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Formation of FePt Nanoparticles Having High Coercivity

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Nanoscale magnetic particles are of interest for developing a more complete understanding of ferromagnetism and as materials 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 $L1_0$ 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] A recent solution synthesis conducted at 389 °C affords the fct FePt phase directly.[7]

Obtaining fct FePt nanoparticles exhibiting high room-temperature coercivity is desired for high-density magnetic storage. FePt coercivity is maximized at a slightly iron-rich alloy composition ($Fe_{55}Pt_{45}$)[1] and by thermal annealing fcc FePt particles at ca. 650 °C. Annealing at higher temperatures decreases observed coercivity owing to phase separation or twinning.[10] Sintering effects have been reduced by using rapid thermal annealing (annealing times of only 5 s),[11] binding fcc FePt nanoparticles to the surface of oxidized Si wafers prior to annealing,[12] or by Fe-oxide surface passivation.[13,14]

As part of a continuing study of the preparation of metal alloy nanoparticles using single-source molecular precursors,[15−19] we now report the synthesis of FePt nanoparticles exhibiting high room-temperature coercivity. To a solution of 2 mL of toluene, 0.323 mL of oleic acid, and 0.28 mL of oleylamine is added 60 mg of the known[20] polyheteronuclear cluster complex, $Pt_3Fe_3(CO)_{15}$, **1** [prepared here by reaction of $Fe(CO)_5$ and tris(norbornylene)-platinum(0) (see Supporting Information (SI))]. The resulting solution is sonicated (Branson Digital Sonifer, Model 450, 1-cm diameter Ti horn, 20 kHz, 160 W) under N_2 for 1 h. Solids formed are removed by centrifugation (5100 rpm). Surface-capped FePt nanoparticles precipitate upon the addition of 20 mL of ethanol and are collected by centrifugation.

A TEM micrograph (Figure 1) of surface-capped FePt powder reveals 2 nm aggregate-like particles due to surfactant van der Waals interactions. An EDS spectrum (see SI) confirms the presence of Fe and Pt in a nearly 1:1 atomic stoichiometry, and a powder XRD scan (see SI) shows very broad peaks centered at 2θ values expected for diffraction from the (111), (200), (220), and (311) planes of fcc FePt.

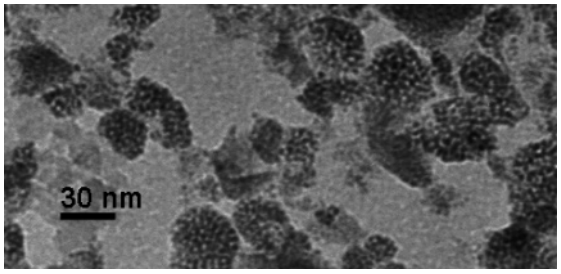

Figure 1. TEM micrograph of surface-capped fcc FePt nanoparticles.

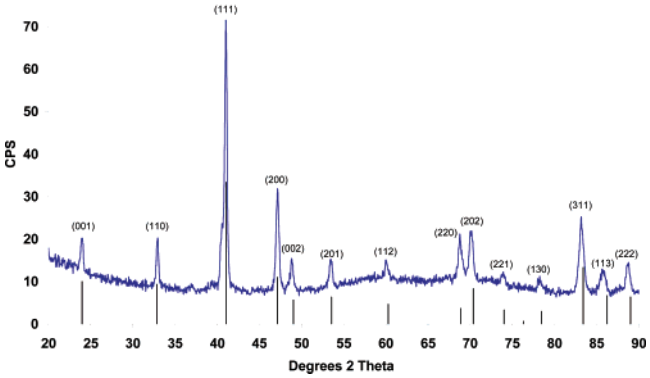

Figure 2. Powder XRD (Cu Ka radiation) of annealed FePt powder along with the line pattern and peak indices of bulk fct FePt.

Metal ordering is accomplished by annealing surface-capped fcc FePt powder in a tube furnace at 775 °C for 3 h under getter gas (9:1 N_2/H_2). An XRD scan of annealed as-isolated FePt powder (Figure 2) confirms formation of highly crystalline fct FePt under these conditions. Expected fct superlattice peaks are observed with excellent differentiation of the (200)/(002) pair of peaks. Some sintering occurs giving FePt particles 29 nm in diameter (Scherrer's analysis). Appearance of the (111) diffraction peak at 40.84 degrees in 2θ is consistent with a Fe content of ca. 50.2 atom %.[21]

Dispersions of surface-capped fcc FePt nanoparticles in (1:1) hexane/octane solution[22] form self-assembled particle arrays on SiO TEM grids (Ted Pella, Inc.) and on oxidized Si wafers when using [3-(2-aminoethylamino)propyl]trimethoxy- silane as a linker molecule.[23] Annealing fcc FePt/grid and Si wafer arrays under the conditions described above gives the corresponding fct FePt/grid and Si wafer nanoparticle arrays.

TEM micrographs of a fct FePt/grid array (Figure 3) reveal nanoparticles exhibiting high contrast and single-crystal nanoparticles at high resolution showing lattice-fringe spacings consistent with *d*-spacings known for the (111) and (110) planes of fct FePt. Fe/Pt atomic ratios determined by on-particle HR-EDS for 19 fct FePt nanoparticles (see SI) indicate good particle-to-particle compositional uniformity.

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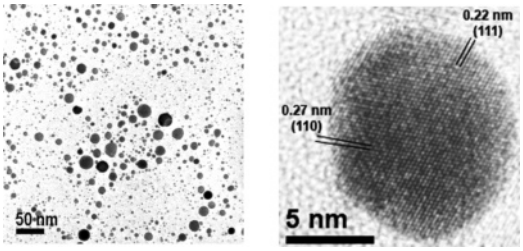

Figure 3. TEM micrographs at low (left) and high (right) resolution of annealed fct FePt nanoparticles. Selected lattice fringes are identified.

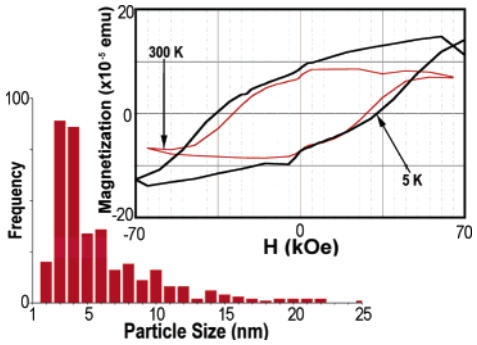

Figure 4. Magnetization hysteresis loops of a fct FePt/Si wafer nanoparticle array with corresponding particle-size histogram.

SEM micrographs (SI) of fct FePt/Si wafer arrays reveal nanoparticles well dispersed on the Si wafer surface. The presence of (001) and (110) superlattice peaks expected of fct FePt is confirmed by powder XRD (SI). Magnetic hysteresis loops (at 5 and 300 K) of a fct FePt/Si wafer array are shown in Figure 4 along with a particle-size histogram constructed from the corresponding fct FePt/TEM grid array. FePt particles of 5.8 nm average diameter are observed with 80% of the particles having diameters between 2−8 nm. The corresponding volume-weighted average diameter is 8.7 nm (see SI). A room-temperature coercivity of 22.3 kOe is recorded with higher coercivity at 5 K, although this sample cannot be saturated at a maximum available applied field of 6.5 T. Oe.[12]

Experiments to determine which synthesis parameters enhance the magnetic ordering within these nanoparticles are underway. Use of zerovalent heteropolynuclear clusters as single-source metal precursors might afford more intimately randomized fcc FePt nanoparticles than can be obtained from dual-source or dinuclear precursors requiring chemical reduction. Also, the formation of fcc FePt nanoparticles at the extremely high local temperatures generated during microsecond sonochemical cavitation events[24] may be a contributing factor. Optimization of this synthesis strategy for the preparation of size-selected fct FePt nanoparticles having high coercivities at 300 K are in progress.

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Supporting Information Available: Experimental details including synthesis procedures, TEM, SEM, EDS, HR-EDS, XRD, and particle-size histogram data. This material is available free of charge via the Internet at http://pubs.acs.org.

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