NDnano
Center for Nano Science and Technology

ND*nano* Summer Undergraduate Research
2019 Project Summary

1. Student name & home university: Caroline Howell, University of Notre Dame

2. ND faculty name & department: Ryan K. Roeder, Aerospace and Mechanical Engineering, and Anthony J. Hoffman, Electrical Engineering

3. Summer project title: Phononic nanoparticles for low-loss, tunable nanophotonics in the mid- and far-IR

4. Briefly describe new skills you acquired during your summer research:

This was my first time conducting lab work outside of a classroom setting. I began by learning basic skills like how to operate a centrifuge and follow an SOP. I quickly became more independent, started to set my own schedule, and chose what reaction parameters I wanted to investigate. By the end of the summer, I feel confident in my ability to perform a synthesis, modify a procedure, communicate results, write technically, and troubleshoot when things don't go as planned.

5. Briefly share a practical application/end use of your research:

Plasmonic nanotechnologies have transformed areas such as spectroscopy, data processing, imaging, sensing, and medical therapy. However, the utility of plasmonic optical modes is limited in the long-wavelength IR by the dominance of optical phonons over plasmons. This project proposes leveraging the use of optical phonons to extend the technological impact of nanophotonics to the mid- and far-IR. The ability to tune the surface phonon resonance of a material could be used to enhance textile-based thermal camouflage. Additional applications have been proposed that use phononic resonances in the mid- and far-IR to detect explosives and industrial toxins.

6. 50- to 75-word abstract of your project:

Phononic nanoparticles are optical materials that resonate with and absorb light in the mid- and far-infrared region of the electromagnetic spectrum. The influence of particle size and morphology on a material's optical properties in this region has not yet been investigated. Commercially-available zinc oxide nanoparticles were used to prepare samples for optical characterization. Later, zinc oxide was synthesized by a variety of methods with the goal of creating monodispersed nanoparticles with tunable physical properties.

7. References for papers, posters, or presentations of your research:

1. W. L. Barnes, A. Dereux, and T. W. Ebbesen, "Surface Plasmon Subwavelength Optics," *Nature* 424, 824–30 (2003). doi:10.1038/nature01937
2. S. Eustis and M. A. El-Sayed, "Why Gold Nanoparticles Are More Precious than Pretty Gold: Noble Metal Surface Plasmon Resonance and Its Enhancement of the Radiative and Nonradiative Properties of Nanocrystals of Different Shapes," *Chem. Soc. Rev.* 35, 209–217 (2006). doi:10.1039/b514191e
3. K. M. Mayer and J. H. Hafner, "Localized Surface Plasmon Resonance Sensors," *Chem. Rev.* 111, 3828–3857 (2011). doi:10.1021/cr100313v
4. Y.-C. Yeh, B. Creran, and V. M. Rotello, "Gold Nanoparticles: Preparation, Properties, and Applications in Bionanotechnology," *Nanoscale* 4, 1871–80 (2012). doi:10.1039/c1nr11188d
5. J. D. Caldwell, L. Lindsay, V. Giannini, I. Vurgaftman, T. L. Reinecke, S. A. Maier, and O. J. Glembocki, "Low-Loss, Infrared and Terahertz Nanophotonics Using Surface Phonon Polaritons," *Nanophotonics* 4, 44–68 (2015). doi:10.1515/nanoph-2014-0003
6. K. Feng, W. Streyer, Y. Zhong, A. J. Hoffman, and D. Wasserman, "Photonic Materials, Structures and Devices for Reststrahlen Optics," *Opt. Express* 23, A1418 (2015). doi:10.1364/OE.23.0A1418

One-page project summary that describes problem, project goal and your activities / results:

Over the past 30 years, advances in understanding of the structure-property relationships governing the surface plasmon resonance of noble metal nanoparticles (NPs) have enabled the development of plasmonic materials and nanotechnologies [1-4]. Surface plasmons are free electrons on the surfaces of noble metal NPs which resonate with and absorb specific frequencies of light. The surface plasmon resonance (SPR) of a material can be tuned by altering the physical properties of the material. For example, the SPR can be tuned from visible to near-IR frequencies by adjusting the thickness-to-diameter ratio of the particle [1-4] and to mid-IR using doped semiconductors and patterned nanostructures [5,6]. However, despite all these advances there is still a lack of actionable knowledge regarding phononic NPs, which absorb in the mid to far-IR [5]. Therefore, the objective of this project was to establish a basic understanding of the structure-property relationships for interactions of phononic NPs with mid and far-IR and to engineer tunable surface phonon resonant modes in phononic NPs.

Commercially-available ZnO NPs, 1000, 500, 80-200, 30-40, 18, and 10-30 nm in size were investigated. X-ray diffraction (XRD) was used to confirm the phase of each sample as ZnO and measure the crystallite size using the Scherrer equation. The mean crystallite size did not correspond to the specifications of the commercial supplier. The three larger NP samples (1000, 500, and 80-200 nm) exhibited a mean crystallite size of 61-85 nm and the three smaller NP samples (30-40, 18, and 10-30nm) exhibited a mean crystallite size of 19-27 nm (Fig. 1).

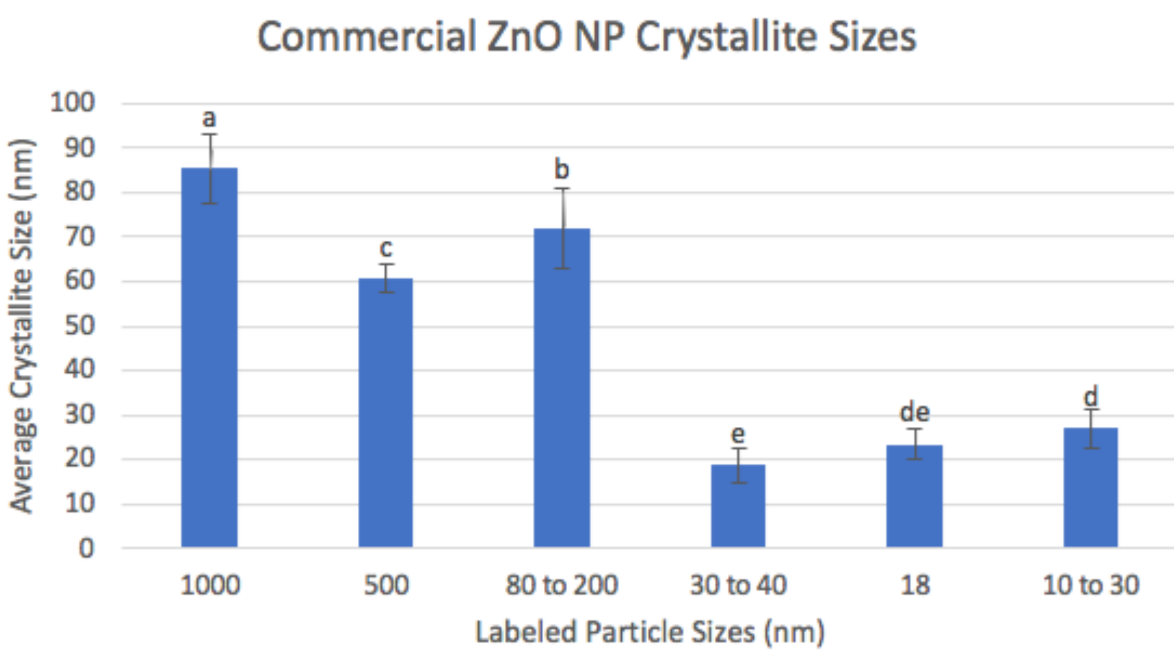

Figure 1. Mean crystallite size measured by XRD for commercial samples of ZnO NPs.

Samples were prepared for optical characterization of absorption and transmission by mixing NPs with KBr to create transparent pellets. The smaller NPs exhibited lower optical transmissions than larger NPs at the same NP:KBr mass ratio. Methods were investigated for assembling a monolayer of NPs on gold-coated slides for emission measurements. This part of the project remains ongoing due to difficulty obtaining reproducible results and agglomeration of the commercial NPs.

Finally, the synthesis of monodispersed ZnO NPs was investigated to overcome the inaccurate size and poor quality (agglomeration) of the commercial NPs. Optical and electron microscope images revealed that the as-synthesized NPs are monodispersed. Moreover, the size and morphology can be tailored by varying reaction parameters such as the cooling rate, reactant concentration, and solvent type. Therefore, these NPs will be used for future optical characterization of ZnO NPs in the mid- and far-IR.

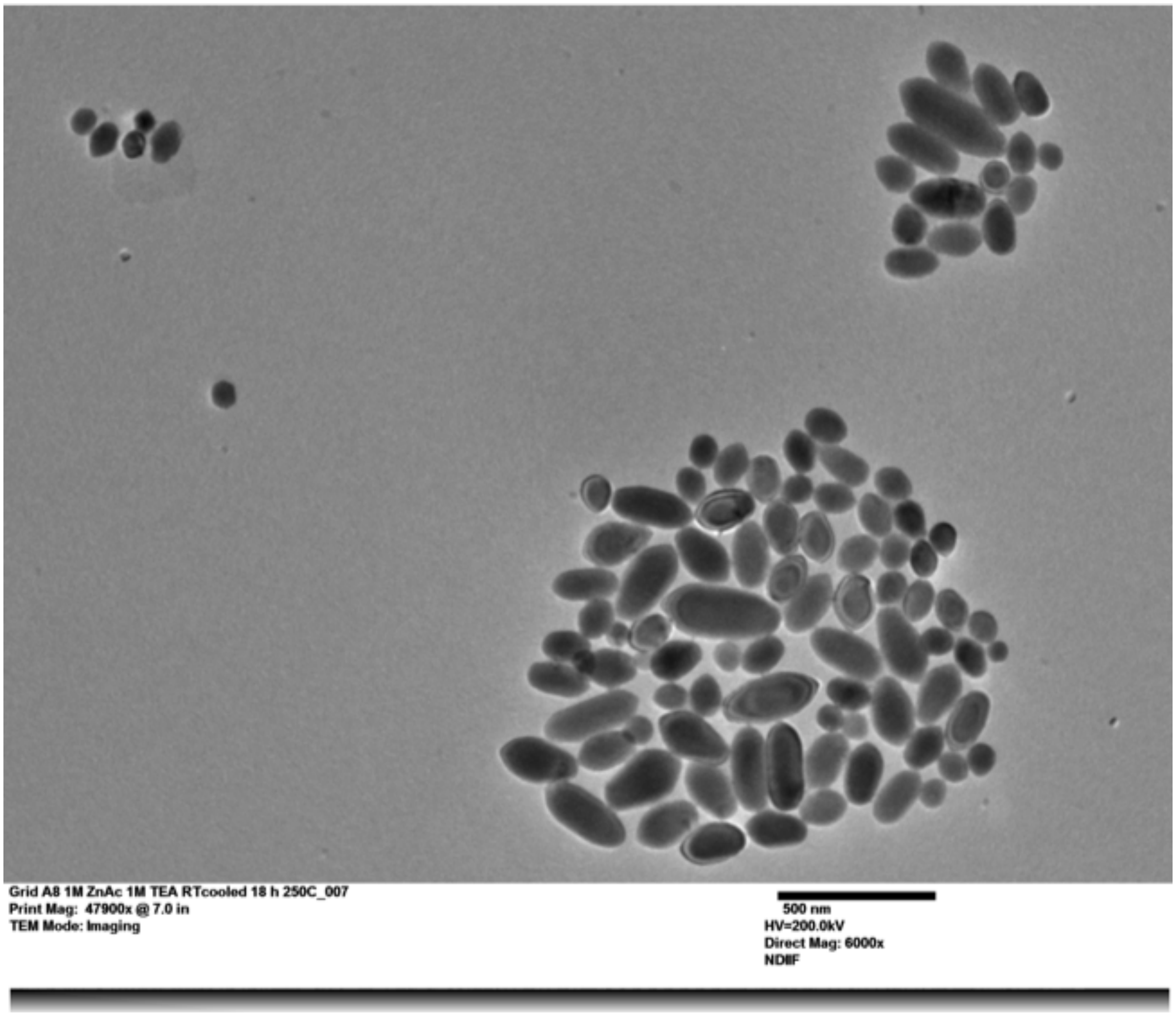

Figure 2. TEM micrograph of as-synthesized ZnO NPs.