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Fabrication and Characterization of Nanofiber Nylon-6-MWCNT as an Electrochemical Sensor for Sodium Ions Concentration Detection in Sweat

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Fabrication and Characterization of Nanofiber Nylon-6-MWCNT as an Electrochemical Sensor for Sodium Ions Concentration Detection in Sweat

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Honors Project

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In Coordination with the University of Akron Honors College

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Executive Summary

The purpose of the research is to further understand, fabricate, and characterize nanofiber nylon-6-MWCNT as an electrochemical sensor to identify sodium ions concentration in sweat. This process includes fabricating and testing various electro-spun polymer nanofiber materials to determine the effects of the components on absorption, specifically in sweat. The focus of this report is analyzing the wettability of various electrospun polymer nanofibers using contact angle testing using Drop Shape Analysis and Image J, and chronoamperometry data to characterize treated sensors, noticing variation based on different fabrication parameters to assist in the development of a wearable sensor.

From contact angle analysis, with concentrations below 2 g/L, there was not evidence of a deviation in the wettability of the polymer fibers. Contact angle results supported Wujcik, Blasdel, Trowbridge, and Monty showing that there is not much variation in sensitivity for loading below the threshold showing that the largest factor on the sensor is the solvent and carbon isomer concentration, but below the threshold of 4.5 weight percent MWCNT, there is little variation. This opened the opportunity for fabrication with any MWCNT isomer and concentration understanding that as the isomer concentration increase, so does opportunity for agglomeration, poor dispersion, and a gradient of multi-walled carbon nanotubes (MWCNT) on the fiber.

Based on chronoamperometry testing, sensors concentration of MWCNT and amount of time dip-coated did not significantly affect the categorization of sensors as ‘good’ ($R^2 \geq .8$). Based on the tests completed, after moving the scale out from under the hood (sensor 61 and beyond) and the choice of series of sodium ion solutions is what impacted being characterized as ‘good’ sensors. The “New Solution” (NS), which consisted of a series of sodium ion solutions with

concentrations ranging from 10 mM to 150mM, was more selective with labeling sensors as ‘good’ than the “Old Solution” (OS) which consisted of a series of sodium ion solutions with concentrations ranging from 10 mM to 60 mM. Overall reproducibility of a ‘good’ sensor is 49% (not including the unknown sensors). Reproducibility for the OS is 63% and for the NS is 35%.

Through the processes of electrospinning, sensor fabrication, and chronoamperometry testing, sensors were able to be characterized to determine usability for further development in wearable sensors. The sensors developed and analyzed paved the way for testing and prototyping the sensor’s ability to detect sodium ion levels on subjects in real time.

Treatment of the polymer fibers with multi-walled carbon nanotubes (MWCNT) and calixarene takes 48 + hours to complete, so time is the largest limitation for this project. Use of the DSA was a limiting factor as often, the DSA was not functioning or being temperamental.

Understanding that the 1 cm by 1 cm sensors are too small for the body testing, there will be an increase in the number of 2 cm by 1 cm sensors developed. Understanding the sensitivity of the sensors when measuring and fabricating, it is important to notice outside factors that may affect measurements.

When stepping into research project similar to this, undergraduates have the opportunity to gain insight into electrochemical processes, experience the overlap of biomedical basics, electrical engineering, and chemical engineering. Students can gain a better understanding for the necessity of precise measurement techniques and the analysis process that follows changes in process variables. Students gain the opportunity to be a significant role in the development of a technology that can change future in exercise-science by utilizing and maturing one’s lab skills,

knowledge on safety, confidence in lab practices, independence in research, and improvement on data analysis.

Introduction

For my honors research credits, I continued research under Dr. Chelsea Monty's supervision. My research has been developing for the past 2 and a half years while not on co-op. The purpose of the research is to further understand, fabricate, and characterize nanofiber nylon-6-MWCNT as an electrochemical sensor to identify sodium ions concentration detection as in sweat. This process includes fabricating and testing various electro-spun polymer nanofiber materials to determine the effects of the components on absorption, specifically in sweat. The testing includes optimization of several carbon nanofiber materials at varying concentrations paired with multiple polymer compositions, electro spun into nanofiber like sheets, completing chronoamperometry testing on the developed sensors, and testing of scaled-up optimized sensors.

The fabrication is first based on a procedure for electrospinning polymer sheets developed by Nate Blasdel (Appendix 4). Once formed, the fibrous polymer sheets are treated with a combination of nanofibers, TritonX, and calixarene to engineer the absorptive characteristics of the fabric. The variables being tested for the contact angle portion of the research project include the material of the electro-spun fabric, the carbon nanotube solutions, and the concentrations of the carbon nanotube. After crafting the nanosensor, testing occurs using the Drop Shape Analysis (DSA) and Image J to perform contact angle analysis on surface adhesion and to identify the most effective combination of material and nanotube to develop an absorptive sensor. Using the Gamry Instrument Reference 3000, electrochemistry data is used to identify the effects of changing sodium ion content on the electrical current through the sensor, later used to in application of the wearable sensor.

This new technology could be used in several applications because of its capacity and selectivity to detect lactate, pH, and sodium levels in sweat. Nanosensors can be utilized to accurately track

internal body factors compared to what external fitness trackers measure like steps, activity, heart rate, and sleep based on movement.

With more development, the abilities of this technology to easily detect internal body chemistry in sweat could be used in the athletic or medical field.

Background

The market for wearable sensors is growing. According to Research and Markets, global wearable sensor market was estimated to be worth about 4.71 billion USD in 2015 with a compound annual growth rate (CAGR) of just under 26% from 2015-2020 (Research and Markets, 2016). With increased awareness of health and fitness, wearable sensors are lucrative to the growth in the health care industry. North America followed by developing countries in the Asia pacific like India and China, are early partakers of new technology and have both access and great desire for wearable sensors.

The majority of wearable sensors measure external physical states of the human body, like steps, etc. “These sensors can continuously monitor the wearer’s health status, track exercise activity, and access soldier performance. The field could rapidly grow if challenges to wearability, comfort, device and material compatibility, power back-up and analytical performance are address” (Shrivastava et. al., 2016). Polymer nanocomposites, materials made of conductive polymers and another nanomaterial like carbon nanotubes (CNT), are excellent transducers for electrochemical sensors. Conductive polymers have unique properties like flexibility, light-weight, scalability, corrosion resistant, low cost, and ability to be customized that other materials are not able to offer, making them ideal for sensor fabrication.

In 2009, Schazmann, Morris, Slater, Beirne, Fay, Reuveny, Moyna, and Diamond worked to develop a wearable compact Sodium Sensor Belt (SSB) to be worn on the lower back. The SSB included an impermeable plastic for holding a sodium Ion Selective Electrode (ISE) that continually sensed sweat to be used during exercise, a sweat wicking pump, and a potentiometer. The sensor, when developed, will have a wide range of application from high performance athletics to potentially monitoring Cystic Fibrosis. The sensor transfers information on both the chemical and physical state of the human body (Schazmann & others, 2009). With use of the belt, conditions such as dehydration (low plasma water content) and hyponatremia (low sodium concentration) can be monitored and avoided during athletic performance. The team demonstrated on-body sampling and sensing of sodium ions in sweat demonstrating the relationship between sodium electrolytes, sweat, and chemical/physical state of the human body for both healthy subjects and subjects with Cystic Fibrosis. Evaporation of sweat was the largest source of error for the team.

In 2013, Wujcik, Blasdel, Trowbridge, and Monty worked to quantify sodium ion's ability to be sensed in sweat effectively using Nylon-6/MWNT/calixarene nanocomposites. The team used thermal gravimetric analysis (TGA) to examine the amount of MWCNT adsorbed to the surface of the nylon nanofiber using low (.25 g/L) and high (2.5 g/L) weight percent MWNT. As sensors are dip coated in higher concentrations of MWCNTs, it led to a higher weight percent of carbon adsorbed. However, as MWCNT weight percent increases, agglomeration was observed using SEM which caused poor dispersion and a gradient of dense and sparse MWCNTs on the nanofibers. TGA and SEM analysis concluded that sensor sensitivity decreases as MWCNT loading increases.

Based on the increased affect in sensor sensitivity and response, the ion sensor experimental methods determined the use of TritonX-100 as surfactant and dispersing agent over TritonX-114 while utilizing calixarene's ability to introduce vibrational absorbance and selectivity to sodium ions sets these sensors apart from simple sweat conductivity sensors.

The team determined that an optimized sensor scheme includes .25 mg/mL MWCNT in .3 weight percent TritonX-100 in water utilizing calixarene's functionalized surface to improve selectivity to sodium ions. Nylon-6/MWNT/calixarene nanocomposites were effectively used for selective and sensitive sodium ion detection in liquids like sweat.

Experimental Methods

Treating of Polymer Fabric with Nanotubes

To treat the polymer fabric, one must first determine the desired concentration for the sample.

Table 1 depicts the necessary measurements depending on the concentration of the solution.

TABLE 1 shows the formulas for each desired concentration of carbon nanotubes.

Concentration	Amount of MWCNT	Amount of .03% TX solution
.25	1 mg	4 mL
.5	1 mg	2 mL
1	1 mg	1 mL

To create a 1 mg CNT solution, 2 mgs of Carbon Nanotubes (CNT) would be combined with 2 mL of .03% TX solution. A 1 cm by 1 cm square of the polymer fabric is cut. After sonicating the solution for 60 minutes without heat, the square is immersed in the solution for the desired amount of time (60 - 120 seconds), called dip coating, followed by an immersion in clean DI

water for the same amount of time before being set to dry for 24 hrs. Several types of carbon nanotubes were tested at various concentrations including CNT, CNT-OH, and CNT-COOH. Later, tests altered the soaking time in the CNT solution and the DI water rinse from 60 seconds to 120 seconds.

Creation of Calixarene Solution

Following the 24-hour drying period for the CNT treated polymer square, it must be treated with a calixarene solution. 12.5 mg of calixarene and 5 mL of toluene should be combined and stirred until all the calixarene has dissolved. The polymer square was added to the calixarene solution, sonicated for 5 minutes and left to sit overnight. Once the square soaked for 24 hrs, it was removed and set out to dry.

Contact Angle Testing Using the Drop Shape Analysis

Several CNT, CNT-COOH, and CNT-OH solutions were prepared for testing and sonicated for several minutes before beginning contact angle testing. Each test required an unused one 1 cm by 1 cm polymer square. Using Drop Shape Analysis (DSA) software, each concentration of the CNT solutions was tested. 5 μ L of CNT solutions were loaded into the drop needle to be dropped onto the untreated nylon.

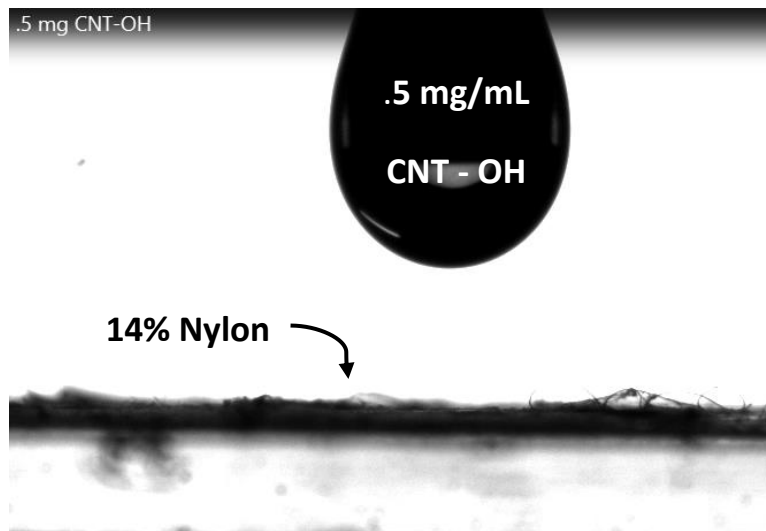


Figure 1 displays the image from DSA dropping .5 mg/mL CNT-OH solution onto 14% nylon.

Using video recording, contact angles were measured at 0, 1, 2, 3, and 6 seconds after dropping

the solution to determine wettability properties of the materials with time. Between testing, the drop needle was rinsed with acetone, DI water, and dried with air.

Chronoamperometry Testing

Using the Gamry Instrument Reference 3000 Potentiostat/Galvanostat/ZRA via direct-current (DC), each piece of treated polymer fabric (sensor) was tested using a series of sodium ion solutions. The sensor was connected using 2 electrodes. The response of the electric current through the sensor was plotted during the addition of solution. The



Figure 2 shows the electrode sensor connection for the chronoamperometry testing.

testing included increments of 30 μL drops starting with the lowest sodium ion concentration and increasing to the largest concentration. The sensors were tested using 2 separate sodium ion solution series fabricated within the lab. The solution series, ‘Old Solution’(OS), had sodium ion concentrations ranging from 10 to 60 mM solutions at intervals of 10 mM. The second series, ‘New Solution’ (NS), consisted of solutions ranging from 10 to 150 mM solutions at intervals of 10 mM. When testing NS, not all solutions were used in series to mimic the potential sodium ion level changes that sweat of the body would produce.

Each sensor was tested using the Gamry application and a PotentioStat to track the changes in the voltage through each sensor as sodium ion concentration changed. The uninterrupted data for each sensor was analyzed using a derivative calculation method to determine a regression line for each sensor.

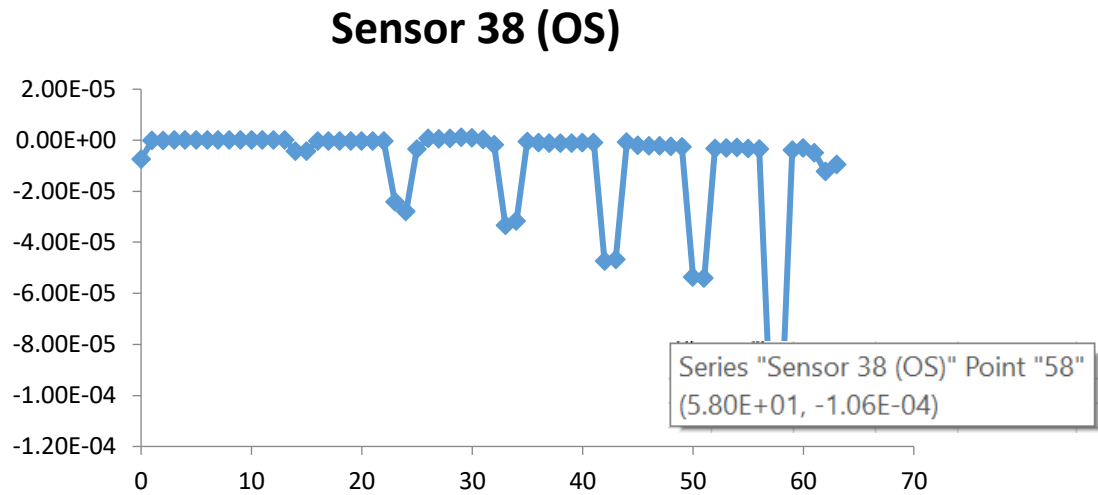


Figure 3 above shows the graphical representation of the derivative calculation used to create the regression relationship for each sensor.

The derivative data like in **Figure 3** is used to collect the derivative voltage response for each change in sodium ion level to develop a regression value for each sensor to determine if the sensor is usable for the next phase or not. Regression values greater than .8 are classified as ‘good’ sensors.

Table 2 shows sensor 38 (OS) derivative data at each concentration tested.

Na+ Concentration	Voltage Response
10	-4.20E-06
20	-2.80E-05
30	-3.33E-05
40	-4.74E-05
50	-5.41E-05
60	-1.05E-04
Slope	-1.70E-06
Intercept	1.43E-05
R2	0.879

For specifics on the electrospinning procedures, see appendix III.

Data and Results

Contact Angle Results

Using DSA, each contact angle calculation was taken from the images at the left and right side 3 times using Image J. The angles were averaged together and gathered in the graphs below. Error bars represent the standard error of the angle measurements collected.

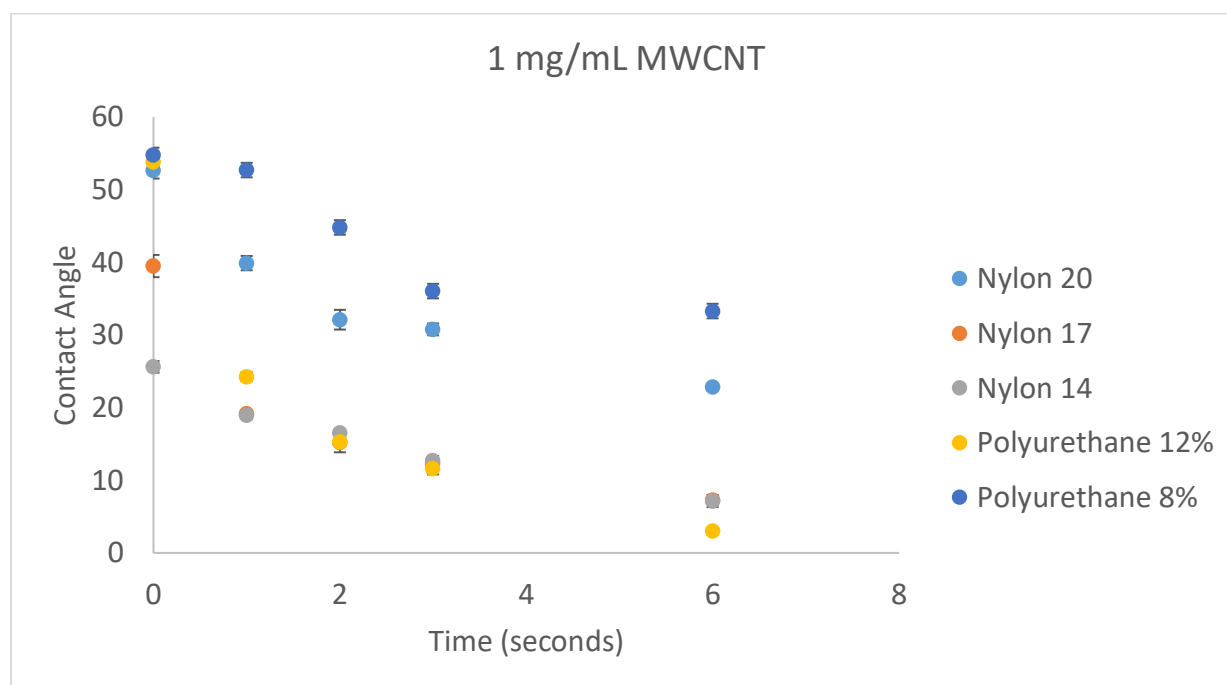


Figure 4 above shows the contact angle values for each polymer fabric tested at 0,1,2, and 6 seconds for 1 mg/mL concentration of MWCNT. Error bars represent the standard error of the measurements.

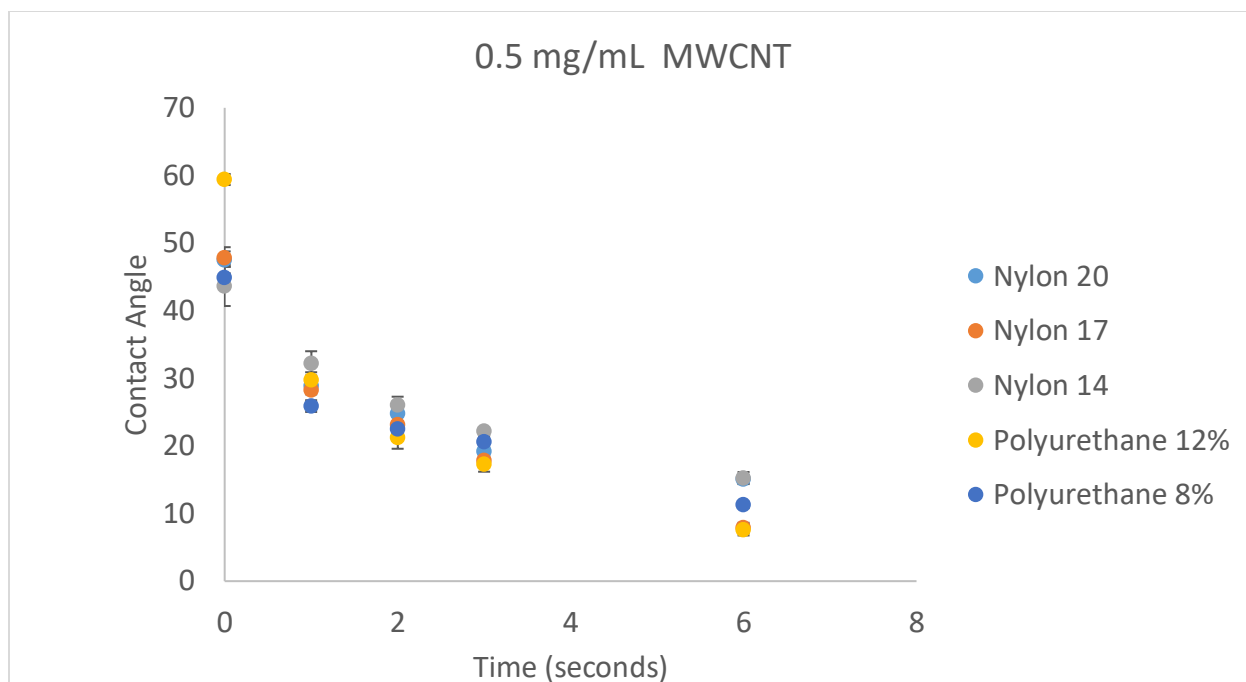


Figure 5 above shows the contact angle values for each polymer fabric tested at 0,1,2, and 6 seconds for .5 mg/mL concentration of MWCNT. Error bars represent the standard error of the measurements.

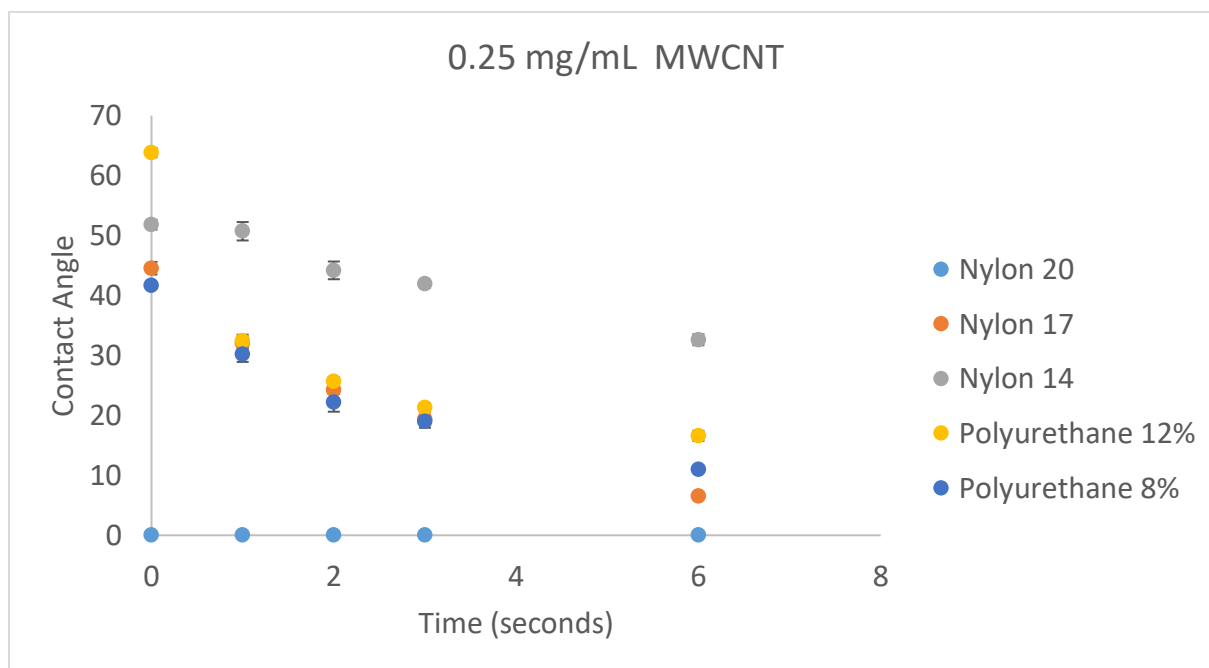


Figure 6 above shows the contact angle values for each polymer fabric tested at 0,1,2, and 6 seconds for .25 mg/L concentration of MWCNT. Error bars represent the standard error of the measurements.

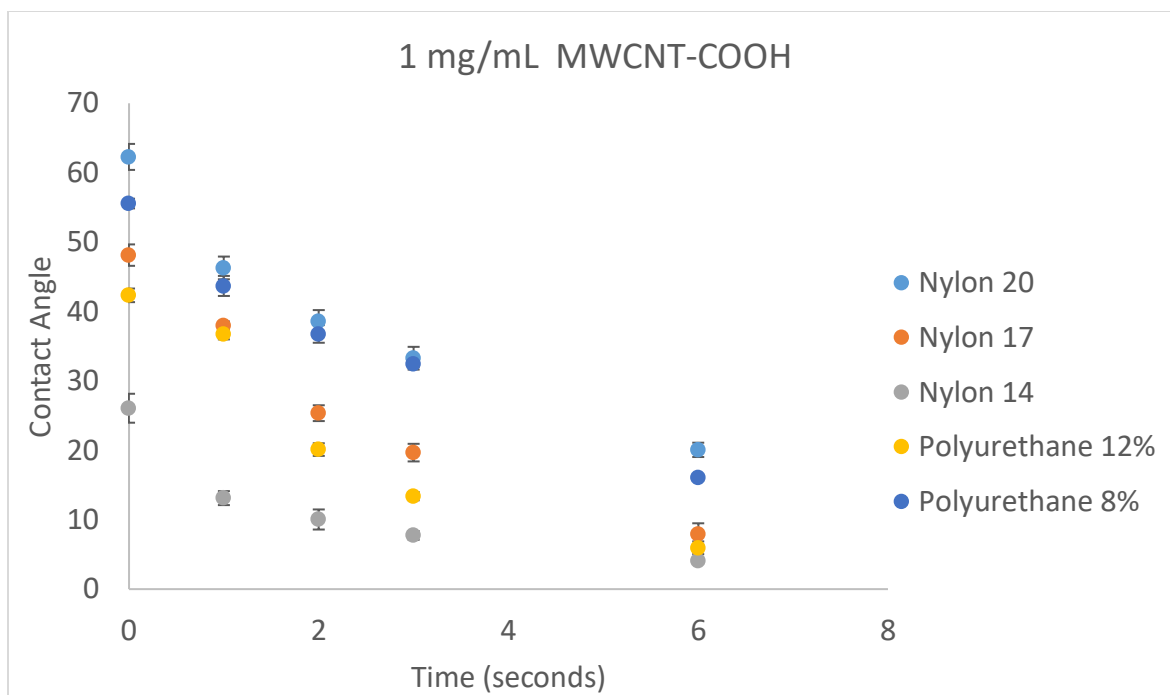


Figure 7 above shows the contact angle values for each polymer fabric tested at 0,1,2, and 6 seconds for 1 mg/mL concentration of MWCNT-COOH. Error bars represent the standard error of the measurements.

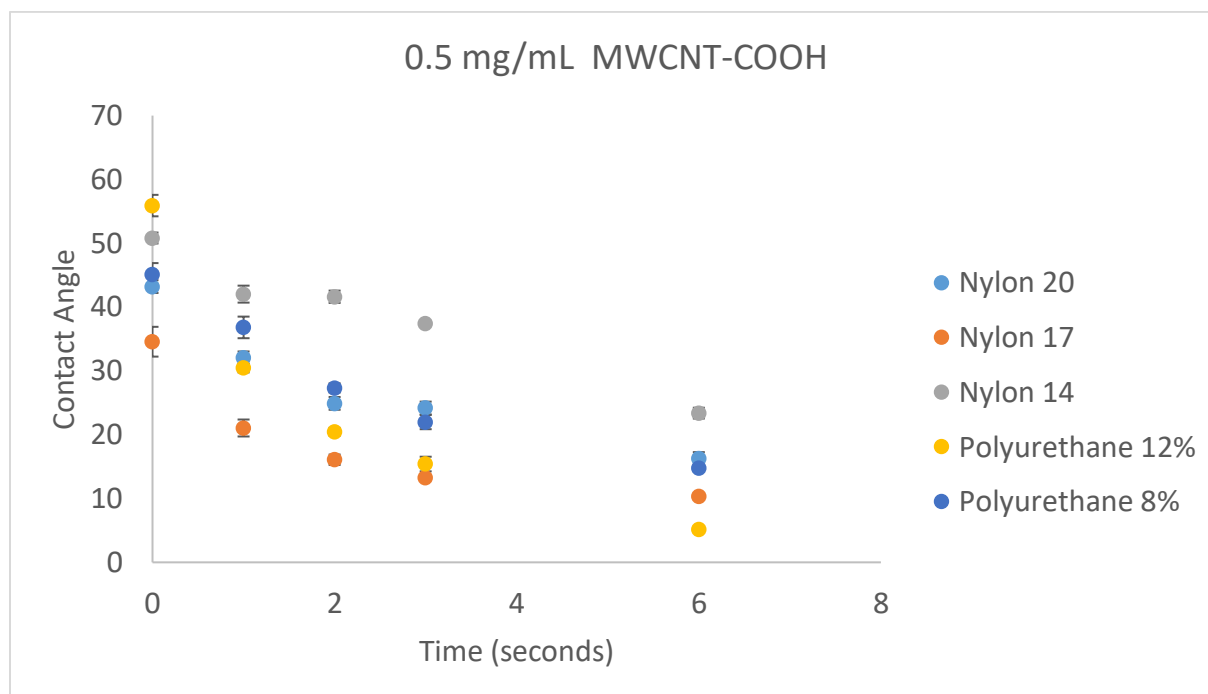


Figure 8 above shows the contact angle values for each polymer fabric tested at 0,1,2, and 6 seconds for .5 mg/mL concentration of MWCNT-COOH. Error bars represent the standard error of the measurements.

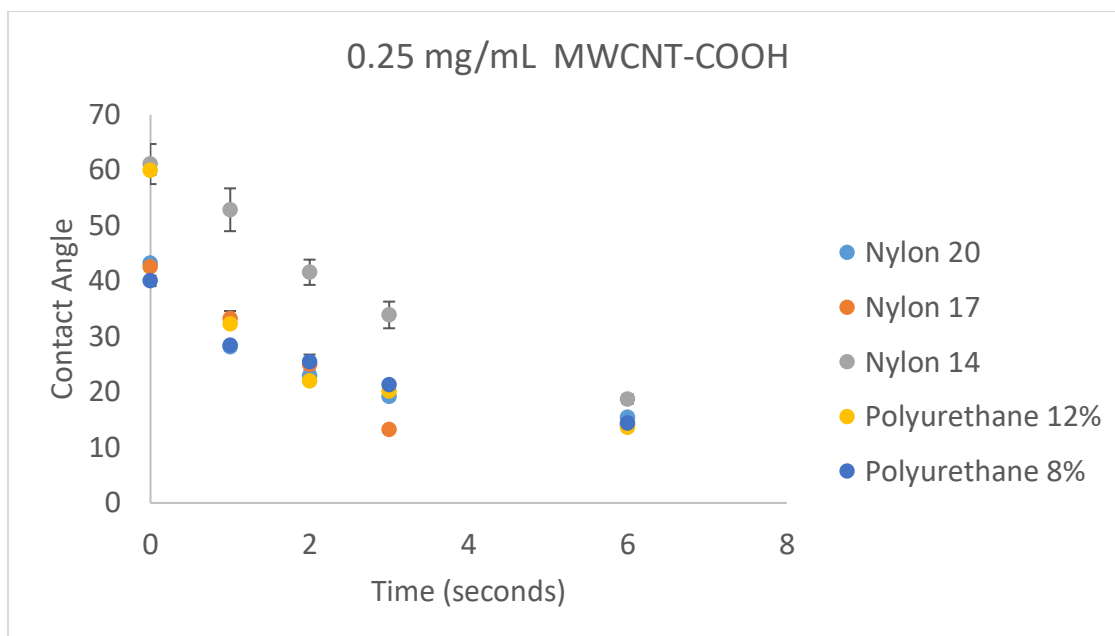


Figure 9 above shows the contact angle values for each polymer fabric tested at 0,1,2, and 6 seconds for .25 mg/mL concentration of MWCNT-COOH. Error bars represent the standard error of the measurements.

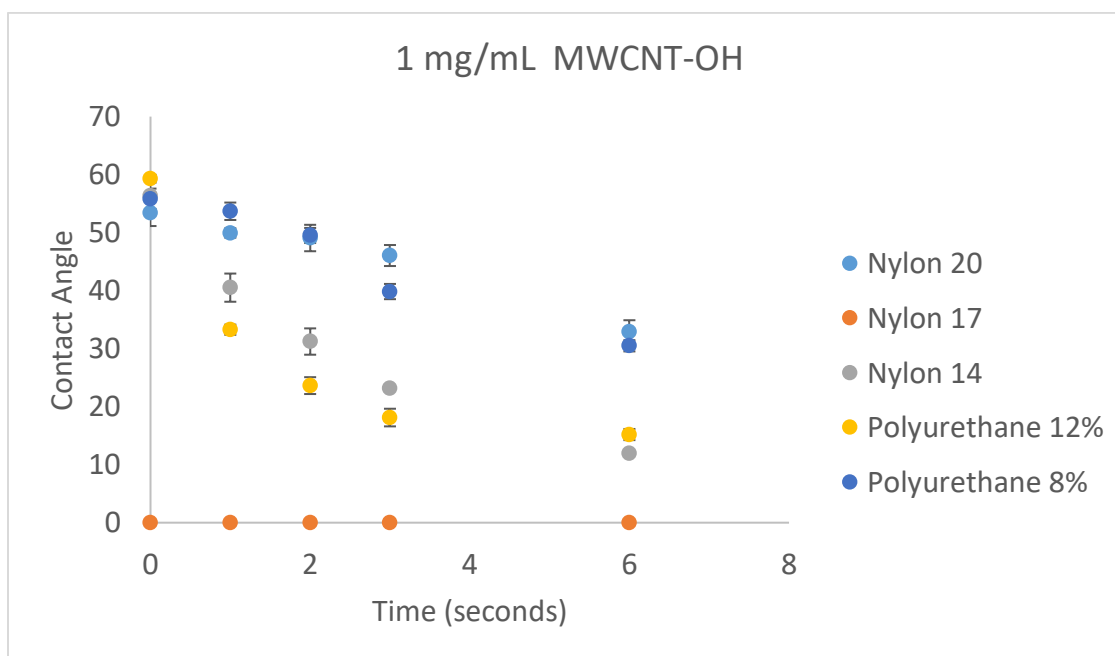


Figure 10 above shows the contact angle values for each polymer fabric tested at 0,1,2, and 6 seconds for 1 mg/mL concentration of MWCNT-OH. Error bars represent the standard error of the measurements.

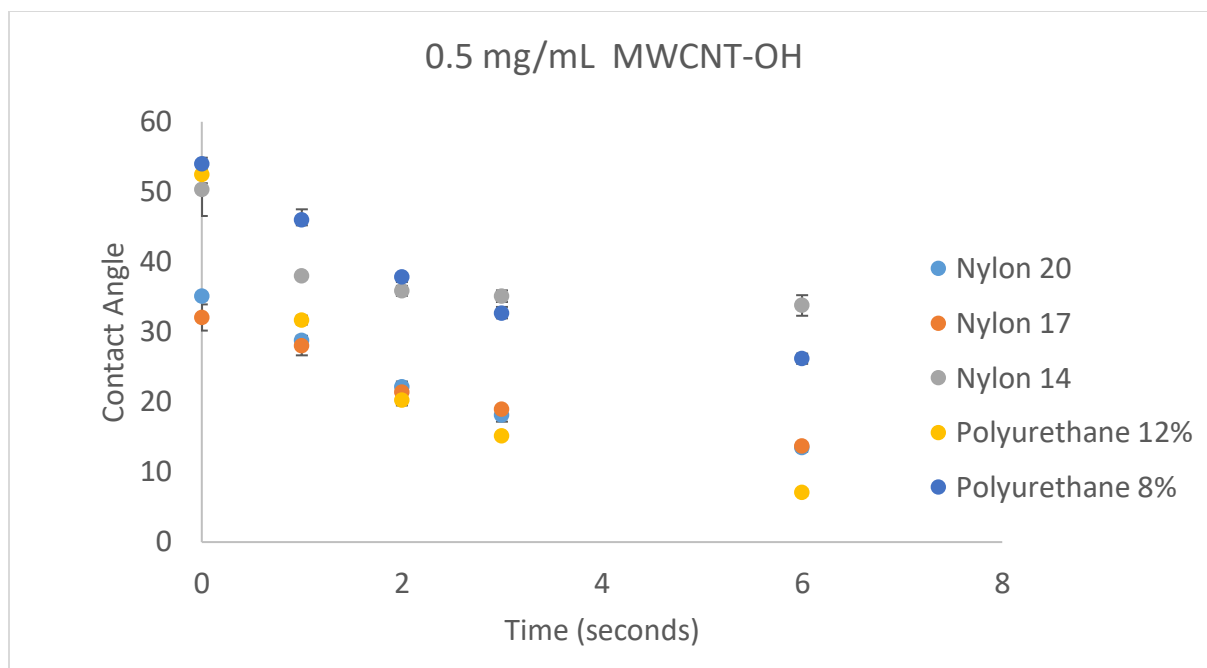


Figure 11 above shows the contact angle values for each polymer fabric tested at 0,1,2, and 6 seconds for .5 mg/mL concentration of MWCNT-OH. Error bars represent the standard error of the measurements.

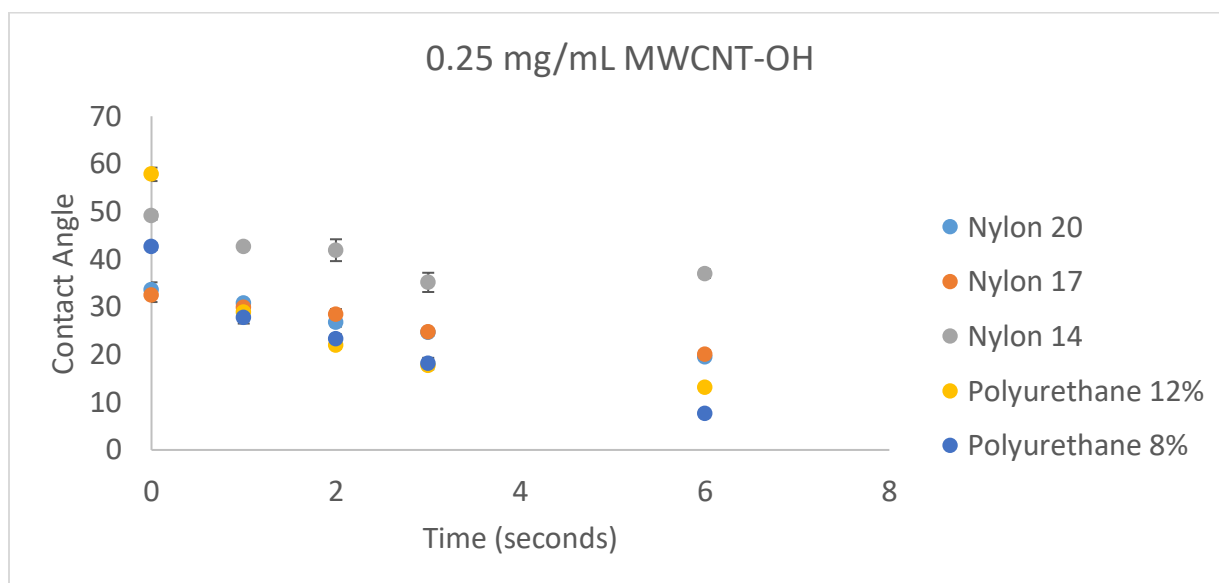


Figure 12 above shows the contact angle values for each polymer fabric tested at 0,1,2, and 6 seconds for .25 mg/mL concentration of MWCNT-OH. Error bars represent the standard error of the measurements.

Chronoamperometry Results

Each sensor was tested using the PotentioStat on Gamry Instrument Reference 3000 to track the changes in the voltage as sodium ion concentration is changed. The uninterrupted data for each sensor was analyzed using a derivative calculation method to determine a regression line for each sensor. The regression values are used to determine if the sensor is satisfactory for the next phase of development. If the regression value is greater than .8, it was considered a “Good Sensor”.

Table 2 shows each sensor’s regression value for the ‘Old’ sodium solution (OS) and the ‘New’ Sodium Solution.

Sensor #	Coat Weight (g)	Nanotube Concentration	Time Dip coated (Sec)	OS R ²	NS R ²
20	?	?	?	0.848	
26	?	?	?	0.734	
27	?	?	?	0.688	0.589
31	?	?	?	0.404	0.009
32	?	?	?	0.621	0.758
33	?	?	?	0.723	
34	?	?	?	0.604	
35	?	?	?	0.252	0.891
36	?	0.25	60	0.376	0.342
37	26	0.25	60	0.581	0.633
38	26	0.25	60	0.879	0.822
39	26	0.25	60	0.928	0.959
40	26	0.25	60	0.884	0.968
41	26	0.25	60	0.984	0.814
42	26	0.25	60	0.829	0.418
43	26	0.25	60	0.932	0.769
44	26	0.25	60	0.681	0.889
45	26	0.25	60	0.807	0.454
46	26	0.25	60	0.635	0.213
47	26	0.25	60	0.894	0.790
48	26	0.25	60	0.505	0.538
49	26	0.25	60	0.733	0.116
50	26	0.25	60	0.892	0.879
51	26	0.25	60	0.607	0.941

53	25.3	0.5	60	0.061	0.006
54	25.3	0.5	60	0.037	0.429
55	25.3	0.5	60	0.038	0.554
56	25.3	0.5	120	0.838	0.874
57	25.3	0.5	120	0.018	0.202
58	25.3	0.5	120	0.001	0.009
59	25.3	0.25	90	0.357	0.298
60	25.3	0.25	90	0.060	0.227
61	25	0.5	120	0.826	0.984
62	25	0.5	120	0.927	0.119
63	25	0.5	120	0.912	0.891
64	25	0.5	120	0.861	0.171
65	25	0.5	120	0.895	0.651
66	25	0.5	120	0.829	0.882
67	25	0.25	60	0.605	0.714
68	25	0.25	60	0.853	0.838
69	25	0.25	60	0.620	0.460
70	25	0.25	60	0.920	0.521
71	25	0.25	60	0.987	0.630
72	25	0.25	60	0.607	0.604
73	25	0.25	60	0.785	0.694
74	25	0.25	60	0.891	-
75	25	0.25	60	0.941	0.650
76	25	0.25	60	0.877	0.918
77	25	0.25	60	0.879	0.897
78	25	0.25	60	0.216	0.281
79	25	0.5	120	0.772	0.644
80	25	0.5	120	0.823	0.312
81	25	0.5	120	0.857	0.013
82	25	0.5	120	0.803	-
83	25	0.5	120	0.984	0.912
84	25	0.5	120	0.923	0.883
85	26	0.25	60	0.761	0.251
86	26	0.25	60	0.695	0.550
87	26	0.25	60	0.978	0.737
88	26	0.25	60	0.894	0.019
89	26	0.25	60	0.839	0.803
90	26	0.5	120	0.962	0.550
91	26	0.5	120	0.992	0.598
92	26	0.5	120	0.957	0.406
93	26	0.5	120	0.928	0.850
94	26	0.5	120	0.916	0.738

95	26	0.5	120	0.911	0.824
96	26	0.25	60	0.933	0.459

Discussion and Analysis

Contact Angle

The contact angle graphical data shows that in general as more water is added into the solution the material the contact angle of the material decreases, and the contact angle decreases with time which is to be expected. From the data, it appears there is not evidence that the polymer nanofibers response influences surface adhesion meaning no material is significantly better across all MWCNT concentrations for wettability than another. This supports Wujcik, Blasdel, Trowbridge, and Monty's understanding that the largest factor on the sensor is the solvent and carbon isomer concentration, but below the threshold of 4.5 weight percent MWCNT, there is little variation. **Figure 13** shows the differences in the polymer water works of adhesion (Wslv) depending on the type of material and the nanotube, backing the claim that the change in wettability does not affect sensor response. Wslv derives from the contact angle values understood in **Equation 1** below.

$$(1) \quad Wslv = 30 * (1 + \cos(\text{radians of contact angle}))$$

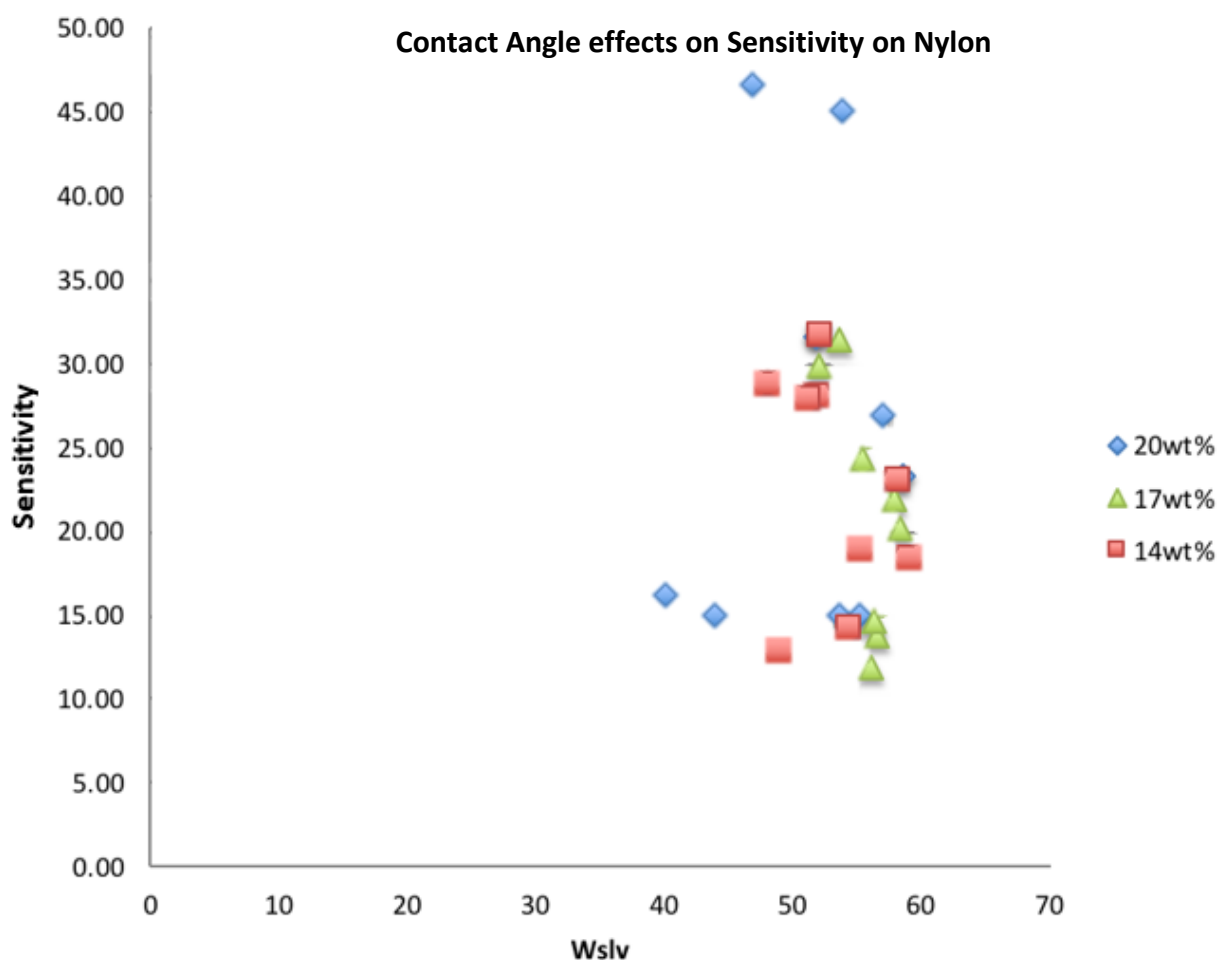


Figure 13 shows the relationship between the contact angle results through polymer water works of adhesion (Wslv) and the sensitivity of each nylon tested.

Chronoamperometry

Sensors 31 through 96 were fabricated with Evan Fritz. Each sensor was treated according to lab requests, recorded in **Table 2**. Variables included the MWCNT concentration and the amount of time dip-coated.

A two-sample T test was carried out comparing the old solution R^2 values to new solution R^2 values. The p-value for a two tailed T test was .012 meaning there is evidence to reject the null hypothesis and conclude that the two-population means are different at the 0.05 significance

level (alpha). Knowing there is a significant difference in the means, exemplifies that ‘old solution’ is more likely to result in a ‘good’ sensor than ‘new solution’ tests. The sensors were tested using 2 separate sodium ion solution series fabricated in the lab. NS was more selective with labeling sensors as ‘good’ seen in [Table 3](#).

Table 3 shows statistics for the population of sensors that were tested. *Before* represents sensor number 60 and below while *after* refers to sensor 61 and after. It is separated into the MWCNT concentrations used for creation of the sensor and the labels that each sensor was given based on its R^2 value.

	<i>Old Solution</i>	<i>New Solution</i>
Before	32	32
0.25	18	18
<i>bad</i>	9	11
<i>good</i>	9	7
0.5	6	6
<i>bad</i>	5	5
<i>good</i>	1	1
?	8	8
After	36	36
0.25	18	18
<i>bad</i>	7	13
<i>good</i>	11	5
0.5	18	18
<i>bad</i>	1	10
<i>good</i>	17	8
Grand Total	68	68

Looking at the data collected on the treated sensors, as the sensor number grew, so did the likelihood of the sensor being classified as ‘good’, illustrating reproducibility of sensor treatment. However, between the fabrication of sensor 60 and 61, the lab scale was relocated outside of the hood. Following that change, the average regression value for the sensors increased.

A two sample T test was carried out to compare the R^2 values for before the scale moving and after. The p-value for a two tailed t-test was .0012 meaning that there is evidence to reject the null hypothesis and conclude that the two-population means are different at the 0.05 significance level (alpha). This means there is a significant difference in the mean regression values for sensor numbers 60 and below and sensors greater than 60.

Based on the small sample size, it seems that after moving the scale, sensors dip coated in MWCNT at .5 concentration resulted in a higher R^2 seen in [Table 4](#). The decrease in the number of ‘good’ sensors could come from the larger range of sodium ion concentration from 10 mm to 150 mm, or the method used to create the sodium ion solutions.

Table 4 shows statistics for the population of sensors that were tested. *Before* represents sensor number 60 and below while *after* refers to sensor 61 and after. It is separated into the MWCNT concentrations used for creation of the sensor.

	<i>Old Solution</i>			<i>New Solution</i>		
	Count	Average R^2	Std Dev R^2	Count	Average R^2	Std Dev R^2
Before	32	0.576	0.319	28	0.550	0.322
0.25	18	0.698	0.249	18	0.615	0.291
0.5	6	0.166	0.330	6	0.345	0.340
	8	0.609	0.193	4	0.562	0.389
After	36	0.843	0.149	36	0.617	0.272
0.25	18	0.793	0.190	18	0.604	0.243
0.5	18	0.893	0.064	18	0.629	0.305
Grand Total	68	0.718	0.277	64	0.587	0.295

Based on the limited data, it appears that as dip-coat time increased so did the likelihood of the sensor being classified as ‘good’. However, Two Two-sample T tests were carried out to comparing the means of sensors characterized as ‘good’ for sensors dip-coated for 60 seconds and dip-coated for 120 seconds and the means of sensors characterized as ‘good’ for sensors with a .25 MWCNT concentration and .5 MWCNT concentration using alpha values equal to .05.

Both tests resulted in not enough evidence to reject the null hypothesis. Based on the sample size, concentration of the sensor treatment and the amount of time dip-coated does not significantly affect the regression values.

Overall, out of 68 sensors tested with both solutions, 49% are characterized as ‘good’ sensors (not including the unknown sensors). When reviewing just the old solution 63% are characterized as ‘good’ sensors and for just the new solution, 35% are characterized as ‘good’ sensors.

Conclusions

Contact angle results supported Wujcik, Blasdel, Trowbridge, and Monty showing that there is not much variation in sensitivity for loading of MWCNT below the threshold. This opened the opportunity for fabrication with any MWCNT isomer and concentration understanding that as the isomer concentration increase, so does opportunity for agglomeration, poor dispersion, and a gradient of MWCNT on the fiber. Using contact angle testing determined that “clumping” of nanotubes was due to the nanotubes liking to be clustered together vs. being dispersed on the polymer sheet.

Based on the chronoamperometry sensor data, dip coat time and MWCNT concentration does not significantly affect sensor characterization as ‘good’. However, sensors treated after sensor 60 and the old solution result in more sensors characterized as ‘good’. With the small sample size, the fabrication of more sensors would further validate the findings.

Overall reproducibility of a ‘good’ sensor is 49% (not including the unknown sensors).

Reproducibility for the OS is 63% and for the NS is 35%.

In the future, further chronoamperometry testing of the sensors will validate the ability for sensors to be used in the next phase, prototyping. The chronoamperometry data can then be used in reverse, taking sweat in real time and relaying the sodium ion levels continually. Further optimization and fabrication of the nanocomposites using calixarene and .3% TritonX-100 in water and MWCNT is necessary to try to increase reproducibility and develop a simple, usable application for real time sodium ion sensors.

Appendices

I. References

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II. Additional Data Tables

Table 5 shows the contact angle data averages from 3 readings of each drops the left and right-side angles.

Polymer	Time (sec)	TritonX and Water		1 mg MWCNT		0.5 mg MWCNT		0.25 mg MWCNT		1 mg MWCNT-COOH	
		CA	Wslv	CA	Wslv	CA	Wslv	CA	Wslv	CA	Wslv
Nylon 20	0	25.98	56.97	52.64	55.12	47.46	50.28	-	-	35.32	54.48
	1	20.75	58.05	39.90	53.02	28.86	56.27	-	-	28.77	56.30
	2	16.38	58.78	32.11	55.41	24.79	57.24	-	-	25.58	57.06
	3	11.79	59.37	30.77	58.28	19.16	58.34	-	-	24.28	57.35
	6	8.56	59.67	22.81	58.87	15.07	58.97	-	-	23.66	57.48
Nylon 17	0	25.98	56.51	39.49	52.99	47.76	50.17	44.55	51.38	48.13	50.02
	1	20.75	58.05	19.14	58.34	28.23	56.43	32.05	55.43	37.93	53.66
	2	16.38	58.78	15.18	58.95	23.08	57.60	24.24	57.35	25.35	57.11
	3	11.79	59.56	12.36	59.22	17.80	58.56	19.35	58.31	19.67	58.25
	6	8.56	59.70	7.30	59.71	7.85	59.72	6.49	59.81	7.93	59.71
Nylon 14	0	55.41	47.03	25.60	57.06	43.58	51.73	51.80	48.55	26.06	56.95
	1	50.72	48.99	18.98	58.37	32.21	55.38	50.71	49.00	13.11	59.22
	2	48.61	49.84	16.49	58.77	26.01	56.96	44.18	51.51	10.03	59.54
	3	45.79	50.92	12.68	59.27	22.14	57.79	41.96	52.31	7.74	59.73
	6	39.66	53.10	7.15	59.77	15.25	58.94	32.61	55.27	4.07	59.92
Polyurethane 12%	0	-	-	53.85	47.70	59.40	45.27	63.81	43.24	42.33	52.18
	1	-	-	24.27	57.35	29.73	56.05	32.40	55.33	36.74	54.04
	2	-	-	15.28	58.94	21.24	57.96	25.63	57.05	20.11	58.17
	3	-	-	11.64	59.38	17.30	58.64	21.30	57.95	13.39	59.18
	6	-	-	2.99	59.96	7.02	59.78	16.59	58.75	5.96	59.84
Polyurethane 8%	0	-	-	54.79	47.30	44.91	51.25	41.66	52.41	55.54	46.98
	1	-	-	52.71	48.18	25.89	56.99	30.22	55.92	43.69	51.69
	2	-	-	44.81	51.28	22.46	57.73	22.22	57.77	36.77	54.03
	3	-	-	36.05	54.26	20.60	58.08	18.95	58.37	32.45	55.32
	6	-	-	33.30	55.07	11.26	59.42	10.94	59.45	16.05	58.83

Table 6 shows the contact angle data averages from 3 readings of each drops the left and right-side angles.

Polymer	Time (sec)	.5 mg MWCNT-COOH		.25 mg MWCNT-COOH		1 mg MWCNT-OH		.5 mg MWCNT-OH		.25 mg MWCNT-OH	
		CA	Wslv	CA	Wslv	CA	Wslv	CA	Wslv	CA	Wslv
Nylon 20	0	43.85	51.63	43.20	51.87	53.44	47.87	35.05	54.56	33.60	54.99
	1	19.08	58.35	28.89	56.27	49.94	49.31	28.73	56.31	30.79	55.77
	2	17.43	58.62	22.98	57.62	49.07	49.66	22.14	57.79	26.73	56.79
	3	13.18	59.21	19.15	58.34	46.05	50.82	18.13	58.51	24.65	57.27
	6	9.96	59.55	15.46	58.91	32.89	55.19	13.45	59.18	19.54	58.27
Nylon 17	0	34.57	54.70	32.41	55.33	-	-	32.06	55.42	32.41	55.33
	1	21.05	58.00	29.85	56.02	-	-	28.03	56.48	29.85	56.02
	2	16.08	58.83	24.93	57.21	-	-	21.39	57.93	28.48	56.37
	3	13.29	59.20	13.18	59.21	-	-	18.94	58.38	24.76	57.24
	6	10.32	59.51	13.96	59.11	-	-	13.66	59.15	20.09	58.17
Nylon 14	0	50.82	48.95	61.11	44.50	56.35	46.62	50.31	49.16	49.13	49.63
	1	42.02	52.29	52.86	48.11	44.72	51.32	37.95	53.66	42.65	52.07
	2	41.61	52.43	41.59	52.44	31.22	55.66	35.87	54.31	41.90	52.33
	3	37.41	53.83	33.90	54.90	23.19	57.58	35.10	54.54	35.15	54.53
	6	23.38	57.54	18.73	58.41	11.97	59.35	33.78	54.94	36.96	53.97
Polyurethane 12%	0	55.90	46.82	59.98	45.01	59.29	45.32	52.45	48.28	57.81	45.98
	1	30.45	55.86	32.27	55.37	33.26	55.09	31.69	55.53	28.94	56.25
	2	20.46	58.11	21.93	57.83	23.63	57.49	20.25	58.15	21.98	57.82
	3	15.40	58.92	20.16	58.16	18.12	58.51	15.14	58.96	17.67	58.58
	6	5.18	59.88	13.56	59.16	15.19	58.95	7.08	59.77	13.13	59.22
Polyurethane 8%	0	45.10	51.18	40.03	52.97	55.84	46.85	53.96	47.65	42.62	52.08
	1	36.81	54.02	28.44	56.38	53.68	47.77	45.95	50.86	27.75	56.55
	2	27.33	56.65	22.11	57.79	49.50	49.48	37.86	53.69	23.33	57.55
	3	21.97	57.82	21.33	57.95	39.84	53.04	32.67	55.25	18.10	58.51
	6	14.72	59.02	14.41	59.06	30.49	55.85	26.18	56.92	7.61	59.74

Table 7 shows the 2- tailed T test for comparing the number of sensors characterized as ‘good’ for the old solution and new solution using an alpha value equal to .05.

	<i>OS</i>	<i>NS</i>
Mean	0.716	0.587
Variance	0.077	0.087
Observations	68	64
Pooled Variance	0.082	
Hypothesized Mean Difference	0.000	
df	129	
t Stat	2.559	
P(T<=t) one-tail	0.006	
t Critical one-tail	1.657	
P(T<=t) two-tail	0.012	
t Critical two-tail	1.979	

Table 8 shows the 2- tailed T test for comparing the means of sensors characterized as ‘good’ for sensors below and including sensors 60 and after sensor 60 using an alpha value equal to .05.

	<i>Before</i>	<i>After</i>
Mean	0.564	0.730
Variance	0.101	0.060
Observations	60	72
Hypothesized Mean Difference	0	
df	110	
t Stat	-3.316	
P(T<=t) one-tail	0.0006	
t Critical one-tail	1.659	
P(T<=t) two-tail	0.0012	
t Critical two-tail	1.982	

Table 9 shows the 2- tailed T test for comparing the means of sensors characterized as ‘good’ for sensors with a .25 MWCNT concentration and .5 MWCNT concentration using an alpha value equal to .05.

	<i>0.25</i>	<i>0.5</i>
Mean	0.719	0.635
Variance	0.059	0.124
Observations	52	48
Pooled Variance	0.090	
Hypothesized Mean Difference	0	
df	98	
t Stat	1.403	
P(T<=t) one-tail	0.082	
t Critical one-tail	1.661	
P(T<=t) two-tail	0.164	
t Critical two-tail	1.984	

Table 10 shows the 2- tailed T test for comparing the means of sensors characterized as ‘good’ for sensors dip-coated for 60 seconds and sensors dip-coated for 120 seconds using an alpha value equal to .05.

	<i>60</i>	<i>120</i>
Mean	0.662	0.699
Variance	0.074	0.101
Observations	74	42
Pooled Variance	0.084	
Hypothesized Mean Difference	0	
df	114	
t Stat	-0.662	
P(T<=t) one-tail	0.254	
t Critical one-tail	1.658	
P(T<=t) two-tail	0.509	
t Critical two-tail	1.981	

III. Procedures

1. Treating Nylon with Nanotubes Procedure

A. Creation of Polymer nanocomposites

1. 1 mg CNT solution:
2. Measure [2 mgs] of nanotube (CNT, CNT-OH or CNT-COOH)
3. Combine [2 mgs] of nanotubes with [2 mL] of .03% TX solution.
 - a. To create .03% tritonX (TX) solution:

- i. Make a 3% TX solution with 3 ml of TX and 97 mL of DI water
- ii. Take 10 mL of 3% TX and combine with 90 mL of DI water
4. Sonicate without heat for 60 minutes. *
5. Cut [1 cm by 1 cm] of the nylon sheet**
6. Dip-coat the 1 cm² into mixed solution for [60 seconds]. ***
7. Immediately Dip-coat the nylon in clean DI water (as a rinse) for [60 sec]. ***
8. Place nylon on aluminum Petri dish to dry for 24 hrs.

TABLE 11 shows the recipes for each desired concentration of carbon nanotubes.

Concentration	Amount of CNT	Amount of .03% TX solution
.25	1 mg	4 mL
.5	1 mg	2 mL
1	2 mg	2 mL

*Be sure to seal the vials with parafilm to reduce contamination.

**For prototype testing cut the polymer into 2 cm by 1cm and double amounts of CNT and TX solution.

*** The amount of time the polymer square was soaked/rinsed was a varied variable for some tests.

B. Creation of Calixarene Solution

1. Combine 12.5 mg of Calixarene (be sure to store this in a “closed container” to reduce humidity effects on calix.) and 5 mL of toluene. **
2. Stir using stir plate for about 15 minutes until the calixarene is dissolved. *
3. Place nylon treated with nanotubes in the calix/toluene solution and sonicate for 5 minutes without heat. *
4. *Leave the nylon in the solution overnight
5. Remove from solution and Place nylon on aluminum Petri dish to dry.

*Be sure to seal the vials with parafilm to reduce contamination.

**For prototype testing cut the polymer into 2 cm by 1cm and double amounts of CNT and TX solution.

C. Contact Angle Procedure using Drop Shape Analysis and Image J

1. Sonicate the CNT/TX solutions before testing.
2. Cut 1 cm by 1 cm of [nylon] sheet. This nylon should not be treated. You will need 1 square for each test.
3. In Dr. Chase's Lab, login to the DSA computer. Turn on machine and then open software.
4. Remove specified CNT needle from cabinet. This needle has a larger gauge to transfer carbon nanotubes.
5. Use software to fill needle with 15 μmL of solution. 5 μmL is all that is needed, but often excess is necessary.
6. Place one untested, untreated 1 cm by 1 cm polymer fabric on a slide using double sided tape. This will keep the fabric in place, without affecting the adhesion properties.
7. Begin recording and drop μmL of the solution. On the screen, a droplet should appear at the base of the needle. Use the platform adjuster to move the fabric up to the droplet. Bring the nylon back down and watch the drop dissipate.
8. Stop recording and save for later analysis using Image J.
9. Empty the drop needle and syringe using the DSA software.
10. Rinse needle with acetone and DI water and dry with air.
11. Repeat steps 5 – 10 for the remainder of solutions to be tested. Each material should test 10 Solutions (1 mg, .5 mg, .25mg concentrations of CNT, CNT-OH, and CNT-COOH and TX/water),

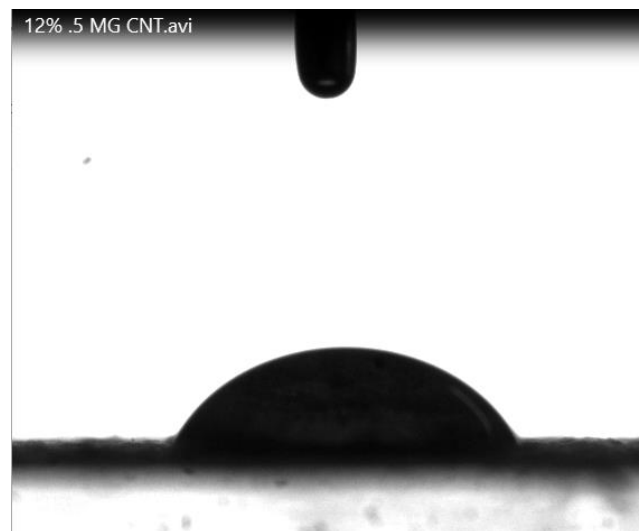
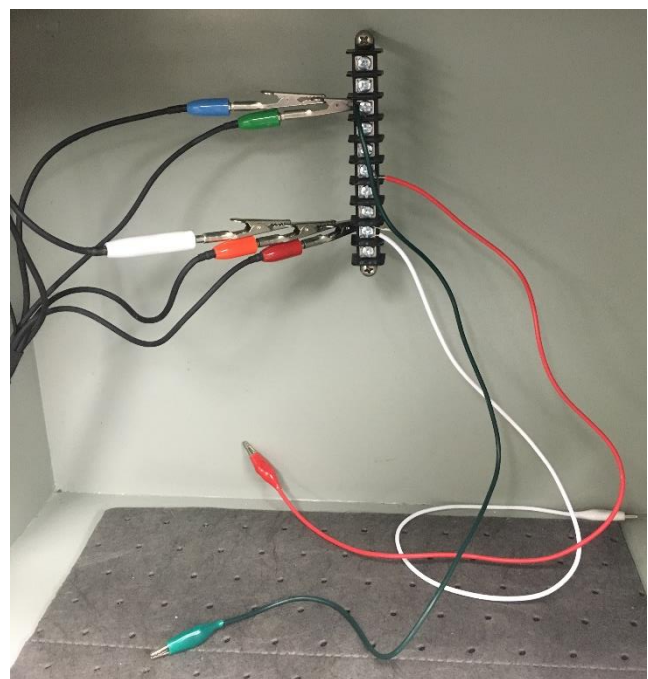


Figure 14 displays the image from 12% nylon dropping .5 mg/mL CNT solution.

2. Chronoamperometry Testing

1. Setup Gamry Instrument Reference 3000 Potentiostat/Galvanostat/ZRA via direct-current (DC)
 - a. Connect electrodes properly into a 2-electrode set up according to image.
 - i. Blue clip should be connected to the green clip which is connected to the 3rd screw from the top creating the working electrode.

Figure 15 displays the correct alligator clip formation for electrode connection when using the Gamry Instrument Reference.



- ii. White clip connects to the orange clip attached to the red clip which acts as the counter electrode when connected to the 2nd screw from the bottom
 - iii. If the electrode is not connected to the Potentiostat, do so using the free green and white alligator clips.
 - b. Wash glass slide and clips.
 - c. Open Gamry software on connected computer.
 - i. Experiment → Physical Chemistry → Chronoamperometry
 - d. Begin Chronoamperometry Testing of various levels of sodium ion concentration.
 - i. Creation of sodium ion concentrations uses milliQ water.
2. Place both clips on opposite sides of the treated sensor. Be sure that the clips are not touching each other. See image.
3. Begin recording data on Gamry software.
4. Using a pipette, drop 30 μL onto the treated sensor starting with the lowest sodium concentration.
5. After graphed response has leveled, continue with the next concentration without stopping the recording.
6. Repeat steps 2 - 4 for each concentration.
7. Stop recording responses.
8. Be sure to save the responses for chronoamperometry derivative analysis.



Figure 16 shows the electrode sensor connection for the chronoamperometry testing.

3. Preparation of Large Sensor

- a. Treating Nylon with Nanotubes Procedure for Large Sensor

Table 12 displays formulas for fabrication of a large sensor.

Concentration	Amount of CNT	Amount of .03% TX solution	Amount of Calixarene	Amount of Toluene
.25	25 mg	100 mL	250 mg	100 mL
.5	50 mg	100 mL	250 mg	100 mL
1	1 mg	1 mL	250 mg	100 mL

To create a .25 mg CNT solution:

1. Measure [25 mgs] of nanotube (CNT, CNT-OH or CNT-COOH).
2. Combine [25 mgs] of nanotubes with [100 mL] of .03% TX solution.
3. Sonicate without heat for 60 minutes. *
4. Cut [4.25 in by 4.25 in] of the nylon sheet.
5. Soak polymer square into mixed solution for [60 seconds].
6. Immediately place the nylon in clean DI water (as a rinse) for [60 sec].
7. Place nylon on aluminum Petri dish to dry for 24 hrs.

*Be sure to seal the vials with parafilm to reduce contamination.

b. Creation of Calixarene Solution for Large Sensor

1. Combine 250 mg of Calixarene (be sure to store this in a “closed container” to reduce humidity effects on calixarene) and 100 mL of toluene.
2. Stir using stir plate for about 15 minutes until the calixarene is dissolved. *
3. Place nylon treated with nanotubes in the calixarene/toluene solution and sonicate for 5 minutes without heat. *
4. *Leave the nylon in the solution overnight
5. Remove from solution and Place nylon on aluminum Petri dish to dry.

*Be sure to seal the vials with parafilm to reduce contamination.

4. SSCS Electrospinning Procedure

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1. Polymer Solution Preparation

- a. Approximately 10 mL of X% nylon-6 solution is made to use to electrospin.
 - i. Make sure enough polymer solution is ready when needed by mixing it the night or day before spinning.
 - ii. See **Table 9** for recipes of the different weight % solutions

Table 13: Recipe for Polymer Electrospun Fabric

Component	Grams of component for X% PA-6 solution				Amount (mL)
	10%	12%	14%	20%	
PA-6	1.1111	1.3636	1.6279	2.5000	
Calculated %	10.00	12.00	14.00	20.00	
Formic Acid ~98%	5.000				4.095
Acetic Acid 99%	5.000				4.765

- b. In a plastic weigh-boat, weigh out desired amount of polymer (since polymer is in pellet form the exact amount in grams from above may be hard to obtain, get within one pellet) and record the weight.
- c. In a hood, dispense 4.095 mL of formic acid and 4.765 mL of acetic acid into a new labeled scintillation vial using a pipette.

- d. Place a clean and dry magnetic stir bar (there is one that continually used in ES box in the SSCS cabinet) into the acid solution and put on a stir plate, stirring at about half to three quarters speed.
- e. With the acids stirring, pour in the PA-6 pellets, ensuring that all pellets enter the vial (the pellets will start to stick together, this is normal).
- f. Put cap on vial and ensure vial is clamped so it doesn't walk off the stir plate during stirring.
- g. Allow stirring overnight or until all the PA-6 pellets are dissolved.
- h. This solution can be stored (with the cap on tightly) for short periods of time (approximately 1 week) for use. If the solution sits too long the PA-6 wt.% will change, as these acids are volatile.
- i. **MAKE SURE TO REMOVE AND CLEAN THE STIR BAR**
 - i. Remove stir bar using a magnet, which should be stuck to the cabinet underneath the dry chemical storage. Do this in a hood and clean the polymer and acid off the magnet as well.
 - ii. Put the stir bar in a medium sized beaker with 2 successive aliquots of approximately 1:15 parts 70% HNO_3 solution and stir for about 1 minute on a stir plate (2 successive aliquots means to do this twice) and empty the acid/polymer solution into a waste beaker. Be sure to add acid to the water.
 - iii. Put 20 mL DI H_2O into the beaker and stir for about 1 min, and empty into the waste beaker.
 - iv. Put 20 mL acetone into the beaker and stir for about 1 min, and empty into the waste beaker
 - v. Wipe off the stir bar using a Kim-wipe and ensure that all dried polymer is removed from its surfaces.
 - vi. Empty the waste beaker into the aqueous waste drum and record on the aqueous waste form.

2. Electrospinning Setup

- a. **Materials and supplies:** ES box from SSCS cabinet should contain the following: roll of tubing (Cole-Parmer, Item#:06605-27, 1/16" ID x 1/8" OD), a scintillation vial of female luer thread style to 200 series barbs (Cole-Parmer, Item#: 45500-00, 1/16" ID tubing), scintillation vial of male luer to 500 series barbs (Cole-Parmer, Item#: 455503-41, 1/16" ID tubing), a tubing cutter, a copper sheet wrapped around PVC pipe, a scintillation vial of HNO_3 cleaning solution (about 1 mL 70% HNO_3 to 15-20 mL DI H_2O), a scintillation vial of DI H_2O , a blue holder of stainless steel reusable needles (20 G x 1") sanded, some cotton balls, some 5 mL syringes (BD, Lure-Lok Tip, w/ 21g x 1" needle) we do not use the plastic/metal needle, but please save), some gloves, a marker, scissors, a stir bar, a roll of masking tape, a role of scotch tape, and a razor blade.
 - i. *****Note: Keep ES box stocked periodically and let a grad student know if you are running low on any of the above supplies.**
- b. **Cleaning of the Copper Sheet**

- i. **NOTE: BE CAREFUL NOT TO BEND, CRINKLE, AND/OR KINK THE COPPER SHEET. WE WOULD LIKE THE SHEET TO STAY AS UNIFORM A SURFACE AS POSSIBLE.**
 - ii. In a hood, tear two long pieces of paper towel and put the copper sheet on one of them (Do one side at a time, each on a dry piece).
 - iii. Make sure to have 2 small pieces of paper towel to wipe off the copper sheet with DI H₂O and acetone after acid cleaning.
 - iv. Wet a cotton ball with the HNO₃ cleaning solution and wipe off the oxidation from the entire copper sheet (this will be visibly apparent as it will go from a dullish brown to a shiny copper).
 - v. Wipe the HNO₃ solution off the copper sheet with the DI water wet paper towel and wipe it off with an acetone-wet paper towel.
 - vi. Dry the copper sheet using a dry paper towel.
 - vii. Repeat steps (ii) through (v) for the other side of the copper sheet.
- c. **Wrapping Copper Sheet with Paper Towel**
 - i. **NOTE: BE CAREFUL NOT TO BEND, CRINKLE, AND/OR KINK THE COPPER SHEET. WE WOULD LIKE THE SHEET TO STAY AS FLAT A SURFACE AS POSSIBLE.**
 - ii. Tear off 8 small pieces of masking tape and line them up on the corner of a nearby surface.
 - iii. Once the copper sheet is dry, pull a new piece of paper towel out from the roll, cut the end not attached to the roll flush with a pair of scissors.
 - iv. Put the copper sheet, with the tape side facing up, on the paper towel.
 - v. Pull approximately ½" of the flush end of the paper towel over the copper sheet and tape it to it.
 - vi. Cut the paper towel from the roll about ½" longer than the length of the copper sheet.
 - vii. Fold the ½" of the towel over the end and tape it to the copper sheet.
- d. Wrap the copper sheet tightly around the drum so that the overlap is pointing toward the right side of the cabinet.
 - i. **NOTE: BE CAREFUL NOT TO BEND, CRINKLE, AND/OR KINK THE COPPER SHEET. WE WOULD LIKE THE SHEET TO STAY AS FLAT A SURFACE AS POSSIBLE.**
 - ii. **Tape the paper towel covered copper sheet to itself by taping the overlap at each end of the drum with scotch tape.**
- e. Check the rotation speed of the drum
 - i. Flip the switch on the variac to on (the drum may not start rotating because this set up sits in a harsh/corrosive environment).
 - 1. If the drum doesn't rotate turn the variac voltage up to 35 or 40 to get the wheel rotating and turn it back to around 31 volts.
 - ii. Count the RPM using the black mark on the outside edge of the drum end cap closest to the cabinet door, if not at approximately 7 RPM, adjust the variac voltage accordingly.

- f. Set up of the needle, syringe, and syringe pump:
 - i. If desired, sand needle to a point using a sander (Dr. Chase Lab).
 - ii. Put the SS needle, which at this point should have the male luer tubing connector in the fat end, in the needle stand (Choose a hole and stick to it, there are 2 options).
 - iii. Look through the top of the cabinet and adjust the stand position so that the needle tip is in the center of the collector with at least 1" travel on either side of that center. This is verified on the needle ruler (Note the ruler values that gives 3 stopping points for the needle movement across the drum face while spinning).
 - iv. Measure the distance between needle tip and collector and set to approximately 9 cm by moving the needle stand toward or away from the collector.
 - g. Fold the sided in and tape to the copper sheet.
 - h. Fold corners and tape to the copper sheet
 - i. Wrap and tape the paper towel covered copper sheet around the PVC pipe and put in the ES box to transport to the appropriate lab (Dr. Evans, or Dr. Chase)
3. ES Set up in ES Cabinet.

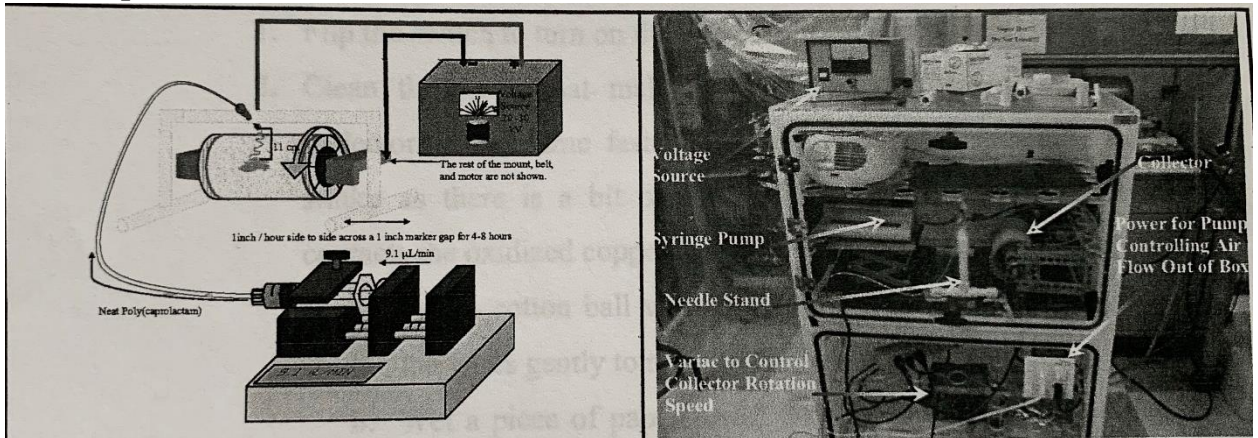


Figure 17: Electrospraying schematic and cabinet

- a. **Check the voltage source (VS):** (we share the VS with other projects and they use the hood, so their wires may be connected).
 - i. **WARNING; THE HIGH VOLTAGE SOURCE CAN CAUSE SERIOUS ELECTRIC SHOCK THAT COULD RESULT IN DEATH. TAKE ALL PRECAUTIONS TO NOT HANDLE OR TOUCH THE ELECTRICAL CONNECTION DURING OPERATION. MAKE SURE TO USE EXTREME CARE WHEN USING A DEVICE OF THIS NATURE.**
 - ii. The positive lead wire has a white plug type end that plugs into the back of the VS and goes through to the interior of the cabinet and will connect to the fat part of the stainless-steel needle by alligator clip on the top side of the needle stand.

- iii. The negative lead wire has an eyelet end that must be clamped to the threaded post on the back of the VS by the post nut and goes through to the cabinet interior connecting to the bracing that holds the rotating drum collector (check periodically that the connection point on the bracing is clean of corrosion; sandpaper, water, and acetone work well to clean).
- iv. Make sure the VS is set to the correct setting by turning on and adjusting the voltage with the center knob on the VS front panel, turn back off until ready to use.

b. Set up the collector:

- i. To reduce humidity within the cabinet, connect fresh air supply and flip the switch to turn on the cabinet airflow out pump. Ensure that the air out is connected to vacuum.
- ii. Clean the wires that make up the face of the rotating drum collector in the same fashion as the copper sheet (the sheet may smell bad based on the smell when nitric acid contacts oxidized copper).
 - 1. Wet a cotton ball with HNO₃ cleaning solution and wipe the wires gently to remove the corrosion.
 - 2. Wet a piece of paper towel with DI H₂O, quickly and gently wipe off the cleaning solution from the wires.
 - 3. Wet another piece of paper towel with acetone, quickly and gently wipe away the water from the wires.
 - 4. Dry the wires with a dry piece of paper towel.
 - 5. HNO₃ should NOT dry on the wires so only clean 7-8 at a time and rotate the drum by hand and repeat the steps until all wires are clean.
 - 6. When all wires are clean, gently pull the drum end caps (polycarbonate wheels that the copper wires are strung too) away from each other on its axel to make the wires taut.
 - 7. Rotate the drum and pull on the middle point between the end caps of each individual wire, lightly, giving a slight hump to each wire point outward from the drum's interior (This helps to ensure good contact between the wires and the copper sheet).
- c. Take a new syringe, put the plastic/metal needle in the ES box, put the female luer tubing connector on the syringe barrel and screw it down, and clamp the barrel in the syringe pump (ensure the syringe barrel is pushed as far to the right as possible in the pump).
- d. Eyeball and cut the amount of tubing needed using the tubing cutter (do this by putting an end of the tubing up to the luer tip in the needle and use a marker to mark the length on the tubing at the luer tip on the syringe barrel in the syringe pump).
- e. Put the needle and syringe barrel together.
 - i. Wearing gloves makes placing the tubing and connectors together easier

- ii. Make sure to expand the end of the tubing that gets the needle luer tip using the barb on the syringe barrel luer tip before putting the needle luer tip barb into the tubing because the barbs on the needle luer tip are cheap and will bend and break if trying to shove it into the tubing alone.
- f. Calculate the required amount of polymer solution for the desired spin time

$$\text{Volume needed } (\mu\text{L}) = \text{syringe pump flowrate } \left(\frac{\mu\text{L}}{\text{min}} \right) * \text{spin time } (\text{min})$$

- g. Turn on the syringe pump and check and adjust the settings (toggle switch in back on right side of the pump).
- h. Volume – set this to the value calculated above and the syringe pump will stop pumping once the volume dispensed reached this value.
 - i. Flowrate = 9.1 $\mu\text{L}/\text{min}$
 - ii. Diameter = 11.81 mm
- i. Once the needle setup is together, fill the syringe barrel with polymer solutions
 - i. Take the needle and tubing off the syringe barrel.
 - ii. Fill the syringe with approximately .5 mL more than the amount calculated above. This excess will be used to fill the tubing.
 - iii. Remove air bubbles from the polymer solution by pulling/pushing the plunger slowly and gently a few times and setting the syringe barrel in the hood on the plunger with the tip pointing straight up for a few minutes to let the air bubbles rise to the top where they will be pushed out when filling the tubing.
 - iv. Reconnect the needle and tubing to the syringe barrel.
 - v. Slowly push the plunger to fill the tubing and needle (watch the solution level closely in the tubing so to not squirt polymer/acid solution everywhere)
 - vi. Put the syringe setup back into the syringe pump and clamp it in making sure the tabs on the syringe barrel are centered and pushed against their support on the pump.
 - vii. Put the needle tip into the needle stand.
 - viii. Check that the pump is pumping.
 - 1. Push the button on the drive plate to disengage the drive plate from the drive screw and push the drive plate up to the syringe plunger.
 - 2. Release the button and wiggle the drive plate to make sure the lock is seated properly in the drive screw thread groove.
 - 3. Push the start/run button and watch the tip of the needle for polymer solution exiting the needle.
 - a. If the solution doesn't seem to come out of the tip (this is an old syringe pump that is finicky and requires finesse at times).
 - i. Wipe the tip with a paper towel.

- ii. Turn the pump flow rate up to 30 or 40 $\mu\text{L}/\text{min}$ and watch the tip (polymer solution will come out fast when it starts to pump at this rate)
 - iii. When the polymer solution starts to flow, press the start/run button again to stop the pump.
 - iv. Readjust the flow rate to 9.1 $\mu\text{L}/\text{min}$.
 - v. The syringe pump should be ready to run.
- ix. Connect the positive lead alligator clip to the fat end of the needle.
- x. Push the needle to the starting ruler mark toward the back of the cabinet.
- j. Now the setup is ready to start spinning

4. Electrospinning

- a. Make sure the collector is rotating and the airflow pump is running.
- b. Clear the volume dispensed on the syringe pump LCD screen by pressing select through all volume and flow rate settings.
- c. Clean off the needle tip with a paper towel.
- d. Start the syringe pump by pressing the start/run button and quickly close the cabinet door and start the VS (MAKE SURE YOUR HANDS ARE OUT OF THE CABINET AND THE CABINET DOOR IS PUSHED SHUT BEFORE STARTING THE VS TO ENSURE THAT YOU DO NOT GET SHOCKED).
- e. Turn the handles to lock the door shut.
- f. Check that polymer is electrospinning by watching for a white band that will start to show on the collector after a few rotations of the drum. Utilize the black background to see the jet exiting the needle tip.
- g. Periodically look at the material and ensure no polymer strands hanging from the needle tip (this will start to happen at relative humidity lower than approximately 30%).
 - i. If so, turn all the handles on the cabinet door to open the cabinet.
 - ii. Shut off the VS.
 - iii. Open the cabinet door and quickly and carefully stop the syringe pump (Be careful when opening the cabinet door, as the cabinet will be full of acetic acid vapor and a breath of this is not pleasant).
 - iv. Open the cabinet door all the way, stand back, and allow the cabinet to air out for a few minutes.
 - v. Wipe the tip of the needle with a paper towel.
 - vi. Restart the syringe pump, close the cabinet door, start the VS, and lock the handles.
- h. After 1 hour, move the needle 1 inch on the ruler.
 - i. Turn the handles on the cabinet door to unlock them.
 - ii. Turn off the VS.
 - iii. Quickly open the door and stop the syringe pump by pushing the start/run button.
 - iv. Let the cabinet air out for a few minutes as before.
 - v. Move the needle 1" in the desired direction.

1. The needle should start at position toward the back of the cabinet and move toward the front of the cabinet on the first two moves, toward the back of cabinet for 2 moves and so on across the face of the drum 1' movement/hr. for the duration of the spun time.
 - i. When getting close to the end of the total spun time check the volume dispensed. The syringe pump will stop pumping at the programmed volume.
 - j. Turn off the VS when the syringe pump stops.
 - k. Stop the rotating drum.
- 5. ES Setup Teardown and Clean Up**
- a. Turn the rotating drum by hand until the overlap seam is seen.
 - b. Using a razor blade cut the tape and PA-6 nanofiber mat to remove the copper sheet and material.
 - i. Make sure not to bend or crinkle the copper sheet when removing it from the drum.
 - ii. Make sure the PA-6 material doesn't touch or run on the shelf floor in the cabinet when removing the copper sheet from the drum.
 - c. Wrap the copper sheet with PA-6 material around the PVC pipe and tape it for transport.
 - d. Remove the needle setup from the needle stand and syringe pump.
 - e. Turn off the syringe pump and cabinet airflow out pump.
 - f. Take the ES box with everything in it back to the lab.
 - g. Clean the needle and needle set up.
 - i. Gather the needle cleaning equipment
 1. In the bottom scintillation vial box in hood 1, there is a syringe barrel in a scintillation vial and a plunger (separate from each other).
 - ii. Grab a 250 mL waste beaker, the HNO₃ from the acid cabinet, DI H₂O and acetone.
 - iii. In the scintillation vial mix approximately 1 mL of HNO₃ to 15 – 20 mL of DI H₂O.
 - iv. Take up 5 mL of this solution with the syringe
 - v. Take the SS needle off the ES syringe setup and put it on the syringe with the cleaning solution.
 - vi. Empty the contents of the cleaning solution syringe through the SS needle into the 250 mL beaker (the needle may plug, if more than a slight pressure is necessary, wipe the tip with a Kim wipe and push the plunger again).
 - vii. Take up the leftover cleaning solution into the syringe through the needle tip and dispense it into the waste beaker through the needle tip.
 - viii. Repeat steps c-g (do not mix HNO₃ in step c for the repeat steps) using DI H₂O and acetone to finish cleaning and drying the needle.
 - ix. Take the needle off the syringe and wipe out the polymer that accumulates in the fat end with a Kim-wipe.

- x. Put the needle back into the blue holder in the ES box.
- xi. Take the cleaning syringe barrel and plunger apart and put them back where they were found.
- xii. Empty the left-over polymer from the ES syringe and tubing into a scintillation vial to air dry in a hood overnight for disposal in the glass waste bucket the next day.
- xiii. Dispose of the waste from the 250 mL beaker into the aqueous waste and record that information on the aqueous waste sheet.
- xiv. Clean all used glassware and put everything back where it was found.
- xv. Put the PA-6 material away for later use.
 - 1. Tear off a piece of paper towel to place the PA-6 material and copper sheet on.
 - 2. Place the paper towel backing wrapped copper sheet, PA-6 material side down onto the torn off paper towel.
 - 3. Remove all the masking taped holding the paper towel to the copper sheet and discard them in the trash (Do not move the PA-6 material around on the torn off paper towel, because we don't want to damage the PA-6 mat surface).
 - 4. Remove the copper sheet from PA-6 and paper towel backing and tape it back to the PVC pipe for next time. Do not bend or crinkle or kink the copper sheet.
 - 5. Fold the PA-6 material and paper towel backing in half so the PA-6 is facing itself and label the end with the most paper towel showing with the material number and date.
 - 6. Put the material in the material box in the SSCS cabinet, where it should sit for at least 2 days to air off the remaining acetic acid vapors before it goes to membrane and sensor construction.