

Fluorescence Dynamic Studies of Cyanine Dyes in Gel-dried Film and Liquid Emulsion by Femtosecond Fluorescence Up-conversion Technique

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Abstract

The fluorescence decays of J-aggregates of the 3,3' - disulfopropyl-5,5' -dichloro-9-ethylthiacarbocyanine (Dye 1) and of the composite J-aggregates by addition of a supersensitizer, 3,3-disulfopropyl-4,5' 4,5' dibenzothiacarbocyanine (Dye 2) on silver bromide crystals were studied by a femtosecond fluorescence up-conversion technique. Crystals having different crystal habits (cubic and octahedral) with the crystal size of 0.2 μ m were used. The average fluorescence decay time became about 2 or 3 times slower in gel-dried film of cubic crystal compared to the liquid emulsion. In the case of octahedral crystal, the average decay time showed relatively small difference between emulsion and gel-dried film conditions. The competition of adsorption between dye molecules and functional groups from gelatin to the surface of silver bromide is considered to explain the difference of the electron injection rate (from the excited J-aggregate to AgBr) between gel-dried film and liquid emulsion..

Introduction

Spectral sensitization makes photographic materials sensitive to green, red, and infrared light by putting sensitizing dyes on the surface of the microcrystals.[1]. The studies of the dynamic processes of sensitization have been studied with time resolution of tens of picoseconds[2-4]. In this work, we measured the fluorescence decay times of the J-aggregates of sensitizing dyes in gel-dried films and liquid emulsion with femtosecond time resolution.

Material and Method

The second harmonic of the chromium-forsterite femtosecond laser (620 nm) beam was used to excite the sample. The instrumental response function was estimated by the cross-correlation of pump and gate beams, which is 70 fs (FWHM) [6]. Decay curves were fitted well by Eq. 1 and the average decay times (τ_{AVE}) were calculated by Eq. 2.

$$y = A_1 e^{-t/\tau_1} + A_2 e^{-t/\tau_2} \quad (1)$$

$$\tau_{Ave} = \frac{A_1 \tau_1 + A_2 \tau_2}{A_1 + A_2} \quad (2)$$

The, K_{ET} , electron transfer rate is defined as

$$K_{ET} = 1/\tau_{Ave}. \quad (3)$$

Emulsions with dyes were made as follows; the methanolic solution of each dye was added into diluted emulsion and agitated for 30 min at 40 °C to make J-aggregate. The J-band of dye aggregate was measured by reflection spectrometer. The preparation of film was the same as above except that emulsions with dyes were coated on PET film.

Results and Discussion

Table 1 gives a comparison of average decay times between liquid emulsion (left) and gel-dried film(right). The fluorescence decays of J-aggregates in the gel-dried film are shown in Fig. 1. The data shown were obtained by averaging 20 scans for one sample. Fluorescence decay time showed much faster decay than that measured with picosecond time resolution by other researchers [3-5].

Sample	τ_{AVE} in emulsion	τ_{AVE} in gel-dried film
Cubic+Dye 1	5.2	15
Cubic+Dye 1+10% SS*	1.3	4.0
Octahedral+Dye 1	2.0	1.6
Octahedral+Dye 1+10% SS*	1.0	1.1

Table 1. The Comparison of decay times(picosecond) between liquid emulsion(left) and gel-dried film(right) .

* compared to dye 1 in weight.

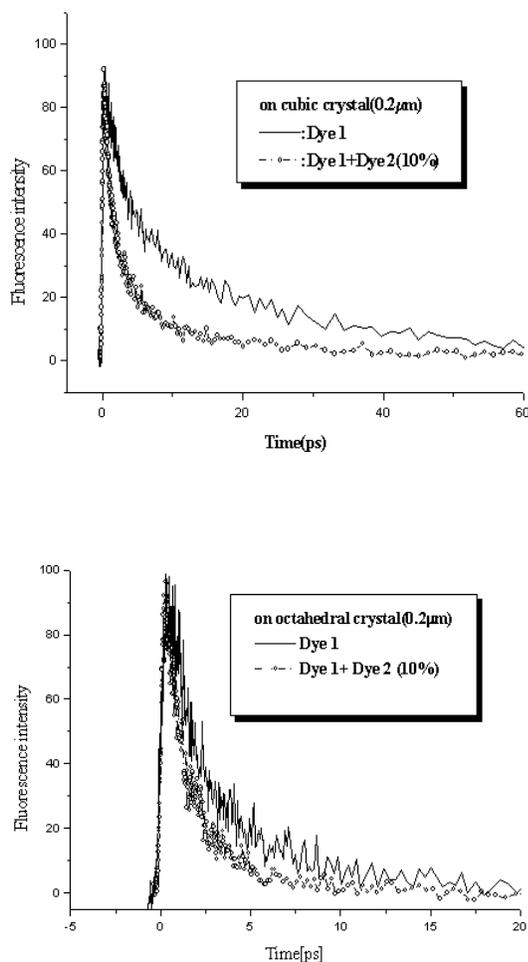


Fig .1. the fluorescence decays of J-aggregates of cyanine dyes in the gel-dried film.

In the case of cubic crystals, the average decay time in gel-dried film was slower than that in liquid emulsion. The competition of adsorption between dye molecules and functional groups from gelatin to the surface of silver bromide can explain why change of decay time was clearly observed for cubic crystals(see Fig . 2). The functional groups from gelatin , which is stabilized with hydroxyl ions in liquid emulsion, adsorb onto crystal surface under dried conditions. The cyanine dye molecules that have positively charged chromophores should compete with gelatin functional groups. Some cyanine dyes are then forced to adsorb into positively charged kink sites[7] .

This situation results in the injection of the silver ions into the interstitial position .The energy band of the space charge layer is shifted up in the case of cubic crystal, which leads to a smaller electron injection rate (see Fig . 4).

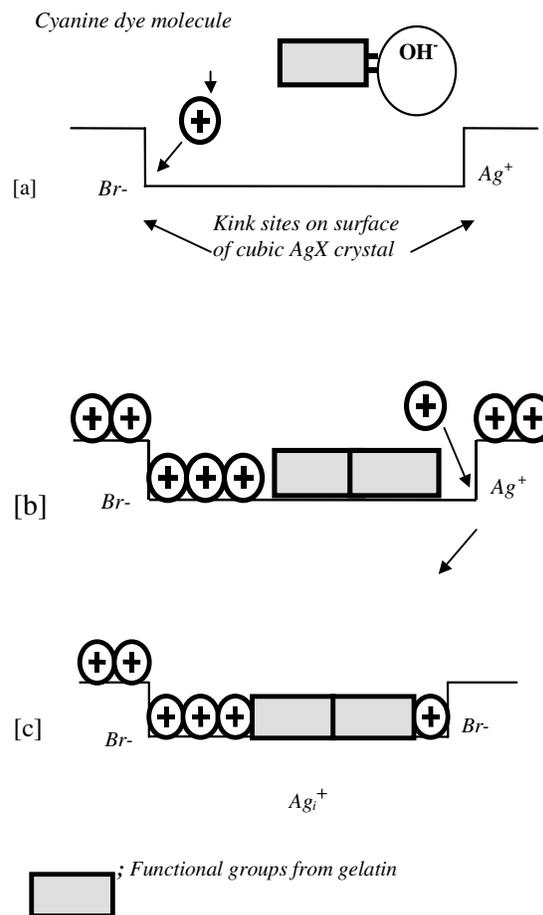


Fig. 2. Schematic illustration of absorption process of cyanine dyes to cubic AgBr crystals where Ag^+ represents an interstitial silver ions[7] .

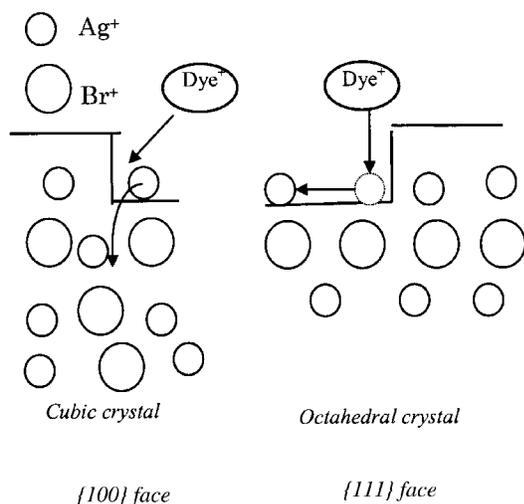


Fig. 3. Schematic illustration showing effect of cyanine dyes on ionic property of AgBr crystals with (100) and (111) faces[8].

In the octahedral crystal, the average time showed relatively small difference between liquid emulsion and gel-dried film conditions. This is due to the fact that the adsorption of cyanine dyes to the octahedral crystals increases, not the concentration of interstitial silver ions, but that of mobile ions on the surface, by repelling silver ions at surface sites, not into interstitial positions, but into surface sites where silver ions are mobile.(see Fig. 3). The ionic conductivity can be change but the surface charge layer, which is effected by interstitial silver ions, is not shifted adsorption of cyanine dyes[8].

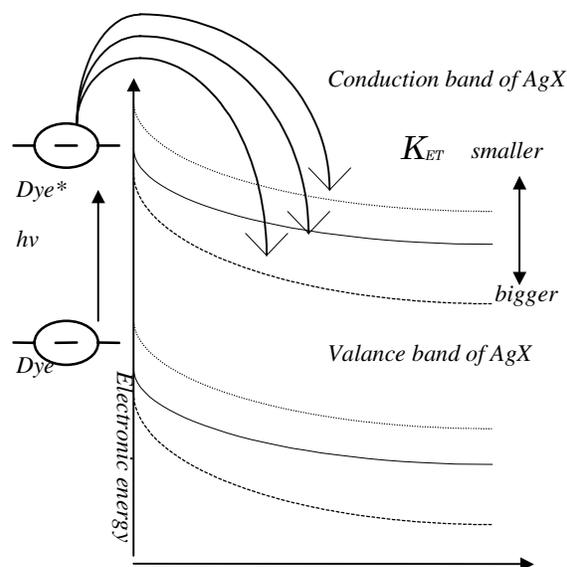


Fig. 4. The relationship between electron injection rate and energy bands of silver halide.

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Biography

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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