Surface enhanced Raman scattering from layered assemblies of close-packed gold nanoparticles

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Abstract

A synthetic method of ordering hydrophilic gold nanoparticles into a close-packed two-dimensional array at a hexane–water interface and subsequent transferring of such structure onto a solid substrate is described. By repeating the transfer process, multilayered gold nanoparticle films are formed without need of linker molecules. Their surface enhanced Raman scattering (SERS) efficiencies are compared as a function of the number of layers. It is shown that both the number of layers and the particle size contribute to SERS phenomenon. Judging from the noticeable dependence of SERS efficiency on the nanometer scale architecture, the close-packed nanoparticle formation at an immiscible interface presents a facile route to the preparation of highly active and relatively clean SERS substrates by controlling both the particle size and the film thickness. Among the investigated samples, the gold nanoparticle film assembled with quintuple layers of 30 nm diameter particles showed the maximum SERS efficiency.

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1. Introduction

The elucidation of the microscopic processes, such as molecular adsorption, catalysis, and corrosion, is of fundamental interest for solving challenging problems in surface chemistry. One of the primary objectives in the study of surface science is the understanding of adsorbate–surface interactions at the molecular level. In order to investigate surface adsorption and its dynamics, a myriad of surface-characterization techniques have been utilized. In particular, surface enhanced Raman scattering (SERS) has been extensively utilized as a major tool for unveiling the vibrational characteristics of adsorbates on noble metal surfaces owing to its enormous signal enhancement effect. It is a general understanding that the SERS from noble metal nanostructures has two major contributions: one is a local field enhancement induced by localized surface plasmon resonance, and the other is a charge-transfer resonance between an analyte and a metal surface [1].
local field enhancement is very sensitive to the size and structure of the noble metal. Especially, sharp edges of the nanometer-sized metals or their gaps may create extraordinarily high local field and serve as “hot spots” in the SERS [2–11].

While investigating the nature of the hot spot and its role in SERS is currently a subject of intensive attention, constructing an effective SERS substrate which takes the best advantage of the nature of the local field enhancement and other SERS effects is a primary interest for practical applications. For the diagnostic purposes, the SERS substrate should be easily prepared and stable in air as well as produces a large enhancement for adsorbate vibrational modes. For this purpose, some of recent developments are worth mentioning; silver nanoparticles tethered to a deposited silver film [12], reduction of Ag⁺ on Cu foil [13], deposition of Ag onto soft-lithographically patterned nanowells [14], silver nanoparticles sitting on porous alumina membrane [15], photochemical modification of gold film [16], and gold-coated photonic crystals [17]. In all the mentioned contributions, a common effort has been exerted on developing stable nanostructures with high signal enhancement.

For synthesizing reproducible SERS substrates, there are two general requirements. One is the tunability of roughness within tenths of nanometer scale, which leads to the generation of the hot spots in a given substrates. Although a particular shape of a single nanoparticle may behave as a hot spot, collective interaction of electromagnetic field within a nanoarchitecture can lead to the generation of hot spots [3–12]. In this respect, assembling nanoparticles into three-dimensional multilayer is worth a special attention since it can create maximum density of hot spots due to the close proximity of nanoparticles of one another. However, construction of the three-dimensional multilayer has commonly required linker or capping molecules to overcome electrostatic repulsion between nanoparticles [18,19]. The presence of the linker or capping materials often prevents the utilization of the structure as SERS substrates for other adsorbates, which significantly limits a scope of material analysis using the SERS technique.

In this paper, we report that it is possible to construct three-dimensional multilayered film with close-packed gold nanoparticles (AuNPs) by using a Langmuir–Blodgett (LB) method. The constructed film is relatively free of linker molecules, and therefore would be more suitable for the SERS substrate. The method is based on entrapping the particles at an interface of water and nonpolar liquid with a tunable contact angle [20–22]. To be more specific, to an aqueous solution of AuNPs is added hexane to form the water–hexane interface. The surface nature of the AuNPs is hydrophilic and prefers the water environment. However, as a small amount of ethanol is added, the dielectric constant of the water layer decreases and the AuNPs become destabilized. As the contact angle of the AuNP at the water–hexane interface approaches 90°, the majority of the destabilized AuNPs are collected at the interface. While hexane is removed spontaneously by evaporation, the AuNPs are floated sparsely on the surface of water. As the solution is compressed along the interface, the AuNPs on the water surface are packed into one large film of a monolayer or a close-packed layer. The resulting AuNP film is transferred to a flat substrate for SERS investigation. This series of transformation is summarized in Fig. 1.

The nanoparticle entrapment at the water/oil interface was recently theoretically studied by Reincke et al. [22]. They considered this process in terms of a thermodynamic evaluation of the self-assembly of charged nanoparticles at the water/oil interface. The chemical potentials of the nanoparticles in the bulk phase and at the water/oil interface were considered by taking into account the interfacial energies, the van der Waals interactions, and the electrostatic interactions. They derived an equation by setting the chemical potential for charged nanoparticles at the interface to be equal to the one in the bulk phase, which showed an isotherm of the interfacial particle coverage as a function of the surface charge density of nanoparticles. The equilibrium interfacial coverage increases with decreasing the surface charge density (σ). When ethanol was added, the σ value decreased, which led to an increase in the interfacial coverage, as represented by the adsorption of nanoparticles to the interface. When the ethanol concentration in the aqueous phase was increased, the interface became completely filled with nanoparticles. However, there is a lower limiting point for the σ value that can be achieved by adding ethanol. Ethanol decreases the dielectric constant of water by forming a mixed phase. The dielectric constants for water and ethanol are 80 and 25 at 293 K, respectively. Therefore, an entrapped nanoparticle must retain a certain electrostatic repulsive force because the com-

Fig. 1 – A schematic representation of AuNP film formation at a water–hexane interface and subsequent transfer onto a 3-mercaptopropyltrimethoxysilane modified substrate.
complete removal of this interaction should lead to the irreversible coagulation of nanoparticles at the interface, which was not observed.

2. Experimental

Aqueous solutions of AuNPs having target diameters of 5.5 nm, 13 nm, or 30 nm were synthesized by reducing HAuCl₄·3H₂O with trisodium citrate and NaBH₄ following the appropriate recipes [23,24]. Then, about 40 mL of the as-made AuNP solution was transferred into a custom-made LB Teflon container having dimensions of 12.5 cm × 4.0 cm × 1.5 cm. Next, 10 mL of hexane was added to form the water–hexane interface, which was followed by the injection of ethanol (ca. 6 mL) in a dropwise fashion to collect AuNPs at the water–hexane interface. Hexane was evaporated away spontaneously, which left the AuNPs on the top surface. The solution was then compressed by sliding two LB barriers from the opposite sides until the solution surface revealed a mirror reflection.

A 0.5-mm-thick silicon wafer, cut into 1 cm × 1 cm segments and cleaned in a standard way, was treated with 1 wt% 3-mercaptopropyltrimethoxysilane in ethanol to form a thiol-terminated surface for better anchoring of AuNPs. The substrate was then dipped into the LB solution with about 45° incident angle and pulled out vertically to transfer the AuNP film. To form multilayer of the AuNPs, consecutive transfer of single monolayers was required.

The structures of the AuNP films formed on the silicon substrates were investigated with a field emission scanning electron microscope (SEM, JEOL JSM6700F). The optical density spectra using an UV-visible spectrometer (Scinco S3100) were obtained for the AuNP films formed on glass substrates.

For the SERS measurements, benzenethiol (or thiophenol, C₆H₅SH) was tested as an analyte. The samples were prepared in two different ways. In the first, a silicon substrate assembled with single-layered or multilayered AuNP film was immersed into 1 × 10⁻⁵ M benzenethiol in ethanol for 1–8 h, depending on the number of layers (1 h per layer). We call these samples “infused”. In the second, the silicon substrate assembled with the first AuNP layer was soaked into the benzenethiol solution for 1 h. This was followed by the formation of a second additional AuNP layer and by a subsequent second soaking in the benzenethiol solution for another 1 h. This was repeated for the desired number of times. We call these samples “sandwiched”.

A micro-Raman spectrometer (Renishaw, InVia) was used to record the SERS. The excitation laser was a He–Ne laser at 632.8 nm in wavelength. The laser power was significantly reduced by lowering the tube current, and further attenuated by pinholes, optics, and filters to less than 0.5 mW before reaching the sample. A 50× objective lens with a numerical aperture value of 0.75 focused the excitation beam onto about 1 μm² area of the sample. The scattered light was collected by the same objective lens and passed through a double super-notch filter (Rayleigh rejection bandwidth <50 cm⁻¹) before introduced into a polychromator with a 1800-grooves-per-mm grating and a Peltier-cooled CCD detector. Each Raman spectrum was obtained with a 10s exposure time of the detector.

3. Results

Fig. 2 shows the SEM images of several AuNP films for the SERS substrate of this study. The left three SEM images are for the single layer film of AuNPs having diameters of 5.5 nm, 13 nm, and 30 nm, respectively. The middle three graphs show the distributions for the diameters of Au particles taken from the SEM images. The average diameters were calculated to be 5.5(±0.8) nm, 13.1(±1.7) nm, and 30.3(±3.5) nm, respectively. When transmission electron microscope images were taken for single layers of these films (not shown in this paper), most particles were isolated from their nearest neighbors. The size distributions of 5.5 nm and 13 nm assemblies were narrow enough that they produced good close-packed structures. The standard deviation of the relative particle-size distribution in the 30 nm film was as good as the others, but the packing efficiency was worse, producing significant portion of the void spaces. The right three SEM images are for the quintuple layer films of AuNPs having diameters that correspond to the far-left side SEM images. As the number of layers increased, the corresponding surface roughness was also increased. As expected from the particle-size distribution and the packing efficiency in the single layer films, the 5.5 nm and the 13 nm multilayer films exhibited less roughness, and the 30 nm multilayer films exhibited the greatest roughness.

In Fig. 3, two Raman spectra of benzenethiol are displayed. Fig. 3a is the SERS spectrum of benzenethiol adsorbed onto a single layer film of 30 nm AuNPs. To identify the peaks, the ordinary Raman (OR) spectrum of neat benzenethiol drop-cast onto a quartz substrate is also displayed in Fig. 3b. Assignments of peaks and their SERS characteristics are found in many references [25–29]. In addition, we obtained a Raman spectrum simulated with a density functional B3LYP formalism. The peak numbers in Fig. 3b are the normal mode numbers in the order of increasing frequencies derived from the simulation. In the absence of benzenethiol, all peaks except the sharp one at 520 cm⁻¹ (indicated with ▲) and the broad one at 2130 cm⁻¹ (indicated with ▼) disappeared. The peak at 520 cm⁻¹ must be from the silicon substrate, but the identity of the broad 2130 cm⁻¹ peak is not clear. This peak should not be assigned to citrate species since no matching peak [30,31] is found. The citrate species on the surface of AuNPs had been minimized during the entrapment process to ‘negligible contribution’ level in the SERS spectrum.

The behavior of other peaks is consistent with other SERS works, performed mostly in colloidal states [25–29]. The following observations are worth mentioning. The S–H stretching (Q₁₉, 2566 cm⁻¹) and the S–H bending (Q₁₃, 917 cm⁻¹) in the OR spectrum disappeared in the SERS spectrum, indicating dissociative chemisorption of benzenethiol onto Au by rupturing S–H bond. A sharp peak at 1470 cm⁻¹, indicated with △, and a broad feature around 2850 cm⁻¹, indicated with ◼, in Fig. 3a, are evidences of the Au–S bond formation. These features generally appeared in SERS spectra of thiols and also in a simulated Raman spectrum of Ag–thiol (see for example Fig. 4.6 of Ref. [1]). The Q₁₉ mode shows the most dramatic change from OR to SERS. Not only was its wavenumber downshifted by 20 cm⁻¹ in SERS but its inten-
Fig. 2 – SEM images of AuNPs layers and their particle diameter distributions. (a) and (c) are SEM images for the single layer and the quintuple layer films, respectively. (b) are the particle diameter distribution determined from the SEM images of the single layer films. The top three figures are for 5.5 nm AuNPs, the middle three figures are for 13 nm AuNPs, and the bottom three figures are for 30 nm AuNPs. In all SEM images, the white scale bars indicate 0.1 μm.

The Q27 mode, C–C stretching, also shows a large downshift and a huge enhancement in SERS. In the SERS spectrum of Fig. 3a, there is no peak assignable to ethanol solvent [32].

By comparing the peak intensities of the two benzenethiol spectra in Fig. 3, the enhancement factor (EF) for each vibrational mode can be estimated. Here, we adopted a definition of EF in a simple way, and used it for all other samples:

\[
EF = \frac{I_{\text{SERS}}}{I_{\text{OR}}} \cdot \frac{C_{\text{OR}}}{C_{\text{SERS}}}
\]

where \(I_{\text{SERS}}\) and \(I_{\text{OR}}\) are the intensities of a peak in the SERS spectrum and in the OR spectrum respectively, and \(C_{\text{SERS}}\) and \(C_{\text{OR}}\) are the corresponding concentrations of the analytes in the solution. This definition of EF is different from the conventional enhancement factor for Raman cross-section, for which estimations such as the adsorption coverage and the confocal volume should be required. The EF compares the Raman intensity from a SERS substrate with that of a non-SERS substrate.
Table 1 – The assignment and the SERS enhancement factor (EF) of several Raman peaks of benzenethiol

<table>
<thead>
<tr>
<th>Mode no.</th>
<th>Assignment</th>
<th>Shift (cm(^{-1}))</th>
<th>EF</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>OR</td>
<td>SERS</td>
</tr>
<tr>
<td>Q4</td>
<td>C–S stretching</td>
<td>412</td>
<td>418</td>
</tr>
<tr>
<td>Q10</td>
<td>C–H out-of-plane def.</td>
<td>697</td>
<td>693</td>
</tr>
<tr>
<td>Q13</td>
<td>S–H in-plane bending</td>
<td>915</td>
<td>–</td>
</tr>
<tr>
<td>Q16</td>
<td>S–H bending + in-plane ring def.</td>
<td>999</td>
<td>997</td>
</tr>
<tr>
<td>Q17</td>
<td>In-plane ring def.</td>
<td>1024</td>
<td>1021</td>
</tr>
<tr>
<td>Q19</td>
<td>C–S stretching + in-plane ring def.</td>
<td>1091</td>
<td>1072</td>
</tr>
<tr>
<td>Q27</td>
<td>C–C stretching</td>
<td>1580</td>
<td>1572</td>
</tr>
<tr>
<td>Q28</td>
<td>S–H stretching</td>
<td>2566</td>
<td>–</td>
</tr>
</tbody>
</table>

Ordinary Raman (OR) peaks are from neat benzenethiol and SERS peaks are from 1 \times 10^{-5} M benzenethiol on the single layered 30 nm AuNPs substrate.

that from a bare substrate [33]. It counts relative number of molecules in the same exposed area irrespective of the adsorption coverage and the confocal depth. This is useful when the SERS substrate is to be developed for a diagnostic purpose. The aforementioned contents of Fig. 3 are summarized in Table 1.

When AuNPs formed multilayered films, the SERS signal further increased. Fig. 4 shows several examples of the SERS

![SERS spectra of 1 \times 10^{-5} M benzenethiol.](image)

Fig. 4 – SERS spectra of 1 \times 10^{-5} M benzenethiol. The top two figures (a1 and a2) are for the 5.5 nm AuNP films, the middle two figures (b1 and b2) are for the 13 nm AuNP films, and the bottom two figures (c1 and c2) are for the 30 nm AuNP films. The left three figures are for the “infused” samples and the right three figures are for the “sandwiched” samples. In each spectral window, three spectra of a single-layered, a double-layered, and a quintuple-layered film are shown from the bottom to the top.
spectra of the multilayered films, Examples are of both the “infused” and the “sandwiched” samples. In each window, the spectra for three different layers: a single, a double, a quintuple, are displayed together. The SERS signals from the 5.5 nm AuNPs films were relatively weak, and those from the 30 nm AuNPs films were the strongest. The SERS signals increased generally as the number of AuNPs layers increased.

4. Discussion

4.1. General characteristics of SERS

There are several factors which are responsible for the enormous intensities in the SERS. First of all, a noble metal substrate which experiences a plasmon resonance with the laser excitation provides a high electromagnetic field at the vicinity of the substrate surface (EM effect). Secondly, the analyte molecule chemisorbed strongly onto the substrate surface induces a charge-transfer state which resonates with the local field (chemical effect). The combination of the substrate and the analyte in this study satisfy both the requirements.

Gold nanoparticles in solution with diameters of a few tens of nanometers have plasmon resonances near 520 nm. As their size increases, the plasmon is less confined and the resonance band gets broadened and shifts to the red. When the gold nanoparticles approach to one another, the plasmon resonance band similarly gets broadened and shifts to the red, as coupling of dipoles between neighboring particles induces multipole-like resonances of the combined particles [34–36]. When the gold forms a tight film, the plasmon resonance weakens substantially and its extinction spectrum appears featureless. When we obtained the visible extinction spectra of our substrates (Fig. 5), the plasmon band survived and appeared broadly between 550 nm and 1000 nm. This red-shifted broad band is the feature of strong coupling of plasmons between individual gold nanoparticles [19,35,36]. The laser wavelength of Raman spectrometer in this study (633 nm) is well suitable to induce the coupled plasmon resonance.

When the optical density at 633 nm was plotted as a function of the number of layers (Fig. 5d), a monotonic increase was found for all three AuNP sizes. However, it should be pointed out that the optical density has contributions from the plasmon absorption, the plasmon scattering, and the nonresonance scattering. While the plasmon absorption and the plasmon scattering induce a local field enhancement, the nonresonance scattering does not, and it increases with the surface roughness. As the number of layers increased, the contribution of the nonresonance scattering must have increased because of the increased surface roughness. This is reflected in the spectral shapes of Fig. 5a–c where the growth of the background was faster than the growth of the plasmon band as the number of layers increased. The growth of the background in the spectra with the number of layers was the fastest for the 30 nm assemblies, because the increase of the surface roughness was the fastest as shown in Fig. 2.

If the contribution of the nonresonance scattering was subtracted from the plots of Fig. 5d, saturation in the increase of the optical density due to the plasmon resonance with the number of layers would be expected. The saturation point of the layer would be lowest for the case of 30 nm.

4.2. Multilayered AuNPs assembly as SERS substrate

In Fig. 6, we plotted the EF of SERS intensities of the Q27 mode vibration as the function of the number of layers. As the number of layers increased, the SERS intensity generally increased. However, the EF change patterns are different for the AuNP sizes and the substrate kinds. In the “infused” samples, there are maximum points of the EF increase: 5th layer for 30 nm AuNPs, 7th layer for 13 nm AuNPs, and higher than 9th layer for 5.5 nm. In the “sandwiched” samples, there are no maxi-
The observed patterns of the EF changes can be explained qualitatively by changes of the number of adsorbed benzenethiol molecules and the plasmon resonance. In the “infused” samples, the saturation of the plasmon resonance due to the increased nonresonance scattering at the increased number of layers would result in the saturation of the EF, at an earlier point for the 30 nm AuNP assemblies and at a later point for the 5.5 nm ones. In addition, there must be saturation in the increase of number of adsorbed benzenethiol molecules. That is, as the number of layers increased, the bottom layers did not adsorb benzenethiols effectively because there is a diffusion barrier for the adsorbate to reach the bottom layer. While some AuNPs in the bottom layers contributed to the plasmon band, they did not contribute effectively to the SERS signal, thereby decreasing the EF at higher layers than the plasmon saturation point. On the contrary, for the sandwiched samples, there is no saturation in the increase of the number of adsorbed benzenethiol molecules since the adsorbate layers were sequentially formed after each AuNP layer formation. Therefore, the EF for the sandwiched samples should be in general higher than the infused samples, and the EF increase with layers does not have a maximum point but a saturation point.

In general, the SERS EFs of the 30 nm AuNPs films are much greater than those of the 13 nm AuNPs films, and those of the 5.5 nm AuNPs films are much smaller. These differences are partly due to the differences in the local field effects induced by the plasmon resonance contribution in the extinction spectra of Fig. 5. As the local field effects affect both the excitation and the scattering processes, the enhancement factor is approximately proportional to the square of the optical density due to the plasmon resonance. However, the differences of the plasmon resonance contribution alone cannot explain the large differences in EF for the three particle-size films. Another factor, the number of chemisorbed benzenethiol, does not necessarily favor the 30 nm AuNPs films, since both the surface area and the packing density are smaller. The local structure created by the packing should also be considered. Yet to be proved, there are suggestions that the local field is much higher at a certain gap structure of particles [7–11]. It is likely that the gap structure favors the 30 nm AuNPs films.

### 4.3. Effectiveness as a SERS substrate

There are many advantages of our substrate for the SERS measurements. First of all, as no linker molecule was used, the AuNPs in the multilayered film prepared in this report were cleaner than other nanoparticle-related SERS substrates. Capping molecules to stabilize the AuNPs in solution were almost uncapped in the LB process. This was demonstrated by the absence of the citrate species in the SERS spectra. When we conducted a cyclic voltammetry on our substrate, the surface showed a conventional gold electrochemistry features, representing its clean surface nature. This point is critical in terms of utilizing such structures as a SERS substrate, because the clean surface is required for firm adsorption of analytes. As indicated, the chemical interaction between substrates and adsorbates plays an important role in SERS mechanism through chemical effects. Secondly, the structure of the assembled nanoparticles maintains the large surface area for the chemisorption and the localized surface plasmon resonance, and thereby extremely large enhancement factor can be obtained. Thirdly, with the high density of spaces between neighboring particles in the close-packing structure, where hot spots or extra enhancement sites may reside, the enhancement factor can be even larger. Fourthly, the preparation of the SERS substrates is easy and fast compared to other preparation methods such as spontaneous adsorption of AuNPs on a substrate.

Although the structures of the SERS substrate in this study are expected to give great local field enhancement and maximum adsorption sites, we have not yet succeeded in getting appreciable SERS signals for many SERS-inactive molecules. No distinctive SERS signals were obtained from ethanol, propanol, and glucose from the “infused” samples when the analytes were completely dried. Their “sandwiched” samples gave somewhat higher SERS signals, probably because the more analytes resided between layers. For example, a 890 cm$^{-1}$ peak of neat ethanol prepared in a “sandwiched” way on the quintuple layered 30 nm AuNPs film gave only 410 counts. Under the same condition, the Q$_{27}$ peak of 1 × 10$^{-5}$ M benzenethiol gave 22,000 counts. This implies that in the SERS mechanism the effect of the charge-transfer resonance via chemical binding to the metal is critical: the local field enhancement effect should operate in conjunction with the chemical effect.

### 5. Conclusion

The presented results on the formation of three-dimensional layered AuNP films, and their SERS dependence on the film
thickness and roughness provide an insight for preparing nanoparticle-related SERS substrates. Although many other examples showed facile preparation of nanostructures for SERS applications, our presented results are unique in terms of controllability of nanometer-scale roughness and electromagnetic coupling. Nanoscopic roughness could be tuned by selecting appropriate size of nanoparticle building blocks, and their electromagnetic coupling density could be further controlled by forming three-dimensional architecture. The close-packed nanoparticle formation at an immiscible interface allows a facile preparation of highly active and relatively clean SERS substrates by controlling both the nanoparticle size and their film thickness. Given that this method of assembly is general for nanoparticles suspended in an aqueous medium, it would be interesting to compare SERS spectra obtained on anisotropic nanoparticles as a function of film thickness and particle shapes. The comparison between spherical and rod-like nanoparticle films constructed by following the present procedure is underway.

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