ORIGINAL PAPER

Photo-Degradation Study of CdTe Nanocrystals by Fluorescence Measurement

Ping Yang · Jinghua Yu

Abstract The photo-degradation of green-, yellow-, orange- and red-emitting CdTe nanocrystals (NCs) in sol–gel SiO$_2$ films was investigated quantitatively by measuring the PL efficiency as a function of the irradiation intensity. The degradation behaviors of the NCs depended strongly on the particle size and the surface state. Green- and yellow-emitting CdTe NCs exhibited a red-shifted PL peak wavelength and decreased PL efficiency after irradiation. In contrast, the PL peak wavelength of red-emitting CdTe NCs remained unchange and their PL efficiency increased. Furthermore, the degraded degree of green-emitting NCs depended linearly on the irradiation intensity (rate constant $k_1 = (1.10 \pm 0.04) \times 10^{-6}$ photon), whereas hat of red-emitting NCs showed a quadratic dependence (rate constant $k_2 = (2.26 \pm 0.1) \times 10^{-26} (\text{cm}^2 \text{ s})/\text{photon}$) at room temperature. This is ascribed to the different surface state of green- and red-emitting CdTe NCs.

Keywords Nanocrystals · Photoluminescence · Photo-degradation · Silica · Film

Introduction

Colloidal semiconductor nanocrystals (NCs) are nanoscale materials whose optical, electronic, and transport proper-ties, due to their strong dependence on size and shape, can be finely tuned by advanced chemical synthesis approaches [1]. Colloidal syntheses of II–VI semiconductor NCs are currently well developed [2] and allow us to obtain nanoscale materials with desirable properties. Compared with organic synthesis routes, aqueous methods are also used to prepare II–VI semiconductor NCs, especially CdTe NCs [3]. Thiol molecules with diverse functional groups, such as thioglycolic acid, 1-thioglycerol, and 2-mercaptoethylamine, are usually used as ligands, which facilitate the conjugation of aqueous NCs with other ions, molecules, or polymers for various applications [4]. The PL properties of CdTe NCs depended strongly on the solution condition. For example, the PL intensity and stability of as prepared NCs greatly increase during storage at room temperature [5].

Recently, the great advances in the surface chemistry of NCs allow them to be effective in practical applications, such as multicolor biological imaging and detection [6]. Photoluminescence (PL) properties of NCs are closely related to the nature of their surface [4, 6]. The trap sites on the NCs surface can dramatically reduce the PL efficiency of NCs. It is believed that these surface properties depended strongly on preparation condition. These surface properties strongly affect other colloidal and photophysical and photochemical properties of NCs. Talapin et al. demonstrated that NCs with a smooth surface have the highest PL efficiency [7]. 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 [8]. The study of the surface chemistry of NCs has attracted widespread interest.

Compared with many ensemble techniques, for exam-ple, UV–vis absorption and fluorescence spectroscopy

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and X-ray photoemission spectroscopy, UV irradiation has been a useful tool for monitoring the change of the surface chemistry and colloidal properties of NCs because the surface state of the NCs is sensitive for such irradiation. UV irradiation has been shown to enhance PL efficiency by creating a passivating layer on the surface [9, 10]. Bao et al. studied such an enhancement effect for water-soluble CdTe NCs in N_2 saturated solution [9]. Bol and Meijerink found a significant increase in the PL efficiency of ZnS:Mn NCs in polymers following UV irradiation [10]. However, these studies cannot reflect the qualitative analysis between irradiation intensity and the properties of NCs. Much more qualitative results are still expected even though CdSe NCs in water [11] have been quantitative analyzed.

Previously, we investigated quantitatively the photo-degradation of films with CdTe NCs as a function of irradiation intensity and temperature. Degradations are almost always related to a diffusion of oxygen from the surroundings [12]. The degradation depended greatly on the surface states of the NCs. Especially, we have found that red-emitting CdTe NCs exhibit two-photon kinetics, whereas green-emitting CdTe ones exhibit one-photon kinetics even though their activation energies are almost the same. In this paper, we reported further study in the degradation. Aqueous green-, yellow-, orange-, and red-emitting CdTe NCs were embedded in sol–gel SiO_2 films. The photo degradation behaviors of the CdTe NCs depended strongly on their size at room temperature. The green- and yellow-emitting NCs exhibited a red-shifted PL peak wavelength and decreased PL efficiency. In contrast, the PL peak wavelength of red-emitting NCs remained unchange and their PL efficiency increased at a low irradiation intensity. The orange-emitting NCs exhibited a different degradation behavior compared with green-, yellow-, and red-emitting NCs. This phenomenon is ascribed to the surface chemistry of the NCs.

Experimental

Preparation of CdTe NCs Water-soluble TGA-capped CdTe NCs were prepared according to the procedure reported in literature [13]. Briefly, by a molar ratio of 5:1 for $NaHB_4$/Te, sodium borohydride was used to react with tellurium in water to prepare a sodium hydrogen telluride (NaHTe) soultion. Fresh solutions of NaHTe were diluted by N_2-saturated deionized water for further use.

For the preparation of TGA-capped CdTe NCs, $CdCl_2 \cdot 2.5H_2O$ (0.4 mmol) and TGA (0.6 mmol) were dissolved in 25 mL of water to get a precursor solution followed by adjustment to a pH value of 11.2 by a NaOH solution of 1 M. The precursor solution was bubbled by N_2
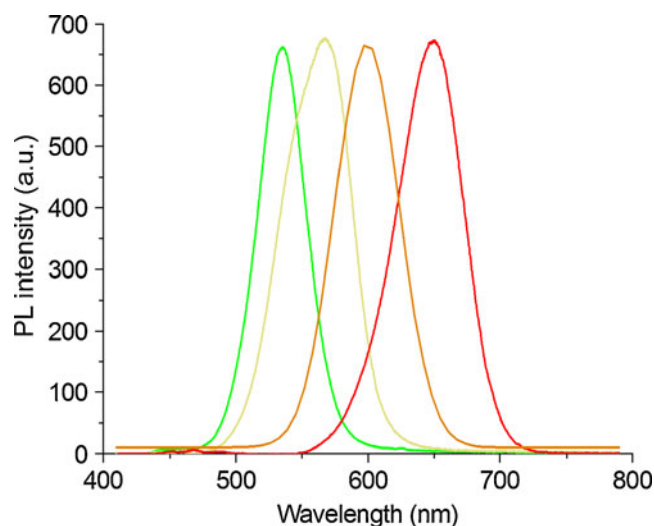

Fig. 1 PL spectra of *green-*, *yellow-*, *orange-*, and *red*-emitting CdTe NCs (from left to right). Their PL peak wavelengths are 540, 570, 600, and 650 nm, respectively

for 30 min. A fresh deoxygenated NaHTe solution was added in the above precursor solution with stirring. The typical molar ratio of Cd:Te:TGA was 1:0.5:1.5. The mixture was subsequently refluxed for different time to synthesize TGA-capped CdTe NCs. To prepare CdTe NCs with different emitting color, the molar ratio of TGA/Cd and the reflux time was adjusted.

Preparation of Functional SiO_2 Films with CdTe NCs A functional SiO_2 precursor sol with CdTe NCs was prepared using a procedure described in detail elsewhere [12]. A precursor 3-aminopropyltrimethoxysilane (APS) sol was prepared by mixing APS with ethanol and H_2O. Typically, the molar ratio of ethanol/H_2O/APS is 30/4/1. The mixture was stirring for 24 h and then heat-treated at 50–70 °C to evaporate ethanol. The aqueous solution of CdTe NCs (1 mL) was mixed with 1 mL of the precursor APS sol with stirring for 5–10 min to get the functional SiO_2 precursor sol with CdTe NCs.

The film samples were prepared by spin-coating using the functional SiO_2 precursor sol with CdTe NCs. Slide

Table 1 Preparation condition and PL properties of initial CdTe NCs

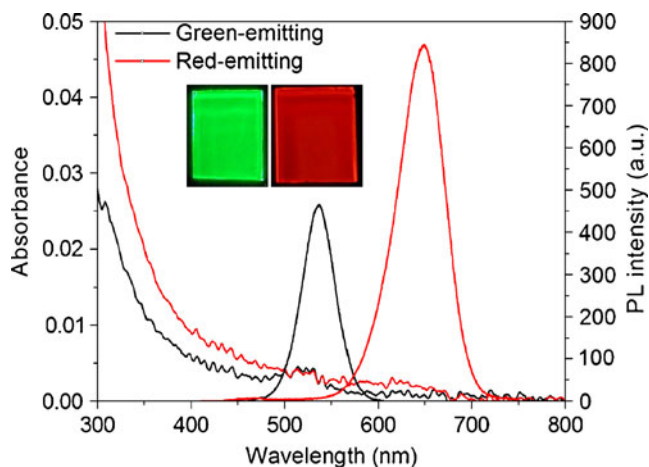| Sample	Reflux time (h)	PL peak wavelength (nm)	PL efficiency (%)
Green-emitting	1.5	539.7	31.2
Yellow-emitting	20	570.3	44.3
Orange-emitting	30	600.4	58.9
Red-emitting	100	650.1	50.4

Fig. 2 Absorption and PL spectra of SiO$_2$ films with green- and red-emitting CdTe NCs. *Insets* show the color images of *green-* and *red-emitting* films upon 365 UV light

glass substrates were immersed in a fresh aqueous solution of acid (v/v=1:3, 30% H$_2$O$_2$/98% H$_2$SO$_4$) until gas evolution ceased. After being rinsed with copious amounts of water and dried, film samples were prepared using the precursor sol. By using an optimized procedure (precursor viscosity was 180 mPa s; spinning speed was gradually increased to 3,000 rpm and kept there for 40 s), we obtained homogenous and transparent functional SiO$_2$ film samples. The thickness of the films was between 15 and 20 μm. The film was dried at a vacuum condition.

Measurement of Photo Degradation and Characteristics The films were irradiated for different time periods using a light of 365 nm from a 250-W xenon lamp (Ushio SP-7 equipped with a B-type lens on top of the fiber) at room temperature. A UV light beam up to 2.0 W/cm^2 was obtained when the irradiation distance between the lens and the film was 22 mm. The absorption and emission spectra during irradiation were measured at room temperature as a function of irradiation time by using Hitachi U-4100 and F-4600 spectrometers, respectively.

The PL efficiencies of CdTe NCs in solutions and in functional SiO$_2$ films were estimated in comparison with a standard rhodamine 6 G solution having a similar optical path length and optical density [14, 15].

Results and Discussion

The PL of CdTe NCs depended strongly on their size. Aqueous green-, yellow-, orange-, and red-emitting CdTe NCs were created by adjusting reflux time. Figure 1 shows the PL spectra of green-, yellow-, orange-, and red-emitting

CdTe colloidal solutions (from left to right). Their PL peak wavelengths are 540, 570, 600, and 650 nm, respectively. Because of optimal preparation conditions, the NCs exhibited high PL efficiencies. Table 1 illustrates the preparation condition and PL properties of initial CdTe NCs.

Figure 2 shows the absorption and PL spectra of functional SiO$_2$ films with green- and red-emitting CdTe NCs. Insets in figure show the color images of green- and red-emitting films upon 365 UV light. Their PL properties are illustrated in Table 2. The result indicated that the PL efficiencies of the green- and red-emitting films are 15 and 30%, respectively. This result is very similar to those reported in our previous paper [12]. These films revealed a relative high PL efficiency compared with other NC-polymer and other NC-SiO$_2$ films [16–18].

An important issue with NCs is the stabilization of particles by encapsulation in inert matrices. Much effort has been undertaken to produce well-defined ultrathin films that may be used to explore potential applications in optoelectronic devices and chemical and biological sensors. One approach developed to achieve stabilization is to produce sol–gel silica films for embedding luminescent NCs. Compared with other silane couple agents, APS has an amino group which can linked with the carboxyl group in TGA. This should be useful to keep TGA-capped CdTe NCs a high PL efficiency in films. Comparing with other NC-polymer and other NC-SiO$_2$ films [16–18], CdTe NCs in the functional SiO$_2$ films exhibited a relatively high PL

Table 2 Evolution of PL properties of SiO$_2$ films with CdTe NCs during irradiation

Sample	Irradiation time (min)	PL peak wavelength (nm)	PL efficiency (%)
Film with green-emitting NCs	N/A	537.4	15.2
	4	539.8	11.1
	30	546.6	9.0
	100	552,6	2.0
Film with yellow-emitting NCs	N/A	570.1	16.4
	4	574.8	14.2
	30	580.4	13.4
	100	586.3	7.3
Film with orange-emitting NCs	N/A	600.8	21.1
	4	599.4	22.1
	30	604.2	24.7
	100	606.4	16;6
Film with red-emitting NCs	N/A	649.5	29.8
	4	649.2	28.6
	30	650.0	36.7
	100	651.0	34.8

Irradiation intensity of 25 mW/cm^2 was used during measurement

efficiency as illustrated in Table 2. This is ascribed to the amino groups in APS prevented the CdTe NCs from agglomeration during incorporation.

The degradation of NCs is always related to the diffusion of oxygen from the surroundings. Because the functional SiO$_2$ film fabricated by APS was thin (15 ∼ 20 μm) sufficiently, transparent, and porous, the photo degradation of CdTe NCs was homogeneous. To investigate the photo degradation degree of CdTe NCs with several sizes, Fig. 3 shows the evolution of PL efficiency of functional SiO$_2$ films with CdTe NCs during irradiation: (a) green-emitting, (b) yellow-emitting, (c) orange-emitting, and (d) red-emitting. Upon irradiation intensity of 25 mW/cm^2, these films with green- and yellow-emitting CdTe NCs exhibited a red-shifted PL peak wavelength and decreased PL efficiency with time. The photo degradation rate of the yellow-emitting NCs was slow compared with the green-emitting ones. Figure 4 shows the absorbance and PL spectra of a functional SiO$_2$

film with green-emitting CdTe NCs before and after irradiation. The absorption spectra remained unchange while the PL spectra revealed a red shift. This is ascribed to the size effect on degradation. Small CdTe NCs were firstly quenched during irradiation.

For functional SiO$_2$ films with orange- and red-emitting CdTe NCs, the PL efficiency of the NCs increased at the initial stage of irradiation as shown in Fig. 3c and d. The PL efficiency of orange-emitting film remained unchanged within 50 min and subsequently exhibited a decrease. In contrast, the red-emitting film remained initial absorption and PL spectra and kept a higher PL efficiency as shown in Fig. 3c. Figure 5 shows the absorption and PL spectra of a functional SiO$_2$ film with red-emitting CdTe NCs before and after irradiation. Table 2 illustrates the evolution of PL properties of functional SiO$_2$ films with CdTe NCs during irradiation. The result indicates that the degradation depended on the size and surface states of the NCs.
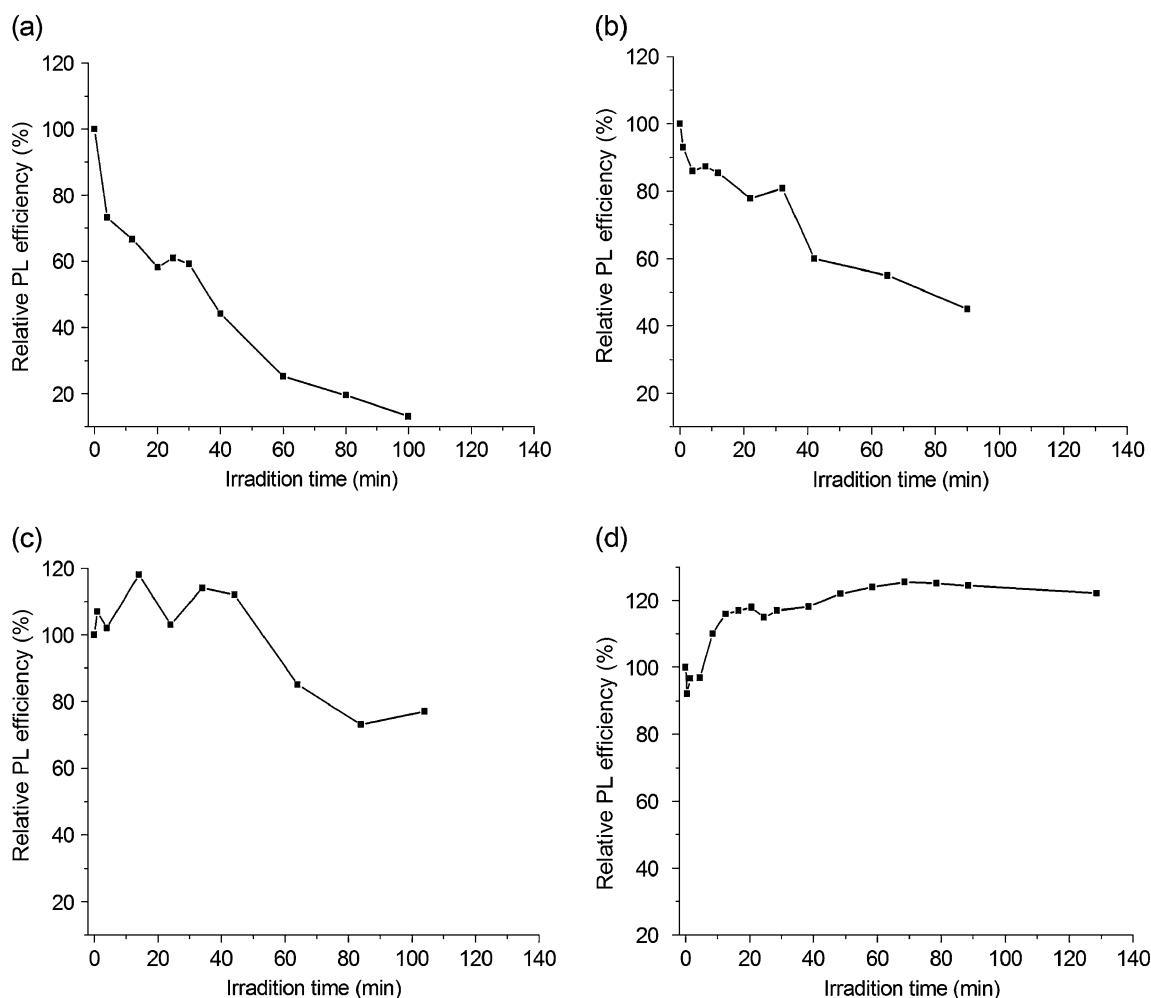

Fig. 3 Evolution of PL efficiency of SiO$_2$ films with CdTe NCs during irradiation. **a** *green*-emitting; **b** *yellow*-emitting; **c** *orange*-emitting; **d** *red*-emitting. Irradiation intensity is 25 mW/cm^2 for four kinds of films
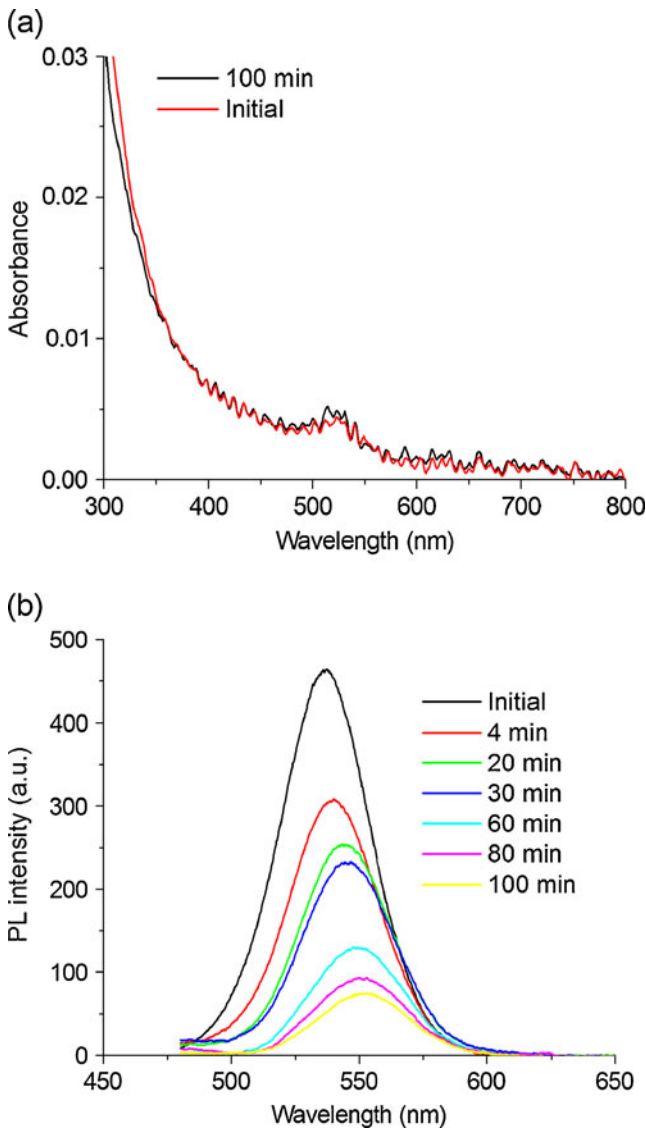
Fig. 4 Absorption (a) and PL (b) spectra of SiO$_2$ film with *green-emitting* CdTe NCs before and after irradiation (irradiation intensity of 25 mW/cm^2). Irradiation time is shown in figures

CdS-like shell was created on the surface of CdTe NCs because of S^{2-} ions generated by the decomposition of TGA during a long reflux. Green-emitting CdTe NCs were fabricated by using a short reflux time, no CdS-like shell was formed on their surface. The photo degradation of green-emitting CdTe NCs was therefore fast. In contrast, the red-emitting ones did not reveal a degradation of PL efficiency within 140 min at irradiation intensity of 25 mW/cm^2. This phenomenon is ascribed to the CdS-like shell on the surface.

Photo irradiation degrades NCs in the films. This is crucially important for their application. We further qualitatively analyzed the UV degradation of green- and red-emitting CdTe NCs in functional SiO$_2$ films because of
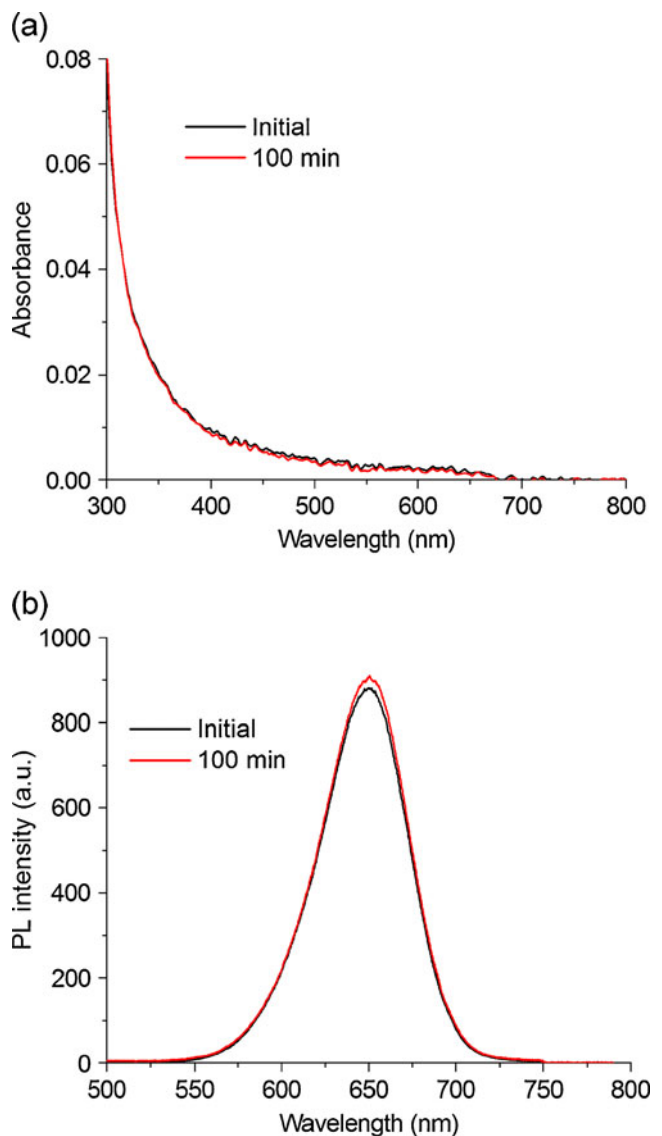

Fig. 5 Absorption (a) and PL (b) spectra of SiO$_2$ film with red-emitting CdTe NCs before and after irradiation (irradiation intensity of 25 mW/cm^2). Irradiation time is shown in figures

The fact that illumination can produce the photo chemical reaction on semiconductor NCs has been reported by several groups [19, 20]. Due to the large ratio of surface to volume, NCs have lots of surface dangling bonds which become reactive upon illumination. In solution, illumination created photochemical etching which resulted in TGA-capped CdTe NCs an increased PL efficiency and a blue shifted PL peak wavelength [9]. Unlike NCs in the solution, UV irradiation degraded CdTe NCs in films. In current experiments, green- and red-emitting CdTe NCs in the film exhibited different degradation behavior. This is ascribed to the difference of their surface state. The surface state of CdTe NCs depended strongly on reflux time. CdTe NCs were fabricated by using TGA as a capping agent. The

their typical photo degradation properties. When the concentration of CdTe NCs in the functional SiO_2 film is M, the concentration of nanocrystals excited by irradiation I (in units of photons/(cm^2 s)) is given by $\sigma I M$, where σ is the cross-section of a single NC at 365 nm. When the excited NC changes to something else, the differential equation can be written using rate constant k_1:

$$\frac{dM}{dt} = -k_1 \sigma I M. \tag{1}$$

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

$$M = M_0 \exp(-k_1 \sigma I t). \tag{2}$$

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

$$\eta_1 = \eta_0 \exp(-k_1 \sigma I t), \tag{3}$$

Where η_0 is the efficiency before irradiation. When the degradation occurs through a level excited by two-photon absorption, Eq. 3 becomes

$$\eta_2 = \eta_0 \exp(-k_2 \sigma I^2 t), \tag{4}$$

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

To investigated the irradiation intensity dependence of degradation rate constant (k_1 and k_2), the irradiation intensity of green-emitting CdTe NCs is up to 60 mW/cm^2 while that of the red-emitting ones is up to 150 mW/cm^2. The degradation curves of green-emitting CdTe NCs show least-squares fitting using Eq. 3. A linear function ($k_1 = C_1 + B_1 I$) was used for getting rate constant k_1. The result indicated rate constant $k_1 (= (1.10 \pm 0.04) \times 10^{-6} \text{photon})$ at room temperature for one-photon kinetics does not depend on the irradiation intensity. For comparison, a similar analysis can be done for red-emitting films. Figure 6 shows a typical photo degradation curve of functional SiO_2 film with red-emitting CdTe NCs. The PL efficiency increased during the initial stage of irradiation. Therefore, we took only the latter slopes, which showed a decrease. Equation 3 does not give a constant k_1 against irradiation intensity, whereas Eq. 4 gives an ideal result. Statistical analysis gives a k_2 value of $(2.26 \pm 0.1) \times 10^{-26} (cm^2 \text{ s})$/photon at room temperature.

The activation energies of the green- and red-emitting CdTe NCs in the functional SiO_2 films are 304 ± 9 and 288 ± 7 meV/particle, respectively [12]. We have indicated that rate constant $k_1 (5.7 \pm 0.8) \times 10^{-7}$ photon for the green-emitting NCs and rate constant $k_2 (1.8 \pm 0.3) \times 10^{-26} (cm^2 \text{ s})$/photon for the red-emitting NCs at 48 °C. According to the Arrhenius plots ($\ln k = \ln A + Ea/RT$,
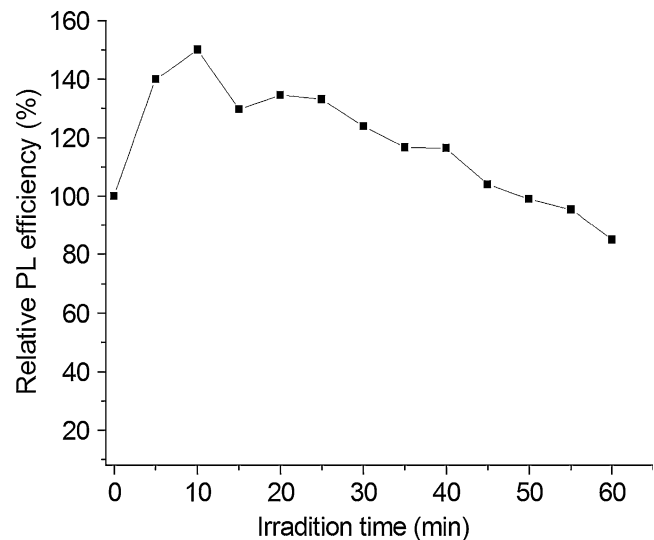

Fig. 6 Relative PL efficiency of functional SiO_2 film with red-emitting CdTe NCs versus irradiation time at irradiation intensity of 130 mW/cm^2

whereas k as rate constant, E_a as the activation energy of single NC, R as gas constant, and T as temperature), the calculated value of rate constants k_1 and k_2 is similar to that obtained by using current experimental data (at room temperature). Therefore, red-emitting CdTe NCs exhibit two-photon kinetics whereas green-emitting CdTe ones exhibit one-photon kinetics at room temperature.

Conclusions

Transparent functional SiO_2 films (15–20 μm) with green-, yellow-, orange-, and red-emitting CdTe NCs were fabricated by using a controlled sol–gel procedure. The photo degradation of the films was estimated by measuring the decrease in PL efficiency as a function of irradiation time for various irradiation intensities. The NCs exhibited different photo degradation behavior because of their size and surface states. The PL efficiency of these films with green- and yellow-emitting CdTe NCs decreased with time. The initial increase in the PL efficiency observed for orange- and red-emitting NCs. The degradation of green-emitting NCs (2.7 nm in diameter) in the film was proportional to the irradiation intensity, while that of red-emitting NCs (3.9 nm in diameter) was proportional to the square of the irradiation intensity. This is ascribed to the surface of red-emitting NCs is covered by CdS-like layer.

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