Time-resolved Surface-enhanced Resonance Raman Scattering Spectra of Thiacyanine Molecules in Water

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We observed change of surface-enhanced resonance Raman scattering (SERRS) spectra of thiacyanine molecules adsorbed on a single Ag nano-aggregate. In water, the SERRS spectrum with background emission changes to temporally-fluctuated spectra without background emission. It seems that the change coincides with dissolution of thiacyanine J-aggregate into the monomers or the dimers.

In surface-enhanced resonance Raman scattering (SERRS) spectroscopy, the spectra of individual molecules adsorbed on noble metal nano-aggregates can be measured by resonance Raman effect and enormous enhanced electromagnetic fields at inter-particle junctions.[1] The structural conversion of single green fluorescent protein due to protonation has been detected by the corresponding vibrational fingerprints.[2] Furthermore, antitumoral drug hypericin shows different SERRS spectra at various pH, which affects the tautomerization, the orientation on the surface, and the aggregation.[3] However, SERRS has not yet detected ionic dyes forming J-aggregates or vise versa.

J-aggregates, which are characterized by a sharp red-shifted absorption band (J-band) from the monomer band, consist of at least several tens of ionic dye molecules that align as staircase or brickwork.[4] However, the formation or decomposition process are still unclear, because their apparent absorption cross-sections per molecule depend on the size of the J-aggregate,[5] and only an ensemble of various sized J-aggregates has been measured by conventional spectroscopy such as time-resolved absorption spectra.[6] Thus, we need to explore the formation or decomposition of J-aggregate one by one using spectroscopy at the single molecule level. Fluorescence spectroscopy for individually-trapped J-aggregate in solution has already been implemented,[7] but precise formation or decomposition of J-aggregates can not be measured owing to diffusion. On the other hand, surfaces of noble metal nanoparticles adsorb J-aggregates.[8] Thus, there is a possibility that J-aggregation or vise versa can be detected by time-resolved SERRS spectra at the single molecule level.

In this study, change of SERRS spectra of 5,5′-dichloro-3,3′-disulfopropyl thiacyanine (TC) molecules at a liquid–solid interface was observed. TC forms J-aggregates (the J-band appears at 464 nm) in an electrolyte and concentrated solution, but exists as the monomers and dimers (the absorption bands appear at 430 and 408 nm, respectively) in a diluted aqueous solution.[9] We measured SERRS spectra of TC J-aggregates adsorbed on a single Ag nanoaggregate in a 1 M NaCl aqueous solution and in water by using an excitation wavelength of 458 nm and our home-built Raman setup.[10] The samples were prepared by adding the mixture of a 0.5 μM TC and 5 mM NaCl aqueous solution to an Ag colloidal solution.

Figure 1a shows typical time-resolved SERRS spectra of TC adsorbed on a single Ag nanoaggregate in a 1 M NaCl aqueous solution. Peak frequencies in the SERRS spectra are almost the same as those in a conventional Raman spectrum of the J-aggregates.[11] The background emission disappeared at low concentration of TC (0.5 nM) or using the longer excitation wavelength (514 nm) than the J-band (464 nm).[11] The maximum and the bandwidth are always almost the same as those of fluorescence of the J-aggregates.[9] Thus, the SERRS spectra may be attributed to the J-aggregates. The peaks and the background emission decreased with time without significant band shifts and then vanished. Thus, any products due to thermal or photodegradation of TC were not observed using SERRS under the present low power laser irradiation (≈0.2 kW/cm^2).

Figure 1b displays typical time-resolved SERRS spectra of TC adsorbed on a single Ag nanoaggregate in water. The initial SERRS spectrum was close to the SERRS spectra in the NaCl aqueous solution (Figure 1a) and the conventional Raman spectrum of the J-aggregates in terms of peak positions. Then, it changed to temporally-fluctuated SERRS spectra without background emission (fluorescence of the J-aggregates). They are similar to those from 0.5 μM 3,3′-disulfopropylthiacyanine aqueous solution or a 0.5 nM TC aqueous solution, in which only the monomers and the dimers exist.[11] In the SERRS spectra at later times (upper spectra in Figure 1b), no peaks were observed in the 1000–400 cm^{-1} region, in which the out-of-plane vibrational modes will be observed.[12] Intensities of these modes are enhanced by resonance Raman effect through the formation of J-aggregates.[12] Thus, lack of the background emission and SERRS peaks in the 1000–400 cm^{-1} region mean the absence of TC J-aggregates on the Ag nanoaggregate. Note that the experimental conditions of Figure 1a, in which peaks due to photo-degradation did not appear, and those of Figure 1b were the same except for the surrounding liquid (NaCl aqueous solution and water, respectively). Thus, the SERRS spectra measured at later times (upper spectra in Figure 1b) may not be attributed to degradation. The change of the SERRS spectra of TC molecules in water coincides with the dissolution of the J-aggregates in surrounding water.

In water, intensities of the SERRS spectra at later times were similar to that of the initial SERRS spectrum (Figure 1b), although the number of TC molecules adsorbed on an Ag nano-aggregate in water decreases due to the dissolution. From this observation, we assume that the SERRS spectra are generated from a limited number of TC molecules adsorbed on the Ag nano-aggregate. Each SERRS-active junction of Ag nano-parti-

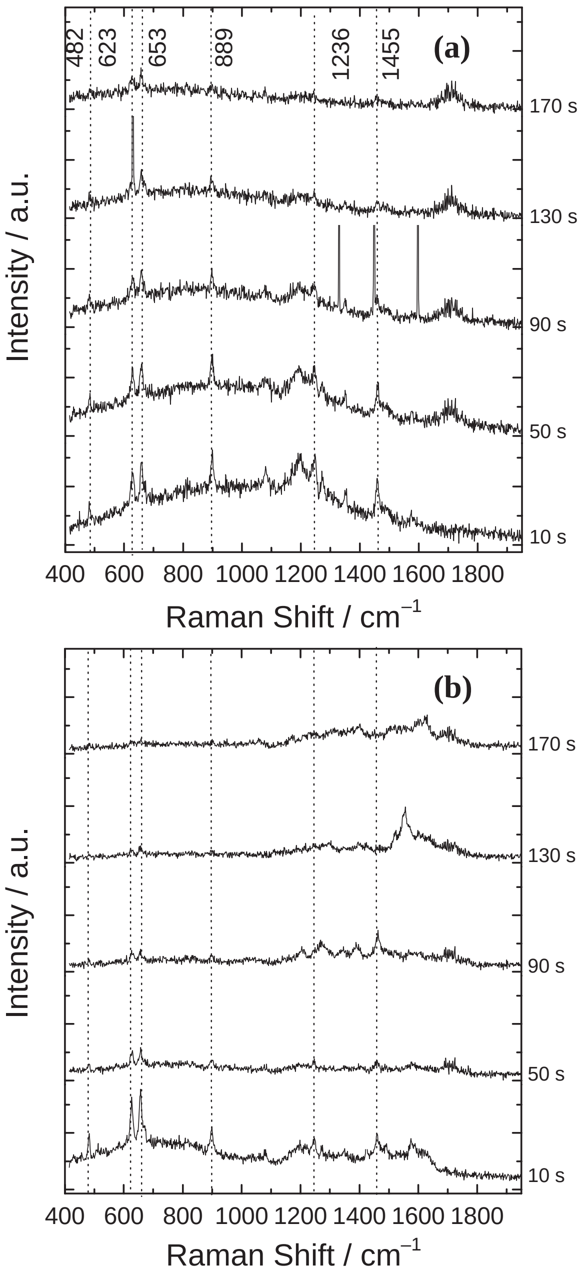

Figure 1. The 458 nm excited time-resolved SERRS spectra of thiacyanine molecules adsorbed on a single Ag nano-aggregate (a) in a 1 M NaCl aqueous solution and (b) in water. The samples were prepared by adding the mixture of a 0.5 μM thiacyanine and 5 mM NaCl aqueous solution to an Ag colloidal solution. Ten seconds integration time per a spectrum. The broad peaks at 1700 cm^{-1} are attributed to artificial noise.

cles is too small to adsorb many molecules and J-aggregates. As shown in upper spectra in Figure 1b, a blinking of SERRS was observed. This means that a few molecules were measured by SERRS. Thus, a few J-aggregate, which consist of at least several tens dye molecules, can be observed at SERRS-active junction in a single Ag nanoaggregate in water.

In a NaCl solution, the intensity of the SERRS spectrum gradually decreased and became zero (Figure 1a). We consider two possible reasons for the decrease in the SERRS intensity. One may be defection of adsorbate from SERRS-active junctions. Monomers or dimers of TC do not defect from J-aggregate adsorbed on an Ag nanoaggregate in a NaCl solution, because the remaining monomers and dimers on a single Ag nanoaggregate were not observed in the NaCl solution. Another reason for the decrease in the SERRS intensity may be a change in the roughness of an Ag nanoaggregate. If an interparticle junction melts and fades away, SERRS intensity at the junction gradually decreases as a result of a gradual decrease in the enhanced electromagnetic field.[13] In this paper, we cannot decide which is the reason of the gradual decrease.

In conclusion, a drastic change of the SERRS peaks of TC molecules adsorbed on a single Ag nanoaggregate in water was observed. We consider that the spectral change coincides with the dissolution of TC J-aggregate into the monomers and the dimers. Thus, SERRS may be applied to explore the formation and decomposition of individual J-aggregate.

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References

1 a) *Surface-Enhanced Raman Scatering–Physics and Applications*, ed. by K. Kneipp, M. Moskovits, H. Kneipp, Springer, Heidelberg and Berlin, **2006**. b) *Surface-Enhanced Vibrational Spectroscopy*, R. Aroca, John Wiley & Sons Ltd., Chichester, **2006**.
2 S. Habuchi, M. Cotlet, R. Grounheid, G. Dirix, J. Michiels, J. Vanderleyden, F. C. De Schryver, J. Hofkens, *J. Am. Chem. Soc.* **2003**, *125*, 8446.
3 G. Lajos, D. Jancura, P. Miskovsky, J. V. García-Ramos, S. Sanchez-Cortes, *J. Phys. Chem. C* **2008**, *112*, 12974.
4 *J-aggregates*, ed. by T. Kobayashi, World Scientific, Singapore, **1996**.
5 R. Weigand, F. Rotermund, A. Penzkofer, *J. Phys. Chem. A* **1997**, *101*, 7729.
6 a) R. F. Pasternack, C. Fleming, S. Herring, P. J. Collings, J. dePaula, G. Decastro, E. J. Gibbs, *Biophys. J.* **2000**, *79*, 550. b) Y. Kitahama, K. Takazawa, *Bull. Chem. Soc. Jpn.* **2008**, *81*, 1282.
7 Y. Tanaka, H. Yoshikawa, H. Masuhara, *J. Phys. Chem. B* **2006**, *110*, 17906.
8 a) G. P. Wiederrecht, G. A. Wurtz, J. Hranisavljevic, *Nano Lett.* **2004**, *4*, 2121. b) T. Uwada, R. Toyata, H. Masuhara, T. Asahi, *J. Phys. Chem. C* **2007**, *111*, 1549. c) I. S. Lim, F. Goroleski, D. Mott, N. Kariuki, W. Ip, J. Luo, C.-J. Zhong, *J. Phys. Chem. B* **2006**, *110*, 6673.
9 H. Yao, S. Kitamura, K. Kimura, *Phys. Chem. Chem. Phys.* **2001**, *3*, 4560.
10 T. Itoh, K. Hashimoto, Y. Ozaki, *Appl. Phys. Lett.* **2003**, *83*, 2274.
11 Y. Kitahama, Y. Tanaka, T. Itoh, M. Ishikawa, Y. Ozaki, unpublished data.
12 D. L. Akins, *J. Phys. Chem.* **1986**, *90*, 1530.
13 F. J. García-Vidal, J. B. Pendry, *Phys. Rev. Lett.* **1996**, *77*, 1163.