Spectroscopic Properties of Noble Metal Nano-Particles Covered with J-Aggregates of Cyanine Dye

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We have found, for the first time, a unique spectroscopic property of noble metal nano-particles (colloidal silver in solution or noble metal island film) covered with a J-aggregate monolayer. The spectral dip or hole at the position of the J-band was observed in the surface plasmon band. The appearance of the hole was related to the interaction between the surface plasmon of the noble metal nano-particles and the Frenkel exciton of the J-aggregate.

Optics and spectroscopy of molecular aggregates have attracted considerable attention in connection with molecular photonic materials.[1] The J-aggregate of cyanine dyes is a particularly interesting molecular aggregate characterized by an unusual sharp absorption band, resonance fluorescence, ultrashort radiative lifetime and Frenkel exciton.[2] Recently, Kawasaki and co-workers have reported a simple fabrication method of monolayer J-aggregates on the flat halide-covered surface of noble metal.[3] Judging from the spectroscopic and STM (scanning tunneling microscopy) observation, the two dimensional J-aggregates were fabricated uniformly and in good reproducibility on the noble metal surface. This method could also be used to make the J-aggregate monolayer adsorb directly on noble metal nano-particles. In connection with the interests in the surface enhanced optical properties of molecules located near the metal nano-particles,[4–7] we have studied in this work what new spectral features evolve in their absorption spectra when the noble metal nano-particles are covered with a J-aggregate monolayer of cyanine dye.

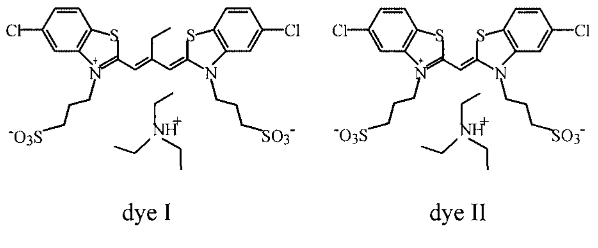

Figure 1. Some cyanine dyes used in this study.

Some cyanine dyes used in this study are shown in Figure 1. As the noble metal nano-particle, we first examined colloidal silver in solution. To make the colloidal silver, 3 cm^3 of $AgNO_3$ aqueous solution (4 mM) (1 M = 1 mol dm^{-3}) was mixed with 12 cm^3 of $NaBH_4$ aqueous solution (8 mM) and the mixture was stirred by a magnetic stirrer for 1 h at room temperature.[8] The absorption spectrum of the resultant solution showed a surface plasmon resonance absorption peak at λ = 385–390 nm, together with its distinct tailing on the longer wavelength side (Figure 2, dashed line). This indicates the formation of small silver particles less than 20–40 nm in diameter that are somewhat aggregated with each other.[9]

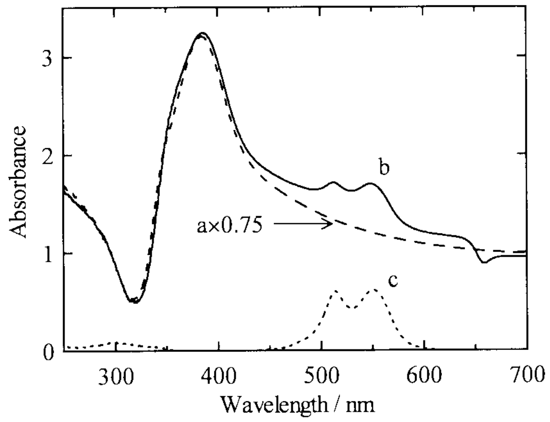

Figure 2. Absorption spectra of colloidal silver before (a) and after (b) dye I adsorption. (a) [Ag]=0.8 mM; (b) [Ag]=0.6 mM, [dye I]=0.01 mM, [NaCl]=1 mM. (c) Absorption spectrum of 0.01 mM dye I solution in the presence of 10 mM NaCl. Note that absorbance of spectrum (a) is reduced by 0.75. Light path length = 1 cm.

The adsorption of dye I (5,5'-dichloro-3,3'-disulfopropyl-9-ethylthiacarbocyanine triethylamine)[10] onto the silver particles was allowed by adding 1 cm^3 of mixed solution containing 0.04 mM dye I and 4 mM NaCl[11] into 3 cm^3 of colloidal silver solution. In a similar manner as in the case of flat silver films,[3] the surface of silver particles is first covered with a pseudo-silver-halide monolayer in the presence of chloride ions, and the cyanine dye forms a J-aggregate monolayer on the thus halogenated silver surface. The resultant colloidal silver solution gave an absorption spectrum as shown by the solid line in Figure 2. In the wavelength range of λ = 300–640 nm, the spectrum is nearly a superposition of the individual spectra of the colloidal silver (dashed line) and the dye I left in the solution as monomer (λ = 550 nm) and dimer (λ = 512 nm). By contrast, we observed an anomalous change of absorption spectrum in the wavelength range of λ = 640–680 nm, where one would generally expect to see the absorption by the adsorbed J-aggregate monolayer. What was actually observed is an anomalous dip or hole at λ = 658 nm in the extended tail of the surface plasmon band. The position of the anomalous hole exactly coincides with that of the dye I J-band, so there is almost no doubt that the unusual spectral phenomenon was caused by the J-aggregate monolayer adsorbed on the silver nano-particles.

Interestingly, when only NaCl was added to the colloidal silver solution prior to the dye adsorption, the extended tailing of the surface plasmon band was removed, which indicates that the previously aggregated silver particles had time to be separated from each other as a result of the surface halogenation.

Subsequent addition of dye I to this better dispersed colloidal silver solution led to the normal (positive) absorption peak by the J-band. In this case, there was no significant overlap between the surface plasmon band and the J-band. These results suggest that the appearance of the anomalous hole at the position of the J-band is due to some unique interaction between the surface plasmon excited in the colloidal silver and the Frenkel exciton in the J-aggregate.

In order to further confirm the appearance of the anomalous spectral feature and clarify the conditions for its appearance, we next employed silver nano-particles deposited on a mica substrate (so-called silver island film). Unlike the colloidal solution studied above, all the dye molecules incorporated in this system in the following manner are in the close vicinity of the silver island. The silver island film was deposited on a freshly cleaved mica by using the DC Ar ion sputtering apparatus.[12] The mica was heated at ~200 °C during 5 min deposition. The apparent thickness of the island film was approximately 20–25 nm. After immersing the silver island film for 5 min in 0.1 mM KBr solution to halogenate the silver surface, the film was immersed in 0.1 mM dye I solution for 5 min.[11] Figure 3 shows the absorption spectra of the silver island film taken before and after dye I adsorption. Before dye I adsorption, the surface plasmon band was observed at λ = 420 nm together with a distinct tailing to the longer wavelength.[13] Adsorption of dye I caused again an anomalous hole at λ = 656 nm, which corresponds to the J-band of dye I. Figure 3 also shows the spectral change caused by the adsorption of another cyanine dye (5,5'-dichloro-3,3'-disulfopropylthiacyanine triethylamine, dye II), which can also form a J-aggregate whose J-band is located at λ = 471 nm. As well as dye I, a distinct hole at the position of the J-band was observed in the surface plasmon band. Thus the anomalous spectral hole seems to be quite a general phenomenon associated with the J-aggregate of cyanine dye in the vicinity of the silver nano-particles.

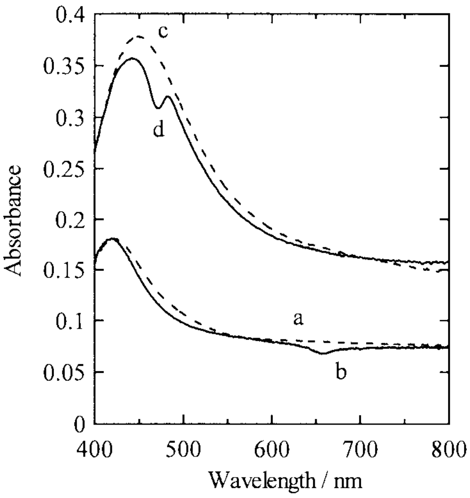

Figure 3. Absorption spectra of silver island films before (dashed line a, c) and after (solid line b, d) adsorption of dye I (b) or dye II (d). Difference between a and c was merely come from the different deposition time.

We have also examined the spectral changes by the adsorption of various other kinds of dyes on silver as well as gold island films.[14] Of these pseudo isocyanine (PIC) that easily forms a J-aggregate gave rise to a spectral hole in the surface plasmon band likewise. However, the hole was never observed for dyes that were adsorbed on the metal particles as monomer or dimer (Rhodamine-B, Rhodamin-6G) or H-aggregate (1,1'-diethyl-2,2'-carbocyanine). There the observed absorption spectra were nearly the superposition of the absorption spectra of the dye and the metal island film. The absorption spectra of gold island films exhibit both a surface plasmon band (λ>500 nm) and an interband transition band (λ<500 nm). The J-aggregates never produced a spectral hole in the region of the interband transition of gold.[15] We therefore conclude that the appearance of the hole at the position of the J-band is due to a characteristic interaction between the surface plasmon of the noble metal nano-particles and the Frenkel exciton of the J-aggregate.

In summary, we have found for the first time a unique spectroscopic property of noble metal nano-particles covered with a J-aggregate monolayer. The spectral hole at the position of the J-band was observed in the surface plasmon band. The appearance of the hole could be related to the interaction between the surface plasmon of the noble metal nano-particles and the Frenkel exciton of the J-aggregate. The simulation of the absorption spectra based on the dipole[16](surface plasmon)–dipole(exciton) interaction model will help us to clarify the origin of the spectral hole, the results of the simulation would be described in detail elsewhere.

References and Notes

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10 The selection of dye I, which has sulfopropyl groups, was very important. For example, the adsorption of cationic cyanine dye (pseudo isocyanine), which consists of only the cationic chromophore, introduced further aggregation and precipitation of colloidal silver. Dye I is adsorbed in the orientation with the cationic chromophore facing the colloidal silver and the sulfopropyl groups being at the outermost surface. The sulfopropyl groups might prevent the colloidal silver from precipitating.
11 The solutions were prepared by use of a mixed water and ethanol solvent of 1:1 volume ratio.
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13 Difference of peak wavelength of surface plasmon band from that of colloidal silver in solution comes from the difference of the particle size, shape and matrix (water or mica/air interface).
14 The preparation method of gold island film covered with dye was almost the same as silver except for immersing KI solution instead of KBr solution for halogenation.
15 On the gold island films, dye II adsorption led to the normal absorption peak by the J-band, although dye I adsorption produced a spectral hole at the position of the J-band.
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