2013

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Yu, Yongsheng; Sun, Kewei; Tian, Yuan; Li, Xingzhong; Kramer, Matthew J.; Sellmyer, David J.; Shield, Jeffrey E.; and Sun, Shouheng, "One-Pot Synthesis of Urchin-like FePd–Fe₃O₄ and Their Conversion into Exchange-Coupled L1₀–FePd–Fe Nanocomposite Magnets" (2013). *David Sellmyer Publications*. 274.
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Published in *Nano Letters* 13:10 (2013), pp. 4975–4979; doi: 10.1021/nl403043d
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Submitted August 14, 2013; revised September 12, 2013; published September 16, 2013.

The authors declare no competing financial interest.

Supporting information for this article is available following the references.

One-Pot Synthesis of Urchin-like FePd–Fe₃O₄ and Their Conversion into Exchange-Coupled L1₀–FePd–Fe Nanocomposite Magnets

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Abstract

We report a one-pot synthesis of urchin-like FePd–Fe₃O₄ nanocomposites, spherical clusters of FePd nanoparticles (NPs) with spikes of Fe₃O₄ nanorods (NRs), via controlled thermal decomposition of Fe(CO)₅ and reduction of Pd(acac)₂. The FePd NPs with sizes between 6 and 9 nm self-aggregate into 60 nm superparticles (SPs), and Fe₃O₄ NRs grow on the surface of these SPs. Reductive annealing at 500°C converts the FePd–Fe₃O₄ into exchange-coupled nanocomposites L1₀–FePd–Fe with their H_c tunable from 0.8 to 2.6 kOe and M_s controlled from 90 to 190 emu/g. The work provides a general approach to L1₀–FePd–Fe nanocomposite magnets for understanding exchange coupling at the nanoscale. The concept may be extended to other magnetic nanocomposite systems and may help to build superstrong magnets for magnetic applications.

Keywords: L1₀-FePd, nanocomposites, reductive annealing, exchange coupling, nanocomposite magnets

Advanced magnets for future high-density power and data-storage applications require a large magnetic coercivity (H_c) and high saturation magnetizations (M_s).¹ Single-component magnets based on NdFeB, SmCo, or FePt (or CoPt) can have very large H_c but generally lower M_s than magnetically soft Fe, Co, or FeCo.²⁻⁴ To further increase magnetization values without sacrificing much coercivity, exchange-spring nanocomposite magnets have been proposed.⁵⁻¹⁰ In this exchange-spring nanocomposite magnet, the magnetically soft phase should be made in intimate contact with the hard phase without forming undesired forms of alloy with the hard phase. Due to the strong exchange coupling, magnetization direction of the soft phase is pinned along the hard phase direction, making the composite possess simultaneously both hard phase (large H_c) and soft phase (high M_s) properties. The key to optimizing the exchange coupling is to control the size of the soft phase. Effective exchange-coupling of the soft phase to the hard phase requires the size of the soft phase to be less than almost half the domain wall width of the hard phase.¹¹⁻¹⁵ Since the domain-wall thickness of the normal hard magnetic materials are in 2–22 nm, the size of the soft phase should be around 4–44 nm.² Despite the theoretical prediction and some early experimental demonstrations, embedding the soft phase with controlled sizes and distribution in a hard magnetic matrix is still extremely challenging.¹⁶⁻²⁰

L1₀-FePt has been prepared as a hard magnetic phase with magnetocrystalline anisotropy constant K_u reaching 6.6×10^7 erg/cm³.²¹⁻²⁵ In a model test, FePt and Fe₃O₄ nanoparticles (NPs)²⁶ or FePt/Fe₃O₄ core/shell NPs²⁷ were assembled and reduced at high temperatures, forming L1₀-FePt-based nanocomposites with a high magnetic performance. However the L1₀-FePt tends to form a solid solution with Fe. As a result, L1₀-FePt-Fe nanocomposite with a distinct Fe phase embedded in the L1₀-FePt matrix cannot be produced easily. In fact, the reductive annealing of FePt and Fe₃O₄ NP assembly gave L1₀-FePt-Fe₃Pt with Fe₃Pt serving as the soft phase.²⁶ Similar to FePt, FePd can also adopt L1₀-type intermetallic structure with K_u at 1.0×10^7 erg/cm³.²⁸ More interestingly, in the FePd alloy equilibrium phase diagram,²⁹ there is a eutectoid reaction at 605°C at the composition of Fe-54 at.% Pd. On cooling from the eutectoid temperature to room temperature, α -Fe and L1₀-FePd can be obtained.³⁰ This simultaneous formation of L1₀-FePd and α -Fe as a thermodynamically stable mixture indicates that L1₀-FePd-Fe is a better model system to study nanocomposite magnets with controlled exchange-coupling.

Herein, we report one-pot synthesis of urchin-like FePd-Fe₃O₄ composites and their conversion into L1₀-FePd-Fe nanocomposite magnets. The unique feature of this synthesis is that FePd NPs (6–9 nm) are first formed and then self-aggregate into 60 nm superparticles (SPs) before the Fe₃O₄ nanorods (NRs) start to grow on the surface of the FePd SPs, giving an urchin-like structure (scheme 1). In the FePd-Fe₃O₄ composite, the Fe/Pd ratios are controlled by the amount of Fe(CO)₅ used in the synthesis and the reaction temperature. Once annealed in a reducing atmosphere at high temperature (up to 500°C), the FePd-Fe₃O₄ can be converted into L1₀-FePd-Fe nanocomposite magnets with L1₀-FePd and α -Fe exchange-coupled. These magnets show the smooth magnetization transition under an external magnetic field and their magnetic properties can be tuned by the amount

of Fe present in the composite. The work provides a general approach to exchange-coupled L1₀-FePd-Fe whose understanding may help to build high performance nanocomposite magnets for superstrong magnet applications.

Scheme 1. Schematic illustration of self-aggregation of FePd NPs into FePd SPs and the formation of urchin-like FePd-Fe₃O₄ composites.

The urchin-like FePd-Fe₃O₄ composites were prepared by one-pot decomposition of Fe(CO)₅ and reduction of Pd(acac)₂ in a mixture of oleic acid (OA), oleylamine (OAm), and 1-octadecene (ODE) (see the Supporting Information). In the synthesis, 0.1 g of Pd(acac)₂, 1.5 mL of OA, 12 mL of OAm, and 8 mL of ODE were first mixed at room temperature and then heated to 90°C. Under a blanket of nitrogen gas, a controlled amount of Fe(CO)₅ was added. Then the solution was heated to 200°C at a heating rate of 5°C/min and kept at 200°C for 1 h before it was cooled to room temperature. The product was separated, purified, and redispersed in hexane. The compositions were analyzed by inductively coupled plasma atomic emission spectroscopy (ICP-AES). Under the described synthetic conditions, FePd NPs self-aggregated into SPs, and Fe₃O₄ NRs grew on the surface of each SP. With the amount of Fe(CO)₅ increased from 0.06 to 0.45 mL, the Fe/Pd ratios of the composites synthesized at 200°C were controlled to be 45:55 to 74:26.

Figure 1A,B shows the typical TEM images of the urchin-like FePd-Fe₃O₄ composite with an overall Fe/Pd ratio at 74:26. In this composite structure, the FePd aggregate has an average size of 60 nm. The HRTEM images (fig. 1C,D) from the central dark part of the single SP reveal that each SP is composed of an aggregate of 6 nm FePd NPs. The interfringe distance of the FePd NP is 0.20 nm, corresponding to (200) interplanar distance (0.192 nm) in the face-centered cubic (fcc) FePd. The Fe₃O₄ grow into 4 nm wide NRs on the FePd SP surface. The amount of Fe(CO)₅ added in the synthesis controlled not only the Fe/Pd ratio but also the morphology of the FePd-Fe₃O₄ composites. By decreasing the amount of Fe(CO)₅ from 0.45 mL to 0.35, 0.15, and 0.06 mL, respectively, urchin-like FePd-Fe₃O₄ composites were still formed, but the Fe₃O₄ NRs became shorter and shorter, as shown in figure S1A–C. The high-resolution TEM (HRTEM) images of a single NR (fig. 1E,F) show that the Fe₃O₄ NR grows directly on a FePd NP. The lattice fringes of the main body of the Fe₃O₄ NRs were measured to be 0.29 nm, which is close to the lattice spacing of the (220) planes (0.296 nm) in the fcc Fe₃O₄ (fig. 1E). These lattice fringes veer away from the growth direction about 45°, indicating the growth in <100> direction, which is further visualized by the parallel fringes close to the FePd-Fe₃O₄ junction area (fig. 1F). The lattice

fringe spacing in the Fe_3O_4 section is 0.22 nm, close to interplane spacing of (400) (0.212 nm) in the fcc Fe_3O_4 , while in the FePd section, it is 0.20 nm, indicating an epitaxial relation between FePd (200) and Fe_3O_4 (400). The syntheses and TEM analyses reveal that, in the current reaction conditions, FePd SPs are formed first and Fe_3O_4 grow on the single FePd NP epitaxially, forming Fe_3O_4 NRs with their length determined by the extra amount of $\text{Fe}(\text{CO})_5$ present in the reaction mixture.

Figure 1. (A and B) TEM images of the urchin-like FePd- Fe_3O_4 composites with an overall Fe/Pd ratio at 74:26. (C) TEM image of the FePd NPs from the central part of the single urchin-like FePd- Fe_3O_4 composite. (D) HRTEM image of a single FePd NP from the central part of the single urchin-like FePd- Fe_3O_4 composite. (E) HRTEM image of a single Fe_3O_4 NR. (F) HRTEM image of the FePd- Fe_3O_4 junction area.

The structure of the urchin-like FePd- Fe_3O_4 composites was further characterized by X-ray diffraction (XRD). Figure 2 shows a series of XRD patterns of the as-synthesized composites with overall Fe/Pd ratios of 74:26, 67:33, 49:51, and 45:55. We can see that both FePd and Fe_3O_4 have the common fcc structure. The relative intensity of the diffraction peaks of Fe_3O_4 increases with increasing Fe concentration, indicating that more Fe_3O_4 NRs are present in the product. The broadened diffraction peaks from FePd NPs indicate small crystal

grain sizes of FePd. As calculated from the (111) peaks by using Scherrer's formula, the average sizes of the FePd NPs vary from ~ 9 to ~ 6 nm with increasing Fe concentration from 45% to 74%, further confirming that the as-synthesized FePd SPs contain the aggregate of the FePd NPs.

Figure 2. XRD patterns of urchin-like FePd-Fe₃O₄ composites with different overall Fe/Pd ratios.

In the synthesis, Fe(CO)₅ was added 10 times more than Pd(acac)₂. When heated, Fe(CO)₅ decomposed to carbon monoxide and Fe, leading to a fast reduction of Pd(acac)₂ to Pd and FePd alloy formation. On the other hand, Fe(CO)₅ could also react with oleic acid, producing hydrogen and Fe-oleate complex that was stable below 200°C.³¹ When 0.45 mL of Fe(CO)₅ was added in the reaction mixture and the heating was controlled at 160°C, only FePd NPs (~ 5.7 nm in crystal sizes) were separated (figs. S2A and S3). When the reaction temperature was raised to 240°C, however, the mixture of FePd and Fe₃O₄ NPs was formed (figs. S2B and S3). Below 200°C, the Fe-oleate complex is stable, and FePd NPs are formed due to the alloying of Fe (from the decomposition of Fe(CO)₅) and Pd (from Fe-induced reduction of Pd salt). At 200°C, the Fe-oleate complex starts to decompose to Fe₃O₄. This decomposition reaction must be very slow, facilitating the direct nucleation and growth of Fe₃O₄ on FePd NPs without separate Fe₃O₄ nucleation/growth. At 240°C, the Fe-oleate complex undergoes relatively fast decomposition, leading to a separate nucleation event and Fe₃O₄ growth. Without OA, the decomposition of Fe(CO)₅ and reduction of Pd(acac)₂ yielded FePd aggregates with FePd in a rod-like morphology (fig. S4).

The urchin-like FePd-Fe₃O₄ composites are ideal precursors for the synthesis of exchange-coupled L1₀-FePd-Fe nanocomposite magnets. The composite with a Fe/Pd ratio of 67:33 was selected for the initial tests and was annealed at different temperatures under Ar + 4% H₂ for 5 h. The corresponding XRD patterns of the powders produced by the annealing are given in figure 3A. When the composite was annealed at 350°C, Fe₃O₄ was reduced to α -Fe, as indicated by the disappearance of Fe₃O₄ and the appearance of the Fe (110) peak in the XRD pattern. Annealed at 450°C, the composite showed the sign of

L1₀-FePd as confirmed by the (200) peak splitting into (200) and (002) peaks. Further increasing the annealing temperature to 500°C led to a more complete phase transformation from chemically disordered fcc-FePd (also called A1-FePd) to chemically ordered L1₀-FePd phase with (110) peak clearly observed in the XRD pattern. However, annealing at even higher temperature at 550°C led to the decrease of the α -Fe (110) peak and increase of the fcc-FePd (200) peak, indicating the diffusion of α -Fe into the L1₀-FePd and reformation of the disordered fcc-FePd. This Fe/Pd randomization temperature (550°C) is lower than that required for the same conversion in the bulk FePd-Fe (605°C) due likely to the nanometer size effect. The average sizes of both FePd and α -Fe were calculated from the FePd (111) and α -Fe (110) peaks in figure 3A using Scherrer's formula. After 350°C annealing, the composite contained 8 nm FePd and 11 nm α -Fe. When the annealing temperature was increased to 500°C, the L1₀-FePd and α -Fe grain sizes reached 24 and 30 nm, respectively.

The optimum annealing condition (500°C for 5 h under Ar + 4% H₂) was also applied to anneal other urchin-like FePd-Fe₃O₄ composites with different Fe/Pd ratios. The corresponding XRD patterns of the annealed samples were given in figure 3B. The samples from the composites of Fe₄₅Pd₅₅ and Fe₄₉Pd₅₁ only gave L1₀-FePd without the sign of α -Fe, while those from the Fe₆₇Pd₃₃ and Fe₇₄Pd₂₆ produced L1₀-FePd and α -Fe phases. The wider angle shift of the diffraction peaks observed from L1₀-Fe₄₅Pd₅₅ is caused by Fe deficiency in the L1₀ structure that should be close to Fe₄₉Pd₅₁. The formation of L1₀-FePd-Fe nanocomposites under the current annealing condition is consistent with what the FePd phase diagram predicts.

Figure 3. (A) XRD patterns of the urchin-like FePd-Fe₃O₄ composites with overall Fe/Pd ratio at 67:33 annealed at 350–550°C. (B) XRD patterns of the FePd-Fe₃O₄ composites with different Fe/Pd ratios annealed at 500°C.

Figure 4A is a typical high-resolution TEM (HRTEM) image of the L1₀-FePd-Fe nanocomposite obtained from the urchin-like FePd-Fe₃O₄ (Fe/Pd = 67:33) annealed at 500°C for 5 h under Ar + 4% H₂. We can see that the annealed sample consists of two different nanoscale domains, one with lattice fringe spacing at 0.27 nm and another at 0.20 nm, corresponding to the (111) planes (interplane spacing of 0.291 nm) in L1₀-FePd and the (110) planes (interplane spacing of 0.201 nm) in α -Fe. The distribution of L1₀-FePd and Fe within

the L1₀-FePd-Fe were analyzed by energy dispersive spectroscopy elemental mappings of Pd and Fe (fig. 4B–D). The color distribution within the map shows two distinct phases with Pd (red) mixing with Fe (green), forming the FePd alloy, and Fe (green) standing out as a separate phase. This indicates that FePd-Fe is indeed formed by reductive annealing of the urchin-like FePd-Fe₃O₄ at 500°C.

Figure 4. (A) HRTEM image of the L1₀-FePd-Fe nanocomposite with nanocrystalline grains of either L1₀-FePd or Fe indicated. (B–D) Elemental mappings of Pd (red)/Fe (green) signals combined (B) and single element Pd (red) (C) and Fe (green) (D).

Magnetic properties of the FePd-Fe nanocomposites were studied by vibrating sample magnetometer (VSM) at room temperature. Figure 5A shows the hysteresis loops of the samples (Fe/Pd ratio of 67:33) annealed at 350 and 450°C. The coercivity of the sample annealed at 350°C is at 0.39 kOe, while that annealed at 450°C has a H_c of 1.16 kOe. The smooth magnetization transition observed from both samples infers that the nanoscale FePd and Fe have effective exchange interactions. Figure 5B summarizes annealing temperature-dependent M_s and H_c of the annealed urchin-like FePd-Fe₃O₄ composites with an overall Fe/Pd ratio at 67:33. Both M_s and H_c of the annealed samples increase with the annealing temperature up to 500°C, due to the increased L1₀-ordering in FePd and the grain growth of α -Fe. However, when the sample is annealed at 550°C, its H_c drops sharply due to the formation of fcc-FePd phase. This is consistent with what is concluded from the XRD studies that the optimum annealing temperature is 500°C and higher temperature annealing results in FePd and Fe diffusion and the formation of fcc-FePd.

Figure 5. (A) Hysteresis loops of the urchin-like FePd-Fe₃O₄ composites with overall Fe/Pd ratio at 67:33 annealed at 350 and 450 °C. (B) Annealing temperature-dependent M_s and H_c of the annealed composite with Fe/Pd = 67:33. (C) Hysteresis loops of the 500 °C annealed composites with Fe/Pd ratios at 45:55 and 67:33. (D) Fe concentration-dependent M_s and H_c for the composites annealed at 500 °C.

Magnetic properties of other urchin-like FePd-Fe₃O₄ composites annealed at 500 °C were also studied. The hysteresis loops of the annealed composites with the Fe/Pd ratios at 45:55 and 67:33 are shown in figure 5C. Both loops show a single phase-like behavior, indicating the effective hard-soft exchange coupling between L1₀-FePd and α -Fe. For the fully ordered L1₀-FePd phases, the domain wall thickness δ_w calculated from $\delta_w = \pi(J/K_U)^{1/2}$, in which $J = 10^6$ erg/cm for the exchange coupling constant and $K_U = 1.0 \times 10^7$ erg/cm³ for the uniaxial anisotropy constant, is about 10 nm.²⁹ This means that the size of the soft phase should be around 20 nm to obtain the effective exchange interaction. However, from both the hysteresis loop and the XRD pattern, we can see that the Fe/Pd 67:33 sample annealed at 500 °C has H_c of 1.4 kOe with the L1₀ ordering parameter only about 0.71. This indicates that the FePd phase is still not fully ordered, and as a result, the uniaxial anisotropy constant should be smaller than 1.0×10^7 erg/cm³. Accordingly, the domain wall thickness may exceed 10 nm, and the critical exchange coupling size of the soft phase should be larger than 20 nm. This is also supported by the fact that the annealed composite containing around 30 nm α -Fe grains (fig. 4B) still shows a single-phase magnetic behavior. Figure 5D summarizes the Fe concentration-dependent M_s and H_c data for the composites annealed at 500 °C. M_s and H_c for the single phase Fe₄₅Pd₅₅ sample are 90 emu/g and 2.6 kOe, respectively. The H_c value of the composite from the Fe/Pd = 74/26 sample decreases to 0.9

kOe, while its M_s increases to 190 emu/g. We can conclude that, in the L1₀-FePd-Fe nanocomposites, L1₀-FePd and Fe are effectively exchange-coupled, and their magnetic properties are tunable by controlling the amount of the Fe phase.

In summary, we have developed a facile one-pot synthesis of urchin-like FePd-Fe₃O₄ composites through controlled thermal decomposition of Fe(CO)₅ and reduction of Pd(acac)₂. The unique feature of the synthesis is the spontaneous self-aggregation of (6–9 nm) FePd NPs into 60 nm SPs followed by the growth of Fe₃O₄ NRs on the surface of SPs. The Fe/Pd ratios are controlled by the amount of Fe(CO)₅ used in the synthesis and the reaction temperature. Once annealed in a reducing atmosphere at high temperatures (up to 500°C), the FePd-Fe₃O₄ composites are converted into L1₀-FePd-Fe exchange-coupled nanocomposite magnets. These magnets show the smooth magnetization transition under an external magnetic field, and their H_c are tunable from 0.8 to 2.6 kOe while their M_s are controlled from 90 to 190 emu/g. The work provides a general approach to L1₀-FePd-Fe with their exchange-coupling strength being optimized for high magnetic performance. The understanding should help to build superstrong nanocomposite magnets for various magnetic applications.

Acknowledgments – This work was supported by the U.S. Department of Energy, Office of Energy Efficiency and Renewable Energy (EERE), under its Vehicle Technologies Program, through the Ames Laboratory. Ames Laboratory is operated by Iowa State University under contract DE-AC02-07CH11358. And research at Nebraska was supported by U.S. DOE/EERE, AROW911NF-09-2-0099 and NCMN-NRI (NSF-DMR-0960110, D.J.S.) for facility use.

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Supporting Information

Materials and Methods

Chemicals and Materials

Oleylamine (OAm, >70%), 1-octadecene (ODE, technical grade, 90%), oleic acid (OA, technical grade, 90%), Pd(acac)₂ (acac = acetylacetonate) (99%), iron pentacarbonyl (Fe(CO)₅, 99.9+% trace metals basis), hexane (98.5%), isopropanol (99.5%), ethanol (100%) were all purchased from Sigma Aldrich. The chemicals and solvents were used as received without purification.

Synthesis of Urchin-like FePd-Fe₃O₄ with Fe/Pd = 45/55

Pd(acac)₂ (0.1 g) and 1.5 ml of OA were added into a 50 ml four-neck flask that contained 8 ml of ODE and 12 ml of OAm under gentle nitrogen (N₂) gas flow. The flask was heated to 90°C at a heating rate of 10°C/min. Under a blanket of nitrogen gas, 0.06 ml Fe(CO)₅ was added. Then the solution was further heated to 200°C at a heating rate of 5°C/min and kept at this temperature for 1 h. The heating source was removed, and the solution was cooled to room temperature, after which the solution was exposed to air. A black product was precipitated by adding 40 ml of ethanol and separating by centrifugation. The dark-yellow supernatant was discarded. The black product was dispersed in 10 mL of hexane and precipitated by adding 40 ml of ethanol and centrifugation.

Characterization

X-ray diffraction (XRD) characterization was carried out on a Bruker AXS D8-Advanced diffractometer with Cu K α radiation ($\lambda = 1.5418 \text{ \AA}$). The inductively coupled plasma-atomic emission spectroscopy (ICP-AES) analyses were carried on a JY2000 Ultrace ICP Atomic Emission Spectrometer equipped with a JY AS 421 autosampler and 2400 g/mm holographic grating. The dried particles were dissolved in warm (~70°C) aqua regia for 30 min to ensure the complete dissolution of metal into the acid. The solution was then diluted with 2% HNO₃ solution to a controlled volume for ICP analysis. Samples for transmission electron microscopy (TEM) analysis were prepared by depositing a single drop of diluted particle dispersion in hexane on amorphous carbon coated copper grids. TEM images were obtained with a Philips CM 20 operating at 200 kV. High-resolution TEM (HRTEM) images were obtained on a FEI Tecnai with an accelerating voltage of 200 kV. Magnetic properties were measured at room temperature by a Lakeshore 7404 high sensitivity vibrating sample magnetometer (VSM) with fields up to 15 kOe.

Figure S1. Typical TEM images of the as-synthesized urchin-like FePd-Fe₃O₄ composites with Fe/Pd ratios at (A) 67/33, (B) 49/51, and (C) 45/55.

Figure S2. TEM images of the FePd SPs synthesized at (A) 160°C and (B) 240°C.

Figure S3. XRD patterns of the FePd-Fe₃O₄ composites synthesized at 160°C and 240°C.

Figure S4. TEM images of the FePd SPs synthesized at (A) 120°C and (B) 200°C in the absence of oleic acid.