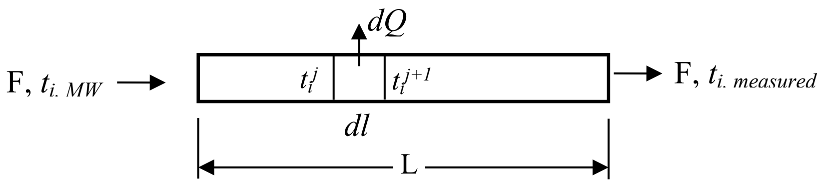
Electronic Supplementary Information

Microwave Promoted Continuous Flow Approach to Self-assembled Hierarchical Hematite Superstructures

M. K. Bayazit, E. Cao, A. Gavriilidis and J. Tang*

Estimation of fluid temperature at the exit of the microwave cavity

The temperature of the reaction fluid measured 5 cm away from the microwave heating zone was 120°C. To estimate the fluid temperature at the exit of the microwave cavity, forced convection heat transfer in the fluid inside the PTFE reactor and natural convection heat transfer in the surrounding air were assumed.



For fully developed internal laminar flow in a circular tube, the Nusselt number

$Nu = \frac{h_i d_i}{\lambda_f}$ is constant.

where:

d_i = tube inside diameter
λ_f = thermal conductivity of the fluid
h_i = convective heat transfer coefficient

For convection with uniform surface heat flux in circular tubes, the Nusselt number is[1]

$$Nu_D = \frac{48}{11} \cong 4.36$$

Taking a small section of the tubing (*dl*), the temperature change of the fluid can be calculated by the heat transfer rate through the tubing wall:

$$dQ = K_o \pi d_o \left(t_i^j - t_o\right) dl \qquad (1)$$

$$K_o = \left[\frac{1}{h_i}\frac{d_o}{d_i} + \frac{d_o}{2\lambda_f} ln \frac{d_o}{d_i} + \frac{1}{h_o}\right]^{-1} \qquad (2)$$

and the heat balance of the fluid:

$$t_i^{j+1} = \frac{dQ}{mCp} + t_i^j \qquad (3)$$

Parameters used for the calculation are listed in Table S1. Since the content of the iron oxide in the reaction fluid was very low (<0.5wt%), the properties of water[2] were used. The results are shown in Table 1.

Table S1. Parameters used in the calculations

PTFE tubing	
Length (L), m	0.05
Tubing O.D (do), m	0.00318
Tubing I.D. (di), m	0.002
Thermal conductivity (λ_{PTFE}), W/m-K	0.25
Water (120°C)	
Density (d), g/ml	0.945
Specific heat capacity (Cp), J/g-k	4.239
Thermal conductivity (λ_f), W/m-K	0.686
Convection heat transfer coefficient (h_i), W/m^2-K	1495
Air outside the tubing	
Temperature (t_o), K	298
Natural convection heat transfer coefficient (h_o), W/m^2-K	10

Estimation of the flow Péclet number, Pe_f

The flow Péclet number was estimated for α-Fe_2O_3 NPs using particle size of 10 nm and the equation below where γ is the shear rate, r is the particle size and d_t is the particle diffusion coefficient.[3]

Flow Péclet number,
$Pe_f=\gamma r^2/d_t$

Shear rate, g, 1/s	21.22066
Pe_f	2.74E-06

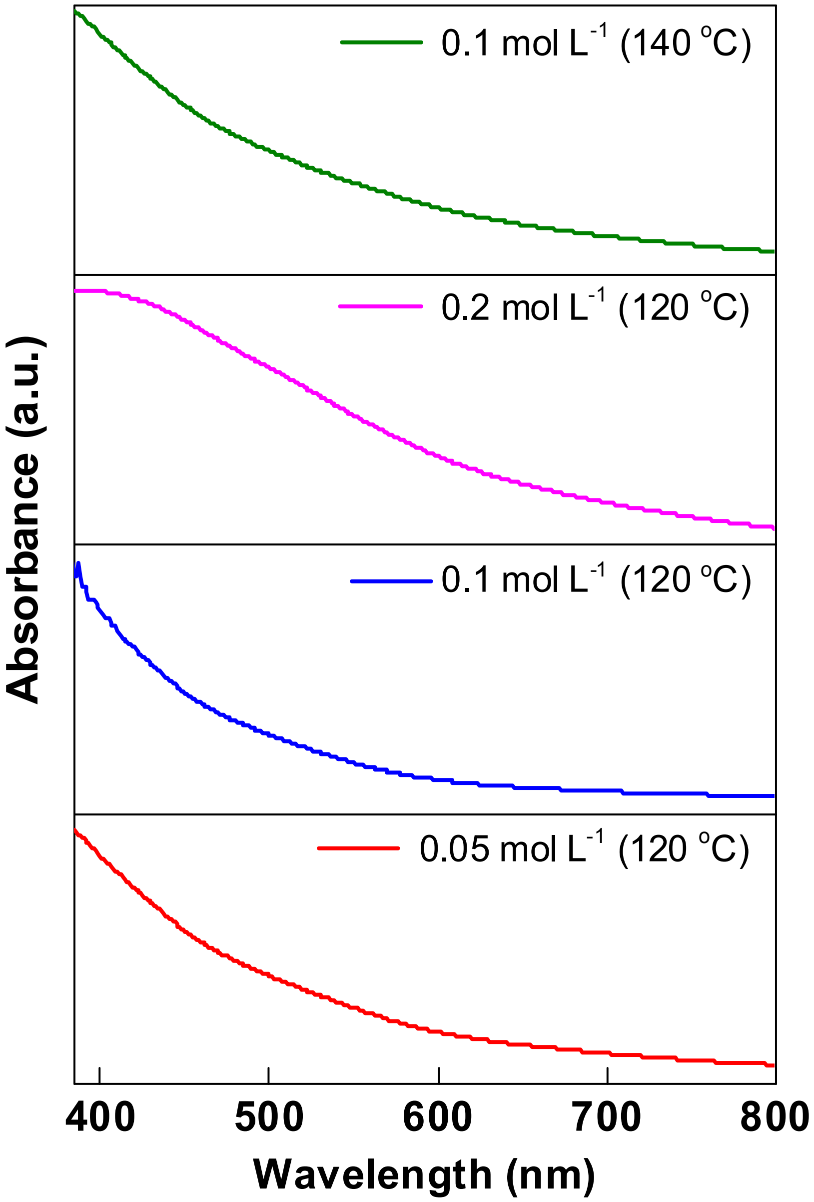


Figure S1. Absorption spectra of particles synthesized by conventional heating flow reactor at 120 °C and 140 °C using 0.05, 0.1 and 0.2 mol L^{-1} $Fe(NO_3)_3.9H_2O$ precursor. No clear hematite related absorption band is observed for the isolated particles synthesized at 120 °C using 0.05 mol L^{-1} and 0.1 mol L^{-1} $Fe(NO_3)_3.9H_2O$ precursor and at 140 °C using 0.1 mol L^{-1} $Fe(NO_3)_3.9H_2O$ precursor. The absorption band observed at *ca.* 400 nm for the isolated particles produced at 120 °C using 0.2 mol L^{-1} $Fe(NO_3)_3.9H_2O$ precursor suggests the presence of hematite particles in isolated product.

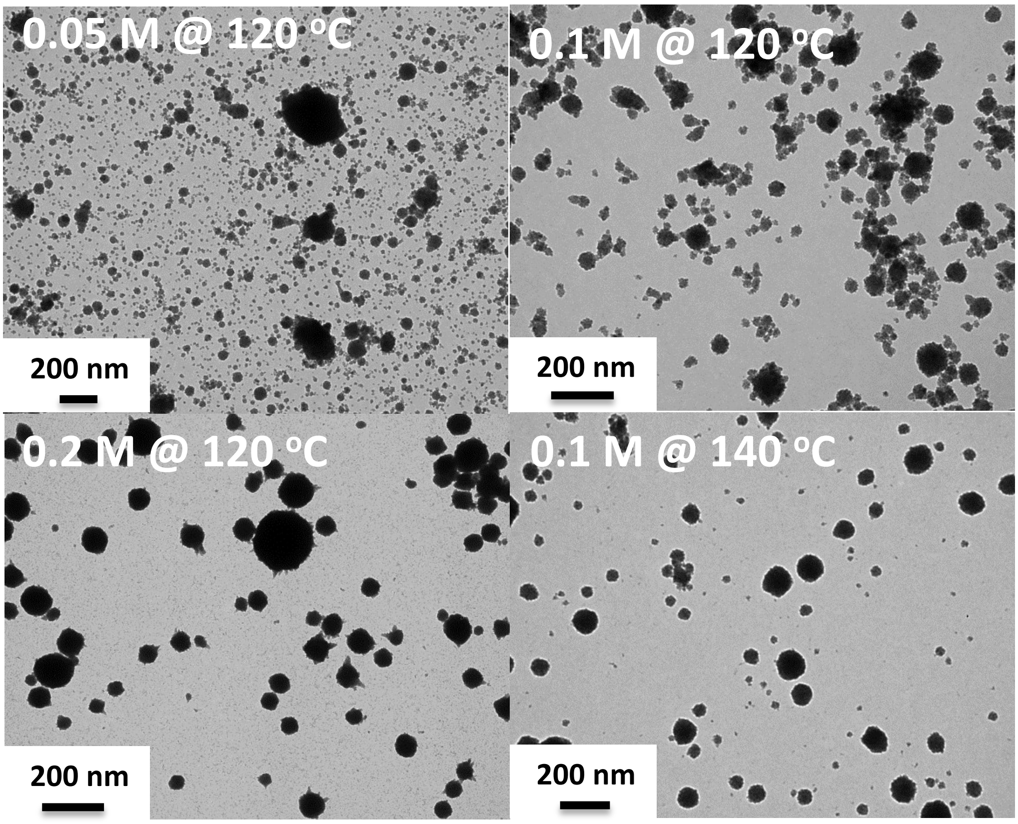


Figure S2. TEM images of particles synthesized by conventional heating flow reactor using 0.05, 0.1 and 0.2 mol L^{-1} $Fe(NO_3)_3.9H_2O$ precursor at 120 °C and 140 °C. No clear ellipsoid hematite particle formation is observed although there are big spherical clusters and small particles are available.

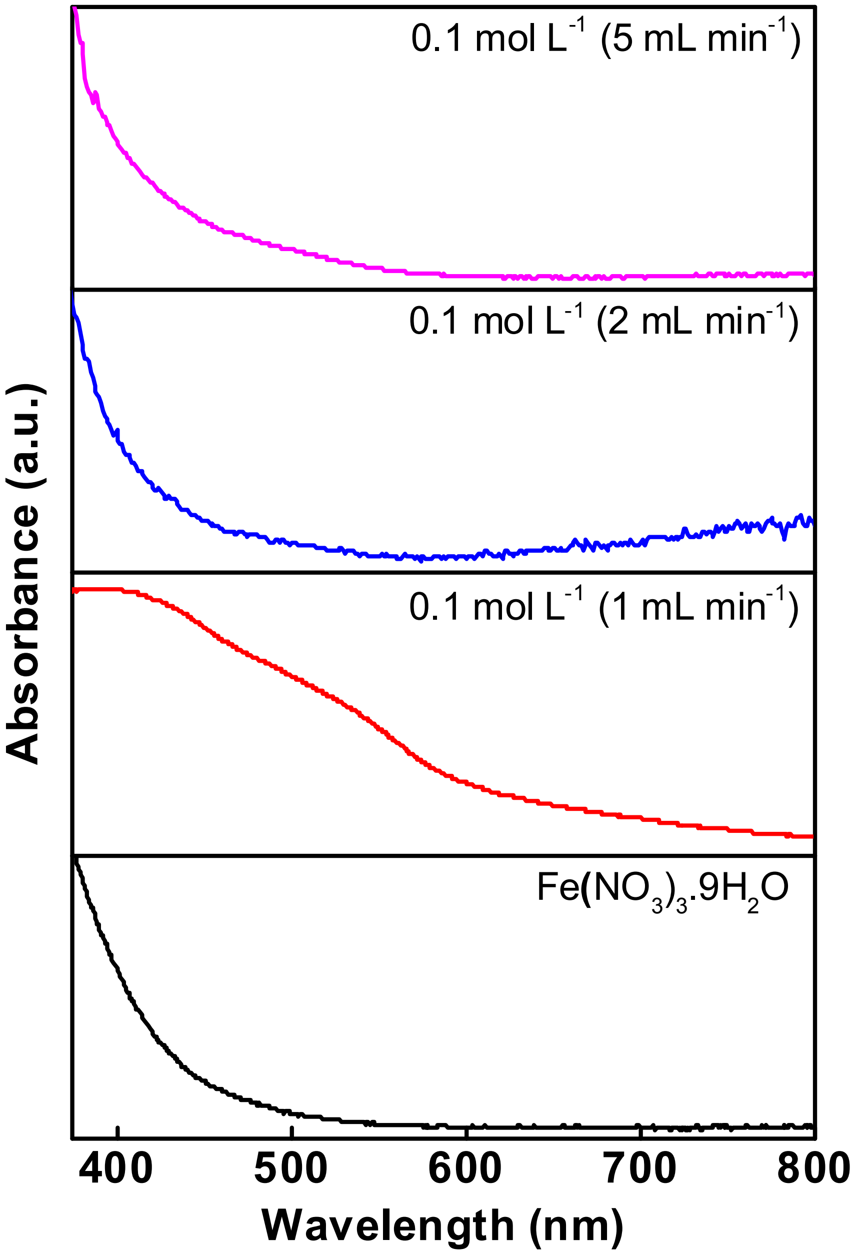


Figure S3. Absorption spectra of particles synthesized by microwave heating flow reactor at using 0.1 mol L^{-1} $Fe(NO_3)_3.9H_2O$ precursor at 1, 2 and 5 mL min^{-1} flow rates. No clear hematite related absorption band is observed for the analyzed crude reaction mixtures obtained at 2 and 5 mL min^{-1} flow rates, compared to 1 mL min^{-1} flow rate. The findings are in good agreement with Raman data.

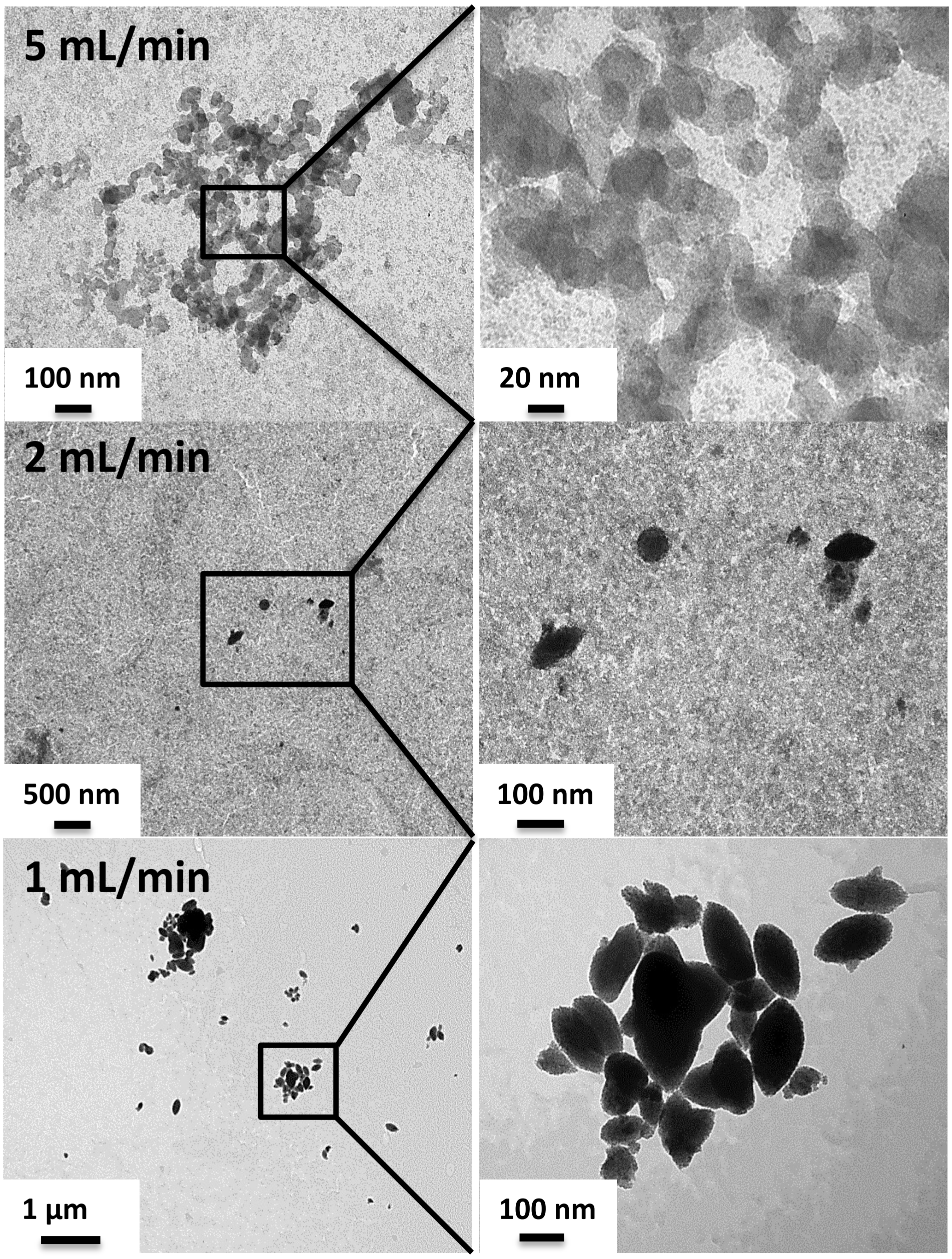


Figure S4. TEM images of particles synthesized by microwave heating flow reactor using 0.1 mol L^{-1} $Fe(NO_3)_3.9H_2O$ precursor at 1, 2 and 5 mL min^{-1} flow rates.

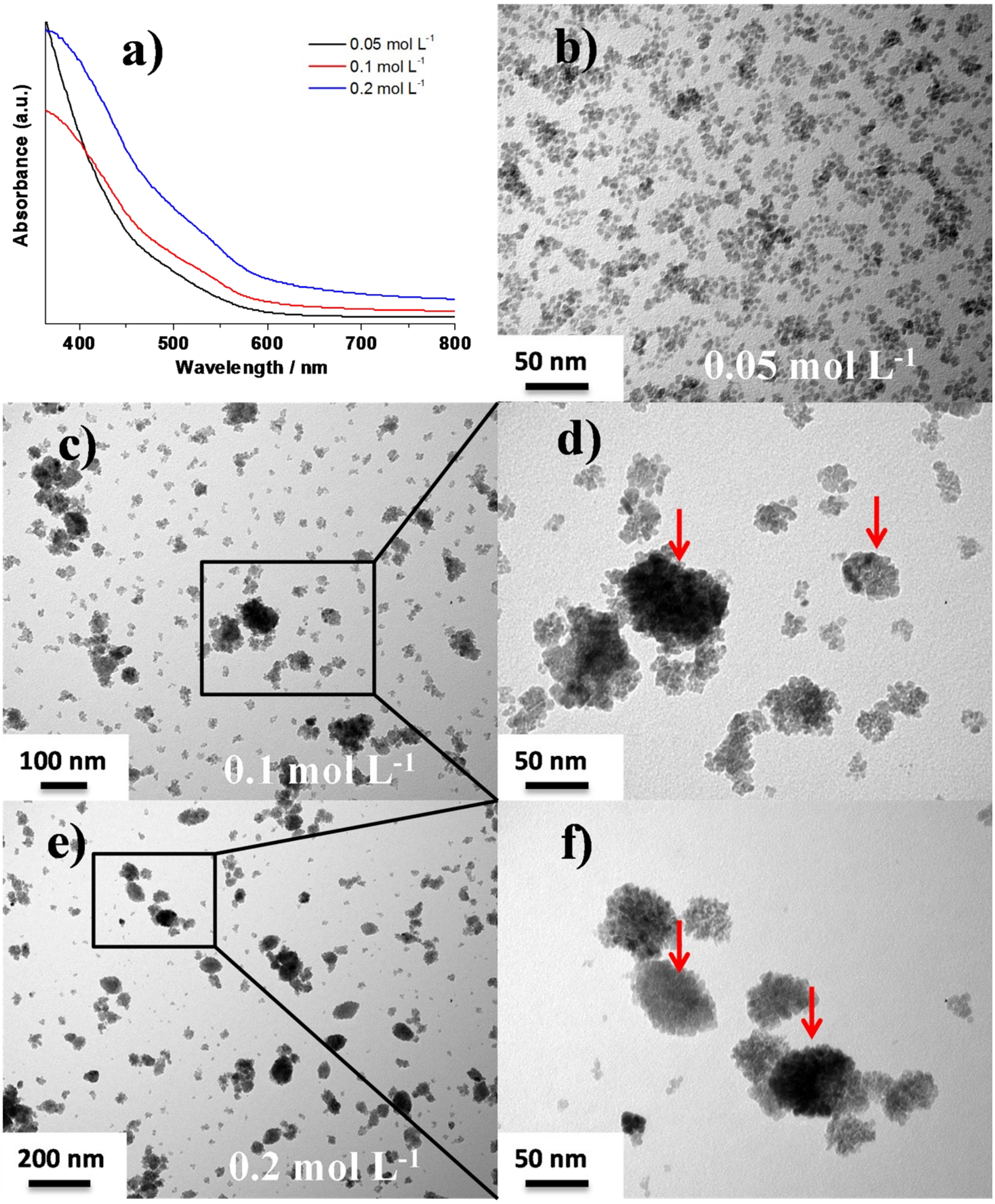


Figure S5. a) Absorption spectra of particles synthesized in a batch reactor by microwave irradiation at 120 °C for 6 min using 0.05, 0.1 and 0.2 mol L^{-1} $Fe(NO_3)_3.9H_2O$ precursor. Hematite related absorption band is observed for the isolated particles synthesized at 120 °C using 0.1 mol L^{-1} and 0.2 mol L^{-1} $Fe(NO_3)_3.9H_2O$ precursor, compared to the analysis of crude reaction mixture of 0.05 mol L^{-1} $Fe(NO_3)_3.9H_2O$ precursor. b) TEM image of the crude reaction mixture obtained by microwave heating batch reactor using 0.05 mol L^{-1} $Fe(NO_3)_3$ precursor at 120 °C. c-d) TEM images of the particles synthesised by microwave heating batch reactor using 0.1 mol L^{-1} $Fe(NO_3)_3$ precursor at 120 °C. e-f) TEM images of the particles synthesised by microwave heating batch reactor using 0.2 mol L^{-1} $Fe(NO_3)_3$ precursor at 120 °C. Red arrows show the possible self-assembled ellipsoid structures. Formation of ellipsoid-like self-assembled clusters and partially/non-assembled particles are observed when 0.1 mol L^{-1} and 0.2 mol L^{-1} $Fe(NO_3)_3.9H_2O$ precursor are used, suggesting that self-assembly of primary hematite nanoparticles is probably directed by microwave irradiation. There are also many non-assembled primary hematite nanoparticles, indicating that the self-assembly of hematite particles in a batch reactor under microwave irradiation is ineffective compared to a flow reactor, probably due to the high volume of the reaction mixture.

[1] Incropera, Frank P.; DeWitt, David P. (2002). *Fundamentals of Heat and Mass Transfer* (5th ed.). Hoboken: Wiley. pp. 486, 487.

[2] Incropera, Frank P.; DeWitt, David P. (1996). *Introduction to Heat Transfer* (3rd ed.). John Wiley&Sons, Inc., New York, USA.

[3] C.-W. Wang, D. Sinton and M. G. Moffitt, Journal of the American Chemical Society, 2011, 133, 18853-18864.