

Dynamic Interactions of CdSe/ZnS Quantum Dots with Cyclic Solvents Probed by Femtosecond Four-Wave Mixing

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Abstract: We studied dynamic interactions between CdSe/ZnS quantum dots (QDs) and cyclic solvents probed by femtosecond four-wave mixing. We found that the dynamic interactions of QDs strongly depend on the existence of π -bonds in solvent molecules.

1. Introduction

Colloidal semiconductor quantum dots (QDs) have attracted enormous interest in the past two decades, since they show excellent photoluminescence (PL) properties such as narrow PL linewidth and high quantum efficiency. The PL of semiconductor QDs can be turned over entire visible region with changing the size of QDs. These excellent properties of semiconductor QDs enable to find wide range of applications such as imaging of biomolecules [1]. Many researches focus on further improving PL properties by the suppression of blinking phenomena in QDs [2].

Another property, optical coherence of exciton in QDs, has been of great interest from the viewpoint of fundamental physics and applications. The optical coherence properties of QDs result from the fluctuation of transition frequency induced by the dynamic interactions of QDs with the surrounding environments. We studied the dynamic interactions of QDs with cyclic solvents by femtosecond four-wave mixing (FWM) signals, and found that QDs in cyclic solvents show particular dephasing behaviour depending on the existence of π -bonds in solvent molecules. In contrast to previous works on the optical coherence in QDs [3,4], we could observe unexpectedly long dephasing times in solvents with no π -bonds, meaning much smaller dynamic interactions of QDs with those solvent molecules. The measured dynamic interactions were compared with the static interaction of QDs such as the peak shifts of PL and absorption bands.

2. Experimental

We used the commercial CdSe/ZnS colloidal QDs (Invitrogen, 655 nm). The purchased QDs were first flocculated by adding methanol/isopropanol mixture and centrifuging. After

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flocculation, the QDs were re-dispersed in four cyclic solvents, benzene, toluene, cyclohexane (CH) and tetrahydrofuran (THF).

In order to study the dynamic interactions of QDs with cyclic solvents, femtosecond FWM spectroscopy on QDs solutions was performed by using the second harmonic light (@ 1.92 eV) of output from optical parametric amplifier which was pumped with femtosecond regenerative amplifier. Pulse duration of the second harmonic light was measured to be approximately 47 fs. We employed conventional two-beam (\mathbf{k}_1 , \mathbf{k}_2) excitation geometry in femtosecond FWM experiments and the FWM signals in $2\mathbf{k}_2 - \mathbf{k}_1$ were measured at room temperature as a function of delay time τ between the two beams [5].

3. Results and discussion

Figure 1 displays the results of femtosecond FWM measurements performed for CdSe/ZnS colloidal QDs in (a) benzene and toluene and (b) CH and THF solutions, where the autocorrelation trace of exciting femtosecond pulses is denoted by a dotted line as a reference. As shown in Fig. 1(a), it is observable that the dominant components of FWM signals in benzene and toluene decay very fast with time constant nearly to or less than our time resolution of about 50 fs. These findings mean that the dynamic interactions of QDs with benzene and toluene molecules are very strong. As these signal decays almost follow the autocorrelation trace of femtosecond pulses, it needs numerical simulation to obtain precise dephasing time. However, we don't carry out the numerical simulation because it is out of our major scope. In addition, one can find the much smaller contributions to the FWM signals with longer dephasing time for $\tau > 200$ fs in both solutions. The optical dephasing times for these contributions are tentatively estimated to be about 604 and 720 fs for benzene and toluene solutions, respectively.

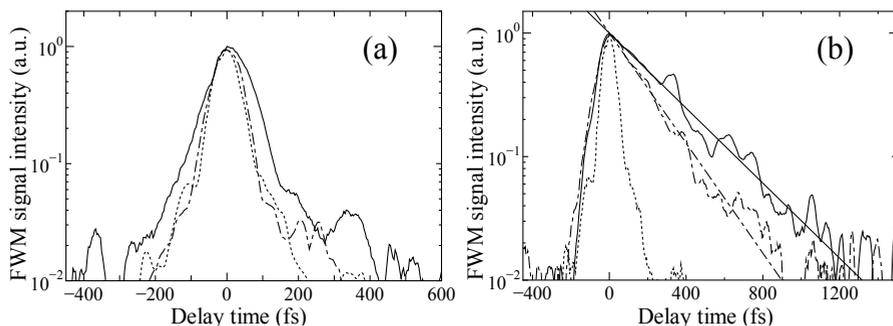


Fig. 1. The FWM signals of QDs observed in four solvents, (a) benzene (solid) and toluene (dot-dashed), (b) CH (solid) and THF (dot-dashed). The dotted lines denote the autocorrelation trace of exciting pulses. The straight solid and dot-dashed lines in (b) show exponential fitting to obtain optical dephasing times in CH and THF solutions.

In sharp contrast to the FWM signals in benzene and toluene, Fig. 1(b) definitely reveals that the FWM signals in CH and THF solutions show extremely slow single-exponential decays. The optical dephasing time of QDs are obtained as 1160 and 720 fs for CH and THF solutions, respectively, with assumption that FWM signal intensity $I(\tau)$ decays following a single exponential function $\exp(-4\tau/T_2)$ with dephasing time T_2 . Since these our findings are contradictory to previous works on optical dephasing of QDs, which indicate the optical dephasing times of QDs at room temperature should be less than 10 fs, we confirmed the reproducibility of the FWM signals of QDs in CH and THF solutions by repeating sample treatment and measurements of FWM signals. We always obtained the same FWM signal traces as in Fig. 1(b) in the confirmation steps. Therefore, we believe that the slow decays of FWM signals in CH and THF solutions manifest the unexpectedly weak dynamic interactions of

QDs with CH and THF molecules. To further examine the origin of FWM signal of QDs in CH and THF solutions, the spectrum of FWM signal at $\tau=0$ was measured and compared with those of the excitation pulses and absorption in QDs, as shown in Fig. 2. As the spectrum peak of FWM signal in THF solution is located at the absorption peak of exciton band in QDs, it is concluded that the FWM signal originates from the exciton transition in QDs, not from the surface state or photo products.

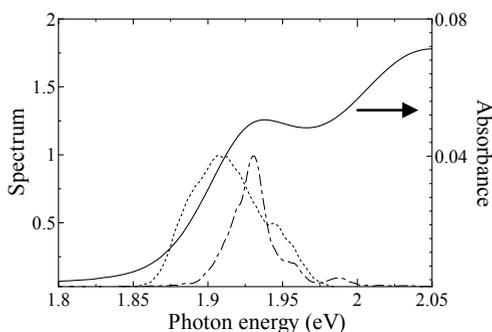


Fig. 2. The spectrum (dot-dashed line) of FWM signal from QDs in THF at $\tau=0$ is compared with the absorption spectrum (solid line) of QDs and the spectrum (dotted line) of exciting femtosecond pulses.

The dynamic interaction between QDs and solvent molecules can be modelled by employing stochastic transition frequency fluctuation $\delta\omega(t)$ of QDs induced by the solvents, which obeys a Gaussian process with $\langle\delta\omega(t)\rangle = 0$ and $\langle\delta\omega(t)\delta\omega(t')\rangle = \Omega^2 \exp(-R|t-t'|)$ with Ω and R being a magnitude and a rate of fluctuation. The $\delta\omega(t)$ gives the decay of FWM signal intensity expressed as $I(\tau) \propto \exp(-4\Omega^2\tau/R)$. According to our FWM measurements described above, it is inferred that the cyclic solvents with benzene ring or π -bonds give much stronger dynamic interaction with QDs than those without π -bonds, which leads to a large values of Ω and resultantly very fast decays of FWM signal in benzene and toluene solutions. It is probably because the density distribution of π -electrons in the cyclic molecule expands from the molecular plane, while the density distribution of σ -electrons in the cyclic molecule is strictly limited in the molecular plane.

4. Conclusion

We have studied the dynamic interactions of QDs with cyclic solvents, benzene, toluene, CH and THF, by femtosecond four-wave mixing and found particular dephasing behaviour depending on the existence or absence of π -bonds in the cyclic solvent molecules. The dependence is interpreted in terms of the density distribution of π - and σ -electrons in the solvent molecules.

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