Interplay between core and shell in a RbCoFe@RbNiCo Prussian blue analogue spin transition heterostructure

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Calculation of percentages of non-transitioning HS Co^{II}-NC-Fe^{III} pairs at 150 K

At 300 K, the RbCoFe-PBA core is at a ferrimagnetic HS state which then transfers to a diamagnetic LS state upon cooling. Because the thermal CTIST process is completed before 150 K, the spins from the core at 150 K can be attributed to the residual non-transitioning HS Co^{II}-NC-Fe^{III} pairs. Therefore, the percentages of non-transitioning HS Co^{II}-NC-Fe^{III} pairs at 150 K can be calculated by equation 1:

$$HS\,\% = \frac{\chi_M T_{core,150\,K}}{\chi_M T_{core,300\,K}} \times 100\,\% \quad (1)$$

Since the $\chi_M T_{core@shell}$ is normalized to moles of core, the calculation of $\chi_M T_{core}$ is based on the equation 2:

$$\chi_M T_{core} = \chi_M T_{core@shell} - \frac{n_{shell}}{n_{core@shell}} \times \chi_M T_{shell} \quad (2)$$

In addition, due to the hexacyanoferrate vacancies in RbCoFe-PBA, the formula of the core is $Rb_{0.28}Co^{II}_{0.24}Co^{III}_{0.76}[Fe(CN)_6]_{0.76}$ at 150 K when all the HS Co^{II}-NC-Fe^{III} pairs have transitioned to LS Co^{III}-NC-Fe^{II}. This means there is a portion of HS Co^{II} centers remain at 150 K which is not considered as the non-transitioning HS Co^{II}-NC-Fe^{III} pairs. As a result, the $\chi_M T_{CoII}$ should be eliminated from $\chi_M T_{core,\,150K}$. Here the $\chi_M T_{CoII}$ value is calculated by equation 3:

$$\chi_M T_{Co^{II}} = \frac{1}{8} g^2 S(S+1) \quad (3)$$

where g of HS Co^{II} is 2.3 with a spin number of 3/2.[1]

Low temperature magnetization

The incomplete HS to LS transition during the CTIST process in CoFe-PBA has been observed commonly in other works.[2-4] It usually shows magnetic ordering below 20 K.[2] But the field-cooled dark state data of the core-shells shows the transition is not even completed at 5 K (Fig. S2), suggesting the magnetic correlation length of the HS Co^{II}-NC-Fe^{III} pairs is limited.

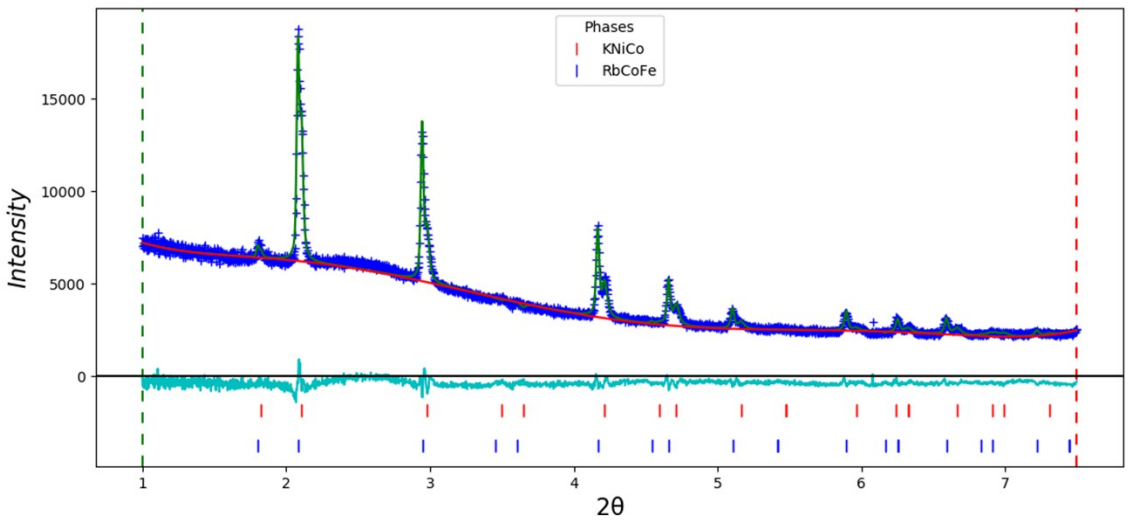

Fig. S1. Pawley refinement of RbCoFe@KNiCo-20 nm.

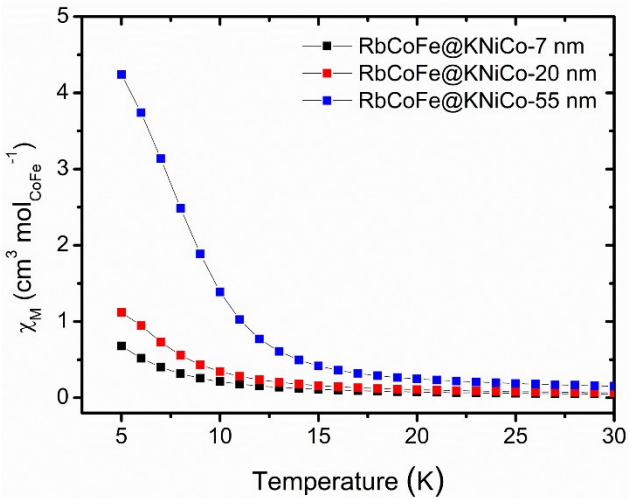

Fig. S2. χ_M vs T plot of the core-shell heterostructures below 30 K.

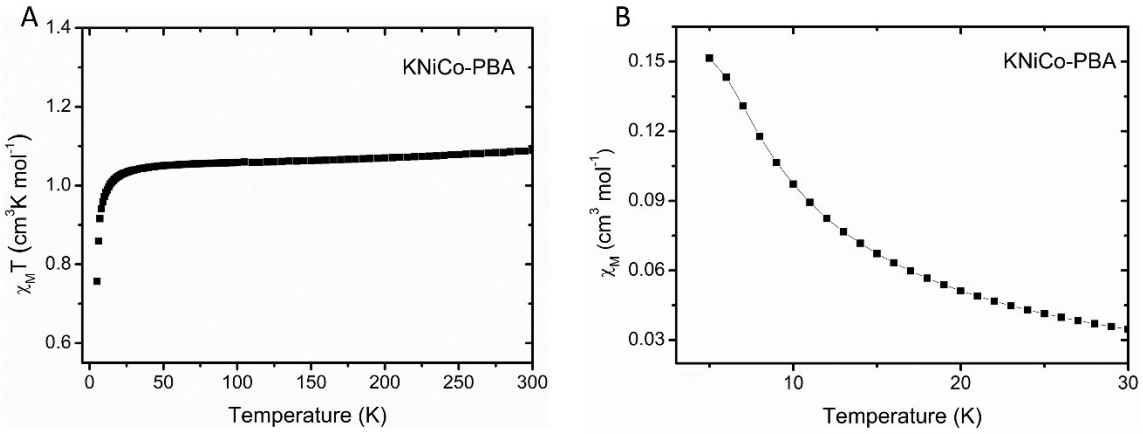

Fig. S3. Magnetism of KNiCo-PBA. (A) $\chi_M T$ vs T plots under a field of 100 G. (B) χ_M vs T plot below 30 K.

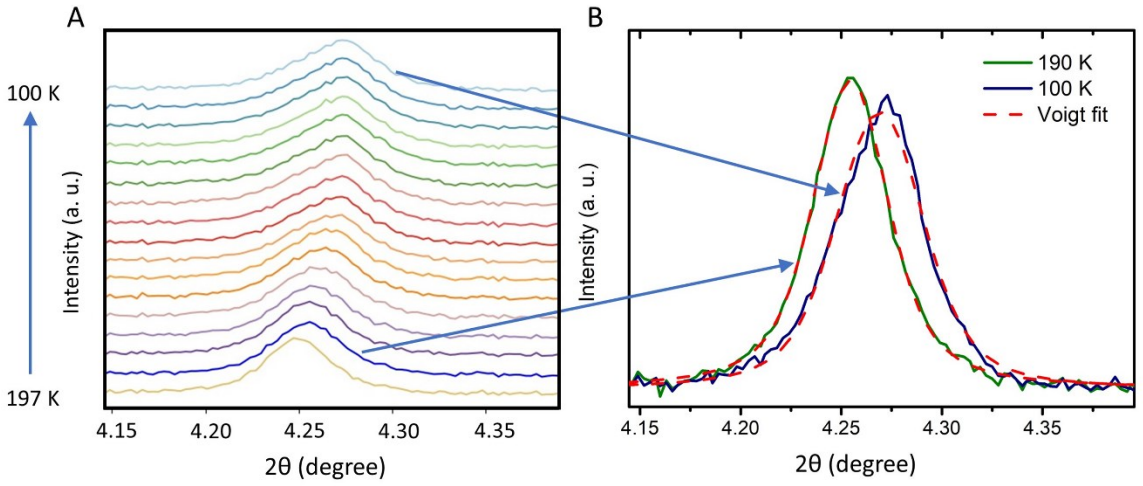

Fig. S4. (A) Stack of PXRD patterns showing the evolution of the 400 reflection of RbCoFe@KNiCo-20 nm upon cooling from 197 K-100 K. Magnetism of KNiCo-PBA. (B) Zoom in view of 400 reflection in RbCoFe@KNiCo-20 nm at 190K and 100K. The peaks were fitted with Voigt formula which are showed as red dash lines. The peak at 100K does not overlap the symettric Voigt fitting curve while the one at 190K overlap with the fitting curve completely.

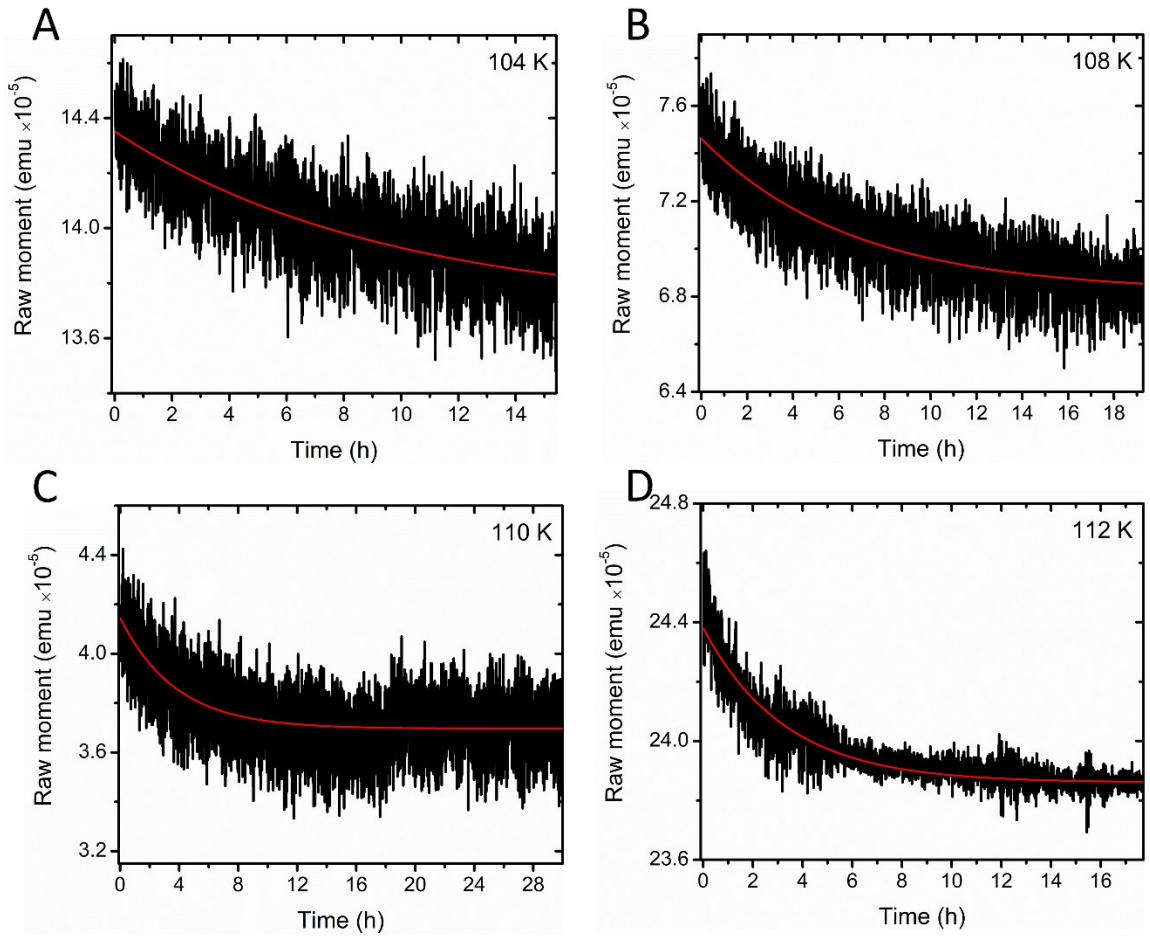

Fig. S5. Magnetization vs time monitoring the isothermal relaxation from the metastable HS state of RbCoFe@KNiCo-20 nm at 4 different temperatures: (A) 104 K, (B) 108 K, (C) 110 K, and (D) 112 K.

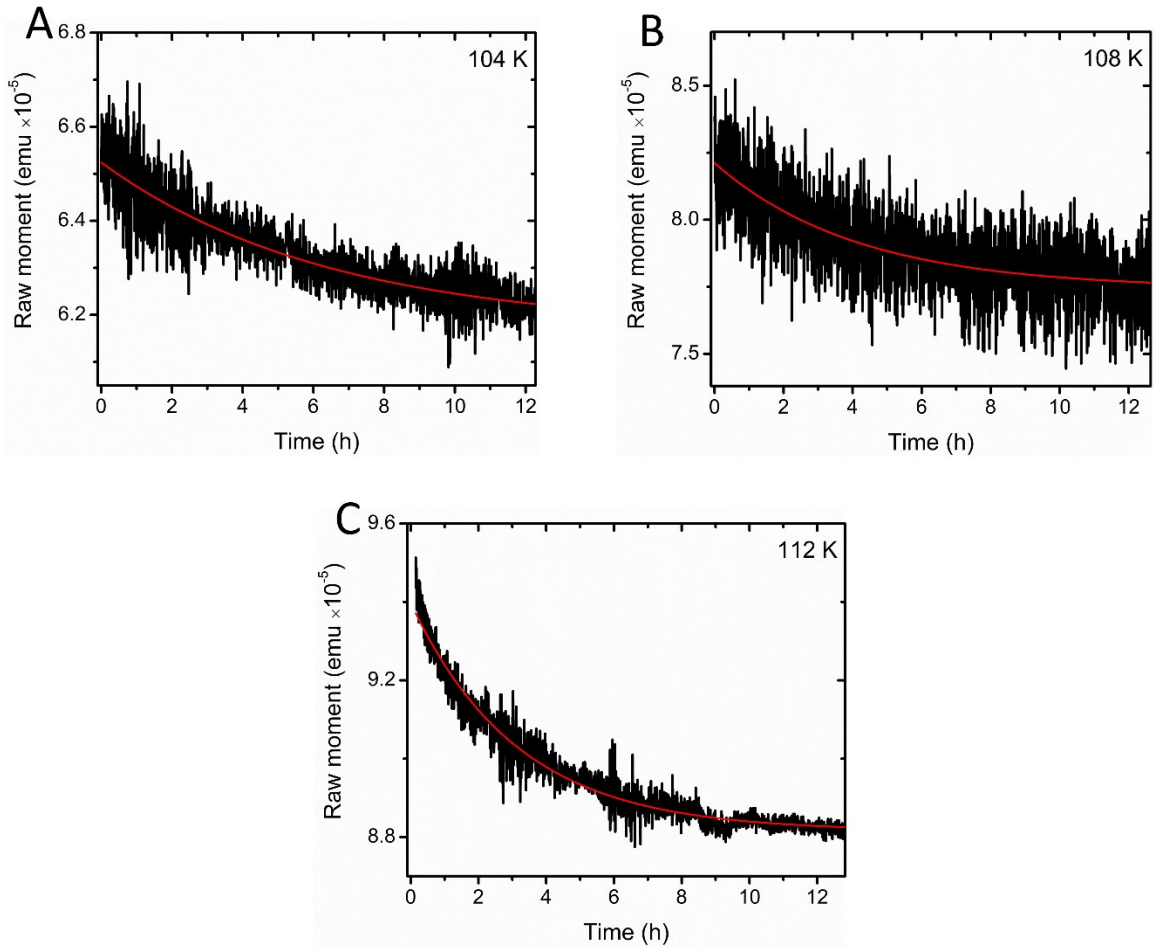

Fig. S6. Magnetization vs time monitoring the isothermal relaxation from the metastable HS state of RbCoFe@KNiCo-55 nm at 3 different temperatures: (A) 104 K, (B) 108 K, and (C) 112 K.

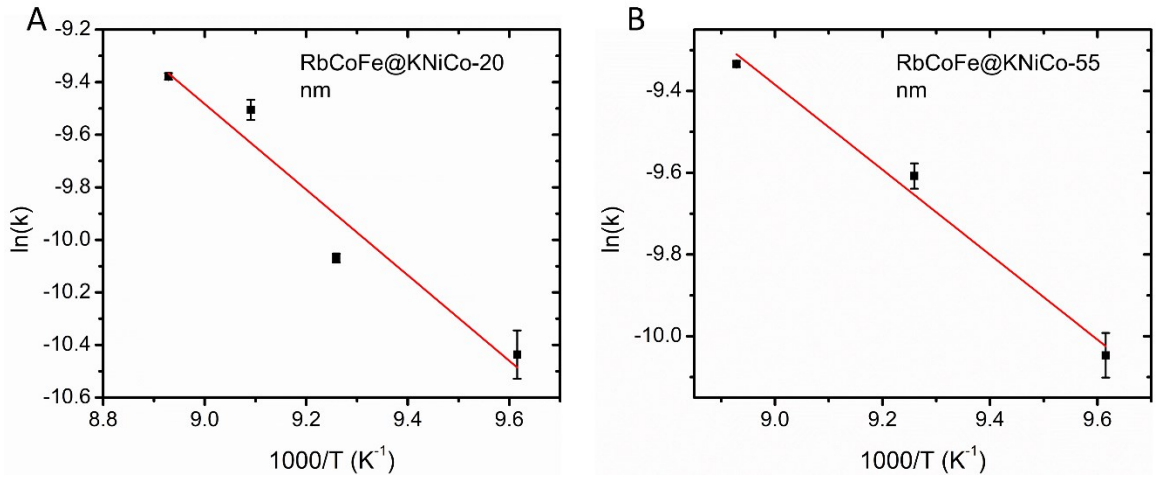

Fig. S7. Arrhenius plots of (A) RbCoFe@KNiCo-20 nm and (B) RbCoFe@KNiCo-55 nm.

Table S1 Magnetization data for RbCoFe@KNiCo core-shell heterostractures.

	$\chi_M T$ at 300K /cm^3 mol^{-1}K	$\chi_M T$ at 150K /cm^3 mol^{-1}K	$\Delta\chi_M T$ /cm^3 mol^{-1}K	Non-transitioning HS pairs %
RbCoFe@KNiCo-7 nm	3.9±0.3	1.6±0.1	2.3±0.4	19±6
RbCoFe@KNiCo-20 nm	4.1±0.3	2.1±0.1	2.0±0.4	23±7
RbCoFe@KNiCo-55 nm	6.3±0.3	4.6±0.2	1.7±0.5	40±10

Table S2 Isothermal relaxation data for RbCoFe@KNiCo core-shell heterostractures.

	$1/\tau_0$, 104 K (s^{-1})	$1/\tau_0$, 108 K (s^{-1})	$1/\tau_0$, 110 K (s^{-1})	$1/\tau_0$, 112 K (s^{-1})	E_{act} (kJ mol^{-1})
RbCoFe@KNiCo-20 nm	2.9×10^{-5}	4.2×10^{-5}	7.4×10^{-5}	8.5×10^{-5}	13.5±2.4
RbCoFe@KNiCo-55 nm	4.3×10^{-5}	6.7×10^{-5}	-	8.8×10^{-5}	8.6±1.0

References

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2. A. C. Felts, M. J. Andrus, E. S. Knowles, P. A. Quintero, A. R. Ahir, O. N. Risset, C. H. Li, I. Maurin, G. J. Halder, K. A. Abboud, M. W. Meisel and D. R. Talham, *J. Phys. Chem. C*, 2016, **120**, 5420-5429.
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