

Supporting Information for

Fabrication, Magnetic Properties and Self-assembly of Hierarchical Crystallined Hexapod Magnetites

Xuzhen Wang,^a Jieshan Qiu,^{*a} Jiangying Qu,^a Zhiyu Wang,^a and Dangsheng Su^b

^a Carbon Research Laboratory, State Key Laboratory of Fine Chemicals, and Liaoning Key Laboratory for Energy Materials & Chemical Engineering; Faculty of Chemical, Environmental & Biological Science and Technology, Dalian University of Technology, Dalian 116024, Liaoning, China.

^b Shenyang National Laboratory of Materials Science, Institute of Metal Reserach, Shenyang 110016, Liaoning, China.

*Corresponding Author. E-mail: jqiu@dlut.edu.cn; Tel/Fax: +86-411-8498-6080

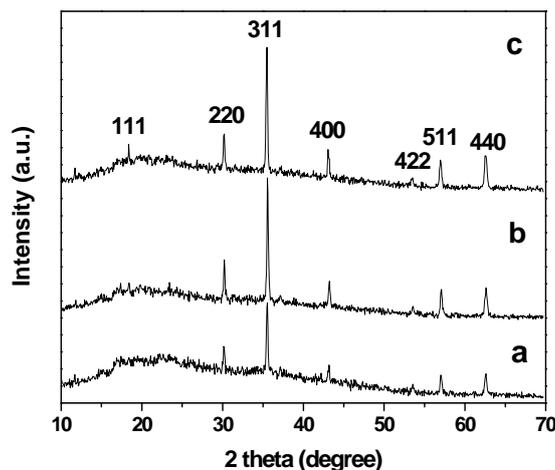


Figure S1. XRD patterns of the typical hexapod magnetite prepared in isopropanol at 350°C for (a) 6 h, (b) 12 h and (c) 24 h.

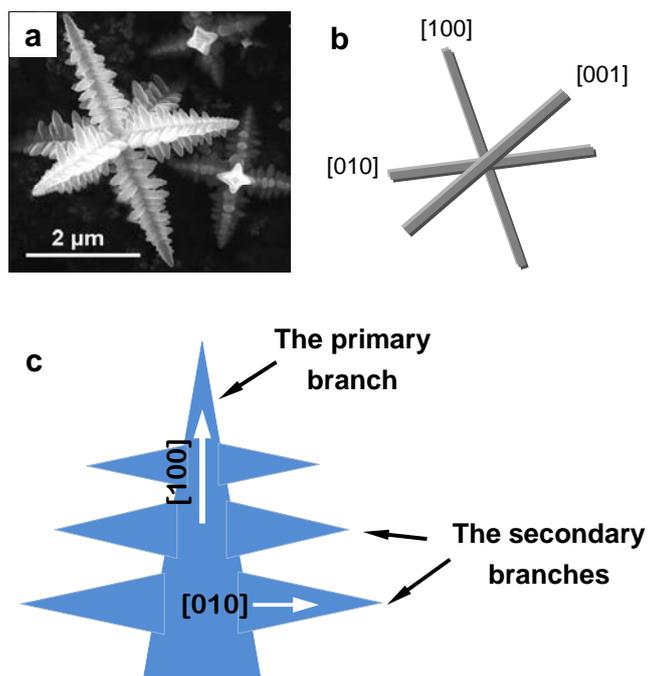


Figure S2. (a) The SEM image of an individual *h*-hexapod Fe_3O_4 and the schematic representation of the crystal growth direction of the primary (b, c) and secondary (c) branches.

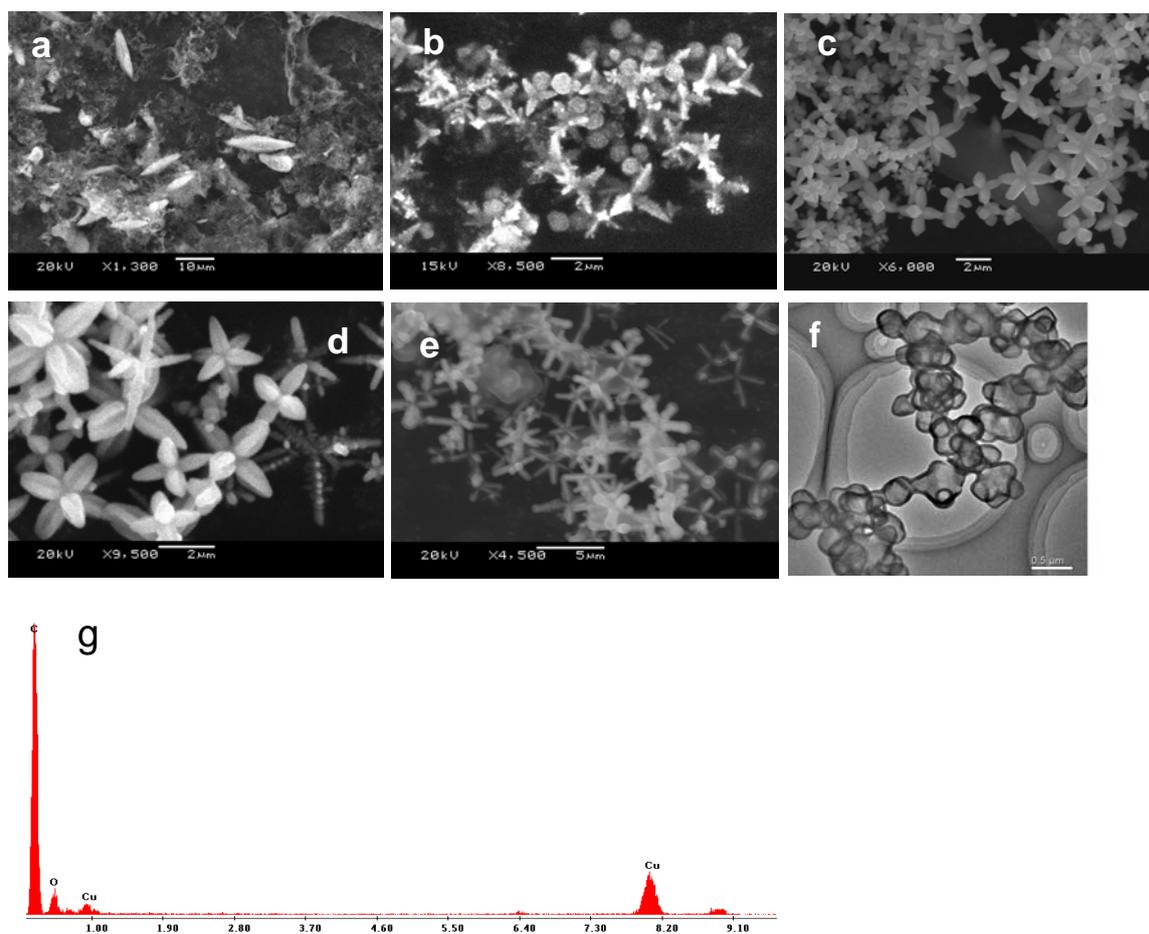


Figure S3. SEM images of the products prepared in isopropanol at different temperature (solvent 2 mL, ferrocene 30 mg, reaction for 24 h). (a) 250°C, (b) 300°C, (c) 400°C, (d) 450°C, (e) 500°C. (f) TEM image of hollow stars from the sample in (e) by acid-etch treatment. (g) EDX spectrum of the product in (e) demonstrates the existence of carbon shell.

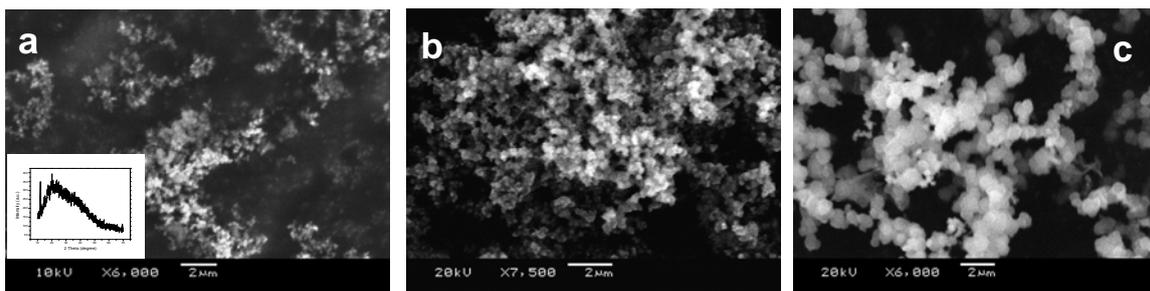


Figure S4. SEM images of irregular particles prepared in (a) cyclohexane and (b) benzene at 400°C for 24 h when ferrocene is 30 mg. The inset in (a) is the XRD pattern of the corresponding product. (c) Quasi-spherical particles obtained from 30 mg pure ferrocene without solvent at 400°C for 24 h in the presence of air.

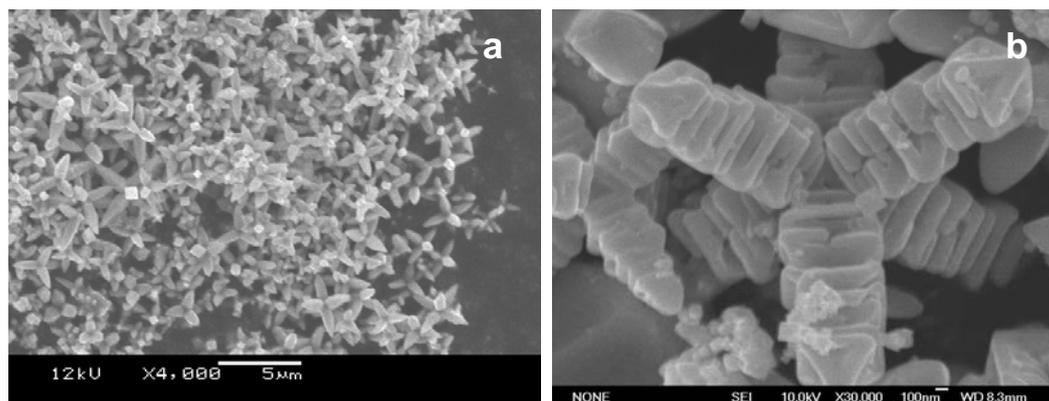


Figure S5. SEM images of Fe₃O₄ pyramid hexapod crystals prepared in methanol at 350°C (a) and 450°C (b) for 24 h.

Table S1. Summary of Various Experimental Conditions for the Fabrication of Magnetite and Their Final Morphologies

Solvent	Vol. (ml)	Ferrocene (mg)	Temp. (°C)	Reaction Time (h)	Morphology characteristics	Representative images
	2	30	300	4-30	MS ^a and star-shaped	Figure S3b
	2	30	350	2	MS	Figure 4c
	2	30	350	4-24	<i>h</i> -hexapods ^b	Fig.2(a,b) and Fig.4(d, e)
	4	10-60	350	6	MS	Figure 6b
Isopropanol (IPA)	6	20-100	350	6	IP ^c and MS	neglected
	2	10-30	400	2	MS	neglected
	2	30	400	4-24	star-shaped hexapods	Figure S3c
	2(N ₂) ^a	30	400	6	IP and multiple-pods	neglected
	2	60	400	6	MS and hexapods	neglected
	2	30	450	4-24	star-shaped hexapods	Figure S3d
Acetone (Ace)	2	30	350-400	4-24	<i>h</i> -hexapods	Figure 3a ₁
	2	30	300	30	<i>p</i> -hexapods ^d	Figure 3(c ₁ ,c ₂ ,c ₃)
Methanol (Meth)	2	30	350	4-24	<i>p</i> -hexapods	Figure S5(a)
	2	30	400-450	2-24	<i>p</i> -hexapods	Figure 3(b ₁ ,b ₂), Figure S5(b)
Benzene or Cyclohexane	2	30-100	300-500	6-24	IP	Figure S4(a, b)

Note: ^a MS refers to micro-sized spheres;

^b *h*-hexapods refer to hierarchical branched hexapods;

^c IP refers to irregular particles;

^d *p*-hexapods refers to pyramid hexapods.

Table S2. Magnetic Properties of Fe₃O₄ Crystals with Different Morphologies at Room Temperature

Sample	$\sigma_s/\text{emu}\cdot\text{g}^{-1}$	$\sigma_r/\text{emu}\cdot\text{g}^{-1}$	σ_r/σ_s	H_c/Oe
<i>h</i> -hexapods	128.0	44.15	0.345	238
<i>p</i> -hexapods	90.2	25.76	0.286	223
microspheres	88.6	16.20	0.183	160
bulk Fe ₃ O ₄	92–100 ^[1]	–	–	115–150 ^[2,3]

[1] R. M. Cornell, U. Schwertmann, *The Iron Oxides: Structure, Properties, Reactions, Occurrence and Uses*. VCH: Germany, **2003**.

[2] X. M. Liu, S. Y. Fu, H. M. Xiao, *Materials Letters*, **2006**, 60, 2979.

[3] B. Geng, J. Ma and J. You, *Cryst. Growth Des.*, **2008**, 8, 1443.