

On Applications of Hydrogel-coated Nanorod Films as Soil Humidity Sensors

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ABSTRACT

Hydrogels are a well-studied class of materials composed of polymer chains, known primarily for absorbing water. Our current multi-step curing process allows us to attach a substrate containing an array of hundreds of nanorods to the surface of a thin hydrogel film. By harnessing the optical properties of gold plasmonic nanorods and the hydrophilic properties of hydrogels, we demonstrate a new hydrogel-based optical humidity sensor that can measure soil wetness. Our preliminary results suggest that this sensor can be modified and produced on a larger scale to eventually serve as a useful tool for agriculturalists interested in measuring their soil's wetness.

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1. INTRODUCTION

Humidity, a term used to refer to water vapor [1] in the air, affects our everyday lives in more ways than weather forecasts. The ability to measure humidity through use of chemical sensors has been important in the fields of indoor air quality, aerospace, agriculture, food, and more [2]. Thus, it comes as no surprise that humidity sensors have been developed to suit the varying needs in which humidity is an important quantity. While there are many different designs for humidity sensors, the two main classes are relative humidity and absolute humidity sensors. Relative humidity sensors are more common than the absolute type because they are cheaper to produce and easier to use [3]. Relative humidity describes the ratio of water vapor present in the environment to the maximum amount of water vapor that environment can hold [1], which is a useful quantity because it can be measured. Polymer-based relative humidity sensors have been extensively studied due to the fact that most of these sensors have porous polymer films on the order of less than a millimeter and are able to gauge changes in humidity by changing some measurable physical property as a result of absorbing water [4].

Hydrogels, a material composed of environmentally-friendly networks of polymer chains [5], have excellent hydrophilic and water absorption properties [6]. After a certain period of time of being exposed to their surrounding environment, hydrogels establish an equilibrium phase between osmotic pressure and the elastic forces within the polymer chains which cause them to swell [6]. Once equilibrium is reached, the swollen hydrogels respond to changes in humidity by absorbing water from the air to maintain equilibrium [6]. Due to the optical properties of water, varied water concentrations within the hydrogel film correspond to changes in refractive indices [7], which can be measured indirectly with a spectrophotometer. This makes hydrogels an excellent candidate for agricultural use, since they can respond well to humidity changes associated with the soil.

2. BACKGROUND

Humidity sensors are used extensively in agriculture for monitoring soil moisture, plantation protection, green-house air conditioning, cereal storage, among other uses [4]. In particular, scheduling when and how much water should be irrigated onto a field of soil is an important function of such sensors, when it comes to non-laboratory uses of humidity sensors [8].

Past experiments have demonstrated that it is possible to create transparent substrates of hydrogel films bound to silver nanoparticles [9]. This is important since nanoparticles correspond to their own unique surface plasmon resonance [10], which can be measured using a spectrophotometer. Since hydrogels experience shifts in their resonance spectra due to humidity fluctuations in the environment, this provides cause to believe that using hydrogel-coated nanoparticle films would allow us to measure how the spectra deviates as humidity changes.

The combined properties of hydrogels and nanoparticles motivate our research in developing soil humidity sensors that use both.

Using a current multi-step curing process developed in the lab, we can attach a substrate containing an array of hundreds of nanorods to the surface of a thin hydrogel film. By making slight modifications to this process, we can bind nanorod arrays to thicker films of hydrogel, thus eliminating the need for a glass substrate. Once this process is complete, the nanorod patterned hydrogel films can be placed directly on top of soil, allowing the water from the soil to be absorbed by (and equilibrate with) the hydrogel. We can then use a scattering device to measure the transmittance spectra of the hydrogel film placed on soil. Using an experimentally determined calibration curve for correlating relative humidities to resonance positions, we can use the resonance position of the spectra to tell us the moisture content of the soil. Furthermore, by measuring the moisture content of the soil's surface, we may be able to aid agriculturalists in determining when to irrigate their fields [8].

3. MATERIALS AND METHODS

3.1 Substrate set-up

A custom-made chemical recipe for hydrogels was prepared in order to make one vial of hydrogel. Using the vial, 1 mL of 2-hydroxyethyl methacrylate (HEMA), 1 gram of acrylamide, and 30 μL of darocur 1173 were mixed together thoroughly. The mixed chemicals-containing vial was exposed in a UV chamber, and then placed aside for an hour. 40 μL of ethylene glycol dimethacrylate and 20 μL of darocur 1173 were then added into the same vial to finally produce the hydrogel we used for the following experiments. Nanoimprinting lithography was used to pattern a square array of hundreds of gold nanorods onto a glass substrate whose size is on the order of a square inch. The patterned substrate was then placed in an oxygen vacuum chamber for approximately 5 minutes. After removed, spacers in the form of layered tape were applied to each side of the patterned substrate area (as demonstrated by the blue area in Figure 1) so as to not

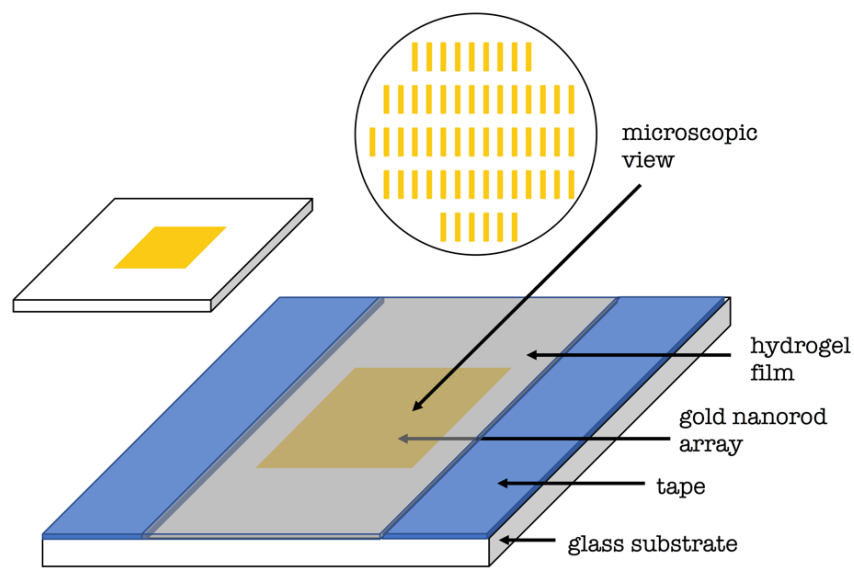


Figure 1: Component breakdown of hydrogel/gold nanorod film fabrication layout.

cover the area of the substrate containing the nanorods. Over the course of several preliminary samples that were tested, the optimal amount of tape layers ended up being between 5-8 in order to create a hydrogel film of adequate thickness.

3.2 Hydrogel Films

The vial containing hydrogel was heated on a hot plate for several minutes (at around 80° F) in order to re-dissolve any remaining crystals. Using a disposable pipette, distilled water was added and mixed together in small amounts (on the order of a few milliliters) in order to give the hydrogel the property of being not too viscous, but viscous enough to attach to substrates when applied. After reaching an optimal viscosity, a disposable syringe was used to drop hydrogel onto the aforementioned gold nanorod patterned substrate with spacers. After applying a few drops of hydrogel to the surface of the patterned substrate between the two spacers (as indicated by the greyed area of Figure 1), a glass slide was then pressed on top so as to flatten the hydrogel layer underneath to a uniform width. By pressing the glass slide tightly on top of the patterned nanorod with hydrogel in between, the viscosity of the hydrogel allowed for the gold nanorod underneath it to adhere to the hydrogel from being previously on the substrate. Using a disposable sealable plastic bag, the substrate/gold nanorod sample with hydrogel and a glass slide atop it were placed inside, and using the output tube end of a nitrogen gas chamber, was deflated with the air inside the bag and pumped with nitrogen gas for about 3-4 minutes. The substrate/glass slide sandwich is then submerged in water for a few hours until both the glass substrate underneath and the glass slide are detached, leaving what's left the hydrogel film attached to the patterned region of nanorods.

3.3 Spectrophotometer set-up

A Cary 5000 UV-Vis-NIR spectrophotometer was used to perform all remaining experiments. Inside the compartment setup of the spectrophotometer is a mount for the patterned hydrogel film to sit on. The spectrophotometer is designed to shine an external source of light from within the compartment over a very small targeted area of the sample. A detector on the other side of the compartment receives the refracted light and is connected to an output that provides us with optometric data (such as absorbance) on a computer screen.

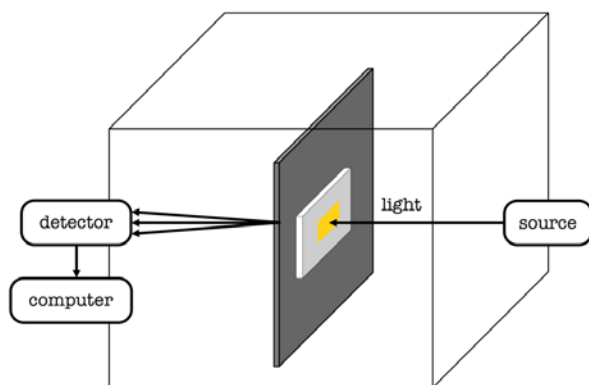


Figure 2: Black box diagram representation of Cary spectrophotometer set-up

3.4 Detection of surface plasmon resonance shift experiment

Our first experiment involved demonstrating that the hydrogel responded to changes in humidity. Using a disposable pipette, a few droplets of water were applied to the surface of a previously prepared patterned hydrogel film. The film was then placed securely onto the mount in the spectrophotometer compartment, after which the compartment was sealed to create a closed environment. Using the corresponding software, we were able to take optometric measurements on the interval of every 2-3 minutes. Specifically, we measured percent transmittance against wavelength in order to see trends in resonance shift.

3.5 Relative humidity experiment

After determining that the hydrogel film sample responds to changes in humidity, we want to now be able to measure how resonance shifts in the patterned hydrogel film sample correspond to the humidity shifts in the external environment. Adding on to the setup of the previous experiment is a cylindrical glass chamber around the mounted sample with water wells placed at the bottom of the enclosed glass chamber and a battery-powered humidity sensor on top of the mount (as shown in Figure 3). Two water wells, filled each with approximately 4 to 5 mL of distilled water, were placed in the enclosed chamber and allowed to disperse uniformly throughout the glass chamber (which is sealed both at both ends). After dispersing and reaching a dynamic equilibrium with the mounted hydrogel film over the course of 30-40 minutes, we were able to take optometric data from the spectrophotometer as well as use the battery-powered humidity sensor to measure the relative humidity for that particular amount of water. Using additional water wells filled with water, we were able to take a variety of data points ranging from 50 to 80 percent relative humidity.

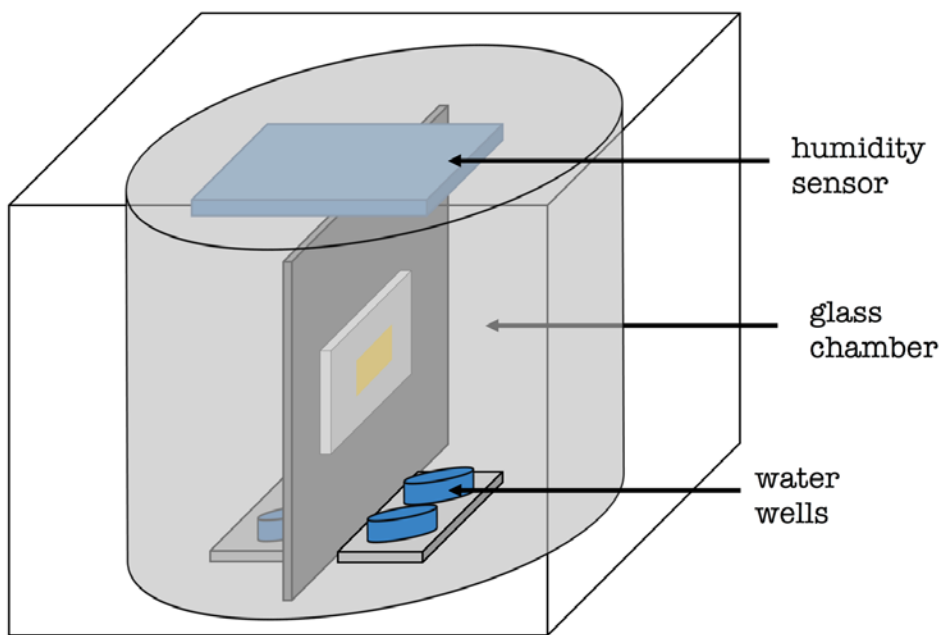


Figure 3: Diagram representation of glass humidity chamber set-up

4. Results

The data collected from our first set of experiments, which served to measure the responsiveness of our hydrogel film sample to water, show that our sample was indeed responsive. As shown in Figure 4, as time passes from the moment water droplets are applied to the surface of the patterned hydrogel film sample, there is a clear blueshift towards shorter resonance positions. The observed blueshift is due to the fact that as the water droplets disperse into the closed chamber, the index of refraction of the patterned hydrogel film lowers since more water is actually absorbed by the film itself. Once the water reaches a dynamic equilibrium between the chamber and the film, the resonance position does not change (as seen at 8 minutes) since the hydrogel film is saturated at equilibrium.

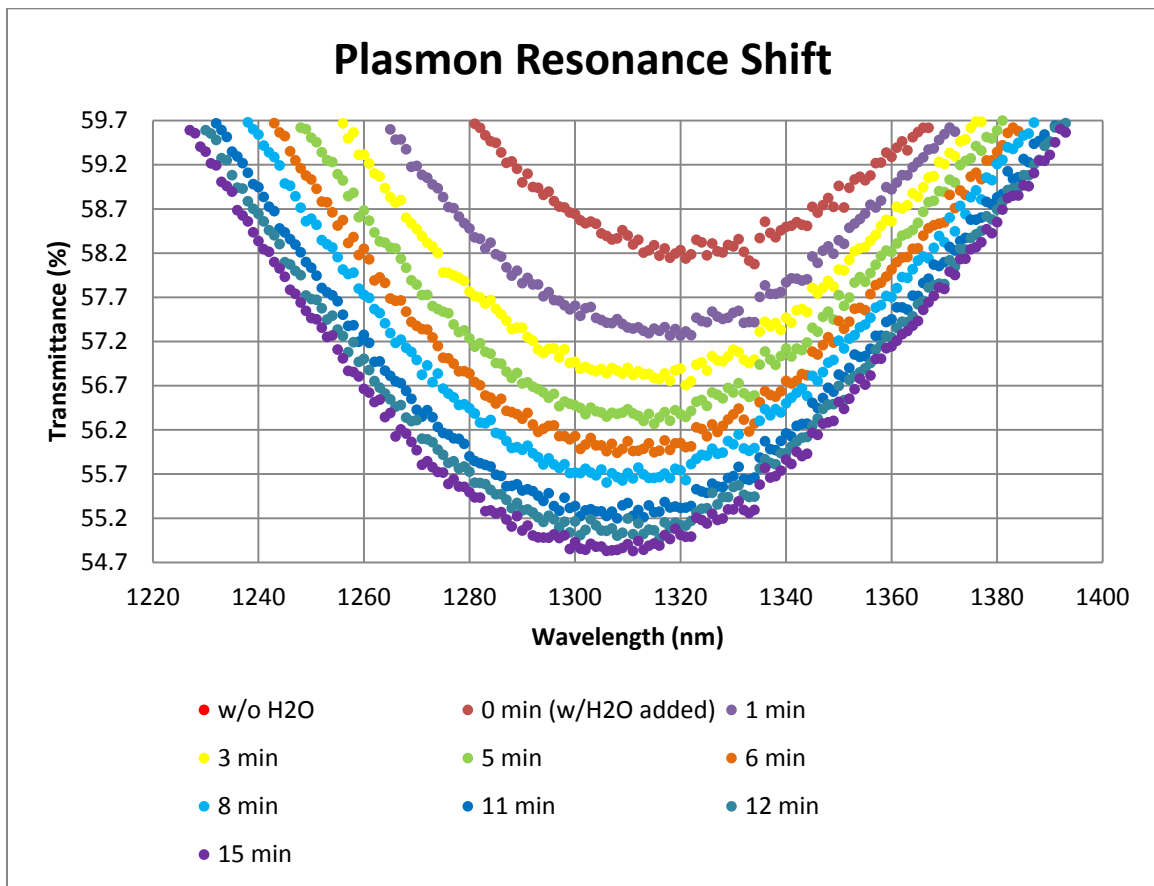


Figure 4: Patterned hydrogel film experiences blueshift after application of water droplet

As demonstrated by Figure 5, the results of the humidity chamber experiment show that as more water is present in the chamber, the shorter the wavelength of the resonance position is. The blueshift of the sample is consistent with Figure 4. A calibration curve, which matches the resonance position to the measured value of relative humidity is

shown in Figure 6. The trendline more visually shows how the sample responds to increases in humidity with decreases in resonance.

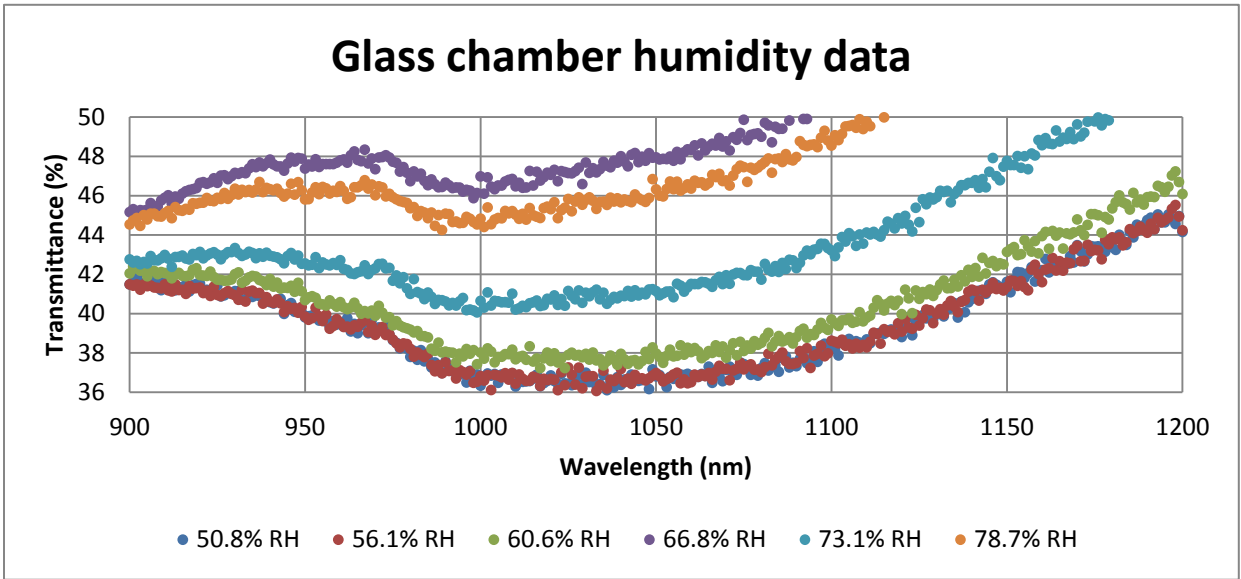


Figure 5: Transmittance spectra at several humidities

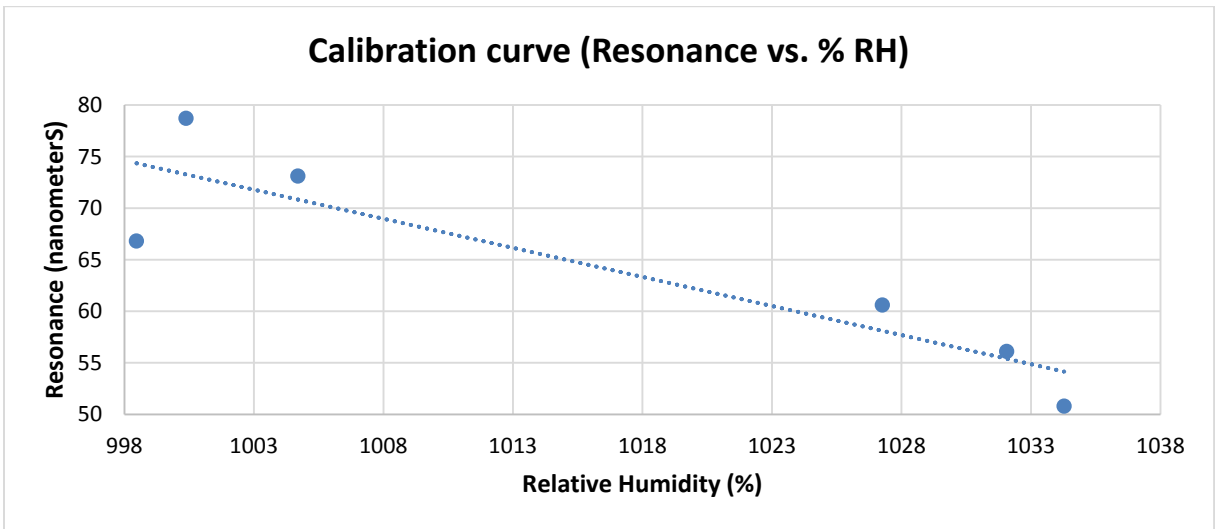


Figure 6: Calibration curve

5. DISCUSSION AND CONCLUSIONS

The results from the first set of experiments were successful in demonstrating that the patterned hydrogel films are responsive to changes in water concentration in the surrounding chamber environment. Although it may seem trivial, demonstrating that the resonance shift of our hydrogel films can be quantitatively measured in different water

concentrations is ultimately necessary in using them as sensors for measuring soil humidity, where we expect to measure soils of various humidities.

For the second experiment, while we tried linearly increasing the amount of water stored in the wells at the bottom of the glass chamber (by about 4 to 5 mL) for each successive measurement (i.e. 50.8 % RH was at current room conditions for the day of experimentation, the successive measurement of 56.1 % RH was with approximately 5 mL of water stored in the wells), it was often the case that adding 4 or 5 mL of water at higher humidities resulted in smaller intervals of humidity increase (i.e. adding 4 mL to the chamber after taking data at the 60.6 % RH resulted in a less than 1 % RH increase, as opposed to the earlier 6 % RH increase from 50.8 to 56.1 % RH). This meant that I had to add an exponentially increasing amount of water to attain the data at the relative humidities displayed in Figure 5, since I was interested primarily in general resonance spectra trends from 50 % RH to 80% RH (and not over small intervals such as from 60 to 61 % RH).

Another concern of the blueshift observed in Figure 5 is that the transmittance curve recorded for 66.8 % RH seems oddly out of place. While all other transmittance curves support the claim that the wavelengths become shorter with an increase in relative humidity, the resonance position for 66.8 % RH seems to be an outlier that does not agree with this trend. In Figure 6, the calibration curve, it is also apparent that this data point seems to disagree with the trend line.

Nonetheless, given that these results are preliminary, we can attribute the oddly placed 66.8 % RH data point to experimental error since all other data seems consistent with the trend in Figure 6 and with the scientific basis for blueshifts.

6. RECOMMENDATIONS

Further experimentation is necessary in the three following areas to ultimately make the patterned hydrogel films effective sensors that can be used in determining soil humidity.

6.1 Hydrogel film thickness

One of the problems we encountered in the early stages of fabricating hydrogel films was that of optimizing the thickness of hydrogel films for both practical and measurable purposes. Before the current method for applying spacers on either side of a nanorod patterned substrate was used, the hydrogels were spin coated at varying speeds from 3000 to 6000 RPM over the course of anywhere from 10 to 60 seconds. This usually resulted in very thin hydrogel films that when attached to the substrate, provided excellent data in the form of clearly defined resonance shifts, but failed to be practical because they were too thin to be detached from the substrate without tearing. The current method of using spacers is an improvement upon the spin coating method, since the spacers method provides slightly thicker hydrogels that detach from the substrate easily. However, making hydrogels too thick could render them unusable for purposes of data collection due to thin film interference and/or compromise the validity of the data for resonance

shifts being reported. Thus, optimizing the thickness of the hydrogel films needs to be further investigated.

6.2 Relative humidity data (continued)

While Figures 5 and 6 show trends that are favorable for continuing the development of the patterned hydrogel film sensors, more data needs to be collected using the humidity chamber in order to ensure that these trends are consistent over a wider range of humidities (i.e. not just from 50 to 80 % RH). Additionally, more data is needed so that the calibration curve can be more clearly defined with a fit that is much better at explaining how our particular hydrogel sensor responds to humidity changes than the generic linear trend line. This is important for the eventual use of these sensors with soil since we want to be able to measure the transmittance spectra in a sample of soil and correspond the resonance to the appropriate relative humidity given by the calibration curve.

6.3 Soil testing

Seeing that these sensors are to eventually be used in soil, it is appropriate that we move beyond the traditional lab setting and test the hydrogel sensor technology on actual samples of moist soil. We are currently in the middle of testing with the use of a scattering device which allows us to place the hydrogel film directly on top of the soil sample and abstract the resonance position of the measured spectra after equilibrating with the water in the soil. The results of these tests will further determine which direction the research should move in, since we will better know for certain if we can use the calibration curve and the scattering device to accurately gauge the humidity of soil samples.

7. ACKNOWLEDGMENTS

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