Correlating Size and Composition-Dependent Effects with Magnetic, Mössbauer, and PDF Measurements in a Family of Catalytically Active Ferrite Nanoparticles

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Abstract: The magnetic spinel ferrites, MFe_2O_4 (wherein 'M' = a divalent metal ion such as but not limited to Mn, Co, Zn, and Ni), represent a unique class of magnetic materials in which the rational introduction of different 'M's can yield correspondingly unique and interesting magnetic behaviors. Herein we present a generalized hydrothermal method for the synthesis of single-crystalline ferrite nanoparticles with 'M' = Mg, Fe, Co, Ni, Cu, and Zn), which can be systematically and efficaciously produced simply by changing the metal precursor. Our protocol can moreover lead to reproducible size control by judicious selection of various surfactants. As such, we have probed the effects of both (i) size and (ii) chemical composition upon the magnetic properties of these nanomaterials using complementary magnetometry and Mössbauer spectroscopy techniques. The structure of the samples was confirmed by atomic PDF analysis of X-ray and electron powder diffraction data as a function of particle size. These materials retain the bulk spinel structure to the smallest size (i.e. 3 nm). In addition, we have explored the catalytic potential of our ferrites as both (a) magnetically recoverable photocatalysts and (b) biological catalysts, and noted that many of our as-prepared ferrite systems evinced intrinsically higher activities as compared with their iron oxide counterparts.

Introduction

Magnetic nanomaterials have become an area of considerable focus, due to their unique physicochemical properties by contrast with their bulk counterparts. Specifically, the so-called metal ferrites, MFe_2O_4 (wherein ‘M’ = Co, Zn, Ni, and Mn), for example, represent a well known and unique class of materials, which have long been studied for their novel magnetic and electronic properties. MFe_2O_4 possesses a cubic spinel structure in which the oxygen atoms are placed in a cubic close-packed arrangement with the metal atoms residing at tetrahedral and octahedral sites, labeled as (A) and [B] sites, respectively.^{1, 2} It is known that altering the occupancies of the (A) and [B] sites can give rise to slight variations of the spinel structure, which can affect the corresponding nature and magnitude of superexchange interactions,³ namely A – A, B – B, and A – B, of which the A – B interactions tend to be highly significant. Exhibiting reliable control over the distribution of M^{2+} and Fe^{3+} cations in each site should result in an intrinsically magnetically tunable system.¹ Hence, by choosing either the appropriate M^{2+} ion or mixture of M^{2+} ions, a wide variety of magnetic behaviors can be observed.

Specifically, below 20 nm in size, ferrite nanoparticles display size-dependent superparamagnetic behavior as well as high saturation magnetization.⁴ In addition, the metal ferrites exhibit high electrical resistivity, high permeability, and excellent chemical stability, thereby rendering them as ideal candidates for electromagnetic applications, spanning both high frequency and wide temperature ranges.¹ Therefore, by combining these properties with the advantages of nanoscale materials (e.g. small sizes, high surface area-to-volume ratios, and often tunable size-dependent properties), ferrite nanostructures inherently possess multiple advantages over other magnetic materials and are also generally lower in cost, thereby enhancing their potential in numerous, wide-ranging applications. Specifically, ferrites have been investigated as active materials for biomedical devices,⁵⁻⁷ sensors,^{8, 9} batteries,¹⁰ magnetic energy storage,¹¹ components for electronics,^{9, 12} magnetically

recoverable catalyst supports,¹³⁻¹⁶ photocatalysts,¹⁷⁻¹⁹ and magnetic resonance imaging (MRI) contrast agents.^{5, 20}

The key to tailoring ferrite nanomaterials for actual real-world applications is by either creating new or modifying existing synthetic protocols to precisely control the size, composition, crystallinity, and morphology of these nanomaterials in order to generate dependable structure-property correlations. Such a strategy entails developing a synthetic methodology, which is not only facile but also reproducible with a number of independent reaction variables which can be reliably adjusted, so as to yield a desired, tailored product.

To date, there have been numerous methods utilized for the synthesis of nanoscale motifs of MFe_2O_4 . These have included methodologies based on hydrothermal^{10, 21} and solvothermal techniques,²²⁻²⁴ thermal decomposition,^{2, 5, 7, 20, 25-28} co-precipitation,^{4, 29-31} electrochemical manipulation,³² microemulsion,^{1, 33, 34} and other solution-based treatments (i.e. sol-gel, polyol, and so forth).³⁵⁻⁴¹ However, an overwhelming majority of the existing literature is primarily associated with developing workable protocols for the production of a *single* spinel ferrite. As such, there are relatively few generalized and established methods that have been practically applied to the controlled synthesis of broad classes of ferrites of various chemical compositions.^{2, 4, 5, 20, 22-24, 28}

Herein our contribution has been to devise a generalized hydrothermal method (Section I) for the reproducible synthesis of pure single-crystalline MFe_2O_4 nanoparticles, wherein ‘M’ = Mg, Co, Ni, Cu, Zn, and even Fe, in which a simple variation of the metal precursor permits for the corresponding production of ferrites of various chemical compositions. We have moreover investigated the role of reaction time, choice of precursor, temperature, pH, and surfactants and correlated their individual effects with the corresponding degree of control over the size, crystallinity, and morphology of our as-prepared nanoparticles. Of the reaction parameters analyzed, the choices of precursor and inclusion of surfactants were determined to have most markedly affected the particle composition, phase

purity, and size, respectively. In addition, unlike prior reports, we also noted that a relatively long reaction time (≥ 12 hours) was not critical and for instance, we were able to significantly reduce the overall reaction time to 3 hours in the case of zinc ferrites.

The key contribution of our work is that we include a comprehensive set (Section II) of magnetic characterization data from Superconducting Quantum Interference Device (SQUID) vibrating sample magnetometry and Mössbauer spectroscopy collected on our family of ferrite nanoparticles as a function of morphology, physical size, and chemical composition, to an extent rarely attempted prior to this current study. Finally, in Section III, we carry out a detailed structural study of the nanomaterials in an attempt to relate the magnetic properties to structural features. The structural analysis combines (i) an atomic pair distribution function (PDF) analysis of X-ray powder diffraction data collected at the National Synchrotron Light Source at Brookhaven National Laboratory (BNL) with (ii) an electron PDF (ePDF) analysis⁴² using electron diffraction data obtained at the Center for Functional Nanomaterials at BNL.

In addition to structural characterization, we have investigated the potential of our ferrite nanoparticles as catalysts (Section IV) for peroxidase-like applications and as magnetically separable photocatalysts. In the presence of methylene blue, we investigated the photocatalytic potential of our ferrite nanoparticles under UV irradiation. These experiments revealed that the photocatalysis process is composition-dependent, with Mg ferrite nanoparticles as the most active of the series studied herein. Moreover, we find that our nanoparticles display enhanced activities even at concentrations of 0.25 g/L, a level which is significantly less than the 1.0 g/L concentrations previously reported in the literature.

Furthermore, we also determined that many ferrite nanoparticles exhibit peroxidase-like activity towards a typical, conventional substrate. Specifically, Mg, Co, and Cu ferrite nanoparticles yielded higher catalytic activities by comparison with iron oxide. Hence, we have highlighted the multifaceted potential of our as-prepared nanostructures, because, in

addition to their robust magnetic properties, our ferrite nanoparticles are also excellent catalysts, with specific chemical compositions consistently yielding intrinsically higher activities. In essence, our novelty herein has been to demonstrate an unprecedented understanding of structure-property correlations in as-prepared nanoscale ferrites.

Experimental

Materials and Reagents. For the metal precursors themselves, different variations were tried, depending on the desired metal ferrite and size. Specifically, we used cobalt (II) chloride (anhydrous, 97 %, Aldrich), cobalt chloride heptahydrate (98%, Aldrich), zinc (II) fluoride (99 %, Aldrich), zinc chloride (Aldrich), copper chloride (Baker), copper (II) nitrate trihydrate (98 %, Alfa Aesar), magnesium boride (Alfa Aesar), magnesium sulfate (Mallinckrodt-Baker), magnesium nitrate (analytical reagent, Mallinckrodt), nickel (II) sulfate hexahydrate (Acros Organics), nickel acetylacetonate (95 %, Sigma Aldrich), nickel chloride hexahydrate (Baker), nickel fluoride (99 %, Aldrich), nickel oxalate (99.9985% metals basis, Alfa Aesar), magnesium chloride (98 %, Aldrich), iron (II) chloride tetrahydrate (99 %, Aldrich), and anhydrous iron (III) chloride (98 %, EM Science) to synthesize cobalt, zinc, copper, magnesium, nickel, and iron ferrites, respectively.

In addition, as solvents, surfactants, as well as catalytic substrates and reagents for our synthesis and catalysis experiments, we also utilized ethanol (99.5+ %, 200 proof, anhydrous, Acros Organics), toluene (ACS reagent, Acros Organics), dimethyl sulfoxide (99.8+ %, anhydrous, Alfa Aesar), meso-2,3-dimercaptosuccinic acid (97%, Alfa Aesar), 3-aminopropyltriethoxysilane (APTES, 99 %, Acros Organics), Igepal CO-630 (Aldrich), polyvinylpyrrolidone with $M_w = 1\,300\,000$ (Acros Organics), Tergital NP-9 surfactant (polyoxyethylene(9)nonylphenyl ether, Aldrich), dextran (from *Leuconostoc spp.*, $M_w = 5\,000$, Sigma Life Sciences), Triton X-100 (EMD Industries), sodium hydroxide (99 %, EMD Science), methylene blue (Mallinckrodt-Baker), hydrogen peroxide (30% by weight aqueous

solution, Sigma Aldrich), glacial acetic acid (Mallinckrodt-Baker), sodium acetate trihydrate (Mallinckrodt-Baker), and 3,3',5,5'-tetramethylbenzidine (liquid TMB substrate, Sigma-Aldrich). All of these reagent chemicals were used, as received, without any additional purification steps involved.

Methodology. MFe_2O_4 (where 'M' = Mg, Fe, Co, Ni, Cu, and Zn) nanoparticles were prepared by using a hydrothermal method, appropriately modified from previous work by Wang *et al.* which had focused on the synthesis of $MnFe_2O_4$ nanorods.²¹ Specifically, a 0.5 M solution of the desired metal precursor (e.g. $CoCl_2$, $NiSO_4$, ZnF_2 , $Cu(NO_3)_2 \cdot 3H_2O$, MgB_2 , $FeCl_2 \cdot 4H_2O$, or $FeCl_3$, depending on the desired ferrite composition) in 16 mL of water was mixed thoroughly by magnetic stirring in a beaker using a micro (flea) type stir bar at ~ 300 rpm. Subsequently, $FeCl_3$ was added to the solution in order to create a 0.1 M solution. It is important to note that the molarities of the precursor solutions were calculated by taking into account of the volume of the final solution, namely 18.3 mL, in order to fill the autoclave to 80% of its capacity. Finally, 2.3 mL of a 4.4 M solution of NaOH was added to the beaker under vigorous magnetic stirring.

After these steps, the progression of the reaction was accompanied by a visible color change from orange/yellow to a dark brown/black color, which varied, depending on the metal precursor employed. The solution was allowed to stir using a micro (flea) type stir bar at ~ 300 rpm for 30 minutes after which it was transferred to a 23 mL Teflon-lined stainless steel autoclave (Parr Instruments) and subsequently sealed. In a typical synthesis, the autoclave was placed in an oven and heated to $190^\circ C$ for 3 - 12 hours. In order to control the ferrites' size regime, surfactants such as NP9 and APTES were employed (Tables 1 and S1) at the reaction temperatures, mentioned previously. For crystalline ultra-small ferrites in particular, the autoclave was heated to $220^\circ C$ for 12 hours, and then allowed to cool naturally to room temperature. The product was subsequently washed four times with aliquots (i.e. 1 aliquot is

~10 mL) of distilled water and once with an aliquot of ethanol, isolated by centrifugation, decantation, and finally placed in a drying oven at ~80°C to remove residual solvent, thereby yielding ~150 mg of sample. As previously mentioned, variations in reaction time, temperature, and pH were explored, and the details of these findings are presented in the Results and Discussion section and the Supporting Information section (Figures S1 – S4) as well as summarized in Tables 1 and S1.

Structural Characterization. Powder samples for X-ray diffraction (XRD) were prepared using sonicated slurries of the product in absolute ethanol, deposited onto glass slides, and allowed to dry under ambient conditions. XRD analysis was conducted using a Scintag diffractometer with Cu K α radiation ($\lambda = 1.54 \text{ \AA}$), scanned with a 1° step size over a range of $20^\circ \leq 2\theta \leq 80^\circ$ in the Bragg configuration.

For transmission electron microscopy (TEM) analysis, as-prepared samples were prepared by first dispersing in ethanol, followed by placing a drop of that dilute solution onto a lacey carbon or ultrathin carbon grid (Ted Pella). We should note that the MgFe₂O₄ nanoparticles (sample Mg1) in particular were ultrasonicated for 90 min and ground with a mortar and pestle for 30 additional min in order to achieve a relatively more homogeneous sample. The samples were then dried at room temperature under air, until all of the ethanol had evaporated. The initial morphology and sizes of the final products were investigated using a FEI-Tecnai12 BioTwinG² instrument for low-resolution imaging. Size measurements were collected from a minimum of 50 particles for each sample in order to compute their average and standard deviation. High-resolution transmission electron microscopy (HRTEM) and selected-area electron diffraction (SAED) analyses were performed using a JEOL 3000F instrument at accelerating voltages of 300 kV.

For energy dispersive X-ray spectroscopy (EDS), samples were dispersed in ethanol, sonicated to ensure reasonable uniformity and homogeneity, and then deposited onto a pre-

cleaned silicon wafer. The samples were secured to an aluminum bar with either conductive carbon or copper tape. The elemental analysis was conducted using a field-emission scanning electron microscope (FE-SEM Leo 1550), operating at an accelerating voltage of 20 kV, and equipped with EDS capabilities.

Samples prepared for BET analysis were initially dried in an oven overnight to remove any residual solvents. Subsequently, ~ 100 mg of material was placed in an analysis tube and degassed for 2 hours at 150°C in order to remove any adsorbed gases on the particle surfaces. After degassing, the BET surface area analysis was conducted with a Quantachrome Nova 2200e Series Instrument with a 10-point sampling method.

Spectroscopy. Optical absorption in the far-infrared (far-IR) region was measured for the as-prepared ferrite samples using a Nexus 670 FT-IR (Thermo Nicolet) instrument, equipped with a single-reflectance zinc selenide (ZnSe) attenuated total reflectance (ATR) accessory, a solid substrate beam splitter, and a DTGS polyethylene detector. These as-prepared solid powders were placed onto the ZnSe crystal and measurements were obtained in transmittance mode using the Smart Performer module. The data shown represent an average of 64 accumulated spectra. Absorption in the UV-Visible region was measured on the solutions of each ferrite nanoparticle dispersed in ethanol. The measurements were taken with a UV1 UV-Visible spectrophotometer (Thermo Scientific).

Magnetic and Mössbauer Characterization. Magnetic data were taken on powders of ferrite nanoparticles, which were encapsulated in paraffin wax within a gelatin capsule placed into a plastic straw in order to allow for immersion into the magnetometer. Magnetization measurements were then taken with a Quantum Design Magnetic Property Measurement System (MPMS) at fields of up to 5 T and temperatures between 2 and 300 K. For Mössbauer spectroscopy, at room temperature (RT), samples were studied, as received, by dispersing in boron nitride powder. Transmission geometry experiments were performed at a constant acceleration mode. Two different spectrometers were used, namely a 1024 channel SEE Co.,

and a 512 channel Halder spectrometer with ^{57}Co radioactive sources embedded in rhodium. Both spectrometers were equipped with Janis Research Co. cryogenic dewars for sample temperature variation from $4.2 \leq T \leq 300$ K. The spectrometers were calibrated with a 6- μm thick metal iron foil enriched in ^{57}Fe as the standard absorber. All measurements were performed at high velocity (± 12 mm/s). Data were collected as counts against source velocity in mm/s. Spectral fits were carried out using either the WMOSS software package licensed by SEE Co. or the NORMOS code (Brand 1995) software package licensed by Wissel Instruments Inc. Spectral analysis was based on a least-square fitting algorithm, assuming each spectrum to be a sum of Lorentzian absorption lines grouped into quadrupole doublets and magnetic sextets, including a distribution of hyperfine fields and intermediate relaxation spectra. The relative amounts of each constituent present were determined by measuring the areas under the relevant spectral peaks, assuming equal recoil-free fractions. The isomer shifts have been given, relative to $\alpha\text{-Fe}$ at RT.

Atomic Pair Distribution Function (PDF) Analysis. PDF data were obtained from synchrotron X-ray data taken on various ferrite nanoparticles (i.e. Co and Ni ferrites), encapsulated in kapton capillary tubes with diameter 1.0 mm, sealed at both ends, and measured at 100 K under nitrogen flow. Synchrotron X-ray total scattering experiments were conducted at the beamline X17A at the National Synchrotron Light Source (NSLS) at Brookhaven National Laboratory. The rapid acquisition pair distribution function (RaPDF) technique⁴³ was applied using a large area 2-D Perkin Elmer detector (2084×2084 pixels and 200×200 μm pixel size), mounted orthogonal to the beam path with a sample-to-detector distance of 208.131 mm for Co and Ni ferrite samples, with an incident X-ray energy of 67.42 keV ($\lambda = 0.1839$ Å). The raw 2D data were azimuthally integrated and converted to 1D intensity versus 2θ using FIT2D program,⁴⁴ where 2θ is the angle between the incident and the scattered X-ray beams.

The PDFgetX3⁴⁵ program was used to correct and normalize the raw diffraction data and then Fourier transform them to obtain the PDF, $G(r)$, according to Equation E1,

$$G(r) = \frac{2}{\pi} \int_{Q_{min}}^{Q_{max}} Q [S(Q) - 1] \sin Qr dQ \quad (E1)$$

Here, $G(r)$ gives the probability of finding a pair of atoms separated by a distance of r , Q is the magnitude of the momentum transfer on scattering and $Q = 4\pi \sin\theta/\lambda$, and $S(Q)$ is the properly corrected and normalized powder diffraction intensity measured from Q_{min} to Q_{max} .⁴⁶ Moreover, to calibrate the sample-to-detector distance and to determine the Q_{damp} and Q_{broad} , the parameters that correct the PDF envelope function for instrument resolution effects, nickel was also measured as the standard material.^{47, 48} The refined values for Q_{damp} and Q_{broad} were $0.0407 \text{ \AA}^{-1}$ and $0.0185 \text{ \AA}^{-1}$, respectively. They were fixed in the subsequent model fits to the PDF data of each nanoparticle sample.

We also used the recently demonstrated ePDF method⁴² on a subset of the smallest nanoparticles of Zn and Ni ferrite. The nanoparticles were dispersed on electron microscope grids. Then the diffraction data were collected using a 20 keV electron beam on a JEOL 1400, utilizing a Gatan CCD camera with a $14 \text{ }\mu\text{m}$ pixel and a 2048×2048 viewing area. A diffraction pattern of a Si calibration standard sample of known lattice parameter was measured prior to the samples of interest (SOI). Then the calibration sample was replaced with the SOI, which were measured without changing any of the experimental parameters. The camera length calibration was performed using the software package, Fit2D,⁴⁴ which has built-in features for performing the calibration. The Debye–Scherrer rings from the Si calibration standard were fit with the known d -spacing fixed but allowing for the camera length and detector non-orthogonality to vary. The 2D diffraction images from SOI were reduced to 1D diffraction patterns using Fit2D, and then further transformed to ePDFs using an in-house program, i.e. PDFgetE.⁴⁹

The ferrite samples share the general formula $(A_{1-x} Fe_x)[A_x Fe_{2-x}]O_4$, where round and square brackets denote the tetrahedral and octahedral sites of the spinel structure, respectively. Here, ‘ x ’ represents the degree of inversion (DOI). The PDF modeling was carried out using the SrFit program.⁵⁰ The structural model of a cubic spinel with the space group of $Fd\bar{3}m$

(No. 227) was used. The fractional coordinates for tetrahedral and octahedral sites are at (1/8, 1/8, 1/8) and (1/2, 1/2, 1/2), respectively, while O atoms are located on (z, z, z). For the Co and Ni samples, the DOIs were derived from previous Mössbauer experiments and were applied in the model fits. The ePDFs from the small nanoparticles were also modeled using the same approach in the SrFit program and the same structural models.

In order to estimate the crystallite size, or the range of structural coherence of the samples, we first assume they are of spherical shape and then we consider PDFs of nanoparticles as the attenuated bulk PDF $G_{\text{Bulk}}(r)$ by an envelope function $\gamma_0(r)$ as follows, according to Equation E2:⁵¹⁻⁵³

$$G(r) = G_{\text{Bulk}}(r)\gamma_0(r), \quad (\text{E2})$$

where $\gamma_0(r)$ is expressed as

$$\gamma_0(r) = \left[1 - \frac{3r}{2D} + \frac{1}{2} \left(\frac{r}{D} \right)^3 \right] \theta(D - r), \quad (\text{E3})$$

and a Heaviside step function ensures $\gamma_0(r)$ is zero beyond the diameter of the nanoparticle,

$$\theta(D - r) = \begin{cases} 0 & D < r \\ 1 & D > r \end{cases}. \quad (\text{E4})$$

Photocatalysis. First, a Beer's law plot of methylene blue was determined using aqueous solutions, ranging from 0.05 - 5 mg/L in concentration. For the photodegradation experiments, 25 mg of the desired ferrite nanoparticles have been added to a beaker containing 100 mL of a 5 mg/L aqueous solution of methylene blue, such that the ferrites maintain a concentration of 0.25 g/L. The solution was stirred magnetically at 400 r.p.m. in order to establish an absorption/desorption equilibrium between the dye and the nanoparticles. The solution was then irradiated at 366 nm with an Entela UVGL-58 Mineralight UV lamp (115 V ~ 60 Hz,

0.16 Amps), placed at a distance of ~ 2 cm from the beaker. Aliquots were taken at hourly intervals, and then subjected to centrifugation at 7000 r.p.m. in order to separate the nanoparticles from the dye. The supernatant was transferred to a quartz cell, and the optical absorbance was measured over the range of 200 - 800 nm with a UV1 UV-Visible spectrophotometer (Thermo Scientific). The absorbance at 664 nm was utilized to calculate the dye concentrations from a linear fit of the Beer's law plot. The final concentration over the initial concentration (C/C_0) was plotted with respect to time to elucidate the reaction order.

Peroxidase-like activity. All experiments were carried out at room temperature in a 3.5 mL quartz cuvette. Aqueous solutions of the ferrite nanoparticles were prepared at 1 mg/mL concentrations in a sodium acetate buffer (0.2 M, pH 4) solution. 1 mL of ferrite solution was mixed with 1 mL of 30% H_2O_2 and 1 mL of the liquid TMB substrate. Upon addition of the generally colorless TMB, a blue color change was observed. Subsequent changes in absorbance, denoting reaction progression, were monitored in rate mode at 652 nm (the maximum absorption wavelength of $TMB^{+•}$, a blue one-electron oxidation product representing the cationic free radical analogue of TMB) as a function of time, using a UV1 UV-Visible spectrophotometer (Thermo Scientific).

Results and Discussion

We systematically investigated several reaction parameters in our hydrothermal synthesis of the spinel ferrites, including reaction time, reaction temperature, the nature of the precursor, concentration of NaOH, and the nature of the surfactants. In our synthesis approach, we found that we could exhibit control over ferrite composition mainly by changing the identity of the metal precursor. Additionally, by utilizing surfactants, specifically Igepal CO-630 (NP-9) and 3-aminopropyltriethoxysilane (APTES), we were able to reliably control particle size. When employing APTES in particular, we were able to generate reasonably

monodisperse ultra-small nanoparticles (i.e. measuring ≤ 4.0 nm in diameter) for a series of Co, Ni, and Zn metal ferrites.

The respective roles of various synthesis parameters such as reaction temperature, reaction time, base concentration, and surfactant were systematically analyzed, highlighted, and ultimately discussed in the Supplementary section (Figures S1, S2, S3, and S4). Specifics for each individual reaction we tried can be found in Table S1. The details for the most relevant and salient products used for our subsequent characterization and catalysis experiments are highlighted in Table 1. Of the experimental parameters probed, we found that (a) the nature of the precursor as well as (b) the surfactant yielded the most significant effect upon the resulting product chemical composition and size, respectively. The effects of all individual parameters tested and the corresponding outcomes on the resulting products yielded are discussed in exhaustive detail in the Supporting Information section.

I. Product Characterization - Size, composition, and morphology of as-generated ferrites

In our efforts to generate our ‘family’ of ferrite systems, we systematically tested out various precursors of different transition metals (Table S1) under standard synthetic conditions (i.e. 190°C for 12 h and in the absence of surfactant). In so doing, we were able to generate ferrite nanoparticles, possessing different chemical compositions. Specifically, we successfully synthesized reasonably pure, ‘optimized’ nanoparticles of MgFe_2O_4 , CoFe_2O_4 , NiFe_2O_4 , CuFe_2O_4 , and ZnFe_2O_4 with precursors of MgB_2 , CoCl_2 , NiSO_4 (or $\text{Ni}(\text{acac})_2$), $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$, and ZnF_2 , respectively, although other precursors were found to work as well in these syntheses to varying degrees. The corresponding, representative XRD data, shown in Figure 1, demonstrate that the samples can be readily indexed to the pure cubic spinel ferrites (space group: $\text{Fd}\bar{3}m$) with no readily detectable impurities, though we found MgFe_2O_4 to possess a minor impurity phase consisting of orthorhombic Fe_2O_3 (JCPDS #72-6233). We also note that to synthesize pure iron oxide (i.e. magnetite, Fe_3O_4), $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$

was specifically used as the precursor (samples Fe1 and Fe2, i.e. Figures S1B and S1E). By contrast, if FeCl_3 were utilized as the precursor, as with the other ferrite systems synthesized, only large spheres of Fe_2O_3 (sample Fe3) could be generated (Figure S1A).

Representative images of transmission electron microscopy (TEM) analysis of typical nanoparticles of metal ferrites, shown in Figure 2, revealed that the nanoparticles were reasonably uniform in size and shape. Subsequent investigation with high-resolution TEM (HRTEM) evinced that the as-prepared nanoparticles were single-crystalline in nature (Figure 3) with no visible defects or dislocations. The corresponding selected-area electron diffraction (SAED) patterns showed a ring-like pattern with relatively sharp discrete spots (Figure 3, respective insets), which are typical for single-crystalline materials, possessing a small particle size with respect to the diameter of the selected-area aperture. The visible rings in the SAED pattern could be indexed to the (111), (220), (311/222), (400), (422), (440), and (511) hkl spacings, respectively, for cubic MFe_2O_4 with 'M' representing a given metal.

In general, we noted that the presence of APTES and NP-9, a cationic and a non-ionic surfactant, respectively, could reduce the size of the ferrite nanoparticles. It is well known that the presence of surfactants can potentially alter the particle size of nanostructures by creating a barrier for mass transfer and correspondingly modulating the surface energy of coated nanoparticles, therefore potentially decreasing their surface tension. This can prevent nanoparticle agglomeration. Furthermore, for our specific reaction protocol, the dissolution of the metal precursors under basic conditions in NaOH allows for the formation of metal hydroxides, which can then intercalate between the NH_3^+ groups of APTES so as to form ion pairs by electrostatic interactions.⁵⁴ That is, the differential selective adsorption and interactions of both APTES and NP-9 with inorganic precursors can impact the nucleation process, and therefore, subsequently affect the resulting crystallite size.

Not surprisingly, TEM and HRTEM images of our crystalline ultra-small Zn and Ni ferrites prepared in the presence of APTES at higher reaction temperatures (220°C) than

conventional standard reaction temperatures (190°C) are shown in Figure 4A-B and Figure 4C-D, respectively. On the basis of statistical measurements of several tens of nanoparticles, pertaining to each sample analyzed, the average diameters of our crystalline as-prepared Zn and Ni ferrites, i.e. the so-called “ultra-small nanoparticles”, were noted to be 3.1 ± 0.7 nm and 3.0 ± 0.6 nm, respectively. Nevertheless, we should note that the expected crystal structure and crystallinity of these ultrathin samples were confirmed by XRD, and are shown in the Figure S5. By contrast, we should note that the ‘ultra-small’ metal ferrites prepared at the standard reaction temperature (190°C) in the presence of APTES (Figure S1B-D and S6) are amorphous and that the average size of these spherical particles (i.e. the Co₃ sample) is ~ 2.6 nm (Figure S6A). For the sake of brevity, all of the characterization data associated with amorphous samples have been placed in the Supplementary Information section.

Moreover, the crystallinity of our ultra-small nanoparticles were further confirmed by HRTEM and SAED patterns (Figure 4C-D and respective insets). HRTEM images in particular revealed interlayer spacings, corresponding to the expected lattice parameters associated with the spinel cubic structure of Zn and Ni ferrites, respectively. Interplanar spacings were estimated to be ~ 0.253 nm and 0.249 nm, respectively, corresponding to the (211) planes. In addition, the associated SAED patterns shown in the insets could be indexed to the reflection of a pure, crystalline spinel cubic structure.

Our ferrite nanoparticles were also analyzed by using energy-dispersive X-ray spectroscopy (EDS) to determine elemental composition. In all cases, we observed the expected peaks for ‘M’, Fe, and O as well as for Si, the last of which could be attributed to the underlying silicon wafer substrate. Moreover, we also employed Fourier transform infrared spectroscopy and UV-visible spectroscopy to confirm the presence, most notably of Fe-O-related signals. All of these data are described in more detail in the Supporting Information section (Figure S7).

II. Magnetic Characterization of Ferrites with SQUID and Mössbauer spectroscopy

We have systematically probed a number of our ferrite nanoparticles by magnetic characterization via SQUID magnetization measurements and Mössbauer spectroscopic analysis in an effort to correlate with the particle size and composition.

AI. Magnetization Analysis of CoFe_2O_4 nanoparticles.

First, we explored the series of CoFe_2O_4 nanoparticles. The M versus H curves at 5 K (Figure 5A) and 300 K (Figure 5B) indicated that particles of different sizes exhibit distinctive hysteresis loops. However, the corresponding zero field-cooled (ZFC) and field-cooled (FC) magnetization curves, shown in Figure 5C, are dominated by interparticle magnetic interactions, as evinced by the rather flat FC magnetization curves. What is observed is the collective magnetic behavior of the particle ensemble, a spin-glass-like magnetic state. Bare nanoparticles interact magnetically via two mechanisms, namely (a) exchange interactions across grain boundaries and (b) dipole-dipole interactions. The former are short-ranged and can be readily eliminated by encapsulating each particle within a thin layer of surfactant. The latter, however, are longer-ranged and are present in all types of nanoparticle assemblies. In fact, they become negligible only at high magnetic dilution, i.e., at large interparticle distances and/or small particle moments.⁵⁵⁻⁵⁸ The bare 23.5 nm particles interact strongly through both mechanisms, whereas the surfactant-coated 14.9 nm diameter particles primarily interact via dipole-dipole magnetic interactions. These interactions prevent superparamagnetic relaxation and result in a collective magnetically blocked state at and below room temperature.

In the Supplementary Information (SI) section, we present additional data for ‘ultra-small’ ferrite nanoparticles possessing an average diameter of ≤ 3 nm. For the ~ 2.6 nm average diameter CoFe_2O_4 surfactant-encapsulated nanoparticles investigated, the total particle moment or “macrospin” is drastically diminished, as indicated by the almost 8-fold reduction in saturation magnetization, observed at room temperature as compared with the larger particles (Table S2 and Table 2). This significantly reduces the strength of the

interparticle dipole-dipole interaction, thereby allowing for single-particle spin reversals and the detection of superparamagnetic relaxation of individual particles. Hysteresis loops and ZFC/FC curves are characteristically different as compared with those of the larger cobalt ferrite particles (Figure S8). The relatively sharp maximum in the ZFC magnetization curve and the $1/T$ -like increase of the magnetization as $T \rightarrow 0$ (Figure S8C) are consistent with superparamagnetism. The maximum in the ZFC magnetization curve determines the superparamagnetic blocking temperature, T_B , to be about 45 K, above which superparamagnetic behavior is expected. Thus, in this case, we observe an over-all behavior, which is consistent with the presence of magnetically non-interacting or weakly interacting magnetic nanoparticles.

It is important to note that in most cases, the magnetization of the samples did not completely saturate, even in the largest magnetic field of 5 T applied. This is a telltale sign of nanoparticle magnetism, attributed to spin canting at the particle surface,⁵⁹ meaning that the surface spins are not perfectly aligned with the core, but tilt away from the particle's anisotropy axis. This effect is very pronounced in the case of sample Co3, measuring 2.6 nm in average diameter, respectively, which exhibits the most pronounced lack of magnetic saturation (Figure S8). Nonetheless, herein, the M_S has been recorded as the value of the magnetization observed at the maximum applied magnetic field of 5 T (Table S2).

The largest 23.5 nm-sized particles analyzed (sample Co1) evince clear expected ferromagnetic behavior, as shown by the hysteresis loops obtained at 5 K and 300 K, since the ZFC/FC curve shows that the magnetization is blocked above 300 K. The saturation magnetization (M_S) and coercivity (H_C) at 300 K are 74.5 emu g^{-1} and 849 Oe, respectively. The M_S is close to the reported value of 80.8 emu g^{-1} for bulk CoFe_2O_4 ,⁶⁰ which is expected, given the relatively large particle size. At 5 K, the M_S value increases to 85.3 emu g^{-1} and the coercivity dramatically increases to 11842 Oe, consistent with previous studies.^{2, 40} The observed increase/decrease in M_S for larger/smaller particles is likely due to the particles'

internal spin structure, which results in the formation of a magnetic core-shell architecture, consisting of a spin-ordered core and spin-disordered shell, due to either spin canting or surface anisotropy.^{40, 61}

The 14.9 nm diameter particles (sample Co2) displayed a highly constricted hysteresis loop, as evinced by the presence of a sharp step at 5 K and 300 K at low applied field (insets to Figures 5A and B). These observations are consistent with some prior reports in the literature^{28, 30, 40} and can be potentially attributed to different phenomena. First, during the synthetic process, the Co^{2+} ions and/or cobalt vacancies can be aligned in a preferential direction, thereby resulting in a highly anisotropic system which produces a net magnetic moment as a result of the aligned spins. Further evidence for a more magnetically anisotropic system is displayed in the higher remanence ratios (M_R/M_S) of the cobalt ferrite nanoparticles (Table 2). Alternatively, this can also be ascribed to competition between different spin ordering structures,⁶² such as spin canting effects⁵⁹ and/or a random distribution of cations between the (A) and [B] subsites, as aging experiments on CoFe_2O_4 have shown.⁶³

Nanostructures are known to trap non-equilibrium states; a lack of cation order within the lattice will fail to establish a clearly preferred anisotropy axis. In this case, under a weak applied field, intrinsic random neighbor spin-spin interactions could trigger the production of a spin disordered state with a sharply reduced magnetization and a constricted hysteresis loop. Therefore, in order to assist in differentiating amongst these various plausible structural scenarios, we have employed Mössbauer spectroscopy to probe the nature of metal cation occupancies in these systems.

A2. Mössbauer analysis of $M\text{Fe}_2\text{O}_4$ nanoparticles.

The room temperature (RT) Mössbauer spectra for samples Co1 and Co2 are shown in Figure 5D. They exhibit six-line absorption spectra, indicative of static magnetic order. They were fit to a superposition of two poorly-resolved iron magnetic sub-sites corresponding to

Fe^{3+} at the tetrahedral Fe(A) and octahedral Fe[B] sites, including distributions of hyperfine fields. The ultra-small 2.6 nm nanoparticles (sample Co3), on the other hand, exhibited a collapsed quadrupolar spectrum at RT (Figure S9, top spectrum), consistent with the presence of superparamagnetism. This spectrum was fit to the superposition of two poorly resolved quadrupolar sub-sites (Table S3), corresponding to the Fe(A) and Fe[B] spinel crystallographic sites, with the larger quadrupole of $\Delta E_{Q1} = 0.94 \pm 0.05$ mm/s, associated with the tetrahedral (A) site, and the smaller quadrupole of $\Delta E_{Q2} = 0.53 \pm 0.05$ mm/s, correlated with the more symmetric octahedral [B] site.

Table 3 summarizes some of the fitted hyperfine parameters values obtained for the various ferrite nanosystems studied. The hyperfine field distributions experienced by the iron nucleus at a particular site is sensitive to the number of M^{2+} nearest neighbors, which gives rise to the observed field distributions. For the case of CoFe_2O_4 , the average magnetic fields at both Fe(A) and Fe[B] sites are considerably reduced as compared with the corresponding bulk values of $B_{\text{HF}}(\text{A}) = 511.5$ kOe and $B_{\text{HF}}[\text{B}] = 550$ kOe, as a result of finite size effects.⁶⁴ We note that depending on particle size, the spectra can exhibit either quadrupole doublets (fast spin relaxation) or magnetic sextets (slow spin relaxation). For example, in the case of the 7.4 nm Ni₂ ferrite sample, Table 3 indicates that satisfactory fits necessitated the inclusion of small contributions of dynamic, intermediate spin relaxation sub-spectra associated with sites (A) and [B] with much reduced hyperfine magnetic fields.

It is also important to highlight the difference in the DOIs, which measure the relative Fe^{3+} site occupancy in tetrahedral and octahedral sites, derived from the ratio of the spectral absorption areas Fe(A)/Fe[B] in the Mössbauer spectra. In a normal spinel structure, M^{2+} ions should all reside at the tetrahedral (A) site, whereas for an inverse spinel structure, these ions are localized at the octahedral [B] site. Indeed, the site occupancies can significantly affect the magnetization values of the sub-lattices and, therefore, the overall magnetization of the sample. Previous reports on both nanosized and bulk CoFe_2O_4 ^{64, 65} have suggested a range of

different degrees of inversion. For example, bulk Co ferrite thermally treated at 1200°C yielded a Fe(A)/Fe[B] value of 0.92 ± 0.04 for slowly cooled samples but an analogous number of 0.65 ± 0.03 for rapidly quenched samples.⁶⁵

For nanosized powders⁶⁴ without any thermal treatment, the ratio of Fe(A)/Fe[B] was found to be 0.73 ± 0.07 . Our CoFe_2O_4 nanostructures exhibited degrees of inversion of 0.39 ± 0.09 , 0.45 ± 0.10 , and 0.37 ± 0.09 for the 2.6 nm (sample Co3), 14.9 nm (sample Co2), and 23.5 nm particles (sample Co1), respectively. These results reinforce observations in the literature that the degree of inversion (DOI) is affected by the synthetic protocol, processing techniques, and processing treatments. More importantly, our analysis shows that both magnetization and the DOI values are highly sensitive to nanoparticle size. Specifically, the increase in the DOI numbers with decreasing particle size implies that more Co^{2+} ions may be occupying more of the [B] sites, as the size is reduced.

A3. SQUID and Mössbauer analysis of Amorphous Ultra-small 2.6 nm CoFe_2O_4 nanoparticles.

Of importance for properly understanding the effect of size, the observation of full superparamagnetic behavior in sample Co3 with a 2.6 nm diameter has allowed for complete micromagnetic characterization of this system.⁶⁶ The superparamagnetic relaxation time (Equation 1) is modeled by the celebrated Néel relaxation process.⁶⁷⁻⁷⁰

$$\tau_s = \tau_0 e^{\frac{KV}{kT}} \quad (1)$$

Here, τ_s gives the relaxation time of the particle's "macrospin", τ_0 is the attempt time for spin reversals, K yields the uniaxial magnetic anisotropy density, V represents the volume of the particle, k is Boltzmann's constant, and T denotes the temperature; KV provides the anisotropy energy or energy barrier for spin reversals. For cubic anisotropy, as is the case for magnetite as well as the spinel ferrites, the uniaxial anisotropy constant K is replaced by $K_1/4$,⁷¹⁻⁷³ where K_1 is the first coefficient of magnetocrystalline anisotropy. Unlike T_B , which is technique

dependent, K and the pre-exponential factor τ_0 represent intrinsic physical properties of the nanoparticles. Determination of the blocking temperature T_B using two magnetic characterization techniques with different characteristic measuring time windows, τ_m , permits for the corresponding analysis of the values of τ_0 and K . Hence, we have combined (i) SQUID magnetization measurements, shown in Figure S8, with $\tau_m \sim 10\text{-}100$ s, and (ii) temperature dependent Mössbauer spectroscopic studies, shown in Figure S9, with $\tau_m \sim 10^{-8}$ s, in order to obtain a complete micromagnetic characterization of this system. As discussed earlier (Figure S8 and S9), Co3 exhibits no evidence for the presence of interparticle interactions, either in its Mössbauer or SQUID behavior. This is due to the extremely small size of the particle and its lack of crystallinity; amorphous samples are expected to exhibit internal spin disorder, which results in a concomitant small “macrospin”, thereby rendering interparticle dipole-dipole interactions negligible.

Figure S9 and accompanying Table S4 provide the Mössbauer spectral profile over the temperature range of $4.2 \leq T \leq 300$ K. A blocking temperature of T_B (Mössbauer) ~ 75 K is observed, while the maximum at T_B (SQUID) ~ 45 K in Figure S8C gives the average blocking temperature for magnetization measurements. As the coexistence of doublets and sextets in the observed Mössbauer spectra extends over a large temperature range, the blocking temperature is determined where the area of the doublets and sextets are equal; this designates the average blocking temperature for the ensemble of the nanoparticles in the sample. Information about the average blocking temperature and average nanoparticle size has been used in Equation (1) to obtain $K = 2.5 \cdot 10^4$ J/m³ and $\tau_0 = 0.5 \cdot 10^{-9}$ s. Bulk CoFe₂O₄, as with all spinels, possesses cubic magnetic anisotropy,⁶¹⁻⁶³ with its first coefficient of magnetocrystalline anisotropy, K_1 , in the range of $(1.8\text{-}3.0) \cdot 10^5$ J/m³, while τ_0 is of the order of a timescale of 10^{-9} s, usually assumed for superparamagnetic nanoparticles. We note that the value of K obtained is an order of magnitude smaller than that of the magnetocrystalline

anisotropy of the bulk, in contradiction to prior reports of increased anisotropy of up to two orders of magnitude for nanoparticles, due to shape, surface, and strain anisotropy contributions.^{74, 75} Moreover, the K value is consistent with use in the PDF studies presented in Section III.

Nevertheless, we believe that this is not necessarily a surprising result, since at a particle diameter of only 2.6 nm, these systems are well below the critical magnetic characteristic exchange length scale for collinear magnetic sublattice formation in CoFe_2O_4 , i.e. $\ell_{ex} = 5.2$ nm.⁷⁶ The critical exchange length is given by $\ell_{ex} = \sqrt{\frac{A}{\mu_0 M_s}}$, where ‘ A ’ represents the Co ferrite lattice exchange stiffness, which depends upon the strength of the superexchange interactions between neighboring spins and the strength of the magnetocrystalline anisotropy.⁷⁷ Therefore, size matters in as much as spin canting and disorder effects permeate throughout the entire volume of this ultra-small Co particle rather than being confined at the surface. This assertion explains the much reduced M_s for this system (Table S2).

B. Magnetic Behavior of nanoscale Mg, Zn, Cu, and Ni ferrites.

The magnetic characterization data for MgFe_2O_4 (samples Mg1), ZnFe_2O_4 (sample Zn1), CuFe_2O_4 (sample Cu1), and NiFe_2O_4 (samples Ni1 and Ni3) are comparatively shown in Figure 6. Details of size and composition effects are explicitly discussed below in Section B1 for Mg and Zn ferrites and Section B2 for the corresponding Cu and Ni ferrites.

Generally speaking, except for the ultra-small 3.0 nm ZnFe_2O_4 nanoparticles (sample Zn2), hysteresis was observed at 5 K, which is characteristic of ferromagnetic behavior. Furthermore, with the exception of Zn1 and Zn2, the ZFC-FC curves of these samples are dominated by the presence of interparticle magnetic interactions, as evinced by the broad maxima of the ZFC curves and the ‘flattened out’ features of the ZF-curve below $T_{\max}$. The

temperature at which the maximum occurs ($T_{\max}$) marks the spin-glass transition temperature in the collective magnetic behavior of the nanoparticle assemblies. The observed $T_{\max}$ values (Table 2) for samples Mg1 (32.9 nm), Cu1 (13.3 nm), Ni1 (87.3 nm), and Ni3 (3.1 nm) were found to be > 300 K, 165 K, > 300 K, and 29 K, respectively. Not surprisingly, the relatively large MgFe_2O_4 nanoparticles still displayed a small degree of hysteresis at 300 K.

Interestingly, although the magnetic spin-freezing temperature was determined to be 165 K, a small hysteresis loop was still present at 300 K for the 13.3 nm Cu ferrite nanoparticles as well as for the 7.4 nm NiFe_2O_4 nanoparticles, a situation which might have been caused either by the trapping field in the superconducting magnets in the SQUID magnetometer or by the presence of some larger or agglomerated nanoparticles in the distribution. Therefore, in some instances, determining T_B from the maximum of the ZFC curve is not necessarily accurate, a finding which has been demonstrated previously.⁴ As for the corresponding as-prepared ultra-small amorphous samples, all of the relevant magnetic and Mössbauer data tables and curves are further discussed in the Supplementary Information section (i.e. Tables S2, S3, and S4, as well as Figures S8, S9, and S10).

B1. SQUID and Mössbauer analysis of nanoscale Mg and Zn ferrites

Sample Zn1 (Figure 6D) shows a relatively sharp maximum at the depressed temperatures of 22 K. This maximum is consistent with superparamagnetic blocking temperatures (T_B). However, the observation that the FC curve does not keep increasing at temperatures below T_B is inconsistent with simple superparamagnetic behavior and may indicate the onset of antiferromagnetic interactions. In the bulk, ZnFe_2O_4 is a normal spinel with the Zn^{2+} ions occupying exclusively tetrahedral (A) sites; it is paramagnetic down to 10 K, where it undergoes a paramagnetic-to-antiferromagnetic phase transition. In the nanostructured state, however, changes in the degree of inversion have been reported, resulting in competing ferromagnetic and antiferromagnetic interactions and the production of

superparamagnetic nanoparticles with blocking temperatures well above 10 K but below room temperature.²⁷ Our 3.0 nm ZnFe₂O₄ particles exhibited a degree of inversion of 0.59, with 33% of Fe³⁺ ions occupying tetrahedral (A) sites, as determined from Mössbauer spectroscopy (Table 3).

In the case of the Mg1 sample, the presence of a magnetic iron signature in the Mössbauer spectra of a relatively large isomer shift (i.e. 0.65 mm s⁻¹ at 300 K, Table 4) points to the partial reduction of Fe³⁺ to Fe²⁺, accompanied by the partial oxidation of Mg²⁺ to Mg³⁺, with concomitant changes in the intrinsic magnetic interactions in this system. This finding may be primarily due to the complicating presence of magnetite, Fe₃O₄, within the Mg1 sample itself (Figure 1), as it appears to comprise ~44% of the magnetic sub-spectrum. Nevertheless, this plausible scenario cannot be readily confirmed through XRD, because the positions of the diffraction peaks for both spinel structures, i.e. Fe₃O₄ and MgFe₂O₄, are very similar. In the magnetic data, the presence of hysteresis gives rise to a higher *M_S* value at 300 K of 34.0 emu g⁻¹ with a small coercivity of 78 Oe. The observation of high saturation magnetization coupled with low coercivities is indicative of ferrimagnetic behavior,⁷⁸ and that fact is consistent with the known behavior of nanoscale Mg ferrite.^{79, 80}

We should note that the DOI of the Mg1 sample is higher than 1, based upon fitting of the Mössbauer spectra (c.f. Table 3). For highly crystalline spinel bulk materials, the maximum DOI expected is 1. In the presence of disorder and/or defects in the nanocrystalline state, DOI could conceivably increase above 1. This may be due to the fact that surface sites, which can dramatically increase in proportion relative to the bulk at the nanoscale, will behave more like (A) sites on account of the distorted/reduced coordination at the surface, thereby explaining the Ni1 and Ni2 data, shown in Table 3.

The 7.8 nm Zn ferrite nanoparticles (sample Zn1) possess *M_S* values of 54.5 emu g⁻¹ and 15.2 emu g⁻¹ at 5 K and 300 K, respectively (Figure 6C). At different temperatures, wide ranges of saturation values have been reported from ~ 20 – 89 emu g⁻¹ at 5 K and 10 – 75 emu

g^{-1} at 300 K for ZnFe_2O_4 nanoparticles.²⁷ Our data fall within these ranges at both temperatures, representative of a Fe^{3+} cation redistribution between the tetrahedral (A) and octahedral [B] sites,⁸¹ which we had also already observed for the Mg ferrite system. Moreover, the 7.8 nm particles exhibit a flatter M versus H curve at 300 K, consistent with the presence of a paramagnetic material, in which M_S is 15.2 emu g^{-1} .

This paramagnetic behavior of the 7.8 nm ZnFe_2O_4 nanoparticles was confirmed subsequently by RT Mössbauer spectroscopy. While this sample (Zn1) also exhibited a collapsed quadrupole spectrum as did the 2.6 nm CoFe_2O_4 sample, the origin is likely to be paramagnetic. The Zn particles exhibited smaller quadrupole splitting along with narrower line widths by comparison (Table 3). This observation is not surprising, given that the Néel temperature (T_N) of bulk ZnFe_2O_4 is 10 K.⁸² Even though cation redistribution at the nanoscale is known to produce ferrimagnetism²⁷ as previously discussed, the sample is likely to be paramagnetic at room temperature.

As expected, the ultra-small ZnFe_2O_4 nanoparticles (sample Zn2) exhibited Mössbauer quadrupole behavior. Spectral fits to the superposition of two poorly resolved quadrupole doublets, corresponding to (A) and [B] crystallographic sites, indicated that the iron coordination within the ultra-small ZnFe_2O_4 nanoparticles is severely distorted away from perfect tetrahedral and octahedral coordination symmetry. The value of the quadrupole splitting for Fe(A) sites was 0.82 mm s^{-1} and that for the Fe[B] sites was 0.44 mm s^{-1} . The corresponding values for the 7.8 nm Zn ferrite particles were 0.61 mm s^{-1} and 0.35 mm s^{-1} , respectively (Table 3). Their degree of inversion also differed; sample Zn1 possessed a degree of inversion of 0.85, while for Zn2, it was reduced to 0.59. To further emphasize size effects, cobalt ferrite particles also displayed a reduction in their degree of inversion with decreasing particle size, with the 2.6 nm Co3 and 14.9 nm Co2 particles, yielding DOI values of 0.39 and 0.45. Interestingly, the amorphous sample, i.e. the 2.6 nm Co3 particles, also evinced a similar temperature-dependent trend, yielding DOI values of 0.39 and 0.51, when measured at room

temperature (Table S3) and at 4 K (Table S4), respectively. This observation either may potentially indicate cation redistribution or may arise from a differential temperature dependence of the recoil free fraction at (A) and [B] sites, or both.

B2. SQUID and Mössbauer analysis of nanoscale Cu and Ni ferrites

The M versus H curves of the copper ferrite system (sample Cu1) are quite distinctive from that of the other ferrite nanoparticle systems (Figure 6E, F). Most notably, at 5 K and 300 K, the nanoparticles exhibited very low M_S values of 4.5 emu g⁻¹ and 5.5 emu g⁻¹, respectively. Hence, we can assume that the magnetic saturation of the sample is largely unaffected by the change in temperature. However, the coercivity decreases from 485 Oe to 2 Oe upon increasing the temperature from 5 K to 300 K. As such, a small, irregular hysteresis is still present. While these values are significantly lower than those associated with other studies on similarly sized CuFe₂O₄ nanoparticles obtained through ball milling⁸³ and chemical methods,⁸⁴ relatively small values similar to ours have been reported for similarly sized CuFe₂O₄ nanoparticles obtained through a sol-gel route.⁸⁵ The composition-dependent Mössbauer spectra evinced the smallest degree of inversion among all ferrite nanosystems studied with a value of 0.28.

Interestingly, the 87.3 nm (sample Ni1), and 7.4 nm (sample Ni2) NiFe₂O₄ samples exhibited rather similar magnetic behavior, regardless of their difference in size (Figure 6G, H). The large Ni1 sample displayed a hysteresis at both 5 K and 300 K, with coercivities of 436 and 43 Oe, respectively, which is expected given that the spin-freezing magnetic transition was found to occur above 300K (Figure 6H). At 300 K, the saturation magnetization was 46.0 emu g⁻¹, which is very close to the value of 47.5 emu g⁻¹ reported for bulk NiFe₂O₄.⁸⁶ It is noteworthy that for the Ni1 sample, an additional contributing factor to the broad maxima may be its relatively large size distribution (see Table 1).⁸⁷ The bulk-like

magnetic behavior of these particles is expected, given the much larger average particle size as compared with the other ferrite systems tested.

However, the ultra-small ~ 3 nm Ni particles (i.e. Ni3 sample) displayed a somewhat different magnetic behavior with a measured spin-glass freezing temperature of 261 K (Table 2) and we also noted the presence of a slight hysteresis at 300 K with a small coercivity of 17 Oe. Interestingly, above 2 K, the increase in field magnitude with temperature of the ZFC curve attained a maximum, observed at approximately $T_B = 29$ K, a phenomenon which could be ascribed to the presence of superparamagnetic crystallites. These ultra-small particles also evinced relatively low M_S values (i.e. 12.1 emu g^{-1}), as opposed to bulk NiFe_2O_4 (i.e. $M_S = 55 \text{ emu/g}$).⁸⁸ This observation overall may be potentially attributed to superparamagnetism at the nanoscale. By contrast, at 300 K, the Ni ferrite systems (i.e. 7.4 nm and 87.3 nm) behaved like soft magnetic materials with high saturation values and low coercivities. This behavior is also consistent with ferrimagnetic behavior.

The observed behavior of the degree of inversion of the Ni samples, as reported in Table 3, is in need of further explanation. In the bulk, NiFe_2O_4 is known to be an inverse spinel with Ni^{2+} ions residing on [B] sites and Fe^{3+} ions residing in (A) and [B] sites. Thus, in the absence of defects, bulk NiFe_2O_4 should exhibit a degree of inversion of 1. Both Ni1 (87.3 nm) and Ni2 (7.4 nm) exhibit degree of inversions larger than 1, which can be explained by the presence of surface sites that behave more like (A) sites, due to the decrease of iron coordination at the surface. One would have expected a monotonic increase in the degree of inversion as the particle size becomes even smaller, namely with our Ni3 (3 nm) samples, as the surface to bulk ratio increases with decreasing particle size. By contrast, the degree of inversion for Ni3 decreases to 0.74. This observation is consistent with previous reports that ultra-small particle sized nanocrystalline NiFe_2O_4 becomes a mixed spinel, with some Ni^{2+} ions forced to occupy (A) sites.⁸⁹ This will decrease the Fe^{3+} occupancy of (A) sites, thereby producing the observed reduction in the degree of inversion in Ni3.

III. Coupling Mössbauer and Magnetic Data of Ferrites with Related PDF Analysis.

The premise of using the pair distribution function (PDF) is that materials are made of multiple elements, have large unit cells, and are often low dimensional or incommensurate structures.⁹⁰ Increasingly also, they have aperiodic disorder with some aspect of the structure that is clearly different from the average crystal structure. In the case of nanoparticles, the very concept of a crystal is invalid, as the approximation of infinite periodicity is no longer a good one. Hence, the value added of a ‘total scattering’ experiment generating PDF data over a conventional powder diffraction analysis is the inclusion of diffuse scattering as well as Bragg peak intensities in the analysis, and the wide range of Q (the magnitude of the scattering vector) over which data are measured. ‘Total scattering’ data can be analyzed by fitting models directly in reciprocal-space.⁹¹

Hence, in light of the extensive magnetization data collected and interpreted, we attempted to further understand and refine the crystal structure of the ferrite samples using PDF analysis, which has already been previously applied to systems ranging from ultra-small CdSe quantum dots, with diameters of 2 nm to 4 nm, as well as to existing metal oxide systems, such as YMnO_3 particles, measuring from 10 nm to ~ 467 nm.^{53, 92} However, though MgFe_2O_4 and CoFe_2O_4 have been analyzed in the past⁹³⁻⁹⁵ using PDF, the size regime of these specific particles was nominally 6 nm or higher, and these ferrite materials conserved their cubic spinel structure. Herein, we are currently the first to report on a PDF analysis of a range of variously-sized nanoparticulate metal oxide samples.

For illustrative purposes, Co, Zn, and Ni ferrites with various size regimes were rigorously analyzed (Table 4). The PDFs of all the ferrite nanoparticles are plotted in the r -range up to 40 Å in Figure 7. The PDF peaks for Co1, Co2, Ni1, and Ni2 samples are still strong at 40 Å where the end point is designated, indicating well-ordered local structures in these materials. By contrast, the PDF peak intensities in Zn1, Zn2, and Ni3 samples diminish

more quickly with increasing r values, indicating a smaller structural coherence for these samples. The PDFs with a high degree of structural coherence (i.e. Co1, Co2, Ni1, and Ni2) are very similar, suggesting these samples share the same structure with each other. However, apart from the reduced size of the particles, PDF patterns of Ni3, Zn1, and Zn2 are similar to the well-ordered Ni and cobalt PDFs, indicating that the underlying structure is the same.

In order to extract more quantitative structural information, we carried out PDF model fits, using the structural model for the cubic spinel space group $Fd\bar{3}m$ (No. 227), and calculated reasonable agreement values with the experimental Synchrotron Light Source XRD and electron microscopy diffraction data (R_w) as shown in Figure 8, with the fit results summarized in Table 4. We should note that due to similar scattering potentials of the Co and Ni samples, the DOIs (as defined in the Experimental section below) were derived from previous Mössbauer experiments (see Table 3) and were used in the model fits. By an inspection of the fits, we observe a good agreement between the measured data and the simulated models for Co1, Co2, Ni1, and Ni2 with an R_w value of ~ 0.1 . The structural features of these larger particles are well described by the cubic spinel model. As the particle size decreases, the fits become worse, being in the vicinity of $R_w = 0.4 - 0.5$. This indicates that there is some ‘unfit’ component in the signal which may originate from ligand effects, for example, of the small nanoparticles. In the ePDFs of Zn2 and Ni3, there is also a residual signal from the carbon grid that supported the nanoparticles, which was not completely subtracted during the background correction. Nonetheless, it is clear that the best-fit PDFs from the models explain the structure well, with calculated peaks lining up well with the measured PDF. We therefore trust the refinements quite well and the poor R_w can be attributed to signals from impurity components as opposed to a poor fit to the nanoparticle structures. The refined parameters in Table 4 show good agreement between the ultra-small and the larger nanoparticles.

The range of signal in the PDF, which indicates the range of structural coherence, is comparable to the physical size of the particles observed in the TEM. Both of these observations suggest that the degree of structural order in the ultra-small nanoparticles is actually rather small. In effect, they appear to be very small chunks of well-defined spinel material. Notably, all the samples, especially the Ni and Zn, exhibit a very high degree of inversion between the tetrahedral and octahedral sites. There appears to be no clear structural explanation for the different magnetic response of the ultra-small nanoparticles. It is interesting to note, however, that this ultra-small particle size range coincides with the characteristic magnetic exchange length scale for magnetic sublattice formation as earlier discussed in light of the Mössbauer analysis of Co₃, and the structural disorder therefore may have a significant effect upon the magnetic properties at the smallest nanoparticle size-scale. The data table of PDF fits for the rest of the ferrite samples analyzed can be found in the Supporting Information section (Table S5).

IV. Catalysis of Ferrites.

(i). Photocatalytic Activity

It has been previously demonstrated that ferrite systems, specifically cobalt and zinc, can be utilized as photocatalysts. Generally, ferrites are utilized in composite systems, since these systems alone are not effective at separating the electron-hole pairs generated by the irradiation process (Equation 2). Hence, a second component, such as graphene, is often present, which is believed to not only provide a pathway for electron transport and prevent undesired recombination but also react with dissolved oxygen in order to produce superoxide anion radicals.¹⁸

Therefore, the holes, remaining on the ferrite, can react with adsorbed water in order to form hydroxyl radical species (Equation 3). Collectively, these active species, including holes and radicals generated by the electron acceptor, can subsequently oxidize the various tested dyes.

In this work, we have probed relatively simple reactions, involving the degradation of methylene blue (MB) under UV irradiation conditions in the presence of our as-synthesized MFe_2O_4 nanoparticles. The photocatalytic activity was determined by monitoring the optical behavior of MB at 664 nm, which represents the peak absorbance of the dye, as a function of time. As shown in Figure 9A, the nanoparticles (at a concentration of 0.25 g/L) are active as photocatalysts as compared with the control sample. Moreover, we found that their chemical composition apparently greatly influences the observed activity. Specifically, we note that our 32.6 nm MgFe_2O_4 (sample Mg1) nanoparticles exhibited the highest photocatalytic activity. This enhancement may be attributed to the interaction of the Mg1 sample with both Fe_2O_3 and Fe_3O_4 potential impurities in the sample, a process which may inhibit recombination and thereby facilitate the generation of oxidative species, such as hydroxyl radicals, relevant for methylene blue degradation.^{96, 97} The high performance of the Mg sample is followed by that of our 7.4 nm NiFe_2O_4 sample (sample Ni2), 13.3 nm CuFe_2O_4 (sample Cu1), 7.8 nm ZnFe_2O_4 (sample Zn1), and 14.9 nm CoFe_2O_4 (sample Co2) nanoparticles, respectively, in order of decreasing activity.

We were able to model the raw data as a pseudo-first-order reaction (Figure 8B), with the kinetics governed by the equation $\ln(C_0/C_t) = kt$, wherein C_0 is the initial concentration of MB, C_t is the concentration of MB at a given time 't', and 'k' is the reaction rate constant derived from the slopes of the 'best' fit lines. From this analysis, we were able to calculate pseudo-rate constants for Mg1, Ni2, Cu1, Zn1, and Co2 of $6.97 \cdot 10^{-4}$, $4.64 \cdot 10^{-4}$, $4.04 \cdot 10^{-4}$, $3.05 \cdot 10^{-4}$, and $2.75 \cdot 10^{-4} \text{ min}^{-1}$, respectively. It is worth noting that the Mg and Zn sample data do not necessarily follow a first-order fit, whereas the remainder of the ferrite nanoparticles essentially do (Table S6). By means of comparison, we have also plotted the data as pseudo-

second-order fits (Figure S13 and Table S7). We have found that the fits improved slightly for both Mg and Zn series, whereas the first order fits were still better for Co, Ni, and Cu ferrites, respectively. Nonetheless, as noted from the linear fits of the data (Figure 9B), the calculated rate constants confirmed reasonable photocatalytic activity for our ferrite nanoparticles.

Most importantly, by comparison with the available literature, our as-prepared ferrite nanoparticles evinced higher activities at lower concentrations. Specifically, Fu *et al.* reported that CoFe_2O_4 nanoparticles at a concentration of 1.0 g/L alone were photocatalytically inert under visible-light irradiation.¹⁸ Although we utilized UV-irradiation in this work, we have demonstrated that CoFe_2O_4 nanoparticles are in fact photocatalytically active, even at a lower concentration of 0.25 g/L. Similarly, in the case of ZnFe_2O_4 , we demonstrated that our nanoparticles are photocatalytically active at 0.25 g/L concentrations, although previous works have reported that ZnFe_2O_4 at a concentration of 1.0 g/L possessed either little or no photocatalytic activity under visible-light irradiation.^{17, 19} To the best of our knowledge, we are the first to report upon the photocatalytic activity of Mg, Ni, and Cu ferrites. In fact, our data suggest that these particular ferrites may be more efficient for photocatalytic applications as opposed to either Zn or Co ferrites, which have been utilized to date.

The UV-visible data for these samples (Figure S7C) may also shed some light on our observations. Of the samples explored, both the Ni and Cu ferrites exhibited evident peaks in their spectra which were large and broad. The Zn ferrite sample also gave rise to a noticeable peak, which was much narrower than that found for either the Ni or Cu samples. Cobalt and iron maintained generally low absorbances over a broad absorption range. Hence, the Ni and Cu samples can apparently absorb more light than the remaining ferrites, and therefore possess enhanced photocatalytic ability.

Although the Mg ferrite particles, like their Zn ferrite analogues, evinced lower absorbance behavior in the UV-visible region, we found that they possessed the highest activity. We utilized Brunauer-Emmett-Teller (BET) analysis to determine the accessible

surface area of the nanoparticles in order to correlate this variable with activity. BET analysis (Table 1) suggests that there is however no simple connection between surface area and photocatalytic activity. For example, highly active Mg1 with a surface area of $27.4 \text{ m}^2/\text{g}$ possesses a significantly lower surface area than many of the other ferrite nanoparticles. Our data moreover show the relative irrelevance of the choice of metal precursors themselves used to generate our metal ferrites, as the resulting photocatalytic properties are not directly correlated (Figure S14). Hence, our results suggest that for photocatalysis, the identity of the metal 'M' may actually in fact be more important than surface area and precursor considerations, presumably through the comparative, differential strengths of various ligand-substrate interactions. Nevertheless, the implication is that one should be able to reliably tune for enhanced activities, primarily by controlling overall ferrite chemical composition. Moreover, we have also demonstrated that these ferrites can be potentially deployed as magnetically separable catalysts, as they are highly responsive to the application of an external magnetic field (Figure S15).

(ii). *Peroxidase-like activity*

Previously, Gao *et al.* showed that Fe_3O_4 nanoparticles possessed the ability to mimic the enzymatic activity similar to peroxidases,⁹⁸ enzymes that can catalyze the oxidation of a variety of organic colorimetric substrates such as 3, 3', 5, 5'-tetramethylbenzidine (TMB). In many cases, the oxidation results in a color change (in our specific experiments, blue), which is typically utilized for immunoassays, sensing, and other detection methods, thereby highlighting the versatility of these materials for applications in biology, medicine, and environmental chemistry. The peroxidase enzymes function by forming a complex with and then subsequently decomposing hydrogen peroxide, which in turn oxidizes the substrate. Interestingly, many peroxidase enzymes rely on an iron-based heme group as the catalytic center. Hence, it is not surprising that iron oxide nanoparticles possess the ability to catalyze the decomposition of H_2O_2 . In this cited work, the group investigated the catalytic roles of

Fe^{2+} and Fe^{3+} , which are both known to catalyze the decomposition of H_2O_2 , and their findings suggested that the Fe^{2+} ions are more dominant in peroxidase-like catalysis as opposed to Fe^{3+} ions. By contrast, in our particular systems, the spinel ferrites lack the presence of Fe^{2+} , and instead possess other M^{2+} ions. Previously, CoFe_2O_4 ⁹⁹ and ZnFe_2O_4 ¹⁰⁰ particles have been shown to display peroxidase-like activity. Hence, we have tried to investigate the potential of our ferrite nanoparticles as peroxidase mimics, and to the best of our knowledge, we are the first to report on the activity of ferrite nanoparticles as a function of chemical composition and particle size.

In effect, by comparison with our Fe_3O_4 nanoparticles, we found that many of our ferrite nanoparticles possess noticeably enhanced peroxidase-like activities, as shown in Figure 10, involving monitoring TMB absorbance variations at 652 nm as a function of catalytic reaction time. We find that our MgFe_2O_4 and CuFe_2O_4 samples as well as the 23.5 nm and 14.9 nm CoFe_2O_4 nanoparticles displayed the highest activities. Moreover, ultra-small ferrite nanoparticles of Ni and Co also evinced enhanced activities by comparison with iron oxide (Figure 10 and S16, respectively). Interestingly, both sizes of Zn ferrite yielded very low peroxidase activity as compared with the 3.0 nm Ni ferrite sample, a finding which stands in contrast with the previous report by Su *et al.*¹⁰⁰ Overall, these observations suggested that other M^{2+} ions may be more efficient at catalyzing the decomposition of H_2O_2 than the corresponding Fe^{2+} ions.

As with our data for photocatalysis, we attempted to correlate activity with the surface areas of our nanoparticles, as we postulated that it may also be playing a role, since many of the smaller sized nanoparticles displayed high activities. However, the ultra-small particles, although they possessed the largest surface areas (Table 1), did not necessarily achieve the highest peroxidase-like activity of all the samples tested. This observation again suggests that the ferrite chemical composition may be the more significant parameter in this reaction. Moreover, we postulate that although more surface sites were likely available, the small size

of these ultra-small particles may have led to decreased activity due to either aggregation, poor accessibility, or surface passivation issues, thereby decreasing the overall reaction rate with the TMB substrate as opposed to the larger, more active ferrite nanoparticles.

Interestingly, we can correlate our Mössbauer spectroscopy results (Table 3), specifically the DOI values, to gain some additional insight into our observed catalytic enhancements. For example, samples Co1 and Co2 possess low degrees of inversion, indicating a predominance of Co^{2+} species at the nanoparticle surface. This inference comes from the fact that a majority of surface sites are (A)-type sites due to the lower metal ion coordination number at the surface, as discussed earlier. Thus, these two systems, demonstrating notable enhancements in peroxidase-like activity, suggest that Co^{2+} is a more active catalytic species as compared with Fe^{2+} . Similarly, samples Mg1 and Cu1 were also noted to yield a majority of M^{2+} ions at their surfaces with correspondingly higher peroxidase-like activities as compared with iron itself. On the other hand, both as-prepared ZnFe_2O_4 samples, which also maintain lower degrees of inversion, yielded lower catalytic activities as compared with Fe_3O_4 itself, suggesting that Zn^{2+} in particular is a less active species. The same behavior was also observed for our nickel ferrite samples.

Hence, the key point of our experiments is that not only are ferrite nanoparticles active as peroxidase catalysts but also, depending on the chemical composition (M^{2+}) and the occupation of the surface sites of the specific ferrite system in question, many of our as-synthesized nanoparticles are significantly more active than Fe_3O_4 alone at catalyzing the decomposition of H_2O_2 , thereby resulting in an appreciable enhancement of the observed peroxidase-like behavior. Additionally, peroxidase activity data associated with our ultra-small ‘amorphous ferrites’ are described and highlighted in Figure S16.

V. Conclusions

We have developed a simple, efficient hydrothermal method for the synthesis of large quantities of pure single-crystalline MFe_2O_4 (where 'M' = Mg, Fe, Co, Ni, Cu, and Zn) nanoparticles. We have explored a variety of experimental parameters in order to reliably tailor our synthesis in order to generate different compositions, sizes, and morphologies. Of the parameters investigated, the nature of the precursors as well as the inclusion of surfactant represented the most critical factors to consider in terms of 'selecting' for chemical composition and particle size. Specifically, by including APTES into the reaction solution, we could generate reasonably monodisperse, ultra-small nanoparticles possessing diameters less than 4.0 nm in size. None of the other reaction variables explored were found to give rise to any significant, controllable effect upon the resulting sample morphology or size.

By this method, we have generated different compositions and sizes of ferrite nanoparticles, which have been investigated for potential applications as (1) photocatalysts and (2) biological catalysts. In discerning practical and relevant structure-property correlations to explain these data, we utilized a combination of SQUID and Mössbauer techniques to systematically correlate nanoparticle size and composition with the observed magnetic behavior of our nanoparticles.

In so doing, we discovered that superparamagnetism is only present in the ultra-small nanoparticles (≤ 4.0 nm), with very magnetic low saturation values. The presence of spin canting, uncompensated surface spins and magnetic anisotropy was observed for a majority of our samples; blocking temperatures and spin-freezing temperatures associated with these systems were also discussed. Mössbauer spectroscopy supported the SQUID data and revealed that the occupancies of the tetrahedral Fe(A) and octahedral Fe[B] sites were significantly altered, thereby emphasizing the importance of the synthetic method, size, and chemical composition.

Moreover, our data are consistent with prior observations reported by other groups^{44, 101, 102} who have noted that (a) differential ligand-surface interactions may be responsible for

altering the observed surface spin-canting disorder and that (b) T_B as well as M_r/M_s and H_c values generally increase with increasing nanoparticle size.

PDF results indicate that the smaller nanoparticle samples are significantly more disordered, but possess the same underlying spinel structure. It is not immediately clear why their magnetic behavior is so strongly modified, though we note that this is the same size where magnetic superexchange interactions associated with the spinel structure were observed to fail by Mössbauer spectroscopy at the particle's critical exchange length scale (*vide supra*).

We also investigated our metal ferrite nanoparticles for potential application as (1) photocatalysts and (2) peroxidase-like catalysts. Our exploration on the photodegradation of MB with our ferrite nanoparticles evinced that they are indeed photocatalytically active under UV irradiation. We found that of the ferrites tested, the 32.6 nm MgFe_2O_4 nanoparticles possessed the highest activity. Moreover, similarly-sized nanoparticles gave rise to different behaviors, e.g. 7.4 nm Ni and 7.8 nm Zn ferrites, suggesting that the observed photocatalysis is primarily dependent on 'M'. By comparison with the available literature (1.0 g/L), we have demonstrated that our as-prepared ferrite nanoparticles overall possess enhanced photocatalytic properties at much lower concentrations (0.25 g/L).

Similarly, we also found that our ferrite nanoparticles are active as peroxidase-like catalysts. Specifically, samples of MgFe_2O_4 and CuFe_2O_4 nanoparticles as well as 23.5 nm and 14.9 nm CoFe_2O_4 nanoparticles evinced very high activities towards TMB oxidation as compared with Fe_3O_4 . Additionally, some of our ultra-small Ni and Co ferrite nanoparticles also displayed enhanced activities. To explain these data, by utilizing the degree of inversion obtained from our Mössbauer spectroscopy data, we were able to quantify the relative amounts of M^{2+} versus Fe^{2+} ions at the surface, thereby elucidating that both chemical composition and surface site occupancies play a significant role in catalytic activity.

Overall, these experiments highlight that our hydrothermal method generates robust, multifunctional, and fundamentally useful ferrite nanoparticles. The fact that we can tailor not

only their size and degree of crystallinity, especially in the ultra-small range below 3 nm, but also their chemical composition to a large degree therefore renders these ferrites as a highly versatile family of valuable materials, which are not only practically advantageous from an applications' point-of-view but also crystallographically significant from a fundamental science perspective.

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Supporting Information Available:

In addition to photocatalysis data, a table of samples systematically prepared by altering a number of reaction variables and the corresponding images for the synthesis optimization as a function of surfactant, reaction time, NaOH concentration, and reaction temperature as well as additional characterization data from PDF measurements in addition to results from low-temperature Mössbauer, magnetization, FT-IR, UV-visible, and EDS spectroscopies for representative ferrite nanoparticles. This material is available free of charge *via* the Internet at <http://pubs.acs.org>.

Table 1. Reaction specifics, product characterization data, and surface area for MFe_2O_4 nanoparticles. All reactions were conducted at 190°C for 12 hours without the presence of surfactant, unless explicitly specified under ‘Additional Notes’.

'M'	Sample #	Product Characterization (morphology and size)	Additional Notes	Surface area (m^2/g)
Mg	1	particles; 32.9 ± 17.9 nm	MgB_2 precursor	27.4
Fe	1	cubes; 68.9 ± 42.7 nm	$\text{FeCl}_2 \cdot 4 \text{H}_2\text{O}$ precursor	9.87
	2	particles; 4.0 ± 1.0 nm	$\text{FeCl}_2 \cdot 4 \text{H}_2\text{O}$ precursor, 1 mL of APTES used; amorphous	183
	3	Fe_2O_3 ; spheres; 222 ± 38 nm	FeCl_3 precursor	-
Co	1	particles; 23.5 ± 4.9 nm	$\text{CoCl}_2 \cdot 7 \text{H}_2\text{O}$ precursor	78.7
	2	particles; 14.9 ± 3.6 nm	$\text{CoCl}_2 \cdot 7 \text{H}_2\text{O}$ precursor, 1 mL of NP-9 ^[c] used	54.3
Ni	1	cubes; 87.3 ± 26.2 nm	NiSO_4 precursor	18.0
	2	particles; 7.4 ± 2.5 nm	$\text{Ni}(\text{acac})_2^{\text{[d]}}$ precursor	59.4
	3	particles; 3.0 ± 0.6 nm	NiSO_4 precursor, 1 mL of APTES ^[b] used; run at 220°C	345.4
Cu	1	particles; 13.3 ± 3.9 nm	$\text{Cu}(\text{NO}_3)_2 \cdot 3 \text{H}_2\text{O}$ precursor	5.8
Zn	1	particles; 7.8 ± 2.0 nm	ZnF_2 precursor	132
	2	Particles 3.1 ± 0.7 nm	ZnCl_2 precursor, 1 mL of APTES ^[b] used; run at 220°C	239.2

[a] 'particles' refers to a spherical morphology, [b] APTES = 3-aminopropyltriethoxysilane,

[c] NP9 = Igepal CO-630, and [d] (acac) = acetylacetonate.

Figure 1. XRD data (red, upper curves) associated with the pure, crystalline MFe_2O_4 products synthesized by optimizing the metal precursors used, wherein 'M' is Mg (A, Sample Mg1), Co (B, Sample Co1), Ni (C, Sample Ni1), Cu (D, Sample Cu1), Zn (E, Sample Zn1), and Fe (F, Sample Fe1). The JCPDS standards (black, lower curves) used to index the ferrites are #73-2410, 22-1086, 74-2081, 77-0010, 82-1049, and 85-1436 for Mg, Co, Ni, Cu, Zn, and Fe ferrites, respectively.

Figure 2. Representative TEM images associated with magnesium (A, sample Mg1), cobalt (B, sample Co2), nickel (C, sample Ni2), copper (D, sample Cu1), and zinc (E, sample Zn1) ferrite nanoparticles. All scale bars represent 40 nm.

Figure 3. Representative high-resolution TEM images showing single-crystalline nanoparticles of magnesium (A, sample Mg1), cobalt (B, sample Co2), nickel (C, sample Ni2), copper (D, sample Cu1), and zinc ferrite nanoparticles (E, sample Zn1). The selected-area electron diffraction patterns (A-E insets) can be indexed to the cubic spinel structure of the ferrites. All scale bars are 5 nm, except for nickel ferrite (C) in which the scale bar represents 2 nm.

Figure 4. TEM images associated with nickel (A, Ni₃) and zinc (B, Zn₂) metal ferrites prepared at 220°C. High-resolution TEM images showing single-crystalline nanostructures of nickel (C, sample Ni₃) and zinc (D, sample Zn₂) metal ferrite samples. All scale bars associated with low resolution TEM are 40 nm. The selected-area electron diffraction patterns (C-D insets) can be indexed to the cubic spinel structure of the ferrites.

Figure 5. M versus H curves at 5 K (A) and 300 K (B) with insets showing a magnified view along with ZFC-FC curves at an applied field of 500 Oe (C) for the 23.5 nm (red) and 14.9 nm (green) CoFe_2O_4 nanoparticles, along with room temperature Mössbauer spectra (D) with the solid black line, dotted green line, and dashed purple line corresponding to the theoretical fit, contribution of the Fe(A), and contribution of the Fe[B] sites, respectively. (D). Left panel: Mössbauer spectra of Co1 (bottom) and Co2 (top) at RT fitted to a superposition of two groups of magnetic hyperfine fields associated with (A) (green) and [B] (purple) sites. Right panel: Derived hyperfine field distributions for each subsite, (A) green line, [B] purple line, overall, black line, assuming Gaussian distributions.

Table 2. Magnetic characterization data associated with MFe₂O₄ nanoparticles, obtained from M versus H curves at 5 K and 300 K, along with ZFC-FC curves at an applied field of 500 Oe. Note that the unit emu/g is calculated for the total mass of the material.

Sample	Size (nm)	T (K)	H_C (Oe)	M_S (emu/g)	M_R (emu/g)	M_R/M_S	T_{max}/T_B (K)
Mg1	32.6	5	339	43.8	9.56	0.22	> 300
		300	77	34.0	3.86	0.11	
Co1	23.5	5	11842	85.3	65.52	0.77	> 300
		300	849	74.5	23.44	0.31	
Co2	14.9	5	444	88.4	54.12	0.61	> 300
		300	179	75.9	21.68	0.29	
Ni1	87.3	5	436	52.5	19.11	0.36	> 300
		300	43	46.0	3.36	0.07	
Ni2	7.4	5	364	52.0	16.8	0.32	270
		300	39	44.8	3.69	0.08	
Ni3	3.0	5	160	40.8	8.69	0.21	29
		300	17	12.1	0.19	0.01	
Cu1	13.3	5	485	5.5	1.91	0.35	165
		300	2	4.5	0.02	0.004	
Zn1	7.8	5	259	54.5	7.81	0.14	22
		300	-	15.2	-	-	
Zn2	3.1	5	18.3	7.5	0.59	0.08	6
		300	-	6.4	-	-

Figure 6. M versus H curves at 5 K and 300 K with insets showing a magnified view along with ZFC-FC curves at an applied field of 500 Oe for 32.6 nm MgFe₂O₄ (A, B), 3.0 nm and 7.8 nm ZnFe₂O₄ (C, D), and 13.3 nm CuFe₂O₄ (E, F) nanoparticles, as well as 3.1 nm, 7.4 nm, and 87.3 nm NiFe₂O₄ (G, H) nanoparticles, respectively. FC and ZFC curves are shown as solid and open markers, respectively. Note that the unit emu/g is calculated for the total mass of the material.

Table 3. Fitted ^{57}Fe Mössbauer parameters of selected MFe_2O_4 nanoparticles at 300 K.

Sample	Size (nm)	Site ^[a]	Γ ^[b] (mm/s)	δ ^[c] (mm/s)	ΔE_Q ^[d] (mm/s)	B_{HF} ^[e] (T)	HFD ^[f] (FWHM) (T)	Area ^[g] (%)	Fe(A)/Fe[B] (inversion) ^[h]
Co1	23.5	1	0.36	0.27	-	43.2	7.1	27	0.37 ± 0.09
		2	0.36	0.30	-	47.9	4.1	73	
Co2	14.9	1	0.36	0.25	-	44.1	8.1	31	0.45 ± 0.10
		2	0.36	0.35	-	47.7	4.0	69	
Zn1	7.8	1	0.34	0.35	0.61	-	-	46	0.85 ± 0.17
		2	0.27	0.35	0.35			54	
Zn2	3.1	1	0.35	0.35	0.82	-	-	37	0.59 ± 0.13
		2	0.30	0.34	0.44	-	-	63	
Ni1	87.3	1	0.31	0.26	-	48.4	2.8	56	1.27 ± 0.25
		2	0.31	0.37	-	51.7	2.4	44	
Ni2	7.4	1	0.66	0.28	-	49.9	2.1	46	1.35 ± 0.29
		2	0.66	0.38	-	51.8	1.9	31	
		SPD	0.75	0.36	0.70	-	-	6	
		1(IR)	0.50	0.31	-	27.0	15.0	8	
		2(IR)	0.75	0.31	-	44.0	8.0	9	
Ni3	3.0	1	0.50	0.30	0.86	-	-	20	0.74 ± 0.32
		2	0.50	0.31	0.43	-	-	27	
		1(IR)	0.36	0.33	-	2.0	15.2	47	
		2(IR)	0.36	0.30	-	23.7	12.1	6	
Cu1	13.3	1	0.55	0.33	-	45.8	7.8	22	0.28 ± 0.08
		2	0.28	0.38	-	51.5	2.0	78	
Mg1	32.6	SPD	0.55	0.39	0.80	-	-	36	1.06
		1	0.55	0.65	-	48.6	7.2	33	
		2	0.40	0.31	-	51.9	2.1	31	

[a] Site 1 = tetrahedral Fe(A) site, Site 2 = octahedral Fe[B] site, SPD = superparamagnetic doublet, IR = intermediate relaxation [b] full width of absorption lines at half maximum with error ± 0.03 mm/s, [c] isomer shift relative to Fe at 300 K with error ± 0.03 mm/s, [d] quadrupole splitting with error ± 0.05 , [e] hyperfine field with error of ± 0.5 , [f] Hyperfine field distribution (full width half maximum), [g] area below the spectrum with error ± 5 , and [h] degree of inversion with associated errors..

Figure 7. Measured PDFs for Co, Ni, and Zn ferrite nanoparticles of various sizes plotted in a r -range up to 40 Å.

Figure 8. PDF fits for as-prepared Co, Ni, and Zn ferrite NPs in an ‘r-range’ from 1 Å to 40 Å. The blue circles and red solid lines correspond to measured and simulated PDFs, respectively. The green solid lines offset below are the difference curves. Agreement factors, R_w , are displayed beside each model fit.

-	R _w	DOI ^a	DOI ^b	<i>a</i> (Å)	<i>z</i> (O)	<i>U</i> _{iso} (M)(Å ²) ^c	<i>U</i> _{iso} (Fe)(Å ²)	<i>U</i> _{iso} (O)(Å ²)	Structural Coherence (Å) ^d	Size (Å) ^e
Co1	0.107	---	0.540	8.365	0.256	0.0057	0.0077	0.0194	106 ^f	235(49)
Co2	0.101	---	0.621	8.381	0.256	0.0062	0.0067	0.0178	130.5 ^f	149(36)
Ni1	0.118	---	1.119	8.346	0.255	0.0037	0.0062	0.0120	1198.5 ^f	873(262)
Ni2	0.139	---	1.149	8.348	0.254	0.0030	0.0072	0.0120	174 ^f	74(25)
Ni3	0.465	---	0.561	8.417	0.262	0.0038	0.0066	0.0051	15.92	30(6)
Zn1	0.425	0.509	0.850	8.367	0.256	0.0044	0.0762	0.0181	20.23	78(20)
Zn2	0.522	1.209	0.590	8.660	0.265	0.0043	0.0048	0.0023	18.97	31(6)

Table 4. Summary of PDF fits associated with Co, Ni, and Zn ferrite nanoparticles. For fits with R_w values greater than 50% (Co3 and Ni3), the fit results are not valid therefore not shown in the table.

^a Degree of inversion values originate from PDF modeling.

^b Degree of inversion values come from the Mössbauer data (Table 3).

^c “M” stands for metal ions other than Fe. If the sample is Fe₃O₄, M is Fe.

^d Structural coherence arises from PDF fit using a spherical characteristic function.

^e Particle sizes are obtained from transmission electron microscopy (TEM) measurements (Table 1).

^f The precision of these values is low and limited by the poor instrumental resolution. The range of structural coherence refined from PDF becomes less accurate the larger the particles are above ~65 Å, which represents the radial distance where the signal of the bulk nickel calibration standard vanishes.

Figure 9. Photodegradation of methylene blue under 366 nm UV irradiation in the presence of magnesium (yellow, ▼), nickel (green, ▲), copper (red, ◆), zinc (purple, ■), and cobalt (blue, ●) ferrite nanoparticles as a function of irradiation time as compared with a control (black, ■) of methylene blue without any nanoparticles present (A). Pseudo-first-order fits of the data as a logarithmic change in concentration as a function of UV irradiation time (B).

Figure 10. Peroxidase-like activity of ferrite nanoparticles (at 1 mg mL^{-1} concentration) towards TMB, measured at 652 nm as a function of reaction time.

TOC Figure Caption. By generating ferrite nanoparticles of controlled sizes and compositions, variations in nanoscale structure can be rigorously correlated with magnetic and catalytic properties.

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