

## Time-resolved luminescence study of biexcitons in CuCl quantum dots

Yasuaki Masumoto, Satoshi Katayanagi, and Tomobumi Mishina

*Institute of Physics, University of Tsukuba, Tsukuba, Ibaraki 305, Japan*

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Population dynamics of excitons and biexcitons in nanometer-sized CuCl microcrystallites (nanocrystals) was studied with a time-resolved luminescence measurement. A recurring process between excitons and biexcitons was clearly observed as a function of the second decay component of the biexciton luminescence and with an increase of the exciton luminescence. They become prominent with an increase in the excitation intensity. The biexciton luminescence is broadened asymmetrically to higher energy with an increase in the biexciton density. These temporal as well as spectral characteristics of biexciton luminescence are inherent to CuCl nanocrystals but are not observed in a CuCl bulk crystal, which shows that biexcitons are much more efficiently formed from excitons in a CuCl nanocrystal than in a CuCl bulk crystal.

Population dynamics of excitons and biexcitons in semiconductors has been studied for a long time.<sup>1-3</sup> With an increase in the excitation intensity, a biexciton is formed as a result of the binary interaction between two excitons. Conversely, when a biexciton is annihilated an exciton and a photon are formed. Excitons can be reformed by the radiative annihilation of biexcitons and subsequently form biexcitons again. This recurring process has been assumed to describe the population dynamics of excitons and biexcitons in CuCl and CuBr,<sup>2,3</sup> which are prototypical materials for the study of biexcitons. However, the recurring process has not allowed one to understand the temporal change of excitons and biexcitons in bulk crystals. In fact, published data of the biexciton luminescence in CuCl bulk crystals show single-exponential decay,<sup>3-6</sup> although the excitation density ranges widely from 50 nJ/cm<sup>2</sup> to 8 mJ/cm<sup>2</sup>. In the present study, we turn to the population dynamics of excitons and biexcitons in nanometer-sized CuCl microcrystallites (CuCl nanocrystals), where quantum confinement of an exciton can be prototypically observed.<sup>7,8</sup> Biexcitons in semiconductor nanocrystals have been a subject of extensive theoretical studies because the spatial confinement modifies the biexciton state considerably.<sup>8,9</sup> The dynamical behavior of biexcitons in nanocrystals in comparison with that in bulk crystals is another interesting subject to be studied. Excitons and biexcitons are spatially confined in nanocrystals, so that the recurring process is expected to take place much more frequently compared with the bulk crystal. In CuCl nanocrystals, biexciton lasing was observed and the optical gain associated with the transition from the biexciton state to the exciton state was much higher than for the bulk crystal.<sup>10,11</sup> A time-resolved luminescence study is expected to help understand these phenomena.

Samples studied were CuCl nanocrystals embedded in NaCl crystal and a CuCl bulk crystal. The growing procedure of the nanocrystal sample and the characterization procedure are described in our previous paper.<sup>10</sup> The size of the bulk single crystal was 7.0×6.5×5.5

mm<sup>3</sup>. Samples were directly immersed in liquid nitrogen and their luminescence was analyzed temporally as well as spectrally. The excitation laser source was a regeneratively amplified output of the self-mode-locked Ti:sapphire laser. The output photon energy was doubled and the excitation ultraviolet pulses had a pulse width of 200 fs, a spectral width of 15 meV, and a pulse energy of 7 μJ. The photon excitation energy was 3.266 or 3.283 eV, which corresponds to the higher-energy part of the Z<sub>3</sub> exciton resonance. The pulse repetition rate was 1 kHz. The luminescence was analyzed by means of a 25-cm subtractive dispersion double monochromator and a synchroscan streak camera. The spectral resolution was set to be 3.3 meV and the time resolution of the system was 23 ps.

Luminescence and absorption spectra are shown in Fig. 1. The absorption spectrum shows a clear but broad Z<sub>3</sub> exciton structure whose energy is higher than the exciton energy of 3.218 eV in a bulk crystal. The blueshift of the Z<sub>3</sub> exciton luminescence, 11 meV, corresponds to the size-quantized energy of the Z<sub>3</sub> exciton in a CuCl nanocrystal whose radius is 4.2 nm.<sup>12</sup> The luminescence spectrum consists of an exciton band and a biexciton band.<sup>10,11,13-16</sup> Biexciton luminescence bandwidth is broader than that in a CuCl bulk crystal. With the increase in the excitation density, the biexciton luminescence increases more than the exciton luminescence, but both of them depend on the excitation density sublinearly.<sup>10,11</sup> The biexciton luminescence in both samples is ascribed to the biexciton annihilation leaving a longitudinal exciton because the induced absorption band related to a transverse exciton was observed at lower energy than the biexciton luminescence band by 7 meV. It is already well confirmed that the exciton band is inhomogeneously broadened because of the size inhomogeneity of nanocrystals.<sup>17</sup> However, the biexciton band cannot be simply considered to be inhomogeneously broadened, because the biexciton luminescence changes its energy little with the change of the nanocrystal radius<sup>15,16,18</sup> and because the biexciton luminescence band is broadened asymmetri-

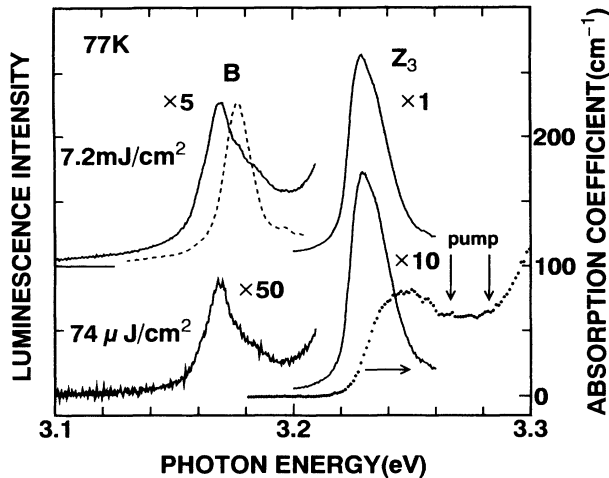


FIG. 1. Absorption spectrum (dotted line) and luminescence spectra (solid lines) of a sample, CuCl nanocrystals embedded in a NaCl crystal, at 77 K. Luminescence spectra are taken under the excitation photon energy of 3.283 eV with excitation densities of 7.2 mJ/cm<sup>2</sup> and 74 μJ/cm<sup>2</sup>. The luminescence spectrum of a CuCl bulk crystal under the same excitation density is shown by a dashed line.

cally to the higher-energy side with the increase in the excitation intensity.

Energy- and time-resolved luminescence of both the exciton and biexciton is shown in Fig. 2. It is clearly observed that the exciton lifetime is much longer than the biexciton lifetime. At the zero time delay, biexciton luminescence is 2.5 times stronger than the exciton luminescence. Then, the biexciton luminescence spectrum is so broad that its high-energy tail merges into the exciton luminescence band.

The temporal change of the exciton and biexciton luminescence at their peak energies is plotted logarithmically or linearly in Figs. 3(a) and 3(b) for two different excitation densities. Biexciton luminescence decay is de-

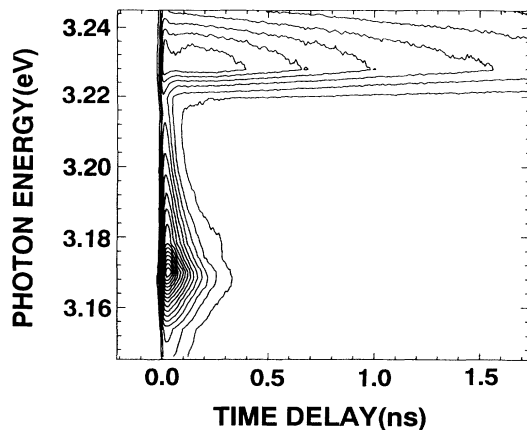


FIG. 2. A contour map of the energy- and time-resolved luminescence of the CuCl nanocrystal sample at 77 K. Excitation photon energy is 3.283 eV and excitation density is 7.2 mJ/cm<sup>2</sup>.

scribed by the double-exponential decay. The time constant of the fast decay is about 70 ps, while the time constant of the slow decay is 800 ps. The slow decay time constant is half of the decay time constant of the exciton luminescence, 1.6 ns. On the other hand, temporal change of the biexciton luminescence in a bulk CuCl crystal under the same excitation condition is expressed by the single-exponential decay. The decay time constant is 85 ps. This decay time constant agrees with the data of previous authors,<sup>3</sup> although the excitation density in our experiment is 10<sup>4</sup> times larger than that of those authors.

Biexciton luminescence is enhanced in comparison with the exciton luminescence with the increase in the excitation intensity. The initial part of the temporal change of the exciton luminescence also depends strongly on the excitation intensity. With the increase in the excitation intensity, a spikelike structure at the zero time delay grows and the initial rise becomes prominent. The decay time constant of the spikelike structure increases and the intensity of the structure increases when the observed photon energy approaches the biexciton luminescence energy. This fact ascertains that the spikelike structure comes from the high-energy tail of the biexciton luminescence. The spikelike structure gives the spectrally (vertically) broadened pattern at the zero time delay to the contour map of Fig. 2.

Population dynamics of excitons and biexcitons is described by the normalized rate equations which take account of the recurring process<sup>1-3</sup>

$$dn_b(t)/dt = -n_b(t)/\tau_b + \alpha n_{ex}(t)^2 + \beta \delta(t), \quad (1)$$

$$dn_{ex}(t)/dt = -n_{ex}(t)/\tau_{ex} + n_b(t)/\tau_b - 2\alpha n_{ex}(t)^2 + \delta(t), \quad (2)$$

where  $n_{b(ex)}(t)$  is the biexciton (exciton) number density,  $\tau_{b(ex)}$  is the biexciton (exciton) radiative decay time con-

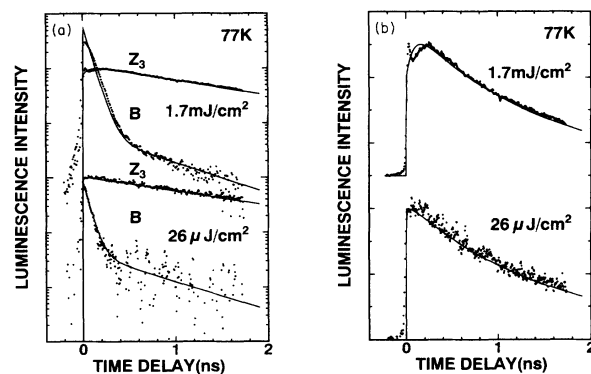


FIG. 3. Temporal change of the luminescence intensity of excitons and biexcitons at two different excitation densities, 1.7 mJ/cm<sup>2</sup> and 26 μJ/cm<sup>2</sup>. Excitation photon energy is 3.266 eV. (a) shows the logarithmic plot of the luminescence intensity at 3.232 (Z<sub>3</sub>) and 3.170 eV (B). (b) shows the linear plot of the luminescence intensity at 3.232 eV. Fitting on the basis of Eqs. (1) and (2) is shown by solid lines. Parameters are  $\tau_{b(ex)} = 76$  ps (1.6 ns),  $\alpha = 0.04$ , and  $\beta = 0.55$  for the excitation density of 1.7 mJ/cm<sup>2</sup>, while  $\tau_{b(ex)} = 68$  ps (1.7 ns),  $\alpha = 0.04$ , and  $\beta = 0.05$  for the excitation density of 26 μJ/cm<sup>2</sup>.

stant,  $\alpha$  is the formation rate of the biexciton as a result of the interaction between two excitons,  $\delta(t)$  is the normalized generation function of excitons and biexcitons, and  $\beta$  is a ratio of the biexciton number density to exciton number density at the zero time delay. Numbers of excitons and biexcitons in nanocrystals are not continuous numbers but integers. However, the ensemble average of numbers in nanocrystals is continuous numbers and is represented by number densities.

Fitting of the experimental results shown in Figs. 3(a) and 3(b) is done by the following procedures. The exciton population decays exponentially after 300 ps, so that the exciton radiative decay rate  $1/\tau_{ex}$  is obtained from the exponential fit without uncertainty. The slower decay rate of the biexciton population is almost equal to twice the exciton radiative decay rate. The faster decay component is obtained by subtracting the slower decay component from the experimental data. Thus the faster decay rate which corresponds to  $1/\tau_b$  is obtained. After that, temporal change of the population of both excitons and biexcitons is fitted by integrating rate equations (1) and (2) numerically with two adjustable parameters  $\alpha$  and  $\beta$ . The fitted results are shown in Figs. 3(a) and 3(b). Here, calculated values  $n_b/\tau_b$  and  $n_{ex}/\tau_{ex}$  are plotted to fit with the luminescence intensity. In addition,  $n_b/\tau_b$  is divided by 1.5 in comparison with  $n_{ex}/\tau_{ex}$ , because the spectral width of the biexciton luminescence is about 1.5 times as broad as that of exciton luminescence. The fitting is very good for every excitation density.

The spikelike structure observed at 3.232 eV at the time origin in Fig. 3(b) comes from the superposition of the biexciton luminescence on the exciton luminescence. Therefore, we omitted the structure to fit the data. Now, characteristic points in the temporal change of excitons and biexcitons are well understood. The slow component of the biexciton decay comes from the second term in the right-hand side of Eq. (1), the formation process of biexcitons, as a result of binary interaction of excitons. The slow rise in the exciton luminescence is explained by the second term in the right-hand side of Eq. (2), the formation of excitons as a result of radiative annihilation of biexcitons. With the increase in the excitation intensity, parameter  $\alpha$  changes little, while parameter  $\beta$  increases.

Parameter  $\beta$  is not zero. Therefore, we consider that biexcitons are formed just after the excitation, even if the excitation photon energy, 3.266 eV, corresponds to the higher-energy side of the  $Z_3$  exciton absorption. It should be noted that we could explain the quick rise in the biexciton luminescence not by the second term in the right-hand side of Eq. (1) but by the last term. Biexciton formation takes place most efficiently just after the excitation. Biexciton lifetime in nanocrystals is almost the same with that in a bulk crystal. This fact indicates that the biexciton envelope function is not so deformed.<sup>2</sup> This is reasonable because the interexciton distance in a CuCl biexciton, 1.5 nm, is still smaller than the radius of nanocrystals, 4.2 nm. In nanocrystals, absence of spatial diffusion minimizes the temporal decrease in the number densities of excitons and biexcitons. Therefore, the second term in Eq. (1) becomes larger than the first term before the biexciton density decreases below the detection

limit, because the radiative lifetime of the biexciton is 21 times shorter than that of the exciton. On the other hand, the absence of the slow decay time constant in biexciton luminescence in a bulk crystal suggests the serious temporal decrease of exciton density caused by the spatial diffusion.

The spectral difference in biexciton luminescence between CuCl nanocrystals and CuCl bulk crystals is clearly viewed, when the time-resolved luminescence spectra are compared with each other. Figure 4 shows the time-resolved luminescence spectra of CuCl nanocrystals and CuCl bulk crystals. In CuCl nanocrystals, the biexciton luminescence spectrum is broadened to higher energy at the initial stage. Afterwards, it gradually becomes sharp. On the other hand, in CuCl bulk crystals, the linewidth of the biexciton luminescence does not change and is narrower than that in nanocrystals. The highly asymmetric biexciton luminescence band cannot be interpreted as an inhomogeneously broadened band, because the high-energy shift of the biexciton luminescence is much smaller than that of the exciton with the decrease of the nanocrystal size.

Asymmetric broadening of the biexciton luminescence depends on the excitation intensity and decreases at a

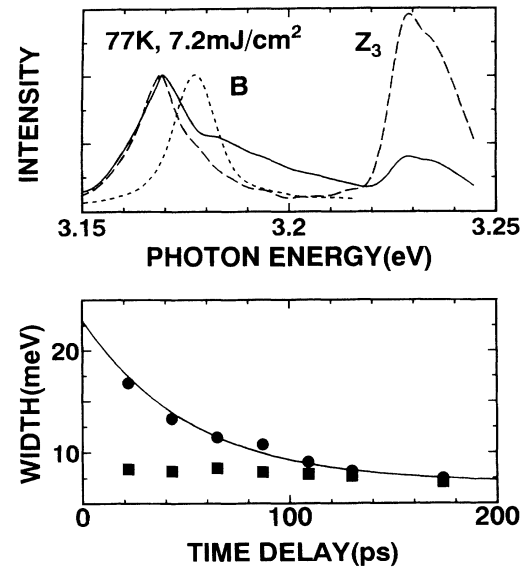


FIG. 4. Time-resolved biexciton luminescence spectra of a CuCl nanocrystal sample. Excitation photon energy is 3.283 eV and excitation density is 7.2 mJ/cm<sup>2</sup>. A solid line shows the time-resolved luminescence at 22 ps. A long-dashed line shows the time-resolved luminescence at 174 ps. A short-dashed line shows the time-resolved luminescence of a bulk CuCl sample at 22 ps. The time-resolved luminescence spectrum of the bulk sample does not change as time proceeds. Biexciton luminescence intensity is normalized. Biexciton luminescence of the nanocrystal sample is broadened asymmetrically to higher energy. The lower figure shows the half-width at the half maximum of the asymmetrically broadened biexciton luminescence band as a function of time. Solid circles show the half-width at the higher-energy side and solid squares show the half-width at the lower-energy side. The broadening decreases at the time constant of 52 ps.

time constant of 52 ps which is almost equal to the biexciton lifetime. This fact shows that the broadening depends on the biexciton density in nanocrystals and, therefore, is ascribed to the strong biexciton-biexciton interaction in nanocrystals. It is noted that the exciton band is inhomogeneously broadened and that the broadening does not depend on the excitation density even just after the excitation. It means that exciton-exciton or exciton-biexciton scattering does not cause the asymmetric broadening of the biexciton luminescence band. In CuCl bulk crystals, the symmetric broadening of biexciton luminescence was reported and was interpreted as the biexciton-biexciton collision.<sup>13</sup> Therefore, asymmetric broadening observed in CuCl nanocrystals is interpreted not as simple biexciton-biexciton collision but may be interpreted as excited states of biexcitons which are induced by the biexciton-biexciton interaction.<sup>9</sup> We imagine the biexciton excited states are composed of an exciton at the ground ( $n=1$ ) quantum state and an exciton at the excited ( $n=2,3,\dots$ ) quantum state or two excitons at the excited quantum state. Energy separation between the ground biexciton state and its first excited state is estimated to be three times the quantum confinement energy of excitons, 11 meV, for CuCl nanocrystals 4.2 nm in radius. This energy separation is almost equal to the biexciton binding energy. Therefore, biexciton luminescence broadens asymmetrically up to the exciton luminescent energy as a result of smearing by the size distribution, if the excited-state biexcitons annihilate leaving excitons at the ground quantum state. The possible instan-

taneous formation mechanism of biexcitons is the direct two-photon creation of the biexciton excited states. Further study is necessary to clarify the physical process.

In summary, the exciton luminescence and the biexciton luminescence in CuCl nanocrystals were investigated with time-resolved spectroscopy. The biexciton luminescence shows two-component decay behavior and the slower decay time constant is half of the decay time constant of the exciton luminescence. Exciton luminescence shows a clear increase. These characteristics are pronounced with the increase in the excitation intensity and are well explained by the recurring process between excitons and biexcitons. Biexcitons are created just after the excitation, even if the exciton band is excited. Simultaneously, biexciton luminescence spectra are broadened asymmetrically to the higher energy depending on the excitation intensity. These observations are interpreted as a result of frequent exciton-exciton and biexciton-biexciton interactions in CuCl nanocrystals. Characteristic features observed temporally as well as spectrally are not observed in a CuCl bulk crystal. This is because excitons and biexcitons are spatially confined in nanocrystals while not in a bulk crystal.

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sample show that the mean radius of nanocrystals is 3.0 nm. The blueshift of  $Z_3$  exciton luminescence is not reflected by the mean size of nanocrystals but by the size of luminescent nanocrystals. When the size distribution is large, the luminescence spectrum shows Stokes shift from the absorption peak.

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