# Preparation of Anisotropic Metal Dimer Array on Glass Substrate Showing Intense Surface-Enhanced Raman Scattering

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Structure of the Ag and Au dot dimers arrayed on a glass substrate was optimized to exhibit intense surface-enhanced Raman scattering (SERS) of adsorbed 4,4'-bipyridine molecule in an aqueous solution. The substrates with the Ag and Au dimers show clear optical anisotropy correlated to the polarization direction of the array. The SERS intensity also showed the same polarization anisotropy, suggesting that the gap of the dimer induced intense SERS. Empirical enhancement factor of the present system was estimated to be between  $10^5$  and  $10^9$ . The SERS activity of the Au dimer was kept even under intense light irradiation, while the structure of the Ag dimer was damaged under the similar conditions. Localization of the SERS active site was shown by Raman imaging measurement. Polarization dependence of the SERS image proves that the uniformity of the structure of the Ag and Au dimer array showing intense SERS.

Key words: surface-enhanced Raman scattering, metal nano-particle, metal nano-gap, surface plasmon, angle-resolved nanosphere lithography

### **1. INTRODUCTION**

Recognition and detection of a small number of molecules have been the central issue of recent nanotechnology. To establish the method for ultrasensitive molecular detection, novel system should be developed to obtain very stable and highly reproducible signal containing vibrational information on target molecules. Surface-enhanced Raman scattering (SERS) from metal nanostructure may provide a chance to solve the problem.<sup>1</sup>

From the early stage of its discovery of SERS, the phenomenon has been expected to be applied for the ultra-sensitive molecular detection and discrimination. Raman scattering cross section can be significantly increased when a molecular is located in the vicinity of plasmon-active metals. Enhancement of the cross section by a factor of  $10^{14}$ - $10^{15}$  leads to single molecular detection by Raman.<sup>2-3</sup> In spite of the expectation, the use of SERS for analytical method has been quite limited. A large number have been carried out to prepare SERS active substrate.<sup>4-14</sup> Studies using Ag resulted in successful preparations on the SERS active structures with relatively large empirical enhancement factors, which give the measure of the SERS activity, show discrepancies ranging from  $10^4$  to  $10^{11}$ , depending on the experimental condition and the substrate preparation.<sup>4-14</sup>

Recently, we have succeeded in optimizing the structure of Ag substrate for the observation of intense SERS.<sup>15-17</sup> The SERS activity was well correlated to the optical scattering property of the Ag dimer with distinct gap distance, suggesting that the intense SERS originates from the gap part of the dimer. In-situ spectral measurements of individual dimers were carried out in an aqueous solution containing equal amounts of 4,4'-and 2,2'-bipyridines. Characteristic time-dependent

spectral changes were observed in the system. Detailed analysis of the observed spectra using solutions with different concentration proved that the spectra originated from a very small number of molecules at the active SERS site of the dimer. The Ag structure should be promising for the SERS application. But it was found that the Ag structure was not chemically stable and was damaged under intense light irradiation. Thus, the preparation method should be extended using other chemically stable material.

In this report, structure of the Ag and Au dot dimers arrayed on a glass substrate was optimized to observe intense SERS of adsorbed 4,4'-bipyridne molecule in aqueous solution. Characteristics on the SERS activity of the Au dimer array were carefully evaluated based on the comparison with those of the Ag dimer array. Possibility on the use of the Au structure for SERS active substrate showing very stable and highly reproducible signal was discussed.

## 2. EXPERIMENTAL

Detailed experimental procedure in the present study was described previously.<sup>15-17</sup> Briefly, the Ag dot dimer array showing intense SERS were prepared by an angleresolved nanosphere lithography technique (AR-NSL)<sup>18-20</sup> using repeated vapor depositions with different angles

using repeated vapor depositions with different angles onto the polystyrene (PS) particle (Polysciences Inc.; d =350 nm) monolayer prepared on a glass substrate. Similar procedure was adopted to prepare the Au dimerarrayed substrate showing intense Raman scattering. For Raman measurement, a commercial Raman microprobe spectrometer (Ramanscope, Renishaw) was specially modified for NIR laser light ( $\lambda_{ex} = 785$  nm). The estimated spot size of irradiation ca. 1 µm. Extinction spectrum of the Ag dimer array in the visible-near infrared region were recorded utilizing a multi-channel spectrometer (MCPD-2000, Ohtsuka Electronics, observed area: ca. 0.3 cm<sup>2</sup>). The structure of the dimer on the glass substrate was inspected by an atomic force microscope (AFM, Nanoscope-IIIa, Digital Instruments) in air.

### 3. RESULTS AND DISCUSSION

Optical properties of the Au dimer can be controlled by the size and thickness of the unit structure as well as the gap distance between the units. Figure 1 shows extinction spectra and AFM images of the Au dot units prepared by different evaporation thickness. As the thickness increased from 20 nm to 30 nm, peak of the extinction spectra slightly shifted to shorter wavelength. Further increment in the thickness led to unstable adhesion of Au dot on the glass substrate. The Au unit structure was removed during the PS removal procedure, leading to lost of the optical extinction. These results indicate that evaporation of Au with 20 nm in thickness gives stable Au dot unit structure showing optical anisotropy.

Figure 2 shows AFM images and extinction spectra of Ag and Au dimer structures optimized for the present SERS measurements. The images exhibit the dimmer aligned as parallel triangle structure. Triangle corner had a round shape because of the surface energy of the metals. Smaller Au dimmer seems to be coupled roundshape dots rather than triangles. At the Ag dimer array, extinction spectra measured by polarized light showed distinct peaks attributed to a transverse and a longitudinal mode (Fig. 2 (c)). When the polarization of the illuminated light coincides with the long axis of the dimer structure, extinction maximum is observed at longer wavelength. Polarized excitation with the short axis leads to extinction at shorter wavelength. Oberved change in the absorption maximum depending upon the polarization angle proves the formation of well-ordered anisotropic dimer structure. The Au dimer array also showed optical anisotropy. Parallel polarization to the long axis of the dimer structure resulted in relatively strong extinction of the illuminated light. Although peak due to a transverse mode at the short axis excitation was not clearly oberved at the Au dimer, polarization anisotropy in the extinction spectra proved successful preparation of periodic array of the Au dimer a glass substrate at relatively large area (> 1 cm<sup>2</sup>), as has been observed for the Ag dimer array, which was previously reported.

Near-infrared SERS activity of the Ag and Au dimer arrays was evaluated in an aqueous solution. Both dimer arrays exhibited relatively intense SERS. Figure 3 shows the SERS spectrum measured using an aqueous solution containing 4,4'-bipyridine using the dimers arrays. Normal Raman spectra of the bulk crystal and homogeneous aqueous solution under conditions without the enhancement were also shown for comparison. All of the spectra exhibited Raman bands, which can be attributed to the vibrational modes of the 4,4'-bipyridine molecule. In the case of the Ag dimer array, peak assignments are as follows; 1016 cm<sup>-1</sup> (ring breathing), at 1080 cm<sup>-1</sup> (in-plane ring deformation, C-H bending), at 1240 cm<sup>-1</sup> (in-plane C-H beFnding), and at 1300 cm<sup>-1</sup> (inter-ring stretching). The Au dimer array showed slightly blue-shifted peaks in the SERS spectra. The



Fig. 1. Absorption spectra (left) and AFM images (right) prepared using PS particles with the diameter of 350 nm; the thickness of evaporated Au was 20 nm; solid line and (a), 30 nm; dashed line and (b), 40 nm; dot-dashed line and (c), 50 nm; dotted line and (d).



Au (d, e, f); AFM images (a, b, d, e), polarized absorption spectra (c, f), polarization angle to the long axis  $\theta$  was 0° (solid line), 90° (dashed line).

shift was clearly observed at the ring breathing mode at 1020 cm<sup>-1</sup>, reflecting the state of metal-dependent adsorption. It should be noted that characteristics of the SERS spectra are comparable to those of unenhanced normal Raman spectra of the bulk crystal and homogeneous aqueous solution.

Enhanced scattering at these dimer arrays was clearly demonstrated by relatively low excitation power  $(I_{ex})$ and short exposure time  $(t_{ex})$  compared with those for bulk cry

stals and in homogeneous aqueous solutions of relatively high concentration. An empirical signal enhancement factor (EF) of the Au dimer was estimated from the peak integration ratio of the SERS vibration at 1020 cm<sup>-i</sup> to the unenhanced signal from the solution of a defined sample concentration. The EF was found to be in the range between 3.1 x  $10^5$  and 1.2 x  $10^9$ , assuming the number of molecules on the surface as full monolayer adsorption  $(2.2 \times 10^6 \text{ molecules}/\mu\text{m}^2)$  and projection of the amount in solution (600 molecules/ µm<sup>2</sup>), respectively. The value of the Ag dimer array is approximately one order higher than that of the Au dimer. The value of EF at the present Au dimer array is comparable or larger than the recently reported values of the SERS from a self-organized large gold nano-particle array<sup>21</sup> and structured gold substrate,<sup>22</sup> possessing a precisely controlled structures. Although estimated value of EF is significantly dependent upon the number of molecules at the SERS active site, relatively large value of EF at the Au dimer array proves that optimization of the Au dimer structure is achieved in the present system.

Advantage of the Au system is superior chemical

4 6 Time / sec. Fig.4. SERS spectra from the dimer arrays of Ag (a), Au (b), and time course of SERS signal at 1018 cm<sup>-1</sup> (c): Ag (solid line), Au (dotted line).

10

8

stability than that of Ag. Generally, intense photoirradiation to Ag nanoparticles leads to structural deformation due to photo- and/or thermal-chemical degradation. At the present Ag dimer array, stability of the SERS intensity was dependent upon the power of the excitation. Relatively stable scattering signals were observed during the measurement at the irradiation with the power less than 100 µW. However, higher irradiation power of greater than 500  $\mu$ W led to immediate change in the scattering signal due to the degradation. In this case, unstable signal blinking was observed during the experiment under the intense photoirradiation. Even in the case of 200 µW irradiation, continuous observation for a few tens seconds led to irreversible change in the spectral shape as shown in Figure 4 (a) after the reversible spectra blinking possibly due to change in absorption state of molecules on the Ag surface. The Au dimer array, however, did not show appreciable signal fluctuation even under intense photoirradiation. Figure 4 (b) shows SERS spectra observed at the Au dimer array under the irradiation with the power of 1740  $\mu$ W, which was approximately one order higher than that for the Ag. Time-courses of the SERS intensity at 1018 cm<sup>-1</sup> observed using the Ag and Au dimer arrays were shown in Figure 4 (c). Highly stable SERS from the Au dimer array compared with the Ag was shown in the Figure. Although the SERS intensity of the Au was weaker than that from the Ag, which is due to relatively small EF, signal fluctuation was less than a few percent. Present result demonstrates that the Au dimer array with optimized structure maintains its SERS activity under intense light irradiation.

Relatively strong SERS enhancement occurs at specific "hot" sites of the dimer. Figure 5 shows Raman images using expanded NIR laser beam with the diameter of approximately 30 µm. These image



300 counts

1100

Raman Shift / cm<sup>-1</sup> Fig. 3. NIR Raman spectra of 4,4'-bipyridine;

observed at Au dimer ((a), irradiation power

(I) = 200 mW, exposure time  $(t_{ex}) = 5 \text{ s}$ ,

concentration (n) = 1 mM), Ag dimer ((b), I =

200 mW,  $t_{ex} = 1$ s, n = 1 mM), aqueous solution ((c), I = 39.2 mW,  $t_{ex} = 2000 \text{ s}$ , n =

10 mM), crystalline solid ((d), I = 200 mW,

1200

1300

(d)

 $t_{\rm ex} = 10 \, {\rm s}$ ).

1000

C 900 (a)

a.u.

Raman Intensity /

0

2





Fig.5. Raman images observed at 1018  $cm^{-1}$ , (I = 30 mW,  $t_{ex}$  = 10 sec.).

measurements prove that the intense SERS signals are originated from highly localized specific sites on the dimer array. The intensity of the spots was dependent on the polarization angle of the excitation. When the polarization direction aligned to the long axis of the Ag dimer array, the intensity of the bright spots of Raman scattering became maximized. Intensity became weak when the polarization direction was close to the perpendicular direction to the long axis of the dimer. Clear polarization angle dependence observed in the present system reflects uniformity of individual dimer array showing intense SERS.

It should be noted that former estimation of the enhancement factor is based on the assumption that the molecules are homogeneously distributed at the observed area. Thus, further detailed measurement on the hot site observed at the Raman image in Figure 5 may give several orders of magnitude higher, because of expected smaller number of molecules at the gap part. Further detailed analysis on the SERS intensity and the number of molecules at the hot site is undergoing.

Highly stable SERS active substrate composed of the Au dimer may provide ultra-sensitive Raman sensor discriminating molecules with matrix high reproducibility. One of serious problems on the application of SERS, i.e., poor reproducibility and luck of stability, could be solved by the use of the Au dimer array having optimized structure. As well as these possibilities on the practical application, higher stability under intense light irradiation may open up novel application for manipulation of small number of molecules at the gap. Theoretical estimation suggested that the irradiation in the order of 10<sup>5</sup> W/cm<sup>2</sup> can trap a molecule at the gap part of Ag spherical dimer at room temperature.<sup>23</sup> In the present system, the Au dimer array, however, was found to be stable under the irradiation concentrated at the diameter of a few µm with the power of 1740  $\mu$ W, which corresponding to 10<sup>5</sup> W/cm<sup>2</sup>. Further careful control in the filed at the gap part of the Au dimer could open the possibility of the molecular manipulation. Further optimization on the structure is in progress to clarify the possibility of the molecular manipulation at the gap of the Au dimer.

#### 4. SUMMARY

Structure of the Ag and Au dot dimers arrayed on a glass substrate was optimized to observe intense SERS of adsorbed 4,4'-bipyridne molecule in aqueous solution. The substrates with the Ag and Au dimer shows clear optical anisotropy correlated to the polarization direction of the array. The SERS intensity showed the same polarization anisotropy, suggesting that the gap of the dimer is the origin of intense SERS. The SERS activity of the Au dimer was maintained even under intense light irradiation, in which the structure of the Ag dimer was damaged. Localization of the SERS active site was shown by the Raman image measurements.

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