Supplementary Information

Assembly of Magnetite Nanoparticles into Spherical Mesoporous Aggregates with a 3-D Wormhole-Like Porous Structure

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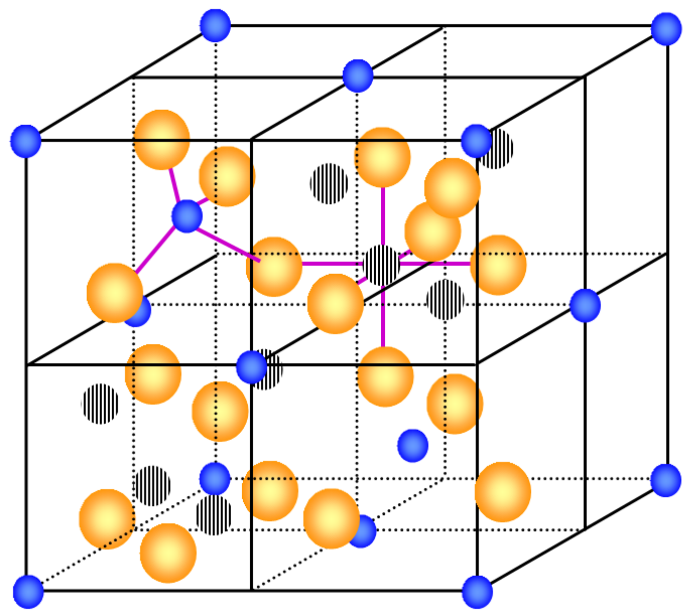
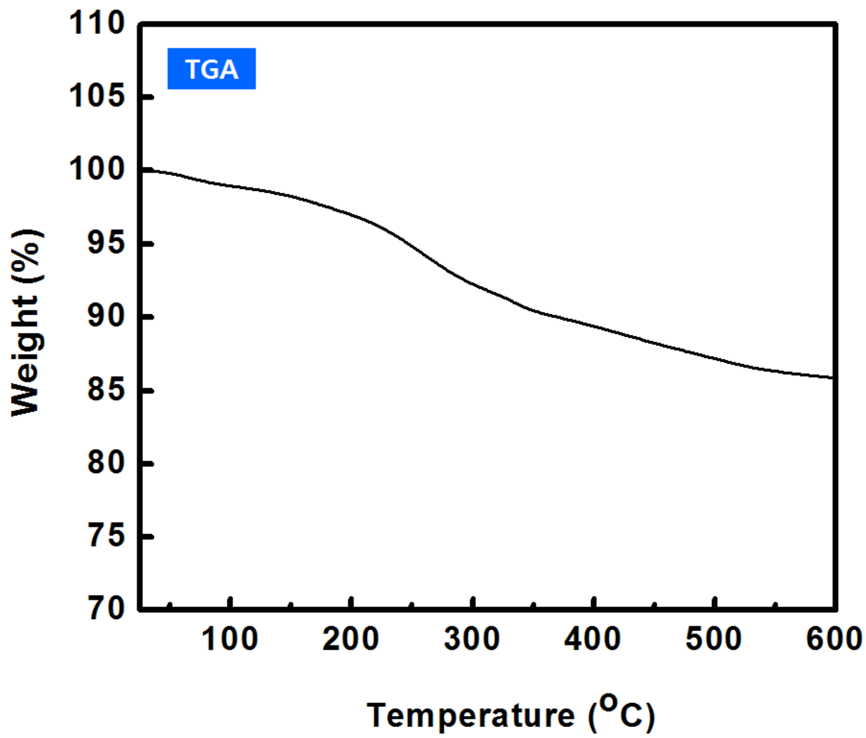


Figure S1. Schematic diagram for a unit cell of magnetite (Fe_3O_4): ● Fe^{3+} (tetrahedral coordination), ◍ Fe^{2+}/Fe^{3+} (octahedral coordination), ● oxygen



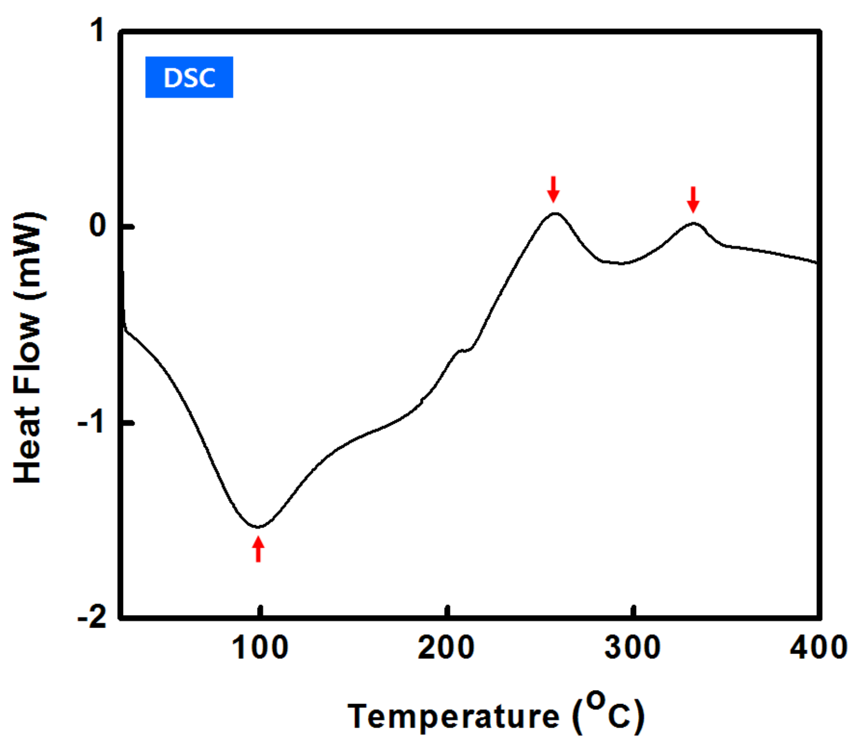


Figure S2. TGA and DSC curves of as-prepared mesoporous magnetite before calcination

Table S1. The standard 2θ values and relative intensity for magnetite (Fe_3O_4) with respective diffraction planes (JCPDS file, No. 19-0629)

2θ (deg)	Intensity (a.u.)	h k l	2θ (deg)	Intensity (a.u.)	h k l
18.269	8	1 1 1	62.515	40	4 4 0
30.095	30	2 2 0	65.743	2	5 3 1
35.422	100	3 1 1	70.924	4	6 2 0
37.052	8	2 2 2	73.948	10	5 3 3
43.052	20	4 0 0	74.960	4	6 2 2
53.391	10	4 2 2	78.929	2	4 4 4
56.942	30	5 1 1	86.617	4	6 4 2

Ref. *Natl. Bur. Stand. (U.S.) Monogr.* 1967, 25, 5, 31

Table S2. The standard 2θ values and relative intensity for maghemite (γ-Fe_2O_3) with respective diffraction planes (JCPDS file, No. 04-0755)

2θ (deg)	Intensity (a.u.)	h k l	2θ (deg)	Intensity (a.u.)	h k l
18.392	5	1 1 1	43.472	24	4 0 0
21.238	1	2 0 0	53.886	12	4 2 2
23.836	**5**	**2 1 0**	57.166	33	5 1 1
26.110	2	2 1 1	59.597	<1	5 2 0
30.272	34	2 2 0	60.457	10	5 2 1
32.172	**19**	**3 0 0**	62.726	53	4 4 0
33.928	1	3 1 0	65.185	1	5 3 0
35.597	100	3 1 1	71.401	7	6 2 0
37.280	1	2 2 2	74.677	11	5 3 3
38.783	**6**	**3 2 0**	75.372	3	6 2 2

Ref. R. Haul and T. Schoon. Z. *Phys. Chem.* 1939, **44**, 216.

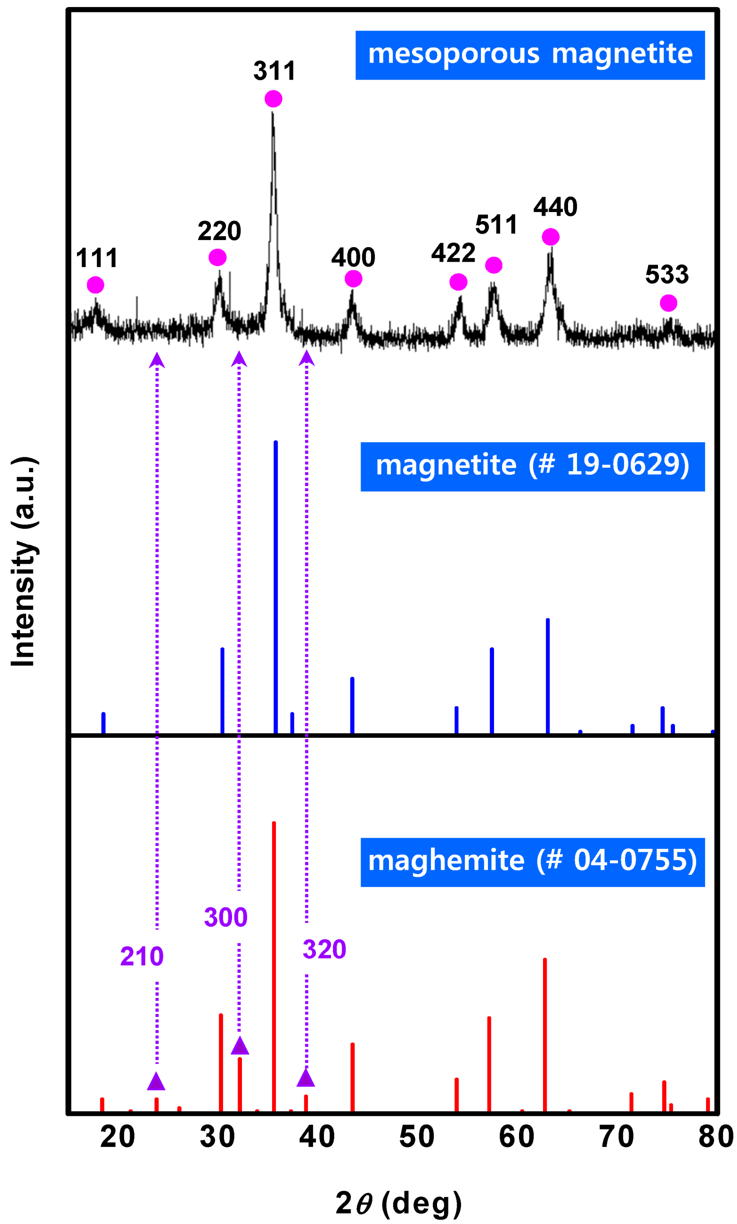


Figure S3. X-ray diffraction patterns of mesoporous magnetite and the standard JCPDS patterns for magnetite and maghemite

Table S3. FWHM values of the main diffraction peaks and crystallite size for mesoporous magnetite

h k l	Position (2θ)	FWHM (2θ)	Crystallite size (nm)
2 2 0	30.153	1.461	5.570
3 1 1	35.461	1.432	5.761
4 0 0	43.097	1.451	5.823
4 2 2	53.553	1.454	6.053
5 1 1	56.972	1.547	5.779
4 4 0	62.671	1.596	5.764

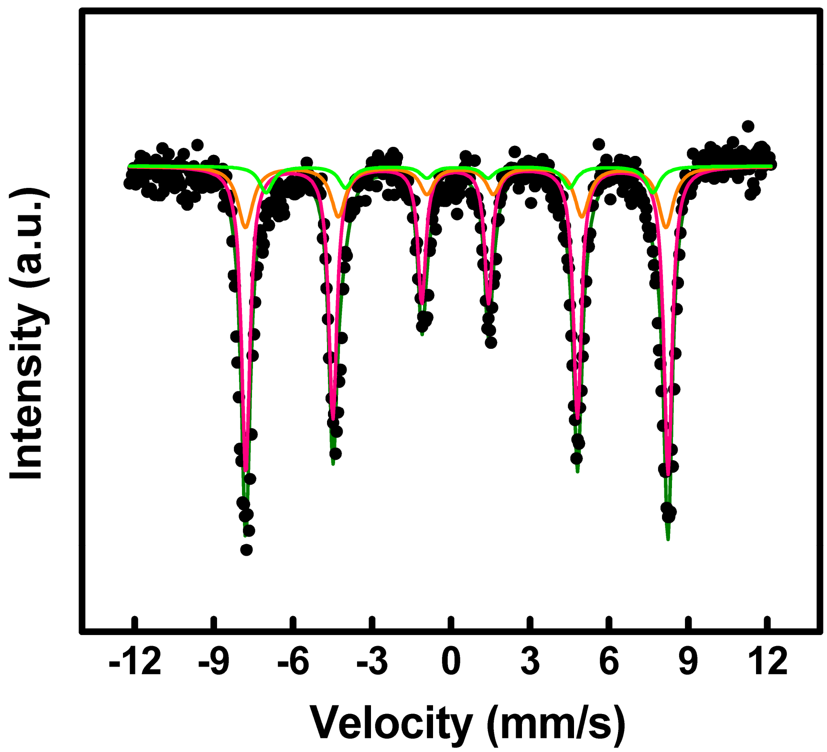


Figure. S4 ^{57}Fe-Mössbauer spectra of the maghemite (γ-Fe_2O_3) at room temperature (full cirles: experimental data; solid lines: best fit)

The maghemite sample (nanopowder - avg. part. size: 5~25 nm) was purchased from Sigma-Aldrich (CAS number: *1309-37-1*).

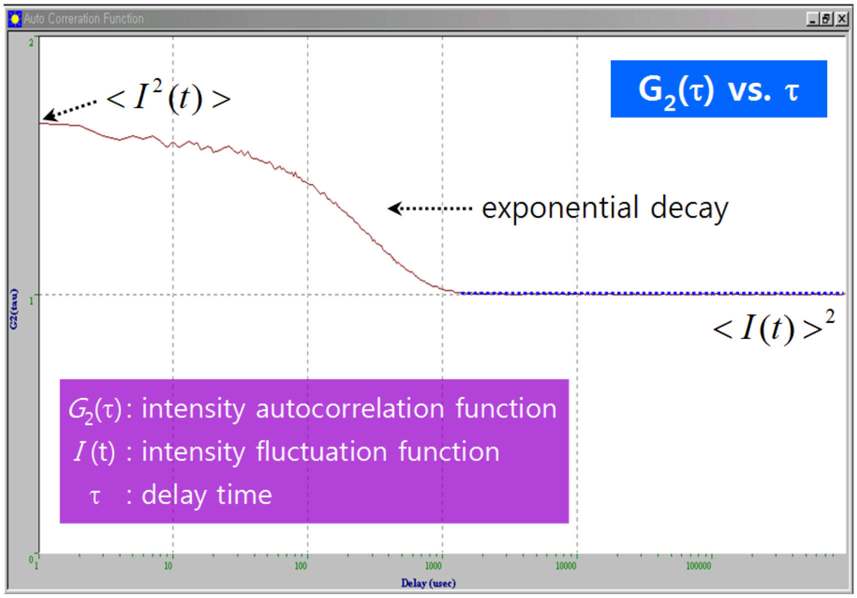


Figure S5. Intensity auto-correlation function (ACF), $G_2(\tau)$ in DLS

The second-order correlation function $G_2(\tau)$ can be expressed in the first-order correlation function, $G_1(\tau)$ according to the Siegert relation: $G_2(\tau) = B\left(1 + \beta G_1(\tau)^2\right)$, where B is the baseline constant and β is a coherence constant. In the case of a perfect setup, both equal unity. In the case of single-exponential decay, $G_1(\tau)$ can be expressed in terms of a typical decay rate, Γ and time, t; $G_1(\tau) = \exp(-\Gamma\tau)$. The apparent translational diffusion coefficient, D is given by equation: $\Gamma = Dq^2$, where q is the magnitude of the scattering vector; $q = 4\pi n \sin(\theta/2)/\lambda$, where n is the refractive index of the solvent, θ is the scattering angle, and λ is the wavelength of the incident light. For spherical particles, the translational diffusion coefficient can be related to the hydrodynamic radius, R according to the Stokes-Einstein equation: $D = k_B T / 6\pi\eta R$, where D is the diffusion coefficient of the Brownian motion of spherical particles, k_B is the Boltzmann constant, T is the absolute temperature, and η is the viscosity of the solvent. The hydrodynamic radius distribution of particles, G(R) was estimated using the COTIN algorithm, which is conventionally used to determine the inverse Laplace transform of the measured amplitude autocorrelation function.[1, 2]

(1) R. Finsy, *Adv. Colloid Interfac.* 1994, **52**, 79.

(2) I. K. Voets, A. De Keizer, M. A. Cohen Stuart and P. De Waard, *Macromolecules* 2006, **39**, 5952.

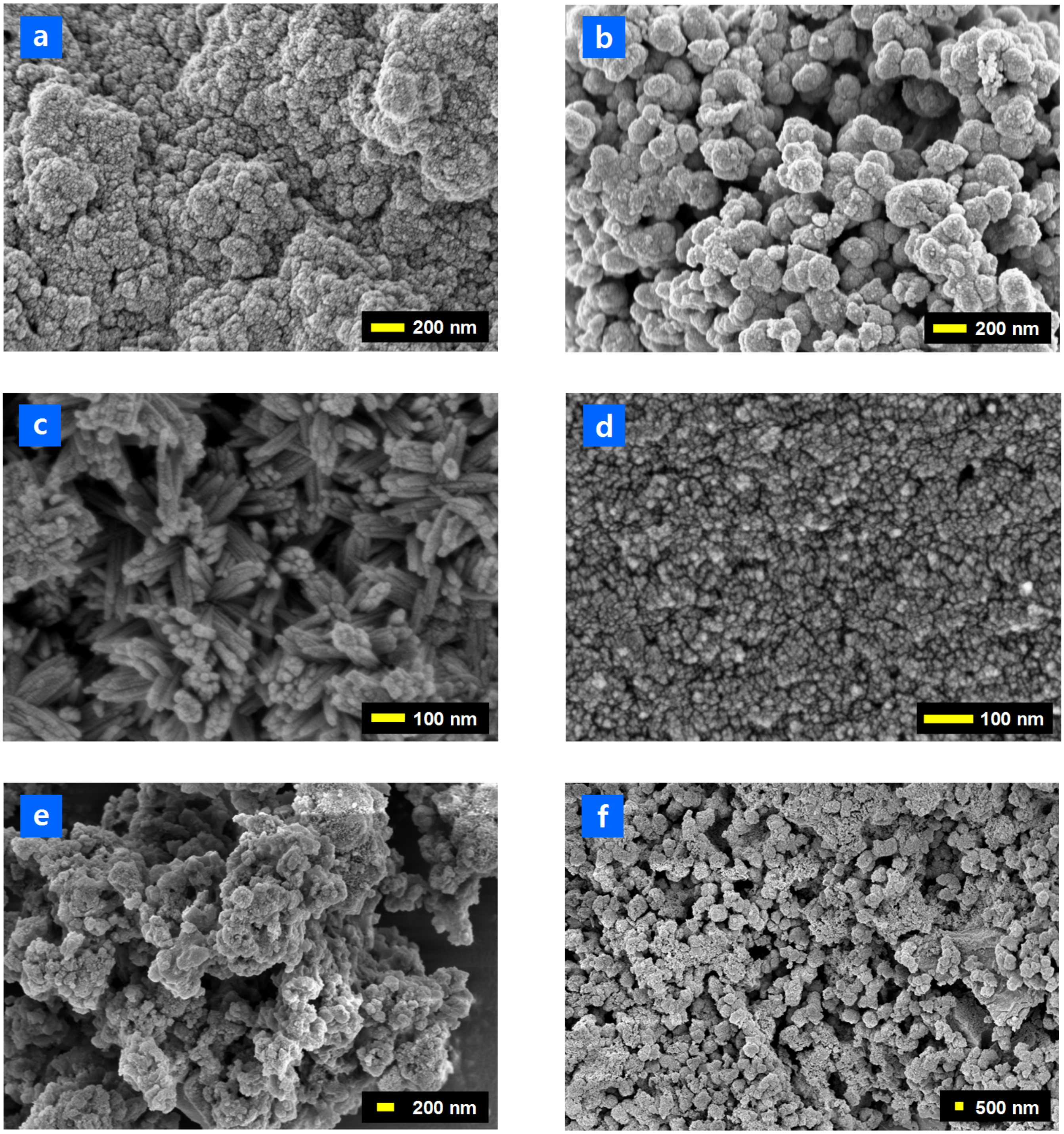


Figure S6. Representative FE-SEM images of synthesized magnetite particles under various reaction conditions: (a) with stirring, (b) low reaction temperature (below 40 ^{o}C), (c) high triblock copolymer concentration, (d) without the triblock copolymer, (e) decreased triblock copolymer/precursor molar ratio, and (f) decreased reaction time