Electronic Supplementary Information (ESI)

for

Designing Large Scale Synthesis Strategy of High Quality Magnetite Nanocrystals on the Basis of Solution Behavior Regulated Formation Mechanism

Xueyi Guo,*[a] Weijia Wang,[a] Ying Yang[a] and Qinghua Tian[a]

[a] School of Metallurgy and Environment, Central South University, Changsha, Hunan 410083, China

* Address correspondence to xyguo@csu.edu.cn

1. Experiment Details

1.1 Synthesis conditions of MNCs with diverse size distributions and morphologies.

Table S1. Synthesis conditions of MNCs with diverse size distribution and morphologies.

No.	ODE	Iron Source		OA	OAm	Temperature/ Time
		$Fe(acac)_3$	$Fe(OA)_3$			
	(mmol)	(mmol)	(mmol)	(mmol)	(mmol)	(°C / hours)
Figure 3(b)	62.58	/	3.00	3.00	32.00	Step 1: 200°C/0.5 h Step 2: 220°C/2 h
Figure 5(a)	62.58	3.00	/	12.00	32.00	Step 1: 200°C/0.5 h Step 2: 220°C/2 h
Figure 5(b)	62.58	4.00	/	12.00	32.00	Step 1: 200°C/0.5 h Step 2: 220°C/2 h
Figure 5(c)	62.58	5.00	/	12.00	32.00	Step 1: 200°C/0.5 h Step 2: 220°C/2 h
Figure 5(d)	62.58	6.00	/	12.00	32.00	Step 1: 200°C/0.5 h Step 2: 220°C/2 h
Figure 6(a)	62.58	3.00	/	4.00	40.00	Step 1: 200°C/0.5 h Step 2: 220°C/2 h
Figure 6(b)	62.58	3.00	/	20.00	24.00	Step 1: 200°C/0.5 h Step 2: 220°C/2 h
Figure6(c)	62.58	3.00	/	26.00	18.00	Step 1: 200°C/0.5 h Step 2: 220°C/2 h
Figure 6(d)	62.58	3.00	/	30.00	14.00	Step 1: 200°C/0.5 h Step 2: 220°C/2 h
Figure 7(a)	62.58	3.00	/	12.00	32.00	Step 1: 200°C/0.5 h Step 2: 220°C/4 h
Figure 7(b)	62.58	3.00	/	12.00	32.00	Step 1: 200°C/0.5 h Step 2: 220°C/6 h
Figure 7(c)	62.58	3.00	/	12.00	32.00	Step 1: 200°C/0.5 h Step 2: 240°C/2 h
Figure 8	1250	60.00	/	200.00	640.00	Step 1: 200°C/0.5 h Step 2: 230°C/4 h

1.2 Preparation conditions of FTIR samples.

Table S2. Preparation conditions for FTIR samples.

No.	$Fe(acac)_3$	ODE	OA	OAm	Description
	(mmol)	(mmol)	(mmol)	(mmol)	
F1	3.00	0.00	0.00	0.00	Pure $Fe(acac)_3$/120 °C, 2 h
F2	0.00	62.58	0.00	0.00	Pure ODE/120 °C, 2 h
F3	0.00	0.00	12.00	0.00	Pure OA/120 °C, 2 h
F4	0.00	0.00	0.00	32.00	Pure OAm/120 °C, 2 h
F5	3.00	62.58	0.00	0.00	$Fe(acac)_3$ in ODE/120°C, 2 h
F6	0.00	62.58	12.00	0.00	OA in ODE/120°C, 2 h
F7	0.00	62.58	0.00	32.00	OAm in ODE/120°C, 1 h
F8	3.00	62.58	12.00	0.00	Precursor-1/120°C, 2 h
F9	3.00	62.58	12.00	32.00	Precursor-2/120°C, 1 h
F10	3.00	62.58	12.00	32.00	Precursor-2/200°C, 0 min
F11	3.00	62.58	12.00	32.00	Precursor-2/200°C, 30 min
F12	3.00	62.58	12.00	32.00	Precursor-2/220°C, 0 min
F13	3.00	62.58	12.00	32.00	Precursor-2/220°C, 120 min

1.3 Preparation conditions of UV-vis samples.

Table S3. Preparation conditions for UV-vis samples.

No.	$Fe(acac)_3$	ODE	OA	OAm	Description
	(mmol)	(mmol)	(mmol)	(mmol)	
U1	3.00	62.58	0.00	0.00	Pure $Fe(acac)_3$
U2	3.00	62.58	3.00	0.00	$Fe(acac)_3$/OA=1:1 (m/m)
U3	3.00	62.58	6.00	0.00	$Fe(acac)_3$/OA=1:2 (m/m)
U4	3.00	62.58	9.00	0.00	$Fe(acac)_3$/OA=1:3 (m/m)
U5	3.00	62.58	12.00	0.00	$Fe(acac)_3$/OA=1:4 (m/m)

$Fe(acac)_3$ and OA were dissolved in ODE at room temperature. The mixture was heated to 120 °C and maintained for 2 hours with stirring. OAm was then added to the mixture and stirred for another one hour at 120 °C. And 200 μL sample was dissolved in 3 mL hexane for UV-vis measurement.

1.4 Preparation of XRD samples

2 mL concentrated MNCs/hexane suspensions (50mg/mL) were drop casted onto zero background silicon substrate and dried in vacuum at 60 °C for 6 hours. The MNCs were then deposited on silicon substrate and used for XRD measurement.

2. Supplementary Data

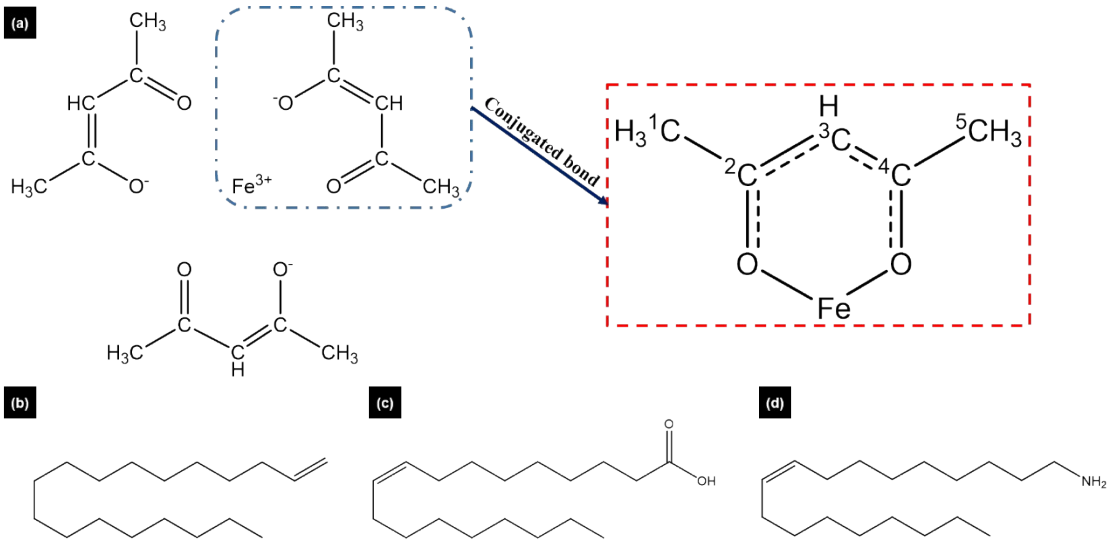

Figure S1. Chemical structure diagrams of reactants used for MNCs synthesis. (a) $Fe(acac)_3$, (b) ODE, (c) OA, (d) OAm.

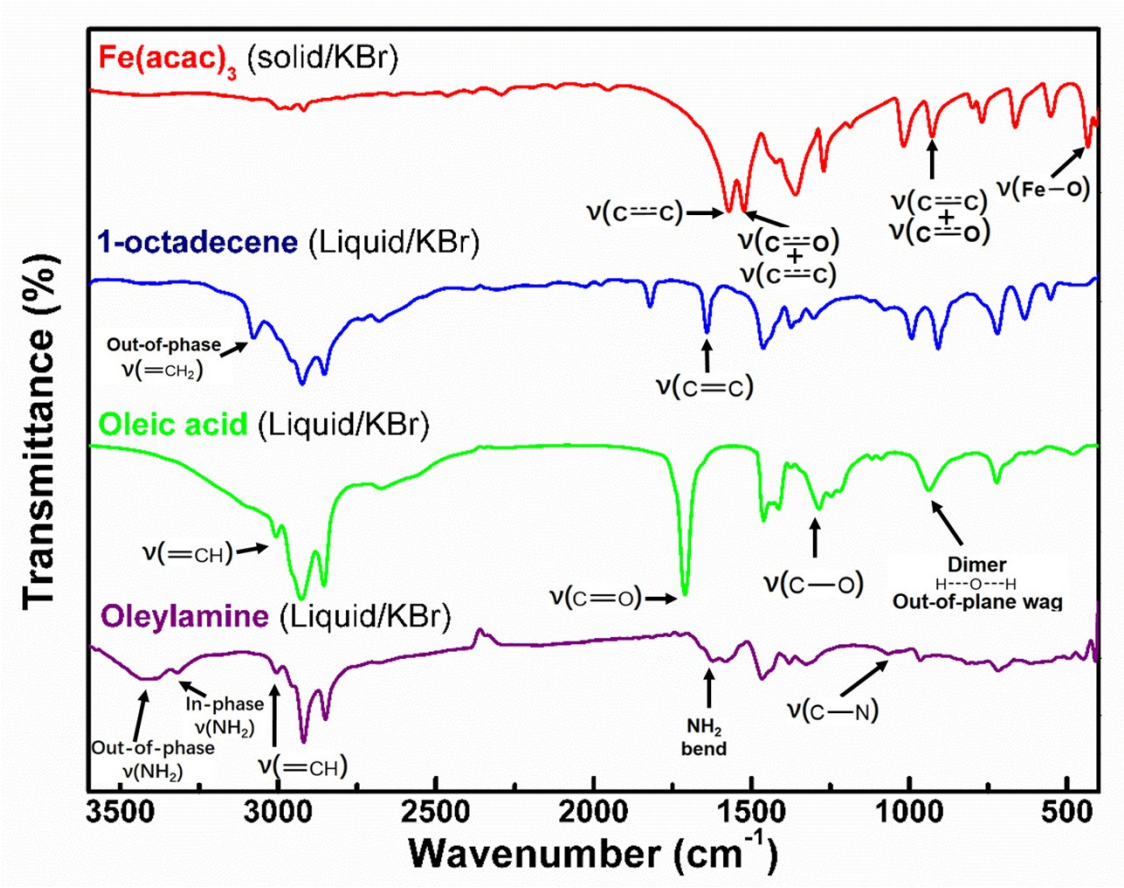

Figure S2. FTIR spectra of reactants used for MNCs synthesis.

Table S4. Observed frequencies and band assignments of reactants used in MNCs synthesis.

$Fe(acac)_3$	Band Assignment	1-Octadecene	Band Assignment
1571	$\nu(^2C{=}{=}{=}^3C)+\nu(^3C{=}{=}{=}^4C)$	3076	$\nu(=CH_2)$
1523	$\nu(C{=}{=}{=}O)+\nu(C{=}{=}{=}C)$	2923	$\nu(CH_2)$ Out-of-phase
1385		2853	In-phase
1360	$\delta_s(CH_3)$	1821	908 cm^{-1} overtone band
1271	$\nu(H_3C{-}C)+\nu(C{=}{=}{=}C)$	1641	$\nu(C{=}C)$
1188	$\delta(CH)+\nu(H_3C{-}C)$	1462	$\delta(CH_2)$
1018	$\rho_r(CH_3)$	1373	$\delta_s(CH_3)$
927	$\nu(C{=}{=}{=}C)+\nu(C{=}{=}{=}O)$		
800	$\pi(CH)$	992	$^{+}H\diagup C{=}C\diagdown H^{+}$
770			
664	$\nu(H_3C-C)+$ Ring deformation $+\nu(Fe-O)$		
551	Ring deformation $+\nu(Fe-O)$	908	$=C\begin{matrix}\diagup H^{+}\\ \diagdown H^{+}\end{matrix}$
433	$\nu(Fe-O)$		

Oleic acid	Band Assignment		Oleylamine	Band Assignment
3006	$\nu(=CH)$		3384	$\nu(NH_2)$ Out-of-phase
2926	$\nu(CH_2)$	Out-of-phase	3318	In-phase
2854		In-phase	3004	$\nu(=CH)$
1710	$\nu(C=O)$	Out-of-phase	2919	$\nu(CH_2)$ Out-of-phase
1461	$\delta(CH_2)$		2849	In-phase
1285	$\nu(C-O)$		1623	$\delta(NH_2)$
938	Dimer O…H…O out-of-plane wag		1465	$\delta(CH_2)$
723	$\rho_r(CH_2)$		1380	$\delta_s(CH_3)$
			1326	
			1066	$\nu(C-N)$
			814	NH_2 wag
			788	

v: stretching; $\mathbf{v_s}$: symmetrical stretching; $\mathbf{v_{as}}$: asymmetrical stretching; **δ**: in-plane bending or deformation; $\mathbf{\delta_s}$: in-plane bending; $\mathbf{\rho_r}$: rocking; **π**:out-of-plane bending.

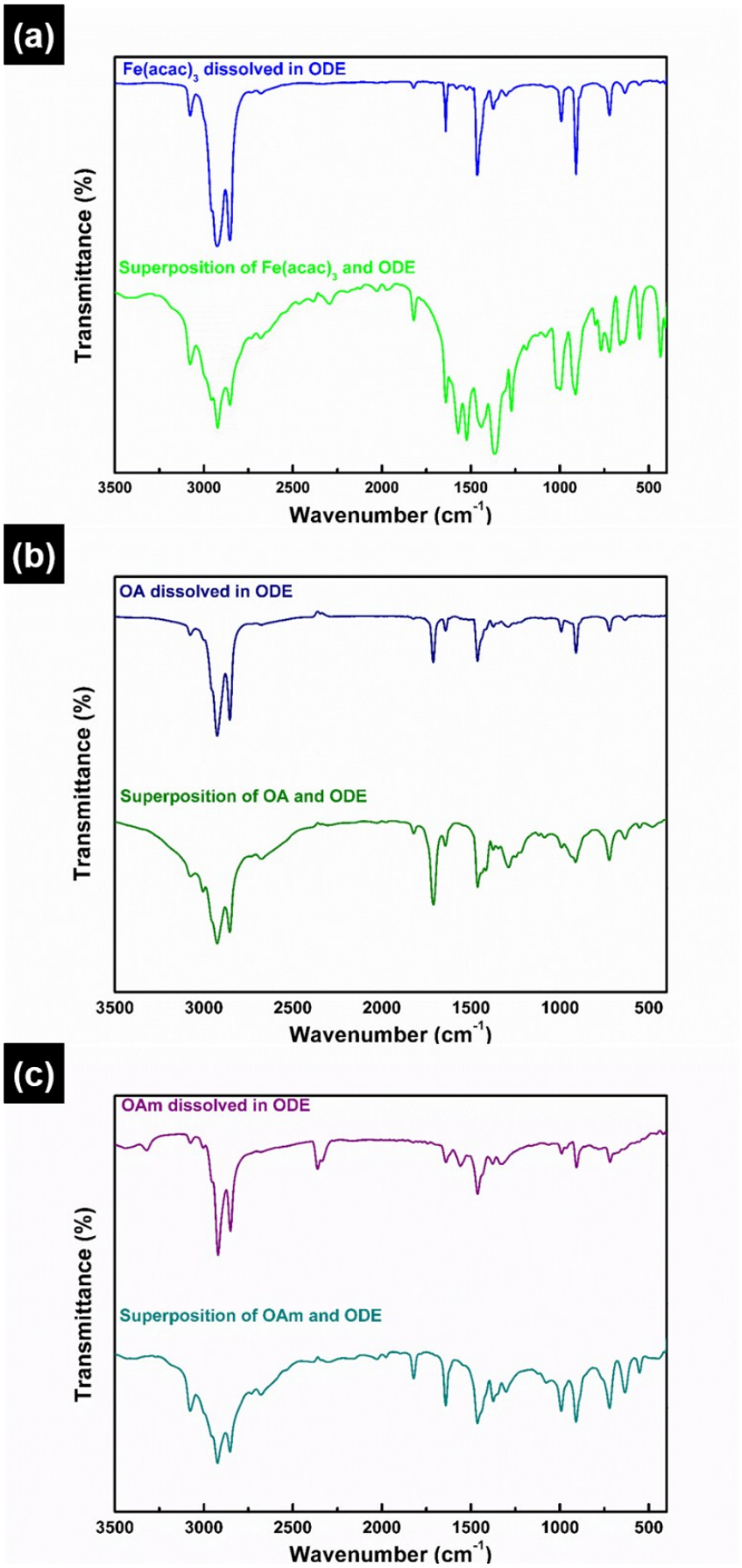

Figure S3. FTIR spectra of reactants dissolved in ODE. (A) $Fe(acac)_3$, (b) OA, (c) OAm.

Table S5(a). Observed frequencies and band assignments of $Fe(acac)_3$ dissolved in ODE.

Wavenumber (cm^{-1})	Band Assignment	Attribution
1821	908 cm^{-1} overtone band	ODE
1641	$\nu(C=C)$	ODE
1579	$\nu(^2C=^3C)+\nu(^3C=^4C)$	$Fe(acac)_3$
1524	$\nu(C=O)+\nu(C=C)$	$Fe(acac)_3$
1464	$\delta(CH_2)$	ODE
1374	$\delta_s(CH_3)$	ODE
992		ODE
908		ODE
721	$\rho_r(CH_2)$	ODE
437	$\nu(Fe-O)$	$Fe(acac)_3$

Table S5(b). Observed frequencies and band assignments of oleic acid dissolved in ODE.

Wavenumber (cm^{-1})	Band Assignment		Attribution
3076	$\nu(=CH_2)$		ODE
2924	$\nu(CH_2)$	Out-of-phase	ODE&OA
2854		In-phase	ODE&OA
1711	$\nu(C=O)$		OA
1642	$\nu(C=C)$		ODE
1462	$\delta(CH_2)$		ODE&OA
1373	$\delta_s(CH_3)$		ODE
1289	$\nu(C-O)$		OA
992			ODE
909			ODE
721	$\rho_r(CH_2)$		ODE&OA

Table S5(c). Observed frequencies and band assignments of oleylamine dissolved in ODE.

Oleylamine dissolved in ODE	Band Assignment		Attribution
3384	$\nu(NH_2)$	Out-of-phase	OAm
3318		In-phase	OAm
3075	$\nu(=CH_2)$		ODE
3003	$\nu(=CH)$		OAm
2918	$\nu(CH_2)$	Out-of-phase	ODE&OAm
2849		In-phase	ODE&OAm
2360	$\nu(NH^+)$		OAm
1824	~906 cm^{-1} overtone band		ODE
1624	$\delta(NH_2)$		OAm
1558	$\nu(NH_3^+)$		OAm
1461	$\delta(CH_2)$		ODE&OAm
1377	$\delta_s(CH_3)$		ODE&OAm
1327			ODE&OAm
1064	$\nu(C-N)$		OAm
990			ODE
906			ODE
781	NH_2 wag		OAm
718	$\rho_r(CH_2)$		ODE

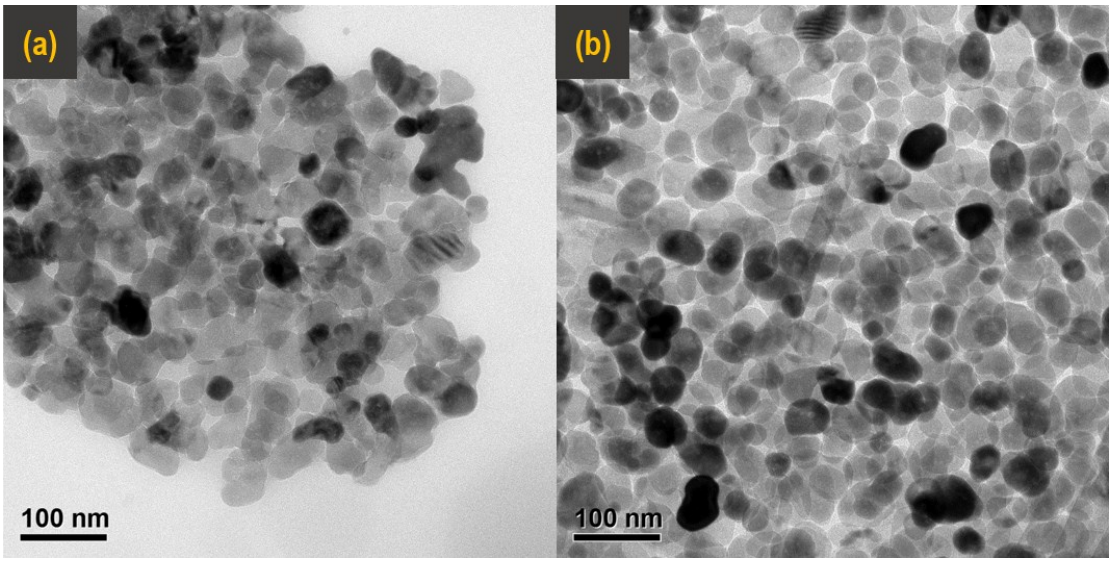

Figure S4. TEM images of MNCs with various $Fe(acac)_3$ addition: (a) 1 mmol, (b) 2 mmol.

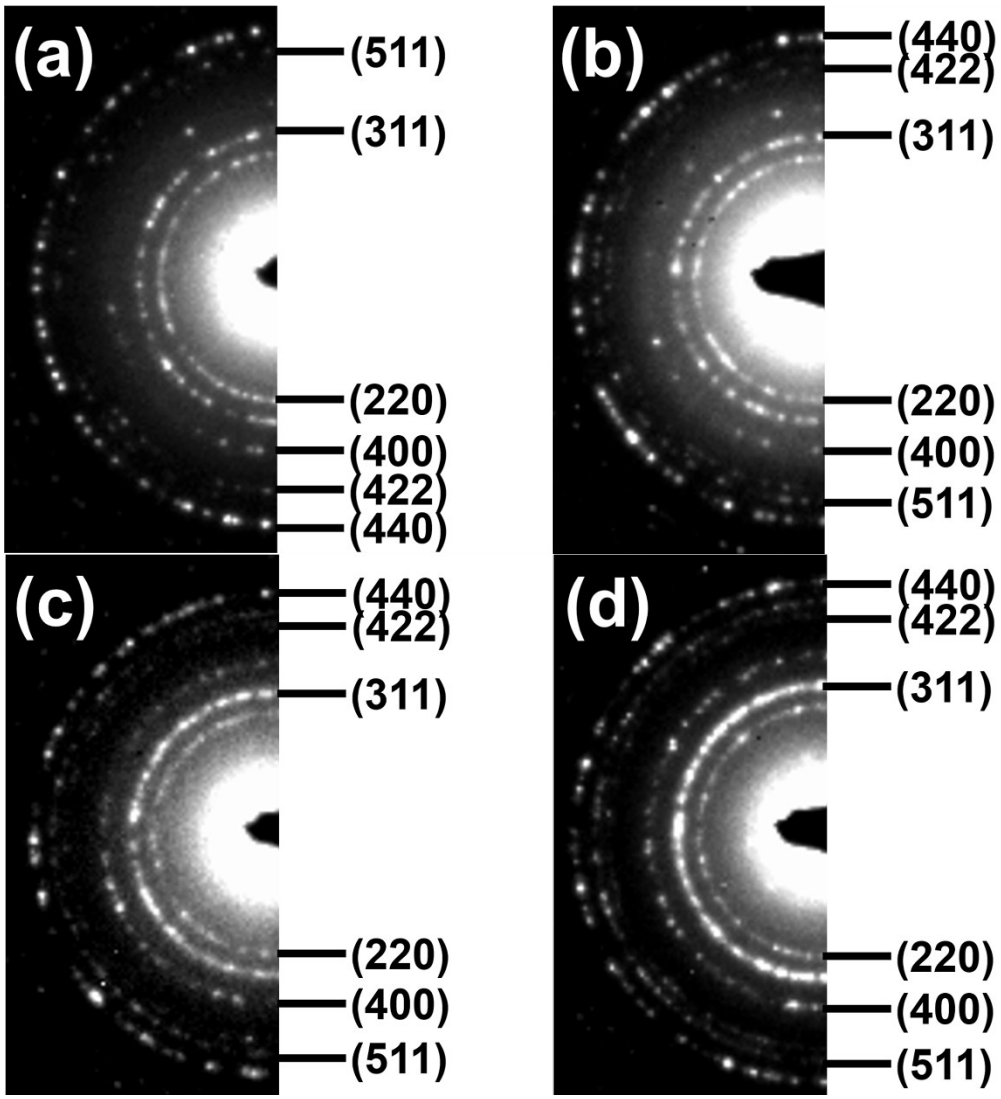

Figure S5. SAED patterns of MNCs synthesized with various $Fe(acac)_3$ amounts. (a) 3 mmol, (b) 4 mmol, (c) 5 mmol, (d) 6 mmol.

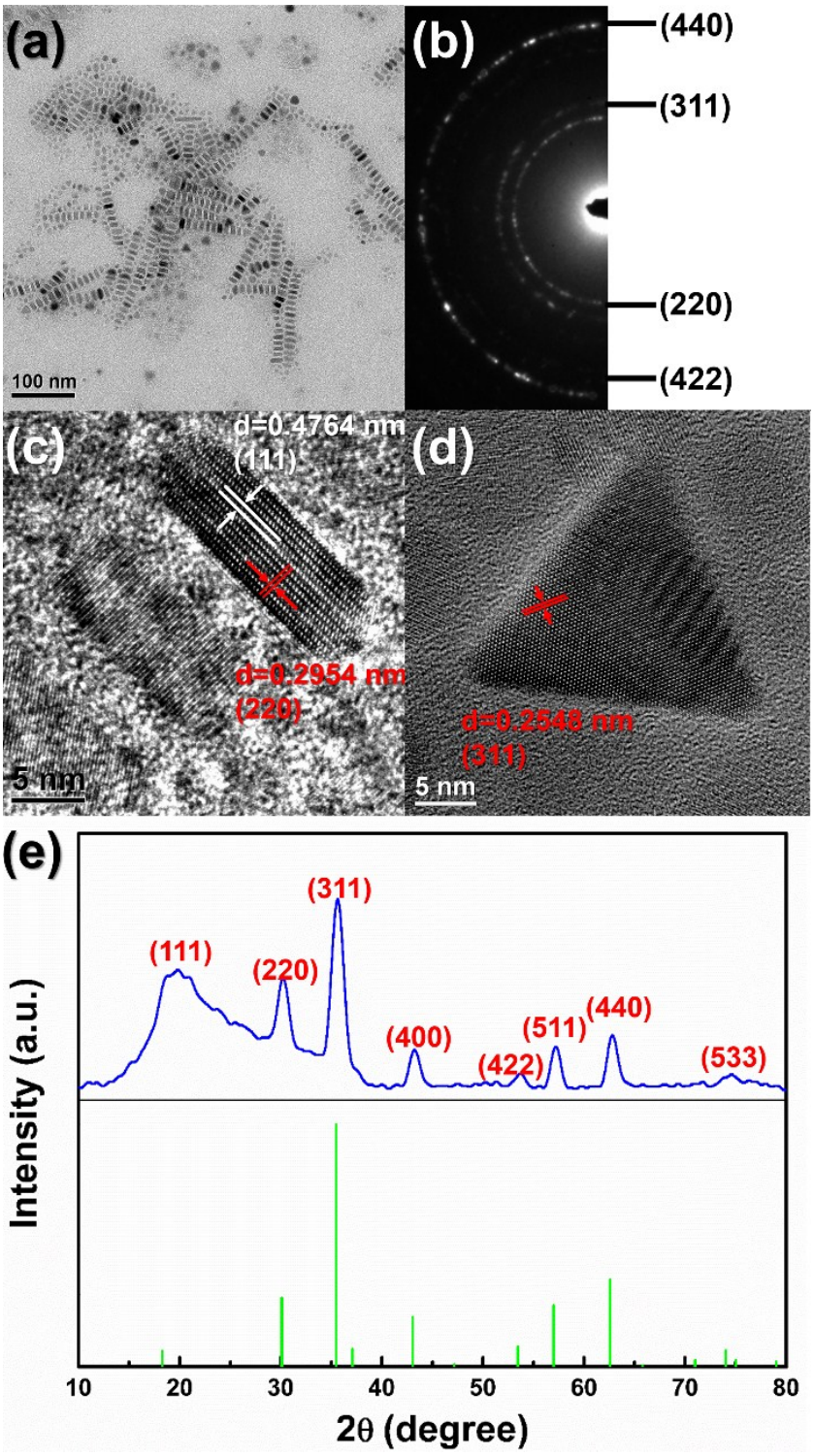

Figure S6. TEM images (a), selected area electron diffraction (SAED) pattern (b), HRTEM images from side face projection (c) and top face projection (d) and XRD pattern (e) of triangular prism shape MNCs.

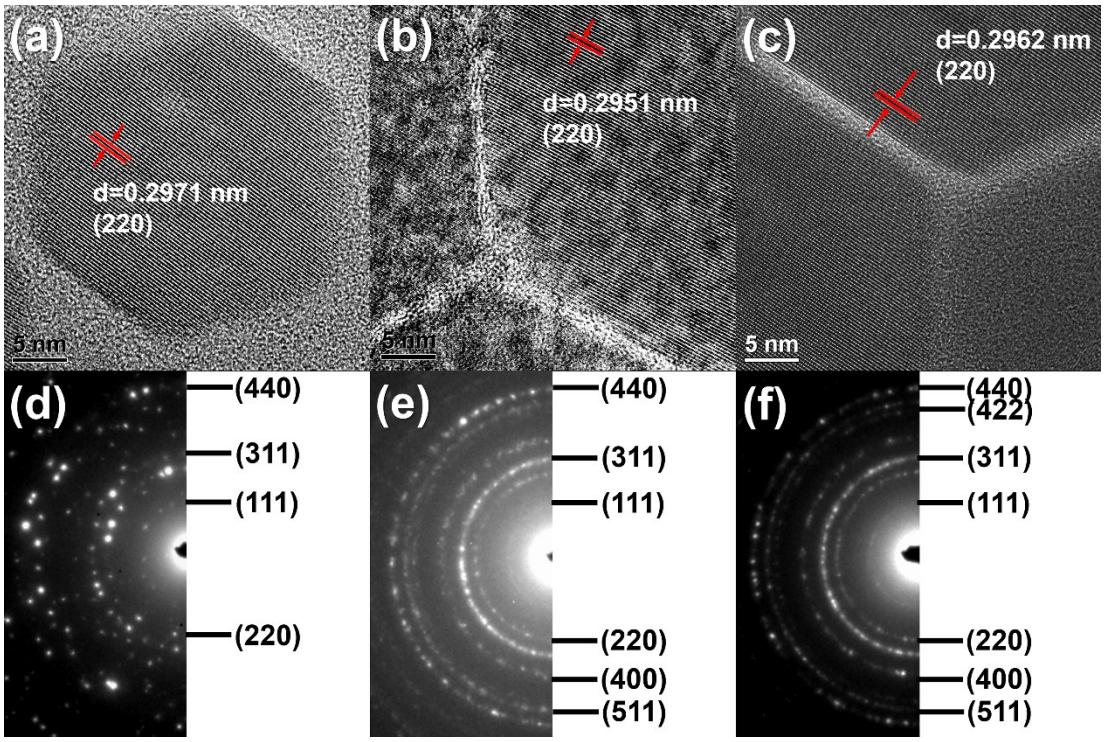

Figure S7. HRTEM images and SAED patterns of MNCs synthesized with various OA/OAm molar ratios. (a, d) 5/6 (20 mmol/24 mmol), (b, e) 13/9 (26 mmol/18 mmol), (c, f) 15/7 (30 mmol/14 mmol).

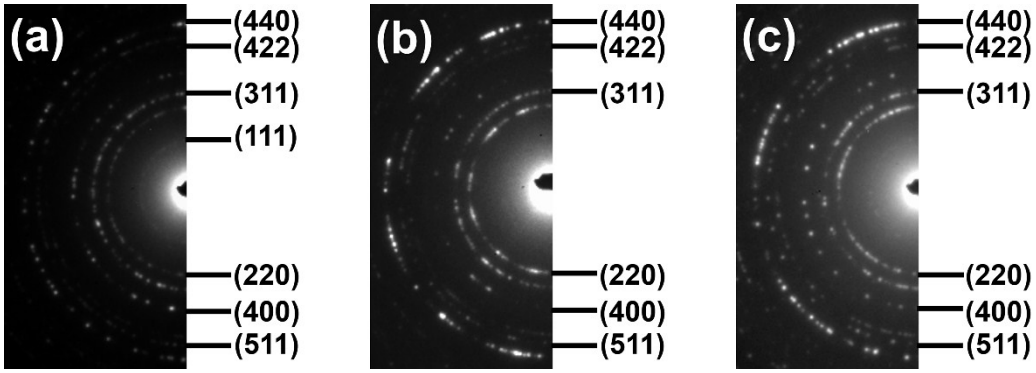

Figure S8. SAED patterns of MNCs synthesized under different reaction temperatures and times. (a) 220 °C, 4 hours, (b) 220 °C, 6 hours, (c) 240 °C, 2 hours. Amounts of $Fe(acac)_3$, OA, OAm and ODE used in synthesis are 3 mmol, 12 mmol, 32 mmol and 62.58 mmol, respectively.

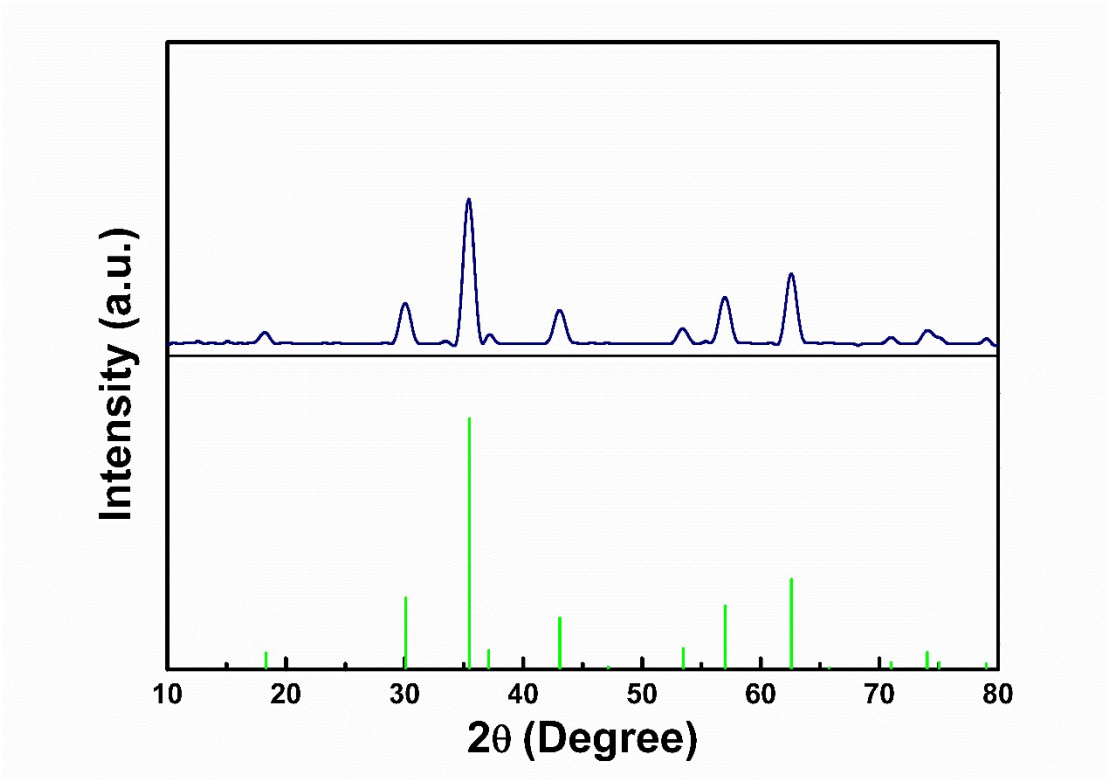

Figure S9. XRD pattern of MNCs using iron oleate ($Fe(OA)_3$) as reactant.

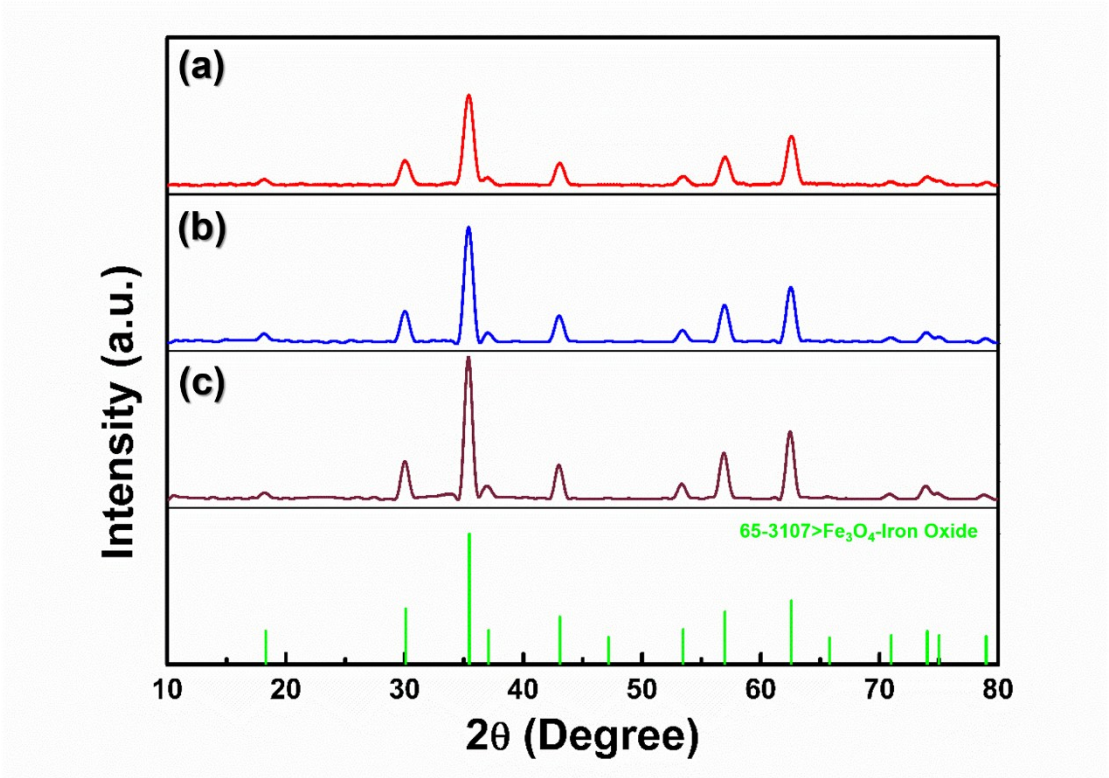

Figure S10. XRD patterns of MNCs synthesized with various $Fe(acac)_3$ amounts. (a) 3 mmol, (b) 4 mmol, (c) 5 mmol.

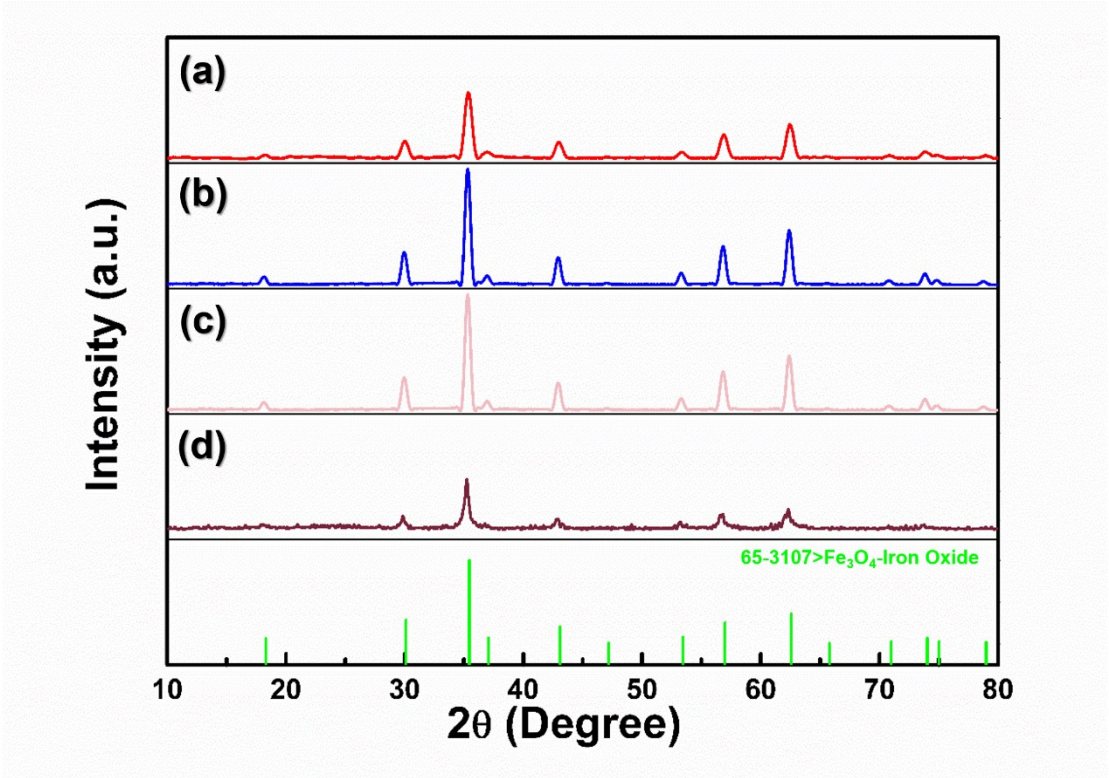

Figure S11. XRD patterns of MNCs synthesized with various OA/OAm molar ratios. (a) 1/10 (4 mmol/40 mmol), (b) 5/6 (20 mmol/24 mmol), (c) 13/9 (26 mmol/18 mmol), (d) 15/7 (30 mmol/14 mmol).

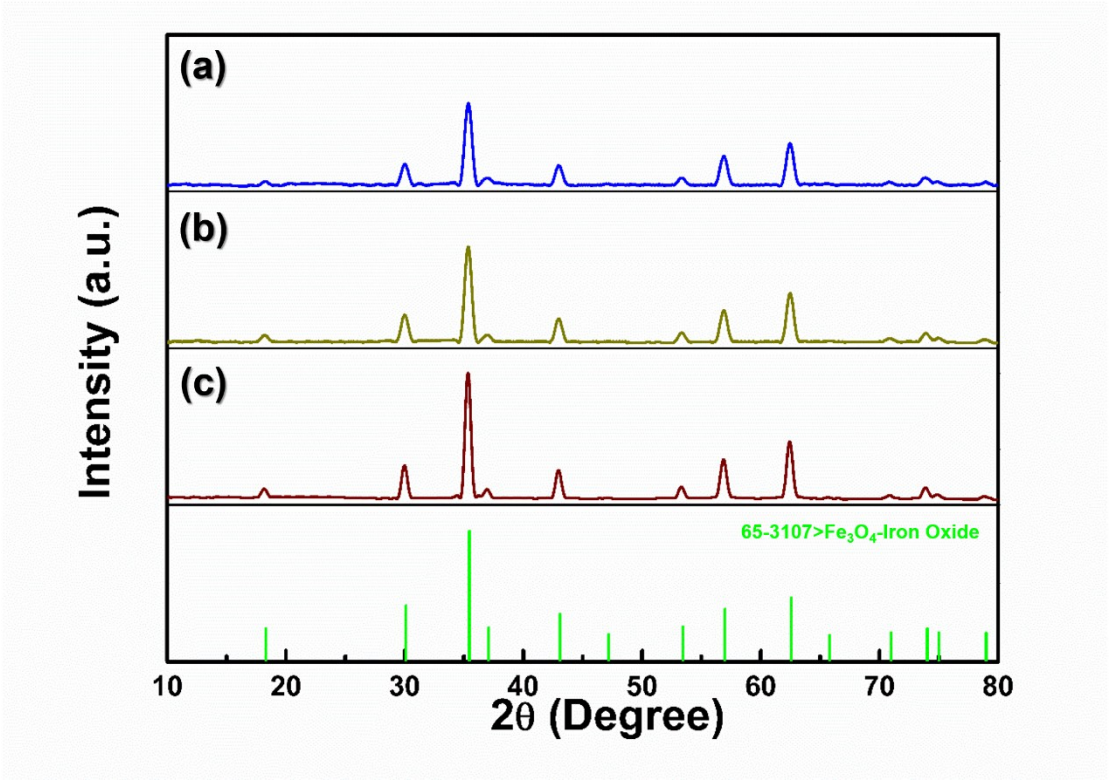

Figure S12. XRD patterns of MNCs synthesized under different reaction temperatures and times. (a) 220 °C, 4 hours, (b) 220 °C, 6 hours, (c) 240 °C, 2 hours. Amounts of $Fe(acac)_3$, OA, OAm and ODE used in synthesis are 3 mmol, 12 mmol, 32 mmol and 62.58 mmol, respectively.

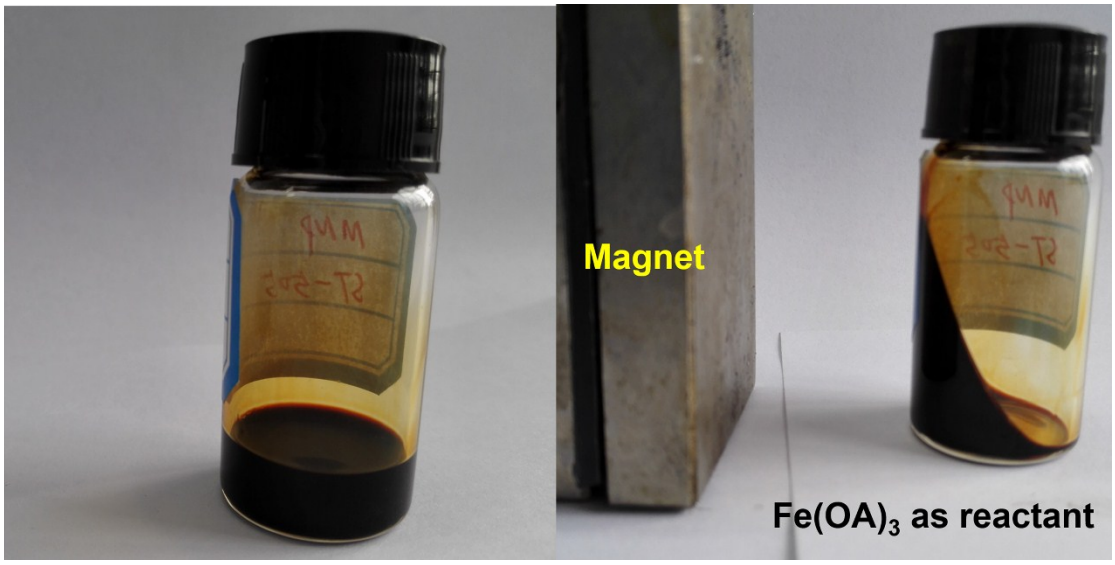

Figure S13. Photographs of MNCs using iron oleate ($Fe(OA)_3$) as reactant dispersed in hexane with and without magnet bar.

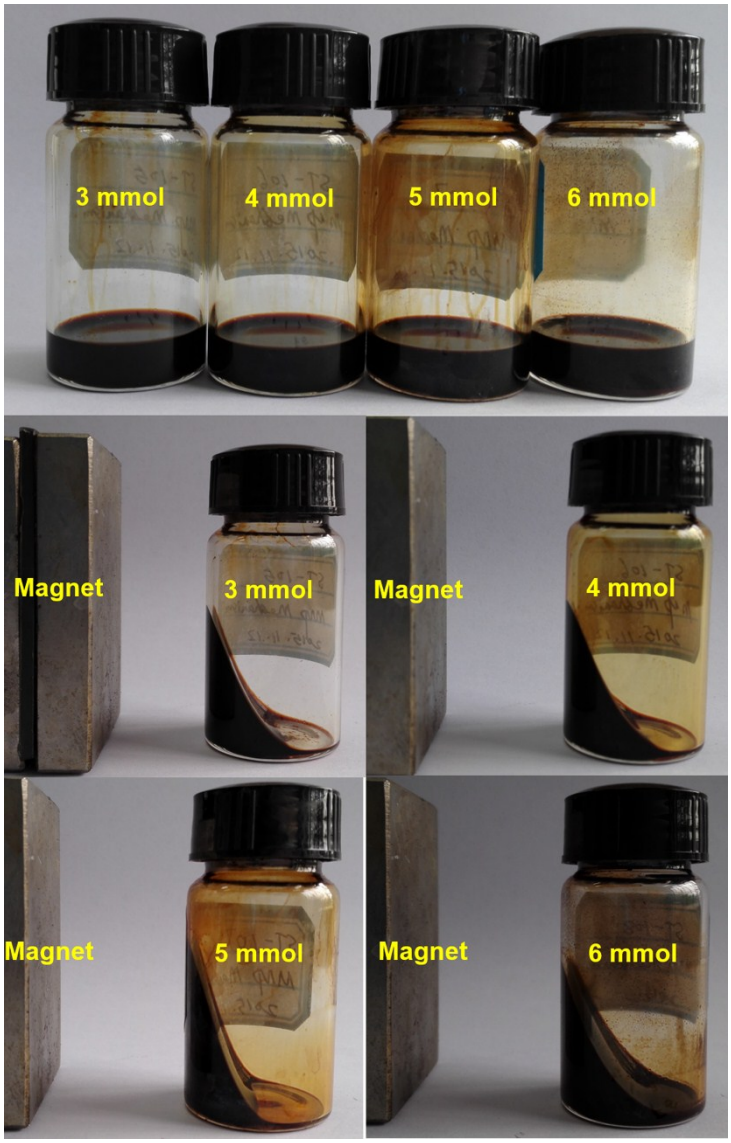

Figure S14. Photographs of MNCs synthesized with various $Fe(acac)_3$ amounts and dispersed in hexane with and without magnet bar.

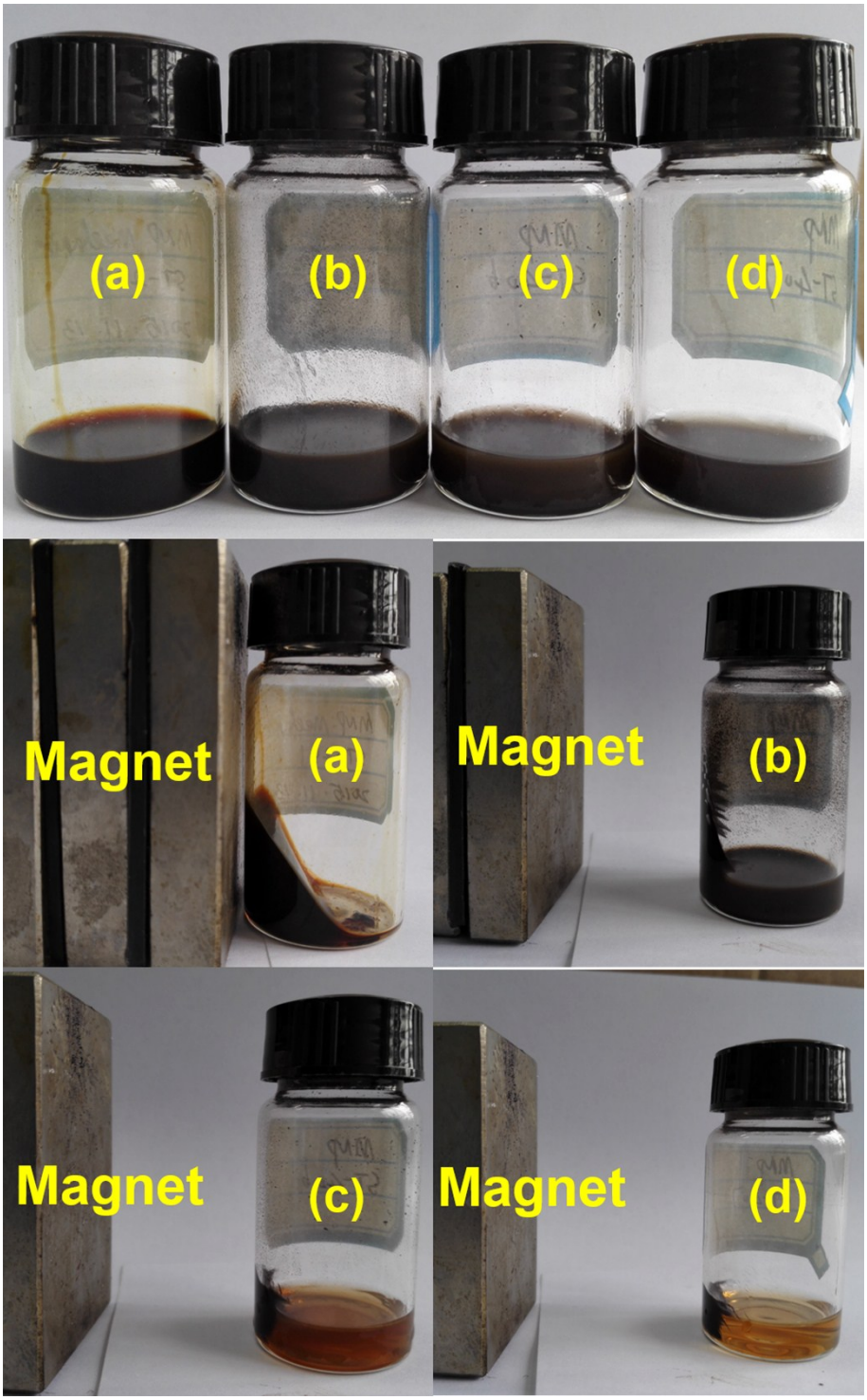

Figure S15. Photographs of MNCs synthesized with various OA/OAm molar ratios and dispersed in hexane with and without magnet bar. (a) 1/10 (4 mmol/40 mmol), (b) 5/6 (20 mmol/24 mmol), (c) 13/9 (26 mmol/18 mmol), (d) 15/7 (30 mmol/14 mmol).

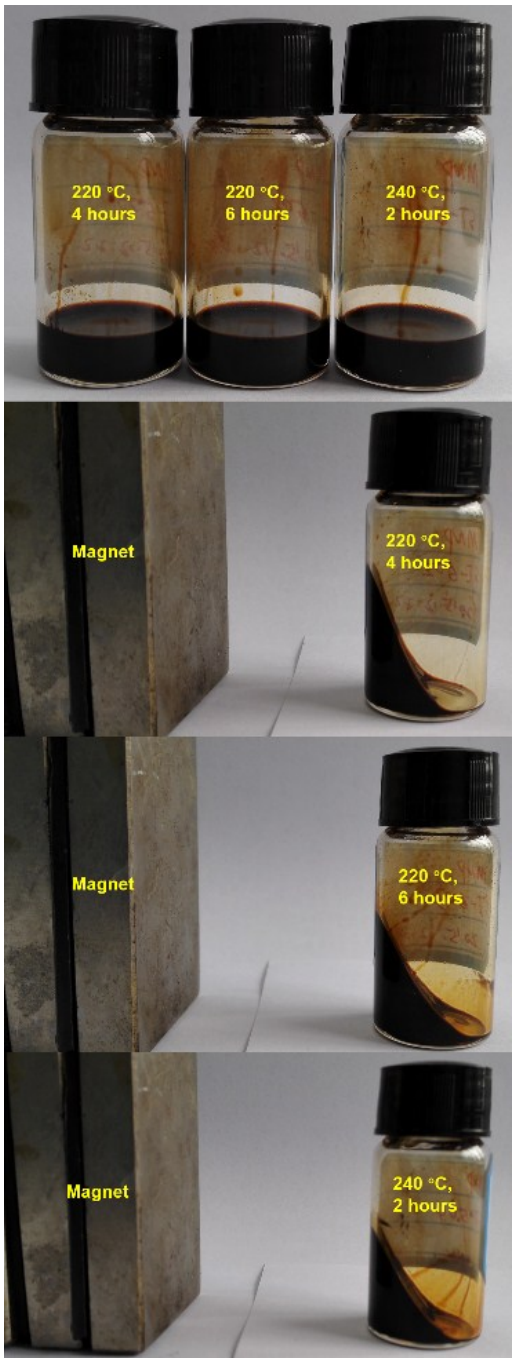

Figure S16. Photographs of MNCs synthesized under different reaction temperatures and times and dispersed in hexane with and without magnet bar.

Figure S17. Photographs of 6 gram MNCs dispersed in hexane with and without magnet bar.