Luminescence kinetics of CdSe-based quantum dots in toluene

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Abstract. Luminescence kinetics of quantum dots (CdSe-CdS core-shell nanoparticles) in toluene were studied. Quantum dots were obtained through colloidal synthesis method in aqueous-organic media with the average size estimated as 2 nm and 2.9 nm from the position of the exciton absorption peak. A biexponential luminescence decays with time constants of a few and tens of picoseconds were observed via up-conversion technique.

1. Introduction
CdSe-CdS nanoparticles have gained a particular interest due to their unique optical properties [1]. The evolution of photoinduced charge carriers and, therefore, the luminescence kinetics strongly depends on the size of the nanocrystallite and the properties of its surface. As a rule, the reported optical responses decay within picoseconds which is associated with exciton-phonon interaction processes [2]. Auger recombination processes [3] can also occur, leading to rapid subpicosecond decay. Generally, multicomponent luminescence decays are being observed, e.g. [1], with time constants up to hundreds of nanoseconds [1], depending on the quantum dot sizes.

The problem of the quantum dots synthesis is the aggregation of single dots into clusters of tens and hundreds of nanometers. This process greatly suppresses the confinement effect, and therefore, makes it less appealing to applications in optoelectronics. To address this problem, we have obtained quantum dots of 2 nm and 2.9 nm in size, consisting of CdSe cores coated with CdS shell. Those are less likely to get aggregated, while retaining all the confinement-related optical properties.

2. Experimental
CdSe nanoparticles were synthesized using colloidal method in aqueous organic media [4]. Cadmium acetate and sodium selenosulfate were used as a source of cadmium and selenium ions. In order to obtain quantum dots (QD) dispersible in organic solvents, like toluene, hexane, chloroform, etc., oleic acid was chosen as the stabilizer. The organic component of the medium necessary to dissolve the oleic acid was ethanol or glycerin. Depending on the required optical characteristics, the synthesis of CdSe QD was carried out at different temperatures.

CdSe nanocrystallites with a luminescence maximum at 500 nm (Fig.1 (3)) were obtained in a water-ethanol medium at 50°C. The QD were purified by reprecipitation from a mixture of ethanol-hexane. The absorption spectrum of QD contains a wide wing in the range of 400-500 nm, corresponding to exciton absorption. The average size of QD was estimated from the position of the exciton absorption peak at 457 nm [5]. According to these values, the average size of CdSe QD was 2 nm.
CdSe nanocrystallites with a luminescence maximum at 570 nm were obtained in an aqueous glycerin medium at 170 ° C. These nanocrystallites absorb light in a wider range, and the exciton peak is at 543 nm (Fig. 1 (4)). The average size of CdSe QD was estimated as 2.9 nm.

**Figure 1.** Absorbance (1,2) and luminescence (3,4) spectra of 2 nm (1,3) and 2.9 nm (2,4) CdSe-CdS QD in toluene.

Time-resolved fluorescence up-conversion technique [6] was applied to both samples. To excite the luminescence of the samples, the second harmonic of Ti:Sapphire laser (pulse duration of 50 fs, carrier wavelength of 770 nm, average power of 450 mW) was used with a wavelength of 385 nm and the average power of 20 mW. A suspension of QD in toluene was pumped through a quartz cuvette 2 mm thick. The remaining part of 770 nm laser beam with an average power of 330 mW was passed through the optical delay line and used as a temporal gate. The luminescence emission was collected by a parabolic mirror and, along with the gate beam, focused onto a BBO type 1 crystal of 0.5 mm thickness, where sum frequency signal was generated. This signal was isolated by a monochromator and recorded by the photon counting system.

3. Results

The recorded experimental data (Fig. 2) is the convolution of the QD luminescence emission and the gate pulse. The width of spread function can be estimated as 100 fs (considering the duration of femtosecond pulses), which is significantly less than typical luminescence decay times. It was established [2-3] that different relaxation processes of photoexcitation must predominate depending on the QD size, namely, electron-phonon relaxation for larger dimensions and Auger recombination for smaller crystallites. As we have studied QD of two sizes, 2 nm and 2.9 nm, we expected to find a significant difference in the ratio of "faster" (sub-picosecond) and "slower" (tens of picoseconds) contributions.
As evident from Fig. 2, the basic shape of the luminescence kinetics curve does not depend on the size of the QD, so the relaxation processes for larger and smaller QD are arguably the same. However, the parameters of the two-exponential decay of the luminescence kinetics depend significantly on the size of the QD: the decay times of 1.8 ps and 26.8 ps correspond to 2 nm QD, and 4.5 ps and 68 ps are detected for 2.9 nm QD. We should note that in a single CdS crystal the carrier thermalization time within the conduction band is of the same order [7], which may indicate some agglomeration of QD in the suspension.

4. Conclusion
The application of time-resolved fluorescence up-conversion technique revealed a two-component nature of the luminescence decay. For QD with average size estimated as 2 nm the decay times were found to be 1.8 and 26.8 ps, and for 2.9 nm QD the decay times were 4.5 and 68 ps. The established correlation between the decay times and the size of the QD fits with the existing data [2-3]. More detailed analysis of the dependence of the relaxation processes in QD on their size will require additional experimental and theoretical studies.

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