

Ultrafast Carrier Dynamics in CdS₂ Nanocrystals in Glass Matrix

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(Received November 2, 2007; accepted January 5, 2008)

We report on photoexcited carrier dynamics in CdS₂ nanocrystals in a glass matrix studied by ultrafast photoluminescence spectroscopy. The results of photoluminescence up-conversion measurements are compared with those of transient absorption and degenerate four-wave mixing (DFWM) experiments. The fast component (about 1 ps) of the photoluminescence and transient absorption decay is attributed to hole trapping in a surface state.

KEYWORDS: semiconductor, nanocrystal, glass, photoluminescence

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Semiconductor nanocrystals are promising for applications in optoelectronics.^{1,2)} Semiconductor-doped glasses are now considered as a model system of II-VI semiconductor nanocrystalline assemblies and are one of the most studied nanocrystalline systems. Carrier dynamics in semiconductor nanocrystals are of great importance both from the basic physics and application viewpoints. Several papers were devoted to investigation of photoexcited carrier dynamics in CdS and CdSe nanocrystals on picosecond and femtosecond time scales.^{3,4)} The relaxation and recombination paths of electrons and holes were identified, the role of surface states of individual CdSe nanocrystals was emphasized, and the consequences for applications in lasers were discussed.⁵⁾ However, it turned out that the knowledge of properties of a semiconductor-glass interface and consequently of surface states of nanocrystals is rather poor. Unfortunately, surface states of nanocrystals affect strongly physical properties of nanocrystals. It is for example well known that light irradiation of semiconductor nanocrystals in glass can lead to photodarkening, which affects optical properties of materials and carrier dynamics within nanocrystals.²⁾ Extensive experimental data on a series of samples are therefore needed for understanding relevant microscopic processes.

In a previous paper,⁶⁾ we reported on ultrafast carrier dynamics in CdSSe nanocrystals in glasses, which were measured by femtosecond degenerate four-wave mixing (DFWM) experiments and transient absorption in the infrared range. Here, we report on ultrafast photoluminescence dynamics of a series of CdSSe nanocrystals in glass matrixes, which were measured by a femtosecond up-conversion technique. The obtained results were compared with those reported in the previous paper,⁶⁾ The photoluminescence dynamics complete the information on carrier relaxation as they reflect relaxation of both electrons and holes, whereas the transient absorption and DFWM are affected by electrons. The results were also compared with those for the ultrafast photoluminescence dynamics of CdS nanocrystals in glass matrixes,⁷⁾ in order to examine the effect of alloying on carrier dynamics.

The samples investigated were commercial CdSSe-doped filter glasses: Hoya R-64, R-66, and R-68; Asahi R-64 and R-66; Corning 2-58 and 2-64; and Schott RG645 and RG665. Absorption edges of these filter glasses were approximately 630 nm for R-64, 2-58, and

RG645; 650 nm for R-66, 2-64, and RG655; and 670 nm for R-68. Different positions of the absorption edge were due to different nanocrystal sizes (effect of quantum confinement) and different alloy compositions of CdSSe. The alloy compositions are listed in Table I, and these values were from ref. 8. Thicknesses of samples were about 2.5 mm. The concentration of CdSSe was about 0.4 wt%.⁹⁾ Sizes of CdSSe nanocrystals were approximately 8 to 30 nm.¹⁰⁾ Glass compositions were 50 wt% SiO₂, 20 wt% K₂O, 20 wt% ZnO, 4 wt% Na₂O, and 4 wt% B₂O₃ for Hoya, 70 wt% SiO₂, 6 wt% K₂O, 10 wt% ZnO, 10 wt% Na₂O, and 3 wt% B₂O₃ for Asahi, 70 wt% SiO₂, 10 wt% ZnO, 6 wt% Na₂O, and 10 wt% B₂O₃ for Corning, and 50 wt% SiO₂, 20 wt% K₂O, 20 wt% ZnO, and 4 wt% B₂O₃ for Schott.⁹⁾

Photoluminescence dynamics were measured at 300 K. The excitation source was a frequency-doubled Ti:sapphire laser (Spectra Physics Tsunami 3960; wavelength = 405 nm, pulse duration = 80 fs, energy per pulse = 1 nJ, repetition rate = 82 MHz). Since the peak power density of laser light was high (about 100 MW/cm²), samples were photodarkened before measurement. The luminescence dynamics were measured using a standard up-conversion technique with a time resolution of approximately 0.5 ps. In this setup, luminescence light was overlapped spatially with the switching femtosecond pulse at a fundamental laser wavelength in a nonlinear BBO crystal to produce the light at the sum frequency. This up-converted signal was detected by a photon-counting photomultiplier module (Hamamatsu). The luminescence dynamics were monitored by changing the time delay between the excitation pulse and the switching pulse using an optical delay line.

An example of ultrafast photoluminescence dynamics is shown in Fig. 1, where dynamics of photoluminescence at its peak wavelength (665 nm) for Hoya R-68 is indicated (symbols). The luminescence dynamics were fitted well by a single-exponential decay function with a time constant of 1.3 ps (smooth curve). Time constants depended slightly on the wavelengths of luminescence: 1.2 ps (650 nm), 1.3 ps (665 nm), and 1.4 ps (680 nm). Similar results were also obtained using the other samples. In the measurement, we used the excitation with a photon energy above the ground-state absorption. With the high photon energy of the photoluminescence signal, we monitored the higher states of CdSSe

nanocrystals. The carrier dynamics of the higher states were affected by relaxation.²⁾ On the other hand, the effect of relaxation was small for the lower states. Therefore, the decay constant was small for the high photon energy of the photoluminescence signal.

Figure 2 shows dynamics of luminescence of Asahi R-64 at its peak wavelength (615 nm). The decay constant was 0.8 ps. The decay constants of all the measured samples are summarized in Table I. For each sample, the wavelength of photoluminescence maximum, where dynamics were measured, the decay constant obtained from fitting, and the molar fractions x of $\text{CdS}_x\text{Se}_{1-x}$ nanocrystals in glasses taken from ref. 8 are shown in the table. The decay constants of all the samples were about 1 ps. These results are similar to those for CdS-doped glasses.⁷⁾ Therefore, the effect of alloying on carrier dynamics is considered to be small in CdSSe nanocrystals in glass.

It is interesting to compare the photoluminescence dynamics with the results of transient absorption in the infrared range ($3\mu\text{m}$) and DFWM experiment we reported recently.⁶⁾ The dynamics of transient absorption of Hoya R-68 are shown in Fig. 3. The data were fitted by a two-exponential decay function shown by a smooth curve in Fig. 3. The small decay time constant was 1.1 ps, and the large one was about 200 ps. The small decay time constant agreed well with that of the luminescence dynamics (1.3 ps, cf. Fig. 1). The DFWM signal of Hoya R-68 (Fig. 2 in ref. 6) was also fitted well by a two-exponential decay function. The small decay time constant was 4 ps, and the large one was about 200 ps. The decay time was larger than those for transient absorption and luminescence dynamics. A difference in decay time was also observed in Asahi Y-64: 2 ps and 200 ps for the DFWM experiment⁶⁾ and 0.8 ps for the present experiment.

The photoluminescence intensity was proportional to the product of the electron and hole populations at a particular energy. The decay constants we obtained were in agreement with those observed by Klimov and coworkers^{3,4)} in CdS and CdSe nanocrystals. They showed that the ultrafast photoluminescence decay is due to the trapping of holes in the surface states. They suggested that the hole traps are intrinsic nanocrystal states or intrinsic interface states. Consequently, the decay times are almost independent of the type of sample. The transient absorption measurement probed by infrared pulses monitors absorption attributed to carriers excited by a visible pump pulse. Because of

the position of energy states of carriers confined within nanocrystals, the excited state absorption in infrared is dominated by the contribution of the hole population. That is why the same fast decay component appears in both the photoluminescence and transient absorption decay. The slower 200 ps component is most likely attributed to electron dynamics. The dynamics measured by the DFWM technique with 780 nm pulses reflects the dynamics of the space modulation of a complex index of refraction of the sample. The real excitations of carriers, which lead to picosecond signal responses, differ from those in the two other ultrafast experiments. That is why the direct comparison of decay times is not straightforward. Indeed, the 780 nm pulse can lead to the two-photon absorption in the energetically high carrier states and to the single-photon absorption in the surface states (energetically located below the absorption edge energy). For these states, the hole relaxation is slower (no fast trapping). The response of the whole assembly of nanocrystals is thus slower. The equality of decay time constants (200 ps) of the slow components in transient absorption and DFWM measurements enables one to assign the faster decay to the hole dynamics and the slower one to the electrons.

In summary, the ultrafast photoluminescence dynamics of a series of CdSSe-doped glasses were measured and compared with those of transient absorption and DFWM experiments. The initial decay times of luminescence and transient absorption were about 1 ps. Their values were found to be almost independent of the type of sample. We interpret this initial fast photoluminescence decay in terms of efficient hole trapping in surface states.

The authors acknowledge the support of the Grant Agency of the Academy of Sciences of the Czech Republic (Grant No. A1010316) and of the research center LC510 of the Ministry of Education of the Czech Republic. This work is part of the research plan MSM 0021620834 that is financed by the Ministry of Education of the Czech Republic.

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Figure captions

Fig. 1. Dynamics of photoluminescence of Hoya R-68 measured by up-conversion technique. The excitation wavelength is 405 nm, and photoluminescence is monitored at about 665 nm. The smooth curve is a single-exponential fit.

Fig. 2. Dynamics of photoluminescence of Asahi R-64 measured by up-conversion technique. The excitation wavelength is 405 nm, and photoluminescence is monitored at about 615 nm. The smooth curve is a single-exponential fit.

Fig. 3. Transient absorption of Hoya R-68 in infrared range. The peak power density of pump light is 0.75 TW/cm^2 . The wavelength of pump light is 482 nm, and that of probe light is $3 \mu\text{m}$. Data points are from ref. 6, and the smooth curve is a two-exponential fit.

Table I. Decay times of luminescence at peak wavelengths in all samples investigated. The excitation wavelength is 405 nm. The molar fractions x of $\text{CdS}_x\text{Se}_{1-x}$ nanocrystals in glasses are from ref. 8. The x values of Hoya R-66 and R-68 are smaller than 0.04, and that of Asahi Y-64 is smaller than 0.06.

Sample	Luminescence Wavelength (nm)	Luminescence Decay time (ps)	Composition x
R-64(H)	630	1.0	0.04
R-66(H)	650	1.4	
R-68(H)	665	1.3	
R-64(A)	615	0.8	0.06
R-66(A)	650	1.0	
2-58	600	0.8	0.29
2-64	615	0.5	0.11
RG645	615	0.6	0.23
RG665	615	0.6	

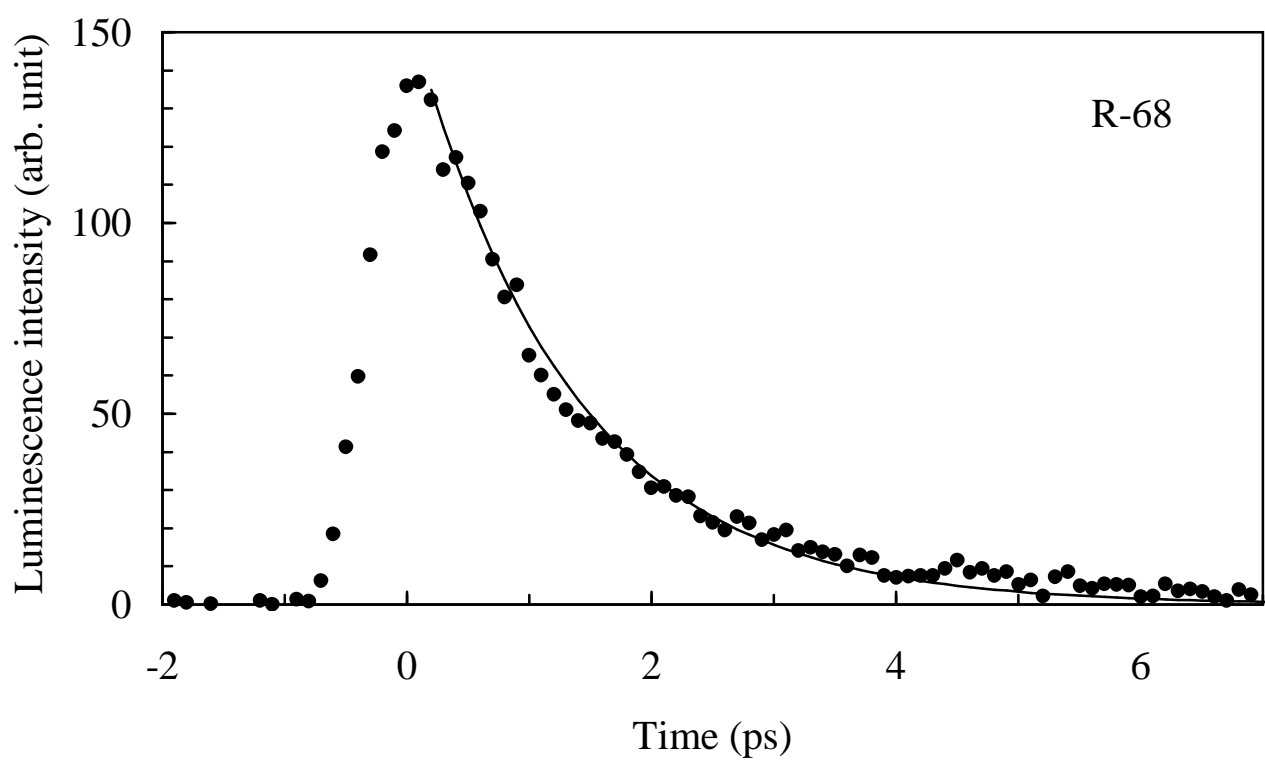


Fig. 1

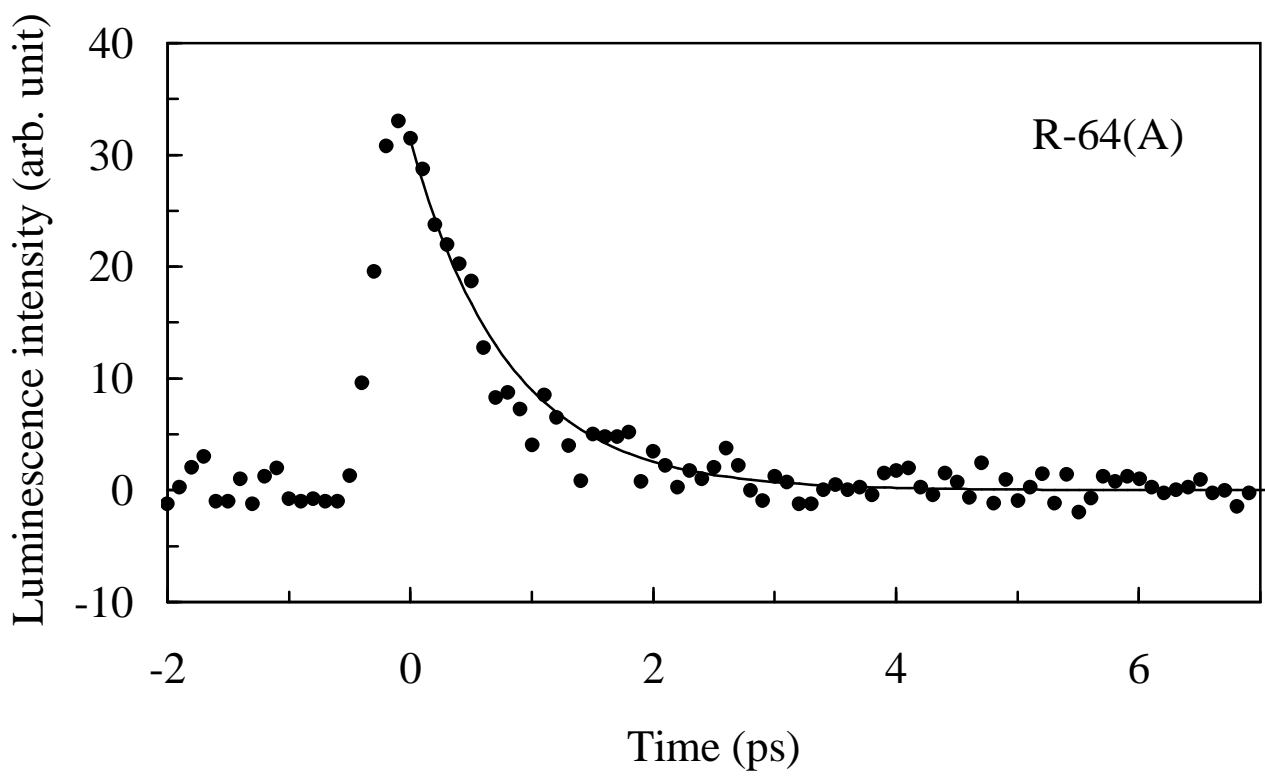


Fig. 2

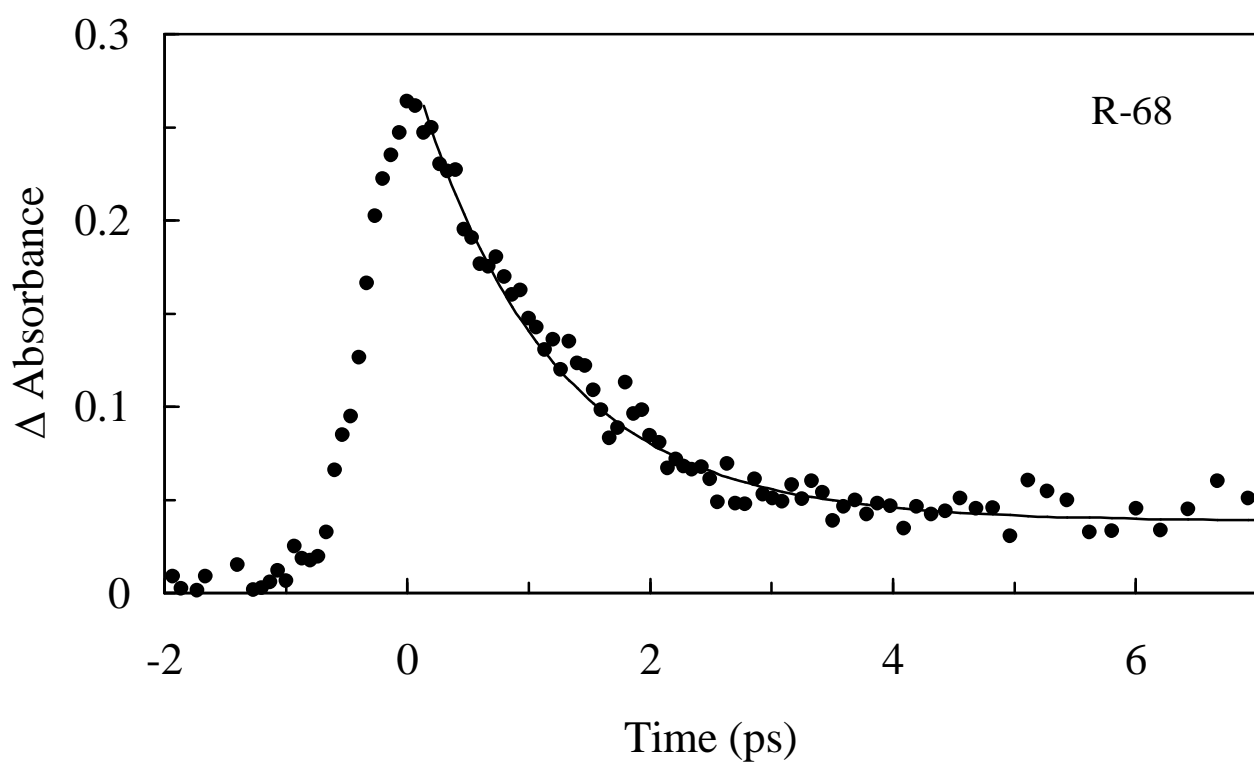


Fig. 3