Biexciton and Triexciton States in Quantum Dots in the Weak Confinement Regime

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Biexciton and triexciton states in CuCl quantum dots were studied by means of time-resolved size-selective pump-and-probe technique. A clear induced absorption band is observed on the high-energy side of the excitation photon energy. The new induced absorption is assigned to the transition from the exciton ground state to one of the weakly correlated exciton pair states which were theoretically predicted to exist and to play an important role in nonlinear optical processes. Its pump energy dependence and temporal evolution strongly support this assignment. Under high-density or two-color excitation condition, a triexciton state in quantum dots is observed for the first time. [S0031-9007(97)04397-4]

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Semiconductor nanocrystals dispersed in a large-bandgap matrix can be treated as quantum dots. Three-dimensional quantum confinement of electrons, holes, and excitons makes it possible to observe quantum size effect in quantum dots [1–3]. We can classify the quantum confinement effects into two main categories according to the ratio of the quantum dot radius R to the exciton Bohr radius a_B. One is the *strong confinement* ($R < a_B$) where electrons and holes are quantized individually, and the other is the *weak confinement* ($R > a_B$) where the translational motion of excitons is quantized. A CuCl quantum dot is known as a prototypical system in the weak-confinement regime because of its small exciton Bohr radius and has often been used to investigate excitons and biexcitons.

The study of the quantum confinement effect on many-exciton states, e.g., biexciton and triexciton, is still in the elementary stage. There are many experimental reports showing unique nonlinear optical properties of quantum dots, for example, enhancement of the biexciton binding energy [4], a nonmonotonic size dependence of the optical nonlinearity [5], and biexciton lasing [6]. Through these studies, the importance of weakly correlated exciton pair states has been pointed out [7]. The weakly correlated exciton pair state is one of the excited biexciton states. Roughly speaking, that state is an antibonding state of two excitons and has a higher energy and a larger spatial extent than the biexciton ground state, leading to a larger oscillator strength of transition from the exciton state. This state is of general character and is expected to be present as well in other low-dimensional structures, e.g., quantum wells and quantum wires. However, the actual observation was successful for the first time in the quantum dot as reported here, because the continuum states overlapping the weakly correlated exciton pair state inhibit clear observation of this state in other structures. So far, the experimental study of the excited biexciton states has been limited to the strong-confinement regime where the excited biexciton state is blurred by the size inhomogeneity and the ground state biexciton is masked by the broad exciton bleaching [8,9]. Therefore, it is important and interesting to study the excited biexciton states in the weak-confinement regime, making use of the advantageous situation that the exciton and biexciton binding energies are quite large. In this Letter, the excited biexciton states are identified unambiguously in CuCl quantum dots from comparison between theory and experiments. Furthermore, a triexciton state in quantum dots is observed for the first time. Along this line of approach, we can study the many-exciton states in a quantum dot successively. From details of the exciton addition spectrum, we can clarify the exciton correlation with renewed interest and investigate, for example, the ionization threshold of excitons and biexcitons which has been discussed so far only in the mean-field approximation. Thus, the present study holds a great promise of revealing new aspects in many-body physics.

We used the time-resolved size-selective pump-and-probe method. The sample was CuCl quantum dots embedded in a NaCl crystal. The absorption band of the sample was inhomogeneously broadened because of the size inhomogeneity of the quantum dots. The laser source was a self-mode-locked titanium sapphire laser and a titanium sapphire regenerative amplifier. After amplification, the output pulse has a pulse duration of 300 fs at a repetition rate of 1 kHz, and a pulse energy of 200 μJ/pulse. The amplified laser pulses were converted to their second harmonic. The second harmonic pulses were spectrally filtered by means of a spectral filter stage made of a grating and were used as pump pulses for the size-selective excitation. Their typical spectral width was 1.7 meV. A part of the amplified laser pulse was focused in pure water to produce a white continuum which was used as a probe beam. The transient absorption spectra were recorded by a spectrometer and a liquid-nitrogen cooled charge-coupled device multichannel detector.

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A solid line in the upper part of Fig. 1 shows the absorption spectrum of the sample at 77 K. The Z_3 exciton and $Z_{1,2}$ exciton absorption structures are observed. These exciton absorption energies are shifted to the higher energy side compared to those of the bulk material due to the quantum confinement effect. The Z_3 exciton energy of bulk CuCl is shown by a downward arrow. The spectrum of the spectrally filtered pump pulse is shown in the inset by a solid line together with that of the unfiltered pulse shown by a broken line. According to the well-known relation between the quantum confined exciton energy and the quantum dot radius [10], the pump pulse energy of 3.259 eV excites quantum dots of 2.3 nm radius. The dashed line shows the absorption spectrum at 10 ps after the excitation. The solid line in the lower part of Fig. 1 shows the difference between two spectra in the upper part. The spectrum consists of a spectral hole at the pump photon energy and two induced absorption structures at both sides (3.180 eV, 3.296 eV) of the spectral hole. Persistent hole burning was much smaller than the transient hole burning at 77 K [11]. Bleaching around 3.335 eV is related to the $Z_{1,2}$ exciton.

Differential absorption spectra are shown at the lower part of Fig. 1 for four different pump photon energies. Two prominent induced absorption bands shift with the change of the excitation photon energy. The energies of the spectral hole and the induced absorption bands are plotted in Fig. 2 as a function of the excitation photon energy. The solid circles show spectral hole energies, and they are on a line of slope 1.0, since their energy coincides with the excitation photon energy. Open (solid) triangles exhibit the energies of the induced absorption located at the higher (lower) energy side. Open circles show the energies of induced absorption measured previously by nanosecond pump-and-probe method [4] which was identified as the transition from the exciton to the biexciton ground state. The coincidence between open circles and solid triangles confirms the proper present measurement.

The solid line through the open triangles is a fitted line by the least squares method. The slope of this line is 2.0. This line crosses the line of slope 1.0 near the Z_3 exciton energy of bulk CuCl. Furthermore, the spectral hole and the induced absorption on the higher energy side exhibit almost the same temporal evolution. They show an exponential decay with a time constant of 480 ps which almost coincides with the luminescence decay time of excitons in CuCl quantum dots [12]. This fact indicates that the induced absorption on the higher energy side arises from the excitons preexcited in the quantum dots. These features agree well with those of the theoretically predicted [7] strong induced absorption transition from the exciton state to excited biexciton states.

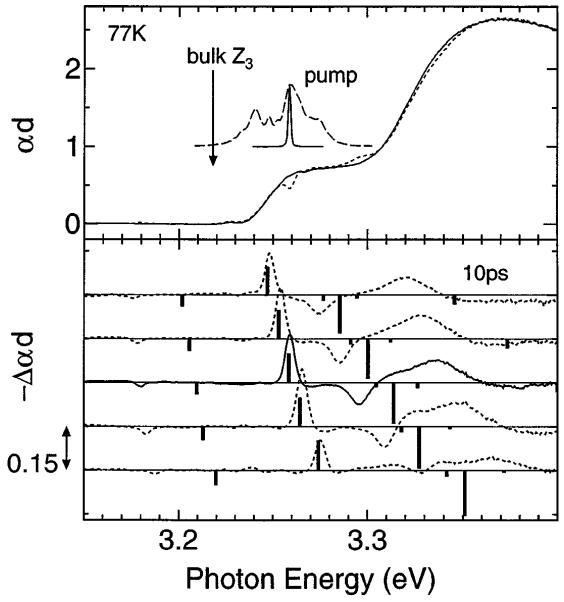

FIG. 1. Upper panel: The solid line shows absorption spectrum of CuCl quantum dots embedded in a NaCl crystal at 77 K, while a dashed line represents that at 10 ps after photoexcitation. Lower panel: The solid line shows differential absorption spectrum corresponding to the upper figure, while dashed lines are those for different excitation photon energies. The radii of quantum dots which were excited are 2.65, 2.46, 2.32, 2.19, and 2.03 nm from top to bottom, respectively. Thick solid bars are theoretical results normalized at the spectral hole. In the inset, filtered and unfiltered pump spectra are shown by a solid line and a dashed line, respectively.

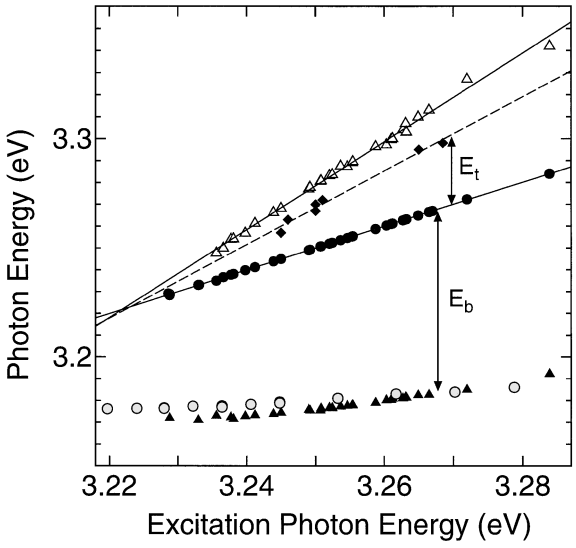

FIG. 2. Excitation energy dependence of the structures appearing in the differential absorption spectrum. The solid circles represent spectral hole energies, and they are on a line of slope 1.0. Open (solid) triangles show the energy of the induced absorption located at the higher (lower) energy side of the spectral hole. Open circles indicate the energy of the induced absorption measured by nanosecond pump-and-probe method in Ref. [4]. Solid diamonds correspond to additional induced absorption under high-density excitation. E_b denotes the biexciton binding energy defined by $2E_X - E_{XX}$ and E_t shows $E_{XXX} - E_{XX} - E_X$. Then the triexciton binding energy defined by $3E_X - E_{XXX}$ is given by $E_b - E_t$.

In CuCl where both the uppermost valence band and the lowermost conduction band are doubly degenerate, the angular momentum of the Bloch part exciton wave function is either 0 or 1. Then the angular momentum of the biexciton can be either of 0, 1, and 2. The explicit biexciton wave function for $J = 0$ and 2 can be written as $\Psi_{XX0} = \sqrt{3}/2\Phi_{XX}^{++}\chi_{00}^{00} - 1/2\Phi_{XX}^{--}\chi_{00}^{11}, \Psi_{XX2} = \Phi_{XX}^{--}\chi_{2M}^{11}$, where $\chi_{JM}^{j_e j_h}$ denotes the Bloch part wave function which has the total angular momentum (J, M) and is composed of two-electron wave function of angular momentum j_e and two-hole wave function of angular momentum j_h. In the limit of weak confinement, it has been shown that the weakly correlated exciton pair states may be approximated by product states of two independent excitons [7], namely,

$$\Phi_{XX}^{\pm\pm} = \frac{1}{\sqrt{2}}[\phi_X^g(r_{e1}, r_{h1})\phi_X^g(r_{e2}, r_{h2}) \pm \phi_X^g(r_{e1}, r_{h2})\phi_X^g(r_{e2}, r_{h1})], \quad (1)$$

where ϕ_X^g is the envelope function of the exciton ground state and r_{e1} and r_{e2} (r_{h1} and r_{h2}) denote the electron (hole) coordinates. The oscillator strengths of transitions from the ground state exciton X to these excited biexciton states are calculated as $f(X \rightarrow XX0) = 2/3 f_0, f(X \rightarrow XX2) = 4/3 f_0$, where f_0 is the oscillator strength of the excitonic transition.

The theoretical induced absorption spectrum from the exciton ground state is shown by thick solid bars in Fig. 1. The energy shifts of strong bands show good correspondence with experiments. Furthermore, the relative strengths of the induced absorption lines and the spectral hole are reproduced quite well by the theory, although there is a discrepancy in the energy positions of the induced absorption lines. Hence the strong peak above the pump energy can be assigned to the induced absorption transition to $XX2$ states.

Next we discuss experimental observation of triexciton states in CuCl quantum dots. At the upper part of Fig. 3(A), we exhibit the excitation density dependence of the differential absorption spectrum at 10 ps after photoexcitation. Under low density excitation, spectra in Fig. 3(A) are similar to those in Fig. 1, and the biexciton luminescence cannot be observed. Under high density excitation condition, we observed an additional induced absorption band which is shown by an arrow. Simultaneously the biexciton luminescence became observable.

In Fig. 3(B), the time evolution of the additional induced absorption is shown. Together with it, the temporal evolution of the spectral hole and the higher energy induced absorption band are also presented in the figure, although the excitation density was slightly low. Two solid curves through the solid circles and open triangles show an exponential decay with a time constant of 480 ps. On the other hand, the decay time constant of the additional induced

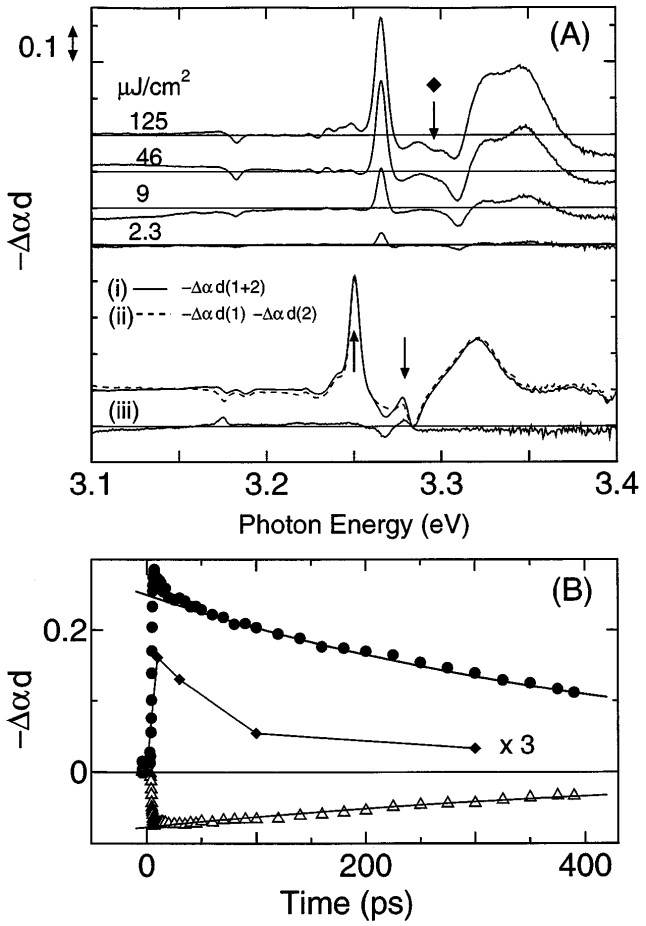

FIG. 3. (A) Upper panel: Excitation density dependence of the differential absorption spectrum at 10 ps after photoexcitation with the excitation photon energy fixed at 3.265 eV. Additional induced absorption shown by an arrow appears with the increase of the excitation. Lower panel: Experimental results of the two-color pump-and-probe measurement. The photon energy of the first (second) pump pulse is indicated by an upward (a downward) arrow. (i) Shows the differential absorption spectrum induced by both the first and second pulses. (ii) Exhibits the sum of differential absorption spectra induced by the first pump pulse and by the second one alone. (iii) = (i) − (ii). (B) Time evolution of the additional induced absorption under high-density excitation together with the spectral hole and the higher energy induced absorption. Symbols are the same as in Fig. 2.

absorption is less than 100 ps and corresponds to the luminescence lifetime of biexciton which is known to be 70 ps for CuCl nanocrystals [13]. If a triexciton state consists of a biexciton and an exciton, the intensity of the induced absorption transition from a biexciton to a triexciton should be proportional to the number of biexcitons. Therefore the time evolution and the excitation density dependence suggest strongly that the additional induced absorption can be assigned to transition from the biexciton ground state to a triexciton state.

We examined this assignment by the two-color pump-and-probe method. The energy of the second pump pulse is tuned to the induced absorption caused by the

first pump pulse. This combination produces biexciton effectively only in quantum dots of particular size and enables us to observe the induced absorption to triexciton states. At the lower part of Fig. 3(A), results of the experiment are shown. Photon energy of the first or second pump pulse is represented by an upward or a downward arrow, respectively. Time delay between two pump pulses was 5 ps, and the probe pulse delay to the second pump pulse was also 5 ps. The solid line (i) shows the differential absorption spectrum induced by two successive pump pulses, while the dotted line (ii) exhibits the sum of differential spectra induced by the first pump pulse and by the second one alone. Spectrum (iii) shows the difference between two spectra. If the second pump pulse increases (decreases) the absorption of the quantum dots excited selectively by the first pulse, we would observe negative (positive) signal in spectrum (iii). In fact, we observed an increased absorption region between the spectral hole and the induced absorption in spectrum (iii). The relative peak position is similar to that of the additional induced absorption in the upper part of Fig. 3(A). Hence both structures should be of the same origin. Excitation energy dependence of this induced absorption is shown in Fig. 2 by solid diamonds. The fitted line has a slope of 1.7, and this line also crosses the other two lines near the bulk Z_3 exciton energy.

In addition to an increased absorption region, we observed two decreased absorption regions in spectrum (iii). The lower or higher energy one indicates the decrease of the transition from the exciton state to the biexciton ground state or excited biexciton state, respectively. This can be explained by noticing that the biexcitons are produced size-selectively by the second pump pulse.

The linear proportionality of the induced absorption energy to the exciton confinement energy suggests that the exciton addition energy is primarily determined by the increase in the kinetic energy proportional to the inverse square of the quantum dot radius. As proposed previously [7], since the weakly correlated exciton pair state ($XX2$) is an antibonding state of two excitons, its kinetic energy can be assumed to be equal to that of two excitons independently confined in a region of half the volume of the quantum dot. Then its energy is written as $E_{XX2} = 2E_{bk} + 2\sqrt[3]{4}\,(E_X - E_{bk})$, where $E_X(E_{bk})$ is the exciton energy in a quantum dot (bulk material) and the slope in Fig. 2 is estimated as $2\sqrt[3]{4} - 1 \cong 2.2$ in good agreement with the experiment. The observed triexciton state has an energy greater than that of an independent biexciton-exciton pair but smaller than that of three excitons. Thus, while this state is a bound state, it may be regarded as an antibonding combination of a biexciton and an exciton. Therefore the above argument may be extended to the case of exciton addition to the biexciton ground state assuming the added exciton to occupy half the volume of the quantum dot without affecting the biexciton ground state. Then we have $E_{XXX} - E_{XXg} = \sqrt[3]{4}\,(E_X - E_{bk}) + E_{bk}$ with $E_{XXX(XXg)}$ being the energy of the triexciton (biexciton ground) state, and this gives the slope in Fig. 2 as $\sqrt[3]{4} \cong 1.6$, again in good agreement with the experiment. These qualitative arguments provide a strong support to the identification of the newly observed induced absorption as the transition from the biexciton to a triexciton state.

In conclusion, we studied biexciton and triexciton states in quantum dots in the weak-confinement regime by using the time-resolved size-selective pump-and-probe technique. One of the observed induced absorption bands was unambiguously identified as the transition from the exciton state to the weakly correlated exciton pair state whose presence was theoretically predicted. We observed a triexciton state in quantum dots for the first time by two independent methods employing high-density excitation and two-color excitation scheme. These experiments open a new direction of research and hold a great promise of revealing new aspects of many-exciton states in confined systems.

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