

Quantitative Analysis of the Photodegradation of Emitting CdTe Nanocrystals Dispersed in Glass Films

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CdTe nanocrystals (NCs, green- and red-emitting) prepared by an aqueous method were embedded into transparent glass films (15–20 μm thick) using a sol–gel method. Photodegradation of the NCs in the films due to UV irradiation (365 nm) was investigated quantitatively by measuring the PL efficiency as a function of the irradiation time for various irradiation intensities at several temperatures. Since CdTe NCs prepared by an aqueous method incorporate sulfur atoms from the surfactant (thioglycolic acid) during prolonged reflux in an alkaline region, the surface of red-emitting NCs (3.9 nm Φ) is much more sulfur rich than that of green-emitting ones (2.6 nm Φ), as previously reported. Due to this composition difference, the degradation behaviors of the two types of NCs differ significantly. The photodegradation of green-emitting glass films depended linearly on the irradiation intensity, whereas that of red-emitting ones showed a quadratic dependence. The activation energies of the photodegradation for both types of films were similar, 304 ± 9 and 288 ± 7 meV/particle, respectively. The NCs in the film were more than 2 orders of magnitude more robust than those in colloidal solutions. Comparison of the degradation of the glass films in air and in an Ar atmosphere revealed that the main mechanism of the photodegradation of the green-emitting NCs was oxidization from the first electronically excited state. The mechanism of the red-emitting NCs was not oxidization but a surface change probably related to a surfactant reaction.

I. Introduction

Semiconductor nanocrystals (NCs) with a high photoluminescence (PL) efficiency have shown great potential in photonic crystals,^{1–3} light-emitting devices,⁴ and biological labels^{5,6} because their band gap is a function of crystal size and can thus be tailored. Since a large portion of the atoms are located on or near their surfaces, surface functionality is one of their most attractive properties. Talapin et al. demonstrated that NCs with a smooth surface have the highest PL efficiency.^{7,8} Gaponik et al. reported that the photostability of mercaptoethylamine-capped CdTe NCs is lower than that of thioglycolic acid (TGA)-capped ones because of the difference in their surface structures.⁹ Together with these surface structures, UV irradiation has been shown to enhance PL efficiency by creating a passivating layer on the surface. Bao et al. studied such an enhancement effect for water-soluble CdTe NCs in N₂ saturated solution.¹⁰ Bol and Meijerink found a significant increase in the PL efficiency of ZnS:Mn NCs in polymers following UV irradiation.¹¹ However, UV irradiation degrades the NCs as well, which is crucially important for their application. Even though the mechanisms should be closely related to UV enhancement, there has been little research in this direction. To our knowledge, qualitative results have been reported only for CdSe NCs in water,¹² CdSe NCs in toluene, CdTe NCs in water,⁹ silica-coated CdSe NCs in a buffer solution,¹³ and silica-coated CdS in solution¹⁴ at room temperature. There have been fewer reports on degradation in solid matrixes, where molecule mobility is greatly restricted. The mechanism of this degradation is highly important for applications.

We recently fabricated glass phosphor with embedded aqueously prepared semiconductor NCs (CdTe) using a sol–gel method in both bulk^{15,16} and powder forms.¹⁷ Glass has several superior properties such as high transparency, robustness against atmospheric attack, and UV irradiation compared with polymers. Thin-film luminescent devices made of glass should thus be of great technological interest.

We have now fabricated transparent glass films (15–20 μm thick) by modifying our previously reported method for preparing bulk phosphor.¹⁵ The photodegradation of these films was investigated quantitatively by measuring the PL efficiency as a function of the irradiation time and temperature for various intensities. The degradation was almost always related to the diffusion of oxygen from the surroundings. Since the prepared films were sufficiently thin and transparent, the photodegradation was homogeneous, making quantitative analysis feasible. The measured degradation greatly depended on the surface states of the NCs. We found that red-emitting CdTe NCs exhibit two-photon kinetics whereas green-emitting CdTe ones exhibit one-photon kinetics.

II. Experimental Section

A. Preparation of Glass Films. An aqueous colloidal solution of TGA-capped CdTe NCs was prepared using a procedure described in detail elsewhere.^{18,19} (The TGA molar ratio was ~ 1.25 against Cd²⁺.) The NCs in the crude colloidal solution had a PL efficiency of 30% for green and 50% for red.

A precursor sol was prepared using a method similar to one described elsewhere.¹⁵ Briefly, 10 mL of a mixture of 3-aminopropyltrimethoxysilane (APS) and methanol was prepared with

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a molar ratio of 1:50. After 2 mL of water was added, the solution was kept for 12 h under atmospheric conditions. This made the viscosity of the sol 500–1500 mPa s. The precursor sol was then obtained by adding 1.3 mL of aqueous colloidal solution containing CdTe NCs into the viscous sol.

Slide glass substrates (Matsunami, no. S9112, 76 mm × 52 mm) were immersed in a fresh aqueous solution of acid ($v/v = 1:3$, 30% $\text{H}_2\text{O}_2/98\%$ H_2SO_4) until gas evolution ceased. After being rinsed with copious amounts of water and dried, the surface-treated substrates were spin coated (3000 rpm for 40 s). The central part of the substrates (18 mm × 25 mm) was cut to obtain transparent glass film samples having a uniform thickness (15–20 μm). As previously reported,¹⁵ the PL efficiency of NCs in a colloidal solution is retained in a bulk sample (free-standing plate) when prepared in a Petri dish for 2 days. However, the quick drying of the spin coating method degraded the PL efficiency to less than that in bulk glass, as described below. Even with the low PL efficiency, the PL peak wavelength and width remained unchanged. This means the dispersion of the NCs in the film was successful. Their concentration was of the order of 10^{-5} mol/L.

B. Measurement of Photodegradation. The films were irradiated for different lengths of time using a 365-nm light from a 250-W mercury lamp (Ushio SP-7 equipped with a B-type lens on top of the fiber). A light beam with an intensity of up to 1.8 W/cm^2 was obtained when the distance between the lens and the film was 20 mm. A digital hot plate (Barnstead International, 722A-1) was used to keep the films at the desired temperature (up to 95°C). The film temperature was closely monitored using a thin ($\sim 0.1 \text{ mm}\Phi$) thermocouple. Following the irradiation, the sample was removed from the hot plate, and the absorption and PL spectra were measured at room temperature as a function of irradiation time for various irradiation intensities using two conventional spectrometers (Hitachi U-4000 and F-4500). Before each UV irradiation, we ensured that the light beam irradiated vertically toward the same spot ($\sim 5 \text{ mm}\Phi$) on the film sample. To get a flat spectral baseline, we took special care to position the sample at the same place in the spectrometer reproducibly. A blank film without NCs was prepared, and the absorption and PL spectra for that film were subtracted from those for the sample films.

To determine the activation energy of the photodegradation, we measured the irradiation-time dependence of the PL efficiencies at various temperatures from 20 to 95°C and several irradiation intensities from 190 to 840 mW/cm^2 for green-emitting films and from 0.40 to 2.0 W/cm^2 for red-emitting films.

The PL efficiencies of the CdTe NCs in sol–gel glass films were estimated in comparison with a standard dye solution (quinine in 1 N H_2SO_4 solution, 55%²⁰) having a similar optical path length and optical density. The details are described elsewhere.²¹ A 10% error bar was added to each PL efficiency based on the deviation in the calculated PL efficiency.

When testing was done in an inert atmosphere to determine the effect of oxygen, a glovebox (Miwa, DBO-1.5L, Ar atmosphere, oxygen less than 10 ppm during irradiation) was used. To prevent the generation of cracks during irradiation in Ar, the films were slowly heated to 80°C in the dark and kept at this temperature for 5 h before measurement. For the purposes of comparison, the samples for irradiation in air were also heat-treated in the same way.

III. Results and Discussion

A. Typical Examples of PL Degradation. Figure 1 shows examples of PL spectra of CdTe NCs in diluted colloidal

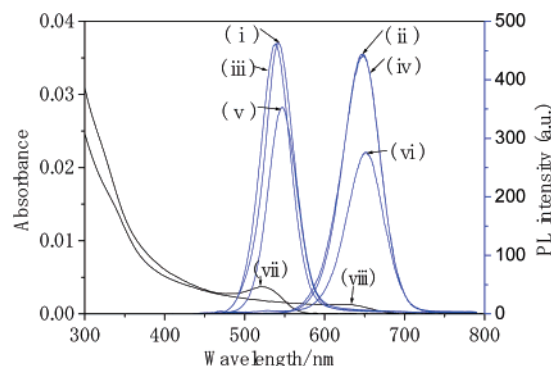


Figure 1. Examples of absorption and PL spectra of CdTe NCs in diluted colloidal solution and glass films: (i and ii) diluted colloidal solution; (iii and iv) glass film before irradiation; (v and vi) glass film after irradiation. Absorption spectra of green- and red-emitting solutions (vii and viii) are shown for comparison. The irradiation levels were 230 mW/cm^2 for 30 min for green-emitting films and 2.0 W/cm^2 for 40 min for red-emitting films at room temperature in air. The PL intensities for green- and red-emitting NCs (i–iv) are normalized for the purpose of comparison.

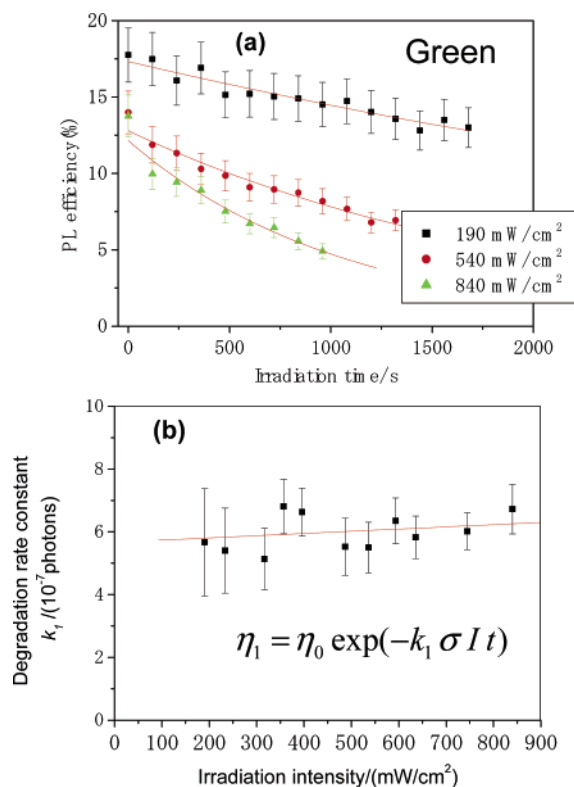


Figure 2. (a) Irradiation intensity dependence of the PL efficiency of green-emitting films at 48°C . The PL efficiency decreased with irradiation time for three different irradiation intensities. (b) Rate constant k_1 for one-photon kinetics as a function of irradiation intensity. It did not depend on irradiation intensity.

solution and glass films. The absorption spectra of the colloidal solution are shown as well for comparison. We found no change in the absorption spectra of the glass films within the irradiation energy used (up to 4.2 kJ/cm^2 for green and 22 kJ/cm^2 for red). The PL peak wavelengths were slightly red-shifted by the irradiation, for both the green- and red-emitting films.

B. Irradiation Intensity Dependences of PL Efficiency. We estimated the PL efficiencies from a spectrum shown, for example, in Figure 1. Figures 2a and 3a present some of the efficiencies thus derived and their decrease for green- and red-emitting glass films with UV irradiation at 48°C . As the

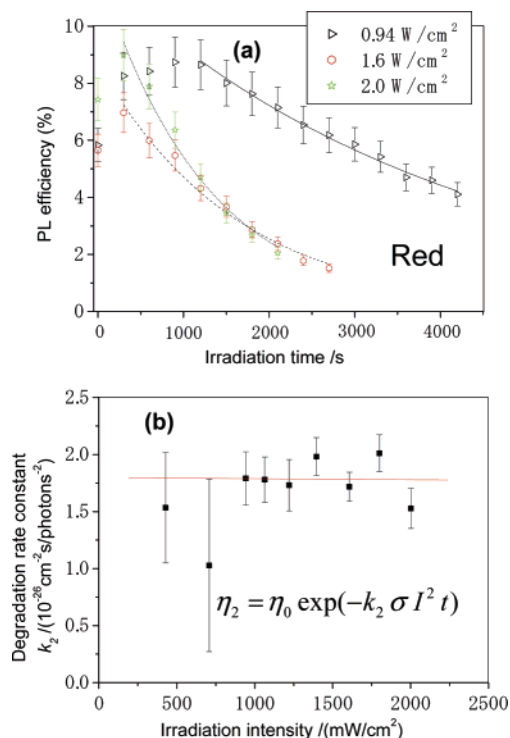


Figure 3. (a) Irradiation intensity dependence of the PL efficiency of red-emitting films at 48 °C. The PL efficiency increased and then decreased with irradiation time for three different irradiation intensities. Only the decreases were used for analysis. (b) Rate constant k_2 for two-photon kinetics as a function of irradiation intensity. It did not depend on irradiation intensity.

irradiation intensity increased, the degradation accelerated. We analyzed these efficiency decreases quantitatively.

If the concentration of CdTe NCs in glass film is M , the concentration of nanocrystals excited by irradiation I (in units of photons/(cm² s)) is given by σIM , where σ (in units of cm²) is the cross section of a single NC at 365 nm. When the NCs react and change to something else due to the excitation, the differential equation can be written using rate constant k_1 :

$$\frac{dM}{dt} = -k_1 \sigma IM \quad (1)$$

Therefore, the temporal evolution of the concentration of not-reacted CdTe is

$$M = M_0 \exp(-k_1 \sigma I t) \quad (2)$$

If we consider the concentration of emitting NCs is $M_0 \eta_1$ for a film with PL efficiency η_1 , the decrease in efficiency due to UV irradiation can be expressed using irradiation time t :

$$\eta_1 = \eta_0 \exp(-k_1 \sigma I t) \quad (3)$$

where η_0 is the efficiency before irradiation. If the degradation occurs from a level excited by two-photon absorption, eq 3 becomes

$$\eta_2 = \eta_0 \exp(-k_2 \sigma I^2 t) \quad (4)$$

where rate constant k_2 reflects the parameters of the first excited state such as the excited-state lifetime (τ) and absorption cross section toward a higher energy level (σ^*), namely, $k_2 \propto \tau \sigma^*$.

The absorption cross sections of green- and red-emitting CdTe NCs at an irradiation wavelength of 365 nm are estimated to

be $9.1 \times 10^{-16} \text{ cm}^2/\text{particle}$ (2.6 nm Φ) and $4.6 \times 10^{-15} \text{ cm}^2/\text{particle}$ (3.9 nm Φ), respectively, based on the reported extinction coefficient of the first absorption peak and its wavelength dependences.^{22,23}

The three curves in Figure 2a show examples of least-squares fitting using eq 3. The k_1 values and their errors were derived assuming a 10% error in each η value; they are plotted for a total of 11 irradiation intensities in Figure 2b. If we use a linear function ($k_1 = C_1 + B_1 I$) for the fitting in Figure 2b, the mean value of C_1 is $(5.7 \pm 0.8) \times 10^{-7}$ photons and the slope B_1 is $(1 \pm 1) \times 10^{-10}$ (photons cm²)/mW. Therefore, rate constant k_1 ($= (5.7 \pm 0.8) \times 10^{-7}$ photons) at 48 °C for one-photon kinetics does not depend on the irradiation intensity.

Although a similar analysis can be done for red-emitting films, the PL efficiency increased during the initial stage of irradiation. Therefore, we took only the latter slopes, which showed a decrease, as depicted in Figure 3a for three examples. Equation 3 does not give a constant k_1 against irradiation intensity, whereas eq 4 gives a good result, as shown in Figure 3b. The error bars in Figure 3b were derived by adding a 10% error to each η , as shown in Figure 3a. The k_2 value was invariant for a total of nine irradiation intensities. Statistical analysis gives a k_2 value of $(1.8 \pm 0.3) \times 10^{-26} \text{ (cm}^2 \text{ s)/photon}^2$ at 48 °C and a slope (intensity dependence) of $(0 \pm 0.2) \times 10^{-29} \text{ (cm}^4 \text{ s)/(photon mW)}$.

When we prepared red-emitting colloidal solution, the reflux time was several tens of hours, whereas with green-emitting solution it was less than an hour. After the lengthy reflux of red-emitting NCs in the highly alkaline region (pH 11.3), a significant number of sulfur atoms originating from the hydrolysis of TGA had been incorporated into the NC lattices,^{9,24} making the surface of the red-emitting NCs sulfur rich. The difference in kinetics originated from this surface condition.

C. Initial PL Efficiency Dependence. Unlike the bulk glass,¹⁵ the PL efficiencies of the films were not the same even when the same initial colloidal solution was used in their preparation. This is because the sol–gel reaction conditions during spin coating varied from sample to sample. Therefore, we investigated the photodegradation of samples having different initial PL efficiencies for both green- and red-emitting films. The results are shown in parts a and b of Figure 4 for green- and red-emitting films, respectively. By using the equations above, we were able to keep the reaction constants (k_1 for green-emitting NCs, k_2 for red-emitting NCs) the same within the experimental error. This validates the analysis based on eqs 3 and 4 in subsection B.

D. Irradiation Temperature Dependence of PL Efficiency. Since the photodegradation of green- and red-emitting films can be expressed using k_1 and k_2 , respectively, we investigated its temperature dependence, as shown in Figures 5a and 6a. By measuring at about 10 different temperatures from 20 to 95 °C, we constructed the Arrhenius plots depicted in Figures 5b and 6b. They show that the activation energies of the green- and red-emitting CdTe NCs in the glass films were 304 ± 9 and 288 ± 7 meV/particle, respectively.

E. Comparison with Other Work. The derived activation energy for photodegradation (~ 300 meV, 30 kJ/mol) was 1 order of magnitude larger than the exciton binding energy and 1 order of magnitude less than the typical dissociation energy of an ionic bond.²⁵ It is also different from the thermal energy at room temperature (26 meV). However, this difference accounts for the significant temperature dependence of degradation, as described above.

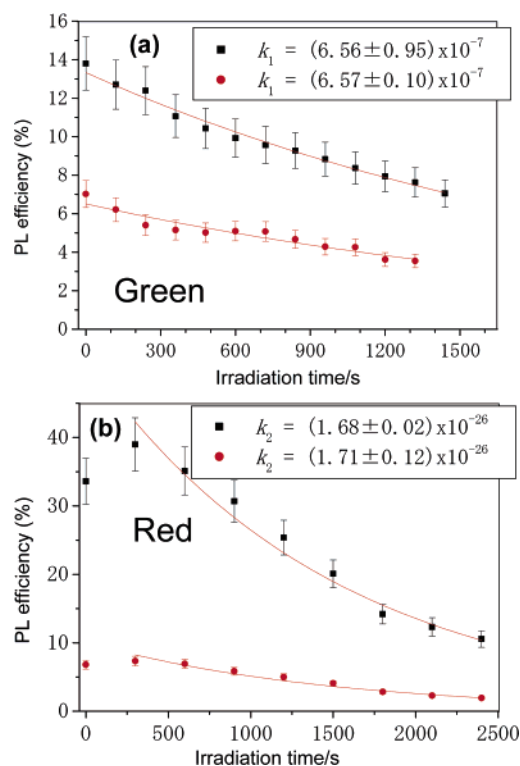


Figure 4. PL efficiencies of (a) green- and (b) red-emitting glass films with different initial PL efficiencies against irradiation time. The irradiation intensities of green- and red-emitting glass films were 350 and 1600 mW/cm², respectively. The sample temperature was 48 °C.

The number of excitations before degradation is an important factor for any application. If we consider the degradation point to be a 20% decrease in initial PL efficiency, Figure 2a shows that 3.9×10^5 excitations result in degradation at 48 °C for any irradiation intensity with the green-emitting NCs. Figure 3a presents the situation for red-emitting NCs at 48 °C. 6.3×10^6 excitations result in degradation at an intensity of 940 mW/cm², whereas 3.4×10^6 excitations result in degradation at an intensity of 2.0 W/cm². At room temperature (20 °C), the number of excitations becomes 2.8 times higher because the activation energy of both types of nanocrystals is ~ 300 meV.

As mentioned in the Introduction, a few reports have described photodegradation. Gaponik et al. investigated the photostability of TGA-capped CdTe NCs in water and TOPO-capped CdSe NCs in toluene at room temperature.⁹ They used 400-nm light from a 450-W xenon lamp after band-pass filtering. Even though they did not give the size of the NCs investigated, we can assume the emission wavelength was in the red region because there was an increase in PL intensity at the beginning of irradiation. Judging from the standard specifications of the apparatus they used, we estimated their irradiation intensity to be roughly 10 mW/cm². This means the number of excitations before 20% degradation of their CdTe NCs (degradation time is measured from the time when the NCs show the highest PL intensity) was of the order of 10^4 , whereas that of their CdSe NCs was of the order of 10^5 at room temperature. For CdTe NCs, this is 3 orders of magnitude lower than for the films we investigated. We also investigated the photodegradation of red-emitting CdTe NCs in the crude colloidal solution we used for film preparation. After an increase during the initial stage of irradiation, the PL efficiency drastically dropped accompanied by a significant red shift of the spectral peak wavelength (see the Supporting Information). The degradation speed compared

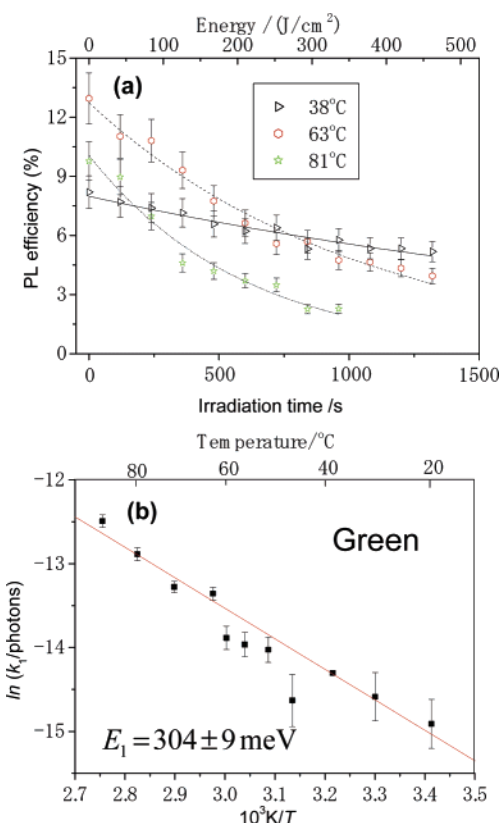


Figure 5. (a) Temperature dependence of the PL degradation of green-emitting films with an irradiation intensity of 350 mW/cm². The PL efficiency decreased with irradiation time for three different heating temperatures. (b) Arrhenius plot of PL degradation; $\ln(k_1)$ changed as a linear function of $1/T$.

with that of the corresponding red-emitting film was a couple of orders of magnitude higher.

Alivisatos' group investigated the photodegradation of silica-coated CdSe/ZnS in buffer solution with 488-nm irradiation at 130 mW/cm².¹³ They did not detect any degradation after irradiation for 4000 s. For red-emitting CdSe NCs, this corresponds to 3.8×10^6 excitations at room temperature, which is probably similar to that for CdTe NCs in glass.

Peng's group measured the decrease in absorption of thiol-coated CdSe NCs in water with 254-nm irradiation.¹² If we roughly estimate the absorption cross section at 254 nm to be 10 times that at the first absorption peak, 4.7×10^5 excitations occurred before degradation at room temperature. This is at least 1 order of magnitude less than for the CdTe NCs in glass because the PL apparently degrades much faster than the absorption decreases.

F. Possible Mechanism of Photodegradation. To clarify the origin of the photodegradation, we did a degradation experiment in a glovebox in which the concentration of oxygen was more than 4 orders of magnitude lower than under atmospheric conditions. As explained in the Experimental Section, we had to heat-treat the film additionally to avoid the formation of cracks during irradiation in a glovebox. This is because the concentration of H₂O is less than 1 ppm in the glovebox. For comparison, another heat-treated sample was irradiated under atmospheric conditions at room temperature. As shown in Figure 7a, photodegradation did not take place in Ar (upper part of Figure 7b, $k_1 \sim 0$ photons) for green-emitting films. The degradation in air (lower part of Figure 7a) was similar to that shown in Figure 2a, and the rate constant, $\ln(k_1/\text{photons})$, was -15.2 ± 0.3 . This is close to the track of the curve in Figure

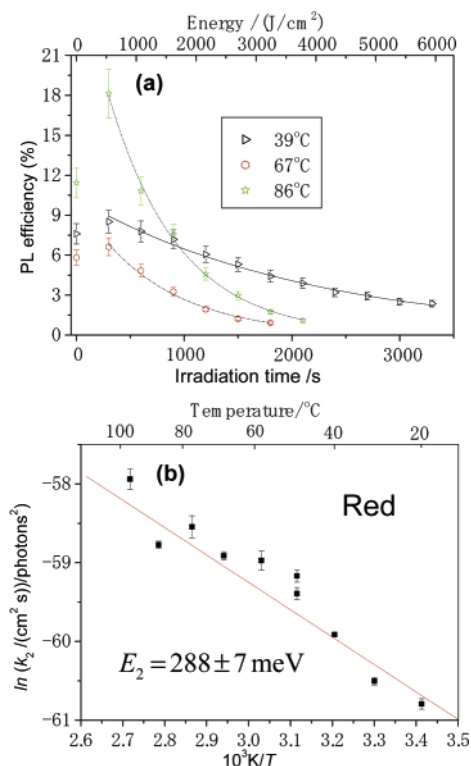


Figure 6. (a) Temperature dependence of the PL degradation of red-emitting films with an irradiation intensity of 1.8 W/cm². The PL efficiency increased and then decreased with irradiation time for three different heating temperatures. (b) Arrhenius plot of PL degradation; $\ln(k_2)$ changed as a linear function of $1/T$.

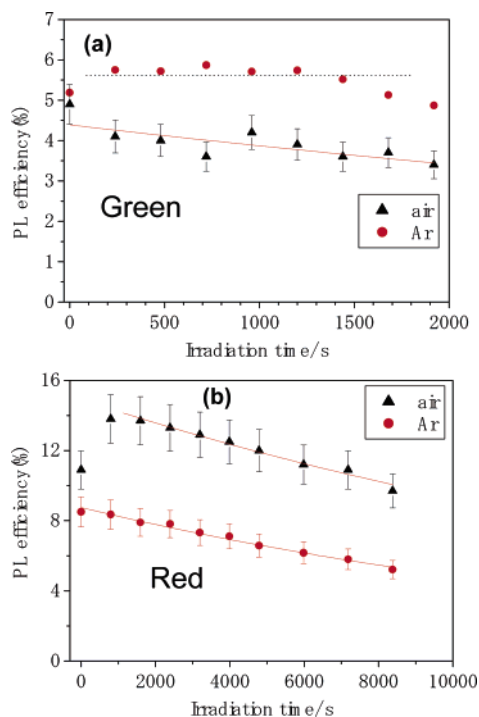


Figure 7. (a) Irradiation-time dependence of the PL efficiency of heat-treated green-emitting films in air and in Ar atmosphere at room temperature. The irradiation intensity was 350 mW/cm². (b) Irradiation-time dependence of the PL efficiency of heat-treated red-emitting films in air and in Ar atmosphere at room temperature. The irradiation intensity was 1330 mW/cm².

5b for 20 °C. Figure 7b shows the case for red-emitting films both in air and Ar. When the film was in air, the efficiency went up at the beginning of irradiation. It then decreased by a

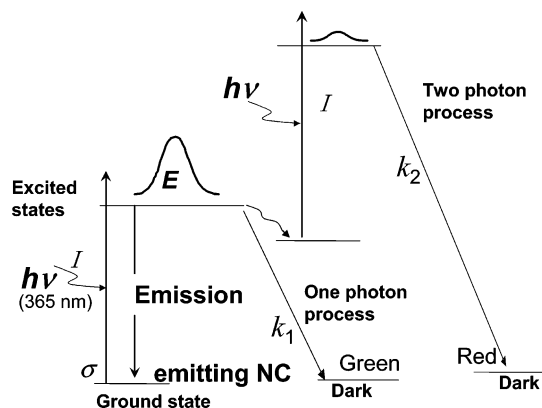


Figure 8. Possible degradation mechanism of emitting CdTe NCs in glass films during UV irradiation. The reaction paths of green- and red-emitting NCs are different.

constant rate during irradiation. These tendencies are the same as those shown in Figure 3a. The rate constants, expressed by $\ln[k_2/((\text{cm}^2 \text{ s})/\text{photons}^2)]$, in Ar and air were -60.60 ± 0.06 and -61.45 ± 0.02 , respectively. This means that the degradation speed does not depend significantly on the atmosphere for red-emitting films. However, the value in air was a little bit lower than that of normal (not heat-treated) samples, for which the Arrhenius plot of degradation is shown in Figure 6b at 20 °C. This is probably due to the difference in the amount of water and the extent of the network structure in glass. After the network grew and the amount of water was reduced by heat treatment, the photodegradation rate became small.

We can say from Figure 7a that the photodegradation of green-emitting NCs in glass film is due to simple oxidation from the first excited state, whereas the main mechanism for the red-emitting NCs is not oxidation but related to a surface condition change, probably the reaction of surfactant molecules upon irradiation through higher electronic states. Oxidation of Te was strongly inhibited because the surface of the red-emitting NCs was covered by sulfur atoms from the surfactant. Since the activation energies of the green- and red-emitting NCs in the films were roughly the same ($E \sim 300$ meV/particle), a possible mechanism of the photodegradation, as shown in Figure 8, is as follows. For green-emitting NCs, the oxidation takes place directly from the electronically excited state by electrons passing through the activation barrier E . On the other hand, degradation of red-emitting films takes place due to excitation from some metastable level after electrons pass through the barrier. This excitation causes additional surface deterioration.

Figure 9 shows the development of the PL spectral width (fwhm) during irradiation for the two glass films (green and red) and two conditions (Ar and air). The green-emitting films did not show any width change during irradiation, whereas the red-emitting ones showed a decrease by irradiation. These tendencies did not depend on the atmosphere. Therefore, the deterioration of the surface of red-emitting NCs upon irradiation is not “destructive”. Instead, NCs probably having some unstable surface sites, where the PL wavelength from them deviates from the peak ensemble PL wavelength, that are quenched preferentially upon irradiation. This may narrow the PL width during irradiation. From the spectral point of view, green- and red-emitting CdTe NCs are different substances.

Finally, we attempted to detect a change in the surfactant conditions of red-emitting films accompanying a PL decrease by measuring the surface Fourier transform infrared (FTIR) spectra. However, no difference was detected by the irradiations, as shown in the Supporting Information.

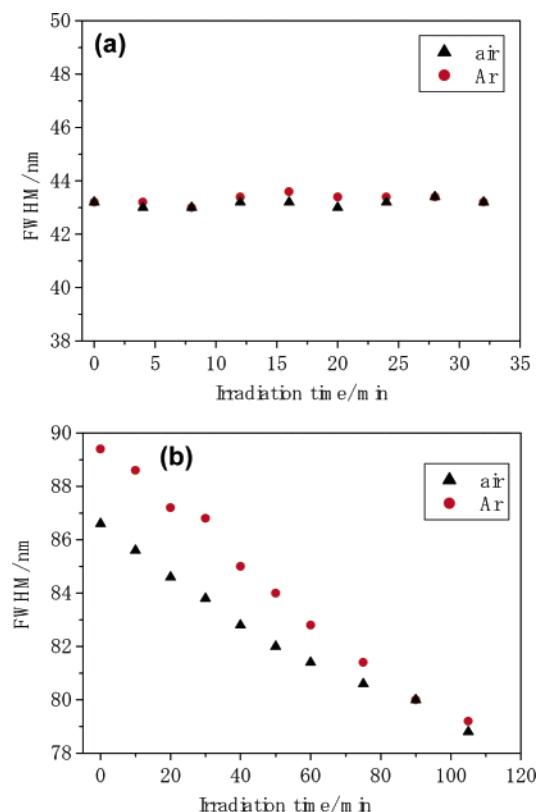


Figure 9. PL spectral width (fwhm) of heat-treated (a) green-emitting film and (b) red-emitting film as a function of irradiation time in air and Ar. The irradiation intensity was 350 mW/cm² for green and 1330 mW/cm² for red at room temperature.

The observation, analysis method, and intensity dependence of photodegradation described here should be useful for other materials and applications such as single-particle spectroscopy.^{26,27}

IV. Conclusion

Transparent photoluminescent glass films (15–20 μm thick) were fabricated by dispersing CdTe NCs prepared from an aqueous solution. The photodegradation of the films was estimated by measuring the decrease in PL efficiency as a function of irradiation time for various irradiation intensities at several temperatures. The films were sufficiently thin and homogeneous to permit quantitative analysis.

The degradation of green-emitting NCs (2.6 nm Φ) in the film was proportional to the irradiation intensity, while that of red-emitting NCs (3.9 nm Φ) was proportional to the square of the irradiation intensity. This was ascribed to the difference in the surface composition, because the surface of red-emitting NCs is covered by sulfur supplied by hydrolysis of the surfactant (TGA) during synthesis in a highly alkaline region.^{9,24} The activation energy of the degradation was estimated to be ~ 300 meV for both green- and red-emitting NCs. Comparison of the degradation in Ar and air atmospheres revealed that the main mechanism of the photodegradation for green-emitting film was

oxidization from the first electronically excited state and that the main mechanism for red-emitting film was not oxidization but probably related to the change in the surfactant. The initial increase in the PL efficiency observed only for red-emitting NCs in air was due to oxidization of the surface. The NCs in glass film were more than 2 orders of magnitude more robust than those in colloidal solution.

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Supporting Information Available: Figures showing the degradation of red-emitting NCs in solution and glass films and infrared spectral information. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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