Excitonic optical nonlinearity and exciton dynamics in semiconductor quantum dots

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Two salient features of the excitonic state in semiconductor quantum dots are theoretically clarified. One is the enhanced excitonic optical nonlinearity arising from the state filling of discrete levels due to the quantum size effect. The calculated third-order nonlinear susceptibility explains successfully the recent experimental results. The other feature is the exciton dynamics in semiconductor quantum dots. A comprehensive interpretation is presented for the fast- and slow-decay components in phase conjugation and luminescence measurements.

Recently, the excitonic states in semiconductor microstructures have attracted much attention due to the enhanced excitonic optical nonlinearity and fast response time.[1-9] In semiconductor microstructures of lower dimensionality, the energy levels of carriers are discrete due to the quantum size effect. The oscillator strength becomes concentrated on the sharp transitions of the lower energy and the mechanism of excitonic optical nonlinearity is simply the state filling of these sharp excitonic transitions in contrast to the band filling of continuum states in the bulk material. As a consequence, the excitonic optical nonlinearity is enhanced while the saturation power is reduced, relative to the bulk semiconductor. The response time of the optical nonlinearity is determined by the buildup time and recombination lifetime of photogenerated carriers. The dynamics of photogenerated carriers in semiconductor-doped glasses have been studied extensively by the transient-grating method,[1,5-9] pump-probe method,[3] and photoluminescence.[5-7,10-12] Some controversies exist about the origins of the fast and slow components of the electron-hole recombination.[1,5-12]

In this Brief Report the excitonic spectra in a semiconductor quantum dot (spherical microcrystallite) are calculated and their size dependence is clarified for the first time, taking into account the effect of the surface polarization energy. The excitonic optical nonlinearity is then calculated based on these excitonic spectra and wave functions, and its frequency dispersion is compared with that obtained in recent experiments.[2] The theoretical and experimental results are in good agreement. Also, the calculated radiative recombination lifetime of excitons in quantum dots is in good agreement with the recent experimental values of carrier lifetime in semiconductor-doped glasses. Furthermore, the dependence of exciton lifetime on quantum-dot size is predicted for the first time. Finally, a comprehensive interpretation of the controversial aspects of exciton dynamics in semiconductor quantum dots is presented.

First of all, the excitonic states in semiconductor quantum dots are discussed. It is now well known that the effective-mass approximation is applicable even for semiconductor microcrystallites containing as few as 100 atoms.[13] The following considers mainly the excitonic state associated with the lowest electron and hole subbands. This treatment is justified because the intersubband energy is of the order of tens of meV in semiconductor microcrystallites having a radius of about 100 Å and is much larger than the homogeneous linewidth of excitons. Then the s-like excitonic wave function is given by

$$F(r_e,r_h)=C_F j_0(\pi r_e/R)j_0(\pi r_h/R)\exp(-\alpha\,|\,r_e-r_h\,|\,)\,, \tag{1}$$

where C_F is the normalization constant, j_0 the zeroth-order spherical Bessel function, R the radius of a quantum dot, r_e (r_h) the coordinate of the electron (hole),

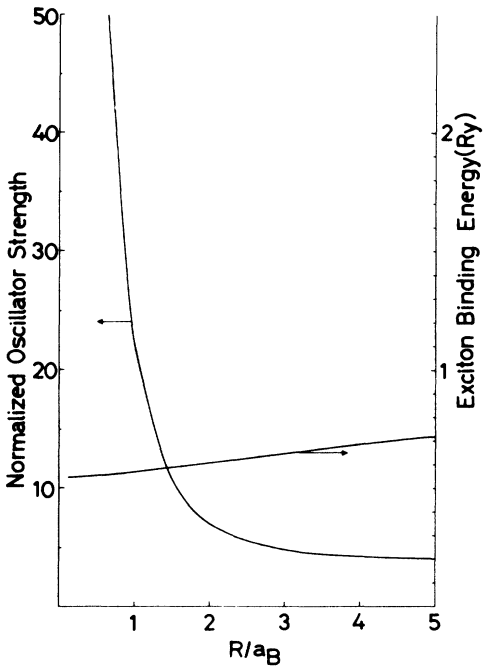

FIG. 1. Exciton binding energy in units of the effective Rydberg and normalized oscillator strength in spherical semiconductor particles plotted as a function of particle radius. a_B is the exciton Bohr radius in bulk semiconductors.

and α the variational parameter for energy minimization. Here the usual boundary condition is employed.[14] The exciton binding energy in a semiconductor quantum dot is obtained from the energy difference between the exciton state and a state with a free electron-hole pair. It should be noted that the Coulomb energy of a free electron-hole pair in a quantum dot is not zero, because of the three-dimensional confinement, whereas it is zero in the cases of bulk crystal, quantum-well, and quantum-wire structures. Figure 1 shows the dependence of the exciton binding energy on the quantum-dot radius normalized by the exciton Bohr radius a_B in bulk crystals. It is important to note that the rather small exciton binding energy implies the ionization of excitonic states at room temperature. In fact, for semiconductor (CdS) quantum dots with radii in the range shown in Fig. 1, the excitonic state may be ionized to the free-electron-hole-pair state at room temperature.

The radiative recombination lifetime τ_R of excitons in a quantum dot can be estimated from the oscillator strength f of the excitonic transition.[15] For a free electron-hole pair in a semiconductor (CdS) quantum dot, the oscillator strength f_0 is estimated to be 8.14 using the relevant parameters,[16] and the corresponding radiative lifetime τ_R is 440 ps. These values are independent of quantum-dot size. When the excitonic effect, namely the electron-hole correlation, is included, the oscillator strength f is enhanced since it is proportional to the probability of finding an electron and a hole at the same position. The enhancement factor of the oscillator strength due to the excitonic effect is given by

$$f/f_0=\pi^3/4aI(a)\ , \tag{2}$$

with $a=2\alpha R/\pi$ and

$$I(x)=\int_0^\infty dk\frac{1}{(k^2+x^2)^2}\{S_i(k\pi)-[S_i((k+2)\pi)+\mathrm{sgn}(k-2)S_i(|k-2|\pi)]/2\}^2\ , \tag{3}$$

where S_i is the sine integral function. This enhancement factor and the corresponding radiative recombination lifetime are given in Fig. 2 as a function of the normalized radius of the quantum dot. The oscillator strength increases with increasing quantum-dot size. This is based on the assumption that the excitation is coherent throughout a quantum dot. On the contrary, the normalized oscillator strength per volume of $4\pi a_B^3/3$ increases when the quantum-dot size is reduced as shown in Fig. 1. This is a consequence of the quantum confinement effect on the spatial correlation between an electron and a hole. For a CdS quantum dot with 100 Å radius, the radiative recombination time is estimated to be 20 ps. This value is of the same order as the time constants of the fast-decay component reported so far in transient grating measurements.[5-9]

The excitonic optical nonlinearity in semiconductor quantum dots can be enhanced due to the large oscillator strength of the exciton and the discrete energy levels, which lead to an easily attainable state filling. The third-order excitonic optical nonlinearity $\chi^{(3)}$ corresponding to optical mixing between two incident light beams with frequencies ω_1 and ω_2 is calculated as[17,18]

$$\chi^{(3)}(-2\omega_1+\omega_2;\omega_1,\omega_1,-\omega_2)=\frac{-2i\mu^4N}{[i\hbar(\omega_0-2\omega_1+\omega_2)+\hbar\gamma_\perp][i\hbar(\omega_2-\omega_1)+\hbar\gamma_\parallel]}\left[\frac{1}{i\hbar(\omega_0-\omega_1)+\hbar\gamma_\perp}+\frac{1}{i\hbar(\omega_2-\omega_0)+\hbar\gamma_\perp}\right]\ , \tag{4}$$

where μ denotes the dipole moment of the excitonic transition, ω_0 the transition frequency, $\gamma_\perp(\gamma_\parallel)$ the transverse (longitudinal) relaxation constant, and N is the number density of quantum dots. Actually the size of the semiconductor microcrystallites is not uniform but rather is describable by a distribution. Here the distribution function derived theoretically by Lifshitz and Slezov[19] is assumed for the radius of quantum dots. The dependence of $\gamma_\perp$ and $\gamma_\parallel$ on the size of the quantum dots is also included as follows:

$$\hbar\gamma_\parallel=\hbar/\tau_R,\quad \hbar\gamma_\perp=\tfrac{1}{2}\hbar\gamma_\parallel+\hbar\gamma_0\ , \tag{5}$$

where τ_R is the radiative recombination lifetime. $\hbar\gamma_0$ represents the dephasing arising from scattering and/or trapping by defect states or surface states and is taken to be 3.29 meV, corresponding to a dephasing time of 200 fs.[20] The calculated frequency dispersions of $\chi^{(1)}$ and $\chi^{(3)}$ for the degenerate case, i.e., $\omega_1=\omega_2$, are shown in Fig. 3. The out-of-phase behavior between $\chi^{(3)}$ and $\chi^{(1)}$ for both real and imaginary parts explains the experimental results[2] very well. The absolute value of $\chi^{(3)}$ for CdS quantum dots is estimated to be about 3.8×10^{-8} esu for a number density N of 10^{14} cm^{-3} and for the Lifshitz-Slezov distribution of quantum-dot radius with an average of 100 Å. This value is also in good agreement with the experimental value at room temperature.[1] In this calculation the oscillator strength of the free electron-hole pair is employed in consideration of the aforementioned possibility that the excitonic state is ionized at room temperature. At low temperatures the ex-

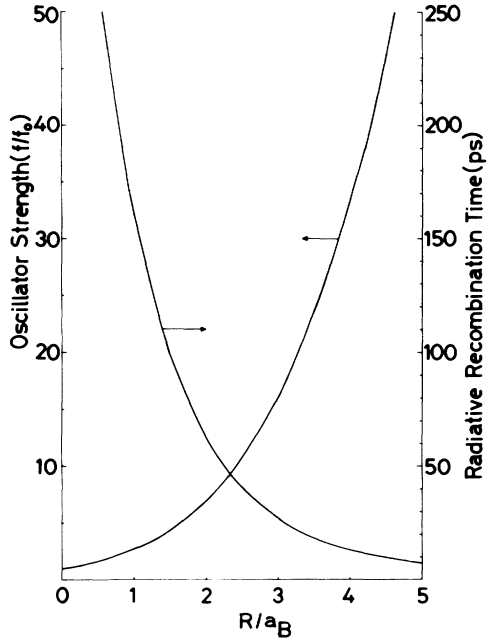

FIG. 2. Enhancement factor of the oscillator strength of an exciton relative to that of a free (uncorrelated) electron-hole pair, and the radiative recombination time in spherical semiconductor particles plotted as a function of particle radius.

citonic state is stable and its large oscillator strength is available to enhance the optical nonlinearity. In fact, the excitonic optical nonlinearity at low temperatures is calculated to be as large as 10^{-4} esu. A higher value of $\chi^{(3)}$ can be realized by choosing a suitable number density and quantum-dot radius.

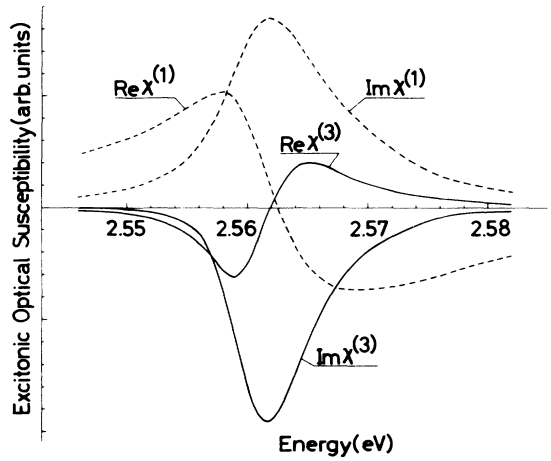

FIG. 3. Frequency dispersion of linear optical susceptibility $\chi^{(1)}$ and third-order nonlinear susceptibility $\chi^{(3)}$ of spherical semiconductor (CdS) particles. Particle size distribution is taken into account by the Lifshitz-Slezov distribution function for an average radius of 100 Å.

Our comprehensive interpretation of the controversial exciton dynamics in semiconductor quantum dots is presented with respect to the exposure-time dependence of the decay characteristics[7,9] and the darkening of the glass.[7] The slow-decay component can be attributed to the radiative recombination of an electron and a hole trapped by a donor-acceptor pair. The rate of this process is dependent on the distance between the donor and the acceptor and it gives rise to a broad luminescence spectrum. This assignment is corroborated by the recent measurement of the donor-acceptor pair recombination rate in bulk CdS.[21] In the course of this recombination process, the emitted phonons induce some kind of structural change around the donor-acceptor pair and efficient nonradiative recombination centers will be formed. The temperature rise due to laser irradiation, regarded as uniform in semiconductor microcrystallites, is estimated to be rather small. This suggests the importance of local phonon modes in inducing the structural change. After repeated exposure to laser irradiation, these nonradiative recombination centers are accumulated and the photogenerated carriers lose their energy via these centers. Thus the radiative recombination via a donor-acceptor pair becomes quenched, leading to the disappearance of the broad luminescence spectrum[7] and also of the slow-decay component in the transient grating measurements.[7,9] This accumulated structural change may be a cause of the permanent holographic grating and the darkening of the glass. This kind of photoinduced structural change is seen extensively in amorphous materials, such as *a*-Si,[22] chalcogenide glasses,[23] and Eu-doped glasses.[24] However, the details of the structural change have not yet been identified experimentally. On the other hand, the fast-decay component can be considered as arising from the radiative recombination of free excitons as calculated above. This interpretation is consistent with the experimental result[7] that the narrow luminescence line attributed to the excitonic recombination shows a very rapid decay. However, we have to keep in mind the possibility that the fast-decay component arises from the nonradiative recombination of an electron-hole pair via defect states or surface states. Thus it is crucial to examine the size dependence of the decay time constant in identifying the origin of the fast-decay component. A preliminary study of this size dependence has been carried out at low temperatures.[25] Although the results seem to suggest the relevance of mechanisms other than the radiative excitonic recombination, a more systematic study of the dependence of the decay-time constant on particle size and temperature is necessary to clarify the mechanism of the fast decay.

In conclusion, the calculated third-order excitonic optical nonlinearity of semiconductor microcrystallites (quantum dots) and its frequency dispersion are in good agreement with recent experimental results. A comprehensive interpretation of exciton dynamics in semiconductor quantum dots is presented. Especially, the radiative recombination lifetime of excitons in quantum dots is estimated in order to explain the experimental time constants of the fast decay in the transient grat-

ing and the luminescence measurements. Dependence of the radiative recombination lifetime on the quantum-dot size is predicted for the first time and is expected to play a key role in clarifying the mechanism of the fast decay.

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