

Terpene Gas Detection Device Based on Localized Surface Plasmon Resonance Phenomenon of Au Nanoparticles

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**Terpene Gas Detection Device Based on Localized Surface
Plasmon Resonance Phenomenon of Au Nanoparticles**

金ナノ粒子の局在プラズモン共鳴現象を用いた
テルペンガス検知デバイスに関する研究

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Contents

Chapter 1 Introduction	1
1.1 Necessity of gas detection	1
1.2 Terpene detection	2
1.3 Gas detection methods	3
1.3.1 Instrumental gas analysis methods	3
1.3.2 Commonly used gas sensor.....	5
1.4 Localized Surface Plasmon Resonance Sensors of Noble Metal Nanoparticles	12
1.4.1 LSPR introduction and principle.....	12
1.4.2 LSPR based sensors.....	17
1.5 Aim and results in this research	19
1.6 Thesis outline	20
Reference	22
Chapter 2 Sputtered Au nano-islands on glass for fast speed vapor detection	27
2.1 Introduction	27
2.2 Experimental	29
2.2.1 Au and Ag NPs fabrication	29
2.2.4 Vapor generation device.....	30
2.2.5 Fabrication of LSPR sensor device	31
2.3 Results and discussion	32
2.3.1 Optical properties of sputtered AuNPs	32
2.3.2 Morphology characteristics of sputtered NPs.....	33
2.3.3 Influence of thermal annealing treatment on NP's morphology.....	34
2.3.4 LSPR response of Au and Ag NPs	36
2.3.5 The real-time response characters of AuNPs films	39
2.3.6 Response time of LSPR sensing device.....	40
2.4 Conclusion	41
Reference	41
Chapter 3 Layer-by-layer Structured AuNPs Sensors for Terpene Vapors Detection	46

3.1 Introduction	46
3.2 Experimental	47
3.2.1 Preparation of Aqueous Au colloidal solution	47
3.2.2 Fabrication of layer-by-layer structured AuNPs films	48
3.3 Results and discussion	49
3.3.1 UV-vis spectra of layer-by-layer structured AuNPs film	49
3.3.2 UV-vis spectra of dithiol linked AuNPs in solution	55
3.3.3 The refractive index sensitivity of AuNPs multilayer sensors	57
3.3.4 The LSPR response of AuNPs multilayer sensors	59
3.4 Conclusion	60
Reference	61
Chapter 4 Terpene Detection Based on Localized Surface Plasma Resonance of Thiolate Modified Au nano-islands	65
4.1 Introduction	65
4.2 Experimental	66
4.2.1 Thiolate Au nano-islands surface modification	66
4.2.2 Terpene vapors generation	66
4.3 Results and discussion	67
4.3.1 Optical and morphological characters of sputtered AuNPs on glass	67
4.3.2 LSPR spectrum response	70
4.3.3 Thiolate-modified AuNPs for terpene detection	73
4.3.4 Response mechanism discussion	75
4.4 Conclusion	77
Reference	77
Chapter 5 Terpene Vapor Detection Using Molecularly Imprinted Polymer Coated Au Nanoparticle Sensor	81
5.1 Background information of MIP and MIP in sensors	81
5.2 MIP coated AuNPs sensor design	82
5.3 Experimental	85
5.3.1 MIP Powder Fabrication	85
5.3.2 MIP Film Fabrication	85

5.3.3 MIP-coated AuNP Film Fabrication.....	85
5.3.4 GC-MS Analysis	86
5.3.5 AFM and SEM Images	87
5.4 Results and discussion.....	88
5.4.1 The selectivity of MIP powder to the template molecules.....	88
5.4.2 The selectivity of MIP films to the template molecules.....	89
5.4.3 Dependence between polymer thickness and spin coating speed	92
5.4.4 Optical characteristics of polymer-coated AuNPs film	93
5.4.5 The refractive index sensitivity of polymer-coated AuNP sensor	94
5.4.6 The LSPR response of polymer-coated AuNP sensors.....	96
5.5 Conclusion.....	97
Reference.....	98
Chapter 6 Conclusion.....	102
6.1 Conclusion.....	102
6.2 Prospect.....	104
Reference.....	105
Appendix.....	107
Acknowledgement.....	127

Figures list

Chapter 1

Fig. 1.1 GC/MS analysis	4
Fig. 1.2 Infrared gas detector	5
Fig. 1.3 Typical structure of a conductivity sensor.....	6
Fig. 1.4 The schematic graph of the metal oxide sensor	8
Fig. 1.5 SAW sensor	9
Fig. 1.6 Quartz crystal microbalance with polymer coating.....	10
Fig. 1.7 PID sensor.....	12
Fig. 1.8 The sketch of a homogeneous sphere placed into an electrostatic field.....	15
Fig. 1.9 The schematic sensing diagram of AuNP LSPR film.....	17
Fig. 1.10 A flow chart about this work	20

Chapter 2

Fig. 2.1 The schematic graph of the electric field coupling between two special NPs	28
Fig. 2.2 The schematic vapor generation device	31
Fig. 2.3 Diagram of LSPR-VOC sensing device	32
Fig. 2.4 UV-vis spectra of sputtered Au and Ag NPs	33
Fig. 2.5 SEM images of Au NPs with different sputtering condition	34
Fig. 2.6 AFM images of AuNPs before and after 200 °C 20 h annealing treatment	36
Fig. 2.7 AFM images of AuNPs the same sputtering condition but different annealing time	36
Fig. 2.8 LSPR response of Au and Ag NPs on glass	38
Fig. 2.9 Spectra of Au and Ag NPs in air versus annealing time	38
Fig. 2.10 LSPR response ($\Delta\lambda_{\min}$ and $\Delta T_{\min}$) of Au and AgNPs versus annealing time	39
Fig. 2.11 Real-time response signal of NPs films	40
Fig. 2.12 Real-time response signal of LSPR sensing device	41

Chapter 3

Fig. 4.1 Chemical structures of thiolate and terpenes used in this study	66
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Fig. 4.2 The LSPR spectra of AuNPs prepared with different sputtering condition	68
Fig. 4.3 AFM images of AuNPs	70
Fig. 4.4 LSPR spectra of AuNPs in air and ethanol gas	71
Fig. 4.5 The normalized local refractive index sensitivity of thiol modified AuNPs to terpenes	74
Fig. 4.6 Real-time response signal of AuNPs LSPR–VOC sensor	75
Fig. 4.7 The schematic sensing mechanism of thiolate modified AuNPs	77

Chapter 4

Fig. 3.1 The sensing scheme and molecular structures of dithiol in this research ...	49
Fig. 3.2 UV/vis spectra of AuNPs multilayers (diameter: about 10 nm) linked with (a) 1,4-benzenedithiol and (b) 1,10-decanedithiol	50
Fig. 3.3 The UV-vis spectra of AuNPs multilayer structures (a) AuNPs multilayers cross-linked by DDT, (b) BDT	51
Fig. 3.4 AFM images of APTES modified glass substrate	53
Fig. 3.5 SEM image of Au NPs multilayer cross-linked by 1,10-decanedithiol with 10 depositions	53
Fig. 3.6 The schematic diagram of Au NPs films	55
Fig. 3.7 The UV-vis spectra of AuNPs solution adding dithiol	56
Fig. 3.8 The refractive index sensitivity (RIS) of Au NPs multilayer sensors: (a) cross-linked by DDT, (b) cross-linked by BDT	58
Fig. 3.9 Real-time response signal of AuNPs multilayer sensor to terpene the real-time response signal of AuNPs multilayer sensors to (a) α -pinene, (b) myrcene, (c) β -caryophyllene	60

Chapter 5

Fig. 5.1 The schematic graph of MIP-coated AuNPs film for α -pinene detection .	84
Fig. 5.2 The schematic diagram of mixed terpene vapors absorption by polymer powder and GC/MS measurement	87
Fig. 5.3 The selectivity coefficient (S_i) of α -pinene imprinted polymer powder to α -pinene, limonene, and γ -terpinene	89
Fig. 5.4 Template molecular absorption amount of MIP film normalized by that of NIP (H_n) versus the the molar ratio of template to monomer (the data shown in	

the graph is the average values of two times detection of three samples)	91
Fig. 5.5 The selectivity coefficient (S_i) of α -pinene imprinted polymer films to terpenes : α -pinene, limonene, and γ -terpinene (the molar ratio of template to monomer is 1:4, the data shown in the graph is the average values of two times detection of three samples)	91
Fig. 5.6 The dependence of NIP thickness on the spin coating speed on Au substrate (the data shown in the graph is the average values of three times detection of two samples at each spin coating speed)	92
Fig. 5.7 AFM images of bare AuNPs (A) and NIP coated AuNPs on glass at spin coating speed of 600 rpm (B)	93
Fig. 5.8 Dependence of the optical features ($\lambda_{\min}$ and $T_{\min}$) of NIP-coated AuNP sensors on the spin coating speed	94
Fig. 5.9 The dependence of RIS ($\Delta\lambda_{\min}$ and $\Delta T_{\min}$) of MIP and NIP coated AuNP sensor on the spin coating speed for α -pinene vapor detection (The red solid triangle and square represent MIP, while the blue solid triangle and square represent NIP. T represents transmittance)	95
Fig. 5.10 The selectivity of MIP-coated AuNP sensor.....	96
Fig. 5.11 The real-time response of MIP coated AuNPs sensor	97

Chapter 6

Fig. 6.1 LSPR gas sensing system	104
Fig. 6.2 Gas molecules visualization based on AuNPs-MIP sensing system.....	105

Tables list

Tab. 4.1 The local refractive index sensitivity of ethanol gas	72
Tab. 4.2 The normalized local refractive index sensitivity of naked AuNPs to terpenes	73
Tab. 1 Average value of morphological parameters of Au islands deposited on glass substrate processed under various conditions, parameters in the table were calculated using Image j.....	114

Chapter 1 Introduction

1.1 Necessity of gas detection

Gas sensing technologies have been widely used in various fields of daily life, such as environment, industry, and medical treatment. The application of various gas sensors and networks in environmental has been become one of the most major applications. The recent emergence of concern over environmental pollution and efficiency in a variety of combustion processes and of increased awareness over a need to monitor potentially hazardous gases has stimulated substantial research and development in the field of gas sensors¹. These gases include, CO, CO₂, NO_x (x = 0.5, 1, and 2), SO_x (x = 2 and 3), a fraction of unburned hydrocarbons [including liquefied petroleum gas (LPG) also known as cooking or town gas] and hydrogen. LP gas can form explosive mixture with ambient air and can lead to personal injury upon continuous exposure, even in small concentrations². The accidental escape or leak of either CO or H₂ from industrial factories with a high temperature and pressure system can be a source of explosion and health hazard. Nitrogen oxides, NO and NO₂ are the most common and dangerous pollutants of the atmosphere. Together with the oxides of sulfur, these compounds contribute to the formation of acid rain, which exerts very harmful environmental effects. Photolytic decomposition of NO₂ by cosmic radiations results in ozone formation, which when combined with hydrocarbons, forms smog. The ultimate accumulation of carbon dioxide by fuel burning under "lean" conditions in combustion furnaces and in automobile engines, has been anticipated as the main reason for "global warming" and "greenhouse effects"³. In view of these facts, monitoring the progress and control of combustion processes and from the viewpoints of anthropogeneous, industrial, and automobile exhaust pollution control, reliable and long-life sensors capable of detecting and measuring gases in the ambient and at the generating source are needed.

With the increase of world population, the demand for food has been growing fast. As a result, we have to grow more food on the same or less and less arable land. Increase the field production and reduce pests and diseases are the most effective means to achieve this purpose. The real-time field conditions supervision is a thorny issue, and

many advanced technologies, especial sensors and sensor network have been attempting to develop. Gas sensors are more applicable than the other sensors in agriculture due to the complex environmental factors in agriculture. In this research, our target gas is terpene. Plants synthesize and emit a large amount of volatile organic compounds (VOCs) during their normal growth process as metabolites ^{4,5}. In the case of herbivore or pathogen attack, the emission amount of certain volatile compounds, such as terpenoids, phenylpropanoids, fatty acid derivatives, and amino acid derivatives increases significantly. Among these compounds, terpenes are accounted for a large part and play a specific role in serving as attractants or deterrents for herbivores ^{6,7}. The basic molecular formulae of terpenes are multiples of isoprene (C_5H_8) with a head-to-tail linkage or a ring-structure arrangement. Terpenes are often strong smelling and thus have a protective function for plants. The emission amounts of terpenes are linked to the endogenous biological clock of plants ⁴. The releasing amounts and species of terpenes by various plants in their secondary metabolites process have been considered as indicators of biological states to analyze the growth status ^{8,9}. For instance, terpenoid compounds emitted from Lima bean plants infested with spider mites can act as airborne signals, which activate the defense responses and thus enhance the resistance against spider mites in the leaves of neighboring conspecific plants ^{4,10}. Therefore, real-time terpene detection is of importance in plant growth status evaluation and pest and disease controlling in agriculture.

1.2 Terpene detection

Instrumental approaches have already been used for terpene detection. A reversed-phase (RP)- high-performance liquid chromatography (HPLC) method with evaporative light scattering detection (ELSD) was developed for the analysis of terpene compounds including actein, 27-deoxyactein and cimicifugoside in traditional Chinese medicine of *Cimicifuga foetida* L ¹¹. Li and Fitzloff used HPLC with photodiode array (PDA) detection to compare flavonol aglycone content in various pharmaceutical products ¹² and published a method to simultaneously determine terpene lactones and flavonol aglycones using HPLC with evaporative light scattering detection (ELSD) ¹³. Gas chromatography mass spectrometer (GC/MS) is another commonly used means to

detect terpenes. For instance, GC (with an ultra-sensitive low volume photoionization detector) was undertaken to measure the ambient concentrations of a few selected terpene hydrocarbons with better frequency including isoprene, α -pinene and β -pinene¹⁴. The monoterpenes and sesquiterpenes extracted from the milk fat were semi-quantified by dynamic headspace–gas chromatography–mass spectrometry (DHS-GC-MS). All the milk samples were correctly classified according to their geographical origin irrespective of seasonal herd management pattern, which show that the assay of terpene compounds can provide useful fingerprints for the characterization of dairy produce according to geographical area and production conditions¹⁵. In addition, A plasma based ambient ionization technique that enables rapid ionization of small molecules with high sample throughput was coupled to an orthogonal time-of-flight mass spectrometer, and the system was optimized for successfully analyzing a vital hormonal regulator in insects, juvenile hormone and its terpene precursors, namely, farnesol, farnesoic acid, and methyl farnesoate¹⁶. A solid-phase extraction method (SPE) is proposed as a novel sample preparation method for the simultaneous determination of α -, β -thujone, and anethole in absinthe, followed by capillary gas chromatography with flame ionization detection (FID) or mass spectrometry (MS) for final quantitation of the terpenes¹⁷. Furthermore, quartz crystal microbalance (QCM) sensor and sensor arrays have also been applied for terpene and terpene derivatives detection. QCM sensor which covered by molecular imprinted polymer (MIP) with various composition ratio of cross-linker, functional monomer and template molecule for terpene: α -pinene, limonene, limonene oxide was fabricated¹⁸. A piezoelectric multichannel QCM, coated with six molecularly imprinted polystyrene artificial recognition membranes have been developed for selective quantification of terpenes emanated from fresh and dried Lamiaceae family species, i.e., rosemary (*Rosmarinus Officinalis* L.), basil (*Ocimum Basilicum*) and sage (*Salvia Officinalis*) i.e., α -pinene, limonene, eucalyptol, β -pinene, terpinene and estragole¹⁹.

1.3 Gas detection methods

1.3.1 Instrumental gas analysis methods

Instrumental techniques such as gas chromatography²⁰ and infrared absorption are widely used for accurate gas detection. The technique of GC is a form of partition chromatography in which the mobile phase is a gas and the stationary phase is a liquid. As shown in Fig. 1.1, a sample is injected into the gas phase where it is volatilized and passed onto the liquid phase, which is held in some form in a column. Components spend different times in the mobile phase and the stationary phase, depending on their relative affinities for the latter, and emerge from the end of the column exhibiting peaks of concentration, ideally with a Gaussian distribution. These peaks are detected by some means which converts the concentration of the component in the gas phase into an electrical signal, which is amplified and passed to a continuous recorder, and perhaps to an integrator, so that the progress of the separation can be monitored and quantified.

Mass spectrometer could also be used to detect gas samples. The gas molecules are partially ionized into ions. The speed of a charged particle may be increased or decreased while passing through the electric field, and its direction may be altered by the magnetic field in the analyzer part. The magnitude of the deflection of the moving ion's trajectory depends on its mass-to-charge ratio. The detector records the relative abundance of each ion type. This information is used to determine the chemical element composition of the original sample and the isotopic composition of its constituents.

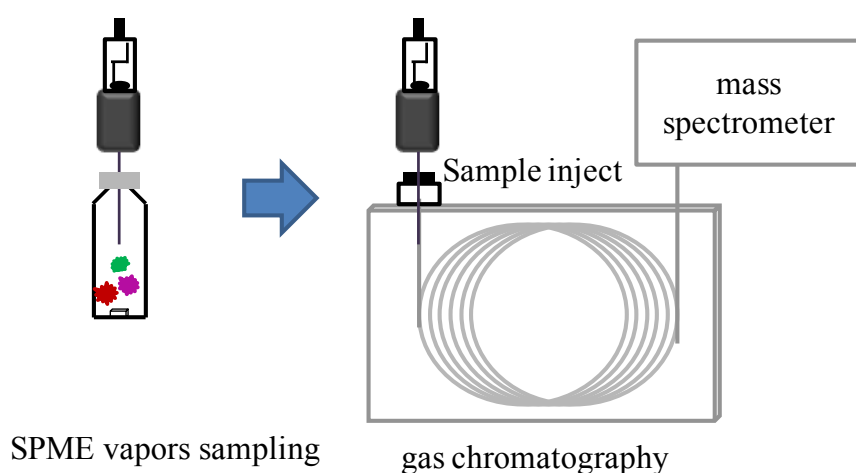


Fig. 1.1 GC/MS analysis

In the infrared gas detector²¹ as shown in Fig. 1.2, an infrared source illuminates a volume of gas that has entered inside the measurement chamber. The gas absorbs some

of the infrared wavelengths as the light passes through it, while others pass through it completely unattenuated. The amount of absorption is related to the concentration of the gas and is measured by a set of optical detectors and suitable electronic systems. The change in the intensity of the absorbed light is measured relative to the intensity of light at a non-absorbed wavelength. The microprocessor computes and reports the gas concentration from the absorption. When there is no gas present the signals of reference signal detector and measurement signal detector are balanced. When there is combustible gas present, there is a predictable drop in the output from measurement signal detector because the gas is absorbing light.

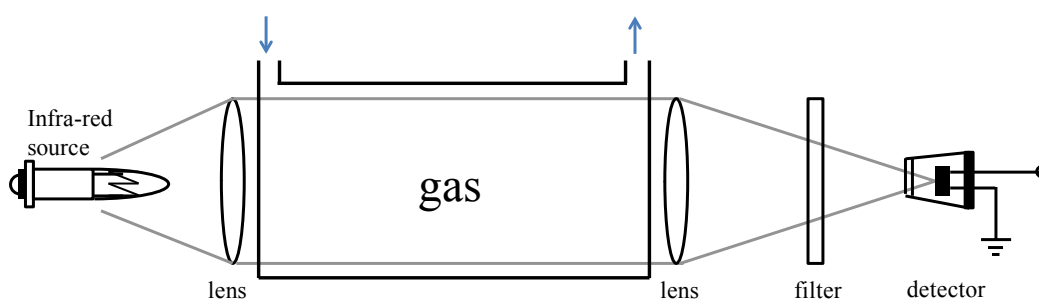


Fig. 1.2 Infrared gas detector

However, installation of these conventional instruments is costly, requires a sampling system and complicated maintenance, and in situ continuous monitoring in most gaseous environments becomes time consuming and unrealistic.

1.3.2 Commonly used gas sensor

Conductivity sensors²²

Conducting polymer composites, intrinsically conducting polymers and metal oxides are three of the most commonly utilized classes of sensing materials in conductivity sensors as shown in Fig. 1.3. These materials work on the principle that a change in some property of the material resulting from interaction with a gas/odor leads to a change in resistance in the sensor.

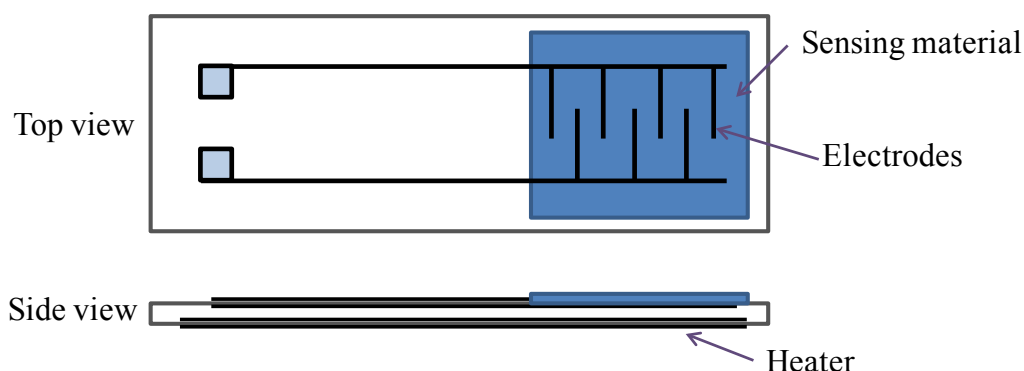


Fig. 1.3 Typical structure of a conductivity sensor

Conducting polymer composite sensors

Conducting polymer composites consist of conducting particles such as polypyrrole and carbon black interspersed in an insulating polymer matrix. When the polymer composite sensor is exposed to a vapor, some of the vapor permeates into the polymer and causes the polymer film to expand. The vapor-induced expansion of the polymer composite causes an increase in the electrical resistance of the polymer composite because the polymer expansion reduces the number of conducting pathways for charge carriers²³. The response time of conducting polymer composite sensor depends on the rate of diffusion of permeate into the polymer. The diffusion rate mainly depends on the nature of the polymer, permeate and the cross linking, the concentration of permeate and thickness of the film, and on the effects of fillers, plasticizers and temperature.

Conducting polymer composites offer many advantages over other materials when utilized as gas sensors²². High discrimination in array sensors can be easily achieved using these materials due to the wide range of polymeric materials available on the market. This is due to the fact that different polymers give different levels of response to a given odor. Conducting polymer composites are also relatively inexpensive and easy to prepare. The signal conditioning circuitry required for these sensors is relatively simple as only a resistance change is being measured. The main drawbacks of using conducting polymer composites sensors are aging problem.

Intrinsically conducting polymer sensors

Intrinsically conducting polymers (ICP) have linear backbones composed of unsaturated monomers, i.e. alternating double and single bonds along the backbone,

which can be doped as semiconductors or conductors ²⁴. Yasufuku ²⁵ describes them as π electron conjugated polymers where the π symbol relates to the unsaturated structure of the monomer containing an unpaired carbon electron. The principle of operation for ICP sensors is that the odorant is absorbed into the polymer and alters the conductivity of the polymer including: intra-chain conductivity, intermolecular conductivity, and ionic conductivity.

Intrinsically conducting polymer sensors have a number of advantages. Increased discrimination when developing sensor arrays can easily be achieved with these materials as a wide range of intrinsically conducting polymers is available on the market ²⁶. ICP sensors operate at room temperature ²⁷, thereby simplifying the required system electronics. Conducting polymers show a good response to a wide range of analytes and have fast response and recovery times especially for polar compounds. Problems related to intrinsically conducting polymer sensors include poorly understood signal transduction mechanisms, difficulties in resolving some types of analytes, high sensitivity to humidity and the sensor response can drift with time. In addition, the lifetime of these sensors can be quite short, typically 9-18 months, due to oxidation of the polymer ²⁸.

Metal oxide sensors

The principle of operation of metal oxide sensors as shown in Fig. 1.4 is based on the change in conductance of the oxide on interaction with a gas, and the change is usually proportional to the concentration of the gas. There are two types of metal oxide sensors. n-type (zinc oxide, tin dioxide, titanium dioxide or iron (III) oxide) which respond to reducing gases and p-type (nickel oxide, cobalt oxide) which respond to oxidizing gases. The n-type sensor operates as follows: oxygen in the air reacts with the surface of the sensor, and traps any free electrons on the surface or at the grain boundaries of the oxide grains. This produces large resistance in these areas due to the lack of carriers and the resulting potential barriers produced between the grains inhibit the carrier mobility. However, if the sensor is introduced to a reducing gas like H_2 , CH_4 , CO , C_2H_5 or H_2S the resistance drops because the gas reacts with the oxygen and releases an electron. This lowers the potential barrier and allows the electrons to flow, thereby increasing the conductivity. P-type sensors respond to oxidizing gases like O_2 , NO_2 , and Cl_2 as these

gases remove electrons and produce holes, i.e. producing charge carriers. The sensitivity of the metal oxide sensor depends on the film thickness and the temperature at which the sensor is operated.

The main advantages of metal oxide sensors are fast response and recovery time which mainly depend on the temperature and the level of interaction between the sensor and gas ²⁹. Thin film metal oxide sensors are small, and relatively inexpensive to fabricate, have lower power consumption than thick film sensors, and can be integrated directly into the measurement circuitry ³⁰. However, they have many disadvantages due to their high operating temperatures, which results in increased power consumption over sensors fabricated from materials other than metal oxides. They also suffer from sulphur poisoning due to irreversible binding of compounds that contain sulphur to the sensor oxide ³¹, and ethanol can also blind the sensor from other volatile organic compound (VOC) gases ²⁸.

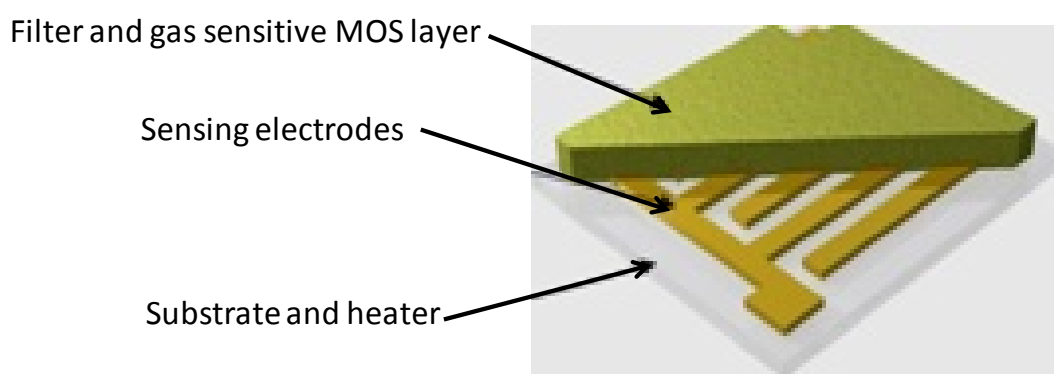


Fig. 1.4 The schematic graph of the metal oxide sensor

Piezoelectric sensors

There are two types of piezoelectric sensors used in gas sensing, the surface acoustic wave (SAW) device and the quartz crystal microbalance (QCM). The SAW device produces a surface wave that travels along the surface of the sensor while the QCM produces a wave that travels through the bulk of the sensor. Both types of devices work on the principle that a change in the mass of the piezoelectric sensor coating due to gas absorption results in a change in the resonant frequency on exposure to a vapor ²⁶.

Surface acoustic wave (SAW)

Surface acoustic wave sensors as shown in Fig. 1.5 are a class of

microelectromechanical systems (MEMS) which rely on the modulation of surface acoustic waves to sense a physical phenomenon. The sensor transduces an input electrical signal into a mechanical wave which, unlike an electrical signal, can be easily influenced by physical phenomena. The device then transduces this wave back into an electrical signal. Changes in amplitude, phase, frequency, or time-delay between the input and output electrical signals can be used to measure the presence of the desired phenomenon. The SAW device is composed of a piezoelectric substrate with an input (transmitting) and output (receiving) interdigital transducer deposited on top of the substrate³². The sensitive membrane is placed in between. The mass of the gas sensitive membrane of the SAW device is changed on interaction with a compatible analyte and causes the frequency of the wave to be altered. The change in frequency with sorption of a vapor is given by^{26, 33}

$$\Delta f = \Delta f_p c_v K_p / \rho_p \quad (1-1)$$

Where Δf_p is the change in frequency caused by the membrane, c_v is the vapor concentration, K_p is the partition coefficient, ρ_p is the density of the polymer membrane used. The sensitivity of the SAW device to a particular odor depends on the type sensitive membrane and the uptake of vapors by polymers.

SAW devices can detect a broad spectrum of odors due to the wide range of gas sensitive coatings available³⁴ and they also offer high sensitivity and fast response times and their fabrication is compatible with current planar IC technologies³³. However, SAW devices suffer from poor signal to noise performance because of the high frequencies at which they operate²⁸, and the circuitry required to operate them is complex and expensive.

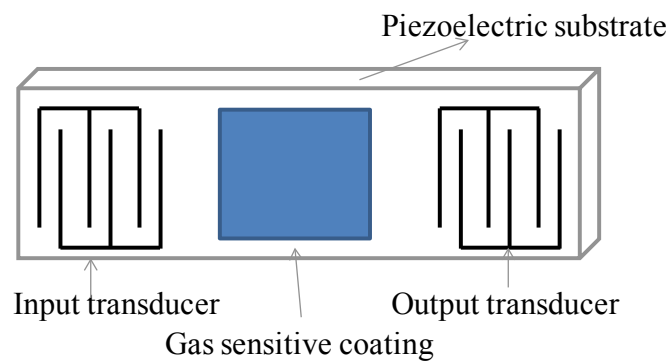


Fig. 1.5 SAW sensor

Quartz crystal microbalance (QCM) sensors

Quartz crystal microbalance (QCM) gas sensors as shown in Fig. 1.6 operate on the same principle as SAW devices. When an AC voltage is applied across the piezoelectric quartz crystal the material oscillates at its resonant frequency, normally between 10 and 30 MHz ²⁸. The three-dimensional wave produced, travels through the entire bulk of the crystal. A membrane is deposited onto the surface of the crystal and this layer adsorbs gas when exposed to the vapor, which results in an increase in its mass. This increase in mass alters the resonant frequency of the quartz crystal and this change in resonant frequency is therefore used for the detection of the vapor ²⁶. The sensitivity of QCMs is given by

$$\frac{\Delta f}{\Delta c} = \frac{(-2.3 \times 10^{-6})f^2}{A}$$

(1-2)

Where f is the fundamental frequency, c is the concentration and A is the area of the sensitive film ³⁵.

The advantages of using QCMs are fast response times, typically 10 s ³⁶, while response times of 30 s to 1 min have been reported ³⁷. However, QCM gas sensors have many disadvantages which include complex fabrication processes and interface circuitry ³³, and poor signal to noise performance due to surface interferences and the size of the crystal.

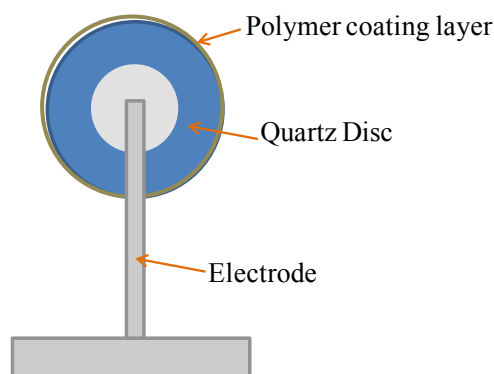


Fig. 1.6 Quartz crystal microbalance with polymer coating

Photoionization (PID) sensor

In a photoionization detector ³⁸⁻³⁹ as shown in Fig. 1.7 process high-energy photons, typically in the ultraviolet (UV) range, break molecules into positively charged ions. As compounds elute from the GC's column they are bombarded by high-energy photons and are ionized when molecules absorb high energy UV light. UV light excites the molecules, resulting in temporary loss of electrons in the molecules and the formation of positively charged ions. The gas becomes electrically charged and the ions produce an electric current, which is the signal output of the detector. The greater the concentrations of the component, the more ions are produced.

Photoionization detectors (PIDs) are fast responding and easy-to-use for parts per million (ppm) detection of many hazardous volatile organic compounds (VOCs) ³⁸⁻³⁹. PIDs are capable of effectively detecting and monitoring many hazardous substances. PIDs are non-destructive detectors. They do not appreciably destroy/consume the components they detect. Therefore they can be used before other detectors in multiple-detector configurations. Typical photoionization detectors measure volatile organic compounds and other gases in concentrations from sub parts per billion to 10000 parts per million (ppm). The photoionization detector is an efficient and inexpensive detector for many gas and vapor analytes. A PID may produce instantaneous readings and operate continuously. These hand-held, battery-operated detectors are widely used in military, industrial, and confined working facilities for safety. PIDs are broad band detectors and are not selective, as these may ionize everything with an ionization energy less than or equal to the lamp output. A PID is highly selective when coupled with a chromatographic technique or a pre-treatment tube such as a benzene specific tube. The PID will only detect components which have ionization energies similar to or lower than the energy of the photons produced by the PID lamp used in the detector. This selectivity can be useful when analyzing mixtures in which only some of the components are of interest. The signal produced by a PID may be quenched when measuring in high humidity environments, or when a compound such as methane is present in high concentration. This attenuation is due to the ability of water, methane, and other compounds with high ionization potential (IP) values to absorb the photons emitted by the UV lamp without leading to the production of ion current. This reduces the number of energetic photons available to ionize target analytes.

External influences such as temperature and humidity variation limit detection below ppm levels.

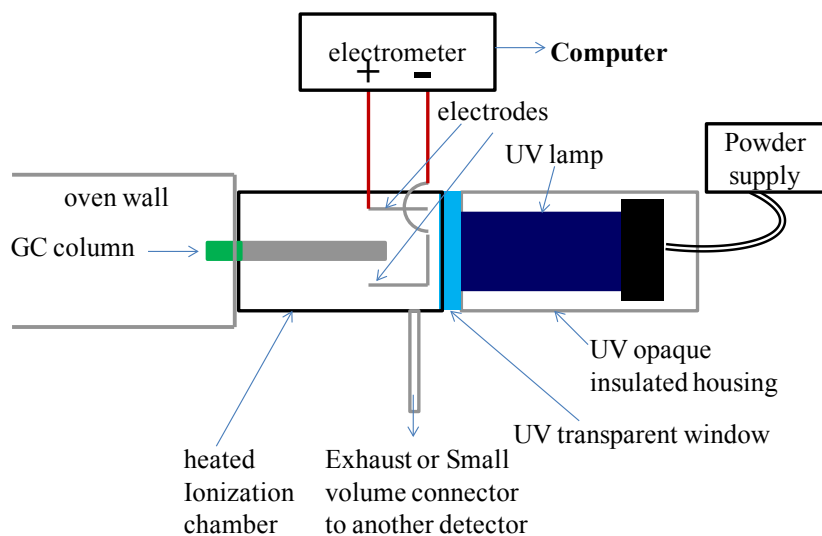


Fig. 1.7 PID sensor

1.4 Localized Surface Plasmon Resonance Sensors of Noble Metal Nanoparticles

The real-time detection of various terpene vapors requires the sensors have not only a fast, sensitive, and selective response, but also portability in agricultural environment. Based on this premise, the localized surface plasmon resonance (LSPR) of noble metallic nanoparticles, such as gold nanoparticles was proposed to detect our target gas-terpene.

1.4.1 LSPR introduction and principle

Coinage metals, such as Au, Ag, and Cu, have been important materials throughout history⁴⁰. Although in ancient cultures they were admired primarily for their ability to reflect light, their applications have become far more sophisticated with our increased understanding and control of the atomic world. Today, these metals are widely used in electronics and catalysis and as structural materials, but when they are fashioned into structures with nanometer-sized dimensions, they also become enablers for a completely different set of applications that involve light. These new applications go far beyond merely reflecting light and have renewed our interest in maneuvering the interactions

between metals and light in a field known as plasmonics⁴¹⁻⁴⁵. Plasmonics is related to the localization, guiding, and manipulation of electromagnetic waves beyond the diffraction limit and down to the nanometer-length scale⁴⁴. The key component of plasmonics is a metal, because it supports surface plasmon polariton modes, which are electromagnetic waves coupled to the collective oscillations of free electrons in the metal. The ability of a metal nanoparticle to support a surface plasmon resonance is dependent on its dielectric function ϵ , which includes a real part (ϵ_r) and an imaginary part (ϵ_i), both of which vary with excitation wavelength (λ). The dielectric function of a material reflects the unique interaction between its electrons and the light.

Although there are a rich variety of plasmonic metal nanostructures, they can be differentiated based on the plasmonic modes they support: localized surface plasmons (LSPs) or propagating surface plasmons (PSPs). Surface propagating plasmons are electromagnetic excitations propagating at the interface between a dielectric and a conductor, evanescently confined in the perpendicular direction. These electromagnetic surface waves arise via the coupling of the electromagnetic fields to the oscillations of the conductor's electron plasmon. Localized surface plasmons on the other hand are non-propagating⁴⁵. When a surface plasmon is confined to a particle of a size comparable to the wavelength of light, that is, a nanoparticle, the particle's free electrons participate in the collective oscillation, and it is termed a localized surface plasmon (LSP). In LSPs, the time varying electric field associated with the light (E_0) exerts a force on the gas of negatively charged electrons in the conduction band of the metal, and drives them to oscillate collectively. At a certain excitation frequency, this oscillation will be in resonance with the incident light, resulting in a strong oscillation of the surface electrons, commonly known as a localized surface plasmon resonance (LSPR) mode⁴⁶. The curved surface of the particle exerts an effective restoring force on the driven electrons, so that a resonance can arise, leading to the field amplification both inside and in the near field zone outside the particle.

LSPR of noble metal NPs arises when electromagnetic radiation induces a collective oscillation of the conduction electrons of the individual NPs, which produces a large degree of absorption and scattering cross sections in narrow spectral ranges and depends mainly on the NPs' shape, size, and dielectric effect⁴⁷⁻⁵¹. LSPR is theoretically possible

in any metal, alloy, or semiconductor NPs that have a large negative real dielectric constant and a small imaginary dielectric constant; LSPR is especially possible in Au and Ag NPs ⁴⁷⁻⁴⁹. The LSPR has two important effects. First, electric fields near the particle's surface are greatly enhanced, this enhancement being greatest at the surface and rapidly falling off with distance. Second, the particle's optical extinction has a maximum at the plasmon resonant frequency, which occurs at visible wavelengths for noble metal nanoparticles. This extinction peak depends on the refractive index of the surrounding medium and is the basis for the sensing applications ⁴⁷⁻⁵¹. Plasmonic NPs can act as transducers that convert small changes in the refractive index into spectral shifts in the intense NP extinction and scattering spectrum through the electromagnetic field generated by the LSPR in the NP ⁵². In terms of gas detection, the use of the LSPR of NPs is attributed to the changes in LSPR due to the adsorption of gas molecules on NPs surface. This detection principle requires the absorption of gas molecules onto a thin layer of NPs layer, where the formation of almost a single layer changes the LSPR spectrum. Thus, high-speed gas sensing can be realized by LSPR sensors. Chemical sensor based on noble metallic nanoparticles on gas detection very common. For instance, the LSPR of Ag or Au NPs and Au-Co₃O₄ composite films deposited on glass substrates was used to detect CO₂, H₂, toluene, octane, chlorobenzene, n-Xylene, and pentanol, producing a linear response with increasing gas concentration until saturated concentrations were obtained ^{53, 55}. In addition, when combined with surface modification technologies such as thiol surface modification, LSPR sensors can generate certain a chemical selectivity ⁵⁴. For gold and silver nanoparticles, the resonance falls into the visible region of the electromagnetic spectrum. A striking consequence of this is the bright colors exhibited by particles both in transmitted and reflected light, due to resonantly enhanced absorption and scattering. Ag nanostructures are considered to be toxic, although passivating the surface can greatly increase their stability and thus attenuate or eliminate their toxicity ⁵⁶. In contrast, Au is well-known for its bio-inertness, and its surface is believed to be oxide-free. For these reasons, Au nanostructures are well-suited for in vivo applications ⁵⁷. Next, we discuss the LSPR in AuNPs specific completely.

The interaction of a particle of size d with the electromagnetic field can be analyzed

using the simple quasi-static approximation provided that $d \ll \lambda$ ⁴⁵⁻⁵¹, i.e. the particle is much smaller than the wavelength of light in the surrounding medium. In this case, the phase of harmonically oscillating electromagnetic field is partially constant over the particle volume, so that one can calculate the spatial field distribution by assuming the simplified problem of a particle in an electrostatic field. The harmonic time dependence can then be added to the solution once the field distributions are known. As we will show below, this lowest-order approximation of the full scattering problem describes the optical properties of nanoparticles of dimensions below 100 nm.

We start with the most convenient geometry for an analytical treatment: a homogeneous, isotropic sphere of radius a located at the origin in a uniform, static electric field $\mathbf{E} = E_0 \hat{\mathbf{z}}$ as shown in Fig. 1.8. The surrounding medium is isotropic and non-absorbing with dielectric constant ϵ_m , and the field lines are parallel to the z -direction at sufficient distance from the sphere. The dielectric response of the sphere is further described by the dielectric function $\epsilon(\omega)$.

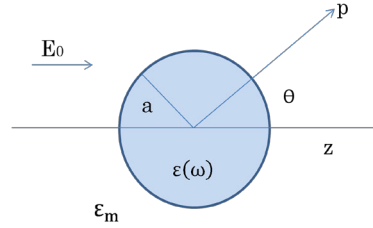


Fig. 1.8 The sketch of a homogeneous sphere placed into an electrostatic field

In the electrostatic approach, the solution of the Laplace equation for the potential, $\nabla^2 \phi = 0$, for the absence of unpaired electric charge. According to the Gauss's law of Maxwell equation and Poisson's equation,

$$\nabla E = \frac{\rho}{\epsilon_0} \quad (1-3)$$

$$\nabla^2 \phi = -\frac{\rho}{\epsilon_0} \quad (1-4)$$

$$\text{Hence, } E = -\nabla \phi \quad (1-5)$$

Due to the azimuthal symmetry of the problem, the general solution is of the form

$$\phi(r, \theta) = \sum_{l=0}^{\infty} [A_l r^l + B_l r^{-(l+1)}] P_l(\cos \theta) \quad (1-6)$$

$P_l(\cos \theta)$ is the Legendre polynomials (the most general solution to Legendre's Equation

and Legendre polynomials are solutions that are azimuthally symmetric) of order l , and θ the angle between the position vector $\mathbf{r}$ at point p and the z -axis. Due to the requirement that the potentials remain finite at the origin, the solution of the potentials ϕ_{in} inside and ϕ_{out} outside the sphere can be written as

$$\phi_{\text{in}}(r, \theta) = \sum_{l=0}^{\infty} A_l r^l P_l(\cos\theta) \quad (1-7)$$

$$\phi_{\text{out}}(r, \theta) = \sum_{l=0}^{\infty} [B_l r^l + C_l r^{-(l+1)}] P_l(\cos\theta) \quad (1-8)$$

The coefficients of A_l , B_l and C_l can now be determined by the boundary condition at $r \rightarrow \infty$ and at the sphere surface $r = a$. The requirement that $\phi_{\text{out}} \rightarrow -E_0 z = -E_0 r \cos\theta$ as $r \rightarrow \infty$ demands that $B_1 = -E_0$ and $B_l = 0$ for $l \neq 1$. The remaining coefficients A_l and C_l are defined by the boundary conditions of $r = a$. Equality of the tangential components of the electric field demands that

$$-\frac{1}{a} \frac{\partial \phi_{\text{in}}}{\partial \theta} \Big|_{r=a} = -\frac{1}{a} \frac{\partial \phi_{\text{out}}}{\partial \theta} \Big|_{r=a} \quad (1-9)$$

the equality of the normal components of the displacement field

$$-\epsilon_0 \epsilon \frac{\partial \phi_{\text{in}}}{\partial r} \Big|_{r=a} = -\epsilon_0 \epsilon \frac{\partial \phi_{\text{out}}}{\partial r} \Big|_{r=a} \quad (1-10)$$

Application of these boundary conditions leads to $A_l = C_l = 0$ for $l \neq 1$, and via the calculation of the remaining coefficients A_1 and C_1 the potentials evaluate to

$$\phi_{\text{in}} = -\frac{3\epsilon_m}{\epsilon + 2\epsilon_m} E_0 r \cos\theta \quad (1-11)$$

$$\phi_{\text{out}} = -E_0 r \cos\theta + \frac{\epsilon - \epsilon_m}{\epsilon + 2\epsilon_m} E_0 a^3 \frac{\cos\theta}{r^2} \quad (1-12)$$

ϕ_{out} describes the superposition of the applied field and that of a dipole located at the particle center.

Rewrite the ϕ_{out} by inducing the dipole moment $\mathbf{p}$ as

$$\phi_{\text{out}} = -E_0 r \cos\theta + \frac{\mathbf{p} \cdot \mathbf{r}}{4\pi\epsilon_0\epsilon_m r^3} \quad (1-13)$$

$\mathbf{p}$

$$= 4\pi\epsilon_0\epsilon_m a^3 \frac{\epsilon - \epsilon_m}{\epsilon + 2\epsilon_m} \mathbf{E}_0$$

(1-14)

We therefore see that the applied field induces a dipole moment inside the sphere of magnitude proportional to $|\mathbf{E}_0|$, if we induce the polarizability α , defined by $\mathbf{p} = \epsilon_0\epsilon_m\alpha\mathbf{E}_0$, which arrive at

$$\alpha = 4\pi a^3 \frac{\epsilon - \epsilon_m}{\epsilon + 2\epsilon_m}$$

(1-15)

According to this equation, the resonant enhancement appear under the condition that $|\epsilon + 2\epsilon_m|$ is a minimum, which for the case of small $\text{Im}(\epsilon)$ around the resonance simplifies to

$$\text{Re}[\epsilon(\omega)] = -2\epsilon_m$$

(1-16)

The schematic LSPR phenomenon in AuNPs on glass substrate is shown in Fig. 1.9.

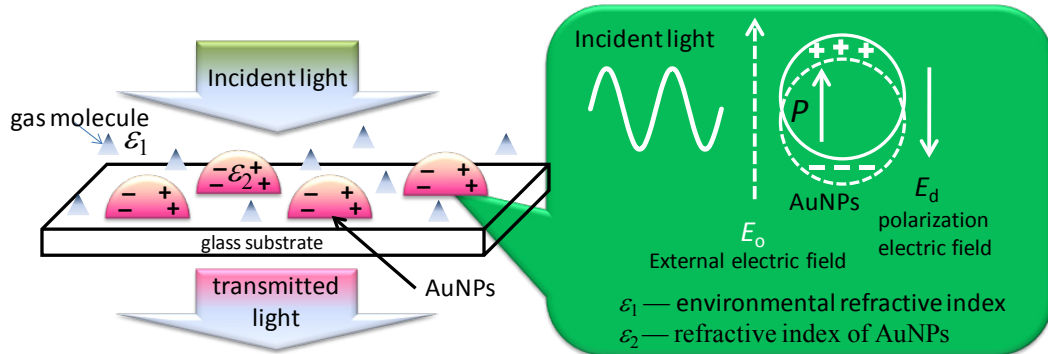


Fig. 1.9 The schematic sensing diagram of AuNP LSPR film

1.4.2 LSPR based sensors

The simplest sensing application of LSPR-active particles is to detect changes in the bulk refractive index of their environment through shifts in the LSPR peak wavelength. LSPR peaks are typically detected by spectral extinction measurements on a dense film or spectral scattering measurements on single nanoparticles. The LSPR peak wavelength shift is approximately linear with changes in refractive index of the surrounding medium. Therefore, the refractive index sensitivity of a particular nanoparticle type is usually reported in nanometers of peak shift per refractive index

unit (nm/RIU) ⁴⁷⁻⁵⁰. In addition, electronic field enhancements due to LSPR decay rapidly with distance from the nanoparticle surface ^{55-56,58}. Therefore, spectral LSPR shifts only probe a nanoscale region around the particle. This highly localized sensing volume allows one to observe molecular interactions near the nanoparticle surface because they result in changes in the local refractive index ^{55-56,58}.

1.4.2.1 LSPR-Based Biological Sensors

Several aspects of LSPR sensing suggest its suitability for biological and biomedical assays ⁵⁹⁻⁶¹. This allows a continuous measurement of the target concentration on the sensor and enables the analysis of real time binding kinetics. One of the typical examples is Biotin-streptavidin. Biotin-streptavidin is especially well suited to LSPR sensing because biotin, a small organic molecule, can be conjugated to the nanoparticle surface, while the index of refraction of the larger streptavidin protein is detected ⁵⁹. The other commonly known example is the LSPR sensors which have been applied in immune-assay. Capture antibodies are typically conjugated to the nanoparticle surface via a SAM and standard bioconjugate linkers ⁵⁹⁻⁶¹. Antibodies would achieve their natural affinity while bound to nanoparticles given their relatively large size as compared to biotin. However, their larger size also increases the separation between the nanoparticle and target antigen, thus lowering the sensitivity and ultimately the limit of detection.

1.4.2.2 LSPR-Based Chemical Sensors

Gas sensor

A variety of LSPR sensing schemes have been developed for organic vapors. Cheng et al. have demonstrated LSPR sensing of volatile organic compounds (VOCs, e.g. toluene) in gaseous form ⁵⁵. In their studies, the adsorption of these compounds to silver, gold nanoparticles, and gold nanoshells was monitored through both the peak wavelength and the integrated total magnitude of the particles' extinction. The response was verified to be fast and reversible. Another case for LSPR-based gas sensing was developed by Karakouz et al. ⁶², where the evaporated gold island films were coated

with the polymers polystyrene sulfonic acid and polystyrene. These polymers swell and/or shrink upon exposure to the various gases applied (chloroform, water vapor, etc.), affecting the local refractive index and inducing LSPR peak shift.

Metal detection sensor

Monitoring the levels of potentially toxic metal (PTM) ions (e.g., Hg^{2+} , Pb^{2+} , Cu^{2+}) in aquatic ecosystems is important because these ions can have severe effects on human health and the environment ⁶³. Gold nanomaterials are attractive sensing materials because of their unique size and shape-dependent optical properties. A gold nanoparticle-based sensor for copper ions based upon plasmonic resonance energy transfer was developed by Choi et al and coworkers ⁶⁴. In their research, specific ligands were coated on gold nanoparticles, which would form complexes with copper ion. The sensing principle is based on that the electronic absorption of the metal-ligand complex matched the plasmon resonance of the nanoparticles, which would result in a quenching of nanoparticle scattering on copper ion binding. In addition, a review on optical assays for Hg^{2+} , Pb^{2+} , and Cu^{2+} ions using functionalized Au nanomaterials are discussed by Y. Lin and coworkers ⁶³. The sensing approaches based on changes in absorbance resulting from metal ion-induced aggregation of Au nanoparticles (NPs) or direct deposition of metal ions onto Au NPs. The super-quenching properties of Au NPs allow them to be employed in ‘turn on’ and ‘turn off’ fluorescence approaches for the sensitive and selective detection of Hg^{2+} , Pb^{2+} , and Cu^{2+} ions. The sensing principle is based on fluorescence quenching through analyte-induced aggregation or the formation of metallophilic complexes of Au nanodots.

1.5 Aim and results in this research

The final target of this research is to detect terpene vapors in agriculture. As described in chapter one, terpene is an important class of biomarker vapors, especially in the conditions of diseases or herbivores. Compared with the instrumental gas sensing methods and commonly used gas sensors, such as QCM and SAW, noble metal nanoparticles sensor is a more suitable candidate based on the sensing characteristics.

In the first stage, we investigated the bare AuNPs deposited on glass substrate using Au ion sputtering methods and chemical synthesized colloidal. The sensitivity

enhancement was realized by appropriate thermal annealing or the multilayer structure.

Next, thiolate surface modification we adopted to generate affinitive selectivity between terpene molecules and the thiolate capping layer. The mutual selectivity between terpene and thiolate was accomplished by choosing the favorable structures of thiolates.

In the final stage, molecular imprinted polymer (MIP) technique was combined with the LSPR phenomenon to achieve the specific selectivity of the sensor to terpene vapors. We have successfully realized the selective detecting α -pinene from limonene and γ -terpinene. For the purpose of real field application, more kinds of MIP films to the other commonly generated terpene by plants still have to be developed. In addition, the effect of temperature and humidity from the environment needs more consideration. These plans are under way by our research group.

A flow chart shown in Fig. 1.10 depicts the research progress and the related results in this work.

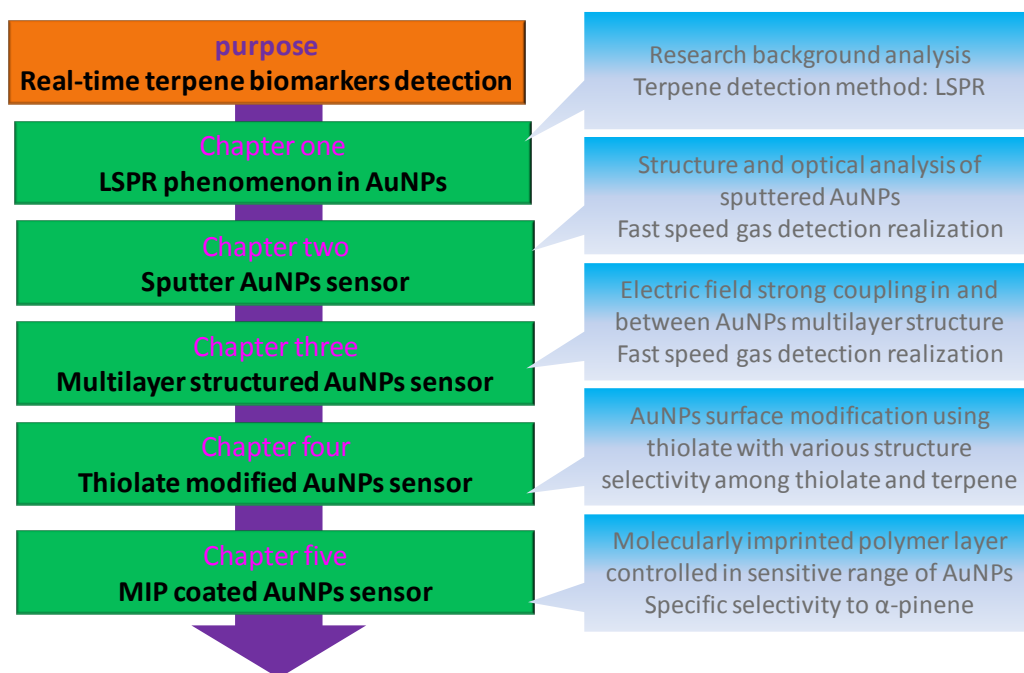


Fig. 1.10 A flow chart about this work

1.6 Thesis outline

This research is mainly related to the LSPR phenomenon of noble metallic nanoparticles and their application as the gas sensor.

In chapter one, we mainly introduce the backgrounds on the necessity of gas detection, the gas sensing technology, and the LSPR phenomenon. The main object of this research is to realize the fast, sensitive, selective terpene detection.

Chapter two describes the application of sputtered Au nano-islands for vapor detection. The effect of sputtering conditions on the formed nanostructure is discussed in detail. In addition, Thermal annealing is applied to tune the size, shape, and distribution of sputtered nano-islands further at various temperatures. As a result, the fast speed ethanol gas detection is realized in less than 2 s.

So as to further improve the sensitivity of AuNP sensor, multilayer structured Au NP sensor is proposed in chapter three based on the enhanced electric field generated by coupled Au NPs in the multilayer structure. The result shows that AuNP multilayers linked by 1, 4-benzenedithiol showed the largest RIS with four layers, which was mainly attributed to the enhanced electric field generated by larger sized Au clusters and the coupling effect in and between Au clusters.

However, bare Au nano-islands lack the selectivity to gas molecules. Therefore, thiolate surface modification is adopted to form the capping layer on Au nano-islands as demonstrated in chapter four. According to responses of thiolate modified Au nanoparticle sensor to terpene vapors, certain selectivity of Au nano-island sensor to terpene is realized through the structural characteristics of thiolate capping layers.

In chapter five, MIP coated AuNPs sensor is presented. MIP was prepared using methacrylic acid as monomer, ethylene glycol dimethylacrylate as cross-linker, and α -pinene as template. The MIP adsorption character was evaluated using GC-MS. Through modulating the molar ratio of template molecule to monomer, a larger absorption ability of MIP layer to α -pinene is achieved. The optical features of MIP coated AuNPs layer is studied under various spin coating speeds. The specific selectivity of the MIP coated AuNPs sensor to α -pinene vapor is compiled at the spin coating speed of 1400 rpm. The real-time response of α -pinene imprinted polymer coated AuNP sensor to three terpene vapors: α -pinene, limonene, and γ -terpinene is selective, rapid, and reversible.

In the last section, the research is summarized, and the possible research prospect is proposed.

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Chapter 2 Sputtered Au nano-islands on glass for fast speed vapor detection

2.1 Introduction

The enhanced electric fields are confined within only a tiny region of the nanometer length scale near the surface of the particles and decay significantly thereafter⁸. This localized field enhancement provides a field gradient that is much greater than that of any far-field optical tweezers¹¹. Therefore, it may be possible to trap single molecules or other nanoparticles in regions near an elliptical metal nanoparticle or tip or between two nanoparticles. In addition, this near-field interparticle coupling takes effect on the particle plasmon resonances, especially the shift of the plasmon resonant wavelength as a function of particle separation³⁷. This shift decays approximately exponentially with increasing particle spacing. W. Rechberger and coworkers found that the shift drops to zero when the gap between the two particles reaches about 2.5 times the particle size³⁶. It is also found that the exponential decay of the peak shift with the particle gap is size and shape-independent^{36, 37}. This E field coupling behavior can be explained by a simple weakening/ enhancing of the restoring forces for the plasma electrons due to the presence of the charge distribution of the neighboring particles^{11, 36, 37}. The schematic diagram of electric field coupling between two special NPs versus inter-particle distance

was drawn as shown Fig, 2.1.

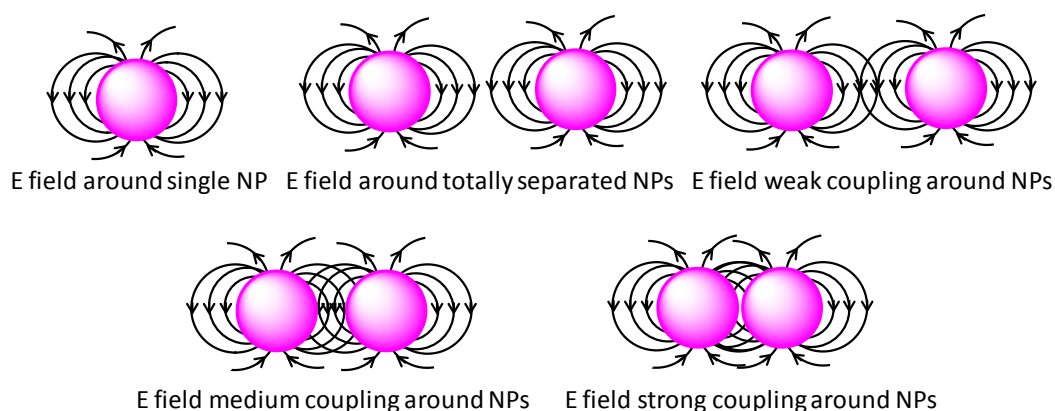


Fig. 2.1 The schematic graph of the electric field coupling between two special NPs

When the distance between neighboring NPs is far enough, there could be thought that there is no electric field inference. With the interparticle distance decrease, weak electric field mutual coupling occurs. With the interparticle distance further decrease, the electric field coupling becomes stronger. When the interparticle distance is as short as a few nanometers, the strong electric coupling would cause the generation hot electrical spots between NPs, which is extremely sensitive to the variation of the refractive index. Hence, could be used for the single molecule detection in the biosensing field.

In summary, the most important features of Plasmon coupling between NPs are (1) a significant red-shift in terms of resonance wavelength and broadening of the UV-vis spectral bandwidth, (2) distance dependent E-field enhancement in the gaps, (3) extreme localization of the near-field (hot spot), and extreme sensitivity of near-field properties to the size of the gap. For gas molecules detection, the molecules would form the layer structure, and when the gas concentration is high enough, the layer would be dense to a thin liquid layer on the surface of NPs. Hence, the medium electric field coupling of monolayer structured NPs as shown in Fig. 2.1 are more suitable for gas detection.

High-speed gas sensing devices have already been studied and applied in the detection of the gas distribution or determination of the gas source ¹. For instance, the combination of high-speed gas sensors with mobile robots has proved useful in a number of application areas. Therefore, the development of high-speed and compact gas

sensing devices has already become a subject of strong interest. There are several types of widely-known sensors that are capable of detecting volatile chemicals in air, such as surface acoustic wave (SAW),² monolayer protected nanocluster (MPC),³ quartz crystal microbalance (QCM),⁴ metal oxide (MOX),⁵ and photoionization (PID) sensors. However, SAW, MPC, and QCM sensors require a finite time for the vapor molecules to diffuse through the sensing film during the response process, and the typical response time of these three sensors exceed 10 s⁶. MOX sensors are low cost and compact, and can detect a variety of reductive volatile chemicals (VOCs). Although they have been commercially used in various areas, their response time is long because a chemical reaction is required in the thick reaction layer of the metal oxide. PID sensors, which can be applied in high-speed gas detection, ionize gas molecules by means of a deep ultraviolet light. However, they suffer from a lack of selectivity except when coupled with a chromatographic technique (GC) or a pre-treatment tube such as a benzene specific tube.

In this part, we focus on the LSPR of noble metal nanoparticles (NPs) based on their gas sensing ability and response characteristics. We studied the morphological and optical properties of Au and Ag NPs that were prepared by sputtering onto transparent glass substrates, which were then employed as LSPR transducers for high-speed gas sensing. Because the substantial mobility of Au or Ag NPs that has been sputtered onto common substrates such as glass reduces their reusability, we addressed this problem via the evaporation of NPs on aminosilane-modified glass substrates to provide an environment with a chemical affinity for silica. We investigated the influence of sputtering conditions on Au and Ag NPs' transmittance spectra and related morphological characteristics. Next, we focused on the function of thermal annealing on NP reshaping and the LSPR response to changes in the refractive index. Finally, we explored an LSPR sensor using sputtered Au NPs as a sensing layer based on the different electric field coupling conditions. The responses show that the LSPR sensor can be applied for high-speed gas detection.

2.2 Experimental

2.2.1 Au and Ag NPs fabrication

Before the sputtering of the NP, glass substrates were first cut to dimensions of 26 × 10 mm, then cleaned thoroughly with detergent, distilled water, acetone, and ethanol in an ultrasonic cleaner, and then dried in a stream of N₂. The substrates were processed in a plasma cleaner (PDC-001, HARRICK) in an argon atmosphere (110 V, 10.2 W) for 5 min and then placed in a 1:10 (volume ratio) solution of 3-aminopropyl triethoxysilane (APTES) (Shin-Etsu Chemical) in ethanol for 1 h. These surface-modified glass substrates were rinsed thoroughly with ethanol to remove non-chemically adsorbed APTES molecules. The processed glass substrates were placed into a quick coater (SC-701HMC, Sanyu Denshi) for sputtering with Au and Ag NPs using various sputtering currents and time periods. Thermal annealing treatment of the glass substrates with Au or Ag NPs was carried out in an oven (OF-300S, Asone) with an air atmosphere at 200 °C for various time periods. The annealed substrates were left to cool in air at room temperature.

2.2.2 UV-vis spectrum

The transmittance spectrum was obtained by an UV-vis spectrophotometer (UV1800, Shimadzu), whose scanning range was set from 400 to 1000 nm with a 0.5 nm resolution, using an optical cell containing air as a baseline.

2.2.3 Atomic force microscopy and scanning electron microscope images

Images of the NPs on glass were collected using a scanning electron microscope (SE-3400, Hitachi High-Technologies) and an atomic force microscope (AFM) of scanning probe microscope (SPM) (Digital Instruments Nanoscope) operating in tapping mode, separately. Pointprobe-silicon SPM-sensors (Digital Instruments, Nanosensors) were used. The typical technical data was as follow: thickness: 4 μm; length: 125 μm; width: 30 μm; resonance frequencies: 320 kHz; force constant: 42 N/m; coating: none.

2.2.4 Vapor generation device

We constructed our own gas generation device to generate variable concentrations of organic vapor for testing of the LSPR sensors. A schematic experimental setup is shown

in Fig. 2.2. Here, we used the bubbling method to produce ethanol gas in the testing cell in the spectrophotometer. The bubbling speed was set to be 0.1 and 1 L/min for generate refractive index changes around the NPs.

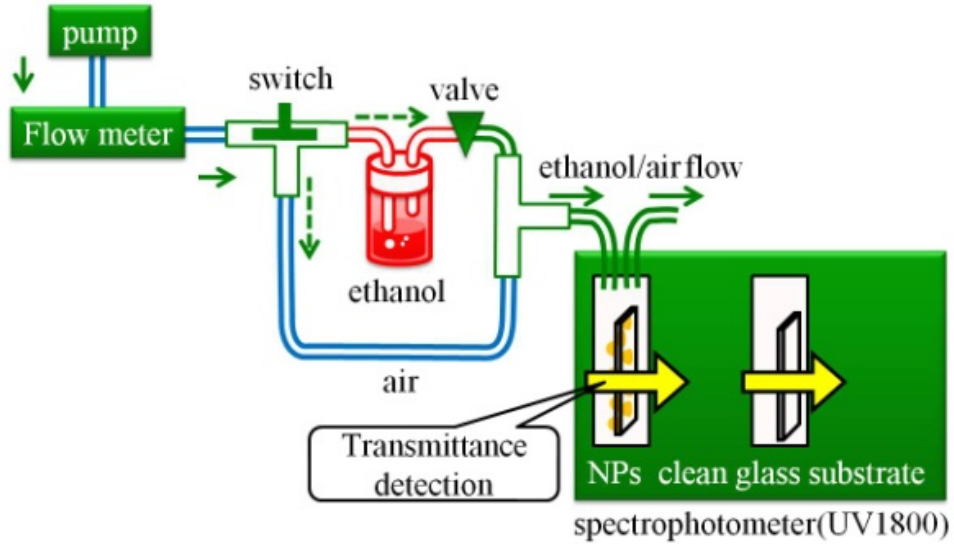


Fig. 2.2 The schematic vapor generation device ³⁸

2.2.5 Fabrication of LSPR sensor device

A compact LSPR-VOC sensing device was constructed to test its possible use as a high-speed gas detection device, as shown in Fig. 2.3. The bubbling method was chosen to generate ethanol gas at a given concentration, and a fan in the testing chamber was used to exhaust the testing vapor around the NPs. Ethanol gas was switched on for 20 s and then switched off. A glass substrate with Au NPs (sputtering current: 1.5 mA; sputtering time: 90 s) was fixed between a light-emitting diode (MPG5373X, STANLEY, dominant wavelength λ_d : 567 nm) and a light-receiving photodiode (S2281-01, Hamamatsu photonics, wavelength range: 190~1000 nm, λ_{peak} : 720 nm). The wavelength range of the emitting light was chosen such that it would be at around the LSPR peak wavelength of the NPs. The light intensity at the light-receiving photodiode was changed when the refractive index around the NPs on the glass substrate changed from that of air to that of ethanol gas, and was then converted into the related voltage signal.

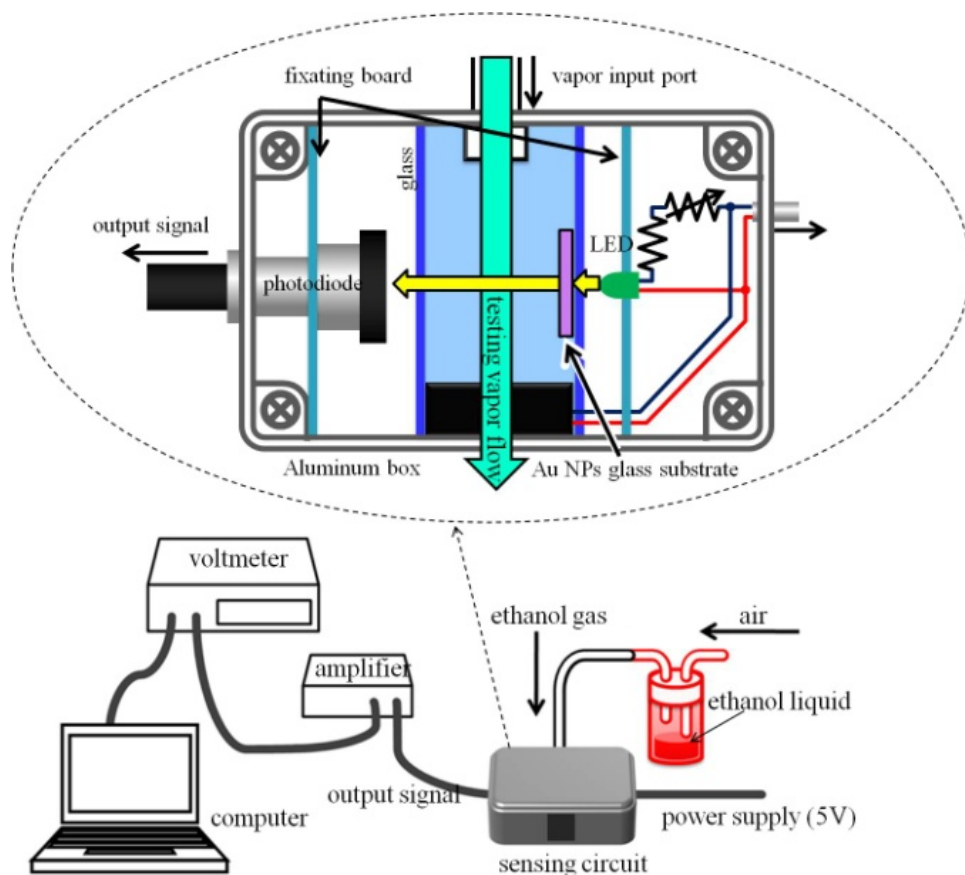


Fig. 2.3 Diagram of LSPR-VOC sensing device ³⁸

2.3 Results and discussion

2.3.1 Optical properties of sputtered AuNPs

For understanding the influence of sputtering conditions on the optical characteristics of the AuNPs, the transmission spectra of AuNPs on glass versus the sputtering time in air was investigated; the results are shown in Fig. 2.3. The sputtering current was controlled at 1mA and 4 mA with an increase in sputtering time from 20 s to 60 s. The minimum transmittance ($T_{\min}$) decreased from about 93.6 % to 72.6 %, and the wavelength of the minimum transmittance ($\lambda_{\min}$) shifted from about 531 nm to 579 nm for the Au NPs (sputtering current: 1.5 mA, sputtering time: increasing from 20 s to 60 s). The same tendency toward change in the LSPR spectrum was also observed for the AuNPs (sputtering current: 4 mA, sputtering time: from 20 s to 60 s). It is worth mentioning that when the sputtering current was as high as 4 mA, the spectral bandwidth showed an obvious broadening or even loss of peak features with increasing

sputtering time. The optical characters of AgNPs were also studied, and the results are shown in Fig. 2.3(c). The LSPR spectra of the AgNPs (sputtering current: 1.5 mA, sputtering time: from 20 s to 100 s) shows a similar tendency to change as was the case for the Au NPs. These results indicate that with sputtering time or sputtering current increase, there is a decrease in transmittance and a spectral red-shift in wavelength for both Au and Ag NPs.

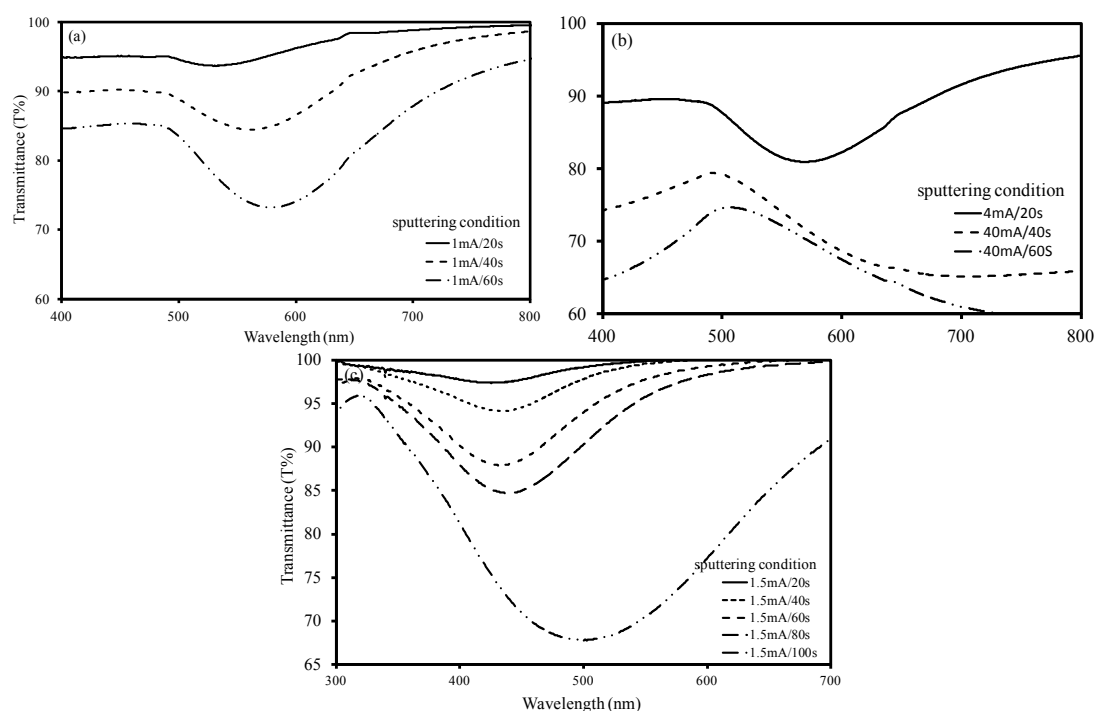


Fig. 2.4 UV-vis spectra of sputtered Au and Ag NPs ³⁸

- (a) Transmission spectra of Au NPs (1.0mA/20s to 60s) (b) Transmission spectra of AuNPs (4.0mA/20s to 60s) (c) Transmission spectra of AgNPs (1.5mA/20s to 100s)

2.3.2 Morphology characteristics of sputtered NPs

SEM images of the NPs were investigated to study the geometric size and shape characteristics of the NPs that were sputtered under various sputtering conditions. The SEM images of AuNPs under different sputtering conditions (sputtering current: 1 mA, sputtering time: 20 s (1 mA/20 s), 1 mA/60 s, 4 mA/20 s, and 4 mA/60 s) are shown in Fig. 2.4. With an increase in the sputtering current or time, the number of NPs and their

in-plane width became larger, and the inter-particle distance became narrower. When the sputtering current increased to 4 mA with a sputtering time as long as 60 s, larger and irregularly-shaped nanostructures were formed, and the NPs underwent severe aggregation reflected by the yellow-blue color of the AuNPs film, which indicates a tendency toward a transition from separate NPs to a continuous film. The morphological characteristics of the NPs can be used to explain their optical features. A red shift in the optical spectra and an increase in the optical density are attributed to the increase in NPs' in-plane width and number ⁷⁻⁸. The increase in spectral bandwidth with increased sputtering time or current is mainly due to the heterogeneity of the NPs' size distribution, their irregular shape, and the plasmon resonance coupling between aggregated NPs ^{31-35, 9-11}. The spectral broadening or even the loss of peak features with an increase in sputtering time indicates that the dipole plasmon resonance in a single NP was affected by the NPs' irregular shape, and a certain degree of quadruple or even multipole plasmon resonance may have taken place as well ^{17, 18}. In addition, these complex resonances in the irregularly shaped NPs may affect one another, in that the inter-particle distance is shortened by the NP aggregation ¹⁹.

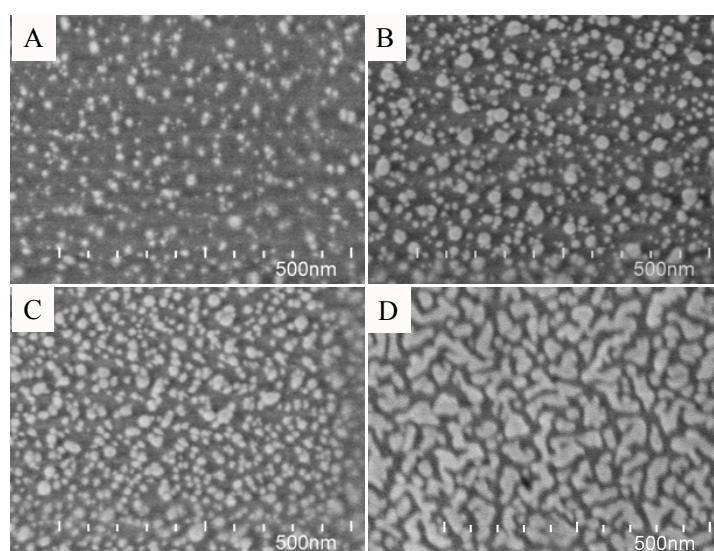


Fig. 2.5 SEM images of Au NPs with different sputtering condition ³⁸

(A) 1 mA 20 s, (B) 1 mA 60 s, (C) 4 mA 20 s, (D) 4 mA 60 s.

2.3.3 Influence of thermal annealing treatment on NP's morphology

For investigating the influence of the morphological characteristics on the NPs' LSPR response, thermal annealing treatment was applied to control the NPs' reorganization²⁰⁻²⁷. Here, the annealing temperature was set to be 200° C (a low temperature) to protect the organic adhesive layer (APTES)^{20,22}. It is known that the morphological features of the Au film depend mainly on the initial film thickness, annealing atmosphere, time, and temperature²⁰⁻²². The entire annealing process was conducted in air. Thus, we focused on the effects of the sputtering conditions and the annealing time on the modification of the NPs' morphology. First, we considered the influence of the sputtering conditions on the NPs' morphology. Au NPs on glass substrates under sputtering conditions of 1.0 mA/60 s, 1.5 mA/60 s, and 1.5 mA/80 s were annealed at 200° C for 20 h. The AFM images of the AuNPs before and after thermal annealing are shown in Fig. 2.5.

Before annealing, the height scales of NPs under sputtering conditions of 1.0 mA/60 s, 1.5 mA/60 s, and 1.5 mA/80 s were 4.76 nm, 7.26 nm, and 9.27 nm; these values increased to 16.52 nm, 20.01 nm, and 22.98 nm, respectively, after annealing treatment. NPs under sputtering conditions of 1.5 mA/80 s exhibited the maximum in-plane width and out-of-plane height both before and after annealing treatment. Similarly, NPs under sputtering condition of 1.0 mA/60 s exhibited the minimum in-plane width and out-of-plane height both before and after annealing. These results suggest that when treated under the same annealing conditions (200° C/20 h in air), the NPs' final morphology is to a certain extent dependent upon their initial morphology.

Next, we investigated the effect of the annealing time on the modification of the NPs' morphology. Here, we studied the morphological characteristics of AuNPs under the same sputtering conditions of 1.5 mA/80 s but with different annealing times (5 h, 15 h, and 30 h). As shown in Fig. 2.6, with an increase in annealing time from 0 h to 30 h, the NPs' out-of-plane height increased slightly from 20.24 nm to 21.86 nm. With a further increase in annealing time, the NPs' in-plane-width first increased, and then decreased. These results indicate that the NPs' aspect ratio at first increased in a short annealing time, after which it decreased. In addition, with increasing annealing time, the NPs' shape became round. When the annealing time was as long as 30 h, we found that the NPs' size distribution tended to be uniform.

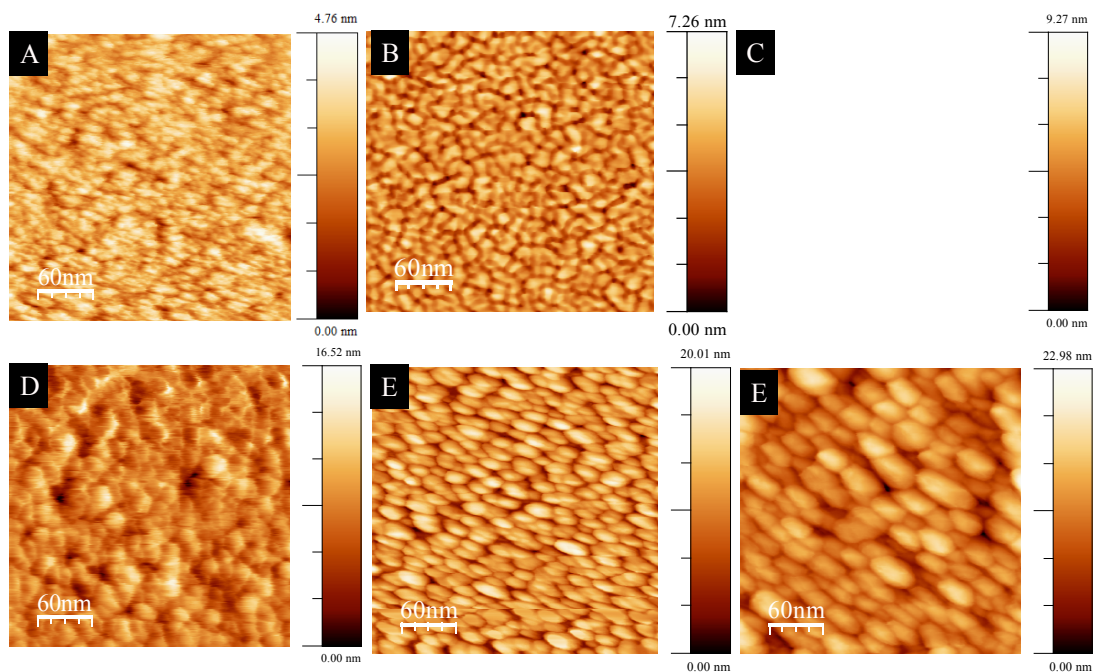


Fig. 2.6 AFM images of AuNPs before and after 200 °C 20 h annealing treatment ³⁸
(A and D: 1.0 mA/60 s before and after annealing, B and E: 1.5 mA/60 s before and after annealing, C and F: 1.5 mA/80 s before and after annealing)

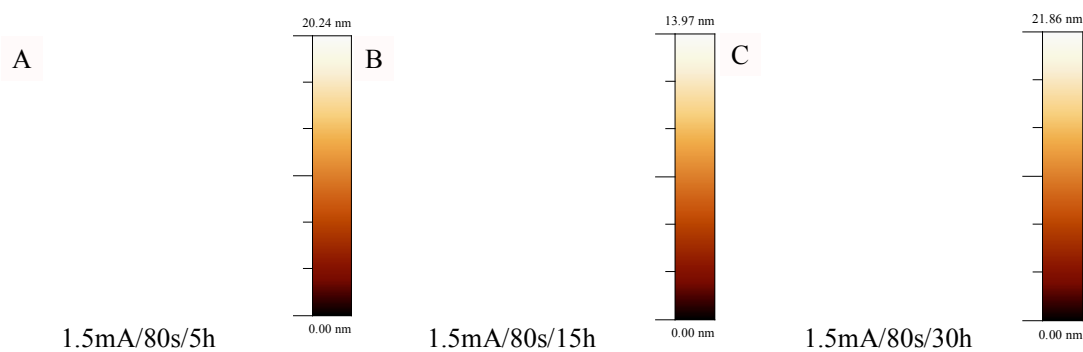


Fig. 2.7 AFM images of AuNPs the same sputtering condition but different annealing time ³⁸

(AuNPs with the same sputtering condition: 1.5 mA/80 s, annealing time from the left side to the right side are 5 h, 15 h, and 30 h).

2.3.4 LSPR response of Au and Ag NPs

The transmission spectra of AuNPs (1.5 mA /100 s) or AgNPs (2 mA /90 s) on glass

substrates in air and ethanol gas were compared, and the results are shown in Fig. 2.8. A red-shift of the minimum transmission in wavelength ($\Delta\lambda_{\min}$) and a decrease in the minimum transmittance ($\Delta T_{\min}$) occurred when the local refractive index around Au NPs is changed from that of air to that of ethanol gas. For AgNPs, the spectral peak ($\lambda_{\min}$) shifts from about 476 nm in air to 492.5 nm in ethanol gas, and the minimum transmittance ($T_{\min}$) decreases from 70.7% in air to 64.7% in ethanol gas. For AuNPs, the spectral peak ($\lambda_{\min}$) shifts from about 628.5 nm in air to 646.5 nm in ethanol gas, and the minimum transmittance ($T_{\min}$) in the spectrum decreases from 72.7% in air to 67.2% in ethanol gas.

The spectra of AuNPs (1.5 mA/100 s) and AgNPs (2 mA/90 s) in air with an annealing time that varies from 0 to 20 h were investigated shown in Fig. 2.9. For both Au and Ag NPs, with an increase in annealing time, there is a blue shift in the optical spectrum and conspicuous spectral bandwidth narrowing. These effects are mainly attributed to the change in morphology caused by the annealing treatment. In other words, plasmon resonances in NPs with a smaller aspect ratio and a round shape after annealing treatment shift to blue in the spectra. In addition, the regular plasmon resonance in the round NPs and weakened inter-particle plasmon resonance coupling also had an impact on the spectral changes ¹⁹.

Next, we studied the effect of thermal annealing on the NPs' LSPR response ($\Delta\lambda_{\min}$ and $\Delta T_{\min}$) in air and ethanol gas. As shown in Fig. 2.10, for AuNPs, both $\Delta\lambda_{\min}$ and $\Delta T_{\min}$ show an increasing trend after a short annealing time (less than one hour), and then decrease with a further increase in the annealing time, in that NPs treated by a short annealing time possess a larger aspect ratio ⁷⁻⁹. However, for AgNPs, both $\Delta\lambda_{\min}$ and $\Delta T_{\min}$ decrease versus the annealing time, a result that may be attributed to the thermal stability of AgNPs ^{20, 21}. In the annealing process (in air at 200° C), AgNPs may be oxidized, so their LSPR response will decrease with an increase in the oxide thickness on AgNPs ²³.

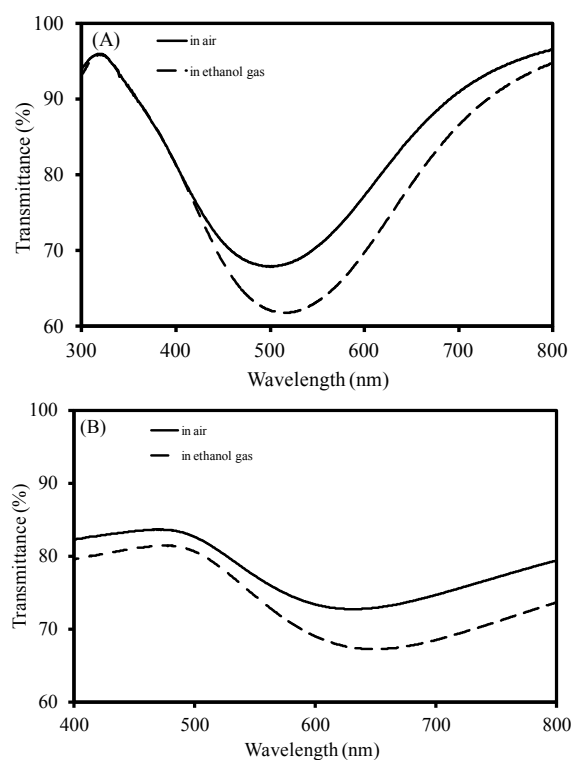


Fig. 2.8 LSPR response of Au and Ag NPs on glass ³⁸

(A: AgNPs, B: AuNPs)

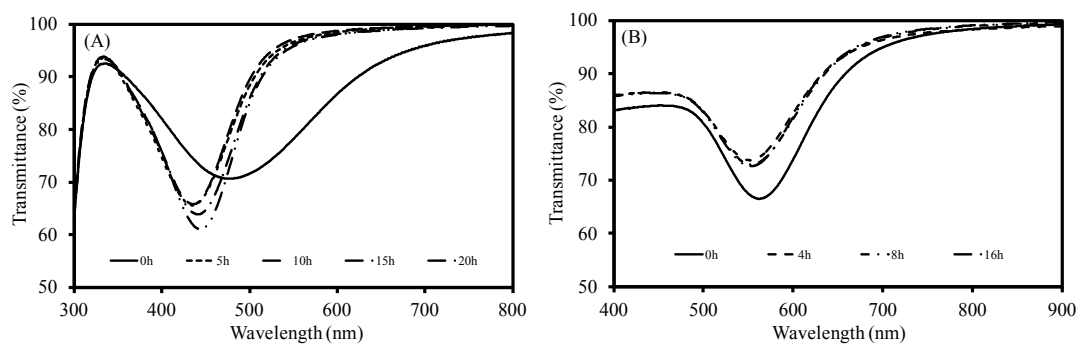


Fig. 2.9 Spectra of Au and Ag NPs in air versus annealing time ³⁸

(A: LSPR spectra of AgNPs in air versus annealing time, B: LSPR spectra of AuNPs in air versus annealing time)

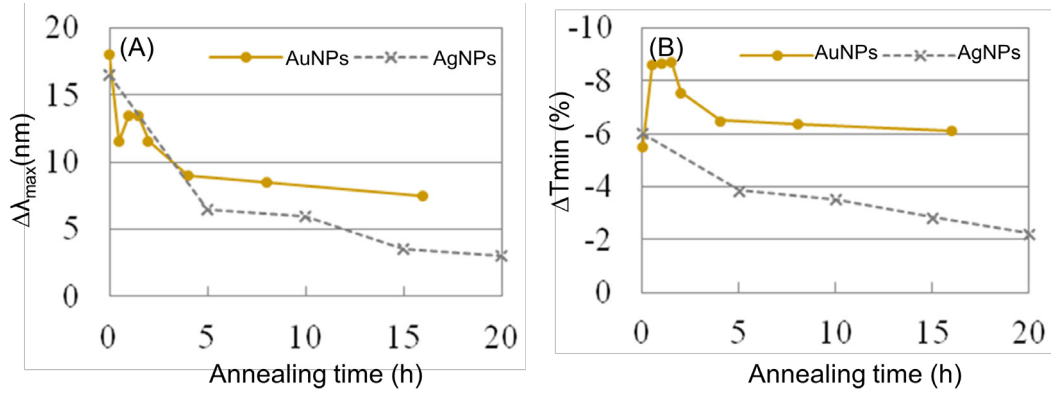


Fig. 2.10 LSPR response ($\Delta\lambda_{\min}$ and $\Delta T_{\min}$) of Au and AgNPs versus annealing time ³⁸

2.3.5 The real-time response characters of AuNPs films

The dynamic vapor response signals of AuNPs (sputtering conditions: 1.5 mA, 100 s) to ethanol gas in different concentrations are shown in Fig. 2.11. The bubbling method was adopted to generate ethanol gas with concentrations of 32780 ppm and 47100 ppm at air-flow rates of 1 L/min and 0.1 L/min, respectively. The ethanol gas was switched on for 30 s and 120 s respectively, and then switched off. The response signal of single point transmittance is at $\lambda = 628$ nm. We define the response time (T_{90}) as the time period needed to reach 90% of the final transmittance in ethanol gas, and the time period to reach 90% of the final transmittance in air, when the refractive index is changed from that of ethanol gas to that of air, is defined as the recovery time. This recovery time was about 1.5 s and 1.8 s, as shown in the results in Fig. 2.11 (a). The limit of detection (3 δ) for ethanol was calculated to be 74.4 ppm based on the response signal shown in Fig. 2.10 (a). The delayed response characteristic shown in Fig. 2.11 (b) can be attributed to the gas mixing speed in the testing chamber. The LSPR response shows a nonlinear increase to ethanol gas, which may be attributed to the near-saturated sensing range of the AuNPs film in ethanol gas at a high concentration.

We summarized the presence of a fast sensing mechanism based on the morphology of the sensing film. The thicknesses of Au or Ag NPs films are quite small (less than 10 nm), so gas molecules can quickly adsorb on the NPs' surface. Although the NPs' height was increased (less than 20 nm) by thermal annealing treatment, its influence on the time extension for gas molecule adsorption can still be neglected. In addition, thermal annealing treatment makes the NPs' surface smooth, and thus suitable for

surface modification, which gives the sensor molecular recognition ability on the basis of increasing the response time. Annealed Au/Ag NPs, on the other hand, have a small LSPR response to a change in the refractive index.

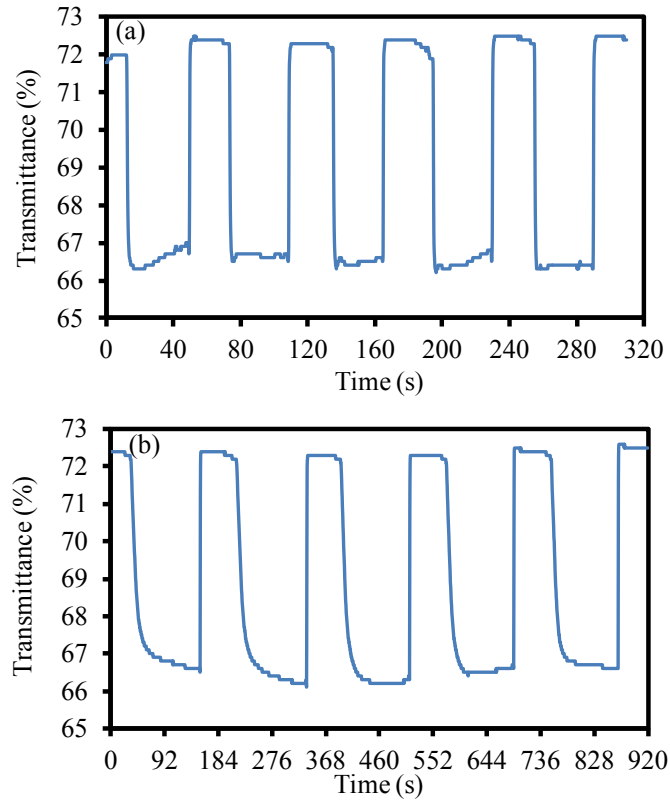


Fig. 2.11 Real-time response signal of NPs films ³⁸

(a) Response signal of AuNPs sensor with vapor flow rate 1 L/min, (b) Response signal of AuNPs sensor with vapor flow rate 0.1 L/min.

2.3.6 Response time of LSPR sensing device

Before analyzing the response characteristics of the LSPR sensing device, we need to define two parameters. (1) The response time (T_{90}) is defined as the time period it takes to reach 90% of the final voltage in ethanol gas when the refractive index is changed from that of air to that of ethanol gas. ²⁾ The recovery time is defined as the time period it takes to reach 90% of the final stable voltage in air when the refractive index is changed from that of ethanol gas to that of air. As shown in Fig. 2.12, both the response time and the recovery time of this LSPR sensor device are less than 10 s, times that are

limited by the speed of gas mixing in the testing chamber, which is nonetheless faster than the typical T_{90} of SAW and MPC sensors, which are both greater than 10 s⁶⁾.

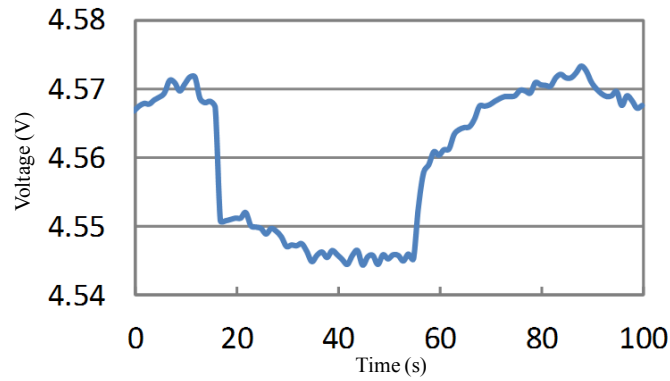


Fig. 2.12 Real-time response signal of LSPR sensing device³⁸

2.4 Conclusion

In this part, we demonstrated a high-speed LSPR gas sensor that was realized by directly sputtering Au or Ag NPs onto glass substrates. By varying the sputtering conditions, we obtained consistent knowledge of the NPs' optical characteristics and determined the relationship between the NPs' spectral characteristics and their morphology. Thermal annealing treatment in air at 200° C for different time periods was applied to reshape the initial sputtered NPs. By comparing the LSPR response ($\Delta\lambda_{\min}$ and $\Delta T_{\min}$) of the NPs to ethanol gas, we ascertained that AuNPs with a larger aspect ratio generate a larger response to the same refractive index change, and that the thermal stability of AuNPs is better than that of AgNPs. The real-time response characteristics of this LSPR sensor show that it can be applied in robots for high-speed gas detection.

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Chapter 3 Layer-by-layer Structured AuNPs Sensors for Terpene Vapors Detection

3.1 Introduction

Based on the results shown in chapter 2, it is hard to realize the strong electric field coupling in the sputtered Au nano-islands monolayer. Hence, in this part, the Au colloid was synthesis using the wet method to control the interparticle distance of AuNPs easily. Three-dimensional assemblies of NPs into multilayer structures on substrates obtained by the layer-by-layer self-assembly technique using bi-functional compound acted as a linker unit has succeeded in controlling the physical and chemical properties of organically encapsulated metal NPs ¹⁻⁷. This procedure can be repeated many times to built up an arbitrary number of well-defined layers. It has been reported that the optical properties of such multilayer structures can be tuned by varying the size of the metal particles ⁸⁻⁹ or the molecular structure of the encapsulating organic component ⁸⁻⁹. Researches on the layer-by-layer self-assembly of AuNPs films linked by alkanedithiol have shown that the electrical resistances of such multilayer structures depend on the length of the dithiol linkers ⁹⁻¹². In addition, it has been verified that the molecular structures of cross-linker could decide the optical characters of metal nanoparticle multilayers ¹⁻⁷.

Fabrication of patterned collections of nanoparticles has potentially important implications in nanoelectronic device fabrication and biosensing. One of interesting applications of AuNPs multilayer is as chemiresistor-type gas sensors ⁵. AuNPs linked by alkanedithiol with varying alkyl chain length showed a fast, reversible, and sensitive increase of their resistance when exposed to vapors such as toluene and tetrachloroethylene (TCE) ¹³. The vapor-sensitivity of such sensors is attributed to the film swelling and changes of the dielectric environment of NPs and the selectivity is controlled mainly by the solubility features of linker molecules to the target vapors. Other researchers have reported that the selectivity of this kind of sensor can be tuned by introducing chemical functionality into the cross-linkers which encapsulate the nanoparticles ¹³⁻¹⁴.

According to our previous studies, both bare AuNPs sensor ^{15, 16} can be used to detect

refractive index change induced by vapors through comparing the changes in their LSPR spectrum, and their response time is verified to be fast. The goal of our present study is to improve the sensitivity of the LSPR sensor and investigate the influence of molecular structure and natural characteristics of dithiol cross-linkers on the optical characters of AuNPs multilayer sensors and their vapor-sensing properties. AuNPs multilayers were fabricated via layer-by-layer self-assembly in AuNPs solution. In this layer by layer structured AuNPs, the number of electrical hot spots generated by the NPs coupling would increase greatly, compared with the AuNPs monolayer. Therefore, this structure is expected to increase the refractive index sensitivity of AuNPs sensor. The refractive index sensitivity of the layer-by-layer structured AuNPs sensors was investigated by detecting the red-shift of the minimum transmittance in wavelength ($\Delta\lambda_{\min}$) and the decrease of the minimum transmittance ($\Delta T_{\min}$) upon exposure to terpene vapors in LSPR spectra. Their response character was investigated by monitoring their spectra changes in three kinds of terpenes, α -pinene, β -caryophyllene, and myrcene, respectively. The sensing scheme is shown in Fig. 3.1.

3.2 Experimental

3.2.1 Preparation of Aqueous Au colloidal solution

3.2.1.1 Method 1³⁰

Solutions of Au nanoparticles in toluene were prepared as described by Brust and coworkers¹⁷. 30mL of 30mM aqueous solution of hydrogen tetrachloroaurate was mixed with 80 mL of a 50 mM solution of tetraoctylammonium bromide in toluene and stirred vigorously for at least 1h, and then waited for stratification. Extracted the organic phase tetrachloraurate and slowly poured 25 mL 0.5 M sodium borohydride aqueous solution with vigorous stirring. After the ruby-colored organic was separated, washed once with 0.1 M sulfuric acid, five times with water, respectively, and the final solution was thoroughly dried with anhydrous magnesium sulfate. The Au nanoparticles solution used was diluted to ~1000 mg/L. The average size of AuNPs is less than 10 nm.

3.2.1.2 Method 2^{28, 29}

AuNPs were prepared by sodium citrate reduction of HAuCl_4 ¹⁸. Sodium citrate tribasic dehydrate (SCTD) (SIGMA-ALDRICH) and hydrogen tetrachloroaurate (HTA) (Wako) were directly used as received. 7.25 mg of HTA in 20 ml distilled water was brought to a vigorous boiling with stirring in a round-bottom flask fitted with a reflux condenser, and a solution of SCTD (42.35 mg) in 15 ml distilled water was then rapidly added to the flask. The solution was boiled for another 15 min. During the process, the color of the solution was changed from pale yellow to deep red. The solution was allowed to cool to room temperature with continuous stirring. The final solution was stored at 4°C until further use, conditions under which the nanoparticles are stable for several months. The average size of AuNPs is about 48 nm.

3. 2. 2 Fabrication of layer-by-layer structured AuNPs films

3. 2. 2. 1Methods 1

APTES modified glass substrates were immersed into freshly prepared Au nanoparticles solution overnight. In the following, thoroughly rinsed with toluene and immersed in a 2 mM dithiol toluene solution for 1 h. Dithiol used in this study were 1,4-benzenedithiol (BDT) and 1,10-decanedithiol (DDT) without further process. Subsequently, layers were deposited alternately immersion in Au nanoparticles for 3 h and dithiol solution, respectively.

3. 2. 2. 2 Methods 2

APTES modified glass substrates were rinsed in ultrasonic bath of ethanol again for 5 min and dried at 105°C for 10 min¹⁸. Next, the silane-functionalized substrates were exposed to AuNPs solution for 12 h to form AuNPs monolayer on both sides of the glass substrates, and then rinsed copiously with distilled water. For the subsequent layers formation, the substrates were immersed in a 2 mM ethanolic solution of BDT and DDT, respectively. After 1 h, they removed, rinsed with copious amounts of ethanol, and dried in N_2 stream. Afterwards, they were immersed in AuNPs solution for another 12 h and rinsed thoroughly with distilled water. This process was repeated till the desired number of multilayer was obtained¹⁶. The molecular structures of dithiol are shown in Fig. 3. 1.

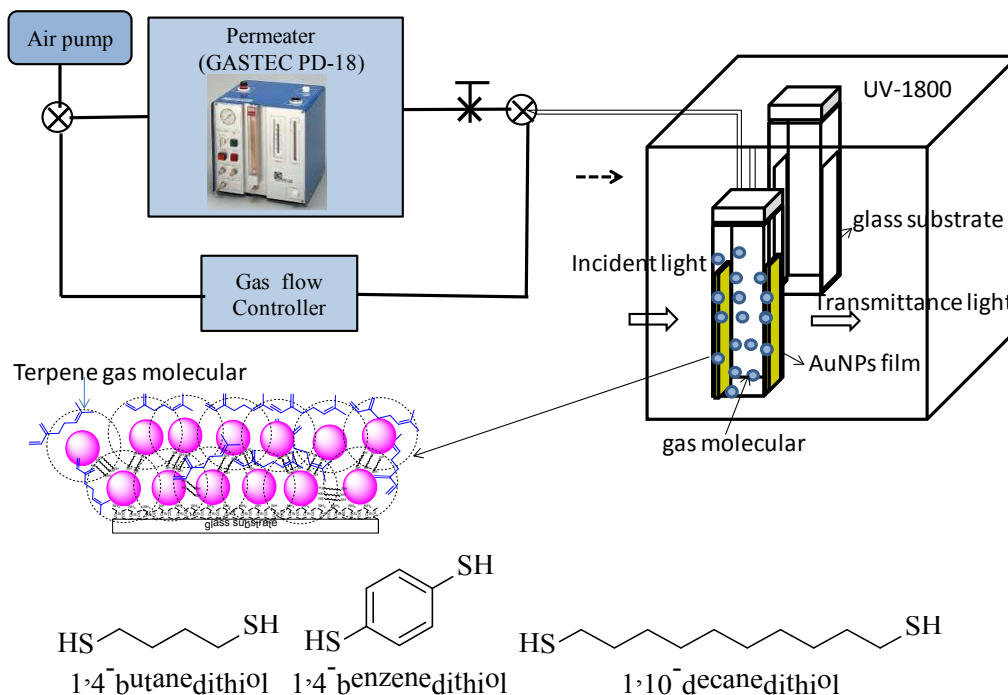


Fig. 3.1 The sensing scheme and molecular structures of dithiol in this research (A standard gas generator was adopted to generate terpene vapors, and concentrations of α -pinene, myrcene, and β -caryophyllene were calculated to be approximately 387 ppm, 194 ppm, and 5 ppm, respectively.)

3. 3 Results and discussion

3.3.1 UV-vis spectra of layer-by-layer structured AuNPs film

The UV-vis spectra of AuNPs (diameter: about 10 nm) multilayer are shown in Fig. 3.2. The spectra of four consecutive layers linked with 1,4-benzenedithiol and 1,10-decanedithiol both show no further broadening and loss of peak features after the deposition of four layers. Spectral wavelength of the minimum transmittance linked by 1,4-benzenedithiol and 1,10-decanedithiol shift from ~ 530 nm to ~ 570 nm and ~ 565 nm, respectively. Comparing the color of four layer structured 1,4-benzenedithiol and 1,10-decanedithiol linked Au films, the 1,4-benzenedithiol linked film is light purple while the color of 1,10-decanedithiol linked Au films is dark purple. The similarity of these two different AuNPs multilayer is presented by that for both longer cross-linker

1,10-decanedithiol and 1,4-benzenedithiol linked AuNPs multilayer, the transmittance in the visible region decreases linearly as a function of colloid coverage. In addition, the spectra of AuNPs multilayer always keep the one peak characteristic.

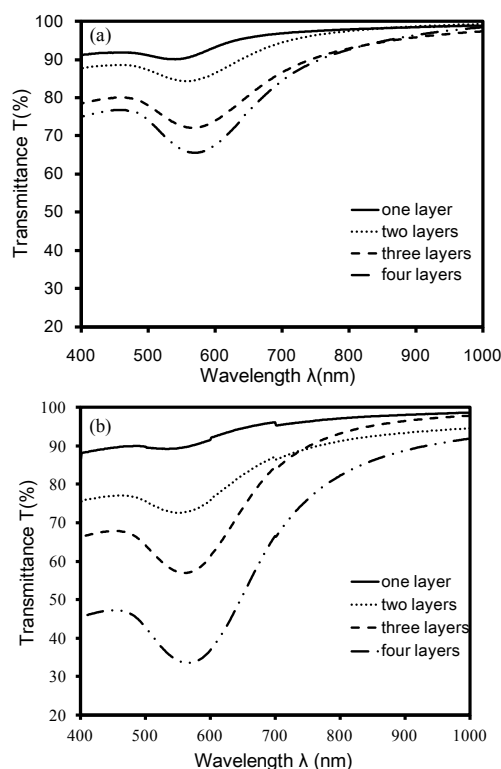


Fig. 3.2 UV/vis spectra of AuNPs multilayers (diameter: about 10 nm) linked with (a) 1,4-benzenedithiol and (b) 1,10-decanedithiol ³⁰.

In comparison, spectra of AuNPs (diameter: about 48 nm) multilayers linked by DDT and BDT in air are shown in Fig. 3.3. With the spectrum from the particle solution that was used for film preparation. Compared to the solution-phase spectrum, the plasmon adsorption of the film is broadened and significantly shifted to longer wavelengths (red shift). This phenomenon is due to differences in the dielectric environment (water and glass substrate) of the nanoparticles as well as the interactions between particles (coupling between nanoparticles) ^{7, 13}.

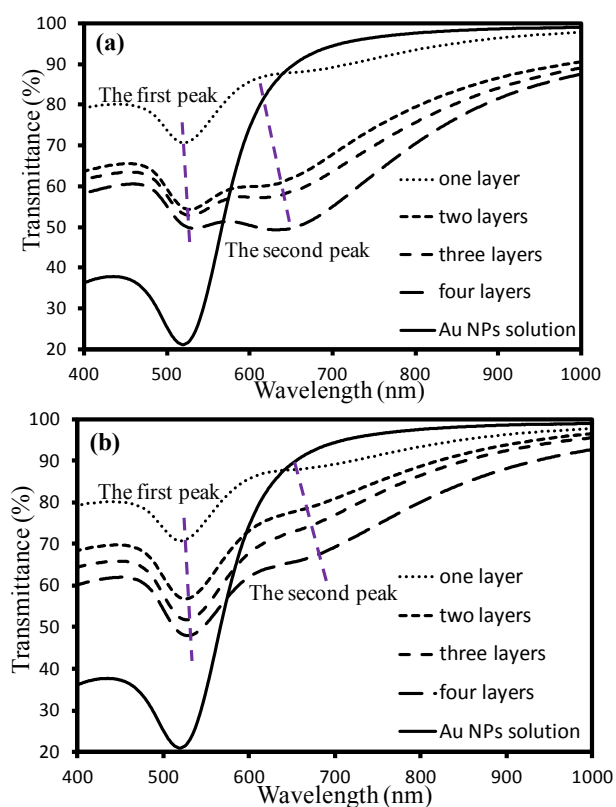


Fig. 3.3 The UV-vis spectra of AuNPs multilayer structures (a) AuNPs multilayers cross-linked by DDT, (b) BDT ^{28, 29}.

Fig. 3. 3 (a) shows the spectra of AuNPs multilayers linked by DDT. It was observed that there were two transmission peaks for all multilayer structures cross-linked by DDT with the exception of the first deposition, which is different from AuNPs multilayer comprised of small sized AuNPs as shown in Fig. 3.2. The first minimum transmission peak (λ_1) and the second minimum transmission peak (λ_2) appeared at around 520 nm and 615 nm, respectively. With layer number increase, the wavelength of both λ_1 and λ_2 slightly shifted to the red. The first peak can be attributed to the LSPR dipole polarization from single AuNPs and aggregates in self-assemble process, while the second peak comes from the dipole-dipole interaction between NPs and their aggregates ¹⁶. The slope of the second transmission peak gradually increased with the deposition process, which suggested that more AuNPs contribute to the plasmon dipole-dipole coupling. This two-band feature is different from the previous results of our group ¹⁹, in which small-sized AuNPs (smaller than 10 nm in diameter) were used to form the

multilayer structure, and only one plasmon band was observed even with the layer number of AuNPs multilayers increased to 4. We attributed the difference to be the size effect of AuNPs (less than 10 nm in diameter), which leads NPs in multilayers to aggregate easily on the influence of dithiol cross-linker, and make NPs pack closely and display the characteristic plasmon resonance as coupled clusters^{8, 19}.

AFM images of APTES modified glass substrate and DDT linked AuNPs multilayers are shown in Fig. 3.4. The quality of formed APTES layer depends on surface hydroxyl group, concentration of silane and ambient water and CO₂^{20, 21}. Here, the RMS roughness APTES layer is 0.4731 nm. Hence, the layer is thought to be a relatively uniform monolayer as shown in Fig. 3.4 (a). It could be clearly seen that AuNPs formed a submonolayer after the first deposition as shown in Fig. 3.4 (b). Most NPs (about 50 nm) were isolated with each other, and uniformly distributed on glass surface. With deposition cycle increase, Au clusters were formed randomly. After 4 deposition cycles, as shown in Fig. 3.4 (e), continuous interacting NP clusters were produced. When the deposition cycles reached to 10, a more condensed NPs layer was gained, and the thickness increased to about 600 nm as shown in Fig. 3.5. Both AFM and SEM images revealed that the average thickness of the multilayer structures increased with deposition process.

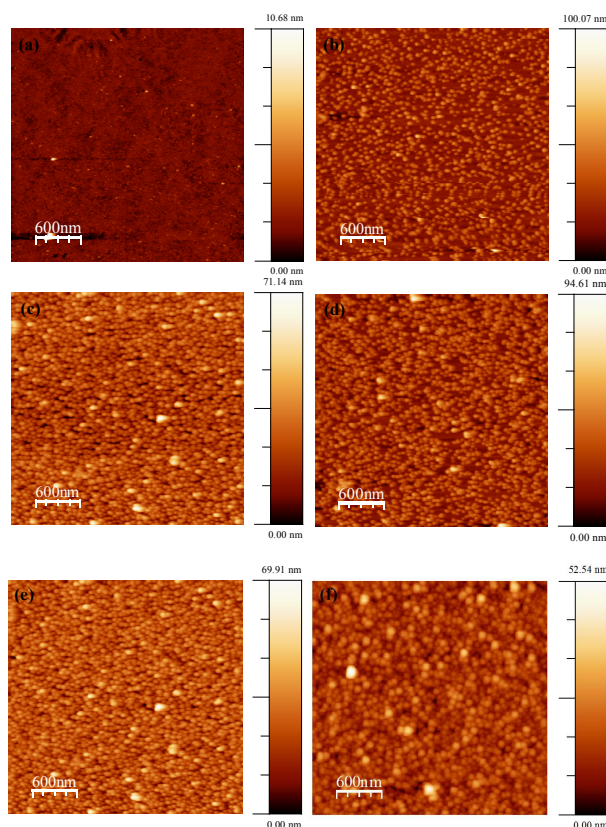


Fig. 3.4 AFM images of APTES modified glass substrate²⁸
 (a) and Au NPs multilayers with (b) 1, (c) 2, (d) 3, (e) 4 depositions cross-linked by 1,10-decanedithiol; (f) 4 depositions cross-linked by 1,4-benzenedithiol.

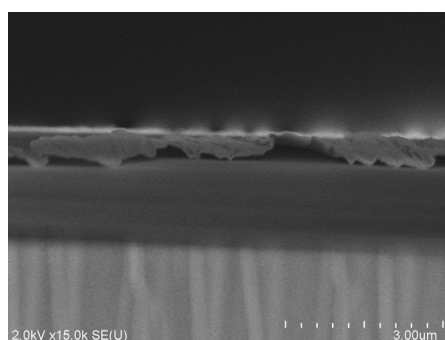


Fig. 3.5 SEM image of Au NPs multilayer cross-linked by 1,10-decanedithiol with 10 depositions²⁸

The study of the activation energies indicates that in the case of noncovalently organized particles only the cluster spacing is of relevance, and the linking molecules simply act as spacers, independent of their chemical nature²². The simple relation

proposed by Neugebauer and Webb was often adopted to describe the conductivity of alkanethiol²³ even alkanedithiol^{13,24} stabilized AuNPs networks.

$$\sigma = \sigma_0 \exp[-E_a/RT] \quad (3-1)$$

In this expression, σ_0 is a constant, T represents the absolute temperature, R is the gas constant, and E_a is the electrostatic activation energy of charge transport.

$$E_a = (1/2) \frac{e^2}{4\pi\epsilon\epsilon_0} [r^{-1} - (r + s)^{-1}] \quad (3-2)$$

In which r is the radius of the particle, s is the interparticle spacing given by the length of the dithiol spacer arm, and ϵ is the relative permittivity of the material between the particles. We assumed that different dithiol linkers will not generate big difference in ϵ ¹. According to these two equations, when the particle size is a constant, E_a will increase with the length of the dithiol spacer, while the σ will decrease with it. While covalently cluster-linking species, possessing delocalized π -electrons (the case of BDT), enable inter-cluster electron transfers by lower activation energies, not only on their lateral extension²².

The spectra of AuNPs multilayers linked by BDT in Fig. 3.3 (b) show one distinct transmission peak at about 528 nm. While when the layer number increased to four, there was tendency to emerge second plasma peak at about 650 nm, which were different from the spectral characters cross-linked by DDT. AFM image of BDT linked Au multilayer with 4 depositions was shown in Fig. 3.4 (f). The continuous interacting NPs and clusters were produced, but the average size of NPs and clusters here were larger. We speculated that the differences in spectra and morphology were mainly attributed to the molecular nature of dithiol linkers. Electrical conductance of BDT (with conjugated π system) is much larger than that of DDT, and the molecular size of BDT (7.44 Å) is much smaller than DDT (15.23 Å). As a result, NPs in intra- and inter- layers linked by BDT cannot be separated well electrically and show the plasmon resonance feature as larger Au clusters instead of separated NPs. Based on the above fact, a schematic three-dimensional multilayer structure of Au NPs assembled on glass substrate cross-linked by DDT and BDT with two deposition cycles were ideally drawn and shown in Fig. 3.6. BDT linked multilayers shows the character of NP clusters, while DDT linked one still keep the

feature of separated NPs, which is consistent with their optical properties as shown in Fig. 3.3.

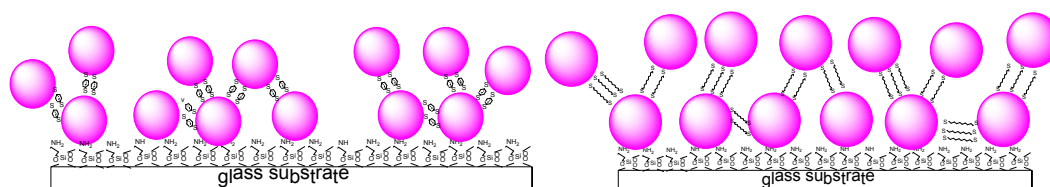


Fig. 3.6 The schematic diagram of Au NPs films ^{28, 29}

3.3.2 UV-vis spectra of dithiol linked AuNPs in solution

NPs solution-phase spectra linked by 1,4-butanedithiol (UDT) (molecular length: 7.825 Å), BDT(7.44 Å), and DDT (15.23 Å) were detected. The spectra AuNPs solution (2.5 mL) mixed with 2 mM BDT, DDT, and UDT ethanol solution (0.5 mL) after 2 h were investigated, respectively. As shown in Fig. 3.7 (a), adding BDT solution, the transmission band (TB) of the original AuNPs solution was broadened, the minimum transmittance ($T_{\min}$) was decreased, and the wavelength of minimum transmittance ($\lambda_{\min}$) shifted to longer wavelengths, which was similar with the spectra of NPs multilayers on glass substrate. Adding the same amount of DDT solution, the broadening of TB, decreasing of $T_{\min}$, and the red-shift of $\lambda_{\min}$ were more conspicuous than adding BDT. It worth mentioning that there was only one transmission peak, which was different from DDT linked AuNPs multilayers on glass substrate. These differences could be attributed to the reason that the length or chemical nature (or both) of dithiol linkers such as DDT in bathing medium were different from the particle film, and the inter-particle distance in solution is larger than that on glass substrate ²⁴. As a result, the interparticle distance linked by DDT in solution is not short enough, so particle-particle interaction (coupling) is weak. Adding the same amount of UDT solution, the spectra showed two peak features. Molecular length of UDT is much shorter than DDT, so the distance between UDT linked NPs is short enough in solution-phase. Therefore, the particle-particle interaction is enhanced by UDT linked NPs. Here, we found that although UDT and BDT share the similar molecular length but different spectra.

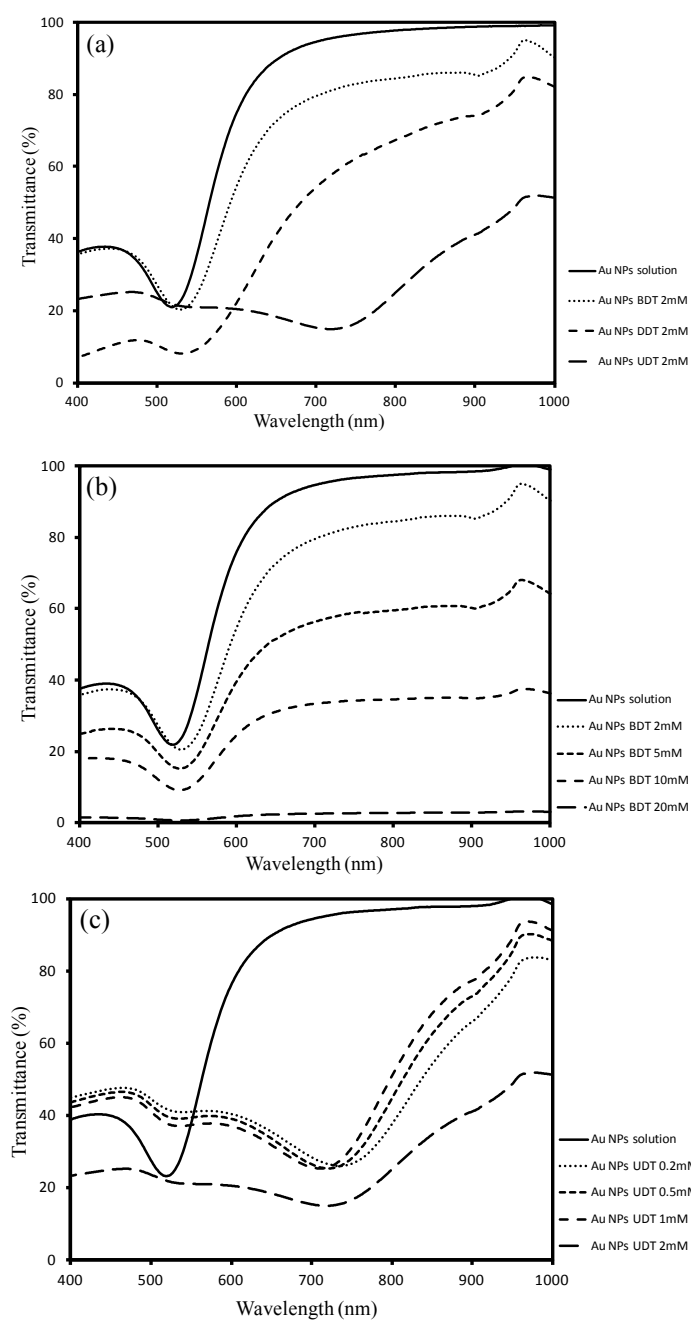


Fig. 3.7 The UV-vis spectra of AuNPs solution adding dithiol

(a) AuNPs solution adding with the same amount of BDT, DDT, and UDT, (b) AuNPs solution adding different amount of BDT, (c) Au NPs solution adding different amount of UDT ²⁸.

For further analyzing the spectra difference linked by BDT and UDT, the spectra of AuNPs solution (2.5 mL) mixed with difference molar ratio of UDT and BDT ethanol

solution (0.5 mL) were detected. In Fig. 3.7 (b), with the increase of BDT molarities from 2 mM to 20 mM, the TB became more pronounced, and the $T_{\min}$ decrease became more conspicuous, while the spectra still kept one-peak feature. Conversely, we decreased the molarities of UDT solution from 2 mM to 0.2 mM, the spectra still demonstrated two-peak feature as shown in Fig. 3.7 (c). Upon the addition of a small amount of UDT, the intensity of the plasmon absorbance at about 520 nm was reduced and a band at about 721 nm was formed. According to Michal Lahav and coworkers⁵, the intensity of the second absorbance was enhanced at the expense of the plasmon absorbance of individual particles. When the concentration of UDT was high enough, the solution turned blue and the particles ultimately precipitate. Based on all the above analysis, we gained two speculations. The spectral differences were caused by the molecular characteristics of dithiols instead of their amount. The other was that not only the molecular length but also their chemical nature (electron conductive characteristic) took effect on the final LSPR characteristics of AuNPs multilayer structures.

3.3.3 The refractive index sensitivity of AuNPs multilayer sensors

The refractive index sensitivity (RIS) of AuNPs multilayer sensors is defined by a red-shift of the minimum transmittance in wavelength ($\Delta\lambda_1$ and $\Delta\lambda_2$) and a decrease in the minimum transmittance (ΔT_1 and ΔT_2) induced by the refractive index change. We detected the RIS of sensors to water. As shown in Fig. 3.8 (a), for Au multilayers sensors linked by DDT, the RIS of both individual NPs or aggregates ($\Delta\lambda_1$ and ΔT_1) and dipole-dipole coupled NPs or aggregates ($\Delta\lambda_2$ and ΔT_2) increase with the number of AuNPs layer, and arrived to the maximum value at three layers (depositions). We attributed this result to that with layer number increase, the electric field coupling of AuNPs in intra- and inter- layers was enhanced because of NPs number increase. As a result, the RIS of the multilayer sensor was also enhanced. However, with NPs number or density continuing increase, the LSPR in individual NPs or aggregates and dipole-dipole coupling between them in the bottom layers could be covered by those in the top layers¹⁶, so the RIS decreased when the layer number was 4. On the contrary, the RIS of AuNPs multilayer sensors cross-linked by BDT kept an increasing tendency versus layer number as shown in Fig. 3.8 (b). As shown in Fig. 3.4 (e), the average size

of aggregated NP clusters in BDT cross-linked multilayers was bigger. Hence, we speculated that their LSPR characters were also similar with large-sized Au clusters. Large-sized Au clusters could generate longer and stronger electromagnetic field ²⁵⁻²⁶, and the electric field coupling would be stronger. Therefore, the refractive index sensitivity would be improved as well. We choose the transmittance peak change per refractive index unit, $\Delta\lambda_1/\text{RIU}$ and $\Delta\lambda_2/\text{RIU}$, as the normalized RIS of the multilayer AuNP film to the changes in refractive index. Here, $(\Delta\lambda_1/\text{RIU})$ of AuNPs monolayer and BDT linked one (with four depositions) were calculated and compared. The refractive index change was 0.33 (n change from 1 (air) to 1.33 (water)), and the related RIS was calculated to be 21.21 nm/RIU and 60.99 nm/RIU, respectively. Therefore, we concluded that the sensitivity enhancement could be attributed to the electrical field coupling from multilayer structure. The normalized RIS here is almost the same with that of AgNPs (37 ± 4 nm in diameter ²⁷).

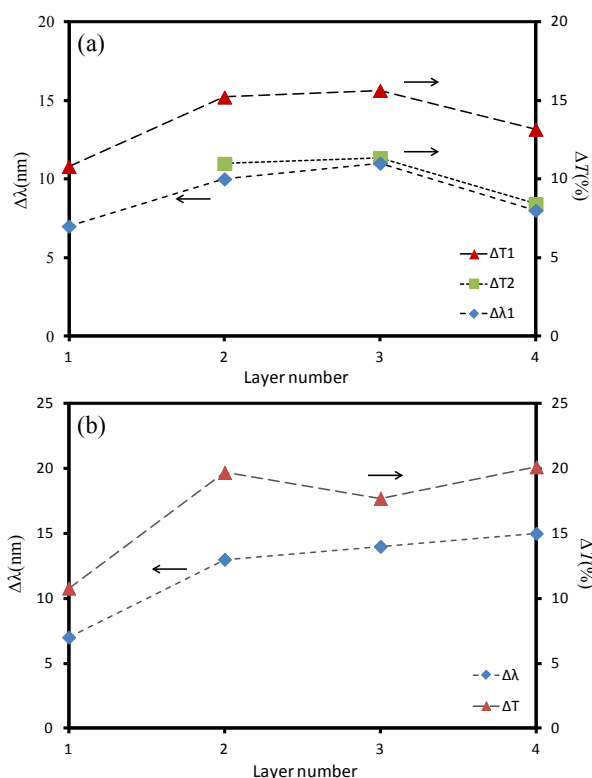


Fig. 3.8 The refractive index sensitivity (RIS) of Au NPs multilayer sensors: (a) cross-linked by DDT, (b) cross-linked by BDT ²⁸.

3.3.4 The LSPR response of AuNPs multilayer sensors

Comparing all RIS results, AuNPs multilayer sensors cross-linked by BDT with 4 layers were used to detect their real-time response to three kinds of terpene vapors: α -pinene, myrcene, and β -caryophyllene. Fig. 3.9 (a), (b), and (c) show the response signal of single point transmittance at $\lambda=528$ nm to these three kinds of vapors, separately. Terpene vapor flow were switched on for 120 s and switched off for 120s during all the test cycles. Transmittance values were sampled at 1s interval. The response time (T_{90}) was defined to be the time period for reaching 90% of the final transmittance in terpene gas, and the time period for recovering 90% of the final transmittance in air was defined as the recovery time (T'_{90}). As described in our previous research ¹⁵, the speed of gas mixing in the testing chamber affects the final response time and recovery time, so we only calculated response time and recovery time of β -caryophyllene, and the values T_{90} and T'_{90} were about 2 s and 3 s neglecting the delays in manual operation. Its related detection limit (3δ) was calculated to be 2.45 ppm for β -caryophyllene. The responses of AuNPs multilayer sensors to changes in terpene vapor concentration were rapid, reversible, and reproducible. The single wavelength transmittance response appeared to be noisy due to the small background vibrations of the UV-vis spectrophotometer.

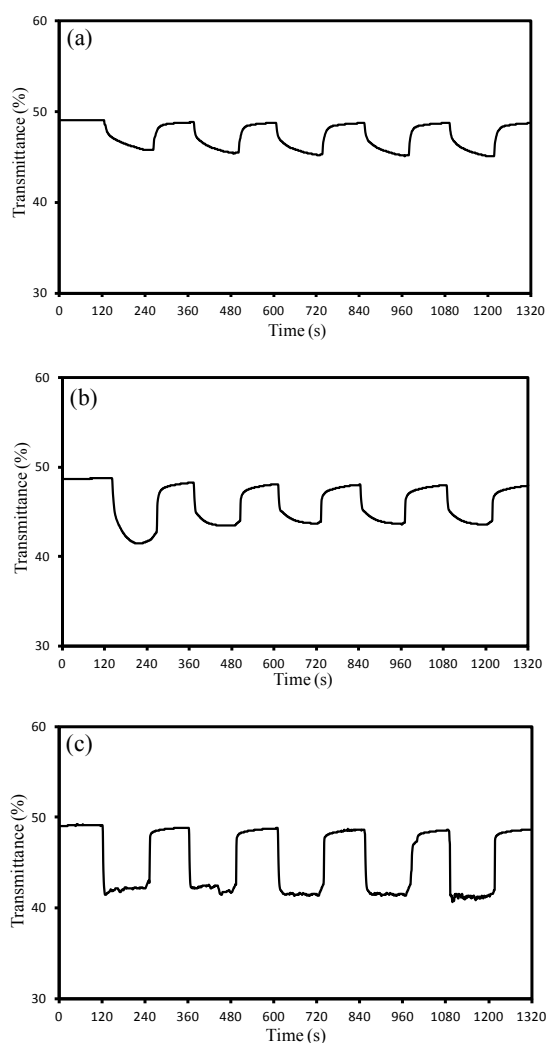


Fig. 3.9 Real-time response signal of AuNPs multilayer sensor to terpene the real-time response signal of AuNPs multilayer sensors to (a) α -pinene, (b) myrcene, (c) β -caryophyllene²⁸.

3.4 Conclusion

We have successfully fabricated the AuNPs self-assembled multilayer structures on glass substrate by using the layer-by-layer self-assembly technique to detect terpene vapors. The LSPR optical characteristics of multilayer structures were verified to be mainly attributed to the dithiol molecular length and their chemical nature. The normalized RIS of AuNP multilayer was increased to about three times, compared with the monolayer structure. The refractive index sensitivity of resulting AuNPs multilayer sensors to three kinds of terpene vapors was investigated. The results showed that

AuNPs multilayers linked by BDT with four NP deposition cycles exhibited the highest sensitivity, which was attributed to the plasmon coupling and NPs' size effect. The real-time responses of AuNPs multilayer sensors to changes in terpene vapor concentration were verified to be rapid, reversible, and reproducible. However, the refractive index sensitivity improvement of this multilayer structured AuNPs sensor to terpene vapors was very limited. In addition, there is no specific selectivity of multilayer structured AuNP sensor to gas molecules.

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Chapter 4 Terpene Detection Based on Localized Surface Plasma Resonance of Thiolate Modified Au nano-islands

4.1 Introduction

An intrinsic feature of the AuNPs is the large fraction of atoms located at the surface that are modified when the particle is capped with different chemical species. Thus the capping agents can alter significantly the whole NP properties. An example of strong interaction between the NPs and the capping agent are the thiol-capped AuNPs. It has been shown that the thiols induce changes in the electronic configuration of the NPs, increasing the hole density at the $5d$ Au level ^{1-7, 12}. As a consequence of these changes in the electron configuration, the physical properties of the NPs change significantly ³. Thiol-capped AuNPs also exhibit a wider SPR than bare NPs, which is associated with an extra damping due to the interaction of conduction electrons with the thiols ^{8, 9}.

There are two proposed explanations for the changes induced in the SPR of AuNPs by thiol capping: the reduction of electron density in the NPs and the increase of damping due to charge localization at the NP surface. In a recent work ⁹, Lica et al. proposed that the changes in the SPR of thiol-capped NPs are due to the decrease in Au $5d$ electrons because of the charge transfer from Au atoms at the NP surface to S atoms at the end of the thiol chain. The other argument proposed to explain the changes induced in the SPR by thiol capping is the charge localization at the Au-S bond. This covalent bond blocks the electrons involved in the bond at the NP surface. The localized charge will have an electrostatic interaction with the NP conduction electrons, inducing an extra damping in the electrons oscillation called chemical interface damping and therefore, enhancing the SPR bandwidth ^{1,2,3}.

In this study, a sensor based on LSPR of AuNPs sputtered on transparent glass substrates was proposed to detect terpene vapors. The dependence of transmission spectra of AuNPs with different sputtering conditions was investigated. A decrease in transmittance and a red-shift was observed when exposed to three terpene vapors: β -caryophyllene, α -pinene, and myrcene. AuNPs were modified by thiolate to enhance the selectivity and sensitivity of the LSPR sensor. The structural characters of thiolate-capping layers on LSPR responses were discussed. The mutual inference

between terpene molecules and the thiolate layer is expected to generate certain selectivity.

4.2 Experimental

4.2.1 Thiolate Au nano-islands surface modification

Thiolate agents (TOKYO Chemical Industry) were directly used as received. The molecular structures of thiolate and terpene are shown in Fig. 4.1. The solutions of thiolate (2.5×10^{-4} M) were prepared by dissolving 1-dodecanethiol, hexyl mercaptan, 2-mercaptobenzothiazole, 4-methoxy- α -toluenethiol, 3-methoxybutyl 3-mercaptopropionate, methyl 3-mercaptopropionate, 1-octadecanethiol, and 11-mercapto-1-undecanol in ethanol, respectively. Glass substrates with sputtered Au NPs (sputtering condition: 1.5 mA 60 s, 200 °C 5 h annealing) were immersed in the thiolate solutions for 1 h to form the thiolate-capping layers. The substrates were rinsed thoroughly with ethanol to remove unreacted thiolates, dried by N₂ stream, and preserved in vacuum before use.

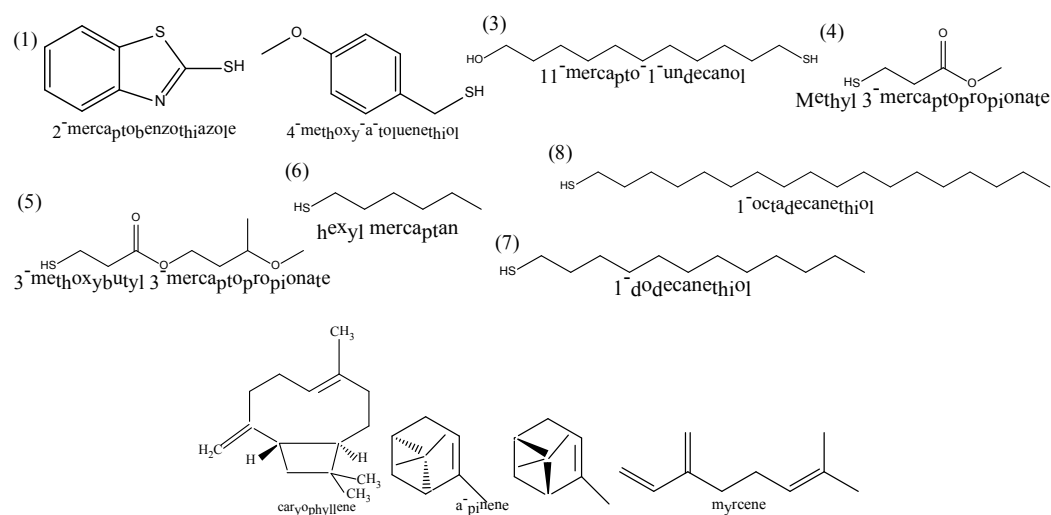


Fig. 4.1 Chemical structures of thiolate and terpenes used in this study²⁵

4.2.2 Terpene vapors generation

A bubbling method was used to generate terpene vapors with standard concentrations. A water bath was used to control the temperature. For α -pinene, myrcene, and ethanol,

the temperature was set to be 30°C, and the temperature was set as 60°C for generating β -caryophyllene vapor. The concentrations of terpene vapors were calculated in the light of following formula:

$$C = \frac{K \times Dr \times 10^3}{F} \quad (4-1)$$

where C (ppm) is the standard gas concentration, Dr ($\mu\text{g}/\text{min}$) is diffusion rate at the set temperature, F (mL/min) is the flow rate of diluent gas, and was set to be 0.475L/min in bubbling process. K is the factor for converting gas weight to gas volume which can be calculated according to the formula as follow:

$$K = \frac{22.4}{M} \times \frac{273+t}{273} \times \frac{760}{P} \quad (4-2)$$

where M is molecular weight, t is 25°C, and P is 760 mmHg. The values of Dr for three kinds of terpene were obtained by calculating the weight-loss of terpene liquid under the dilute gas (air) at a flow rate of 0.475 L/min for 30 min. For the bubbling method, the values of Dr for ethanol, α -pinene, myrcene, and β -caryophyllene were measured to be 85385 $\mu\text{g}/\text{min}$, 17943 $\mu\text{g}/\text{min}$, 10533 $\mu\text{g}/\text{min}$, and 1113 $\mu\text{g}/\text{min}$, separately. Substituted Dr into formula (4-1), the final concentrations of ethanol, α -pinene, myrcene, and β -caryophyllene were approximately 95137 ppm, 6780 ppm, 3980 ppm, and 280 ppm, respectively.

A dilution method was used to generate terpene vapors with low concentrations. The temperature of the gas generating chamber in a permeator was set to be 50°C, and the flow rate of dilute gas (air) was set to be 0.2 L/min lasting for 30 min. The values of Dr for α -pinene, myrcene, and β -caryophyllene were measured to be 431 $\mu\text{g}/\text{min}$, 216 $\mu\text{g}/\text{min}$, and 8.33 $\mu\text{g}/\text{min}$, and the final concentrations of were calculated to be approximately 387 ppm, 194 ppm, and 5 ppm, respectively.

4.3 Results and discussion

4.3.1 Optical and morphological characters of sputtered AuNPs on glass

The transmission spectra of Au NPs with different sputtering time were investigated. Controlling the sputtering current to be 1.5mA and sputtering time increasing from 20 s to 80 s, as shown in Fig. 4.2 (a), decreases in transmittance and the spectral red-shift in wavelength were observed. The minimum transmittance ($T_{\min}$) decreases from about

88.1% to 49.5%, and wavelength of the minimum transmittance ($\lambda_{\min}$) shifts from 549 nm to about 649 nm with sputtering time increasing to 80 s.

Thermal annealing treatment is a commonly used method for NPs reshaping, which is based on the fact that the difference in thermal expansion coefficient between the metal and substrates leads to NPs reorganization due to the relaxation of the thermal stress during the course of the annealing process¹⁰. Here, a relatively low temperature (200°C) and a long annealing time (20 h) were chosen to protect the organic adhesive layer (low temperature) while enable AuNPs reorganization (long time). Hence, both annealed and unannealed AuNPs demonstrated the good adhesion provided by the APTES interlayer¹¹). Transmission spectra of thermal annealed AuNPs with the same sputtering conditions on glass are shown in Fig. 4.2(b). After annealing treatment, the decreases in transmission spectra and the spectral red-shift were also observed. With sputtering time varying from 20 s to 80 s, $T_{\min}$ decreases from 88% to 53.8%, and $\lambda_{\min}$ shifts from 526 nm to 549 nm. In addition, annealing treatment induces a blue shift in wavelength and a marked bandwidth narrowing of transmission spectrum comparing with the unannealed ones.

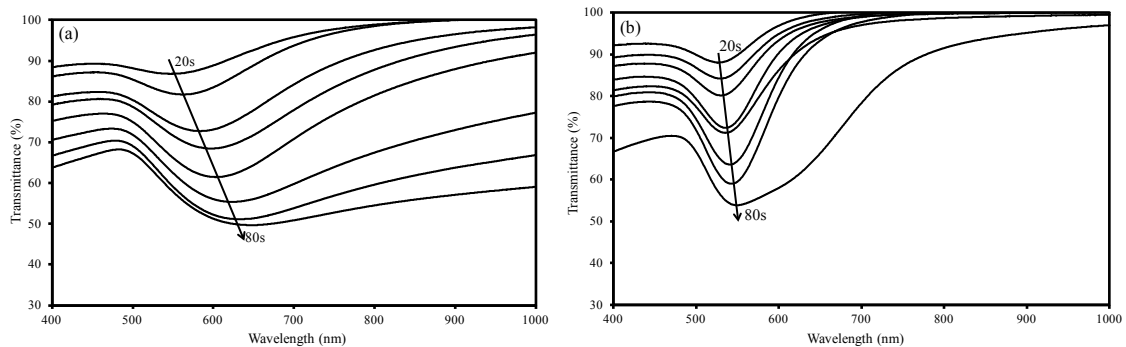


Fig. 4.2 The LSPR spectra of AuNPs prepared with different sputtering condition. The sputtering current is 1.5 mA, the sputtering time increases from 20 s, 25 s, 30 s, 40 s, 50 s, 60 s, 70 s to 80 s; (a) and (b) shows the LSPR spectra of Au NPs before and after 200°C, 20 h annealing treatment²⁵.

AFM images of Au NPs deposited on glass were investigated and shown in Fig. 4.3 (a). Both the in-plane width and out-of-plane height of NPs increase with increasing in

sputtering time. Through calculating the profile height of AuNPs on glass, we observed that the out-of-plane height of NPs increases from 3.59 nm to about 9.27 nm, while the in-plane width increases from 10 nm to larger than 30 nm with sputtering time increasing from 20 s to 80 s. This result indicated that the increase in sputtering time resulted in the increase of aspect ratio of AuNPs. In addition, the shape of NP varied from sphere to irregular ellipse with one axis obviously extended with sputtering time increase to 80 s.

Thermal annealing treatment can lead to neighboring NPs combine with each other and form larger clusters¹³, which phenomenon is verified by the result shown in Fig. 4.3 (b). The out-of-plane height of AuNPs with 60 s sputtering time is less than 7.26 nm, after annealing treatment, this value increases to 20 nm. However, NPs' in-plane width does not show conspicuous increase. The obvious out-of-plane height increase and neglectable in-plane width increase trend illustrates that NPs' aspect ratio decreased by thermal annealing treatment. Moreover, thermal annealing treatment makes the shape of NP become round, which means that the irregular edges and sharp points of NP will disappear. This result indicates that the stronger EM field induced by these irregular edges and sharp points will also disappear after annealing treatment. According to the above results, we suggest that the decrease in NPs' aspect ratio induced by thermal annealing leads to the blue-shift of $\lambda_{\min}$ in LSPR spectra. While the spectral bandwidth narrowing are primarily attributed to the aspect ratio decrease and the round shape of thermal annealed NPs.

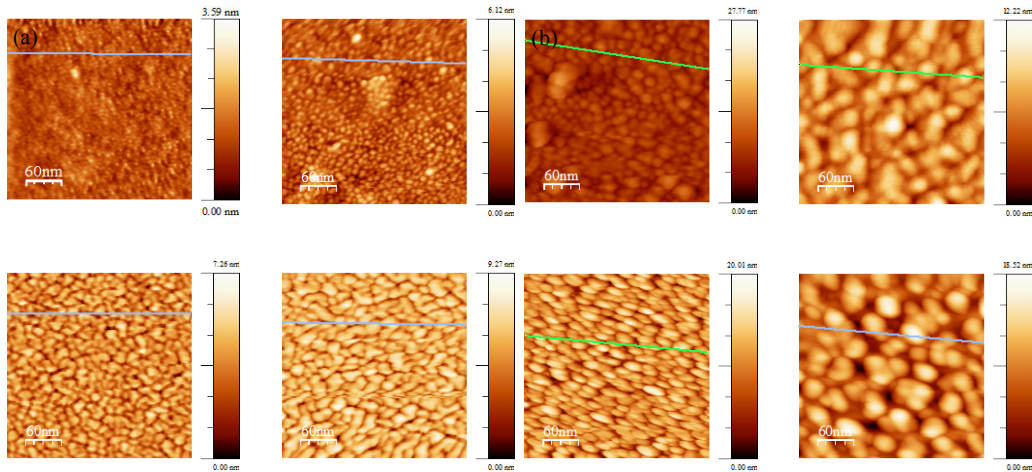


Fig. 4.3 AFM images of AuNPs ²⁵.

(a) the morphology of AuNPs on glass before annealing with sputtering current 1.5 mA and sputtering time 20 s (1.5 mA/20 s), 1.5 mA/40 s, 1.5 mA/60 s, and 1.5 mA/80 s from the left to the right; (b) the morphology of AuNPs on glass after annealing with sputtering conditions: 1.5 mA/20 s, 1.5 mA/40 s, 1.5 mA/60 s, and 1.5 mA/80 s after annealing treatment.

4.3.2 LSPR spectrum response

LSPR response of AuNPs to local refractive index change can be ideally explained by the bi-layer structure formed by volatile organic chemicals. A thin adsorbed film of uniform thickness d and index of refraction n_a is bonded to the metal surface. Refractive index of the medium above this adsorbate layer is n_s , and the LSPR response R ($\Delta\lambda_{\min}$) to the effective refractive index of the bi-layer can be written as ^{14, 15}

$$R = m(n_a - n_s)[1 - \exp(-2d/l_d)] \quad (4-3)$$

where m is the refractive index unit, l_d is the electromagnetic field decay length. According to this equation, it can be roughly considered that the LSPR response to the same local refractive index change is proportional to l_d , which is mainly related with the structural characters of AuNPs such as size and shape.

In order to test the response character of AuNPs, the LSPR response of NPs to ethanol gas was investigated. LSPR responses of AuNPs to ethanol gas generated by bubbling method are shown in Fig. 4.4. The response is defined by the minimum transmittance shift in wavelength ($\Delta\lambda_{\min}$) in addition with the minimum transmittance

decrease ($\Delta T_{\min}$). The normalized LSPR response ($\Delta\lambda_n$ and ΔT_n) of AuNPs to the ethanol gas were calculated and shown in Table 4.1. LSPR response ($\Delta\lambda_n$) reaches its maximum 20.75 nm when the sputtering time is 60 s, and then decreases with sputtering time further increase. ΔT_n shows the similar response tendency. After annealing treatment, the LSPR responses ($\Delta\lambda_n$ and ΔT_n) of NPs decrease. AuNPs with the sputtering time 70 s has the largest $\Delta\lambda_n$ (12.66 nm) which is smaller than its value before annealing. These results can be explained by NPs' morphology (shape and aspect ratio). It has been reported that the sharp structural features of NPs tend to increase charge separation and reduce the restoring force for the dipole oscillation in NPs, so around the sharp corner, the hot spot of electromagnetic field (sensitive field to local refractive index change, namely, larger m in Eq. 4-3 can be generated. In addition, the number of resonances increases as the symmetry of a structure decreases¹⁶. Hence, nanostructure with larger aspect ratio produces strong a electromagnetic field (larger m) and longer l_d . This can be used to explain the variance of LSPR responses of NPs before and after annealing treatment.

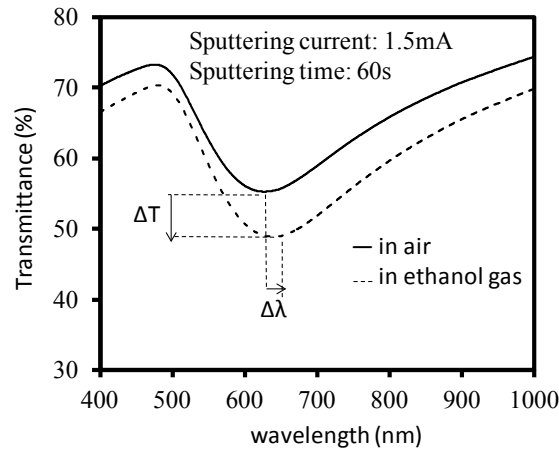


Fig. 4.4 LSPR spectra of AuNPs in air and ethanol gas²⁵.

Tab. 4.1 The local refractive index sensitivity of ethanol gas ²⁵

Sputtering time (s)	unannealed				annealed			
	$\Delta\lambda/\lambda*1000$	SD	$\Delta T/T*100$	SD	$\Delta\lambda/\lambda*1000$	SD	$\Delta T/T*100$	SD
20s	0	0	1.61	0.22	7.11	0.47	3.95	0.99
30s	12.88	2.60	4.34	0.29				
40s	15.49	1.24	5.95	0.35	5.35	0.72	6.20	0.84
50s	17.96	3.08	7.87	0.86				
60s	20.75	0.01	11.79	0.33	11.11	0.93	11.13	0.66
70s	14.61	8.27	12.80	0.45	12.66	0.23	15.00	0.09
80s	17.20	7.19	12.51	0.39	12.28	0.45	5.08	0.11

$\Delta\lambda/\lambda*1000$ and $\Delta T/T*100$ are the normalized LSPR local refractive index sensitivity $\Delta\lambda_n$ and ΔT_n , SD: standard derivation.

Based on the LSPR response of Au NPs to ethanol gas, we selected the optimum sputtering condition (1.5 mA/60 s) to deposit AuNPs on glass without annealing to test the LSPR responses to terpenes β -caryophyllene, α -pinene, and myrcene. As shown in Table 4.2, the normalized LSPR responses to these three terpenes are different due to the different local refractive indexes generated by terpenes. The normalized LSPR responses ($\Delta\lambda_n$) to α -pinene, myrcene, and β -caryophyllene are 30.39 nm, 17.63 nm, and 7.21 nm, respectively. This result demonstrated that terpene vapors can be detected by the LSPR phenomenon of AuNPs. In addition, the LSPR response increased with the increase in concentrations of vapors, but the response did not show the linear relationship with the increase in concentrations, which indicated that this concentration range of terpene vapors may have exceed the saturated concentrations of the LSPR response ^{17,18}.

Tab. 4.2 The normalized local refractive index sensitivity of naked AuNPs to terpenes ²⁵

terpenes	unannealed			
	$\Delta\lambda/\lambda*1000$	SD	$\Delta T/T*100$	SD
β -caryophyllene	7.21	1.76	3.16	0.49
α -pinene	30.39	6.58	14.34	1.06
myrcene	17.63	6.74	10.90	0.44

$\Delta\lambda/\lambda*1000$ and $\Delta T/T*100$ are the normalized LSPR local refractive index sensitivity $\Delta\lambda_n$ and ΔT_n , SD: standard derivation.

4.3.3 Thiolate-modified AuNPs for terpene detection

Thiolate surface modification was applied based on the hypothesis ¹⁶ that the selective dissolving ability of thiol-capping layers to vapors and affinity between thiol-capping layer and vapor molecules can be used to improve the selectivity and sensitivity of the LSPR sensor. Eight kinds of thiolate were applied to modify AuNPs for detecting their LSPR responses to β -caryophyllene, α -pinene, and myrcene. As shown in Fig. 4.5, the LSPR responses ($\Delta\lambda_n$) of 2-mercaptobenzothiazole-modified AuNPs to β -caryophyllene and 4-methoxy- α -toluenethiol-modified Au NPs to myrcene is 15.91 nm and 24.72 nm, which are larger than the LSPR responses of naked Au NPs 7.21 nm and 17.63 nm. In contrast, the LSPR responses of 11-mercapto-1-undecanol, methyl 3-mercaptopropionate, 3-methoxybutyl 3-mercaptopropionate-, hexyl mercaptan, 1-dodecanethiol, and 1-octadecanethiol-modified AuNPs to all these three kinds of terpene are smaller than those of naked AuNPs. For instance, the LSPR responses of 1-octadecanethiol-modified AuNPs to β -caryophyllene, α -pinene, and myrcene were 3.41 nm, 4.45 nm, and 2.58 nm, respectively. This result indicated that the thiolate-capping layers were formed after thiolate modification, and different thiolates could form characteristic monolayers on the surface of AuNPs, which affected the sensing ability of LSPR sensors to vapors. In addition, the LSPR responses of naked NPs to β -caryophyllene vapor (280 ppm) were obviously improved by 2-mercaptobenzothiazole and 4-methoxy- α -toluenethiol surface modification.

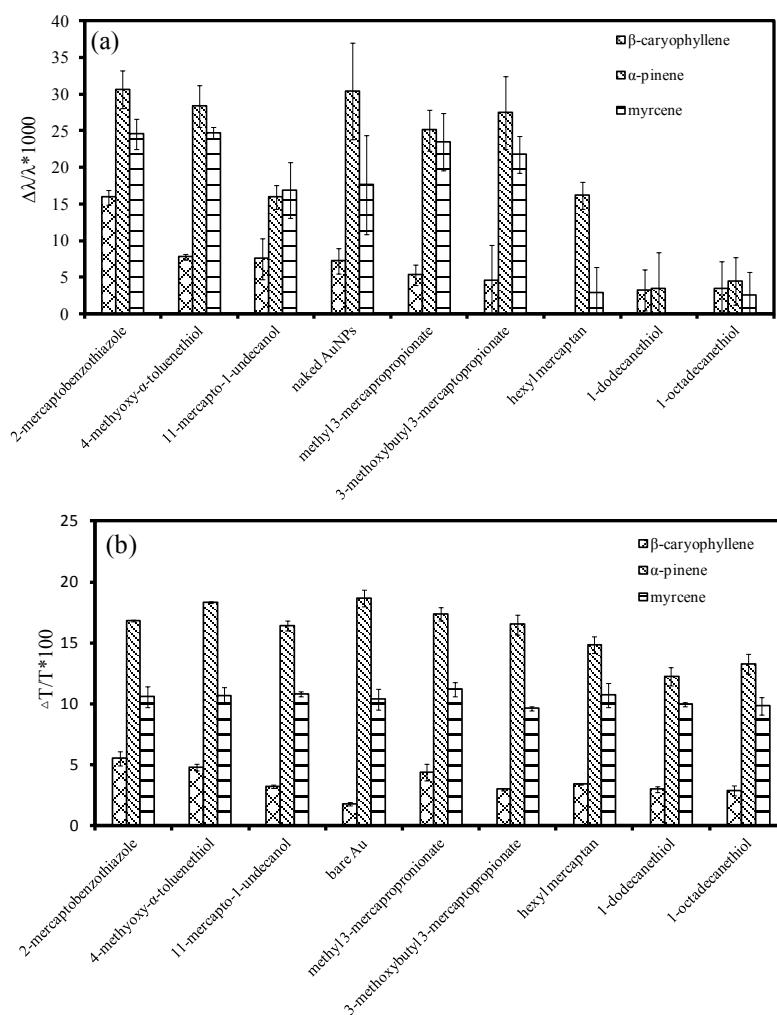


Fig. 4.5 The normalized local refractive index sensitivity of thiol modified AuNPs to terpenes

(a) and (b) shows the LSPR responses ($\Delta\lambda/\lambda * 1000$, and $\Delta T/T * 100$) of thiolates modified AuNPs to terpenes β -caryophyllene, α -pinene, and myrcene, respectively ²⁵.

Fig. 4. 6 shows the real-time signal changes of single point transmittance at λ equals to 620 nm of AuNPs modified by 1-dodecanethiol, 1-octadecanethiol, and 4-methoxy- α -toluenethiol in clean air and three kinds of terpene vapor: α -pinene, myrcene, and β -caryophyllene, respectively. The diluted terpene vapors were switched on for 300 s then switch off for 300 s during every test cycle. The LSPR spectra were

collected at 1 s intervals. As shown in Fig. 4.6, the LSPR responses ($\Delta T_{\min}$) of 4-methoxy- α -toluenethiol-modified Au NPs to α -pinene (400 ppm), myrcene (200 ppm), and β -caryophyllene (5 ppm) are 1.4%, 0.6%, and 0.4%, respectively. While those of 1-octadecanethiol-modified Au NPs to α -pinene, myrcene, and β -caryophyllene are 0.5%, 0.1%, and 0.3%, respectively. It is worth mentioning that the LSPR response of 4-methoxy- α -toluenethiol-modified AuNPs to β -caryophyllene 0.4% is comparable to that to myrcene 0.6%. This result illustrated that the thiolate-surface-modification could detect terpene vapors with low concentrations as well. In addition, the response characters of the LSPR sensors to changes in vapor concentration were verified to be reversible and reproducible.

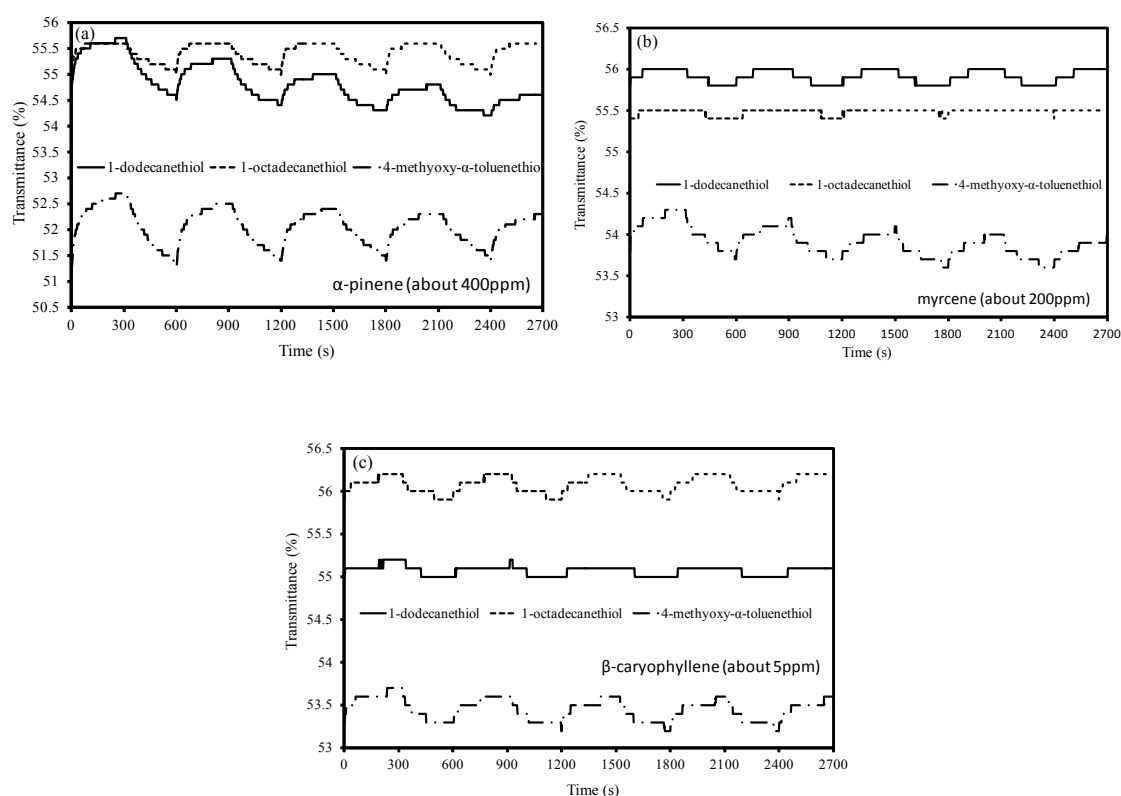


Fig. 4.6 Real-time response signal of AuNPs LSPR-VOC sensor ²⁵.

4.3.4 Response mechanism discussion

A schematic sensing mechanism of thiolate-capping layers was proposed to explain the above results shown in Fig. 4.5 and Fig. 4.6. The ring-structured thiolate capping

layer improved the LSPR responses of Au NPs to all these three terpene vapors, especially, to the larger ring-structured β -caryophyllene. Thiolates can form monolayers on AuNPs by binding sulfur atom with Au atom^{7, 20-23}. When the LSPR phenomenon in AuNPs is excited, the decaying distance of generated electromagnetic fields l_d can exceed the thickness of thiolate-capping layer²⁴. In addition, structural characters of thiolate molecules determine the steric distribution of the formed monolayer^{22, 23}. As shown in Fig. 4.7, we suggested that ring-structured thiolates form relatively loosely-packed disordered monolayer, while long chain-structured thiolate form relatively closely-packed ordered monolayer. In the same vapor micro-environment, a loosely-packed thiolate monolayer may adsorb more vapor molecules than a closely-packed one. Gas molecules enclosed inside the monolayer will contribute more to the effective local refractive index change than the ones located far outside. Therefore, the loosely-packed monolayer structure will result in greater change in AuNPs' effective local refractive index. Furthermore, small-sized vapor molecules are expected to penetrate thiolate monolayer and get directly adsorbed on the surface of AuNPs. On the contrary, large-sized vapor molecules are mainly adsorbed close to or inserted into the thiolate-capping layer¹⁸. When the vapor concentration is high, both vapor molecules inside and outside the thiolate-capping are condensed. Terpene molecules in this study include two-irregular ring structures (β -caryophyllene), one hexagonal ring structure (α -pinene), and a short chain structure (myrcene). Here, we suggest that the affinities and the mutual selective solubility of ring-structured thiolate capping layer to terpene vapors are better than the long-chain-structured thiolates. However, the specific selectivity of AuNPs through thiolate modification is hard to realize.

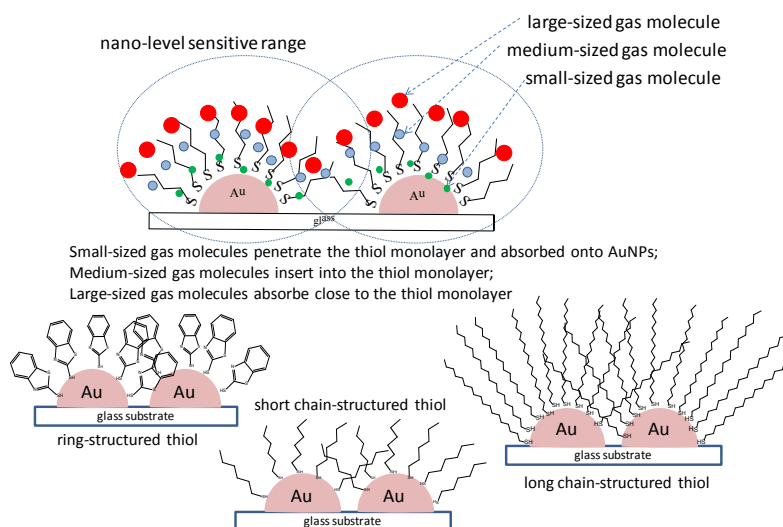


Fig. 4.7 The schematic sensing mechanism of thiolate modified AuNPs ²⁵.

4.4 Conclusion

We demonstrated an LSPR sensor that using sputtered AuNPs with VOC-sensitive and –selective thiolate monolayer. We studied the LSPR spectra and morphology of AuNPs versus sputtering time. Through comparing the LSPR response of thiolate modified AuNPs to terpenes, the thiolate-surface-modification provides reversible and reusable to the LSPR sensor was verified. A sensing mechanism was proposed in that affinities and the mutual selective solubility between thiolate-capping layer and terpene vapors took the main effect on the improvement of the NPs' LSPR response. Studies to further enhance the VOCs specific sensitivity of LSPR sensor and apply them in optical sensing system are underway.

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Chapter 5 Terpene Vapor Detection Using Molecularly Imprinted Polymer Coated Au Nanoparticle Sensor

5.1 Background information of MIP and MIP in sensors

Molecular imprinting is the template polymerization process for synthesizing complementary binding sites for given molecules with tailor-made fashion ¹. It is an established method for the production of polymeric artificial receptors for specific molecular recognition ². Molecular imprinting of synthetic polymers is a process where functional and cross-linking monomers are co-polymerized in the presence of the target analyte (the imprint molecule), which acts as a molecular template ³. The template molecules take two main functions: one is space-filling three-dimensional object around which a complementary polymer cavity could be formed. The other is to organize complementary interactions between groups on the template and functional monomers during polymerization. Thus, the selectivity is realized by forming specific recognition sites in the polymer matrix through adding template molecules in the polymerization process ⁴⁻⁵. The functional monomers initially form a complex with the imprint molecules, and following polymerization, their functional groups are held in position by the highly cross-linked polymeric structure. Subsequent removal of the imprint molecule reveals binding sites that are complementary in size and shape to the analyte. In that way, a molecular memory is introduced into the polymer, which is now capable of rebinding the analyte with a very high specificity. There are two distinct approaches to molecular imprinting. The ease of this method makes it competitive with other synthetic organic methods of molecular recognition ⁶. The polymer network itself provides immobilization of binding sites on a solid support that can be utilized in many applications ⁷.

Chemical sensors and biosensors are of increasing interest within the field of modern analytical chemistry. The central part of a chemical or biosensor is the recognition element. The recognition element is responsible for specifically recognizing and binding the target analyte in an often complex sample. Biosensors rely on biological entities such as antibodies, enzymes, receptors, or whole cells as the recognition elements ⁸⁻⁹. Unfortunately, in general, poor chemical and physical stability of biomolecules

sometimes prevents their use in harsh environments. Another important technique that is being increasingly adopted is molecular imprinting in polymers. An important aspect in the design of a MIP-based sensor is to find an appropriate way of interfacing the polymer with the transducer. In most cases, the MIP has to be brought into close contact with the transducer surface. Generally applicable are standard surface coating techniques such as spin coating and spray coating, which have both been used to apply a thin film of monomer solution to acoustic transducer surfaces ¹⁰⁻¹¹. A rather simple way to synthesize a polymer layer on a flat surface is to use a sandwich technique. The imprinting solution is cast between the transducer surface and another flat surface such as a glass or quartz disk, whereafter the polymerization is initiated ¹²⁻¹³.

Widely applied MIP sensors are the mass-sensitive acoustic transducers including SAW and QCM sensors. For example, polymers of the polyurethane type have been synthesized at the surface of SAW and QCM oscillators in the presence of a certain organic solvent ¹⁰. The polymer films subsequently showed a preferential uptake of the “imprinting” solvent over other solvents. Via the change in oscillation frequency resulting from the mass change at the oscillator surface the selective absorption of MIP layer could be realized. Other sensors have been designed based on conductometric transducers ¹⁴. Two electrodes are separated by an imprinted polymer, in the form of a membrane. As a result, binding of the analytes to the polymer changes its conductivity which is translated into an electrical signal ^{15, 16}.

5.2 MIP coated AuNPs sensor design

Au nanoparticles (AuNPs) exhibit a strong extinction band in UV-visible range when the incident photon frequency is resonant with the collective oscillation of the conduction electrons, which is known as the localized surface plasma resonance (LSPR) ¹⁷. The extinction band can be modulated by the size, shape, materials, and inter-particles distance of noble metallic NPs ¹⁸. The unique electronic and optical properties of metallic NPs added new dimensions to the area of sensors ¹⁹. Applications of the optical properties of noble metal NPs as chemical and biological sensors have attracted much attention ^{20, 21, 22, 23-25}. It has been demonstrated that noble metal NPs sensors show a real-time high-speed sensing ability and repeatability to the change of

environmental refractive index²⁶. Our recent research on AuNPs generated by Au atom sputtering method shows that the responses of AuNPs sensor to the refractive index change induced by gases are less than two seconds²⁶.

Volatile terpenes are a large and diverse class of organic compounds, produced by a variety of plants and insect²⁷⁻²⁸. In the event of herbivore, insect, pathogen attack or the environmental pressures, the emission amount of terpenes would increase remarkably²⁸⁻²⁹. Terpenoid compounds emitted from Lima bean plants infested with spider mites act as airborne signals, activating jasmonic acid/ethylene-induced defense responses and enhancing the resistance against spider mites in the leaves of neighboring plants²⁹⁻³¹. *Vicia faba* plants exposed to (*Z*)-jasmone, a volatile jasmonate metabolite emitted from flowers and damaged tissues, had elevated levels of the monoterpene β -ocimene³². Volicitin has been shown to stimulate the expression of genes involved in the biosynthesis of indole and sesquiterpenes in maize³³. Isoprene, a simple C₅ terpene is released from the foliage of many species, especially trees. Sharkey and coworkers³⁴ suggest that rather than simply increasing the general thermal tolerance of photosynthesis, they suggest that isoprene helps the photosynthetic apparatus to recover from brief episodes of temperatures over 40°C. As a result, the monitoring of the amount of specific terpene is a promising approach to predict the potential herbivore in agriculture.

Plasmonic NPs can act as transducers that convert small changes in the refractive index into spectral shifts in the intense NP extinction and scattering spectrum through the electromagnetic field generated by the LSPR in the NP. In terms of gas detection, the use of the LSPR of NPs is attributed to the changes in LSPR due to the adsorption of gas molecules on NPs surface. This detection principle requires gas molecules enter close to or adsorbed onto NPs. There is no chemical reactions occur. Thus, high-speed gas sensing can be realized by LSPR sensors. However, bare AuNP sensors lack the specific selectivity to different molecules. In this work, we proposed terpene sensor based on the MIP combined AuNPs LSPR sensor. The sensor was fabricated by spin coating MIP mixture on AuNPs. We chose methacrylic acid as monomer, ethylene glycol dimethylacrylate as crosslinker, and α -pinene as the template molecules to fabricate MIP matrix. The schematic sensing mechanism of MIP-coated AuNP sensor is as shown

in Fig. 5.1. Template molecules (α -pinene) adsorbed onto or absorbed into cavities in polymer matrix will induce the refractive index change surrounding AuNPs, which would change the electron polarization in NPs. This change expresses as the surface plasmon peak position ($\lambda_{\min}$) shift and the transmittance variation in spectrum. The spectral characteristics of MIP-coated AuNPs films versus spin coating speed were investigated. The results demonstrated that both good sensitivity and selectivity can be obtained when the thickness of polymer layer on AuNPs was controlled in a suitable range.

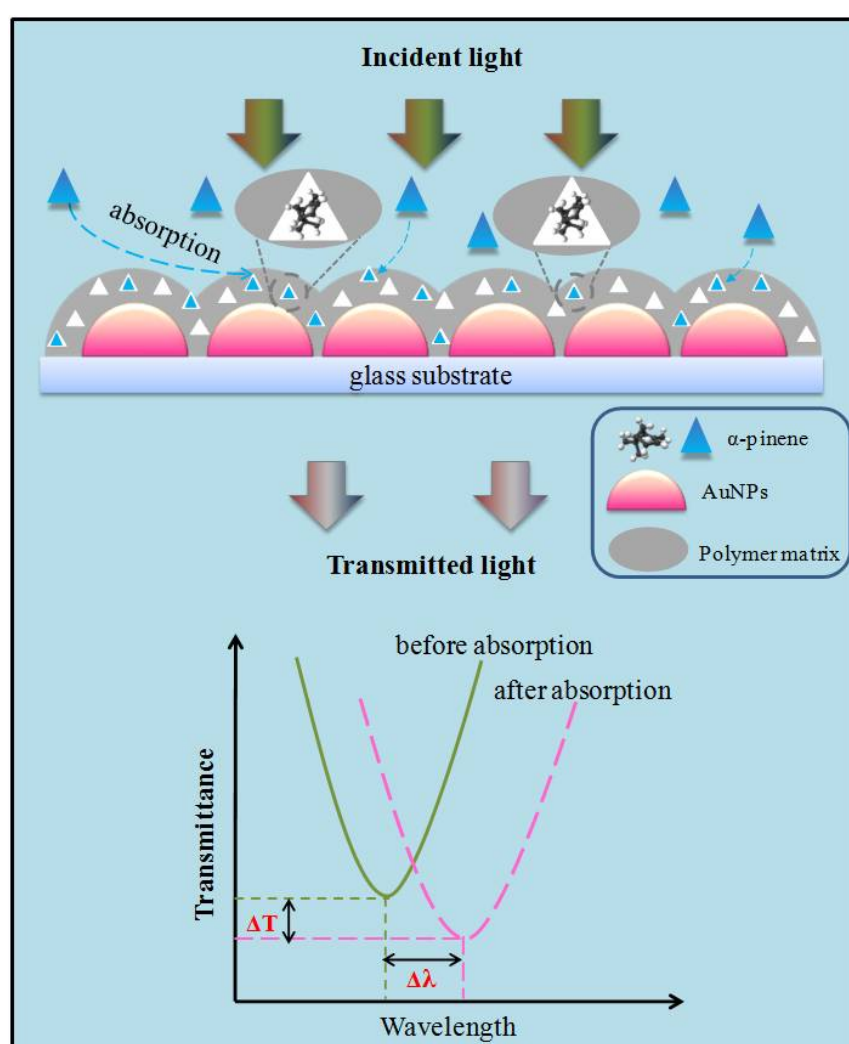


Fig. 5.1 The schematic graph of MIP-coated AuNPs film for α -pinene detection ³⁹.

5.3 Experimental

5.3.1 MIP Powder Fabrication

The reagents were directly used as received. The polymerization of 5.88 mmol MAA (Wako Pure Chemical Industries, LTD.), 29.41 mmol EGDMA (Wako Pure Chemical Industries, LTD., Japan), 18.38 mmol hexane (Wako Pure Chemical Industries, LTD.), 1.47 mmol α -pinene (SIGMA-ALDRICH, CO., USA) and 0.15 mmol azobisisobutyronitrile (AIBN) (Tokyo Chemical Industry Co., LTD., Japan) was carried out at 60°C in water bath for 6 h. The bulk MIP polymer was grinded into powder and sieved with a mesh (diameter of sieve pore: 100 μ m). The MIP powder was heated at 60°C overnight to evaporate solvent and template molecules. There is no terpene residual according to the GC/MS analysis result (data not shown). Fabrication of non-imprinted polymer (NIP) was carried out under the same procedure without adding α -pinene.

5.3.2 MIP Film Fabrication

The pre-polymerization of MAA, EGDMA, hexane, and AIBN (the same amount as powder fabrication) was carried out at 60°C in water bath for 3.5 h. After that, terpene liquid was added to the pre-polymerized solution and stirred thoroughly. Pre-polymerized MIP (20 μ L) were casted on the clean glass substrate and heated at 60°C for another 8 h to finish the whole polymerization and template evaporation process. NIP solution without adding α -pinene was prepared under the same condition. The residual amount of template molecule in MIP film before the adsorption test was measured using GC/MS. The result showed that no detectable residual of α -pinene in MIP films after template molecule removal.

5.3.3 MIP-coated AuNP Film Fabrication

Plasma cleaned substrate was immersed in a 1:15 (volume ratio) ethanol solution of 3-aminopropyl triethoxysilane (APTES) (Shin-Etsu Chemical, Japan) for 3 h. After washing with ethanol and drying in nitrogen flow, glass substrates were put into a quick coater (SC-701HMC, Sanyu Denshi, Japan) for AuNPs deposition. The sputtering current and time was set to be 1.5 mA for 70 s. After deposition, AuNP substrate was

annealed in air atmosphere at 200 °C for 5 h. After annealing, the substrate was treated in the plasma cleaner for 1 min and then immersed in 1 mM 2-aminoethanethiol (AET) (Wako Pure Chemical Industries, LTD.) ethanol solution for 1 h, followed by rinsed thoroughly with ethanol. 5 μ L pre-polymerized mixture was casted on the AuNP deposited substrate and spin coated at speeds varying from 600 rpm to 1600 rpm for 1 min (with 5 s acceleration time). Finally, samples were heated at 60 °C for another 8 h to finish the polymerization process.

Surface of AuNP film is not smooth, which results to the difficulty in establishing model for thickness detection using ellipsometry method. Therefore, the polymer layer was spin coated on Au substrate instead of AuNP film. Polymer thickness on Au substrate (Au layer: 200 nm, Cr layer: 20 nm on glass slide) was measured using spectroscopic ellipsometer (SpecEI-2000-Vis, Mikropack).

5.3.4 GC-MS Analysis

Absorption test of MIP powder to mixed terpene vapors including α -pinene, limonene, and γ -terpinene (Wako Pure Chemical Industries, LTD.) shown as Fig. 5.2: three vessels filled with three terpene bulk solutions (10 mL) was sealed in a desiccator (volume: 13.5 L) for 6 h to reach their saturation concentrations ³⁶. The same quality of NIP and α -pinene imprinted polymer powders (template molecules removed) (50 mg) were put in the desiccator to absorb the mixed terpene vapors for 30 min. Then, the powders were taken out and sealed in the septum-capped vial for GC/MS analyzing.

Terpene vapor absorption test of the MIP film (with different molar ratio of template to monomer) was done as follow: four small capsules with 20 μ L of α -pinene solution were put into four containers with the same volume, respectively, and evaporated for about 30 min to generate terpene atmosphere. After that, the NIP and MIP samples were put into these four containers respectively for 30 min.

Three kinds of terpene liquid (each 20 μ L) were put in capsules, respectively. These capsules were placed into a sealed container, and let terpene liquids evaporate for 30 min. The samples of MIP and NIP films were then set into the container for 30 min to absorb terpene vapors. After that, all the samples were packed in septum-capped vials, and the headspace of vials was analyzed by SPEM fiber through GC/MS.

The adsorption amounts of the MIP films and powders to terpene molecules were analyzed using (solid-phase microextraction) SPME-GC/MS (QP2010-SE SHIMADZU, Japan). A SPME fiber of divinylbenzene/carboxen on polydimethylsiloxane (CAR/DVB on PDMS) 50/30 μm fiber (SUPELCO) was used for auto-sampling at extraction conditions of 70 $^{\circ}\text{C}$, 30 min. The column used was a 60 m $\times$ 0.32 mm, 0.5 μm film thickness DB-WAX. Helium was used as a carrier gas with a flow rate of 2.5 mL/min. The analytes were desorbed in the injection port of the GC using an inlet temperature of 240 $^{\circ}\text{C}$. The 53 min GC method began with an initial oven temperature of 40 $^{\circ}\text{C}$ for 5 min, followed by a ramp of 5 $^{\circ}\text{C}/\text{min}$ to 230 $^{\circ}\text{C}$, and ending with a 10 min hold. The quadruple mass analyzer was operated in electron ionization (EI) mode, and scanned over a mass ranged of m/z 35–550 in full scan mode ³⁵.

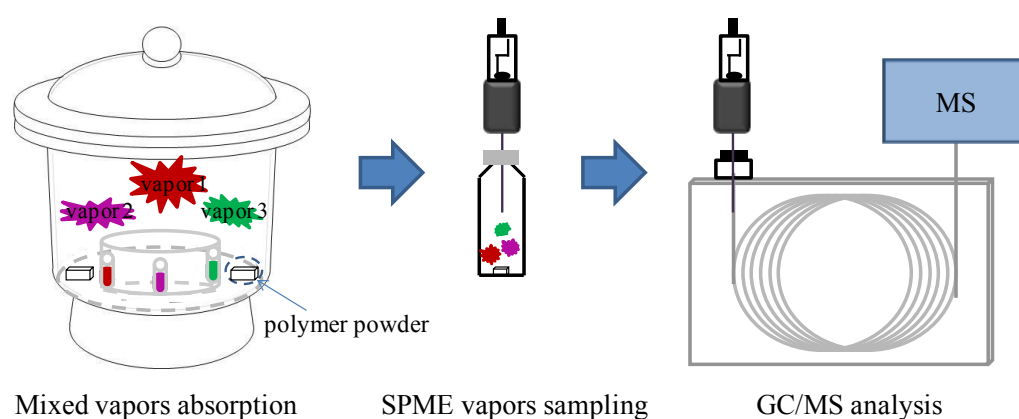


Fig. 5.2 The schematic diagram of mixed terpene vapors absorption by polymer powder and GC/MS measurement ³⁹.

5.3.5 AFM and SEM Images

Atomic force microscopy (AFM, Nanoscope IIIa, Digital Instrument) was utilized to analyze the morphology and distribution characters of AuNPs before and after polymer deposition. AFM was operated in a tapping mode. Typical technical data of point probe-silicon SPM-sensor (Digital Instruments, Nanosensors) include: thickness: 4 μm , length: 125 μm , width: 30 μm , resonance frequencies 320 kHz, force constant: 42 N/m, and Coating: none. Response of MIP coated AuNP Sensor

The transmittance spectra recorded using an UV-vis spectrophotometer (UV1800, Shimadzu). Transmittance values were sampled at 1 s interval. A bubbling method was utilized for vapor generation as our previous research ^{22, 26}, two samples of polymer-coated NP slide were put inside the optical cell, and the single point transmittance ($\lambda = 562$ nm) was recorded. Terpene vapor flow was switched on for 120 s and switched off to clean air for 120 s during all the test cycles. The concentrations of terpenes: α -pinene, Limonene, and γ -terpene were calculated to be 315, 625, and 469 ppm, respectively.

5.4 Results and discussion

5.4.1 The selectivity of MIP powder to the template molecules

The selective absorption of MIP powder (molar ratio of template to monomer: 1:4) to mixed terpenes is as shown in Fig. 5.3. In this study, the absorption property of each sample to terpene mixture was analyzed using the values of total ion current, an absorption response from GC/MS. The selectivity was evaluated by the coefficient (S_i) of each vapor, expressed by the quotients of the TIC values of vapors absorbed by α -pinene imprinted polymer and those by non-imprinted polymer ³⁶.

$$S_i = \text{TIC}_{\text{mip}} / \text{TIC}_{\text{nip}}$$

(5-1)

Where i represents the corresponding vapors, including α -pinene, limonene, and γ -terpene. The TIC values of NIP was used as the reference responses. Hence, when S_i is larger than 1, more vapor molecules are trapped by MIP than NIP. It is shown that the selectivity coefficient of α -pinene imprinted polymer powder to α -pinene is larger than 1, while S_i of α -pinene imprinted MIP to limonene and γ -terpinene is less than 1.

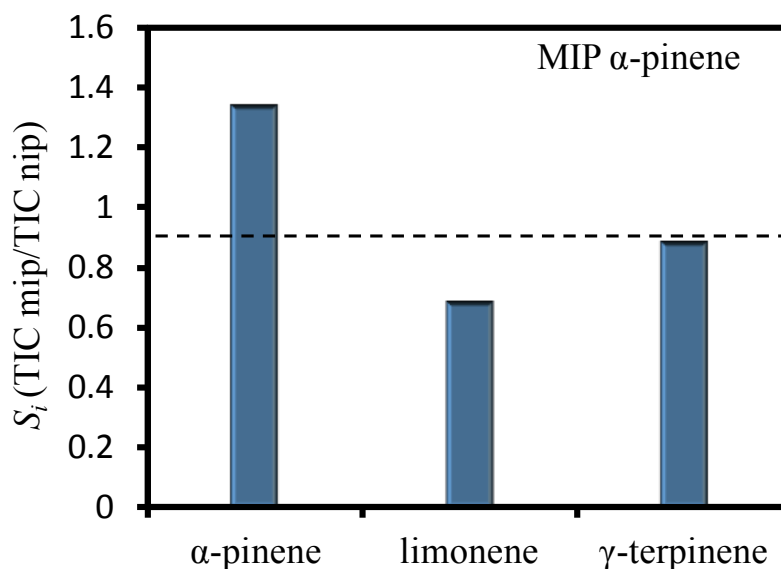


Fig. 5.3 The selectivity coefficient (S_i) of α -pinene imprinted polymer powder to α -pinene, limonene, and γ -terpinene ^{38, 39}.

5.4.2 The selectivity of MIP films to the template molecules

Many researches have indicated that the selective absorption property of MIP was influenced by the polymerization conditions ¹⁻⁷. For instance, increasing in the concentration of binding sites in the MIP could be realized by optimizing the ratio of the functional monomer to template ¹⁻³. Hence, the effect of monomer concentration in the MIP composition was investigated by variation of the molar ratio of template to monomer employed in the polymer mixture. Template molecular absorption amount of MIP films was normalized by that of NIP film and expressed by H_n as shown in Fig. 5.4. n represents the molar ratio of template to monomer. When the molar ratio of α -pinene to monomer is as low as 1:16, H_n is approximately equal to 1. With the increase in the molar ratio of α -pinene to monomer, H_n increases as well. The largest H_n is obtained when the molar ratio of template to monomer is 1:4. In addition, when the molar ratio of α -pinene to monomer increased to 1:2, H_n decreases to a small value (approximately zero). This result might be attributed to the extremely large amount of template molecule, which will impede the normal polymerization process because excessive target molecules worked as impurity in polymerization reaction.

The selectivity of α -pinene imprinted polymer (molar ratio of template to monomer: 1:4) to α -pinene, limonene, and γ -terpinene was investigated. The results shown in Fig. 5.5 illustrated that the S_i of α -pinene is the largest. In addition, the S_i of γ -terpinene is larger than that of limonene, which is also consistent with the S_i features of MIP powder. Template (α -pinene) molecule does not have specific functional groups such as carboxyl group, which could form strong bonding with the polymer matrix. Hence, it is suggested that the weak hydrogen bond and Vander Waals force are the main binding and rebinding force between α -pinene molecules and the polymer matrix. The cavities in polymer matrix due to the effects of template molecular size and shape become the key factor in molecular identification process ³⁻⁷. The selectivity of α -pinene imprinted polymer to α -pinene vapor is mainly attributed to the rebinding of α -pinene molecules to the specific cavities formed in polymer matrix during polymerization process, while the absorption of α -pinene imprinted polymer to γ -terpinene and limonene molecules might be attributed to the unspecific rebinding. The three-dimension structures of α -pinene, γ -terpinene, and limonene molecules are drawn, and the largest distances between H atoms (molecule length) of these three molecules are calculated using ChemBioDraw software. The molecular length of α -pinene, γ -terpinene, and limonene is 6.67 Å, 7.24 Å, and 8.33 Å, respectively. Hence, it is speculated that the unspecific absorption of α -pinene imprinted polymer to γ -terpinene might be higher than that to limonene.

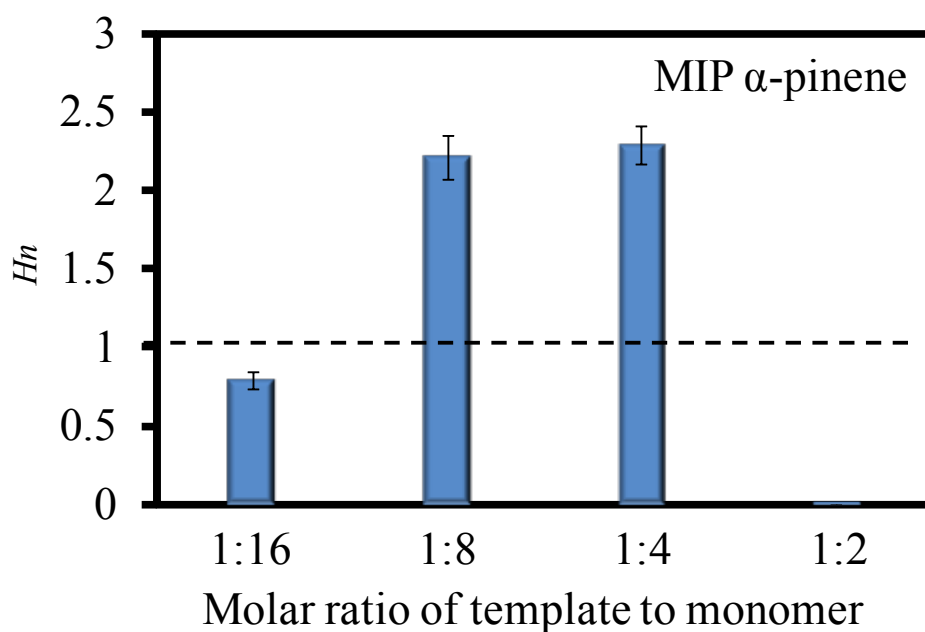


Fig. 5.4 Template molecular absorption amount of MIP film normalized by that of NIP (H_n) versus the the molar ratio of template to monomer (the data shown in the graph is the average values of two times detection of three samples) ³⁹.

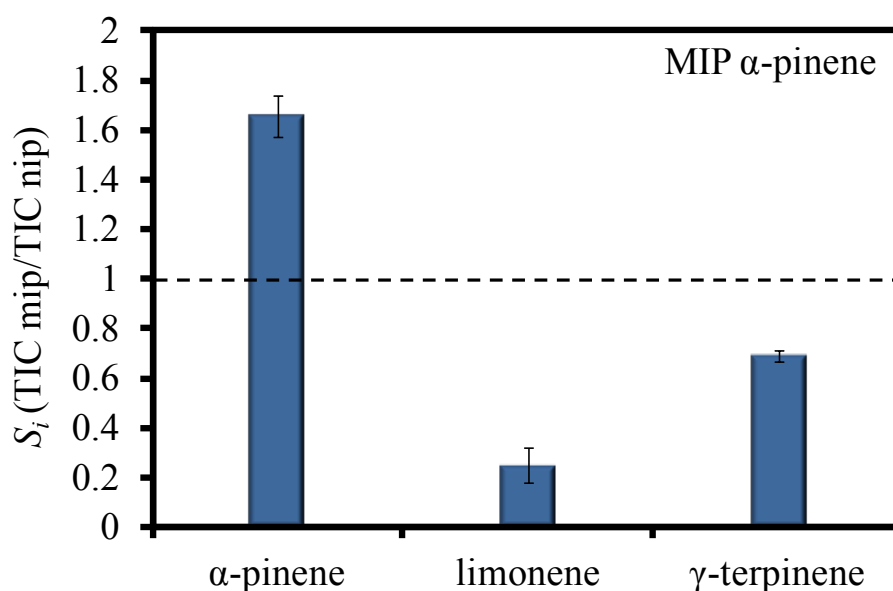


Fig. 5.5 The selectivity coefficient (S_i) of α -pinene imprinted polymer films to terpenes : α -pinene, limonene, and γ -terpinene (the molar ratio of template to monomer is 1:4, the data shown in the graph is the average values of two times detection of three samples) ³⁹.

5.4.3 Dependence between polymer thickness and spin coating speed

Fig. 5.6 shows the relationship of polymer thickness on Au substrate versus spin coating speed. As the spin coating speed is 600 rpm, the polymer thickness is about 7 nm. When the spin coating speed increased to about 1000 rpm, polymer thickness decreases to less than 2 nm. With spin coating speed further increase, there is no obvious polymer thickness decrease. In addition, AFM images of AuNP film and NIP coated AuNP film at a spin coating speed of 600 rpm were investigated as shown in Fig. 5.7. The RMS roughness of AuNP film and NIP coated AuNP films is 1.88 and 0.56, respectively, which verifies that the polymer layer could be successfully formed on NP film through spin coating method.

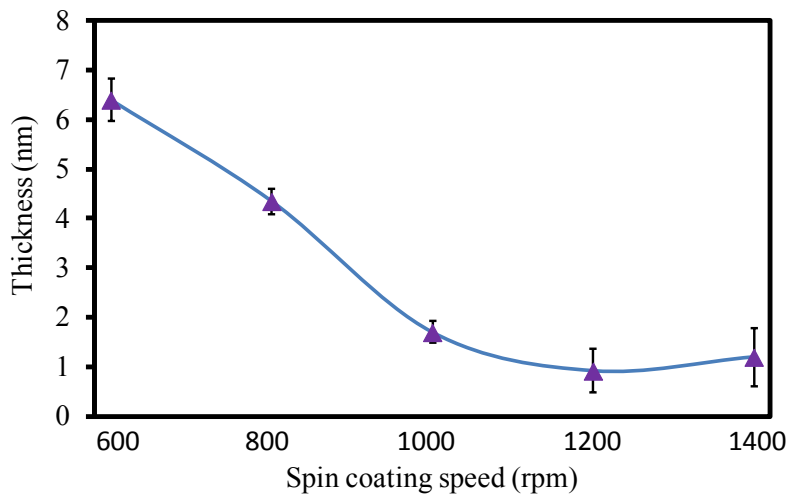


Fig. 5.6 The dependence of NIP thickness on the spin coating speed on Au substrate (the data shown in the graph is the average values of three times detection of two samples at each spin coating speed) ^{38, 39}.

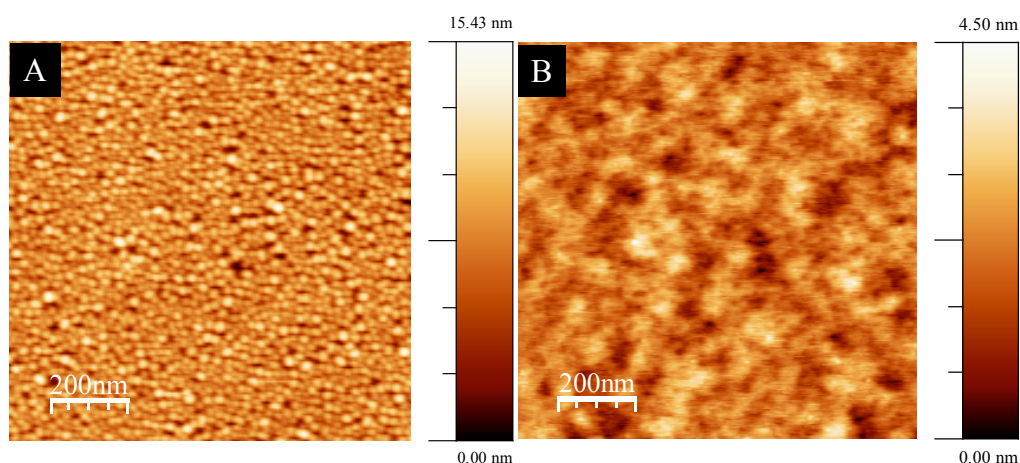


Fig. 5.7 AFM images of bare AuNPs (A) and NIP coated AuNPs on glass at spin coating speed of 600 rpm (B) ³⁹.

5.4.4 Optical characteristics of polymer-coated AuNPs film

Au sputtering method is adopted to generate AuNPs film on glass, and the average size is approximately 30 nm with an oblate shape after 200 °C 5 h annealing treatment as shown in Fig. 5.7 (A). According to our previous research ^{22,26}, AuNPs sensing film has higher sensitivity at this condition. Optical characteristics of NIP coated AuNPs films at different spin coating speeds were investigated as shown in Fig. 5.8. NIP topping layer made the plasmon adsorption peak $\lambda_{\min}$ shifts to the red, and the transmittance decreases. The increase in spin coating speed made the plasmon adsorption peak $\lambda_{\min}$ shift to the blue, and the transmittance increase. This phenomenon is due to the decrease of polymer thickness with the increase of spin coating speed. In addition, when the spin coating speed increased from 600 rpm to 800 rpm, there was no obvious transmittance increase as the spin coating speed further increase from 800 rpm to 1600 rpm. The effective refractive index change could be detected in the range of a few tens of nanometers from NPs' surface ³⁷, and the most sensitive sensing range is in a shorter range less than 5 nm ³⁸. Therefore, it is suggested that the thickness value of polymer topping layer generated at lower spin coating speed such as 600 rpm is almost equivalent to or exceed the sensing distance of NPs. While high spin coating speed make the polymer layer left on NPs thin.

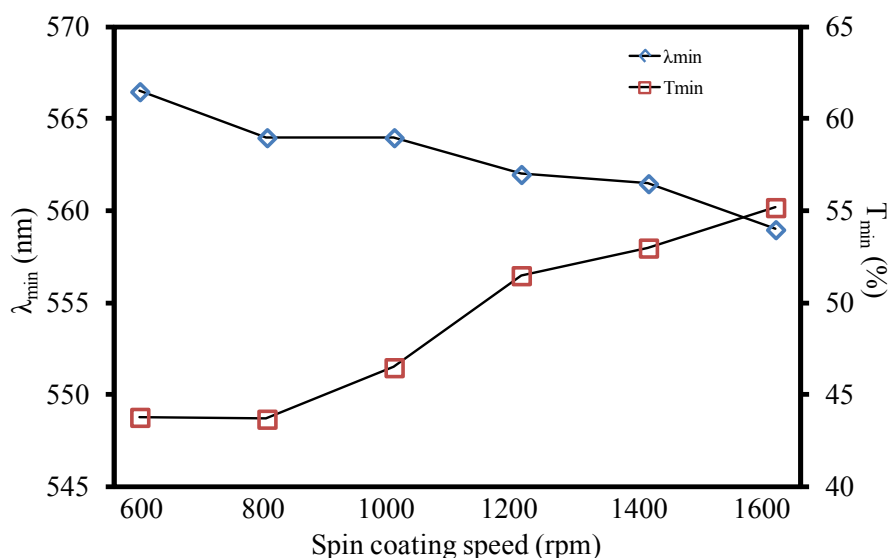


Fig. 5.8 Dependence of the optical features ($\lambda_{\min}$ and $T_{\min}$) of NIP-coated AuNP sensors on the spin coating speed ³⁹.

5.4.5 The refractive index sensitivity of polymer-coated AuNP sensor

The sensitivity of MIP-coated AuNP sensor is decided by the refractive index sensing ability of NPs. Thus, the sensing range of NPs has to be taken into consideration. In this research, the refractive index sensitivity (RIS) of polymer-coated AuNP sensors is defined by a red shift of the SP peak position ($\Delta\lambda_{\min}$) and a decrease in the minimum transmittance ($\Delta T_{\min}$) induced by the refractive index change by α -pinene vapor. RIS of NIP and MIP coated AuNPs sensors to α -pinene vapor was measured as shown in Fig. 5.9. Two samples of polymer-coated NP slide were put inside the optical cell. Bubbling method (vapor flow rate: 1 mL/min) was used to generate α -pinene vapor. The result shows that when the spin coating speed is as slow as 600 or 800 rpm, the RIS of both NIP and MIP is low, and there is no difference between them. As the spin coating speed exceeds 1200 rpm, RIS of MIP-coated substrate is higher than NIP-coated one. When the spin coating speed is as high as 1600 rpm, there is nearly no difference between the RIS of NIP and MIP. Those results could be explained to the polymer thickness variation. The schematic selectivity of MIP-coated AuNP sensor is as shown in Fig. 5.10. The thick polymer layer that exceed the sensing range of AuNPs generated at a low spin coating speed will impede α -pinene molecules to go into the sensitive range of NPs,

which leads to a small or no RIS. Hence, the specific selectivity of MIP layer is hard to realize. While a too thin polymer layer formed on NPs at a high spin speed such as 1600 rpm allow the template molecules to go into the sensitive range of NPs, which would cause the detective refractive index change. In addition, the selective feature of MIP layer is hard to be kept because of the small absorption ability of a too thin polymer layer. Only when the polymer thickness is well controlled close to the sensitive range of NPs, the amount of template molecules absorbed onto and into MIP layer is larger than that of NIP. As a result, the specific selective absorption could be realized.

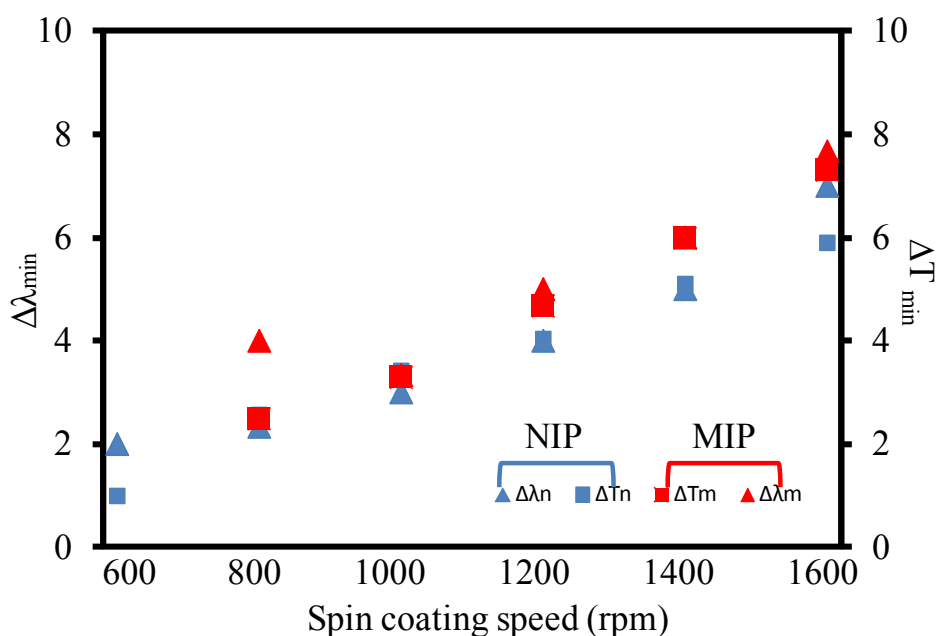


Fig. 5.9 The dependence of RIS ($\Delta\lambda_{\min}$ and $\Delta T_{\min}$) of MIP and NIP coated AuNP sensor on the spin coating speed for α -pinene vapor detection (The red solid triangle and square represent MIP, while the blue solid triangle and square represent NIP. T represents transmittance) ^{38, 39}.

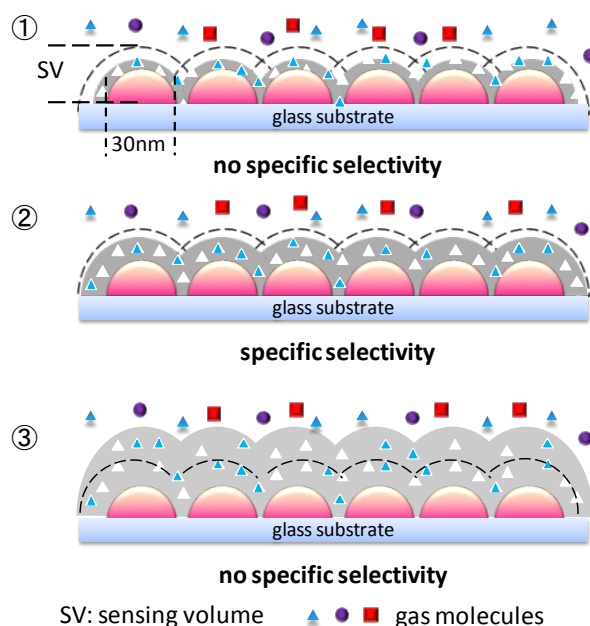


Fig. 5.10 The selectivity of MIP-coated AuNP sensor

5.4.6 The LSPR response of polymer-coated AuNP sensors

The real-time response characters of α -pinene imprinted polymer (molar ratio of template to monomer: 1:4) coated AuNP sensor (spin coating speed: 1400 rpm) to α -pinene (315 ppm), limonene (625 ppm), and γ -terpinene (469 ppm) vapors were investigated. Fig. 5.11 shows the normalized responses at the single point transmittance ($\lambda = 562$ nm). The formula below is adopted to normalize the LSPR response.

$$K_j = 100 * (T_0 - T) / T_0 * 100 / C_j \quad (5-2)$$

Where j is on behalf of three kinds of terpenes: α -pinene, limonene, and, γ -terpinene. T represents the transmittance value in terpene vapors, and T_0 is the transmittance value in air. C_j delegates the concentration of terpene vapors. It is noticed that the corresponding response signal of α -pinene is the largest. In addition, the air baseline recover effect ($K_j=0$) of α -pinene is slower than the other two vapors, which may be attributed to the specific binding effect of α -pinene with MIP layer. The response time (T_{90}) is defined as in our previous research^{25,26}. T_{90} of polymer-coated AuNP sensor to the refractive index change induced by terpene vapors are rapid (less than 3 s), reversible, and reproducible, which is comparable with the response time of bare AuNP sensors²⁵. This result is mainly attributed to that the top polymer layer on NPs is as thin as in a few of nanometer. Hence, the terpene vapor could saturate the layer in a short time. Moreover,

the speed of gas mixing in the testing cell affects the final response time, while the single wavelength transmittance response noise is attributed to the small background vibrations of the UV-vis spectrophotometer.

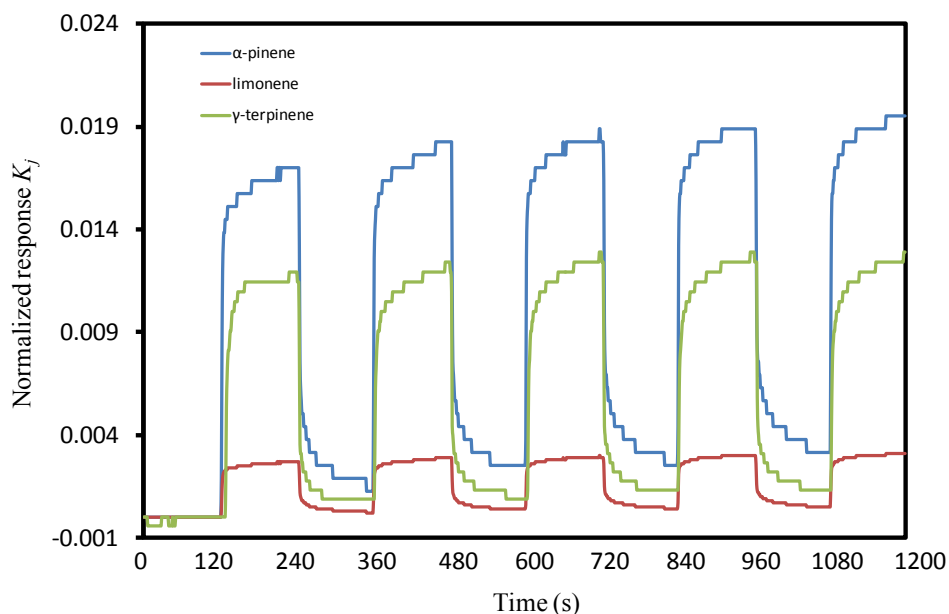


Fig. 5.11 The real-time response of MIP coated AuNPs sensor ³⁹.

5.5 Conclusion

In this research, MIP coated AuNP sensor was explored to detect α -pinene vapor. MIP was spin coated on sputtered AuNPs film. The absorption characteristics of α -pinene imprinted polymer powder and film were evaluated by GC/MS. Compared with the other two terpene vapors, the selectivity feature of MIP powder to α -pinene was verified. In addition, the largest absorption amount of MIP powder and film to α -pinene vapor is appeared when the molar ratio of template to monomer is 1:4. Relationship between spectral and polymer thickness versus spin speed was studied. The results showed that higher RIS and selectivity of MIP coated AuNPs sensor was realized when the spin coating speed is about 1400 rpm. The real-time responses of MIP coated AuNP sensor to three kinds of terpene vapors were verified to be selective, rapid, reversible, and reproducible. For the purpose of the real-field application, development of more types of MIP sensing films of terpenes and their derivatives is necessary. In

addition, more complex interference factors from environment such as temperature and humidity need careful consideration. The sensitivity and selectivity further improvement is also necessary for the real field application.

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Chapter 6 Conclusion

6.1 Conclusion

There are many odor substances distributed in the space. In addition, the odor type and concentration will be strongly dependent on the surrounding environment. Hence, odor type, concentration, and distribution detection is a necessary and challenge task. In this research, terpene vapors become our detection target since terpene evaporation amount is one of the indexes to supervise the field condition. Plants are famous for their ability to produce a diversity of secondary metabolites, some of which are released into the air after attack or egg deposition by herbivores¹⁻⁵. These herbivore-induced plant volatiles (HIPVs) mainly comprise terpenoids, fatty acid derivatives, phenyl propanoids and benzenoids^{6,7} and can be emitted either at the site of damage or systemically from undamaged parts of affected plants⁸. The blends can be complex, comprising hundreds of compounds⁹, some of which are not produced by intact or mechanically damaged plants and others of which are synthesised de novo in response to herbivore attack¹⁰. However, most studies of the function of HIPVs are laboratory based and only a few have demonstrated an HIPV mediated increase in carnivore attack rates on herbivores under field conditions¹⁰⁻¹².

In our research, we developed the AuNP sensors to detect terpene vapors. In the first stage, we adopt the Au atoms sputtering method to sputtering Au nano-islands on glass substrate. For the purpose of tuning the size, shape, and distribution of sputtered nano-islands further, thermal annealing was set at various temperatures. The results showed that both low and high temperature annealing could make the irregular shaped islands round, and high temperature annealing could make nano-islands more separated. In addition, high temperature annealing increased the refractive index sensitivity (RIS). Furthermore, the response of Au nano-islands sensor to the RI change induced was fast (less than 1 s). It is conclude that Au nano-island LSPR sensor with fast response was realized.

So as to further improve the sensitivity of Au nanoparticle (NP) sensor, multilayer structured AuNP sensor was proposed based on the enhanced electric field generated by coupled AuNPs. Influence of molecular structure and natural characteristics of dithiol

linkers on the optical characters and the related terpene vapor-sensing ability of AuNPs multilayer sensors were investigated. AuNPs multilayers were fabricated via layer-by-layer self-assembly in AuNPs and dithiol solution. The dithiol linkers include 1, 4-benzenedithiol (A), 1, 10-decanedithiol (B), and 1, 4-butanedithiol (C). The transmittance spectra of AuNPs multilayer on glass linker by linker B and AuNP clusters linked by linker C in solution showed two localized surface plasmon peaks, while AuNP multilayers linked by linker A on glass and in aqueous solution showed one surface plasmon peak, which were attributed to the molecular conductivity features of dithiol linkers. The linker possessing delocalized π -electrons (the case of 1, 4-benzenedithiol), enable inter-cluster electron transfers by lower activation energies has larger conductivity. As a results, Au NP multilayers linked by 1, 4-benzenedithiol showed the largest RIS with four layers, which was mainly attributed to the enhanced electric field generated by lager sized Au clusters and the coupling effect in and between Au clusters.

It is known that bare Au nano-islands do not have selectivity to gas molecules. In the next stage, the thiolate surface modification was adopted to form the capping layer on Au nano-islands. Thiolates with characteristics structures, including irregular circle, short and long chain shaped were chosen. RIS of thiolate modified Au nano-islands to three kinds of terpene vapors: α -pinene (hexagonal ring structure), myrcene (short chain structure), β -caryophyllene (two-irregular ring structures), and ethanol gas was compared. Based on the results, it is suggested that ring-structured thiolates form relatively loosely-packed disordered monolayer, while long chain-structured thiolate form relatively closely-packed ordered monolayer. In addition, a loosely-packed thiolate monolayer may adsorb more vapor molecules than a closely-packed one. Schematic sensing mechanism is that affinities and the mutual selective solubility between thiolate-capping layer and terpene vapors took the main effect on final response. Hence, certain selectivity of Au nano-island sensor was realized through thiolate surface modification.

In the last stage, on the purpose of improving of the selectivity of AuNPs sensor, the molecular imprinted polymer (MIP) layer on AuNPs was attempted to combine. The sensitivity of polymer-coated AuNP sensor is mainly decided by the RI sensing ability of NPs. Thus, the sensing range of AuNPs has to be taken into consideration. Terpene

molecules have no specific functional groups such as hydroxyl or carboxyl to form covalent or strong non-covalent interaction with monomer. Therefore, the size and shape of template molecular become key factors in molecular identification process. MIP was prepared using methacrylic acid as monomer, ethylene glycol dimethylacrylate as cross-linker, and α -pinene as template. The MIP adsorption character was evaluated using GC/MS. The highest affinitive absorption of polymer film appeared when the molar ratio of template to monomer is 1:4. The results showed that the refractive index sensitivity of MIP coated AuNPs sensors increase with spin coating speed, and better sensitivity and selectivity of were realized at a suitable spin coating speed 1400 rpm. The real-time response of α -pinene imprinted polymer coated AuNP sensor to three terpene vapors: α -pinene, limonene, and γ -terpinene was verified to be selective, rapid, and reversible.

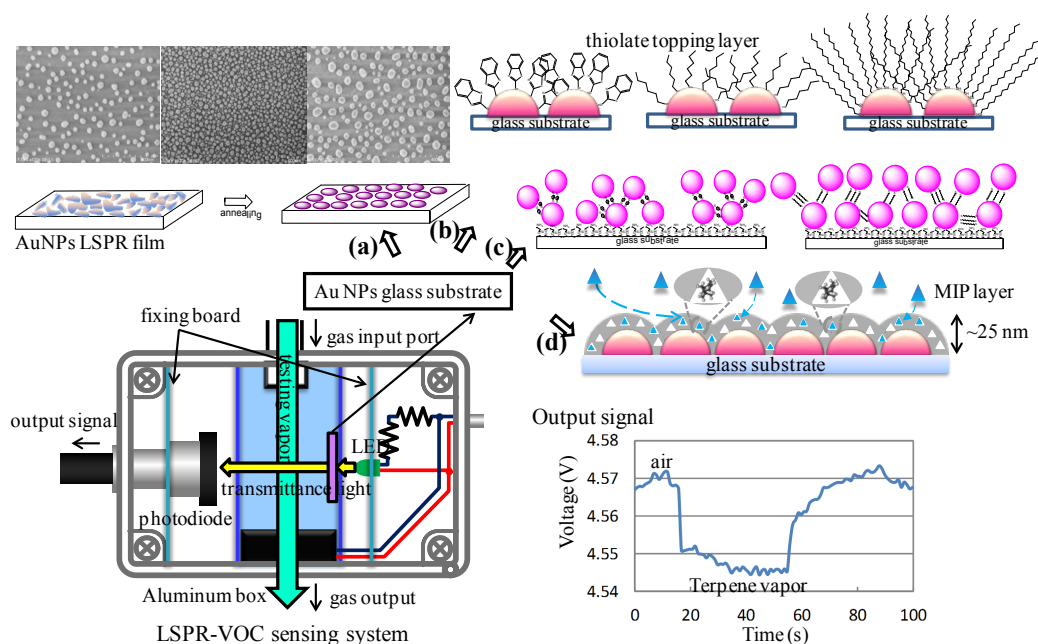


Fig. 6.1 LSPR gas sensing system

6.2 Prospect

My present research is mainly on development of various AuNPs LSPR sensors for gas detection. In the present stage, through combined with the molecular imprinted polymer (MIP) technology, we realized the selective identification of α -pinene vapor

from limonene, α -pinene, and γ -terpene. Hence, we propose that using molecular imprinted polymer doped with AuNPs and dye molecules processing characteristics absorption in certain light wavelength band would become a more precise and sensitive method to detect, identify, and visualize gas molecules distributed in the space. In order to realize agricultural biomarker gas detection in the future research, we suggest that through effective acquisition and analysis the real-field biomarker gases and the gases variation when certain abnormal condition happened such as insect pest, the biomarker gases for some kinds of plants could be successfully confirmed. Combined with the MIP technique, the precise identification to the biomarker gases is hopeful. In addition, we have verified that the MIP- AuNPs sensor is long term use possible, which also provided a platform for the real-field use in agriculture. Based on the above situations, we have a bold assumption that a sensor network based on MIP-AuNPs sensor could be an effective means to realize the purpose of real-time field supervision.

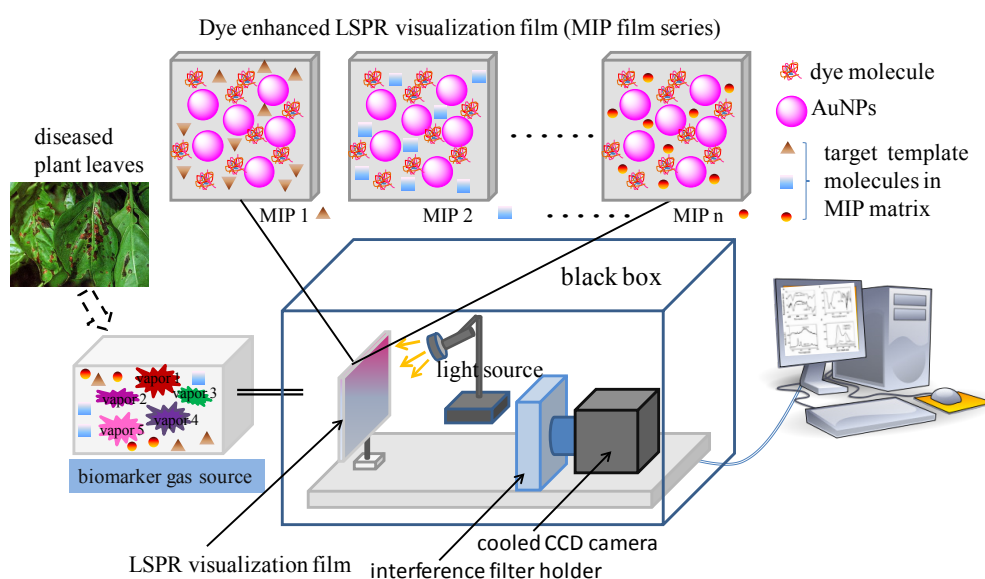


Fig. 6.2 Gas molecules visualization based on AuNPs-MIP sensing system

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Appendix

Structure and localized Surface Plasmon Tuning of Sputtered Au Nano-islands on Glass through Thermal Annealing

Introduction

Noble metal (e.g., gold, silver, copper) nanostructures exhibit special optical and electronic properties, notably different from those of bulk materials ^{1, 2, 3}, which are derived from excitation of LSPR by electromagnetic radiation in the UV-vis spectral range. The LSPR phenomena are expressed as strong light scattering, the appearance of intense surface plasmon adsorption bands, and enhancement of local electromagnetic fields near the metal surface ^{1, 3-5}. Noble metal nanostructures supporting excitation of surface plasmon (SP) polaritons are of special interest in the rapidly developing nano-sensing technology. The refractive index sensitivity (RIS) of SP extinction bands to the dielectric properties of the surrounding medium has been studied as the fast speed and sensitive sensors applied in chemical and biological sensing ^{3, 5}.

The spectral properties of NPs are sensitive to the size, shape of nanostructures, neighboring distance, and the effective refractive index of the surrounding environment ^{2-4, 6-7}. The size of NP determines plasmonic features including the ratio of absorption to scattering, the number of LSPR modes, and the peak position of an LSPR mode ^{1-3, 8-10}. As the size of the particle becomes larger and larger, the energy levels will continue to split and finally merge into the quasi-continuous band structure for the bulk solid ²⁻³. Furthermore, it has been revealed that the sharpness of corners, edges or the specific geometry of a nanostructure can have a large effect on the plasmonic properties of nanostructures. For instance, the plasmon peak of the cubic nanostructures with sharp corners shifts to the red when compared to rounded structures of similar sizes, which is attributed to the reduced restoring force which caused the greater charge separation during the dipole oscillation ²⁻³. In addition, the geometry of nanostructures also change the position of the LSPR peak, number of resonances, and the scattering and absorption cross sections ^{2-3, 8}. Moreover, the distance between NPs influences the LSPR characteristics due to the electronic-field coupling between nanoparticles during excitation ^{1-3, 11-14}. The effect from surrounding refractive index is dependent on the

electron transfer occurs between NPs and the adsorbents. Generally speaking, a red shift is expected if electron transfer occurs from NPs to the adsorbent, and a blue shift results from electron transfer from the adsorbent to NPs ¹⁵⁻¹⁸. NPs applied in LSPR sensors field, the sensing response is affected by the feature of nanostructure. Hence, tuning the shapes, sizes, orientations, and inter-particle distance is significant for the development of LSPR sensors with higher performance.

The structure of NPs can be tuned by the techniques include both the top-down technique, such as electron-beam lithography (EBL) ¹⁹ and the bottom-up fabrication methods, such as colloidal lithographies (CL) ²⁰⁻²². These methods have become the popular selection in making metallic NPs with various structures. However, EBL requires costly instrumentation, and is hard to control due to machine difference. In addition, CL includes colloidal fabrication and self-assembly process which are hard to realize, and the production rate is very limited. Hence, a more easily controllable, efficient, and economic method for making and tuning nanostructure has yet to be developed.

In the last part, a simple procedure of Au ion sputtering is promoted to deposited nano-island arrays on transparent glass substrate ²³⁻²⁴. Through controlling the sputtering conditions such as current or time, added with thermal annealing, we gain Au nano-islands on glass with different morphology, size, and optical characters ²⁵. The prepared Au nano-islands films were utilized to fabricate LSPR gas sensors which showed a rapid response to ethanol gas, which demonstrate a potential application in the field of sensor-loaded robot for the fast speed environment gases detection ²⁶.

As mentioned, the sensitivity of LSPR sensors is influenced by complicated factors related to the structure of NPs. In this research, we explored a simple method to tune the structure Au nano-islands including size and inter-particle distance. The method is based on the time and temperature control in the thermal annealing procedure, and is combined with a re-sputtering and re-annealing process. The sensing performance of Au nano-islands films with tunable structures was evaluated by their refractive index sensitivity and figure of merit (FOM), according to their spectra change induced by their surrounding medium change. The results demonstrated that nano-islands film annealed at 500 °C showed higher RIS, and nano-islands film generated by the

re-sputtering procedure and re-annealed at 500°C realized the RIS improvement. Furthermore, RIS, surface plasmon band position, and FOM of Au nano-islands films are dependent on each other.

Experimental

Au Nano-islands Fabrication

Cleaned and dried glass substrates were processed in a plasma cleaner (PDC-001, HARRICK) in argon atmosphere (110V, 10.2W) for 5 min. After that, the substrates were immersed in a 1:15 (volume ratio) solution of 3-aminopropyl triethoxysilane (APTES) (Shin-Etsu Chemical) in ethanol for 3 h, and then rinsed thoroughly with ethanol to remove physically adsorbed APTES molecules. Au was deposited on glass substrate using a quick coater (SC-701HMC, Sanyu Denshi, Japan) through controlling sputtering current and time. Thermal anneal treatment was carried out in air atmosphere at a serial of temperature varying from 100°C to 600°C in an muffle furnace (ISUZU SSTS-13K, ISUZU Seisakusho co., Ltd). Beginning of the heating was taken as zero time for the kinetics. A stationary temperature of 500°C was reached within about 20 min, and maintained constant within $\pm 5^\circ\text{C}$ for the desired time. The heating rate was approximately $25^\circ\text{C min}^{-1}$. The substrates after annealing were left to cool till room temperature before spectra detection.

Evaluation of RIS

The bulk refractive index sensitivity (RIS) is one of the commonly used methods to assess the sensing performance of noble metallic NP sensors, and is defined as the change of spectral parameters of the LSPR transducer in response to change in the refractive index (RI) of the bulk solution ²⁴. The extinction spectra of Au nano-islands films in water-glycerol mixtures of varying glycerol volume ratios were compared. With the increase in the volume percentage of glycerol, plasmon peak of Au nano-islands film shifted toward the red direction. The refractive index of the liquid mixture was calculated according to the Lorentz-Lorenz equation as shown in reference ²⁷:

$$\frac{n_{12}^2 - 1}{n_{12}^2 + 2} = \varphi_1 \frac{n_1^2 - 1}{n_1^2 + 2} + \varphi_2 \frac{n_2^2 - 1}{n_2^2 + 2}$$

(1)

where n_{12} is the refractive index of the liquid mixture, n_1 and n_2 are the indexes of water (1.333) and glycerol (1.475), respectively, and ϕ_1 and ϕ_2 are the volume fractions of the two components. The calculated refractive index of the liquid mixture as a function of the volume percentage of glycerol are approximately 1.340 (5%), 1.347 (10%), 1.357 (15%), and 1.361 (20%).

Results and discussion

Morphology of Au Nano-islands on Glass

T. Karakouz and coworkers' research show that as-prepared Au nano-islands (10 nm in thickness on glass) show a marked change when the heating temperature reaches at about 200 °C, while a surface plasmon band appears at around 300°C, which is attributed to the completion of the thermal dewetting and formation of well-defined islands²⁸. In light of this result, the annealing temperature was initially set at 300 °C in this research to study the dependence of morphology of islands on the annealing time. SEM images of Au nano-island films (deposited under 1.5 mA current for 70 s sputtering) annealed at 300°C with different time are shown in Fig. 1. The as-sputtered islands (Fig. 1 (A)) present a rather irregular shape, reflecting the concurrent accumulation of Au on the substrate surface and coalescence of primary nucleated islands during the sputtering process. According to the height distribution and cross section images shown in Fig. 3 (A), the average height of as-prepared Au islands was about 6 nm. The major change in island morphology of Au islands during annealing proceeds on the tens of hours at 200 °C and 10 min at 500°C in the reference 7 and 28. In this work, the annealing time period was set in the range of 10 min to 5 h. After 300°C 10 min annealing, the irregular shaped Au islands had changed to a spheroid-like shape (Fig. 1(B)), which was mainly attributed to the fast dewetting of islands from glass. With the annealing time further increase from 10 min to 5 h at 300°C, the average in-plane size of nano-islands increased from about 244.6 nm² to about 323.41 nm² as shown in Table 2-1.

Next, the influence of annealing temperature on the morphology change of islands was investigated. SEM image of Au nano-islands annealed at 500°C for 5 h is shown in

Fig. 2 A. Annealing at a high temperature made the in-plane size of nano-islands become large and extremely separated. The average size and inter-island distance of islands increased from approximately 323.41 nm² to 1308.95 nm² and 13.55 nm to 47.51 nm, respectively. As a result, the density of islands on glass was decreased.

In order to tuning the density of nano-islands, Au was re-sputtered on the sample prepared under 500°C 5 h annealing. SEM images of re-sputtered islands (1.5 mA 70 s re-sputtering), and the re-sputtered islands re-annealed at 300°C and 500°C for 5 h were studied as shown in Fig. 2 (B), (C), and (D). For the purpose of understanding the proposed “sputtering, annealing, re-sputtering, and re-annealing” process better, AFM images of related Au nano-islands were also investigated. It is demonstrated that after re-sputtering, the size of initially annealed islands are increased as shown in Fig. 2 (B) and Fig. 3 (C). In addition, the newly generated islands are also distributed among those big islands. As a result, the increase in islands density was realized. In the normal condition, the newly sputtered islands would prefer to settle on those previously formed islands. However, 500 °C 5 h annealing makes islands separated in a large distance (Fig. 2 A and Fig. 3 B). Hence, the newly sputtered Au islands could also settle among the space of those big islands on glass, directly. In the nest stage, re-annealing was adopted to eliminate the size and shape difference of the islands after re-sputtering. SEM images of nano-islands re-annealed at 300°C and 500°C are shown in Fig. 2 C and D. It is demonstrated that newly generated small islands in the re-sputtering process merge with the neighboring after re-annealing process. As a result, the small spheroid-like islands were formed among those big islands after 300°C re-annealing. Moreover, with the re-annealing temperature continuing increasing from 300°C to 500°C, the small islands generated during 300°C re-annealing continue merging with adjacent islands, which leads to the enlargement of both the newly formed islands and those big islands (Fig. 2 D and Fig. 3 D). There are certain differences of the average size and inter-particle distance of Au islands between SEM and AFM images, which is mainly attributed to the tip convolution effect.

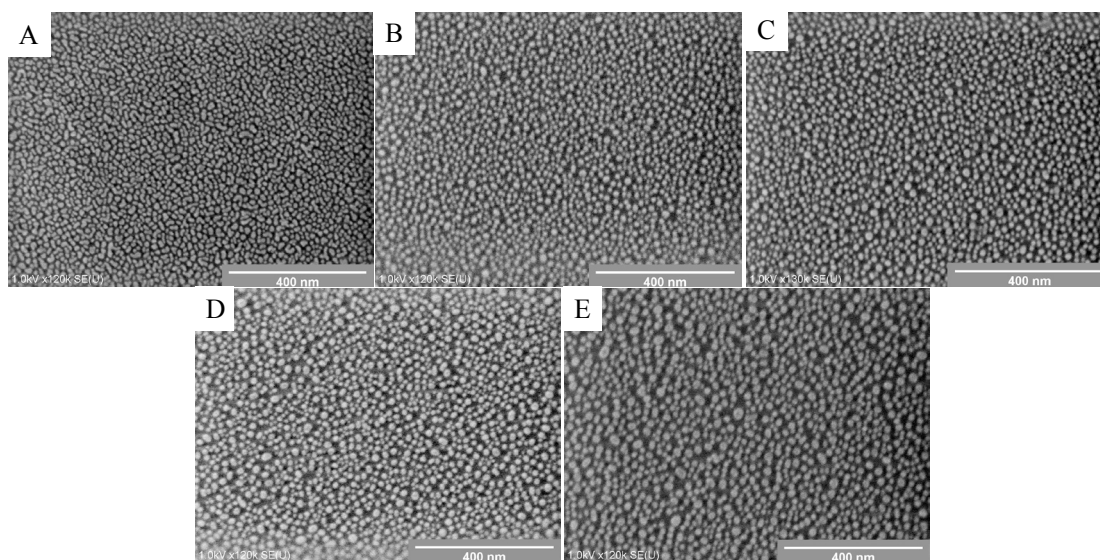


Fig. 1 SEM images of Au nano-islands film (1.5 mA 70 sputtering) on glass substrate without annealing (A) and annealed at 300 °C for 10 min (B), 30 min (C), 100 min (D), 300 min (E) ³⁸.

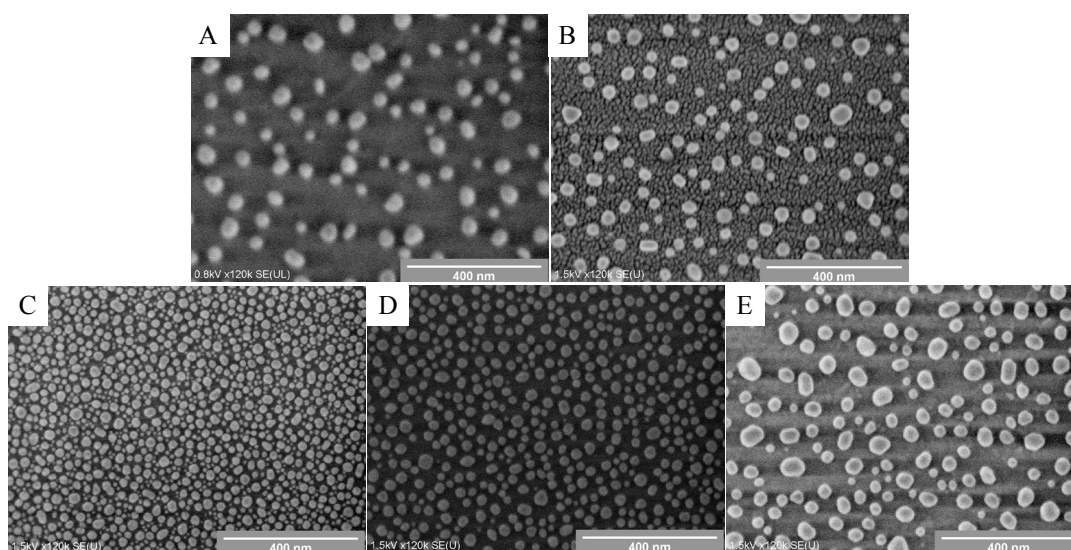


Fig. 2 SEM images of Au nano-islands film (1.5 mA 70 s sputtering) on glass substrate annealed at (A) 500 °C. The re-sputtered nano-islands on the islands shown in A with re-sputtering condition: 1.0 mA 20 s (B), 1.0 mA 40 s (C), and 1.5 mA 70 s (D). Re-annealing treatment to sample shown in (D) at 300 °C and 500 °C are shown in (E) and (F). (G) shows the SEM image of nano-islands film sputtered 1.5 mA 140 s and annealed at 500 °C for 10 h ³⁸.

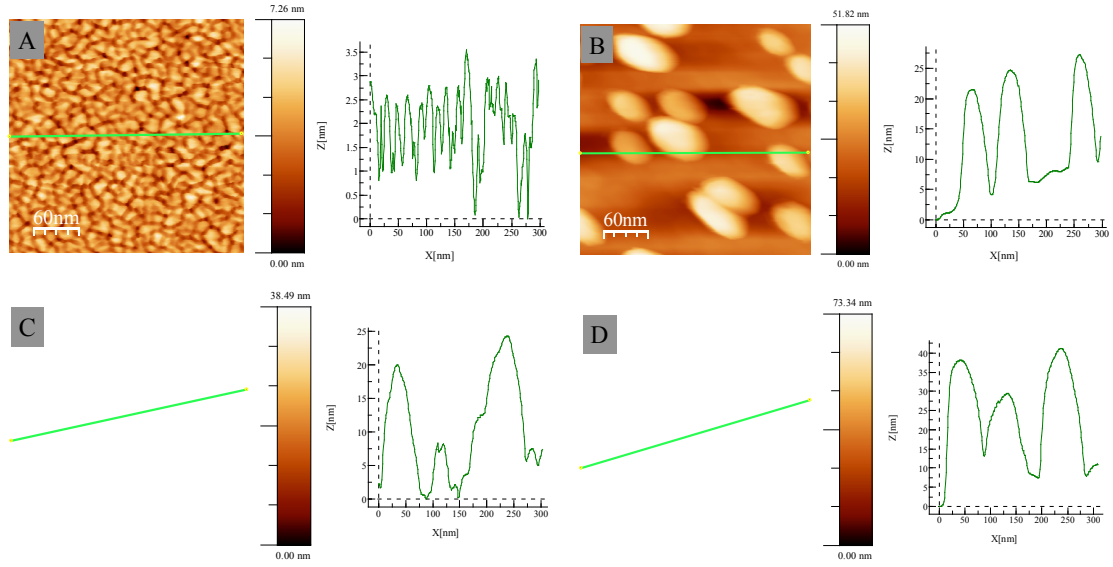


Fig. 3 AFM images of Au nano-islands on glass (A) 1.5mA 70 s sputtering, (B) 1.5mA 70 s sputtering and 500 °C 5 h annealing, (C) 1.5mA 70 s sputtering, 500 °C 5 h annealing, and 1.5mA 70 s re-sputtering, (D) 1.5mA 70 s sputtering, 500°C 5 h annealing, 1.5mA 70 s re-sputtering, and 500 °C 5 h re-annealing ³⁸.

Tab. 1 Average value of morphological parameters of Au islands deposited on glass substrate processed under various conditions, parameters in the table were calculated using Image j³⁸.

preparing condition	Size (nm ²)	aspect ratio	Circularity	r _e (nm)
1.5 mA 70 s sputtering	254.27	1.83	0.52	9.25
1.5 mA 70 s sputtering, 300 °C 10 min annealing	244.60	1.90	0.42	12.11
1.5 mA 70 s sputtering, 300 °C 30 min annealing	294.56	1.86	0.52	12.99
1.5 mA 70 s sputtering, 300 °C 100 min annealing	306.46	1.81	0.47	13.24
1.5 mA 70 s sputtering, 300 °C 5 h annealing	323.41	1.76	0.42	13.55
1.5 mA 70 s sputtering, 500 °C 5 h annealing	1308.95	1.59	0.19	47.51
1.5 mA 70 s sputtering, 500 °C 10 h annealing	1481.15	1.32	0.29	38.48
1.5 mA 70 s sputtering, 500 °C 5 h annealing, 1.5 mA 70s re-sputtering, 500 °C re-annealing	572.29	1.17	0.30	25.45

r_e is the inter-particle distance calculated using the formula, $r_e = \frac{1}{2\sqrt{\rho_0}}$ ($\rho_0 = \frac{N}{A}$, N is the number of particle in the area A), $\text{Circularity} = 4\pi \frac{\text{Area}}{[\text{Perimeter}]^2}$, with a value of 1.0 indicating a perfect circle. As the value approaches 0.0, it indicates an increasingly elongated shape.

LSPR Spectroscopy of Au Nano-islands on Glass

The influence of annealing time on the optical properties of Au nano-islands (1.5 mA 70 s) on glass was investigated. Fig. 4 A shows the transmittance spectra of Au nano-islands on glass annealed at 300 °C with annealing time increasing from 10 min to

300 min. It is demonstrated that the SP band position shifts to the blue, and the spectral bandwidth is narrowed with annealing time elongation. The effect of annealing temperature on the spectra of Au nano-islands on glass is shown in Fig. 4 B. It is illustrated that $\lambda_{\min}$ shifts to the blue, and the spectral bandwidth become narrow with temperature increase from 100 °C to 500 °C, which shares the similar spectral varying tendency as shown in Fig. 4 A. In reference 29, authors suggest that upon nanostructure size enlargement, the scattering efficiency gradually increases, eventually becoming dominant, and the SP band becomes much broader and shifts considerably to longer wavelength. Although the size of nano-islands annealed at high temperature such as 500 °C is much larger than those of low temperature annealed ones, related SP band is narrower, and $\lambda_{\min}$ shifts to the blue. The blue shift and the spectral bandwidth narrowing with annealing temperature increase might be mainly attributed to the inter-particle distance increase of islands. In addition, the recrystallization and an increase in the crystal size of islands during annealing, especially at high temperature, result in a decrease in the electron scattering at grain boundaries and roughness are also thought to be one of the important reasons for explaining the optical features of islands, as suggested in reference ²⁸. Furthermore, with annealing temperature continuing increasing to 550 °C or 600 °C, $\lambda_{\min}$ shows a reversely red shift, and the spectral bandwidth is broadened. According to the reference 7 and 28, when the annealing temperature were near the glass-transition temperature T_g of the cover-glass substrate ($T_g=557^\circ\text{C}$) or higher, the depression depth of islands and rim height in the glass are much larger. Hence, it was suggested that the effect of the refractive index of glass substrate to Au nano-islands become larger when the annealing temperature achieve to 550 °C or higher. In addition, islands faceting ¹¹, producing a more even crystal shape at higher temperature was speculated to contribute to the LSPR characteristics as well.

Spectra of Au nano-islands formed by re-sputtering on the nano-island film after 500 °C 5 h annealing were studied and presented in Fig. 4 C. The position of SP band does not show notable change with re-evaporation time increase in the first 40 s, while shifts to the red clearly with re-evaporation time continuing increasing. In addition, the bandwidth of SP is broadened outstandingly with re-evaporation time increase. It was suggested that the strong electric field coupling among nano-islands might be one of the

important reasons for spectral broadening and the SP band red shift. The coupling effect between NPs leads to weakening of the restoring force for the plasma electrons due to the presence of the charge distribution of the neighboring particle when the distance is short ^{7, 14, 30}. In addition, the polycrystalline property the newly formed islands and the enlargement of the initial islands induced by the re-sputtering process were also inferred to be one of the significant reasons for the transmittance decrease. Besides, the increase in scattering efficiency with the enlargement in islands size was also thought to contribute to the broadening of SP band and the SP position red shift.

Spectra of Au nano-island films under the same re-sputtering condition (1.5 mA 70 s) but different re-annealing temperature are presented in Fig. 4 D. Compared with the spectra of nano-islands film shown in Fig. 4 C, re-annealing made the position of SP band shift to the blue and the spectral bandwidth become narrow. Especially, when re-annealing temperature increased to 500 °C, the SP band position is nearly the same with nano-islands film formed by the once sputtering and 500 °C annealing process, which could also be explained by the decay length of electromagnetic fields from the surface of nanostructures, namely, the efficient coupling distance among the neighboring nano-islands. At the same time, the recrystallization and an increase in the crystal size during the re-annealing process could become one of the significant factors of the SP band blue shift and the spectral bandwidth narrowing.

Based on the above spectral varying characteristics versus sputtering and annealing conditions, we further investigated the spectral tuning range of Au nano-islands on glass under various processing conditions shown in Fig. 5. The sputtering conditions varied from 1.5 mA 20 s to 100 s, the annealing temperature changed from 100 °C to 600 °C, and the annealing time increased from 10 min to 5 h. the surface plasmon resonance peak could be tuned from about 510 nm to 610 nm, and the spectral full bandwidth tuning was realized from approximately 50 nm to 800 nm. Hence, it was concluded that both the SP resonance peak and the full bandwidth of spectrum could be successfully tuned in a relatively wide range using this means.

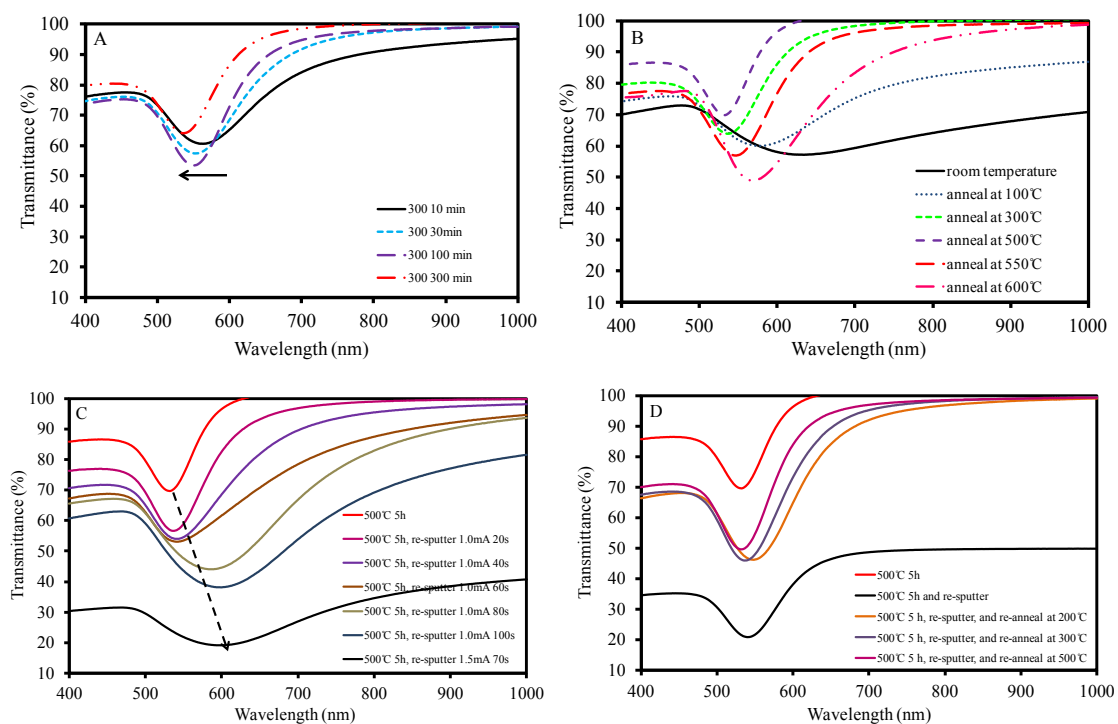


Fig. 4 Transmission UV-vis spectra of Au nano-islands on glass under sputtering current and time: 1.5 mA 70 s, and annealed at 300 °C for 10 min, 30 min, 100 min, and 300 min (A), (B) Au nano-islands on glass with 1.5 mA 70 s sputtering and annealed at temperatures from 100 °C to 600 °C for 5 h, (C) Au nano-islands on glass with 1.5 mA 70 s sputtering, annealed at 500 °C and re-sputtered with different time periods, (D) Au nano-islands on glass with 1.5 mA 70 s sputtering, annealed at 500 °C, re-sputtered (1.5 mA 70 s), and re-annealed at different temperature³⁸.

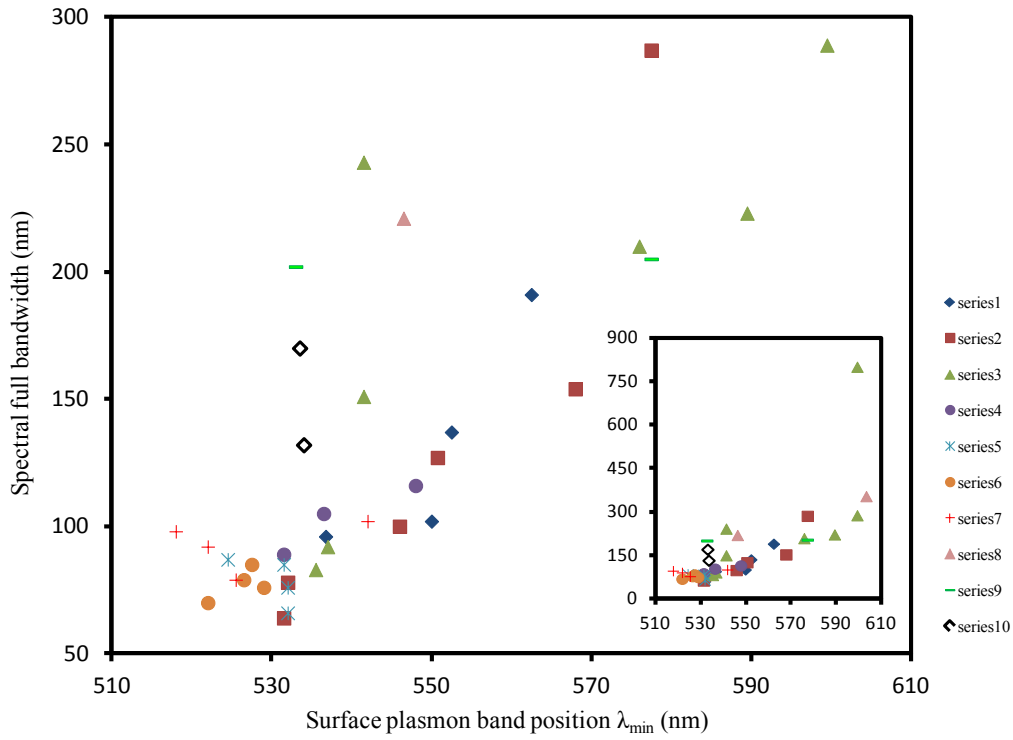


Fig. 5 The phase diagram of spectral tuning range (series delegate the sputtering and annealing condition) ³⁸

series 1: sputtering condition: 1.5 mA 70 s, annealed at 300 °C for (10 min, 30 min, 100 min, 300 min); **series 2:** 1.5 mA 70 s, annealed at (100, 200, 300, 400, 500, 550, 600 °C for 300 min); **series 3:** re-sputter on Au nano-islands (1.5 mA, 70 s 500 °C anneal) under 1 mA for 10 s, 20 s, 40 s, 60 s, 70 s, 80 s, 100 s, and 1.5 mA for 70 s; **series 4:** re-anneal of re-sputtered 1.5 mA 70 s at 200 °C, 300 °C, and 500 °C; **series 5:** 1.5 mA 20 s, 40 s, 70 s, and 100 s annealed at 500 °C for 300 min; **series 6:** 1.5 mA 20 s, 40 s, 70 s, and 100 s annealed at 500 °C for 100 min; **series 7:** 1.5 mA 20 s, 40 s, 70 s, and 100 s annealed at 500 °C for 10 min; **series 8:** 1.5 mA 20 s, 40 s without anneal, **series 9:** 1.5 mA 20 s, 40 s annealed at 100 °C for 10 min; **series 10:** 1.5 mA 20 s, 40 s annealed at 300 °C for 10 min.

Refractive Index Sensitivity (RIS) and Theoretical Approximations

To explain the structural independence of the RIS on the LSPR band position, we adopted the quasistatic theory analysis given by ^{9, 31} as an approximate analytical expression for the RIS, $d\lambda_{\min}/dn$, of the resonance wavelength to the RI of the medium.

Here, the wavelength of plasmon peak at the resonance condition is expressed by $\lambda_{\min}$, the real part of the dielectric function of gold is expressed by ϵ_r at resonance condition, and the related RI of surrounding medium is expressed by n ($n=\sqrt{\epsilon_m}$).

$$d\lambda = (d\epsilon_r / d\lambda |_{\lambda = \lambda_{\text{LSPR}}})^{-1} d\epsilon_r \quad (2)$$

We consult the relax assumption of a spherical NP shape. A treatment of the scattering problem in ellipsoidal coordinates leads to the following expression for the polarizabilities α_j along the principal axes a_i ($i=1, 2, 3$)³²:

$$\alpha_j = 4\pi a_1 a_2 a_3 \frac{\epsilon(\omega) - \epsilon_m}{3\epsilon_m + 3L_i(\epsilon(\omega) - \epsilon_m)} \quad (3)$$

L_i is a geometrical factor, while $\epsilon(\omega)$ is the particle dielectric function. Resonance occurs at poles of the polarizability. The resulting resonance condition is show as below:

$$3\epsilon_m + 3L_i(\epsilon(\omega) - \epsilon_m) = 0 \quad (4)$$

As a result, the derivative of the above equation is written as:

$$d\epsilon_r = \left(1 - \frac{1}{L_i}\right) d\epsilon_m \quad (5)$$

Thus, equation (2) can be written as

$$d\lambda = (d\epsilon_r / d\lambda |_{\lambda = \lambda_{\text{LSPR}}})^{-1} \left(1 - \frac{1}{L_i}\right) d\epsilon_m \quad (6)$$

We obtain that the RIS is proportional to the material characteristics, ϵ_m , and $\left(1 - \frac{1}{L_i}\right)$.

When material and $d\epsilon_m$ are the same, RIS is determined by $\left(1 - \frac{1}{L_i}\right)$. For sputtered gold nano-islands, a quantification of the average deviation from circularity for the island nanostructure will be convenient for a description of their optical and RIS properties. We use the definition of eccentricity e of an ellipse³³ to describe the deviation of island nanostructure from circularity as following:

$$\bar{e}^2 = 1 - \left(\bar{b}/\bar{a}\right)^2 \quad (7)$$

$\bar{a}$ and $\bar{b}$ are the averaged major axes and minor axes, and the geometrical factor L_i are given as follows:

$$L_1 = \left[(1 - \bar{e}^2) / 2\bar{e}^3 \right] \{ \ln[(1 + \bar{e})/(1 - \bar{e})] - 2\bar{e} \} \quad (8)$$

$$L_2 = L_3 = 1/2(1 - L_1) \quad (9)$$

It is suggested that that nano-island with prolonged shape would has smaller

geometrical factor (shape-dependent depolarization parameter), which process a higher RIS. In addition, thermal annealing made the size and inter-particle distance of nano-islands change obviously. Hence, investigation on the dependence of RIS of nano-islands on the size and inter-particle distance is also necessary. According to the “plasmon ruler equation” for dipolar-coupling model promoted by Prashant K. Jain and coworkers^{34, 35}

$$\Delta\lambda/\lambda_0 = \frac{14.3\varepsilon_m(1+\gamma)^2}{(12\Lambda(s/D)^3 - (1+\gamma))(464.6 + 14.3\varepsilon_m\gamma)} \quad (10)$$

Where $\Delta\lambda/\lambda_0$ is the fractional plasmon shift, λ_0 denoted as the single-particle resonance wavelength maximum as (for $s/D \rightarrow \infty$), γ is a factor which depends on the nanoparticle shape, e.g. $\gamma = 2$ for sphere. D is the particle dimension along the axis of inter-particle interaction, and Λ depends on the other particle dimensions, e.g. $\Lambda = 1$ for sphere and $\Lambda = (1/\text{Aspect ratio})$ for oblate spheroids interacting along the long-axis. s is the inter-particle edge-to-edge separation. From this equation, we knew that the SP band position shift is dependent on s/D , ε_m , and γ . When all the spectra were detected in air, and we roughly thought that γ is nearly the same for nano-spheroids after annealing. Then, we suggested that the fractional plasmon shift was affect by s/D .

The dependence of RIS and SP position on annealing temperature, re-sputtering condition, and re-annealing procedure was studied and shown in Fig. 6 A to C. RIS of Au nano-islands on glass under the same evaporation conditions while different annealing temperature is shown in Fig. 6 A. RIS increases with the raising of annealing temperature. In addition, RIS of nano-island generated by re-sputtering shown in Fig. 6 B first decreases with re-sputtering time extension. Specially, when the re-evaporation time is long (1.5 mA 70 s) the RIS decreases to the negative. In the reference 19 and 31, authors suggest that coherent coupling of the plasmon resonance of closely spaced particles is responsible for the blue shift. Here, it was suggested that the optical shifts observed for the immobilized gold islands relative to solution, as a function of particle size, might be also due to the complex interplay between several additional factors. Apart from inter-island coupling, the presence of the glass substrate in contact with the NPs also causes an anisotropic increase in the effective refractive index of the local environment of NPs.

RIS and SP band position showed the opposite trend. Namely, the larger RIS appeared at a short SP wavelength position. Combined morphological with the optical characteristics of Au nano-islands, it was suggested that high temperature annealing and re-annealing could make the E-field coupling among nano-islands weak, and the appropriate nano-islands density increase, which leads to the increase in the RIS. In addition, the average size and the crystal structure of islands in this proposed “sputtering, annealing, re-sputtering, and re-annealing” process are another two significant factors which would concern the final RIS. Another important index to evaluate the performance of LSPR sensor is FOM which defined as that the RIS divided by the full bandwidth at half-maximum of the extinction peak of Au nano-islands, expressed as ^{15, 36, 37}:

$$\text{FOM} = \frac{\text{RIS}}{\text{full bandwidth at half-maximum extinction peak}} \quad (11)$$

The transmittance spectra were asymmetry. Hence, the full bandwidth at half-maximum extinction peak was calculated using the two times of $[\lambda_{\text{half-maximum extinction}} - \lambda_{\text{min}}]$ ($\lambda_{\text{half-maximum extinction}}$ is the wavelength where the corresponding extinction equals to half of the maximum extinction from the longer wavelength side of λ_{min}). FOM versus the annealing and re-annealing temperature is shown in Fig. 6 D. It is manifested that the varying trend of FOM is the same with the RIS variation tendency shown in Fig. 6 A and C. The large FOM values occur at nano-islands films under the 500 °C annealing and re-annealing conditions.

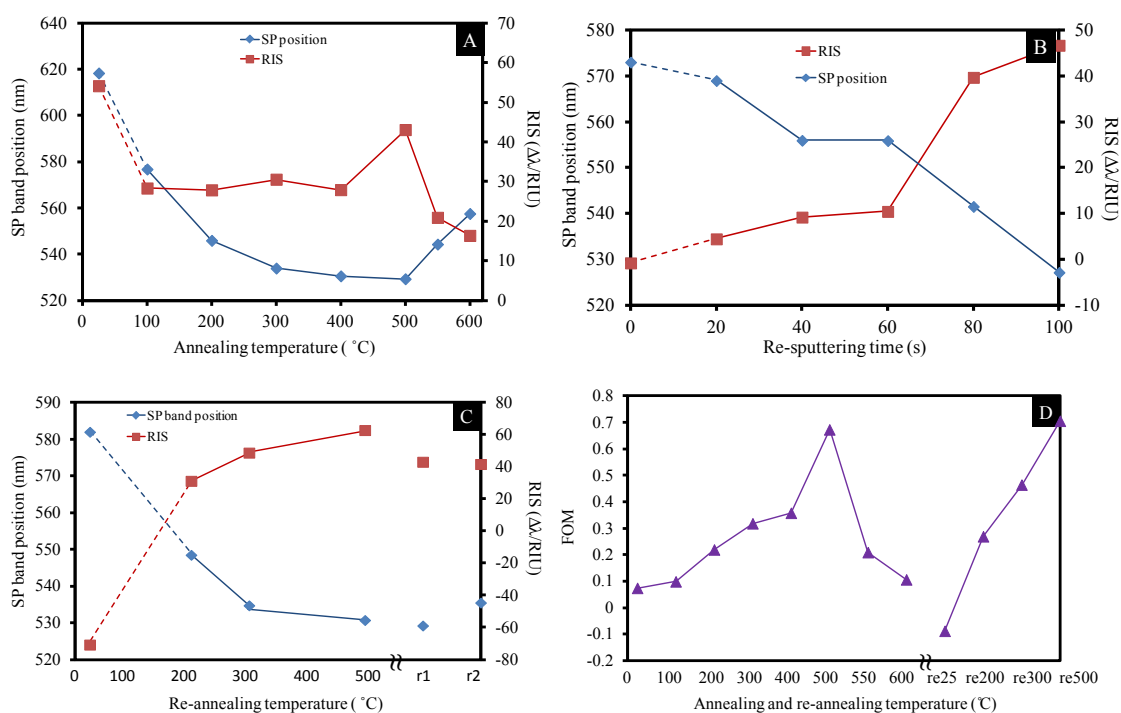


Fig. 6 The RIS of nano-islands on glass with different sputtering, annealing, re-sputtering, and re-annealing treatment, and the varying tendency of FOM of nano-islands³⁸.

Conclusion

Sputtered Au nano-islands on glass substrate followed by annealing in air is a convenient scheme to obtain Au islands films displaying characteristics LSPR property. Annealing was verified to take effect on nano-islands re-shaping and structure tuning. In addition, high temperature annealing such as 500 $^{\circ}\text{C}$ could generate well-separated larger-sized nano-spheroids. Moreover, through the re-sputtering and re-annealing process, we successfully realized nano-islands structure further tuning, which is different from the once sputtering and annealing procedures. Moreover, Re-sputtering and re-annealing process improved the RIS. The RIS and FOM showed the same varying tendency, while the SP band position showed the opposite trend versus annealing and re-annealing temperature. However, the bare AuNPs don't have specific selectivity to terpene gas molecules.

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