NDnano Summer Undergraduate Research
2022 Project Summary

1. Student name & home university: Juwan Jeremy Jacobe, University of Notre Dame

2. ND faculty name & department:
Prof. Anthony Hoffman, Department of Electrical Engineering
Prof. Ryan Roeder, Department of Aerospace and Mechanical 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 summer involved learning a lot of lab equipment operation and benchwork chemistry, especially nanoparticle synthesis and sample preparation for FTIR measurements. This project was also generally very helpful in developing general skills in working in a lab, especially in practicing awareness and caution while running experiments and remembering to take note of everything for reference in the future.

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

Phononic nanomaterials could be applied for nanophotonic technology with operationality in the mid- and far- IR spectral ranges. A practical application already being explored within this project is molecular sensing, i.e. using phononic nanomaterials to enhance detection sensitivity of signatures of molecules. Many complex molecules, especially those of interest for biomedical and astrochemistry applications, have unique signature spectra in the IR, which makes extending the operationality of nanophotonics further into the mid- and far- IR desirable.

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

ZnO nanoparticles exhibiting surface phonon polariton (SPhP) modes between 600cm^{-1} and 400cm^{-1} were synthesized using a solvothermal method to investigate applications for molecular sensing in the mid- and far-IR. Thymine, the analyte-of-interest, was adsorbed onto the nanoparticles' surface, and the IR spectra of adsorbed samples were measured using FTIR spectroscopy. Thymine adsorbed on ZnO nanoparticles displayed new/enhanced spectral features between 1300cm^{-1} to 1100cm^{-1}, potentially due to interactions with the second harmonic of SPhP modes.

7. References for papers, posters, or presentations of your research:
[1] Anker, J., Hall, W., Lyandres, O. et al. Biosensing with plasmonic nanosensors. Nature Mater 7, 442–453 (2008). https://doi.org/10.1038/nmat2162
[2] Mueller, et. al. (2021). Surface-Enhanced Raman Scattering and Surface-Enhanced Infrared Absorption by Plasmon Polaritons in Three-Dimensional Nanoparticle Supercrystals. ACS nano, 15(3), 5523–5533
[3] Caldwell, Joshua D., et. al. "Low-loss, infrared and terahertz nanophotonics using surface phonon polaritons" Nanophotonics, vol. 4, no. 1, 2015, pp. 44-68
[4] I. Khan, et al., "Surface Phonon Polariton Modes in Zinc Oxide Nanoparticles," 2020 Conference on Lasers and Electro-Optics (CLEO), 2020, pp. 1-2

[5] A. Barzinjy, Azeez (2020) Structure, Synthesis and Applications of ZnO Nanoparticles: A Review. Jordan Journal of Physics, 13 (2). pp. 123-135

[6] J. Hammond, et. al., “Localized Surface Plasmon Resonance as a Biosensing Platform for Developing Countries,” Biosensors, vol. 4, no. 2, pp. 172–188, Jun. 2014

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

Previous work on plasmonic nanomaterials[1] has shown that the phenomenon of surface plasmon resonance, the coupling of charge carriers at the surface of these materials to incident light, can be utilized for sensing technology. Surface enhanced infrared absorption (SEIRA) studies[2] have especially shown that surface plasmons can confine and enhance incident electric fields, leading to higher optical detection sensitivity of molecules on the surface of plasmonic materials in the UV-Vis and near-IR spectral ranges.

Phononic nanomaterials exhibit a similar phenomenon through surface phonon polaritons (SPhPs), the coupling of lattice vibrations to incident light, but with lower optical losses in the mid- and far- IR spectral ranges[3]. The goal of this project was to investigate ZnO nanoparticles (NPs) as phononic NPs and to examine if SPhP-induced SEIRA is observed when performing optical measurements on molecules adsorbed onto the surfaces of ZnO NPs.

ZnO NPs were synthesized using a low cost solvothermal method, which yielded spherical nanoparticles between 100-500 nm in diameter as measured by dynamic light scattering. These as-synthesized ZnO NPs exhibit a Reststrahlen band between 600 cm^{-1} and 400 cm^{-1} due to SPhP modes[4]. Analyte molecules of interest were loaded onto ZnO NP surfaces through adsorption in an aqueous colloidal solution. These adsorbed samples were mixed with KBr and pressed into pellets for optical measurements. Pellets containing the analyte alone, the NPs alone, and the analyte physically mixed with NPs were also prepared as control. IR spectra of pellets were measured from 4000 cm^{-1} to 370 cm^{-1} using Fourier transform infrared (FTIR) spectroscopy. FTIR measurements were performed under atmospheric conditions but with N_2 gas constantly purging the blackbody measurement chamber to reduce noise from H_2O and CO_2 present in the air.

Experiments previously done by a graduate student also working on this project have investigated leucine-adsorbed ZnO NPs. Leucine, an essential amino acid, was initially chosen as it was a biorelevant molecule. The IR spectra of the leucine-adsorbed ZnO NPs (see Figure 1) displayed significant changes from the reference spectra of leucine alone, signifying strong chemical interactions through chelation between the ZnO NPs and leucine. Most of the peak shifts/enhancements could be attributed to chelation, so any peak shifts/enhancements solely due to SPhP interactions with the adsorbed molecule were difficult to find. Further experiments were done with other biorelevant molecules that weren’t known to have strong chemical interactions with ZnO.

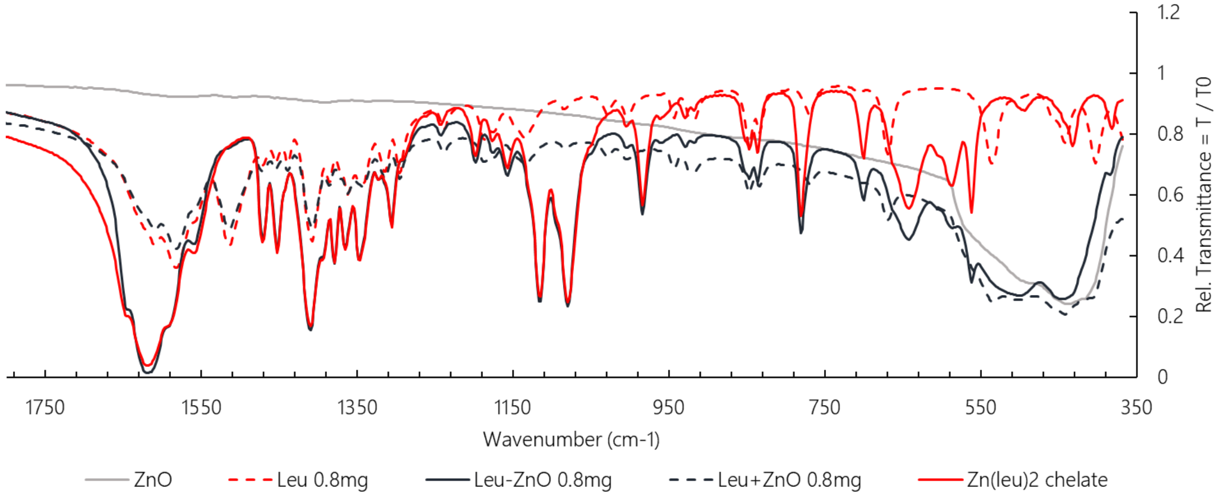

Figure 1. FTIR Spectra of leucine-adsorbed ZnO NPs and its associated controls

After initial experiments, work on this project focused on thymine, one of four nucleobases making up DNA. Results of FTIR measurements of thymine-adsorbed ZnO NPs as well as its associated control sample groups can be seen below in Figure 2.

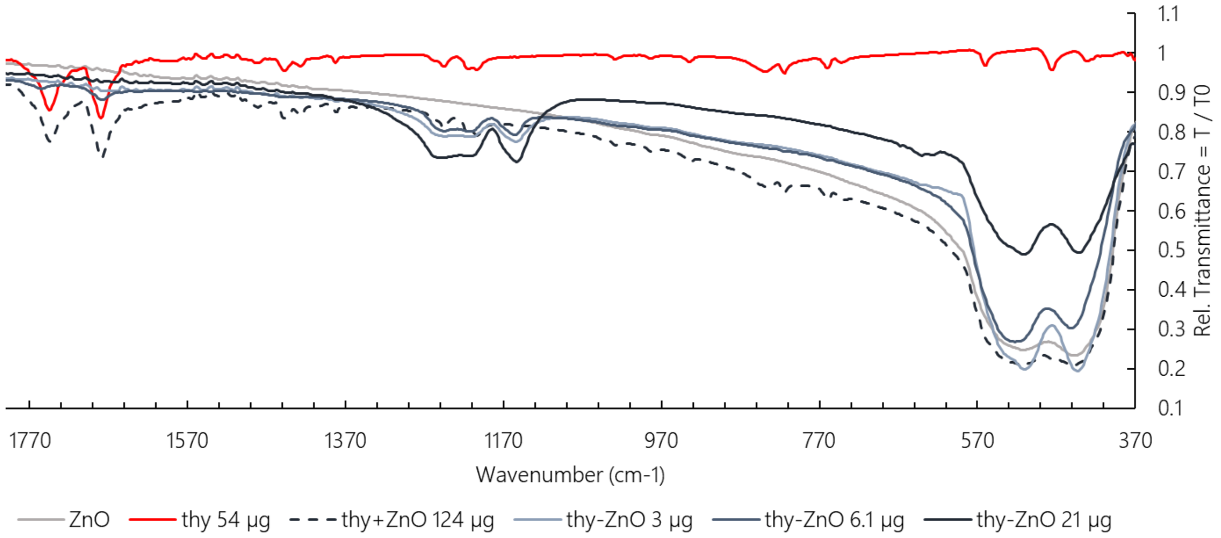

Figure 2. FTIR spectra of thymine-adsorbed ZnO NPs and its associated controls

The most significant changes in the thymine-adsorbed ZnO NPs are the new features between 1350 cm^{-1} and 1100 cm^{-1}, which may be enhancements of existing thymine features within that range. As more thymine is adsorbed onto the surface, the multimode band between 1300 cm^{-1} and 1180 cm^{-1} gets broader and deeper and the dip at 1155 cm^{-1} gets deeper. This may be due to interactions between the second harmonic of SPhP modes and the vibrational bands of these regions, but further investigation is needed to prove this line of thought. Further work in general is needed with different analyte molecules as well as with different ZnO nanostructures with varying morphologies to better understand how ZnO nanomaterials can be leveraged for SEIRA.