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Kinetics study of ultrafast electron transfer from sensitized dyes to silver halide microcrystals*

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Spectral sensitization micromechanism of cyanine dyes J-aggregate adsorbed on the tabular and cubic AgBr microcrystals with different dye concentrations is studied by using picosecond time-resolved fluorescence spectroscopy, and the dependences of electron transfer and spectral efficiency sensitization on different conditions are analysed in detail. With the steady spectroscopy, the wavelengths of absorption and fluorescence of J-aggregate adsorbed on AgBr microcrystals are found to shift to red relative to dye monomer. The spectrum of fluorescence has a red shift relative to the absorption peak. With the time-resolved fluorescence spectroscopy, the fluorescence decay curves of cyanine dyes J-aggregate adsorbed on the tabular and cubic AgBr grains are found to be fitted well by a double-exponential decay function. The fitting curves consist of a fast and a slow component. Because of the large amplitude of the fast component, this fast decay should be attributable mainly to the electron transfer from J-aggregate of dye to a conduction band of AgBr.

Keywords: spectral sensitization, electron transfer, fluorescence lifetime, silver bromide
PACC: 7220J, 0768, 7200

1. Introduction

The formation of multicolour images is one of important properties of photographic materials. The primary colours required for photosensitive materials are blue, green and red. Silver halide microcrystals can intrinsically absorb ultraviolet and blue lights only. So it is only sensitive to the blue light in a visible range. West and Gilman[1] investigated spectral sensitization, which was used to make silver halide sensitive to lights with wavelengths longer than those of blue, green, red and infrared lights, by absorbing the sensitizing dyes. The spectral sensitization is realized by the electron transfer mechanism presented by Tani[2,3] The conduction electrons react with interstitial silver ions to form silver spots of latent-image.[4−6] To obtain multicolour images, sensitizing dye should absorb the light with a required wavelength and make excited electron transfer to conduction band of silver halide. So it is very important to comprehend the dye adsorption on silver halide grains and interaction between them.

The relative quantum yield of spectral sensitization is defined as a ratio of the quantum yields for creating latent-images in two types of excitations: the dye excitation and the AgBr grains excitation without dye. The relative quantum yield of spectral sensitization ($\Phi_{\rm r}$) is directly proportional to the efficiency of the electron transfer($\Phi_{\rm r}$) in this process.[7] Generally, ($\Phi_{\rm r} = \Phi_{\rm s}$, i.e. the efficiency of electron transfer efficiency is equal to that of the spectral sensitization.

The relaxation rates of radiation and no-radiation of the excited dye each compete with that of the electron transfer. So the electron transfer and the efficiency of spectral sensitization can be discussed by the fluorescence emission of dye on silver halide

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grains. To explain the essential process of spectral sensitization and enhance the sensitization efficiency, time-resolved dynamic spectrum is commonly used. Two techniques are usually used: time-correlation single photo count technique (TCSPC) and high-speed streak photography technique (streak camera). Their time-resolved rates have both reached a picosecond range. TCSPC is used widely, but its time-resolved rate is larger than 20–50 ps. And the full wave at half maximum (FWHM) of instrument response is below 50 ps. Tani *et al*[8,9] and Lanzafame *et al*[10] investigated the sensitization process of a silver halide system using TCSPC. With the improvement in laser source, other relevant experimental conditions and equipments, streak camera has developed greatly over the last several decades. Tani and his co-workers have performed dynamics study of silver halide sensitization at a time-resolved rate more than 20 ps.[11,12] Because of its higher time-resolved rate and other excellent properties, the streak camera is used to measure time-resolved fluorescence spectrum in our work at a time-resolved rate of 5 ps.

In our work, the time-resolved fluorescence spectrum of cyanine dye J-aggregates adsorbed on cubic and tabular microcrystals of AgBr is observed using the streak camera. The dependences of the ultrafast electron transfer from J-aggregate to a conduction band of AgBr on the dye concentration and shape of microcrystals are analysed. The influence of these dependences is also analysed. Some interesting conclusions are obtained.

2. Experimental principle and equipment

2.1. Preparation of sample

The emulsions used in this work were composed of the suspension of the AgBr grains in aqueous gelatin solution, and prepared by using the controlled double-jet precipitation method.[13−17] The edge lengths of the AgBr microcrystals were 0.4μm for cubic grains and 1.7μm for tabular grains. The values of pH and pBr of the above emulsions were 6.4 and 2.8, respectively. The added amounts of dye methanol solution with a concentration of 2g/L were 2, 3, 4, 5 and 10mL for T-grains and cubic grains gelatin emulsions, both containing 5g AgBr (AgBr is 2.78 mmol and gelatin 4.5 g). The dye concentrations contrasted with AgBr were 2.26, 3.38, 4.51, 5.64 and 11.28mmol/mol, respectively. The ambient temperature was 45°C during the preparation of samples. The above emulsions were agitated for 30 minute to make dye form J-aggregate on AgBr grains. The molecule structure of Dye1 is shown in Fig.1.

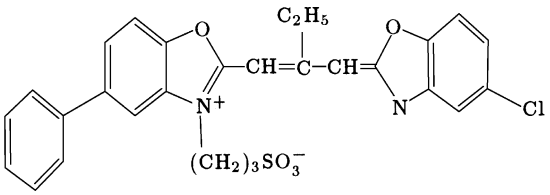


Fig.1. The molecular structure of Dye1.

2.2. Experimental setup

A Millennia laser was used to pump a mode-locked Ti:sapphire laser Tsunami. Briefly, pulses with 100 fs of duration, 8nJ/pulse of energy and 800 nm of wavelength at a repetition rate of 82 MHz were generated and amplified in a regenerative amplifier which was pumped at 527 nm by a Nd:YL laser. The output energy of the amplifier was typically 600μJ. Then the laser was tuned in an optical parameter amplifier (OPA). The setup is described in Fig.2. An electric signal of 1 KHz given by the regenerative amplifier created a gate pulse through the delay Dly1 determined by a delay generator. And the gate pulse chose an electric signal of 82 MHz created by a photojunction diode. The chosen electric signal which gave a scan signal through the delay Dly2 to trigger off a periodic sawtooth high voltage that is added to the deflexion electric field of the streak camera. This caused different shifts of photoelectrons generated by the excitation of the fluorescence that passed through the electric field. Therefore, the time resolution of any wavelength is attained. The scan signal was created by a high frequency signal through a short delay. So its time-domain dithering is far weaker than that of the regenerative amplifier, and time resolution is much higher. Improving time resolution is an important matter in streak camera experiment. And the key factor is time-domain dithering of triggering scan signal generated by a photodiode. So it is required to adjust the position of the photodiode to make it be over against laser beam, and adjust the input power to 2–5 mW synchronously. Furthermore, it is required to optimize the electric triggering delay signal to make the time range of laser scanning image on the display screen as narrow as possible. To improve time resolu-

tion, the electric triggering signal should be optimized also. In addition, the intensity of signal received by the photodiode can be adjusted to make laser images in the lowest time-domain. During the experiment, the damage to streak camera, caused by the excessive light and excessive pulses, should be avoided.

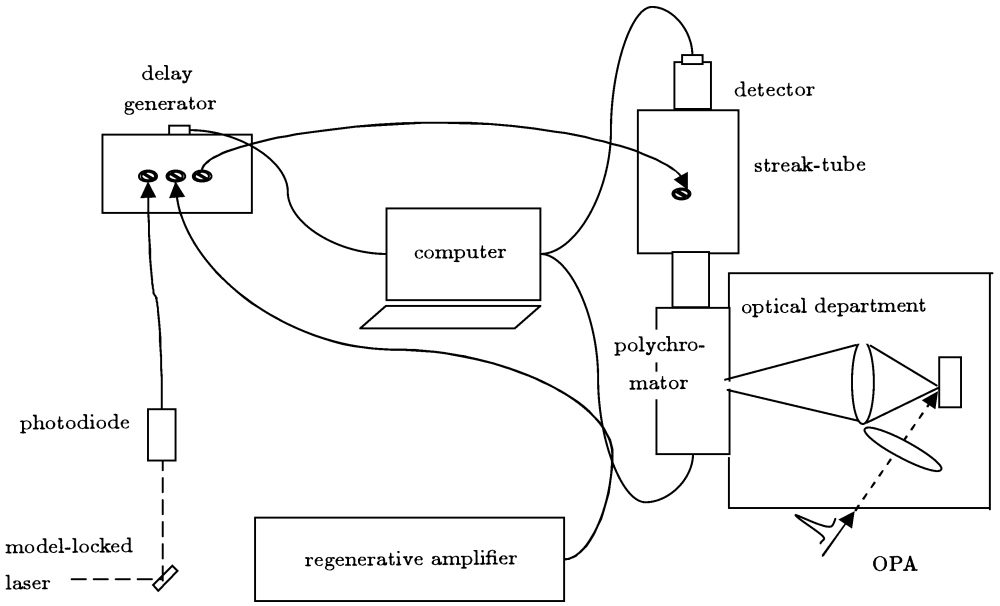


Fig.2. Experiment setup.

3. Analysis of experimental date

3.1. Steady spectroscopy

In our work, the steady absorption and fluorescence are measured by HITACHI U-3310 Spectrophotometer and F-2500 Fluorescence Spectrophotometer, respectively. All the measurements were carried out under the conditions of no ambient light because all samples were photosensitive.

It is shown in Fig.3 and Fig.4 that the peak of fluorescence of Dye1 has a slight red shift relative to that of absorption for cubic grains or for T-grains. The absorption and fluorescence spectra have an obvious red shift relative to that of monomer.

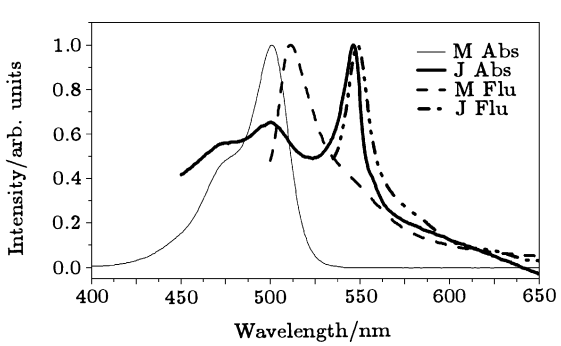


Fig.3. The absorption and the fluorescence spectra of Dye1 monomer and J-aggregate on cubic grains.

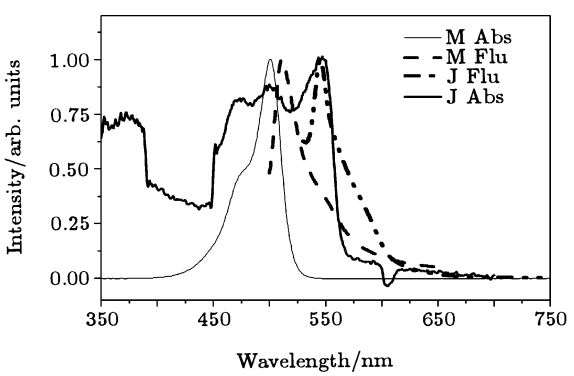


Fig.4. The absorption and the fluorescence spectra of Dye1 monomer and J-aggregate on T-grains.

3.2. Dynamics analysis of time-resolved fluorescence decay

The fluorescence decay curves can be fitted by a double-exponential function, which is defined as

$$A_1 \exp(-t/\tau_1) + \exp A_2(-t/\tau_2). \qquad (1)$$

From Figs.5 and 6 and Table 1, it is clearly seen that the fluorescence decay lifetime of J-aggregate on the cubic grains is shorter than that of dye monomer. The former is less than 31 ps, and the later is 70 ps. Especially the faster decay component becomes shorter markedly; τ_1 reduces twice. This confirms assuredly

that electron transfer takes place from excited J-aggregation to conduction band (CB) of AgBr. The course competes with the fluorescence decay, which makes the fluorescence lifetime shorter, but decay faster. With the increase of dye, the fluorescence decay becomes slower, but lifetime longer. k_{ave} reduces from 0.05 ps^{-1} to 0.033ps^{-1}, and τ_{ave} increases from 19.735 ps to 30.155 ps. So the electron transfer rate from excited dye to CB of AgBr, competing with the fluorescence emission, becomes shorter. The fast decay component is less dependent on the dye concentration. Its lifetime has no obvious change (10.6–12.1ps). And it has a larger amplitude (76–89%). Because of the larger amplitude and the larger quantum yield of electron transfer, it can be believed that the electron transfer of J-aggregate occurs. The electron transfer results in the increase of the decay rate of the faster component in the fluorescence decay. So the fast decay component should be attributable mainly to the electron transfer from excited J-aggregation to CB of AgBr. The slow component is taken into account also, because it contributes to the statistical quantum yield of spectral sensitization. The slow component is more dependent on the dye concentration. Total change of the fluorescence decay rate is attributable mainly to the influence of the slow. It is shown obviously in Fig.7 and Table 1 that the fluorescence decay of J-aggregate on T-grains at the lowest concentration (2.63mmol/mol) is far faster than that at each of the other four higher concentrations. The average decay lifetime τ_{ave} reaches 21.157 ps and the decay rate k_{ave} is 0.047 ps^{-1}. It can be seen in Table 1 that the fluorescence decays of four samples with higher concentrations change slightly. The fast component has a larger amplitude in the fitted curve, especially for the sample with the lowest concentration the associated fast component reaches 96.2%. As analysed above, this fast component is still attributable to the electron transfer.

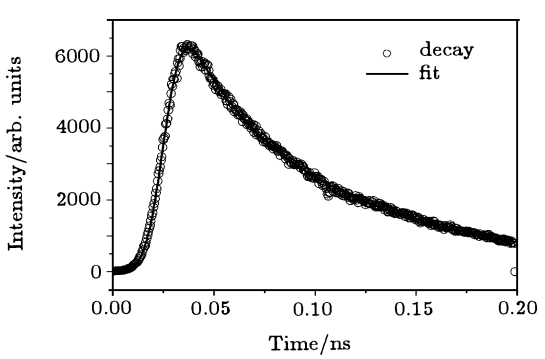


Fig.5. The decay dynamics curves of time-resolved fluorescence of Dye1 monomer and their fitted curves. The excited wavelength is 450nm.

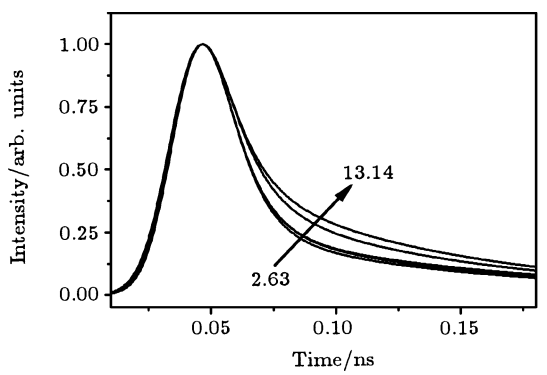


Fig.6. The dynamics decay fitted curves of time-resolved fluorescence of Dye1 J-aggregate on the cubic grains with different concentrations relative to AgBr. The dye concentrations are 2.63, 3.96, 5.26, 6.57, and 13.14mmol/mol.

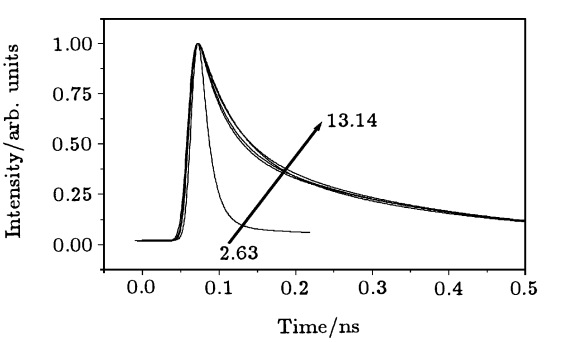


Fig.7. The dynamics decay fitted curves of time-resolved fluorescence of Dye1 J-aggregate on the T-grains with different concentrations relative to AgBr. The dye concentrations are 2.63, 3.96, 5.26, 6.57, and 13.14mmol/mol.

Table 1. The dynamics fitted curve parameters of the time-resolved fluorescence decay. Spectral lines are all fitted by a sum of the double exponential function (τ_1, τ_2, A_1, A_2). C stands for cubic grains and T for T-grains. Time is in units of ps. The dye concentration is in units of mmol/mol.

Dye concentration	A_1/%	τ_1	A_2/%	τ_2	τ_{ave}	k_{ave}
monomer	28.2	25.1	71.7	87.7	70.0	0.014
C-2.63	89.5	10.6	10.5	97.6	19.7	0.050
C-3.96	88.2	10.9	11.8	97.4	21.1	0.047
C-5.26	88.4	11.1	11.6	106.4	22.1	0.045
C-6.57	81.1	12.1	18.9	91.6	27.1	0.037
C-13.14	76.4	11.7	23.6	89.9	30.1	0.033
T-2.63	96.2	13.5	3.8	215.1	21.1	0.047
T-3.96	62.2	47.8	37.8	273.8	133.2	0.008
T-5.26	58.9	34.7	41.1	260.5	127.5	0.008
T-6.57	56.9	41.0	43.1	265.8	126.8	0.008
T-13.14	61.8	33.4	38.2	270.1	123.8	0.008

It can be concluded from the analysis of above experimental results that the fluorescence peaks of Dye1 J-aggregate on cubic grains and on T-grains have no obvious distinction. Their spectral sensitization ranges are close to each other. The fluorescence decay rates of Dye1 J-aggregate adsorbed on the two kinds of grains are approximately the same at a low concentration (2.63 mmol/mol). With the increase of dye concentration, the fluorescence decay of J-aggregate on cubic grains is faster obviously than that on T-grains. And the decay rate is larger markedly than that on T-grains. At the low concentrations, the electron transfer rates from dye J-aggregate to CB of AgBr are comparatively close to each other. As the dye concentration increases, the transfer rate of J-aggregate on cubic grains is larger obviously than that on T-grains. The sensitization efficiency is directly proportional to the electron transfer rate. So the sensitization efficiency of Dye1 on cubic grains is higher than that on T-grains.

4. Conclusions

It is found that the absorption and fluorescence spectra of Dye1 J-aggregate in AgBr emulsion both are shifted to long wavelengths. The shift of fluorescence spectrum is slightly more than that of absorption spectrum. The dynamics curves of time-resolved fluorescence decay can be fitted by a sum of the double exponential functions. There exist two components, the fast and the slow. The fast one has larger amplitude, which can be attributable mainly to the electron transfer from excited dye J-aggregation to CB of AgBr. It is concluded that the sensitization efficiency of Dye1 on cubic grains is higher than that on T-grains.

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