Two-photon excitation spectra of confined excitons in CuCl nanocrystals

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We investigated two-photon excitation spectra of confined excitons of CuCl nanocrystals embedded in a NaCl matrix. The spectra exhibit a sharp increase that is attributed to transitions into higher Coulombic states (nP) of the confined excitons, and its position shifts to a higher energy side with decreasing crystal size. We also discuss the difference in peak positions between one- and two-photon absorption spectra in the presence of a broad inhomogeneous width due to the size distribution. [S0163-1829(99)04320-9]

I. INTRODUCTION

Recently, the electronic and optical properties of semiconductor nanocrystals, i.e., ''quantum dots,'' have attracted much attention because of their potential for electronic and optical applications.[1] In such a system, an electron and a hole exhibit various characteristic properties that are much different from those in a bulk crystal, on account of quantum confinement effects. With regard to the confinement of excitons in nanocrystals, there are two extreme cases, depending on the ratio of the nanocrystal size (a) to the effective exciton Bohr radius (a_B). One extreme case is known as that of ''electron-hole individual confinement'' or ''strong confinement.'' This corresponds to the situation $a \ll a_B$, in which the confinement energy of an electron and a hole overwhelms the Coulomb interaction between them. Most III-V and II-VI semiconductor nanocrystals belong to this regime. These nanocrystals have been studied extensively. The other extreme case, in which $a \gg a_B$, is referred to as ''exciton confinement'' or ''weak confinement.'' Here the Coulomb interaction is much greater than the individual confinement energy and hence the translational motion of the exciton is constrained. Excitons in CuCl nanocrystals are typically classified into the exciton confinement regime[2] and the optical properties of the nanocrystals have been studied in several contexts. Most of these studies are concerned with the lowest excited state of the confined exciton. For higher excited states there are very few studies, in spite of the importance of obtaining a thorough understanding of the energy diagram of the confined exciton. For instance, the exciton confinement picture may no longer be valid for higher Coulombic states because of their extended internal motion. Two-photon spectroscopy[3,4] and infrared transient absorption spectroscopy[5,6] are promising methods for the study of the higher excited states of the nanocrystals. The former is of particular interest because the use of two photons can cause excitation into higher states that are difficult to observe using usual one-photon excitation spectroscopy. Moreover, two-photon excitation will provide interesting information concerning such phenomena as nanocrystal orientation in a crystalline matrix,[3] resonant second harmonics,[7] and resonant hyper-Raman scattering.[8] Recently, several authors have reported on two-photon spectroscopy for nanocrystals in both the strong confinement regime [CdS and CdSe (Refs. 9 and 10)] and the weak confinement regime [CuCl (Refs. 11–13)]. Theoretical calculation of two-photon transitions in the strong confinement regime has also been presented.[14] In this paper we report on two-photon excitation spectra of confined excitons in CuCl nanocrystals embedded in NaCl matrices and show a pronounced two-photon excitation band that is probably due to transition to higher Coulombic nP-like states.

II. EXPERIMENT

CuCl nanocrystals embedded in a NaCl crystal matrix were grown using a customized heat treatment.[15] Samples with mean effective radii $a^* = 1.6$, 2.7, and 6.3 nm were used for the present experiment. The mean effective radii were estimated from the peak position of the one-photon absorption band and/or the luminescence band due to the confined Z_3 excitons. The samples were cooled in a conduction-type cryostat down to liquid nitrogen temperature. The sample was excited by a continuous-wave mode-locked (CW-ML) dye laser (Pyridine-2, line width of approximately 0.1 nm, pulse width 20 ps, and peak intensity at the sample of approximately 10 MW/cm^2) synchronously pumped by the second harmonics of a CW-ML Nd:YAG laser (where YAG denotes yttrium aluminum garnet). The excitation light was vertically incident on the sample along the [001] direction of the matrix (NaCl) crystal. The excitation light was linearly polarized with the electric vector parallel to the [110] or [100] direction, using an achromatic half wave plate. Emitted and scattered light from the sample was collected along the [010] direction and detected by an intensified charge coupled device camera (Princeton Instruments ICCD-576G/6) through a grating spectrometer (Acton Research SpectraPro-500). The total spectral resolution of this apparatus was ~ 0.1 nm.

III. RESULTS AND DISCUSSION

Figure 1 shows the emission spectra under one-photon band-to-band excitation (curve a) and under two-photon excitation at various excitation energies ranging from the band-to-band (curves b and c) to the $Z_{12}(1S)$ exciton band region (curves d and e). For these excitation energy regions, the emission spectra under one- and two-photon excitations are quite similar to each other. The emission intensity under two-photon excitation rapidly increases with increasing excitation energy, while the shape and the energy position do not

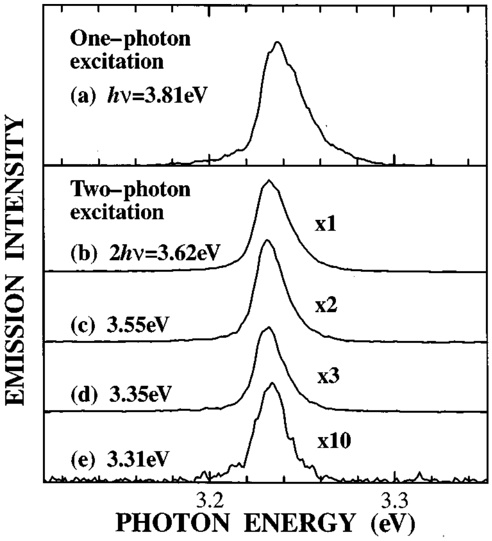

FIG. 1. Emission spectra of the CuCl nanocrystals ($a^* = 2.7$ nm) in a NaCl matrix at 77 K under one-photon band-to-band excitation (curve a) and two-photon excitation (curves b–e). Each spectrum was magnified by the factor indicated on the corresponding curve.

change distinguishably. It is noteworthy that the emission band under the two-photon excitation is slightly (~5 meV) shifted to the lower energy side with respect to that under the one-photon excitation.

Figure 2 shows the two-photon excitation spectra for the spectrally integrated intensity of the total emission band. Open and closed circles represent the spectra for incident polarizations parallel to the [100] and [110] axes of the NaCl single crystalline matrix, respectively. A one-photon absorption spectrum is also shown for comparison. In the two-photon excitation spectra for [110] polarization, peaks are observed at 3.24 and 3.32 eV. These are attributed to the lowest (1S) states of the Z_3 and Z_{12} exciton bands, respectively. These peak positions in the two-photon excitation are shifted to the lower energy side with respect to that in the one-photon absorption. This difference, as well as the similar difference observed in the emission spectra for one- and two-photon excitation (Fig. 1), is probably caused by the difference in the size dependence between one-photon and two-photon transition rates, as discussed later. The incident polarization dependence of these peaks indicates that the CuCl nanocrystals are grown with their crystal axes parallel to those of the NaCl matrix.[3] In the energy region above 3.45 eV, which is higher than the 1S exciton bands, there exists a distinct absorption edge that has almost no polarization dependence, whereas there is no distinguishable structure of the one-photn absorption spectra in this region. The two-photon absorption efficiency in the energy region above this edge reaches a value more than ten times greater than that of the Z_3 or Z_{12} exciton band. This pronounced two-photon absorption is possibly due to transitions to Coulombic nP-like states of the confined excitons, since the energy separation between the absorption edge and the Z_3 1S band, approximately 240 meV, is comparable to the peak energy of the infrared transient absorption (~280 meV) due to the transition from Coulombic 1S to 2P states of the confined Z_3 exciton.[5,6] This sharp increase in the two-photon absorption was similar to that theoretically predicted[16] and observed in bulk CuCl crystal,[17,18] except that no discrete structures due to transitions to 2P or 3P excitons were resolved in our spectra. In the bulk crystal, discrete structures due to these transitions were clearly observed in the two-photon absorption spectra.[18,19] The possible reason for this difference is the inhomogeneous broadening due to size distribution of our nanocrystalline sample.

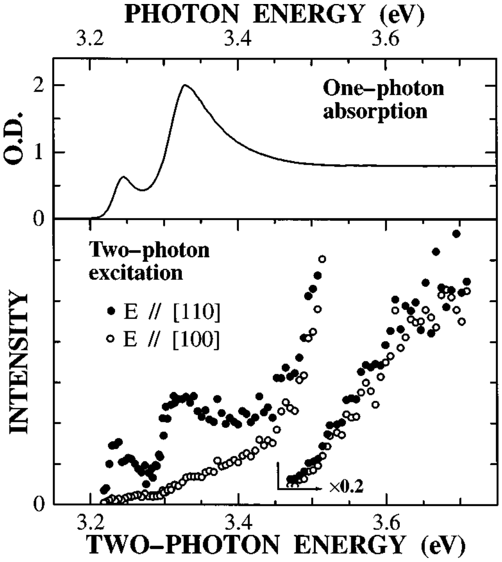

FIG. 2. One-photon absorption spectrum (top) and two-photon excitation spectra for the integrated emission intensity (bottom) for CuCl nanocrystals ($a^* = 2.7$ nm) in a NaCl matrix at 77 K. Open and closed circles represent the spectra for incident polarizations parallel to the [100] and [110] axes of the NaCl single crystalline matrix, respectively.

Figure 3 presents the two-photon excitation spectra for some samples with different mean nanocrystal size. We see that, in addition to the edge position of the two-photon excitation spectra (indicated by thick vertical arrows in the figure), the separation between the edge and the Z_3 1S band (indicated by thin arrows) also becomes larger with decreasing mean nanocrystal size. Provided that the absorption edge can be attributed to the transitions to higher Coulombic states of the confined excitons, this finding indicates that the energy positions of the higher Coulombic states depend more strongly on the nanocrystal size than that of the lowest 1S state. In other words, it implies that the higher Coulombic states of the confined exciton deviate considerably from the ideal exciton confinement model, in which the exciton binding energy should be independent of the nanocrystal size. This result is qualitatively consistent with the theoretical calculation for S-like confined exciton states,[20] where the separation between 1S- and 2S-like states becomes larger with the decrease of nanocrystal size. In Fig. 4 we plot the energy separation between the edge position and the $Z_3(1S)$ peak under two-photon excitation versus the mean effective radius (a^*) of the nanocrystal (filled circles). In the figure the peak positions observed in infrared transient absorption spectra[6] (open squares) and the theoretical 1S-2S separation[20] (solid line) are also plotted for comparison. We see that the experimental results for the two-photon excitation and the infrared absorption both agree qualitatively with the theoretical cal-

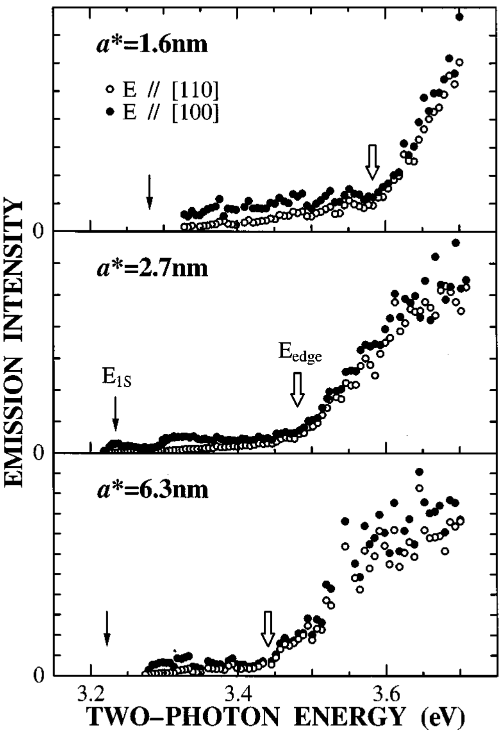

FIG. 3. Two-photon excitation spectra for the spectrally integrated emission intensity of CuCl nanocrystals ($a^*=1.6$, 2.7, and 6.3 nm) in a NaCl matrix at 77 K. Open and closed circles represent the spectra with incident polarization parallel to the [100] and [110] axes of the NaCl matrix, respectively.

culation. However, a more detailed study, including the calculation of two-photon transition energy and the transition probability from the ground state to the higher Coulombic (nP-like) states, is necessary to facilitate quantitative comparison between experimental and theoretical results.

Next we discuss the shift of the two-photon excitation peak from the one-photon absorption observed in the present experiment and show that it is attributed to the difference between the size dependence of one- and two-photon excitation (or absorption) rates.[21] For usual nanocrystalline samples, there is a certain degree of size distribution.[22] The distribution was studied theoretically in detail by Lifshitz and Slezov.[23] Here, for simplicity, we assume a Gaussian distribution $f(a)$ of the nanocrystal size a, which is practically used to approximate the size distribution of semiconductor nanocrystals grown in glass matrices:[24]

$$f(a)=\frac{1}{\sqrt{2\pi}\sigma}\exp\{-(a-\bar{a})^2/2\sigma^2\}. \tag{1}$$

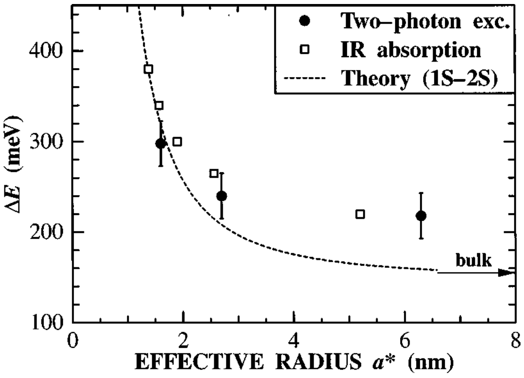

FIG. 4. Energy separation between the edge position and the $Z_3(1S)$ peak in the two-photon excitation spectra (filled circles). Peak positions of the infrared absorption spectra [open squares, following Yamanaka, Edamatsu, and Itoh (Ref. 6)] and the theoretical $1S$-$2S$ separation of confined excitons in spherical nanocrystals [solid curve, following Kayanuma (Ref. 20)] are also shown.

Under the condition of the ‘‘exciton confinement’’ regime, the lowest confinement energy (E) of the exciton is

$$E(a)=\frac{\hbar^2}{2M}\left(\frac{\pi}{a}\right)^2\equiv\left(\frac{k}{a}\right)^2, \tag{2}$$

where M is the translational mass of the exciton and a represents the radius of the spherical nanocrystal. Thus, in the energy domain, the distribution function $f(a)$ is transformed to

$$g(E)dE=f(a)\left|\frac{da}{dE}\right|dE=\frac{a^3}{2k^2}f(a)dE. \tag{3}$$

For a nanocrystal of a certain size (a), the one-photon excitation rate is proportional to the volume of the nanocrystal (a^3), while the two-photon excitation rate is proportional to the square of the volume, provided that the electronic states of relevance to the transition maintain their coherence within the nanocrystal. Thus the spectra of the one- and two-photon excitation (I_1 and I_2, respectively) are described by

$$I_n(E)dE\propto a^{3n}g(E)dE\propto a^{3(n+1)}f(a)dE \quad (n=1,2). \tag{4}$$

Here it is assumed that the homogeneous width of the exciton is negligible in comparison to the inhomogeneous width due to the size distribution. After a short calculation, we find the peak energy positions E_n $(n=1,2)$ for $I_n(E)$:

$$E_n=4k^2[\bar{a}+\sqrt{\bar{a}^2+12(n+1)\sigma^2}]^{-2}. \tag{5}$$

By fitting $I_1(E)$ to the $Z_3(1S)$ exciton band of the observed one-photon absorption spectrum [Fig. 2(a)] we can estimate the values of $\bar{a}$ and σ and thus E_1-E_2. The resultant values are $\bar{a}=1.0$ nm, $\sigma=0.7$ nm, and $E_1-E_2=7.8$ meV. The calculated curves of $g(E)$, $I_1(E)$ and $I_2(E)$ using the above parameters and $M=2.3m_0$ (hence $k=0.16$ eV/nm^2) for CuCl are shown in Fig. 5. The value of E_1-E_2 is comparable to the observed one (~ 10 meV), indicating the adequacy of the estimation. It should be noted that the mean size ($\bar{a}=1.0$ nm) estimated above is considerably smaller than the ‘‘mean radius’’ ($a^*=2.7$ nm) estimated by the peak position of the one-photon absorption spectrum or the luminescence spectrum under band-to-band excitation. From the above considerations, we conclude that a^* should be regarded as the ‘‘one-photon optical’’ mean radius, which is expressed by the mode of $I_1(E)$, i.e., the peak position of the size-distribution function weighted by the square of the nanocrystal volume, but not as the mean value ($\bar{a}$) of the raw size distribution. Although the actual size distribution may be different from an ideal Gaussian distribution, this effect should be taken into account when-

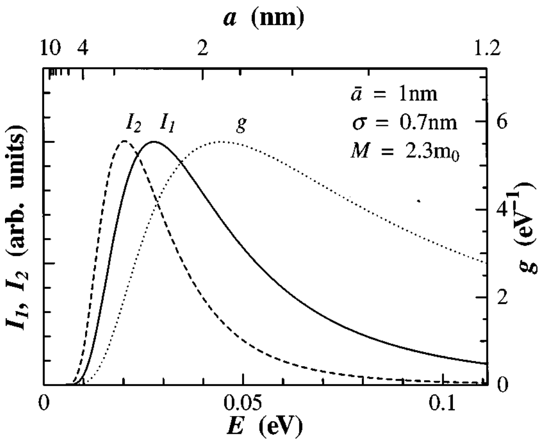

FIG. 5. Size-distribution function $g(E)$ (dotted curve), one-photon excitation spectrum $I_1(E)$ (solid curve), and two-photon excitation spectrum $I_2(E)$ (dashed curve), calculated for $\bar{a} = 1.0$ nm, $\sigma = 0.7$ nm, and $k = 0.16$ eV/nm^2.

ever one refers to the mean radius estimated from optical measurements. We emphasize that this must be a general phenomenon for such nanocrystals the optical spectra of which have broad inhomogeneous width due to considerable size distribution.

IV. CONCLUSION

In conclusion, we have studied the two-photon excitation spectra of confined excitons in CuCl nanocrystals embedded in NaCl matrices. We have found the pronounced two-photon absorption whose edge position is located above the lowest exciton absorption band. The edge position corresponds to the energy position of the Coulombic $2P$ state of a confined exciton and the energy separation between $1S$ and $2P$ states is dependent on the nanocrystal size. This finding indicates that the higher Coulombic states of the confined exciton differ significantly from those in the exciton confinement regime because of the large spatial extension of wave functions. Also, we have discussed the difference in peak positions between one- and two-photon absorption spectra in the presence of the broad inhomogeneous width due to the size distribution of the nanocrystal.

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