SURFACE ENHANCED RESONANCE RAMAN SCATTERING AND LOCALIZED SURFACE PLASMON OF TETRAPHENYLPORPHYNE ADSORBED ON SINGLE SILVER NANO-AGGREGATES

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Abstract: We have been investigating the relation between surface plasmon resonance and surface enhanced resonance Raman scattering (SERRS) of adsorbed molecules to explore the mechanism of SERRS. Using the most appropriate optical conditions, we measured SERRS of a model compound of heme proteins with the extremely low concentrations and discussed newly found results

• Introduction • Surface-enhanced resonance Raman scattering (SERRS) has been expected for application of a single molecule detection or high-sensitive detection of biomolecules because of the enormous enhancement factor by 10^{10}-10^{14}.We have been investigating the relationship between SERRS and surface plasmon resonance (SPR) to explore the mechanism of SERRS using single nanoparticles spectroscopy under single Ag nano-aggregates/Rhodamine 6G system[1-3]. It has been found that under single Ag nano-aggregates, polarization dependence of SPR is the same as that of SERRS[1] and SERRS excitation profile changes with the SPR peak energy shifts[3]. We have attempted the single biomolecule detection by applying our previous knowledges about SERRS experimental conditions to SERRS measurement of porphyrin. We measured the adsorption and desorption process of TPP molecules at the SERRS active junction under the single Ag nano-aggregates/Tetrapheylporphine (TPP) (Fig. 1) system. The intense blinking was observed on Ag aggregates. It was found that the on-off response of SERRS is sometimes the same as that of the emission and sometimes different from that. This emission is considered to localized surface plasmon (LSP) emission, which is a radiative decay of a SP localized at SERRS active junction excited by electrons tunnelling between metal and adsorbed molecules through the charge transfer state. In our previous studies, it was found that the variations of LSP bands reflect those of the geometry of SERRS active junctions. We report that the relationship between SERRS and LSP under the unstable state such as the intense blinking is observed.

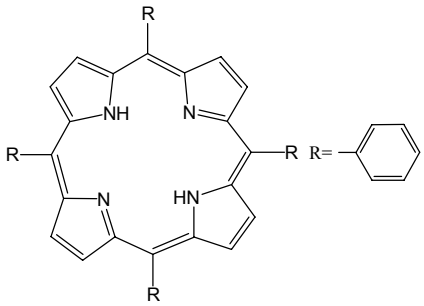

Figure 1. the structure of tetraphenylporphine

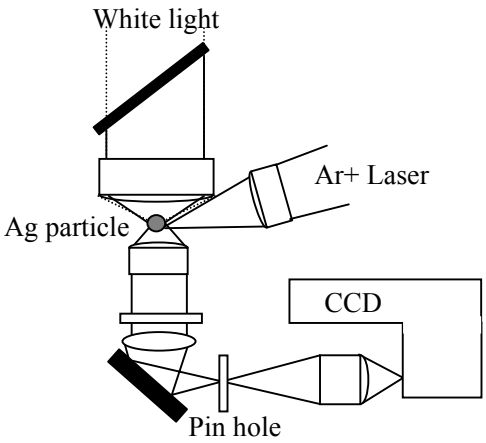

Figure 2 optical system

• Experiment • Figure 2 shows the experimental setup used. Optical images and inelastic scattering were obtained using the white light and the laser with the excitation line of 457 nm, respectively. The mixture of a TPP aqueous solution (3.0×10^{-7} M), NaCl aqueous solution (10 mM) and an Ag colloid solution (1.7×10^{-12} M) was spin-coated onto a glass plate after a 1hour incubation period at room temperature. We measured inelastic scattering from SERRS-active Ag

nano-aggregates selectively on the microscope. LSP and SERRS time-resolved spectra from SERRS-active Ag nano-aggregates were detected.

• Result and Discussion • Figure 3 shows the inelastic scattering spectrum of an aggregate of Ag nanoparticles by the collective Raman measurement. This spectrum consists of three bands due to fluorescence, LSP and SERRS of TPP. The fluorescence band is almost the same as that of TPP aqueous solution. This LSP band from 510 to 620 nm has a complicated shape because the different energy emissions from many SERRS active junctions are accumulated. However, single nano-aggregate has only several hotspots and the LSP band should correspond to a dipolar oscillation mode unlike collective measurement. Such LSP band was observed by single nano-aggregates

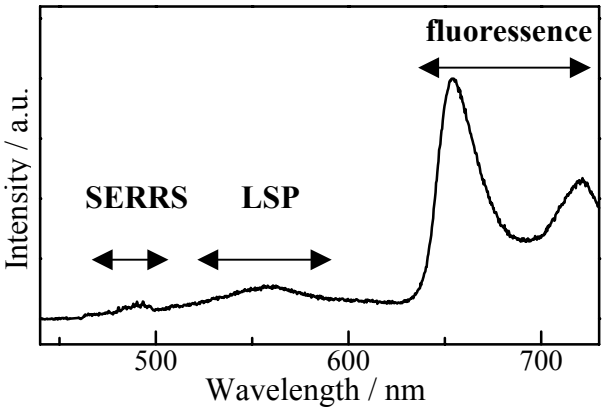

Figure.3 the inelastic scattering from an Ag micro-aggregate was assigned to fluoressence (650-740 nm), LSP(550-650 nm) and SERRS(460-500 nm) band

measurement. The peak energy of LSP bands of single nano-aggregates was almost the same as that of R6G molecules adsorbed on them. This suggests that the variety of SERRS active nano-structures do not depend on the variety of molecules.

Figure 4 shows ten inelastic scattering spectra of single Ag nano-aggregates measured every 5 sec. These spectra include SERRS bands from 460 to 500 nm and LSP bands at 570 nm. As shown in Fig. 4(b) SERRS bands are observed at the same time as LSP bands. On the other hand, in Fig.4 (a), SERRS bands are observed even after the disappearance of LSP bands. This result may be the directly demonstration of the process that TPP molecules adsorb on or desorb from the metal. These temporal profiles of SERRS and emission spectra shows that SERRS active nano-structure would have two types at least, such as only SERRS occurs or SERRS and LSP emission occur. These results also indicate that SERRS and LSR occur independently.

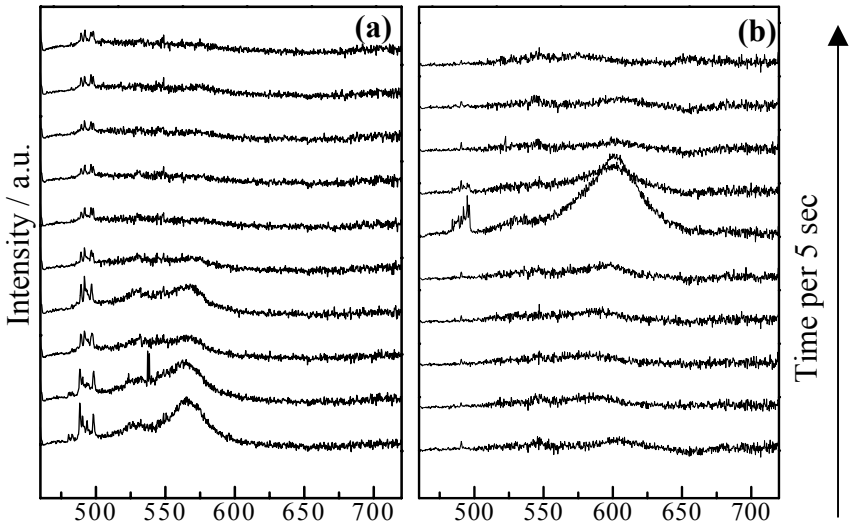

Figure.4 SERRS 460 to 500 nm and LSP(600 nm) spectra per 5sec

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