

Observation of enhanced biexcitonic effect in semiconductor nanocrystals

Young-Nam Hwang,¹ Koo-Chul Je,² Dongho Kim,¹ and Seung-Han Park²

¹National Creative Research Initiatives Center for Ultrafast Optical Characteristics Control, Yonsei University, Seoul 120-749, Korea

²Department of Physics, Yonsei University, Seoul 120-749, Korea

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We have observed enhanced biexcitonic effect in CdS_{0.6}Se_{0.4} nanocrystals by means of femtosecond two-photon pump-probe spectroscopy. In contrast to a weak biexcitonic photoinduced absorption in the presence of $|1S_e1S_h\rangle$ or $|1P_e1P_h\rangle$ excitons due to one-photon excitation, we have found a pronounced photoinduced absorption arising from a strong Coulomb coupling between a $|1S_e1S_h\rangle$ exciton and a two-photon excited $|1S_e1P_h\rangle$ exciton. We have also theoretically shown that $|1S_e1S_h;1S_e1P_h\rangle$ biexcitons have a large binding energy compared with $|1S_e1S_h;1S_e1S_h\rangle$ and $|1S_e1S_h;1P_e1P_h\rangle$ biexciton states.

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Semiconductor nanocrystals whose sizes are comparable to or less than the exciton Bohr radius exhibit a number of novel physical and optical properties due to the confinement of carriers in all three dimensions.¹ The three-dimensional confinement modifies the electronic states in the nanocrystals significantly and induces quasidiscrete energy levels.² Coulomb interaction between electrons and holes has also a large influence on these confined states, even in small nanocrystals showing strong confinement.^{3,4} Therefore, the electron-hole states in semiconductor nanocrystals are usually referred to as exciton states.⁵

Furthermore, it has been theoretically demonstrated that Coulomb interaction between the excitons could be strong enough to form stable biexciton states whose binding energy increases with decreasing nanoparticle size.⁵⁻⁷ Even excited biexciton states have been found to be stable in semiconductor nanoparticles by investigating the weak photoinduced absorption on the high energy side of the bleached exciton resonance in pump-probe experiments.^{4,7,8} In addition, the ground biexciton state has been observed when homogeneous and inhomogeneous broadenings are severely reduced by lowering temperature ($T=15K$) and saturating relatively large nanoparticles.⁹

In contrast, the biexcitonic effects at room temperature in CdSe nanocrystals, arising from $|1S_e1S_h\rangle$ and $|1P_e1P_h\rangle$ excitons, have been reported.¹⁰ The observed $|1S_e1S_h;1P_e1P_h\rangle$ biexciton state was attributed to the weak dependence on homogeneous broadening, based on the assumption of the same biexciton binding energies of $|1S_e1S_h;1S_e1S_h\rangle$, $|1S_e1S_h;1P_e1P_h\rangle$, and $|1P_e1P_h;1P_e1P_h\rangle$ states. However, the measured $|1S_e1S_h;1P_e1P_h\rangle$ biexciton binding energy was different from the $|1S_e1S_h;1S_e1S_h\rangle$ biexciton binding energies obtained in other experiments.⁹

In this paper, we report on observation of enhanced biexciton interaction from $|1S_e1S_h\rangle$ and $|1S_e1P_h\rangle$ excitons, indicating its strong dependence on the composite exciton states. To populate $|1S_e1P_h\rangle$ state in CdS_{0.6}Se_{0.4} nanocrystals, we have used infrared femtosecond pulses of 1.11 eV which efficiently induce two-photon absorption. Note that one-photon excitation is not easily achieved for the exciton state due to selection rules.¹¹ For comparison, the $|1S_e1S_h\rangle$ and $|1P_e1P_h\rangle$ excitons are also excited by one-photon exci-

tation with the pump pulses of 2.18 and 3.10 eV, respectively. In the presence of these excitons, $|1S_e1S_h\rangle$ excitons are excited by delayed continuum pulses to probe the photoinduced absorption due to biexciton formation. The dependence of biexciton states on various exciton states has been also theoretically investigated. The result clearly shows a significantly increased Coulomb interaction of the $|1S_e1S_h;1S_e1P_h\rangle$ biexciton state.

The sample employed in our experiment is CdS_{0.6}Se_{0.4} nanocrystals doped in a glass matrix (Schott Glass, OG 590). The average radius of $R=3.0$ nm with the size dispersion of 10–15 % has been estimated by small angle neutron scattering method.^{12,13} To investigate the effect of the exciton states on the biexciton binding energies, femtosecond pump-probe experiments have been performed by populating $|1S_e1S_h\rangle$, $|1P_e1P_h\rangle$, and $|1S_e1P_h\rangle$ states in the nanocrystals. The $|1S_e1S_h\rangle$ excitons are resonantly excited at 2.18 eV (570 nm) with the pump fluence of ~ 75 $\mu J/cm^2$. The $|1P_e1P_h\rangle$ state is populated by intraband relaxation of carriers excited at high photon energy of 3.10 eV (400 nm) with the pump fluence of ~ 225 $\mu J/cm^2$, while the $|1S_e1P_h\rangle$ excitons are created by two photon excitation at 1.11 eV (1120 nm) with the pump fluence of ~ 750 $\mu J/cm^2$.¹¹ The details of the experimental techniques may be found in the literature.¹³

The chirp-corrected transient absorption spectra in early delay times are shown in Fig. 1. In the case of one-photon excitation at 2.18 eV [Fig. 1(a)], the transient absorption spectra are dominated by the $|1S_e1S_h\rangle$ bleaching at 2.15 eV (A1 band). Since all three valence bands are coupled to one conduction band in CdS_{0.6}Se_{0.4} nanocrystals, the state filling of the exciton resonance from the spin-orbit split-off band ($\Delta_{so} \approx 250$ meV),¹⁴ also induces a small bleaching at 2.43 eV (A2 band). The assignment is further confirmed by similar recovery behavior of A1 and A2 bands as shown in Fig. 2(a), since the bleaching dynamics is mainly determined by the shared electron population.^{15,16} Although $|1S_e1S_h;1S_e1S_h\rangle$ biexciton states can be formed in this case, the photoinduced absorption indicating the biexciton effect is not observed due to the broadening of A1 band. The biexciton binding energy is not large enough to surpass the broadening of the bleach band.

For the photoexcitation at 3.10 eV [Fig. 1(b)], a photoinduced absorption (B band) is observed at the low energy side

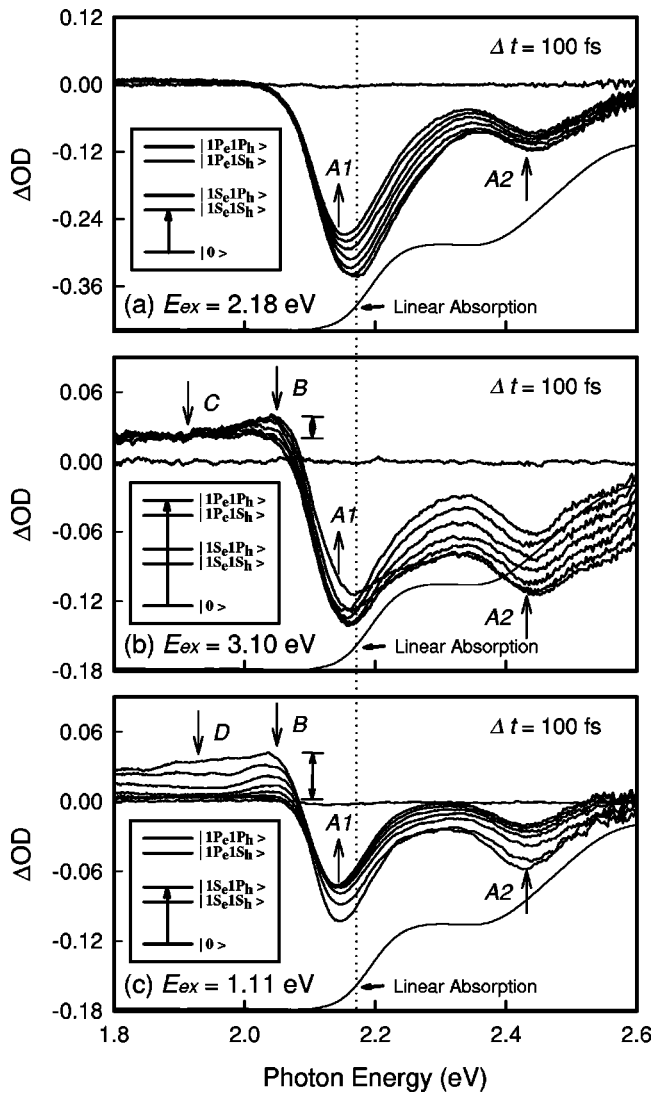


FIG. 1. The transient absorption spectra excited at (a) 2.18 ($|1S_e1S_h\rangle$), (b) 3.10 ($|1P_e1P_h\rangle$), and (c) 1.11 eV ($|1S_e1P_h\rangle$) and linear absorbance of $\text{CdS}_{0.6}\text{Se}_{0.4}$ nanocrystals. The spectra shown are in the initial decay stage with time intervals of 0.1 ps. The inset shows the scheme of energy levels of $\text{CdS}_{0.6}\text{Se}_{0.4}$ nanocrystals.

of A1 band. The considerable increase in the A2 bleaching magnitude strongly implies the population in the $|1P_e1P_h\rangle$ excitons, although it is spectrally overlapped by $|1S_e1S_h\rangle$ transitions from the split-off band [Fig. 1(a)]. Note that the two-exponential decay dynamics of A2 band shown in the inset of Fig. 2(b) also indicates that the A2 band includes the $|1P_e1P_h\rangle$ contribution as well as the $|1S_e1S_h\rangle$ transition from the spin-orbit split off band since the energy difference between the $|1P_e1P_h\rangle$ transition energy and the split-off $|1S_e1S_h\rangle$ transition is only ~ 40 meV.^{4,16}

The kinetic behaviors [Fig. 2(b)] show that the relatively slow build-up of A1 band still continues during ~ 0.3 ps, while A2 band follows a decay dynamics. The intraband relaxation also provides further evidence for the contribution of $|1P_e1P_h\rangle$ population to A2 band, as previously observed in CdSe nanoparticles.¹⁶ The A1 and A2 kinetics at long delay times are determined by the 1S electron relaxation

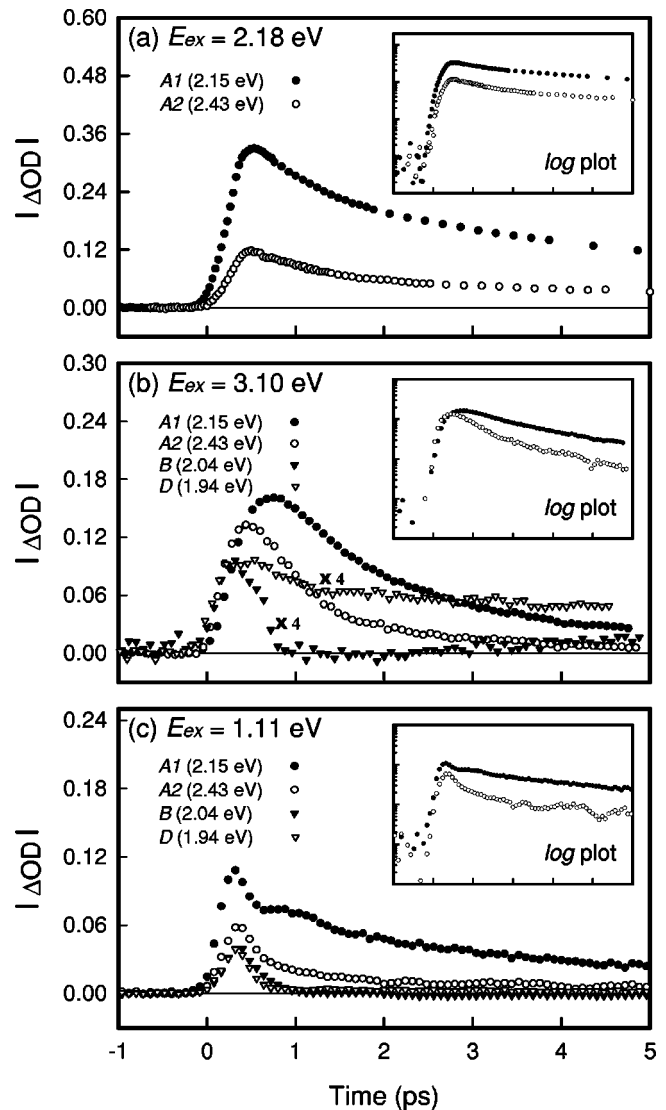


FIG. 2. Temporal profiles of characteristic bleaching and photo-induced absorption bands in $\text{CdS}_{0.6}\text{Se}_{0.4}$ nanocrystals excited at (a) 2.18 ($|1S_e1S_h\rangle$), (b) 3.10 ($|1P_e1P_h\rangle$), and (c) 1.11 eV ($|1S_e1P_h\rangle$). The insets show the kinetics of A1 and A2 bands in log scale.

after the fast $1P$ -to- $1S$ relaxation in the early decay stage, resulting in the similar bleaching recovery [inset of Fig. 2(b)]. Since $|1S_e1S_h;1S_e1S_h\rangle$ biexciton state induces no change on the spectra [Fig. 1(a)], the observed photoinduced absorption of B band can be ascribed to the formation of $|1S_e1S_h;1P_e1P_h\rangle$ biexcitons.

The biexcitonic features are still obscured by another spectrally broad and long-lived photoinduced absorption (C band) originating from the transition of trapped electrons within a broad distribution of surface states.^{17,18} dc Stark effects as well as the biexcitonic interaction can lead to a derivativelike feature in the differential absorption spectra due to the shift of exciton band. In the case of the dc Stark effect, the electric field is generated by the charge separation due to the trapped holes at the surface of semiconductor nanocrystals. According to the previous report, the holes are

trapped for a quite long time so that the derivative feature can be observed even at ~ 300 ps after photoexcitation.¹⁶ In contrast, the biexcitonic effect shows a subpicosecond decay dynamics.¹⁰ To clarify the biexciton dynamics, the B band kinetics is extracted by considering the almost constant decay of C band. As shown in Fig. 2(b), the B band exhibits an ultrafast dynamics which is consistent with the dynamics of $A2$ band at the early stage. It indicates that the relaxation in both of the bands is determined by the $|1P_e1P_h\rangle$ population. All the observed features of $|1S_e1S_h;1P_e1P_h\rangle$ biexcitons are in a good agreement with the previous works on CdSe nanocrystals.^{10,16}

However, we have observed that the biexcitonic photoinduced absorption of B band is enhanced in the case of two-photon excitation at 1.11 eV. As shown in Fig. 1(c), the bleaching of $A1$ and $A2$ bands is also observed because of $1S$ electrons in the conduction band. The $A1$ bleaching magnitude comparable to that of one-photon excitation [Fig. 1(b)] indicates an efficient two-photon generation of $|1S_e1P_h\rangle$ excitons. Therefore, the strong B band can be directly assigned to the active formation of $|1S_e1S_h;1S_e1P_h\rangle$ biexciton states with a large Coulomb interaction energy. As well as the enhancement of photoinduced absorption of the B band, the gradual red-shift of $A1$ band has been also observed as the B band reaches its maximum [Figs. 1(a)–1(c)]. The observed spectral features strongly suggest an increased Coulomb coupling between $|1S_e1P_h\rangle$ and $|1S_e1S_h\rangle$ exciton states.

The kinetics of biexciton state is now determined by the intraband relaxation of holes from $1P$ to $1S$ states in the valence bands. Even a simple strong confinement model predicts that the intraband transitions between different angular momentum states are allowed.¹¹ Moreover, the energy difference between $1S$ and $1P$ hole states are very small compared with the corresponding electron energy difference due to the large hole effective mass in nanocrystals. Therefore, an ultrafast relaxation of holes is expected with a time constant shorter than or comparable to that of electron intraband relaxation. The biexciton dynamics of B band shown in Fig. 2(c) indeed shows a subpicosecond decay process. It is believed (despite of our limited time resolution) to be even faster than the biexcitonic dynamics in Fig. 2(b), depending on the electron intraband relaxation.

We have also theoretically studied the binding energies of various biexcitons, in which a $|1S_e1S_h\rangle$ exciton is coupled to another exciton state including $|1S_e1S_h\rangle$, $|1P_e1P_h\rangle$, $|1S_e1P_h\rangle$, $|1S_e2P_h\rangle$ states and so on. Since one-pair and two-pair systems with Coulomb interactions in quantum dots cannot be solved analytically, several groups have calculated the biexciton binding energies by using numerical matrix-diagonalization scheme⁵ and variational method.⁶

We have basically followed the numerical approach given by Hu, Lindberg, and Koch.⁵ For this approach the exciton and biexciton states are computed by numerical matrix diagonalization using expansion of the exciton and biexciton wave functions into appropriate sets of basis functions. The exciton state has the general form of

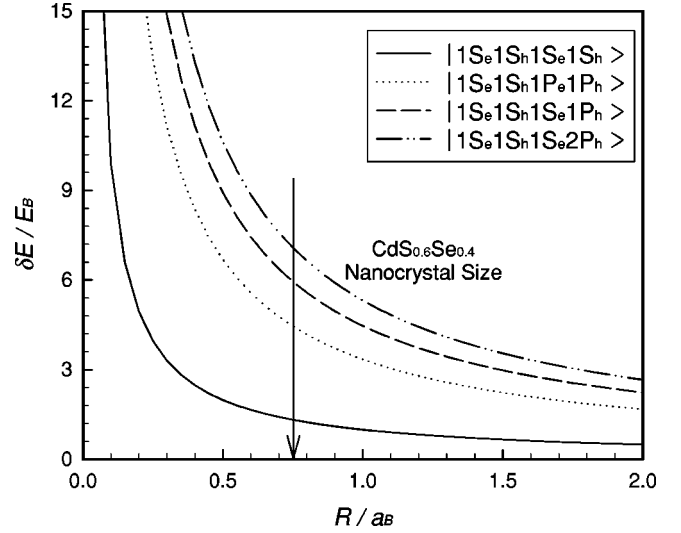


FIG. 3. Biexciton binding energies calculated in the presence of excitons in various quantum-confined states. The $|1S_e1S_h;1S_e1P_h\rangle$ biexciton binding energy surpasses the others in ambient nanoparticle sizes.

$$|\Phi_1\rangle = \int \int dr_e dr_h \phi_{n_1 n_2 l_1 l_2; LM}^{(1)}(r_e, r_h) \times \sum_{s_e, s_h} \chi(s_e, s_h) \psi_e^\dagger(r_e, s_e) \psi_h^\dagger(r_h, s_h) |0\rangle,$$

where $\chi(s_e, s_h)$ is related to the spin part, $\psi_e^\dagger(\psi_h^\dagger)$ is the creation operator of an electron(hole) and

$$\begin{aligned} \phi_{n_1 n_2 l_1 l_2; LM}^{(1)}(r_e, r_h) \\ = \sum_{m_1, m_2} \langle l_1 m_1 l_2 m_2 | LM \rangle \phi_{N_1}(r_e) \phi_{N_2}(r_h) \end{aligned}$$

is the exciton wave function. Here, $\phi_N(r_e)$ is the single-particle wave function, $N = \{n, l, m\}$ is the short-notation for the set of quantum numbers, L and M are the quantum numbers of the total angular momentum and its z component and $\langle l_1 m_1 l_2 m_2 | LM \rangle$ is the Clebsch-Gordan coefficient in Condon-Shortley convention.¹⁹ The biexciton wave functions can be expanded by using the two one-pair basis wave functions as in the case of one-pair state. The Coulomb matrix elements for exciton and biexciton states can be calculated by using the expansion formulas of Coulomb interaction with the Legendre function. It contains radial and angular integrations which provide selection rules. Through these calculations the binding energy of the ground-state biexciton δE_2^{ij} is defined relative to the ground-state energy of two unbound excitons as $\delta E_2^{ij} = (E_1^i + E_1^j) - E_2^{ij}$, where E_1^i is the exciton energy of the exciton state i and E_2^{ij} is the corresponding biexciton energy of the biexciton state ij . We include angular momentum states up to $l=3$ and numerically compute all integrals.

The results are shown in Fig. 3 where the nanoparticle size and the binding energy are normalized by the Bohr radius (a_B) and the binding energy (E_B) of bulk exciton

to eliminate material dependence. It is obvious that the biexciton binding energy depends strongly on the constituent exciton states in all nanoparticle sizes. For $\text{CdS}_{0.6}\text{Se}_{0.4}$ nanocrystals with $R \approx 0.75a_B$, the biexciton energies are $1.32E_B$, $4.45E_B$, and $5.95E_B$ for $|1S_e1S_h;1S_e1S_h\rangle$, $|1S_e1S_h;1P_e1P_h\rangle$, $|1S_e1S_h;1S_e1P_h\rangle$ states, respectively. The Rydberg energy E_B is estimated to be ~ 17.2 meV based on the value of $a_B = 40$ Å. The biexciton binding energy increases with asymmetric feature in the composite exciton states and the biexciton states because symmetric states induce a compensation between Coulomb attraction and repulsion and have no net Coulomb interaction. The theoretical calculations are in a good agreement with the observed experimental results, showing an enhancement of photoinduced absorption of B band and a gradual redshift of $A1$ band as the $|1S_e1S_h\rangle$, $|1P_e1P_h\rangle$, and $|1S_e1P_h\rangle$ excitons are excited by the pump beam.

Finally, it should be mentioned that the broad photoinduced absorption tail, designated as D band in Fig. 1(c), has a completely different feature from C band in Fig. 1(b). The D band shows as an extremely fast dynamics as the biexcitonic B band [Fig. 2(c)]. The biexciton states whose hole state is higher than $1P$ may be responsible for the induced absorption because the binding energy of $|1S_e1S_h;1S_e2P_h\rangle$ state is larger than $|1S_e1S_h;1S_e1P_h\rangle$ biexciton binding energy (Fig. 3). However, the fast initial decays observed in $A1$ and $A2$ bands in Fig. 2(c) could hardly be explained because they are determined by the relatively slow population relaxation of $1S$ electrons [Figs. 2(a) and 2(b)]. The observed D band strongly suggests the existence of localized biexcitons in the nanocrystals due to the constituent excitons trapped

into surface states or crystal defects. However, no long-lived photoinduced absorption has been observed by the photoexcitation at 1.11 eV in contrast to the case of excitation at 3.10 eV [Figs. 1(b) and 2(b)], although the $A1$ bleaching magnitudes are comparable to each other. Therefore, the trapped excitons are not mainly produced by pump excitation. Instead, it is possible that the $|1S_e1S_h\rangle$ excitons excited by probe beam can be trapped with the simultaneous formation of $|1S_e1S_h;1S_e1P_h\rangle$ biexcitons. Then, the spectrally broad photoinduced absorption of D band can be explained by ample surface states. Moreover, the fast decays of $A1$ and $A2$ bands manifest the rapid decrease of $|1S_e1P_h\rangle$ exciton population due to the formation of the localized biexciton states. The second build-up of $A1$ band after the fast decay is caused by the $|1S_e1P_h\rangle$ excitons set free from the localized biexcitons.

In summary, we have observed that the biexciton binding energies are significantly affected by the constituent exciton states. In particular, we have found the enhanced photoinduced absorption due to the strong Coulomb interaction between $|1S_e1S_h\rangle$ and $|1S_e1P_h\rangle$ excitons in the $\text{CdS}_{0.6}\text{Se}_{0.4}$ nanocrystals. We have also theoretically confirmed that the biexciton binding energies depend on the constituent exciton states, resulting in the enhanced biexcitonic effect of the $|1S_e1S_h\rangle$ and $|1S_e1P_h\rangle$ excitons.

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