Enhancing Heating Efficiency in Magnetic Nanoparticles Doping Effects in Single-Core and Core-Shell Structures

JaeHyun Kim[3], Jaemog Jung[1,2], Jae-Hyun Lee[1,2]

[1]Center for Nanomedicine, Institute for Basic Science (IBS), Seoul, Republic of Korea
[2]Department of Nano Biomedical Engineering (NanoBME), Advanced Science Institute, Yonsei University, Seoul, Republic of Korea
[3]Department of NanoScience and Engineering, Yonsei University, Seoul, Republic of Korea

Introduction

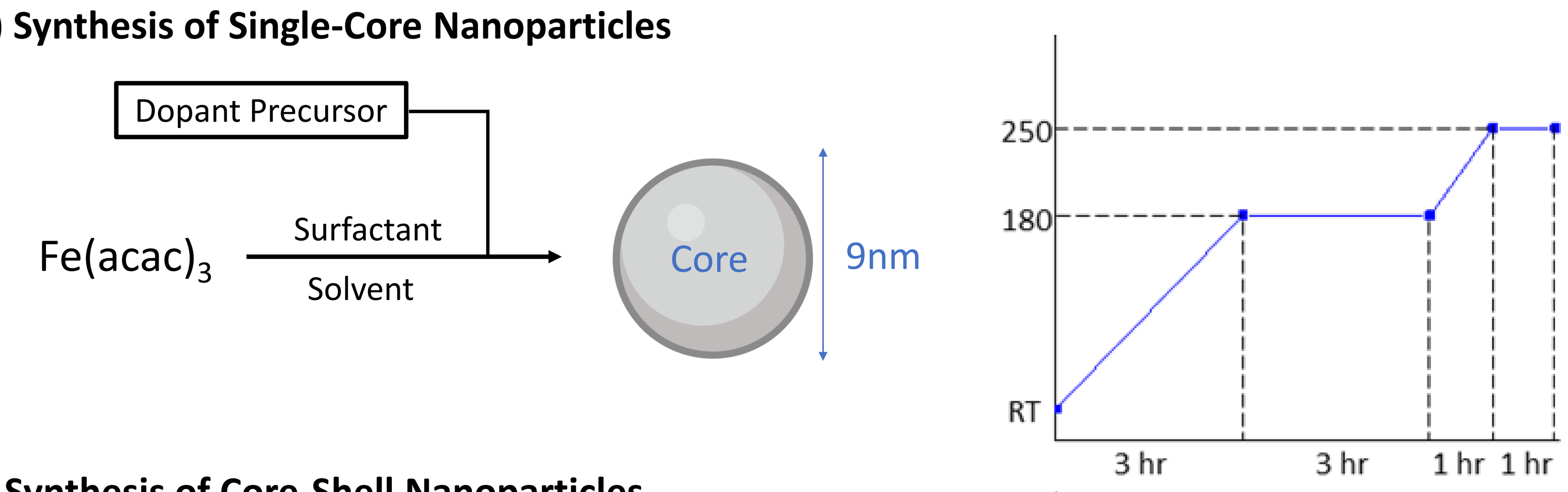
Magnetic nanoparticles (MNPs) are promising for biomedical applications like hyperthermia treatment due to their unique properties, such as non-invasiveness, deep tissue penetration, remote controllability, and molecular-level specificity. However, their low energy conversion efficiency remains a challenge.

To address this, core-shell magnetic nanoparticles, which combine a hard core and a soft shell, have been developed to enhance magnetic performance. The choice of core and shell materials plays a crucial role in optimizing key magnetic properties such as saturation magnetization and anisotropy, which ultimately improve energy conversion efficiency.

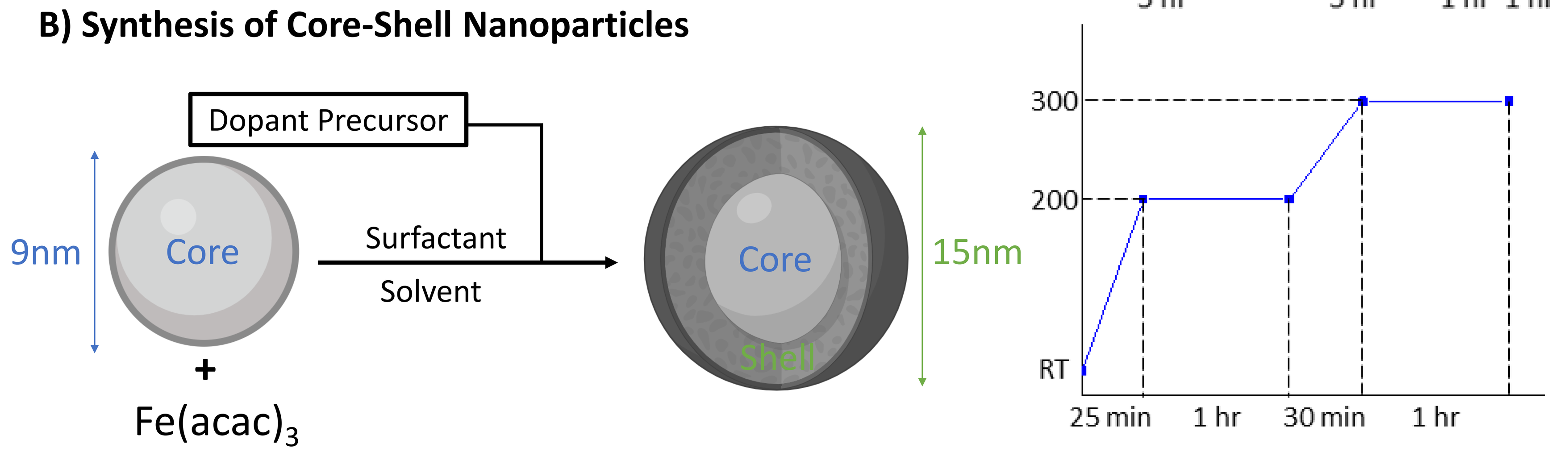
In this study, we explored the effects of different doping elements on nanoparticles. We compared three types of single-core nanoparticles ($CoFe_2O_4$, $ZnFe_2O_4$, and $CoZnFe_2O_4$) and three core-shell nanoparticles, where $CoFe_2O_4$ nanoparticles were used as seeds and grown by thermal decomposition. Magnetic properties were measured to evaluate how doping composition influences saturation magnetization, anisotropy, and SLP.

Experimental Methods

A) Synthesis of Single-Core Nanoparticles



B) Synthesis of Core-Shell Nanoparticles



Results

Figure 1 | Effects of precursor, solvent, and surfactant on nanoparticle morphology

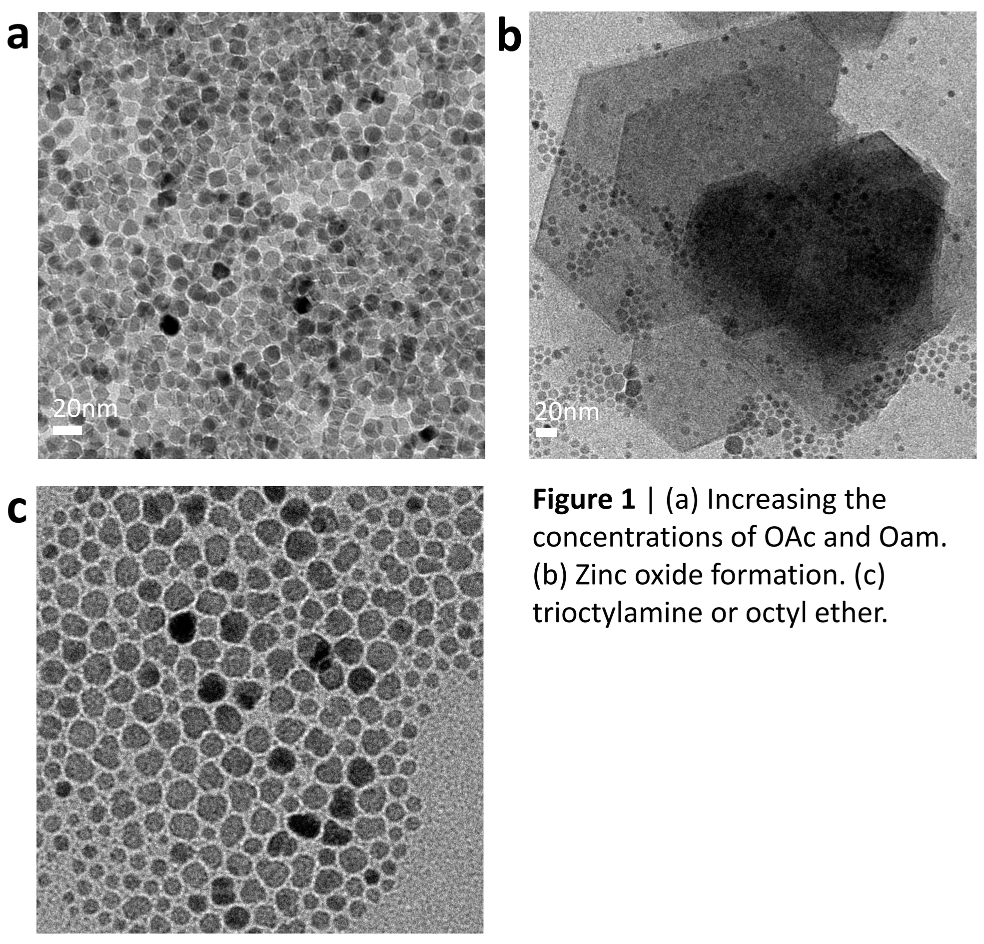


Figure 1 | (a) Increasing the concentrations of OAc and Oam. (b) Zinc oxide formation. (c) trioctylamine or octyl ether.

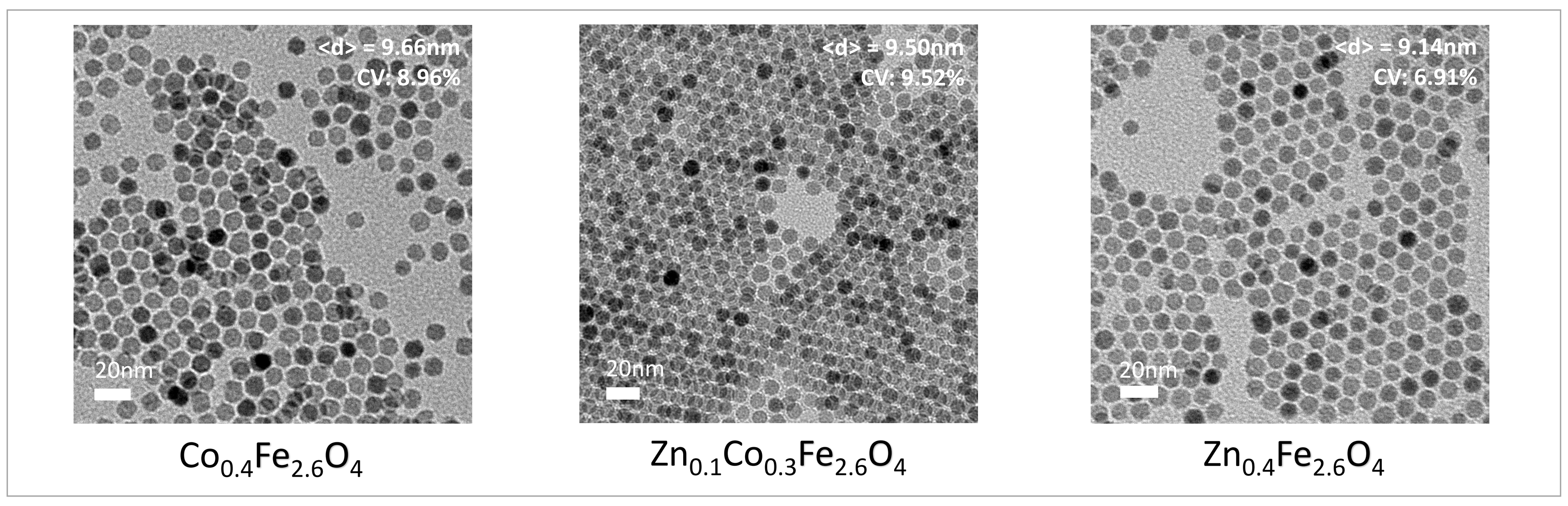
Various experimental conditions were explored to synthesize **9 nm spherical iron oxide nanoparticles**.

(a) Surfactant experiment: It was found that 10 mL of oleic acid and 30 mL of oleylamine are optimal to achieve spherical nanoparticle shapes.

(b) Precursor experiment: It was found that 1.0 g of $ZnCl_2$ leads to the formation of zinc oxide. Concentrations greater than 1.0 g resulted in the undesirable formation of zinc oxide.

(c) Solvent experiment: It was found that using octyl ether or trioctylamine led to irregular nanoparticle shapes, unlike Benzyl ether, which consistently produced spherical particles.

Figure 2 | TEM images of selected nanoparticles



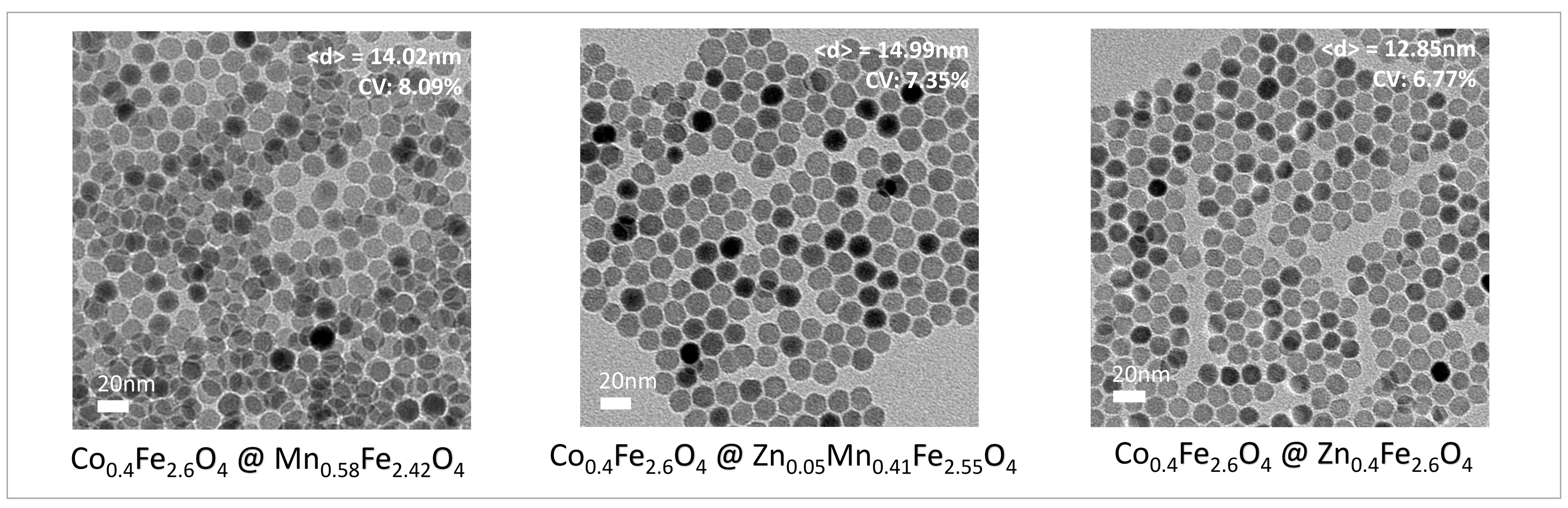
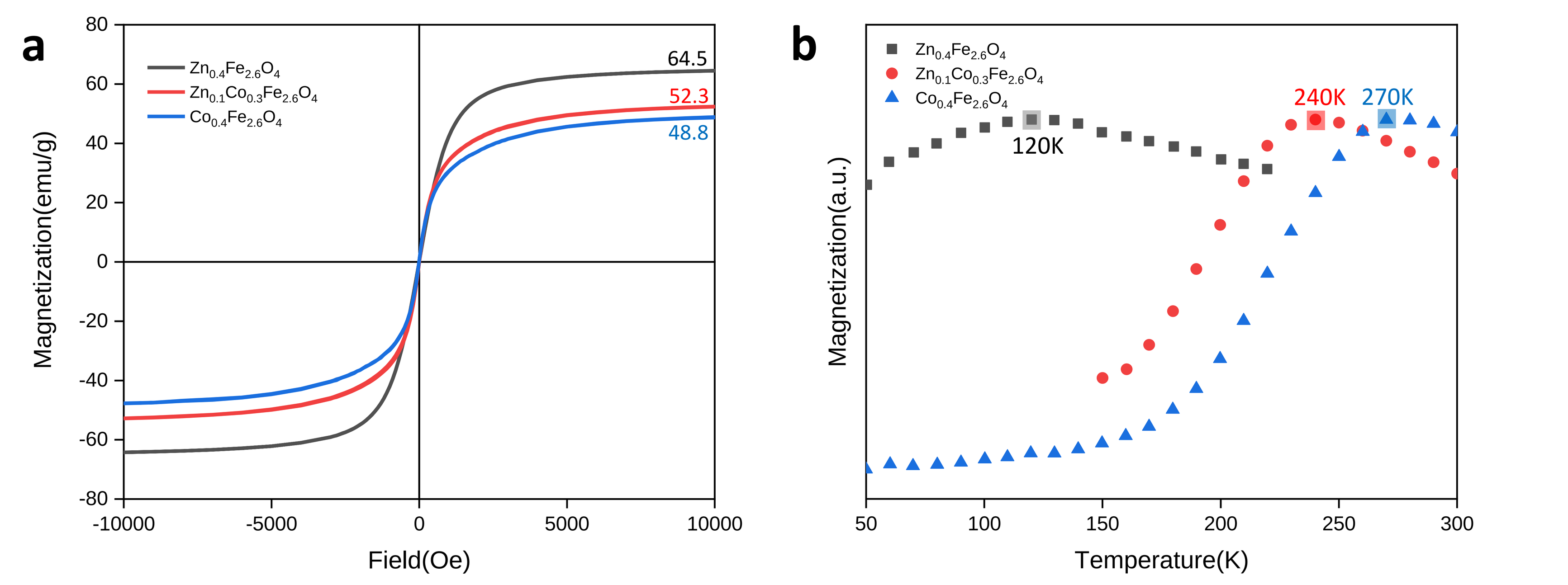


Figure 2 | (a) TEM images of single-core nanoparticles synthesized under optimized conditions. (b) TEM images of core-shell nanoparticles synthesized under optimized conditions.

Figure 3 | M-H and M-T Curves of nanoparticles



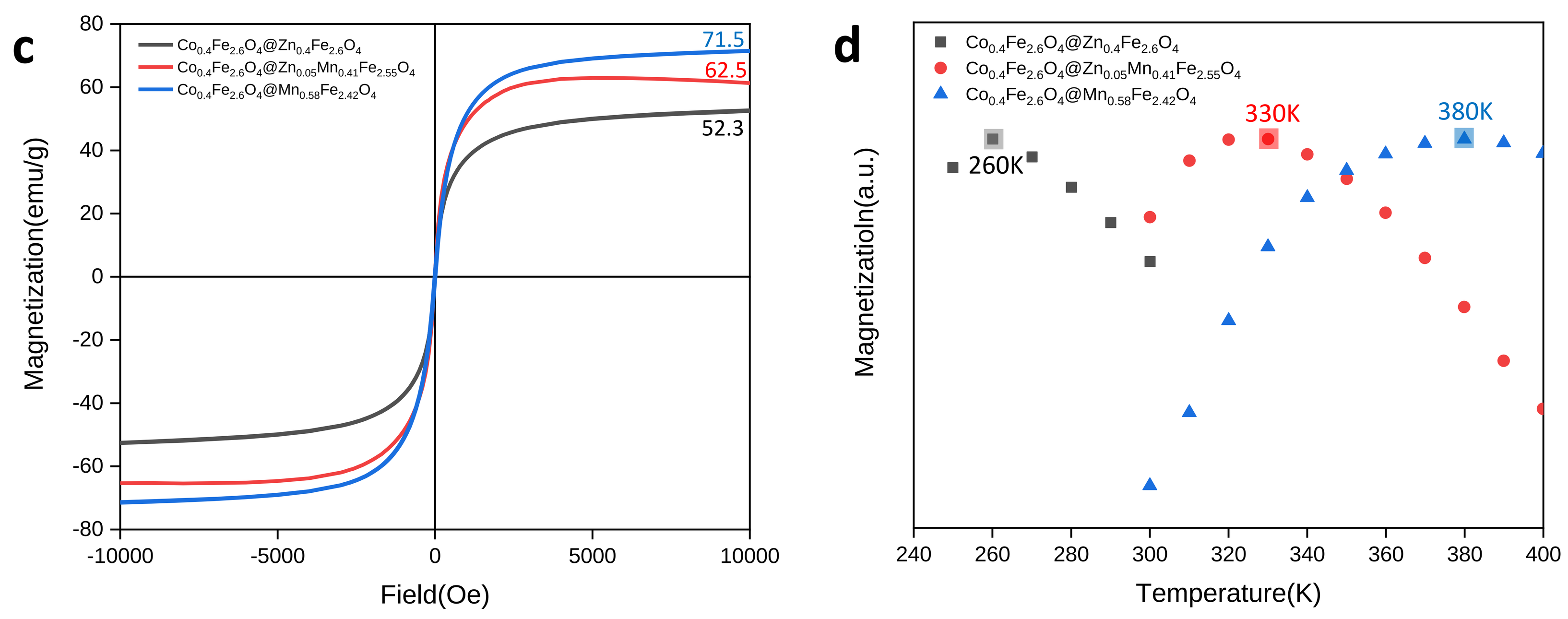


Figure 3 |
(a) M-H curves of single-core nanoparticles measured by VSM.
(b) M-T curves of single-core nanoparticles measured from ZFC.
(c) M-H curves of core- shell nanoparticles measured by VSM.
(d) M-T curves of core- shell nanoparticles measured from ZFC.

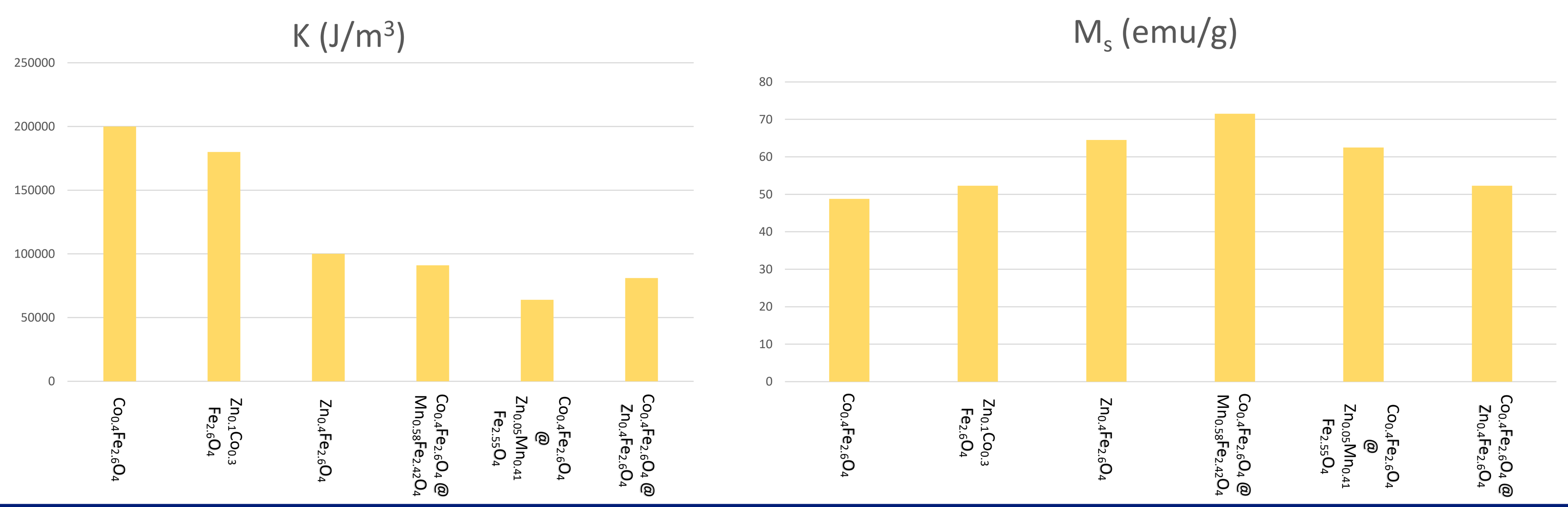
(a) Single-core M_s: $Zn_{0.4}Fe_{2.6}O_4 > Zn_{0.1}Co_{0.3}Fe_{2.6}O_4 > Co_{0.4}Fe_{2.6}O_4$

(b) Single-core T_B: $Co_{0.4}Fe_{2.6}O_4 > Zn_{0.1}Co_{0.3}Fe_{2.6}O_4 > Zn_{0.4}Fe_{2.6}O_4$

(c) Core-shell M_s: $Co_{0.4}Fe_{2.6}O_4$ @ $Mn_{0.58}Fe_{2.42}O_4 > Co_{0.4}Fe_{2.6}O_4$ @ $Zn_{0.05}Mn_{0.41}Fe_{2.55}O_4 > Co_{0.4}Fe_{2.6}O_4$ @ $Zn_{0.4}Fe_{2.6}O_4$

(d) Core-shell T_B: $Co_{0.4}Fe_{2.6}O_4$ @ $Mn_{0.58}Fe_{2.42}O_4 > Co_{0.4}Fe_{2.6}O_4$ @ $Zn_{0.05}Mn_{0.41}Fe_{2.55}O_4 > Co_{0.4}Fe_{2.6}O_4$ @ $Zn_{0.4}Fe_{2.6}O_4$

Figure 4 | K and M_s Calculation of nanoparticles



Conclusion & Further Study

In this study, we investigated the effects of core and shell doping on the magnetic properties and specific loss power (SLP) of magnetic nanoparticles (MNPs). By systematically varying the dopant composition, we examined how saturation magnetization (M_s), blocking temperature (T_B), and SLP were influenced by both single-core and core-shell structures.

- In zinc doped ironoxide, Zn^{2+} substitution for Fe^{3+} at tetrahedral sites reduces spin disorder, enhancing superexchange interactions and leading to the highest M_s.
- In cobalt doped ironoxide, the strong spin-orbit coupling of Co^{2+} leads to a high K.
- The lower K of cobalt doped ironoxide@mangan doped ironoxide compared to single-core nanoparticles is likely due to Mn making the shell softer.
- The high M_s of cobalt doped ironoxide@mangan doped ironoixde is likely due to strong exchange coupling between the core and shell.
- According to the K- M_s -SLP 3D graph, zinc,cobalt doped ironoxide exhibits the highest SLP among single-core nanoparticles, while cobalt doped ironoxide@zinc,mangan doped ironoxide shows the highest SLP among core-shell structures.

Further study:

1. Investigate the effect of elemental composition by analyzing Co, Zn, and Fe atomic % variations to optimize M_s, K, and SLP.
2. Explore shape anisotropy effects by synthesizing octahedral nanoparticles and comparing their magnetic behavior with spherical counterparts.
3. Apply silica coating to prevent nanoparticle aggregation during VSM and ZFC measurements, ensuring accurate characterization.

Reference

[1] J. Cheon et al., *Nano Today*. 2017, 13, 61-76. [2] J. Cheon et al., *Nature Nanotechnoly*. 2011, 6, 418–422. [3] L. Qiao et al., *ACS Nano*. 2017, 11, 6370–6381.