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Piezoelectric sensor for ethylene based on silver(I)/polymer composite

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ABSTRACT

The postharvest stability of fruits is influenced by the atmospheric ethylene. Thus, it is important to detect ethylene accumulation in the fruit environment to avoid economic losses due to premature rotting. In this study, an ethylene sensor was fabricated by drop-casting a $AgBF_4$/polyvinylpyrrolidone composite onto a quartz crystal microbalance (QCM). Upon exposure to ethylene, the oscillation frequency of the QCM decreased immediately, and reached steady state after 10 min. This response could be attributed to the binding of ethylene to immobilized Ag(I), causing a change in the surface mass of the sensor. The sensor can be regenerated by purging it with nitrogen gas, indicating reversibility of the response. The response was repeatable with RSD of <5% (n = 11) against 25% ethylene. The mole ratio of Ag(I) to monomer unit and the amount of coating material influenced the sensor response, and were optimized. The sensor exhibited a linear working range from 1 to 7 ppm (R = 0.9896) with RSD of <15% (n = 3). The sensitivity and limit of detection were determined to be 51 Hz ppm^{-1} and 420 ppb, respectively. The sensor also produced responses to higher ethylene level (from 10 ppm to 1,000,000 ppm) but with a much lower sensitivity. The sensor output correlated well with the results of gas chromatograhic measurements. Good selectivity to ethylene was shown against other volatile organic compounds. The sensing paradigm for ethylene based on $AgBF_4$/PVP coated QCM can be applied to ethylene monitoring in post-harvest technology.

1. Introduction

The measurement of low ethylene concentration is important in agriculture and horticulture, particularly in post-harvest management [1]. Ethylene plays a regulatory role in the ripening of fruits [2]. It is released by plants and fresh products, and its accumulation within the fruit environment, especially during storage and transportation, accelerates ripening [3] and could result to premature rotting [1]. Thus, monitoring ethylene concentration is important to optimize the freshness of fruits when these products reach the consumers.

Several detection methods have been used to measure ethylene. These methods include gas chromatography detection, electrochemical and optical methods [4]. However, most of the effective and precise ethylene detection methods are expensive and difficult to apply to in-field and real-time measurement. The development of simple and affordable method is particularly challenging due to the limited chemical functionality of ethylene [5].

Sensor technology offers an alternative detection method for ethylene [5]. Sensors can simplify and lower the cost of the conventional ethylene analysis. Ethylene sensors have been fabricated based on amperometric [6], conductimetric [1,7–10], luminescence [2,11], colorimetric [12], and piezoelectric [13] sensing principles. Commercially available ethylene sensors have been developed based on electrochemical and optical transductions [4].

A number of reagents have been employed in the molecular recognition phase of ethylene sensors. Among these are redox reaction reagents [6–9,12], semiconductor metal oxides [14]; and a Mn/SiO nanomaterial [15]. Supramolecular macrocycles of platinum and palladium that can entrap ethylene within its cavities were applied in a piezoelectric sensor for ethylene [13]. Metal ions such as copper(I) [1] and silver(I) [2], which form complexes with ethylene, have been employed in a chemoresistive [1] and luminescence sensors [2] for ethylene.

In this study, a piezoelectric sensor is described which is based on a silver(I)/polymer composite coupled with a piezoelectric quartz crystal microbalance (QCM). Piezoelectric transducers, such as the QCM, are mass sensors anchored to the principle of gravimetry [16]. These sensors were initially thought not to be sensitive enough for the detection of ethylene which has a low molecular weight. However, the sensitivity was improved by coating the

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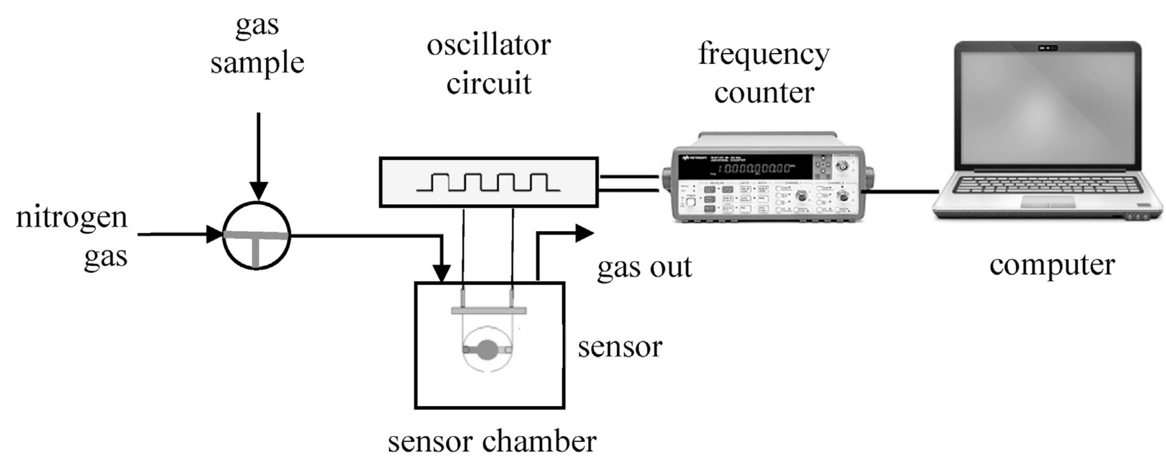

Fig. 1. Instrumentation for the piezoelectric sensor for ethylene.

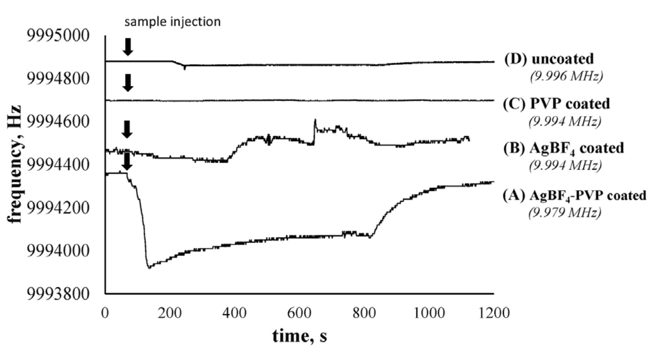

Fig. 2. Response to 250,000 ppmV ethylene of (A) $AgBF_4$/PVP composite-coated quartz crystal; (B) $AgBF_4$-coated quartz crystal; (C) PVP-coated quartz crystal; and (D) uncoated quartz crystal.

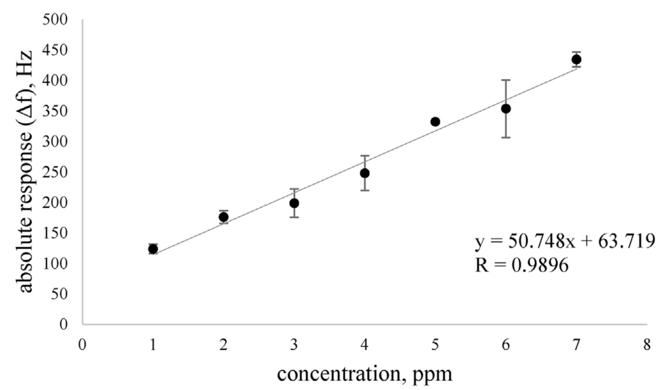

Fig. 4. Calibration curve of the ethylene sensor. (number of replicates = 3).

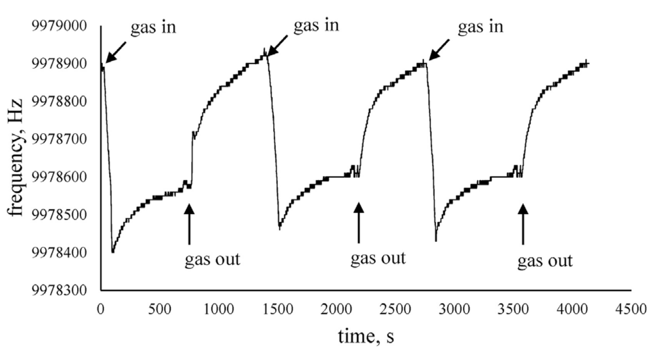

Fig. 3. Sensor response to repeated ethylene measurements of a 250,000 ppmV ethylene gas mixture.

crystal with a layer of an efficient ethylene-binding reagent, such as supramolecular macrocycles [13]. Silver(I)/polymer composites bind with ethylene through a complexation reaction, and could make the piezoelectric crystal sensitive to ethylene. This binding reaction has been applied in the separation of alkenes from alkanes in the refining and petrochemical industry [17].

2. Material and methods

2.1. Materials

The silver salts used as sensing reagents were $AgNO_3$ (99.0%, Ajax) and $AgBF_4$ (98%, Sigma-Aldrich). The polymers studied as immobilizing agents were polystyrene (280,000 g/mol, Sigma-Aldrich), polyethylene glycol (3350 g/ mol, Sigma-Aldrich) and polyvinylpyrrolidone (10,000 g/mol, Sigma-Aldrich). The solvents used to dissolve the polymer were acetonitrile (100.0%, J.T. Baker) for polyethyleneglycol and polyvinylpyrrolidone, and tetrahydrofuran (99.8%, RCI Labscan) for polystyrene. The volatile organic compounds used in the selectivity studies were diethyl ether (99.5%, RCI Labscan), ethanol (99.9%, RCI Labscan), ethyl acetate (99.8%, RCI Labscan) and *n*-hexane (95%, RCI Labscan). All the reagents mentioned above were used as-received without further purification.

Gas mixtures of different ethylene concentrations (1–250,000 ppmV ethylene) were prepared by diluting ethylene gas (99.95%, Sigma-Aldrich) with high purity N_2 gas (United Compact, Manila). Low concentration of ethylene were prepared through serial dilution.

2.2. Sensor fabrication

An AT-cut 10-MHz piezoelectric crystal (Seiko, aluminum electrode) was employed for the fabrication of the sensor. The crystal was cleaned with acetone (99.9%, Sigma-Aldrich). It was initially coated with the pristine polymer by drop-casting 1.00 μL of the polymer solution (0.1 g/L) on the surface of the crystal. The polymer-coated crystal was dried for 30 min under a continuous stream of high purity N_2 gas at room temperature.

A solution of the silver salt/polymer (1:4) composite was prepared by dissolving the silver salt (1.0-μg Ag^+) and the polymer in this solvent. Acetonitrile was the solvent used for the composites based on polyethyleneglycol and polyvinylpyrrolidone, and tetrahydrofuran was used for the polystyrene composites. The solution was placed in an ultrasonicator for 5 min. A small amount