Surface Plasmon Resonance of Two-Dimensional Gold Colloidal Crystals Formed on Gold Plates

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The free electrons inside precious metals such as Au vibrate when the surface of the metal is irradiated with an electromagnetic wave of an appropriate frequency. This oscillation is referred to as surface plasmon resonance (SPR), and the resonance frequency varies with permittivity of the medium around the metal. SPR sensors are widely applied in the fields of bioscience and pharmaceutical sciences, including biosensing for drug discovery, biomarker screening, virus detection, and testing for food safety. Here, we fabricated a metal–insulator–metal (MIM) SPR sensor by constructing two-dimensional (2D) regular array of Au colloidal particles (2D colloidal crystals) on an insulator layer over a thin Au film coated on a glass substrate surface. The 2D crystals were fabricated by electrostatically adsorbing negatively charged three-dimensional colloidal crystals onto a positively charged thin insulator formed on Au film. The plasmon peaks/dips from the MIM structure were measured in aqueous solutions of ethylene glycol (EG) at various concentrations. Multiple plasmon peaks/dips were observed due to the localized SPR (LSPR) of the Au particles and the Fano resonance between the Au particles and thin film. The plasmon peaks/dips shifted to higher wavelengths on increasing EG concentrations due to an increase in the refractive index of the media. The observed peak/dip shift was approximately twice that of LSPR from an isolated Au particle. We expect the present MIM substrate will be useful as a highly sensitive sensor in the pharmaceutical field.

Key words two-dimensional colloidal crystal; gold particle; metal–insulator–metal structure; surface plasmon resonance; Fano resonance

Introduction

When the surface of a precious metal such as Au or Ag is irradiated with an electromagnetic wave of an appropriate frequency, the free electrons inside the metals collectively vibrate. This phenomenon is referred to as surface plasmon resonance (SPR).1,2 and the resonance frequency varies with the permittivity of the medium surrounding the metal. SPR has been used to quantify molecules attached to metal surfaces and is widely applied in chemistry and bioscience.2–9 The use of SPR has been widely explored in pharmaceutical sciences, including biosensing for drug discovery,10 biomarker screening,11,12 virus detection,13 nucleic acid detection,14 and testing for food safety.15,16 Additionally, medical sensors based on antigen–antibody reactions are developed using SPR.6–8,17

In applications such as the aforementioned sensors, propagating plasmons produced using flat metal plates are commonly used.2,6,7,18 Oppositely, the plasmon resonance produced using fine Au colloidal particles, where the plasmon is localized within the particles (localized SPR; LSPR), is used for sensing.1,5,8,18,19 Recently, plasmon resonance in various microstructures of metals such as the metal–insulator–metal (MIM) structure,3,20–23 has attracted considerable attention. Nicolas et al.21 reported fabrications of the MIM structure, where Au cylinders (diameter, 80–200 nm; height, 50 nm) were periodically arranged (gap size, approximately 300–600 nm) on the insulator layer (thickness, 6 nm) covered on an Au film (50 nm). They observed several peaks in the extinction spectrum of the MIM structure, owing to the interference between SPR and LSPR, which is called Fano resonance.3,20–24 The Fano resonance is advantageous for material sensing because it is more sensitive to changes in the ambient permittivity than the regular LSPR peak.

Such high sensitive sensing of molecules is an important technology, not only in basic research but also in the clinical field, since it can lead to early detection of diseases and reduce the amount of specimens needed for e.g., blood tests. We believe that the MIM structure described above is one of the useful materials for high-sensitivity SPR analysis in the pharmaceutical field. However, currently electron beam lithography is used to fabricate the MIM structures, which requires a complicated process for substrate fabrication and makes mass production for practical use difficult.

To solve this problem, we used the “crystal” structure of charged Au colloidal particles as the regular arrangement part (the top layer) of the above structure. In reference 21, a two-dimensional (2D) regular array of Au pillars of several hundred nanometers in size was created on an insulator. We fabricated regular structures using Au particles with diameters ranging from approximately 150 to 250 nm, by the method which will be described below.

Colloidal dispersions of charged particles are stabilized against aggregation due to long-range electrostatic repulsive forces acting between the particles. When the electrostatic repulsion is weak, the particles are randomly arranged in the dispersion [Fig. 1(a) left]. On the other hand, when the repulsion is strong enough, the particles are regularly arranged in

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a body-centered cubic or face-centered cubic lattice [Fig. 1(a) right]. This structure is referred to as “charged colloidal crystalline.”25–27) In the crystal state, the particles are not in contact with each other, but are regularly arranged with gaps between them. The distance between the particle surfaces reach as much as 1 µm, when the electrostatic interparticle repulsion is sufficiently strong.

Recently, we reported that 2D crystals were obtainable by electrostatic adsorption of the three-dimensional (3D) charged colloidal crystals onto the oppositely charged flat plate.28) In the present study, we fabricated MIM structures by adsorbing 2D Au colloidal crystals on the oppositely charged insulator layer, over a thin Au film coated on a glass substrate surface29) [Fig. 1(b)]. As illustrated in Fig. 1(c), multiple plasmon peaks were observed from the MIM substrates because of the Fano resonance.

Generally, the plasmon peak shifts on changing the permittivity of the surrounding medium. The relative permittivity \( \varepsilon_r \) of a material varies with the frequency \( \omega \) of the incident electromagnetic wave. For non-polar molecules, the basic equation of electromagnetism between \( \varepsilon_r \) and the refractive index \( n \)

\[
\varepsilon_r = n^2
\]

is well established, for a wide range of \( \omega \). For polar molecules such as water, equation (1) does not hold for small \( \omega \), but it holds well for \( \omega \) of visible light. In this study, we will discuss the plasmon peak shift by using the refractive index as an index.

The peak shift of the MIM substrate fabricated in this study was approximately twice as large as that of a single Au particle. The present MIM substrate is expected to be useful as a highly sensitive SPR sensor that is applicable in the field of pharmaceutical sciences.

### Experimental

**Colloidal Particles** The characteristics of the colloidal particles used are listed in Table 1. Silica particles (Sicaster®-GreenF) were purchased from Polyscience Inc. (Warrington, PA, U.S.A.) as an aqueous dispersion and deionized by adding a mixture of anion- and cation-exchange resin beads (AG 501-X8(D), 20–50 mesh, Bio-Rad Laboratories, Inc., CA, U.S.A.). Au colloidal particles, Au 1 (Au colloidal solution-SC), were purchased from Tanaka Precious Metal Co., Ltd. (Tokyo, Japan); Au 2 and Au 3 (Au colloidal aqueous dispersion, AMS-Au) were synthesized by Fuji Chemical Co., Ltd. (Osaka, Japan). Although Au 3 had a high surface charge for the crystallization, the charge number of Au 1 and Au 2 particles were low. To facilitate crystallization, we introduced negative surface charges to Au 1 and Au 2 particles using 3-mercapto-1-propanesulfonate as follows. First, an aqueous solution of 0.05 M MPS (0.08 mL) was added to water (3.92 mL) and homogenized by ultrasonification for 5 min. Afterward, 4 mL of

| Sample | \( d \) (nm) | \( \zeta \) (mV) | \( Z \) |
|--------|------------|-------------|------|
| Silica | 510 ± 53   | −56         | −5060|
| Au 1   | 152 ± 41   | −33         | −375 |
| MPS-Au 1 | 152 ± 41 | −50         | −606 |
| Au 2   | 216 ± 25   | −22         | −359 |
| MPS-Au 2 | 216 ± 25 | −45         | −910 |
| Au 3   | 243 ± 28   | −41         | −978 |

\( a \) Determined through dynamic light scattering; \( b \) Zeta potential; \( c \) Labeled with green fluorescent dye; \( d \) Modified 3-mercapto-1-propanesulfonate.
the aqueous Au colloid (approx. 0.01 wt%) was added, and the solution was homogenized by ultrasonification for 10 min to introduce MPS to the Au particles. The samples were purified by centrifugation, and ion exchange resin beads was added for deionization. Hereinafter, the particles that underwent surface modification using MPS are denoted by MPS-Au 1 and MPS-Au 2.

Particle diameters \( d \) were obtained by dynamic light scattering (DLS) and are listed in Table 1. The zeta potential \( \zeta \) was calculated from the mobility determined by microscopy electrophoresis, using Henry's equation.\(^{30}\) The effective charge number \( Z \) of the particle was estimated from the \( \zeta \) value, based on the Poisson–Boltzmann equation.\(^{30}\)

The water was purified using a Milli-Q system (Millipore Co., Ltd., MA, U.S.A.).

**Dynamic Light Scattering (DLS)** DLS measurements were performed using an FDLS-300 (Photal Co., Ltd., Osaka, Japan) equipped with a helium–neon laser (100 mW; wavelength, 532 nm). The \( d \) of the colloidal particles was estimated from the diffusion coefficient measured under the conditions of the particle volume fraction \( \varphi \leq 10^{-4} \) and NaCl concentration \([\text{NaCl}] = 10^{-4} \) M, assuming the Stokes–Einstein relation.

**Electrophoretic Mobility Measurements** The mobility of the colloidal particles was measured using a microscopic electrophoresis apparatus, ZC-3000U (Microtec Co., Ltd., Chiba, Japan). The number concentration of the particles was set at \( 10^9–10^{11} \) L\(^{-1}\) and at \([\text{NaCl}] = 10^{-7} \) M. The average value was obtained from the measured values of the mobility for more than 100 particles.

**Surface Modification of Glass Substrates** For the microscopic observation, a NEO microcover glass (24 mm × 24 mm, Matsunami Glass Co., Ltd., Tokyo, Japan) was used as a glass substrate. Au-deposited glass (22 × 26 × 0.55 mm; thickness of Au-deposited film, 30 nm) was purchased from Kenis Co., Ltd. (Osaka, Japan). Both glasses were immersed in concentrated sulfuric acid for more than one day and thoroughly washed with ultrapure water.

Positively charged glass substrates were prepared by modifying the cover glass with 3-aminopropytriethoxysilane (APTES, Shin-Etsu Chemical Co., Ltd., Tokyo, Japan) with objective lenses (×100 oil immersion and ×40, Plan Flour, Nikon Co., Ltd.).

**Spectroscopy** Absorption spectra were recorded using an UV-visible (UV–VIS) spectrophotometer (UV-2400PC, Shimadzu Co., Ltd., Kyoto, Japan). The reflectance spectrum of the substrate was measured using a fiber spectrometer (USB2000, Ocean Optics, Inc., FL, U.S.A.). Ethylene glycol (EG; FUJIFILM Wako Pure Chemical Corporation, Osaka, Japan) was used to confirm the sensing ability of the substrates.

**Results and Discussion**

**Crystallization of Au Colloidal Particles in Aqueous Dispersions** First, we describe the preparation of 3D charged Au colloidal crystals. This structure is essential for the construction of the MIM substrates to be fabricated in the present study. As mentioned earlier, the driving force of the charged colloidal crystals is the electrostatic repulsive force between the particles. At lower salt concentration, the electrostatic shielding effect is weaker, and the electrostatic repulsion between the particles is stronger. Thus, the colloidal crystals are formed under low salt condition.\(^{25–27}\)

We prepared colloidal crystals by deionizing the samples; this was performed by adding methanol. The
crystallization occurred from the vicinity of the ion exchange resin beads. Figures 3(a) and (b) show the microscopic images of the Au 2 particle dispersion (0.07 wt%) one day after the addition of the ion exchange resin beads. After one day, the Au particles were settled at the bottom. Figure 3(a) is obtained using a 40× objective lens. The images of the ion-exchange resin beads are indicated by a white dashed line. The bright regions surrounding the resin beads are the crystal region.

Figure 3(b) shows the image of the crystals obtained using a 100× objective lens. Although the size of the Au particles (216 nm) was below the optical resolution of the microscope, the particles were observed extremely brightly because of the surface plasmon. Figure 3(c) shows the radial distribution function $g(r)$ obtained from the image analysis of Fig. 3(b). The horizontal axis of the figure is the distance between the particle centers normalized using the particle radius $a_p$. An or-
dered periodic structure was observed to have been generated. The distance between the centers of the particles was 560 nm, as calculated from the peak position of $g(r)$, and the distance between the nearest surfaces was calculated to be 340 nm. Thus, 3D charged colloidal crystals of Au colloidal particles with a distance between the particles were obtained.

**Fabrication of MIM Substrates Using Au Colloidal Crystals** We previously reported that 2D crystals with a non-close-packed structure can be obtained by electrostatic adsorption of the 3D crystal structure on an oppositely charged substrate. Here we fabricated 2D crystals on an insulator layer formed on the Au-deposited glass substrate. Figure 4(a) shows a schematic diagram of the fabrication. Prior to the adsorption experiments of the Au particles, we examined 2D crystals of silica colloidal particles on the APTES-modified Au-deposited glass substrate (see Supplementary 2). Supplementary Figure S2 shows a microscopic image of the 2D silica crystals.

The 2D Au colloidal crystals were similarly obtained using the APTES-modified Au-deposited glass substrate. We used MPS-Au 2 particles, which had high charge, to facilitate crystallization. Figures 4(b) and 4(c) show the micrographs and $g(r)$ of the resulting 2D crystals, respectively. The interparticle distance in the 2D crystal was 560 nm, indicating that the gaps between the particles were approximately 340 nm. In the following experiments, we used this MIM substrate, which has 2D Au colloidal crystal in the top layer.

**Optical Properties of Au Particle Dispersions** Au colloidal particles scatter light as nonmetallic particles and exhibit absorption because of LSPR. When the particle size is close to the wavelength of the light used in the measurement, light scattering is described as Mie scattering rather than Rayleigh scattering. The absorption spectra of Au particles were calculated based on Mie scattering theory using the program described in Ref. 2. The details of the calculation are given in Supplementary 3. On the calculation, $\varepsilon$ value of the Au par-
articles was estimated in terms of the Drude model. Figures 5(a) and (b) show the theoretical spectra for particle sizes $d = 150$ and $200$ nm, respectively. The solid, dashed, and dotted lines represent the extinction cross-section $C_{\text{ext}}$, scattering cross-section $C_{\text{sca}}$, and absorption cross-section $C_{\text{abs}}$, respectively. Here, $C_{\text{ext}} = C_{\text{sca}} + C_{\text{abs}}$ and the extinction of the sample were equal to $C_{\text{ext}} n_p$, where $n_p$ is the number density of the particles in dispersions.

The measured absorption spectra of Au 1 and Au 2 are shown in Fig. 5(c) (particle concentration approx. 0.01 wt%). For Au 1 ($d$ approx. 150 nm), peaks were observed at wavelengths of 540 and 650 nm, whereas for Au 2 ($d$ approx. 200 nm) a peak was observed at a wavelength of 560 nm. These results correlated with the calculated curves. For both cases, the contribution of scattering was smaller in the experiment than in theory. This may be due to the effect of the particle size distribution.

Optical Properties of the Substrates The optical properties of the substrates were examined by reflection fiber spectroscopy. Three substrates were used: (1) Au-deposited glass, (2) Au particles adsorbed on a cover glass substrate, and (3) MIM structure (2D Au crystal/insulator/Au-deposited glass). Hereafter we refer to these substrates as substrate (1), (2) and (3), respectively. Here we used MPS-Au 1 ($d$ approx. 150 nm) and Au 3 ($d$ approx. 200 nm) particles to facilitate crystallization. Figures 6(a) and (b) show the reflection spectra of substrates prepared by using MPS-Au 1 and Au 3, respectively. For substrate (1), a minimum was observed around 480 nm. At $d$ approx. 150 nm, a peak around 590 nm was observed for substrate (2). This correlated with the scattering peak of the
aforementioned single particle. For substrate (3), peaks appeared at even longer wavelengths, compared with the first two substrates. At \( d \approx 150 \text{ nm} \), multiple peaks/dips were also observed for substrate (3). This was considered to be caused by the Fano resonance. At \( d \approx 200 \text{ nm} \), the single particle-derived peak and Fano resonance-derived peak overlapped, resulting in a distorted peak shape.

The surface plasmon peak shifted in response to changes in the refractive index of the surrounding medium.\(^2\)\(^,\)\(^3\) We confirmed the peak shift of the SPR using mixtures of water \((n_{\text{water}} = 1.33)\) and EG \((n_{\text{EG}} = 1.43)\) at various concentrations as media. We chose EG because it has relatively high value of refractive index, and EG is miscible with water in any ratio. By using EG aqueous solution, the refractive index of the medium was continuously variable over a wide range. The substrates were the same as those in Fig. 6. The substrate was initially wetted with water, but was replaced by adding a sufficiently large amount of water/EG on top of the substrate. Microscopic observation of the solvent-displaced substrate without drying confirmed that the particle arrangement structure did not change significantly.

Figures 7(a), (b), and (c) show the results for MPS-Au 1 \((d \approx 150 \text{ nm})\); and Figs. 7(d), (e), and (f) are the results for Au 3 \((d \approx 200 \text{ nm})\). Figures 7(a) and (d) show the spectral changes versus EG concentrations for substrate (2), and Figs. 7(b) and (e) show those for substrate (3). The peak/dip positions were indicated by dashed lines. For both cases, the plasmon peaks/dips shifted to longer wavelengths as the EG concentration increased. Supplementary Figure S4 (Supplementary 4) shows the results for substrate (1), indicating that the peak/dip shift did not significantly vary on changing the EG concentration.

To evaluate the sensing ability, the wavelength changes per refractive index change (refractive index unit, RIU) were determined. Figures 7(c) and (f) show the plots of the peak/dip shift against the refractive index. The solid and dashed lines are the data of substrate (3) and substrate (2). The maximum peak shift was observed for substrate (3) at \( d \approx 200 \text{ nm} \) (wavelength = 600–650 nm, 363 nm/RIU). The presence of peaks in the wavelength region of \( > 700 \text{ nm} \) was indicated, although they could not be accurately and sufficiently measured with the optical system used in this experiment. They were more than twice those of substrate (2) (wavelength = 540 nm, 145 nm/RIU) and larger than the reported value of 300 nm/RIU.\(^2\)\(^,\)\(^3\) Thus, it was suggested that high sensing ability could be achieved using MIM structures. We note that the peak shift of 200 nm Au particles calculated by Mie scattering theory was 196 nm/RIU, and the observed value (145 nm/RIU) was approximately 74% of the theoretical value. This difference may suggest that water molecules are more likely to be distributed near the surface of the Au particles than EG molecules (selective solvation). We are currently investigating the difference between experiment and theory.

However, at \( d \approx 150 \text{ nm} \) [Fig. 7(c)], the maximum change (wavelength = 700–750 nm, 138 nm/RIU) for substrate (3) was lower than that for substrate (2) (wavelength = 600 nm, 209 nm/RIU). This was considered to be due to the overlap of the single particle-derived peak and Fano resonance-derived peak, which reduced the shift. We expect that these findings will be useful for fabricating plasmon sensors with high sensitivity.

**Conclusion**

Here, we fabricated MIM-structured substrates by immobilizing a regular array of Au colloidal particles on the surface of an insulator film on Au-deposited glass substrates via electrostatic adsorption. This method was facile because the Au colloidal particles formed the crystal structure by self-assembly. We examined the optical properties of the fabricated MIM substrates. Multiple peaks/dips caused by Fano resonance were observed. We investigated the peak shifts in response to changes in the refractive index of the solvent using an aqueous EG solution. The shift of the MIM substrate was larger than that of the Au particles/glass substrate. These results indicated a high sensing ability in the MIM structure. The method used in this study is expected to enable easy fabrication of 2D ordered structures with spacing between particles, leading to increased sizes and mass production.

SPR is expected to have a wide range of applications in the field of pharmaceutical sciences, and has already been utilized as various biosensors in basic research. Here, although we used a mixture of solvents with different refractive indices (permittivities) as model materials, the SPR method can detect the change of permittivity around the particles, on adsorbing biomolecules. As numbers of reports have already shown, the coupling with antigen–antibody reactions can be used to provide selectivity. Particularly, we expect the MIM substrates to be used as disposable diagnostic chips. We expect the present MIM substrate will be useful as a highly sensitive biosensor in the pharmaceutical field.

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**Conflict of Interest** The authors declare no conflict of interest.

**Supplementary Materials** This article contains supplementary materials.

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