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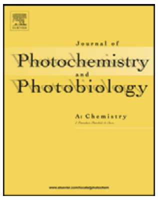

Photoluminescence developed from polystyrene and CdS/polystyrene nanocomposite films in picosecond time range by repetitional irradiation of excitation femtosecond pulses in PL up conversion measurements

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ABSTRACT

A CdS/SPS nanocomposite film in which CdS nanoparticles were embedded into partially sulfonated polystyrene (SPS) was synthesized and its subpicosecond time resolved photoluminescence (photoluminescence up conversion: PL Up-C) measurements were carried out. A similar measurement was also done for pure SPS and polystyrene (PS) films that were used as the matrix. For a CdS/SPS, PL Up-C signals (sum frequency signal; SFS) were observed at the first measurement. They were also observed for pure SPS and PS films by repetitional measurements though they were not observed at the first measurement. It seems that the development of SFS for SPS and PS films is due to relatively stable luminescent substances formed from themselves by exposing them to intense femtosecond laser pulse (for excitation) during the measurements. The SFS development process was also readily observed for a CdS/SPS film by reducing excitation pulse intensity in the measurements. Therefore, PL that was observed for a CdS/SPS film is also mainly due to luminescent substances formed from the SPS matrix but CdS nanoparticles. CdS nanoparticles embedded into a SPS film may act as an accelerator for PL development from the SPS matrix. The origin of PL may be several luminescent substances formed by photo- or thermal-degradation of SPS via multiphoton (probably two photons) absorption of SPS itself and/or photo-excitation of CdS nanoparticles. Although the luminescent substances could not be assigned, they might be oxidative decomposition products of SPS that have long conjugated π bonds with a PS main polymer chain that absorbs the excitation femtosecond pulse (λ_{max} = 396 nm).

1. Introduction

CdS/polymer nanocomposites, in which CdS nanoparticles are embedded into polymer substrates that exhibit long-term stability and flexible reprocessability, attracted much attention due to their possibility for practical application to molecular electronics, optics, photoelectrochemical cell and nonlinear optical materials. Although there are many studies on their stationary photo-properties, primary photo-events of such semiconductor/polymer nanocomposite films in several picoseconds time regions have hardly been studied [1–7].

Recently we have conducted PL Up-C measurements for CdS/SPS nanocomposite films in order to clarify their primary photo-events in the time region within several decade picoseconds. In these measurements, SFS development and its decay time profile observed by repetitional PL Up-C measurements showed interesting behavior in which the observed PL seems not attributable to CdS nanoparticles. In the PL Up-C measurements of SPS and PS films which were carried out to confirm both the origin and development mechanism of PL, we observed interesting phenomenon that the SFS from the pure PS and SPS films became observable by repetition of the measurements though it was not observed at the first measurement. Namely, it is suggested that PL from the PS and SPS films was developed by repeated exposure of the PS and SPS films to the excitation femtosecond laser pulse during the PL Up-C measurements.

A large number of studies on photo- and thermal-stability of PS and its co-polymers have been conducted even recently and it is known that they are stable to the light with the wavelength longer than 300 nm as they do not absorb the light in this wavelength region though they decompose and turn yellow by UV light or at high temperature [8–13]. As the excitation wavelength (λ_{max} = 396 nm) at the PL Up-C measurements in the present study is longer than the edge wavelength of absorption band of PS, one-photon absorption by PS does not occur usually at the excitation wavelength. However, as the excitation laser pulse that was used in the present study is the femtosecond laser pulse with extremely intense peak power, there is a possibility that multiphoton (probably two photon) absorption of the excitation pulse by PS occurs and

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consequently photo- and/or thermal-reactions occur via excited states of PS.

In the present study, we mainly report on SFS behavior in the time range within several decade picoseconds and on the expected mechanism of PL development at PL Up-C measurements of CdS/SPS, PS and SPS films.

2. Experimental

2.1. Preparation of samples

PS with m.w. ca. 250,000 used in the present study was purchased from Kanto Chem. Co. The synthesis of SPS which is used for the synthesis of CdS nanoparticles *in situ* was carried out according to the literatures [1,14] as follows: acetylsulfate solution (1 M; synthesis from acetic anhydride and sulfuric acid) was added to PS in 1,2-dichloroethane and the mixture solution was heated at 50 °C for 5 h. Thereafter, insoluble material was precipitated from the reaction mixture by adding hexane and then separated from the solution by centrifugation. After the obtained solid was washed with ethanol several times and dried *in vacuo* for 8 h. The sulfonation ratio for the synthesized SPS was determined by titration with KOH methanolic solution (0.1 M). The SPS sample was dissolved in the mixed solvent of toluene and ethanol prior to titration.

The synthesis of the CdS/SPS nanocomposite was carried out *in situ* as follows [1]: a DMF solution of cadmium acetate dihydrate was added slowly to a DMF/1,2-dichlorethane solution of SPS with stirring. And further stirring at 70 °C, a DMF solution of thioacetoamide (molar ratio of S/Cd = 2) was added dropwise slowly to the mixed solution. The mixed solution was then refluxed for 1 h to form CdS nanoparticles in SPS. After the solution, which turned yellow, was allowed to stand to cool down until room temperature, insoluble material was precipitated from the solution by adding hexane. The precipitate was separated from the solution by centrifugation and then washed with ethanol several times. The precipitate was dried *in vacuo* for 10 h.

CdS/SPS films on a slide glass were prepared by the repetition of dropping of a CdS/SPS solution (DMF solvent) onto a slide glass and dried at room temperature. Both pure SPS and PS films on slide glasses were prepared similarly to CdS/SPS films by using SPS in a DMF solution and PS in a toluene solution, respectively.

The typical thickness of the films used in the present study was about 5 μm. Absorption and photoluminescence spectra of the films on a slide glass were recorded using an UV–vis–NIR spectrophotometer (Shimadzu, UV-3600) and a fluorescence spectrophotometer (Hitachi F-4500), respectively. Both spectra of a slide glass were also recorded for the background correction.

All reagents were used without further purification. Slide glasses used as a supporting plate for films were purchased from Matsunami glass Co.

2.2. Measurements of subpicosecond time resolved photoluminescence by PL Up-C method

Subpicosecond time resolved PL measurements were conducted by the PL Up-C method using the home-made PL Up-C system which was previously reported in Ref. [15]. Outline of the PL Up-C measurement is as follows: the excitation pulse was a 396 nm pulse generated by frequency doubling of the fundamental output (λ_{max} = 792 nm) from a femtosecond mode-locked Ti:Sapphire laser (76 MHz, FWHM = ca. 170 fs, MIRA 900 Basic, Coherent) using a BBO crystal. The gate pulse (mixing pulse) was the residual of the fundamental output. The intensity of the laser pulses was measured with a laser power meter (NOVA, OPHR) before every PL Up-C measurements.

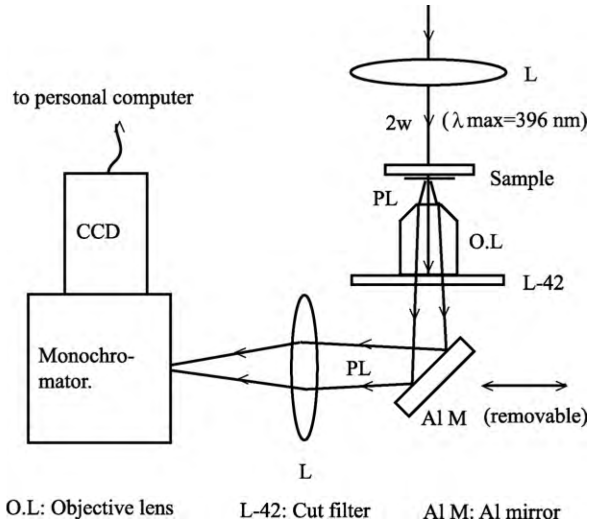


Fig. 1. Schematic representation of a set-up for PL measurement by the femtosecond pulse excitation.

The PL generated by photo-excitation of film samples on a slide glass was collected by an objective lens just behind the samples and focused after passed through a cut filter (L-42, HOYA) in a BBO crystal together with the gate pulse, which passed through an optical delay stage, to generate their SFS. The generated SFS was introduced into a monochrometer and then detected by using a photomultiplier tube (R585, Hamamatsu) and a gated photon counter (SR400, Stanford Research Systems Inc.). Applied voltage for the photomultiplier tube was −1200 V. The signals of the photomultiplier tube were amplified to 5-fold by a fast pre-amplifier (SR440, Stanford Research Systems Inc.) before they were introduced into the gated photon counter (gate time: 6 s). SFS was measured as a function of the delay time between the excitation pulse and the gated pulse by operating the optical delay stage. Acquisition of the data and operation of the delay stage were carried out using a personal computer equipped with software for the operation. The optimization of the optics for the PL Up-C measurements of film samples on a slide glass was done by utilizing the fluorescence (at 490 nm) of coumarin 151 in ethanol/water and thereafter by utilizing that of an identical CdS/SPS nanocomposite film. The PL Up-C measurements were usually carried out with ca. 13 mW as the excitation pulse intensity and ca. 160 mW as the gate pulse intensity in two delay time ranges (a short time range: −2 to 6 ps and a long time one: −5 to 40 ps). It took about 10 min for the measurement in the short time range and about 20 min for that of the long time one. Therefore, the samples were exposed to the intense excitation pulse for ca. 10 or ca. 20 min in the PL Up-C measurement.

2.3. Measurements of ordinary PL spectra by the femtosecond pulse excitation using a CCD detector

None-time resolved (ordinary) PL spectra of film samples by the femtosecond laser pulse excitation were recorded with a CCD detector (DV420-OE, Andor) by a set-up as shown in Fig. 1. Their excitation condition was the same as that for PL Up-C measurements. The other conditions for the measurements were 0.021 s for the gate time and 100 times for the integration frequency of the acquisition data, 372–717 nm for spectral region measured. Accumulation of the data was carried out by a personal computer equipped with analytical software (Andor SOLIS for Spectroscopy, Andor Tech.).

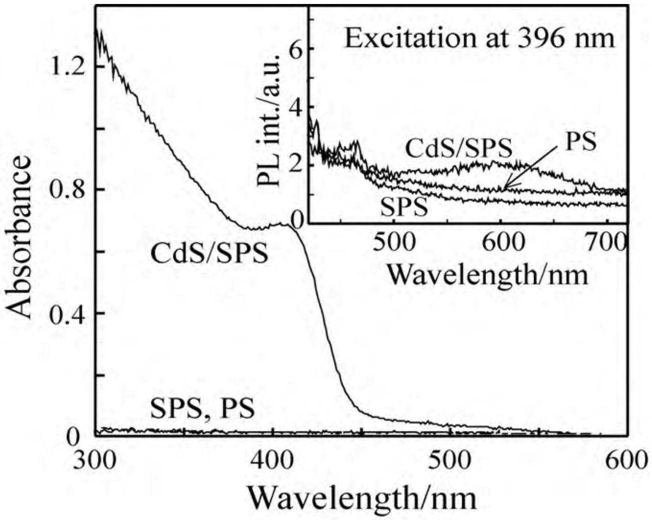


Fig. 2. Absorption and photoluminescence spectra of CdS/SPS, SPS and PS films.

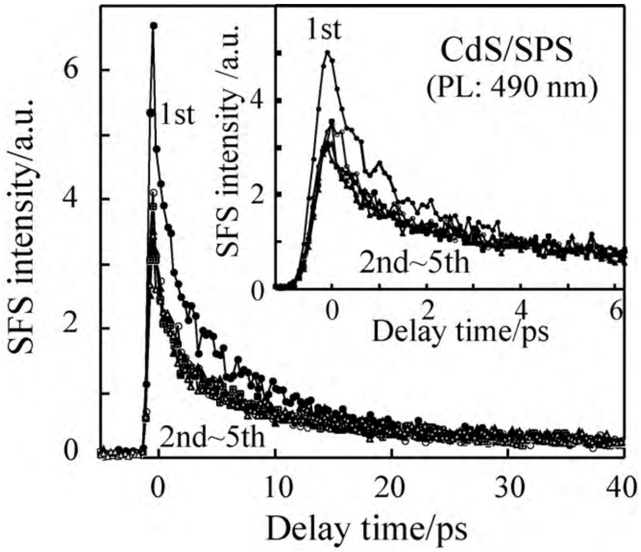


Fig. 3. SFS time profiles of a CdS/SPS film obtained by the repititional PL up conversion measurements using the 13 mW pulse excitation.

3. Results and discussion

3.1. Characterization of a CdS/SPS nanocomposite and its film

Sulfonation ratio of SPS synthesized in the present study was 8.1%, which was estimated by its acid–base titration using a KOH methanolic solution. An absorption spectrum of a CdS/SPS nanocomposite film used in the present study is shown in Fig. 2 together with those of PS and SPS films. As is clear from the figure, the edge of the absorption band of a CdS/SPS nanocomposite film prepared is around 450 nm and blue-shifts compared with that of a bulk CdS crystal whose band edge is 512 nm [16]. According to the relationship between the edge wavelength of absorption band and particle size of CdS [16], the size of CdS particles in the CdS/SPS nanocomposite film used was ca. 2.5 nm. Their ordinary PL spectra are also shown in the inset of Fig. 2. Although there is the report in Ref. [2] that CdS nanoparticles embedded into a PS film have an intense band-gap luminescence band, it was hardly observed for CdS/SPS nanocomposite films synthesized in the present study as well as their PL spectra that was previously reported in Ref. [1]. Both SPS and PS films used were transparent and there were no absorption bands in the wavelength region longer than 300 nm.

3.2. PL Up-C measurements of CdS/SPS nanocomposite films

3.2.1. Influence of the excitation pulse in the repetitional measurements

The results of repetitional PL Up-C measurements for a CdS/SPS nanocomposite film are shown in Fig. 3. The measurements were carried out with the excitation pulse intensity of ca. 13 mW and the PL wavelength of 490 nm (corresponds to the sum frequency wavelength of 303 nm). As seen from the figure, SFS rises up immediately after incidence of the excitation pulse and thereafter decayed considerably within a few picoseconds from the first time of the repetitional measurements at both long (it takes ca. 20 min per one measurement) and short (it takes ca. 10 min per one measurement) time ranges. A sample film was exposed to the intense femtosecond excitation pulse during the measurements owing to the feature of the PL Up-C method. The SFS intensity and its decay time profile did not change after the several measurements though the SFS intensity for the first time measurement is large compared to others (there is the case that the SFS intensity at the first time measurement is almost the same as others). However, the SFS intensity tended to decrease when the repetitional measurements were further repeated. Similar repetitional PL Up-C measurements were also carried out for PL at 460 nm (sum frequency wavelength: 291 nm) and 520 nm (sum frequency wavelength: 314 nm) under the same conditions as that at 490 nm. SFS decay time profiles for PL at both wavelengths were almost the same as that for PL at 490 nm. SFS decay dynamics in the long time range were analyzed by curve fitting using Eq. (1) consisting two exponential components and a constant one:

$$S(t) = A_1 \exp\frac{-t}{\tau_1} + A_2 \exp\frac{-t}{\tau_2} + \text{const.} \qquad (1)$$

where $S(t)$ is SFS intensity at the delay time t, A_i contribution ratio of component i to $S(t=0)$ and τ_i lifetime of component i. In the following, $i=1$ and 2 correspond to a short lifetime component and a long one, respectively. For a CdS/SPS film, the results of the curve fitting for SFS concerning PL at three wavelengths (460, 490 and 520 nm) are shown in Fig. 4. The best fitted curves estimated by Eq. (1) were also shown in the figure. Their decay dynamics factors obtained by the curve fitting are shown in Table 1. The PL components at

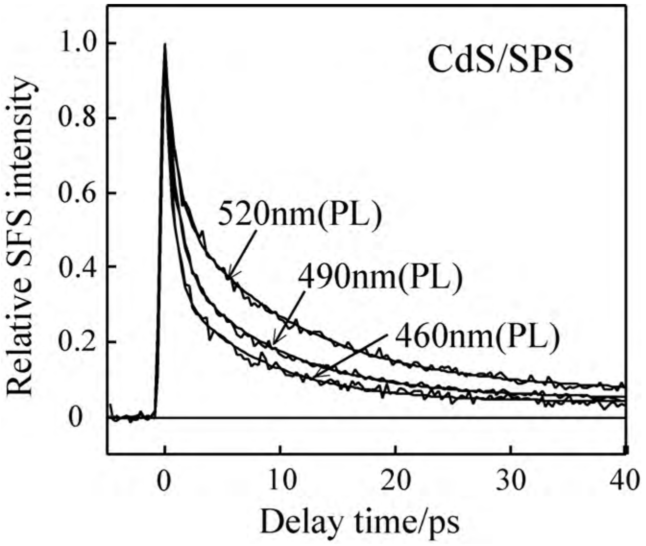


Fig. 4. SFS time profile and its best fitted curve for a CdS/SPS film at the different PL wavelength.

Table 1
Lifetimes (τ_1, τ_2) of PL components and their contribution ratios (A_2/A_1) estimated by the curve fitting for the decay part of SFS profiles of CdS/SPS, SPS and PS films by use of Eq. (1).

Film	PL wavelenght[a] (nm)	τ_1	τ_2	A_1	A_2	Const.[b]	A_2/A_1
CdS/SPS	460	0.71	7.70	0.63	0.33	0.04	0.52
	490	0.97	9.05	0.57	0.38	0.05	0.67
	520	0.96	10.87	0.42	0.51	0.07	1.21
SPS	460	0.55	5.68	0.63	0.34	0.03	0.54
	490	0.67	6.64	0.61	0.36	0.03	0.59
	520	0.97	8.41	0.56	0.40	0.04	0.71
PS	460	1.15	12.12	0.46	0.44	0.11	0.96
	490	1.41	13.31	0.41	0.47	0.12	1.15
	520	1.31	14.69	0.30	0.52	0.18	1.73

[a] The wavelength at which PL was observed as SFS.
[b] The constant used in Eq. (1) in the text.

all wavelengths observed as SFS consist of a fast decay component (τ_1) with a lifetime shorter than 1 ps, a relatively longer one (τ_2) with around 10 ps lifetime and a constant one (const.) which decays hardly in the time range of the measurements, as described by Eq. (1). However, τ_2 and A_2 for the long lifetime component increase slightly with increasing the observation PL wavelength. This result suggests that several luminescent substances might exist in the film.

3.2.2. *Influence of the excitation pulse intensity*

In order to clarify the dependence of the excitation pulse intensity on the SFS appearance process observed in the repetitional PL Up-C measurements of a CdS/SPS film, the measurements were carried out at 490 nm PL wavelength under the excitation pulse intensity of ca. 5 mW (Fig. 5). In contrast to our expectations, the SFS appearance tendency under the 5 mW excitation was considerably different from that observed under the 13 mW excitation described above. Namely, although it was expected that the SFS intensity decreases to some extent when the excitation pulse intensity was lowered from ca. 13 mW to ca. 5 mW at the first PL Up-C measurement, the intensity was extremely lower than expected value. Thereafter, the SFS intensity increased remarkably by repeating the PL Up-C measurement. If the origin of PL observed is attributable to the emission from CdS nanoparticle in the film, it may be considered that the identical SFS intensity and its time profile should be observed every time at the repeating PL Up-C measurements, of course, though the SFS intensity decreases by lowering the excitation pulse intensity from ca. 13 mW to ca. 5 mW. Naturally, it was also considered that the remarkable increase in the SFS intensity and the different SFS time profile were not observed by repeating of PL Up-C measurements. As seen from the figure, however, the SFS grows up with repeating the measurements and it is not explicable if its origin is PL of CdS nanoparticles. Therefore, it seems that the origin of the PL observed as SFS in PL Up-C measurements of the CdS/SPS nanocomposite film is not CdS particles but the luminescent substances formed from the SPS (PS main part) matrix itself by photochemical or thermal-reactions due to absorption of the intense femtosecond excitation pulse because PS does not have PL at least in visible region.

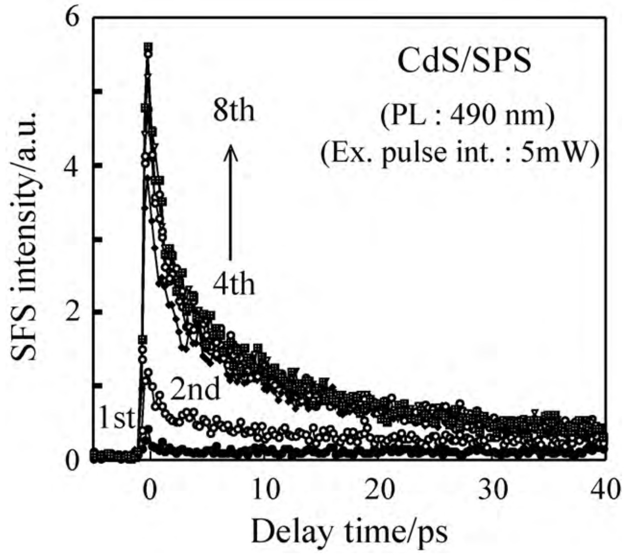


Fig. 5. SFS time profiles of a CdS/SPS film obtained by the repititional PL up conversion measurements using the 5 mW pulse excitation. The data for the 3rd measurement were accidentally not saved, although the measurements were carried out 8 times successively.

3.3. *PL Up-C measurements of PS and SPS films*

3.3.1. *Influence of the excitation pulse in the repetitional measurements*

Although it was doubted that the PL observed as SFS for a CdS/SPS film could be attributed to the near band-gap PL of CdS nanoparticles from the comparison to that of CdS colloidal solutions previously reported in Ref. [15], this was ruled out because the SFS intensity increases remarkably and its time profile changes considerably by repeating of PL Up-C measurements under the excitation condition of low intensity. Therefore, we concluded that the PL at 490 nm observed as SFS is attributed to luminescent substances which were formed from SPS (PS main part) as the matrix. In order to confirm the supposition for the origin of the PL, the repetitional PL Up-C measurements were also carried out for PS and SPS films as well as that for a CdS/SPS film. For a PS film, the results observed at 490 nm (observation PL wavelength) in a long time range (−5 to 40 ps) and a short time one (−2 to 6 ps) by the 13 mW excitation were shown in Fig. 6. As seen from the result in a shorter time range (the insert in the figure), SFS appears and grows up gradually by repeating the measurement several times though SFS was not observed at the first measurement. The growth of SFS time profiles was achieved maximum in the sixth repetition times, and it was almost fixedly kept afterwards. It seems that the appearance and enhancement of SFS were observed because stable luminescent substances, which are not transient, were gradually accumulated by exposing the PS film to the excitation pulse during the measurements. For 460 and 520 nm of PL observation wavelengths, similar appearance and decay time profiles of SFS were also observed, respectively.

As it takes ca. 10 min for the short time range measurement and ca. 20 min for the long time one, it turned out that the maximum in the concentration of the formed luminescent substances is sixth times for the short time range measurement and third times for

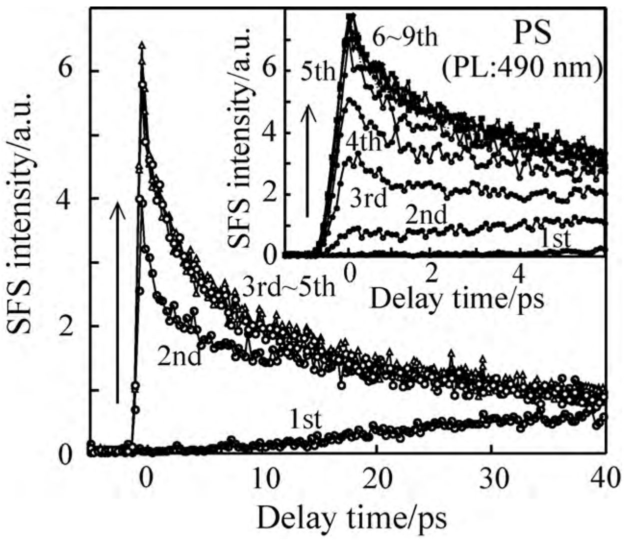


Fig. 6. SFS time profiles of a PS film obtained by the repititional PL up conversion measurements using the 13 mW pulse excitation in a long time range (inset: a short time range).

the long one. In both cases, therefore, the SFS intensity (namely, the concentration of luminescent substances in a PS film) would be achieved its maximum by exposing the PS film to the excitation pulse for ca. 40–50 min. A similar appearance and enhancement process of SFS was also observed for a SPS film.

Curve fitting of the time profiles of SFS decay part at each wavelength for both PS and SPS films was also carried out by using Eq. (1) similar to that of a CdS/SPS film. Their decay dynamics factors such as a lifetime obtained are shown with those for a CdS/SPS film in Table 1. It may also be suggested that the luminescent substance in the both films is not single because the wavelength dependence of dynamics factors for PS and SPS films is similar to that for a CdS/SPS film though their values are somewhat different from those for a CdS/SPS film. According to a report by Kaczmarek et al. [13], when PS is decomposed, dehydogenation occurs from the carbon adjacent to the phenyl group and consequently the conjugate double bond is formed in the hydrocarbon main chain. Therefore, it is considered that many luminescent substances with PL maximum at different wavelengths form depending on the length of the chain with the conjugated double bonds and their further formation mechanism is complicated.

For CdS/SPS, PS and SPS films, the SFS intensity at delay time zero under the excitation pulse intensity of ca. 13 mW was plotted for total exposure time for the repetitional measurements in Fig. 7. As seen from the figure, the appearance of PL from a CdS/SPS film was faster than that from SPS and PS films which are matrices. For a CdS/SPS film, SFS was already observed at delay time zero at the first measurement. The sample films were exposed to the excitation pulse for a few minutes before the delay time zero and consequently luminescent substances were formed before delay time zero owing to the particularity of PL Up-C method. That may be a reason why the SFS signal was observed even at delay time zero for the CdS/SPS film. Namely, it is considered that the luminescent substances are rapidly formed from matrices by the reaction of matrices with electrons and/or holes generated by one-photon absorption of the excitation pulse by CdS nanoparticles in a CdS/SPS film before delay time zero or by the heat generated instantly by non-radiative recombination of their carriers and consequently a large SFS was observed even at delay time zero at the first measurement. However, SFS was hardly observed at delay time zero at the first measurement for SPS and PS films in which the rate of the formation of the luminescent substances was probably slower compared to that for a CdS/SPS film due to the absence of CdS nanoparticles. The growth and decay rates of SFS for a SPS film are somewhat larger than those for a PS film. Although a possibility of the influence due to the difference in morphology between SPS and PS films cannot be ruled out, there is the possibility that the formation of the luminescent substances and quenching of their PL in a SPS film were influenced by the introduced sulfonyl group.

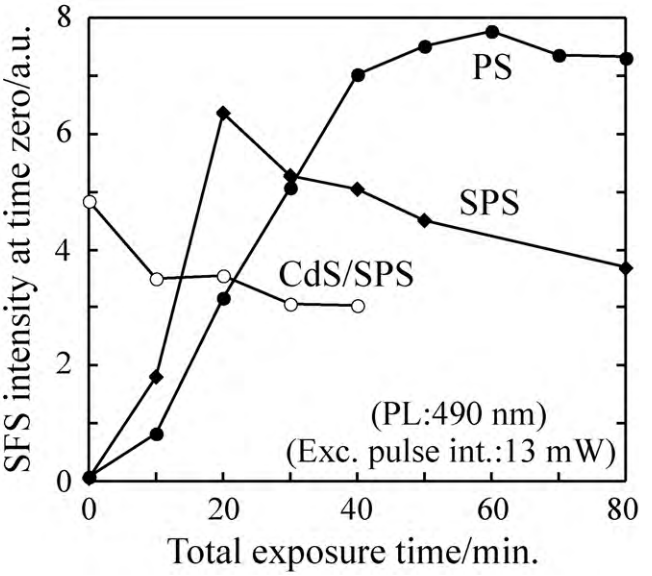


Fig. 7. Relationship between SFS intensity at time zero vs. total exposure time of the excitation pulse. Note that the films were exposed to the excitation pulse for a few minutes at total exposure time zero owing to the particularity of PL Up-C method.

On the other hand, the maximum of the SFS intensity for a CdS/SPS film is smaller than those for SPS and PS films and its further decay begins at early exposure time than those for SPS and PS. It may be suggested that the existence of CdS nanoparticles enhances the influence of the femtosecond laser pulse to the formation and decay dynamics of luminescent substances in their films.

In order to confirm exactly the growth profile of SFS for a CdS/SPS film, the SFS intensity at delay time zero was recorded in real-time

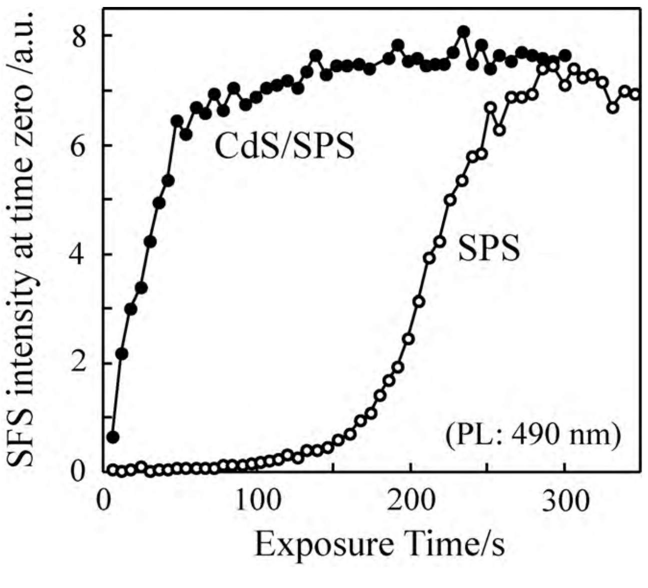


Fig. 8. Exposure time dependence of SFS intensity at time zero for CdS/SPS and SPS films under the 13 mW femtosecond pulse irradiation.

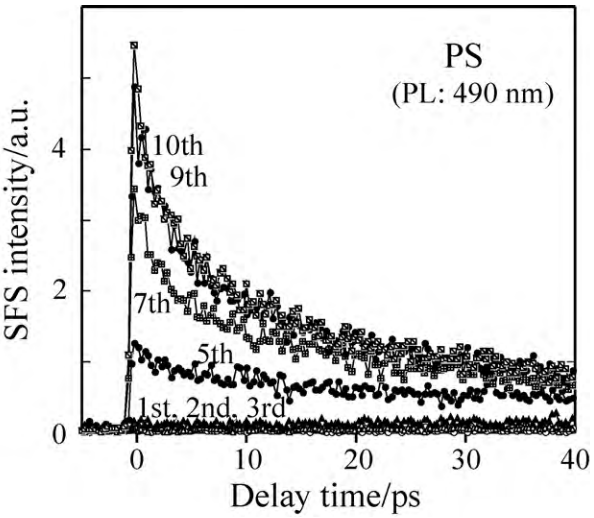


Fig. 9. SFS time profiles of a PS film obtained by the repititional PL up conversion measurements using the 5 mW pulse excitation. For clarify odd numbered experimental data were cited except for 2nd and 10th data, although the measurements were carried out 10 times successively.

from immediately after the irradiation of the excitation pulse under the delay stage fixed at delay time zero. The result was shown together with that for a SPS film in Fig. 8. For a CdS/SPS film, the SFS intensity reached almost at the maximum for ca. 1 min after irradiation of the excitation pulse. The time that the SFS reached at the maximum was shorter than that for a SPS film about five times. It also suggests that CdS nanoparticles existing in the film is contributing significantly to the formation of luminescent substances.

3.3.2. *Influence of the excitation pulse intensity*

In order to clarify the influence of the excitation pulse intensity on the growth and decay behavior of the SFS for PS and SPS films, the repetitional PL Up-C measurements were also carried out at 490 nm (PL observation wavelength) under the condition of the 5 mW excitation pulse intensity. The result for a PS film in the long time range was shown in Fig. 9.

The figure shows that, although SFS was not observed until the second time measurement, it developed at the third time measurement and then grew up gradually until ninth time measurement by repeating the measurements. The decay part of the SFS time profile became clear with increasing the repetition number. The growth of SFS slowed evidently by dropping the excitation pulse intensity. It seems that both the intensity and the time profile of SFS are nearly stable but do not reach fully to the maximum intensity at tenth measurement though the measurement was done only to tenth time in the present study. Therefore, it would take more than ca. 180 min until the concentration of luminescent substances was reached completely at the maximum in a PS film under the condition of the 5 mW excitation pulse intensity. It turned out that the rate of the formation of luminescent substances in a PS film was slower than that for the excitation with ca. 13 mW about five times by dropping the excitation pulse intensity to ca.5 mW. Probably, it is due to that probability of two-photon absorption of the excitation pulse by a PS film becomes greater together with increasing the excitation pulse energy. Similar excitation pulse intensity dependence was observed for a SPS film except for the time that reaches maximum is shorter than that for a PS film. However, it is not provided yet whether the formation of luminescent substances by multiphoton excitation of PS occurs via photochemical process concerning excited states of PS or via thermal process by a local rise in a temperature by two-photon absorption.

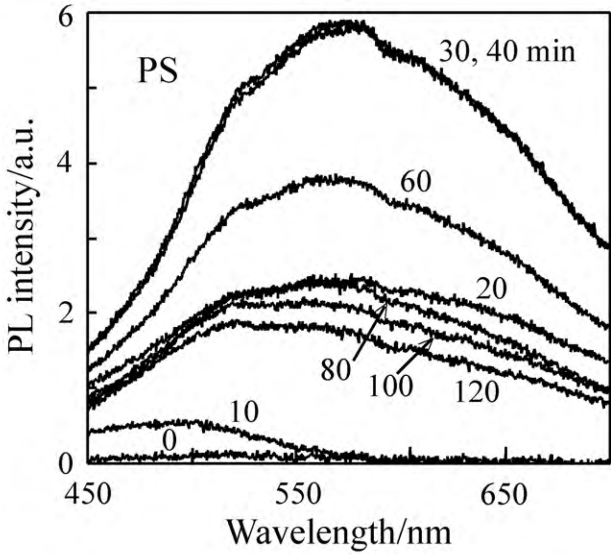


Fig. 10. Exposure time dependence of PL spectrum of a PS film measured by the 396 nm pulse excitation using a CCD detector. Exposure and excitation pulse intensities were 13 mW the same as the excitation condition in PL Up-C measurements. The times in the figure denote the exposure time to the 396 nm femtosecond pulse.

3.4. *Exposure time dependence of PL spectrum of a PS film recorded by the femtosecond laser pulse excitation*

In order to observe the change in PL spectrum of a PS film by exposing it to the excitation pulse in the repetitional PL Up-C measurements, its PL spectrum was measured repeatedly by using a CCD detector under the excitation condition that was identical with the repetitional PL Up-C measurements. The PL spectra of a PS film at various exposure times are shown in Fig. 10. As shown in the figure, a PL spectrum of a PS film in the 450–700 nm range increased with increasing the exposure time to the excitation pulse with red-shift of its PL maximum. The evolution of PL from a PS film occurs evidently by exposing it to the femtosecond excitation pulse for a long time. Its tendency is almost consistent with the above results of PL Up-C measurements for a PS film in which the relatively stable luminescent substances are generated by photo- and/or thermal-decomposition initiated by the multiphoton absorption by a PS film. Furthermore, the tendency that its PL intensity decreases by the femtosecond laser pulse irradiation for a long time is similar to the exposure time dependence of the SFS intensity for a PS film in the PL Up-C measurements. As the reason for that the intensities of PL and SFS for a PS film decrease by exposing it to a femtosecond laser pulse for a long time, it may be considered that decomposition of the formed luminescent substances or ablation of a PS matrix occur by the excitation laser pulse. In the latter case, the incident of the excitation pulse or the passage of the emitted PL in the film may be interfered by its morphological change by the ablation. However, experimental evidences for the decomposition of the luminescent substances and the morphological change of a PS film have not yet been obtained thus far.

3.5. *Mechanism of PL development from PS and CdS/SPS films*

According to Kaczmarek et al. [13], photodegradation of PS by UV (254 nm) light is a result of excitation of its phenyl group and the main primary reaction is elimination of a hydrogen atom from carbon at the α-position to the phenyl group and then the reaction proceeds by the reaction of the formed radical with molecular oxygen. It is considered that ordinary one-photon absorption does not occur in PS and SPS films even by irradiation with a 396 nm laser pulse used as the excitation pulse in the present PL Up-C measurements because PS and SPS do not have any absorption bands in the wavelength range longer than ca. 300 nm [1]. However, as SFS was developed for PS and SPS films, which did not contain CdS nanoparticles, by repeating PL Up-C measurements for the same position of identical films in the present study, it was proven that the luminescent substances were evidently formed from PS by the 396 nm excitation pulse. This result suggests that PS and SPS absorb multiphoton (probably two photon) simultaneously by the excitation with the 396 nm femtosecond laser pulse.

Although there is the possibility that PS degradation occurs via photochemical formation of radicals as mentioned above, there is another possibility that the reaction occurs via thermal processes [11] by elevating temperature of the films due to absorption of the excitation pulse. The experimental evidence that judges the formation process of the luminescent substances under the femtosecond laser pulse excitation not yet been obtained.

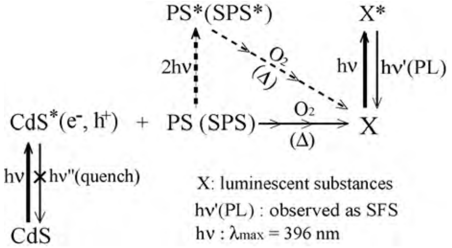
As a CdS/SPS film contains CdS nanoparticles with the absorption band in the wavelength region shorter than ca. 450 nm as shown in Fig. 2, it is considered that the formation of luminescent substances occurs mainly via the degradation of PS due to one-photon absorption of the excitation pulse by CdS nanoparticles rather than the degradation route owing to multiphoton absorption of the excitation pulse by PS itself. One of the degradation routes of PS in CdS/SPS process is a thermal process in which the degradation of PS is induced by the heat due to non-radiative recombination of the photo-generated electron and hole in CdS nanoparticles. Another route is photocatalytic process in which the photo-generated hole and/or electron are directly concerned in the degradation of PS. Whether the luminescent substances in a CdS/SPS film had formed by which process of photocatalytic and thermal were also not clarified.

As described in Section 3.2.2, however, it seems that the contribution of PL of CdS to SFS of a CdS/SPS film is very small because the development process of SFS from a CdS/SPS film slowed down and then was observed clearly when the excitation pulse intensity was dropped. Therefore, CdS nanoparticles in a CdS/SPS film will solely accelerate the formation of luminescence substances from SPS matrix (PS main part).

As shown in Table 1, the lifetimes (τ_1 and τ_2) and the ratios of pre-exponential factors (A_2/A_1) for SFS (therefore PL) were estimated by curve fitting of the decay part of SFS time profiles for three kinds of films. The lifetimes (τ_1 and τ_2) and the ratios of pre-exponential factors increased approximately in order of SPS < CdS/SPS < PS at any PL wavelength. However, there are no difference between SPS and CdS/SPS for the values of τ_1 at 520 nm and A_2/A_1 at 460 nm. These results suggest that different luminescent substances might be formed for each film. However, as the difference between PS and SPS films is only whether it has sulfonyl group or not, it is difficult to consider that the different luminescent substances have been formed in both films due to the above difference. It may be natural to consider that the formed luminescent substances are almost similar in both PS and SPS films and sulfonyl group in a SPS film maybe act as a quencher for the PL.

For any film, the lifetime and ratio of SFS (PL) components depend on the PL observation wavelength as shown in Table 1. If one luminescent substance only is formed in a film, there is no difference in the decay dynamics factors of SFS among the PL observation wavelength in the identical film. Therefore, it is considered that several luminescent substances were formed in a film. And further the lifetime of SFS increases with increasing the PL observation wavelength in any films.

According to the report in Ref. [13], various substances are formed from PS by its photolysis with a UV light. Namely, if PS absorbs a UV light, radicals are formed by elimination of a hydrogen atom from the carbon adjoining the phenyl group of PS and subsequently, benzoic acid, acetophenone, methybenzonate, styrene, stilbene, double bonds in main chain, etc. are formed by reaction of the radical with oxygen. Although stilbene among these has intense PL around 370 nm, it seems that SFS corresponding to PL in wavelength range longer than 460 nm, which was observed in the present study, is not due to stilbene because the PL observation wavelength is in fairly longer wavelength region. It seems that the PL observed as SFS in the present study is attributable to several luminescent substances with long conjugated double bonds containing the phenyl group and the double bonds of PS main chain which were formed by repetitional irradiation of the excitation femtosecond pulse. Therefore, the luminescent substances have the PL maximum in visible region which can be excited with a single photon of the 396 nm pulse. It is considered that the presence of several luminescent substances is due to the difference in the number of the conjugated double bonds. It is for sure that PL is emitted from luminescent substances by one-photon excitation with the 396 nm pulse because it is experimentally confirmed that the SFS intensity at delay time zero is linearly proportional to the excitation pulse intensity which will be reported elsewhere.



Scheme 1. The proposed mechanism for the development of PL from a PS (or SPS) film with and without CdS nanoparticles.

4. Conclusion

The proposed mechanism for the formation of luminescent substance and the SFS development for PS and CdS/SPS films is shown in Scheme 1. The experimental results in the present study can be explained as shown in the scheme. Namely, for PS and SPS films, the excited state of PS is generated by absorbing multiphotons (probably two photons) of the 396 nm excitation pulse and subsequently relatively stable luminescent substances are formed from the excited state of PS directly or via thermal-reactions after its non-radiative deactivation. The generated luminescent substances were excited by one-photon absorption of the excitation pulse and their PL in visible region was observed as SFS in the PL Up-C measurements. In the case of a CdS/SPS film, CdS nanoparticles are entirely contributed to the formation of the luminescent substances from SPS matrix (PS main part) by the reaction of electrons and/or holes generated by one-photon absorption of the excitation pulse with PS or by thermal oxidative decomposition of PS by heat generated by non-radiative recombination of the carriers. At present, the additional study on the PL development process in their films is in progress.

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