Molecularly Imprinted Sol-gel Modified Localized Surface Plasmon Resonance Sensor for *cis*-Jasmone Detection

Liang Shang, Chuanjun Liu, Kenshi Hayashi
Graduate School of Information, Science and Electrical Engineering
Kyushu University
Fukuoka, Japan

***Abstract*—The detection of *cis*-jasmone is meaningful to sense potential threat in agriculture. In present study, a nanocomposite imprinted LSPR sensor was developed for determination of *cis*-jasmone vapors. Molecular imprinted sol-gels (MISG) were fabricated on the surface of Au nano-islands via spinning coating. For enhancing the sensitives of sensors, AuNPs was sputtered on the MISG layers. The sensitives and selectivelies of samples recoated divers thickness of AuNPs were compared and discussed. The result indicated that the sensitivity of AuNPs/MISG/AuNPs was higher than that of AuNPs/MISG. In addition, AuNPs/MISG coated with 3 nm AuNPs shown a better sensitive and selectively. In-situ response was verified to be fast, selective and reversible. The absorbance spectra of *cis*-jasmone vapors linearly increased with its concentration in the range of 10 to 75 ppm, with the limit of detection of 3.45 ppm (*S*/*N*=3). The research offered useful technologies for developing *cis*-jasmone sensor in agriculture area.**

Keywords—Molecular imprinted sol-gel; Au nano-island; Localized surface plasmon resonance; Gas sensor; Layer by layer; cis-Jasmone

I. INTRODUCTION

Plants damaged by herbivore feeding can release stress-related signals, or agriculture volatile organic components (AVOCs), such as *cis*-jasmone and indole [1]. These AVOCs can not only affect pathogen development, but also attract other insects that prey on or parasitize the herbivores [2]. *cis*-Jasmone, formally related to the plant hormone jasmonic acid (JA), is well known as a defense-related component of AVOCs for plants [3]. Therefore, the investigation and determination of *cis*-jasmone in atmosphere is important for pest controlling in agriculture.

The phenomenon of localized surface plasmon resonance (LSPR) could be employed as transducers that convert change in the refractive index (RI). The superiorities of LSPR sensors are rapid recovery and response speed, which had been applied in some areas [4]. However, LSPR sensors are non-specificity sensors. To overcome above drawback, recognition sites, such as molecular imprinted polymers (MIPs) and metal organic frameworks (MOFs), are coated on Au nano-islands for developing LSPR sensors [5]. Recently, molecular imprinted sol-gels (MISGs) has widely applied in developing biosensors and quartz crystal microbalance (QCM) sensors via their chemical and thermal stability [6].

To our knowledge, few LSPR-MISGs methods have been proposed for plant related vapor detection. In present study, Au nano-islands coated with MISGs were used for developing *cis*-jasmone sensors. The schematic of AuNPs/MISG/AuNPs sensor is show in Fig. 1. MISGs were spin coated on the Au nano-islands firstly. Then, AuNPs were sputtered on the MISG layers to form hot spots for enhancing sensitives. Based on the cavities generated by templates in sol-gel matrix, *cis*-jasmone vapor would be absorbed selectively, which would induce the change of absorbance spectra. By detecting these variations, an optical sensor was developed for *cis*-jasmone vapor detection.

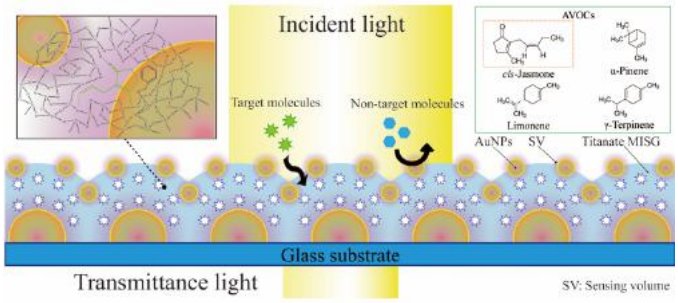

Fig. 1. The schematic graph of AuNPs/MISG/AuNPs film for selective cis-jasmone detection.

II. EXPERIMENTS

A. MISG reaction solutions preparation

MISG reaction solution was prepared by dissolving 150 μL tetrabutoxy titanium as a precursor, 50 μL *cis*-jasmone as template molecules and 50 μL TMP as functional monomer in 2 mL of *iso*-propanol. 25 μL titanium tetrachloride was added to initialize the reaction. Then, the solution was heated in a 60 °C water bath for 1 h to finish prehydrolyzing.

B. AuNPs/MISG/AuNPs film fabrication

Clean and dried glass substrates were processed in a plasma cleaner in argon atmosphere (110V, 10.2W) for 5 min. After immersing in a 1:10 (v:v) 3-aminopropyl triethoxysilane ethanol solution for 8 h, substrates were put into a quick coater for AuNPs deposition (thinkness: 3 nm), and annealed in air atmosphere at 500 °C for 2 h. We repeated this process for twice to obtain high sensitive LSPR substrates. MISGs film was constructed on the AuNPs film by spin coating 20 μL of

MISG solution at a spinning rate of 3000 rpm. Then, samples were heated at 130 °C for 1 h to remove template molecules from the MISGs. Afterwards, samples were put into the quick coater again for AuNPs deposition on MISGs and annealed at 130 °C for 1 h.

C. *Instrument and testing system*

SEM was employed for analyzing the morphologies characteristics of AuNPs/MISG/AuNPs films in present study. Vapor generation and spectra testing system are shown in Fig 2. Vapor generation system included an air pump, an air filter, two mass flow controllers (MFC), a glass bottle and a gas valve. The system was controlled by Labview software. The concentration C (ppm) can be calculated by (1) and (2).

$$C = \frac{k \times D_r \times 10^3}{F} \tag{1}$$

where D_r (μg/min) indicted the diffusion rate at the appoint temperature, F (L/min) indicated the flow rate of diluent gas, k indicated the factor for converting gas weight to gas volume, which can be calculated as follows:

$$k = \frac{22.4 \times (273 + t) \times 760}{M \times 273 \times P} \tag{2}$$

where M indicated the molecular weight of organic acid molecule, t is the gas temperature and P is the gas pressure (760 mmHg).

Spectra testing system was consisted of a light source, a spectrometer, a personal computer and a gas room. The scanning range was set from 400 to 900 nm and the wavelength resolution was 0.1nm. By the OPwave+ software, the absorbance spectra in real-time were detected and recorded.

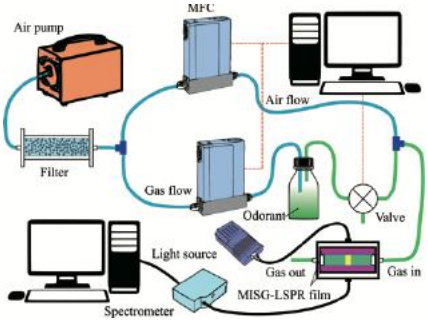

Fig. 2. Schematic of vapor generation and spectra testing system.

III. RESULTS AND DISCUSSION

A. *Optical and morphology characteristics of AuNPs/MISG/AuNPs films*

Spectral characteristics of bare and MISG coated Au nano-islands were studied as shown in Fig. 3. It demonstrated that sol-gel layer made the plasmon peak shift to the red. In addition, the maximum absorbance (A_{max}) was increased and the spectral peak position (λ_{max}) was shifted to the red via the increasing of thickness for recoating AuNPs. The surface morphological analysis of MISG recoated with different thickness of AuNPs were studied in Fig. 4. It illustrated that Au nano-islands are covered by MISG films. The modified Au nano-islands was very rough, which increased the specific surface area. Compared with AuNPs/MISG coated samples (Fig. 3-b), AuNPs were observed on the surface of MISGs (Fig. 3-d), which indicated that AuNPs/MISG/AuNPs film was constructed on the substrate. In addition, the size of Au nano-islands on the MISGs was depended on the thickness of recoating AuNPs.

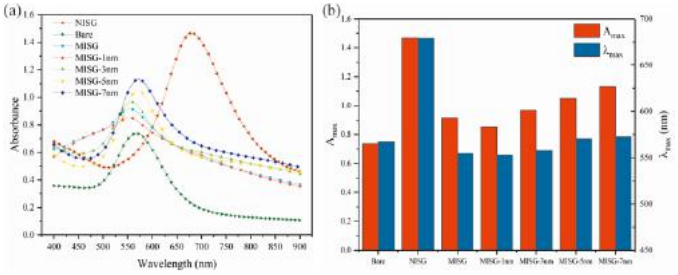

Fig. 3. Absorbance spectra (a) and optical features (b) of bare, non-imprinted sol-gel (NISG), molecular imprinted sol-gel (MISG) and MISG/AuNPs coated samples.

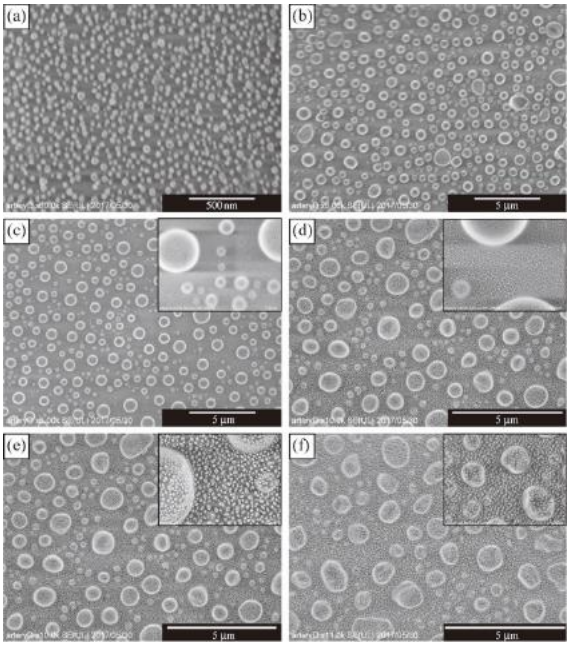

Fig. 4. SEM images of bare Au nano-island (a) and coated with MISG (b), MISG/1nm-AuNPs (c), MISG/3nm-AuNPs (d), MISG/5nm-AuNPs (e) and MISG/7nm-AuNPs (f).

B. *Selectivity of AuNPs/MISG/AuNPs sensor*

The purpose for preparing AuNPs/MISG/AuNPs films is to improve the sensitivity and selectivity of LSPR sensor. Although, particular cavities can be generated in MISGs by imprinting technology, molecules with similar structures to the template would be adsorbed on the surface of polymer and they can be captured in the cavities sites of MISGs. Therefore, α-pinene, limonene and γ-terpinene were chosen as interference AVOCs to evaluate the selectivity of the prepared sensor (Fig. 1). Considered the different concentrations of AVOCs, all responses were normalized for further processing (3).

$$R_{normalized} = \frac{A_{gas} - A_{air}}{\lg(C_j)} \tag{3}$$

where, A_{gas} and A_{air} indicated the absorbance in gas and air. C_j is on behalf of four types of AVOCs. Here, the concentrations of *cis*-jasmone, α-pinene, limonene and γ-terpinene were 86.87±9.48, 2316.54±352.27, 443.33±120.58 and 795.53±77.96 ppm, respectively.

The normalized responses of MISG coated AuNPs are shown in Fig. 5. Compared with MISG, the sensitivities of MISG coated AuNPs are higher, which can be explained by the hot spots between the bottom and surface AuNPs. In addition, too large Au nano-island would induce a worse selectivity for LSPR sensors. Real-time response of MISG coated with 3 nm AuNPs are shown in Fig. 6. It illustrated a fast, selective and reversible response was obtained in present research.

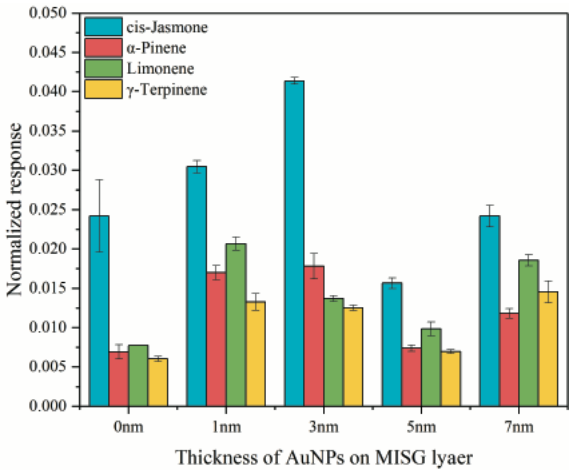

Fig. 5. Comparison selectivities of the MISG recoated with 1 nm, 3 nm, 5 nm and 7nm AuNPs sensors for cis-jasmone and other AVOCs detection.

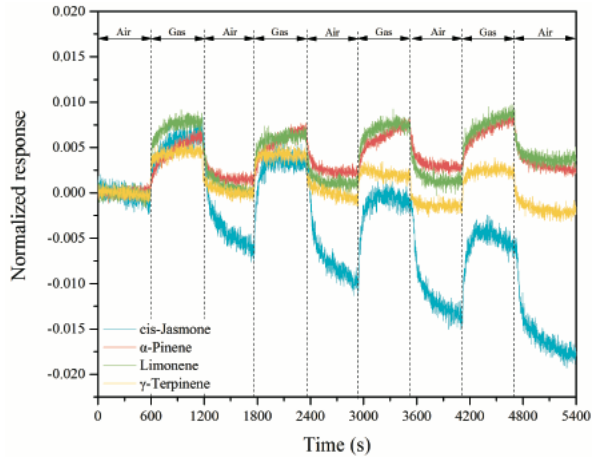

Fig. 6. Real-time responses of AuNPs/MISG/3nm-AuNPs sensor to 4 AVOCs. Responses were normalized by the concentration of AVOCs. Gas responses were obtained by keeping the switch on to AVOC vapor flow for 600 s and then to air flow for 600 s.

Calibration curve of *cis*-jasmone sensor in different concentrations is shown in Fig. 7. A linear range is observed with the equation of y=0.05219+0.00103x (R^2=0.91287). The limit of detection (LOD) was calculated to be 3.45 ppm based on 3δ.

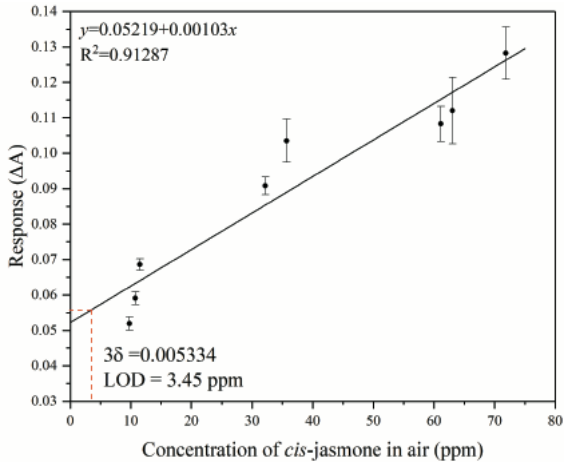

Fig. 7. The change of absorbency of MISG/AuNPs modified Au-island in cis-jasmone detection. The limit of detection (LOD) for cis-jasmone LSPR sensor was 3.45 ppm.

IV. Conclusion

In this study, a novel and simple strategy was proposed for preparation of a LSPR sensor for determination of *cis*-jasmone vapors selectively. A layer by layer method was used for constructing AuNPs/MISG/AuNPs films on substrates. The results indicated that combination of sol-gel technology and AuNPs, hot spots were constructed for enhancing the sensitivities of MISG coated LSPR sensors. In-situ response was verified to be fast, selective and reversible. The research offers useful technologies for developing *cis*-jasmone sensor in agriculture area.

Acknowledgment

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