Electronic Supplementary Material (ESI) for Chemical Communications

Supporting information

Enhancement of fluorescence intensity by silicon particles and its size effect

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The fluorescence dye solution of malachite green (MG) was prepared in a similar manner. The concentration of methanol solution of MG was 3.7 x 10^{-5} M. The fluorescence spectrum was measured in a similar manner, i.e. *in situ* photoluminescence microscopy (Horiba Jobin Yvon, HR800) at the excitation wavelength of 632.8 nm with a He-Ne laser. To obtain the spectra with good signal/noise ratio, the laser power, in front of an optical cell, was adjusted to each sample solution, i.e., crystal violet (CV) = 17.6 μW and MG =1.7 μW. The enhancement substrate was immersed in the solution of optical cell and the solution in the cell was sealed by a cover glass. The used enhancement substrate was prepared using the Si submicron particles with the average diameter of 500 nm, giving the largest EF for the case of CV solution. The fluorescence spectra with and without the enhancement substrate were measured and used to estimate the enhancement factor (EF).

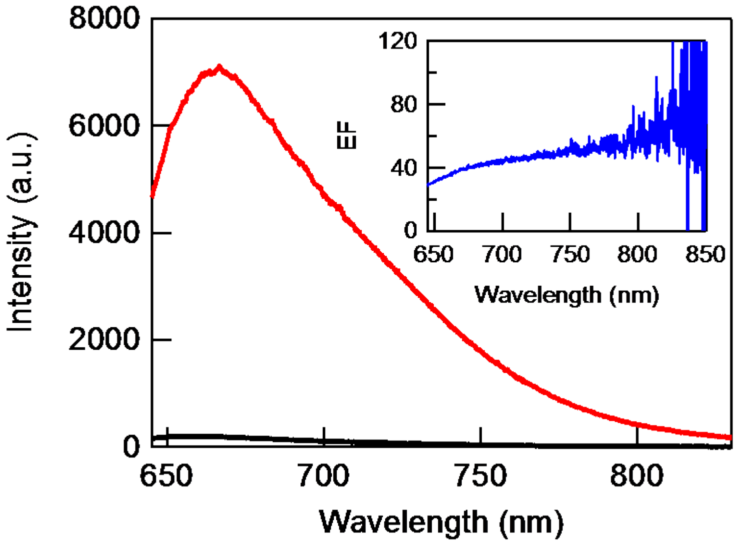

Figure S1. Fluorescence spectrum of the malachite green (MG) solution. The red curve shows the spectrum in the presence of Si nanoparticles, and the black curve shows the spectrum in the absence of Si nanoparticles. The inset is the spectrum of fluorescence enhancement factor (EF) as a function of fluorescence wavelength.

Figure S1 shows the fluorescence spectra of MG solution with the enhancement substrate and with a fluorescence-free quartz plate, which correspond to a sample (red) and a reference (black), respectively. It was revealed that the fluorescence intensity is enhanced by the excitation using the silicon (Si) submicron particle. We obtained the EF by dividing the fluorescence intensity of spectrum in the presence of the enhancement substrate by that in the absence of the substrate. The inset of Fig. S1 shows the enhancement spectrum. The obtained EF of MG is large value (EF_{max} = 60), which is 4 times larger than the EF typically reported using the enhancement substrate made of gold or silver (EF=15).[1] On the other hand, the EF of MG is smaller than that of CV (EF_{max} = 180). The difference of EF between CV and MG will be due to complex processes, e.g., interaction between dye molecule and Si particle, intermolecular interaction between dye and solvent molecules, the perturbation of the near-field to dye molecule, and the dynamics of relaxation processes. According to the recent study on the fluorescence enhancement of silver nanoparticle, it was suggested that the relaxation process of excited molecule affects the enhancement process.[2] Namely, the magnitude of vibrational-relaxation rate in the first electronic excited state against that of irradiative decay rate to the electronic ground state is a key factor for characterizing the enhancement process. Based on this mechanism, the relaxation processes of CV and MB molecules would be differently affected by the near field on the Si submicron particle. In near future, we would investigate the EF by changing various parameters to understand the difference of EF by Si particle.

References

1. C. D. Geddes Editor, Metal-enhanced fluorescence, Wiley, 2010.
2. T. Itoh, Y. S. Yamamoto, H. Tamaru, V. Biju, N. Murase, and Y. Ozaki, Phys. Rev. B, 87, 235408 (2013).