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Study of Surface-Enhanced Infrared Spectroscopy

2. Large Enhancement Achieved through Metal–Molecule–Metal Sandwich Configurations

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In this paper we report a versatile and effective strategy to attain strong surface-enhanced infrared absorption by employing a sandwich system consisting of metal island films and self-assembled monolayers (SAMs) of 4-pyridinethiol. The observed larger enhancement factor stems from coupling of the electric fields induced by excitation of the surface plasmon resonance of the overlayer and underlayer Au island films, and from enhanced chemical interactions of the Au island films and the pyridine molecule in the sandwiched structures, compared to the corresponding SAM–Au configuration. © 2001 Academic Press

Key Words: **surface-enhanced infrared absorption spectroscopy (SEIRAS); electromagnetic mechanism; chemical origin; Au island film; self-assembled monolayer (SAM); metal sandwich configuration; surface plasmon resonance; 4-pyridinethiol.**

INTRODUCTION

In the preceding paper (1), we described the dependence of the enhancement of infrared (IR) absorption on structure and vibration modes of the chemisorbed molecules using the self-assembled monolayers (SAMs) of 4-pyridinethiol and 4-nitrothiophenol measured by IR reflection–absorption spectroscopy (IRAS). Important conclusions obtained include that (1) optimization of experimental conditions using Au island films as active substrates for surface-enhanced infrared absorption (SEIRA) yields enhancement comparable to or even larger than that reported using Ag island films; and (2) the strong SEIRA enhancement observed stems from electromagnetic and chemical origins, with the former contributing predominantly to the overall SEIRA enhancement. In this paper, we report on a feasible and versatile method by which a large enhancement of IR absorption measured in transmission mode can be gained. An enhanced IR absorption can be achieved by preparing two Au island films sandwiching a SAM of 4-pyridinethiol, and a system with a second SAM on the top of the sandwiching Ag films.

Knoll *et al.* (2) investigated the conformational structures of Langmuir–Blodgett (LB) films of cadmium arachidate by surface IR and SERS techniques. They found that evaporation of an Ag island film on the monolayer LB film deposited on a flat Ag surface imposes no practical changes on the IR spectra, suggesting that there is no SEIRA effect for such a configuration. The phenomenon was also observed by others (3) and was later interpreted within the framework of the theoretical model for SEIRA proposed by Osawa (4). In contrast, Raman signals of the LB film of cadmium arachidate sandwiched between a flat Ag film and an Ag island film are clearly detected in comparison with the case for LB film on a flat Ag surface, due to the presence of the Ag island film operating as a SERS-active substrate. Later, by measurement of ATR SEIRA spectra of 20-nm-thick films of *p*-nitrobenzoic acid derivatives sandwiched by Ag island films, Badilescu and co-workers (5) suggested that the overall IR enhancement observed in the sandwich configuration is due to an increase in the number of interfaces where metal–sample chemical interaction takes place. Recently Yu *et al.* (6) investigated the electromagnetic effect in surface-enhanced Raman scattering (SERS) by employing SAMs of azobenzene derivatives sandwiched by Ag island films. Their work implies that coupling of the electric fields of the overlayer and underlayer metal island films occurs, and it interacts with the SAM within the Ag film sandwich. We demonstrate in the present study that a sandwiched configuration can substantially improve the enhancement of IR absorption, which, as a continuation and deepening of our preceding work, will aid in a better understanding of the enhancement mechanisms operating in SEIRA. A schematic representation of the Au island film–SAM configurations is shown in Fig. 1.

EXPERIMENTAL SECTION

4-Pyridinethiol and other chemicals used are the same as those described in the preceding paper (1). As for the preparation of sandwiches between the Au island film and the SAM of 4-pyridinethiol and SEIRAS measurment, it can be described briefly as follows: after deposition of an Au island film at a rate of 0.1 Å/s onto IR-transparent CaF_2 substrates (for measuring

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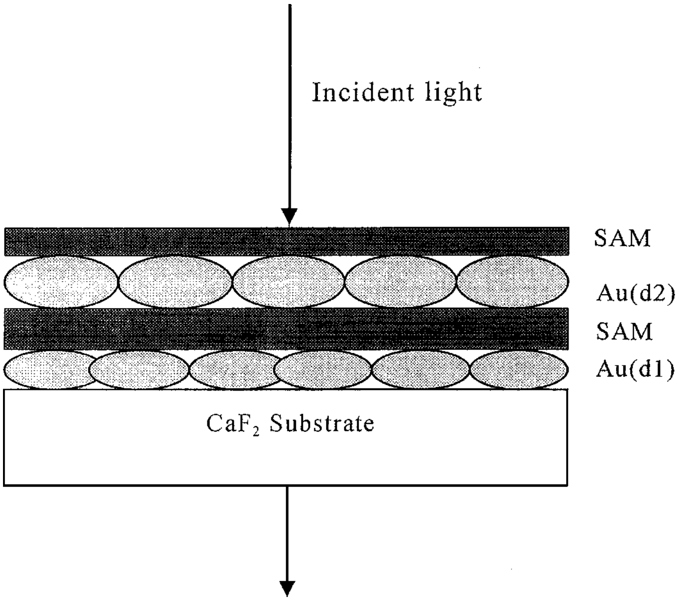

FIG. 1. Schematic presentation of the Au island film SAM of 4-pyridinethiol configuration.

IR spectra in the transmission mode), a background spectrum is measured immediately. A SAM of 4-pyridinethiol is then formed on the Au island film according to the preceding paper (1). An IR spectrum of the SAM is then measured. Followed by deposition of the overlayer Au island film, a background spectrum was recorded. Finally, an IR measurement is taken after a second SAM is formed on the Au island overlayer. The single beam spectrum of the Au films recorded before the formation of the SAM was always used as the background spectrum unless specified otherwise.

RESULTS AND DISCUSSION

4-Pyridinethiol molecules chemisorbed on Au island films thermally deposited onto CaF_2 substrates successfully form SAMs, as evidenced by the IR transmission spectra. The transmission SEIRA measured for these SAMs have spectral patterns similar to those of the RAS SEIRA of the 4-pyridinethiol SAMs on the island films deposited on glass substrates (1). According to our previous assignment of the IR absorption bands, the bands at 1607, split 1569/1561, and split 1471/1462 cm^{-1}, are due to ring stretching modes 8*a*, 8*b*, and 19*a* of the pyridyl group, respectively. The presence of the split bands at 1572/1565 and 1471/1462 cm^{-1} in the SAM spectrum but the absence of these bands in the KBr may be due to changes in intermolecular interactions in the film environment compared with that in the KBr pellet. The bands due to 8*b* and 19*a* modes in the transmission SEIRA of the SAM show some distortion and dispersive features, a phenomenon frequently observed in the SEIRA spectra that is due to the dispersion of the refractive index of the composite film (7, 8). Therefore, we choose the band at 1607 cm^{-1}, which shows less distortion than the other two bands, to estimate the relative enhancement factor, that is, the ratio of absorbance of a band in the transmission IR spectrum of the SAM of 4-pyridinethiol on the Au island films to that of the same band in IRAS of the SAM on a thick Au film. We then discuss the surface enhancement mechanisms on the basis of the relative enhancement factors for different metal–SAM structures. The relative enhancement factors calculated for all Au–SAM configurations are listed in Table 1. It should be noted that the dispersive feature of the band for thicker Au films may induce some calculation errors, but it does not affect the conclusions drawn from the experiment.

SAM–Au Configuration

Figure 2 shows transmission SEIRA spectra of the SAM of 4-pyridinethiol on Au island films of different thicknesses on CaF_2 substrates. The spectral profile is similar to the IRAS and RA SEIRA spectra we reported in the preceding paper (1). As in the case of our investigation on SEIRA reported in the preceding paper, an increase in the Au film thickness yields an increase in the relative enhancement factor, but the amplitude is remarkably smaller than the analogous one in the RAS SEIRA. This is due to a smaller sampled area in transmission SEIRA than that in RAS SEIRA. Johnson and Aroca (9) investigated SEIRA of Langmuir–Blodgett (LB) films of N-(2-phenylethyl)perylenetetracarboxylic monoimide on Ag island films and found that the enhancement factor in SEIRA measured in transmission is about one-third that in RAS mode for the same LB film. In the present work, no attempt is made to compare the relative enhancement factor in the transmission SEIRA of the SAM of 4-pyridinethiol on island films on CaF_2 substrates with that in the corresponding RAS SEIRA on glass substrates since different substrates impose different effects on enhancement of the IR absorption. It seems that the enhancement is not yet saturated even when the thickness of the Au island film is increased to 15 nm.

TABLE 1

Relative Enhancement Factors in Transmission SEIRA Spectra of Au–SAM Systems with Different Configurations (Value in Parentheses was Obtained by Using a 15-nm Au Island Film on a CaF_2 Plate as a Background)

Configuration	Relative enhancement factor[a]
SAM–5 nm Au	2
SAM–10 nm Au	6
SAM–15 nm Au	11
Au–SAM–5 nm Au	7
Au–SAM–10 nm Au	14
Au–SAM–15 nm Au	28
SAM–Au–SAM–5 nm Au	27
SAM–Au–SAM–10 nm Au	24
SAM–Au–SAM–15 nm Au	33 (59)

[a] The values for all SAM–Au–SAM–Au configurations refer to the relative enhancement factors of the upper SAMs only, except for the value in parentheses that includes contributions from both the upper SAM and the sandwiched SAM.

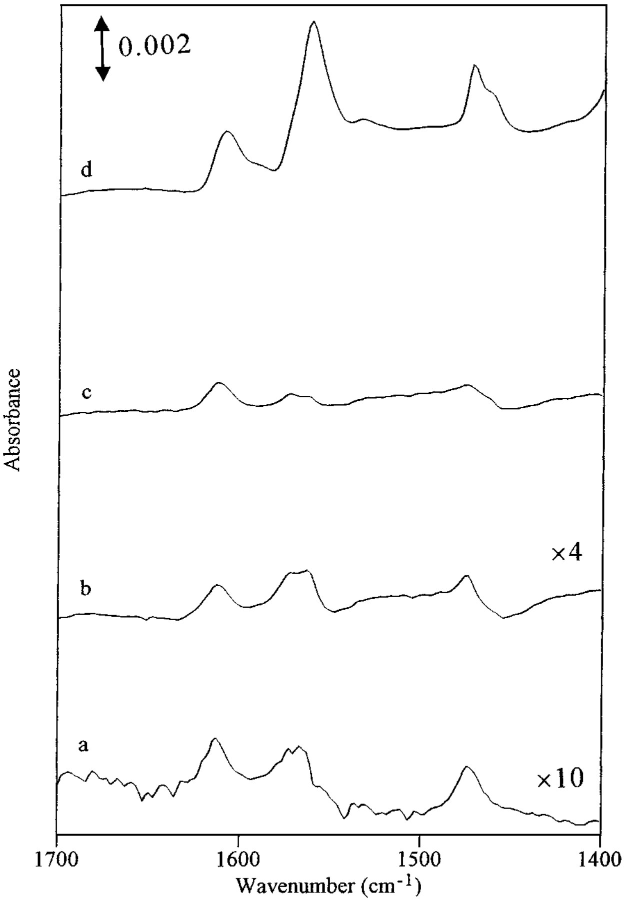

FIG. 2. IRA spectrum of the SAM deposited on a thick Au film evaporated on glass substrates (a) and transmission SEIRA spectra in region from 1700 to 1400 cm^{-1} of a SAM of 4-pyridinethiol on Au island films with thicknesses of (b) 5, (c) 10, and (d) 15 nm deposited on CaF_2 substrates.

Au–SAM–Au Configuration

Interesting results were obtained when we deposited an overlayer of Au island film 10 nm thick on the SAM on the Au island used above (shown in Fig. 1). Figure 3 exhibits the transmission SEIRA spectra of the Au–SAM–Au sandwiches. In the present experiment we kept the thickness of the overlayer Au film to be constant (10 nm) and adjusted that of the underlayer film. It has been found that with the increase in the thickness of the underlayer Au films, the relative enhancement factor increases about twice for every 5 nm increase of the Au film thickness, having almost the same tendency as the SAM–Au structure illustrated in Fig. 2. Nevertheless, relative enhancement factors more than 2 times larger than those of the corresponding SAM–Au configurations were observed, in all cases. It is reasonable to assume that the introduction of the overlayer Au film on the SAM gives rise to considerably larger enhancement. Formation of the sandwiched structure enables the SAM to interact with the enhanced electric field via coupling of the surface plasmons excited from the overlayer and underlayer Au films as suggested by Yu and collaborators (6). Moreover, the access of the overlayer Au film to the N atom of the pyridine group may facilitate the charge transfer from the overlayer Au film to the pyridine, as suggested in previous literature on SEIRA (5) and on SERS (10–12).

It should also be noted that deposition of an Au overlayer may alter the orientation of the pyridine group in the SAM to some extent, resulting probably in lessening of the enhancement of the bands due to in-plane vibrations, if the pyridine plane becomes more tilted toward the surface of the Au underlayer film. To investigate this effect, we compare the RAS spectra of the SAM formed on a thick Au surface with and without the presence of a 5-nm Au overlayer film, as shown in Fig. 4. The reason we chose this system is that there is no enhancement caused by the electromagnetic mechanism in this case (2, 4). Therefore, the change in intensity, when inducing an overlayer Au film, only comes from the chemical effect, especially alteration in the molecular orientation. The intensity of the bands for the SAM on a thick Au layer with the presence of a 5-nm Au island film was approximately 80% compared to the SAM on a thick Au surface without a Au overlayer (see Fig. 4). Apparently, the presence of an Au overlayer has no significant influence on the intensities

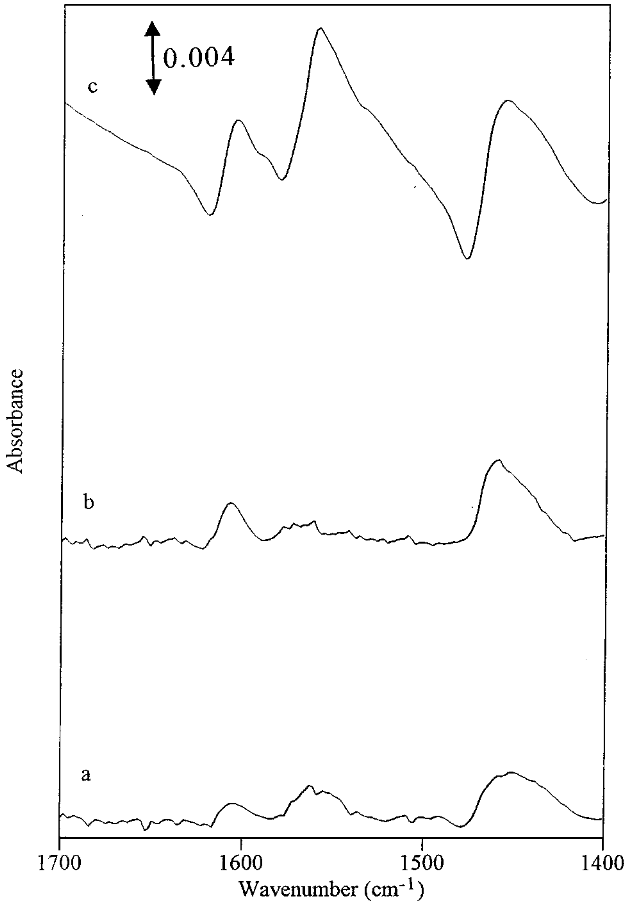

FIG. 3. Transmission SEIRA Spectra of (a) 10 nm Au–SAM–5 nm Au, (b) 10 nm Au–SAM–10 nm Au, and (c) 10 nm Au–SAM–15 nm Au on CaF_2 substrates.

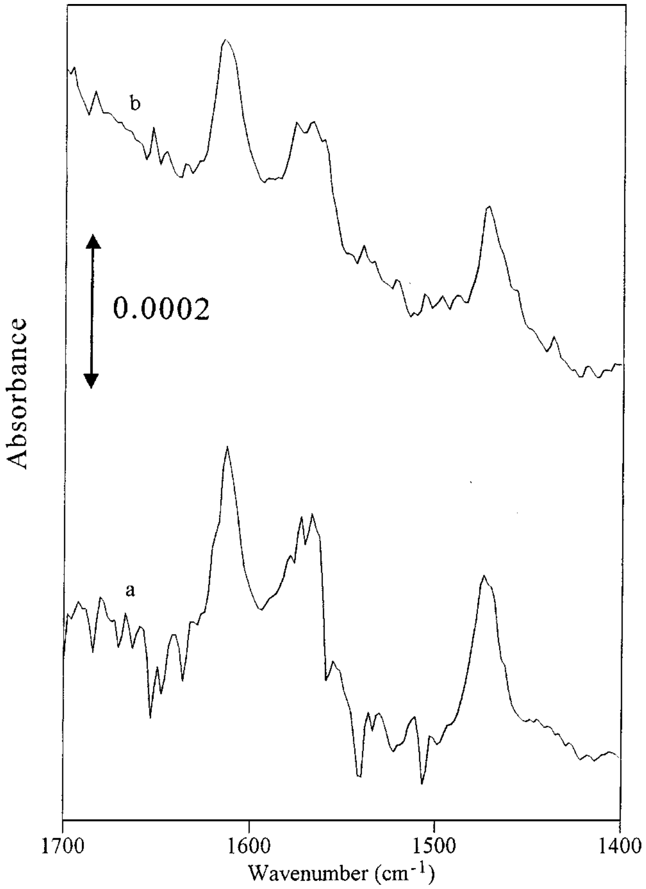

FIG. 4. IRA spectra of the SAM on the 200-nm Au surface (a) without and (b) with a 5-nm Au overlayer on the top of the SAM.

of the IR bands. A similar phenomenon was also observed by Knoll and collegues (2).

SAM–Au–SAM–Au Configuration

By extending the above-mentioned work, we formed a second SAM of 4-pyridinethiol on the top of the sandwiches (see Fig. 1) and measured their transmission SEIRA spectra. The results are given in Fig. 5. Compared with the corresponding Au–SAM–Au and the SAM–Au configurations, all SAM–Au–SAM–Au configurations give an increase in the relative enhancement factor to different extents, depending on the configuration as indicated in Table 1. It is important to note that the observed relative enhancement factors for the SAM–Au–SAM–Au structures originate almost, if not absolutely, from the upper SAM, since we eliminated the IR absorbance of the sandwiched SAM during the spectral measuring process by using an Au–SAM–Au sample as the background spectrum. That is, the contribution of the sandwiched SAM to the total IR absorption can be eliminated if we use the Au coated with the SAM as a background. Such a contribution will be present if a bare Au surface is used as a background. To clarify this point, we measured two SEIRA spectra of the same sample, SAM–10 nm Au–SAM–15 nm Au by using two different background spectra of the 10 nm Au–SAM–15 nm Au and the 15-nm Au configurations, respectively. The two spectra thus obtained are presented in Fig. 6. The SEIRA with the former background shows a relative enhancement factor of 33, while that with the latter is 59. Assuming that the relative enhancement factor of 28 for the 10 nm Au–SAM–15 nm Au configuration remains unaltered before and after formation of a second SAM on the top of the sandwich, we can then estimate the relative enhancement factor of the upper SAM by simply subtracting the relative enhancement factor of 28 for the sandwiched SAM from the total relative enhancement factor of 59. We then get a relative enhancement factor of 31 for the top SAM. The value is in good agreement with the experimental value of 33. Therefore, we infer that the relative enhancement factors for the SAM–Au–SAM–Au configurations shown in Table 1 are merely from the upper SAM.

That the upper SAM in the SAM–Au–SAM–Au configurations gives a larger enhancement than that in the corresponding SAM–Au configurations can be explained by the following two possible reasons. One is that the surface morphology of the overlayer Au is different from that of the Au films in the SAM–Au configuration, since the overlayer Au is deposited on the SAM, while the Au film in the SAM–Au structure was deposited directly on the bare CaF_2 substrate. It was reported that

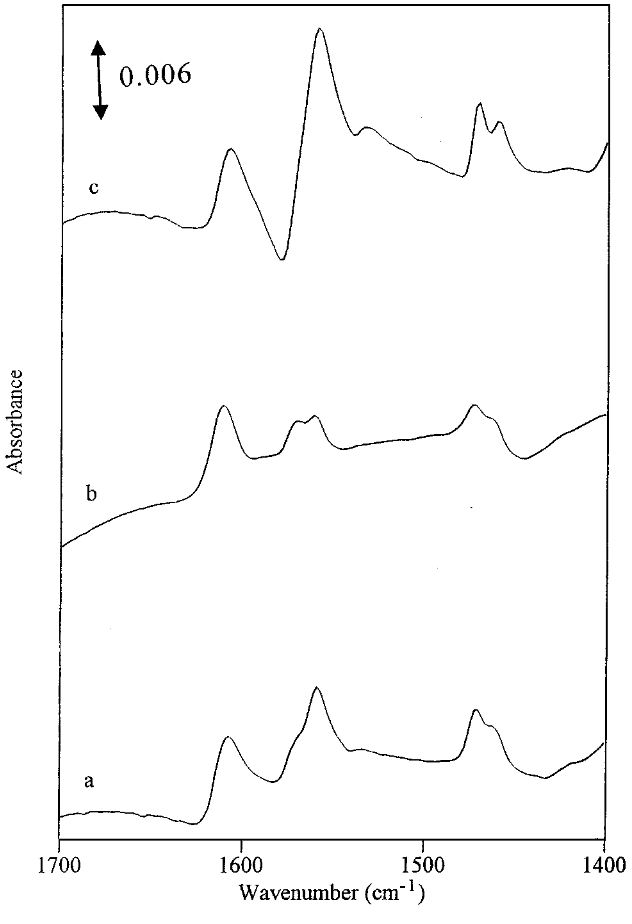

FIG. 5. Transmission SEIRA spectra of (a) SAM–10 nm Au–SAM–5 nm Au, (b) SAM–10 nm Au–SAM–10 nm Au, and (c) SAM–10 nm Au–SAM–15 nm Au on CaF_2 substrates.

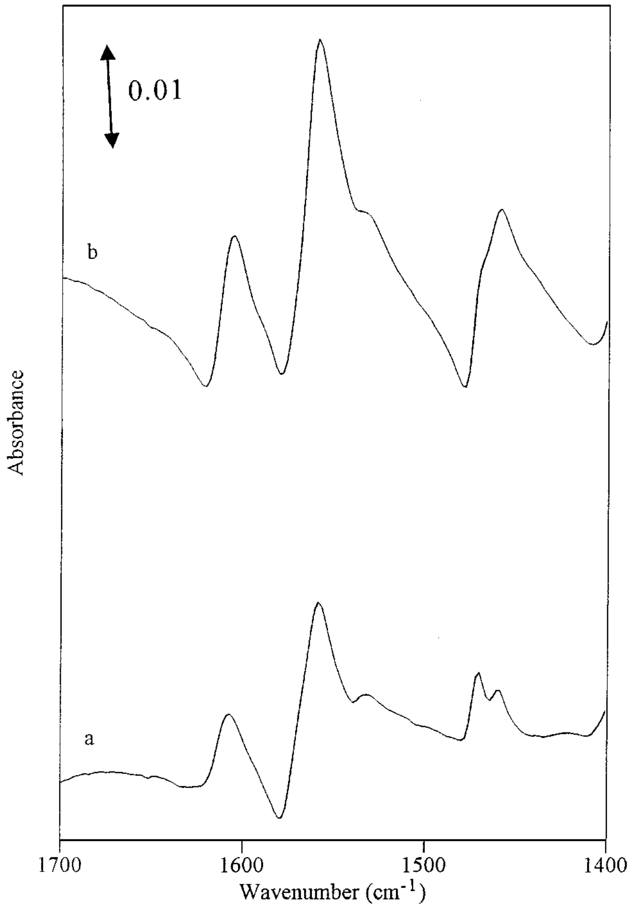

FIG. 6. Transmission SEIRA spectra of SAM–10 nm Au–SAM–15 nm Au on CaF_2 substrates with (a) 10 nm Au–SAM–15 nm Au and (b) 15 nm Au on a CaF_2 substrate as the background spectrum.

the metal films deposited onto a chemically modified substrate surface could bring about changes in the surface structure, and thus in optical and electronic properties of the metal films (13, 14). The second possibility is that there is, at or near the surface of overlayer Au island film where the upper SAM is formed, a strongly enhanced electric field induced by coupling of the surface plasmons from the underlayer and overlayer Au films. Such a possibility is very likely because the electric field created by exciting surface plasmons at or near the metal surface extends to 5–10 nm in distance from the adsorbate to the metal (4, 9, 15). Considering that the thickness of the 4-pyridinethiol SAM is only about 0.5 nm at most when the pyridine is oriented perpendicular with respect to the metal surface (16), the upper SAM will be able to interact with the electric field produced from both overlayer and underlayer Au island films. Consequently, it is not unreasonable to conclude that a coupled electric field from overlayer and underlayer Au films contributes to large enhancement for the upper SAM in the SAM–Au–SAM–Au configurations.

It seems strange to observe a larger relative enhancement factor for the upper SAM than for the sandwiched SAM. It was originally expected that the sandwiched SAM should exhibit relative enhancement factors larger than the corresponding upper one since the electric field within the sandwich should be stronger than that outside the sandwich. The possible alteration in the orientation of the pyridine molecules in the Au-sandwiched SAM results in a relatively smaller SEIRA enhancement, but to a very limited degree, as we discussed earlier. Further work is desired to clearly elucidate the phenomenon.

CONCLUSION

In the present work we discussed the large enhancement in SEIRA resulting from the presence of an Au island film-chemisorbed molecule in sandwiched structures. The coupling of the electric fields from both upper and lower Au films and the increase in molecule–Au film interactions are presumably responsible for the strong enhancement. The strategy is versatile and effective for observation of a strong enhancement in SEIRA, and thus may assume general significance in surface-enhanced spectroscopies.

There are still some problems that remain unsolved. For example, why the upper SAM gives a larger relative enhancement than the sandwiched SAM is not definitely clear at present. Further work to understand the phenomenon is currently in progress in our laboratory and will be reported in a separate paper.

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