

# DIRECT INVESTIGATION OF SURFACE PLASMON SENSITIVE SURFACE ENHANCED RAMAN SCATTERING USING SINGLE Ag NANO-AGGREGATES

T. Itoh, K. Hashimoto, Y. Kikkawa, A. Ikehata, and Y. Ozaki\*

Department of Chemistry, School of Science and Technology, Kwansei-Gakuin University, 2-1, Gakuen, Sanda 669-1337, Japan; E-mail: [ozaki@ksc.kwansei.ac.jp](mailto:ozaki@ksc.kwansei.ac.jp)

**Keywords:** SERS, surface plasmon, single Ag nano-aggregate

**Abstract:** We investigated polarization dependences of surface enhanced resonance Raman scattering (SERRS) and surface plasmon resonance (SPR) to identify the SERRS yielding SPR bands. We also studied SERRS excitation spectra for single Ag nano-aggregates with the SPR bands to explore the electromagnetic (EM) and resonance contribution to SERRS.

Surface enhanced resonance Raman scattering (SERRS) has recently been a matter of great interest from the points of its applications as well as basic science because it allows one single molecule detection due to its enormous enhancement factor by  $10^{10}$  to  $10^{14}$ . However, the varieties of molecules and metal substrates that yield SERRS are quite limited and its mechanism is still unclear. Recently, experimental studies on relationship between surface plasmon resonance (SPR) and SERRS have rapidly been advanced because several groups achieved SERRS detections using single Ag nano-aggregate and/or single adsorbed dye molecule systems [1-5]. These SERRS researches are valuable to optimize the electromagnetic (EM) interactions at metal nano-structure/adsorbed molecule systems for single-molecule bioanalysis and nano-biodevice.

In the present study, polarization dependences of SERRS and SPR are investigated for identification of the SERRS yielding SPR bands. SERRS excitation spectra are investigated for single Ag nano-aggregates with the SPR bands to exam the EM and resonance contribution to SERRS.

A mixture of a NaCl (10 mM) aqueous solution and that of Rhodamine 6G (R6G) ( $1.1 \times 10^{-9}$  M) is added to the Ag colloidal solution, and is spin-coated onto a glass plate. White and resonance Raman excitation light are introduced into a stage of optical microscope through the same pass with a dark and bright-field condenser, and focused onto a glass plate with dispersed Ag particles. The scattered light from an Ag particle is collected with an objective lens and passed a polarizer and led to a polychromator. The SERRS active Ag particles always look nano-aggregates consisting of many particles by AFM measurements.

Fig. 1(a) show the SPR bands of single Ag nano-aggregate for the polarization angles of  $0^\circ$  (min) and  $60^\circ$  (max), respectively. The insets in Fig. 1 (a) depict the corresponding SERRS spectra with excitation wavenumber ( $\omega_{ex}$ ) of  $18800\text{ cm}^{-1}$ . SPR band have lower ( $\omega_{SP1}$ ;  $\sim 14500\text{ cm}^{-1}$ ) and higher ( $\omega_{SP2}$ ;  $22000\text{ cm}^{-1}$ ) peak energy. Fig. 1(b) presents polarization dependences of peak intensities of SPR with  $\omega_{SP1}$  (open circles) and  $\omega_{SP2}$  (closed circles), respectively. Their polarization dependence curves of SPR bands with  $\omega_{SP1}$  and  $\omega_{SP2}$  fit in well with the square of cosine curves (dotted lines) whose phase differences are  $90^\circ$  to each other, and therefore, these bands with  $\omega_{SP1}$  and  $\omega_{SP2}$  correspond to transverse and longitudinal modes of SPR, respectively. Fig. 1(c) shows polarization dependence of peak intensities of SPR with  $\omega_{SP1}$  (open circles) and SERRS bands with the  $\omega_{ex}$  of  $18800\text{ cm}^{-1}$  (open squares) and  $15790\text{ cm}^{-1}$  (open triangles)  $\text{cm}^{-1}$ . All the polarization dependence curves in the lower panels fit with the square of cosine curves (dotted lines) that have the same phase functions. These polarization experiments strongly suggest that EM field generated by the SPR band with  $\omega_{SP1}$  enhances the Raman signals [5].

We chose four Ag nano-aggregates with different dipolar SPR band positions, and these SPR bands are shown in Fig. 2(a) as solid lines ((1), (2), (3), and (4)). The broken lines in Fig. 2(a) and (b) represent the fitted optical transition band of adsorbed R6G molecules. SPR bands shown in Fig. 2(b) as solid lines ((1), (2), (3), and (4)) are the ones fitted by Lorentzian curves because their SPR bands are thought to be due to dipolar electric oscillations [5].

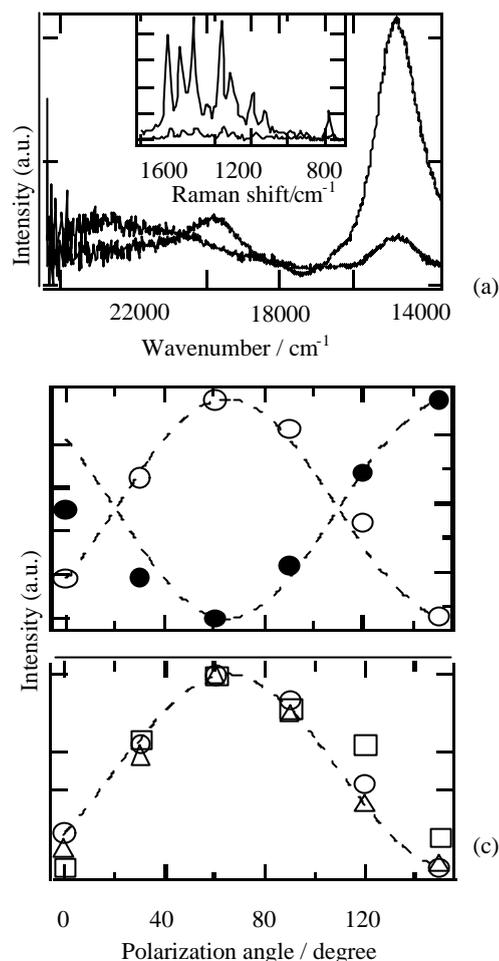


Fig. 1. (a): the SPR and SERRS (inset) bands for the polarization angle of  $0^\circ$  (min) and  $60^\circ$  (max). (b): polarization angle dependences of peak intensities of SPR bands with  $\omega_{SP1}$  (open circles) and  $\omega_{SP2}$  (closed circles), respectively, and their fitted curves (dotted lines). (c): polarization dependences of peak intensities of SPR bands with  $\omega_{SP1}$  (open circles) and SERRS bands with  $\omega_{ex}$  of  $18800\text{ cm}^{-1}$  (open squares) and  $15790\text{ cm}^{-1}$  (open triangles)  $\text{cm}^{-1}$ .

Fig. 3 (a), (b), (c), and (d) show the excitation profiles of the three SERRS bands for the four Ag nano-aggregates with the SPR bands shown as (1), (2), (3), and (4) in Fig. 2, respectively. It is noted that these excitation profiles become broad and shift to lower energy side as the SPR bands shift to lower energy side. To clarify these variations in the SERRS excitation profiles, we estimate SERRS excitation profiles for each Ag nano-aggregate by using SPR and R6G optical transition bands fitted by Lorentzian curves. For simplification of the estimation, SERRS excitation profiles are calculated by multiplying each fitted SPR band by the optical transition band of R6G shown in Fig. 2(b). These estimated profiles are overdrawn in Fig. 3(a) to 4(d) as dotted lines. The estimated excitation profiles qualitatively reproduce their tendencies of peak shifts and broadening of these experimental profiles. This yields the direct evidence for the decrement of spectral overlap between the contribution of resonance and that of enhanced EM field on SERRS.

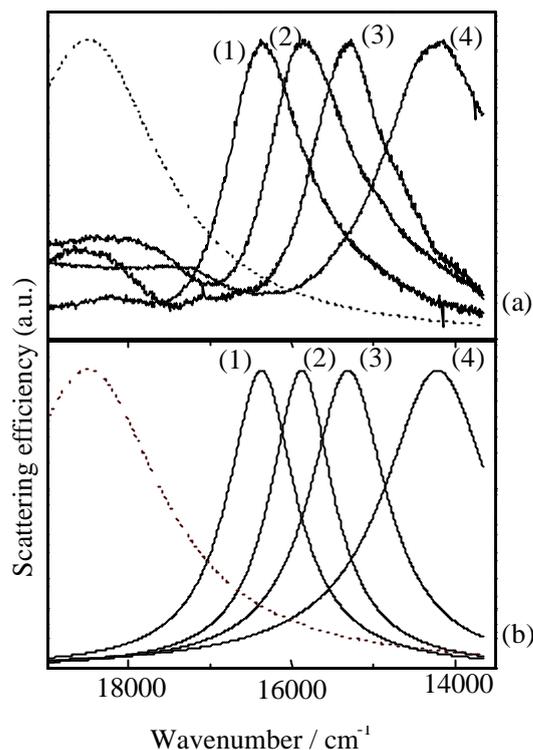


Fig. 2. (a): SPR bands of SERRS active single Ag nano-aggregates (solid lines (1), (2), (3), (4)) and the fitted optical transition band of R6G (broken line). (b): SPR bands fitted by Lorentzian curves (solid lines (1), (2), (3), (4)) and the fitted optical transition band of R6G (broken line).

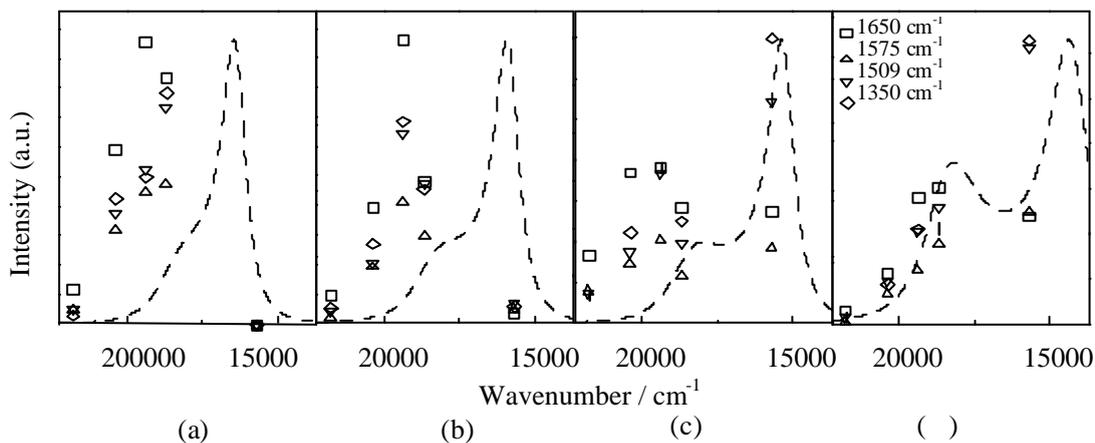


Fig. 3. Calculated (solid lines) and experimental (makers) excitation profiles of SERRS. The Ag nano-aggregates corresponding to (a), (b), (c), and (d) are the same as those corresponding to (1), (2), (3), (4) in Fig. 2, respectively. Open circles, triangles, and squares represent peak intensities of SERRS bands at 1650, 1575, and 1509  $\text{cm}^{-1}$ , respectively.

In conclusion, under the single nano-aggregate measurement conditions, we can investigate the SERRS anisotropy and the excitation profiles induced by the dipolar SPR band. It has been found that these results clearly reflect the contribution from EM enhancement. We expect that an application of a tunable laser to this method enable us directly to evaluate the amplified EM near-field at SERRS active area. Our experimental method will contribute to the optimization of SERRS active substrates and the selection of suitable excitation laser wavelength and polarization.

#### References:

1. K. Kneipp, Y. Wang, H. Kneipp, I. Itzkan, R.R. Dasari, and M.S. Feld, *Phys. Rev. Lett.* **78**, 1667 (1997).
2. S. Nie and S.R. Emory, *Science* **275**, 1102 (1997).
3. A. M. Michaels, M. Nirmal, and L. E. Brus, *J. Am. Chem. Soc.* **121**, 9932 (1999).
4. M. Futamata, Y. Maruyama, and M. Ishikawa, *Vib. Spectrosc.* **30**, 1714 (2002)., Y. Maruyama, M. Ishikawa, and M. Futamata, *J. Phys. Chem. B.* **108**, 673 (2004).
5. T. Itoh, K. Hashimoto, and Y. Ozaki, *Appl. Phys. Lett.*, **83**, 2274 (2003). T. Itoh, K. Hashimoto, A. Ikehata, and Y. Ozaki, *Appl. Phys. Lett.*, **83**, 5557 (2003). T. Itoh, K. Hashimoto, A. Ikehata, and Y. Ozaki, *Chem. Phys. Lett.* **38**, 225 (2004).