FLEXIBLE BIODEGRADABLE LEAF-WEARABLE SENSOR FOR MONITORING STRESS-INDUCED METHANOL EMISSION FROM PLANTS

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ABSTRACT

In this study, we present a novel flexible, biodegradable, and leaf-wearable sensor to directly monitor methanol gas emitted from plants in response to various stress factors, including water stress, light stress, and physical wounding. We fabricated the methanol sensor by first screen-printing interdigitated electrodes on a biodegradable substrate, which was then coated with a composite of zinc oxide nanorods (ZnONRs) and platinum nanoparticles (PtNPs). The morphological characterization of the sensor, featuring PtNPs/ZnONRs on carbon electrodes, was conducted using scanning electron microscopy. The sensor demonstrated a sensitivity of 0.1718 pF/ppm, and a limit of detection of 6.79 ppm. The sensor operated at room temperature and was tested on tomato plants under water stress, artificial wounds, and light stress conditions. The sensor exhibited its highest capacitance change of 9.4 pF during water stress over 24 hours of time frame.

KEYWORDS

Wearable sensor, plant sensor, methanol, interdigitated electrodes.

INTRODUCTION

Plants emit gaseous methanol (CH_3OH), a key volatile organic compound (VOC), as a signaling molecule in plant-plant and plant-animal communication [1]. Moreover, methanol plays a vital role in the plant's defense mechanisms and stress adaptation [1]. The methanol gas sensors reported in the literature require long hours to fabricate, yet not wearable on plants [2]. Although some plant-wearable VOC sensors are reported in the literature, they either incur complex chemical synthesis procedures [3], or do not explore the role of methanol in plant's stress adaptation strategies [4]. Moreover, non-biodegradable sensors contribute to environmental pollution, highlighting the importance of designing biodegradable sensors for plants. Typically, metal oxide sensors (e.g., ZnO and TiO_2) require high operating temperatures of 240-400°C, reducing sensor lifespan and energy efficiency. To address these issues, we employ nanorods of ZnO to enhance surface-to-volume ratio and enable operation at room temperature, while also controlling the number of reactive sites on the sensor surface.

SENSOR FABRICATION PROCESS

Biodegradable substrate preparation. The biodegradable substrate was prepared by dissolving polyvinyl alcohol and corn starch in deionized (DI) water for 2.5 hours. Glycerol was added to the solution and stirred for 30 mins. Polyvinyl alcohol, corn starch, and glycerol were used at a weight ratio of 16:0.4:1.5. The resulting solution was poured in a 7.0 cm x 5.0 cm mold and kept in the oven at 60°C for 72 hours. Finally, the film was peeled off from the mold.

Synthesis of PtNPs/ZnONR composite. The ZnONR were synthesized using a hydrothermal method as reported in [2]. Platinum nanoparticles (PtNPs, 1000ppm) dispersed in water were purchased from an external vendor and diluted to 200 ppm using DI water. A mixture of 60mg of ZnONR and 2mL of PtNPs was dissolved in 1mL *N*,*N*-dimethylformamide. The solution was stirred at 300 rpm at 70°C for 6 hours.

Sensor fabrication. Interdigitated electrodes (IDE) were fabricated by transferring the design to the biodegradable substrate and coating with carbon ink through a screen-printing procedure, as shown in Figure 1a-b. Next, the synthesized PtNPs/ZnONR composite was drop-casted on the IDEs and spin-coated at 200 rpm for 10 seconds to create a uniform layer (Figure 1c). The sensors were dried at room temperature for 6 hours. Figure 1d shows the schematic illustration of the sensor installed on the leaf and measured with an LCR meter.

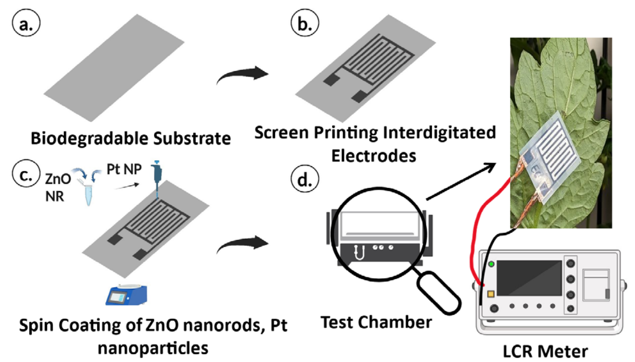

Figure 1: Fabrication process flow and the experimental setup.

RESULTS AND DISCUSSION

Gas sensing setup. The sensors were characterized using a custom-designed gas sensing setup (Figure 2). Different concentrations of methanol were prepared by controlling the flow rate of gaseous methanol and air flown into the sensing chamber through flow controllers. The mass flow meters (MFMs) precisely measured the gas flow rate. The sensor was enclosed inside the sensing chamber and the response was measured with an LCR meter.

Biodegradable test. The biodegradability of the substrate was tested by dissolving it in distilled water. It took ~4 hours for the

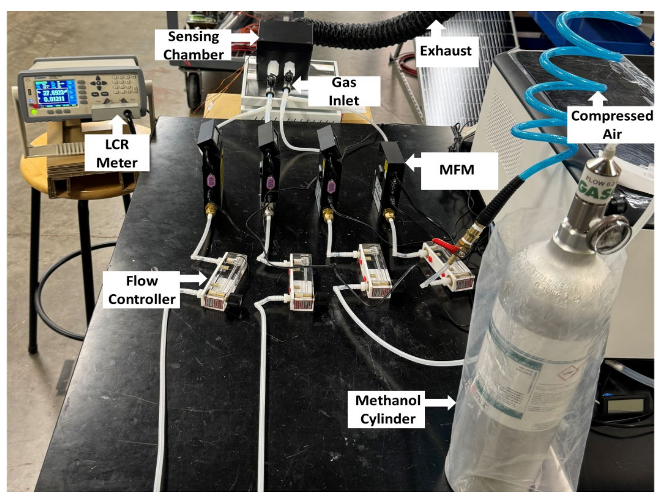

Figure 2: A custom-built gas sensing setup to calibrate the methanol sensors.

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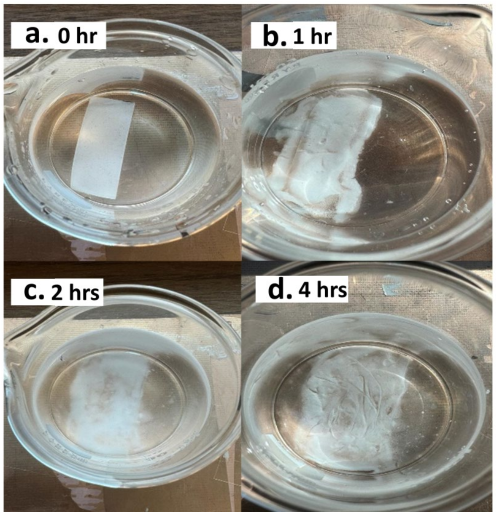

Figure 3: (a) Biodegradable substrate placed in 40 mL of distilled water. Optical images taken after (b) one hour, (c) two hours, and (d) four hours in distilled water.

substrate to completely dissolve in water, as shown in Figure 3.

Sensor characterization. The morphological characterization of the PtNPs/ZnONR-coated IDE electrodes was conducted using scanning electron microscopy (SEM), as shown in Figure 4a-b. Additionally, energy dispersive X-ray spectroscopy (EDS) was utilized to confirm the presence of Zn and Pt on the electrode surface, as depicted in Figure 4c-d.

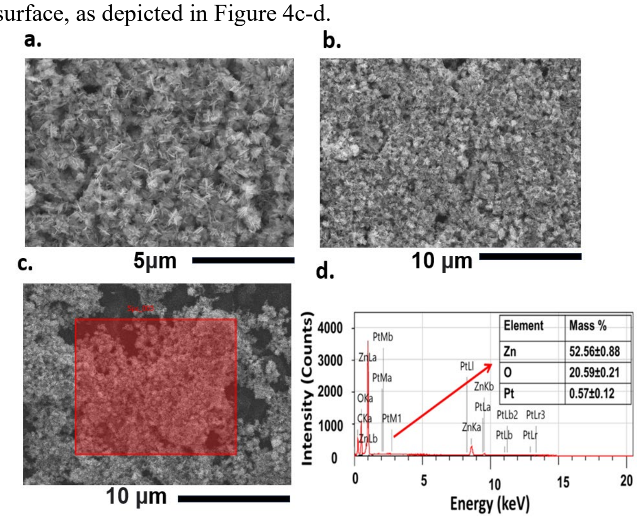

Figure 4: SEM images of PtNPs/ZnONRs at (a) 5 µm and (b)10 µm magnifications. (c-d) EDS results confirming the presence of zinc (Zn), oxygen (O) and platinum (Pt) at mass percentages of 52.56%, 20.59%, and 0.57%, respectively.

Calibration tests. Upon exposure to air, the sensor captures oxygen molecules on the surface, which ionize into oxygen ions (O_2^-) by capturing electrons from the conduction band of ZnONRs. In the presence of methanol gas, the absorbed O_2^- and methanol molecules react, liberating the trapped electrons to the conduction band of the ZnONRs. The sensor was evaluated at 22°C, 25°C and 30°C temperatures for methanol concentrations ranging from 2.92 ppm to 99.33 ppm (Figure 5a). The sensor exhibits a sensitivity of 0.1718 pF/ppm, and a limit of detection is 6.79 ppm, as determined from the calibration curve in Figure 5b.

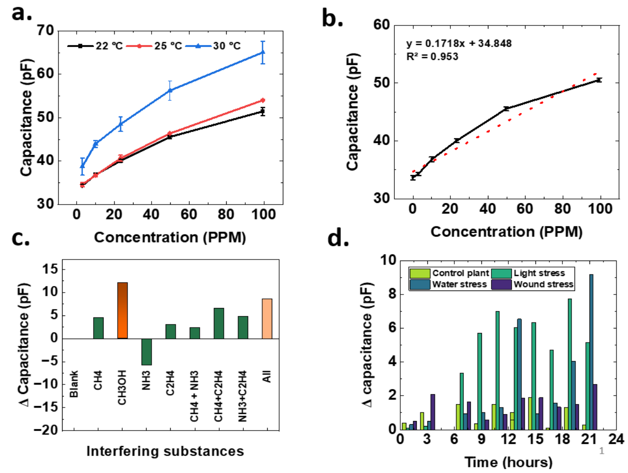

Figure 5: (a) Sensor response measured at 22°C, 25°C and 30°C. (b) Calibration curve at 22°C demonstrating a sensitivity of 0.1718 pF/ppm. (c) Selectivity test conducted with different gases, including methane (CH_4), ammonia (NH_3), ethylene (C_2H_4) and methanol (CH_3OH). (d) Sensor response over 24 hours from tomato plants subjected to light, water, and wound stressors.

Selectivity tests. To determine the selectivity of the sensor, the sensor was exposed to 50 ppm each of methane, ammonia, ethylene gases, and then a mixture of all gases (Figure 5c). The sensor showed a capacitance change of 12.35pF in response to 50 ppm of methanol which is relatively higher compared to the responses for the interfering gases, i.e., ammonia, methane and ethylene which had -5.7pF, 4.612pF and 3.09pF capacitance change, respectively.

In-situ tests in live plants. Tomato plants were subjected to various stress conditions, including water stress (deprived of irrigation for 24 hours), wounds (injury on the plant node), and light stress (plants in the dark for 24 hours). The sensor was attached to the leaves and methanol emissions were measured. Light stress resulted in a 7.4pF capacitance change while the sensor showed the highest capacitance change of 9.4 pF during 24-hour water stress (Figure 5d).

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REFERENCES

[1] H. Ibrahim, S. Moru, P. Schnable, and L. Dong, "Wearable Plant Sensor for In Situ Monitoring of Volatile Organic Compounds Emissions from Crops", *ACS Sens.*, 7, 8, 2293-2302 (2022).

[2] L. Malepe, D. T. Ndinteh, P. Ndungu, and M. A. Mamo, "Selective detection of methanol vapour from a multicomponent gas mixture using CNPs/ZnO@ZIF-8 based room temperature solid-state sensor", *RSC Adv.*, 12, 27094-27108 (2022).

[3] N. I. Hossain and S. Tabassum, "A hybrid multifunctional physicochemical sensor suite for continuous monitoring of crop health", *Sci. Rep.*, 13, 9848 (2023).

[4] N. I. Hossain, T. Noushin, and S. Tabassum, "Tattoo-like flexible ethylene sensor for plant stress monitoring in Real-time", *IEEE Sens. J.,* (Early Access), 31 October 2023, 10.1109/JSEN.2023.3327547.

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