

Growth of FePt nanocrystals by a single bimetallic precursor $[(\text{CO})_3\text{Fe}(\mu\text{-dppm})(\mu\text{-CO})\text{PtCl}_2]^\dagger$

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A new single source approach was developed to synthesize face-centered tetragonal (fct) FePt nanoparticles using bimetallic compound $(\text{CO})_3\text{Fe}(\mu\text{-dppm})(\mu\text{-CO})\text{PtCl}_2$, which has been characterized by single crystal X-ray diffraction and was used as the precursor to ensure the accurate stoichiometry of the final FePt product; the ability of the molecular complex to act as a single source precursor for the formation of fct FePt nanocrystals with an average diameter of 3.2 nm has been demonstrated.

There has been considerable interest in face-centered tetragonal (fct) FePt nanoparticles because they possess large magnetocrystalline anisotropy and high chemical stability. These properties make fct FePt nanoparticles applicable in high density recording media, permanent magnetic nanocomposites and for use in biological separation.¹ Monodisperse FePt nanoparticles are typically synthesized through the simultaneous reduction of a metal salt and the thermal decomposition of a metal carbonyl in the presence of mixed surfactants.² In this technique, the FePt nanoparticles are prepared using a variety of starting compounds, such as $\text{FeCl}_2/\text{Pt}(\text{acac})_2$ or $\text{Fe}(\text{CO})_5/\text{Pt}(\text{acac})_2$ in a ratio of about 1 : 2. The resulting disordered cubic FePt nanoparticles are generally converted into fct FePt ones by annealing at temperatures above 550 °C under a reducing atmosphere.^{3,4} This conventional method, based on dual-source precursors, demonstrates the feasibility of smooth solid-state conversions to produce nanocrystals, but at the same time often suffers from difficulties with stoichiometric control. This is largely due both to premature reactions between the Fe and Pt nanoparticles and non-stoichiometric starting compositions of the dual Fe and Pt sources. An alternative approach that overcomes this problem is to use a bimetallic complex involving a Fe–Pt direct bond as a single source precursor. It is expected that this approach will be useful in the synthesis of stoichiometric FePt nanoparticles of high purity.

Here we report a new synthetic approach that allows the formation of 1 : 1 ordered FePt nanocrystals by using the well-characterized bimetallic precursor $[(\text{CO})_3\text{Fe}(\mu\text{-dppm})(\mu\text{-CO})\text{PtCl}_2]$

(**1**)⁵ ($\text{dppm} = \text{Ph}_2\text{PCH}_2\text{PPh}_2$). This compound was found to be a very effective source for synthesizing fct FePt nanoparticles under comparatively mild conditions, mainly due to the intimate mixing of the Fe and Pt species at a molecular level. It is remarkable that both the stoichiometry and diffusion barrier required to yield FePt nanocrystals can be easily controlled by utilizing this bimetallic precursor. To the best of our knowledge, this study is the first demonstration of the utilization of a single source for the synthesis of magnetic intermetallic alloys, although such a soft chemical approach has been used to produce various other functional materials.⁶

Bimetallic precursor **1** was prepared by the reaction of $[(\text{CO})_4\text{Fe}(\text{dppm})]$ with $\text{Pt}(\text{COD})\text{Cl}_2$ ($\text{COD} = 1,5\text{-cyclooctadiene}$) in toluene at room temperature. The chelating nature of the dppm ligand appears to restrict the number of coordinating sites, allowing for the formation of 1 : 1 FePt adducts exclusively. As shown in Fig. 1, the compound contains a direct Fe–Pt bond that is bridged by dppm and CO groups. The Fe–Pt distance is 2.638 Å, which is comparable to those found in other mixed metallic complexes,⁷ and indicates that the Fe and Pt atoms are directly bonded. In the presence of surfactants, treatment of **1** with lithium triethylborohydride leads to the formation of FePt nanoparticles in 64% yield after washing with ethanol. This result suggests that the

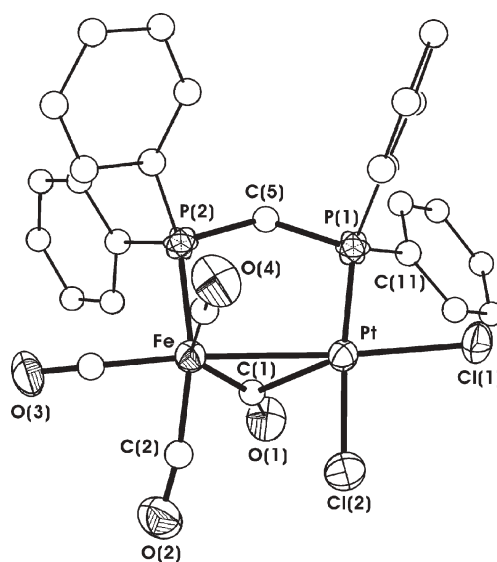


Fig. 1 ORTEP drawing of the molecular structure of $[(\text{CO})_3\text{Fe}(\mu\text{-dppm})(\mu\text{-CO})\text{PtCl}_2]$ (**1**). Selected inter-atomic distances (Å): Fe–Pt 2.638, Fe–P(2) 2.269, Pt–P(1) 2.234, Fe–C(1) 1.872 and Pt–Cl(1) 2.350.

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† Electronic Supplementary Information (ESI) available: Spectroscopic results (NMR, crystallographic data and FT-IR spectrum) for $[(\text{CO})_3\text{Fe}(\mu\text{-dppm})(\mu\text{-CO})\text{PtCl}_2]$ along with XRD and TEM images of the FePt nanoparticles. See DOI: 10.1039/b516831g

precursor undergoes a decomposition reaction that presumably proceeds *via* loss of the dppm and CO ligands, followed by the liberation of chloride to yield the FePt nanocrystals. The bridging dppm ligands appear to prevent the unwanted segregation of Fe and Pt in the course of the FePt formation, permitting the decomposition and crystallization processes to occur at conditions milder than those required for conventional dual source reactions.⁸ Evidence of stoichiometric FePt composition was also provided by elemental analysis using inductively coupled plasma mass spectroscopy (ICP-MS), in which the final composition of the nanoparticles was determined to be Fe_{0.52}Pt_{0.48}.

Low resolution transmission electron microscopy (TEM), shown in Fig. 2, reveals that the average diameter of the as-prepared FePt nanocrystals is 3.2 nm. It is worthwhile mentioning that the FePt sample also contains non-spherical nanoparticles. This might be due to the monoclinic nature of the starting precursor compound. Namely, the precursor compound is smoothly transformed into fct FePt nanocrystals by maintaining its structural integrity, which might lead to a non-spherical shape in the resulting nanocrystals. On the other hand, in the dual-source approach, individual Fe and Pt atoms are condensed into a solid-state cluster within the surrounding surfactant molecules, which would thus prefer to form a spherical shape. The crystallinity of these nanoparticles was carefully examined using high resolution TEM, as shown in Fig. 2(b).

Lattice distances of 1.996 Å and 2.271 Å were measured from the fringes, indicating the presence of the tetragonal phase; these distances corresponding to the (200) and (111) planes, respectively. Clearly, the TEM data coincides well with the X-ray powder diffraction (XRD) data from tetragonal FePt (Fig. 3). The remarkable low temperature growth of the tetragonal phase seen in the present study occurs even at relatively low temperatures owing to the intimate contact between the Fe and Pt fragments. This implies that post-annealing might not be a requisite step in the production of the fct FePt phase.

The XRD pattern of the as-synthesized FePt sample, shown in Fig. 3, displays very broad peaks due to nanometer-sized grains. Annealing at high temperature transformed the as-prepared sample into the desired tetragonal phase. Clearly, there is a narrowing of the XRD peaks, indicative of grain growth. Using the Debye-Scherrer equation, the average particle size was determined from the XRD data of the FePt sample annealed at 550 °C to be approximately 7.6 nm.⁹ This is much larger than the

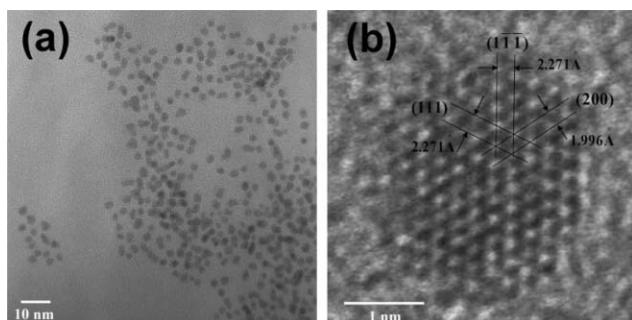


Fig. 2 (a) Low resolution TEM micrograph of as-synthesized FePt nanocrystals. (b) High resolution TEM image of the as-synthesized FePt nanocrystals. The lattice distances correspond to the (200) and (111) lattice planes of fct FePt.

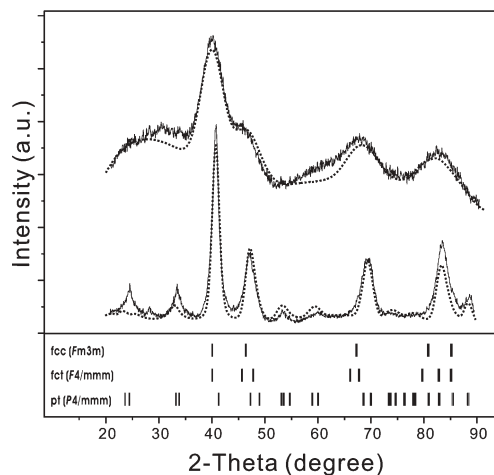


Fig. 3 XRD powder patterns of the as-synthesized (top) and annealed FePt nanocrystals (bottom). The Rietveld fit is plotted as a dotted line. The vertical bars are the calculated peak positions for the corresponding fct and primitive tetragonal (pt) symmetries.

size of the as-synthesized FePt particles estimated from the TEM images, suggesting that interfacial melting occurs in the sintering process. The as-synthesized FePt nanocrystals prepared by our single source method adopt the tetragonal structure, which is evident by refining the XRD data using the Rietveld method. The intimate and controlled mixing of the metal species at the molecular level allows the formation of the bimetallic phase under mild conditions.¹⁰ The heat treatment, however, drastically affects the magnetic properties of the FePt nanoparticles, as shown in Fig. 4.

The magnetic properties of the as-synthesized FePt nanocrystals reveal a superparamagnetic feature with a blocking temperature of about 40 K, as shown in Fig. 4(b). Below this blocking temperature, the magnetization reversal curve measured at 10 K shows a hysteric behavior, with a coercivity of about 1.9 kOe. On

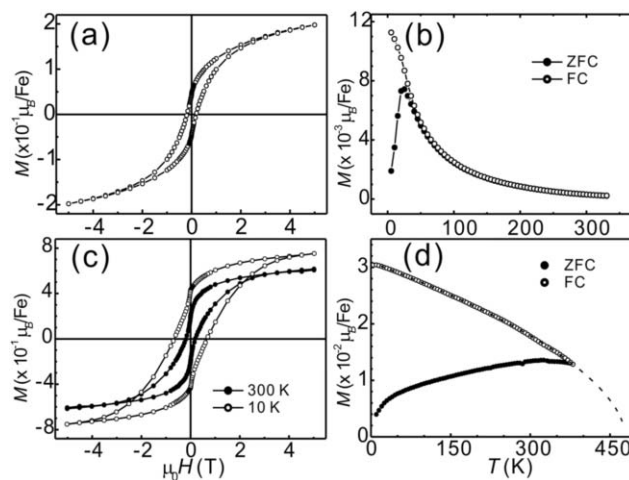


Fig. 4 Typical field-dependent magnetization curves at 10 K (○) and 300 K (●) of (a) as-synthesized and (c) annealed FePt nanoparticles. Zero-field-cooled (ZFC, ●) and field-cooled (FC, ○) magnetization data of (b) as-synthesized and (d) annealed FePt nanoparticles measured in an applied field of 100 Oe. The dashed line in (d) illustrates the power law fit to the data.

the other hand, the FePt nanoparticles annealed at 550 °C are shown to have a larger coercivity and higher blocking temperature than the as-prepared ones. As can be seen from the $M(H)$ curves in Fig. 4(c), the coercivity of the FePt sample is close to 9.2 kOe, showing that the sample possesses high magnetocrystalline anisotropy. A remarkable feature in the $M(H)$ curve of Fig. 4(d) is that the FePt nanoparticles remain ferromagnetic at temperatures over 300 K, despite having an average particle size of 7.6 nm. The power law fit with $M(T) = M_0(1 - T/T_c)^\beta$, where $M(T)$ is the temperature dependent magnetization, M_0 is the magnetization at $T = 0$, T_c is the Curie temperature, and β is the critical exponent, given by the dashed line in Fig. 4(d), yields a Curie temperature of 479 K, indicating that interfacial melting, driven by annealing at high temperature, converts the superparamagnetic nanoparticles completely into ferromagnetic ones.¹¹

In conclusion, we have demonstrated a single source approach to the synthesis of fct FePt nanocrystals using a bimetallic precursor without post-annealing at high temperature. The present method enables us to synthesize fct FePt nanoparticles under relatively mild conditions by utilizing a bimetallic precursor which can be modulated at the nanometer scale. It is thus expected that this single source approach will be applicable to the synthesis of other functional materials, even generating new metastable intermetallic alloys. We are currently working on a more detailed analysis of their magnetic properties, focusing on the correlation between the nanoparticle size and the Curie temperature.

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 5 Crystal data for 1: $C_{29}H_{22}O_4P_2Cl_2FePt$, $M = 818.27$, monoclinic, space group $P2_1/n$ (no. 14), $a = 12.535(1)$, $b = 17.662(1)$, $c = 13.211(1)$ Å, $\beta = 102.2(1)^\circ$, $Z = 4$, $V = 2859.2(7)$ Å³, $\mu_{\text{expt}} = 5.728$ mm⁻¹, $T = 293(2)$ K, $d_{\text{calc}} = 1.901$ g cm⁻³, $\lambda(\text{Mo-K}\alpha) = 0.71073$ Å, 15966 reflections measured, 5624 were unique and used in all calculations. The structure was solved by direct methods (SHELXL-97) and refined by full-matrix least-square methods on F^2 with 353 parameters, R_1 ($I > 2\sigma(I)$) = 0.0294 and $wR_2 = 0.0561$, GOF = 0.948, residual density 1.212/−1.014 e Å⁻³. CCDC 291487. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b516831g.
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