SUPPORTING INFORMATION

In situ liquid transmission electron microscopy reveals self-assembly-driven nucleation in radiolytic synthesis of iron oxide nanoparticles in organic media

Nathaly Ortiz Peña,[1,2] Dris Ihiawakrim, [1] Sorina Creţu,[1] Geoffrey Cotin,[1] Céline Kiefer,[1] Sylvie Begin-Colin,[1] Clément Sanchez,[3,4] David Portehault,[3] Ovidiu Ersen[1]*

[1] Institut de Physique et Chimie des Matériaux de Strasbourg (IPCMS), UMR 7504 CNRS Université de Strasbourg, BP 43 Strasbourg Cedex 2, France
[2] Université Paris Cité, CNRS, Laboratoire Matériaux et Phénomènes Quantiques, 75013 Paris, France
[3] Sorbonne Université, CNRS, Collège de France, Laboratoire de Chimie de la Matière Condensée de Paris (CMCP), 4 place Jussieu, F-75005, Paris, France
[4] University of Strasbourg Institute for Advanced Studies (USIAS), 67083 Strasbourg, France
** corresponding author*

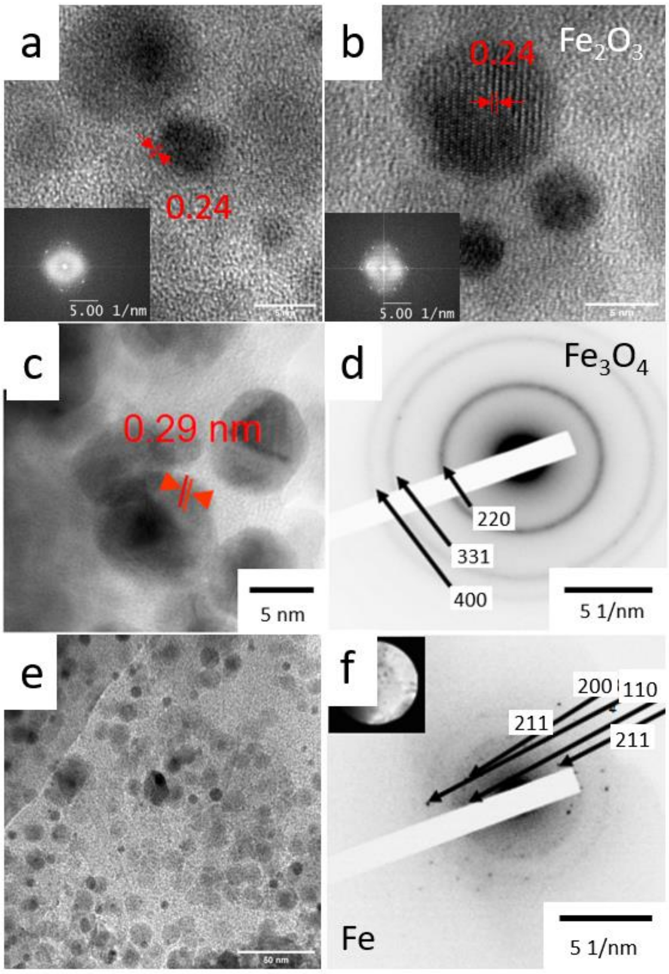

Figure S1. HRTEM images (a-c and e) and corresponding SAED pattern of c and e (d and f respectively) of nanoparticles of iron oxide spinel and metallic iron nanoparticles obtained by *in situ* liquid-phase radiolytic decomposition within the transmission electron microscope. These particles are analyzed *post mortem*, after blanking the electron beam and drying the *in situ* cell out of the microscope. The Selected Area Electron Diffraction pattern is indexed along a typical iron oxide spinel and metallic iron nanoparticles structure. Fe may arise from reduction under the electron beam.

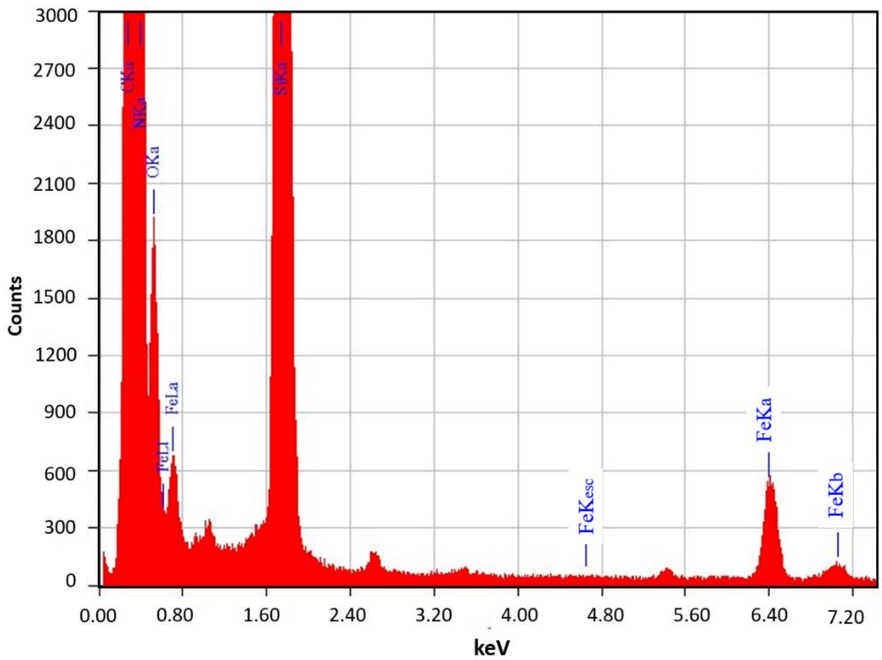

Figure S2. Energy dispersive spectrum obtained during the *in situ* experiment depicted in Figure 2. The signature Kα of iron was detected at 6.40 keV.

MAXIMUM TEMPERATURE RISE CALCULATION DUE TO THE ELECTRON BEAM[1]

$$\Delta T_{max} = \frac{S\ 10^2}{\pi \alpha_{th} C_p}\ I\left(1 + \frac{t}{\lambda}\right)\left(\frac{1}{4} + \frac{1}{2}\ Ln\left[\frac{L}{a}\right]\right)$$

I = beam current; a= beam radius; t = thickness; L = Window size; λ = Mean free path

Parameter	Water	Organic solvent
S = stopping power (MeV cm^2 g^{-1}) (200 kV)	2.79 [2]	2.99 (paraffin wax) [2]
C_p = specific heat at constant pressure (J mol^{-1} K^{-1}) (300 K)	75.28	564.4 (octadecane) [3]
α_{th} = thermal diffusivity (10^{-6} m^2 s^{-1}) (300 K)	0.148 [4]	0.06 (octadecane) [5]

Hence,

$$\Delta T_{max-Water} < 4\ K$$

$$\Delta T_{max-Octadecane} < 10\ K$$

Supporting movie S1. Decomposition of the iron (II) stearate $FeSt_2$ in 80% of sodium oleate and 20% of oleic acid surfactants in octadecene. No nuclei are initially observed. Apparition of vesicle-like structures.

Supporting movie S2. Octadecene under irradiation.

Supporting movie S3. Dynamic interaction of vesicles upon irradiation. Apparition of nuclei upon bursting of the vesicles.

Supporting movie S4. Nucleation and growth under TEM illumination at a high electron dose of 9400 $e^-/nm^2 \cdot s$.

Supporting movie S5. Nucleation and growth under TEM illumination at a medium electron dose of 6900 e^-/nm^2s.

Supporting movie S6. Nucleation and growth under TEM illumination at a low electron dose of 2500 $e^-/nm^2 \cdot s$.

Supporting movie S7. Nucleation and growth under STEM illumination at a low electron dose of 900$e^-/nm^2 \cdot s$.

Supporting movie S8. Nucleation and growth under STEM illumination at a low electron dose of 230$e^-/nm^2 \cdot s$.

REFERENCES

(1) Schneider, N. M. Electron Beam Effects in Liquid Cell TEM and STEM. In *Liquid Cell Electron Microscopy*; Cambridge University Press, 2017; pp 140–163.

(2) Berger, M. J.; Seltzer, S. M. *Stopping Powers and Ranges of Electrons and Positrons*; 1983.

(3) U.S. Secretary of Commerce on behalf of the United States of America. Octadecane https://webbook.nist.gov/cgi/cbook.cgi?ID=C593453&Units=SI&Mask=FFF (accessed Oct 14, 2019).

(4) Water - Thermal Diffusivity https://www.engineeringtoolbox.com/water-steam-thermal-diffusivity-d_2058.html (accessed Oct 14, 2019).

(5) Vélez, C.; Khayet, M.; Ortiz De Zárate, J. M. Temperature-Dependent Thermal Properties of Solid/Liquid Phase Change Even-Numbered n-Alkanes: N-Hexadecane, n-Octadecane and n-Eicosane. *Appl. Energy* **2015**, *143*, 383–394.