

Halide-ion-assisted increase of surface-enhanced hyper-Raman scattering: a clear observation of the chemical effect

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We show that the increase of surface-enhanced hyper-Raman scattering (SEHRS) intensity of organic dye molecules adsorbed on single silver (Ag) colloid aggregate in the presence of halide ions is a direct evidence of the chemical effect in the enhancement mechanism. Time-dependent SEHRS measurements before and after adding halide ions enabled us to distinctly observe the chemical effect. The presence of the halide ions results to a more stable chemical interaction between metal and dye molecule, making it more resistant against photodegradation effects. This study can contribute in elucidating the chemical effect mechanism and aid in the development of SEHRS as a useful spectroscopic tool. Copyright © 2008 John Wiley & Sons, Ltd.

Keywords: surface-enhanced hyper-Raman scattering; chemical effect; halide ions

Introduction

Hyper-Raman scattering (HRS) is a nonlinear Raman effect in which the scattered light is Raman-shifted relative to twice the frequency of the incident light. It contains rich molecular vibrational information that complements infrared (IR) absorption and Raman scattering.^[1] The extremely small scattering cross-section of HRS has so far limited its application, indicating the need for a good enhancement technique. One technique to amplify the HRS signal is to use the enhancement effects at the surface of metallic nanostructures,^[2–4] a technique known as surface-enhanced hyper-Raman scattering (SEHRS). In Raman scattering, the enhancement at the surface of a metallic nanostructure is generally believed to have two enhancement mechanisms, namely the electromagnetic (EM) effect and the chemical effect. Studies in SEHRS have mainly been focused on the EM effect,^[5–7] while it is not very clear thus far whether or not chemical effect can make a significant contribution to SEHRS. Recently, we have shown that the increase in SEHRS intensity of crystal violet dye molecules in the presence of halide ions is due mainly to the chemical effect.^[8] In the present study, we extend the investigation of the chemical effect in SEHRS to other dye molecules and clarify the role of halide ions by performing time-dependent SEHRS measurements on a single Ag aggregate adsorbed with the dye molecule before and after adding halide ions.

Experimental

Silver colloid nanospheres (~65 nm diameter) were prepared using the standard citrate reduction method.^[9] The dye molecules examined were malachite green (MG), crystal violet (CV) and rhodamine 6G (R6G). Samples were prepared by incubating Ag colloid solution with aqueous solutions of the dye and halide ions (Br⁻ or Cl⁻) in final concentrations of 10⁻⁶ M and 10⁻³ M,

respectively. A drop (10 µl) from this mixture was cast on a glass substrate and dried in air. The experimental setup used a mode-locked Ti:sapphire laser (884 nm, 80 MHz, 5 ps) for excitation, and a confocal Raman microscope coupled to a spectrograph equipped with a charge-coupled device (CCD) detector. A single isolated aggregate (~1 µm diameter) of Ag colloids incubated with the dye molecules was selected in the illumination focus spot for SEHRS measurement. We took extra care in selecting exactly similar isolated aggregates in every experiment so that the results could be readily compared.

Results and Discussion

Figure 1 shows that the intensity of the hyper-Raman modes of the three dye molecules in the halide-ion-treated aggregates is significantly increased in comparison with the halide-ion-free aggregates. The bar graph in Fig. 1 is plotted from independent observations of 12 single Ag aggregates of similar size and shape under the same experimental conditions to confirm the statistical consistency and reproducibility. In a previous study,^[8] we have established by hyper-Rayleigh scattering that the presence of halide ions does not cause any significant change in the EM

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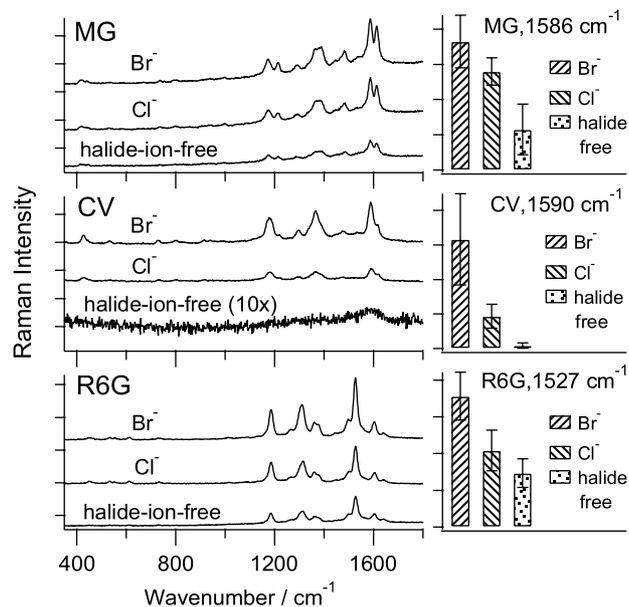


Figure 1. Average SEHRS spectra of three organic dye molecules in the presence and absence of halide ions. Bar graphs show specific SEHRS peak representing one standard deviation. Laser power at the sample was 400 μ W, and the integration time for each spectrum was 60 s. Spectra were offset for viewing.

enhancement, therefore, ruling out the possibility that the increase of SEHRS intensity in the presence of halide ions, observed in Fig. 1, is due to an EM effect. Figure 1 shows different degrees of intensity enhancement among the three dye molecules, with the largest enhancement observed in CV, by about a factor of 10–40, and moderate enhancements in MG and R6G, by about a factor of 2–3. Since the increase in SEHRS intensity might also be due to an increased adsorption of dye molecules induced by the halide ions, we performed fluorescent measurements on the same samples and observed an average increase in fluorescence intensity in the halide-ion-treated aggregates by a factor of 2. Therefore, for MG and R6G, it is difficult to distinguish the enhancement contributions between chemical effect and increased adsorption. However, for CV, the increase in SEHRS intensity is clearly dominated by the chemical effect.

In order to separate the enhancement contribution between chemical effect and increased adsorption for R6G, we performed time-dependent SEHRS measurement before and after adding halide ions. A single Ag aggregate with adsorbed R6G molecules (before this experiment, the aggregates were thoroughly rinsed with water to remove any loosely bounded R6G molecules), was immersed in 200 μ l of water and SEHRS spectra were obtained sequentially with integration time of 10 s. After 30 s, 20 μ l NaBr (or NaCl) solution was added. Figure 2 shows that the SEHRS intensity initially decreased from 10 to 30 s, due mainly to photodegradation of the R6G molecules. However, after adding the halide ions at 30 s, the SEHRS intensity increased at 40 s, achieving a maximum at 50 s, and then decreased gradually at longer times. Noticing that SEHRS intensity first decreased with time and then increased by about a

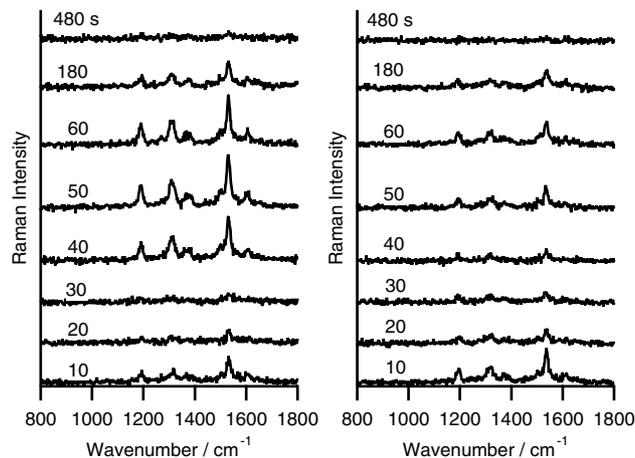


Figure 2. Time-dependent SEHRS spectra obtained from R6G adsorbed on single aggregate. After 30 s, Br⁻ (left) or Cl⁻ (right) ions were added to a final concentration of 10⁻³ M. Laser power was 400 μ W. The integration time for each spectrum was 10 s. Spectra were offset for viewing.

factor of 3–5 after addition of halide ions shows beyond doubt that the main effect of the halide ions in the increased SEHRS intensity is ascribed to a chemical effect. Increased adsorption was not possible in this experiment because the initial number of adsorbed molecules was fixed and the effects of photodegradation actually decreased the possible number of adsorbed molecules that could participate in the enhancement process. The SEHRS signal was stable for a longer time period, between 40 and 180 s, which means that the presence of halide ions results in a more stable chemical interaction between Ag and R6G making it more resistant to photodegradation effects. In comparison, the results for CV and MG did not clearly show the same effect due to the much weaker SEHRS signals. Interestingly, this halide-ion-induced stabilization and enhancement were also observed in a similar time-dependent surface-enhanced Raman scattering (SERS) measurements on R6G-covered Ag nanoparticles^[10] which suggests that the R6G-halide-Ag surface complex, when properly excited, can enhance both SERS and SEHRS intensities.

References

- [1] L. D. Ziegler, *J. Raman Spectrosc.* **1990**, *21*, 769.
- [2] C. K. Johnson, S. A. Soper, *J. Phys. Chem.* **1989**, *93*, 7281.
- [3] S. Nie, L. A. Lipscomb, S. Feng, N. T. Yu, *Chem. Phys. Lett.* **1990**, *167*, 35.
- [4] H. Kneipp, J. Kneipp, *J. Raman Spectrosc.* **2005**, *36*, 551.
- [5] A. A. Leng, S. Yasseri, S. Sharma, Z. Li, H. Y. Woo, D. Vak, G. C. Bazan, A. M. Kelly, *Anal. Chem.* **2006**, *78*, 6279.
- [6] C. Hulthen, M. A. Young, R. P. Van Duyne, *Langmuir* **2006**, *22*, 10354.
- [7] X. Y. Li, Q. J. Huang, V. I. Petrove, Y. T. Xie, Q. Luo, X. Yu, Y. Yan, *J. Raman Spectrosc.* **2005**, *36*, 555.
- [8] A. Palonpon, T. Ichimura, P. Verma, Y. Inouye, S. Kawata, *Appl. Phys. Express* **2008**, *1*, 092401.
- [9] P. C. Lee, D. Meisel, *J. Phys. Chem.* **1982**, *86*, 3391.
- [10] M. Futamata, Y. Maruyama, *Anal. Bioanal. Chem.* **2007**, *388*, 89.