

Communication

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Room Temperature Blocked Magnetic Nanoparticles based on Ferrite Promoted by a Three-Step Thermal Decomposition Process

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Supporting Information

ABSTRACT: Exchange coupled nanoparticles that combine hard and soft magnetic phases are very promising to enhance the effective magnetic anisotropy while preserving sizes below 20 nm. However, the core-shell structure is usually insufficient to produce rare earth-free ferro(i)magnetic blocked nanoparticles at room temperature. We report on onion-type magnetic nanoparticles prepared by a three-step seed mediated growth based on the thermal decomposition method. The core@shell@shell structure consists of a core and an external shell of $Fe_{3-\delta}O_4$ separated by an intermediate Codoped Ferrite shell. The double exchange coupling at both core@shell and shell@shell interfaces results in such an increased magnetic anisotropy, that onion-type nanoparticles of 16 nm mainly based on iron oxide are blocked at room temperature. We envision that these results are very appealing for potential applications based on permanent magnets.

Hard-soft coupled magnetic nanoparticles have gained a tremendous amount of interest during the last decade for short-term development of advanced applications related to spintronics (magnetoresistive sensors, magnetic recording ...).¹ Indeed, they are a potential alternative to produce permanent magnets.² in order to circumvent supply storages caused by the critical need for rare earth elements in communications and mobility applications. With this purpose, the main goal is to overcome superparamagnetism, which results from size reduction to the nanoscale.3 A very attractive approach is the design of core-shell nanoparticles that combine hard and soft magnetic phases in direct contact.⁴ Thanks to the large core-shell interface, exchange coupling between interfacial spins of both phases can be finely modulated by a collection of parameters such as core size and shell thickness,^{5,6} as well as crystal lattices mismatch, defects⁷

and cationic diffusion.^{8,9} Therefore, exchange coupling results in the enhancement of thermal stability (higher blocking temperature, T_B) and magnetic stability (higher coercive field, H_C). In this field, iron oxide is certainly the first choice to avoid rare earth components because of its abundance, non-toxicity and cheapness.¹⁰ Indeed, ferr(i)magnetic (F(i)M) Ferrites are usually combined with an antiferromagnetic (AFM) phase such as MnO@Mn₃O₄,¹¹ Fe₃₋₈O4@CoO,^{5,12} CoO@CoFe₂O₄,¹³ ZnO@Co_xZn_{1-x}Fe₂O₄.¹⁴

Nevertheless, the AFM order vanishes below the Néel temperature (for instance, $T_N = 290$ K for CoO) which results in the disappearance of the exchange bias coupling. It is an important drawback for the design of room temperature permanent magnets. Recently, the magnetic anisotropy energy of Co@CoO nanoparticles incorporated in a NiO matrix ($T_N = 520$ K) was enhanced above room temperature thanks to proximity effects.¹⁵ However, in this approach, nanoparticles cannot be manipulated as separate building blocks for the production of advanced technological devices. An alternative to AFM components is the design of nanoparticles that combine multiple F(i)M phases. Ferrites $(MFe_2O_4, with M: Co, Mn, Ni)$, which exist in several chemical compositions, allow the fine modulation of hardness and softness of the magnetic phases.^{6,16} For instance, the diffusion of Co^{2+} in the surface layer of a $Fe_{3-\delta}O_4$ core resulted in the formation of a Co-doped Ferrite shell which markedly increased of magnetic anisotropy energy.5,17 Furthermore, recent advances in synthesis techniques allowed the production of multiple shell nanoparticles.¹⁸⁻²⁰ Although T_B remains below room temperature, onion-type nanoparticles offer the potential to produce permanent magnets at room temperature.

Here, we report on an original strategy to synthesize oniontype nanoparticles that are ferrimagnetic at room temperature and mainly consist of iron oxide with a mean size that does

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not exceed 16 nm. These nanoparticles consist of a core@shell@shell structure, with a intermediate shell which mostly consists in Co-Ferrite The significant enhancement of the magnetic properties at room temperature is ascribed to double interfacial exchange coupling at core/shell and shell/shell interfaces.

Nanoparticles were synthesized by a three-step thermal decomposition method. First, $Fe_{3-\delta}O_4$ nanoparticles (C) were prepared by performing the thermal decomposition of iron stearate in dioctyl ether at 290 °C in presence of oleic acid. Second, cobalt stearate was decomposed in octadecene at 310 °C in order to grow a CoO shell on the $Fe_{3-\delta}O_4$ surface (CS). Third, iron stearate was again decomposed in order to grow a second shell of $Fe_{3-\delta}O_4$ (CSS). Both shells were formed successively through a seed mediated growth by controlling

carefully the synthesis conditions. Nanoparticles were isolated after each step in order to avoid any side reactions resulting from the presence of side products and remaining metal stearate.

TEM micrographs show the increase of the mean nanoparticle size after each decomposition step from 10.1 ± 1.1 nm (C), 14.0 ± 1.5 nm (CS) to 15.6 ± 2.3 nm (CSS), respectively (Figure 1a-d). XRD patterns display typical peaks of the spinel structure (Figure 1e). Additional peaks corresponding to the wüstite CoO phase were observed in the CS pattern and almost vanished in the CSS pattern. Furthermore, spinel peaks became narrower after each growth step which corresponds to the increase of larger crystal sizes (6.1 ± 0.1 Å (C), 7.9 ± 0.1 Å (CS) and 11.0 ± 0.1 Å (CSS)) and agree with larger nanoparticles. EDX analysis



Figure 1. TEM micrographs of (a) C, (b) CS and, (c) CSS nanoparticles. (d) Size distributions measured from TEM micrographs. e) XRD patterns. Black and red bars correspond to the spinel structures (Fe_3O_4 JCPDS card n° 19-062 and $CoFe_2O_4$ JCPDS card n° 22-1086) and the CoO wüstite structure (JCPDS card n° 70-2856), respectively.

performed on several nanoparticles showed the presence of Co with a Fe:Co atomic ratio of 45:55 in CS which increased to 73:27 in CSS, consistent with the growth of a Fe-rich shell.

Furthermore, the STEM-EELS elemental mapping recorded at Fe-L and Co-L edges showed that Co is not homogenously distributed across CSS nanoparticles (Figure 2b,d). This result was confirmed by EELS spectra recorded in different areas (Figure 2d,e) which show different Co content. STEM-EELS analysis on CS also showed that CoO seems to grow preferentially on specific facets of the $Fe_{3-\delta}O_4$ core and resulted in an irregular shell shape (Figure S1).⁵ This is consistent with the more faceted morphology of CS nanoparticles in comparison with C nanoparticles (Figure 1a,b). Nevertheless, the overall amount of CoO-rich phase is much lower in CSS than in CS as shown by XRD. Indeed, CSS edge (area B) displays a Fe:Co ratio of 2.0 ± 0.3 , consistent with a Co-doped Ferrite.

STEM HAADF micrographs revealed lattice fringes across CSS (Figure 2a and S2) which agree with the high crystallinity of the spinel structure. A d spacing of 2.423 Å, consistent with the [222] direction and a cell parameter of 8.893 Å, were calculated from Fast Fourier Transform (FFT) (Figure S3). The doubling of lattice fringes was also observed in Co-rich areas with a d-spacing of 2.461 Å, consistent with the [111] direction of wüstite CoO phase. The perfect interpenetration of fringes corresponding to spinel and wüstite structures shows the

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good epitaxial relationship. Indeed, geometric phase analysis revealed a lattice expansion of 1-2 % which agrees with the small lattice mismatch of 1.6 % when crossing spinel wüstite structures.



Figure 2. CSS nanoparticle. a) Dark field STEM-HAADF micrograph. STEM-EELS micrographs showing the distribution of Fe (red), Co (green) and O (blue) species: b) composite image, c) Fe map, d) Co map and e) EELS spectra corresponding to different areas as selected on d).

To confirm these results, we investigated the chemical composition of CSS and site occupancy of Fe and Co cations by performing XMCD measurements (Figure 3).²¹ At the Fe-L_{2,3} edge, peaks correspond to Fe²⁺ and Fe³⁺ cations in Oh sites (S1), Fe³⁺ in Td sites (S2) and Fe³⁺ in Oh sites (S3) of the Ferrite spinel structure. The S1+S2/S2+S3 ratio (0.95) is intermediate to Fe₃O₄ (1.27) and γ -Fe₂O₃ (0.61).¹⁷ It agrees with the low occupancy of Fe²⁺ in Oh sites. At the Co-L_{2,3} edge, a peak (S4) corresponds to Co²⁺ in Oh sites of a Co-Ferrite.²² Such an intense peak cannot be ascribed to the CoO AFM phase. Indeed, XMCD being sensitive to the polarization of magnetic moments, spins of Co²⁺ which are coupled antiparallel in CoO cannot contribute to the signal.



Figure 3. XMCD spectra of CSS.

The magnetic properties of the nanoparticles were studied by SQUID magnetometry. M(H) curves of CSS nanoparticles display a coercive field (H_C) of 500 Oe at 300 K in contrast to C and CS nanoparticles ($H_{C}=0$) (Figure 4b). This result was confirmed by M(T) curves (Figure S₄) and the corresponding distribution of blocking temperatures (T_B) (Figure 4a),^{14,23} i.e. the temperature below which the magnetic moments of nanoparticles are blocked. T_B gradually increases with the formation of shells and clearly raises up above room temperature (340 K) for CSS. This value is much higher than the one of $Fe_{3-\delta}O_4$ nanoparticles of 15 nm (150 K),²⁴ and is similar to smaller CoFe₂O₄ nanoparticles of 12 nm.²⁵ Given the lower Co-Ferrite content in CSS and its larger size, it clearly shows that exchange coupling contributes to the enhancement of T_B in CSS.

FC M(H) curve recorded for CSS at 10 K after cooling under a field of 7 T showed a wide-open hysteresis cycle corresponding to H_C of 15 000 Oe and a very small shift to negative fields corresponding to an exchange field (H_E) of 500 Oe. In contrast, a very large shift corresponding to H_E of 5 000 Oe was observed for CS which is ascribed to strong exchange bias coupling at the $Fe_{3-\delta}O_4/CoO$ interface. Therefore, we expect that the contribution of this phenomenon to T_B enhancement in CSS is negligible. It confirmed that the CoO shell, which is very thin at the surface of the $Fe_{3-\delta}O_4$ core, mostly vanished in CSS and became Co-Ferrite upon the third decomposition step. The smooth profiles of the M(H) curves agree with the strong exchange coupling of soft $Fe_{3-\delta}O_4$ and hard Co-Ferrite phases. It results in the non-saturation of the M(H) curves in contrast to C which agree with the high magnetic anisotropy of exchange coupled nanoparticles. The magnetization of CSS at 7 T (72 emu/g) which is dramatically higher than that of CS (41 emu/g) also confirmed the transformation of CoO in Codoped Ferrite (Ms for CoFe2O4 nanoparticles is about 80 emu/g).²⁵ It is worth to note that such a M_S is even much higher than the Fe_{3- δ}O₄ core (56 emu/g),²⁴ thus increasing the energy product as required for permanent magnets.





Figure 4. Magnetic properties of C, CS and CSSC nanoparticles. a) Distribution of blocking temperatures M(H) curves recorded at b) 300K (ZFC) and c) 10K (FC under 7 T).

In summary, we have reported on the synthesis of magnetic nanoparticles with an onion-type structure produced by a three-step thermal decomposition process. Besides each decomposition step resulted in the increase of the nanoparticle size, this study shows that the third one accelerated the conversion of the CoO in Co-Ferrite. This is due to two different mechanisms promoted by the high temperature in the reaction medium: (i) the interdiffusion of Co and Fe cations at the $Fe_{3-\delta}O_4$ /CoO interface promoted by vacancies at the $Fe_{3-\delta}O_4$ core surface^{8,17} and, (ii) the solvation of CoO in presence of Fe monomers (resulting from the third decomposition of Fe(Stea)₂) which led to Co-–Ferrite.²⁶ According to EDX performed on a large number of CSS nanoparticles, we expect the large amount of Fe monomers during the third decomposition step in comparison to solvated Co monomers to result in the growth of a second layer of $Fe_{3-\delta}O_4$ after the formation of the $CoFe_2O_4$ layer.

Therefore, we expect the CSS nanoparticles to consist of two $Fe_{3-\delta}O_4/Co$ -doped Ferrite and Co-doped Ferrite/ $Fe_{3-\delta}O_4$ interfaces which both generate hard-soft exchange coupling. Such a CSS structure resulted in the significant enhancement of T_B and H_C which was not observed in previous works on trimagnetic type nanoparticles. Therefore, room temperature blocked magnetic nanoparticles mostly based on iron oxide with a size not exceeding 16 nm can be synthesized. Such a strategy opens huge perspectives for the design of rare-earth-free nanoparticles with tunable magnetic properties for a wide range of applications including high density data storage, therapeutics and sensors. Work is in progress to achieve a deeper understanding of the structure of CSS nanoparticles and the structure-property relationship.

ASSOCIATED CONTENT

Supporting Information

Experimental details Figure S1: TEM-HAADF, STEM-EELS and EELS analysis on CS. Figure S2: STEM and STEM-HAADF on CSS. Figure S3: STEM HAADF and FFT on selected area. Figure S4: Details on FC-ZFC measurements. Figure S5: Magnetization curve against a magnetic field of C, CS and CSS at 300 and 10 K. Table S1: Table of the magnetic characteristics of C, CS and CSS.

The Supporting Information is available free of charge on the ACS Publications website.

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Notes

The authors declare no competing financial interests.

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REFERENCES

(1) López-Ortega, A.; Estrader, M.; Salazar-Alvarez, G.; Roca, A. G.; Nogués, J. Applications of Exchange Coupled Bi-Magnetic Hard/Soft and Soft/Hard Magnetic Core/Shell Nanoparticles. *Phys. Rep.* **2015**, 553, 1–32.

(2) Gutfleisch, O.; Willard, M. A.; Brück, E.; Chen, C. H.; Sankar, S. G.; Liu, J. P. Magnetic Materials and Devices for the 21st Century: Stronger, Lighter, and More Energy Efficient. *Adv. Mater.* 2011, 23 (7), 821.

(3) Bedanta, S.; Kleemann, W. Supermagnetism. J. Phys. Appl. Phys. 2009, 42 (1), 013001.

(4) Nogués, J.; Sort, J.; Langlais, V.; Skumryev, V.; Suriñach, S.; Muñoz, J. S.; Baró, M. D. Exchange Bias in Nanostructures. *Phys. Rep.* **2005**, *422* (3), 65–117.

(5) Liu, X.; Pichon, B. P.; Ulhaq, C.; Lefevre, C.; Greneche, J.-M.; Begin, D.; Begin-Colin, S. Systematic Study of Exchange Coupling in Core-Shell Fe₃-DO4@CoO Nanoparticles. *Chem. Mater.* **2015**, *27* (11), 4073.

(6) Song, Q.; Zhang, Z. J. Controlled Synthesis and Magnetic Properties of Bimagnetic Spinel Ferrite CoFe2O4 and MnFe2O4 Nanocrystals with Core-Shell Architecture. *J. Am. Chem. Soc.* **2012**, *134* (24), 10182.

(7) Chai, Y.; Feng, F.; Li, Q.; Yu, C.; Feng, X.; Lu, P.; Yu, X.; Ge, M.; Wang, X.; Yao, L. One-Pot Synthesis of High-Quality Bimagnetic Core/Shell Nanocrystals with Diverse Exchange Coupling. *J. Am. Chem. Soc.* **2019**.

(8) Lopez-Ortega, A.; Estrader, M.; Salazar-Alvarez, G.;
Estrade, S.; Golosovsky, I. V.; Dumas, R. K.; Keavney, D. J.;
Vasilakaki, M.; Trohidou, K. N.; Sort, J.; Peiro, F.; Surinach, S.;
Baro, M. D.; Nogués, J. Strongly Exchange Coupled Inverse
Ferrimagnetic Soft/Hard, MnxFe₃-XO₄/FexMn₃-XO₄,
Core/Shell Heterostructured Nanoparticles. *Nanoscale* 2012, 4 (16), 5138.

(9) Skoropata, E.; Desautels, R. D.; Chi, C. C.; Ouyang, H.; Freeland, J. W.; van Lierop, J. Magnetism of Iron Oxide Based Core-Shell Nanoparticles from Interface Mixing with Enhanced Spin-Orbit Coupling. *Phys. Rev. B* 2014, *89* (2), 024410.

(10) Tartaj, P.; Morales, M. P.; Gonzalez-Carreño, T.;
Veintemillas-Verdaguer, S.; Serna, C. J. The Iron Oxides Strike
Back: From Biomedical Applications to Energy Storage
Devices and Photoelectrochemical Water Splitting. *Adv. Mater.* 2011, 23 (44), 5243.

(11) López-Ortega, A.; Tobia, D.; Winkler, E.; Golosovsky,
I. V.; Salazar-Alvarez, G.; Estradé, S.; Estrader, M.; Sort, J.;
González, M. A.; Surinach, S. Size-Dependent Passivation
Shell and Magnetic Properties in
Antiferromagnetic/Ferrimagnetic Core/Shell MnO
Nanoparticles. J. Am. Chem. Soc. 2010, 132 (27), 9398–9407.

(12) Baaziz, W.; Pichon, B. P.; Lefevre, C.; Ulhaq-Bouillet,
C.; Greneche, J.-M.; Toumi, M.; Mhiri, T.; Begin-Colin, S. High
Exchange Bias in Fe₃O₄@CoO Core Shell Nanoparticles

Synthesized by a One-Pot Seed-Mediated Growth Method. *J. Phys. Chem. C* **2013**, *117* (21), 11436.

(13) Lima, E.; Winkler, E. L.; Tobia, D.; Troiani, H. E.; Zysler, R. D.; Agostinelli, E.; Fiorani, D. Bimagnetic CoO Core/CoFe $_2$ O $_4$ Shell Nanoparticles: Synthesis and Magnetic Properties. *Chem. Mater.* **2012**, *24* (3), 512–516.

(14) Lavorato, G. C.; Lima, E.; Troiani, H. E.; Zysler, R. D.; Winkler, E. L. Tuning the Coercivity and Exchange Bias by Controlling the Interface Coupling in Bimagnetic Core/Shell Nanoparticles. *Nanoscale* **2017**, *9* (29), 10240–10247.

(15) De Toro, J. A.; Marques, D. P.; Muñiz, P.; Skumryev, V.; Sort, J.; Givord, D.; Nogués, J. High Temperature Magnetic Stabilization of Cobalt Nanoparticles by an Antiferromagnetic Proximity Effect. *Phys. Rev. Lett.* **2015**, *115* (5), 057201. https://doi.org/10.1103/PhysRevLett.115.057201.

(16) Daffé, N.; Sikora, M.; Rovezzi, M.; Bouldi, N.; Gavrilov, V.; Neveu, S.; Choueikani, F.; Ohresser, P.; Dupuis, V.; Taverna, D.; Gloter, A.; Arrio, M.-A.: Sainctavit, P.; Juhin, A. Nanoscale Distribution of Magnetic Anisotropies in Bimagnetic Soft Core–Hard Shell MnFe2O4@CoFe2O4 Nanoparticles. *Adv. Mater. Interfaces* **2017**, *4* (22), 1700599.

(17) Kevin Sartori, Geoffrey Cotin, Corrine Ulhaq, Christophe Lefevre, Valérie Halté, Sylvie Bégin-Colin, Fadi Choueikani, Benoit P. Pichon. Strong Interfacial Coupling through Exchange Interactions in Soft/Hard Core-Shell Nanoparticles as Function of Cationic Distribution. *Submitted*.

(18) Salazar-Alvarez, G.; Lidbaum, H.; Lopez-Ortega, A.; Estrader, M.; Leifer, K.; Sort, J.; Surinach, S.; Baro, M. D.; Nogues, J. Two-, Three-, and Four-Component Magnetic Multilayer Onion Nanoparticles Based on Iron Oxides and Manganese Oxides. *J. Am. Chem. Soc.* **2012**, *133* (42), 16738.

(19) Krycka, K. L.; Borchers, J. A.; Laver, M.; Salazar-Alvarez, G.; Lopez-Ortega, A.; Estrader, M.; Surinach, S.; Baro, M. D.; Sort, J.; Nogués, J. Correlating Material-Specific Layers and Magnetic Distributions within Onion-like Fe₃O₄/MnO/g-Mn₂O₃ Core/Shell Nanoparticles. *J. Appl. Phys.* **2013**, *11*3 (17).

(20) Gavrilov-Isaac, V.; Neveu, S.; Dupuis, V.; Taverna, D.; Gloter, A.; Cabuil, V. Synthesis of Trimagnetic Multishell MnFe2O4@CoFe2O4@NiFe2O4 Nanoparticles. *Small* **2015**, *11* (22), 2614–2618.

(21) Ohresser, P.; Otero, E.; Choueikani, F.; Chen, K.; Stanescu, S.; Deschamps, F.; Moreno, T.; Polack, F.; Lagarde, B.; Daguerre, J.-P.; Marteau, F.; Scheurer, F.; Joly, L.; Kappler, J.-P.; Muller, B.; Bunau, O.; Sainctavit, P. DEIMOS: A Beamline Dedicated to Dichroism Measurements in the 350–2500 EV Energy Range. *Rev. Sci. Instrum.* **2014**, *85* (1), 013106.

(22) Daffé, N.; Choueikani, F.; Neveu, S.; Arrio, M.-A.; Juhin, A.; Ohresser, P.; Dupuis, V.; Sainctavit, P. Magnetic Anisotropies and Cationic Distribution in CoFe2O4 Nanoparticles Prepared by Co-Precipitation Route: Influence of Particle Size and Stoichiometry. *J. Magn. Magn. Mater.* **2018**, *4*60, 243–252. (23) Bruvera, I. J.; Mendoza Zélis, P.; Pilar Calatayud, M.; Goya, G. F.; Sánchez, F. H. Determination of the Blocking Temperature of Magnetic Nanoparticles: The Good, the Bad, and the Ugly. *J. Appl. Phys.* **2015**, *118* (18), 184304.

(24) Baaziz, W.; Pichon, B. P.; Fleutot, S.; Liu, Y.; Lefevre, C.; Greneche, J.-M.; Toumi, M.; Mhiri, T.; Begin-Colin, S. Magnetic Iron Oxide Nanoparticles: Reproducible Tuning of the Size and Nanosized-Dependent Composition, Defects, and Spin Canting. J. Phys. Chem. C 2014, 118 (7), 3795–3810.

(25) Song, Q.; Zhang, Z. J. Shape Control and Associated Magnetic Properties of Spinel Cobalt Ferrite Nanocrystals. *J. Am. Chem. Soc.* **2004**, *126* (19), 6164–6168.

(26) Sytnyk, M.; Kirchschlager, R.; Bodnarchuk, M. I.;

Primetzhofer, D.; Kriegner, D.; Enser, H.; Stangl, J.; Bauer, P.; Voith, M.; Hassel, A. W.; et al. Tuning the Magnetic Properties of Metal Oxide Nanocrystal Heterostructures by Cation Exchange. *Nano Lett.* **2013**, *13* (2), 586–593.



