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High-performance Molecular Imprinted Sol-gel LSPR Array for Plant Volatile Organic Components Sensing

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Introduction

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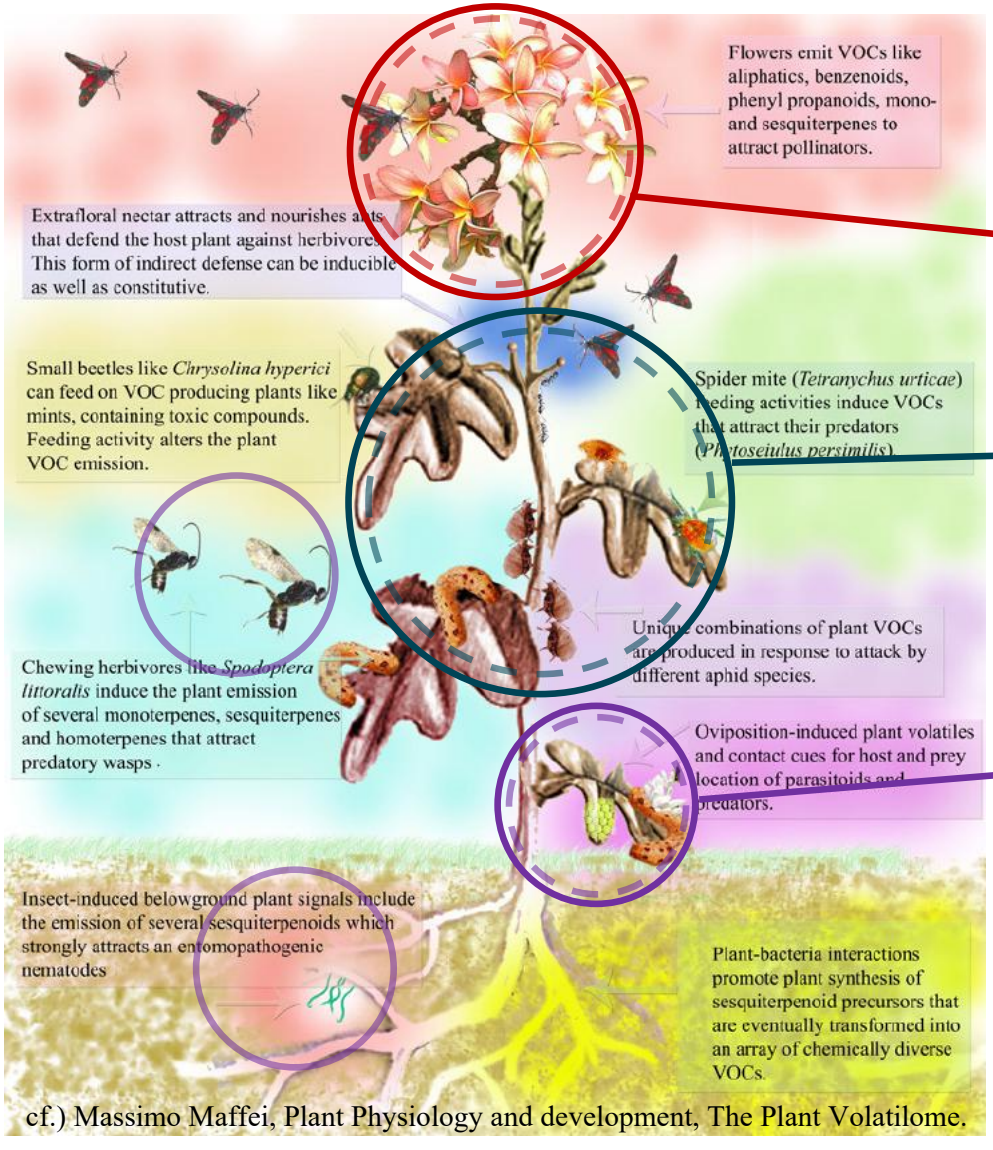
Plant Volatile Organic Compounds (PVOCs)



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

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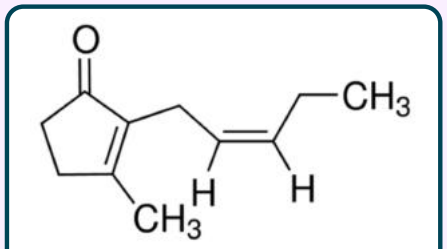
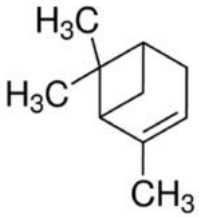
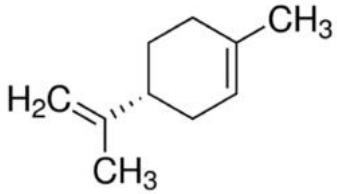
PVOCs



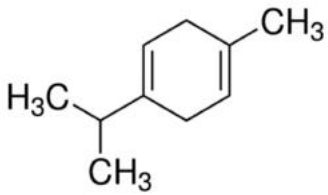
cis-Jasmone



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

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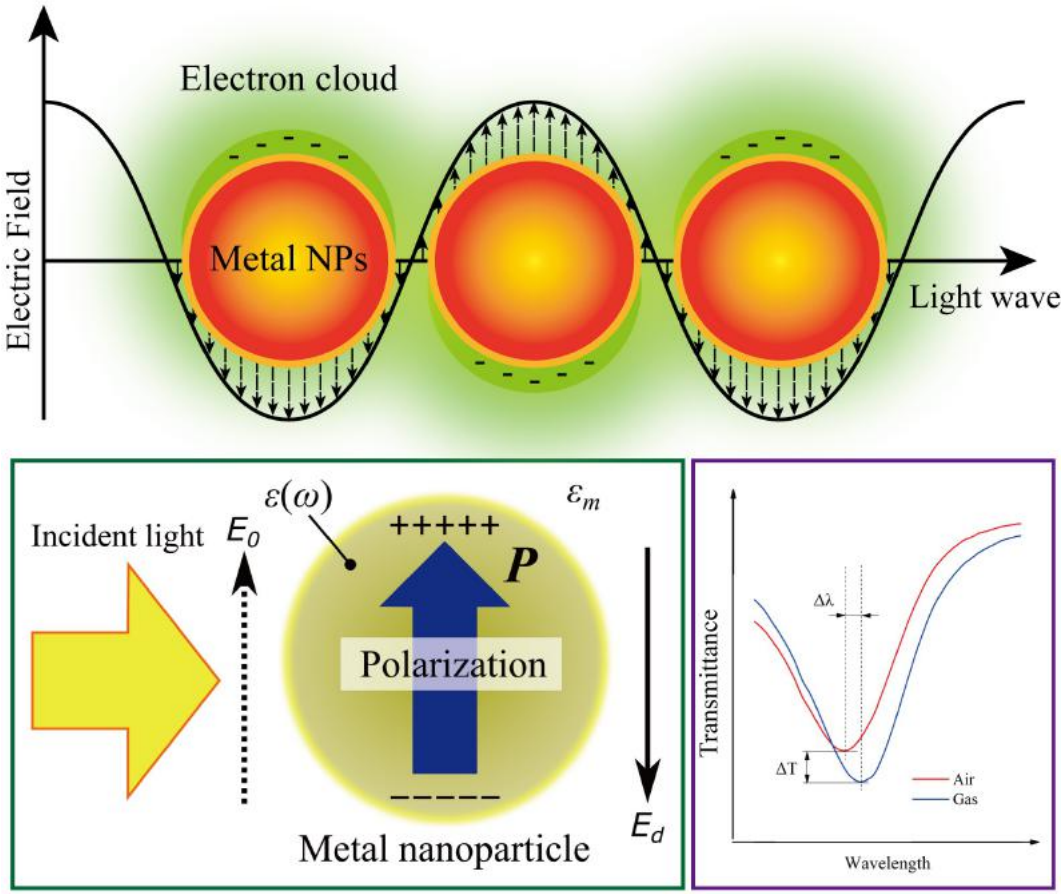
Localized surface plasmon resonance (LSPR)



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

Absorption spectra

Particle size, shape, composition

Surrounding media

Merit & drawback

Fast response/recovery speed

Non specificity

Introduction

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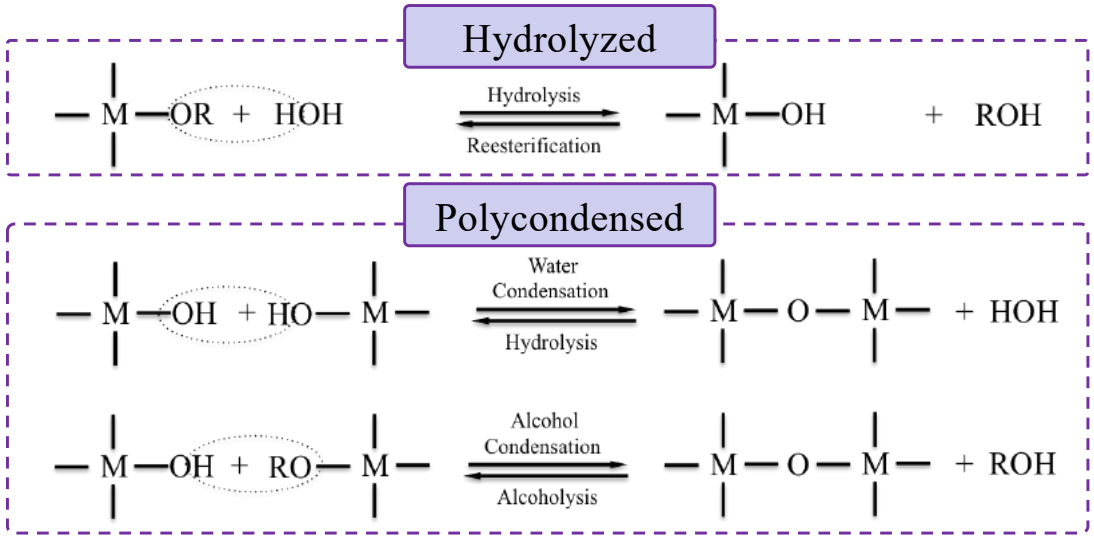
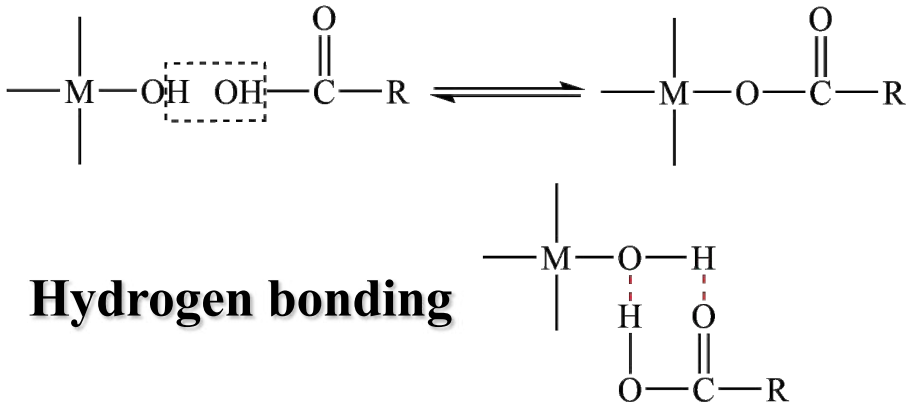
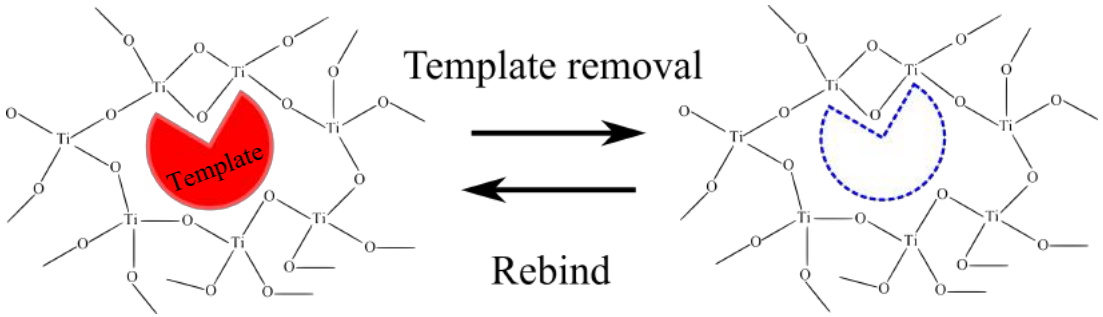
Molecularly Imprinted Sol-gel （ MISG ）

Reaction principle



Imprinting method





(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

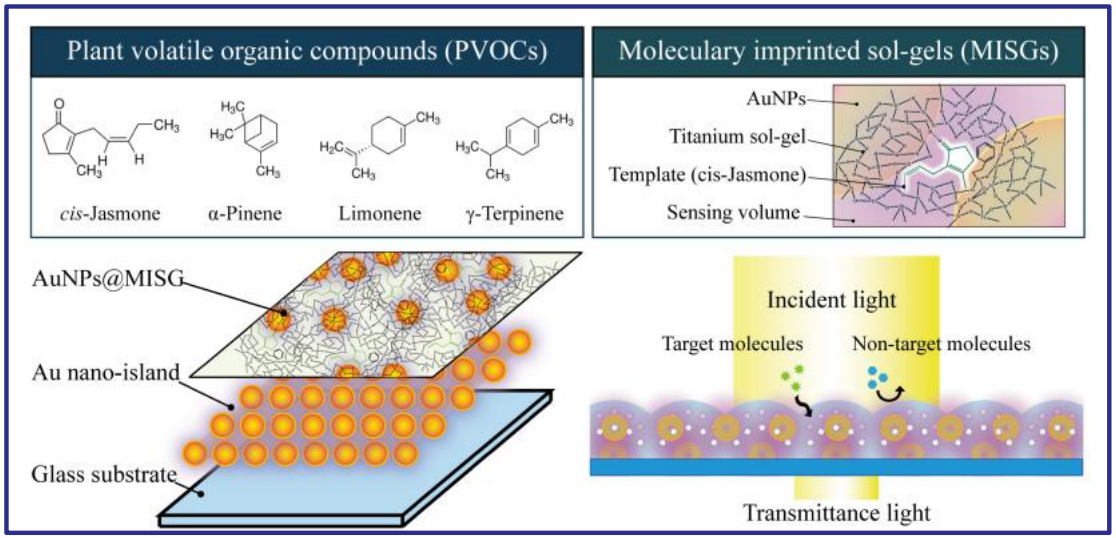
Selective adsorption layer

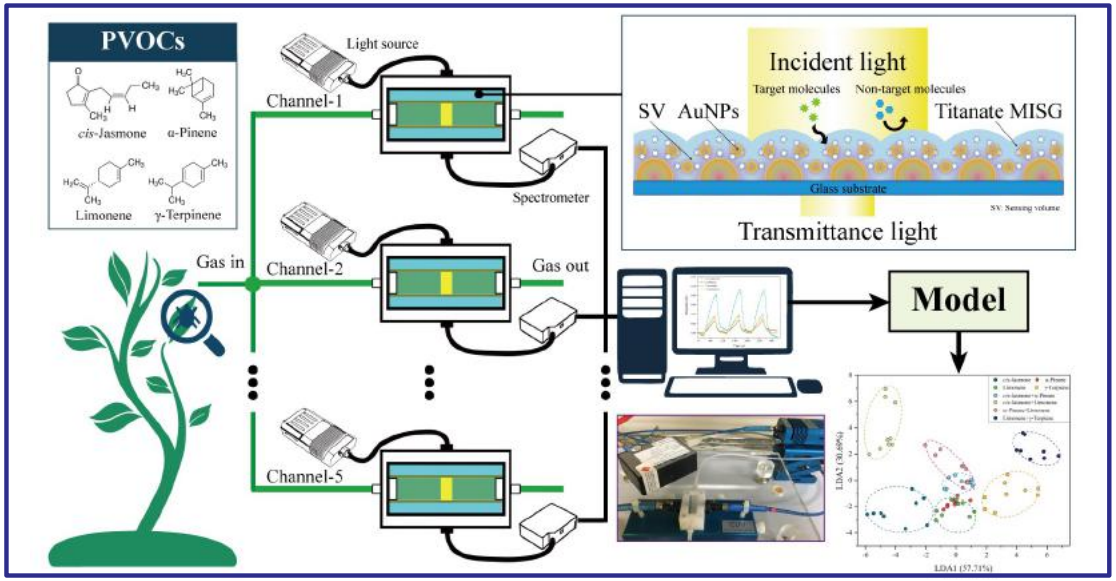
AuNPs layer

LSPR sensing layer

Detecting the change of the spectra

The target PVOC vapor would be selective detected.





Experiment

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MISG-AuNPs

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

60 ºC water bath, 1h

AuNPs solution

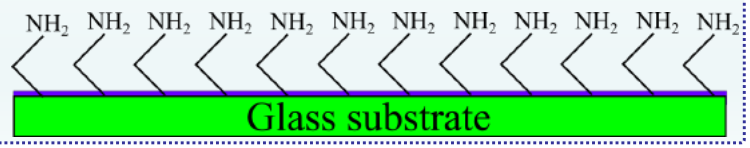
Stirring 4h

MISG-AuNPs film fabrication

Step 1 APTES modification

(3-Aminopropyl) triethoxysilane

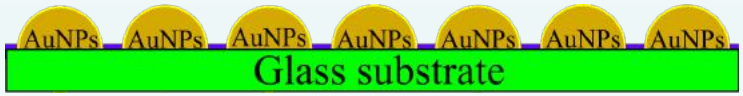
APTES ethanol solution (v:v = 1:10), 8 h



Step 2 Sputtered AuNPs and anneal

Sputtering AuNPs thinkness: 3nm

Anneal: 500 ºC, 2 h, 2 times, air

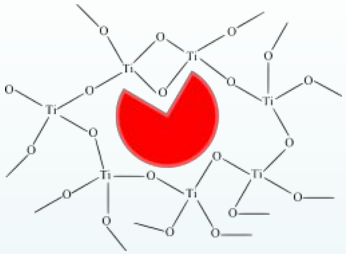


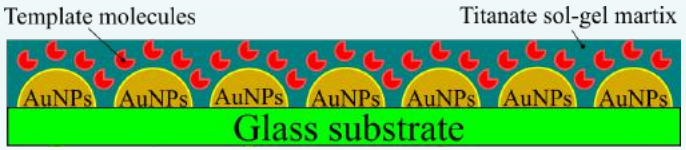
Step 3 MISG reaction solution spin coating

MISG solution: 20 μL

Spin coating speed:

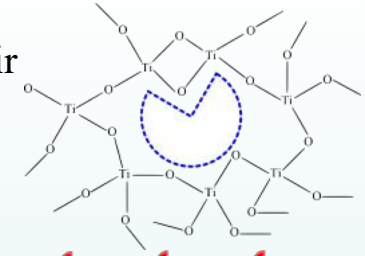
1000/3000/5000 rpm

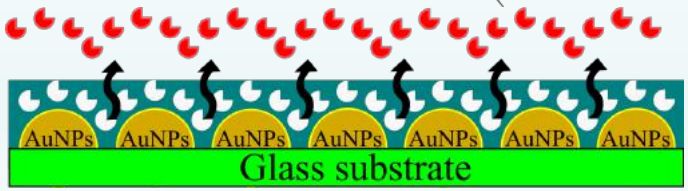




Step 4 Annealed for removing templates

Anneal: 130 ºC, 1h, air





Experiment

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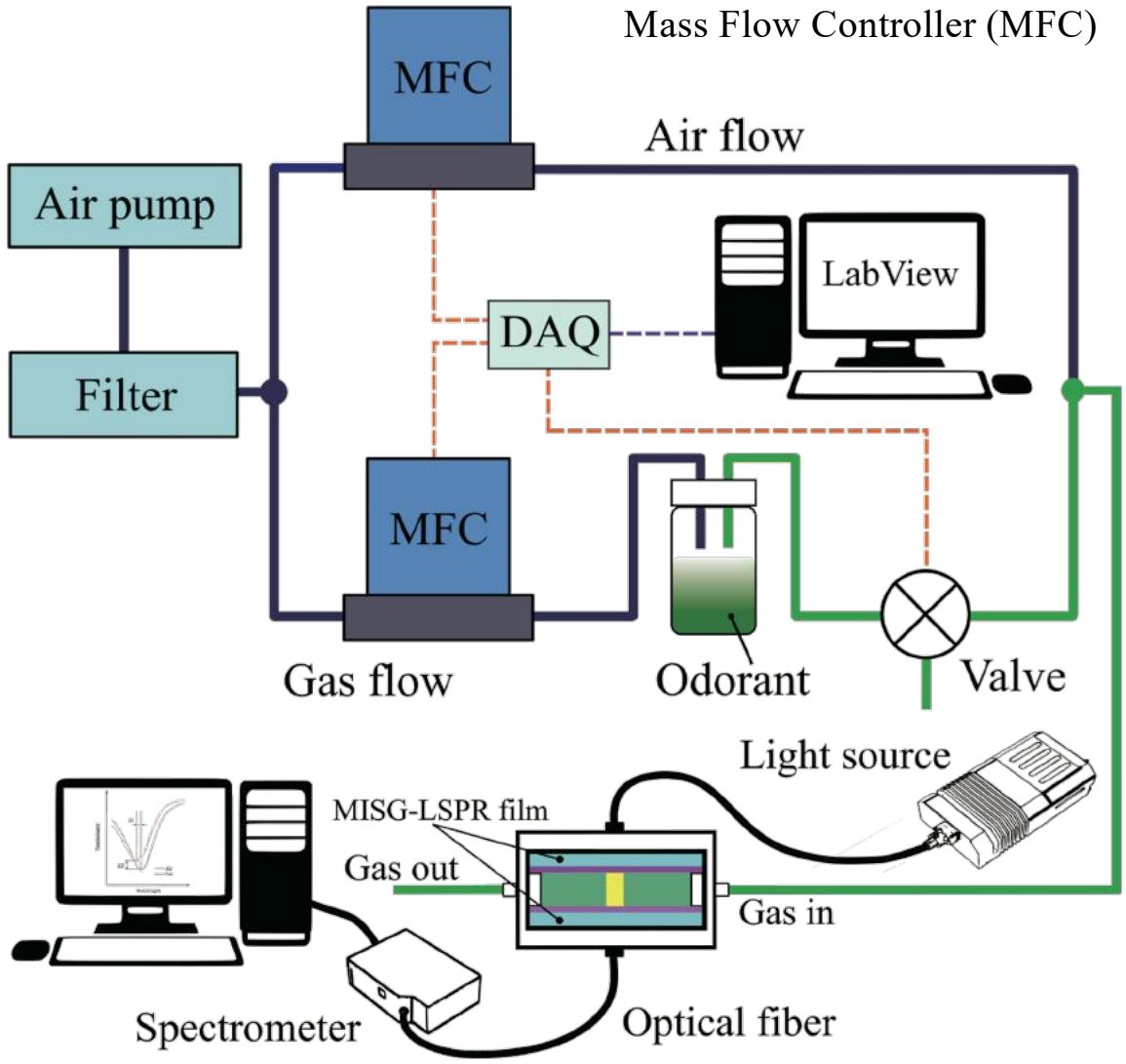
Vapor generation and LSPR spectra testing system



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

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

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

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

Results and discussion

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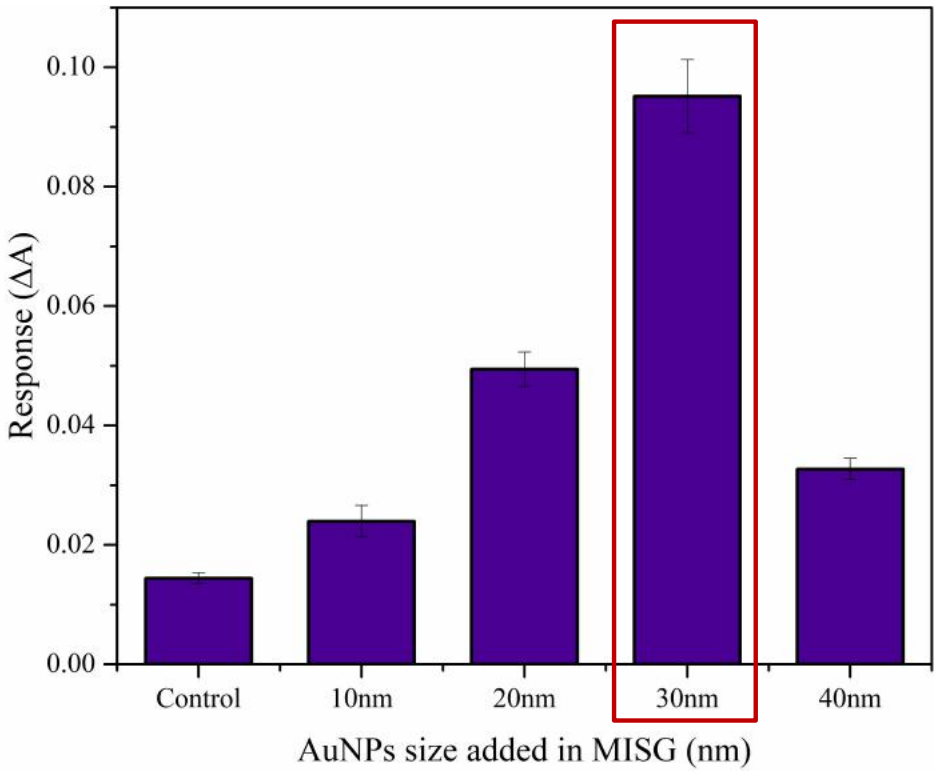
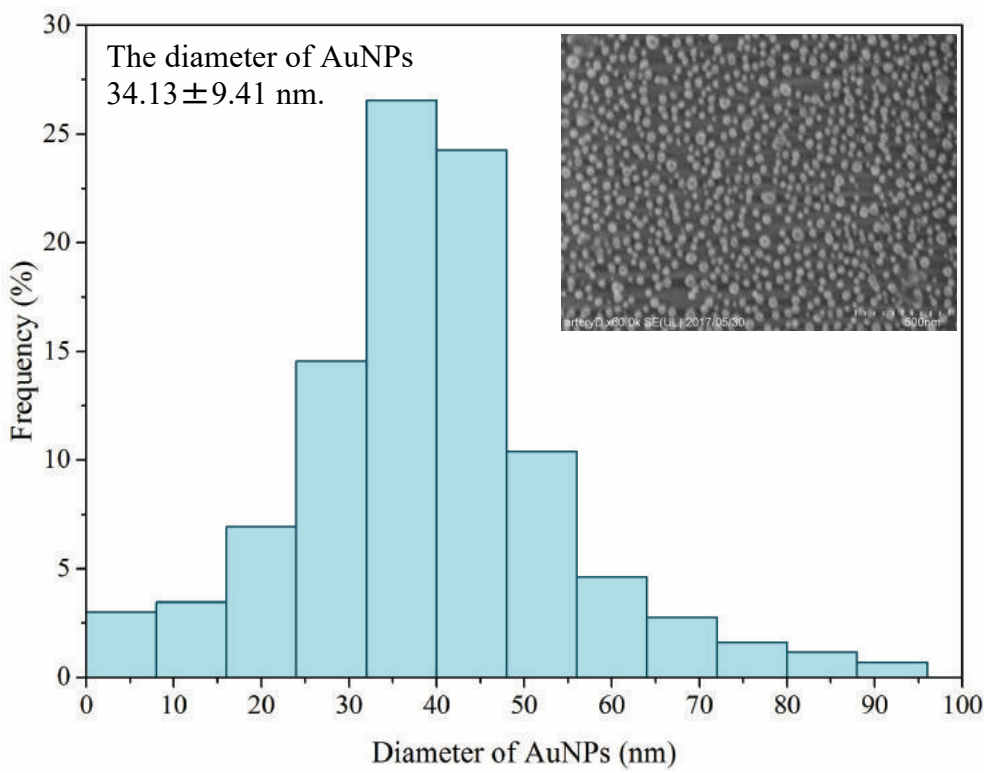


Response response effected by AuNPs size in MISGs.



Particle size distribution histogram of spherical AuNPs determined from bare sample.

- Response of AuNPs@MISG-coated with 30-nm AuNPs was **6.33 times** that without NPs.
- The diameter of the AuNPs on the substrate is close to that of the AuNPs in the MISG (30 nm).
- The high sensitivity of the sensor was contributed by **hot-spot coupling**.

Results and discussion

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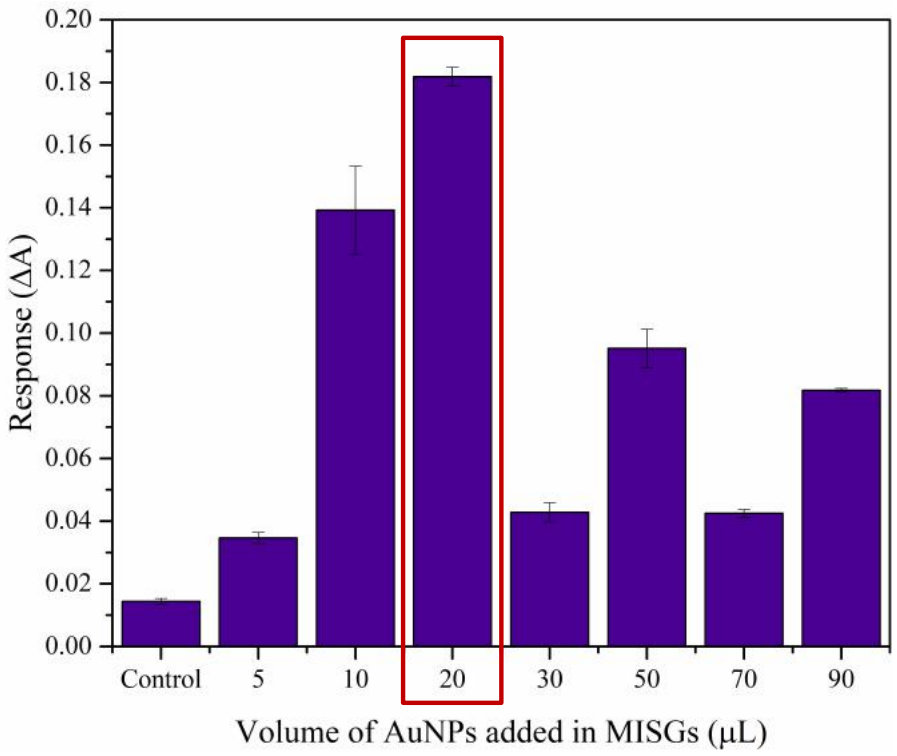
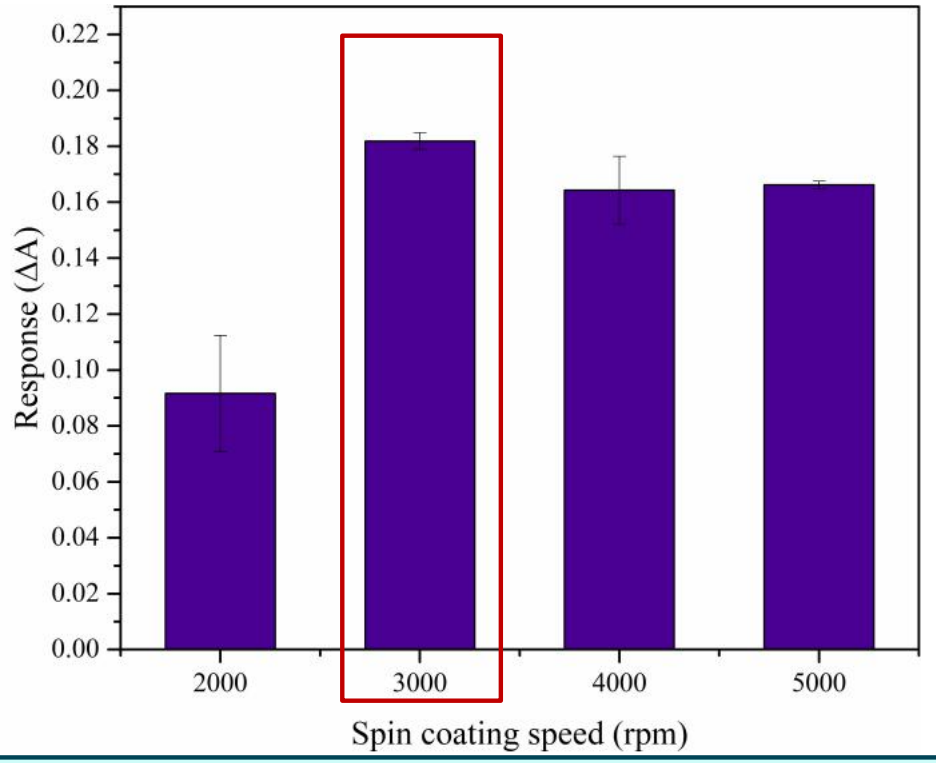


Response effected by AuNPs (30 nm) amount in MISGs.



Response effected by spin coating speed.

- Sensitivity of the sensors increased with the AuNP concentration firstly and then decreased.
- Sensor coated with the MISG containing 20 μL of 30-nm AuNPs had the highest sensitivity.
- The thickness of the sensing film influences the sensitivity of LSPR sensors.
- Optimal spin coating speed was selected as **3000 rpm** in the present study.

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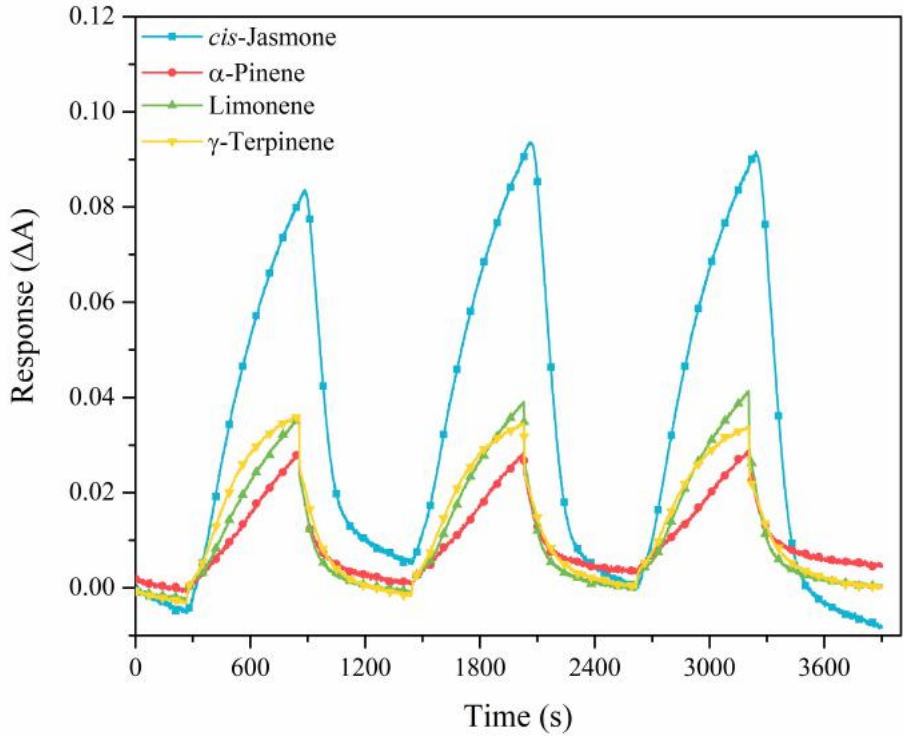
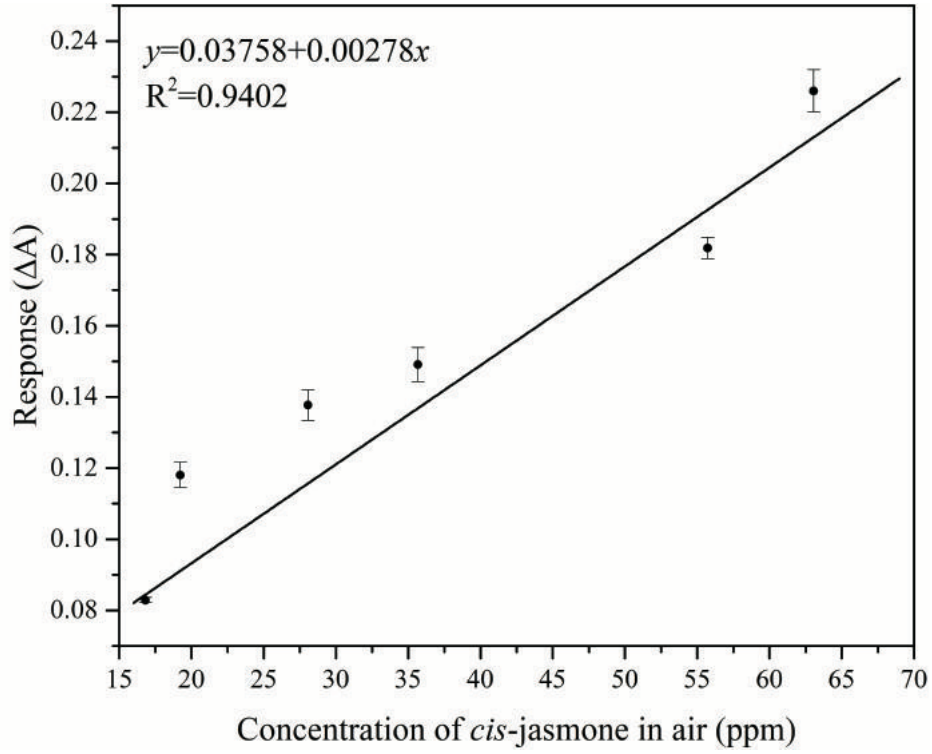


Real-time responses of AuNPs@MISG-modified Au-islands to 4 PVOCs.



Linear response vs. CJ concentration in air.

- Response to CJ was higher than interfering PVOCs (Interference immunity).
- The limited of detection (LOD) was calculated as 3.07 ppm (S/N=3).
- The developed sensor has sufficient interference immunity for use in agricultural applications.

Results and discussion

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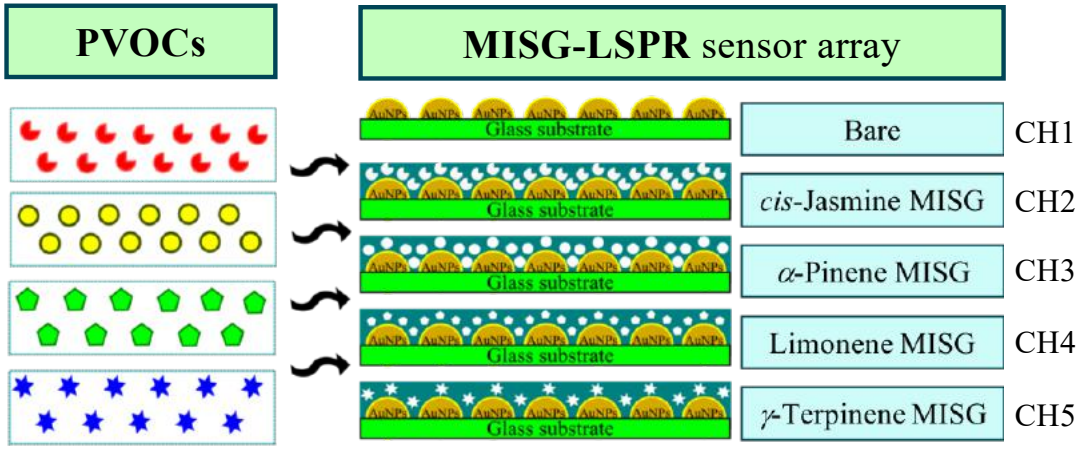
Sensor response matrix to PVOCs

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.
- 72 samples (8 PVOCs × 3 flow rates × 3 repeats) were obtained in this study.
- All responses were scaled for former processing.

Correlation matrix for channels

	CH1	CH2	CH3	CH4	CH5
CH1	1	0.06	-0.05	-0.17	-0.34
CH2	0.06	1	0.53	0.31	0.06
CH3	-0.05	0.53	1	0.59	0.1
CH4	-0.17	0.31	0.59	1	0.51
CH5	-0.34	0.06	0.1	0.51	1

- Low correlation between each channels.
- More information can be obtained in MISG sensor array.

Results and discussion

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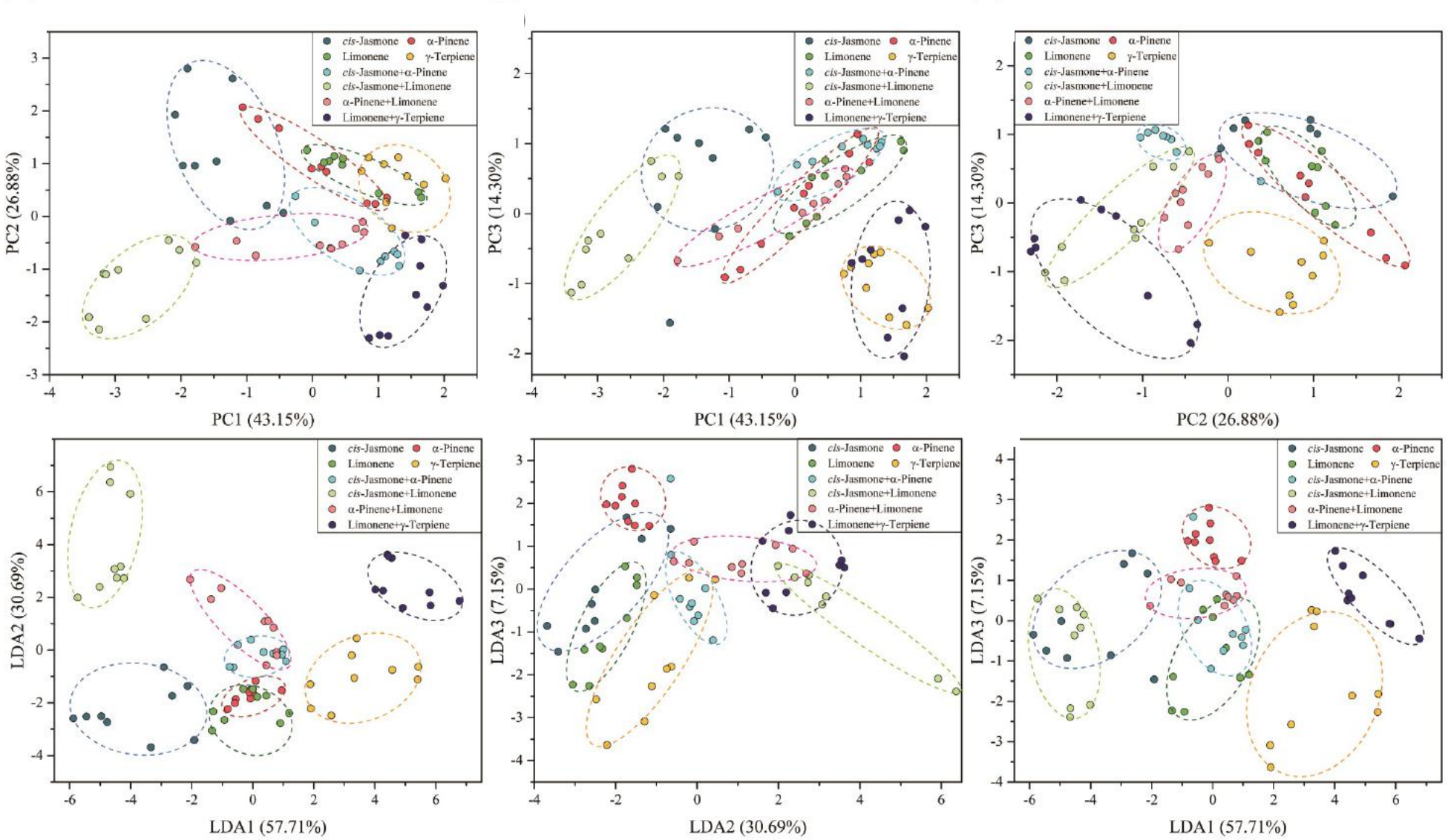

Mapping samples in PCA space and LDA space

Results and discussion

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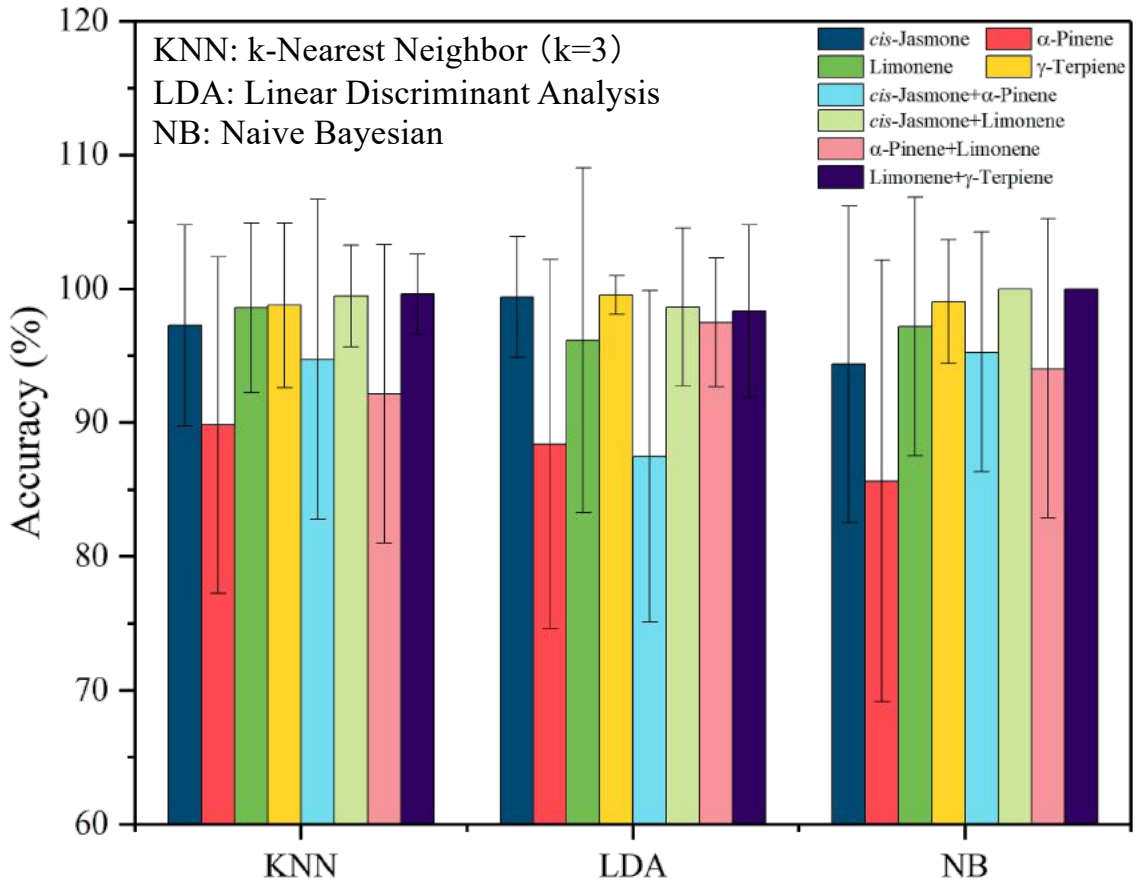
Models established by KNN, LDA, and NB.



- Data sets were divided by random selection method.
- Train set : test set = 7:3. Repeat 100 times.

Models evaluation

Model	Accuracy	SD.
KNN	96.76 %	9.36 %
LDA	95.67 %	11.06 %
NB	95.72 %	11.48 %

Discussion

- PVOCs from single or mixture can be recognized and classified.
- Low accuracy in detecting α-pinene.
- In summary, KNN shown the best result than other models.
- Better result would be obtained by more samples.

Conclusion

- An **LSPR sensor** coated with an **MISG containing AuNPs** to amplify the sensing signal was developed for PVOC detection.
- The sensitivity of the AuNPs@MISG-coated sensor was **12.33 times** higher than that of the sample without AuNPs.
- The real-time responses of the sensor displayed good **interference immunity and repeatability.**
- A five-channel AuNPs@MISG LSPR **sensor array** was designed to detect and identify **four plant VOCs alone and in binary mixtures**.
- KNN displayed high accuracy (96.03%), identifying plant VOCs quickly and efficiently.
- This study may become a useful technology for agricultural applications.

Thank you for your attention

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