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Direct synthesis of partially ordered tetragonally structured FePt nanoparticles by polyol method for biomedical application

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ABSTRACT

We report the direct soft chemical synthesis and characterization of a family of face centered cubic (fcc) and partially ordered face centered tetragonal (fct) FePt nanoparticles (NPs) suitable for biomedical applications. Both fcc and partially ordered fct-FePt NPs are synthesized by employing a simple polyol method. By using polyvinyl pyrolidone (PVP) as a stabilizer in various ratios during synthesis, fcc-FePt NPs have been converted into partially ordered fct-FePt NPs at low temperature $(300^\circ C)$. The advantages of this process are its simplicity, the short reaction time, easy preparation and dispersibility of the NPs in aqueous media.

Keywords: *FePt; Nanopartcles; Ferromagnetism; DC magnetization; Transmission electron microscopy.*

INTRODUCTION

Iron-platinum alloy nanoparticles (FePt NPs) are extremely promising candidates for the next generation of magnetic nanomaterial for nanomedicine applications like magnetic hyperthermia and magnetic resonance imaging (MRI) [1,2] because of their high Curie temperature (Tc), saturation magnetic moment (Ms), magneto-crystalline anisotropy, and chemical stability. Recently, superparamagnetic chemically disordered face-centered cubic (fcc) FePt nanoparticles have been demonstrated as superior negative contrast agents for MRI [3]. Superparamagnetic FePt nanoparticles, which show high saturation magnetization compared to SPION, are expected to be a high performance nanomagnet for magnetic medicine [4-6]. Even though FePt NPs exists in disordered fcc and ordered fct structures, the synthesis of fct FePt NPs is not so easy. Further, such structural difference in fcc-FePt and fct-FePt NPs leads to distinctive property change not only in magnetism [7, 8] but also in the chemical stability.

Conventionally, as prepared fcc FePt NPs are converted into fct NPs by a slow rate heating of fcc structure above 550°C for 4-6 h [7, 8], which results in agglomeration of these NPs.

This conventional complicated synthesis procedure and hydrophobicity has limited the potential usage of both forms of FePt NPs in vitro, in vivo and in clinic. In this work, we report the direct soft chemical synthesis and characterization of a family of fcc and partially ordered fct-FePt NPs dispersible in aqueous media suitable for biomedical applications. Both fcc and partially ordered fct-FePt NPs are synthesized by employing a simple polyol method. By using PVP in various ratios during synthesis, fcc-FePt NPs have been converted into partially ordered fct-FePt NPs. The advantages of this process are its simplicity, the short reaction time and facile chemistry. The structure, composition and magnetic properties of the FePt NPs were characterized by XRD, TEM and magnetic measurements. The initial studies show that FePt NPs can exhibit low cytotoxicity. This paves the way for several future applications of FePt NPs, including regenerative medicine and stem cell therapy in addition to enhanced MR diagnostic imaging.

EXPERIMENTAL

In this method, iron (III) acetyl acetonate (Fe(acac)$_3$) and chloro platinic acid are used as the main reactants in tetra-ethylene glycol solvent with different ratios of polyvinyl pyrolidone (PVP) as a stabilizer. In a typical process to synthesize fcc phased FePt NPs, 1:1 molar ratio of Fe(acac)$_3$ and chloro platinic acid were refluxed in tetra ethylene glycol taken in a round bottomed flask at 300oC for 2h. The obtained product dried at room temperature after washing using acetone and ethanol several times. Partially ordered fct phased FePt NPs were synthesized in a similar manner by adding different ratios of PVP (1:1, 1:2 and 1:3) with respect to Fe and Pt precursors taken during reaction. Phase purity and the structure of the fine powder obtained were analyzed by powder X-ray diffraction using Cu Kα radiation of a Philips Diffractometer (model PW 1071) fitted with graphite crystal monochromator. DC magnetization measurements, as a function of field were carried out using an E.G.& G P.A.R vibrating sample magnetometer

(model 4500). The electron diffraction and high-resolution transmission electron microscopic (HRTEM) images were acquired on a TEM JEOL 2010F.

RESULTS AND DISCUSSION

Energy dispersive X-ray analysis (EDAX) indicates that all samples show the Fe:Pt ratio in the range 60:40 for both fcc and fct phased FePt NPs. The XRD pattern of fcc-FePt samples showed the peaks (111), (200) and (220) with the lattice constant a = 3.848(2) Å, corresponding to cubic phase (fcc) of FePt (Figure 1a and d). The emergence of additional peaks (001) and (110) in the XRD pattern (Figure 1b and c) confirms the partial transformation of fcc-FePt to tetragonal structured fct-FePt. Analysis of the X-ray diffraction pattern of fct-FePt revealed that the lattice constant is 3.862 Å and c is 3.722 Å, with c/a ratio being 0.964. This is quite consistent with the lattice constant for near-equiatomic FePt bulk material with L10 phase [9]. It is worth to note that the sample without PVP is fcc structured and the fct-FePt phase started to form only in the presence of PVP (Figure 1b and c). However, it is observed that the fct phase formation is PVP ratio dependent and above FePt:PVP = 1:3 ratio, the fct phase disappears and the fcc phase re-emerges (Figure 1d).
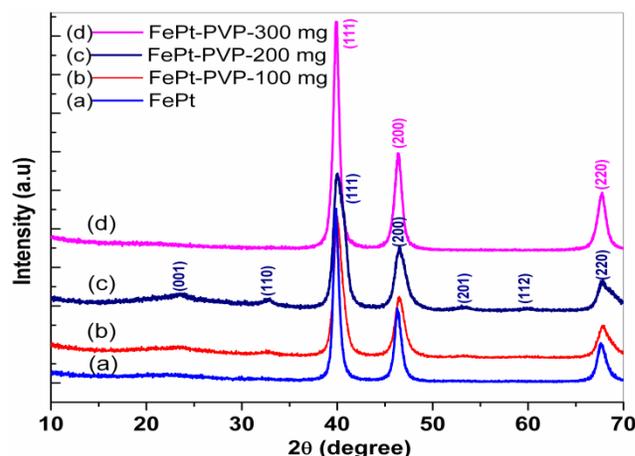
Fig.1. Room temperature powder x-ray diffraction patterns of (a) FePt without PVP, (b) FePt with FePt:PVP = 1:1, (c) FePt with FePt:PVP = 1:2 and (d) FePt with FePt:PVP = 1:3.

The crystallite size calculated for these samples using Scherrer's equation (after correction for broadening due to standard sample) is approximately in the range 7-10 nm. It is worth to note that the crystallite size is marginally less for PVP stabilized samples. A marginal shift in the peak positions to higher angles (Figure 1) is observed in the case of fct phased FePt samples (Figure 1b and c).

Figure 2 shows the TEM, HRTEM and SAED pattern of fcc phased FePt NPs synthesized without adding PVP. The TEM (Figure 2a and b) shows that the particle diameter is in the range of about 10 nm in agreement with the XRD results. The HRTEM and indexed SAED pattern show that the samples are highly crystalline fcc structured FePt.
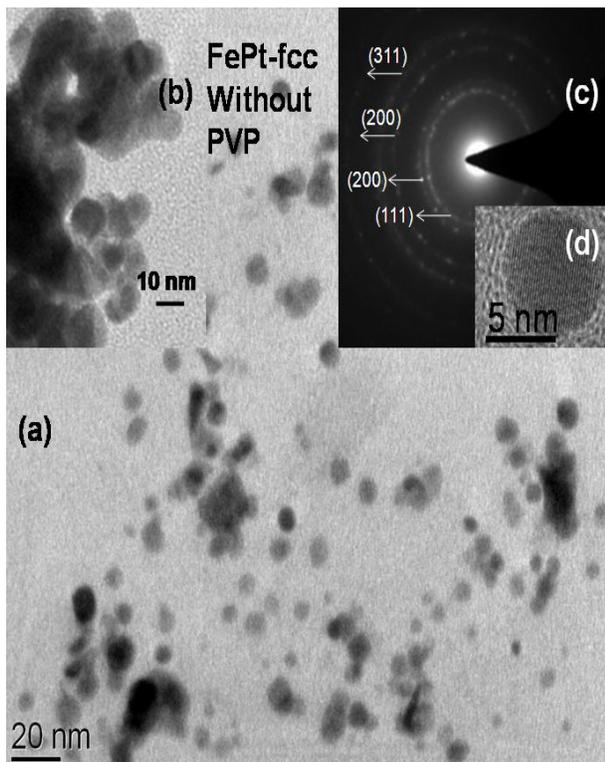
Fig.2. (a, b) TEM, (c) SAED and (d) HRTEM images of fcc-FePt nanoparticles without PVP coating.

FePt NPs with fct structure prepared using PVP (FePt:PVP=1:2) showed particle diameter of about 8 nm (Figure 3a and b). The indexed SAED pattern (Figure 3c) shows that the FePt particles are highly crystalline with fct structure. On increasing the PVP ratio to FePt:PVP = 1:3, the particle size

marginally decreased to about 6-7 nm as is evident from Figure 3d.
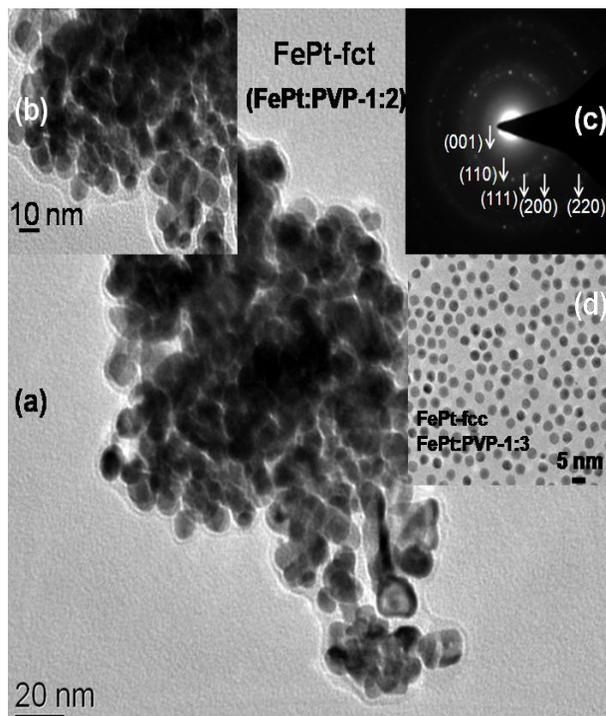
Fig.3. (a, b) TEM, (c) SAED of fct-FePt nanoparticles with FePt:PVP = 1:2 and (d) TEM image of fcc-FePt nanoparticles with FePt:PVP = 1:3.

The magnetic hysteresis loops and magnetization as a function of temperature of fcc and fct phased FePt NPs prepared using different ratios of PVP are given in Figure 4. The saturation magnetization (Ms) of fcc phased FePt NPs synthesized without PVP is ~50 emu/g. It is worth to note that the saturation magnetization increases systematically as a function of increasing PVP ratio upto an optimum value of FePt:PVP = 1:2. The Ms value observed for FePt nanoparticles prepared using PVP ratios FePt:PVP = 1:1 and FePt:PVP = 1:2 were 105 and 142 emu/g, respectively. Above PVP ratio of 1:2(eg. FePt:PVP = 1:3), the saturation magnetization decreases and the M vs H curve showed a superparamagnetic type of behavior. Both FePt without PVP (fcc-FePt) and with PVP (FePt:PVP = 1:1) showed ferromagnetic behavior with weak coercivities (Hc=430 and 250 Oe respectively) and remanences (Mr=16 and 26 emu/g respectively) (Figure 4a and b). The M vs T curve (inset of Figure 4a) of fcc-FePt NPs, synthesized without PVP, further confirmed their

ferromagnetic behavior. However, in the case of fct-FePt NPs obtained by using higher PVP ratio (FePt:PVP = 1:2), the saturation magnetization (Ms~142 emu/g), coercivity (Hc~4 kOe) and remanence (Mr~90 emu/g) increased significantly as expected for fct phased FePt NPs. Its ferromagnetic behavior is further confirmed from the M vs T plot (inset of Figure 4c). The interesting aspect is that the fcc to fct phase transformation in FePt NPs is PVP ratio dependent for a given concentration of Fe and Pt salts. When the PVP ratio is increased to 1:3 (FePt:PVP = 1:3) by keeping other conditions same, the FePt NPs showed fcc phase (Figure 1d) with superparamagnetic type of behavior (Figure 4d) with blocking temperature (TB) ~175 K (inset of Figure 4d).

We have carried out preliminary studies on FePt, for their effects on the metabolic activity and viability of human endothelial cells. Considering the magnetic properties shown by this material, it appears to be promising for T2 weighted imaging in MRI applications. It may be noted that FePt nanoparticles without PVP showed slight toxicity character wherein at 10µg/ml, cell started showing adverse effects on their viability leading to apoptosis. We believe that the presence of platinum contributed to the toxicity character for this material. However, considering the clinical use of platinum based chemodrugs such as cisplatin and oxaliplatin, it is possible that, with proper surface chemistry modifications, it will be appropriate to test for the anticancer activity of this materials at lower doses (< 10µg/ml). The PVP coated FePt samples showed promising results in this respect and further studies on these materials using different size-scale, shape, composition and surface chemistry are in progress for better understanding of the properties and their possible bio-medical applications.
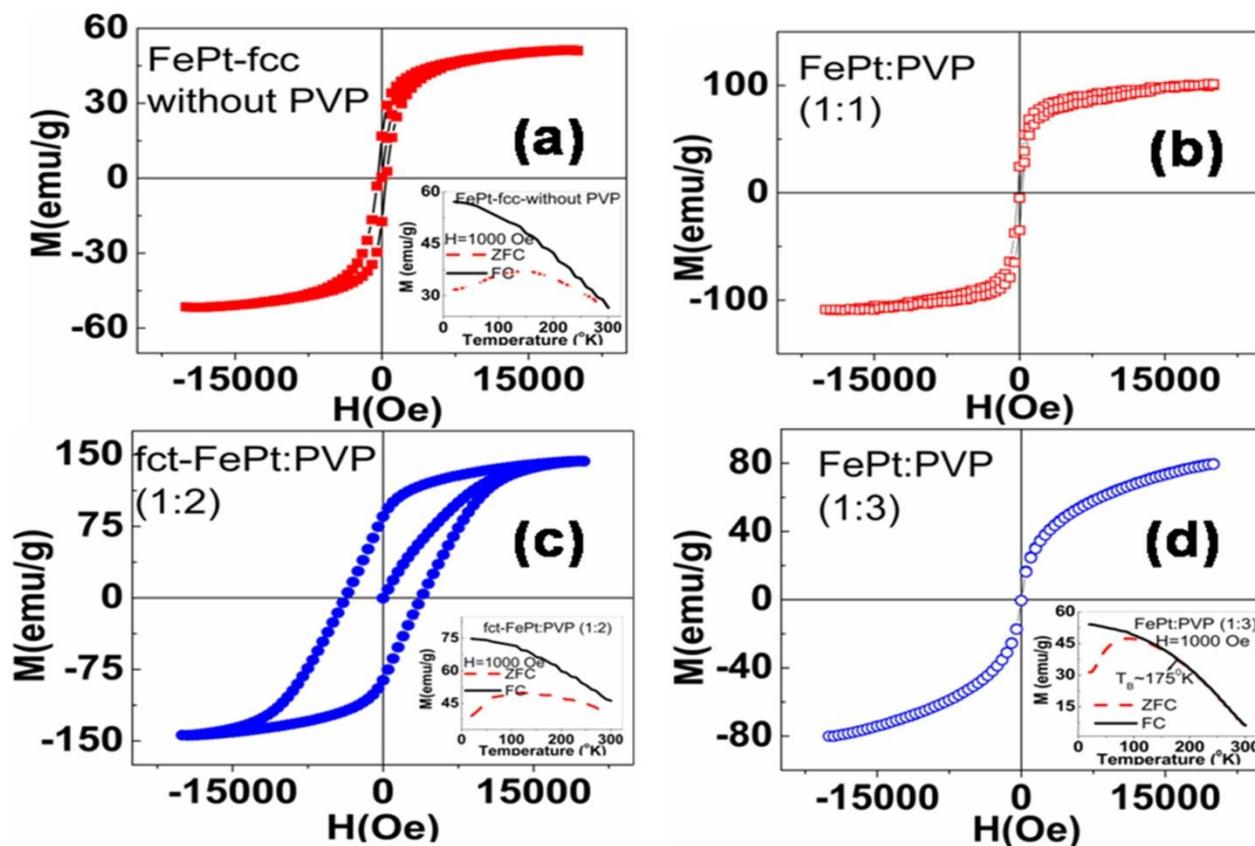
Fig.4. M vs H curves of (a) FePt without PVP and inset shows its M vs T curve, (b) M vs H curve of FePt with FePt:PVP = 1:1, (c) fct-FePt with FePt:PVP = 1:2 and inset shows M vs T curve and (d) fcc-FePt with FePt:PVP = 1:3 and inset shows the M vs T curve.

CONCLUSION

In conclusion, a soft chemical method of preparing fct phased FePt from fcc phased FePt nanoparticles at low temperature has been developed using PVP as a protective agent. The preliminary results suggest that, in addition to unique functional properties, these nanomaterials also show typical nano-bio interactions leading to varied toxicity characteristics.

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