

Supplemental Information for

**Densely arranged two-dimensional silver nanoparticle assemblies with optical
uniformity over vast areas as excellent surface-enhanced Raman scattering
substrates**

Yoshimasa Tanoue,^a Kosuke Sugawa,^{*a} Takahiro Yamamuro^a and Tsuyoshi Akiyama^{*b}

^a *College of Science and Technology, Nihon University, Tokyo, Japan*

^b *Department of Materials Science, School of Engineering, The University of Shiga Prefecture, Shiga,
Japan*

This file includes:

1. Calculation procedure for obtaining the enhancement factor of the Raman signal from PATP on metal nanoparticle assemblies.
2. Characterization of gold nanoparticle assemblies.
3. Raman signals from PATP on the gold nanoparticle assemblies.

1. Calculation procedure for obtaining the enhancement factor of the Raman signal from PATP on metal nanoparticle assemblies.

To quantitatively evaluate the enhancement effect of SERS signals, the enhancement factor (EF) values were estimated based on the following equation, as previously reported:^{S1-S3}

$$EF = \frac{I_{SERS}/N_{surf}}{I_{bulk}/N_{bulk}}, \quad (1)$$

where I_{SERS} is the intensity of a vibrational mode on the SERS spectrum of PATP and I_{bulk} is the intensity of the same vibrational mode for the normal Raman spectrum of the 10 M PATP methanol solution. In this study, the peak appearing at $\sim 1070 \text{ cm}^{-1}$ (a_1 mode) was selected in order to calculate the EF values because the a_1 vibrational mode is largely associated with the EM mechanism (SPR effect). In equation 1, N_{surf} and N_{bulk} are the number of PATP molecules effectively excited by laser irradiation of the nanoparticle assemblies and solutions, respectively. N_{surf} can be calculated as follows:

$$N_{surf} = \frac{RA}{\sigma}, \quad (2)$$

where R is the roughness factor of the nanoparticle assemblies, A is the area of the focal spot of the laser, and σ is the surface area occupied by immobilized PATP molecules. PATP molecules occupy $\sim 0.20 \text{ nm}^2$ at full coverage on gold and silver assuming that the PATP molecules have been immobilized perpendicular to the metal surface via metal-sulfur atom bonding. In this case, σ can be assumed to be $\sim 0.20 \text{ nm}^2/\text{molecule}$.^{S3,S4} In this study, metal nanoparticles formed almost 2-D assemblies and therefore the roughness factor (R) can be calculated as follows:

$$R = \frac{\Gamma \times A_{sphere}}{A_{pro}}, \quad (3)$$

where Γ , A_{sphere} , and A_{pro} denote the surface coverage of the nanoparticle, surface areas of the nanoparticles, and projected surface areas of the nanoparticles on the glass surface, respectively. Thus, N_{surf} can be expressed as follows:

$$N_{surf} = \frac{R \times A \times A_{sphere}}{\sigma \times A_{pro}}, \quad (4)$$

Next, N_{bulk} is calculated using the following equation:^{S1,S2}

$$N_{bulk} = AhcN_A, (5)$$

where h is the height of the volume of PATP solution contributing to the Raman signal, c is the concentration of the PATP solution (10 M), and N_A is the Avogadro's number.

We determined h for the measurement configuration by transferring a silicon (100) wafer across the focal plane of the objective lens ($\times 100$) and recording the intensity of the Raman signal from the silicon at 520 cm^{-1} . We then obtained the values for $h = 6\text{ }\mu\text{m}$ (532 nm) and $17\text{ }\mu\text{m}$ (785 nm) by integrating the intensity of the Raman signal over distance and dividing the calculated value by the largest observed Raman signal. Based on the above results, we determined the EF values for the system under laser excitation wavelengths of 532 and 785 nm.

2. Characterization of gold nanoparticle assemblies.

Synthesis of the colloidal aqueous solution of gold nanoparticles was performed using a modified version of the previously reported method.^{S5} The diameter of the resultant AuNPs estimated from transmission electron microscope (TEM) images (Figure S1(A)) was $61 \pm 6\text{ nm}$. The SEM image of gold nanoparticle assemblies prepared from the gold colloidal aqueous solution by the organic solvent-mediated liquid-liquid interface assembly technique is shown in Figure S1(B). It was confirmed that the gold nanoparticles formed what appeared to be dense almost 2-D assemblies (coverage: ca. 76%).

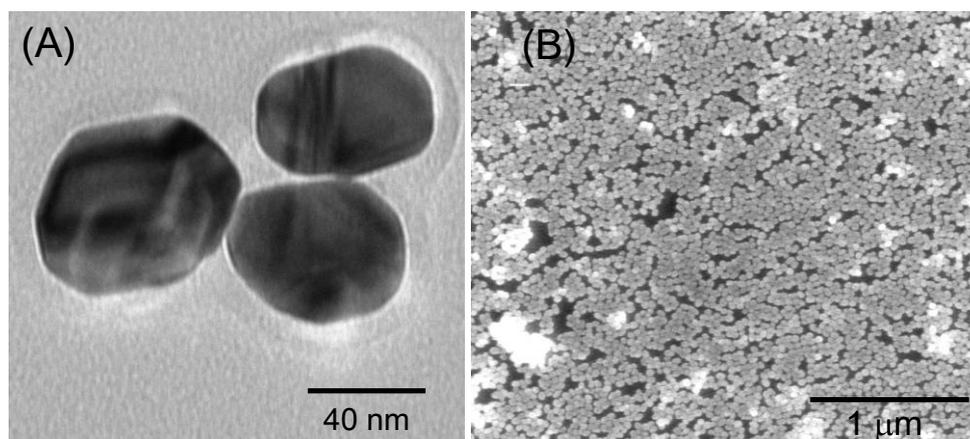


Figure S1(A) TEM image of synthesized gold nanoparticles and (B) SEM image of gold nanoparticle assemblies.

The transmission extinction spectrum of the gold nanoparticle assemblies is shown in Figure S2. The extinction spectrum of the assemblies contains two broad extinction bands at ~550 and 700-1100 nm. The former band can be assigned to the plasmon mode of the isolated gold nanoparticle, and the latter band can be assigned to the longitudinal plasmon mode of coupling nanoparticles.^{S6,S7} Therefore, for the SERS measurements, the laser line at 785 nm is seen to overlap significantly with the broad peak of the longitudinal plasmon mode as well as with the peak from the AgNP assemblies.

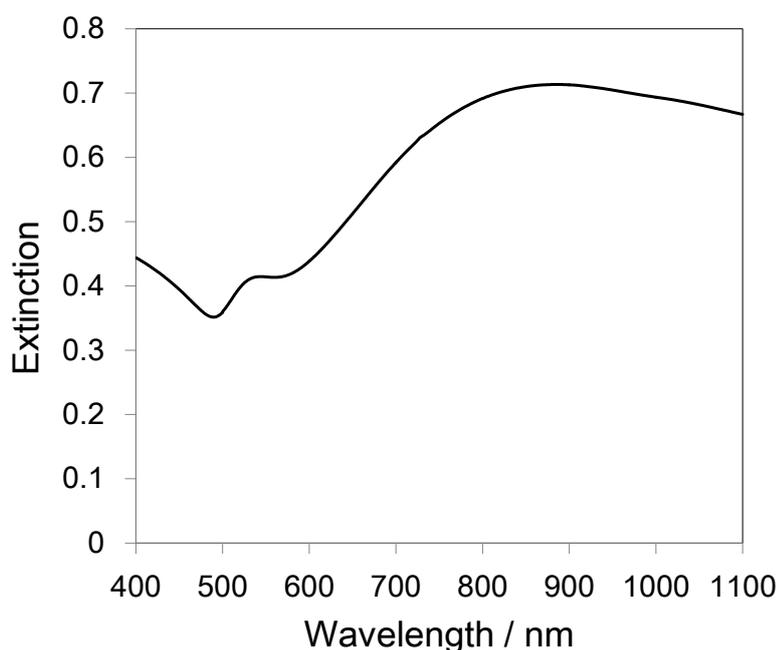


Figure S2 Extinction spectrum of the gold nanoparticle assemblies.

3. Raman signals from PATP on the gold nanoparticle assemblies.

PATP molecules were immobilized on the gold nanoparticle assemblies as a result of the strong bonding taking place between the thiol group of the PATP and the metal surface. As shown in Figure S3, for laser excitation at 785 nm, the spectral pattern obtained was characteristic of PATP, as it appears in AgNP assemblies.

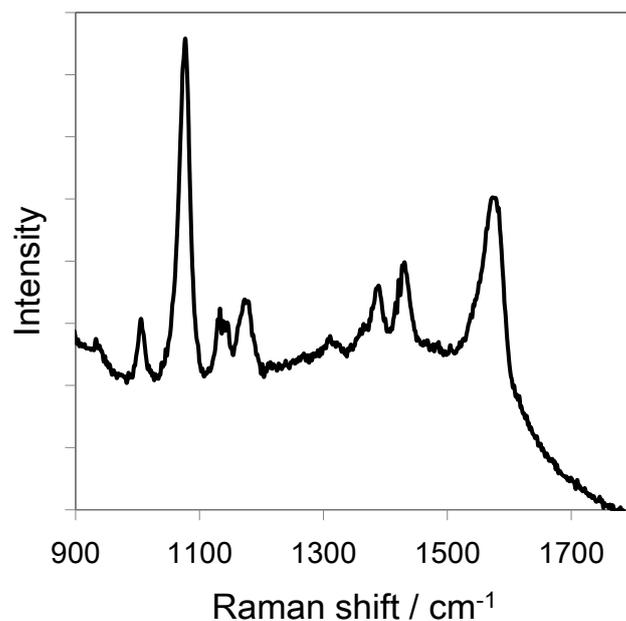


Figure S3 SERS spectrum from PATP immobilized on the gold nanoparticle assemblies measured at 785 nm.

References

- S1. W. B. Cai, B. Ren, X. Q. Li, C. X. She, F. M. Liu, X. W. Cai, Z. Q. Tian, *Surf. Sci.*, 1998, **406**, 9.
- S2. E. J. Smythe, M. D. Dickey, J. Bao, G. M. Whitesides, F. Capasso, *Nano Lett.*, 2009, **9**, 1132.
- S3. Y. Wang, X. Zou, W. Ren, W. Wang, E. Wang, *J. Phys. Chem. C*, 2007, **111**, 3259.
- S4. K. Kim, J. K. Yoon, *J. Phys. Chem. B*, 2005, **109**, 20731.
- S5. J. Turkevich, P. C. Stevenson, J. Hiller, *Discuss. Faraday Soc.*, 1951, **11**, 55.
- S6. W. Lee, S. Y. Lee, R. M. Bridger, O. Rabin, *Adv. Funct. Mater.*, 2011, **21**, 3424.
- S7. P. M. Jais, D. B. Murray, R. Merlin, A. V. Bragas, *Nano Lett.*, 2011, **11**, 3685.