

Synthesis and characterization of CoFe₂O₄ building blocks and hard magnetic supercrystals with interparticle interaction

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Introduction

Experimental Methods

Cobalt ferrite ($CoFe_2O_4$) is a magnetic material of the spinel group that is widely studied due to its physical, chemical, and magnetic properties. Due to its chemical and mechanical stability, moderate saturation magnetization, high coercivity, and strong anisotropy, cobalt ferrite is widely utilized in biotechnology, catalysis, biomedicine, magnetic drug delivery, solar cells, magnetic cards, recording devices, and sensors.



Among the various magnetic properties of cobalt ferrite, it is important to adjust the coercivity value for various applications. For soft magnetic materials with low coercivity values, they can sensitive reaction as sensors to external magnetic fields. For hard magnetic materials with high coercivity values, they can be magnetized in the direction of the magnetic field, serving as permanent magnets regardless of external magnetic fields.

I. Synthesis of Octahedral Nanoparticles

 $Co(acac)_2 + Fe(acac)_3 \xrightarrow{OA, BE, \Delta} CoFe_2O_4$

*acac: acetylacetonate, OA: oleic acid, BE: benzyl ether





In this study, the synthesis method of cobalt ferrite was devised by controlling precursors, ligands, reaction time, and its magnetic properties were analyzed. Furthermore, by adjusting the distance between particles, the collective properties were confimed. Additionally, through the synthesis of supercrystals with interparticle dipolar interaction, It was possible to improve and control the properties of magnetic nanomaterials.



Results

I. Synthesis of Cobalt Ferrite Nanoparticle with Octahedral Shape

A. Controlling the ratio of atoms $[Co(acac)_2 : Fe(acac)_3]$



I . Dependence of the coercivity on the distance between nanoparticles

TEM images of $CoFe_2O_4@SiO_2$ NPs with shell thickness of (a) 0nm, (b) 5 nm, (c) 10 nm, (d) 15 nm, (e) 20 nm, (f) 25 nm. (g) Dependence of the coercivity value on the interparticle distance, d_{ii} (nm).

$\operatorname{High}^{\operatorname{high}}_{\operatorname{High}}$					
Ms (emu/g) Hc (Oe) composi	tion				
1 7 0 CoO					
1.5 6 170 CoO					
.75 20 800 CoO, CoFe ₂ O ₄					
:2 43 600 CoFe ₂ O ₄ Co _{0.7} Fe ₂	. ₃ O ₄				
2.5 48 800 CoFe ₂ O ₄ Co _{0.7} Fe ₂	. ₃ O ₄				
:3 67 1070 CoFe ₂ O ₄ Co _{0.5} Fe ₂	.5 ⁰ 4				

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 $CoFe_2O_4$

 $CoFe_2O_4$

CoFe₂O₄

Analysis of physical and crystallographic properties. (a) Analysis of the monodispersity: transmission electron microscope (TEM), (b) Analysis of the crystal structure: x-ray diffraction (XRD), (c) ,(d) Analysis of the magnetism: vibrating sample magnetometer (VSM)

B. Controlling the morphology of nanoparticles

(a)	Oleic acid	7 mmol	8 mmol	8 mmol
	Time	1 h	1 h	3 h
	yield	-	32.3 %	43.5 %

III. Supercrystal with Dipolar Interaction Energy

Analysis of supercrystals. (a) TEM images of supercrystal (b) Hysteresis loops of the supercrystal and single magnetic nanoparticle, (c) Normalized isothermal remanence (IRM), DC demagnetization remanence (DCD), and ΔM curves of the supercrystal and single magnetic nanoparticle.

Conclusion & Further Study

Analysis of Cobalt ferrites, which are synthesized under different conditions. (a) Analysis of the morphology and the size (TEM), (b) Analysis of the crystal structure (XRD), (c) Hysteresis loops and the magnetism of Cobalt ferrites.

To analysis the magnetic properties of cobalt ferrite, the following three experiments were conducted.

The first experiment is synthesis of cobalt ferrite. Nanoparticles with a Co:Fe ratio of 1:2 composition and an octahedral shape were synthesized by adjusting the ratios of the precursor and the amount of ligand.

The second experiment is to confirm the coercivity values based on the distance between particles. It was observed that the coercivity value increases as the distance between particles decreases.

Lastly, Supercrystals were synthesized by assembling MNPs. It was confirmed that supercrystals exhibited greater coercivity compared to single nanoparticles due to the interparticle interaction energy.

In the future, we plan to investigate the differences in interaction energy and magnetic properties based on the packing structure of the supercrystals.

- J. Cheon et al, Nat., Nanotech 2011, 6, 418-422.

- M. T. Swihart et al., ACS Nano 2017, 6, 6370-6381.
- Angang Dong et al., *J. Am. Chem. Soc* **2018**, 140, 15038–15047.
- Jose Rivas et al., Adv. Sci. 2022, 10, 2203397.