Temperature dependence of spectra and exciton-phonon coupling in semiconductor CdSe/ZnS quantum dots

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Based on spectral-kinetic data for individual amine-capped semiconductor quantum dots CdSe/ZnS-AM QD, and their nanoassemblies with perylene bisimide molecules (DPP) in methylcyclohexane-toluene (6:1), it was found that the temperature lowering (273 K → 77 K) is accompanied by conformational transformation of surface ligand layer (AM) which accelerates upon attachment of DPP molecules to the QD surface. Using exciton-phonon coupling approach, it was argued for these QDs that the formation of the absorption band for the first excitonic transition takes place with participation of CdSe core LO phonons influenced by surface stabilizing ligand low-temperature conformational effects.

Keywords: amine-capped semiconductor quantum dots CdSe/ZnS-AM; $(pyridyl)_2$-perylene diimide (DPP) dye molecules; temperature dependence of absorption and photoluminescence spectra; exciton-phonon coupling; phase transition of stabilizing ligand layer.

Температурная зависимость спектров и экситон-фононной связи в полупроводниковых квантовых точках CdSe/ZnS

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На основании спектрально-кинетических данных для индивидуальных стабилизированных амином полупроводниковых квантовых точек CdSe/ZnS-AM КТ, и наноансамблей, включающих эти КТ и молекулы перилен-бисимида (DPP) в метилциклогексан-толуоле (6:1), обнаружено, что понижение температуры (273 K → 77 K) сопровождается конформационной перестройкой поверхностного слоя лиганда (AM), которая усиливается при связывании молекул DPP на поверхности КТ. В модели экситон-фононных взаимодействий обосновано, что для этих КТ формирование полосы поглощения первого экситонного перехода происходит с участием оптических фононов ядра CdSe при воздействии низкотемпературных конформационных эффектов в поверхностном слое стабилизирующего лиганда.

Ключевые слова: стабилизированные амином полупроводниковые квантовые точки CdSe/ZnS-AM; молекулы красителя (пиридил)2-перилен-бисимда (DPP); температурные зависимости спектров поглощения и фотолюминесценции; экситон-фононные взаимодействия; фазовая перестройка стабилизирующего слоя лиганда.

Introduction

It is well documented that in semiconductor quantum dots (QDs) the electronic energy levels as well as the lattice vibrational modes (phonons) become discrete due to the three-dimensional confinement [1, 2]. One long standing question in QD physics is the effect of quantum confinement on the strength of exciton-phonon coupling and phonon frequency, a topic that has received considerable experimental attention [3]. Experimentally, the analysis of this coupling is based on two types of observations, namely *(i)* the intensity ratios of the spectrally resolved pure (phonon-less) electronic transition intensities and phonon side bands (Raman spectroscopy [4]), and *ii)* temperature dependence of optical transition intensities, contributions to the homogeneous spectral line widths and energies of absorption and/or photoluminescence (PL) emission together with experimentally determined Stokes shift [5].

Upon studying exciton-phonon coupling in semiconductor QDs, the majority of previous temperature experiments have been carried out for QDs dissolved in rigid matrixes (polymers, resins, *etc*.). On the other hand, in typical solvents (freezing at low *T*) a possible low-temperature phase transition of the capping ligand layer may be accompanied by QD surface relaxation or reconstruction what was described by us for TOPO-capped CdSe/ZnS QDs and their nanoassemblies with porphyrin molecules in methylcyclohexane-toluene (6:1) glass forming mixture at $T < 240$ K [5]. Here, based on combination of absorption/PL data, we discuss temperature dependent exciton-phonon coupling for CdSe/ZnS-AM QDs capped by long-chain amines (AM) and their nanoassemblies with perylene bisimide molecules (DPP) embedded into such solvent mixture.

Results and Discussion

The non-covalent coordination interaction between ZnS surface of amine-capped CdSe/ZnS-AM QD and perylene bisimide molecule (DPP) is shown in Fig. 1 where basic spectral effects upon temperature lowering are presented also.

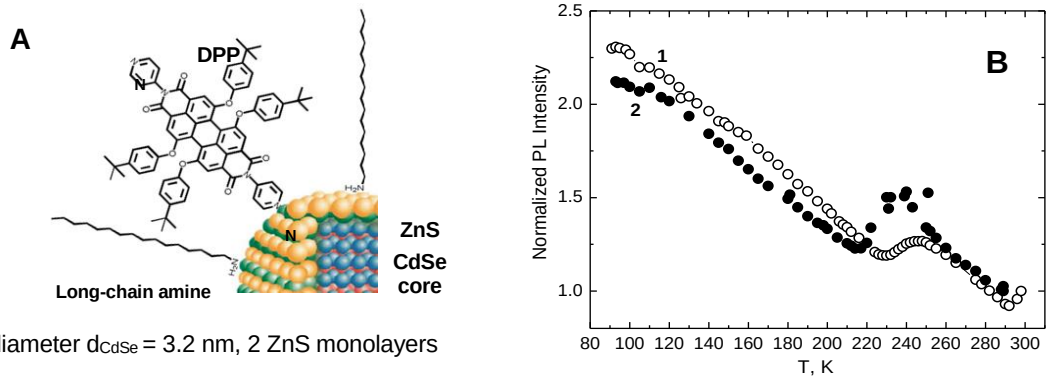

Fig. 1. (*A*) Schematic presentation of the interaction between surface of amine-capped CdSe/ZnS-AM QD and perylene bisimide molecule, DPP; (*B*) Temperature dependence of the normalized photoluminescence (PL) intensity (λ_{exc} = 450 nm, (λ_{max} = 618 nm) for CdSe/ZnS-AM QDs (1, open circles) and for nanoassemblies based on CdSe/ZnS-AM QDs and DPP molecules at molar ratio $x = [C_{DPP}]/[C_{QD}] = 1$ (2, closed circles) in a methylcyclohexane/toluene (6:1) mixture

Figure 1, *B* shows that upon temperature lowering, the maximum of PL spectra for alone QDs are blue shifting. In addition, the PL line width (FWHM) becomes essentially narrower, while the PL intensity becomes higher. Interestingly, that a non-monotonous behavior (which is called as "kink", for simplicity) is observed for CdSe/ZnS-AM QDs between 220 K and 250 K, far from the glass transition temperatures for a methylcyclohexane-toluene (6:1) mixture (151.6 K). In addition, the temperature PL dependence for a nanoassembly of CdSe/ZnS-AM QDs with a DPP molecule shows also a kind of "amplification" of the PL intensity jump at T_{crit} which is accompanied with a shift of T_{crit} by about 10 K towards lower temperatures. We have argued [6, 7] that unusual "luminescence anti-quenching" at a well defined temperature of T~250 K (like "kink" in our experiments) is connected with low-temperature surface relaxation and/or surface reconstruction (some strain-induced deformations of ZnS shell), which are strongly dependent on the type of capping ligand molecules (TOPO or AM) and, in turn, may cause a spatially-energetic reordering of trap states. Correspondingly, we took into account this phase transition upon analysis of exciton-phonon coupling for CdSe/ZnS-AM QDs.

For wide band materials, such as CdSe/ZnS QDs, where the exciton binding energy is much smaller than the band gap energy (E_g), the corresponding E_g values may be approximated as the energy of the first exciton peak (the band edge exciton) measured in optical absorption and PL spectra at various temperatures. The obtained temperature dependences were fitted using Debye [6] and Einstein [7] model for electron-phonon coupling, correspondingly:

$$\text{Debye approach:} \qquad E_g(T) = E_g(0) - \alpha T^2/(T + \theta_D) \tag{1}$$

where $E_g(0)$ is the band gap at 0 K, α is a constant and θ_D the Debye temperature;

$$\text{Einstein approach:} \qquad E_g(T) = E_g(0) - k/[\exp(\theta_E/T) - 1] \tag{2}$$

where k is a constant, and θ_E is the Einstein temperature.

In addition, exciton-phonon coupling adds to dephasing processes resulting in homogeneous line width broadening. In this case exciton-phonon coupling may be deduced from temperature dependent PL line width (FWHM) data using the following equation [8]:

$$\text{FWHM}(T) = \Gamma(T) = \Gamma_{inh} + \sigma T + \Gamma_{LO}/[\exp(E_{LO}/k_B T) - 1] \tag{3}$$

where Γ_{inh} is the inhomogeneous broadening, Γ_{LO} represents the exciton-LO-phonon coupling strength and E_{LO} is LO-phonon energy, a linear coupling to temperature follows a coupling constant σ, the temperature dependent terms represent the direct dephasing processes via acoustic phonons and an Orbach-type dephasing process caused by LO phonons.

Finally, assuming a temperature-independent radiative lifetime due to the strong confinement regime, the temperature dependence of the QD PL intensity (caused by a temperature activated increase of non-radiative channels) was fitted according to [9]

$$I_{PL}(T) = I_0/\{1 + a\cdot\exp(-E_a/k_B T) + b\cdot[\exp(E_{LO}/k_B T) - 1]^{-m}\} \tag{4}$$

where I_0 is PL intensity at T=0, E_a is the activation energy for excitation of non-radiative traps, E_{LO} the energy of either CdSe or ZnS phonons, and m is the number of phonons needed to populate the next higher excitonic QD state which promotes exciton-phonon induced radiationless transitions, a and b respond to the relative contribution of these two processes.

The results of the fitting procedures for CdSe/ZnS-AM QDs at various temperatures are shown in Figs. 2 and 3.

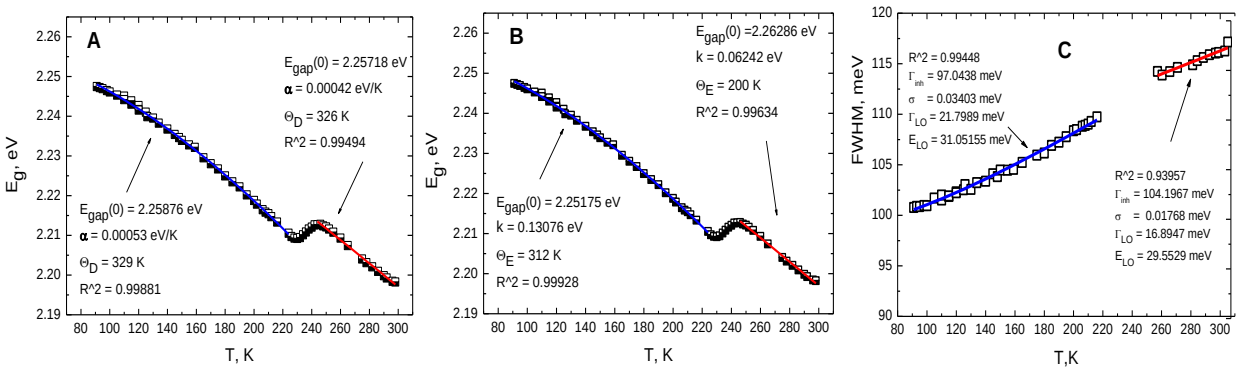

Fig. 2. A, B: Temperature dependence of energy gap values E_g for CdSe/ZnS-AM QDs in methylcyclohexane/toluene (6:1) mixture based on PL band measurements and fitting according to Equ. 1 (*A*) and Equ. 2 (*B*); experimental points present energy E_{max} of the PL band maximum; red and blue lines show simulations above and below the phase transition temperature (~240 K), correspondingly. C: Fit of the temperature dependent PL line widths FWHM (λ_{exc}= 450 nm) according to Equ. 3; fit parameters are included; lines show above (red) and below (blue) the phase transition temperature (~240 K)

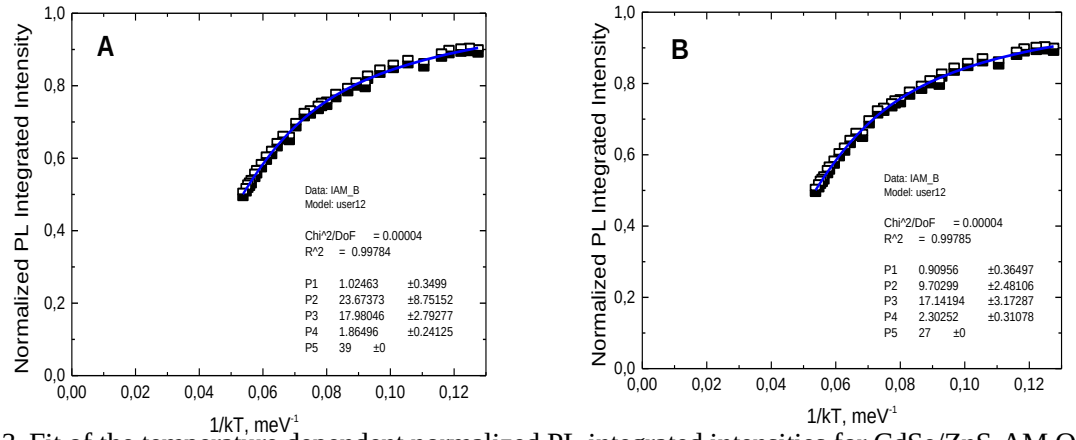

Fig. 3. Fit of the temperature dependent normalized PL integrated intensities for CdSe/ZnS-AM QDs in methylcyclohexane/toluene (6:1) mixture (λ_{exc} = 450 nm) according to Equ. 4 below the phase transition temperature (~240K) with fixed phonon energies E_{LO} = 39 meV (***A***) and 27 meV (***B***) for ZnS and CdSe phonons, respectively. Fits are restricted to the temperature range below the phase transition. Fitting procedure has been performed at ratio I/I_0=0.9. Note the 1/*kT* presentation

The analysis of these results shows the following. While the energy gap E_g (0) = 2.26 eV for all temperature range, we observe differences in the respective temperatures: the average Θ_D and Θ_E values are systematically larger for high temperature range (before phase transition of AM layer) compared to low temperature range (after phase transition). Debye and Einstein temperatures are related to the heat capacity of solids. Since we observe in PL strong contributions from PL at the ZnS/CdSe interface we suggest that ligand depending exciton-phonon coupling might increase the Debye and Einstein temperature.

According to fits of the temperature dependent FWHM (Fig. 2, *C*) it follows that the phonon coupling constant Γ_{LO} for AM-capped CdSe/ZnS QDs seems to be on average somewhat smaller as compared to TOPO-capped QDs. This might be due to the fact that it is only possible to fit FWHM data below and above T_{crit} separately due to the pronounced

jump at this temperature. Nevertheless, also in this case E_{LO} is larger than expected for CdSe phonons. Evaluation of exciton-phonon coupling from FWHM according to Equ. 3 results in Γ_{in} = 97 meV, σ = 30 μeV; Γ_{LO} = 22 meV, and E_{LO} = 34 meV. This latter value is very close to the LO (ZnS) phonon of 39 meV [5] while comparison with results from literature reveals that E_{LO} (CdSe) is expected to be close to 25 meV [5]. This means that the energy shift upon temperature lowering is due to the temperature-dependent phonon induced band-gap shrinkage of the CdSe core material.

Conclusions

Our temperature dependent optical experiments on CdSe/ZnS-AM QDs are in almost quantitative agreement with experimental reports on the PL detected influence of electron-phonon coupling on optical properties. While in most of those reported experiments PL data (PL energy; PL band width, or Stokes shifts) have been used to determine electron-phonon coupling parameters, we used in parallel temperature dependent absorption data which provided in combination with PL emission the identification of the temperature dependence of the Stokes shift, which reveals temperature dependent Huang-Rhys factors. We like to remark that the apparent Stokes shift might by enlarged by an energy cascade from near-band edge states to traps close to the band edge. As a consequence, a simple determination of exciton-phonon coupling from Stokes shifts from absorption/PL data will generally result in too large couplings. Finally, it would be interesting to get further information on such processes via analysis of blinking and spectral diffusion experiments with respect to exciton-phonon coupling

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