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# Quantum dot based superstructures: PL decay analysis

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Abstract. The analysis of the optical properties, including transient photoluminescence (PL), of CdSe quantum dots (QDs) self-assembled in supercrystals shows that supercrystals possess efficient QD PL. Although PL band is slightly broadened and blueshifted as compared with QD colloidal solution, PL kinetic is the same showing absence of induced channels of the energy dissipation. The data indicate the opportunity to create quantum dot solids with efficient PL.

#### 1. Introduction

Quantum dots (QDs) are semiconductor nanocrystals which sizes are close or less than the exciton Bohr radius and where movement of charge carriers is space limited in all three directions. This results in size dependent discrete energy spectra of the electronic transitions in ODs often called, therefore, "artificial" atoms. Development of the nanotechnology allows to design novel nanostructured materials based on QDs as building blocks. These materials possess unique optical and electronic properties, which can be tuned by varying the size, shape and chemical composition of the building blocks and, at the same time, by changing the inner morphology of the superstructure. One of the types of nanostructured materials is the supercrystals (SCs) formed from QDs [1]. These materials are very attractive for application in devices with improved performance for photovoltaics, biosensing and elements for telecommunications [2, 3]. However, these materials are far from the mass production, since there are lots of challenges to solve, for instance, there is a lack of information on optical properties, e.g. photoluminescence (PL), of SCs with different chemical composition, morphology and other parameters.

Thus, the investigation of optical properties, including PL kinetics, of SCs formed from CdSe QDs in comparison with that of QDs in colloidal solution is of great interest.

#### 2. Experimental

2.1. Materials. Colloidal 4 nm in diameter CdSe QDs with surface stabilized by trioctylphosphine oxide (TOPO) molecules have been synthesised by standard hot-injection method [4]. Then TOPO molecules have been replaced with oleic acid (OA) ones needed for SCs growth from colloidal QD solution. Absorption (ABS) and PL spectra of QDs in a tetrachlormethane (TCM) solution are shown in figure 1(a). SCs have been obtained by self-assembly of QDs on a glass substrate by slow evaporation of the saturated QD colloidal solution with initial QD concentration of around 10<sup>-5</sup> M. The obtained SCs have a shape of polyhedra with pronounced edges (see figure 1(b)). The size of typical SC used for investigation is of about  $68.5 \times 9.5$  um (see figure 1(b)). This QD sample also contains areas with disordered QD ensembles, formed in excess of OA molecules. For comparison a sample

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with QDs deposited on a glass substrate has been prepared. In this case, a solution with QD concentration around 10<sup>-7</sup> M has been used. A drop of this colloidal solution has been dripped on the substrate and evaporated in ambient atmosphere leading to QD agglomeration into clusters (hereafter called "QDs in aggregates"). It should be noted that the evaporation process has been much faster than that for the saturated QD solution. Microphotographs of typical SC and of QDs in aggregates on the substrate obtained with a confocal microscope Olympus BX-51 are shown in figure 1(b) and 1(c), respectively.



**Figure 1.** (a) ABS and PL spectra for 4 nm CdSe QDs, covered with OA molecules, in TCM. (b) and (c) 100x100 um microphotographs of QD SC and of QDs in aggregates, respectively.

2.2. Methods. For optical spectral analysis of the samples a spectrophotometer UV-3600 (Shimadzu) and spectrofluorimeter Carry Eclipse (Varian) have been used. PL spectra of QD samples on the substrates have been obtained with a laser scanning microscope LSM-710 (Zeiss). PL decay at room temperature has been investigated by a laser scanning confocal microscope MicroTime 100 (PicoQuant), which implements the method of time-correlated single photon counting. Obtained PL decay curves from the samples have been fitted by biexponential function:

$$I(t) = I_0 + A_1 \exp(-t/\tau_1) + A_2 \exp(-t/\tau_2).$$
(1)

The average PL lifetime has been calculated with:

$$\langle \tau \rangle = \frac{\sum I_i \tau_i^2}{\sum I_i \tau_i}.$$
 (2)

#### 3. Results

The investigation of the steady-state spectral properties of QD in SCs and in aggregates shows that their ABS and PL bands are broadened and blueshifted in comparison with those in the colloidal solution. Obtained spectra are shown in figure 2.



Figure 2. ABS (a) and PL (b) spectra of samples of QDs: (1) in solution, (2) in aggregates, (3) in SCs.

The changing in the optical properties is mainly caused by interactions between the nanocrystals and their chemical environment in solution, in aggregates, and in SCs [5]. The concentration of OA molecules nearby QD is increasing in the series: QDs in solution, QDs in aggregates, disordered QD ensembles and QD SCs. Thus, QDs in SCs and in disordered ensembles are surrounded by a matrix formed from OA molecules.

We have investigated luminescence properties of QD samples on the substrates (QD SCs, QD in aggregates and disordered QD ensembles) by means of confocal microscopy. The obtained PL spectra together with PL images of the samples are shown in figure 3. Comparison of the PL images shows an unusually sharp spatial distribution of PL intensity through SC, where only edges of SC are highly luminescent. As it is seen from the figures 3(b) - 3(d), such PL spatial distribution is not observed for QDs in aggregates and disordered QD ensembles.



Figure 3. (a) PL spectra of QDs: (1) in solution, (2) in aggregates, (3) in SC, (4) in disordered ensembles. PL images of QDs: (b) in aggregates, (c) in SC, (d) in disordered ensembles.

PL spectral analysis of the samples shows that PL maximum is blueshifted and for SCs this shift is maximal and is of 63 nm compared to QD colloidal solution. This comes, most likely, from differences in QD environment for TCM solution and OA matrix.

A comparison of PL decay curves for QDs in initial colloidal solution and for QD samples on the substrates is presented in figure 4(a).



**Figure 4.** PL decay curves (a) and average PL lifetime dependence on emission peak wavelength (b) for QDs: (1) in solution, (2) in aggregates, (3) in SC, (4) in disordered ensembles.

PL decay analysis shows that the average PL lifetime of QDs in initial colloidal solution is 25.3 ns with 6.7 ns and 30.9 ns of "short" and "long" decay components, which are in agreement with literature [6]. The average PL lifetime of QDs in aggregates is reduced to 9.9 ns that has been expected due to increasing interaction between close packed QDs. At the same time, for disordered QD ensembles in OA the average PL lifetime is close to that in solution and for SCs is as high as 29.9 ns, which is slightly higher that PL decay value for isolated QDs in solution.

For spectrally resolved PL decay analysis interference filters to cut a 5 nm spectral band within PL spectra have been used. The maximum positions of the bands are shown by dashed lines in figure 3(a). In figure 4(b) the average PL lifetimes, estimated by equation (2), are shown. As it was expected, the average PL lifetime of QDs in solution is independent from the emission wavelength. For QDs in aggregates and disordered QD ensembles in OA the increase of PL lifetime with emission wavelength is observed. In case of QDs in aggregates PL lifetime increases from 5.7 to 13.3 ns. It can be explained by taking into account FRET between QDs in aggregates. Contrary to these data PL lifetime of QDs in SCs is independent from the emission wavelength, as it is observed for QDs in solution. This indicates that the interaction of QDs in SCs does not affect PL decay of quasi-isolated QDs.

#### 4. Conclusion

Optical properties of CdSe QDs with diameter of 4 nm self-assembled in supercrystals on the glass substrate have been investigated in comparison with QDs in TCM solution and with QDs in aggregates and disordered QD ensembles on the substrates. The spectral analysis shows that ABS and PL bands of QDs in SCs are broadened and blueshifted in comparison with the colloidal solution. The transient PL analysis shows that QDs in superstructure possess almost the same PL lifetimes comparing to those in colloidal solution, showing absence of induced channels of the energy dissipation. This data indicate the opportunity to create quantum dot solids with efficient PL.

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#### References

[1] Nie Z, Petukhova A and Kumacheva E 2010 Nat Nanotechnol 5(1) 15-25

[2] Nag A, Zhang H, Janke E and Talapin D V 2015 Zeitschrift für Physikalische Chemie **229**(1-2)

85-107 Jiao Y, Han D, Ding Y, Zhang X, Guo G, Hu J, Dong Y and Dong A 2015 *Nature* communications **6** Yu W, Qu L, Guo W and Peng X 2003 *Chemistry of Materials* **15**(14) 2854-2860

 [3] Ushakova E, Cherevkov S, Litvin A, Parfenov P, Zakharov V, Dubavik A, Fedorov A and Baranov A 2016 Opt Express 24(2) A58-A64

[4] Wang X, Qu L, Zhang J, Peng X and Xiao M 2003 Nano Lett 3(8) 1103-1106