

Studies on the Surface-Enhanced Infrared Spectroscopy of Langmuir–Blodgett Monolayers of Azobenzene Carboxylic Acid on Silver Island Films

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Thin silver island substrates with different sizes and different states of aggregation of the silver particles are prepared by evaporation and a thermal annealing process. The Langmuir–Blodgett monolayer of 4-octyl-4'-(3-carboxytrimethyleneoxy)azobenzene are deposited on these silver-coated substrates, and their infrared spectra are studied. The experimental results reveal that the enhancement factor decreases as the silver particles become less aggregated.

I. Introduction

Surface-enhanced spectroscopy, such as surface-enhanced Raman spectroscopy, surface-enhanced luminescence spectroscopy, surface-enhanced infrared spectroscopy, and so forth, have been attracting considerable research interests because of their importance in fundamental physical and chemical research, and also their prospective practical applications. Since their discoveries, extensive studies have been conducted and many important works have been reported.^{1–15} Among the surface-enhanced spectroscopies, it is in recent years that the surface-enhanced infrared spectroscopy (SEIRS) has become more and more popular.^{16–26} SEIRS is believed

to be an important method in many areas, such as in situ monitoring of surface chemical reactions,^{27–31} structural investigation of ultrathin organic films,^{22,32–33} and trace adsorbate analysis,^{34–36} and so forth.

In these surface-enhanced phenomena, the enhancement-active substrates (usually island metal films) are found to play an important role because of the two main mechanisms of the surface-enhanced spectroscopies: one is attributed to the enhanced local surface electromagnetic (EM) field generated through the coupling of the incident EM field into the metal film surface by the roughness of metal surfaces (called electromagnetic mechanism, i.e., *EM mechanism*),^{1–5,16,23,32} and the other is called *chemical mechanism*, which is due to the electron transferring from the molecules and substrates, resulting in a larger dipole moment and consequently leading to an enhanced absorption.^{1,19,21,36–38} All of these factors show a very close relationship of surface-enhanced spectroscopy with the nature of the enhancement-active substrates. This feature has been observed in many works on surface-enhanced

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Raman spectroscopy (SERS),^{6–14} as well as in surface-enhanced infrared spectroscopy (SEIRS).^{23,32–33,38}

In the previous works on SEIRS,^{23,38} the thickness of the enhancement-active substrates (silver island film) is tuned to examine the enhancement effects, and also the thickness is relatively larger (≥ 10 nm), in which case the silver particles are already in a highly aggregated state. In this paper, we adopted the method of vacuum evaporation and rapid thermal annealing to prepare very thin silver island films (thickness ≤ 10 nm) and to tune the morphology of them. The silver films are found to be consisting of silver particles of different sizes and different aggregation states, characterized by morphological study and optical absorption study. By the Langmuir–Blodgett (LB) technique, monolayers of azobenzene carboxylic acid were fabricated on these silver island substrates. The enhanced infrared absorption of the LB monolayers on different silver substrates allow us to make an investigation into the dependence of SEIRS on the morphology of the silver film, especially the aggregation of the silver particles.

II. Experimental Section

SEIRS-active silver island films were prepared by vacuum evaporation and thermal annealing. The morphological study on these substrates were done by an atomic force microscope (AFM), and the UV–visible spectroscopy was adopted to investigate the absorption of the surface plasma resonance of the silver film. LB monolayers of azobenzene carboxylic acid were deposited on these substrates, and the infrared spectra of these systems were measured.

Plates of CaF_2 ($30 \times 10 \text{ mm}^2$) and mica wafers ($10 \times 10 \text{ mm}^2$) were used as supporting substrates for spectroscopy and AFM studies, respectively. Prior to the evaporation of silver, the CaF_2 plates were carefully cleaned in acetone, chloroform, and a mixture of $\text{K}_2\text{Cr}_2\text{O}_7$ and concentrated H_2SO_4 solution, and then rinsed with Milli-Q water and absolute ethanol. The surfaces of mica wafers were treated by peeling off the top mica layers. Thin silver films were deposited on the substrates by a vacuum evaporator at a pressure of 4×10^{-5} Torr. The thickness was measured by a quartz thickness gauge, and the deposition rate was kept at 0.1 nm/s.

For thermal annealing of the silver film, a rapid thermal processor was used (Model KST-2, Beijing Instrument Factory, China). The annealing temperature was tuned in the region of 100–600 °C. In experiment, silver film coated substrates annealed at the temperatures of 100, 200, 250, 300, 350, 400, 500, and 600 °C were prepared, respectively. Each silver-coated substrate was annealed at its fixed temperature for 20 s. The whole system is protected by N_2 during the process of annealing to prevent oxidation of silver.

The morphological studies were done with a Nanoscope III AFM (Digital Instruments, USA), operated in ambient air. Standard 200- μm , V-shaped, Si_3N_4 cantilevers with integrated pyramidal tips (DI) were used (spring constant = 0.06 N/m). Images were acquired at a scan rate of 3.97 Hz, with imaging forces being around 2 nN. Lateral (x – y) calibration of the microscope was achieved by scanning freshly cleaned HOPG and mica. Vertical (z) calibration was performed using an e-beam-defined metal square pattern.

UV–visible spectra of silver-coated CaF_2 substrates were recorded by a Shimadzu UV-3100 UV–visible spectrophotometer at a resolution of 2 nm. In the measurement, the bare CaF_2 plate was used as the reference.

4-Octyl-4'-(3-carboxytrimethyleneoxy)azobenzene (Dojindo, Japan, referred to as ABD) was adopted as the compound for Langmuir–Blodgett (LB) monolayer fabrication. The LB monolayers of ABD were deposited onto the silver-coated CaF_2 substrate by a commercialized Langmuir trough (FACE, Japan). Milli-Q water ($> 17 \text{ M}\Omega \text{ cm}$) was used as the subphase. Chloroform was used as the spreading solvent of ABD. The π – A isotherm of the Langmuir monolayer of ABD on water is presented in Figure 1. All of the LB films were prepared by vertical

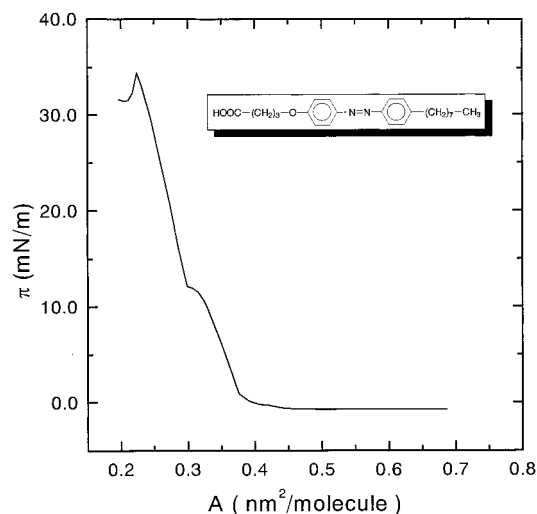


Figure 1. The π – A isotherm of the Langmuir monolayer of 4-Octyl-4'-(3-carboxytrimethyleneoxy)azobenzene (ABD) on the water surface at 20 °C.

transferring at a constant surface pressure of 20 mN/m and at the constant subphase temperature of 20 °C. The transferring ratios for both coated and uncoated substrates were identical and were nearly unity.

Infrared spectra were measured with a Perkin-Elmer System 2000 FT-IR spectrometer, equipped with a liquid nitrogen cooled narrow band MCT detector. All the spectra were obtained by referencing 100 sample scans to 100 bare CaF_2 background scans at 4-cm^{-1} resolution with strong apodization. The sample chamber was purged with dry N_2 to eliminate the spectral interference from water vapor in air.

III. Results and Discussion

A. Fabrication and Characterization of SEIRS-Active Substrates. The as-prepared silver films and the silver films after an annealing treatment are found to be consisting of small silver particles, showing their island nature. As an example, the AFM image of the silver film after annealing treatment at 250 °C is shown in the inset of Figure 2, in which small separation between the particles can also be seen. The annealing process is found to have a profound effect on the morphology of the silver island films. Table 1 summarizes the results of the morphological studies and optical absorption studied on the silver films. Obviously, the height and lateral diameter of the silver particles are increased by the annealing treatment: the average lateral diameter changes from ~ 12 to ~ 56 nm, and the average height changes from ~ 2 to ~ 11 nm. Regarding the changes in the shape of the particles, similar to other studies,³⁸ we model the silver particles as ellipsoids, whose rotation axes are normal to the substrate surface and adopt the ratio (η) between the average diameter (a) and the average height (h) of the particle as the parameter ($\eta = a/h$, see ref 38). From Table 1, it is also seen that the ratio η increases with the annealing temperature, although there are two exceptions (as-prepared and 600 °C annealed silver films). In other words, the silver particles have become more and more “flat” after being annealed. From the AFM images, another important feature of these morphological results is noted: larger and larger separation is created between the silver particles as the annealing temperature increases (i.e., the distance between the particles increases with the annealing temperature, though its value is difficult to measure definitely).

Optical absorption is very important in characterizing the active substrate for surface-enhanced spectroscopy,

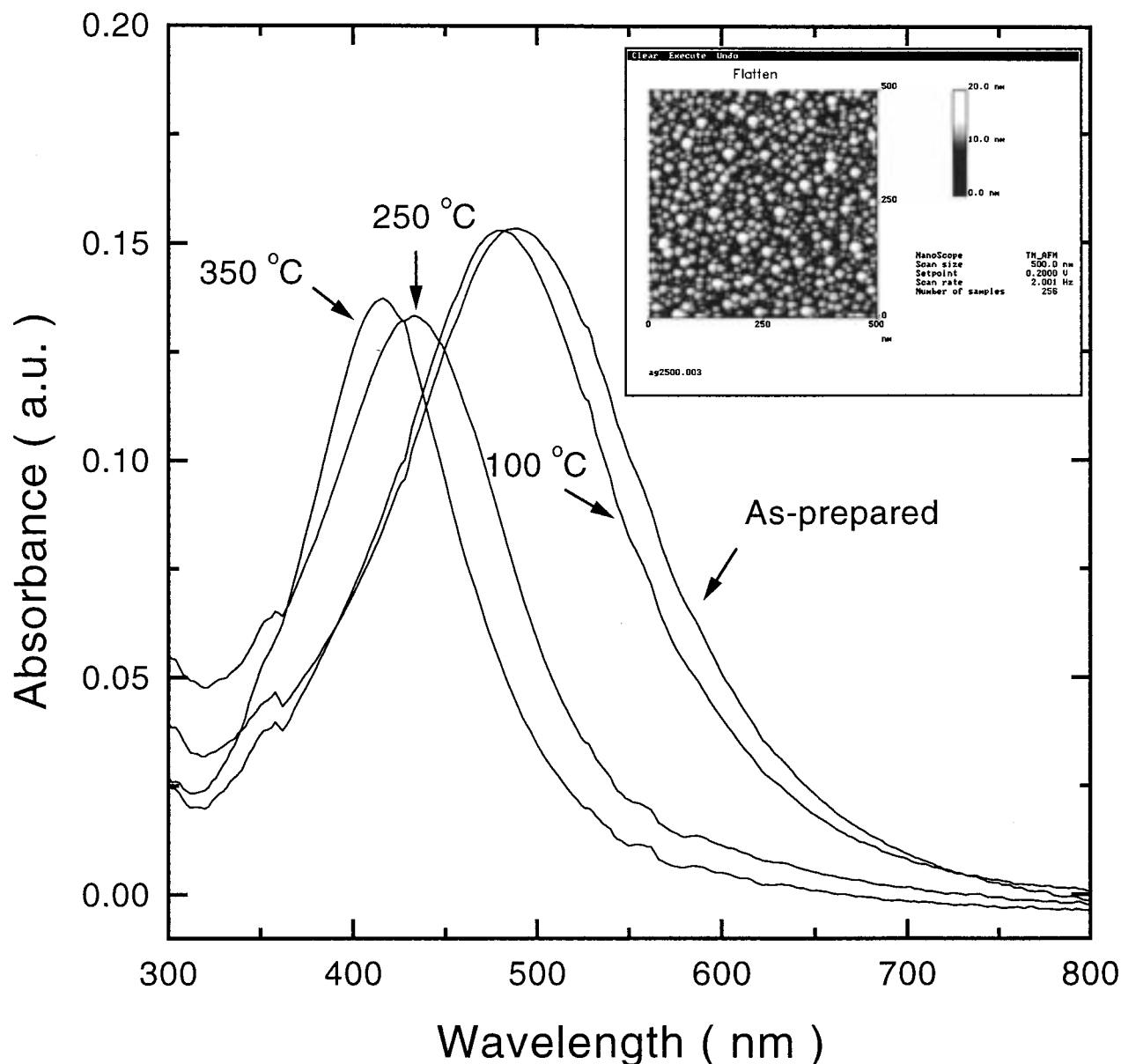


Figure 2. The UV-visible absorption spectra of CaF_2 substrates coated with as-prepared silver films and silver films annealed at 100, 250, and 350 °C. Inset: the AFM image of the surface of silver film annealed at 250 °C.

Table 1. Results of Characterization of the Silver Island Film Annealed at Different Temperature

annealing temp. (°C)	peak position (nm)	lateral diameter (nm)	height (nm)	η^a
0 (as-prepared)	488	11.78 ± 4.6	2.16 ± 1.1	5.45
100	478	13.77 ± 7.3	3.19 ± 1.2	4.31
200	438	18.00 ± 5.8	3.53 ± 1.4	4.58
250	432	18.62 ± 7.7	3.68 ± 1.3	5.05
300	416	20.80 ± 8.2	3.75 ± 1.4	5.55
400	412	21.60 ± 8.2	3.95 ± 1.1	5.48
500	402	32.52 ± 6.11	5.23 ± 1.5	6.21
600		52.62 ± 6.3	11.17 ± 3.0	4.71

^a η = lateral diameter/height.

such as silver island films, because it reflects the surface plasma resonance in the films. Figure 2 is the UV-visible absorption spectra of CaF_2 substrates coated with as-prepared silver films and silver films annealed at 100, 250, and 350 °C. The absorption peak of surface plasma resonance is found to be around 400–500 nm, and a blue-shift of the maximum absorption is clearly seen as the annealing temperature increases. As summarized in

Table 1, the peak position of surface plasma resonance experiences a blue-shift of ~ 90 nm as the temperature increases from 0 to 500 °C. (“0 °C” is “without annealing” or “as-prepared”).

Extensive studies have been made on the optical response of silver island films, and it has been found that its UV-visible absorption peak position mainly depends on the size and the aggregation of the silver particles: larger size and more aggregated states result in an absorption at a longer wavelength than the smaller size and less aggregated systems. As in this study, the absorption peak experiences a blue shift with the increasing of the annealing temperature, despite the enlargement of the particles, which is expected to red shift the maximum absorption. Therefore, the changes in the particle's aggregation exerts a more pronounced effect than the changes in the particle size.

B. Surface-Enhanced IR Spectra of Azobenzene LB Monolayers. When the series of silver island films coated CaF_2 substrates were prepared, LB monolayers of ABD molecules were deposited on them and their trans-

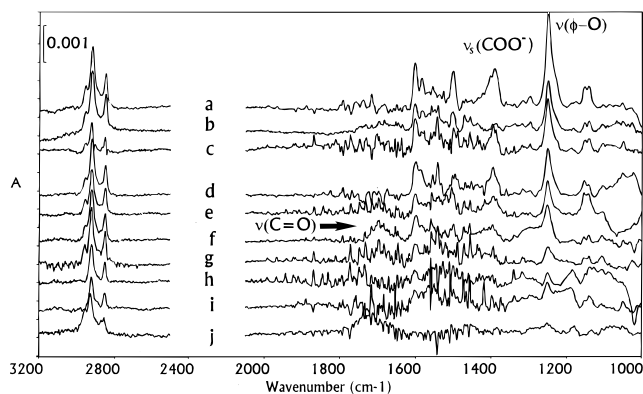


Figure 3. The infrared spectra of LB monolayers of ABD on different silver island coated CaF_2 : As-prepared (a), 100 °C (b), 200 °C (c), 250 °C (d), 300 °C (e), 350 °C (f), 400 °C (g), 500 °C (h), 600 °C (i), and no silver island films (j).

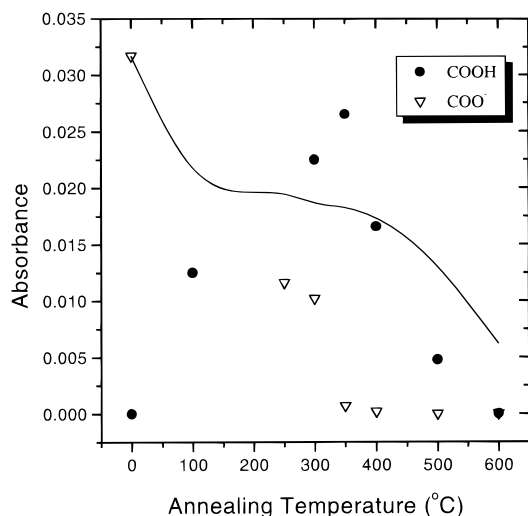


Figure 4. The variation of the intensity absorbance of $\nu_s(\text{COO}^-)$ (∇) and $\nu(\text{C}=\text{O})$ (\bullet) with the annealing temperature. The solid line demonstrates the variation of the number of molecules on silver particles.

mission infrared spectra are measured. Figure 3 displays these infrared spectra, and as a comparison, the spectra of the LB monolayer on a bare CaF_2 substrate is also shown. Several important features should be noticed:

(1) The infrared absorption is enhanced to some extent due to the existence of the silver films, and the spectra bear the characteristics of the ABD molecules, which can be evidenced by a series of characteristic absorption bands, such as those at 2960, 2920, and 2850 cm^{-1} of the stretching mode of methyl groups ($\nu_{\text{as}}(\text{CH}_3)$), the anti-symmetric and symmetric stretching of the methylene groups ($\nu_{\text{as}}(\text{CH}_2)$ and $\nu_s(\text{CH}_2)$), the bands at 1597, 1499, and 1473 cm^{-1} of the in-plane stretching vibration modes of aromatic rings, and the bands at 1253 and 1153 cm^{-1} of the Phen-O stretching modes and Phen-N stretching modes, $\nu(\phi-\text{O})$ and $\nu(\phi-\text{N})$, respectively.

(2) The intensities of most vibration modes decrease on the silver-coated substrates annealed at higher temperatures. As an example, Figure 5 shows the absorbance of the stretching vibration mode of the Phen-O bond ($\nu(\phi-\text{O})$) versus the annealing temperature, in which a monotonic decreasing of absorbance with the increase of the temperature is observed.

(3) The carboxyl group (COOH) and carboxylate group (COO^-) are found to coexist on the substrates. The existence of COO^- is clearly evidenced by the strong

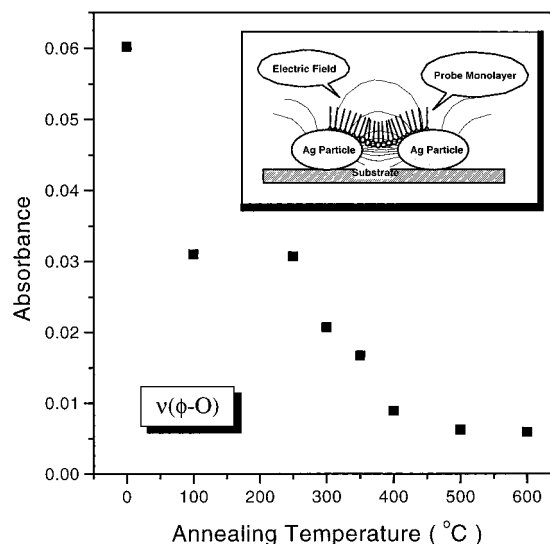


Figure 5. The absorbance of the stretching vibration mode of the Phen-O bond, $\nu(\phi-\text{O})$, versus the annealing temperature. Inset: A sketch of mutual coupling of the EM field of different silver particles.

absorption peak at 1390 cm^{-1} ($\nu_s(\text{COO}^-)$). (The absence of the absorption of $\nu_{\text{as}}(\text{COO}^-)$ is due to the selection rule of the surface-enhanced infrared spectroscopy.²³) The existence of the COOH group is evidenced by the absorption around 1710 cm^{-1} in spectrum e-g ($\nu(\text{C}=\text{O})$ of the carboxyl group). The coexistence of COOH and COO^- can be understood as the following: When the silver island films have been annealed at higher temperatures, along with the increase of size of the silver particles, the distance between the particles also increases, resulting in many gaps, or separations, between the silver particles. When the monolayer of ABD is transferred onto such a substrate, the COOH group will react with silver and be converted to COO^- on the silver particles, while the COOH group will remain unchanged within the gaps between the silver particles. The coexistence of the carboxyl and carboxylate groups, and the sensitive distinguishing ability of these two groups by infrared spectroscopy, will allow us to make a direct comparison between the enhancement effect on the silver particles and in the separation between them.

Figure 4 shows the variation of the absorbance of $\nu_s(\text{COO}^-)$ and $\nu(\text{C}=\text{O})$ with the annealing temperature. The characteristics of these two modes are quite different. The intensity of $\nu_s(\text{COO}^-)$ decreases monotonically with the increase of the annealing temperature, while the absorbance of $\nu(\text{C}=\text{O})$ experiences first an increasing and finally decreasing process. The decrease in the absorption of $\nu_s(\text{COO}^-)$ may have two contributions: the decrease of the amount of COO^- groups and the decrease in the enhancement factor. The decrease in the COO^- group's amount is due to the decrease of the silver surface, and the resulting reduction of absorption is estimated by the solid line in Figure 4.³⁹ It is seen that the experimental data shows a much faster decrease, indicating that, apart from the decrease in the COO^- group's amount, the

(39) Since the silver films were prepared at the same time by vacuum evaporation, the amount (volume) of silver per unit area on each substrate is assumed to be identical, and therefore, the increase in the size of the silver particle will result in a decrease in its surface area. As modeled as an ellipsoid of revolution, the volume (V) and surface area (A) of the silver particle can be expressed as the following: $V = \frac{4}{3}a^2H$ and $A = 2\pi(a^2 + (H^2/2e) \log((1 + e)/(1 - e)))$, where $a' > H$, $e^2 = 1 - (H^2/a'^2)$, and $a' = a/2$ and $H = h/2$, as defined in Table 1. The solid line in Figure 4 is generated by calculating the A/V value, using the average value of a and h presented in Table 1 and normalizing to the absorbance on as-prepared silver substrate.

enhancement factor for COO^- groups on the silver particle is also decreasing, as the silver film is annealed at higher temperatures. As for the COOH groups, due to the increase of the separation between the silver particles, the amount of the COOH group in the LB monolayer will increase, which will bring about an increase in the absorbance of $\nu(\text{C}=\text{O})$. However, the unique varying behavior of the $\nu(\text{C}=\text{O})$ absorbance shows that there must be a decrease of the enhancement factor between the silver particles, causing the absorbance of $\nu(\text{C}=\text{O})$ to decrease as the annealing temperature rises. It is the competition of these two factors that results in the special feature of the variation of $\nu(\text{C}=\text{O})$'s absorbance. To summarize, as the silver island films are annealed, the separation between the silver particles become larger and larger and less aggregation of the particles results, leading to a reduction in the enhancement factor of infrared absorption.⁴⁰

It is believed that, in the surface-enhanced infrared absorption, the excitation of the surface plasma oscillation places an important role in generating an intense, localized EM field around the metal particles.²⁰ However, the wavelength of surface plasma excitation radiation is usually in the visible region (~ 400 nm for silver), far away from the infrared region ($\sim 2\text{--}3$ μm). To generate surface plasma in the infrared measurement, absorption of infrared probe radiation by the silver films is needed. To shift the plasma resonance absorption into the infrared region, the silver particles should be much aggregated (i.e., they should be very close to each other).¹²⁻¹⁴ In this case, different particles can interact with each other through their surface EM field, and the collective electron resonance is excited, which lowers the resonance frequency and therefore brings about the absorption in the infrared region by the assembly of the particles. This effect in surface-enhanced infrared spectroscopy is evidenced by the linear dependence of IR enhancement on the IR background absorption of the silver island in refs 23 and 38.

Mutual interaction between the metal particles is believed to have important effect on the surface-enhanced spectroscopy.¹⁵ Regarding the enhanced IR absorption in this study, as sketched in Figure 5, the mutual interaction between different particles will result in a

concentrated electric field flux between the particles, creating the very intense EM field in these places. If the silver particles are more separated, their mutual interaction will be reduced and the absorption of infrared radiation, and as a result, the intensity of the EM field between and on the particles, will be reduced. Consequently, the infrared energy absorbed by the adsorbed molecules will decrease, and therefore, a reduction in the enhancement factor results.

It should be noted that the IR enhancement has been found to depend also on the shape of the particles,³⁸ in which larger enhancement is observed on island films with a larger value of the diameter-to-height ratio (η). As in this study, the annealing treatment raises the value of η (Table 1), which is expected to increase the enhancement factor. However, the decrease in the enhancement factor with the rise of the annealing temperature indicates a more predominant effect of the mutual interaction between the particles.

IV. Summary

By vacuum evaporation and thermal annealing, silver island films with different sizes and different distributions of silver particles are fabricated: the annealing treatment has enlarged both the silver particles' size and their mutual separation and has also made the particles be more "flat". UV-visible spectra of the silver film reveals a blue shift in the surface plasma resonance peak, due to less aggregation of the silver particles, resulting in the decrease of mutual interaction of the EM field between them. The enhanced IR spectra of the LB monolayer of ABD molecules on these silver substrates are measured. While the absorption of most vibration modes decrease on silver film annealed at higher temperatures, the absorption of the $\nu(\text{C}=\text{O})$ mode of COOH shows first an increasing and later decreasing behavior versus the increase of the annealing temperature. It is concluded that the enhancement factor decreases when the aggregation between the silver particles is reduced.

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(40) The molecular orientation may have its effect on the IR absorption, which is difficult to evaluate in the present case. However, it is reasonable to assume that the LB monolayers in this study have similar structure and do not bear drastic change from substrate to substrate.