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RESEARCH PAPER

Development of ZnO Nanorod Sensor for Detection of Malathion

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Abstract

Residues of different pesticide are commonly found in tea leaves, and the possible health implications of exposure to these residues are a key reason for concern among tea manufacturers and consumers. Apprehensions are being raised about environmental dangers connected with exposure to pesticides via different pathways due to the fact that their mechanisms of action are not species-specific (e.g., residues in food and drinking water). Short-term effects include skin and eye irritation, headaches, dizziness, and nausea, while long-term effects can be severe damage to organs and cancer. Therefore, it is crucial to keep a close eye on pesticide levels in tea samples, as these chemical traces continue to build up in the environment and in living organisms, posing a threat to both human and animal health. In order to detect pesticide residues in various sample matrices, researchers are developing a variety of sensor platforms. This work reports the development and testing of a sensor based on ZnO nanorods capable of detecting the widely used insecticide Malathion. The reported sensor has been successfully used to detect Malathion levels in spiked samples with good repeatability.

Keywords: *Sensor, Pesticide, ZnO, Nanorod, Malathion*

1 Introduction

Herbicides, insecticides, fungicides, and rodenticides are examples of pesticides, which are among the few hazardous compounds introduced on purpose into the environment to destroy living organisms. Despite common misconception, the term "pesticide" can refer to a wide variety of compounds beyond just "insecticides" including "herbicides" and "fungicides"(1). Since pesticides can lessen the amount of food that is wasted and increase both the quantity and quality of crops that can be grown at a reasonable price, it is commonly acknowledged that they contribute significantly to agricultural progress(2). Concerns about the environment arise from the overuse of pesticides. Chemical pesticides, such as dichlorodiphenyltrichloroethane (DDT), dichlorodiphenyldichloroethylene (DDE), parathion, malathion, chlordane, and atrazine, are the most dangerous to humans and the environment(3). Reports on poisoning and the effects of synthetic chemicals on human health indicate that many farmers, rural workers, and their families were poisoned during pesticide applications. Overexposure and improper usage of harmful substances are major causes of the estimated 355,000 annual deaths caused by accidental poisonings around the world(4). Both humans and ecosystems can be seriously harmed by pesticides and herbicides. Humans can have both short-term (such as discomfort, nausea, dizziness, and headaches) and long-term (such as diabetes, neurological diseases, cancer, and asthma) effects from pesticides and herbicides(5). India is also the world's largest producer and consumer of tea, making it the beverage's undisputed champion. A large application of pesticides to the tea crop and the average consumption of six grams of dried (made) tea per day per person make tea a major potential source of human exposure to pesticide residues(6). Hot tea can act as a solvent for numerous pesticides, including ethion, quinalphos, malathion, and dimethoate, all of which are used on tea plants during cultivation and leave behind detectable residues in the finished product. In order to ensure the safety of consumers, it is important to regularly test for the presence of pesticide residues in tea. This is because a single cup of tea has the potential to contain traces of several different classes of chemicals(7). The detection of pesticide residues by gas/liquid chromatography attached with mass spectrometry is considered the gold standard method. However, these techniques have their own limitations, such as time-consuming and labor-intensive pretreatment and cleanup procedures. The development of new detection methods has been spurred by the rapid progress made in surface-enhanced Raman spectroscopy (SERS). The ultra-sensitivity and straightforward methods of SERS make it a valuable detection tool(8). As a result of the drawbacks of the prevalent commercial methods, it is important to explore alternative approaches that can reliably detect pesticides and herbicides with short detection time at affordable cost while yet being specific and sensitive. As such, the advent of nanomaterials opened up new opportunities for the sensing industry to reach these benchmarks. As part of our research, we have developed a ZnO nanorod based sensor for quantitative analysis of Malathion spike samples. We have examined the sensor's output pattern as a function of concentration.

2 Materials and Methods

2.1 Fabrication of the Sensing Electrode

First, DipTrace software is used to plan out the interdigitated electrodes. The mirror image of the layout is printed onto an OHP sheet by a laser printer.

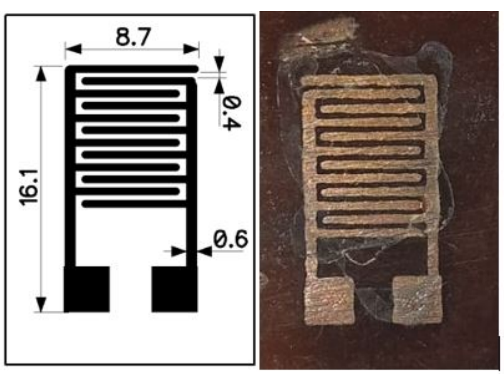

Figure 1: Design of the Interdigitated Electrode in PCB for the Sensor (in mm)

The foundation is a FR_4 board, which is cut to size based on the design. The ink traces are then pasted onto the copper of FR_4 board using a tonal heat transfer mechanism. After the design has been placed onto the copper plate, it is dipped into a ferric chloride solution to remove the excess copper. As demonstrated in the figure, the sensor's response is optimal with a spacing of 0.4 mm.

2.2 Synthesis of ZnO Seed Nanoparticles

The ZnO nanoparticles were synthesized by dissolving 4 mM of zinc acetate dihydrate $Zn(CH_3COO)_2 \cdot 2\,H_2O$, Merck, 99% purity) in 20 ml of ethanol C_2H_5OH, also from Merck, and heating the mixture to 50˚C while stirring constantly. After allowing the solution to cool in air, another 20 ml of fresh ethanol was added, and then 20 ml of 2 mM sodium hydroxide in ethanol was added dropwise while stirring. After 2 hours in a water bath at 60˚C, the mixture was cooled to room temperature(9).

2.3 Growth of ZnO Nanorods on Seeded Substrate

The Copper electrode substrate was dipped for 15 minutes into a solution of pre-synthesized ZnO nanoparticles to seed the substrate.

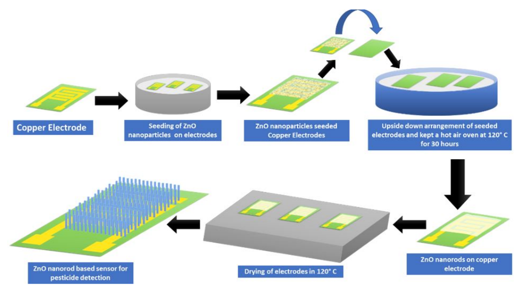

Figure 2: Process for Growth of ZnO Nanorods on Copper Electrode

After each of these three dippings, the substrate was rinsed in deionized water to remove any unattached particles and then heated to 120˚C for 15 minutes.

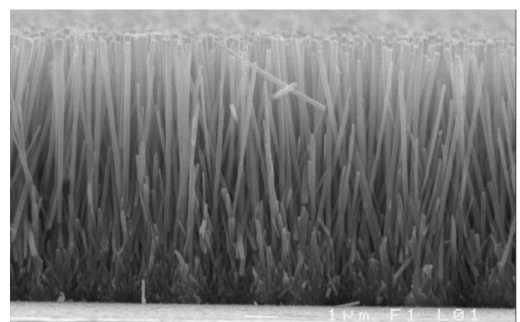

Figure 3: Scanning Electron Micrograph of the ZnO Nanorods Grown on the Cu Electrodes With Average Width ~ 100nm and length ~ 7µm

The substrate was preheated to 100˚C and then annealed at 120˚C for an hour(10). To grow ZnO nanorods, the seeded substrate was placed inverted in a petri dish containing an equimolar (20 mM) solution of zinc nitrate hexahydrate $Zn(NO_3)_2 \cdot 6\,H_2O$, Merck, 99% purity and hexamethylenetetramine $C_6H_{12}N_4$, both from Merck and placed in a hot air oven set to 90˚C for 30 hours. The growth solution was changed every 5 hours, and once the process was complete, the substrate was rinsed extensively with deionized water and dried at 120˚C for an hour(11; 12).

2.4 Preparation of Test Solution

Malathion 50% EC, which is routinely used in tea gardens, was used in our investigation. As the insecticide is accessible in liquid form, we used deionized water as a solvent to dilute it. The spiked samples were prepared at concentrations of 1%, 0.8%, 0.6%, 0.4%, and 0.2% by v/v dilution using the formula $C_1V_1 = C_2V_2$, where C is the solute concentration and V is the volume in ml.

2.5 Pesticide Sensing Setup

The testing setup consists of the as developed ZnO nanorod sensor, potential divider circuit, Arduino based Data acquisition system and LabVIEW interfacing with PC.

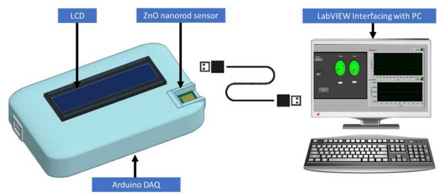

Figure 4: Pesticide Sensing Setup

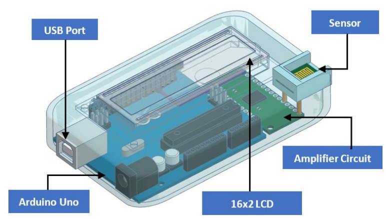

Figure 5: Schematic Diagram of the Device

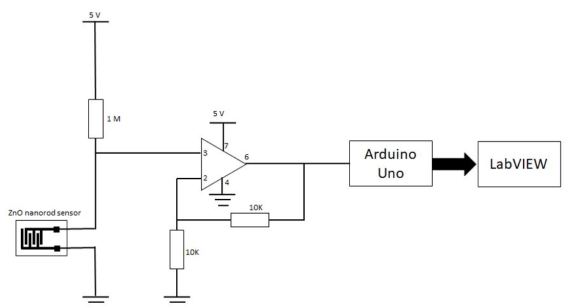

Figure 6: Circuit Diagram of the Pesticide Sensor

As seen from the Figure 4, the device is attached with the developed ZnO nanorod sensor. The spike samples can be dropped on the sensor surface for data collection and analysis. The device schematic diagram is shown in Figure 5 and the circuit diagram in Figure 6. When different concentrations of pesticides are dropped on the sensor, the electrical resistance of the sensor changes. Because of this, there is a change in the voltage across the sensor, which depends on the concentration of pesticides in the spike solution. This voltage is amplified even more so that it can be used as an input to a microcontroller in a sensitive way. The data from the microcontroller is recorded in real time by using LabVIEW interface in a PC.

3 Results and Discussion

It has been discovered that the resistance of the sensors lies in the range of 170 to 190 MΩ, and this resistance decreases when exposed to UV light.

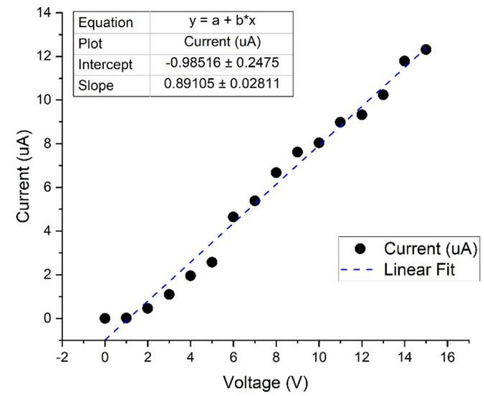

Figure 7: VI Characteristic of the Sensor Showing Linear Response

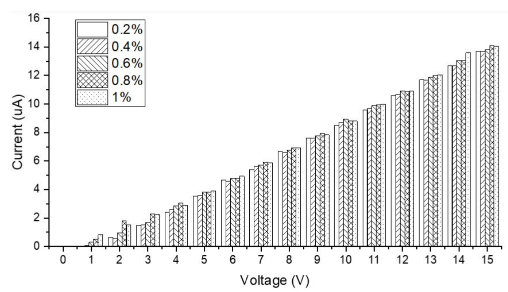

Figure 8: VI Characteristic of the Sensor at Different Concentrations of Malathion

This is because of the electron hole pair generation and excitation of free electrons on to the conduction band. The voltage- current (VI) characteristics of the sensor is shown in the Figure 7, which clearly indicates ohmic linear response confirming that the sensor is a resistive one.

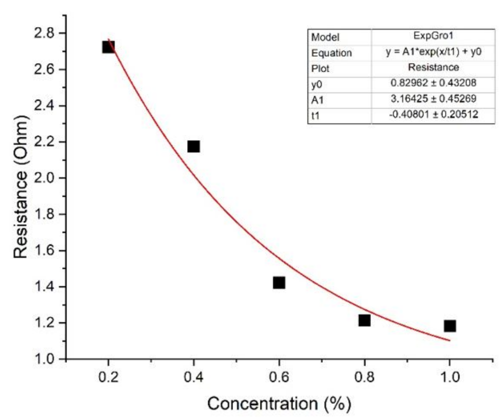

Figure 9: Concentration vs Resistance from VI Characteristics

The change in current was found to follow the linear equation y=0.9x-1. Different concentrations of Malathion spiked samples were used to record the sensor's VI characteristics.

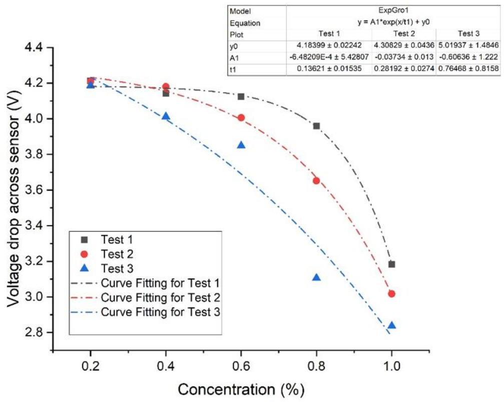

Figure 10: Concentration vs Voltage Drop Across Sensor

As shown in Figure 8, the current at a certain voltage level is different for different concentrations of Malathion. At any given voltage level, it is clear that the current goes up as the concentration increases. This indicates that the resistance goes down as the concentration increases. Figure 9 shows how the average resistance of the sensor changes at each concentration level. The sensor output is evaluated with the device shown in Figure 4, and a potential divider and amplifier circuit as depicted in Figure 6 are utilized. The change in sensor resistance causes a change in voltage across the potential divider. Utilizing a system based on a microcontroller allows for future development portability. The sensor's repeatability is examined thrice and as observed in the concentration vs voltage drop plots Figure 10, the voltage across the sensor decreases as concentration increases, meaning that sensor resistance likewise decreases, as observed in the Concentration vs. Resistance plot in Figure 9. The exponential decay in resistance with increase in concentration following the expression y=3e-2.5x+0.8 can be attributed to the transfer of electrons from the outer shell of malathion to the semiconducting ZnO nanorods through adsorption. Higher the concentration of malathion, more is the adsorption on the ZnO nanorods and more will be the transfer of electrons. Being a semiconductor, electron injection decreases the bandgap leading to more electron transitions to the conduction band and a subsequent decrease in resistance. The 3 tests showed similar variations in conductivity following exponentially decaying response.

4 Conclusion

ZnO nanorod-based sensor was fabricated for the detection of a pesticide (Malation). The sensor's capability of identifying Malathion pesticide was extensively tested. A drop in the sensor's resistance was observed with increase in Malathion concentration. These changes were found to be repeatable and the response time short. The fabricated sensor's high sensitivity and repeatability suggest that ZnO nanorods are promising candidates for the development of efficient pesticide sensors.

Conflict of Interest

The authors declare no conflict of Interest in this reported communication.

Acknowledgments

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