Ultrafast Dynamics of Spectral Sensitization

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Abstract

Dynamics of spectral sensitization and supersensitization of the silver bromide microcrystals were studied by the femtosecond fluorescence up-conversion technique with sub-one-hundred femtosecond time resolution. In order to obtain information on electron transfer from the excited dyes to the conduction band of silver bromide, an annihilation-free fluorescence from J-aggregates of cyanine dye adsorbed on silver bromide microcrystals of a different shape (cubic and octahedral) was measured. A very fast fluorescence decay with a component as fast as 400 fs is observed. The average fluorescence decay time is several times longer on cubic grains than that on octahedral grains. Upon addition of a supersensitizer (SS), which is co-adsorbed on the surface of silver bromide grains, the average fluorescence decay became several times faster. Different models of supersensitization were examined and the results were analyzed in the framework of the "hole-trapping" supersensitization model.

Introduction

While the whole scheme of spectral sensitization is known for a long time, the individual processes are not well defined yet. The reason is experimental difficulties in studying highly photosensitive materials and particularly J-aggregates, adsorbed on silver halide surface. It was shown in numerous works, that the fluorescence decay of the excited J-aggregates strongly depends on the excitation intensity [1-3]. The larger aggregate size and longer lifetime of the exciton, the larger is the distance of exciton migration. As a result, small excitation intensity should be used to avoid annihilation. While several works have been made at sufficiently low excitation intensity the time resolution was in a range of tens of picoseconds [5-7]. In this work we present the fluorescence study with femtosecond time resolution on J-aggregates adsorbed on AgBr surface.

The other molecule co-adsorbed on AgBr grains in much smaller concentration than sensitizing dye, which is called supersensitizer (SS), is often used in photography to improve the quantum yield of spectral sensitization particularly in the red region. Two main mechanisms were proposed for the supersensitization effect. One is the "hole-trapping" mechanism in which the electron from supersensitizer (SS) fills the hole in the HOMO of the excited sensitizing dye (Figure 1) [8-10]. Another is the "aggregate-partitioning" mechanism, where it is considered that SS molecules work as J-aggregate partitioners, and decrease the size of the aggregates [9,11]. This causes an increase in radiative lifetime and/or increase in electron injection rate, and hence increase in the quantum yield of the electron injection. The dynamic studies of supersensitization process are very limited and restricted to our best knowledge to the case of "aggregate-partitioning" mechanism.

Experimental Section

The emulsions used in this work were composed of the suspensions of AgBr microcrystals in aqueous gelatin solutions. The edge lengths of the AgBr microcrystals were controlled from 0.04 to 0.9 μm. The dyes were adsorbed on AgBr grains during the agitation at 40 °C of the above-stated emulsions, to which methanol solution of Dye 1 or Dye 1 / SS was added. The "hole-trapping" supersensitization mechanism is possible if the HOMO level of the SS is higher than the HOMO level of J-aggregates. This is the case for Dye 1 / Dye 2 (SS) pair studied in this work. The sensitizer used in this work is 3,3'-disulfopropyl-5,5'-dichloro-9-ethylthiacarbocyanine (Dye 1)(Figure 2) which forms J-aggregates on the surface of AgBr grains. Addition of SS (3,3'-disulfopropyl-9-ethyl-4,5,4',5'-dibenzothiacarbocyanine) changes the dynamics of fluorescence decay of the sensitizer.

A second harmonic of the chromium-forsterite femtosecond laser tunable from 610 to 660 nm was used to excite the sample. The pulse duration of the SH pulses was about 44–55 fs and the repetition rate

of the laser is 4 MHz. The excitation power was carefully controlled and was around 0.1 mW, which corresponds to the excitation intensity of about $(0.5–1)\times10^{12}$ photons cm^{-2} $pulse^{-1}$. During experiments the sample was circulated in a 0.5 mm thick sample cell. Special care was taken to prevent the sample illumination by the room light during preparation of the sample and the experiment.

Results and Discussion

Time-resolved fluorescence was measured from the sample which contained AgBr grains with J-aggregates on the surface suspended in gelatin solution (Table 1). The fluorescence decays observed for the 0.2 μm cubic AgBr grains are not exponential, and can be fitted well by a two exponential decay function. The fluorescence decay of Dye 1 on 0.2 μm octahedral grains (without SS) is also nonexponential and it appears to be about 2.5 times faster than that on cubic grains. Addition of the SS makes the fluorescence decays faster for both cases, cubic and octahedral grains. The effect of SS is rather large for cubic grains, about 4 times, and much smaller for octahedral grains, 1.6–2.1 times, except for the 0.04 μm grains. The weighted-average rate constants were calculated for non-exponential decays (Table 1).

Two mechanisms of supersensitization were previously considered: the "aggregate-partitioning" and "hole-trapping" [9] mechanisms. In the "aggregate-partitioning" mechanism, also called as the "exciton-trapping" supersensitization, the J-aggregate size in the presence of a SS is considered to play an essential role. It is assumed that the ends of J-aggregates work both as traps for excitons and as reaction sites for electron injection. According to this model formation of J-aggregates in the presence of SS makes the J-aggregate size smaller, which gives faster exciton trapping at the sites where injection rate is suppose to be fast. As a support for the "aggregate-partitioning" mechanism the decrease of the injection rate with increase of J-aggregate size was observed [11]. On the other hand the increase of the electron injection rate for larger aggregates was reported [6,12].

The "hole-trapping" mechanism of supersensitization assumes that a hole in the HOMO level of excited J-aggregates is filled by an electron transfer (ET) from SS followed by the electron injection from the reduced J-aggregate to AgBr grains (Figure 1). To make the hole-trapping process efficient, the HOMO level of SS must be higher than that of J-aggregates. It was reported that the HOMO level of Dye 2 is slightly higher than that of Dye 1 J-aggregates. So, we think that for the present system of Dye1 / Dye 2 (SS) the "hole-trapping" mechanism is readily applicable to supersensitization.

The following observations support this statement. The increase in the trapping plus injection rate of about 5 times was observed upon addition of SS. In the presence of SS the J-band becomes slightly broader, which can be assigned to a smaller size of the aggregates, as well as to a change of the environment for J-aggregates in the presence of SS. Even if one attributes the absorption peak broadening upon addition of SS solely to a shortening of the aggregates, the change of the coherence size would be for example from 10 to 6 without and with SS, respectively. We think it is unrealistic to attribute such a large change of the rates to a slight change of the coherence size, if any. The experiments with different amount of Dye 1 adsorbed on the surface of AgBr grains support this assumption (data not shown). At smaller ratio of Dye/AgBr the average size of J-aggregates is smaller. If the ET rates would increase in smaller aggregates we should have observed faster fluorescence decay upon decreasing of the Dye/AgBr ratio. One can see the opposite effect; when the ratio of Dye / AgBr decreased by ten times, the fast component of the decay became longer. This is not in favor of the "aggregate-partitioning" mechanism. Thus, we consider that the "aggregate-partitioning" mechanism is not the major mechanism and its contribution is negligible in the present systems. Further quantitative analyses including the measurements of rates of electron transfers and quantum yields.

It is analyzed that the rate constant of ET from SS to the excited J-aggregates, k_{SS}, is larger than k_{ET} by about 8 times for cubic and only about 1.5 times for octahedral grains. This determines the relatively high quantum yield of photographic process with octahedral grains and rather small improvement by addition of SS. On the cubic grains the quantum yield without SS is small because of small k_{ET} and thus a large effect of SS is observed. This large increase of the quantum yield by SS is caused by the large k_{SS} constant, namely $k_{SS} \sim 8k_{ET}$ for cubic grains.

Table 1: Results of the fluorescence decay fit with two exponentials (τ_1, τ_2, A_1, A_2), average time $\bar{\tau}$, and observed decay constant k_{obs} for AgBr grains of different size and surface type

AgBr type	AgBr size	τ_1 ps	A_1	τ_2 ps	A_2	$\bar{\tau}$ ps	k_{obs} and k_{obs}^{SS} ps^{-1}
Cubic (100)	0.2 μm	1.77	0.64	10.8	0.36	5.0 ± 0.2	0.20 ± 0.01
	0.2 μm + SS	0.77	0.78	3.35	0.22	1.34 ± 0.06	0.75 ± 0.04
	0.2 μm ^{a}	2.5	0.58	9.3	0.42	5.4 ± 0.2	0.19 ± 0.01
	0.2 μm + SS	0.8	0.87	4.4	0.13	1.3 ± 0.07	0.77 ± 0.05
Octahedral (111)	0.04 μm	1.5	0.66	13	0.34	5.5 ± 0.7	0.18 ± 0.02
	0.04 μm + SS	0.79	0.88	4.5	0.12	1.25 ± 0.15	0.80 ± 0.10
	0.2μm	1.08	0.80	5.40	0.20	1.95 ± 0.15	0.51 ± 0.03
	0.2 μm + SS	0.66	0.84	2.5	0.16	0.95 ± 0.06	1.06 ± 0.06
	0.4 μm	0.69	0.55	2.26	0.45	1.40 ± 0.07	0.72 ± 0.04
	0.4 μm +SS	0.56	0.68	1.1	0.32	0.73 ± 0.04	1.37 ± 0.08
	0.9 μm	0.66	0.85	3.3	0.15	1.07 ± 0.05	0.94 ± 0.04
	0.9 μm + SS	0.40	0.78	1.35	0.22	0.61 ± 0.03	1.64 ± 0.08

^{a} The two experiments are shown for cubic AgBr of 0.2 μm to demonstrate the reproducibility of the measurements, as the grains were newly synthesized for each experiment.
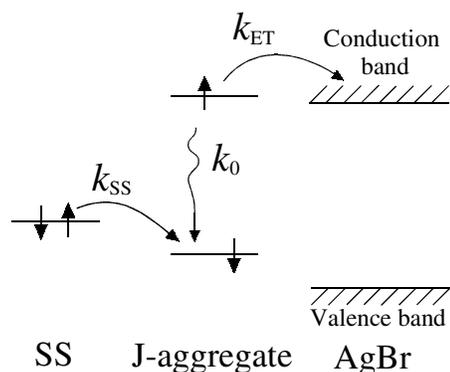
Figure 1. Reaction scheme of the "hole-trapping" supersensitization.
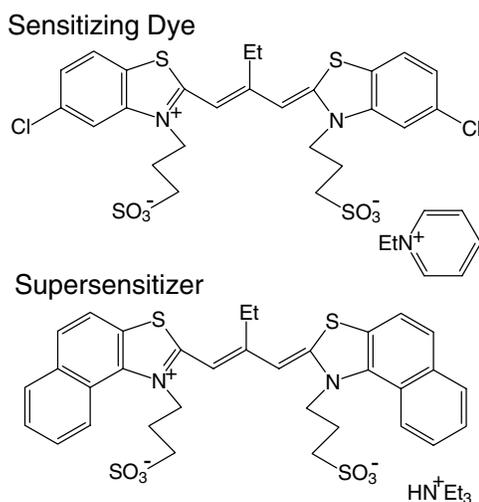
Figure 2. The molecular structure of the sensitizing dye and supersensitizer used in the present work.

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Biography

Keitaro Yoshihara received his Ph.D. in Chemistry from University of Tokyo in 1976. He worked in University of Tokyo, Institute of Physical and Chemical Research (RIKEN), and Institute for Molecular Science. In 1997 he joined Japan Advanced Institute of Science and Technology (JAIST). His work has primarily focused on the dynamical processes of excited molecules, including photochemistry and photosynthesis, and development of several methods in ultrafast spectroscopy.