

Direct Synthesis and Size Selection of Ferromagnetic FePt Nanoparticles

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A one-step synthesis of L1₀ FePt nanoparticles ca. 17.0 nm in diameter by reductive decomposition of the single-source precursor, FePt(CO)₄dppmBr₂, on a water-soluble support (Na₂CO₃) is demonstrated. Direct conversion of a FePt(CO)₄dppmBr₂/Na₂CO₃ composite to a L1₀ FePt/Na₂CO₃ nanocomposite occurs at 600 °C under getter gas with metal-ion reduction and minimal nanoparticle coalescence. Triturating the resulting nanocomposite with water simultaneously dissolves the sodium carbonate solid support and precipitates the formed fct FePt nanoparticles. As-prepared FePt nanoparticles are ferromagnetic and exhibit coercivities of 14.5 kOe at 300 K and 21.8 kOe at 5 K. When capped by functionalized methoxypoly(ethylene glycol) surfactant molecules, as-prepared, polydisperse ferromagnetic FePt nanoparticles can be dispersed and size-selected by fractional precipitation.

Introduction

Nanoscale magnetic particles are of interest for developing a more complete understanding of ferromagnetism and as materials potentially suitable for high-density magnetic storage.¹ FePt nanoparticles exist in a chemically disordered face-centered cubic (fcc) structure having very small coercivity and soft magnetic properties or in a L1₀ chemically ordered face-centered tetragonal (fct) structure having a large magnetic anisotropy, high coercivity and hard magnetic properties. An excellent timely review of the synthesis and properties of FePt nanoparticle materials is now available.²

Methods for preparing FePt nanoparticles usually involve initial formation of fcc FePt nanoparticles followed by thermal annealing to effect a fcc to fct phase transformation. While different precursors are commonly employed as sources of Fe and Pt atoms,^{3–7} use of single-source precursors has been reported recently.^{8,9} Direct formation of fct FePt

nanoparticles from precursors has been achieved in a solution-phase synthesis conducted at 389 °C⁷ and within a solid-phase TiO₂ sol–gel matrix at 600 °C.¹⁰

Obtaining fct FePt nanoparticles exhibiting significant room-temperature coercivity is desired for high-density magnetic storage. FePt coercivity is maximized at a slightly iron-rich alloy composition (Fe₅₅Pt₄₅)¹ and by thermal annealing fcc FePt particles at ca. 650 °C. Annealing at higher temperatures decreases observed coercivity due to particle sintering and to phase separation at temperatures of 800 °C or above.¹¹ Sintering effects have been reduced by using rapid thermal annealing (annealing times of only 5 s),¹² by binding fcc FePt nanoparticles to the surface of oxidized Si wafers prior to annealing,¹³ by intentional use of Fe-oxide surface passivation,^{5,14} by coating fcc FePt nanoparticles with a silica shell,¹⁵ or by annealing preformed fcc FePt nanoparticles on NaCl as a support.¹⁶

As part of a continuing study of the preparation of metal alloy nanoparticles using single-source molecular

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- (1) Wirth, S.; von Monnar, S. *Handbook of Advanced Magnetic Materials*; Springer: New York, 2006; Vol. 1.
- (2) Sun, S. *Adv. Mater.* **2006**, *18*, 393.
- (3) Sun, S.; Murray, C. B.; Weller, D.; Folks, L.; Moser, A. *Science* **2000**, *287* (5460), 1989.
- (4) Sun, X.; Kang, S.; Harrell, J. W.; Nikles, D. E.; Dai, Z. R.; Li, J.; Wang, Z. L. *J. Appl. Phys.* **2003**, *93* (10, Pt. 2), 7337.
- (5) Chen, M.; Liu, J. P.; Sun, S. *J. Am. Chem. Soc.* **2004**, *126*, 8394.
- (6) Harrell, J. W.; Wang, S.; Nikles, D. E.; Chen, M. *Appl. Phys. Lett.* **2001**, *79*, 4393.
- (7) Howard, L. E. M.; Nguyen, H. L.; Giblin, S. R.; Tanner, B. K.; Terry, I.; Hughes, A. K.; Evans, J. S. O. *J. Am. Chem. Soc.* **2005**, *127*, 10140.
- (8) Song, H. M.; Hong, J. H.; Lee, Y. B.; Wan, S. K.; Youngmee, K.; Kim, S.; Hur, N. H. *Chem. Commun.* **2006**, 1292.

- (9) Siani, J.; Captain, B.; Alexeev, O. S.; Stafyla, E.; Hungria, A. B.; Midgley, P. A.; Thomas, J. M.; Adams, R. D.; Amiridis, M. D. *Langmuir* **2006**, *22*, 5160.
- (10) Sort, J.; Surinach, S.; Baro, M. D.; Muraviev, D.; Dzhardimalieva, G. I.; Golubeva, N. D.; Pomogailo, S. I.; Pomogailo, A. D.; Macedo, W. A. A.; Weller, D.; Skumryev, V.; Nogues, J. *Adv. Mater.* **2006**, *18*, 466.
- (11) Zeng, H.; Li, J.; Wang, Z. L.; Liu, J. P.; Sun, S. *IEEE Trans. Magn.* **2002**, *38*, 2598.
- (12) Zeng, H.; Sun, S.; Sandstrom, R. L.; Murray, C. B. *J. Magn. Magn. Mater.* **2003**, *266*, 227.
- (13) Mizuno, M.; Sasaki, Y.; Yu, A. C. C.; Inoue, M. *Langmuir* **2004**, *20*, 11305.
- (14) Liu, C.; Wu, X.; Klemmer, T.; Shukla, N.; Weller, D.; Roy, A. G.; Tanase, M.; Laughlin, D. *Chem. Mater.* **2005**, *17*, 620.
- (15) Lee, D. C.; Mikulec, F. V.; Pelaez, J. M.; Koo, B.; Korgel, B. A. *J. Phys. Chem. B* **2006**, *110*, 11160.
- (16) Elkins, K. E.; Li, D.; Poudyal, N.; Nandwana, V.; Jin, Z.; Chen, K.; Liu, J. P. *J. Phys. D: Appl. Phys.* **2005**, *38*, 2306–2309.

precursors,^{17–21} we now report (1) the direct synthesis of fct FePt nanoparticles (5–55 nm in diameter) by thermal reduction of a (1:1) Fe, Pt-dinuclear precursor deposited onto a water-soluble solid support, and (2) subsequent size selection of as-prepared ferromagnetic FePt nanoparticles by fractional precipitation using functionalized long-chain PEG molecular surfactants. This synthesis strategy provides a one-step, solid-state preparation of fct FePt nanoparticles on a readily removal solid support and a protocol for effecting significant size selection of ferromagnetic nanoparticles.

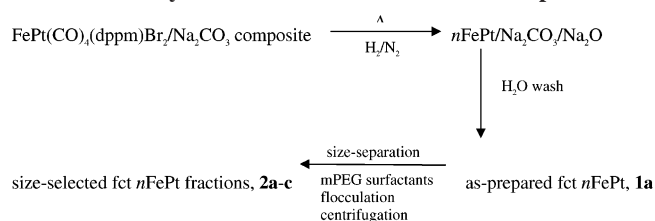
Experimental Section

Reagents and General Methods. Methoxypoly(ethylene glycol) (mPEG) (MW 2000) derivatives thiol (mPEG-SH) and succinic acid (mPEG-COOH) were purchased from Sun Bio Corporation, Inc. Organometallic reagents were purchased from Strem Chemicals, Inc., and all other reagents were purchased from Aldrich. The complexes $\text{Fe}(\text{CO})_4(\text{dppm})^{22}$ and $\text{FePt}(\text{CO})_4(\text{dppm})\text{Br}_2^{23}$ and the surfactant mPEG-dopamine²⁴ were prepared as described in the literature.

Thermal treatments were conducted inside a quartz tube under a continuous gas flow using a 1 foot Linberg/Blue tube furnace. Sonication was done via a glass container immersed in a Bransonic 2510R sonifier. Powder X-ray diffraction (XRD) scans were obtained on a Scintag X1 θ/θ automated powder X-ray diffractometer with a Cu target, a Peltier-cooled solid-state detector, and a zero-background Si(510) sample support. TEM bright-field micrographs were recorded on both a 200 kV Phillips CM20T TEM and HR-TEM 200 kV Philips CM200 FEG TEM coupled with an Oxford light-element EDS detector and EMiSPEC Vision data acquisition system. HR-EDS data was collected in Nanoprobe mode with an acceleration voltage of 200 kV and a collection time of 100 s for each particle. NMR spectra were obtained on a Bruker 500 MHz spectrometer. Magnetic measurements were performed at Oak Ridge National Laboratory using a SQUID magnetometer. Microanalyses were performed by Galbraith Laboratories, Knoxville, TN.

Direct Preparation of L1₀ FePt Nanoparticles. In a typical preparation, 0.150 g (0.165 mmol) of $\text{FePt}(\text{CO})_4(\text{dppm})\text{Br}_2$ was dissolved in a minimum of CH_2Cl_2 (5 mL) under N_2 . To achieve a final composite of 9 wt % total metal loading, we added 0.415 g (3.92 mmol) of ball-milled anhydrous Na_2CO_3 to the above solution and allowed it to stir for 1 h. Solvent was removed under reduced pressure, producing a free-flowing orange powder. The sample was placed in a glazed ceramic boat and inserted in the center of a tube

Scheme 1. Synthesis of Size-Selected FePt Nanoparticles



furnace. The tube volume was purged with N_2 (20 min) and 1:9 $\text{H}_2:\text{N}_2$ (20 min), followed by reductive decomposition at 600 °C under 1:9 $\text{H}_2:\text{N}_2$ (4 h). The resulting black powder was allowed to cool to room temperature before being removed from the furnace. This solid was very responsive to an applied magnetic field of an external magnet. FePt nanoparticles were isolated by adding this black powder to 5 mL of water followed by mixing, mild sonication, and centrifugation to give a dark precipitate of metal powder. This procedure was repeated two times to ensure complete dissolution of excess water-soluble support and once with acetone to facilitate drying. The wet metal powder was dried in air to give 0.0350 g (84% based on total metal) of a free-flowing black, ferromagnetic, as-prepared FePt powder (**1a**). Anal. by ICP-OES (Element (wt%)): Fe (20.1); Pt (68.7). The chemical composition of the flow gas during the thermal treatment was not analyzed.

L1₀ FePt Nanoparticle Size Separation. For size separation, ca. 20 mg of as-prepared fct FePt nanoparticles were first sonicated (2 h) and then shaken (24 h) in methylene chloride solution (11 mL) containing 0.1 mL (0.73 mmol) of triethylamine, 110 mg (0.06 mmol) of mPEG-dopamine, and 110 mg (0.06 mmol) of mPEG-SH, producing a golden brown solution with some solid phase evident. The supernatant was removed and further processed for FePt size selection. Solubilized nanoparticles were precipitated from solution by diluting 2-fold with ethanol and centrifuging at 5500 rpm (1 h). The precipitated powder was dispersed into 5 mL of ethylene glycol by low-power sonication (30 min). The solution was centrifuged at 1000 rpm (15 min) to yield a small amount of precipitate (**2a**) and a golden supernatant. The supernatant was placed into a test tube and centrifuged again at 5500 rpm (15 min). A second precipitate (**2b**) was collected for further characterization. The supernatant was then doubled in volume by adding isopropyl alcohol as a flocculant. The mixture was homogenized using low-power sonication (30 min). The solution was then centrifuged at 5500 rpm (1 h), and a final precipitate (**2c**) was collected for further characterization. Nanoparticle fractions **2a–2c** can be re-dispersed in ethylene glycol with dispersion stability increasing as **2a** < **2b** < **2c**. Fraction **2c** can be precipitated through the addition of isopropyl alcohol only with difficulty.

Results and Discussion

Evaporation of solvent from slurries of $\text{FePt}(\text{CO})_4(\text{dppm})\text{Br}_2$ with fine, dry sodium carbonate powder in methylene chloride gives orange $\text{FePt}(\text{CO})_4(\text{dppm})\text{Br}_2/\text{Na}_2\text{CO}_3$ composite powders (Scheme 1). Thermal treatment of such composites at 600 °C under getter gas (1:9 $\text{H}_2:\text{N}_2$) in a tube furnace leads to minor calcination of Na_2CO_3 to form Na_2O ,²⁵ precursor degradation with reduction of the metal atoms, and formation of fct $\text{FePt}/\text{Na}_2\text{CO}_3$ nanocomposites as black powders. Variation of the precursor: Na_2CO_3 mass ratio determines the total metal weight percent of the final nanocomposite and provides some control over FePt mean

- (17) Kwiatkowski, K. C.; Milne, S. B.; Murkerjee, S.; Lukehart, C. M. *J. Cluster Sci.* **2005**, *16*, 251.
- (18) King, W. D.; Steigerwalt, E. S.; Deluga, G. A.; Boxall, D. L.; Moore, J. T.; Chu, D.; Jiang, R.; Kenik, E. A.; Lukehart, C. M. In *Nanotechnology in Catalysis*; Zhou, B.; Hermans, S.; Somorjai, G. A., Eds.; Kluwer Academic/Plenum Publishers: New York, 2004; Vol. 1, Chapter 10, p 201.
- (19) Anderson, A. D.; Deluga, G. A.; Boxall, D. L.; Vergne, M. J.; Hercules, D. M.; Kenik, E. A.; Lukehart, C. M. *J. Nanosci. Nanotechnol.* **2003**, *4*, 809.
- (20) King, W. D.; Corn, J. D.; Murphy, O. J.; Boxall, D. L.; Kenik, E. A.; Kwiatkowski, K. C.; Stock, S. R.; Lukehart, C. M. *J. Phys. Chem. B* **2003**, *107*, 5467.
- (21) Moore, J. T.; Chu, D.; Jiang, R.; Deluga, G. A.; Lukehart, C. M. *Chem. Mater.* **2003**, *15*, 1119.
- (22) Jacobsen, G. B.; Shaw, B. L.; Thornton-Pett, M. *J. Chem. Soc., Dalton Trans.* **1987**, 1509.
- (23) Jacobsen, G. B.; Shaw, B. L.; Thornton-Pett, M. *J. Chem. Soc., Dalton Trans.* **1987**, 3079.
- (24) Hong, R.; Fischer, N. O.; Emrick, T.; Rotello, V. M. *Chem. Mater.* **2005**, *17*, 4617.

- (25) Steigerwalt, E. S.; Lukehart, C. M. *J. Nanosci. Nanotechnol.* **2002**, *2*, 25.

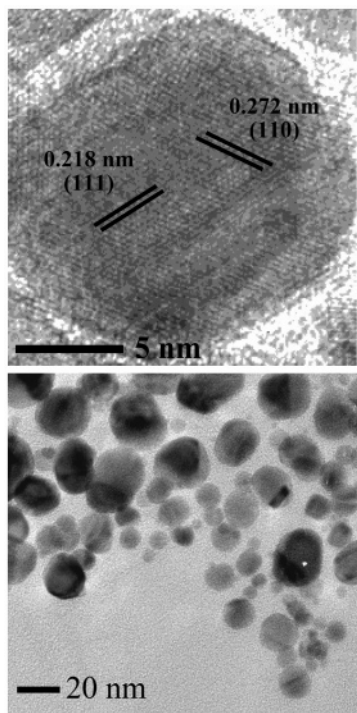


Figure 1. TEM micrographs of as-prepared fct FePt nanoparticles **1a** at low (bottom) and high magnification (top). The HR-TEM image reveals a single-crystal morphology and lattice fringes having interplanar spacings of 0.218 and 0.272 nm assigned to diffraction from the (111) and (110) planes of fct FePt.

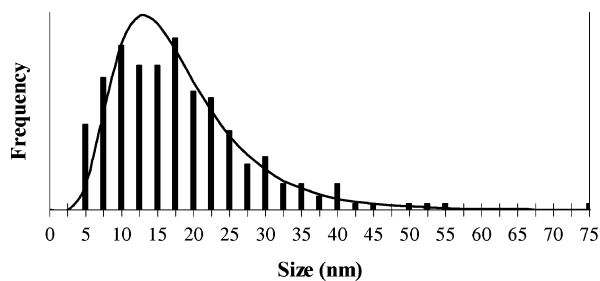


Figure 2. Particle-size histogram of as-prepared fct FePt nanoparticles **1a**.

particle size. When treated with water, the $\text{Na}_2\text{CO}_3/\text{Na}_2\text{O}$ solid support dissolves, and as-prepared fct FePt nanoparticles can be isolated as a free-flowing black powder **1a** having a Fe:Pt atomic ratio of 1.02, as determined by commercial, bulk elemental analysis (ICP-OES). Early termination of this thermal treatment afforded poorly ordered L_{10} FePt and no crystalline impurities, as determined by XRD.

TEM micrographs of as-prepared FePt powder **1a** at low and high resolution are shown in Figure 1. Particles having slightly irregular shapes are observed in good contrast at low magnification. At high resolution, particles appear as uncapped nanocrystals with rounded facets and exhibit continuous fringe-pattern lines consistent with single-crystalline nanoparticles. Interplanar distances of 0.218 and 0.272 nm measured from orthogonal cross fringe patterns within a single nanoparticle correspond to the (111) and (110) d -spacings expected for fct FePt having an ordered L_{10} atomic structure. A histogram of fct FePt nanoparticle sizes (see Figure 2) reveals particle diameters ranging from 5 to 55 nm with a nearly log-normal distribution, consistent with

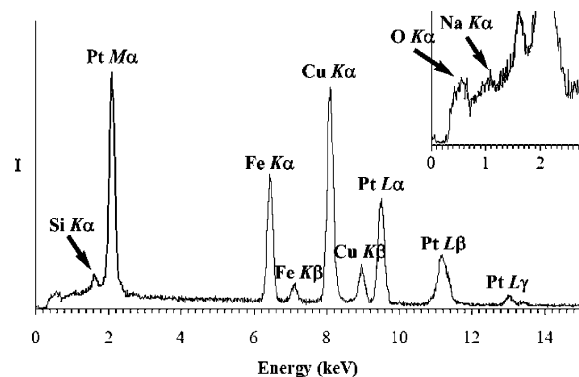


Figure 3. EDS spectrum of as-prepared fct FePt nanoparticles **1a** with magnification of the low-energy range as an insert.

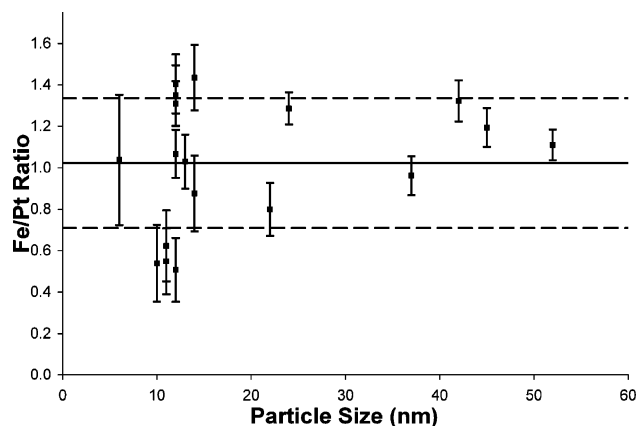


Figure 4. Fe:Pt atomic ratios determined by on-particle EDS for 19 as-prepared fct nanoparticles **1a**. Dashed lines indicate a calculated range of ± 1 standard deviation.

particle growth via a surface-diffusion process.²⁶ The average FePt particle size is 17 ± 10 nm with a calculated volume-weighted average particle size of 20 nm.

An EDS spectrum of as-prepared fct FePt nanoparticles **1a** supported on a SiO_x -coated TEM grid is shown in Figure 3. Strong X-ray emission lines are observed from Fe and Pt, as expected, along with emission lines from Cu, Si and oxygen present within the TEM grid. Weak emission is also observed from Na, probably present as Na^+/OH^- or $\text{Na}^+/\text{HCO}_3^-$ ion pairs providing surface passivation of the fct FePt nanoparticles.

Fe:Pt atomic ratios determined by on-particle HR-EDS for 19 as-prepared fct FePt nanoparticles (see Figure 4) indicate good particle-to-particle compositional uniformity. The average Fe:Pt atomic ratio calculated from these measurements of 1.0 is the same as that determined by bulk elemental analysis (Fe:Pt = 1.02) within experimental error of the bulk analysis method. Although atomic ratios determined by on-particle HR-EDS have very low precision due to the counting statistics associated with measuring weak emission intensities, gross phase separation of Fe and Pt is not observed within this limited set of measurements.

Successful formation of a highly ordered L_{10} lattice for the as-prepared FePt powder **1a** is confirmed by powder XRD (see Figure 5). Superlattice peaks expected for the fct FePt phase are clearly observed, with the (001) and (110)

(26) Granqvist, C. G.; Buhrman, R. A. *J. Catal.* **1976**, *42*, 477.

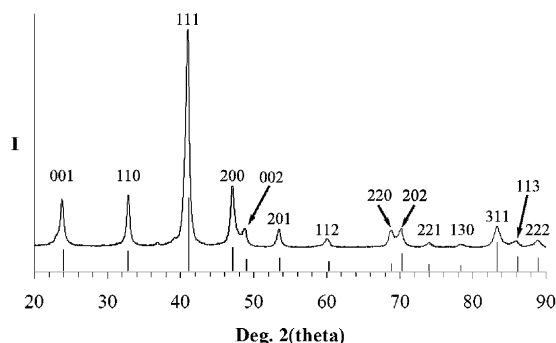


Figure 5. XRD scan (Cu K α radiation) of as-prepared fct FePt nanoparticles **1a** along with the XRD line pattern and peak indices of bulk fct FePt (PDF Card 46-1359).

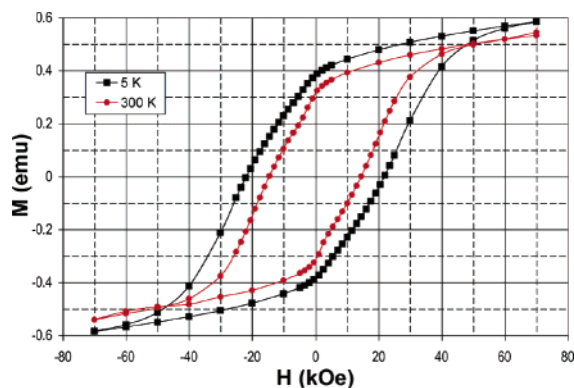


Figure 6. Magnetic hysteresis loops of as-prepared fct FePt nanoparticles **1a** at 300 and 5 K.

diffraction peaks having strong intensity and with good definition of the (200)/(002) pair of reflections. Appearance of the (111) diffraction peak at 40.89° in 2θ correlates to a Fe content of ca. 52 at %.²⁷ This composition is consistent with the alloy stoichiometry of Fe₅₁Pt₄₉ determined by bulk elemental analysis. For pure FePt fct (L₁₀), the unit-cell constants of $a = 3.8525 \text{ \AA}$ and $c = 3.7133 \text{ \AA}$ give an a/c ratio of 1.037. Calculated unit-cell parameters from the XRD scan of **1a** gives unit-cell parameters of $a = 3.857 \text{ \AA}$ and $c = 3.728 \text{ \AA}$ and an a/c ratio of 1.035, confirming synthesis of only L₁₀ material. Scherrer's analysis of XRD peak widths gives a calculated average crystallite size of 16 nm, which compares well to the average particle size of 17 nm determined by TEM.

Magnetic hysteresis loops recorded for as-prepared FePt powder **1a** at 5 and 300 K are shown in Figure 6. Symmetrical loops are evident with coercivities of 21.8 and 14.5 kOe at 5 and 300 K, respectively, confirming the formation of hard ferromagnetic nanoparticles, as expected for fct FePt. A remanence of $(2/\pi)M_{\text{sat}}$ is observed, consistent with a random uniform distribution of magnetocrystalline orientations, likely resulting in a reduction of measured coercivity due to magnetic dipole coupling between neighboring nanocrystals.

Having achieved a direct one-step synthesis of polydisperse fct FePt nanocrystals from a single-source precursor and isolation of these nanocrystals by simple dissolution of a

water-soluble support, we attempted to separate these as-prepared nanoparticles into narrower size ranges for specialized applications, such as magnetic data recording. A common method for effecting nanoparticle size selection is fractional precipitation of surfactant-stabilized particles. Application of this method to size selection of fct FePt nanoparticles requires (1) identification of surfactants capable of dispersing FePt nanoparticles into solvents, and (2) a strategy for minimizing ferromagnetic interparticle attractive forces.

Fortunately, previous work by others confirms that mixtures of methoxypoly(ethylene glycol) of 550 Da average molecular weight, m-PEG550, terminated with thiol and dopamine functional groups²⁴ or trifluoroester-PEG597-thiol²⁸ are effective surfactants at dispersing supermagnetic fcc FePt nanoparticles into water or methylene chloride. Minimizing ferromagnetic attractive forces can be achieved by preventing close interparticle contact. The magnetic attractive force between two identical bar magnets favorably oriented decreases with increasing separation distance, x , with an approximate power-law dependence of $x^{-3.76}$, when the intermagnet separation distance is from 1 to 5 times the length of the bar magnets.²⁹ PEG surfactants (MW 2000) increase the hydrodynamic radius of proteins by ca. 1.8 nm,³⁰ so mPEG2000 derivatized with thiol and dopamine functional groups were chosen as likely surfactants to effect practical size separation of ferromagnetic fct FePt nanoparticles. Assuming that this model applies to two ferromagnetic FePt nanoparticles of diameter 16 nm, then the magnetic attractive force between two ferromagnetic nanoparticles of 16 nm diameter will be reduced by ca. 50% if each particle possesses a surfactant layer ca. 1.8 nm thick.

As-prepared fct FePt nanoparticles **1a** disperse in a methylene chloride solution containing triethylamine, mPEG-dopamine, and mPEG-thiol, producing a golden-brown solution. Fractional precipitation of fct FePt nanoparticles using centrifugation with ethanol and isopropanol as flocculants occurs in stages to give three isolable precipitates (**2a–2c**). TEM micrographs of these powders (shown in Figure 7) reveal particles of good contrast trending toward decreasing particle size with successive fractional precipitation. Larger FePt particles have highly irregular shapes, whereas smaller particles have more spherical morphology. A HR-TEM image of a 10-nm particle from fraction **2c** reveals continuous cross fringe lattice patterns with interplanar spacings of 0.281 and 0.271 nm consistent with the (111) and (110) d -spacings of fct FePt. This particle has a single-crystal, spherical morphology. Sulfur emission present in the HR-EDS spectrum of this material confirms the presence of mPEG-thiol surfactant.

Particle-size histograms for fractions **2a–2c** are shown in Figure 8 and confirm a significant degree of size selection. Particles in fraction **2a** range in size from 16 to 90 nm, with an average diameter of $31 \pm 12 \text{ nm}$; fraction **2b** contains particles ranging in size from 10 to 35 nm, with an average diameter of $16 \pm 6 \text{ nm}$; and particles in fraction **2c** range in

(27) Klemmer, T. J.; Shukla, N.; Liu, C.; Wu, X. W.; Svedberg, E. B.; Mryasov, O.; Chantrell, R. W.; Weller, D.; Tanase, M.; Laughlin, D. E. *Appl. Phys. Lett.* **2002**, *81*, 2220.

(28) Latham, A. H.; Williams, M. E. *Langmuir* **2006**, *22*, 4326.

(29) Gram, F. <http://instruct.tri-c.edu/fgram/web/Mdipole.htm>.

(30) Sharma, U.; Carbeck, J. D. *Electrophoresis* **2005**, *26*, 2086.

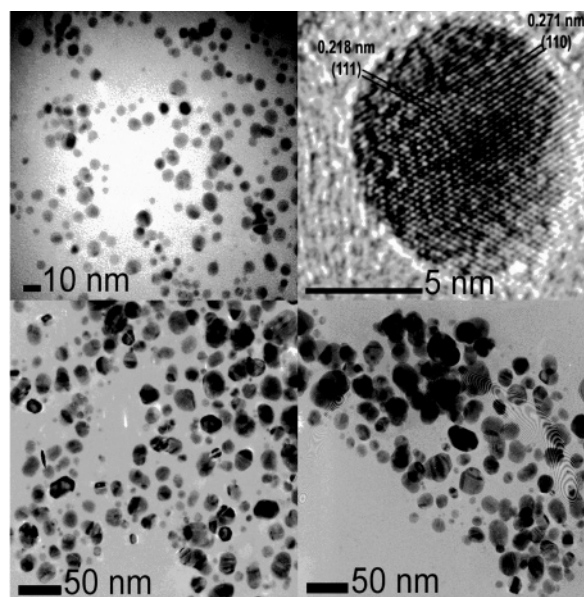


Figure 7. TEM micrographs of size-separated fct FePt nanoparticles having average diameters of 5 nm (top left, **2c** at low magnification; top right, **2c** at high magnification), 16 nm (bottom left, **2b**) and 31 nm (bottom right, **2a**).

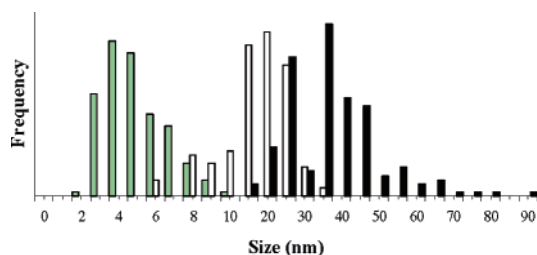


Figure 8. Particle-size histograms of size-selected fct FePt nanoparticles fractions (**2a**, black; **2b**, white; **2c**, gray).

size from 1.5 to 10 nm and have the smallest average diameter of 5 ± 2 nm. Because fraction **2a** consists of a fairly broad range of large particles in a distribution overlapping with that of fraction **2b**, further characterization was acquired only for fractions **2b** and **2c**.

Magnetic hysteresis loops recorded at 5 and 300 K for fct FePt nanoparticles of fractions **2b** (16 nm) and **2c** (5 nm) are shown in Figure 9. Nearly symmetrical magnetic loops are evident for fraction **2b** nanoparticles with coercivities of 12.0 and 9.5 kOe at 5 and 300 K, respectively, confirming the formation of hard ferromagnetic nanoparticles. However, hysteresis loops for fraction **2c** nanoparticles exhibit much lower coercivity (ca. 1.3 kOe) at both 5 and 300 K and approach coercivity values expected for soft ferromagnetic behavior. A trend of decreasing coercivity for fct FePt nanoparticles experiencing prolonged exposure to mPEG surfactants is consistent with some degree of Fe loss from the fct FePt alloy phase during size selection. SAED patterns of **1a**, **2b**, and **2c**, analyzed with ProcessDiffraction³¹ software, corroborate this hypothesis. The relative intensity of the observed $L1_0$ superlattice peaks decreases with increasing time of exposure to surfactants. In addition, the “constricted” hysteresis loops observed for fractions **2b** and

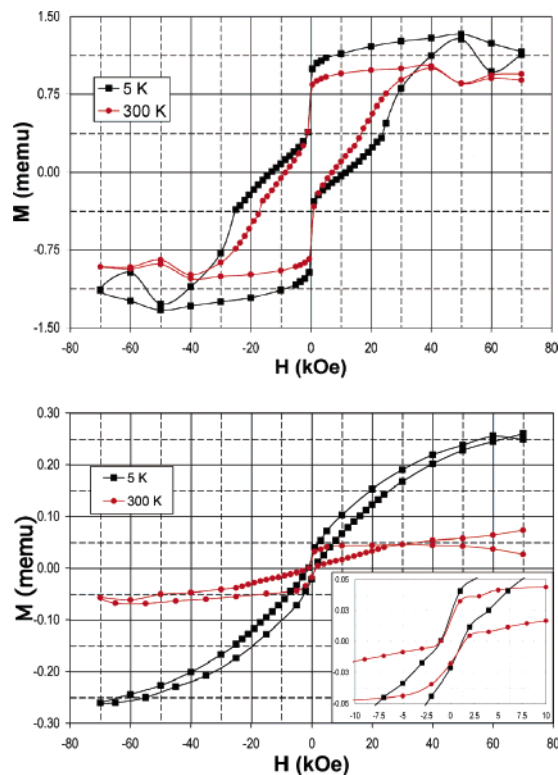


Figure 9. Magnetic hysteresis loops at 300 and 5 K for size-selected fct FePt nanoparticles having average diameters of 16 nm (top, **2b**) and 5 nm (bottom, **2c**).

2c (near-zero applied field) are consistent with a mixture of ferromagnetic and superparamagnetic FePt phases.³² Because broad-area EDS data reveal a constant Fe/Pt atomic ratio for **1a**, **2b**, and **2c**, we speculate that the coordinating mPEG surfactants used for size selection extract Fe atoms from near-surface layers of the fct lattice upon prolonged exposure. This effect is greatest for fraction **2c** nanoparticles; the fraction having the smallest average particle size and nanoparticles of greatest surface area. Compositional or structural alteration of fct FePt nanoparticles upon prolonged exposure to coordinating mPEG surfactants needs further clarification.

Conclusions

Thermal reduction of $\text{FePt}(\text{CO})_4\text{dppmBr}_2/\text{Na}_2\text{CO}_3$ composites provides a one-step, direct synthesis of fct FePt/ $\text{Na}_2\text{CO}_3/\text{Na}_2\text{O}$ nanocomposites from which fct FePt nanocrystals can be harvested by dissolution of the water-soluble support. This synthesis strategy is both convenient and readily scalable. Size selection of polydisperse, ferromagnetic FePt nanoparticles can be achieved by fractional precipitation using mPEG-dopamine and mPEG-thiol as surfactants to enhance the dispersibility of FePt nanoparticles and minimize ferromagnetic attractive forces. Care should be taken to avoid prolonged exposure of FePt nanoparticles to the conditions of size selection, as some ionization of Fe atoms appears to occur.

(32) Stahl, B.; Ellrich, J.; Theissmann, R.; Ghafari, M.; Bhattacharya, S.; Hahn, H.; Gajbhiye, N. S.; Kramer, D.; Viswanath, R. N.; Weissmüller, J.; Gleiter, H. *Phys. Rev. B: Condens. Matter Mater. Phys.* **2003**, *67*, 014422/1.

(31) Labar, J. L. *Microscopy Anal.* **2002**, *9*.

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