N}\,(energy\ per\ pulse) \tag{3}$$

$$E = 3.5\,mJ \tag{4}$$

$$f = 35\,mm\,(local\ length\,of\ plano - convex\,focusing\ lens) \tag{5}$$

$$s = 12\,mm\,(measured\ diameter\,of\ unfocused\ beam) \tag{6}$$

$$\lambda = 527\,nm\,(laser's\ central\ wavelength) \tag{7}$$

$$d = \frac{2 \cdot 1.22 \cdot \lambda \cdot \frac{f}{s}}{\sqrt{2 \cdot ln(2)}}\,(diameter\,of\ focused\ beam) \tag{8}$$

$$d = 3.19 \cdot 10^{-4}\,cm \tag{9}$$

$$S = \pi \cdot \left(\frac{d}{2}\right)^2\,(area\,of\ focused\ laser\ beam) \tag{10}$$

$$S = 8 \cdot 10^{-8}\,cm^2 \tag{11}$$

$$J = \frac{E}{S}\,(laser\,fluence) \tag{12}$$

$$J = 4.3 \cdot 10^4\, J/cm^2 \tag{13}$$

The calculation of the fluence threshold for heating-melting-evaporation model was determined according to the following set of formulas:

$$E_{abs} = \frac{E_0}{S_0} \cdot \sigma_{abs} = \Psi \cdot \sigma_{abs} \tag{14}$$

where E_0 represents the energy of a single pulse, S_0 the laser beam cross-section (the area of light that is perpendicular to the beam direction), $\Psi = E_0/S_0$ the laser fluence and σ_{abs} the particle absorption cross-section, which describes the energy absorbed by the irradiated particle.

$$\Psi \cdot \sigma_{abs} = m_p \cdot \int_{T_0}^{T} c_p(T) \cdot dT \tag{15}$$

where $m_p = \rho_p \pi d_p^3/6$ is the particle mass, ρ_p is the density of the particle, d_p is the diameter of the particle and T_0 is the initial temperature of the particle and T is the final temperature of the particle.

$$\Psi \cdot \sigma_{abs} = m_p \cdot \int_{T_0}^{T_m} c_p^s(T) \cdot dT + m_p \cdot \Delta H_m + m_p \cdot \int_{T_m}^{T_b} c_p^l(T) \cdot dT + m_p \cdot \Delta H_{ev} \tag{16}$$

Here, c_p^s represents the heat capacity of the material in the solid state, c_p^l the heat capacity in the liquid state, T_m the melting temperature, T_b the boiling temperature and as previously mentioned, ΔH_m the enthalpy of the melting and ΔH_{ev} the enthalpy of the evaporation.

$$\Psi \cdot \sigma_{abs} = m_p \cdot [(H_{T_m} - H_{T_0}) + \Delta H_m + (H_{T_b} - H_{T_m}) + \Delta H_{ev}] \tag{17}$$

where $H_{T_m} - H_{T_0}$ represents the relative enthalpy to reach the melting point and $H_{T_b} - H_{T_m}$ the relative enthalpy to reach the boiling point.

$$\sigma_{abs}(d_p) \cdot \mathbf{d}(\Psi) = \Delta H_{ev} \cdot \mathbf{d}(m_p) \tag{18}$$

which after the substitution of m_p and the editing takes the following form

$$\mathbf{d}(\Psi) = \frac{\pi}{2} \cdot \rho_p \cdot \Delta H_{ev} \cdot \frac{d_p^2 \cdot \mathbf{d}(d_p)}{\sigma_{abs}(d_p)} \tag{19}$$

Then, the final equation that enables to calculate the required fluence to fully evaporate micro particles will be

$$\begin{aligned} \Psi \quad = \quad & \frac{\pi \cdot d_p^3 \cdot \rho_p}{6 \cdot \sigma_{abs}} \cdot [(H_{T_m} - H_{T_0}) + \Delta H_m + (H_{T_b} - H_{T_m})] + \\ & \frac{\pi \cdot \rho_p}{2} \cdot \Delta H_{ev} \cdot \left(\int_{d_p}^{0} \frac{d_p^2}{\sigma_{abs}(d_p)} \cdot \mathbf{d}(d_p) \right) \end{aligned} \tag{20}$$

Note, the particle cross-section was calculated by Mie-theory calculator [1] and the required values of the quantities were taken from the database [2].

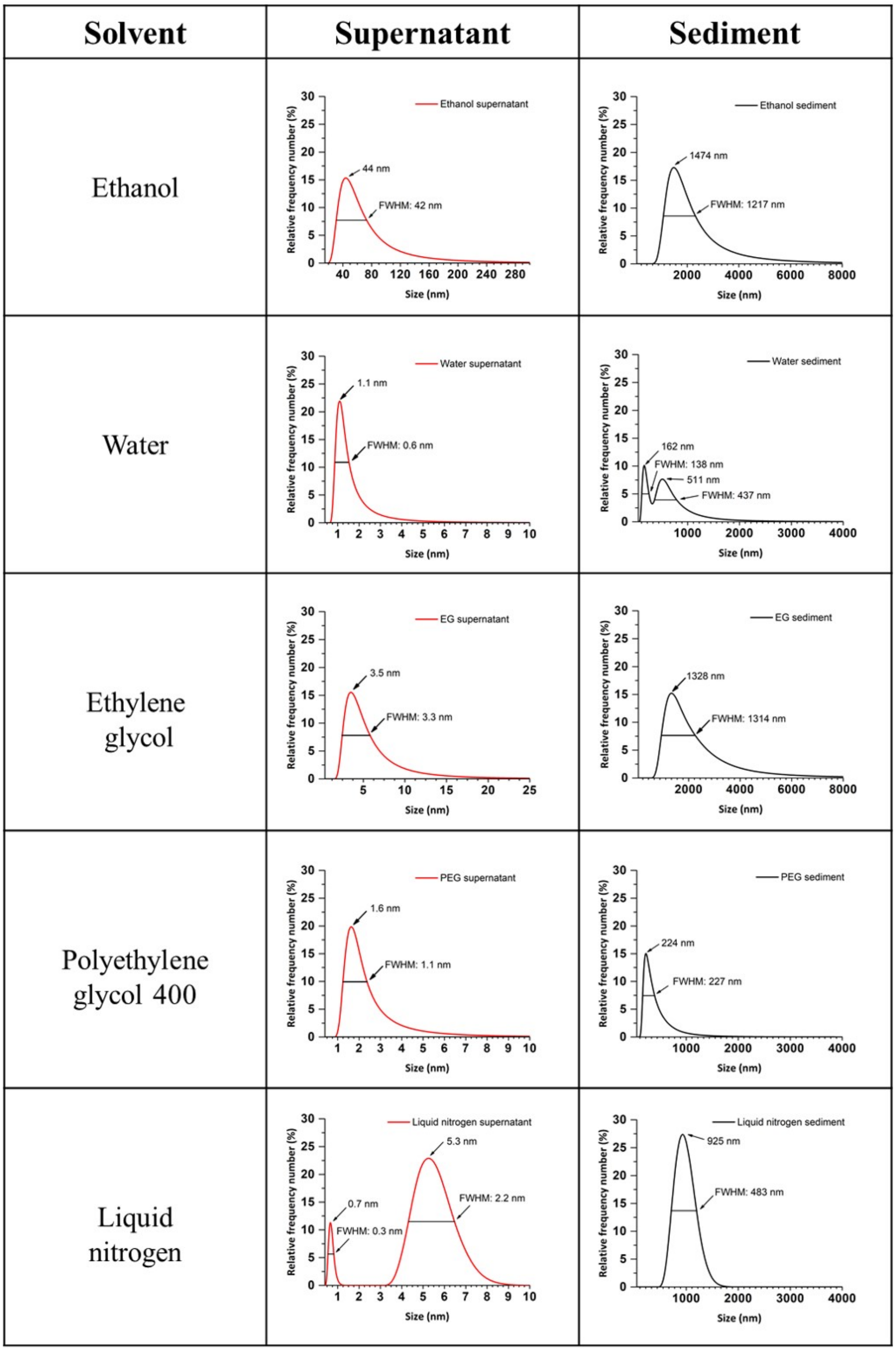

Figure S.1. Representative DLS images of sediment and supernatant samples.

Table S1. SAED parameters of samples corresponding to the specific crystallographic families in Fe-based crystals. Tetragonal Fe_2O_3 crystal (ICDD file: 65-390), cubic Fe_3O_4 crystal (ICDD file: 65-3107), hexagonal Fe crystal (ICDD files: 34-529), and the monoclinic Fe_5C_2 crystal (ICDD file: 20-508)

Ethanol				**Crystal type**	**Water**				**Crystal type**
No	**1/2r (nm^{-1})**	**d-spacing (A)**	**hkl**		**No**	**1/2r (nm^{-1})**	**d-spacing (A)**	**hkl**	
1	6.741	2.967	(220)	Fe_2O_3 / Fe_3O_4	1	7.830	2.554	(311)	Fe_2O_3 / Fe_3O_4
2	8.001	2.500	(311)	Fe_2O_3 / Fe_3O_4	2	11.719	1.707	(422)	Fe_2O_3 / Fe_3O_4
3	9.544	2.096	(400)	Fe_2O_3 / Fe_3O_4	3	13.780	1.451	(440)	Fe_2O_3 / Fe_3O_4
4	10.970	1.823	(101) / (312)	Fe / Fe_5C_2	4				
5	13.455	1.486	(440)	Fe_2O_3 / Fe_3O_4	5				
Ethylene glycol				**Crystal type**	**Liquid nitrogen**				**Crystal type**
No	**1/2r (nm^{-1})**	**d-spacing (A)**	**hkl**		**No**	**1/2r (nm^{-1})**	**d-spacing (A)**	**hkl**	
1	6.816	2.934	(220)	Fe_2O_3 / Fe_3O_4	1	7.957	2.514	(311)	Fe_2O_3 / Fe_3O_4
2	7.966	2.511	(311)	Fe_2O_3 / Fe_3O_4	2	9.652	2.072	(400)	Fe_2O_3 / Fe_3O_4
3	9.511	2.103	(400)	Fe_2O_3 / Fe_3O_4	3	13.608	1.470	(101)	Fe_2O_3 / Fe_3O_4
4	13.597	1.471	(440)	Fe_2O_3 / Fe_3O_4	4				

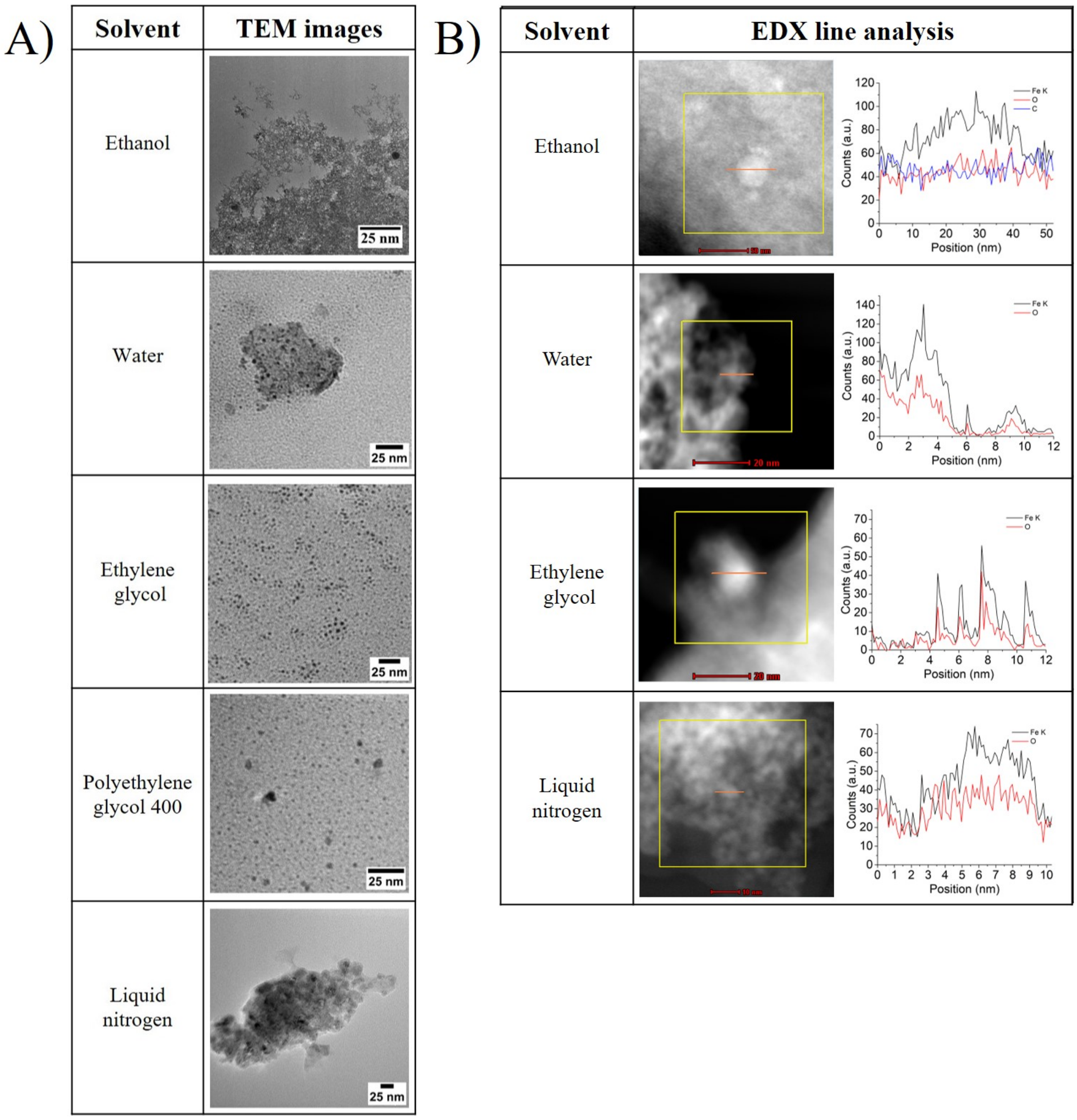

Figure S.2. A) Representative TEM images of the different samples where the bar scale is 25 nm. In these images, it is possible to appreciate the oxide matrices containing the iron-based particles synthesized in ethanol, and the agglomerates of the sample synthesized in liquid nitrogen and further redispersed in ethanol. B) Representative EDX line scans of the individual ultra-small NPs found in the samples' supernatant.

[1] https://omlc.org/calc/mie_calc.html [online 21-04-2021]
[2] https://www.webelements.com/iron/thermochemistry.html [online 25-04-2021]

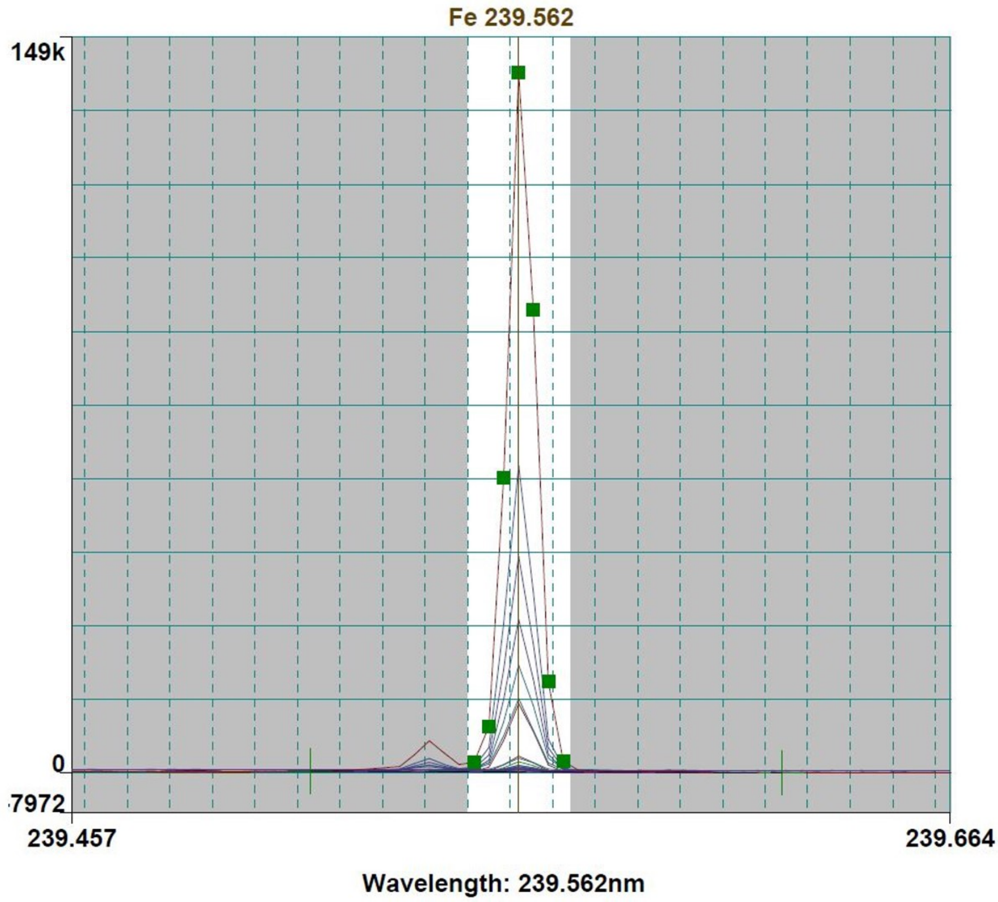

Figure S.3. Details from ICP-OES measurements. The main iron peak was measured at 239.56 nm, and is possible to observe smaller peak at 239.54 nm, also belonging to the iron.