Direct Chemical Synthesis of L1$_0$ FePt Nanostructures

Irene Zafiropoulou, Eamonn Devlin, Nikos Boukos,
Dimitrios Niarchos, Dimitrios Petridis, and
Vassilios Tzitzios*

Institute of Materials Science, NCSR "Demokritos", Aghia Paraskevi, 15310 Athens, Greece

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Bimetallic FePt and CoPt nanoparticles in the ordered face-centered tetragonal phase (fct) combine chemical stability, high magnetocrystalline anisotropy ($K_u \approx 7 \times 10^6$ J/m^3), and high coercivity values. These unique properties allow reduction of the particles size below 10 nm with simultaneous stabilization of their magnetization against thermal fluctuations and demagnetizing effects; such properties are necessary for ultrahigh-density magnetic storage applications.[1−4]

Nowadays, a plethora of chemical routes for the synthesis of ultrafine, monodispersed FePt nanoparticles in the sub-10 nm range size have been developed.[5−13] The as-made nanoparticles have a disordered face-centered cubic (fcc) structure and reveal superparamagnetic behavior. A thermal treatment (annealing) of the as-made nanoparticles at temperatures above 550 °C is required in order to obtain the magnetically interesting face-centered tetragonal (fct) phase.[1] However, annealing at these temperatures induces complete decomposition of the protective organic layer surrounding the surface of each particle and consequently leads to an undesirable aggregation and sintering. As a result, the nanoparticles lose their solubility and most importantly their size and shape homogeneity, which is essential for self-assembly.

Recently, different methods have been used to attempt to lower the FePt phase-transition temperature. Introduction of a third metal, such as Ag,[15] Au,[16] and Sb,[17] into FePt chemically synthesized nanoparticles has lowered the fcc to fct transformation temperature to approximately 400 °C. Recently, Howard et al.[18] reported the direct synthesis of fct FePt nanoparticles using Collman's reagent, $Na_2Fe(CO)_4$, as reducing agent for the Pt^{2+}. The reaction occurs in hydrocarbon solvents at 330 °C in the presence of surfactants under an inert atmosphere. The as-made FePt nanoparticles are partially ordered with an average particle size of 6−8 nm and reveal coercivities of ∼1300 and 3100 Oe at room temperature and 10 K, respectively. Kang et al.[19] synthesized partially ordered FePt nanoparticles by thermal decomposition of $Fe(CO)_5$ and reduction of $Pt(acac)_2$ in hexadecylamine at 360 °C in the presence of 1-adamantanecarboxylic acid. The particles exhibit coercive fields of 500 and 800 Oe in the perpendicular and parallel directions, respectively. A similar procedure has been reported by Jia et al.[20] for FePtAu nanoparticles of different compositions, with coercivities varying from a few hundred to a few thousand Oe.

In this work, the direct synthesis of hard magnetic L1$_0$ FePt and FePtAu nanoparticles, without any postannealing step is reported. The nanoparticles synthesized present considerable ordering and a high coercive field of 5.8 kOe.

In a typical synthesis route, 2 mL of oleylamine (Fluka), 2 mL of oleic acid (Fluka), 0.26 mmol $Fe(acac)_3$ (Aldrich), 0.25 mmol $Pt(acac)_2$ (Alfa Aesar), and 0.077 mmol $AuCl_3$ (Alfa Aesar) are added to 20 mL of liquid paraffin (Fluka) to synthesize a material with $Fe_{44}Pt_{43}Au_{13}$ composition, which has been proved to present the lowest transformation temperature.[16] Liquid paraffin is used as a high-boiling-point solvent, whereas oleylamine plays the role of mild reducing agent and surfactant, along with oleic acid. The mixture is heated to 200 °C under a N_2 atmosphere for 20 min; subsequently, the temperature is raised to reflux conditions (390−400 °C) for 3 h. The synthesis procedure was also performed under a 4% H_2−96% Ar atmosphere. To control the morphology of the nanoparticles synthesized, instead of oleic acid, which leads to the formation of worm-like nanostructures, we used PVP (polyvinyl pyridine, Fluka, MW = 1500, 30 mg) and pluronic tri-block copolymer (F-127, Sigma, 30 mg). The resulting black precipitant is magnetically separated and washed several times with a hexane−ethanol mixture. The same procedure was followed for the synthesis of bimetallic FePt nanoparticles, without Au addition.

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* Corresponding author. E-mail: tzitzios@ims.demokritos.gr.

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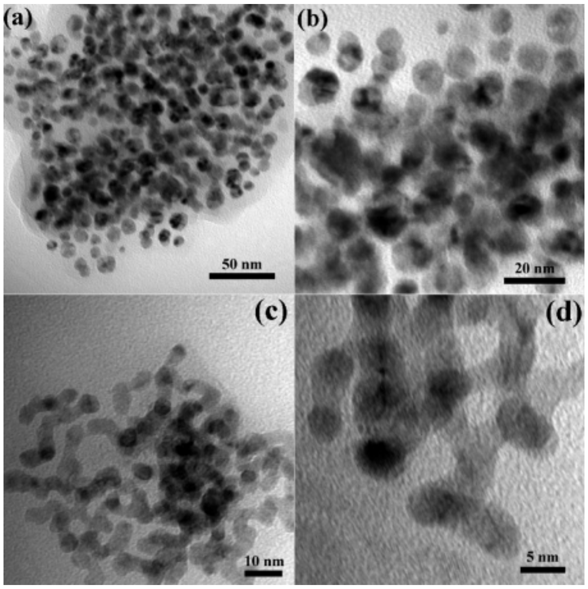

Figure 1. TEM images of FePtAu nanostructures, synthesized under 4% H_2 atmosphere, in the presence of pluronic (a) and (b) and oleic acid (c) and (d).

A Siemens D500 diffractometer, with CuK$_a$ radiation (λ = 1.5418 A) was used for the structure study, whereas the magnetic properties were measured at room temperature using a VSM PAR model 155. Mössbauer spectrometry was carried out using a constant acceleration spectrometer with a ^{57}Co-(Rh) source calibrated at room temperature using an iron metal foil. The low-temperature measurements (4.2 K) were carried out using an Oxford Variox cryostat. TEM images were collected using a Philips CM20 operated at 200 kV microscope. The samples were dispersed in chloroform and drops of the solution were allowed to dry on a carbon-coated Cu grid.

TEM images from the materials synthesized in the presence of oleic acid or pluronic are shown in Figure 1. It is worth mentioning that, despite the high reaction temperature, the material synthesized in the presence of oleic acid forms wormlike nanostructures. Their size is kept relevantly small, because the width is less than 5 nm (images c and d of Figure 1). In images a and b of Figure 1, TEM images of the material synthesized in the presence of pluronic are presented. As indicated by the images, individual nearly spherical nanoparticles were formed, with an ~8.7 nm mean diameter and narrow size distribution ($\sigma \approx 17\%$). The composition of this material, as calculated by EDX, is found to be $Fe_{45}Pt_{44}Au_{11}$, which is very close to the theoretical composition. In the case of PVP, similar nanoparticles were formed, but with a broader size distribution ($\sigma \approx 30\%$). The anisotropic growth of the particles when oleic acid was used can be attributed to the high reaction temperature (>380 °C), at which this surfactant is probably unstable and cannot bind strongly to the particle surface. In general, the nanomaterials synthesized via the above-mentioned procedure form dispersions that are stable at least overnight in nonpolar organic solvents, such as hexane and chloroform. In future work, pluronic and other polymers will be studied in various concentrations to produce nanoparticles with narrower size distribution, or other anisotropic shapes.

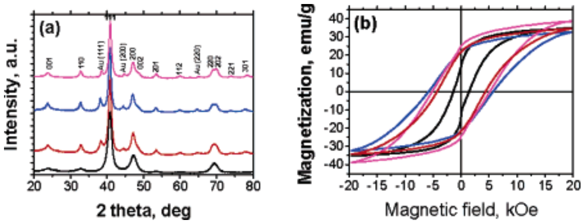

Figure 2. (a) XRD patterns of the FePt (black) and FePtAu nanoparticles in the presence of oleic acid (red), PVP (blue), pluronic (magenta), synthesized under 4% H_2. (b) Magnetic hysteresis loops of FePt (black) and FePtAu nanoparticles in the presence of oleic acid (red), PVP (blue), pluronic (magenta).

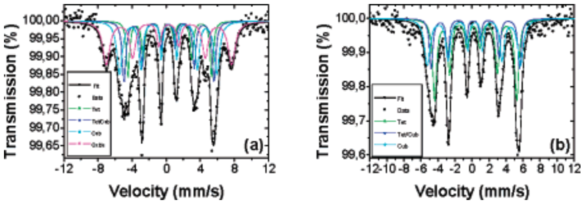

Figure 3. Mossbauer spectra of FePt (a) and FePtAu with oleic acid (b) samples.

The FePt particles synthesized under both atmospheres (inert and reducing) and in the presence of all kinds of surfactants clearly show a significant degree of ordering, but the presence of 4% H_2 reduces the quantity of Fe oxides in FePt and almost excludes it from FePtAu. The XRD patterns of the nanostructured materials are presented in Figure 2(a). The black line shows the pattern of the FePt, whereas the red, blue, and magenta show the FePtAu synthesized in the presence of oleic acid, PVP, and pluronic-F127 block copolymer, respectively. The formation of the fct phase is verified by the evolution of (001) and (110) characteristic planes of the fct phase, at 24 and 32.8°, respectively.[21] The addition of Au in the FePt alloy doubly affects the material obtained: it promotes the fcc to fct transformation, leading to a material with a larger volume of the hard magnetic phase, and also favors the formation of the FePt alloy over oxide phases, leading to a magnetically hard material.

To confirm the above-mentioned conclusions and fully investigate the structure of the materials synthesized under a H_2 atmosphere, we performed Mossbauer spectroscopy on both FePt and FePtAu (with oleic acid or pluronic) samples. The spectrum of the FePt sample, Figure 3a, revealed components attributed to tetragonal, cubic, and oxide phases. The tetragonal phase, identified by its hyperfine field (HF), 306 KG, and its quadrupole splitting (QS), 0.14 mm/s, comprised 18% of the total iron content, which is a very satisfying value for the bimetallic alloy without annealing. A second component with a hyperfine field of 356 KG and a quadrupole splitting of −0.05 mm/s is unambiguously assigned to the cubic FePt phase and comprises 29% of the iron content. A third component with a hyperfine field of 329 KG and a QS of just 0.05 mm/s is attributed to a disordered phase intermediate between the cubic and tetragonal phases on the basis of its intermediate HF and QS values. This phase comprises 23% of the Fe content. The existence of both cubic and tetragonal phases is in accordance with the XRD pattern, because the 111 FePt peak is observed at 40.822°, whereas the peaks for the fcc and fct structures are at 40.298 and 41.031°, respectively.[21] Last, a broad component with a hyperfine field of 458 KG is observed. This subspectrum (30%) is assigned to amorphous oxide phases that are formed during the high-temperature preparation of the FePt nanostructures. The fact that these oxides do not appear on the XRD pattern can be ascribed both to their low crystallinity and the high scattering of FePt alloy and Au. The Mossbauer spectra of the gold-containing with pluronic sample (not shown) is distinguished by the absence of oxide phases and the increased fraction of tetragonal phase formed, which in fact confirms the dual effect of the Au addition. In this case, only two phases are observed, the tetragonal phase representing the 45% (HF = 307 KG, QS = 0.14 mm/s), an appreciable value taking into account the lack of postannealing (further discussion is following). The second phase observed, holding 55% of the sample, is cubic, with HF = 328 KG and QS = 0.02 mm/s. In the gold-containing FePtAu with the oleic acid sample Mossbauer spectrum, Figure 3b, the presence of Fe-oxides is also not indicated. The tetragonal phase (HF = 300 KG, QS = 0.14 mm/s) comprises 43% of the total, as in the case of the sample with pluronic. The cubic phase (HF = 342 KG, QS = −0.07 mm/s) comprises 35%. Again a third component is observed (HF = 324 KG, QS = 0.11 mm/s), which we again attribute to a tetragonal-cubic intermediate phase. In this case, the intermediate phase may lie closer to the tetragonal phase than in the FePt sample, as indicated by its large quadrupole splitting, close to that of the pure tetragonal phase. The large percentage of the tetragonal phase is also indicated by the 111 peak of FePt at 40.926°, very close to the theoretical position of the 111 peak of fct FePt (41.031°). Thus, the Au addition promotes the formation of the fct phase as well as eliminates the presence of oxides.

FePt and FePtAu nanoparticles were magnetically characterized using VSM measurements at room temperature (Figure 2b). In accordance with the above results, all materials have hard magnetic properties right after the chemical synthesis. The material that demonstrates the best magnetic behavior, i.e., the largest value of coercive field, is the FePtAu synthesized under a H_2 atmosphere in the presence of pluronic (magenta line). This material has a 5.2 kOe coercivity, a value reported for the first time in the literature, for as-prepared nanoparticles synthesized by metal salts without any postannealing. The FePtAu material synthesized in the presence of oleic acid and PVP has developed a 4.3 and 5.8 kOe coercive field, respectively, whereas the FePt has a coercive field of 1.4 kOe. These values are also outstanding (especially the case of PVP), but the particles do not have a satisfying morphology, as mentioned above. All the coercivity values are in accordance with the results obtained by both the XRD and Mossbauer measurements, i.e., the ratio of the hard magnetic fct phase. The higher value of coercivity displayed by all the FePtAu materials can be ascribed both to the higher percentage of fct phase and to the lack of γ-Fe_2O_3. As far as the materials with polymers are concerned (coercivities of 5.2 and 5.8 kOe for pluronic and PVP. respectively) the higher coercive field values originate from the different behavior of polymers as surfactants compared with organic acids and amines. Polymers tend to cover the particles, without bonding on the surface atoms like carboxy and amine groups. This different behavior most probably affects the transformation of the particles to the fct phase. The difference between the two polymers can be ascribed to the different morphology of the particles. According to the literature, the coercivity of these materials does not exceed the value of 500 Oe without any postannealing; the value of ∼5.8 kOe is obtained only after annealing at 500 °C for FePt[7] and at 375 °C for FePtAu (work under progress), whereas in relevant works the higher value reported is only 1.3 kOe at RT[18] and 5 kOe when $Fe(CO)_5$ is used.[20]

In conclusion, $L1_0$ FePt and FePtAu nanostructures have been chemically synthesized in high-boiling-point solvent without the use of toxic reagent such as $Fe(CO)_5$. The coercivities displayed by the materials are up to 5.8 and 1.4 kOe for FePtAu and FePt, respectively, without any post-annealing, whereas the higher coercive field value for as-made FePt reported until now is 1.3 kOe (RT). Au addition led to a higher content of fct phase along with elimination of Fe oxides, resulting in a magnetically harder material. When pluronic was used as surfactant, individual nanoparticles with spherical shape and size of ∼8.7 nm were synthesized. The nanostructures synthesized in the presence of oleic acid and PVP have a wormlike shape (because of the high temperature during the synthesis procedure). In future work, different kinds of surfactant-like high-molecular-weight polymers in various concentrations will be studied in order to obtain nanoparticles with size and shape homogeneity along with solubility. These properties combined with the high coercivity of the material without annealing are very promising for a variety of applications.

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