Generation processes of superfluorescence of biexcitons in CuCl quantum dots by one- and two-photon resonant excitation

K Kawamura1, T Yoshida1, M Nasu1, J Ishihara1, A Ishikawa2 and K Miyajima1*

1Department of Applied Physics, Graduate School of Science, Tokyo University of Science, 6-3-1 Niijuku, Katsushika-ku, Tokyo 125-8585, Japan
2Department of Science for Advanced Materials, Graduate School of Engineering, University of Yamanashi, 4-3-11 Takeda, Kofu-city, Yamanashi 400-8511, Japan

*Corresponding Author
E-mail address: miyajima@rs.tus.ac.jp

Abstract. We investigated the influence of excitation processes of a biexciton on the generation of superfluorescence, which is pulsed radiation from coherently coupled two-level systems, from biexcitons in CuCl quantum dots. Two excitation processes of biexcitons were examined: resonant two-photon excitation of biexcitons, and resonant one-photon excitation of excitons. The excitation density dependence of the time-resolved photoluminescence was measured. The results showed that for one-photon excitation, a stronger peak intensity, longer delay time and wider pulse width were observed compared to resonant two-photon excitation. The high density of the excited dots in the one-photon excitation process results in the strong pulse, while an initial population of excitons results in a suppression of coherent coupling.

1. Introduction
Superfluorescence (SF) is defined as cooperative spontaneous emission from coherently-coupled many excited two-level systems [1]. In the generation process of SF, complete population inversion of many two-level systems is formed by a strong excitation pulse. Their dipole moments are then synchronized by interaction with a radiation field, which is triggered by a spontaneous emission. They then cooperatively emit photons. Therefore, to generate SF, the distance between any given pair of two-level systems should be shorter than the emission wavelength, and a long dephasing time is required to keep synchronization during emission. Until now, most studies on SF reported mainly on atoms and molecules [2]-[4]. However, in recent years, observation of SF in semiconductors has been reported [5],[6]. An exciton or biexciton in a semiconductor has a shorter radiative lifetime compared to an atom or molecule, which induces ultrashort pulses. In addition, semiconductors have an advantage with regard to applications to new light sources owing to the possibility of current injections and miniaturization. Semiconductor quantum dots (QDs) assembly is an appropriate system for generating SF because the fabrication of high-density QD assembly is possible and a QD has quantized energy levels and long dephasing time.
We reported on SF from CuCl QDs assembly [7][8]. CuCl is a suitable material for studying the fundamental properties of excitons and biexcitons because of their large exciton and biexciton binding energies [9][10]. Owing to latter, CuCl QDs assembly has a two-photon absorption band for biexcitons which is below the exciton absorption band [11]. Therefore, a complete population inversion between the biexciton and exciton states can be achieved initially by resonant two-photon excitation of the biexcitons, as shown in Figure 1(a). Under this excitation process, the generation of ultrashort pulsed SF and the transition from a spontaneous emission to the SF are observed for photoluminescence (PL) of biexcitons in CuCl QDs [7][8]. Furthermore, in the case of resonant excitation of the exciton in which a biexciton originates via a relaxation from two excitons in a QD as shown in Figure 1(b), pulsed emissions from the biexcitons were observed [7]. However, the influence of the excitation processes of the biexciton for generating SF has not been investigated. In this study, we measured time-resolved biexciton luminescence under one- and two-photon excitation and their excitation density dependences are discussed. Differences in the actual excited dot density and the initial population density of the excitons and biexcitons affected the time-profiles of the SF.

![Figure 1](image1.png)

**Figure 1.** Energy diagram of resonant two-photon excitation process of biexcitons via virtual level (yellow arrows) (a) and one-photon excitation processes of excitons to generate biexcitons through a relaxation from 2 excitons (blue arrows) (b).

### 2. Experimental setup

We fabricated CuCl QDs embedded in NaCl single crystal using the transverse Bridgman method and the annealing process [12]. The annealing process was performed at 580 °C for 24 hours. The average radius of the CuCl QDs was estimated as ~4.9 nm from the exciton energy obtained by PL excitation measurement. The sample was then cleaved as a plate with a thickness of 1.21 mm and was placed in a holder in a cryostat. During subsequent optical measurement, the sample temperature was kept at 3 K.

The optical Kerr gate method was used for time-resolved PL measurements. A picosecond pulsed laser beam was produced by a regenerative amplified mode-lock Ti:sapphire laser (wavelength, 800 nm; repetition rate, 1 kHz). The laser beam was then divided into two components using a half mirror: one for the gate light and the other for the pump light of an optical parametric amplifier (OPA). The excitation light was obtained from the fourth harmonic generation of a signal beam of the OPA using two β-BaB₂O₄ crystals. The excitation light was focused on the sample with a deformed shape (length, 1870 µm; width, 41 µm) using a cylindrical lens, then, the PL from an edge of the sample was collected. The excitation energy was 3.210 eV for one-photon excitation and 3.185 eV for resonant in two-photon excitation. These values were determined from the PL excitation spectrum of the biexcitons.

### 3. Results and discussion

The excitation density dependences on the time profiles of the biexcitonic PL under one-photon and two-photon excitation are shown in Figure 2(a) and (b), respectively, with scattered excitation light. In both cases, the time profiles changed from exponential decays to the pulsed emissions.

Figure 3 shows the excitation density dependences of the delay time (a), the pulse width (b), and the peak intensity (c). Here, the delay time was defined as the time at the peak of the time profile, and the pulse width was defined as the full-width at half-maximum. When the excitation density increases,
a transition from spontaneous emission to SF occurs, which results in the increase in the delay time and a large superlinearity of the peak intensity. A further increase in the excitation density results in a dominance of the time profile by the SF, which results in a decrease in the delay time [8]. The ideal dependence of the peak intensity is the square of the density of the excited dots. However, because the peak intensity exhibited a similar behavior to that reported in a previous report [8], the generation of the SF is concluded. The origin of the unexpected behavior has not been resolved. It is suggested that the observed time profile consists of a few different SF components. Therefore, for a high excitation density, a new SF component with a long delay time appeared in addition to the main SF component, which results in a long delay time and wide pulse width of the whole profile.

In this case, we focus on the differences between the excitation processes. In Figure 3 (a), the delay time for the one-photon process was approximately 20 ps longer compared to the two-photon process. The generation time for the biexciton from two electron-hole pairs under band-to-band excitation was reported as ~4 ps at 2 K [13]. Therefore, in the case of resonant excitation of the excitons, the biexcitons can be generated more quickly. Therefore, it is concluded that the long delay time resulted not from a relaxation process for two excitons, but from the suppression of coherent coupling of biexcitons. In addition, the pulse width for a one-photon process is wider than that for a two-photon excitation process, except for an excitation density over 4 mJ/cm². This result also supports the idea of a suppression of coherent coupling of biexcitons. We think that an initial population inversion ratio is important for the coherent coupling.

The two-photon process establishes a complete population inversion, while the one-photon process generates biexcitons and excitons simultaneously. For the correlated QDs with three energy levels (ground, exciton and biexciton levels), super-radiant coupling is dominant under a population inversion. However, when the exciton density is higher than the biexciton density, sub-radiant coupling becomes dominant. In the case of one-photon excitation, the initial population of the exciton, which is not negligible for the high excitation density, suppresses the super-radiant coupling. Our theoretical calculation based on the semiconductor luminescence equations [14] showed that the exciton population induces a sub-radiant process of the biexcitons. This agrees with the differences in

Figure 2. Excitation density dependences of time profiles at the peak of the biexcitonic PL obtained under (a) one- and (b) two-photon excitation processes, with photon energies of 3.210 eV and 3.185 eV, respectively. The black broken curves represent the scattered excitation light. The solid black curve shows a fitting by the exponential function. All spectra were normalized by their maximum intensities.
the delay time and pulse width observed for one- and two-photon excitation. On the other hand, the peak intensity for one-photon excitation was stronger than that for two-photon excitation. In the case of the former, the absorption probability of the excitation light is larger than for the case of resonant two-photon excitation. Consequently, the actual density of the excited dots became larger, which results in a strong peak intensity. In addition, one-photon excitation exhibited a stronger power of 5.3 compared to a value of 3.5 for two-photon excitation. When the biexciton density exceeds the exciton density, SF components can be generated. This strong nonlinearity originates from the increase in the number of the cooperative two-level systems and the increase in the population inversion.

4. Conclusions
We investigated the influence of the excitation processes of biexcitons, which are resonant two-photon excitation of biexcitons and resonant one-photon excitation of the excitons, on the generation of SF in CuCl QDs. SF under one-photon excitation processes exhibited a stronger peak intensity, longer delay time and wider pulse width compared to the case of two-photon excitation. The strong peak intensity resulted from the large absorption probability of the excitation light. The actual density of the excited QDs is high for the one-photon excitation process. Furthermore, the longer delay time and wider pulse width indicates the inhibition of synchronization between dipole moments, resulting from the initial population density of the biexcitons and excitons. Our results indicate that the excitation process strongly influences on generating SF.

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Figure 3. Excitation density dependences on delay time (a), pulse width (b) and peak intensity (c) in the time profiles for two-photon excitation (red circles) and one-photon excitation (blue triangles).