

## Direct Evidence of Chemical Contribution to Surface-enhanced Hyper-Raman Scattering

Almar Palonpon<sup>1</sup>, Taro Ichimura<sup>1,2</sup>, Prabhat Verma<sup>1,2,3</sup>, Yasushi Inouye<sup>1,2,3\*</sup>, and Satoshi Kawata<sup>1,2,4</sup><sup>1</sup>Department of Applied Physics, Osaka University, Suita, Osaka 565-0871, Japan<sup>2</sup>CREST, Japan Science and Technology Agency (JST), Kawaguchi, Saitama 322-0012, Japan<sup>3</sup>Graduate School of Frontier Biosciences, Osaka University, Suita, Osaka 565-0871, Japan<sup>4</sup>RIKEN, Wako, Saitama 351-0198, Japan

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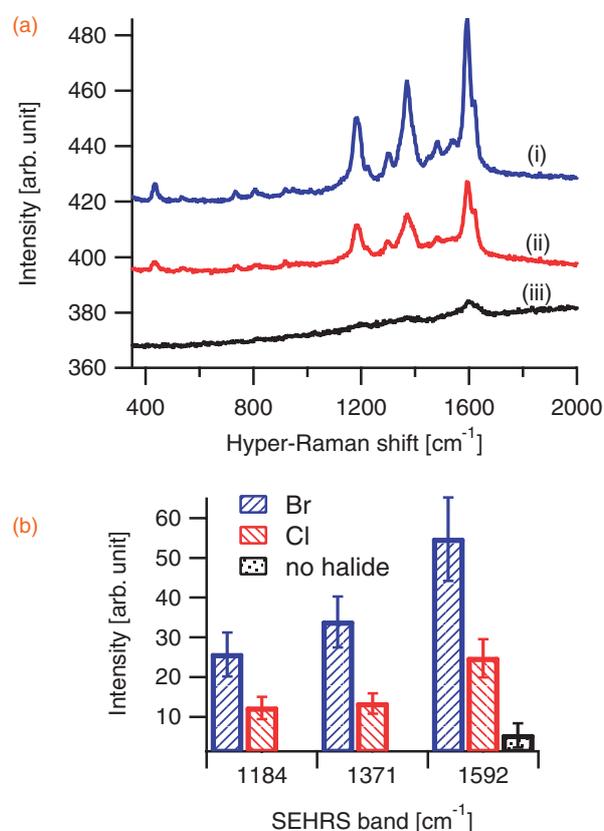
We report on halide-ion-assisted chemical effect in surface-enhanced hyper-Raman scattering of crystal violet (CV) adsorbed on single silver aggregate. A dramatic increase in spectral intensity was observed in the presence of halide ions as compared to their absence. By measuring the hyper-Rayleigh scattering from single aggregate treated with and without halide ions, we established that it was chemical effect, rather than electromagnetic effect that was responsible for this strong enhancement. We attribute the enhancement to a charge transfer mechanism between CV and metal surface mediated by the halide ions similar to surface-enhanced Raman scattering.

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**H**yper-Raman scattering (HRS) is a nonlinear Raman effect in which the scattered light frequency is shifted relative to the second harmonic frequency of the incident light. An HRS spectrum contains rich molecular vibrational information that complements conventional vibrational spectroscopies such as IR absorption and Raman scattering.<sup>1)</sup> Because of the extremely small scattering cross section of HRS, it is often difficult to observe weak HRS modes in experiments. One technique to boost the HRS signal is to use the enhancement of scattering at the surface of metallic nanostructures,<sup>2–5)</sup> a technique known as surface-enhanced hyper-Raman scattering (SEHRS). The studies related to the enhancement in SEHRS have mainly been focused on the electromagnetic (EM) effect,<sup>6–10)</sup> while the nature and the amount of contribution of the chemical effect is not very clear so far. In this study, we report the first direct evidence of chemical enhancement effect in SEHRS of crystal violet (CV) adsorbed on silver (Ag) aggregate. Our approach involves observing the effect of bromide ( $\text{Br}^-$ ) and chloride ( $\text{Cl}^-$ ) ions on SEHRS enhancement, while making sure that the EM contribution remains unchanged by using single isolated Ag aggregate of similar size and shape. This approach allowed us to observe the spectral changes primarily brought about by the chemical effect.

The Ag colloid nanoparticles (~65 nm diameter) were prepared by chemical reduction of silver nitrate.<sup>11)</sup> Aqueous solutions of CV and halide salt (NaCl or NaBr) were added to 2 ml Ag colloid solution and allowed to mix for 5 min at room temperature. The final concentration of CV in all samples was  $10^{-6}$  mol/l, while the concentrations of the halide used in this study varied as indicated in the figures. To prepare the SEHRS sample, a drop from this mixture was cast onto a cleaned glass coverslip and allowed to dry in air. This produced spatially isolated Ag aggregates, with some variation in shape and size, immobilized on the coverslip. In order to keep the EM contribution fixed for all experiments, we carefully selected single isolated Ag aggregates of similar size and shape (~1  $\mu\text{m}$  in diameter) in every SEHRS experiments, because the EM contribution depends primarily on the size and the shape of the aggregate. All the chemicals were purchased from Sigma-Aldrich and used without further purification. The experimental setup used a



**Fig. 1.** (a) Average SEHRS spectra of CV in the presence of (i) 1 mmol/l  $\text{Br}^-$ , (ii) 1 mmol/l  $\text{Cl}^-$ , and (iii) absence of halide ions. Average laser power at the sample position was 400  $\mu\text{W}$ . Acquisition time of each spectrum was 1 min. Spectra are vertically offset for better viewing. The SEHRS spectra were obtained from 20 single Ag aggregates in each sample. (b) Bar graphs show the three strongest SEHRS band of CV. Error bars indicate one standard deviation.

mode-locked Ti:sapphire laser (860 nm, 80 MHz, 5 ps) for excitation and a confocal Raman microscope coupled to a spectrograph equipped with a charge-coupled device (CCD) detector.

Figure 1 compares the SEHRS spectra (averaged from independent observations of 20 single isolated Ag aggregates of similar size and shape) of CV in the presence and absence of halide ions. Strong hyper-Raman modes observed in Fig. 1(a) at 1184, 1371, and 1592  $\text{cm}^{-1}$  are assigned to the

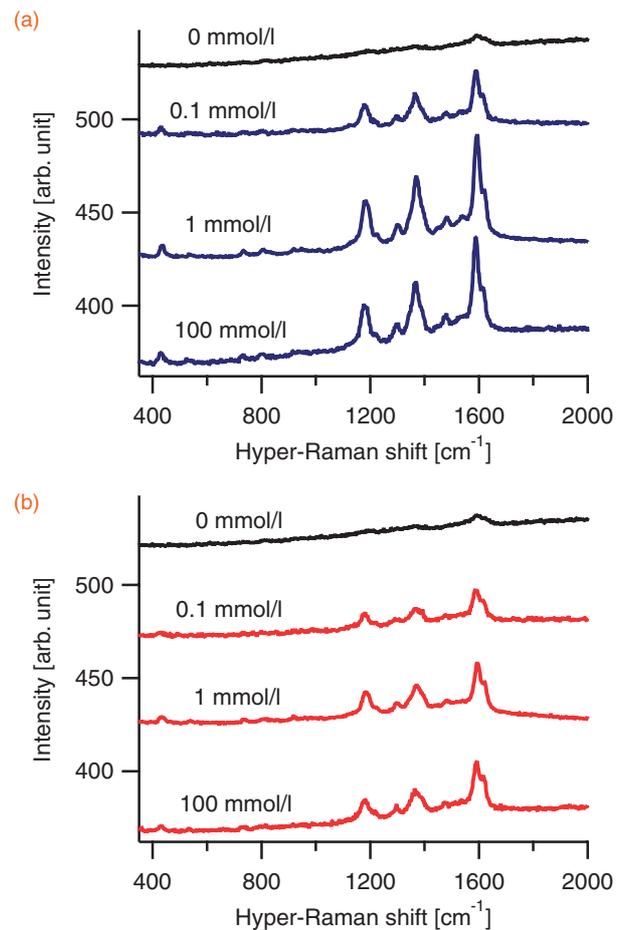
\*E-mail address: ya-inoue@ap.eng.osaka-u.ac.jp

$\nu_9$  CH in-plane bending,  $\nu(\varphi - N)$  stretching and  $\nu_8$  ring stretching vibrational modes of CV, respectively.<sup>12)</sup> In the absence of halide ions, the hyper-Raman active modes of CV could hardly be observed. However, in the presence of halide ions, the intensity of the hyper-Raman modes increased dramatically with several small peaks becoming discernible. The influence of the halide ions on the SEHRS spectra was statistically significant and had good reproducibility as evident from the bar graph in Fig. 1(b). The error bar which indicates one standard deviation was computed from the 20 single isolated Ag aggregates. A comparison between the two halide ions shows  $\text{Br}^-$  ion is more effective in increasing the SEHRS intensity than  $\text{Cl}^-$  ion.

The dramatic increase in SEHRS intensity in the presence of halide ions than in their absence demonstrates the existence and contribution of halide-ion-assisted chemical effect in SEHRS. Surface-enhanced Raman scattering (SERS), which is a linear Raman process and hence has relatively higher scattering efficiency, has also shown the effect of halide ions on enhancement.<sup>13,14)</sup> Similar to SERS, the chemical enhancement effect in SEHRS can be attributed to a charge transfer process between the metal and the adsorbed molecule occupying specific surface active sites at the metal surface.<sup>15)</sup> The halide ions assist in this chemical enhancement by improving the interaction between metal surface and molecule adsorbed at the active sites. There is a possibility that the presence of halide ions may increase the amount of adsorbed CV molecules on the silver aggregate, resulting in increased SEHRS signals. Nevertheless, by measuring the optical absorption and fluorescence spectra of CV molecules in our samples, we confirmed that the increase of adsorbed CV molecules due to the presence of halide ions was small and could not account for the large enhancement in SEHRS intensity. There could be a slight contribution from the increased adsorbed molecules, however, the enhancement in SEHRS intensity should primarily be ascribed to the chemical effect. It must be pointed out here that even in the absence of halide ions, there is still a chemical effect because CV can still adsorb on Ag, albeit a weak one. However, the presence of halide ions creates more chemically active sites in the Ag surface, resulting in a stronger chemical effect. The stronger enhancement observed with  $\text{Br}^-$  ions than with  $\text{Cl}^-$  ions shows the dependence of the chemical effect in SEHRS to the type of halide ion. The  $\text{Br}^-$  ions probably induce more SEHRS-active sites than the  $\text{Cl}^-$  ions on the Ag surface. This explanation is supported by a previous study that showed  $\text{Br}^-$  has a stronger interaction strength (affinity) to Ag surface than  $\text{Cl}^-$  ion.<sup>16)</sup>

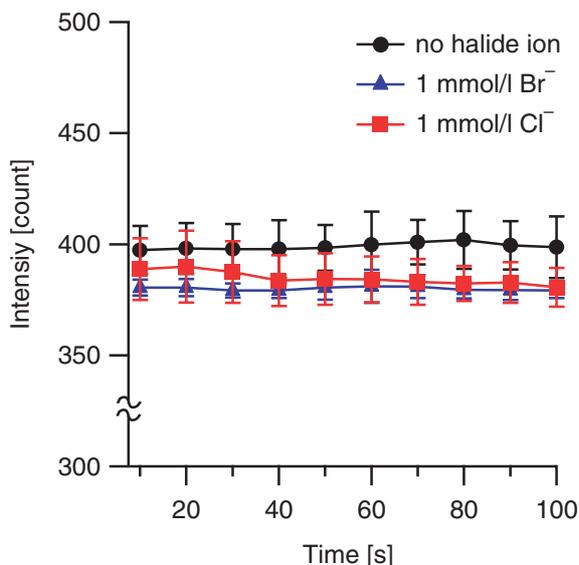
Another strong evidence of the halide-ion-assisted chemical enhancement of CV is the dependence of the SEHRS spectra on halide ion concentration (Fig. 2). The strongest SEHRS intensity was obtained at 1 mmol/l concentration for both  $\text{Br}^-$  and  $\text{Cl}^-$  ions. Even at 0.1 mmol/l, the SEHRS spectra increased which show that it requires only a small amount of halide ions to activate the chemical effect in SEHRS. At high ionic concentrations (100 mmol/l), the SEHRS intensity was comparable to the one at 1 mmol/l concentration which suggests saturation of SEHRS intensity.

Here, we established our approach to distinctly observe the chemical effect from the EM effect. This approach is based on the premise that the EM enhancement effect in a



**Fig. 2.** SEHRS spectra of CV on Ag colloid aggregate at different concentrations of (a)  $\text{Br}^-$  and (b)  $\text{Cl}^-$  ions. Average laser power at the sample position was  $400 \mu\text{W}$ . Acquisition time of each spectrum was 1 min. Spectra are vertically offset for better viewing.

single Ag aggregate is not significantly altered by addition of halide ions. Hence any spectral changes observed between single Ag aggregates treated with and without halide ions should primarily be due to a chemical effect. We have confirmed this premise using hyper-Rayleigh scattering,<sup>17)</sup> which is a very sensitive reporter of nanoparticle aggregation state and hence it is a good measure of the EM enhancement properties of the aggregate. If the EM contribution of a single aggregate increases with addition of halide ions, we should also observe a visible increase in the hyper-Rayleigh intensity between aggregates treated with and without halide ions. However, Fig. 3 shows the contrary, as the hyper-Rayleigh intensity in the presence of halide ions is slightly lower than in the absence of halide ions. This result shows that the hyper-Rayleigh intensity did not increase in the presence of halide ions, which means the presence of halide ions did not contribute to EM enhancement. The slight decrease in intensity could be because the halide ions may block some part of the excitation and scattered light. Additionally, the hyper-Rayleigh intensity did not show any significant variation with time, which confirms that the laser excitation in our experiment was low enough to prevent any laser-induced structural changes in the aggregate. We did not use CV in this experiment because CV possesses a large hyperpolarizability that can mask the true hyper-Rayleigh signal produced by the Ag aggregate.



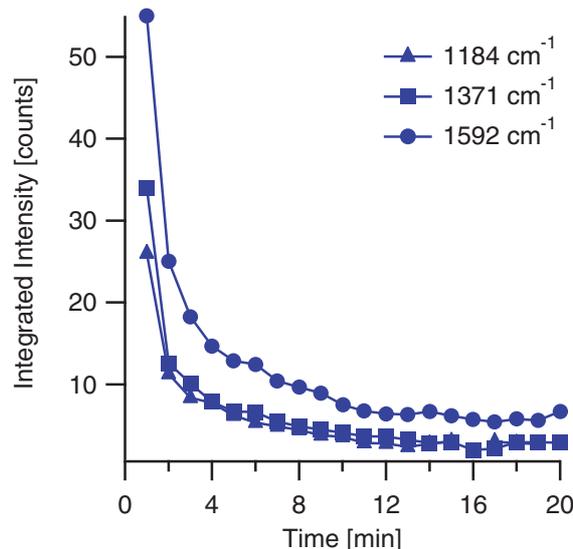
**Fig. 3.** Temporal variation of the hyper-Rayleigh intensity from the Ag colloid aggregate in the presence and absence of the halide ions. Error bars indicate one standard deviation. Acquisition time of each hyper-Rayleigh spectrum was 10 s. Laser power density was the same as in the SEHRS experiment.

Although adsorption of CV on the Ag surface could possibly shift the plasmon resonance of the aggregate, we have confirmed, by observing the surface plasmon absorption, that this effect was negligible in our experiment.

The findings in the hyper-Rayleigh scattering experiment indicate that the immobilized single Ag aggregate does not undergo significant structural changes after addition of halide ions that could bring about any increase in the EM enhancement effect. The effect of the presence of halide ions is therefore believed to be primarily due to atomic-scale changes on the aggregate surface, which might change the chemical properties, and not large-scale changes that would change the EM characteristics of the aggregate.

We also investigated the stability of the SEHRS spectra under prolonged near infrared laser irradiation. Figure 4 shows the time dependence of the three strong hyper-Raman bands of CV in the presence of  $\text{Br}^-$  ions. All the hyper-Raman peak intensities were found to decay, which indicates that the chemical effects are degraded while EM effects are relatively unchanged as established by the hyper-Rayleigh scattering experiment (Fig. 3). A similar decay behavior was also observed for  $\text{Cl}^-$  ions (data not shown). This decay is likely due to the photochemical degradation of CV or CV-halide-Ag complex caused by the two-photon excitation. It becomes clear from Fig. 4 that one must consider a very short exposure time to study the chemical effect in SEHRS.

In summary, we demonstrated for the first time the existence and contribution of halide-ion-assisted chemical effect in SEHRS of CV adsorbed on Ag colloid aggregate, by comparing the SEHRS spectra in the presence and absence of halide ions. The halide ions induced a dramatic increase in SEHRS intensity which can be attributed to a charge transfer mechanism between CV and Ag in complex with the halide ions at surface active sites in the Ag surface. We showed by hyper-Rayleigh measurements that the EM properties of the Ag aggregates treated with and without



**Fig. 4.** Time decay of the SEHRS bands of CV in the presence of 1 mmol/l  $\text{Br}^-$  ions. The solid lines are used only for observing the trend. Average laser power at the sample position was  $400\ \mu\text{W}$ . Acquisition time of each spectrum was 1 min.

halide ions do not change. Hence, this result supported our conclusion that the observed increase in SEHRS intensity is primarily due to a chemical effect. This chemical effect was found to be dependent on the type and concentration of halide ion. This study revealed the important role of halide ions to the chemical enhancement of hyper-Raman scattering opening the doors for the development of SEHRS as a useful spectroscopic tool.

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- 1) L. D. Ziegler: *J. Raman Spectrosc.* **21** (1990) 769.
- 2) C. K. Johnson and S. A. Soper: *J. Phys. Chem.* **93** (1989) 7281.
- 3) L. A. Lipscomb, S. Nie, S. Feng, and N. T. Yu: *Chem. Phys. Lett.* **170** (1990) 457.
- 4) S. Nie, L. A. Lipscomb, S. Feng, and N. T. Yu: *Chem. Phys. Lett.* **167** (1990) 35.
- 5) H. Kneipp and K. Kneipp: *J. Raman Spectrosc.* **36** (2005) 551.
- 6) A. A. Leng, S. Yasserli, S. Sharma, Z. Li, H. Y. Woo, D. Vak, G. C. Bazan, and A. M. Kelley: *Anal. Chem.* **78** (2006) 6279.
- 7) C. Hulthen, M. A. Young, and R. P. Van Duyne: *Langmuir* **22** (2006) 10354.
- 8) X.-Y. Li, Q.-J. Huang, V. I. Petrove, Y.-T. Xie, Q. Luo, X. Yu, and Y. Yan: *J. Raman Spectrosc.* **36** (2005) 555.
- 9) K. Ikeda, M. Takase, Y. Sawai, H. Nabika, K. Murakoshi, and K. Uosaki: *J. Chem. Phys.* **127** (2007) 111103.
- 10) T. Itoh, H. Yoshikawa, T. Ihama, and H. Masuhara: *Appl. Phys. Lett.* **88** (2006) 084102.
- 11) P. C. Lee and D. Meisel: *J. Phys. Chem.* **86** (1982) 3391.
- 12) L. Angeloni, G. Smulevich, and M. P. Marzocchi: *J. Raman Spectrosc.* **8** (1979) 305.
- 13) M. Futamata and Y. Maruyama: *Anal. Bioanal. Chem.* **388** (2007) 89.
- 14) E. J. Liang, X. L. Ye, and W. Kiefer: *J. Phys. Chem. A* **101** (1997) 7330.
- 15) A. Otto, I. Mrozek, H. Grabhorn, and W. Akeman: *J. Phys.: Condens. Matter* **4** (1992) 1143.
- 16) E. J. Liang, X. L. Ye, and W. Kiefer: *Vibrational Spectrosc.* **15** (1997) 69.
- 17) F. W. Vance, B. I. Lemon, and J. T. Hupp: *J. Phys. Chem. B* **102** (1998) 10091.