Supporting Information for

Formation of Strong *L*1₀-FePd/α-Fe Nanocomposite Magnets by

Visualizing Efficient Exchange Coupling

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Fig. S1 Characterization of Pd NCs and XRD patterns of Pd@FeO_x NCs. (a–d) TEM images of the Pd NCs with edge lengths of (a) $15.4(\pm 1.4) \times 13.4(\pm 1.1)$ nm, (b) $20.1(\pm 1.8) \times 17.9(\pm 1.5)$ nm, (c) $24.0(\pm 1.9) \times 21.6(\pm 1.9)$ nm and (d) $27.7(\pm 2.8) \times 24.7(\pm 2.3)$ nm. (e) XRD patterns of the Pd NCs. (f) Comparison between crystalline sizes calculated from the Scherrer equation and the grain sizes observed in the TEM images. The crystalline sizes were calculated from the 200 diffraction peaks by using the Scherrer constant (*K* = 1). These results show that the Pd NCs synthesized by the seeded-growth method were

single crystals. (g) XRD patterns of the $Pd@FeO_x$ NCs with different Fe/Pd compositions. Diffraction peaks assigned to Fe oxide phases did not appear, meaning that the FeO_x shells on the Pd NCs were amorphous.





Fig. S2 Characterization of the $L1_0$ -Fe Pd/ α -Fe NCMs (19 nm-Pd NCs_Fe/Pd = 66/34 at.%) formed by reductive annealing at 540 °C for various times (5, 10, 15, 20 and 25 h). (a) TEM images of the $L1_0$ -FePd/ α -Fe NCMs. (b) XRD patterns of the $L1_0$ -FePd/ α -Fe NCMs. Diffraction peaks assigned to the $L1_0$ -FePd and the α -Fe phases appeared. (c) The tetragonality (*c*/*a*) of the $L1_0$ -FePd phase grains calculated from (b). The crystalline sizes of the α -Fe phase were calculated to be 35.9 nm by the Scherrer equation (K = 0.94) for the 110 diffraction peak. This result means that the partial coalescence of α -Fe phase grains occurred because the crystalline size was larger than expected (Table S1). (d) The change in crystalline size of the $L1_0$ -FePd phase grains with annealing time, estimated by the Scherrer equation (K = 1) from the 001 diffraction peaks. The increase in crystalline size and the partial fusion of particles.



Fig. S3 HRTEM images of L_{10} -FePd/ α -Fe NCMs coated by carbon shells. (a–d) HRTEM images of L_{10} -FePd/ α -Fe NCMs synthesized under various conditions as follows: (a,b) 19-nm Pd NCs_Fe/Pd = 61/39 at.%_570 °C, 10 h; (c) 19-nm Pd NCs_Fe/Pd = 66/34 at.%_560 °C, 3 h; (d) 23-nm Pd NCs_Fe/Pd = 65/35 at.%_550 °C, 3 h. These images show the carbon shells on the NCMs, formed from the protected ligands, such as OAm and OA, by Fe catalysis²⁰. These shells suppressed the coalescence of NCs during reductive annealing.



Fig. S4 Change in spatial distributions of Fe phase grains on Pd NCs during reductive annealing of Pd@FeO_x NCs (26-nm Pd NCs_Fe/Pd = 63/37 at.%). In order to observe the change of phase-segregation structure during the reductive-annealing process, four samples were quenched at 450, 500 and 540 °C and after annealing at 540 °C for 1 h, and two samples were slowly cooled after annealing at 540 °C for 5 and 25 h. These elemental mappings (purple: Fe-K, yellow: Pd-L) obviously showed that the Fe shells homogeneously covered the Pd NCs or the FePd alloys up to 540 °C. In addition, the fraction of the core/shell-like structure in the sample quenched after annealing at 540 °C

for 1 h was larger than those in the samples annealed at 540 °C for 5 and 25 h, indicating that the longer annealing time resulted in the decrease of the amount of core/shell-like structure. These images indicate that the reductive annealing process transforms the core/shell-like structure into the Janus-like structure.



Reductive annealing Ar+4% H₂





 $\begin{array}{c} \text{Reductive annealing} \\ \text{Ar+4\% } H_2 \end{array}$



50 nm

Fig. S5 TEM images before reductive annealing of the $Pd@FeO_x$ NCs and EDS elemental maps before and after annealing. These NCMs were synthesized under optimum conditions, producing a maximum H_c (Table S4). The morphology did not significantly change before and after optimized reductive annealing, though the particles did partially coalesce.



Fig. S6 XRD patterns of various NCMs, and the crystalline sizes and ordering parameters (*S*) of the NCMs with the highest H_c values. (a) XRD patterns of various NCMs. The $L1_0$ -FePd phase appeared in all XRD patterns and the α -Fe phase appeared in samples with Fe/Pd molar ratios of >65/35 at.%. Moreover, fcc-FePd phase appeared in some NCMs, because the transition temperature from $L1_0$ to fcc phases changed with the Fe/Pd composition and the grain size of the $L1_0$ -FePd phase 19,S1 . (b) Observed crystalline sizes of the $L1_0$ -FePd phase, calculated from the Scherrer equation (K = 1) using the 001 diffraction peaks, compared with the theoretical crystalline size (Table S1). These results show that the NCMs formed from 14-nm NCs with Fe/Pd = 61/39 at.% were easy to coalesce and that the $L1_0$ -FePd phase grains were single crystals (Fig. 1a). The *S* values were almost the same among all NCMs.



Fig. S7 L_{10} -FePd crystalline-size-dependent H_c values and the H_c distributions obtained from first-order reversal curves (FORCs) diagrams of NCMs. (a) The H_c and H_c/H_a values of the NCMs formed by optimum reductive annealing (Table S4), as indicated in Fig. S5, where the crystalline sizes of L_{10} -FePd were estimated from Pd crystalline sizes. In both Fe/Pd compositions, the NCMs formed from 19-nm Pd NCs showed the highest H_c . The H_c/H_a value showed almost the same tendency as the H_c value. The external magnetic field was 90 kOe. (b) H_c distributions estimated from the sum of the fractions of hysteron with the same H_c values in the FORCs diagram by using a Gaussian function. The fraction of Janus-like structure increased in the NCMs (23-nm Pd NCs_Fe/Pd = 65/35 at.%; 26-nm Pd NCs_Fe/Pd = 62/38 at.%), because the grain sizes of the α -Fe phase were larger than in other cases (Table S1).



Fig. S8. Change of surface anisotropy constants (*K*_s) and effective micromagnetics constant (*α*) of various NCMs (19-nm Pd NCs, Fe/(Fe+FePd) = 5.20, 19.3, 28.5, 41.9 and 45.8 volume % (vol.%), which corresponds to Fe/Pd = 53/47, 61/39, 66/34, 73/27 and 75/25 at.%, respectively). The *K*_s values can be estimated by using the H_{aexp} (= $2K_{eff}/J_s$) values (Table S3) and the equation $K_{eff} = K_{bulk}+K_s/(6 \cdot D)$, where K_{eff} , K_{bulk} and K_s are the effective, bulk and surface anisotropy constants, respectively, and *D* is the grain size of the NCM^{S2}. The volume fractions of NCMs are calculated from the Fe/Pd molar ratios of the NCMs. We used the K_u (1.8 MJ/m³) of the $L1_0$ -FePd phase as K_{bulk} without that of the α-Fe phase, because the out-of-plane surface anisotropy energy comes from the α-Fe phase^{S3}. Thus, the K_s of the $L1_0$ -FePd/α-Fe phases increased under the existence of the 'efficient' exchange coupling. Intriguingly, the trade-off between the formation of 'efficient' and 'inefficient' exchange coupling of the $L1_0$ -FePd/α-Fe phases made the H_c/H_a and (*BH*)_{max} highest at Fe/Pd = 66/34 at.%, which agreed with the result of FORCs analysis.



Fig. S9 Information obtained from FORCs analysis. (a) Usually, a hysteresis curve gives only average values, although in FORCs analysis, introducing the hysteron, a minimum unit with certain local interaction field (H_u) and H_c values, allows us to discuss the magnetization reversal in terms of the number of hysterons. Thus, the distributions of H_c and H_u are represented by determining the H_c and H_u of hysterons (Fig. 2e). (b) These curves are FORCs of the NCMs synthesized by reductive annealing of $Pd@FeO_x$ NCs (formed from 19-nm Pd NCs) with Fe/Pd = 66/34 at.% at 560 °C for 3 h. These FORCs measurements were performed by the repeat of three steps as follows: (1) the magnetization by magnetic field (5 T); (2) the decrease of magnetic field from 5 T to H_A ; (3) the increase of magnetic field from H_A to 2 T, where each magnetic field in the step was H_B (see experimental section). In each curve, the change in magnetization corresponds to a hysteron with some H_{Ai} switching from -1 to 1. (c) This diagram is obtained by using equation (5) for (b) in the range of $H_B \ge H_A$. The height of a contour line means the number of switches of hysteron from 'down' to 'up'. Thus, from the diagram, we can estimate the fraction of hysterons under different magnetic circumstances such as Janus- and core/shelllike structures (Fig. 2f, g). (d) To simply discuss the contour line of (c), we plotted height of the FORCs diagram ($\rho(H_c, H_u)$) as a function of H_u in the white square region with black dots. Then, the experimental data was fitted by multiple Gaussian functions using kernel

density estimation (bandwidth w = 1)^{S4} with a brown dashed line. The blue and green curves are Gaussian functions, and the red curve is the sum of the blue and green curves. The gray curve is the discrepancy between the brown and red curves. When the gray curve is close to zero, the component number of the H_c distribution is determined. In this case, two types of NCMs exist.



Fig. S10 Determination of α values and effective demagnetization factors (N_{eff}). (a) *J*–*H* curve measured by VSM at 300 K. The inset shows a fit of the *J*–*H* curve using equation (4), from which J_s and H_{aexp} at 300 K were determined. (b) J_s and H_{aexp} obtained at 100, 150, 200, 250 and 300 K. (c) α and N_{eff} determined from J_s and H_{aexp} , according to the micromagnetics model represented by equation (1). This sample was synthesized by 5 h of reductive annealing of Pd@FeO_x NCs with Fe/Pd = 66/34 at.% formed from 19-nm Pd NCs. We conducted the same analysis on all NCMs.

Table S1 Evaluated grain sizes of L_{10} -FePd and α -Fe phases. The L_{10} -FePd/ α -Fe NCMs were synthesized by the diffusion of Fe atoms into the Pd NCs during reductive annealing. The Fe thickness and grain size were estimated by assuming that the α -Fe phase homogeneously covered the L_{10} -FePd phase and was isolated from the L_{10} -FePd phase.

Grain size of Pd NCs (nm)		14	19	23	26
Grain size of <i>L</i> 1 ₀ -FePd phase (nm)		17	23	28	33
Fe/Pd ≈ 62/38 at.%	Fe thickness (nm)	0.66	0.87	1.2	1.3
	Fe grain size (nm)	11	15	18	21
Fe/Pd ≈ 66/34 at.%	Fe thickness (nm)	1.0	1.4	1.5	
	Fe grain size (nm)	13	17	20	

Pd grain size (nm)	Fe(CO)₅ <i>x</i> mmol	Fe/Pd at.%
26	13.3	62/38
23	10.4	65/35
23	13.3	62/38
19	14.8	75/25
19	12.8	73/27
19	11.8	66/34
19	10.4	61/39
19	7.4	53/47
14	12.6	66/34
14	11.8	61/39

Table S2 Synthesis conditions and composition of $Pd@FeO_x$ NCs. The composition of $Pd@FeO_x$ NCs was controlled by tuning the amount of $Fe(CO)_5$. The Fe/Pd molar ratios of the $Pd@FeO_x$ NCs were measured by XRF.

Table S3 K_s and α values of the NCMs with different compositions formed from 19-nm Pd NCs. The J_s , H_{aexp} and α values could be determined from the temperature-dependent magnetic properties (Fig. S10). K_s is found with the following equation^{S2}:

$$K_{\rm eff} = K_{\rm bulk} + K_{\rm s}/(6 \cdot D),$$

where K_{eff} is the effective anisotropy constant calculated from $K_{\text{eff}} = J_s \cdot H_{\text{aexp}}/2$, K_{bulk} is the uniaxial anisotropy constant (K_u) of the $L1_0$ -FePd phase and D is the grain size of the NCMs.

Fe/(Fe+FePd) vol.%	5.20	19.3	28.5	41.9	45.8
J _s (T)	1.11	1.24	1.31	1.43	1.51
H _{aexp} (T)	2.26	3.19	3.11	2.52	2.41
<i>K</i> _{eff} (MJ/m ³)	0.998	1.57	1.62	1.43	1.45
<i>K</i> _{bulk} (MJ/m ³)	1.8	1.8	1.8	1.8	1.8
<i>K</i> s/6 <i>D</i> (MJ/m ³)	-0.802	-0.23	-0.18	-0.37	-0.35
<i>K</i> s (mJ/m²)	-115	-34.2	-28.2	-61.7	-60.7
A	0.427	0.406	0.382	0.305	0.197

Table S4 Dependence of H_c on the reductive annealing conditions of Pd@FeO_x NCs. Reductive annealing was done at several temperatures for 3 or 10 h. The optimum annealing conditions depended on the kind of Pd@FeO_x NCs. The bold values show the highest values among our experiments. The applied H was 20 kOe.

Pd size	14 nm		23 nm		26 nm
Fe/Pd at.%	61/39	66/34	62/38	65/35	62/38
530°C, 3 h		4.07 kOe			
540°C, 3 h	4.39 kOe	4.12 kOe		4.30 kOe	
550°C, 3 h	4.47 kOe	3.87 kOe		4.39 kOe	
560°C, 3 h	4.46 kOe		5.31 kOe	4.31 kOe	
570°C, 3 h			5.52 kOe		3.68 kOe
580°C, 3 h			5.43 kOe		
550°C, 10 h	4.57 kOe			4.04 kOe	3.36 kOe
560°C, 10 h					3.37 kOe
570°C, 10 h			5.56 kOe		3.23 kOe
590°C, 10 h					2.85 kOe
Pd size	19 nm				
Fe/Pd at.%	53/47	61/39	66/34	73/27	75/25
530°C, 3 h				2.66 kOe	2.23 kOe
540°C, 3 h			4.96 kOe	2.76 kOe	2.32 kOe
550°C, 3 h	3.13 kOe		5.17 kOe	2.44 kOe	2.15 kOe
560°C, 3 h		5.29 kOe	5.28 kOe		
570°C, 3 h	3.22 kOe	5.52 kOe	5.10 kOe		
580°C, 3 h		5.49 kOe			
590°C, 3 h	3.34 kOe				
610°C, 3 h	3.25 kOe				
560°C, 10 h			4.95 kOe		
570°C, 10 h		5.55 kOe			
590°C, 10 h	3.21 kOe				

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