LSPR sensor modified by molecularly imprinted sol-gel for selective organic acid vapor detection

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Introduction

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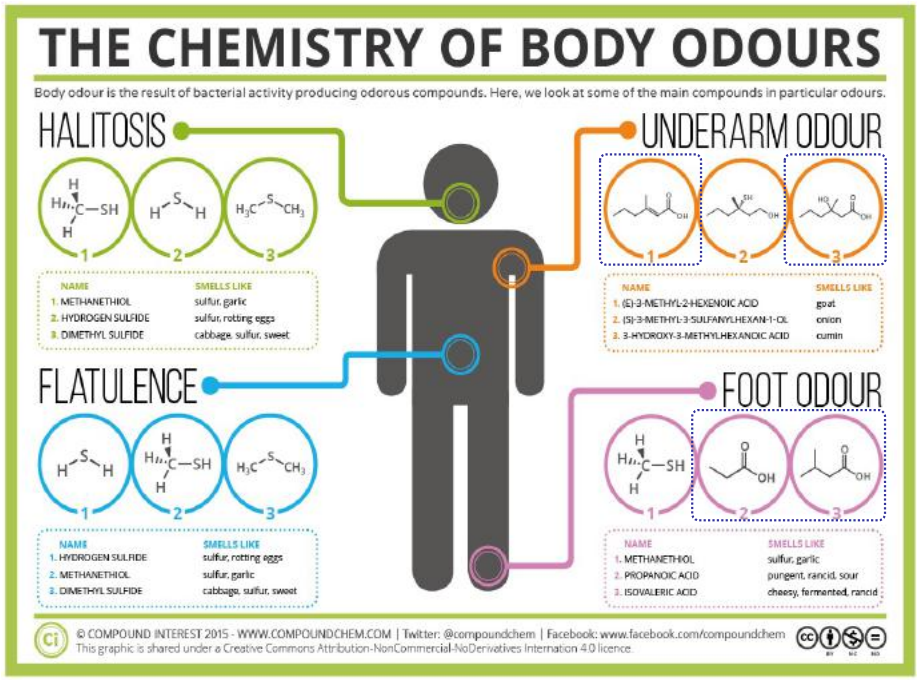
Body odor



Volatile organic compounds (VOCs)

- Fatty acids
- Alcohols
- Aldehydes
- Esters
- Ketones
- Amines

Application

Medical diagnosis

Physiological condition

Forensic

Body odor fingerprint

Introduction

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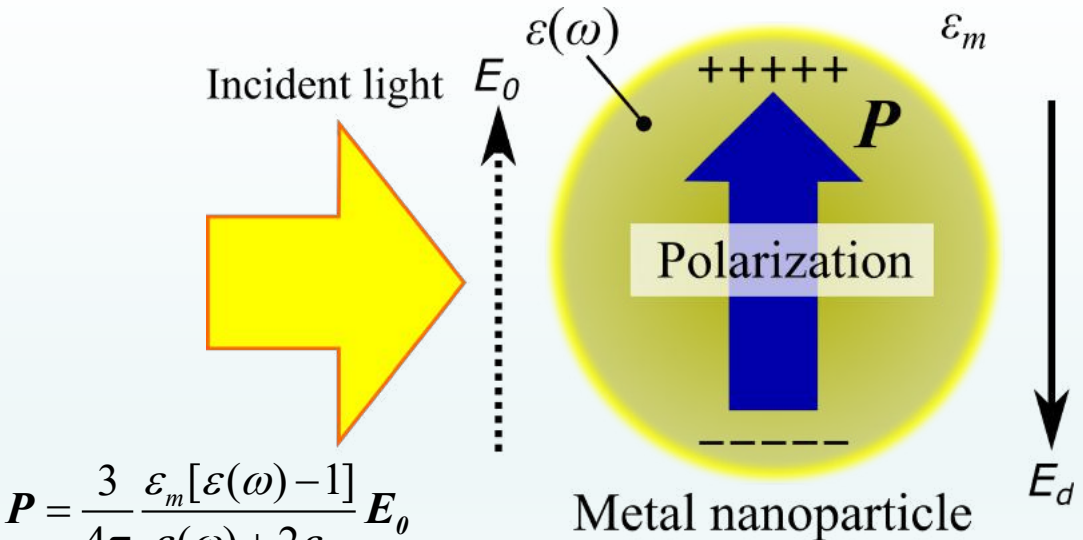
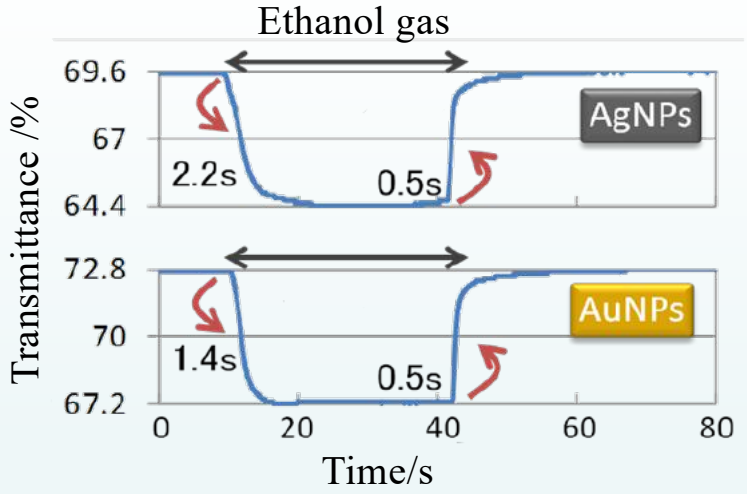
Localized surface plasmon resonance (LSPR)



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



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

Absorption spectra

Particle size, shape and composition

Surrounding media

Merit & drawback

Fast response/recovery speed

Non specificity

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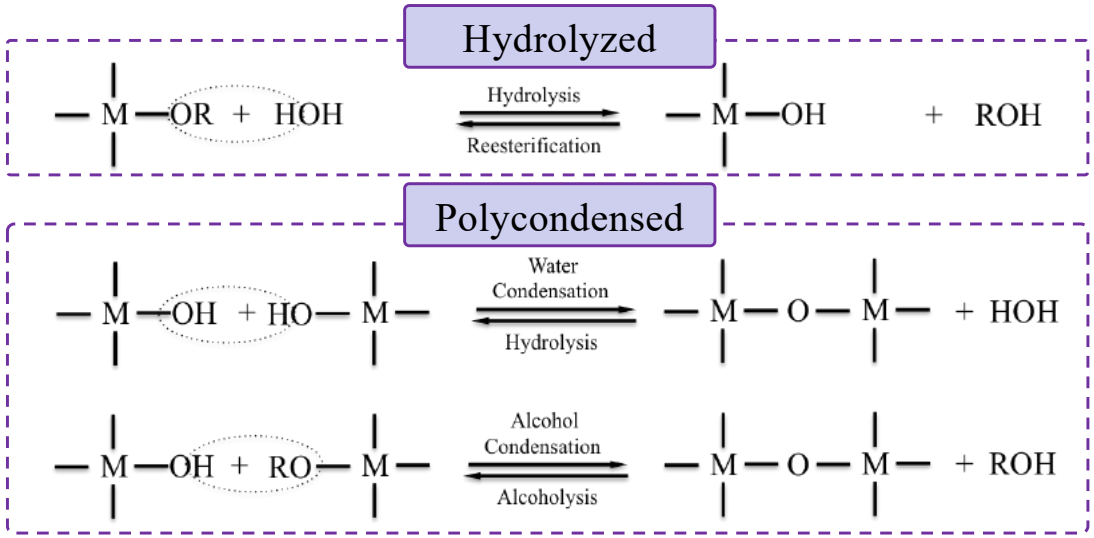
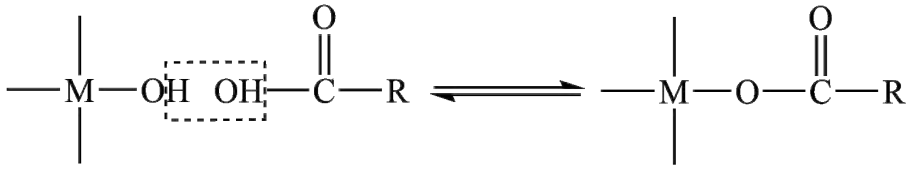
Molecularly Imprinted Sol-gel（MISG）

Reaction principle

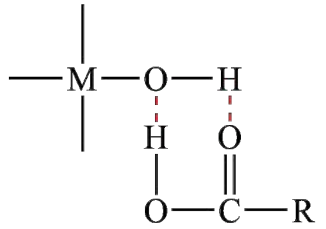


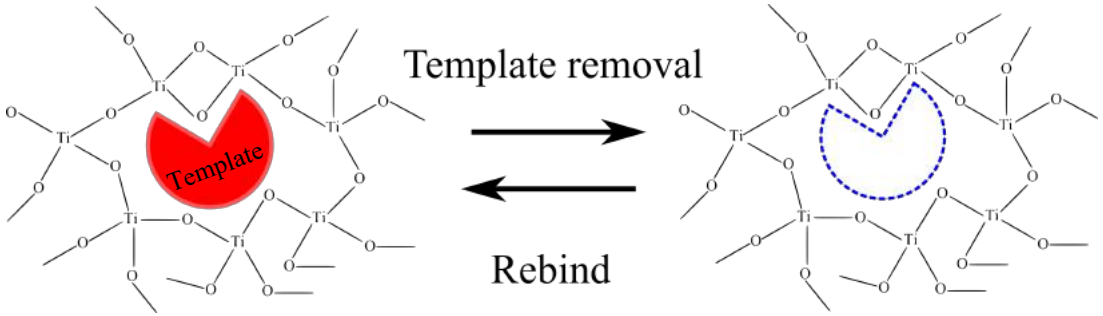
Imprinting method

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 array

MISG layer

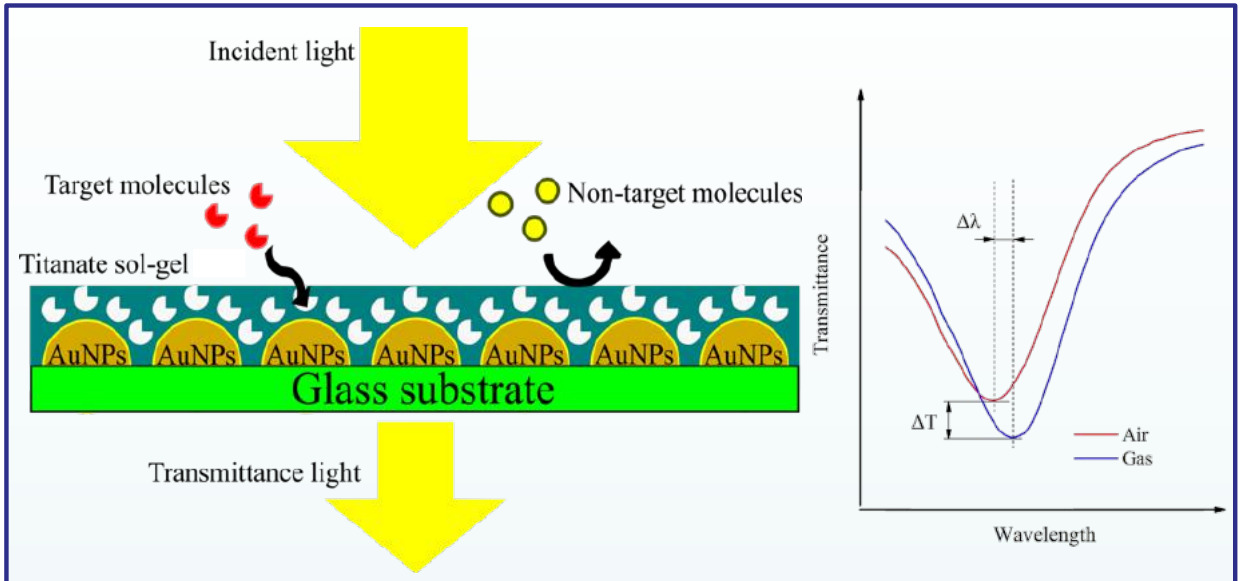
Selective adsorption layer

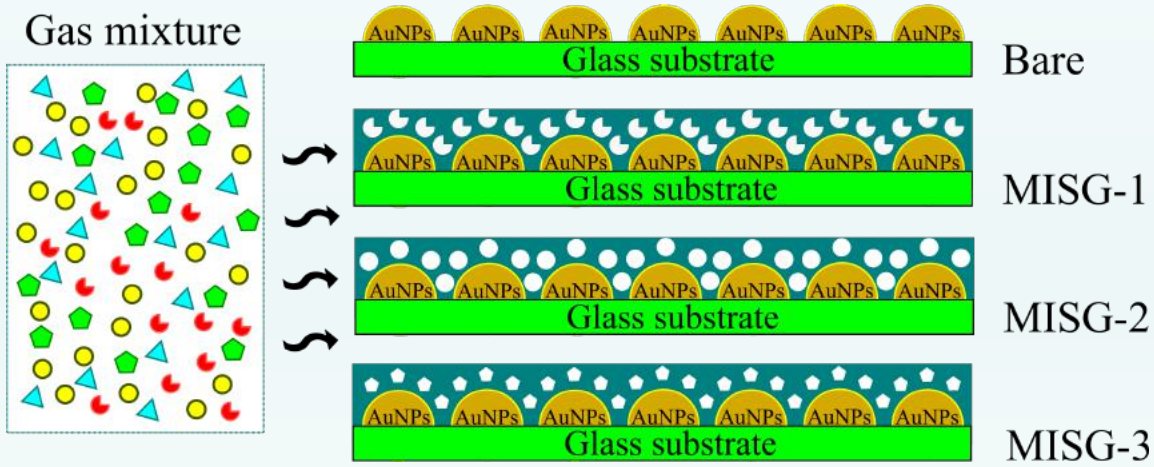
AuNPs layer

LSPR sensing layer

Detecting the change of transmittance light

The target fatty acid vapor would be selective detected.





Experiment

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MISG material

Iso-propanol	2 mL
$Ti(OBu)_4$	136 μL
APTES	24 μL
Template	50 μL
$TiCl_4$	25 μL

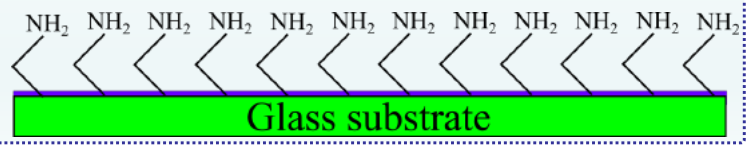
70 ºC water bath, 1h

MISG-AuNPs film fabrication

Step 1
APTES modification

(3-Aminopropyl) triethoxysilane

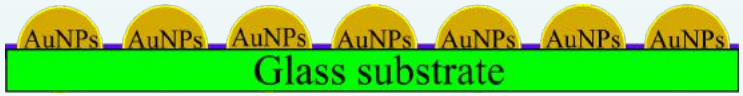
APTES ethanol solution (v:v = 1:10), 8 h



Step 2
Sputtered AuNPs and anneal

Sputtering AuNPs thinkness: 3nm

Anneal: 200 ºC, 5h, air

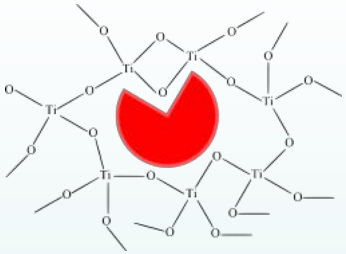


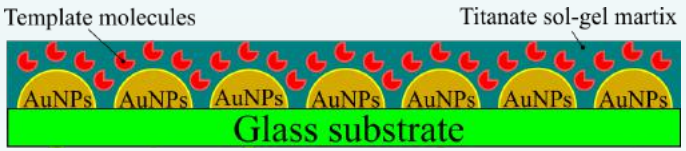
Step 3
MISG reaction solution spin coating

MISG solution: 20 μL

Spin coating speed:

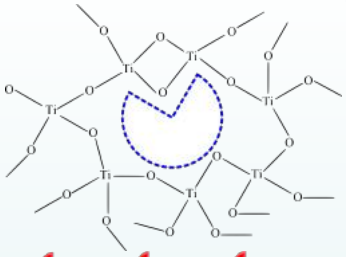
1000/3000/5000 rpm

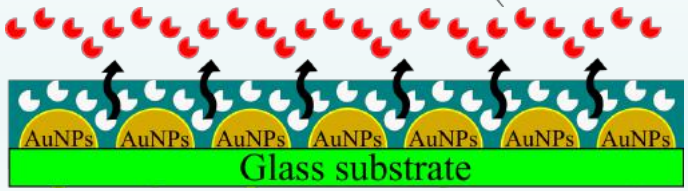




Step 4
Annealed for removing templates

Anneal: 200 ºC, 1h, air





Experiment

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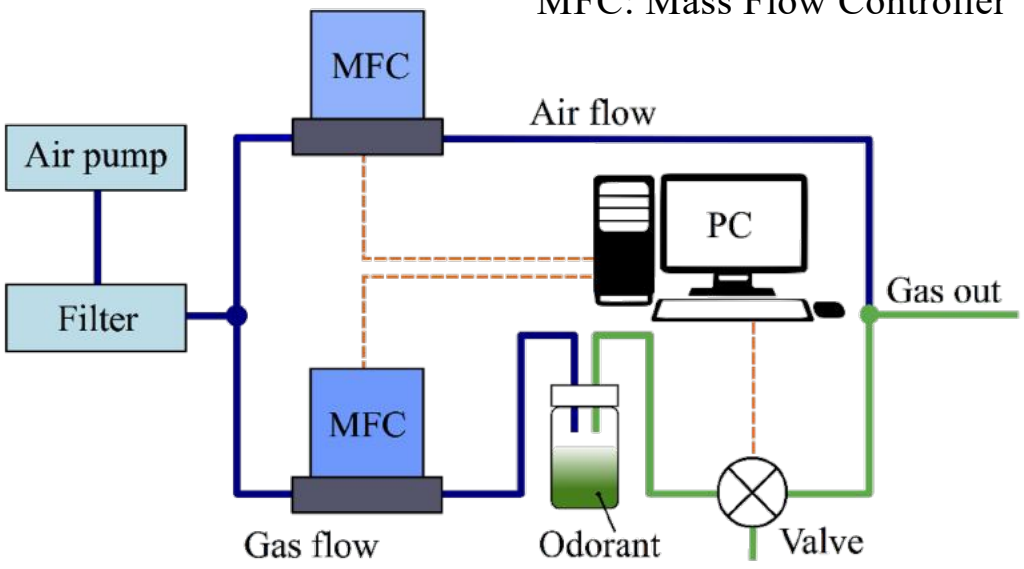
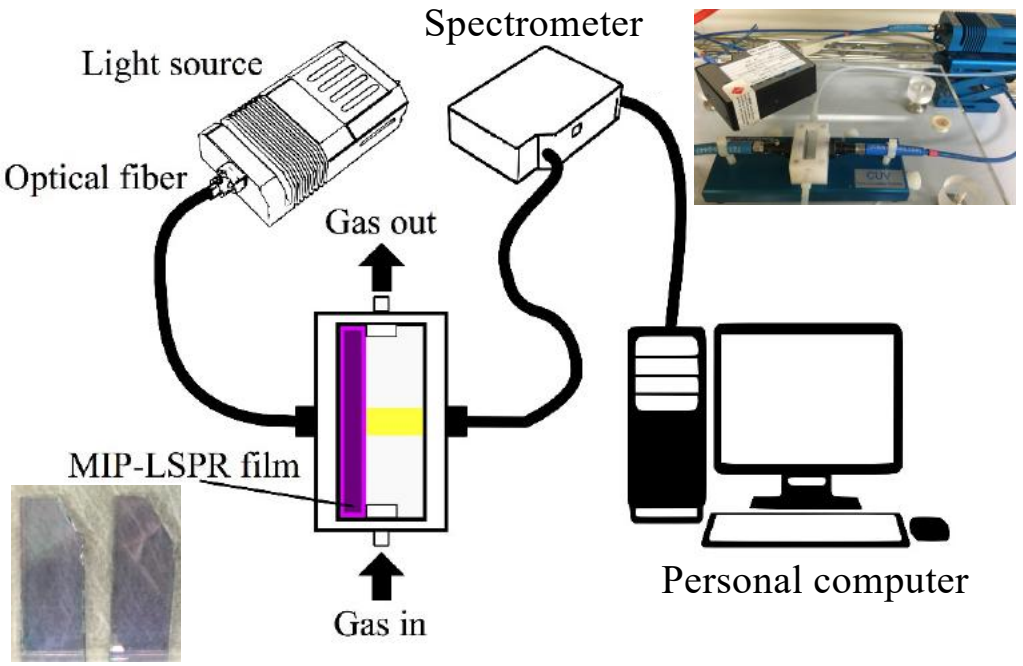
Testing system



Gas generate system



Transmittance spectra testing system

$$k = \frac{22.4\times(273+t)\times760}{M\times273\times P}$$

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

$$C = \frac{k\times D_r\times10^3}{F}$$

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

Results and discussion

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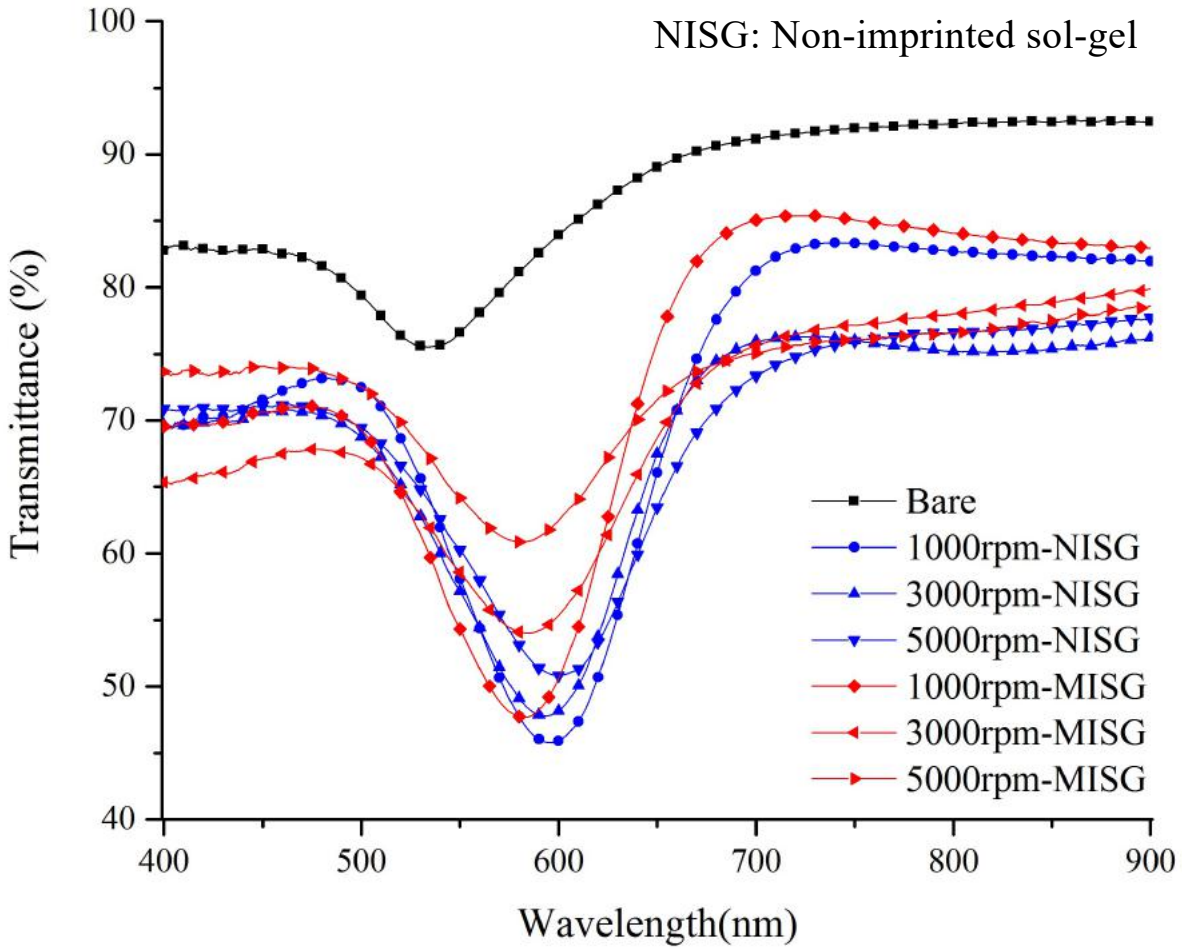
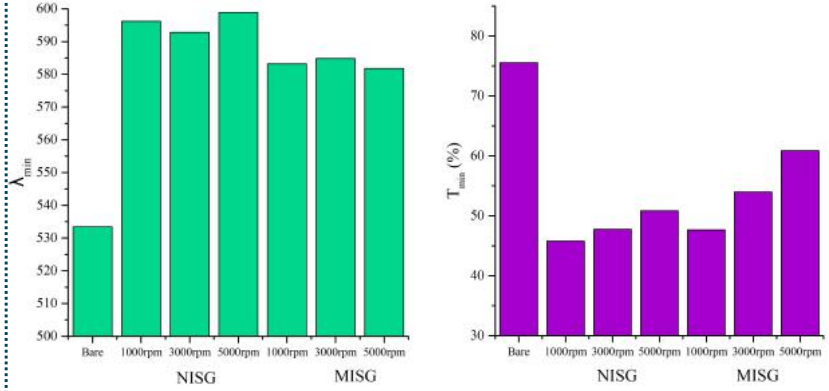
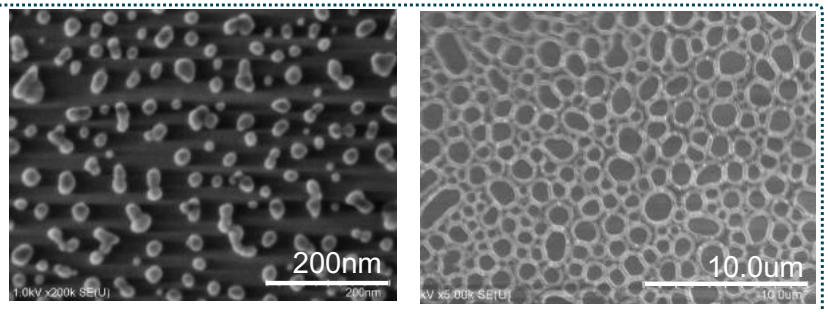
■ Transmittance spectra of MISG-LSPR sensors.



Spectra parameters



SEM image



Bare sample　　MISG coated sample

The changes of transmittance spectra are affected by their different surface features.

Results and discussion

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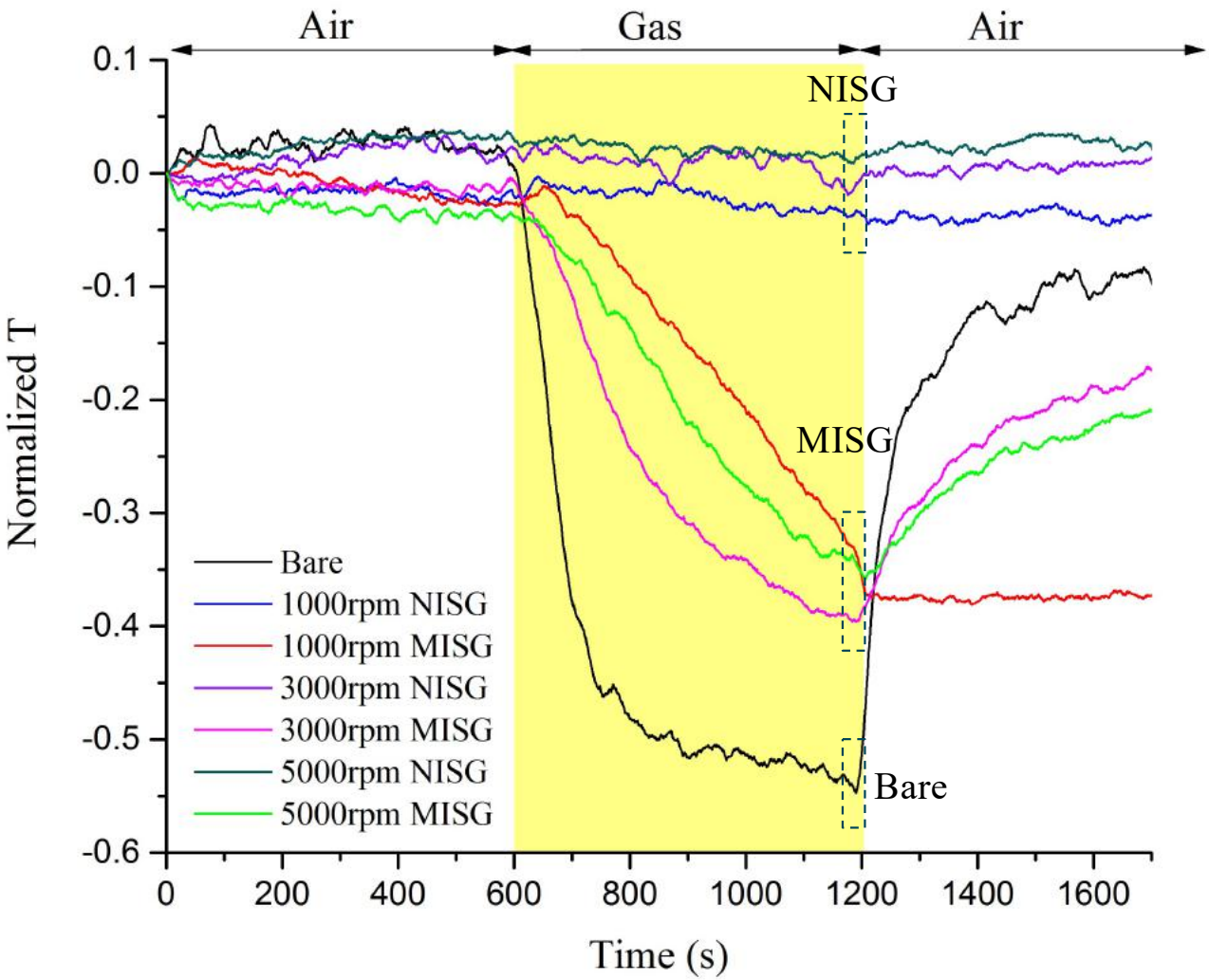
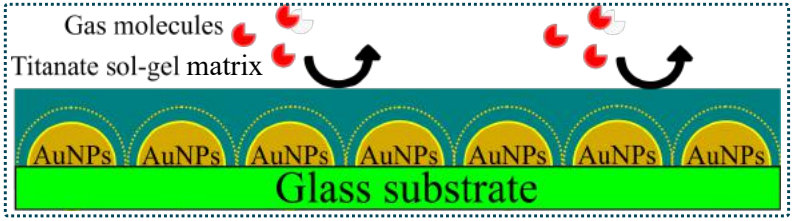
- **Real-time response of HA-MISG and NISG with different coating speeds to HA vapors (Transmittance at λ_{min})**



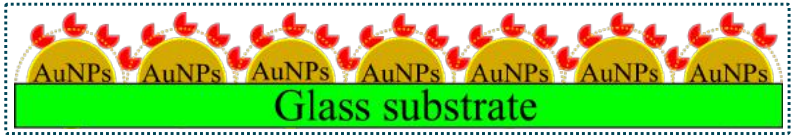
$$Normalized\ T = T_{air} - T_{gas}$$

$R_{bare} > R_{MISG} > R_{NISG}$

NISG coated sample



Bare sample



MISG coated sample

Results and discussion

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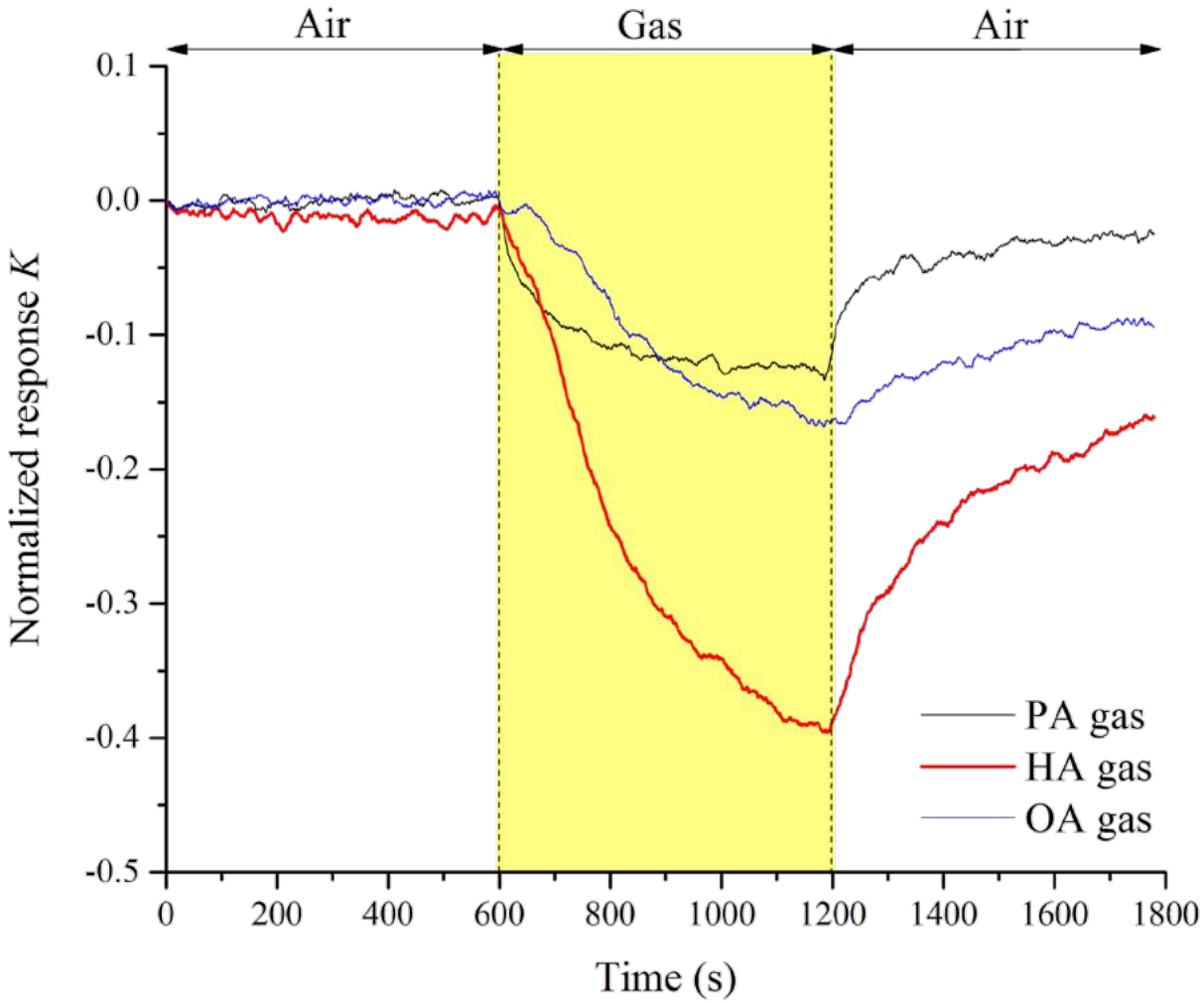
- **Real-time response of HA-MISG-LSPR sensor to three fatty acid vapors (PA/HA/OA)**



HA-MISG-LSPR sensor

Template molecule: HA

Spin coating speed: 3000 rpm

PA: Propanoic acid (40.93 ppm)

HA: Hexanoic acid (21.05 ppm)

OA: Octanoic acid (11.23 ppm)

$K = Normalized\ T/C_{gas}$

A specific selectivity to HA vapors was obtained

Results and discussion

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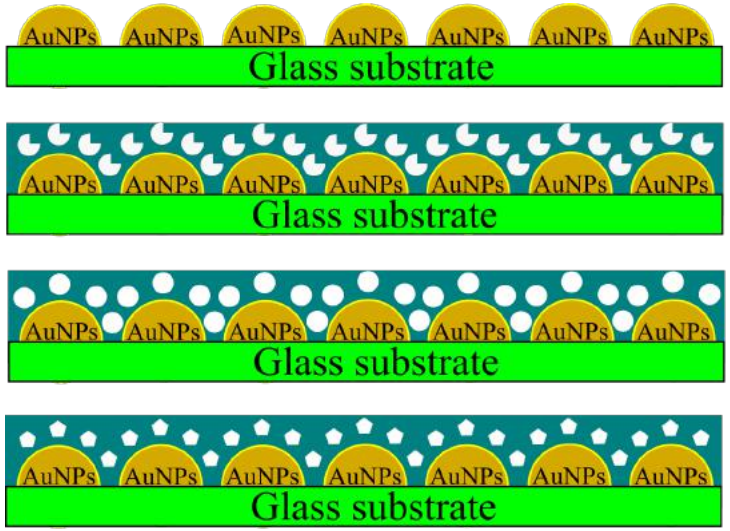
■ MISG-LSPR sensor array for fatty acid vapors discrimination.

Changing the templates in MISG solution

Different types of MISG solution

MISG-LSPR sensor array

1. Bare
2. HA-MISG
3. HPA-MISG
4. OA-MISG



Fatty acid vapors

Propanoic acid (PA)

Hexanoic acid (HA)

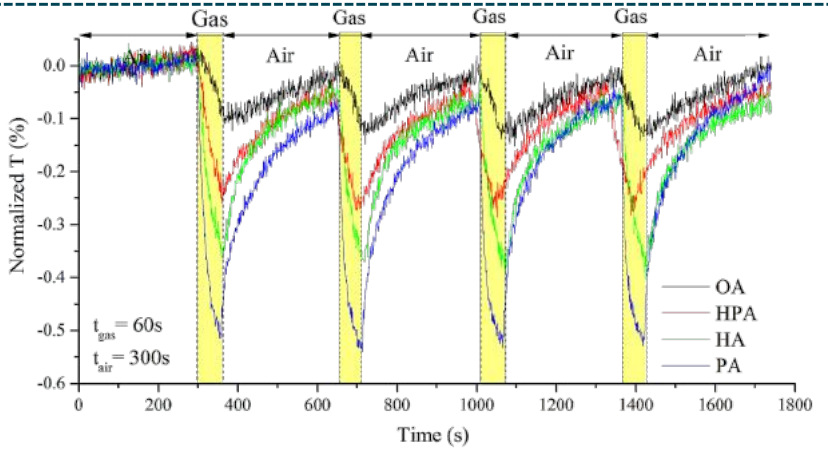
Heptanoic acid (HPA)

Octanoic acid (OA)

Propanoic acid + Hexanoic acid (PA+HA, v:v = 1:1)

Propanoic acid + Octanoic acid (PA+OA, v:v = 1:1)

Hexanoic acid + Octanoic acid (HA+OA, v:v = 1:1)



Typical response of HA-MISG sensor to fatty acid vapors.

Results and discussion

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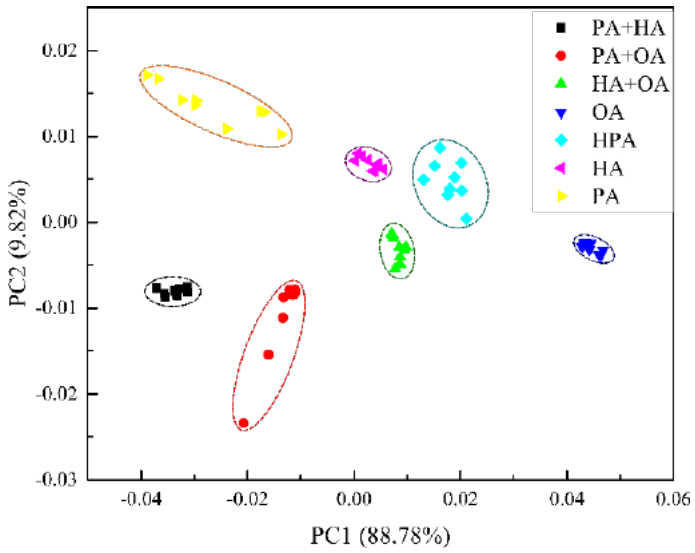
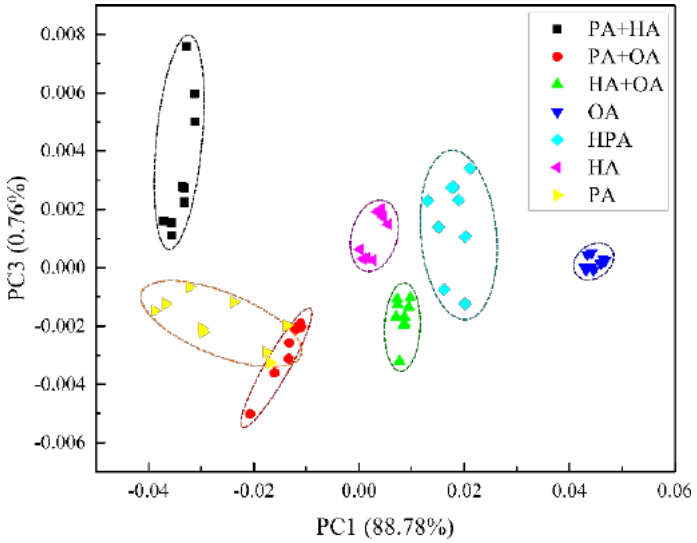
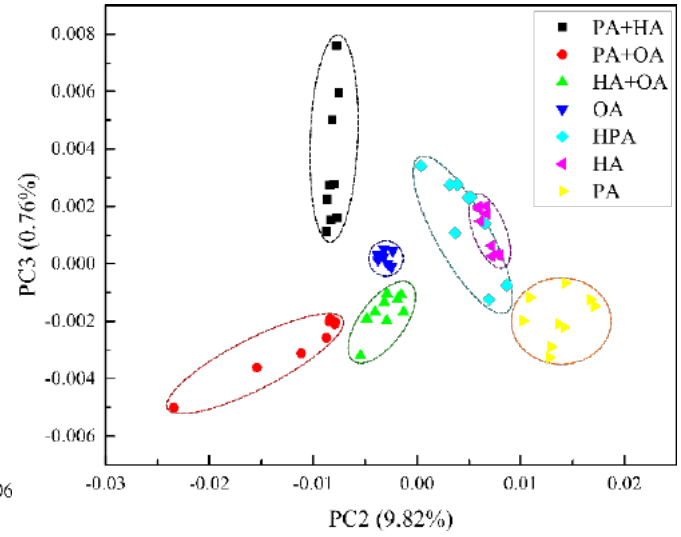
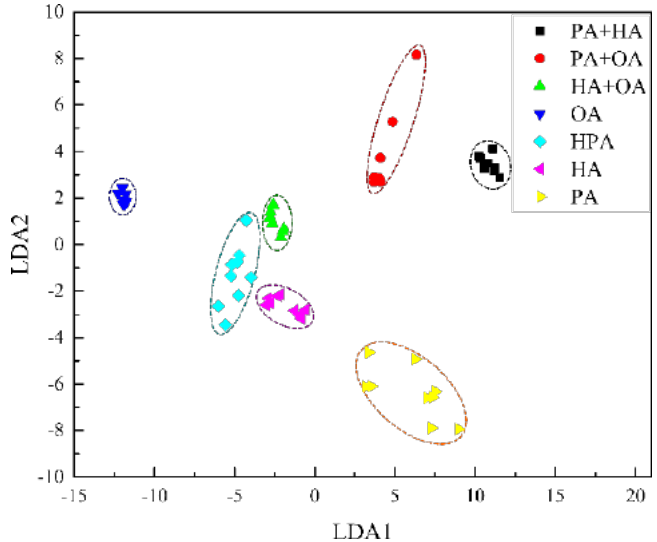
- **PCA and linear discriminant analysis (LDA) results for diverse fatty acid vapors**









- PC1-PC2 space, all the samples were clustered in their groups.
- PC1-PC3 and PC2-PC3 space, an overlapped was observed.
- In LDA space, an acceptable discriminated results was observed.
- MISG-LSPR sensor array would be applied in fatty acid vapors discrimination.

Conclusion

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- An **AuNPs** film combined with **MISG** was utilized for the determination of **fatty acid** vapors **selectively**.
- The **adsorption capacity** of pure titanate sol-gel matrix is **weak.**
- By controlling the **spin coating speed**, the **adsorption ability** of MISG would be controlled.
- Based on the **MISG-LSPR sensor array**, fatty acid vapors would be **detected** and **discriminated**.

Thank you for your attention

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