

The Effects of SiO₂ Shell Coatings on High Temperature Annealing Behavior of FePt Nanocrystals

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Introduction:

Iron Platinum (FePt) nanoparticles (NP's) have been a subject of intense study for many years due to their ease of synthesis, chemical stability, and potential applications in high density data storage [1]. However, as-synthesized NP's exhibit a low Curie temperature, low saturation magnetization, and low coercivity. In order to correct the aforementioned variables, the particles must undergo a high-temperature annealing, after which, through solid state diffusion, the Fe and Pt atoms rearrange from the chemically disoriented face-centered cubic (fcc) phase to the highly ordered face-centered tetragonal (fct) phase, in which Fe and Pt atoms are arranged in alternating layers. In the face centered tetragonal phase, the crystals exhibit a high Curie temperature, high saturation magnetization, and high coercivity, making them ideal candidates for data storage applications, with recording density attainments as high as 1 Tbit/in² estimated. However, exposure to extremely high annealing temperatures required for phase transition (650°C and up) decomposes the organic capping layer, and leads to particle sintering; the particles lose their quantum properties and assume the physical characteristics of a bulk FePt alloy.

By performing a post-synthesis coating of the FePt NP's with SiO₂, it was hoped that the particles could be subjected to high-temperature annealing conditions and rearrange into the fct phase successfully, and due to their isolation within the SiO₂ core-shell structure, avoid the problem of inter-particle sintering.

Experimental Procedure:

FePt nanoparticles were prepared following methods reported by Sun and coworkers [1,2]. A platinum precursor (Pt(acac)₂) in an ether solvent, was reduced either thermally or by addition of the reducing agent 1,2-hexadecanediol, then heated to 100°C and combined with the iron precursor Fe(CO)₅ and organic capping ligands (oleic acid, oleyl amine). This was then allowed to reflux, with an interim incubation temperature and time dependant on desired particle size. The resulting black solution was collected using chloroform, then combined with ethanol (EtOH) as an anti-solvent and centrifuged. The resulting nanoparticle precipitate was dispersed in cyclohexane for silica coating via the inverse micelle method reported by Yi, et al. [3]; the particles were combined with the surfactant Igepal CO-520, a catalytic amount of ammonium hydroxide (30%), and the silica source tetraethylorthosilane (TEOS), and vigorously

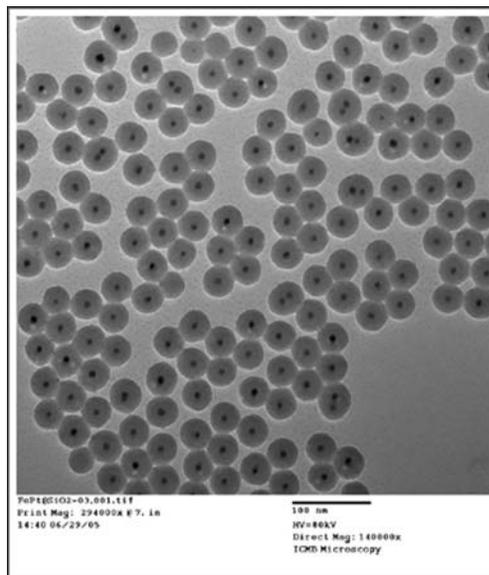


Figure 1:
TEM image of
as-synthesized
silica coated
FePt nano-
particles.

stirred for 72 hours. The brown mixture was then separated using methanol in a separatory funnel. The FePt@SiO₂/MeOH mixture was collected and centrifuged. (“@” denotes a shell material around another core nanocrystal.) The glass-like precipitate was then washed multiple times using various solvents before being re-dispersed into ethanol, forming a colloidal suspension of silica coated particles (Figure 1).

Surface Functionalization:

The as-synthesized silica coated particles were found to exhibit strong interparticle forces, aggregating into large clusters undesirable for data storage applications (Figure 2). Various methods were tried in order to achieve formation of an ordered monolayer. The first two attempts—spin casting and vertical evaporation—proved unsuccessful. The third, a surface functionalization reported by Wei, et al. [4], brought success. In this method, the suspension of FePt@SiO₂ in EtOH was mixed with a small amount of NH₄OH (30%) and a 10% by volume solution of the reactant orthotridecylmethoxysilane (OTMOS) in chloroform, and allowed to react for 24 hours in a vigorously stirred vessel. The result was the grafting of long alkane chains onto the silica surface, making the previously hydrophilic silica particles hydrophobic. By dispersing the hydrophobic particles into an organic solvent then depositing it into a water-filled trough, an ordered monolayer was obtained at the air-water interface.

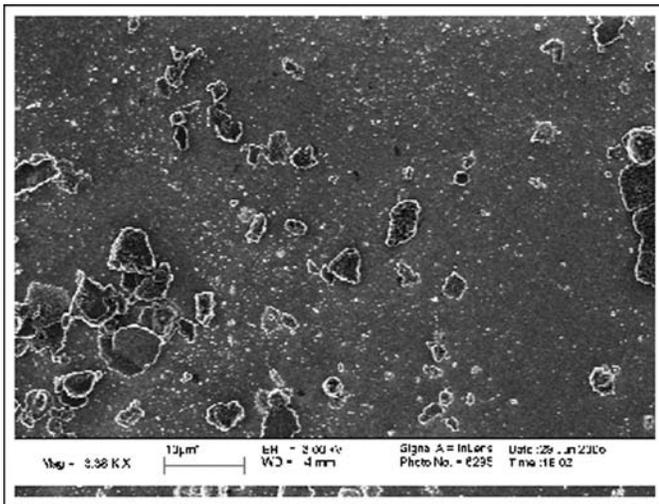


Figure 2: SEM image of agglomerated FePt@SiO₂ nanoparticles.

Annealing:

Two glass substrates were prepared by drop-casting a large amount of FePt@SiO₂ colloidal suspension. The samples were then placed into an x-ray diffractometer (XRD) and annealed *in situ* under air at various temperatures, ranging as high as 800°C.

Results:

From both SEM and XRD studies, it appears that as-synthesized FePt nanoparticles experienced significant inter-particle sintering (Figure 3). However, SiO₂ coated particles exhibited no such sintering (Figure 4). XRD shows that the SiO₂ shells prevented sintering as expected, however, it also appears that they may be inhibiting the fcc to fct phase transition.

Future Work:

Further study of the FePt@SiO₂ nanoparticles is required under different annealing conditions to determine if the

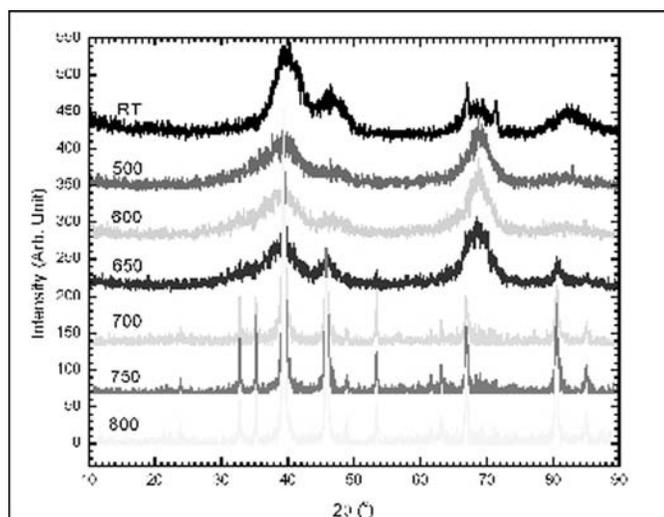


Figure 3: XRD of high-temperature annealing of uncoated 2 nm FePt nanoparticles. Peak sharpening indicates particle sintering.

occurrence of a phase transition on the FePt core is possible. Magnetic characterization of the particles using SQUID or MFM both before and after annealing is required to determine the relevance of FePt@SiO₂ core-shell particles in the field of high-density data storage.

Conclusion:

FePt nanoparticles were prepared using a one-pot synthesis, and then coated with SiO₂ via an inverse micelle method. The particle surfaces were functionalized with OTMOS in order to form a monolayer at the air-water interface. Two substrates were prepared: one using the as-synthesized FePt nanoparticles and one using the SiO₂ coated FePt. The substrates were then placed in an XRD and annealed *in situ*, with as-synthesized nanoparticles exhibiting significant inter-particle sintering, and the SiO₂ coated nanoparticles exhibiting no inter-particle sintering. However, the SiO₂ coating also appears to inhibit the fcc to fct phase transition. The extent of this inhibition is unknown.

Acknowledgements:

Dr. Brian Korgel, Chemical Engineering, University of Texas at Austin; Doh C. Lee, Chemical Engineering, University of Texas at Austin; the Korgel Research Group; NNIN and NSF for funding.

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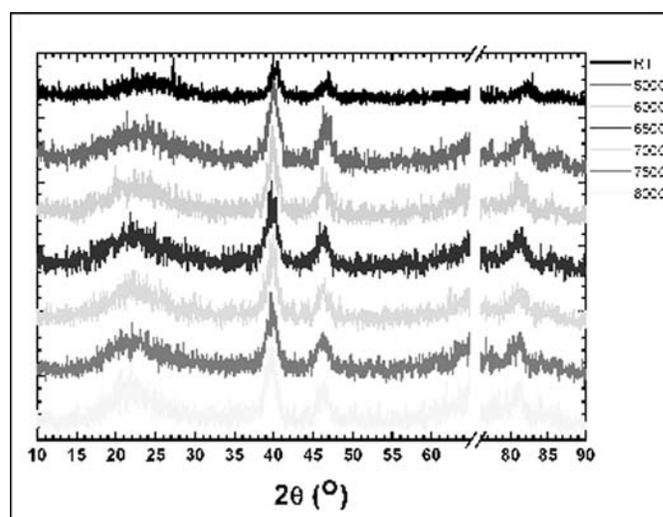


Figure 4: XRD of annealed FePt@SiO₂ nanoparticles at various temperatures. No peak sharpening was observed.