

## One-Step Synthesis of FePt Nanoparticles with Tunable Size

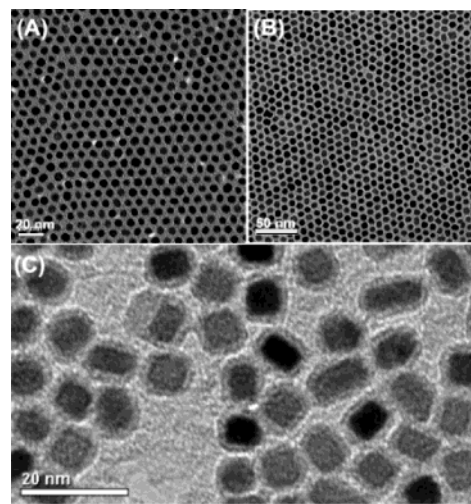
Min Chen,<sup>†,‡</sup> J. P. Liu,<sup>‡</sup> and Shouheng Sun<sup>\*,†</sup>

IBM T. J. Watson Research Center, Yorktown Heights, New York 10598, and Department of Physics, University of Texas, Arlington, Texas 76019

Received April 23, 2004; E-mail: ssun@us.ibm.com

Chemically prepared FePt nanoparticles have generated great interest recently because of their ease of synthesis, chemical stability, and potential applications in high-density data storage<sup>1</sup> and high performance permanent magnets.<sup>2</sup> The surfactants surrounding each FePt nanoparticle can be replaced by other bifunctional stabilizers, rendering the particles water soluble and suitable for site-specific biomolecule attachment and magnetic field-assisted bioseparation.<sup>3</sup> The particles are commonly synthesized via decomposition of iron pentacarbonyl, Fe(CO)<sub>5</sub>, and reduction of platinum acetylacetonate, Pt(acac)<sub>2</sub>,<sup>4</sup> co-reduction of iron salt and Pt(acac)<sub>2</sub>,<sup>5</sup> or seed-mediated growth<sup>4a</sup> where smaller FePt nanoparticles are used as seeds and more FePt is coated over the seeds. Although size distribution of the particles prepared from all these methods can be well-controlled with standard deviation usually within 10%, tuning the size in the desired range along with tight control on composition has been difficult to achieve thus far. The decomposition and reduction or co-reduction methods can yield FePt nanoparticles with controlled composition but fail to produce particles larger than 4 nm, while the seed-mediated growth method gives larger FePt particles without accurate control on Fe/Pt ratio at different sizes. As both structural and magnetic properties of FePt nanoparticles depend not only on the size, but also on the composition of the particles,<sup>4b,6</sup> this size limitation and composition variation at different sizes prevent one from studying property evolution with size and composition of the particles, an understanding that is essential for mapping the scaling limits of future high-density magnetic storage technology.

Here we present a one-step synthesis of FePt nanoparticles with controlled composition and size tunable up to 9 nm in diameter. Different from previous syntheses where either polyalcohol or superhydride was used as reducing agent for particle formation, the current synthesis did not use this additional reducing agent. The extra reducing power introduced by this agent could lead to facile reduction of Pt(acac)<sub>2</sub> to Pt, resulting in fast nucleation of FePt and consumption of metal precursors and, as a result, smaller sized particles. Exclusion of additional reducing agent in the reaction mixture might slow the nucleation rate, allowing more metal precursor to deposit around the nuclei formed in the solution and leading to larger particle size. We found that with benzyl ether as solvent and oleic acid and oleylamine as stabilizers, one-pot reaction of Fe(CO)<sub>5</sub> and Pt(acac)<sub>2</sub> could indeed give larger FePt particles. Size, composition, and shape of the particles were controlled by varying the synthetic parameters such as molar ratio of stabilizers to metal precursor, addition sequence of the stabilizers and metal precursors, heating rate, heating temperature, and heating duration. Further, core/shell-structured FePt/Fe<sub>3</sub>O<sub>4</sub> nanoparticles were also separated by controlled addition of excess of Fe(CO)<sub>5</sub> into the reaction mixture and air oxidation. Preliminary thermal annealing and magnetic study revealed that an assembly of large (6 nm or



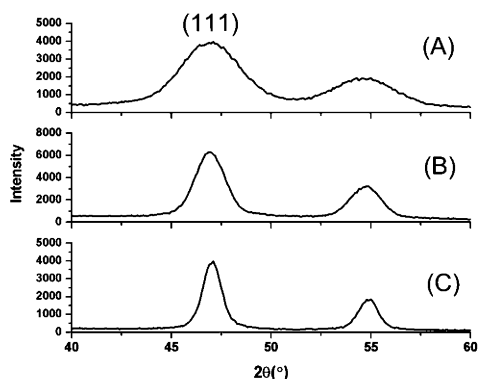
**Figure 1.** TEM bright field images of (A) 6-nm Fe<sub>53</sub>Pt<sub>47</sub>, (B) 9-nm Fe<sub>44</sub>Pt<sub>56</sub>, and (C) 7-nm/1.2-nm FePt/Fe<sub>3</sub>O<sub>4</sub> nanoparticles deposited from their hexane dispersions on amorphous carbon surface and dried at room temperature. The images were acquired from a Philips CM 12 at 120 kV.

above) FePt nanoparticles could withstand higher temperature (650 °C) annealing without noticeable particle sintering. Room temperature coercivity of an assembly containing discrete FePt dots can reach as high as 1.3 T, a value that is suitable for hard magnetic applications.

The size of the particles is tuned by controlling the molar ratio of stabilizers to Pt(acac)<sub>2</sub> and heating conditions. A ratio of at least 8 is essential to make FePt nanoparticles larger than 6 nm. In the synthesis, we first mixed Pt(acac)<sub>2</sub> with Fe(CO)<sub>5</sub> and excess of stabilizers at 100 °C, then heated the mixture to more than 200 °C, and kept it at that temperature for 1h, before it was heated to reflux. We also found that, at the fixed stabilizers/Pt(acac)<sub>2</sub> ratio of 8, both heating rate and interim heating temperature were important in making FePt particles with tunable size. Heating rate of ~15 °C/min and interim heating temperature of 240 °C would finally yield 6-nm FePt, while the rate of ~5 °C/min and heating temperature of 225 °C led to 9-nm FePt.<sup>7</sup> The composition of the particles is controlled by varying the molar ratio of Fe(CO)<sub>5</sub> and Pt(acac)<sub>2</sub>. Under current reaction conditions, Fe(CO)<sub>5</sub>/Pt(acac)<sub>2</sub> ratio of 2 gave 6-nm Fe<sub>53</sub>Pt<sub>47</sub> and 9-nm Fe<sub>44</sub>Pt<sub>56</sub> nanoparticles.<sup>8</sup> Figure 1A,B shows two TEM images of 6-nm Fe<sub>53</sub>Pt<sub>47</sub> and 9-nm Fe<sub>44</sub>Pt<sub>56</sub> nanoparticles obtained from the one-step synthesis. In both cases, the particles have narrow size distribution with standard deviation <10%. Figure 2 shows X-ray diffraction patterns of the assembled FePt nanoparticles with sizes being 3, 6, and 9 nm, respectively. It can be seen that the particles have commonly known chemically disordered fcc structure<sup>4a</sup> and the diffraction peaks are narrower when the size of the particles is larger. Estimation using Scherrer's formula<sup>9</sup> on (111) peak gives the average particle size that is consistent with

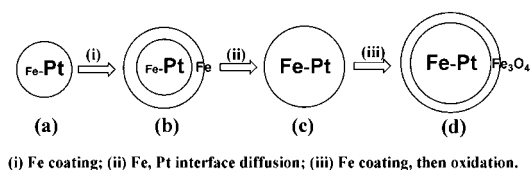
<sup>†</sup> IBM T. J. Watson Research Center.

<sup>‡</sup> University of Texas, Arlington.



**Figure 2.** X-ray diffraction patterns of the as-synthesized FePt nanoparticles with different sizes at (A) 3, (B) 6, and (C) 9 nm. The particles were deposited from their hexane dispersions on silicon (100) substrates. Diffraction patterns were collected on a Siemens D-500 diffractometer under Co K $\alpha$  radiation ( $\lambda = 1.788965 \text{ \AA}$ ).

### Scheme 1



that observed from TEM images, indicating that the as-synthesized FePt nanoparticles are of good crystallinity.

By mixing oleic acid and Fe(CO)<sub>5</sub> with benzyl ether solution of Pt(acac)<sub>2</sub> first and heating the mixture at 130 °C for about 5 min before oleylamine was added, a portion of highly faceted FePt nanoparticles was obtained. If the mixture contained excess of Fe(CO)<sub>5</sub>, by refluxing in a shorter period of time and air oxidation, core/shell-structured FePt/Fe<sub>3</sub>O<sub>4</sub> nanoparticles were separated.<sup>10</sup> Figure 1C is the TEM image of the 7-nm/1.2-nm FePt/Fe<sub>3</sub>O<sub>4</sub> nanoparticles prepared with Fe(CO)<sub>5</sub>/Pt(acac)<sub>2</sub> = 3. Further experiments indicate that various FePt/Fe<sub>3</sub>O<sub>4</sub> nanoparticles with tunable core and shell can be readily prepared in this one-step synthesis.

The synthetic results seem to support the following particle formation mechanism illustrated in Scheme 1. The Pt-rich nuclei (a) are formed from the reduction of Pt(acac)<sub>2</sub> either at temperature >200 °C or by Fe atoms from the decomposed Fe(CO)<sub>5</sub>, or by both. More Fe atoms will then coat over the existing Pt-rich nuclei, forming larger clusters (b). Exposing these clusters to air leads to formation of Pt-rich FePt/Fe<sub>3</sub>O<sub>4</sub> as evidenced by XRD analysis.<sup>7</sup> Heating the clusters (b) to refluxing at 300 °C leads to atomic diffusion and formation of fcc-structured FePt nanoparticles (c), as shown in Figure 1A,B and Figure 2. In the presence of excess of Fe(CO)<sub>5</sub>, the extra Fe will continue to coat over (c), leading to core/shell-structured FePt/Fe<sub>3</sub>O<sub>4</sub> as evidenced by XRD analysis.<sup>7</sup> Heating the clusters (b) to refluxing at 300 °C leads to atomic diffusion and formation of fcc-structured FePt nanoparticles (c), as shown in Figure 1A,B and Figure 2. In the presence of excess of Fe(CO)<sub>5</sub>, the extra Fe will continue to coat over (c), leading to core/shell-structured FePt/Fe<sub>3</sub>O<sub>4</sub> as evidenced by XRD analysis.<sup>7</sup> Heating the clusters (b) to refluxing at 300 °C leads to atomic diffusion and formation of fcc-structured FePt nanoparticles (c), as shown in Figure 1A,B and Figure 2. In the presence of excess of Fe(CO)<sub>5</sub>, the extra Fe will continue to coat over (c), leading to core/shell-structured FePt/Fe<sub>3</sub>O<sub>4</sub> as evidenced by XRD analysis.<sup>7</sup>

The as-synthesized larger FePt nanoparticles with controlled composition are suitable for size-dependent structural and magnetic studies. Annealed at 560 °C for 30 min, 6-nm FePt nanoparticles show a coercivity of 1.2 T, but the 3- to 4-nm particles have a coercivity of only 0.5 T. Annealing results also indicate that the particles can withstand higher temperature than their 4-nm counterparts before they start to sinter. The coating of Fe<sub>3</sub>O<sub>4</sub> around

the FePt core will further stabilize the core. For an assembly containing core/shell 7-nm/1.2-nm FePt/Fe<sub>3</sub>O<sub>4</sub> nanoparticles, annealing at 650 °C did not lead to noticeable aggregation of the FePt core, as evidenced by both TEM and XRD studies,<sup>7</sup> and coercivity of the assembly reached 1.3 T.<sup>7</sup> Considering the fact that larger magnetic particles are thermally more stable than the smaller ones,<sup>1</sup> we believe the FePt nanoparticles prepared from current one-step synthesis will have a great potential for single particle magnetism study and evolve as useful building blocks for the construction of ultrahigh density information and energy storage devices.

**Acknowledgment.** The work was supported in part by US DOD/DARPA under Grant No. DAAD19-03-1-0038.

**Supporting Information Available:** A typical experimental procedure for making 6-nm FePt nanoparticles and particle characterization data. This material is available free of charge via the Internet at <http://pubs.acs.org>.

### References

- (1) (a) Weller, D.; Moser, A. *IEEE Trans. Magn.* **1999**, *35*, 4423–4439. (b) Sun, S.; Weller, D. *J. Magn. Soc. Jpn.* **2001**, *25*, 1434–1440.
- (2) (a) Zeng, H.; Li, J.; Wang, Z. L.; Liu, J. P.; Sun, S. *Nature* **2002**, *420*, 395–398. (b) Zeng, H.; Li, J.; Wang, Z. L.; Liu, J. P.; Sun, S. *Nano Lett.* **2004**, *4*, 187–190.
- (3) (a) Gu, H.; Ho, P.-L.; Tsang, K. W. T.; Yu, C.-W.; Xu, B. *Chem. Commun.* **2003**, 1966–1967. (b) Gu, H.; Ho, P.-L.; Tsang, K. W. T.; Wang, L.; Xu, B. *J. Am. Chem. Soc.* **2003**, *125*, 15702–15703. (c) Xu, C.; Xu, K.; Gu, H.; Zhong X.; Guo Z.; Zheng, R.; Zhang, X.; Xu, B. *J. Am. Chem. Soc.* **2004**, *126*, 3392–3393.
- (4) (a) Sun, S.; Murray, C. B.; Weller, D.; Folks, L.; Moser, A. *Science* **2000**, *287*, 1989–1992. (b) Sun, S.; Fullerton, E. E.; Weller, D.; Murray C. B. *IEEE Trans. Magn.* **2001**, *37*, 1239–1243. (c) Chen, M.; Nikles, D. E. *Nano Lett.* **2002**, *2*, 211–214. (d) Kang, S.; Harrell, J. W.; Nikles, D. E. *Nano Lett.* **2002**, *2*, 1033–1036. (e) Stahl, B.; Gajbhiye, N. S.; Wilde, G.; Kramer, D.; Ellrich, J.; Ghafari, M.; Hahn, H.; Gleiter, H.; Weissmüller, J.; Würschum, R.; Schlossmacher, P. *Adv. Mater.* **2002**, *14*, 24–27. (f) Shevchenko, E.; Talapin, D.; Kornowski, A.; Kötzer, J.; Haase, M.; Rogach, A.; Weller, H. *Adv. Mater.* **2002**, *12*, 287–290. (g) 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* **2003**, *67*, 14422(1–12).
- (5) (a) Sun, S.; Anders, S.; Thomson, T.; Baglin, J. E. E.; Toney, M. F.; Hamann, H. F.; Murray, C. B.; Terris, B. D. *J. Phys. Chem. B* **2003**, *107*, 5419–5425. (b) Jayadevan, B.; Hobo, A.; Urakawa, K.; Chinnasamy, C. N.; Shinoda, K.; Tohji, K. *J. Appl. Phys.* **2003**, *93*, 7574–7576. (c) Jayadevan, B.; Urakawa, K.; Hobo, A.; Chinnasamy, N.; Shinoda, K.; Tohji, K.; Djayaprawira, D. D. J.; Tsunoda, M.; Takahashi, M. *Jpn. J. Appl. Phys.* **2003**, *42*, L350–L352. (d) Iwaki, T.; Kakihara, Y.; Toda, T.; Abdullah, M.; Okuyama, K. *J. Appl. Phys.* **2003**, *94*, 6807–6811. (e) Nakaya, M.; Tsuchiya, Y.; Ito, K.; Oumi, Y.; Sano, T.; Teranishi, T. *Chem. Lett.* **2004**, *33*, 130–131.
- (6) (a) Klemmer, T. J.; Shukla, N.; Liu, C.; Wu, X. W.; Svedberg, E. B.; Mryasov, O.; Chantrell, R. W.; Weller, D. *Appl. Phys. Lett.* **2002**, *81*, 2220–2222. (b) Ulmeanu, M.; Antoniak, C.; Wiedwald, U.; Farle, M.; Frait, Z.; Sun, S. *Phys. Rev. B* **2004**, *69*, 54417(1–5). (c) Takahashi, Y. K.; Koyama, T.; Ohnuma, M.; Ohkybo, T.; Hono, K. *J. Appl. Phys.* **2004**, *95*, 2690–2696.
- (7) See the Supporting Information.
- (8) Particle composition was determined by EDX elemental analysis of the particles on a Leo 1560 SEM at 20 keV. See Supporting Information for an analysis example.
- (9) Klug, H. P.; Alexander, L. E. *X-ray Diffraction Procedures for Polycrystalline and Amorphous Materials*; Wiley: New York, 1962; pp 491–538.
- (10) Note that high-temperature air oxidation of the decomposed product of Fe(CO)<sub>5</sub> usually gives Fe<sub>2</sub>O<sub>3</sub>. See: (a) Hyeon, T.; Lee, S. S.; Park, J.; Chung, Y.; Na, H. B. *J. Am. Chem. Soc.* **2001**, *123*, 12798–12801. (b) Cheon J.; Kang, N.-J.; Lee, S.-M.; Lee, J.-H.; Yoon, J.-H.; Oh, S. J. *J. Am. Chem. Soc.* **2004**, *126*, 1950–1951. However, similar oxidation at room temperature seems to yield Fe<sub>3</sub>O<sub>4</sub> as characterized by the retention of the Fe<sub>3</sub>O<sub>4</sub> structure after thermal annealing. See Supporting Information and Sun, S.; Zeng, H.; Robinson, D. B.; Raoux, S.; Rice, P. M.; Wang, S. X.; Li, G. *J. Am. Chem. Soc.* **2004**, *126*, 273–279.

JA047648M