

Laser-Irradiation Effect on Poly(vinyl alcohol) Films Doped with Nanometer-Sized CdS Particles: Ablation and Third-Harmonic Generation

YOSHIO NOSAKA,* KAZUNORI TANAKA,† and NOBUYUKI FUJII

Department of Chemistry, Nagaoka University of Technology, Nagaoka 940-21, Japan

SYNOPSIS

Ultrasmall CdS particles, whose average size was controlled by thiols to range from 2 to 4 nm, were embedded in poly(vinyl alcohol) films. Shift of the fluorescence peak associates with the shift of the absorption threshold of the films, and the fluorescence intensity increases with the decrease in the size of CdS. Laser ablation at 308 nm was investigated by monitoring the emission spectra. Third-harmonic generation was measured for various sizes of CdS particles, and the optical nonlinearity in the nonresonance region was found to remain almost constant in the diameter range studied. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

Nanometer-sized semiconductor particles have been paid special attention because of their interesting size-dependent properties such as third-order optical nonlinearity.¹⁻³ To apply the semiconductor clusters to optoelectronic devices, transparent supporting materials should be employed. One candidate of such materials is polymer films. Polystyrene,⁴ poly(acrylonitrile-*co*-styrene),⁵ and Nafion^{6,7} were reported as polymers to embed CdS semiconductor clusters. We prepared a poly(vinyl alcohol) (PVA) film doped with methylviologen and ultrasmall CdS particles and tested it as a photochromic device.⁸ A method to control the size of CdS in solution using thiols was also reported.⁹ In the present study, several sizes of CdS particles ranging from 2 to 4 nm were embedded in PVA films and their photophysical properties were evaluated.

When polymer films are applied to optoelectronic devices, micropatterning of the materials is technologically important. Such a micropatterning can be achieved by UV-laser ablation.¹⁰ Masuhara et al.¹¹ and Srinivasan and Braren¹² reported that doping of polymer films with dyes promotes the ablation

sensitivity of the polymer. Being doped with nanometer-sized CdS particles, polymer films may become sensitive to the ablation, because the dopant absorbs the laser light as effectively as it does the dye. In this study, UV-laser ablation of the CdS-doped PVA films was investigated by measuring emission spectra.

Cheng et al.¹³ reported a decrease in third-order susceptibility of CdS clusters with decreasing size. They measured the intensity of third-harmonic generation (THG) for thiophenolate-capped CdS clusters having average diameters of 1.5 and 3.0 nm. However, they used different solvents for the comparison and, furthermore, the mole fraction of two samples differed by a factor of almost two orders of magnitude. Then, in the present study, size dependence on the THG intensity was investigated for nanometer-sized CdS particles embedded in PVA films.

MATERIALS AND METHODS

Cadmium chloride (CdCl_2), sodium sulfide ($\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$), and 2-mercaptoethanol (RSH) (Nacalai Tesque Ltd.) were used without further purification. Poly(vinyl alcohol) (PVA, DP 2000, 99–100% saponified, Nacalai Tesque) was treated with alkaline solution of NaBH_4 in order to reduce

* To whom correspondence should be addressed.

† Present address: Film Laboratory, Teijin Co., Sagamihara.

carbonyl groups in the polymer, followed by neutralization and washing.

Sample films were prepared as follows: One milliliter aqueous solution of 10 mM CdCl₂ was mixed with an aqueous solution of PVA (0.5 mg/10 mL). The desired amount of RSH as 3% aqueous solution was added to the polymer solution followed by stirring for several minutes. Then, 1 mL aqueous solution of 10 mM Na₂S was added to the mixture in the dark. The resultant solution of PVA containing CdS was cast on a Petri dish and dried at 40°C for more than 1 day at normal pressure. The film was peeled from the Petri dish and dried further at 40 mmHg for 1 day and under vacuum for 6 h. Thickness of the films was about 50 μm.

Absorption and fluorescence spectra were measured with a Hitachi U-3210 spectrophotometer and a Hitachi 850 fluorescence spectrophotometer, respectively, at room temperature (about 293 K) and at liquid-nitrogen temperature (77 K). Scanning electron microscopic (SEM) observation was performed with a JEOL JXA-733 microprobe analyzer.

Time-resolved fluorescence spectra and ablation spectra were measured with a spectrometric multichannel analyzer (SMA) equipped with an HR-320 spectrometer (Jobin Yvon) and an IRY-700N/RB multichannel detector (Princeton Instruments). The irradiation was performed with a XeCl laser (Lambda Physik, EMG-202MSC), which produced up to 150 mJ at 308 nm in a 30 ns (fwhm) pulse. The intensity of the laser beam was attenuated by using stainless steel mesh filters. The laser beam

passed a convex lens and irradiated an area of 0.5 mm diameter on the sample film. The light emitted to a 45° direction from the sample was gathered by a convex lens into the glass-fiber probe of the SMA. The sample film was mounted on a holder that can shift the film at a constant rate to avoid repeated irradiation on the same location. The emission intensity was integrated for a certain width of the time gate starting from a certain delay time after the peak of the laser pulse. The output signal of the SMA was accumulated and averaged for 10 laser shots.

As for THG measurements, the irradiation source was an Nd:YAG pulse laser (Spectron SL-803), which produced a 1.064 μm beam of 850 mJ in a 20 ns pulse. The laser beam was loosely focused by a convex lens ($f = 300$ mm) and irradiated the sample film. The transmitted light passed through a CuSO₄ solution filter and a band-pass glass filter (Toshiba UV-D36C), and then the light intensity was measured by another SMA equipped with an IRY-512G multichannel detector (Princeton Instruments) and an MC-25N1 spectrometer (Ritsu Ohyo Kogaku).

RESULTS AND DISCUSSION

Size Dependence of Fluorescence Characteristics

Figure 1 shows the absorption spectra of CdS-doped PVA films prepared with various amounts of RSH. The absorption threshold varied as a function of mole ratio (RSH/CdS) as observed in the similar

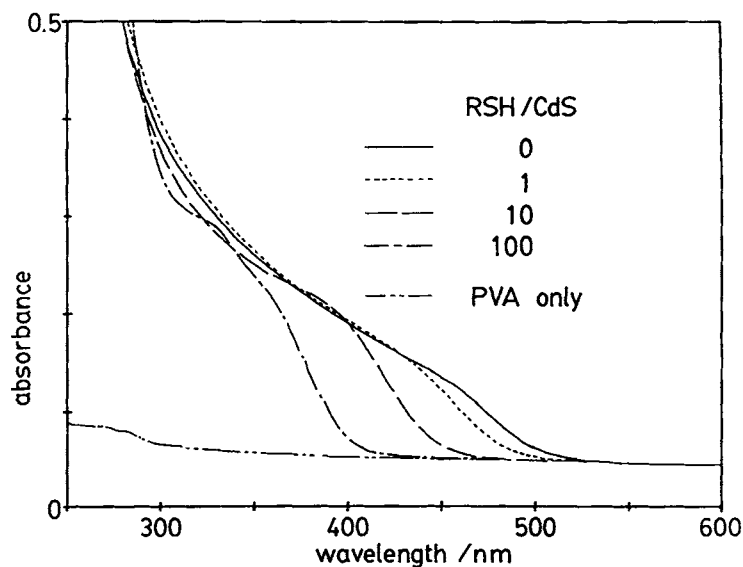


Figure 1 Absorption spectra of PVA films doped with nanometer-sized CdS particles prepared with various amounts of mercaptoethanol (RSH).

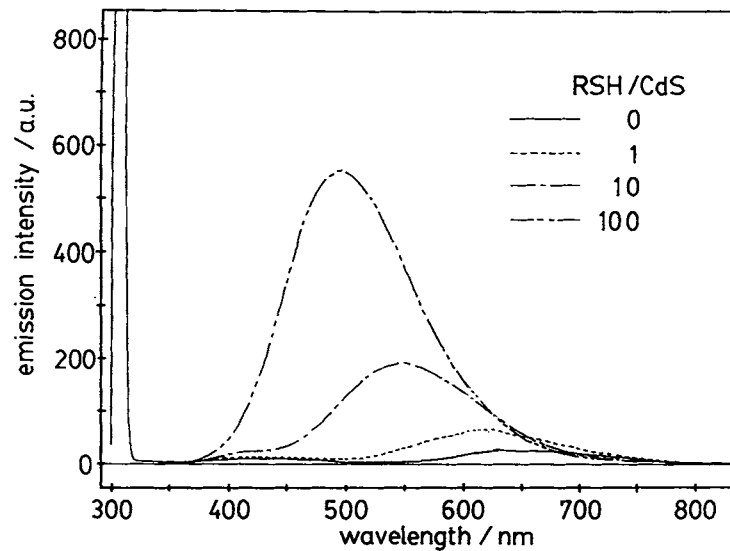


Figure 2 Fluorescence spectra of PVA films doped with nanometer-sized CdS particles, measured at 77 K and 308 nm excitation.

study on CdS in aqueous solution.⁹ The average diameter of the CdS embedded in PVA films is estimated from the threshold wavelength.¹⁴ The diameter ranges from 2 to 4 nm, corresponding to the absorption threshold of 410–500 nm.

Figure 2 represents fluorescence spectra of the CdS-doped PVA films at 77 K. The fluorescence intensity increases with the addition of RSH. In a separate experiment, fluorescence intensity did not increase by adding RSH after the CdS formation, suggesting that the surface complexation with RSH is not responsible for the increase in the CdS fluorescence intensity. Thus, the increase in the fluorescence intensity is based on the decrease in the diameter of the CdS particles. At room temperature, the fluorescence intensity becomes significantly small, indicating that the multiphonon-induced radiationless transition dominates in the deactivation process, as clearly demonstrated for CdS-doped Nafion films.¹⁵

Another observation in Figure 2 is that the peak in the spectra shifts to a shorter wavelength with the increase in the amount of RSH. This observation indicates that the emission level is shifted by the change in the size of CdS. The energies at the emission peak are plotted in Figure 3 as a function of the absorption threshold. For many other CdS/PVA films prepared with various amounts of RSH, fluorescence spectra were measured at two different temperatures, and the energy levels are also plotted in Figure 3. The linear feature between the absorption threshold and the emission peak shows that the emissive levels are closely correlated with the band-

gap levels of the semiconductor microcrystals. The emission peak differs from the absorption threshold by more than 0.6 eV. This difference indicates that the emission is based on the tunneling recombination of shallowly trapped carriers.¹⁶ The carrier pairs

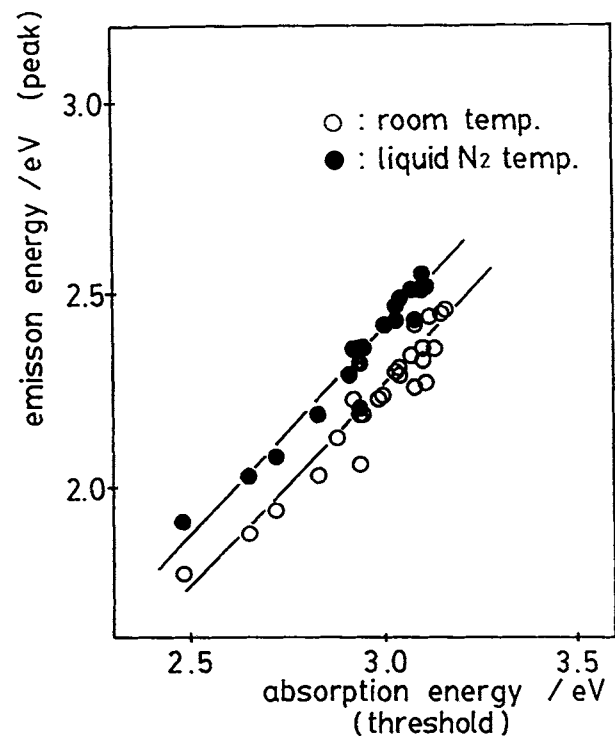


Figure 3 Relationship between absorption threshold energy and emission energy measured at two different temperatures.

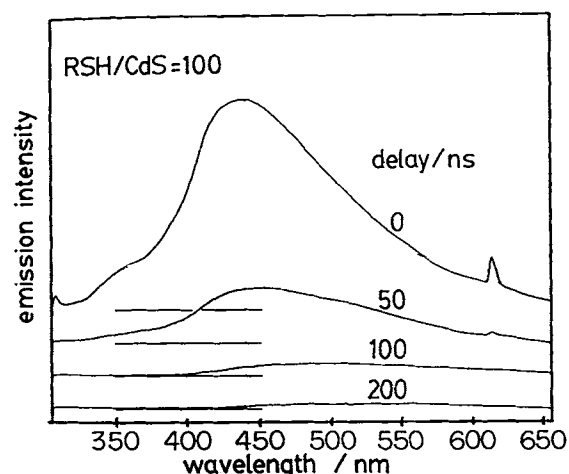


Figure 4 Time-resolved emission spectra of CdS/PVA film. Emission intensity was integrated for 30 ns after the delay time indicated. Fluence of 308 nm laser beam: 3 mJ/cm^2 .

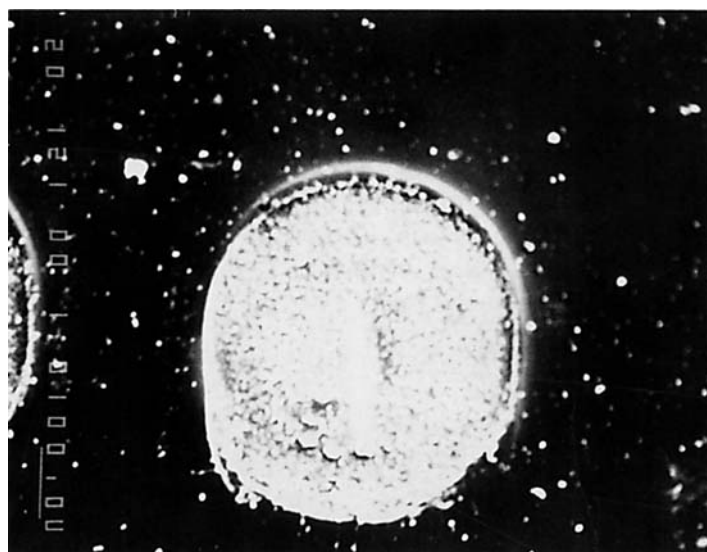
radiate a higher energy and decay faster, the closer they are.¹⁶ Since the carrier pairs are confined in a CdS particle, the decrease in the particle size provides the increase in the rate of the radiative decay. This mechanism explains the observation in Figure

2, where the fluorescence intensity increases with the decrease in size.

Figure 4 shows time-resolved emission spectra of CdS-doped PVA films. An intense broad luminescence peak at 438 nm appears immediately after the laser pulse and it decays in 100 ns. The peak of the emission spectra shifts with time to a longer wavelength and reached 500 nm at 100 ns after the laser pulse. The transient spectrum observed at this delay time corresponds to the stationary recorded fluorescence spectrum in Figure 2. The observation that the decay is faster at a shorter wavelength can be explained by the properties of radiative tunneling decay described above.

Emission Spectra on Laser Ablation

When the 308 nm laser pulse with several hundred mJ/cm^2 irradiates a CdS-doped PVA film, surface etching was observed. The emission spectra observed in the ablation experiments are similar to those in Figure 4 at each delay time, and the intensity is proportional to the fluence up to 1 J/cm^2 . Above this fluence, the emission intensity levels off, because the rate of nonradiative decay increases by local heating. Another likely reason is the decrease in the



100 μm

Figure 5 SEM photograph of the surface of a CdS-doped PVA film (RSH/CdS = 100) irradiated by the 308 nm laser at about 5 J/cm^2 in the air. The white stacks are polymer deposit that was not fully ablated.

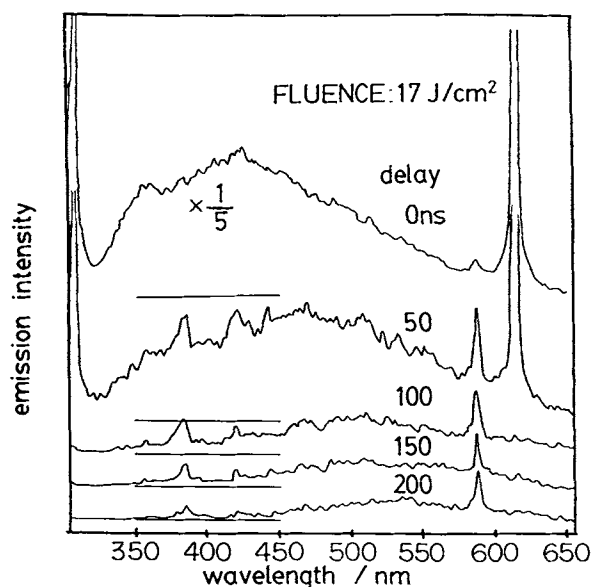


Figure 6 Time-resolved emission spectra of ablated CdS/PVA film (RSH/CdS = 100). Emission intensity was integrated for 30 ns after the delay time indicated. Fluence of 308 nm laser beam: 17 J/cm^2 .

absorbance of CdS by transient band saturation, i.e., transient bleaching.

Figure 5 is an SEM photograph of the etched surface of the film. On the bottom of the etch pits, polymer grains of about $10 \mu\text{m}$ in diameter are observed. For the intention of micropatterning, the conditions of ablation, such as wavelength, fluence, and atmosphere, should be changed to avoid the adhesion of the grains. Below the laser fluence at 5 J/cm^2 , the emission spectrum is attributed to only CdS.

Other emission lines were observed when the laser fluence was as large as 15 J/cm^2 . At this fluence, etching depth is greater than the film thickness of about $50 \mu\text{m}$, i.e., a hole through the film was observed. Optical-microscopic observations revealed that yellow CdS powders, whose average size was the order of $1 \mu\text{m}$, adhered to the film around the hole.

Figure 6 shows the time-resolved emission spectra observed when a 17 J/cm^2 laser pulse irradiates a CdS/PVA film prepared with RSH. Some new peaks appear at 50 ns after the pulse and at longer delay times. The other broad emission is attributed to CdS, as shown in Figure 4.

Figure 7 is the emission spectra at 150 ns after the pulse measured for CdS/PVA films prepared without RSH. Here, CdS emission is very small because of the larger particles as described above, and then the new emission lines associated with the ablation are clearly observed. Furthermore, the intensity of the emission lines itself increases with the particle size, because the contribution of the non-radiative thermal decay to the deactivation processes increases relatively to the radiative tunneling decay as stated above. The dotted line in Figure 7 is the spectrum measured in an argon atmosphere. The intensity of the two emission lines at 359 and 387 nm almost disappears in the argon atmosphere. Some emission lines show a parallel feature to that observed at the ablation of polyimide¹⁷ and poly(methyl methacrylate)¹⁰ films. The two peaks at 359 and 387 nm are attributed to the CN radical, where the nitrogen atom originates from the air. Three peaks at 437, 471, and 513 nm are the emission

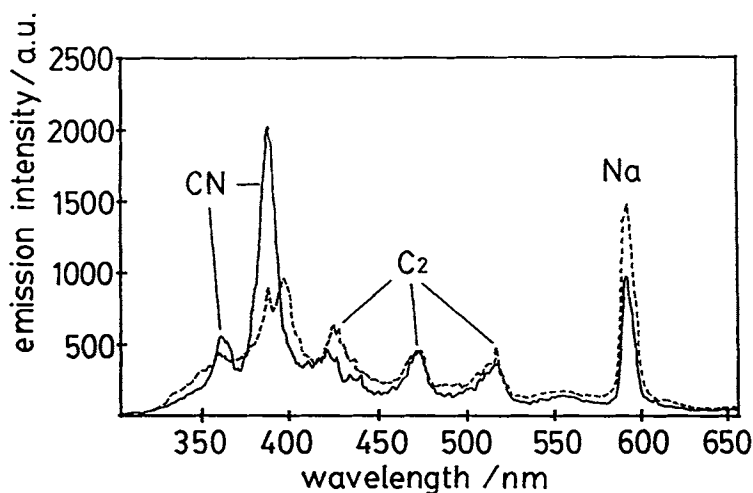


Figure 7 Emission spectra of ablated CdS/PVA film (RSH/CdS = 0). Emission intensity was integrated for 100 ns after the delay of 150 ns. Fluence of 308 nm laser beam: 15 J/cm^2 .

of C_2 radical. Large emission at 589 nm is assigned to the potassium atom, which originates from the Na_2S of the reactant. This emission line is also contributed by the potassium impurity in PVA, because this band could be observed when a PVA film was repeatedly exposed by the laser pulse. The potassium impurity is probably incorporated into PVA on the reduction with $NaBH_4$ and on the saponification at the manufacturer.

When the powder of bulk CdS was ablated by the laser, emission peaks of the cadmium atom were observed at 347 and 361 nm. However, for CdS-doped PVA films, no peaks were observed at these wavelengths. Although the laser light is absorbed by only CdS for both cases, the CdS in the PVA film absorbs energy at a larger volume than does the bulk CdS. Then, the energy can disperse to the matrix polymer, which is thermally decomposed. Since CdS has a higher decomposition temperature than does PVA, the CdS clusters aggregate, forming powders as described above, instead of being ablated.

Third-Harmonic Generation

Evidence for third-order optical nonlinearity is the third-harmonic generation (THG). Cheng et al.¹³ reported THG from 1.91 to 0.64 μm using thiophenolate-capped CdS clusters in solution. They investigated the size effect by comparing the data at different molecular fractions and in different sol-

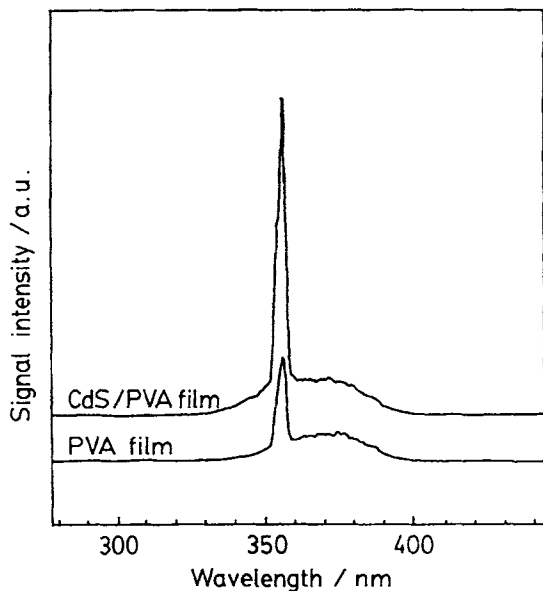


Figure 8 Spectra of the generated third harmonics of 1.06 μm light by CdS-doped PVA film and PVA film (as a reference).

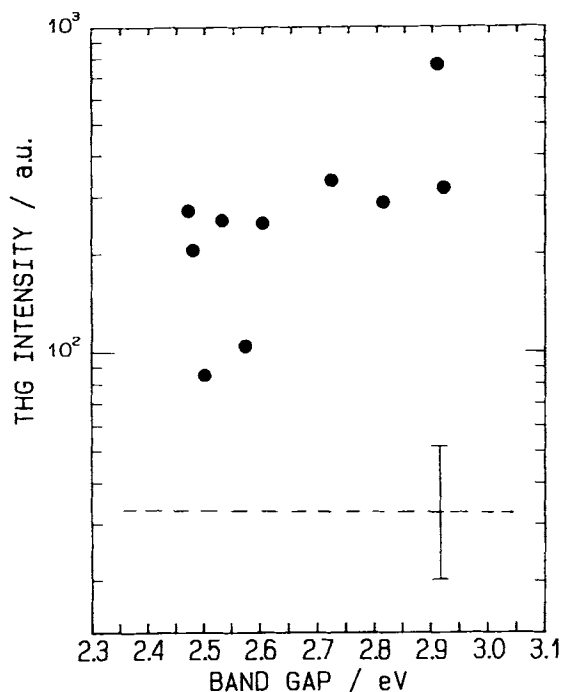


Figure 9 Light intensity of the generated third harmonics (THG) by CdS-doped PVA films as a function of the absorption-threshold energy. THG intensity of PVA films without CdS is shown by dashed line with experimental distribution.

vents. Then, we checked for THG at the same molecular fraction and in the same matrix using the films described above.

When 1.064 μm light was irradiated on CdS-doped PVA films, a spectral line at 355 nm of the third harmonics was observed, as shown in Figure 8. Although third harmonics is observed for PVA films without CdS, the intensity of THG for CdS-doped PVA films is significantly large. THG intensities were measured for several CdS-doped PVA films having different absorption thresholds. Since the CdS-doped PVA films absorb the 355 nm light, the observed light intensity was corrected by multiplying the following factor:

$$2.303A/(1 - 10^{-A})d \quad (1)$$

where A and d represent the absorbance at 355 nm (0.17–0.48) and the thickness (30–73 μm) of the films, respectively. The corrected THG intensity was plotted in Figure 9. Although the data scatter to some extent, the THG intensity increases slightly with the increase in the band-gap energy, i.e., with the decrease in the particle size. This observation does not support the size dependence reported,¹³

where the nonlinearity decreases with the decrease in the size of CdS. Since the third-order nonlinearity in the resonance region is expected to increase with the decrease in the size,¹⁸ the slight increase observed in Figure 9 may be attributed to the resonance effect. In this experiment, absorbing the third harmonics means that the energy of the third harmonics closes to the resonance energy. Although strict THG measurements should be performed in a complete nonresonance region, the present observation suggests that nonresonant optical nonlinearity does not change much for CdS having diameters ranging from 2 to 4 nm.

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