

Field-Effect Gas Sensor Based on Porphyrin and Semiconducting Single-Walled Carbon Nanotubes for Detection of *Phytophthora cactorum* in Strawberries: Post-Print

Authors: Wang Hui, Ruipeng Chen, Zhi-Xue Yu, He Yue, Zhang Fan, Xiong Benhai, Xiong Benhai

Date: 2023-02-17T00:00:00+00:00

Abstract

Phytophthora fragariae causes strawberry leather rot and crown rot, affecting the economic benefits of strawberry cultivation. However, early-stage infected plants exhibit no obvious symptoms and cannot be diagnosed in a timely and accurate manner, thus creating an urgent need for low-cost diagnostic methods to enable early prevention. Strawberry plants infected with *Phytophthora fragariae* release a unique volatile organic compound, 4-ethylphenol, which can serve as a marker gas for rapid disease diagnosis. This study utilizes semiconducting single-wall carbon nanotubes (Single-Wall Carbon Nanotube, SWNT) and field-effect transistors (Field Effect Transistor, FET) to fabricate a semiconductor field-effect gas sensor (SWNT/FET), which is subsequently modified with metalloporphyrin MnOEP that exhibits high sensitivity and selectivity toward 4-ethylphenol to obtain MnOEP-SWNT/FET. The MnOEP-SWNT/FET was characterized through Raman spectroscopy, UV-Vis spectroscopy, and voltammetry to analyze its physicochemical properties and optimize detection conditions, thereby enhancing the gas sensing performance of MnOEP-SWNT/FET toward 4-ethylphenol. Under optimal detection conditions, the MnOEP-SWNT/FET demonstrated a detection range of 0.25%~100% 4-ethylphenol saturated vapor (20 °C), with a limit of detection of 0.15% 4-ethylphenol saturated vapor ($S/N = 3$), and the relative standard error for measurements at different concentrations was below 10%. Testing of actual samples indicated that MnOEP-SWNT/FET detection of healthy strawberry plants may produce false positives, but achieves high detection accuracy for strawberry plants infected with *Phytophthora fragariae*.

Full Text

Preamble

Porphyrin and Semiconducting Single-Wall Carbon Nanotubes based Semiconductor Field Effect Gas Sensor for Determination of Phytophthora Strawberries

WANG Hui¹, CHEN Ruipeng¹, YU Zhixue¹, HE Yue^{1,2}, ZHANG Fan^{1,2}, XIONG Benhai^{1*}

¹ State Key Laboratory of Animal Nutrition, Institute of Animal Science, Chinese Academy of Agricultural Sciences, Beijing 100193, China

² College of Animal Science and Technology, China Agricultural University, Beijing 100193, China

Abstract: Phytophthora cactorum is a highly destructive plant pathogenic fungus that causes strawberry leather rot and crown rot, significantly affecting strawberry yields and economic viability. Early-stage infected plants exhibit no obvious symptoms, making timely and accurate diagnosis impossible with conventional methods. Consequently, low-cost diagnostic tools for early prevention are urgently needed. Infected strawberry plants release a unique volatile organic compound—4-ethylphenol—that serves as a diagnostic marker gas. This study developed a semiconductor field-effect gas sensor by depositing semiconducting single-wall carbon nanotubes (SWNT) onto a field-effect transistor (FET) platform, subsequently modifying the surface with manganese octaethylporphyrin (MnOEP), a metalloporphyrin exhibiting high sensitivity and selectivity for 4-ethylphenol. The MnOEP-SWNT/FET sensor was characterized using Raman spectroscopy, UV-Vis spectroscopy, and voltammetric analysis to optimize detection conditions and enhance gas-sensing performance. Under optimal conditions, the sensor demonstrated a linear response to 4-ethylphenol saturated vapor concentrations ranging from 0.25% to 100% (at 20°C), with a detection limit of 0.15% saturated vapor (S/N = 3). The relative standard deviation across different concentrations was below 10%. Real sample testing revealed that while healthy strawberry plants produced minor false-positive signals, the sensor achieved high detection accuracy for Phytophthora-infected plants.

Keywords: strawberry; fungal infection detection; gas sensor; nanocomposites; field-effect transistor; 4-ethylphenol; semiconducting single-wall carbon nanotubes; field-effect sensor

1. Introduction

Phytophthora cactorum is an extremely destructive plant pathogenic fungus that causes strawberry leather rot and crown rot, with yield losses averaging 20–30% and reaching up to 50% in severe cases, posing a major threat to strawberry

production. Since no cost-effective treatment exists, rapid and accurate diagnosis is critical for preventing disease spread, implementing control measures, and reducing grower losses. Current diagnostic methods include tissue isolation, microscopic analysis, polymerase chain reaction (PCR), recombinase polymerase amplification, fluorescence in situ hybridization, and enzyme-linked immunosorbent assay. Tissue isolation is low-cost and enables quantitative detection of viable pathogens but suffers from long detection times and low accuracy. Microscopic analysis requires sophisticated equipment and trained personnel, making it expensive and time-consuming. Immunological assays offer simple operation and fast response, while molecular hybridization and PCR provide high specificity and sensitivity for pre-symptomatic diagnosis. However, uneven distribution and low pathogen concentrations during early infection stages necessitate large sample volumes, preventing timely and accurate detection.

Research by Jellen et al. and Eikemo demonstrated that *Phytophthora*-infected strawberry plants emit unique volatile organic compounds—4-ethylphenol (vapor pressure 0.13 mmHg at 20°C) and 4-ethyl-2-methoxyphenol (vapor pressure 0.017 mmHg at 25°C)—with concentrations ranging from 1.12–22.56 mg/kg and 0.14–1.05 mg/kg, respectively, correlating positively with disease severity. Given its significantly higher concentration, 4-ethylphenol serves as an ideal diagnostic marker.

Semiconductor field-effect gas sensors offer advantages of low cost, low power consumption, compact size, high sensitivity, and easy integration, making them suitable for real-time monitoring of agricultural volatile organic compounds. The gas-sensitive material is the core component determining sensor performance. Semiconducting single-wall carbon nanotubes (SWNT), formed by rolling single-layer graphene into one-dimensional hollow tubes with diameters of a few nanometers and lengths of 1–100 μm , exhibit high surface adsorption capacity, excellent conductivity, and efficient electron transport properties, making them promising sensing materials. However, pristine SWNT-based sensors suffer from poor selectivity and insufficient sensitivity for specific detection of 4-ethylphenol.

Metalloporphyrins (MPs) are macromolecular heterocyclic compounds consisting of four pyrrole rings linked by methylene groups, forming a central cavity that can coordinate with nearly all metal ions. The unsaturated coordination state of the central metal ion allows gas molecules to interact via van der Waals forces and hydrogen bonds at axial positions, altering the porphyrin's optical and electrical properties. By varying the central metal ion, ring structure, and peripheral substituents, MPs can be tailored for specific gas detection with tunable sensitivity and selectivity. This study combines SWNT-FET sensors with MnOEP modification to achieve early, rapid diagnosis of strawberry *Phytophthora* infection, screening for optimal metalloporphyrins and optimizing detection parameters to enhance practical applicability.

2. Materials and Methods

2.1 Reagents and Materials

Semiconducting single-wall carbon nanotubes (SWNT, 0.01 mg/mL, 95%) were purchased from NanoIntegris (USA). Acetone, isopropanol, sodium hydroxide, and ammonia solution were obtained from Fisher Scientific (China). 3-Aminopropyltriethoxysilane (APTES, 99%) was purchased from Acros Organics (USA). 4-ethylphenol was obtained from Shanghai Macklin (China). Dimethylformamide (DMF) was purchased from Beijing Chemical Industry Co. (China). Metalloporphyrins including tetraphenylporphyrin (TPP), iron porphyrin (FeTPP), zinc porphyrin (ZnTPP), copper octaethylporphyrin (CuOEP), and manganese octaethylporphyrin (MnOEP) were provided by Sigma-Aldrich (USA) and J&K Scientific (USA).

2.2 Experimental Instruments

Raman spectroscopy was performed using a Nicolet Almega XR dispersive microscope with 532 nm laser excitation to detect molecular vibrational (phonon) states. UV-Vis spectroscopy was conducted using a Beckman DU800 spectrophotometer (Beckman Coulter, USA) over 180–780 nm. Scanning electron microscopy images were obtained with a Zeiss Leo SUPRA 55 at 10 kV beam energy. Electrochemical performance including current-voltage (I-V) and current-time (I-T) characteristics was analyzed using a Keithley 2636 semiconductor parameter analyzer. Mass measurements were performed using a BSA224S electronic balance (Sartorius). Chlorobenzene enrichment column sampling tubes were purchased from Pubiao Experimental Equipment Technology (China). A Direct-Q8 ultrapure water system (Millipore, USA) and YG-1206 laboratory tube furnace (Shanghai Yuzhi Mechanical and Electrical Equipment) were used.

2.3 Gas Sensor Preparation

Interdigitated field-effect transistor fabrication followed reference [23]. Silicon wafers with 100 nm SiO₂ surface layer were ultrasonically cleaned in acetone, isopropanol, and ethanol for 20 minutes each to remove organic contaminants, then dried with nitrogen. Positive photoresist was spin-coated onto the wafers, followed by exposure and development to pattern the interdigitated electrodes. Electron beam evaporation deposited 20 nm chromium and 180 nm gold layers, which were annealed at 300°C to enhance adhesion. The wafers were then soaked in acetone for 12 hours to dissolve photoresist, yielding source and drain electrodes with 10 μm gap length and width.

The modification process is illustrated in [Figure 1: see original paper]. Electrodes were cleaned with acetone, isopropanol, and ammonia solution to remove organic and inorganic residues. The transistor was immersed in APTES for 30 minutes, rinsed with ultrapure water, then immersed in SWNT solution for 60 minutes. After washing away residual nanotubes, the device was heated in a tube furnace at 250°C to remove surfactants. Metalloporphyrins were dissolved

in DMF (1 mg/mL), and the SWNT-FET was immersed for 4 hours, followed by annealing at 90°C for 60 minutes under inert gas.

2.4 Gas Generator

The volatile organic gas dilution system is shown in [Figure 2: see original paper]. Solid 4-ethylphenol powder was heated to generate saturated vapor at controlled temperature. Mass flow controllers regulated the mixing ratio of air and 4-ethylphenol vapor to produce various concentrations. The mixed gas flowed through a 1.2 cm³ sealed glass chamber housing the sensor, which was connected via three electrodes (gate, source, drain) to a Keithley 2636 data acquisition system. Source-drain voltage (V_{DS}) was maintained at 0.1 V while gate voltage (V_{G}) varied from -0.1 V to +0.1 V.

2.5 Signal Analysis

Due to variations in initial resistance among different MnOEP-SWNT/FET devices, relative resistance change was used as the response signal, calculated using equations (1) and (2):

$$R = V_{\text{DS}} / I_{\text{DS}}$$
$$\text{Relative resistance} = (R - R_0) / R_0$$

where R_0 is the baseline resistance in dry air, R is the resistance after VOC exposure, V_{DS} is the source-drain voltage, and I_{DS} is the source-drain current.

Carrier mobility (μ) of the semiconductor material was calculated using equation (3):

$$\mu = (L \times g_m) / (W \times V_{\text{DS}} \times C_{\text{OX}})$$

where L and W are the channel length and width, g_m is the transconductance (slope of $I_{\text{DS}}/V_{\text{G}}$), V_{G} is the gate voltage, and C_{OX} is the gate capacitance (11.6 nF/cm²).

3. Results and Discussion

3.1 MnOEP-SWNT Characterization

Raman spectroscopy was used to investigate changes before and after MnOEP modification of SWNT/FET. As shown in Figure 3: see original paper, bare SWNT exhibited four characteristic peaks at 1351 cm⁻¹ (D band), 1579 cm⁻¹ (G band), 1600 cm⁻¹ (G⁺ band), and 2680 cm⁻¹ (2D band). After MnOEP modification, the G band narrowed and shifted to 1598 cm⁻¹, while the D/G intensity ratio increased, indicating non-covalent binding between MnOEP and SWNT with partial sp² to sp³ conversion.

UV-Vis spectroscopy was performed using quartz glass substrates due to poor Si/SiO₂ transparency. Figure 3: see original paper shows that SWNT immobilization significantly enhanced absorbance across 200–800 nm with characteristic peaks at 200–400 nm, consistent with SWNT absorption features [24]. After MnOEP modification, the absorption spectrum showed additional small peaks at 475 nm and 560 nm, confirming successful MnOEP attachment [25].

Electrochemical characterization revealed that both bare and MnOEP-modified SWNT/FET showed linear $I_{\text{DS}}-V_{\text{DS}}$ relationships, but conductivity decreased significantly after modification, indicating electron transfer and $\pi-\pi$ stacking between MnOEP and SWNT. As shown in Figure 4: see original paper, the threshold voltage (V_{TH}) shifted from 0.45 V to -0.15 V after modification. Carrier mobilities were 525 cm²/V · s and 387 cm²/V · s for bare and modified devices, respectively. The conductivity reduction occurs because MnOEP donates electrons to the p-type SWNT, reducing hole concentration and carrier mobility [26].

3.2 Parameter Optimization

[Figure 5: see original paper] compares the performance of different metalloporphyrin-modified sensors for detecting 4-ethylphenol saturated vapor. Bare SWNT/FET showed relative resistance changes of 0.1, 0.24, and 0.49 at 1%, 10%, and 100% vapor concentrations, respectively. After metalloporphyrin modification, sensitivity followed the order: MnOEP-SWNT/FET > ZnTPP-SWNT/FET > CuOEP-SWNT/FET > TPP-SWNT/FET > FeTPP-SWNT/FET, demonstrating MnOEP's superior selectivity for 4-ethylphenol.

Response time was evaluated by monitoring relative resistance versus time at different concentrations. [Figure 6: see original paper] shows that at low concentrations (1% and 10%), MnOEP-SWNT/FET reached maximum response in 5 minutes, while at high concentrations (100%), saturation occurred within 2 minutes. Therefore, 5 minutes was selected as the standard detection time.

Source-drain voltage (V_{DS}) optimization was performed by calculating resistance from $I_{\text{DS}}-V_{\text{DS}}$ curves using Ohm's law. [Figure 7: see original paper] shows that resistance remained constant across most voltages, with discontinuity at 0 V due to equipment limitations in ultra-low current measurement. Since voltage variation did not affect resistance, $V_{\text{DS}} = 0.1$ V was selected for all subsequent experiments.

3.3 4-Ethylphenol Detection Linear Relationship

Under optimized conditions, SWNT/FET and MnOEP-SWNT/FET were tested against 4-ethylphenol saturated vapor concentrations from 0.25% to 100%. Figure 8: see original paper shows the temporal response, while Figure 8: see original paper presents the calibration curve. MnOEP-SWNT/FET exhibited increasing relative resistance with concentration, showing two linear regions: a steep slope from 0.25% to 20% and a gentler slope from 20% to

100%. The linear regression equations were $y_1 = 0.0792x$ ($R^2 = 0.9411$) and $y_2 = 0.0071x$ ($R^2 = 0.9745$), respectively. The detection limit was determined to be 0.15% saturated vapor ($S/N = 3$).

3.4 Consistency

Four independently fabricated MnOEP-SWNT/FET devices were tested for reproducibility. As shown in [Figure 9: see original paper], all devices exhibited consistent positive correlation between relative resistance and 4-ethylphenol concentration, with relative standard deviations (RSD) below 10% across all concentrations, confirming excellent device-to-device consistency.

3.5 Real Sample Analysis

To validate practical applicability, chlorobenzene enrichment tubes were used to collect volatile organic compounds from healthy strawberry plants (samples 1 and 2) and Phytophthora-infected plants (samples 3 and 4). The collected volatiles were analyzed by MnOEP-SWNT/FET and compared with standard 4-ethylphenol vapor at equivalent volumes. Results in show that healthy plants produced minor signals (1.33% and 1.89% relative resistance increase) indicating false positives likely due to environmental interference, while infected plants showed significantly stronger responses (17.34% and 11.65% increase). When spiked with additional 4-ethylphenol, infected samples showed substantially greater signal enhancement (59.35% and 56.34%) compared to healthy plants (52.13% and 47.45%), demonstrating the sensor's diagnostic accuracy.

4. Conclusion

This study leverages the unsaturated coordination state of metalloporphyrin central metal ions, enabling gas molecules to interact via van der Waals forces and hydrogen bonds at axial positions, thereby modulating SWNT sensitivity and selectivity. MnOEP was identified as the optimal metalloporphyrin for 4-ethylphenol detection and integrated with SWNT-FET to create a semiconductor field-effect gas sensor. The MnOEP-SWNT/FET exhibited high selectivity, sensitivity, and rapid response to 4-ethylphenol, enabling accurate diagnosis of Phytophthora infection in strawberry plants, though minor false positives were observed for healthy plants.

Future work will address environmental interference from temperature and other volatile organic compounds by investigating decoupling methods to improve detection accuracy in complex field conditions, further enhancing the practical utility of MnOEP-SWNT/FET for early disease diagnosis.

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