

Tuning the anisotropy constant of magnetic nanoparticles via cation exchange

Min Ji Kim⁴, Mansoo Park^{1,2}, Jongseong Park^{1,2}, Gooreum Kim^{1,3}, Jae-Hyun Lee^{1,2,*}, and Jinwoo Cheon^{1,2,3,*}

¹Center 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 Chemistry, Yonsei University, Seoul, Republic of Korea. ⁴ Department of Materials Science & Engineering, Yonsei University, Seoul, Republic of Korea



Introduction

The engineering of the critical magnetic properties of magnetic nanoparticles (MNPs), encompassing saturation magnetization (M_S), \ge coercivity (H_C), magnetic anisotropy constant (K), blocking temperature (T_B), and magnetic relation time (τ_N and τ_B), is crucial for \underline{a} diverse biomedical systems such as sensing, drug delivery, and 👗 hyperthermia.

Controlling anisotropy constant can be achieved by alterations of size, shape, composition, and architecture of magnetic nanoparticles. Where, cation-exchange, is one of effective approaches for controlling anisotropy constant on magnetic nanoparticles. Soft magnetic Fe₃O₄ has an inverse spinel structure characterized by Fe^{2+/3+} ions occupying octahedral sites (O_h) and Fe³⁺ ions occupying tetrahedral



Schematic illustration of this study



sties (T_d). Substitutional doping occurs with Co²⁺ ions replacing Fe²⁺ ions in the O_h sites.

Here, we studied the reaction kinetics and mechanism of the cation exchange on magnetic nanoparticles, resulting in well-defined Co_xFe_{3-} $_{x}O_{4}$ nanoparticles with preserving morphologies and crystallinity, but also controlling Co contents and anisotropy constant.



Results

(a)



III. Co²⁺ cation exchange with different molar ratio of TOP



Highest coercivity occurred at a TOP/Fe3O4 molar ratio of 1, indicating the role of TOP as strong ligands after cation exchange.



Figure 2. Analysis of Co²⁺ ion exchange with different Co / Fe ratio of X = 0, 1, 2, 4, 6, 10 respectively. (a) STEM EDS maps (Fe in red and Co in blue) (b) Correlation of molar ratio of Co / Fe with cobalt contents for each sample (c) Hysteresis curve of Co²⁺ exchanged samples at 100K (d) Correlation of Co / Fe molar ratio with coercivity and saturated magnetization

Reference

Casu and Falqui et.al., Chem. Mater. 2018, 30, 8099–8112. Kovalenko et al., Nano Lett. 2015, 15, 5635–5640. Donega et al., ACS Nano 2019, 13, 12880-12893. Cheon et al., J. Am. Chem. Soc. 2020, 142, 9130–9134.

Conclusion & Further Study

In this study, we initially confirmed the nucleation and growth of monodisperse Fe₃O₄ nanoparticles with an inverse spinel structure.

Diffusional effects of incoming CoCl₂ was investigated using different molar ratios of Co / Fe. The observed change in coercivity indicates successful cation exchange. However, the cobalt contents substituted into iron oxide nanoparticles do not show linearity, which indicates that other component, potentially trioctylphosphine(TOP), participate as a limiting factor.

The outcoming kinetics of the cation exchange was controlled by changing the molar ratio of the Fe ion extractor, TOP. Highest coercivity was observed at a TOP amount of 16 mmol, with comparable coercivity values noted for 50 mmol and 80 mmol of TOP. This can be explained by a 1:1 ratio of CoCl2-TOP for the cation exchange and excess TOP functioning as strong ligands, binding to Fe atoms and inhibiting further cation exchange. Consequently, the mechanism of cation exchange can be explained as phosphine in TOP forming a lewis acid base complex to extract Fe ion and Co²⁺ instantly being substituted in the vacancy formed. In conclusion, by controlling the kinetics of incoming and outcoming elements of cation exchange, the anisotropy constant was tuned effectively.