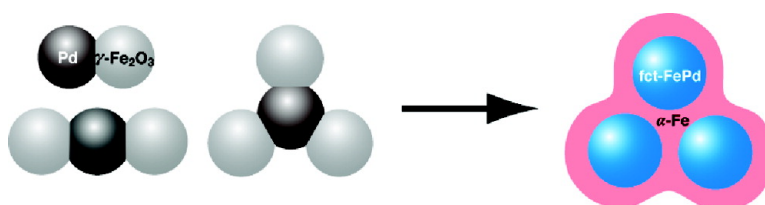


Communication

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Conversion of Anisotropically Phase-Segregated Pd/ γ -Fe₂O₃ Nanoparticles into Exchange-Coupled fct-FePd/ α -Fe Nanocomposite Magnets

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Exchange-coupled nanocomposite magnets consisting of magnetically hard and soft phases are of great importance for advanced permanent magnetic applications due to their large energy product, compared with conventional single-phase magnets.^{1,2} Conventional physical techniques have succeeded in the preparation of exchange-coupled magnets,³ although these techniques are not suitable to control the hard and soft phases at the nanometer scale for efficient exchange coupling. Solid-state reactions of assemblies consisting of two distinct nanoparticles are one approach in solving the above problem,⁴ although the precise control of both phases at the nanometer scale is still a challenging subject. Recently, anisotropically phase-segregated nanoparticles have been accessible and received much attention due to two important features, namely, the simultaneous use of plural functions, such as the luminescent and magnetic properties, and the directed assembly of nanoparticles by anisotropically arranging the different ligands at the surface of these particles.^{5,6} Another important feature of anisotropically phase-segregated nanoparticles is that the atom, ion, and charge transfers can occur at the interface between two inorganic phases. In this communication, we report a new approach for the formation of exchange-coupled face-centered tetragonal (fct)-FePd/ α -Fe nanocomposite magnets via interfacial atom diffusion of anisotropically phase-segregated Pd/ γ -Fe₂O₃ nanoparticles. The fct-FePd nanoparticles were chosen as a magnetically hard phase because the face-centered cubic (fcc)-Pd phase is converted only into fct-FePd phase even in the presence of an excess of Fe.

Monodisperse trioctylphosphine-protected Pd (TOP-Pd) nanoparticles, 4.9 ± 0.3 nm in size, were synthesized according to Hyeon et al.^{7,8} The HRTEM (Figure 1b) and XRD analyses revealed that these Pd nanoparticles are polycrystalline. The anisotropically phase-segregated Pd/ γ -Fe₂O₃ nanoparticles were synthesized by Pd-seed-mediated synthesis. The 4.9 nm TOP-Pd nanoparticles (Pd = 0.17 mmol) were dissolved in 1-octanol (20 mL), to which Fe(acac)₃ (0.43 mmol), oleylamine (6.8 mmol), and oleic acid (6.8 mmol) were added. After stirring the N₂-bubbled solution at 180 °C for 1 h, the heat source was removed to allow the black solution to cool to room temperature. The resulting nanoparticles were purified with 1-hexane/ethanol (1/2, v/v) mixed solvent.

Figure 1a shows the TEM image of the resulting nanoparticles. The nanoparticles made up of dark Pd phases with 1–3 bright phases anisotropically grown at every single Pd nanoparticle surface were predominantly observed, where the size of the Pd nanoparticles is preserved. It was clarified from the HRTEM (Figure 1b), XRD (Figure 2d), and XPS⁸ analyses that the bright phases were composed of γ -Fe₂O₃. The interfacial lattice planes of two distinct phases could be the combination of those with smallest lattice

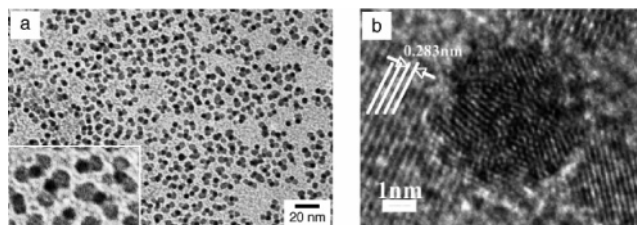


Figure 1. (a) TEM image and (b) HRTEM image of anisotropically phase-segregated Pd/ γ -Fe₂O₃ nanoparticles (inset in (a) is a magnified image).

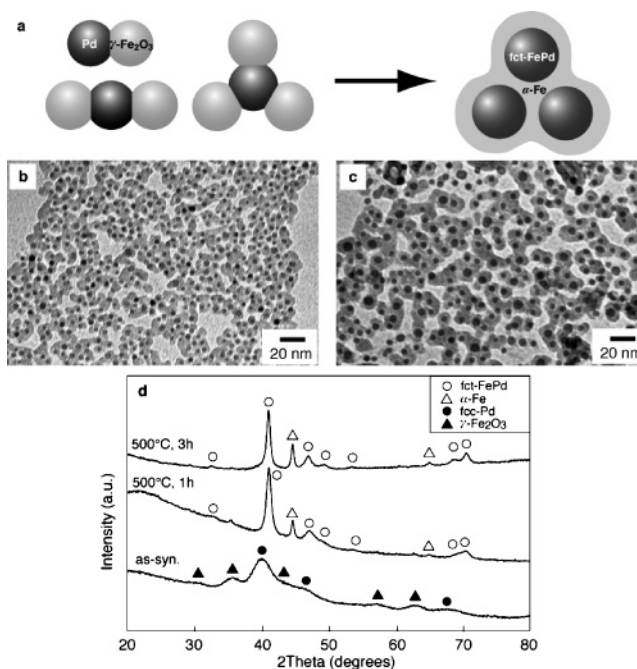


Figure 2. (a) Schematic illustration of the conversion of Pd/ γ -Fe₂O₃ nanoparticles into exchange-coupled fct-FePd/ α -Fe nanocomposite magnets via the interfacial atom diffusion. (b, c) TEM images of Pd/ γ -Fe₂O₃ nanoparticles after annealing under Ar + 4% H₂ at 500 °C for (b) 1 h and (c) 3 h. (d) XRD patterns of as-synthesized and annealed nanoparticles.

mismatch, but this remains unclear at present. The Fe/Pd molar ratio was estimated to be 73/27 from X-ray fluorescence analysis,⁸ which is roughly consistent with that for the feeding precursors. This Fe/Pd molar ratio is large enough to convert the Pd/ γ -Fe₂O₃ nanoparticles into fct-FePd/ α -Fe nanocomposite magnets. In addition, the Pd nanoparticles protected by other ligands such as poly(*N*-vinyl-2-pyrrolidone) (PVP-Pd)⁹ are also candidates to form anisotropically phase-segregated Pd/ γ -Fe₂O₃ nanoparticles.⁸

To convert the Pd/ γ -Fe₂O₃ nanoparticles into exchange-coupled fct-FePd/ α -Fe nanocomposite magnets, the Pd/ γ -Fe₂O₃ nanopar-

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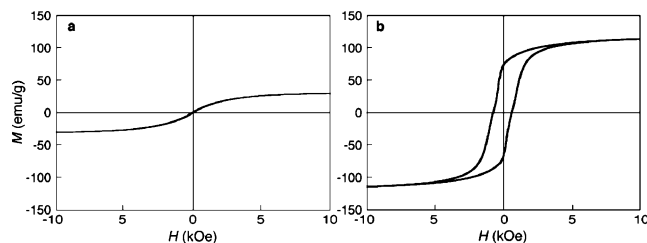


Figure 3. Magnetization curves of Pd/ γ -Fe₂O₃ nanoparticles (a) before and (b) after annealing under a flow of Ar + 4% H₂ at 500 °C for 3 h. The measurement was conducted at room temperature with a maximum application field of 10 kOe.

ticles were annealed under a flow of Ar + 4% H₂ at 500 °C, as illustrated in Figure 2a. Figure 2b and c shows the TEM images of the resulting nanoparticles annealed for 1 and 3 h, respectively. After annealing for 3 h, anisotropically phase-segregated nanoparticles were not observed, and the dark phases were incorporated in the bright phase matrix. It was revealed from the XRD (Figure 2d) and HRTEM⁸ analyses that the γ -Fe₂O₃ phases were completely converted into body-centered cubic (bcc) α -Fe, while the fcc-Pd converted into fct-FePd, which has XRD peaks at 33.0, 41.1, 47.2, 48.8, 53.6, 68.9, and 70.3° corresponding to (110), (111), (200), (002), (201), (220), and (202) lattices, respectively. The long-range-order parameter of fct-FePd of the sample annealed for 3 h was estimated to be 0.25 from the XRD result. It should be noted that the size of the fct-FePd phases (4.9 ± 0.4 nm) is quite similar to that of the fcc-Pd phases. Longer annealing time contributed to an increase in the ordering degree of fct structure of FePd phases together with a slight expansion of the phase volume (6.0 ± 1.0 nm). These results lead us to the following conclusion. First the annealing of the Pd/ γ -Fe₂O₃ nanoparticles under Ar + 4% H₂ reduces the γ -Fe₂O₃ to bcc α -Fe, which is followed by coalescence to form the α -Fe matrix due to the desorption of the organic ligands around each particle. At the same time, interdiffusion between α -Fe and Pd creates the fct-FePd phases in the rich Fe condition, following the phase diagram of FePd alloy, as observed in the Pt/ γ -Fe₂O₃ system.¹⁰ The fct-FePd phases do not grow significantly because they are incorporated into the α -Fe matrix. Finally, magnetically hard fct-FePd phases surrounded by magnetically soft α -Fe phases are obtained. The higher annealing temperature cannot preserve such nanostructures by the severe sintering.

It was then investigated how the interfaces between the Pd and γ -Fe₂O₃ phases in the Pd/ γ -Fe₂O₃ nanoparticles are important in the formation of nanocomposite magnets with the controlled structure at the nanometer scale. For this purpose, 3.6 ± 0.4 nm Fe₃O₄ nanoparticles, which would work as the γ -Fe₂O₃ nanoparticles do under reduced atmosphere, were synthesized by the reaction of Fe(acac)₃ (0.5 mmol) with 1-decanol (10 mL) in the presence of oleylamine (0.5 mL) and oleic acid (0.5 mL) at 220 °C for 2 h.⁸ The mixture of 3.6 nm Fe₃O₄ nanoparticles and 4.9 nm Pd nanoparticles (Fe/Pd = 84/16 (mol/mol)) formed a hexagonal lattice, where two kinds of nanoparticles randomly occupied the site.⁸ When this hexagonal lattice was annealed under Ar + 4% H₂ at 500 °C for 1 h, quite polydisperse nanoparticles having bcc α -Fe and fct-FePd phases were formed.⁸ This result strongly demonstrates the nanoscale interfaces of the Pd/ γ -Fe₂O₃ nanoparticles play an important role in forming nanocomposite magnets with the controlled structure at the nanometer scale.

To ensure efficient exchange coupling between the soft and hard phases, the magnetic property was measured for the fct-FePd/ α -Fe nanocomposites made by the conversion of Pd/ γ -Fe₂O₃ nanoparticles at 500 °C for 3 h using Vibrating Sample Magnetometer

(VSM). Figure 3 shows the magnetization curves of the Pd/ γ -Fe₂O₃ before and after annealing. The saturation magnetization (M_s), remanent magnetization (M_r), and coercivity (H_c) for the annealed specimen were 114 emu·g⁻¹, 73.4 emu·g⁻¹, and 755 Oe, respectively. Considering these values contain carbon contamination (>5 wt %), the M_s value is between those for α -Fe (217 emu·g⁻¹) and fct-FePd (111 emu·g⁻¹), and the H_c value is smaller than that for bulk fct-FePd. This could be mainly due to the low long-range-order parameter of FePd, unoptimized soft/hard volume ratio (58/42), and particle size because the dimension of the soft phase should be smaller than twice the domain wall width of the hard phase for effective exchange coupling to occur within a two-phase magnet.^{1,2} However, the characteristic magnetization process like that of a single-phase hard magnet indicates the existence of an effective exchange coupling between the hard and soft phases in the present specimen. The fabrication of bulk fct-FePd/ α -Fe nanocomposite magnets with optimized long-range-order parameter, soft/hard ratio, optimized particle size, and aligned easy axis of hard phase is now in progress.

In conclusion, a novel approach has been described for the fabrication of exchanged-coupled fct-FePd/ α -Fe nanocomposite magnets by converting anisotropically phase-segregated Pd/ γ -Fe₂O₃ nanoparticles via interfacial atom diffusion. By controlling the volume ratio, nanoscale dimension, and spatial distribution of the hard and soft phases, a further enhanced energy product can be obtained. Our approach has great potential not only for the fabrication of high-performance exchange-coupled magnets but also for the creation of novel advanced materials from various phase-segregated nanoparticles.

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Supporting Information Available: Synthetic procedure and TEM image of TOP-Pd nanoparticles, XPS data for Pd/ γ -Fe₂O₃ nanoparticles, original XRF data, Pd/ γ -Fe₂O₃ nanoparticles obtained from 7.1 ± 0.9 nm PVP-Pd nanoparticles, HRTEM, FFT, and inverse FFT images of fct-FePd/ α -Fe nanocomposite magnets, and TEM images of the mixture of 4.9 ± 0.3 nm Pd and 3.6 ± 0.4 nm Fe₃O₄ nanoparticles before and after annealing. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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