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Mesoscopic enhancement of optical nonlinearity in CuCl quantum dots: Giant-oscillator-strength effect on confined excitons

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We investigate size-dependent nonlinear polarization due to Wannier excitons confined in CuCl quantum dots (QD's) with a radius R of 15–80 Å embedded in glass. The third-order optical susceptibility $\chi^{(3)}$ measured at 80 K increases as a function of radius and subsequently decreases after reaching a maximum value of 2×10^{-6} esu at $R\sim50$ Å. Homogeneous widths and longitudinal relaxation times were also measured and the results were analyzed taking into account a two-level atomic model. We obtain evidence that the size-dependent $\chi^{(3)}$ originates from the size-dependent oscillator strength of coherently generated excitons in the QD. The oscillator strength varies as $R^{2.2}$ for $19<R<40$ Å and is enhanced by a factor of 940 at maximum compared to that of bulk exciton.

In recent years optical nonlinearity of low-dimensional systems of semiconductors has attracted much attention because of the possibility of anomalously high nonlinear polarizabilities. In a quantum-dot (QD) system, photoexcited electron-hole pairs are three-dimensionally confined because of the confinement potential in all three directions. In CdS_xSe_{1-x} microcrystallites embedded in glass, an electron and a hole are independently confined and the size effect on third-order optical susceptibility $\chi^{(3)}$ has been studied both theoretically and experimentally.[1–5]

When a crystallite radius R is larger than an effective Bohr radius a_B of an exciton, a different type of confinement appears. Since the character of an exciton as a quasiparticle is well conserved, the translational motion of the exciton is confined in a QD. The confinement of the excitonic envelope wave function is expected to give rise to enhancement of the oscillator strength f_x per QD by a factor R^3/a_B^3.[3,4] This size-dependent oscillator strength was experimentally confirmed by our previous work from the size-dependent radiative decay rate of the confined exciton in CuCl QD's in glass[6] and by Itoh, Furumiya, and Gourdon using CuCl QD's in NaCl crystals.[7] Such a giant-oscillator-strength effect will result in an enhancement of the nonlinear polarizability. Experimental studies for CuCl microcrystallites have shown that $\chi^{(3)}$ is dependent upon size by measurements of the absorption saturation of the confined excitons[8,9] and degenerate four-wave mixing.[10,11] In the above studies, however, the size dependence of longitudinal and transverse relaxation times T_1 and T_2 was not taken into account. Since the imaginary part of $\chi^{(3)}$ in the resonance regime is affected by not only oscillator strength but also relaxation parameters, it is still an open question as to whether a giant-oscillator-strength effect on a confined exciton enhances certainly the nonlinearity.

In this paper we report experimental evidence for the mesoscopic enhancement of third-order nonlinear susceptibility due to the size-dependent oscillator strength of confined excitons, which was theoretically predicted by Hanamura.[3] We have performed measurements of $\chi^{(3)}$, T_1, and T_2 of CuCl microcrystallites embedded in glass in a wide range of sizes from 15 to 80 Å. Taking into account the measured size dependence of both T_1 and T_2, the size-dependent $\chi^{(3)}$ allows us to find that the oscillator strength depends upon $R^{2.2}$ and is enhanced by the factor of 940 at maximum compared to that of the bulk exciton. The suppression of the enhancement of $\chi^{(3)}$ was observed at larger sizes as well as higher temperatures. This supports the theory that the formation of the coherent excitons within the QD plays an important role in the size-dependent nonlinearity.

The CuCl QD's in the glass matrix were obtained by the double heat-treatment procedure of borosilicate glasses doped with CuCl.[6] This glass was heat treated at temperatures of 550 °C–650 °C to yield CuCl microcrystallites with a wide range of mean radii from 15 to 80 Å. The volume fraction of QD's is 0.1–0.4 %. The peak energy of the absorption spectrum due to the Z_3 exciton is shifted depending on the mean radius,[6,12] and therefore the translational motion is confined in the microcrystallites. The mean radius was determined using the empirical relationship between the radius and the lowest energy of the confined Z_3 exciton. This relationship was derived by measurements of the transmission-electron micrograph for some of the samples studied here and the small-angle x-ray scattering.[12]

Measurements of $\chi^{(3)}$ were carried out using degenerate four-wave mixing (DFWM) with a two-beam configuration by an excimer-laser pumped dye laser with duration of 20 ns. The pumping power level of ~10 kW/cm^2 which was typically used in this experiment ensures that the detected nonlinearity is due to the third-order polarization. T_1 was determined by lifetime measurements of Z_3 exciton luminescence using a cw mode-locked uv laser.[6] T_2 was measured by hole burning experiments and resonant luminescence experiments under the size-selective excitation within an inhomogeneously broadened absorption spectrum of the excitons.

The quantum confined exciton system can be considered to be a two-level atomic system. In the low density regime of the two-level system, the imaginary part of $\chi^{(3)}$ on resonance is given by the following equation:

$$\mathrm{Im}\chi^{(3)}=(e^2/2m_0\omega)^2\hbar f_x^2 N/\Gamma_h^2 T_1^{-1}\ . \qquad (1)$$

Here, f_x and Γ_h are the oscillator strength per QD and the homogeneous width ($\hbar T_2^{-1}$), respectively, and N is the number density of QD's. Since there exists the inhomogeneous broadening due to the size distribution of microcrystallites, we can selectively excite the microcrystallites in which the Z_3 exciton level with Γ_h is resonant with the pumping light. The selective excitation showing the hole-burning effect has been demonstrated in pump and probe experiments in CdSe QD's.[13,14] In this case $f_x N_p$ is proportional to $\alpha\Gamma_h$, where α is the absorption coefficient at the wavelength of the pumping light and N_p is the number density of the QD's selectively excited. Thus, $\mathrm{Im}\chi^{(3)}$ in cgs units is rewritten as

$$\mathrm{Im}\chi^{(3)}=1.3\times10^{17}\times[n/(n^2+2)^2](e^2/2m_0\omega)^2 \times\hbar f_x\alpha/\Gamma_h T_1^{-1} \ , \qquad (2)$$

where n is the refractive index.

The $|\chi^{(3)}|$ spectrum measured by changing the pumping wavelength near the Z_3 exciton band showed the large enhancement at the absorption peak. Such a resonant behavior of the $|\chi^{(3)}|$ spectrum was reported in our previous papers.[10,11] In order to discuss the size-dependent behavior of the nonlinear polarization, we measured values of $|\chi^{(3)}|$ at the peak energy of the Z_3 exciton absorption in CuCl QD's with various mean radii. Figure 1 shows the values of $|\chi^{(3)}|/\alpha$ as a function of R in the temperature range of 80–180 K. $|\chi^{(3)}|/\alpha$ depicts the observed size dependence of $\chi^{(3)}$ even if each sample contains microcrystallites with various volume fractions. As shown in this figure, $|\chi^{(3)}|/\alpha$ measured at 80 K increases monotonically with the increase of R in the range 15–50 Å and subsequently decreases for the larger radii. The fluctuations of the data suggest that the value of $|\chi^{(3)}|/\alpha$ depends on the magnitudes of T_1 and Γ_h which are sample dependent because of the presence of nonradiative processes and phase relaxation due to surface imperfections. The maximum value of $|\chi^{(3)}|$ is 2×10^{-6} esu for the volume fraction of ~0.3%. At 100 K, $|\chi^{(3)}|/\alpha$ exhibits a maximum value at $R_m\sim40$ Å, shown by an arrow in Fig. 1. This value is smaller than $R_m\sim50$ Å at 80 K. The radius R_m at which $|\chi^{(3)}|/\alpha$ has a maximum value becomes even smaller, ~30 Å at 140 K, while it shows no peak at 180 K. These results imply the size-dependent nonlinear polarization and the suppression of the enhancement depending on the temperatures.[15] In order to investigate how f_x, T_1, and Γ_h contribute to the size-dependent $\chi^{(3)}$, we derived size dependence of these parameters by measuring T_1 and Γ_h.

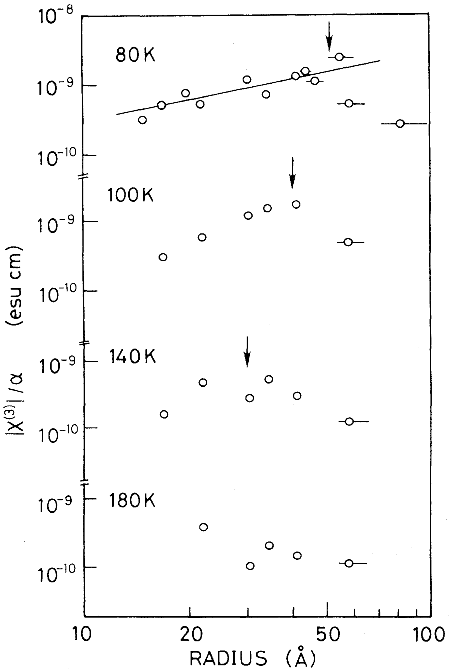

FIG. 1. The size dependence of $|\chi^{(3)}|/\alpha$ measured at the Z_3 exciton peak energy of CuCl microcrystallites for different temperatures. The straight line shows the R^1 dependence. The arrows indicate the radius at which the maximum value of $|\chi^{(3)}|/\alpha$ is obtained.

Figure 2 shows a figure of merit $|\chi^{(3)}|/\alpha T_1$ as a function of R. The figure of merit increases upon an increase of R and subsequently decreases after reaching a maximum value at ~45 Å. The radius dependence for $R<45$ Å is approximately R^3, which is stronger than the observed dependence of $|\chi^{(3)}|/\alpha$. This results from the fact that T_1 is approximately dependent on $R^{-2.4}$. The size-dependent behavior of the figure of merit suggests that f_x and/or Γ_h depend upon the radius.

Γ_h was examined by hole-burning measurements and resonant luminescence measurements. The hole-burning spectrum was found to be weakly dependent on the pumping intensity at the power density of 10–300 kW/cm^2. For $R=36$ Å, Γ_h changed from 1.6 to 1.9 meV at these power densities. This suggests that transverse relaxation of excitons is affected not only by the scattering with phonons and the confinement sphere but also by exciton-exciton scattering. In resonant luminescence experiments, the luminescence line shape exhibited a Lorentzian shape and Γ_h was deduced from half of the

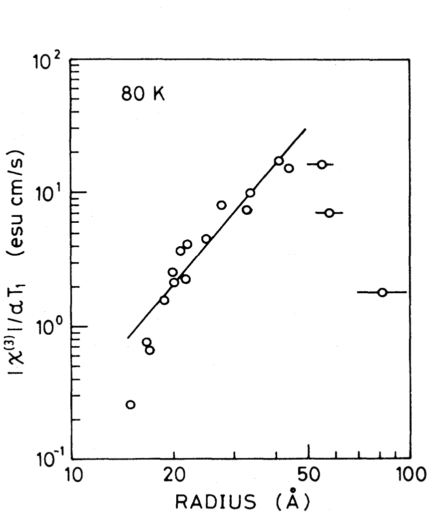

FIG. 2. The figure of merit $|\chi^{(3)}|/\alpha T_1$ as a function of cyrstallite radius. The straight line indicates the R^3 dependence.

half width at half maximum of the shape. Comparing the values evaluated by the two different measurements, we found that the discrepancy is about 20%. Consequently, we used the values of Γ_h which were determined from the linewidth of resonant luminescence at the same pumping power levels as the DFWM experiments (~ 10 kW/cm^2). The value of Γ_h is about 1.9 meV for $R = 20$ Å, while it decreases with increase of R for $R < 50$ Å. For larger radii, the value becomes a constant value of about 0.9 meV.

Using the measured values of Γ_h, α, and T_1, values of $|\chi^{(3)}|\Gamma_h/\alpha T_1$ were calculated. Shown in Fig. 3 is $|\chi^{(3)}|\Gamma_h/\alpha T_1$ as a function of R. This figure demonstrates clearly that f_x increases upon an increase of R in the range of 15–40 Å. For $R > 40$ Å, however, it decreases suggesting the suppression of the enhancement because of the contribution from the higher confined states. The least-square fit of the radius dependence allows us to find $R^{2.2}$ taking the data for $19 < R < 40$ Å. This radius dependence of f_x is in good agreement with the observed dependence of $R^{2.1}$ which was derived from the radiative lifetimes of the Z_3 excitons.[6] It is worth noting that the stronger dependence seen for $R < 19$ Å may be related to the deviation from the exciton confinement since the ratio R/a_B is smaller than 3 in this region.[16]

The smaller radius dependence of the oscillator strength compared to the theoretical expectation of R^3 is mainly due to the finiteness of the confinement potential. In the theoretical model, the infinite and spherical potential is assumed outside the QD consisting of an ideal crystal and the effect of local fields is neglected.[3] In this study, however, the band edge of the borosilicate glass is about 4.3 eV, whereas the band gap of the CuCl crystal is 3.42 eV. Consequently, the wave function can penetrate into the glass, and thereby the weaker confinement effect on the oscillator strength can be expected. The following contributions might also alter the size dependence: (1) the effect of the inhomogeneity in the size of the microcrystallites; the selective excitation cannot exclude completely the contribution from the microcrystallites with different radii which are simultaneously excited within Γ_h; (2) the frequency dispersion effect of $|\chi^{(3)}|$; the microcrystallites which are "off resonant" with the pumping wavelength may contribute to the $|\chi^{(3)}|$ measured with the selective excitation of the mirocrystallites concerned. However, other effects such as polarization charge and the trapping states induced at the interface are ruled out in CuCl, since we observed no luminescence from such centers. We can also ignore an effect of the inhomogeneity in the shape of the microcrystallites. Unlike CuCl microcrystallites embedded in NaCl crystals,[7] the transmission-electron micrograph of our samples gave a confirmation of the absence of a disclike crystallite which causes the stronger confinement in one direction.

For $R > 40$ Å, both f_x and $|\chi^{(3)}|/\alpha$ decrease with increasing R. This decrease suggests that the contribution from the higher states of the quantum confinement cannot be neglected to the third-order polarization. Such a behavior is more clearly demonstrated by the size dependence of $|\chi^{(3)}|/\alpha$ at higher temperatures in Fig. 1. If we calculate the energy separation ΔE between the lowest and the first excited levels of the confinement corresponding to R_m, we obtain 6, 9, and 16 meV for $R_m \sim 50$, 40, and 30 Å, respectively. These energies are comparable to the thermal energies of corresponding temperatures. Therefore, the saturation behavior of the increase of $|\chi^{(3)}|/\alpha$ as well as f_x is interpreted in terms of the thermal distribution of the confined excitons at the higher levels. The contribution from the higher levels cancels out the resonant enhancement at the lowest level. Theoretically, Takagahara demonstrated the decrease of $\chi^{(3)}$ for larger sizes taking into account the redistribution of the oscillator strength under the condition that the many confined levels are included within the homogeneous width.[17] This is in line with the continuous change of the mesoscopic enhancement into the finite nonlinear polarizability of the bulk crystal.

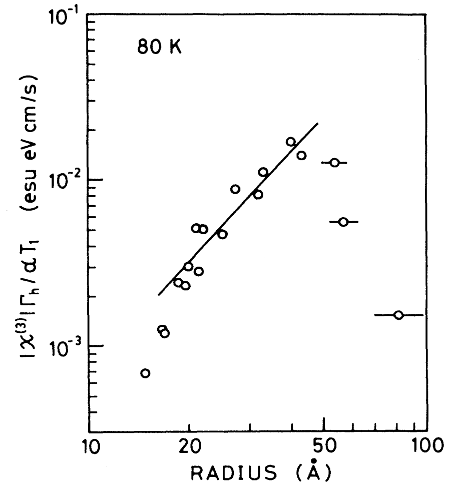

FIG. 3. The size dependence of $|\chi^{(3)}|\Gamma_h/\alpha T_1$ ($\propto f_x$). The straight line indicates the $R^{2.2}$ dependence.

From the above arguments we might expect a higher maximum value of $|\chi^{(3)}|$ at temperatures lower than 80 K. However, such an enhancement cannot be expected if we take into account longitudinal and transverse excitons. A confined exciton with a larger radius corresponds to an exciton with a smaller wave vector where a longitudinal-transverse splitting $\Delta_{\rm LT}$ is important. An exciton of which a confinement energy is smaller than $\Delta_{\rm LT}$ could not contribute to the nonlinear polarization.[18] Using $\Delta_{\rm LT} = 5.7$ meV in CuCl, we obtain a corresponding radius of 50 Å. Therefore, the giant-oscillator-strength effect disappears for $R < 50$ Å.

In what follows, we can estimate values of f_x using the results in Fig. 3 and Eq. (2). Taking the value of 7.5×10^{-4} esu eV cm/s as $|\chi^{(3)}|\Gamma_h/\alpha T_1$ for $R = 15$ Å and 1.7×10^{-2} esu eV cm/s for 40 Å, we estimate $f_x \sim 0.24$ and 5.5 for 15 and 40 Å, respectively. If we compare the value for 40 Å with that of the bulk exciton in CuCl crystal, which is $f_{Z_3} = 5.85 \times 10^{-3}$,[19] the enhancement factor f_x/f_{Z_3} for 40 Å is 940. This value can be compared with that derived from the measured value of the radiative lifetime of the excitons. Taking the lifetime of 200 ps for $R = 40$ Å from Fig. 3 in Ref. 6, we obtain $f_x/f_{Z_3}=950$. The agreement between both values is excellent, and this gives a further confirmation for the mesoscopic enhancement of the oscillator strength in the QD.

Moreover, the large oscillator strength of the confined exciton is comparable to that of biexcitons f_B in the CuCl bulk crystal; $f_B/f_{Z_3}=3200$ which was derived from the radiative lifetime of 50 ps.[19] It is worth noting the difference of the physical picture between the biexciton and the confined exciton. The giant-oscillator-strength effect on the biexciton results from the confinement of two excitons imposed by the Coulomb interaction, while the confinement of the exciton in the QD is externally imposed by the barrier potential. The more interesting and important feature in the QD system is a capability to control the confinement region changing the extent and the height of the barrier potential. This provides a means to engineer optical properties associated with the oscillator strength.

In conclusion, we have unambiguously confirmed that the size-dependent $\chi^{(3)}$ originates from the giant-oscillator-strength effect on the confined exciton in a QD. The oscillator strength compared to the bulk value f_x/f_{Z_3} is enhanced by the factor of 41–940 depending upon the radius from 15 to 40 Å. The suppression of the mesoscopic enhancement for the larger sizes, which is dependent on the temperature, revealed that the resonant enhancement with the lowest confinement state plays an important role in the size-dependent $\chi^{(3)}$. At higher temperatures, the redistribution of the oscillator strength within the homogeneous width causes the saturation and the decrease of the size-dependent polarizability.

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