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Localized Surface Plasmon Resonance Modified with Molecularly Imprinted Sol-gel Sensor array for Plant Volatile Organic Compounds Detection

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Introduction

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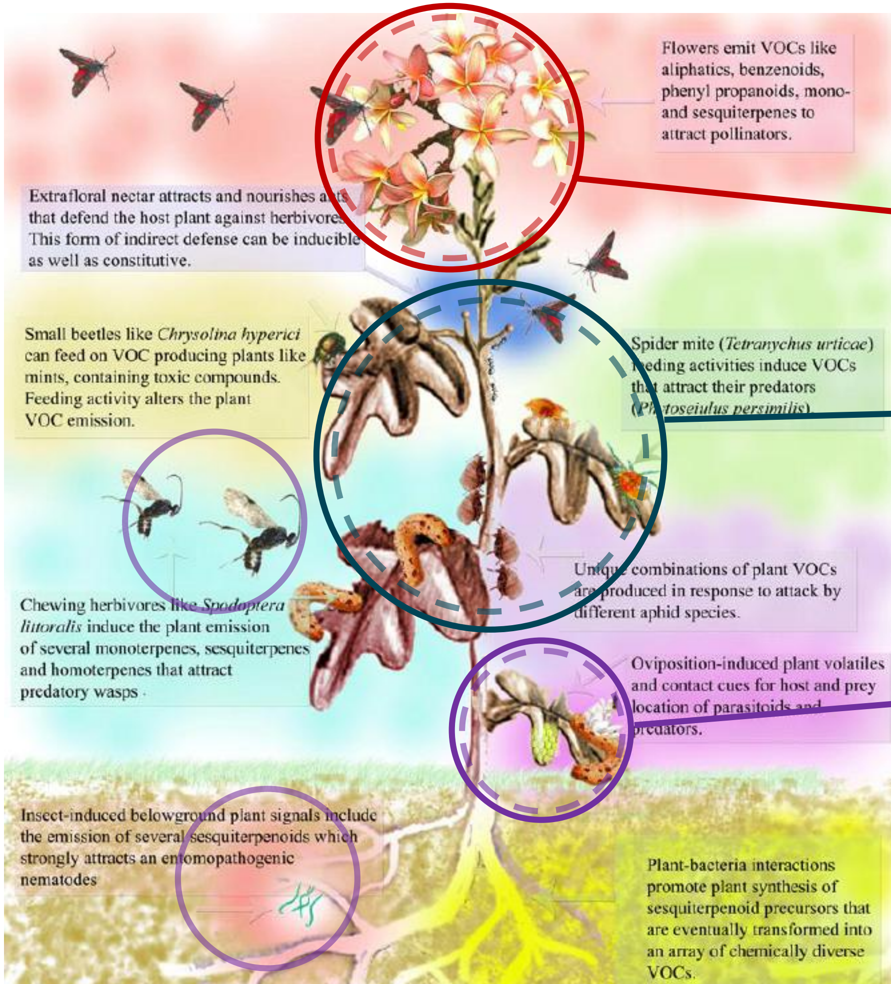
Plant Volatile Organic Compounds (PVOCs)



cf.) Massimo Maffei, Plant Physiology and development, The Plant Volatilome.

Released from flowers, leaves, roots.

Attract pollinators

Plants self-protection

- Spider mite
- Small beetles

Act as wound sealers

Attract predators

Plant–plant communication

Introduction

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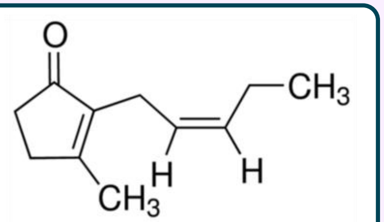
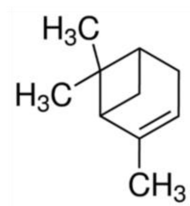
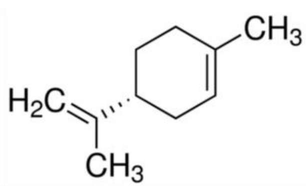
PVOCs



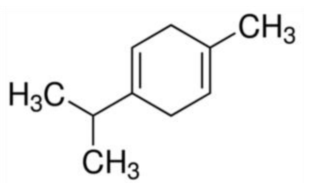
cis-Jasmone



α-Pinene



Limonene



γ-Terpinene




Application

Pest detection

Plant monitoring

Agriculture ICT

We need a translator for plants!

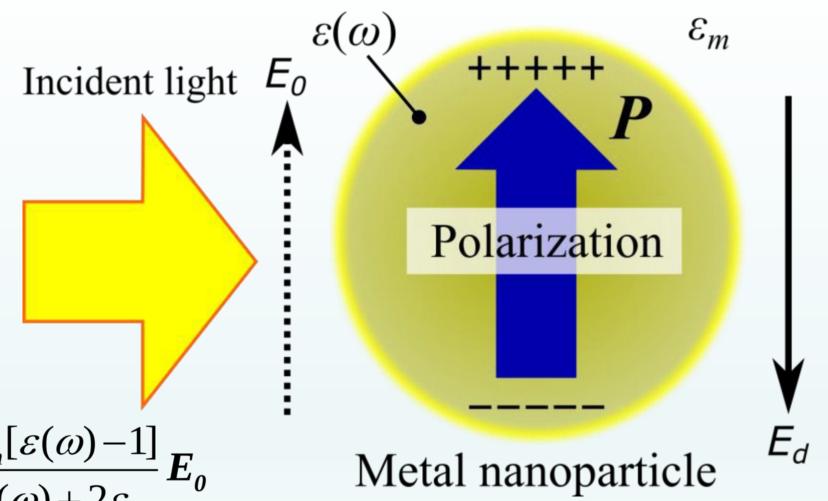
Gas chromatography/mass spectrometry GC/MS

High-cost, not portable and time-consuming

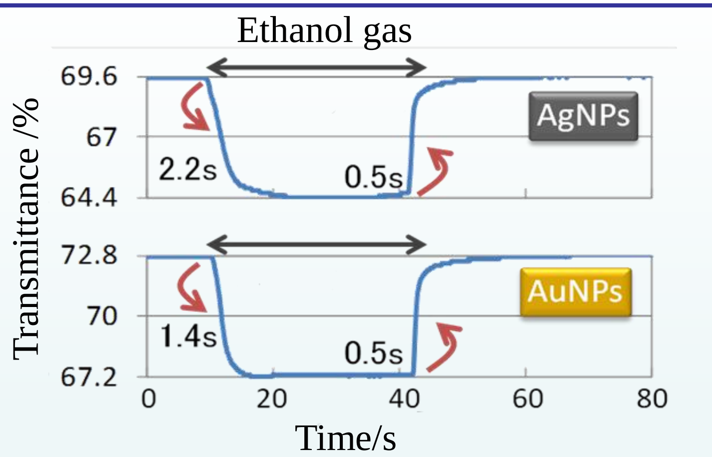
Not suitable for PVOCs real-time monitoring

Introduction

Localized surface plasmon resonance (LSPR)



$$P = \frac{3}{4\pi}\frac{\varepsilon_m[\varepsilon(\omega)-1]}{\varepsilon(\omega)+2\varepsilon_m}E_0$$



Transmittance measurement using LSPR of MNPs.
cf.) B. Chen, M. Ota, K. Hayashi: IEEJ Trans. SM, 133E, 90, 2013

Absorption spectra

Particle size, shape, composition

Surrounding media

Merit & drawback

Fast response/recovery speed

Non specificity

Introduction

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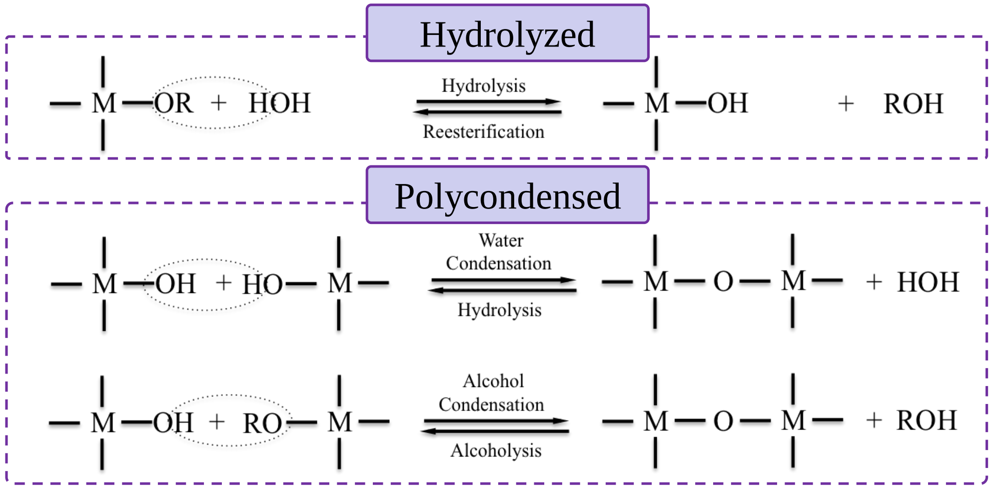
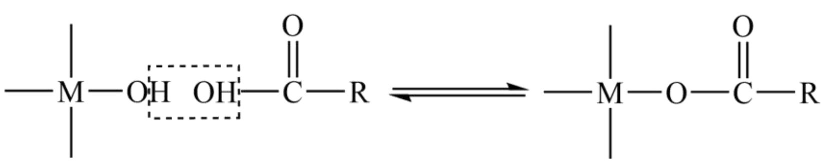
Molecularly Imprinted Sol-gel（MISG）

Reaction principle

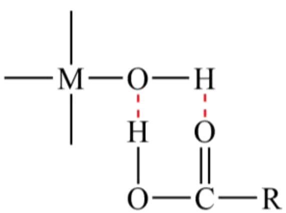


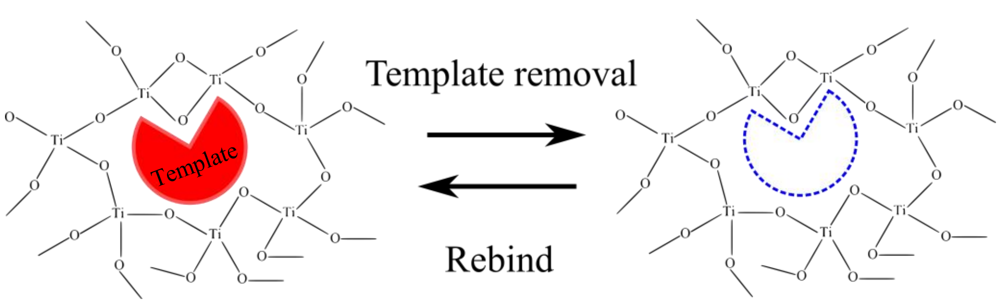
Imprinting method

Covalent bonding



Hydrogen bonding





(Adv. Mater. 2001,13,1327-1330)
(Anal. Bioanal. Chem. 2011, 400, 2457-2462)

Compared with other MIP

Stability of chemical and thermal

Concept

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MISG-LSPR sensor (AuNPs/MISG/AuNPs)

MISG layer

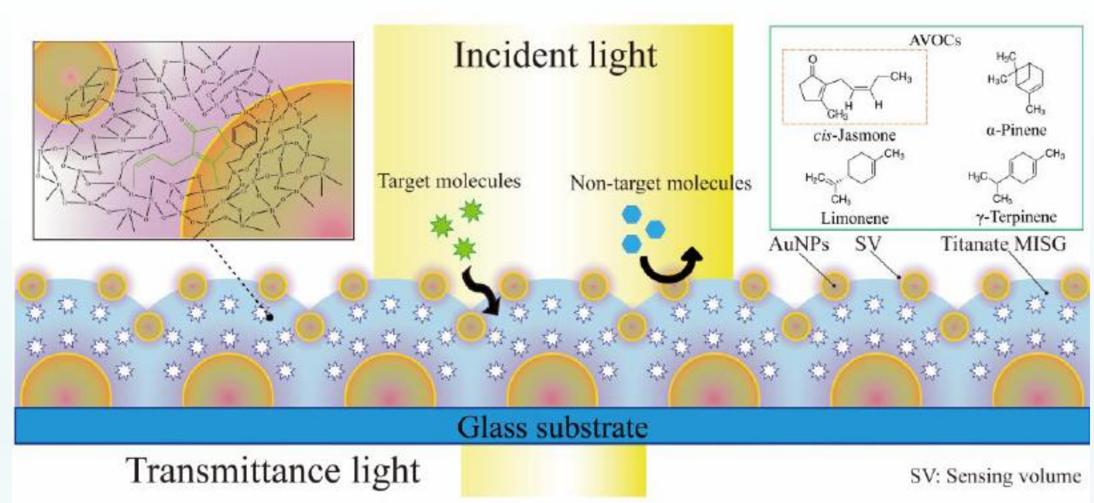
Selective adsorption layer

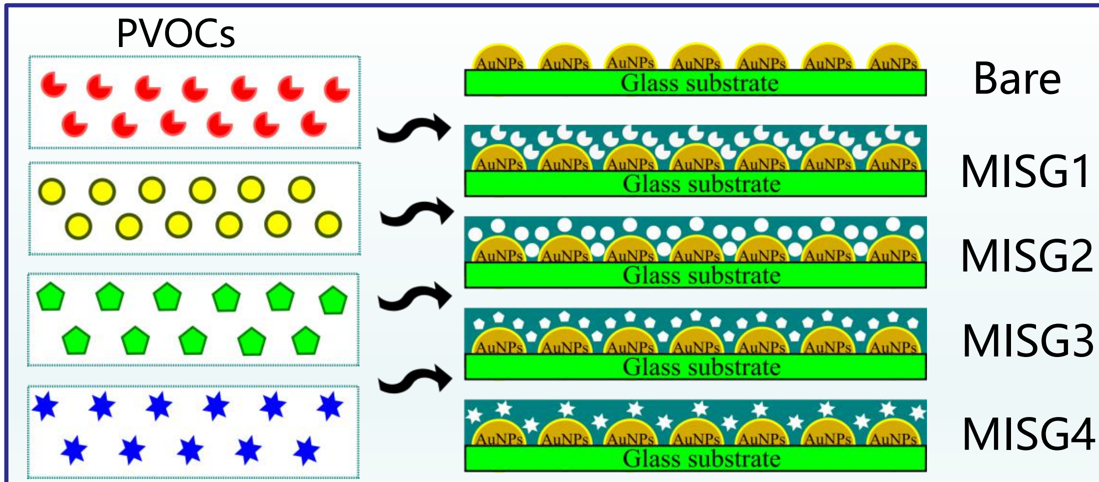
AuNPs layer

LSPR sensing layer

Detecting the change of the spectra

The target PVOC vapor would be selective detected.





Experiment

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MISG material

Iso-propanol	2 mL
$Ti(OBu)_4$	150 μL
TMP	25 μL
Template	50 μL
$TiCl_4$	25 μL

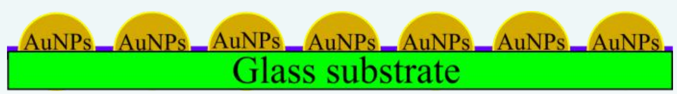
60℃ water bath, 1h

AuNPs/MISG/AuNPs film fabrication

Step 1
Sputtered AuNPs and anneal

Sputtering AuNPs thinkness: 3nm

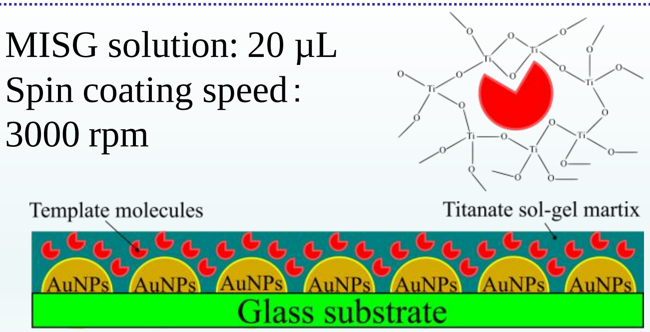
Anneal: 500℃, 2h , air, 2 times



Step 2
MISG reaction solution spin coating

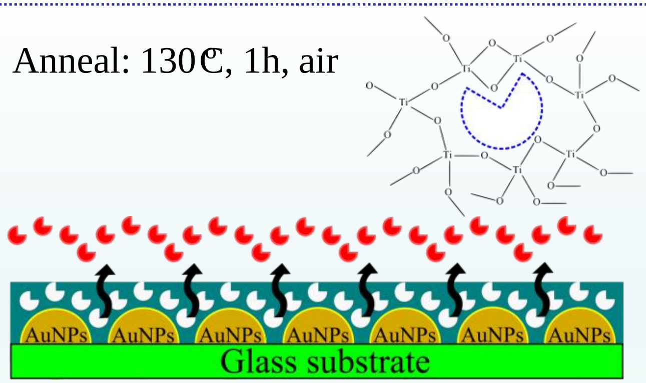
MISG solution: 20 μL

Spin coating speed: 3000 rpm



Step 3
Annealed for removing templates

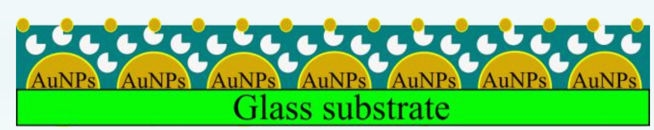
Anneal: 130℃, 1h, air



Step 4
Re-sputtered AuNPs and anneal

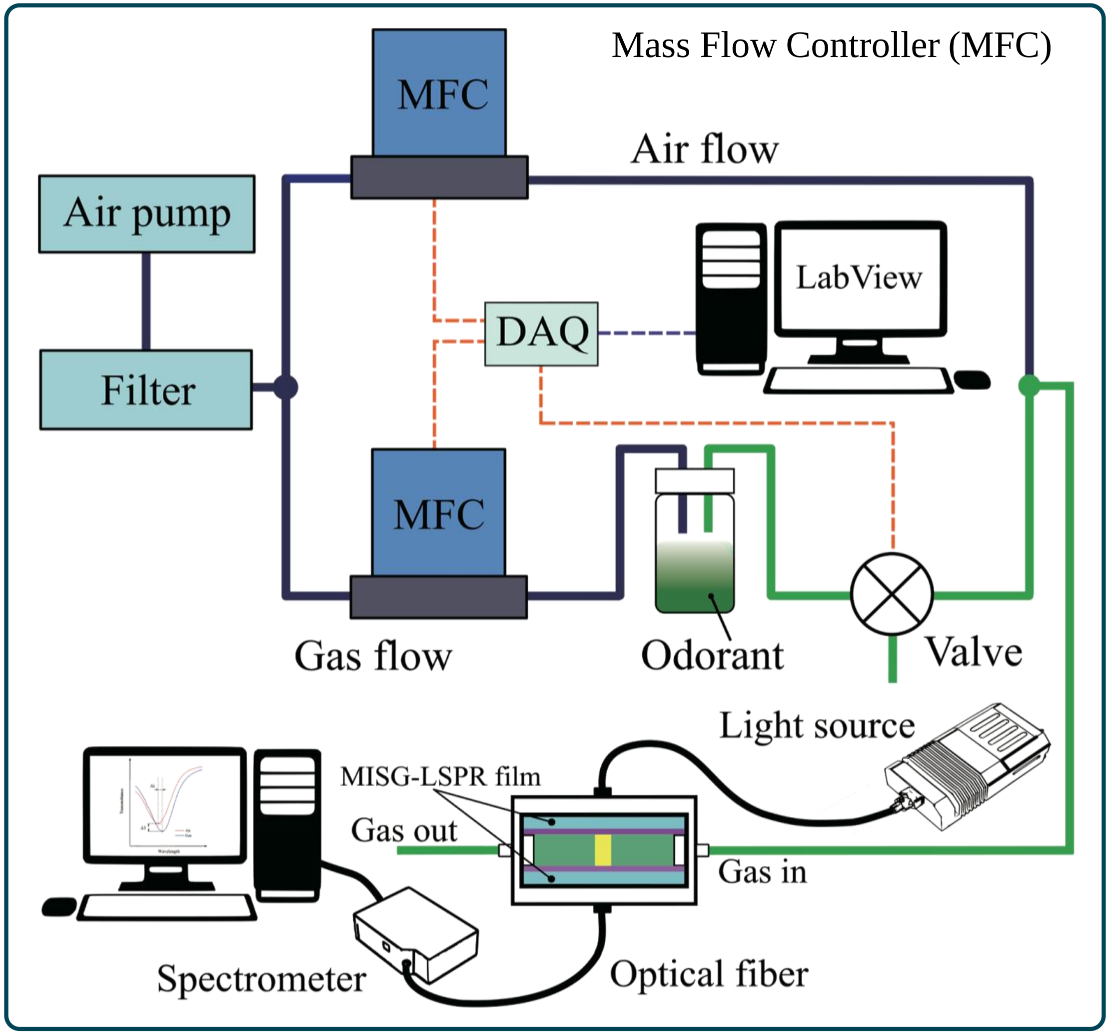
Sputtering AuNPs thinkness: 1, 3, 5, 7nm

Anneal: 130℃, 1h , air



Experiment

Vapor generation and LSPR spectra testing system



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

t – Thermodynamic temperature (℃)
M – Molecular weight (g/mol)
P – Atmosphere (mmHg)

$$C = \frac{k \times D_r \times 10^3}{F} \quad \text{(ppm)}$$

D_r –Diffusion rate (μg/min)
F – Flow rate of dilute gas (ml/min)

Results and discussion

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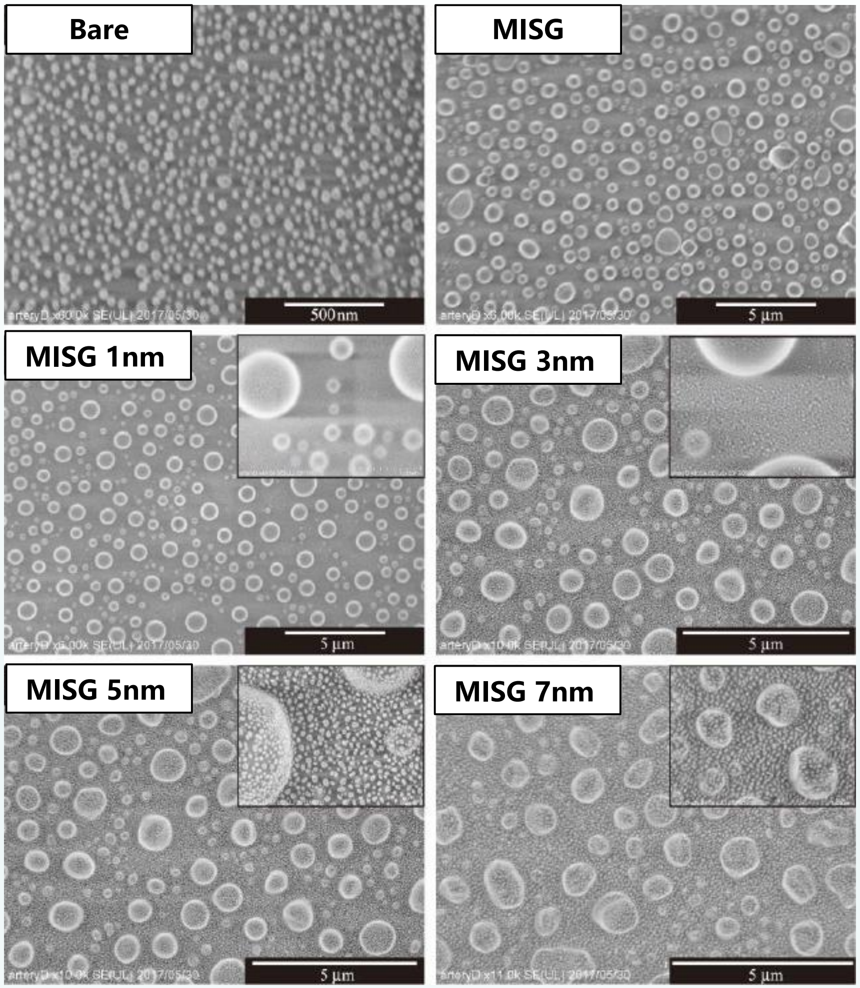
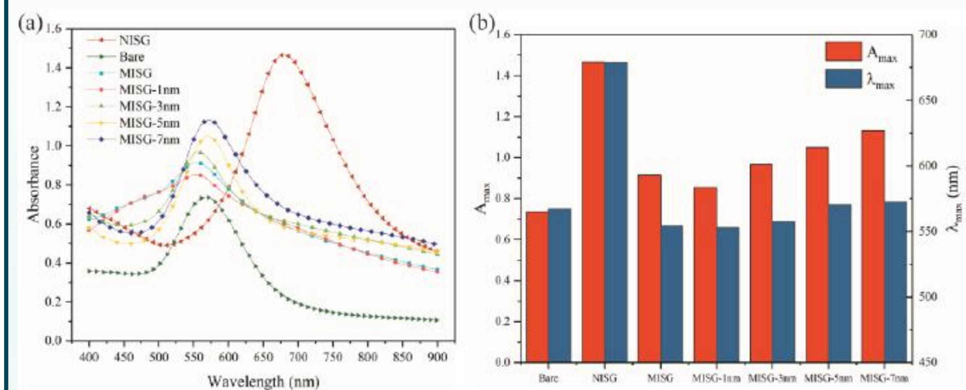
SEM images



Absorbance spectra



Discussion

- Sol-gel layer made the plasmon peak **shift to the red.**
- A_{max} was **increased** and λ_{max} was **shifted to the red** via the increasing of thickness for recoating AuNPs.
- AuNPs/MISG/AuNPs film was constructed on the substrate.
- The size of Au nano-islands on MISG layer was **depended on** the thickness of recoating AuNPs.

Results and discussion

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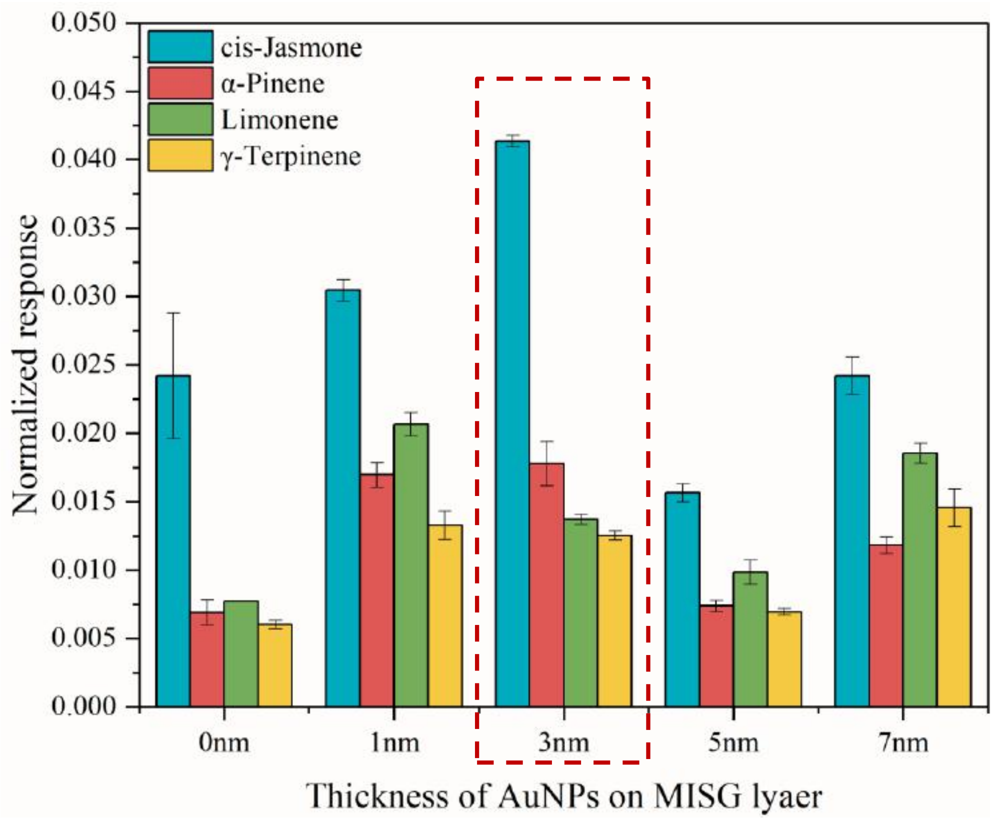
Selectivity of AuNPs/MISG/AuNPs sensor



Comparison selectivity of the MISG sputtered with 0 nm, 1 nm, 3 nm, 5 nm and 7 nm AuNPs sensors for *cis*-jasmone and other AVOCs.

Response Normalization

$$R_{normalized} = (A_{gas} - A_{air}) / \lg(C_j)$$

A_{gas} – Absorbance in gas
A_{air} – Absorbance in air
C_j – Concentration of gas

Concentration

cis-Jasmine	86.87±9.48 ppm
α-Pinene	2316.54±352.27 ppm
Limonene	443.33±120.58 ppm
γ-Terpinene	795.53±77.96 ppm

- The sensitivities of MISG/AuNPs are higher than MISG only.
- It can be explained by the hot spots between the bottom and surface AuNPs.
- Large Au nano-island would induce a worse selectivity for LSPR sensors.

Results and discussion

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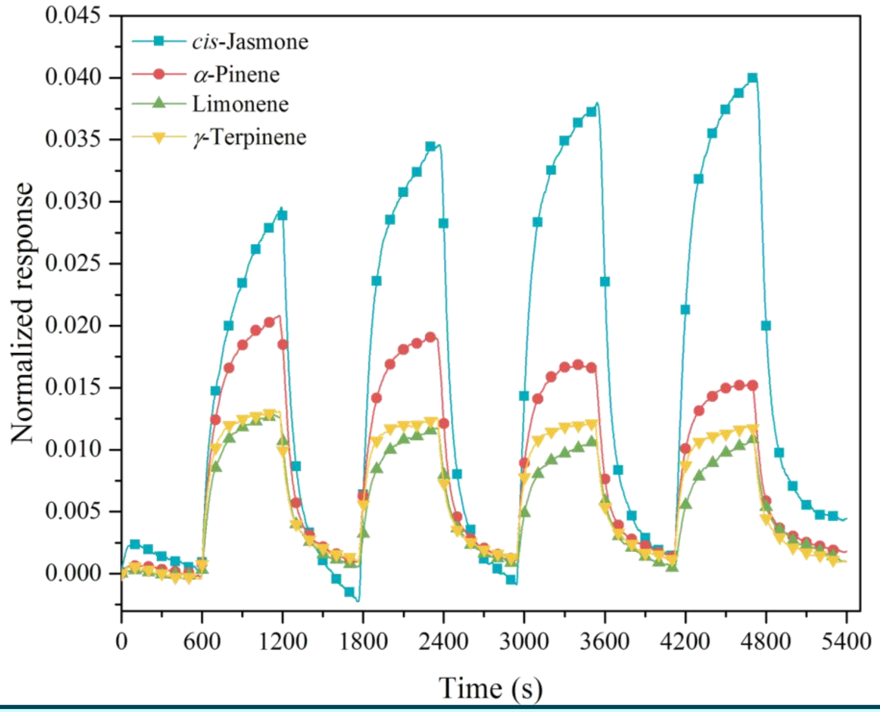
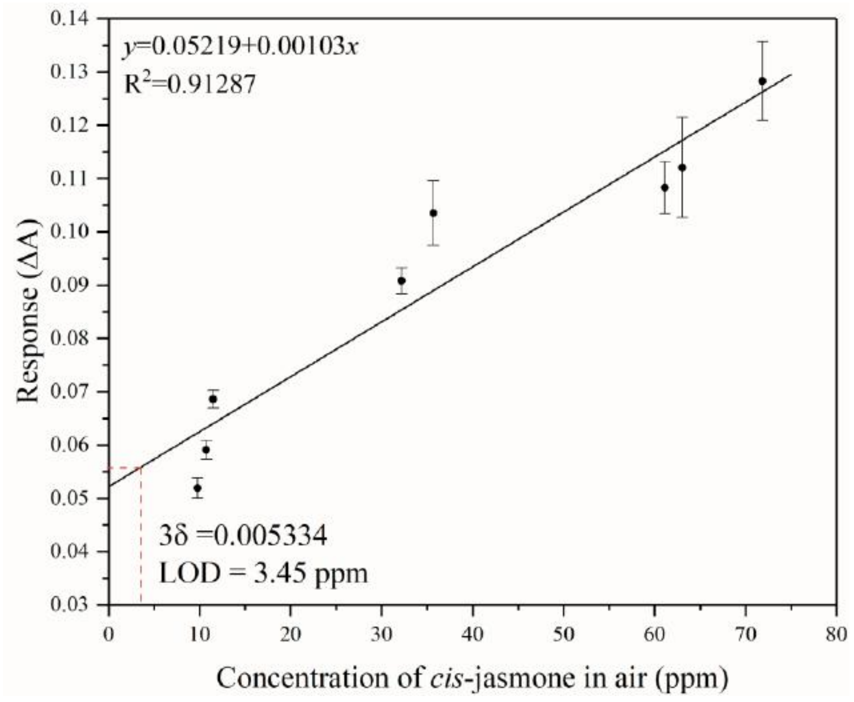
Comparison selectivity of MISGs coated sensor



Real-time responses of AuNPs/MISG/3nm-AuNPs sensor to 4 PVOCs.



The limit of detection (LOD) for *cis*-jasmone sensor was **3.45 ppm**.

A specific selectivity to *cis*-jasmone vapors was obtained.

Results and discussion

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MISG-LSPR sensor array for PVOCs discrimination

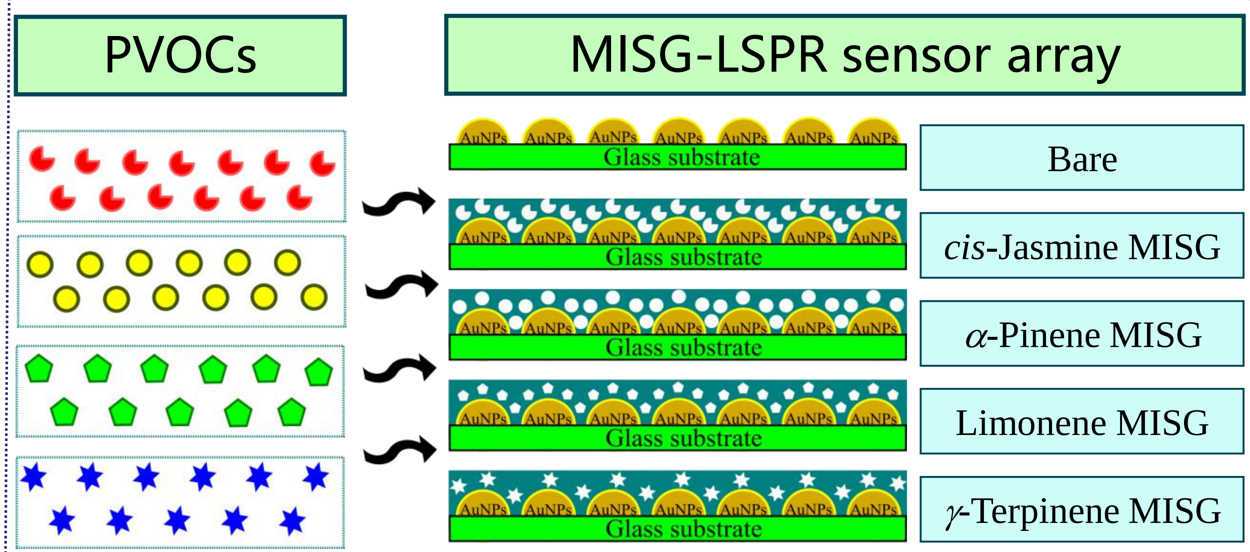
Changing the templates in MISG solution

↓

Different types of MISG solution

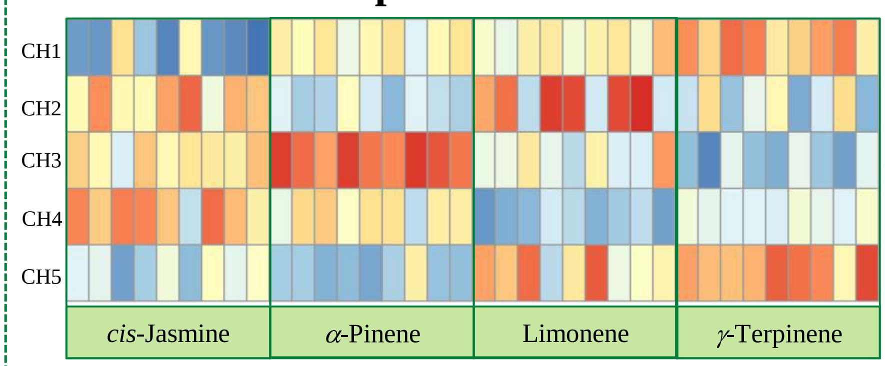
↓

MISG-LSPR sensor array



- By changing the flow rates (0.3, 0.5 and 0.7 L/min), PVOCs with different concentrations would be obtained.
- 36 samples (4 PVOCs × 3 flow rates × 3 repeats) were obtained in this study.
- All responses were scaled for former processing.

Response matrix



Results and discussion

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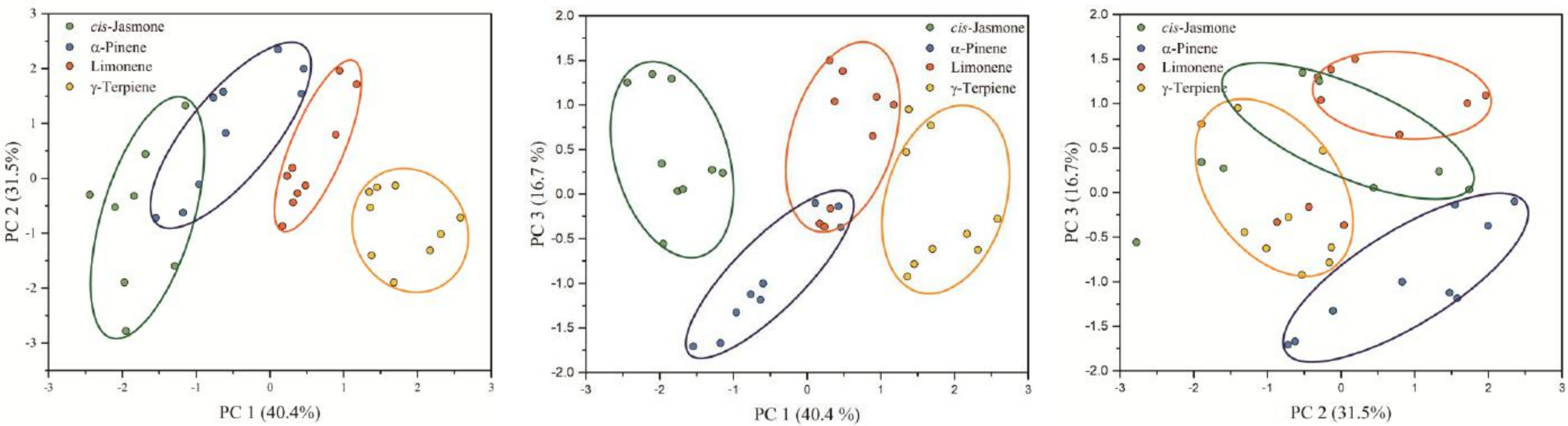
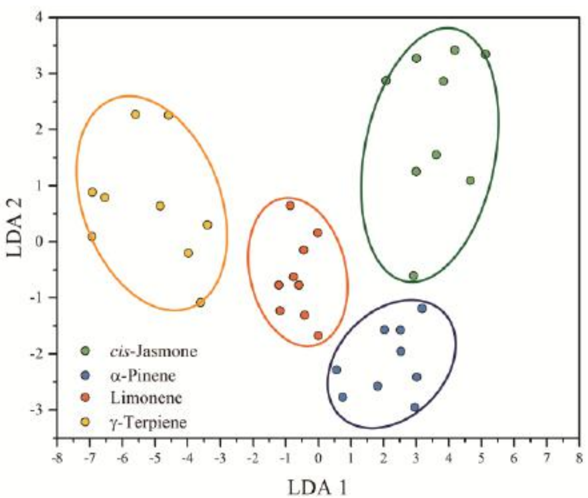
PCA and linear discriminant analysis results for PVOCs





- **Overlapped** were observed in all PCA spaces.
- More information can be obtained in MISG sensor array.
- In LDA space, an acceptable discriminated result was observed.
- Base on LOOCV method, the accuracy of LDA model was **94.4 %**.
- MISG-LSPR sensor array would be applied in PVOCs discrimination.

Conclusion

- An **AuNPs/MISG/AuNPs** film was developed for the determination of **PVOCs selectively**.
- 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 **LOD** for *cis*-jasmone sensor was **3.45 ppm**.
- Based on the **MISG-LSPR sensor array and** the **LDA** model, PVOCs could be discriminated (94.4 %).

Thank you for your attention

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