

Catalytic synthesis, characterization and magnetic properties of iron phosphide nanowires†

Jiun-Hu Chen,^a Ming-Fong Tai^b and Kai-Ming Chi^{*a}

^aDepartment of Chemistry and Biochemistry, National Chung Cheng University, Ming-Hsiung, Chia-Yi, Taiwan 621. E-mail: chekmc@ccu.edu.tw; Fax: 886 5 2721040; Tel: 886 5 2428128

^bDepartment of Electronic Engineering, Wufeng Institute of Technology, Ming-Hsiung, Chia-Yi, Taiwan 621

Received 26th September 2003, Accepted 22nd December 2003
First published as an Advance Article on the web 9th January 2004

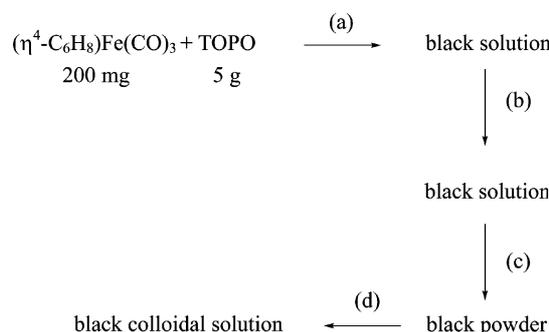
We report on the synthesis of iron phosphide nanowires by thermal decomposition of (η^4 -cyclohexadiene)iron tricarbonyl in the presence of TOP (tri-*n*-octylphosphine) and characterization of the products.

Nanostructured materials are attracting great research interest due to their application as catalysts of organic reactions, as gas sensors and as advanced materials in future optic, electronic and magnetic devices.^{1–3} Recently, the fabrication of Fe-containing magnetic nanomaterials including iron,⁴ iron oxides⁵ and alloys such as FePt⁶ and FeCo⁷ became a very important issue in the potential application of their magnetic characteristics. Iron phosphide, FeP, a low-band gap semiconductor material with special magnetic properties, has traditionally been prepared by high-temperature reactions.⁸ Recently, Lukehart and Brock groups reported the preparation of Fe₂P and FeP nanoparticles, respectively.⁹ Herein, we present the first example of synthesis of iron phosphide FeP nanowires by thermal decomposition of (η^4 -cyclohexadiene)-iron tricarbonyl, (η^4 -C₆H₈)Fe(CO)₃ in the presence of tri-*n*-octylphosphine oxide (TOPO) and tri-*n*-octylphosphine (TOP) as the stabilizing surfactants. In addition, magnetic properties of these products have been investigated in this study.

The preparative procedure summarized in Scheme 1 is modified from the method for generation of Fe nanorods previously reported by Hyeon *et al.*^{4m} Heating a mixture of 200 mg of (η^4 -C₆H₈)Fe(CO)₃ and 5.0 g of TOPO at ~340 °C under a nitrogen atmosphere for 30 min afforded a black solution. To this black mixture in TOPO, was added a set amount of (η^4 -C₆H₈)Fe(CO)₃ (0 mg, sample A; 10 mg, sample B; 25 mg, sample C) in 50 ml of TOP and the solution was continuously heated at ~360 °C for 30 min. This step was repeated once. After the resulting black mixture was cooled to room temperature, excess acetone was added to produce a black precipitate. The black powder product was collected by centrifugation and can be re-dispersed in pyridine or *n*-hexane to form a homogeneous solution.

These products were characterized by transmission electron microscopy (TEM, JEOL JEM-3010), energy-dispersive X-ray spectroscopy (EDS, Noran Nodel Voyager 100 and Link eXL-II), inductively coupled plasma atomic emission spectroscopy (ICP-AES, Jarrell-Ash ICAP 9000), and X-ray powder diffraction analysis (XRD, Rigaku Rotaflex RTP 500RC). The resulting data are summarized in Table 1. TEM examinations revealed that the majority of the products were nanowires

† Electronic supplementary information (ESI) available: TEM images, EDS and XRD data for samples A–D. See <http://www.rsc.org/suppdata/jm/b311943b/>



Scheme 1 Reagents and conditions: (a) Reflux at ~340 °C for 30 min. (b) i. Addition of *x* mg of (η^4 -C₆H₈)Fe(CO)₃ in 5.0 mL of TOP, (*x* = 0, (A); 10, (B); 25, (C)). ii. reflux at ~360 °C for 30 min. iii. repeat i, and ii. (c) i. Addition of excess acetone; ii. centrifugation and washing. (d) Re-dispersed in pyridine or *n*-hexane.

with a diameter of about 5 nm and a length of several hundred nanometers. A TEM image of sample B is shown in Fig. 1a. EDS analysis showed a relatively high phosphorus content in this sample (Fig. 1b). A HRTEM image of a single wire is shown in Fig. 1c and demonstrates the crystalline nature of the nanowire.

A comparison experiment (sample D) conducted by reflux of the precursor in TOPO for 1 h gave spherical nanoparticles whose EDS analysis exhibited a low phosphorus content (see ESI,† Fig. S-4). ICP-AES analysis of the samples provided the Fe and P content (wt%). By subtraction of the weight percentage of C, H, O, and P in the surfactant TOPO, the Fe/P mole ratio in these samples can be calculated and data are listed in Table 1. Iron/phosphorus mole ratios close to one in samples A, B and C indicate the existence of FeP as the major component. Elemental analysis for sample D showed that it contained 98% Fe. XRD patterns for samples A, B and C show nine strong peaks, collected in Table 1. All the peaks are in good agreement with the reported values.¹⁰ These prove that polycrystalline FeP exists in the nanowires.

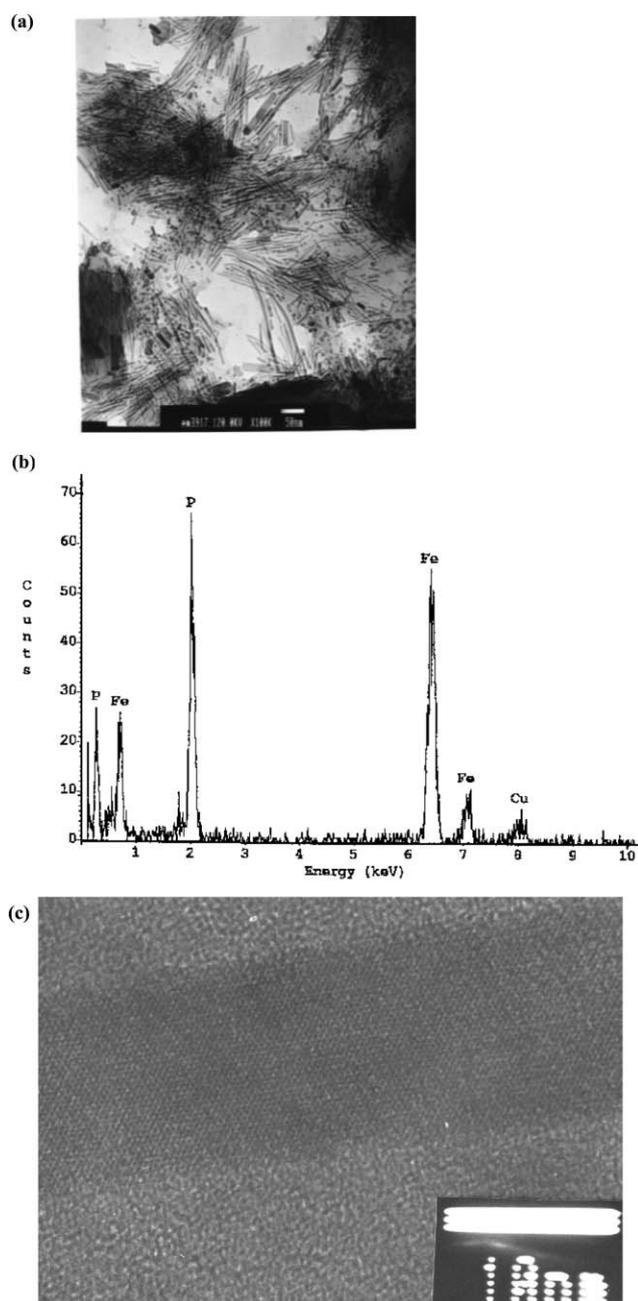
The magnetic properties of sample B have been investigated by a superconducting quantum interference device (SQUID, Oxford MagLab 2000). The temperature dependence of magnetization was measured in an applied magnetic field of 1000 Oe between 2 and 300 K using zero-field cooling (ZFC) and field-cooling (FC) procedures. The result shown in Fig. 2a is typical for magnetic nanoparticles.¹¹ Much higher blocking (140 K) and irreversibility temperatures (233 K) were observed for sample B compared to sample D, probably caused by the high aspect ratio (length/width) and greater thermal energy needed to align the disordered spin. The magnetization hysteresis loop at 2 K is shown in Fig. 2b and exhibits a

Table 1 Summary of the characterization data for nanostructured samples

Sample	Elemental analysis (ICP-AES) ^a		Calc. C, H & O ^b (wt%)	Calc. P _{sample} ^b (wt%)	Fe/P mole ratio	Composition and appearance (TEM)
	Fe (wt%)	P (wt%)				
A	28.9	20.8	50.3	16.4	0.98	FeP nanorods
B	21.8	17.1	61.1	11.8	1.02	FeP nanowires
C	22.8	17.5	59.7	12.3	1.03	FeP nanowires and nanorods
D	24.5	6.3	69.2	0.3	45.29	Fe spherical nanoparticles

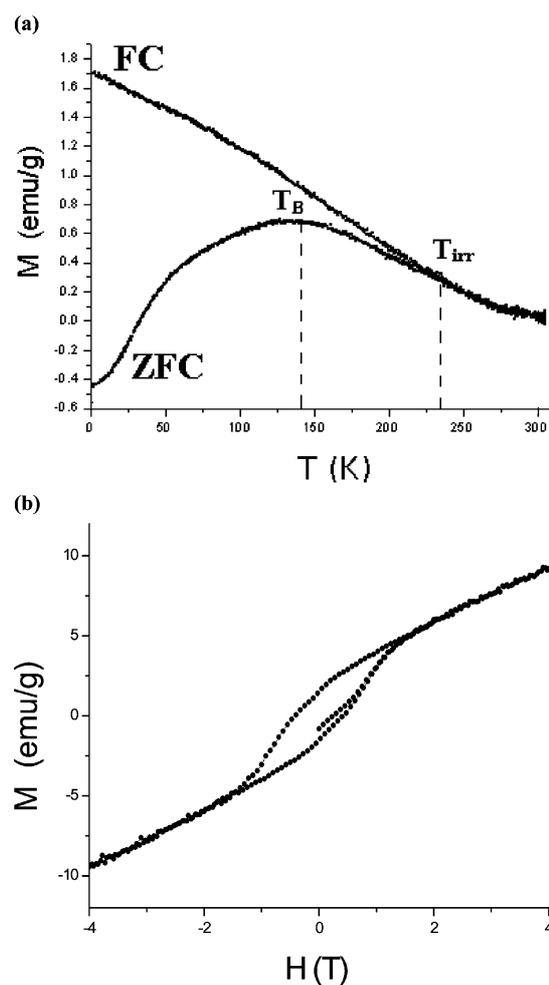
Sample	XRD pattern (2θ/°)								
A	32.88	34.81	35.58	37.16	46.75	48.34	50.54	56.10	59.65
B	32.90	34.68	35.46	37.29	47.13	48.33	—	56.30	59.49
C	32.80	34.70	35.53	37.24	47.05	48.46	50.62	56.10	59.67
FeP ^c	32.74	34.51	35.46	37.14	46.96	48.30	50.38	56.00	59.60
(hkl)	(011)	(200)	(120)	(111)	(220)	(211)	(130)	(031)	(002)

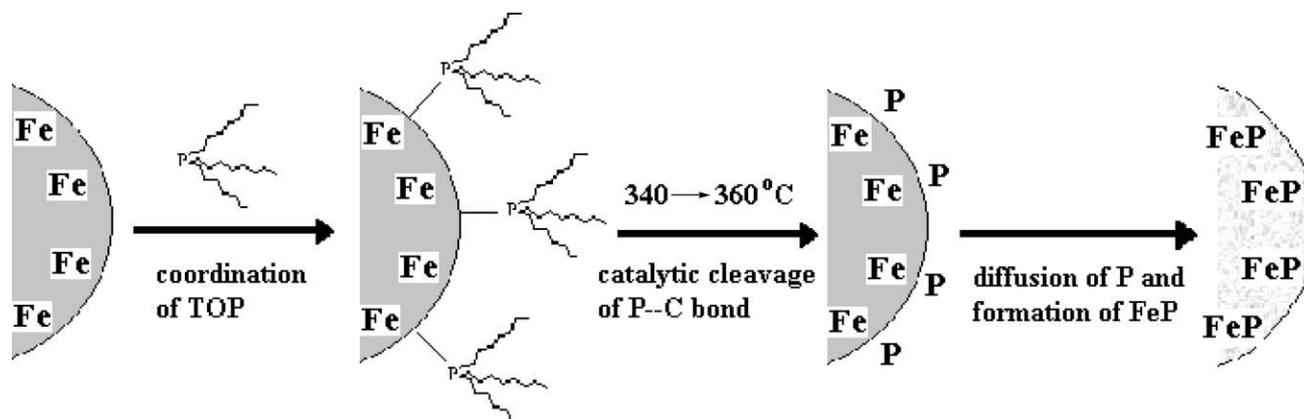
^a The inaccuracy of ICP-AES is 3%. ^b Calc. C, H & O (wt%) = 100 - Fe (wt%) - P (wt%). Calc. P_{sample} (wt%) = P (wt%) - [Calc. C, H & O (wt%)/355.67] × 30.97. ^c ICDD-PDF No. 78-1443.

**Fig. 1** (a) Transmission electron micrograph, (b) EDS data, and (c) high resolution transmission electron micrograph for sample **B**.

coercivity of about 4000 Oe and no saturation up to a magnetic field of 4 T.

A mechanism of formation of FeP nanostructures is proposed in Scheme 2. Reflux of $(\eta^4\text{-C}_6\text{H}_8)\text{Fe}(\text{CO})_3$ in TOPO provided iron nanoparticles. Tri-*n*-octylphosphine was added to the solution and it coordinated to the iron particles first. Then, catalytic cleavage of P-C bonds in TOP occurred and P atoms formed on the surface of Fe particles. Diffusion of phosphorus atoms to the inside of the particles resulted in the

**Fig. 2** (a) ZFC and FC magnetization vs. temperature at an applied magnetic field of 1000 Oe, and (b) magnetization hysteresis loop recorded at 2 K for sample **B**.



Scheme 2

formation of FeP. Powdered FeP has been produced by the sonochemical reaction of $\text{Fe}(\text{CO})_5$ and triethylphosphine via a similar pathway.¹²

Acknowledgements

This research was financially supported by the National Science Council of the Republic of China (NSC 90-2113-M-194-013). We are grateful to Professor C.-R. C. Wang for TEM studies.

Notes and references

- G. Schmid, Ed., *Clusters and Colloids: From Theory to Applications*, VCH, Weinheim, Germany, 1994.
- G.-W. Chow and K. E. Gonsalves, Eds., *Nanotechnology, Molecularly Designed Materials*, ACS Symposium Series 622, ACS, Washington, 1996.
- J. H. Fendler, Ed., *Nanoparticles and Nanostructured Films: Preparation, Characterization and Applications*, Wiley-VCH, Weinheim, Germany, 1998.
- (a) K. S. Suslick, S.-B. Cheo, A. A. Cichowlas and M. W. Grinstaff, *Nature*, 1991, **353**, 414; (b) X. Cao, Yu. Koltypin, G. Kataby, R. Prozorov and A. Gedanken, *J. Mater. Res.*, 1995, **10**, 2952; (c) K. S. Suslick, M. Fang and T. Hyeon, *J. Am. Chem. Soc.*, 1996, **118**, 11960; (d) K. S. Suslick, T. Hyeon and M. Fang, *Chem. Mater.*, 1996, **8**, 2172; (e) D. deCaro, T. O. Ely, A. Mari, B. Chaudret, E. Snoeck, M. Respaud, J.-M. Broto and A. Fert, *Chem. Mater.*, 1996, **8**, 1987; (f) G. Katabi, R. Prozorov, Yu. Koltypin, H. Cohen, C. N. Sukenik, A. Ulman and A. Gedanken, *Langmuir*, 1997, **13**, 6151; (g) A. Sugawara, T. Coyle, G. G. Hembree and M. R. Scheifein, *Appl. Phys. Lett.*, 1997, **70**, 1043; (h) G. Kataby, A. Ulman, R. Prozorov and A. Gedanken, *Langmuir*, 1998, **14**, 1512; (i) D. A. Tulchinsky, M. H. Kelley, J. J. McMilland, R. Gupta and R. J. Celotta, *J. Vac. Sci. Technol., A*, 1998, **16**, 1817; (j) K. T. Wu, Y. D. Yao, C. R. C. Wang, P. F. Chen and E. T. Yeh, *J. Appl. Phys.*, 1999, **85**, 5959; (k) C. Y. Wang, Z. Y. Chen, B. Cheng, Y. R. Zhu and H. J. Liu, *Mater. Sci. Eng.*, 1999, **B60**, 223; (l) G. Kataby, M. Cojocar, R. Prozorov and A. Gedanken, *Langmuir*, 1999, **15**, 1703; (m) S.-J. Park, S. Kim, S. Lee, Z. G. Khim, K. Char and T. Hyeon, *J. Am. Chem. Soc.*, 2000, **122**, 8581; (n) E. E. Carpenter, *J. Magn. Magn. Mater.*, 2001, **225**, 17; (o) G. H. Lee, S. H. Huh, J. W. Park, H.-C. Ri and J. W. Jeong, *J. Phys. Chem. B*, 2002, **106**, 2123.
- (a) C. Pascal, J. L. Pascal, F. Favier, M. L. E. Moubtassim and C. Payen, *Chem. Mater.*, 1999, **11**, 141; (b) C. Yee, G. Kataby, A. Ulman, T. Prozorov, H. White, A. King, M. Rafailovich, J. Sokolov and A. Gedanken, *Langmuir*, 1999, **15**, 7111; (c) T. Fried, G. Shemer and G. Gleiter, *Adv. Mater.*, 2001, **13**, 1158; (d) Y. K. Gun'ko, S. C. Pillai and D. McInerney, *J. Mater. Sci.*, 2001, **12**, 299; (e) E. Strable, J. W. M. Bulte, B. Moskowicz, K. Vivekanandan, M. Allen and T. Douglas, *Chem. Mater.*, 2001, **13**, 2201; (f) K. V. P. M. Shaft, A. Ulman, X. Yan, N.-L. Yang, C. Estournés, H. White and M. Rafailovich, *Langmuir*, 2001, **17**, 5903; (g) T. Hyeon, S. S. Lee, J. Park, Y. Chung and H. B. Na, *J. Am. Chem. Soc.*, 2001, **123**, 12798; (h) Y. Ni, X. Ge, Z. Zhang and Q. Ye, *Chem. Mater.*, 2002, **14**, 1048; (i) K. V. P. M. Shaft, A. Ulman, A. Dyal, X. Yan, N.-L. Yang, C. Estournés, L. Fourrries, A. Wattiaux, H. White and M. Rafailovich, *Chem. Mater.*, 2002, **14**, 1778; (j) A. K. Boal, K. Das, M. Gray and V. M. Rotello, *Chem. Mater.*, 2002, **14**, 2628.
- (a) S. Sun, C. B. Murray, D. Weller, L. Folks and A. Moser, *Science*, 2000, **287**, 1989; (b) Z. R. Dai, S. Sun and Z. L. Wang, *Nano Lett.*, 2001, **1**, 443; (c) S. Sun, S. Anders, H. F. Hamann, J.-U. Thiele, J. E. E. Baglin, T. Thomson, E. E. Fullerton, C. B. Murray and B. D. Terris, *J. Am. Chem. Soc.*, 2002, **124**, 2884; (d) E. Shevchenko, D. Talapin, A. Kornowski, F. Wiekhorst, J. Kötzler, M. Haase, A. Rogach and H. Weller, *Adv. Mater.*, 2002, **14**, 287.
- H. R. Khan and K. Petrikowski, *Mater. Sci. Eng., C*, 2002, **19**, 345.
- N. N. Greenwood and A. E. Earnshaw, *Chemistry of the Elements*, Pergamon Press, New York, 1994.
- (a) C. M. Lukehart, S. B. Milne and S. R. Stock, *Chem. Mater.*, 1998, **10**, 903; (b) K. L. Stamm, J. C. Garno, G. Liu and S. L. Brock, *J. Am. Chem. Soc.*, 2003, **125**, 4038.
- The diffraction pattern for FeP is obtained from ICDD-PDF No. 78-1443.
- (a) Q. Chen and Z. Zhang, *Appl. Phys. Lett.*, 1998, **73**, 3156; (b) S. Sun and C. B. Murray, *J. Appl. Phys.*, 1999, **85**, 4325.
- J. D. Sweet and D. J. Casadonte, Jr., *Ultrason. Sonochem.*, 2001, **8**, 97.