Anti-parallel coupling of Quantum Dots with an Optical Near-Field Interaction

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We report the direct observation of optically forbidden energy transfer between cubic CuCl quantum dots via an optical near-field interaction using time-resolved near-field photoluminescence (PL) spectroscopy. The energy transfer time and exciton lifetime were estimated from the rise and decay times of the PL pump-probe signal, respectively. We found that the exciton lifetime increased as the energy transfer time fell, which strongly supports the notion that near-field interaction between QD makes the anti-parallel dipole coupling. Namely, a quantum-dots pair coupled by an optical near field has a long exciton lifetime and optically forbidden features due to its anti-parallel electric dipole pair. [DOI: 10.1380/ejssnt.2005.74]

Keywords: Photoluminescence; Nano-scale imaging, measurement, and manipulation technology; Alkali halides; Nanoparticles, quantum dots, and supra-molecules; Coupled quantum dots

I. INTRODUCTION

The unique optical properties of a quantum dot (QD) system, i.e., the quantum size effect that originates from the electronic state in QDs, are of major research interest. A coupled QD system has more properties that are unique than a single QD system, including the Kondo effect [1, 2], Coulomb blockade [3], spin interaction [4], and so on. Furthermore, it is possible to control the coupling strength of QDs by using the optical near-field interaction, and to realize unique optical device operation. Recently, we observed an optically forbidden energy transfer between neighboring cubic CuCl QDs via an optical near field [5]. The breaking of the dipole selection rule in the nanometric region has been discussed theoretically [6]. It is based on the fact that the point dipole description of a QD is not suitable for the system that the dots approach each other in a nanometric region. The magnitude of this nanometric dipole-dipole interaction, i.e., the optical near-field interaction, can be estimated by measuring the energy transfer time [7].

The energy transfer between QDs is not only of physical interest, but is also applicable to the novel technology of nanophotonics [8]. We have proposed and demonstrated a nanometric all-optical switch using an optical near field, i.e., the nanophotonic switch [9, 10]. Since the switching time depends strongly on the energy transfer time, observations of the energy transfer time are important for designing nanophotonic switches, and for understanding the phenomenon of energy transfer via an optical near field. It is also important to measure the lifetime of the excitons in a coupled QD pair, because the optical near-field interaction influences the exciton lifetime, and the repetitive switching speed depends on the exciton lifetime [7].

For a coupled QD system, the carrier lifetime is expected to differ from that of an isolated QD. Figure 1 shows schematic drawings of the typical states of coupled QDs. When their electric dipoles are parallel, the carrier lifetime decreases due to the increase in the total oscillator strength, i.e., Dicke’s superradiance [11], as shown in Fig.1 (a). Conversely, when their electric dipoles are anti-parallel, their carrier lifetime increases, because the total oscillator strength decreases, and they ultimately become optically forbidden, as shown in Fig.1 (b).

In this letter, we report the observed energy transfer time from the exciton state in a CuCl QD to the optically forbidden exciton state in another CuCl QD, using time-resolved optical near-field spectroscopy. We also show the nature of the anti-parallel dipole-coupling feature of the optical near-field interaction experimentally.

II. EXPERIMENTAL

Cubic CuCl QDs, i.e., quantum cubes (QCs), embedded in NaCl are suitable for studying the optical near-field interaction, because the possibility of energy transfer due to carrier tunneling and Coulomb coupling can be neglected, since the potential depth exceeds 4 eV and the binding energy of exciton is more than 200 meV with its Bohr radius of 0.68 nm [12]. We fabricated CuCl QCs embedded in a NaCl matrix using the Bridgman method and successive annealing, and found that the average size of the QCs was $L = 4.2$ nm [13]. A 325-nm CW He-Cd laser and 385-nm SHG of CW and mode-locked Ti:sapphire lasers (repetition rate: 80MHz) were used as the light sources. To achieve the selective excitation of the discrete energy levels in the QCs, the duration of the transform-limited pulse of the mode-locked laser was set at 10 ps. A double-tapered fiber probe with a 150-nm aluminum coating and a 40-nm diameter aperture was fabricated by chemical etching and the pounding method [14, 15]. After
FIG. 1: Schematic drawing of a quantum dot (QD) pair and its electric dipoles. (a) The electric dipoles are parallel to each other, i.e., the superradiant state. (b) The dipoles are anti-parallel, i.e., the dipole forbidden state.

the QC pairs in the inhomogeneous size-dispersed sample were found using an optical near-field microscope, the temporal evolution of the photoluminescence (PL) pump-probe signal was detected using the time correlation single photon counting method with a 15-ps time resolution.

III. RESULTS AND DISCUSSIONS

Figures 2(a) and (b) show the near-field PL spectrum of the sample and the spatial distribution of the luminescence intensity from a 6.3-nm QC at 15 K, respectively, with the 325-nm CW probe light only, which excited the band-to-band transition in the sample. The inset in Fig. 2(b) shows the energy transfer between the observed QCs, i.e., from 4.6- to 6.3-nm QCs, where $\tau_i$, $\tau_{sub}$, and $\tau_{ex}$ are the energy transfer time, inter-sub-level transition time, and exciton lifetime, respectively. The energy eigenvalues for the quantized $Z_3$ exciton energy level in a CuCl QC with side length of $L$ are given by $E_{n_x,n_y,n_z} = E_B + \hbar^2\pi^2(n_x^2 + n_y^2 + n_z^2)/2M(L-a_B)^2$, where $E_B$ is the bulk $Z_3$ exciton energy, $M$ is the translational mass of the exciton, $a_B$ is its Bohr radius, $n_x$, $n_y$, and $n_z$ are quantum numbers ($n_z = 1, 2, 3,...$), and $d = (L - a_B)$ corresponds to the effective side length found after considering the dead layer correction [16]. There was resonance between the quantized exciton energy level of quantum number (1,1,1) in the 4.6-nm QCs and the quantized exciton energy level of quantum number (2,1,1) in the 6.3-nm QCs. Note that the transition, induced by the propagating light, between ground state to (2,1,1) excited state is dipole-forbidden. However, optical near-field energy transfer is allowed with the coupling energy represented by the following Yukawa function: $V(r) = A \exp(-\mu \cdot r)/r$ [17, 18]. Here, $r$ is the separation between the two QCs, $A$ is the coupling coefficient, and $\mu$ is the inverse decay length of the Yukawa function, which correspond to the effective mass of our published effective interaction theory [17, 18]. For the $L = 4.6$- and 6.3-nm QC pair with 10-nm separation, the estimated $\tau_i$ is 50 ps, which is much shorter than $\tau_{ex}$, which is a few ns. Since $\tau_{sub}$ is generally less than a few ps and is much shorter than $\tau_i$ [19], luminescence of a 4.6-nm QC decreases due to competitive inhibition and that of a 6.3-nm QCs increases due to the supply of the excitation energy from the neighboring 4.6-nm QC. As a result, the PL signal from the 6.3-nm QC was observed as the spectral peak indicated by the arrow in Fig. 2(a).

Figures 3(a) and (b) show the differential PL spectrum and the spatial distribution of the luminescence intensity from the 4.6-nm QC at 15 K, respectively taken with the 325-nm CW probe light and the 385-nm 10-ps pump pulse. Here, the differential PL spectral intensity is defined as (the PL spectrum with pump and probe light) - (the PL spectrum with the probe light only) - (the PL spectrum with the pump light only). The upward pointing arrow shows the photon energy of the pump pulse tuned to the (1,1,1) exciton energy level in the 6.3-nm QC. The inset in Fig. 3(b) shows the energy transfer between the QCs when the pump pulse excites the 6.3-nm QC. In this case, because the exciton energy in the 4.6-nm QC cannot be transferred to the (1,1,1) exciton...
energy level in the 6.3-nm QC due to the state filling effect, the exciton energy flows back and forth between the (1,1,1) exciton energy level in the 4.6-nm QC and (2,1,1) exciton energy level in the 6.3-nm QC[20, 21], and some excitons recombine in the 4.6-nm QC. Therefore, the PL signal from the 4.6-nm QC was detected as the spectral peak indicated by the arrow in Fig. 3(a). The temporal evolution of this PL signal strongly depends on the \( \tau_i \) and \( \tau_{ex} \) of the coupled QC system.

Figures 4(a) and (b) show the temporal evolution of the PL peak intensity from 4.6-nm QCs on different time scales: (a) from −70 ps to 350 ps, (b) from −400 ps to 4000 ps. The open squares (P1), circles (P2), and triangles (P3) correspond to the experimental results observed for three different 4.6- and 6.3-nm QC pairs. In Fig. 4(a), the longitudinal axis has a linear scale. The solid, broken, and dotted curves are fitted to the experimental values using the rate equation, which is given by

\[
\begin{align*}
\frac{dI_{4.6}}{dt} &= I_0 - \frac{I_{4.6}}{\tau_i} - \frac{I_{4.6}}{\tau_{ex,4.6}} + \frac{I_{6.3}}{\tau_i} + I_{probe}, \\
\frac{dI_{6.3}}{dt} &= I_0 - \frac{I_{6.3}}{\tau_i} - \frac{I_{6.3}}{\tau_{ex,6.3}} + \frac{I_{4.6}}{\tau_i} + I_{probe}. \\
\end{align*}
\]

Here, \( I_{4.6} \) and \( I_{6.3} \) are the exciton populations in the 4.6- and 6.3-nm QCs, respectively and \( I_0 \) and \( I_{probe} \) are the \textit{a priori} population and the exciton population created by the probe laser. The exciton population in the 6.3-nm QC is increased due to the pump pulse at \( t = 0 \). The exciton population in the 4.6-nm QC is also increased due to the prohibited energy transfer to the 6.3-nm QC with the filling effect. This increase in the exciton population of the 4.6-nm QC corresponds to the increase in the PL intensity from the 4.6-nm QC. The rise-time of the PL intensity from the 4.6-nm QC strongly depends on the energy transfer time \( \tau_i \). The energy transfer times
FIG. 4: Time evolutions of the PL peak signal intensity in Fig. 3(a) observed at different positions in the sample, i.e., different QC pairs, (P1:□, P2:○, and P3:△). (a) Evolution in the range \(-70\) ps \(\leq t \leq 350\) ps with a linear longitudinal axis. (b) Evolution in the range \(-400\) ps \(\leq t \leq 4000\) ps with a logarithmic longitudinal axis. (c) Relationship between the energy transfer and decay times for the PL pump-probe signal. Closed squares show the experimental results, which were fitted using the solid curve.

The decay time of the PL intensity from the 4.6-nm QC, which equals the exciton lifetime \(\tau_{ex}\), is given by \(\tau_{ex} \propto 1/F \propto 1/(F_0^2F_\text{ex} \cdot \exp(-a\tau_i))\); then, \(\tau_{ex} = \tau_0/(1 - \exp(-a\tau_i))\), where \(\tau_0\), \(F_0\), and \(a\) are the exciton lifetime of an isolated QC, its oscillator strength, and the fitting parameter, respectively. The solid curve in Fig. 4(c) is the fitted result based on this assumption, and it agrees well with the experimental results.

Next, we discuss the origins of the anti-parallel coupling features of the optical near-field interaction between QDs. In the experiment, we detected the PL signal from QCs, which means that only the transverse exciton was detected, because the longitudinal exciton is optically forbidden and its dispersion differs from that of the transverse exciton, i.e., it has a different energy in the QCs. Since, the direction of the electric dipole in the transverse exciton is perpendicular to the direction of propagation, the dipole never becomes aligned with the direction of propagation after the energy is transferred to the neighboring QC. Although there are two possible eigenstates of the mutual arrangements of the dipoles in excitons, i.e., parallel and anti-parallel, as shown in Figs. 1(a) and 1(b), the occurrence probability of the anti-parallel state exceeds that of the parallel state because the total energy of the system for the anti-parallel state is lower than that for the parallel state. This anti-parallel feature of the optical near-field coupled QCs reduces the recombination of excitons. Consequently, the exciton lifetime increases with the optical near-field interaction.

**IV. CONCLUSION**

We measured the optically forbidden energy transfer time between cubic CuCl QCs via the optical near-field interaction directly using a PL pump-probe technique. The signal rise time, which corresponds to the energy transfer time, was from 25 to 180 ps. We also showed that the QC also differed with the QC pair, as demonstrated in Fig. 4(b), which has a logarithm-scale longitudinal axis. The solid, broken, and dotted lines show the decay time of the PL for QC pairs P1, P2, and P3, respectively, and the respective values are 6.7, 4.2, and 2.9 ns. The solid squares in Fig. 4(c) are the experimental results for the relation between the decay and rise times of the PL from the 4.6-nm QC for several QC pairs including P1, P2, and P3. The decay time exceeds the exciton lifetime of the isolated 6.3-nm QC measured experimentally, and increases as the rise time falls. Rate Equation (1) indicates that the decay time is determined by the exciton lifetimes (i.e., physical properties constant) in the 6.3-nm and 4.6-nm QC. The other dissipative pathways can be negligible in consideration of the exciton luminescence efficiency. Therefore the experimental result in Fig. 4(c) means that the exciton lifetime in the QCs increases with the optical near-field interaction. This increase in the exciton lifetime due to the optical near-field interaction can be understood using the feature of the anti-parallel dipole-dipole coupling of an optical near field. The difference in the total oscillator strength, \(F\), of the excitons in the coupled QD system can be approximated to the lowest order as being inversely proportional to the optical near-field interaction due to its anti-parallel coupling characteristics. Then, the decay time of the PL intensity from the 4.6-nm QC, which equals the exciton lifetime \(\tau_{ex}\), is given by \(\tau_{ex} \propto 1/F \propto 1/(F_0^2F_\text{ex} \cdot \exp(-a\tau_i))\); then, \(\tau_{ex} = \tau_0/(1 - \exp(-a\tau_i))\), where \(\tau_0\), \(F_0\), and \(a\) are the exciton lifetime of an isolated QC, its oscillator strength, and the fitting parameter, respectively. The solid curve in Fig. 4(c) is the fitted result based on this assumption, and it agrees well with the experimental results.
decay time increased as the energy transfer time fell; this was attributed to the anti-parallel dipole-coupling feature of the near-field interaction between the QDs. These features are of interest physically and are applicable to photonic devices, such as optical nanometric sources, long phosphorescence devices, and optical battery cells.

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