Supporting information

# A General Approach to the Synthesis and Detailed Characterization of Magnetic Ferrite Nanocubes

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## 1. Thermal decomposition behavior studies of $M^{2+}$ -Fe<sup>3+</sup> oleate precursors.

The key design for the synthesis of MFe<sub>2</sub>O<sub>4</sub> nanocubes is the step-heating (250 °C–20 min, 320 °C–30 min), where the reaction temperatures were selected based on the TGA studies of  $M^{2+}$ –Fe<sup>3+</sup> oleate precursors (Fig. S1). A similar thermal behavior was observed for various precursors with three different decomposition ranges, where the first weight loss onset was around 150 °C, second one around 250 °C, and third one before 300 °C. Our previous studie<sup>1</sup> suggested that the weight loss in the range of 150 to 250 °C was from partial decomposition of  $M^{2+}$ –oleate, and the dissociation of two symmetric ligands from Fe<sup>3+</sup>–oleate. The continuous weight loss between 250 and 300 °C was due to the complete decomposition of  $M^{2+}$ –oleate, and the dissociation of the last oleate ligand from the Fe<sup>3+</sup>– oleate. The nucleation step normally started around 250 °C, which was the basis of seting up the initial heating step in our nanocube formation. The design was to use slow decomposition at 250 °C for the formation of cubic ferrite structures, and then the heating at 320 °C led to the nanocube growth on the pre-formed seeds. The starting and ending temperatures of this is important to the formation of nuclei, which consequently affected the nuclei concentration, and eventually the metal-ion doping level and final nanoparticle

sizes. A higher ending temperature means a slower decomposition of the mixed precursor ligands, and subsequent lower nucleus concentration, and larger particle size. The final weight loss (300 to 350 °C) was from desorption and decomposition of dissociated ligands. Therefore, the TGA analysis is important to understand the doping level, nanoparticle size, etc.



**Fig. S1** TGA plots of  $M^{2+}$ -Fe<sup>3+</sup> oleate precursors (a) Fe<sup>2+</sup>-Fe<sup>3+</sup>, (b) Mn<sup>2+</sup>-Fe<sup>3+</sup>, (c) Zn<sup>2+</sup>-Fe<sup>3+</sup>, (d) Cu<sup>2+</sup>-Fe<sup>3+</sup>, (e) Ca<sup>2+</sup>-Fe<sup>3+</sup>, (f) Mg<sup>2+</sup>-Fe<sup>3+</sup>.

#### 2. Mechanistic studies of cubic-shape formation.

Regardless of doping ions, the step-heating method allowed the formation of cubic-shapes. Our studies suggested that the step-heating process and extra sodium oleate (NaOA) in the precursor were critical for the cubic-shape formation. Using magnetite as a model system, we have systematically investigate the roles of step-heating and NaOA by varying the reaction temperatures and amount of extra NaOA.

## 2.1 Temperature effect experiments

The temperature effect experiments were set up by varying the nucleation temperatures (250 °C and 270 °C), nucleation temperature heating window (e.g., 250 °C- 0 min, 10 min, 20 min, 30 min, 45 min, and 60 min), and nanocube growth time at 320 °C (20 min, 30 min, 60 min, and 120 min).

## 2.1.1 Variation of nucleation temperatures.

The two nucleation temperatures (250 °C and 270 °C) were chosen in nucleation stage window, one at starting point and the other near the window center. As shown in Fig. S2, the cubic-like nanoparticles were prepared but with round corners and wide size distribution. The cubic-like shape likely resulted from the fast decomposition of metal-oleate complexes at 270 °C, which led to the formation of defective cubic ferrite structures. This relative-high temperature (270 °C) also interfered the decomposition order of oleate ligands of Fe<sup>2+</sup>-oleate and Fe<sup>3+</sup>-oleate, and subsequently, the doping process and the size and size distribution of the pre-seeds.



**Fig. S2** TEM images of Fe<sub>3</sub>O<sub>4</sub> nanoparticles prepared by a modified step-heating method (270 °C-20 min and 320 °C-30 min).

#### 2.1.2 Variation of nucleation temperature heating windows

The effects of nucleation heating window on the nanocube formation were studied at 250 °C with various heating periods (0, 10, 20, 30, 45, or 60 min) (Fig. S3). Direct heating to 320 °C lead to smooth edged but cubic-like nanoparticles (Fig. S3a). Nanocubes were successfully synthesized from the experiments (250 °C-10 min, 250 °C-20 min, and 250 °C-30 min). The size of nanocubes with 10 min heating (Fig. S3b) was slightly smaller than the reactions with 20 and 30 min heating (Fig. S3c and Fig. S3d), which was likely resulted from smaller seeds from the relative short nucleation time. The elongated heating periods (45 and 60 min) did not affect the nanocube size (Fig. S3e and Fig. S3f), but the final nanocubes had much rounded corners.



**Fig. S3** TEM images of Fe<sub>3</sub>O<sub>4</sub> nanoparticles prepared by varying nucleation temperature heating windows. (a) 250 °C-0 min and 320 °C-30 min, (b) 250 °C-10 min and 320 °C-30 min, (c) 250 °C-20 min and 320 °C-30 min, (d) 250 °C-30 min and 320 °C-30 min, (e) 250 °C-45 min and 320 °C-30 min, (f) 250 °C-60 min and 320 °C-30 min.

#### 2.1.3 Variation of nanocube growth time

The effect of growth time on nanocubes were studied at 320 °C with varied periods (20, 30, 60, or 120 min) (Fig. S4). The shorter growth time (320 °C-20 min) also yielded nanocubes, but smaller size and wide size distribution (Fig. S4a). Interestingly, elongated growth time (320 °C -60 min) actually made the size distribution wider with observed tiny nanoparticles (Fig. S4c). This phenomenon was likely due to the nanocube by sodium oleate or residue of NaCl, a by-product from precursor preparation. Continuous heating (320 °C-120 min) led to bigger nanocubes at the expense of tiny nanoparticles with wider size distribution (Fig. S4d), due to the ostwald ripening effect.



**Fig. S4** TEM images of Fe<sub>3</sub>O<sub>4</sub> nanoparticles prepared by varying nanocube growth time. (a) 250 °C-20 min and 320 °C-20 min, (b) 250 °C-20 min and 320 °C-30 min, (c) 250 °C-20 min and 320 °C-60 min, (d) 250 °C-20 min and 320 °C-120 min.

#### 2.2 NaOA effect experiments

In a typical reaction, extra NaOA (equal to the molar amount of  $M^{2+}$  ions) was introduced during precursor preparation to ensure a complete formation of the precursor. To study the NaOA effect, the extra amount of NaOA was removed during the precursor preparation. The weight of the modified precursor was calculated based on the final concentration of Fe<sup>2+</sup>–oleate and Fe<sup>3+</sup>–oleate in our typical reaction. Using the same heating manner (250 °C–20min, 320 °C–30min), the removal of extra NaOA led the formation of Fe<sub>3</sub>O<sub>4</sub> nanoparticles with irregular shapes and sizes (Fig. S5). A possible explanation was that, at high temperature (>200 °C), alkaline metal oleates dissociated and produced a certain amount of ion pairs (sodium cations and oleate anions), which drastically increased the solution conductance.<sup>3</sup> Different from the growth direction facilitated by oleate anions, the sodium cations were capable of inducing nanoparticle morphology transition (to cubic shape) by both surface absorption and inner part incorporation.<sup>4</sup> Moreover, the etching / corrosion by the molten sodium ions should be also considered as the other cubic-shape formation mechanism.<sup>2</sup>



**Fig. S5** TEM images of Fe<sub>3</sub>O<sub>4</sub> nanoparticles synthesized using a modified precursor (no extra NaOA).

#### References

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