NDnano
Notre Dame Nanoscience and Technology

NDnano Summer Undergraduate Research
2021 Project Summary

1. Student name & home university:
Brian Beas – University of Notre Dame

2. ND faculty name & department:
Dr. Nosang V. Myung – Department of Chemical & Biomolecular Engineering

3. Summer project title:
Maximizing the Piezoelectric Response from Inorganic-Organic Composite Electrospun Nanofibers

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

- Nanofiber synthesis using high voltage electrospinning techniques
- Inorganic & Organic chemical synthesis methods
- Data extraction from viscometer, tensiometer, and conductivity lab instruments for experimental analysis
- Image analysis from scanning electron microscope (SEM) images
- Cantilever straining testing for piezoelectric response measurements

5. Briefly share a practical application/end use of your research:
Electrospun nanofiber mats provide a scalable source of piezoelectric generators that, when combined with a gel electrolyte to form a piezoelectrolyte, can be incorporated into existing battery technology to produce Self-Charging Power Cells (SCPC). SCPCs can be used to harvest 'waste energy' from everyday activities such as walking for use in wearable technology.

6. 50- to 75-word abstract of your project:
To reach environmental sustainability and address climate changes, it is critical to develop new renewable energy sources. Piezoelectric materials have been effective at improving energy harvesting and storage in nanogenerators as they couple mechanical stress and electrical polarization processes. By incorporating strong, but brittle, inorganic piezoelectric materials in flexible, weak piezoelectric polymers, we hope to maximize the synergistic piezoelectric response for nanogenerators.

7. References for papers, posters, or presentations of your research:
Beas, B. (July, 2021). *Maximizing the Piezoelectric Response from Inorganic-Organic Composite Electrospun Nanofibers.* Poster Presented at: Notre Dame Summer Undergraduate Research Symposium. Notre Dame, IN.

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

In today's global energy economy there is a constant increasing demand for energy. Therefore, more sustainable and renewable energy sources are essential to fuel the growing energy demand. One way to help solve this growing problem is by using piezoelectric materials in nanogenerators to produce energy. Zinc oxide (ZnO) is a material with a high piezoelectric response but is very brittle, thus incorporating ZnO with a flexible piezoelectric polymer to form a composite material, a synergistic effect between the two can be achieved. The aim of this work is to maximize the piezoelectric response from a ZnO polymer matrix.

ZnO nanoparticles were embedded into polyacrylonitrile (PAN) and polyvinylidene fluoride (PVDF) nanofibers using electrospinning techniques to produce nanofiber mats. Initial experimental designs focused on analyzing how ZnO embedded PAN nanofibers would function and the factors that would impact the morphology of the fibers the most. Different PAN to ZnO ratios were used and electrospun at different conditions in order to gather a systematic data set for the composite nanofibers. Each electrospun nanofiber mat was analyzed using scanning electron microscope (SEM) imaging to determine the morphology of the nanofibers.

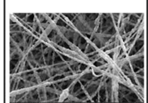
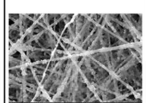
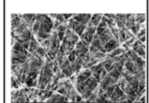
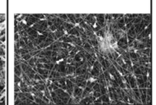
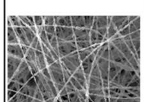
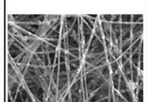
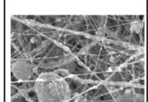
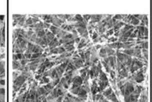
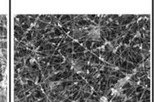
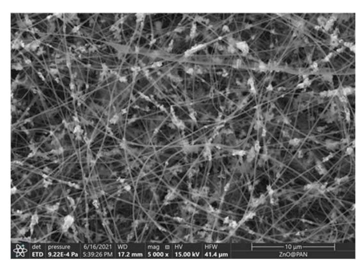
ZnO@PAN						
DOE		++	+-	00	-+	--
Average Diameter (nm)		433, 514	674	548, 523	292, 237	176, 180
Fiber Fraction (mm^2/mm^2)		0.995, 0.907	0.9975	0.980, 0.8196	0.979, 0.931	0.957, 0.950
Bead Density ($beads/um^2$)		0.0009, 0.0112	0	0.00430, 0.0102	0.00779, 0.0182	0.00516, 0.0173
Morphology	**8 kV, 0.5 mL/h**		✖			
	15 kV, 0.5 mL/h					

Table 1. *Average diameter measurements and SEM images from ZnO@PAN experimental design.*

SEM images from the initial ZnO@PAN DOE show various deformities in the nanofiber mats. Multiple samples had signs of ZnO clumps and polymer beading leading to thick nanofibers that were not uniform in diameter or appearance. With all the data that was gathered, a statistical analysis was performed to analyze the factors that had the greatest impact on the nanofibers. It was determined that a 1:1 and 1:2, PAN to ZnO respectively, composite solution would produce the most optimal nanofibers when electrospun at 15.0 kV with a solution feed rate of 0.5 mL/h. When electrospun at these conditions the refined ZnO@PAN composite nanofiber mats had minimal deformities when compared to the initial experimental trials. The average diameter of these nanofibers also greatly decreased from about 500 nm to roughly 160 nm. This decrease in average nanofiber diameter is within the range of nanofiber thickness that would be best to use in



	PAN	PAN:ZnO (1:1 wt%)	PAN:ZnO (1:2 wt%)
Avg fiber diameter (nm)	167	158	162
Fiber fraction (mm^2/mm^2)	0.97	0.98	0.98
Bead density ($beads/mm^2$)	0.035	0.004	0.008

Figure 1. *SEM image of 1:2 wt.% PAN to ZnO nanofiber mat (top) and nanofiber morphology characterization of refined ZnO@PAN DOE (bottom).*

a battery. SEM analysis shows that there were still small clumps of ZnO present on the nanofibers, however the overall uniformity of the nanofibers was deemed satisfactory.

Once uniform ZnO@PAN nanofibers could be synthesized in a consistent manner, cantilever strain piezoelectric testing was performed to measure the electrical output of the nanofibers. This was done by taking a small sample of an electrospun nanofiber mat and enclosing it in between two pieces of brass. Wires were connected to the metal plates and the sample was placed on a speaker to serve as a source of mechanical stress. Once the acoustic vibrator was turned on, an electrical output was measured and recorded as a function of the applied strain on the sample. This was done at increasing strain percentages to gain a better understanding of the magnitude of the piezoelectric output that the nanofiber mats could generate.

To serve as a proof of concept for the increase in the piezoelectric response that ZnO induces, the electrical output of a PAN nanofiber mat without ZnO was measured and compared to that of a 1:2 wt.% PAN to ZnO mat. **Figure 2** shows that the addition of ZnO to a piezoelectric polymer, such as PAN, does increase the piezoelectric response. Each color segment indicates a different amount of applied strain on the sample and as the strain increases, voltage increases. While the measured voltage may be considered low, these results indicate that a synergistic response between ZnO and PAN has been achieved and with more optimization, could be incorporated into a Self-Charging Power Cell (SCPC). With these results work on synthesizing electrospun nanofiber mats from better piezoelectric polymers could be explored.

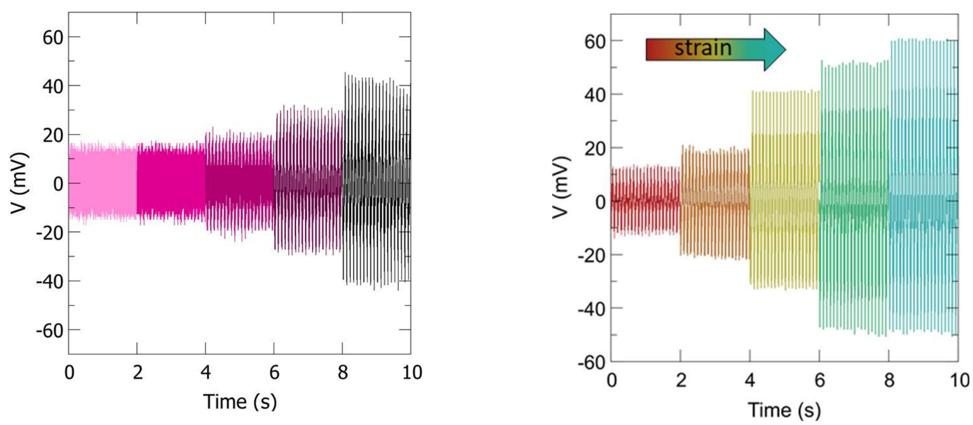


Figure 2. *Voltage output of pristine PAN nanofiber mat (left) and 1:2 PAN to ZnO nanofiber mat (right).*

PVDF, like PAN, is a piezoelectric polymer, but with a higher dielectric constant which gives it a naturally stronger piezoelectric response. Using the data that was gathered from the initial ZnO@PAN experiments and its subsequent refinement, an experimental design for ZnO@PVDF was created and trials with varying ZnO to PVDF weight percent were conducted. PVDF, unlike PAN, proved to be difficult to work with as the prepared solutions were very viscous which in turn affected how they would behave when electrospun. SEM analysis showed that the nanofibers had an ideal average diameter of 150-200 nm but had various deformities such as large clumps of ZnO. While a refined

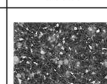
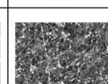
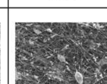
PVDF (MW = 180,000)		ZnO@PVDF			
DOE		--	-+	00	+-
Average Diameter (nm)		176	186	187	226
Fiber Fraction (mm^2/mm^2)		0.805	0.819	0.892	0.801
Bead Density ($beads/mm^2$)		0.0690	0.0173	0.0693	0.0431
Morphology	16.5kV, 1ml/h				

Table 2. *Morphology characterization of ZnO@PVDF trials*

ZnO@PVDF experimental design has not yet been conducted, these preliminary results are promising as the morphology of the nanofibers is not far from what is desired. Future work in this area is still needed and focuses on refining the ZnO@PVDF nanofiber mats, exploring the use of better piezoelectric polymers like P(VDF-TrFE), and aligning ZnO nanoparticles with respect to individual nanofiber direction.