

## 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  $\pi$  bonds with a PS main polymer chain that absorbs the excitation femtosecond pulse ( $\lambda_{\text{max}} = 396 \text{ nm}$ ).

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### 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 ( $\lambda_{\text{max}} = 396 \text{ nm}$ ) 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-dichloroethane solution of SPS with stirring. And further stirring at 70 °C, a DMF solution of thioacetamide (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 ( $\lambda_{\text{max}} = 792 \text{ nm}$ ) 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.

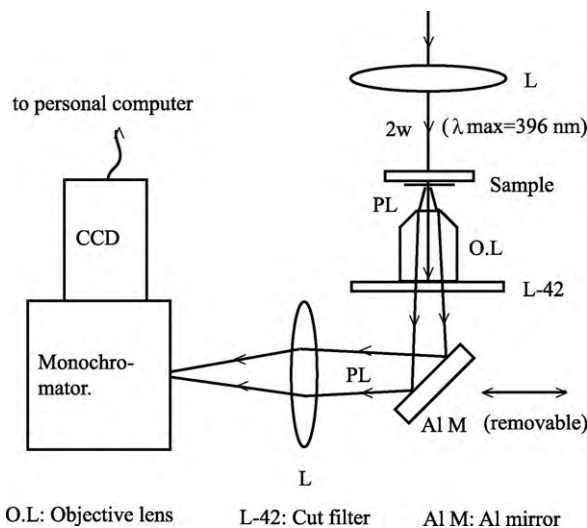


Fig. 1. Schematic representation of a set-up for PL measurement by the femtosecond pulse excitation.

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 monochromator 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  $-1200 \text{ V}$ . 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.).

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