

***In-situ* Electron Microscopy to Inform Superior Magnetic Nanocomposites**

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Recent developments in high switching frequency WBG semiconductors have resulted in increased performance of power electronic circuits.¹ For example, GaN is now a go-to semiconductor for power converters in vehicle electronics, due to its faster switching speed and weight reduction.² The passive magnetic components (e.g., inductors and transformers) however have not matched these advances and now account for a disproportionate size and weight. Traditional magnetic core materials (e.g., ferrites) can suffer from energy loss via heat generation with the two main mechanisms being magnetic hysteresis and the formation of eddy currents.³ Therefore, a material is needed that possesses a high magnetic saturation value (M_{sat}) while eliminating these loss mechanisms. Magnetite (Fe_3O_4) nanoparticles are a promising magnetic material as they are air-stable and possess a high M_{sat} of $92 \text{ Am}^2/\text{kg}$.⁴ When reduced to a specific critical size, Fe_3O_4 nanoparticles display superparamagnetism: a phenomenon unique to magnetic nanoparticles in which the material displays zero hysteresis, by definition.⁵ When the magnetic field is removed, thermal energy randomly reorients the coherent magnetic dipoles of the nanoparticles to yield a total zero magnetic moment. To maintain superparamagnetism at high switching frequencies, nanoparticle relaxation must occur faster than the switching magnetic field. This requires incredibly tight synthetic control as relaxation time is highly dependent on nanoparticle size ($\tau \propto e^V$).⁶ We recently showed that by synthesizing wustite (FeO) nanoparticles and then oxidizing to Fe_3O_4 , we could achieve sub-nm control over nanoparticle diameter.⁴ However, some results indicate that internal defects can be introduced depending on oxidation temperature, which can reduce M_{sat} by up to 60%.⁷

Additionally, the form factor of power circuit componentry is continually being reduced. However due to their brittle nature traditional inductor materials (i.e., ferrites) are not suitable for the most promising techniques for miniaturization e.g., additive manufacturing. Nanoparticles, on the other hand, have the advantage of being dispersible in solvents and can be incorporated into an organic matrix to yield a functional nanocomposite. When formed into a functional nanocomposite determining the packing fraction of the active nanoparticle component is essential. If the nanoparticles pack too closely, magnetic dipole-dipole ($\mu-\mu$) coupling can adversely affect relaxation and introduce hysteretic losses.⁸ If particles are dispersed too distantly, then the nanoparticle loading is not as high as could otherwise be achieved. Therefore, to form a magnetic nanocomposite with superior performance it is essential to observe and eliminate structural defects in the nanoparticles themselves and to understand and control nanoparticle interactions.

Here, we use various advanced electron microscopy techniques to observe and understand the emergence of structural defects in magnetic nanoparticles, and to investigate their collective behavior. We performed *in-situ* experiments using a Titan environmental TEM equipped with a Gatan direct-electron-detection K3-IS camera to identify synthetic conditions that lead to the reproducible formation of high quality, single crystal and compositionally pure Fe_3O_4 nanoparticles. In the presence of an applied magnetic field superparamagnetic nanoparticles are known to form chains, where the nanoparticle magnetic dipoles align

with the direction of the field. In the absence of an applied field magnetic nanoparticles have been shown to form rings, or flux closure loops; however, these are typically discovered upon drying and do not necessarily represent behavior in solution. Therefore we also used cryo-TEM as a powerful tool for investigating nanoparticle assemblies as are present in solution. We show that dimers and longer chain-length structures exist in solution, as well as unique arrangements of nanoparticles that could not be captured by conventional TEM. Finally, we performed cryo-FIB to determine nanoparticle spacing within the resulting nanocomposite, and to investigate the nanoparticle-matrix interface while minimizing beam damage and associated artifacts.

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References

1. F. Roccaforte *et al.*, Emerging trends in wide band gap semiconductors (SiC and GaN) technology for power devices. *Microelectron. Eng.* **187**, 66-77 (2018).
2. H. Amano *et al.*, The 2018 GaN power electronics roadmap. *J Phys D Appl Phys* **51**, (2018).
3. H. Saotome, K. Azuma, H. Kizuka, T. Tanaka, Properties of dynamic magnetic loss of ferrite. *AIP Advances* **8**, 056103 (2018).
4. E. C. Vreeland *et al.*, Enhanced Nanoparticle Size Control by Extending LaMer's Mechanism. *Chem. Mater.* **27**, 6059-6066 (2015).
5. D. L. Huber, Synthesis, properties, and applications of iron nanoparticles. *Small* **1**, 482-501 (2005).
6. B. Cullity, *Introduction to Magnetic Materials*. Addison-Wesley, Ed., (Addison-Wesley Pub. Co., Reading, Massachusetts, 1972).
7. Z. Nedelkoski *et al.*, Origin of reduced magnetization and domain formation in small magnetite nanoparticles. *Sci Rep* **7**, 45997 (2017).
8. T. C. Monson *et al.*, Large enhancements of magnetic anisotropy in oxide-free iron nanoparticles. *J. Magn. Mater.* **331**, 156-161 (2013).