Monodisperse FePt Nanoparticles and Ferromagnetic FePt Nanocystal Superlattices

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Synthesis of monodisperse iron-platinum (FePt) nanoparticles by reduction of platinum acetylacetonate and decomposition of iron pentacarbonyl in the presence of oleic acid and oleyl amine stabilizers is reported. The FePt particle composition is readily controlled, and the size is tunable from 3- to 10-nanometer diameter with a standard deviation of less than 5%. These nanoparticles self-assemble into three-dimensional superlattices. Thermal annealing converts the internal particle structure from a chemically disordered face-centered cubic phase to the chemically ordered face-centered tetragonal phase and transforms the nanoparticle superlattices into ferromagnetic nanocrystal assemblies. These assemblies are chemically and mechanically robust and can support high-density magnetization reversal transitions.

The synthesis of nanoparticles with controlled size and composition is of fundamental and technological interest. The effort to understand the physics of ever smaller structures has been paralleled by attempts to exploit their beneficial properties. The increased surface area and tailored surface chemistry of metal nanoparticles have long been used to optimize the activity and specificity of catalysts (1). Semiconductor nanocrystals show size-tunable optical properties and have been integrated into exploratory optical and electronic devices (2, 3). Engineering the interparticle spacing of metal particle arrays has revealed evidence of tunable metal-insulator transitions (4). Small metal particle arrays have been used to build single-electron devices (5, 6). Progress in ultra-high-density magnetic recording is due in part to the development of metal thin film media with smaller particles, tighter size distributions, and optimized compositions (7, 8). Recently, the study of magnetization processes on nanometer length scales has intensified (9, 10).

We report on the synthesis of monodisperse FePt nanoparticles with controlled size and composition and the fabrication of ferromagnetic FePt nanocrystal superlattices with tunable interparticle spacings. FePt alloys are an important class of materials in permanent magnetic applications because of their large uniaxial magnetocrystalline anisotropy ($K_u = 7 \times 10^6 \text{ J/m}^3$) and good chemical stability. As the magnetic stability of individual particles scales with the anisotropy constant, $K_u$, and the particle volume, $V$, small FePt particles may be suitable for future ultrahigh-density magnetic recording media applications (12). Until now, the synthesis of FePt particle thin films has mainly relied on vacuum deposition techniques (13–15). Postdeposition annealing has proven essential to transform the as-deposited chemically disordered face-centered cubic (fcc) structure into the chemically ordered face-centered tetragonal (fct) phase, which has high $K_u$. Random nucleation in the initial stages of growth, however, typically results in broad distributions of particle sizes, which may be further aggravated by agglomeration during annealing. Solution phase chemical synthesis, in contrast, has been successfully used to prepare monodisperse metal particles (16–19). However, synthetic procedures have not yet been developed to prepare monodisperse hard magnetic FePt nanoparticles.

To prepare FePt nanoparticles, we used a combination of oleic acid and oleyl amine to stabilize the monodisperse FePt colloids and prevent oxidation. The synthesis is based on the reduction of Pt(acac)$_2$ (acac = acetylacetone, $\text{CH}_3\text{COCHCOCH}_3$) by a diol and the decomposition of Fe(CO)$_5$ in high-temperature solutions. The use of diol or polyalcohol (for example, ethylene glycol or glycerol) to reduce metal salts to metal particles is referred to as the “polyl process” (20). We modified this procedure by using a long-chain 1,2-hexadecanediol to reduce the Pt(acac)$_2$ to Pt metal. Thermal decomposition of Fe(CO)$_5$ has been used to produce Fe particles (17). Both chemical reactions were initiated together in the presence of oleic acid and oleyl amine, providing a convenient route to monodisperse FePt nanoparticles (21).

The size and composition of these FePt nanoparticles can be readily controlled. Their composition is adjusted by controlling the molar ratio of iron carbonyl to the platinum salt. For example, with diocetyl ether as solvent, a 3:2 molar ratio of Fe(CO)$_5$ to Pt(acac)$_2$ gave Fe$_3$Pt$_2$ particles, a 2:1 molar ratio yielded Fe$_4$Pt$_2$ and a 4:1 molar ratio produced Fe$_7$Pt$_3$ (22). The FePt particle size can be tuned from 3 to 10 nm by first growing 3-nm monodisperse seed particles in situ and then adding more reagents to enlarge the existing seeds to the desired size. These particles are isolated and purified by centrifugation after the addition of a flocculent (for example, ethanol) and can be redispersed in nonpolar solvents in a variety of concentrations (23).

When the FePt colloids are spread on a substrate and the carrier solvent is allowed to slowly evaporate, FePt nanoparticle superlattices are produced (24). A drop (~0.5 μL) of dilute FePt dispersion (~1 mg/mL) was deposited on a SiO$_2$-coated copper grid for transmission electron microscopy (TEM) studies. The results reveal that the particles are monodisperse with $\sigma < 5\%$ in diameter and readily self-assemble into three-dimensional (3D) superlattices. A TEM image (Fig. 1A) shows a thin section of a hexagonal close-packed 3D array of 6-nm Fe$_5$Pt$_5$ particles with a nearest neighbor spacing of ~4 nm maintained by the oleic acid and oleyl amine capping groups. Room temperature ligand exchange of these long-chain capping groups for shorter RCOOH/RNH$_2$ (R = dodecyl down to hexyl chains) allows the interparticle distance to be adjusted. Ligand exchange with hexanoic acid/hexylamine yields a cubic packed multilayer of 6-nm Fe$_5$Pt$_5$ particles with ~1-nm spacings (Fig. 1B). Such a transition from hexagonal to cubic packing has been observed in monodisperse cobalt nanoparticle assemblies (19). The symmetry of the observed superlattices is influenced by several experimental parameters including the relative dimensions of the metal core and the organic capping, as well as the annealing history of the sample. The FePt particle assemblies show no obvious aggregation upon annealing at temperatures up to 600°C under static N$_2$ atmosphere (1 atm). High-resolution scanning electron microscopy (HRSEM) was used to image the annealed FePt particle assembly on a thermally oxidized Si substrate. For a 180-nm-thick, 4-nm Fe$_5$Pt$_5$ particle assembly annealed at 560°C for 30 min, the HRSEM images of both surface (Fig. 1C) and cross section (not shown in figure) of the assembly show that the particles are well separated with no agglomeration occurring. Interparticle spacings, however, are reduced from ~4 to ~2 nm, as indicated by TEM, HRSEM, and small angle x-ray scattering experiments. Some coherent strain is observed in the superlattices because of this shrinkage. Rutherford backscattering measurements on these annealed 4-nm Fe$_5$Pt$_5$ particle assemblies indicate 40 to 50% (atomic %) carbon content. This shows that annealing at high temperature does not result in the loss of stabilizing ligands; rather, they are converted to a carbonaceous coating.

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around each particle. Energy dispersive x-ray spectroscopy measurements carried out during the SEM and scanning TEM imaging of the films confirm that the average nanocrystals are slightly iron-rich and that the carbon is intimately associated with the particles.

Electron diffraction of the as-synthesized Fe$_{52}$Pt$_{48}$ particles reveals a typical fcc pattern whereas Fe$_{52}$Pt$_{48}$ particles annealed at 560°C show an fct internal structure. Figure 1D is a high-resolution TEM micrograph of individual 4-nm Fe$_{52}$Pt$_{48}$ particles annealed at 560°C for 30 min. The particles are single crystals with a lattice spacing of 2.20 Å, characteristic of the (111) planes in the chemically ordered fct FePt phase (25). The change of the internal particle crystal structure upon annealing is seen in wide-angle x-ray diffraction (XRD) studies. Figure 2 shows a series of such XRD patterns for as-synthesized particles exhibiting the chemically disordered fcc structure. The XRD patterns of the samples annealed above 540°C match those of fct FePt (11, 25). Fitting of the XRD line shapes of the sample annealed at 550°C confirms that the particles are individual single crystals with dimensions matching the average particle size of 4 nm ($\sigma = 5\%$ in diameter) determined by statistical analysis of the TEM images. Annealing 4-nm Fe$_{52}$Pt$_{48}$ particles at higher temperature, for example, 600°C, however, results in an increase of the average particle size and a broadening of the size distribution based on TEM and XRD analyses.

Superconducting quantum interference device magnetometry measurements of 4-nm FePt particles show that the as-synthesized particles are superparamagnetic (coercivity $H_c \approx 0$ Oe) at room temperature. The temperature-dependent magnetization was measured in a 10-Oe field between 5 and 400 K with the standard zero–field-cooling and field-cooling procedures (26). These studies indicate that superparamagnetic behavior is blocked at 20 to 30 K. This low blocking temperature is consistent with low magnetocrystalline anisotropy of the fcc structure. Annealing converts the particles to the high-anisotropy fct phase and transforms them into room temperature superconductors.
nanoscale ferromagnets. The coercivity of these ferromagnetic assemblies is tunable by controlling annealing temperature and time, as well as the Fe:Pt ratio and particle size. Curve A of Fig. 3 shows representative in-plane coercivity data of a series of ~140-nm-thick, 4-nm Fe<sub>48</sub>Pt<sub>52</sub> samples as a function of annealing temperature. There is little difference between in-plane and out-of-plane coercivities and hysteresis behavior, indicating random orientation of the easy axes of individual FePt nanocrystals. FePt stoichiometry-dependent coercivity data (curve B of Fig. 3) demonstrate that Fe-rich Fe<sub>70</sub>Pt<sub>30</sub> nanocrystals have the largest coercivity, consistent with earlier reports on vacuum-deposited FePt thin films (12, 27).

The annealed FePt nanocrystal assemblies are smooth ferromagnetic films that can support high-density magnetization reversal transitions (bits). A ~120-nm-thick assembly of 4-nm Fe<sub>48</sub>Pt<sub>52</sub> nanocrystals with an in-plane coercivity of \( H_c = 1800 \) Oe was selected for initial recording experiments. Atomic force microscopy studies of this sample indicate a 1-nm root-mean-square variation in height over areas of 3 μm by 3 μm. A static write/read tester was used for the recording experiments (28). The read-back sensor voltage signals (Fig. 4A) from written data tracks correspond to linear densities of 500, 1040, 2140, and (d) 5000 fc/mm. (B) Dynamic coercivity measurements \( (H_{cr}) \) of the sample in (A) at 300 K over a range from 5 ns to 65 s. The measured data (○) are fit to a dynamic coercivity law for pulse width \( >10^{-6} \) s (solid curve) (28).

Fig. 4. (A) Magneto-resistive (MR) read-back signals from written bit transitions in a 120-nm-thick assembly of 4-nm-diameter Fe<sub>48</sub>Pt<sub>52</sub> nanocrystals. The individual line scans reveal magnetization reversal transitions at linear densities of (a) 500, (b) 1040, (c) 2140, and (d) 5000 fc/mm. (B) Dynamic coercivity measurements \( (H_{cr}) \) of the sample in (A) at 300 K over a range from 5 ns to 65 s. The measured data (○) are fit to a dynamic coercivity law for pulse width \( >10^{-6} \) s (solid curve) (28).

References and Notes
20. One typical synthetic procedure is as follows: under airless condition, platinum acetylacetonate (197 mg, 0.5 mmol), and dicyclohexyl(20 ml) were mixed and heated to 100°C. Oleic acid (0.16 ml, 0.5 mmol), oleyl amine (0.17 ml, 0.5 mmol), and FeCO<sub>3</sub> (0.13 ml, 1 mmol) were added, and the mixture was heated to reflux (297°C). The refluxing was continued for 30 min. The heat source was then removed, and the reaction mixture was allowed to cool in room temperature.
21. The inert gas protected system could be opened to ambient environment at this point. The product was separated by adding ethanol (~40 ml) and centrifugation. Yellow-brown supernatant was discarded. The black precipitate was dispersed in hexane (~20 ml) and centrifuged. The product was dispersed in hexane (~20 ml) and centrifuged to remove any unsolved precipitation (almost no precipitation was found at this stage), and precipitated out by adding ethanol (~15 ml) and centrifuging. The materials were dispersed...
Efficient Activation of Aromatic C–H Bonds for Addition to C–C Multiple Bonds
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Efficient electrophilic metalation of aromatic C–H bonds leading to new C–C bond formation through regio- and stereoselective addition to alkenes and arenes has been realized by a catalytic amount (0.02 to 5 mole percent) of palladium(II) or platinum(II) compounds in a mixed solvent containing trifluoroacetic acid at room temperature. Various arenes undergo unexpected selectivity in hydroarylation to terminal or internal C=C bonds, inter- and intramolecularly with high efficiency (up to a turnover number of 4500 for palladium), especially for electron-rich arenes, giving thermodynamically unfavorable cis-alkenes, and the oxygen- and nitrogen-containing heterocycles. The simplicity, generality, and efficiency of this process should be very attractive to the possible industrial application for the functionalization of arenes.

Arenes such as benzenes, naphthalenes, phenols, and anilines are the large-quantity chemicals manufactured by chemical industries. Catalytically efficient activation of aromatic C–H bonds leading to useful organic reactions such as new C–C bond formation is of considerable interest for the chemical and pharmaceutical industries and remains a long-term challenge to chemists (1–4). It would provide simple, clean, and economic methods for making aryl-substituted compounds directly from simple arenes because no prefunctionalization, such as halogenation, is involved. The catalytic systems for such a purpose have been sought for many years, although there are many examples of stoichiometric reaction of aromatic C–H bonds with transition metal complexes (1, 2).

The few available catalytic systems based on transition metals (4–12) activate aromatic C–H bonds mainly through two routes. The first route is by chelation-assisted oxidative s-character of low-valent transition metal complexes, such as Ru(0) (4, 5) and Rh(I) (6) complexes, to aromatic C–H bonds in the hydroarylation of C–C multiple bonds. This insertion involves the coordination of a functional group in arenes to the metal complex, followed by the oxidative insertion of the metal to an ortho-aromatic C–H bond, resulting in the addition to unsaturated C–C bonds (2). These systems are apparently limited to functionalized arenes such as aromatic ketones at high temperature and give low stereoselectivity in the hydroarylation of arenes. The second route involves electrophilic metalation of aromatic C–H bonds by Pd(II) complexes to give σ-aryl-Pd complexes in oxidative coupling of arenes with alkynes. The second route involves electrophilic metalation of aromatic C–H bonds by Pd(II) complexes to give σ-aryl-Pd complexes in oxidative coupling of arenes with alkynes.

We report the efficient metalation of aromatic C–H bonds at room temperature by in situ generated highly electrophilic Pd(II) and Pt(II) cationic species in trifluoroacetic acid (TFA), leading to regio- and stereoselective addition of simple alkenes to C–C multiple bonds inter- and intramolecularly (reactions 2 through 4 in Fig. 1). In most cases, the addition to alkenes exclusively affords the thermodynamically unfavorable cis-alkenes, unlike most of the arylation reactions of C=C and C–C bonds that occur mainly in cis fashion and yield trans products, especially in Pd-catalyzed reactions (13, 14). The intramolecular hydroarylation of C=C bonds is very fast and regio- and stereospecific because the electrophilic metalation of aromatic C–H bonds by Pt(II) cationic species is assisted by ethynyl coordination, affording heterocycles in good to excellent yields. In fact, this intramolecular reaction combines the chelation assistance and electrophilic metalation.

The reaction of pentamethylenzene with ethyl phenylpropionate in a mixed solvent TFA/CHCl₃ (4/1 by volume) at 25°C was used to screen catalysts among Pd(OAc)₂, Pd[PhPPH₂]₄(O₂CCF₃)₂ (Ph, phenyl), Pd[PhPPH₂]₄, PdCl₂, PtCl₂, Pt(OAc)₂, RhCl₃, AgOAc, RuCl₃, AgOAc, and Ni(OAc)₂. The highly electrophilic cationic species [M(O₂CCF₃)₃]⁺ (M, metal; L, ligand) are expected to be generated in situ through bonding weakly coordinating anions, CF₃CO₂⁻, to transition metal ions by using TFA as a solvent (15–18). The cationic species should greatly enhance the metalation of aromatic C–H bonds and, at the same time, possibly activate C=C and C–C bonds through the coordination to generate the acceptors of aryl nucleophiles. The reaction was carried out by simply mixing all of the reactants, a catalyst, and the solvent over an ice bath and then warming to room temperature (Table 1 and Fig. 2). The Pd(II) and Pt(II) catalysts were four times as active as other transition metals: Pd(II) > Pt(II) > Rh(III) > Ru(III) > Ni(II), in accordance with the reactivity of these metal ions in electrophilic metalation of aromatic C–H bonds (1). The Pd(II) catalysts Pd(OAc)₂ and Pd[PhPPH₂]₄(O₂CCF₃)₂ are equally active; cis-ethyl 3-pentamethylenylphenyl cinnamate was obtained in 75% yield in 5 hours, and an almost
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*Science* **287**, 1989 (2000);
DOI: 10.1126/science.287.5460.1989

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