Non-Aqueous Synthesis of Graphene Supported Spinel Ferrite Nanoparticles

Nathan Jansen[1], John Yuzon[2], Erin McCardle-Blunk[3], James Barnes[1], Andrea Goforth[1], Jun Jiao[2,3*]

1. Department of Chemistry, Portland State University, Portland, OR, USA.
2. Department of Mechanical & Materials Engineering, Portland State University, Portland, OR, USA
3. Department of Physics, Portland State University, Portland, OR, USA
* jiaoj@pdx.edu

Spinel nanoparticles, such as the ferrite oxides $CoFe_2O_4$ and Fe_3O_4, are of particular interest due to their ferrimagnetic properties. These materials are classified multiferroic, in which their ferromagnetic and ferroelectric properties are coupled. In electrochemical cells such as supercapacitors, multiferroic materials are subject to the magnetoelectric effect (ME), where their intrinsic magnetic moment can be reversibly manipulated by applying an external electric field [1]. When spinel ferrite nanoparticles (NPs) were hybridized with graphene, they have been shown to exhibit enhanced electrochemical properties [2]. The study reported here aims to generate a non-aqueous synthesis for graphene hybridized $CoFe_2O_4$ NPs. Non-aqueous synthesis is advantageous as it eliminates the use of metal halides which may contaminate the crystal structure. The addition of graphene is intended to enhance the electrical properties of the hybrids and in turn the magnetic properties for greater manipulation via the ME.

To synthesize the $CoFe_2O_4$ graphene hybrid, a 1:2 stoichiometric ratio of colbalt(III) acetylacetonate $(Co(C_5H_7O_2)_3)$, and iron(III) acetylacetonate $(Fe(C_5H_7O_2)_3)$, were mixed in an absolute ethanol solvent. A few-layer graphene support was produced via liquid exfoliation and added to the solution to achieve a calculated mass of 88.9% $CoFe_2O_4$. The precursor mixture was magnetically stirred for 2 hours, transferred to a 25 mL Teflon liner, and heated in a stainless steel autoclave at 220°C for 24 hours. The produced NPs were washed several times in DI water then centrifuged at 14,800 rpm for 15 min.

NPs' magnetic property was demonstrated in Figure 1, where (a) and (b) were the NPs solution before and after being exposed to a magnet, respectively. Figure 1 (b) shows that the NPs exhibit strong magnetic response. The XRD spectrum of the NPs in Figure 2 (a) indicates assigned diffraction peaks are consistent with single phase inverse spinel structure, the graphene peaks are also present denoted by asterisks. The Raman spectrum of the NPs in Figure 2 (b) shows peaks at the 5 spinel phonon modes [3]. When comparing Figure 2 (b) to literature values of $CoFe_2O_4$, there are red shifted at 670 and 460 cm^{-1} masking the 620 mode less apparent, this is possibly due to Co^{3+} cations in the sample. TEM image in Figure 3 (a) reveals that large NP clusters (~100 nm in diameter) are surrounded by small NPs. The inset diffraction pattern done on the large clusters shows they are polycrystalline structures. Figure 3 (b) is a HRTEM image of a small NP revealing that it is single crystalline with a diameter ~15nm. The size distribution of the small NPs is 10-20 nm. EDX mapping of the NPs performed in SEM is shown in Figure 4 (a-d). The SEM image in Figure 4 (a) indicates the area of the EDX mapping, EDX map (b) shows the large NP clusters contain higher Co concentration than those of small NPs. EDX maps (c) and (d) show the Fe and O are spread throughout the material, respectively.

The results demonstrated here suggest the synthesis was successful in producing highly magnetic nanoparticles. Further Raman, TEM and EDX experiments will help to achieve the formation of the $CoFe_2O_4$. Optimization of synthesis parameter will be explored to provide control over the species of the material, such as alternative stoichiometric ratios. Additionally Co^{3+} ions in the system will be eliminated by changing the precursor from colbalt(III) to colbalt(II) in future syntheses [4].

References:
[1] A. Molinari, P. M. Leufke, C. Reitz, S. Dasgupta, R. Witte, R. Kruk, and H. Hahn, Nat. Communications, **8**, (2017) p. 15339
[2] W. Qian, Z. Chen, S. Cottingham, W. A. Merrill, N. A. Swartz, A. M. Goforth, T. L. Clare, and J. Jiao, Green Chem., **14**, (2012) p. 371–377
[3] N. Tran, D. H. Kim, T. L. Phan, N. T. Dang, T. N. Bach, D. H. Manh, and B. W. Lee, Phys. B Condens. Matter, **532**, (2018) p. 172–177
[4] The authors would like to thank the support from the NSF under awards No. DMR-1560383 and No. CBET-1507707.
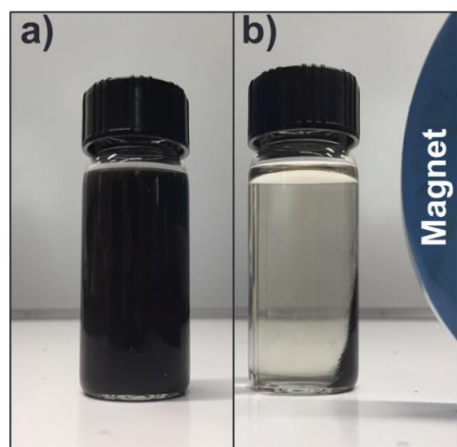
Figure 1. (a) NPs suspended in solvent, (b) NPs responding to external magnetic fields.
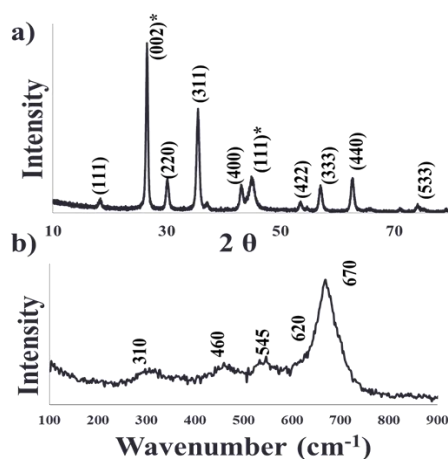

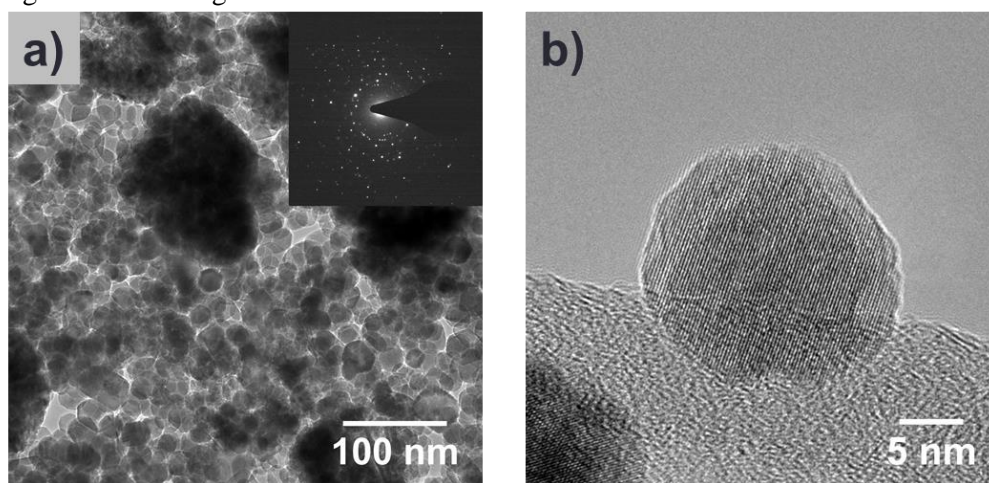**Figure 2.** (a) XRD, and (b) Raman spectra of NPs

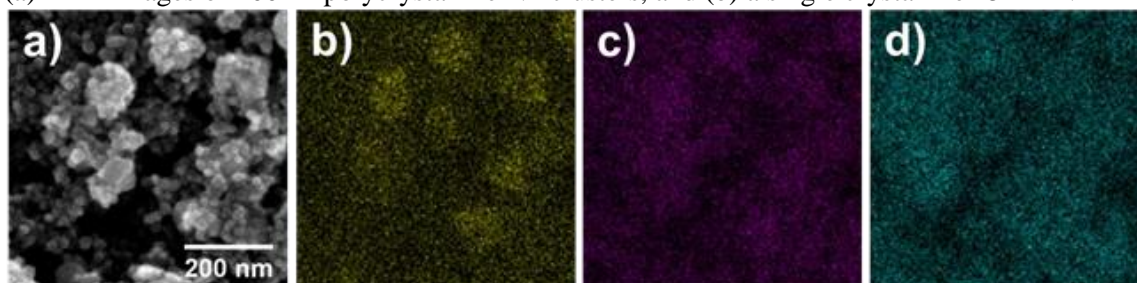**Figure 3.** (a) TEM images of 100nm polycrystalline NP clusters, and (b) a single crystalline 15 nm NP

Figure 4. (a) SEM area to be mapped by EDX. (b) EDX shows large NP clusters have high density of Co. (c) Fe and (d) O distributions can be seen evenly spread throughout the material.