NDnano Summer Undergraduate Research
2022 Project Summary

1**. Student name & home university:** Zuánichi Figueroa Hernández, Polytechnic University of Puerto Rico

2. ND faculty name & department: Dr. Nosang Myung, Chemical and Biomolecular Engineering

3. Summer project title: Enhancement of gas sensing performance based on controlled synthesis of heterojunctions and addition of noble metal dopants in WO_3 nanofibers.

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

- Metal Oxides semiconductor nanofibers synthesis through the electrospinning method.
- Solution properties characterization from equipment such as viscometer, tensiometer and conductivity meter.
- Imagery analysis from scanning electron microscope (SEM) to quantify the diameter.
- X-ray diffraction (XRD) for composition and crystal structure confirmation.

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

The research will be applied to electronic nose (E-nose) system which is a portable, inexpensive, real-time monitoring and reusable device for identification and quantification of various analytes in the complex condition. Such system could be used for various areas such as air quality monitoring, greenhouse gas emissions regulation, and potentially early diagnostic from exhaled breath, etc.

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

Gas sensors are extremely relevant for the detection of gas analytes surrounding us. Among different metal oxide semiconductor sensing materials, WO_3 is one of the best choice because of its low-cost, highly stable, sensitive, and acceptable selectivity. By synthesizing heterojunctions between two dissimilar MOS sensing materials and the addition of noble metal dopants to WO_3, it would be possible to enhance the sensitivity of MOS nanofibers toward analytes.

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

- Dey, A. (2018). Semiconductor Metal Oxide Gas Sensors: A Review. Materials Science and Engineering: B, 229, 206–217. https://doi.org/10.1016/j.mseb.2017.12.036
- Miller, D. R., Akbar, S. A., & Morris, P. A. (2014). Nanoscale metal oxide-based heterojunctions for Gas Sensing: A Review. Sensors and Actuators B: Chemical, 204, 250–272. https://doi.org/10.1016/j.snb.2014.07.074
- Yu, H., Li, J., Li, Z., Tian, Y., & Yang, Z. (2019). Enhanced formaldehyde sensing performance based on ag@wo3 2D nanocomposite. Powder Technology, 343, 1–10. https://doi.org/10.1016/j.powtec.2018.11.008
- Haider, A., Haider, S., & Kang, I.-K. (2018). A comprehensive review summarizing the effect of electrospinning parameters and potential applications of nanofibers in biomedical and biotechnology. Arabian Journal of Chemistry, 11(8), 1165–1188. https://doi.org/10.1016/j.arabjc.2015.11.015

- Yu, H., Li, J., Li, Z., Tian, Y., & Yang, Z. (2019). Enhanced formaldehyde sensing performance based on ag@wo3 2D nanocomposite. Powder Technology, 343, 1–10. https://doi.org/10.1016/j.powtec.2018.11.008
- Miller, D. R., Akbar, S. A., & Morris, P. A. (2014). Nanoscale metal oxide-based heterojunctions for Gas Sensing: A Review. Sensors and Actuators B: Chemical, 204, 250–272. https://doi.org/10.1016/j.snb.2014.07.074

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

Gas sensor, a device that is extremely important for the detection of air pollutants and gas leaks, which could be further upgraded to electronic nose that is able to potentially report health problems such as diabetes and amnesia. However, they need further improvements including higher sensitivity, selectivity and fast response and recovery time to obtain the best sensing performance to accurately provide analyte information. To achieve the previously mention purpose and goal of this research investigation focused on the enhancement of metal oxides semiconductor gas sensors, heterojunctions and noble metal doped electrospun WO_3 nanofibers were synthesized though electrospinning method.

The design of experiment was initially conducted to synthesize two dissimilar heterojunctions between Co and WO_3 and the addition of noble metal dopants to WO_3. In this study we focused on doping it with Ag. This was achieved by preparing multiples solution with varying molar ratios of Co-WO_3 (10%-25%) and Ag-WO_3 (1%-10%). After obtaining homogenous solutions, I performed some solution properties measurements (Table 1).

Sample	Surf. Tension [mN/m]	Viscosity [cP]
10%Co	29.00	34.92
15%Co	38.40	39.11
25%Co	39.37	40.42
1% Ag	36.67	63.31
2% Ag	37.50	62.39
5% Ag	38.30	66.84
10% Ag	37.80	69.72

Table 1: Surface tension and viscosity results of Co-WO_3 and Ag-WO_3.

Parameters	
Temperature [°C]	40
Rel. Humidity [%]	12
Flow Rate [ml/hr]	0.25
Tip to collector distance [cm]	10
Voltage [kV]	13
RPM	450

Table 2: Parameters for electrospinning process.

For the electrospinning set up which consist of an automatic pump, syringes filled up with the precursor solution, a high voltage source and a rotating drum collector. Once the syringes were filled up with the precursor solution which contains the precursors for the metal oxides and polymers, they were loaded on the pump with 10cm between the tip of the needle and the drum collector. The high voltage source (13kV) was applied to the tip of the needle and the parameters for the electrospinning were set up (Table 2). After ~12hrs of electrospinning the sample was collected and calcinated at 500°C for 2hrs to burn the polymer out and assist in the crystallization of metal oxides.

Material characterizations such as SEM was utilized to observe the morphology and measure the average diameter of nanofibers before and after calcination, and XRD was used to determine the composition and crystal structure of these materials after calcination, which were confirmed to be Co_3O_4-WO_3 and Ag-WO_3. Average crystallite size based on the extracted data was shown in Table 3.

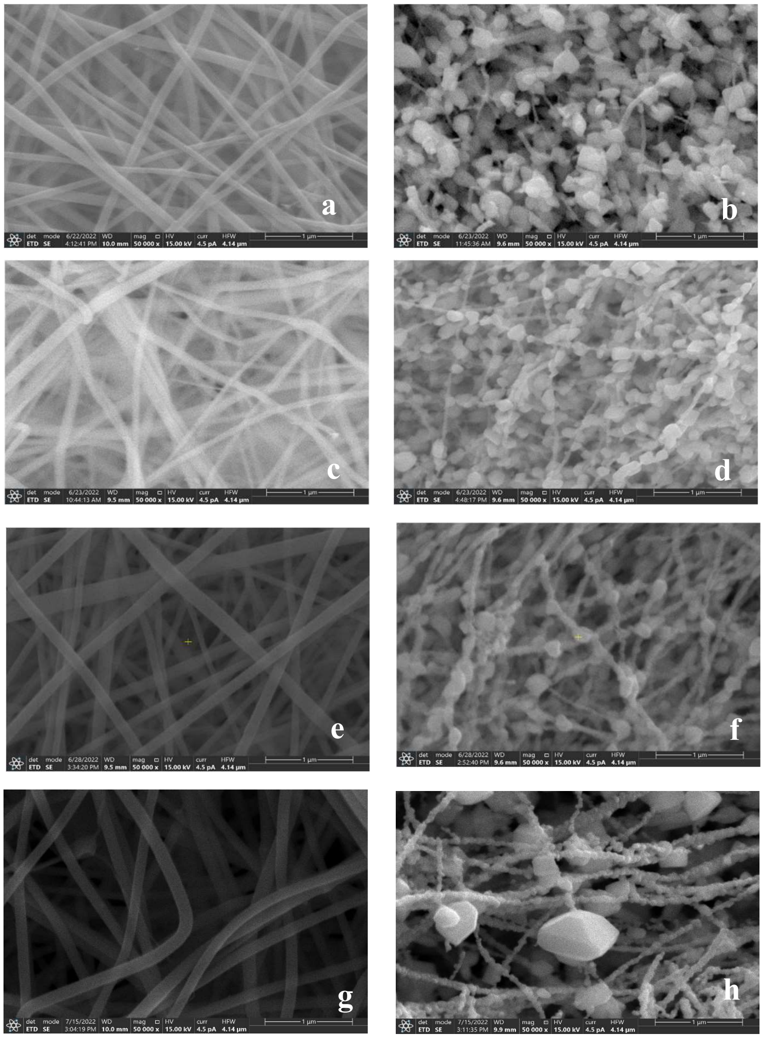

Figure 1: SEM images of (a) 10% Co_3O_4 -WO_3, (b) 10% Co_3O_4-WO_3 after annealing, (c) 15% Co_3O_4 -WO_3, (d) 15% Co_3O_4-WO_3 after annealing, (e) 25% Co_3O_4 -WO_3, (f) 25% Co_3O_4-WO_3 after annealing, (g) 1% Ag-WO_3, (h) 1% Ag-WO_3 after annealing.

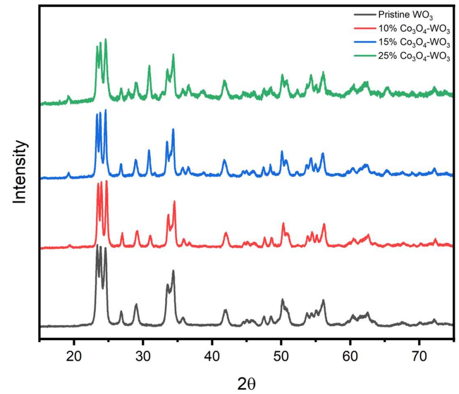

Figure 2: XRD data of Co_3O_4-WO_3.

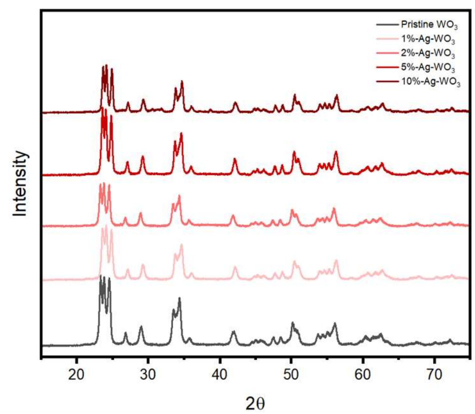

Figure 3: XRD data of Ag-WO_3.

Sample	Ag [nm]	Co_3O_4 [nm]	WO_3 [nm]
10%Co_3O_4 -WO_3	X	22.11	25.57
15%Co_3O_4 -WO_3	X	24.24	28.03
25%Co_3O_4 -WO_3	X	21.65	21.38
10%Ag -WO_3	27.31	X	24.91

Table 3: Average crystallite size in nanometers.

From the imagery taken with the SEM (Figure 1) it was possible to note a decrease in diameter after the annealing process confirming that the polymer was completely burned out of the nanofibers, also in some images its visible some grains that are affirming the formation of the metal oxides. The decrease in diameter was favorable because it increased the surface-volume ratio of the nanofibers giving more active sites for the reactions to occur. X-Ray diffraction results confirmed the crystallization of Co_3O_4 in the peak located around 32.00° and monoclinic tungsten trioxide (WO_3) as seen in Figure 2. The crystallization of silver in WO_3 nanofibers was only visible in the 10%Ag-WO_3 sample at the peak located around 37.00° (Figure 3). All the crystallite sizes were calculated based on the Debye-Scherrer equation as shown below.

$$\mathbf{D = (k\lambda/\beta \cos\theta)}$$

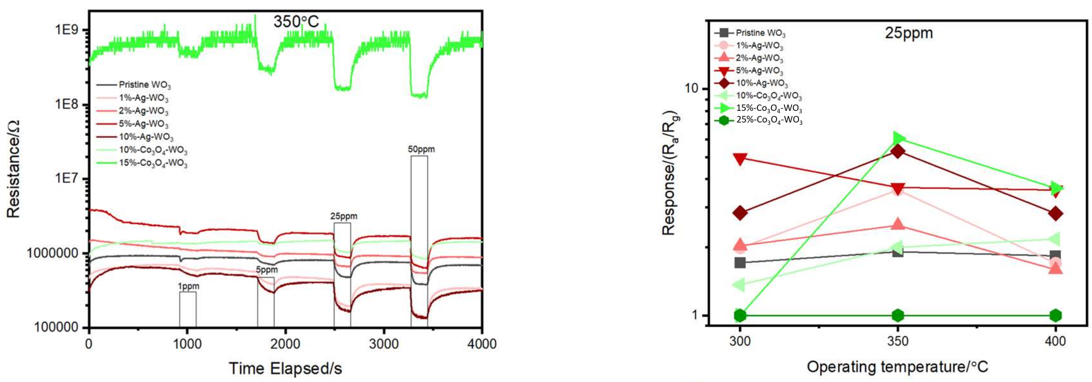

Figure 4: (a) Ethanol sensing raw data of as-synthesized nanofibers. (b) sensing response of 25 ppm ethanol as a function of operating temperature.

Gas sensing experiments were performed by exposing synthesized materials to different concentrations of ethanol (1, 5, 25, and 50 ppm) 350°C as shown in Figure 4(a). 15% Co_3O_4-WO_3 materials and 10% Ag-WO_3 materials showed the highest sensing response towards ethanol at 350°C among heterojunctions and noble metal doped WO_3 nanofibers. It is obvious that both Co_3O_4-WO_3 materials and Ag-WO_3 showed improved sensing response toward ethanol compared with pristine sample, which is expected. For the 25% Co_3O_4-WO_3 nanofiber sample, the resistance was too high to be measured leading to no-response result. However, due to the limit amount of time, only ethanol has been tested. Future work would be more sensing experiments for different analyte detection and data analysis such as sensing response, response/recovery time, limit of detection calculation, correlating with materials properties, and finally machine learning algorithms for identification and quantification of these analytes.