Experimental Evidence of Two-fold Electromagnetic Enhancement Mechanism of Surface-Enhanced Raman Scattering

Samir Kumar*, Kouta Tokunaga, Kyoko Namura, Takao Fukuoka, and Motofumi Suzuki

Department of Micro Engineering, Graduate School of Engineering, Kyoto University, Katsura, Nishikyo, Kyoto 615-8540 Japan.

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ABSTRACT: The surface-enhanced Raman scattering (SERS) electromagnetic (EM) enhancement mechanism is a two-fold enhancement process in which both the incident and scattered Raman fields are enhanced. In this letter, we present new direct evidence of the two-fold EM mechanism by using an Ag nanorod array/SiO₂ dielectric layer/Ag mirror multilayer thin film "local plasmon resonator". The two-fold EM enhancement mechanism of SERS was confirmed by analyzing the optical absorption and Raman scattering spectra of the local plasmon resonator for excitation and scattered light. The effect of light interference was altered by varying the film thickness of the SiO₂ phase control layer (PCL), and the absorbance in the Raman scattering wavelength range was reduced from 90% to 0%. We also demonstrated that the intensity of the background emission is closely related to the enhancement of the scattered field and provides substantial evidence for a two-fold SERS enhancement mechanism.
Surface-enhanced Raman scattering (SERS) is an enormous enhancement of the scattered Raman intensity from molecules on the surface of noble metal particles and can be $10^8$ times or more than that of free molecules.\textsuperscript{1–3} A variety of enhancement mechanisms have been proposed during the early days of SERS.\textsuperscript{4,5} However, only two mechanisms are now widely agreed, namely the chemical enhancement (CE) theory and electromagnetic (EM) theory.\textsuperscript{6} EM enhancement is a two-fold enhancement process; the presence of nanostructured metal surfaces can change the Raman scattering in two ways. The first step involves the enhancement of the excitation field at the nanoparticle surface, and the second step involves the enhancement of the Raman-scattered light from the adsorbed molecule, Fig. 1(a).\textsuperscript{7,8}

There are a few reports in the literature to validate the two-fold EM mechanism of SERS.\textsuperscript{9–12} Yoshida et al. examined the surface-enhanced resonance Raman scattering (SERRS) EM theory by calculating total emission spectra and varying EM enhancement factors, Raman and fluorescence spectra, and excitation wavelengths.\textsuperscript{13} However, the study was inconclusive because the authors hypothesized that the consistency in their experimental and calculated transmission spectra gave strong indications that the SERRS-EM theory is quantitatively correct. McFarland et al. demonstrated that the maximum SERS enhancement occurred at excitation wavelengths slightly shorter than the LSPR, such that both the incident photon and the Raman scattered photon is strongly enhanced.\textsuperscript{12} Nevertheless, their objective was to explore the optimal excitation wavelength as a function of the spectral position of the maximum LSPR extinction, and their method required expensive and complicated instrumentation wherein both the SERS excitation
and detection system can be tuned. To the best of our knowledge, there have been no reports on a clear demonstration of the two-fold EM enhancement mechanism of SERS.

![Diagram of SERS enhancement](image)

**Figure 1.** Schematic illustration of (a) the two-fold electromagnetic SERS enhancement. The first step involves the enhancement of the excitation field at the nanoparticle surface. The localized surface plasmon resonance (LSPR) generates a local electric field near the metal nanoparticles. The molecules around the metal nanoparticles are exposed to the enhanced electric field, thereby enhancing Raman scattering too. This increase in the local electric field at the metallic surface can be termed as the local field enhancement. Second step involves the enhancement in the Raman-scattered light from the adsorbed molecule. The enhanced Raman scattering emitted from the molecule can also partly excite the LSPR of the metal nanoparticles, and further enhance the Raman scattered light and is called radiation enhancement. (b) A schematic diagram of the cross section of multilayer thin film "local plasmon resonator".

To verify the two-fold enhancement mechanism of SERS, it is necessary to fabricate metal nanoparticles that exhibit different responses to excitation and scattered light. This can be realized by using a wavelength-tunable laser for the excitation light, but because the spectroscope's diffraction efficiency and the photodetector's sensitivity depend on the wavelength, quantitative verification is not an easy task. Previously, we reported AgNRAs on shape control layer (SCL) of...
SiO$_2$ having anisotropic surface morphology by using the dynamic oblique angle deposition (OAD) method.$^{14,15}$ The aspect ratio of the Ag nanorods was changed by varying the thickness of the SCL, and hence the plasma resonance was tuned in the wavelength region between 750-950 nm.$^{16,17}$ Therefore, the response to the excitation light and the Raman scattered light was changed to some extent. However, at the same time, the size, shape, and arrangement of the nanostructures also changed, which significantly altered the SERS and is not suitable for two-fold enhancement verification. The optical path length of the light in the multilayer film can be precisely controlled by varying the thickness of the flat and dense PCL. Therefore, in this study, we fabricated an AgNRAs/SiO$_2$ SCL/SiO$_2$ PCL/Ag mirror multilayer thin film "local plasmon resonator" (MLPR) by varying the phase control layer (PCL) thickness and keeping the SCL thickness constant, Fig 1(b).

Herein, we investigate the two-fold EM enhancement mechanism of SERS using a local plasmon resonator and analyzing the optical absorption and Raman spectra of excitation light and scattered light. A close relationship between background generation and SERS enhancement was established, which is a direct indication of the role of the scattered light in the generation of the SERS background. When the absorption of both the excitation light and the Raman scattered light was large, the SERS background and peaks were greatly enhanced, demonstrating the two-fold EM mechanism.

Figure 2 shows the top and cross-sectional views of the SEM images for the MLPR with $d_{PCL} \approx 120$ nm. The direction of the Ag and SiO$_2$ vapor during deposition, are indicated by the white and orange arrows, respectively. When light falls onto a multilayer thin-film structure with several different materials, multiple reflections will take place within the structure. The reflected light may be coherent and interact with each other, depending on the light source and layer thickness. For
precisely tuning of the light coupling to the local plasmons, it is crucial to control the distance
between the AgNRAs and the mirror surface.

Figure 2. (a) Top view; and (b) cross-sectional view of SEM image of MLPR sample with PCL
thickness of 120 nm. The orange arrow indicates the SiO$_2$ vapor deposition direction while the
white arrow shows the Ag deposition direction. A zig-zag dielectric SiO$_2$ layer with an anisotropic
surface morphology was deposited on the PCL layer, and Ag was obliquely deposited thereon so
that Ag was deposited only on the irregular portion of the template. As a result, elongated AgNRs
reflecting the anisotropic surface morphology of the SiO$_2$ template were formed.

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morphology of the SiO$_2$ template were formed, Error! Reference source not found. Fig. 2(a). The
phase can be controlled by changing the thickness of the flat and uniform PCL, while the surface
morphology of the Ag nanoparticles can be kept unaffected by keeping the SCL thickness constant.
This is an essential feature of the local plasmon resonator. The SCL consists of zigzag SiO$_2$
nanostructures, with discontinuous prolate-shaped AgNRAs, with a high aspect ratio along the
long axis in the direction perpendicular to the vapor deposition flow on top.
The reflectance spectra exhibited a strong polarization dependence due to the quasi-prolate morphology of the AgNRAs, Fig. 3. For a fixed value of $d_{PCL}$, the reflectance changed periodically as a function of the photon energy. Besides, the reflectance in the NIR region for $s$-polarized light was much higher than that for $p$-polarized light. The anti-reflective conditions for the $s$-polarized light were found where the reflectance was negligibly small, in the energy range (1.3 eV-1.5 eV) of Raman scattering and the excitation laser ($\lambda = 785$ nm).

![Figure 3](image)

**Figure 3.** (a) $s$-polarized; and (b) $p$-polarized reflectance for $d_{PCL} = 0$ - 210 nm (c) comparison of $s$-polarized reflectance spectra for $d_{PCL} = 0$, 106, and 200 nm. Due to multiple reflections between the film, the interference phenomena by the periodic dark and bright patterns can be distinguished. The brighter part indicates a lower reflection, and the darker part represents higher reflection.

Near the excitation photon energy (1.57 eV, blue dotted line), most of the light was reflected for $d_{PCL} = 0$ nm, but for $d_{PCL} = 106$ nm, there was an absorption peak ($\approx 85\%$), and for $d_{PCL} = 200$ nm, the absorption has a value of approximately 55%, Fig. 3(c). Thus, the absorption can be tuned by simply changing the PCL thickness, which is the most important characteristic of the local plasmon resonator.
As the in situ SERS measurements were performed in the aqueous BPY solution, Fig. S1 shows a comparison of the absorption spectra in air and in water with s-polarized light for $d_{PCL}$ thicknesses of 20 nm, 110 nm, and 200 nm. In each PCL, the absorption spectrum in water was red-shifted by about 50 nm in the short-wavelength range and approximately 100 nm in the long-wavelength range as compared with the absorption spectrum in the air. Figure 4 shows the SERS color map for different $d_{PCL}$ thicknesses. The characteristics SERS peak intensity was minimal for $d_{PCL} = 0$ nm and $d_{PCL} = 200$ nm. The SERS intensity depended on $d_{PCL}$ and became significantly larger for $80 \text{ nm} \leq d_{PCL} \leq 150 \text{ nm}$.

When correlated with the corresponding reflectance spectra (Figure 3(a)), it was confirmed that SERS was strong for the samples with lower reflectance. The SERS characteristic peak intensity was maximum for $100 \text{ nm} \leq d_{PCL} \leq 120 \text{ nm}$ and minimum for $d_{PCL} = 0 \text{ nm}$ and 200 nm. The peak intensity at $d_{PCL} \approx 110 \text{ nm}$ was about 50 times stronger than that for $d_{PCL} = 200 \text{ nm}$. In general, the intensity of the scattered light and absorption are good indicators of the strength of the induced dipole as a dipole induced in metal nanoparticles by the incident light either radiates the scattering light or absorbs the incident light. However, in our case, the intensity of the scattered light strongly depends on the interference condition; thus, only absorption corresponds to the strength of the induced dipole.

In addition, a broad continuous background enhancement was also observed in conjunction with the enhanced Raman characteristic bands.\textsuperscript{2,18} It was observed that not only the Raman scattering peak was enhanced, but the background was also enhanced, and the peak intensity depended on the film thickness, Fig. 4(c). The background emission intensity has been closely associated with SERS enhancement related to plasmon-coupled emission.\textsuperscript{19} Consequently, enhancement of the background electric field occurs in addition to the enhancement of the Raman scattered light.
For $d_{\text{PCL}} \leq 60$ nm in the wavelength range of 800-900 nm, both the absorbance and the background intensity of the SERS spectrum decreased monotonically, Fig. 6[a-c]. For $d_{\text{PCL}} = 20$ and 40 nm, the absorbance increased in the wavelength range of 900-1000 nm. Consequently, the
SERS background also increased slightly. Thus, the increase/decrease in the SERS background is related to the absorbance at that wavelength.

![Absorption and SERS spectrum in water for different PCL thicknesses](image)

Figure 5. Absorption and SERS spectrum in water for $d_{\text{PCL}}$ (a) 20 nm; (b) 40 nm; (c) 60 nm; (d) 110 nm; (e) 150 nm; and (f) 180 nm. The dotted represents wavelengths 785, 851, 874, and 897 nm from the left.

The $d_{\text{PCL}} = 110$ nm sample showed the highest SERS intensity, Fig. 6(c). The absorbance near the excitation wavelength was about 45%, which was small compared to other samples. However, the absorbance for the wavelength at which the Raman scattering peak was approximately 80%,
the highest among all the samples. In other words, one can improve the SERS enhancement using the excitation wavelength such that the absorption is at a slightly higher wavelength than the excitation wavelength. Sample $d_{PCL} = 150$ nm had a broad absorption peak in the wavelength range of Raman scattered light. We obtained the best SERS enhancement when the absorption was maximum for the scattered wavelength (110 nm). The SERS intensity for $d_{PCL} = 150$ nm was about 4 times that of $d_{PCL} = 200$ nm. For $d_{PCL} = 200$ nm, the absorbance near the excitation wavelength was almost zero, and the absorbance in the Raman scattered wavelength range (850-900 nm) was approximately 60% at maximum, resulting in a low SERS intensity and higher background. Hence, for a significant SERS enhancement, the excitation, and scattered wavelengths both should have high absorbance and should be enhanced. The effect of absorbance in the excitation and scattered wavelength on the SERS peak and background enhancement is summarized in Table 1.

Table 1. Effect of absorbance on the excitation and scattered wavelengths, on the SERS peak and background enhancement

<table>
<thead>
<tr>
<th>$d_{PCL}$ thickness (nm)</th>
<th>Absorbance in the wavelength range</th>
<th>SERS</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Excitation 750-800 nm</td>
<td>Scattering 850-900 nm</td>
</tr>
<tr>
<td>20; 40</td>
<td>high</td>
<td>low</td>
</tr>
<tr>
<td>200</td>
<td>zero</td>
<td>medium</td>
</tr>
<tr>
<td>60</td>
<td>high</td>
<td>medium</td>
</tr>
<tr>
<td>150</td>
<td>medium</td>
<td>medium</td>
</tr>
<tr>
<td>110</td>
<td>low</td>
<td>high</td>
</tr>
</tbody>
</table>

*Low implies $\leq 25\%$, medium corresponds to $\leq 50\%$, and high infers $\leq 75\%$ absorbance*

A correlation between the SERS background and absorbance in the Raman scattering wavelength range was found. Both the SERS peaks and background were most strongly enhanced
when the absorbance of the scattering light was high (80%), even for slightly low absorbance around the excitation wavelength. On the other hand, for high or medium absorbance only around the excitation wavelength highest SERS enhancement was not observed. However, the lowest background intensity was observed when the absorbance was minimum for the scattered wavelength, verifying the second step of the EM enhancement. Also, the SERS background was strong even for no absorbance in the excitation wavelength range. This implies that 1) the EM mechanism is a two-step process where the scattered field is also enhanced; 2) the enhancement of the scattered field is a dominating factor for the enhancement of the SERS peaks as well as the SERS background. Our results agree well with previous reports where the maximum enhancement was observed when the excitation wavelength was of higher energy than the LSPR extinction spectrum. Hence, we can conclude that the electric field enhancement of the Raman scattered light exists in addition to the electric field enhancement of the incident light. The understanding of SERS enhancement from this study will be useful in the development of SERS substrates with the best SERS performance.

In conclusion, we have demonstrated that the EM mechanism is a two-step process where the scattered field is also enhanced, and there is a correlation between the SERS peaks, background, and absorption spectra. The absorption can be tuned by simply changing the PCL thickness, which is the most crucial characteristic of the local plasmon resonator. We have also demonstrated that the enhancement of the scattered field is a dominating factor for the enhancement of the SERS peaks as well as the background. The enhancement of the scattered Raman field was verified by using Ag nanorod array/dielectric layer/Ag specular layer whose absorption rate in the near-infrared region was changed significantly by changing the effect of light interference without changing the morphology of the Ag nanoparticles. The best SERS enhancement was observed for
$d_{PCL} = 110 \text{ nm}$ and was about 50 times that of $d_{PCL} = 200 \text{ nm}$. This research will provide crucial evidence for the validity of the two-fold EM mechanism of SERS enhancement and will pave the way for the development of SERS substrates with the best SERS performance.

**MATERIALS AND METHODS**

**A.1 Fabrication of Local Plasmon Resonator.**

The multilayer local plasmon resonator was fabricated using a dynamic OAD technique, in which the deposition angle and/or in-plane direction of the substrate can be changed during deposition, thus allowing to control the complex three-dimensional morphology.\(^1\)\(^-\)\(^3\) The detailed fabrication process also can be found in our previous works.\(^4\)\(^,\)\(^5\) The film thickness of PCL was changed in the range of 0–210 nm. Subsequently, SiO\(_2\) SCL with anisotropic surface morphology was deposited using the serial bideposition (SBD) method.\(^5\)\(^,\)\(^6\) The vapor deposition angle \(\alpha\) for SiO\(_2\) was fixed at 78.6°, and the in-plane angle was swiftly rotated by 180° after each fixed amount of vapor deposition. By repeating 30 cycles of SBD SCL, a thickness of $d_{SCL} = 576 \text{ nm}$ was prepared. Then, Ag was deposited up to thickness, $t_{Ag}$, of 8 nm at a deposition angle, $\alpha_{Ag}$, of 73.4° onto the fabricated SCL layer. The in-plane angle was not changed for the deposition of Ag. The amount of deposition of Ag was small enough to maintain the discontinuous island structure of Ag on SCL.

**A.2 Optical and SERS Characterization**

The reflectance with polarized light for the MLPR was measured in both air and water. For the measurement of reflectance in air, the angle of incidence was sufficiently small to be considered as normal incidence. In the ultraviolet light region, a deuterium light source (DH-2000, Ocean Optics) was used, and in the visible light region, a halogen light source (LS-1, Ocean Optics) was used for reflectance measurements. The light guided by the optical fiber was collimated by the
convex lens and was incident on the MLPR sample perpendicular to the sample plane. Reflectance spectra were collected using a spectrometer (Ocean Optics USB4000). The reflectance measurements were performed for two mutually orthogonal polarizations called "s" (light polarized parallel to the long Ag nanoparticles axis) and "p" (light is polarized perpendicular to the long Ag nanoparticles axis). A 0.5 mm thick silicone cell with a 5 × 5 mm hole in the center was placed on the sample, and 15 µL of pure water was injected into the silicone cell hole and it was sealed with a cover glass. The method for the measurement of reflectance in water was the same as the in air.

For the in situ SERS measurement, on MLPR immersed in a 4,4'-bipyridine (BPY) aqueous solution, a small cell (having a diameter of 3.6 mm and containing a spacer of silicone rubber with a thickness of 0.5 mm) on the sample was created. After the cell was filled with a 10 µL droplet of a 1 mM BPY solution, it was sealed with a cover glass. SERS observations were conducted under both ambient and in water using an inverted Raman spectrometer (RAM200S; LambdaVision, Inc) with a 10× objective lens. A 785 nm laser with an intensity of 30 mW was utilized as the light source for excitation. In addition, a SERS measurement was performed using an s-polarized laser with a polarizing film placed near the objective lens.

ASSOCIATED CONTENT

Supporting Information. (A) Materials and methods; (B) S-polarized absorption spectra in air and water.

AUTHOR INFORMATION

Corresponding Author
*drsamirkumar2017@gmail.com
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