Title	写真の分光増感における超高速過程の研究
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Citation	
Issue Date	2002-03
Type	Thesis or Dissertation
Text version	none
URL	http://hdl.handle.net/10119/2108
Rights	
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Summary of the Doctoral Dissertation. **940005 Ji-Won Oh**

The ultrafast primary process of spectral sensitization in photography is studied by the time-resolved fluorescence decay and fluorescence anisotropy. The fluorescence decay of J-aggregates on AgBr microcrystal surface with a size of 0.2 μm was observed. The decays were obtained in the time resolution of 180fs and analyzed with a one rise and the two decaying exponential components. I could decompose sub-ps and a few ps component, which had not been observed with time-resolution of tens of ps.

Due to the improved time-resolution and time-resolved fluorescence anisotropy measurement, I analyzed the photo-induced electron transfer and excitation energy transfer in the spectral sensitization separately. The fast time component (τ_1) was the main component of electron transfer and slow component (τ_2) was the energy transfer.

The multi component fluorescence decay from J-aggregates on octahedral microcrystal having different dye coverages were observed. The dominant fast component (τ_1 = 0.6~0.8 ps) was observed to show little change in the amplitudes (A_1: 0.7) upon increasing dye coverages. It is attributed to the direct electron transfer of J-aggregates into AgBr. The slow component (τ_2 = 1.9~4.6 ps) and average decay times are increased as dye coverage increases.

The excitation transfer of J-aggregate on AgBr was studied by measuring the time-resolved fluorescence anisotropy, *r(t)*. Two-exponential decay fit of *r(t)* shows a fast component, τ_{A1} about 0.1~0.15 ps. This is close to the ultrafast fluorescence rise components, τ_r about 0.1~0.15 ps. Considering their similarities in time constant, τ_{A1} and τ_r are thought to come from the same origin. The fast anisotropy decay component, τ_{A1}, seems to reflect excitation transfer in a limited area of J-aggregated dyes oriented on {111} of AgBr. It takes place before the direct electron transfer into conduction band of AgBr. The value of slow component, τ_{A2} reflected the exciton migration along long axis of molecular arrays of J-aggregates. The faster τ_{A2} at low coverage (20%) showed that many small J-aggregates with random orientation on AgBr compared to the high coverage (60%).

The time-resolved fluorescence measurements in combination with a quantum yield measurement were applied to J-aggregates adsorbed on cubic and octahedral crystal in gel-dried film and liquid emulsion. It became clear that the τ_1 and τ_2 on octahedral AgBr was faster than that on cubic crystal by 2 or 4 times.

The faster τ_1 on octahedron was explained by the observation that the LUMO level of the J-aggregates on it was higher than that on cube. This result is consistent with the quantum yield (ϕ_r) measurement showing that the ϕ_r on octahedron is greater than that of ϕ_r on cube. The slower τ_2 on cubic AgBr could be explained by the fact the size of J-aggregates on cubic AgBr is bigger than those on octahedron.

The fluorescence decay time of gel-dried films was also shorter than that of liquid emulsions. In the case of cubic AgBr, a clear difference in τ_1 and τ_2 was observed between two types of sample, but no difference was observed in octahedral AgBr. Two possibilities were suggested on this observation. One was that the electron injection on octahedral so optimized close to the barriorless electron transfer in Marcus theory that it was not affected by the phase change of the sample. It is conformed by the fact that τ_1 and τ_2 on octahedral were not changed by the addition of the supersensitizer that enhances electron transfer rate.

The other was based on the experimental observation that interstitial silver ion (Ag_{int}) is generated when the cyanine dyes adsorb to the negatively charged surface caused by the space charge layer in AgBr. Cyanine dyes repel silver ions into cubic AgBr crystal which leads to the generation of Ag_{int}. Therefore, while cubic emulsion was dried into gel-dried film, a band bending is expected to push up potential wall at the surface since Ag_{int} was created and dropped electron injection rate.