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Nanotechnology 20 (2009) 065602 (5pp)

Tailoring the shapes of $Fe_x Pt_{100-x}$ nanoparticles

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Received 12 August 2008, in final form 1 December 2008 Published 15 January 2009 Online at stacks.iop.org/Nano/20/065602

Abstract

 $Fe_x Pt_{100-x}$ nanoparticles of varying composition have been synthesized with various shapes and sizes using a high pressure synthesis method which allows control of synthesis conditions, in particular the reaction temperature. Tailoring the shapes and sizes of $Fe_x Pt_{1-x}$ nanoparticles allows one to control a variety of properties that are relevant to the many potential applications of metallic nanoparticles. Shape and composition can be used to control catalytic activity and to achieve high packing density in self-assembled films. Variation of both nanoparticle size and shape has been achieved by using various different solvents. The solvents used in the nanoparticle synthesis can influence the product because they can play a role as surfactants. Using solvents of various types it has been possible to synthesize $Fe_x Pt_{100-x}$ nanoparticles with a variety of shapes including spherical, rod-like, cubic, hexagonal and high aspect ratio wires. Control of nanoparticle shape opens the door to their being used in various technological applications for which spherical nanoparticles are ineffective.

1. Introduction

Alloy nanoparticles have potential applications in magnetic data recording, catalysis, ferrofluids and other technologies. In some applications, control of nanoparticle shape adds a valuable dimension to their properties. In catalysis for example, shape control allows control of the structure of the exposed surfaces on which catalytic reactions occur and thus, control of catalytic reactivity and selectivity. FePt nanoparticles have interesting potential for use in magnetic data recording. In this application, control of nanoparticle shape would allow higher packing density on the surfaces of magnetic media and has the potential to allow control of crystallographic orientation. The work reported in this paper focuses on the control of the compositions and shapes of chemically synthesized $Fe_x Pt_{100-x}$ nanoparticles

and demonstrates that nanoparticles synthesized in various different solvents can be produced with a wide range of compositions and shapes.

The potential advantage of shape controlled FePt nanoparticles for high density magnetic recording media over existing media is that their high magneto-crystalline anisotropy and anisotropic shapes allow alignment of their magnetic easy axis when deposited in self-assembled films. This has potential impact in magnetic recording where the areal density of magnetic data recording is limited by the superparamagnetic effect [1]. Existing magnetic media based on sputtered CoPt films have reached storage capacities that are limited from further increase by superparamagnetism. The storage density limit imposed by superparamagnetism can only be increased by using media formed of uniformly sized particles rather than the polydisperse particle size distributions produced by sputter deposition. Chemical synthesis methods allow the preparation

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Shape

Spherical

Hexagonal

Rods

Wires

Cubes

Compos.

Fe50Pt50

Fe₁₈Pt₈₂

Fe26Pt74

Fe50Pt50

Fe97Pt3

270

270

2

6 [<mark>9</mark>]

Table 1.	Reaction	mixtures	and	conditions	and	products.
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Table 1. Reaction mixtures and conditions and products.								
Temp. (°C)	Pressure (bar)	Solvent	Reactant/surfactant					
280	1	Dioctylether (Octyl ether)	$\begin{array}{c} 0.0005 \text{ m Pt}(\mathrm{acac})_2 \\ 0.0005 \text{ m Fe}(\mathrm{acac})_2 \\ 0.0005 \text{ m oleylamine} \\ 0.0005 \text{ m oleic acid} \end{array}$					
270	22 [8]	2 ml toluene	$0.00005 \text{ m Pt}(\text{acac})_2$ $0.00008 \text{ m Fe}(\text{CO})_5$ 0.0006 ml oleylamine 0.0006 m oleic acid					
270	6 [9]	20 ml 1,2-dichlorobenzene	$0.0005 \text{ m Pt}(\text{acac})_2$ $0.0009 \text{ m Fe}(\text{CO})_5$ 0.009 m oleylamine					

24 ml oleylamine

20 ml 1,2-dichlorobenzene

of nanoparticles with narrow size distributions. Controlled syntheses that produce nanoparticles with square or hexagonal cross sections would allow higher packing densities than those achievable with spherical particles or shapes with circular cross section [2]. Media formed of closely packed nanoparticles of uniform size could reach the ultimate storage density allowed by media subject to the superparamagnetic limit.

Chemical synthesis of FePt nanoparticles can produce greater monodispersity of grain size than physical methods of FePt film deposition. Furthermore, chemical syntheses can be tailored to produce nanoparticles with controlled shapes. Several reports have suggested syntheses for making nanocubes [3], nanowires [4, 5] and nanorods [6]. One of the issues associated with the use of chemically synthesized nanoparticles is that varying their composition or use of different synthesis methods can give rise to different shapes and impact those properties relevant to data recording, catalysis and other technologies. One of the challenges is to be able to control both the composition and shape of alloy nanoparticles.

The equilibrium shape of an alloy nanoparticle depends upon its size and composition, in addition to external degrees of freedom such as temperature, pressure and the surrounding medium. The surrounding medium plays a role in nanoparticle shape because solvents and other components can act as surfactants and modify the surface energy of the various crystallographic planes exposed by the nanoparticle. Thus, nanoparticles do not necessarily adopt equilibrium shapes that are spherical and minimize surface area. It is also, important to point out that under many circumstances, the shapes exhibited by chemically synthesized nanoparticles may be dictated by their growth kinetics rather than by thermodynamic equilibrium. Understanding of the factors that influence nanoparticle shape is poor, however, it is clear that factors such as synthesis conditions offer means to control nanoparticle shape.

The aim of this work has been to study the shapes of $Fe_x Pt_{100-x}$ nanoparticles with various compositions

synthesized in a variety of solvents under otherwise similar conditions. Although equally important for their ultimate application, we have not focused on the properties of these Fe_rPt_{100-r} nanoparticles. In this work we have used different solvents for nanoparticle synthesis and explored their impact on the resulting shapes, sizes and compositions of the $Fe_x Pt_{100-x}$ nanoparticles. One of the key features of this work is that it has used a high pressure cell for the synthesis, thus allowing all reaction mixtures to be heated to the same temperature (270 °C) independent of the boiling points of the solvents being used. The shapes and compositions of the nanoparticles thus produced are influenced by the properties of the reaction mixture rather than the reaction kinetics dictated by temperature.

0.009 m oleic acid

0.0005 m Pt(acac)₂ 0.0009 m Fe(CO)5

 $0.0005 \text{ m Pt}(\text{acac})_2$ 0.0009 m Fe(CO)5 0.006 m oleylamine 0.006 m oleic acid

2. Experimental details

 $Fe_x Pt_{100-x}$ nanoparticles were chemically synthesized using a variety of solvents and methods. Cubic nanoparticles and nanowires were synthesized using modifications of a previously published methods [3–6]. Nanorods and nanohexagons were synthesized using a new method that makes use of a high pressure cell.

The basic synthesis method used iron pentacarbonyl and platinum (II) acetylacetonate as the metal containing precursors. 1,2-dichlorobenzene, toluene, and pure oleylamine were used as solvents and oleic acid and oleylamine served as surfactants. The details of the reaction mixtures and the conditions are listed in table 1. The reaction mixture consisting of the iron pentacarbonyl, platinum (II) acetylacetonate, surfactants and solvent was placed in a 45 ml Teflon[™] liner. The TeflonTM liner was placed inside the high pressure cell and the pressure cell was heated at a heating rate of 1- $2 \,^{\circ}\text{C} \,^{\text{min}^{-1}}$ to a final temperature of $270 \,^{\circ}\text{C}$. The residual gas in the TeflonTM liner was air. The pressure cell was capable of holding a maximum pressure of 117 bar. In the cases of the reactions performed in solvents with boiling



Figure 1. HRTEM image of hexagonally shaped $Fe_{18}Pt_{82}$ nanoparticles. The $Fe_{18}Pt_{82}$ nanoparticles were synthesized in toluene at a pressure of 22 bar and a temperature of 270 °C.

points that were <270 °C, the reaction pressure was dictated by the vapor pressure of the solvent at 270 °C. In the cases in which the boiling point of the solvent was >270 °C the pressure in the cell was that of air at 270 °C. The reactions were allowed to proceed for a period of 48 h at a temperature of 270 °C. After the completion of the synthesis, the reaction mixture was allowed to cool slowly within the TeflonTM liner. The final solution was a colloidal suspension of surfactant-coated $Fe_x Pt_{100-x}$ nanoparticles and excess surfactant dissolved in solvent.

Following their synthesis, the nanoparticles were washed using polar methanol (CH₃OH), causing them to precipitate. The mixture of nanoparticles and methanol was centrifuged to precipitate the nanoparticles from the solution. The supernatant solvent was discarded to remove the small particles and the precipitated nanoparticles were redispersed in toluene or benzene.

The self-assembled films were prepared by evaporation of the colloidal solution of $Fe_x Pt_{100-x}$ nanoparticles onto a carbon-coated copper TEM grid with 200 mesh. To prepare self-assembled films, 20 μ l of $Fe_x Pt_{100-x}$ nanoparticle solution in hexane was dropped slowly onto a carbon-coated TEM grid at room temperature. The concentration of the $Fe_x Pt_{100-x}$ nanoparticles in solution was very dilute, ~0.1 mg ml⁻¹. The TEM grid was covered with a glass petri dish and the solution of $Fe_x Pt_{100-x}$ nanoparticles was allowed to evaporate slowly overnight.

TEM studies were conducted using a Jeol JEM-2000 EX II microscope operating at 200 keV with a Gatan CCD camera. Energy dispersive x-ray spectroscopy (EDS) was performed using an FEI Tecnai F20 field emission transmission electron microscope with a point resolution of 0.23 nm and scanning transmission electron capability with a resolution of 0.2 nm. The microscope is equipment with an energy dispersive xray and Gatan imaging filter for electron energy loss. The quantitative analysis of EDS was performed by taking an average over clusters of nanoparticles. The accuracy of the methods for determination of the particle compositions is estimated at ± 5 –10%.

The solvents (methanol, toluene, 1,2-dichlorobenzene) and surfactants (oleic acid and oleylamine) were obtained from

Aldrich Chemical Co. and were used as obtained without further purification. The iron pentacarbonyl was obtained from Aldrich and the platinum acetylacetonate (99%) was obtained from Strem chemicals.

3. Results and discussion

Recently, the synthesis of various types of nanoparticles with controlled shapes has been of great interest [3–6]; however, little is understood about the synthesis parameters which impact the shapes of chemically synthesized nanoparticles. We have limited our focus to the use of different solvents to alter the nanoparticle shape. Our previous work [7] showed that synthesis of Fe₅₀Pt₅₀ nanoparticles in dioctylether (b.p.—280 °C) always produces spherical nanoparticles with diameters of 3–5 nm. In this work, we have used solvents with different boiling points in the range 110–350 °C to study the influence of solvent properties on nanoparticle shape and composition.

We find that synthesis in toluene results in the formation of Fe₁₈Pt₈₂ nanoparticles with hexagonal shapes. The Fe₁₈Pt₈₂ nanoparticles shown in figures 1(a) and (b) were synthesized using toluene (b.p.—110°C) as the solvent but at a temperature of 270 °C. At this temperature the vapor pressure of toluene is 22 bar [8]. The heating rates used in this work were $1-2 \circ C \min^{-1}$. We have observed that the rate of heating of the reaction mixture can play an important role in tailoring the shapes of the nanoparticles. Higher heating rates (>5 $^{\circ}$ C min⁻¹) gave only spherical nanoparticles. After the reaction was completed, the reaction mixture was cooled in the high pressure cell. One of the advantages of using the high pressure cell is that there is no oxidation of the $Fe_x Pt_{100-x}$ nanoparticles while at high temperature. Figure 1 shows high resolution TEM images of hexagonally shaped Fe₁₈Pt₈₂ nanoparticles synthesized in toluene. Self-assembly of these nanoparticles results in the orientation of their (111) planes parallel to the plane of the image. The HRTEM image also shows that there are no grain boundaries or defects in the hexagonal particles and they have fairly uniform diameters of ~ 10 nm. Most of the hexagonal nanoparticles have very sharp



Figure 2. HRTEM images of $Fe_{26}Pt_{74}$ nanorods. These $Fe_{26}Pt_{74}$ nanorods were synthesized in 1,2-dichlorobenzene at a pressure of 6 bar and temperature of 270 °C.



Figure 3. HRTEM images of $Fe_{50}Pt_{50}$ nanowires. The $Fe_{50}Pt_{50}$ nanowires were synthesized in oleylamine at a pressure of 2 bar and a temperature of 270 °C.



Figure 4. HRTEM images of $Fe_{97}Pt_3$ nanocubes. These $Fe_{97}Pt_3$ nanocubes were synthesized in 1,2-dichlorobenzene at a vapor pressure of 6 bar and temperature of 270 °C but with less surfactant than used in the synthesis of the nanorods shown in figure 2.

edges with uniform spacing of ~ 1 nm between them. The spacing arises from the layer of surfactant on their surfaces.

Synthesis in 1,2-dichlorobenzene results in Fe₂₆Pt₇₄ nanoparticles with rod-like shapes. Figure 2 shows bright field HRTEM images of Fe₂₆Pt₇₄ nanoparticles which were synthesized using 1,2-dichlorobenzene (b.p.—180 °C) as a solvent. The vapor pressure of 1,2-dichlorobenzene at 270 °C is 6 bar [9]. When using 1,2-dichlorobenzene as the solvent, we observed formation of Fe₂₆Pt₇₄ nanorods. The diameter of the nanorods is 2 nm and these nanorods can be synthesized with lengths in the range of 5–20 nm. The HRTEM images (figures 2(a) and (b)) of the Fe₂₆Pt₇₄ nanorods show uniform growth and deposition with the $\langle 100 \rangle$ direction parallel to the TEM grid. The nanoparticles do not have any grain boundaries or defects. This type of defect free growth of nanoparticles will play an important role in the alignment of their crystallographic axes.

Synthesis in pure oleylamine results in $Fe_{50}Pt_{50}$ nanowires with high aspect ratios. The $Fe_{50}Pt_{50}$ nanowires shown in figure 3 were synthesized using oleylamine as the solvent (b.p.—350 °C). As the boiling point of oleylamine is less than the reaction temperature of 270 °C, the pressure in the reactor is assumed to be that of air at this temperature, ~2 bar. The TEM image in figure 3 shows that these nanoparticles form in the shape of nanowires. The nanowires were 40–200 nm in length with diameters of 1–2 nm. The nanowires showed local self-assembly parallel to one another. The uniform spacing between the nanowires is assumed to arise from adsorbed oleylamine.

Another parameter that can influence the shapes of the nanoparticles is the amount and the type of the surfactant. Synthesis in 1,2-dichlorobenzene but with less surfactant than that used in the synthesis of the nanorods results in $Fe_{97}Pt_3$ nanocubes. The nanocubes shown in the figure 4 were

synthesized using 1,2-dichlorobenzene as the solvent but in this case the amount of surfactant was reduced from that used during the synthesis of the nanorods shown in figure 2. In this experiment the amounts of oleylamine and oleic acid were 2 ml each in 20 ml of 1,2-dichlorobenzene (rather than 3 ml as used previously in the synthesis of nanorods). The HRTEM in figure 4 shows cubic shaped $Fe_{97}Pt_3$ nanoparticles that are very uniform with no grain boundaries and no defects.

The compositions and the shapes of the nanoparticles synthesized in the course of this work are very sensitive to the composition of the reaction mixture. The use of the high pressure cell has allowed all reactions to be conducted at the same temperature (270 °C) thus eliminating the effects of temperature on the reaction kinetics. While the resulting reaction conditions have spanned a wide range of pressures, the sensitivity to pressure is likely to be much less than to temperature and thus the high pressure cell eliminates an important reaction variable. Nonetheless, the reaction conditions (solvent type and surfactant concentrations) have yielded a widely varying distribution of nanoparticle compositions and shapes. In particular, the sensitivity to the concentration of surfactant is highlighted by the production of cubic nanoparticles and nanorods in 1,2-dichlorobenzene solutions containing surfactant concentrations that differ by only 50%. One question that remains is whether the particle shapes are directly dictated by their compositions or whether it is the surfactant and solvent that dictate both shape and composition.

4. Conclusion

Our work demonstrates that under constant reaction temperature conditions, changing the type of the solvent or the amount of the surfactant used in the chemical synthesis of $Fe_x Pt_{100-x}$ nanoparticles can change their shape and composition. The use of a high pressure cell eliminates the role of reaction kinetics dictated by temperature as the source of the variations in nanoparticle size and composition. In the future, we hope to further expand this work to understand the impact of the composition and sizes of these nanoparticles on their magnetic properties and further optimize their synthesis.

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