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Hetero- and low-dimensional structures

Influence of the quantum dots bandgap and their dispersion on the loss of luminescent quanta

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Abstract. The method for estimating the loss of luminescent quanta caused by reabsorption has been proposed. The method is based on the analysis of absorption and luminescence spectra of quantum dots (QDs) with different radii $\bar{r}$ and dispersion of radius $\Delta\bar{r}$. The loss was estimated for QDs of six semiconductor materials with different bulk bandgap E_{g0}: CdS (E_{g0} = 2.42 eV), CdSe (E_{g0} = 1.74 eV), CdTe (E_{g0} = 1.56 eV), InP (E_{g0} = 1.34 eV), InAs (E_{g0} = 0.36 eV), and PbSe (E_{g0} = 0.27 eV). It has been ascertained that, by changing $\bar{r}$ and $\Delta\bar{r}$, one can find the optimal values of these parameters, for which the losses of luminescent quanta are minimal.

Keywords: luminescence, quantum dots, luminophor, reabsorption, quantum loss.

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1. Introduction

The efficiency of solar energy conversion into electricity with a fluorescent concentrator is less than 10% [1, 2]. One of the reasons for the low efficiency is the presence of luminescent quanta reabsorption caused by the existence of luminescence and absorption spectra overlapping [3]. Among the well-known luminophores (rare earth atoms and complexes, dyes, semiconductor quantum dots (QDs)), only QDs can absorb solar quanta in a wide spectral range and emit luminescent quanta in a narrow spectral range. If the luminophores are contained in a transparent dielectric matrix (for example, made in the form of a parallelepiped), due to complete internal reflection luminescent quanta are transferred to the matrix edges with attached solar cells. Then, quantum energy of luminescence is converted into electrical energy. On the transport path, some part of these luminescence quanta is lost as a result of reabsorption. The magnitude of these losses depends on the value of the bandgap of the bulk semiconductor, from which the QDs are made, the size of the quantum dots and their dispersion [1, 4]. The purpose of this work is to determine the value of the aforementioned losses.

2. Reabsorption

The main advantage of QD as compared to other types of phosphors is the ability to accurately match the luminescence band with the maximum sensitivity of the solar cells by changing the size of QD, which diameter varies from 1 to 20 nm [4]. A typical QD with a high quantum luminescence output consists of a core surrounded by one or more shells of semiconductor material and a shell of organic material. The core is made of a narrow-band semiconductor. It absorbs the solar quanta in a wide spectral range and emits luminescent quanta in a narrow luminescent band. The first shell is intended for passivation of dangling surface bonds of the core. The bandgap of this shell exceeds the core bandgap. Each subsequent shell is different from the previous one by extended bandgap. Their main purpose is to match semiconductor lattice parameters, which is necessary to reduce the appearance of dislocations. Organic shell is the set of organic molecules deposited on the last inorganic shell. The primary purpose of the organic shell is to prevent QD aggregation.

The motion of an electron (hole) in QD can be considered as the movement of a quasi-particle in a three-

Table. Roots of the Bessel functions.

l n	1	2	3	4
0	3.142	6.283	9.425	12.566
1	4.493	7.725	10.904	14.066
2	5.764	9.095	12.323	
3	6.988	10.417	13.698	
4	8.183	11.705		
5	9.356	12.967		
6	10.513	14.207		
7	11.657			
8	12.791			
9	13.916			

dimensional potential box. The position of energy levels of the quasi-particle is calculated from the bottom of the potential box (the position of the electron and hole quantization levels is respectively calculated from the bottom of the conduction band and from the top of the valence band). The energy position of QD quantization levels can be calculated using the formula [3]:

$$E^{e,h}_{n,l} = E_{g0} + \frac{\hbar^2\varphi^2_{l,n}}{2r^2}\left[\frac{1}{m_e}+\frac{1}{m_h}\right] - \frac{1.786e^2}{4\pi\varepsilon\varepsilon_0 r} - 0.248E^*_{\mathrm{Ry}}\,, \quad (1)$$

where E^*_{Ry} is the Rydberg energy, ε and ε_0 are the dielectric constants of the medium and vacuum, respectively, $\hbar$ is the Planck constant, m_e and m_h are the effective masses of electron and hole, respectively, e is the electron charge, r – radius of the nanocrystal, $n = 1, 2, 3, ...$ – principal quantum number, $l = 0, 1, 2, ...$ – orbital quantum number, $\varphi_{l,n}$ – universal set of numbers [5], which is given in the table.

The first term of Eq. (1) is the bandgap E_{g0} of a bulk semiconductor; the second term describes the energy position $E^{e,h}_{n,l}$ of the quantum-sized nanocrystal levels; the third term describes the decrease in energy caused by interaction of electron and hole; the fourth term is the Rydberg energy, which magnitude is insignificant and does not depend on the size of the nanoparticle. This energy is commonly neglected except for semiconductors with low dielectric constant.

The absorption spectrum is formed by transitions between the dimensional quantization levels of electrons and holes with the same quantum numbers n and l (see Fig. 1a).

When QD is illuminated by sunlight, electrons gain the energy of absorbed photons and move from the quantum-dimensional levels of the valence band to the corresponding quantum-dimensional levels of the conduction band producing electron-hole pairs. Both electrons and holes quickly (for the picosecond time interval) relax from high energy levels to levels E^e_{01} and E^h_{01}, respectively. Then, conduction band electrons on E^e_{01} level loose energy and re-occupy their position on E^h_{01} level generating photons in the process of recombination.

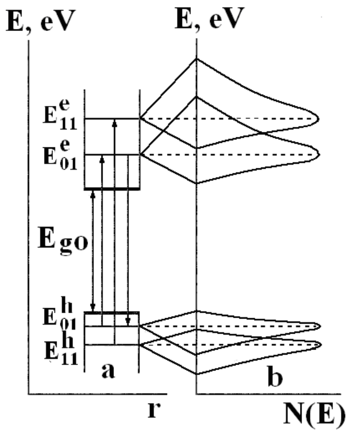

Fig. 1. Diagram of the energy levels of electron and hole under the conditions of dimensional quantization in the absence (a) and presence (b) of nanocrystal dispersion in radius and thermal smearing of quantum-dimensional levels. E_{g0} is the bandgap of bulk crystal, $N(E)$ – density of states.

Temperature smearing of quantized levels is always present in nanocrystals at temperatures other than absolute zero (Fig. 1b). Every technology for the synthesis of nanocrystals leads to a dispersion of nanocrystals in size. So, both the absorption spectrum and the luminescence spectrum are formed by an ensemble of different-sized nanoparticles. To consider these factors, it is sufficient to calculate the absorption spectrum in the region of the first dimensionally quantized absorption maximum and the luminescence spectrum. The absorption can be calculated using the formula

$$\alpha_1(E_{ph}) = A\int_0^\infty \frac{1}{r^3}\exp\left(\frac{(E_{ph}-E_1(r))^2}{2\sigma_E^2}\right)\exp\left(\frac{(r-\bar{r})^2}{2\sigma_r^2}\right)dr\,, \quad (2)$$

which describes the dependence of the absorption coefficient on the energy of photon E_{ph} in the region of the first absorption peak inherent to the quantum dot. In Eq. (2) A is a constant that is determined by the normalization of the absorption peak per unit, and which magnitude is independent of radius. The first exponent describes the temperature smearing (σ_E) of the quantum-dimensional levels of the conduction band and zone of light holes. The second exponent describes variation of QD by radius.

Each QD of the ensemble emits luminescence quanta with their characteristic energy $h\nu$. Therefore, the luminescence intensity I^{En}_{PL} of the QD ensemble consists of a set of luminescence intensities of individual QDs, each of which emits luminescence quanta $I_{PL}(h\nu, r)$ (r is the radius of QD that emits luminescence quanta with the energy $h\nu$). The radius varies within the dispersion of QDs in size. Therefore, the luminescence intensity of the QD ensemble is described by the formula [3]:

$$I_{PL}(E_{ph}) = B\int_0^\infty \frac{1}{r^3}\exp\left(\frac{(E_{ph}-E_{PL}(r))^2}{2\sigma_E^2}\right)\exp\left(\frac{(r-\bar{r})^2}{2\sigma_r^2}\right)dr\,, \quad (3)$$

where B is a constant which value does not depend on the radius and is defined by the condition of luminescence intensity normalization per unity, and $E_{PL}(r)$ is the energy of the luminescence maximum for QD of the radius r.

The energy difference between the first maximum of the absorption band and the maximum of the luminescence band of the QD ensemble is determined as follows [3]:

$$\Delta h\nu = \frac{1.786e^2}{4\pi\varepsilon_0\varepsilon_\infty \bar{r}} - 0.248E^*_{\mathrm{Ry}} , \qquad (4)$$

where $\bar{r}$ is the average radius of the nanoparticle ensemble. It is found that the luminescence band of the QD ensemble luminescence calculated using the formula (4) correctly describes the experimental dependence. In the general case, the coefficients in the formulas (1) and (4) should be selected for each ensemble of QDs in the matrix, while keeping the type of dependences. The effect of size, the variation of QD by radius and thermal smearing of quantum-dimensional QD levels on the loss of the luminescence quanta caused by reabsorption is estimated for the following semiconductors: CdS, CdSe, CdTe, InP, InAs, and PbSe. The absorption and luminescence spectra of QDs made of these semiconductors overlap, and the magnitude of the overlap depends on the size and dispersion of QDs. The presence of such overlap means that the part of luminescent quanta is absorbed, *i.e*. lost as a consequence of reabsorption.

It is known that the error of transmittance measurement does not exceed 0.4% and the error of measurement of luminescence intensity does not exceed 2.6% [3]. Therefore, reliable reabsorption data are obtained for the absorption coefficient and luminescence exceeding 3% in total.

The procedure for estimating the magnitude of luminescent quantum losses related with reabsorption is as follows. Using the known experimental values for the energy position of the first absorption peak and the luminescence peak (Fig. 2), we find the average radius of the QD core according to the formula (4). The absorption spectrum in the region of the first absorption band (Fig. 2, solid curve) and the luminescence spectrum normalized to unity (Fig. 2, dashed curve) are calculated using the formulae (2) and (3). The reliable data for the absorption and luminescence correspond to values greater than a 3% limit shown by the horizontal line parallel to the abscissa in Fig. 2. Then, we draw a line parallel to the ordinate axis from the point of intersection of the curve describing the absorption spectrum with a straight line (parallel to the abscissa axis), which limits the reliability of determining the absorption and luminescence spectra. In the high-energy part of the spectrum, the luminescence quanta are absorbed and the low-energy absorption is absent (see Fig. 2). The procedure for estimating the magnitude of luminescent quantum losses due to reabsorption is as follows. Using the known experimental values for the energy position of the first absorption peak and the luminescence peak (Fig. 2), we find the average core radius of the quantum dot according to the formula (4).

The luminescence quanta of the bounded spectral region (Fig. 2, dashed curve) are absorbed in some spectral range (Fig. 2, shaded area) during the transport through the matrix. To determine the intensity of luminescence after the absorption losses using the formula (3), we first calculate the luminescence intensity of the quantum dot ensemble fulfilling the normalization condition

$$\int_0^\infty I_{PL}\left(E_{ph}\right) dE_{ph} = 1.$$

Then, introducing the mean path of luminescent quantum d_m, we can calculate relative luminescence intensity after this path:

$$QE_{reab} = \int_0^\infty I_{PL}\left(E_{ph}\right) \exp\left[-\alpha\left(E_{ph}\right) d_m\right] dE_{ph} . \qquad (5)$$

The loss of the luminescence intensity due to reabsorption is estimated by the formula

$$I_R = I_{PL}\left(1 - QE_{reab}\right). \qquad (6)$$

To compare the losses in one matrix with different QDs, one can normalize $\alpha(E_{ph})d_m$ in the first absorption maximum to the same value. Fig. 3 shows quantum efficiencies for $\alpha(E_{ph})d_m = 10$ in the first absorption maximum for different $\Delta\bar{r}$ values. Factor 10 means high enough absorption in the maximum. The effect of reabsorption in this case is essential.

In the vast majority of articles devoted to the study of the luminescence concentrator efficiency, the matrix is a PMMA plate containing QDs.

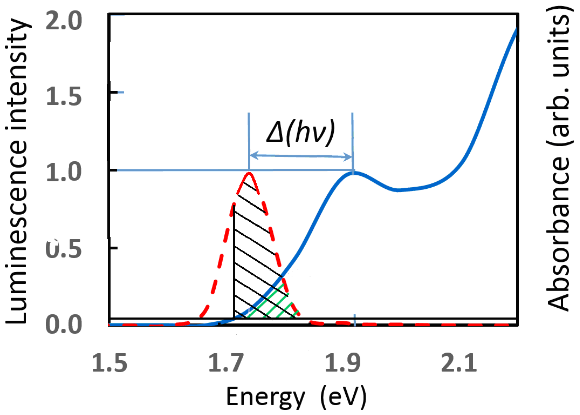

Fig. 2. Absorption spectrum (solid line) and luminescence (dashed line). The horizontal line parallel to the abscissa axis corresponds to the total measurement error of the absorption and luminescence spectra. Luminescence quanta emitted in the spectral region (shown by the hatching) are involved in the absorption. In the spectral region (shown in the figure by a double hatch), the fraction of luminescence quanta that are lost due to absorption is shown. $\Delta h\nu$ is the energy interval between the maximum of the first absorption peak of the quantum dot and the maximum of the luminescence peak.

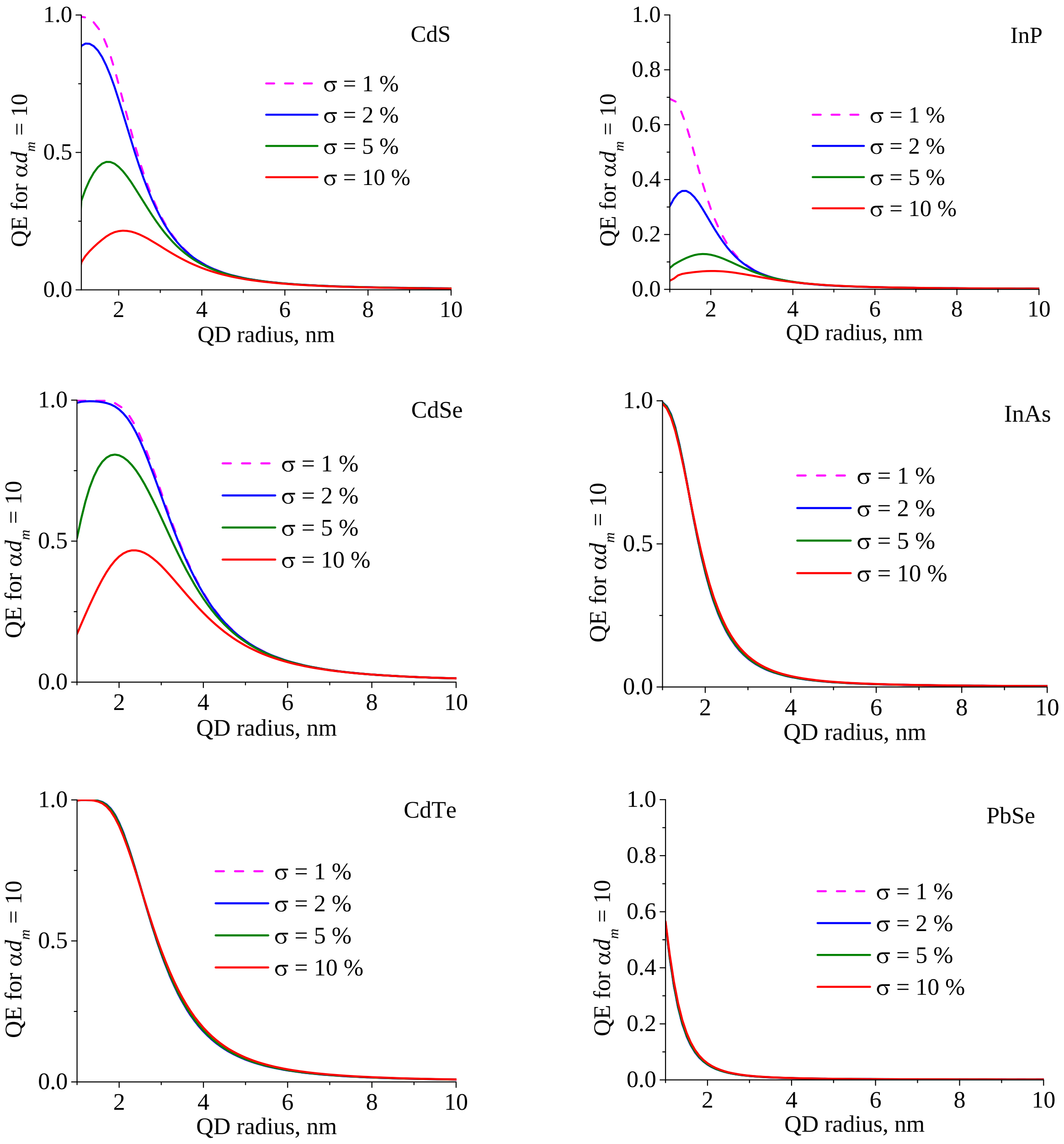

Fig. 3. Dependence of luminescent quanta intensity in the presence of reabsorption on the radius of the quantum dot core for 4 values of variation in radius. Experimental dependences of absorption and luminescence spectra of CdS (E_{g0} = 2.49 eV), CdSe (E_{g0} = 1.74 eV), CdTe (E_{g0} = 1.43 eV), InAs (E_{g0} = 0.355 eV), PbSe (E_{g0} = 0.27 eV).

This plate is transparent in the region 0.4…1 µm (1.2…3.1 eV), so an analysis of the QD core radius influence and the scattering of core sizes on the magnitude of reabsorption for PMMA is actual for QDs of semiconductors with a bandgap E_{g0} in the range 1.2…3.1 eV. In this paper, the set of semiconductors for QDs includes CdS, CdSe, CdTe, InP, InAs, PbSe. The dependence of luminescence quanta losses on the nanoparticle radius is shown (Fig. 3) for the nanoparticle scattering magnitudes of 10, 5, 2, and 1%.

The characteristic features of the curves in Fig. 3 are: i) the decrease in reabsorption with the decrease of $\vec{r}$ down to minimum; ii) the presence of the quantum dot core radius, for which the loss of luminescence quanta is minimal; iii) the shift of $r_{\min}$ into a region of smaller $\vec{r}$ values for the reduce of QD scattering in size; iv) the increase in luminescence quanta losses caused by reabsorption with the increase of QDs radius above $r_{\min}$ related with the decrease in the distance between absorption and luminescence peaks. As the size of quantum dots decreases below $r_{\min}$, the role of temperature smearing of quantum-dimensional levels increases, which is accompanied by the increase in reabsorption.

3. Conclusions

The features of fluorescence quantum losses dependence on the size of the core, the magnitude of QD size dispersion, and the bandgap of semiconductor are considered. It has been shown that, with the core size decrease, the magnitude of these losses is minimal for a certain optimal radius of the QD core. As the size of the QD core decreases or increases relatively to the optimum one, loss of fluorescent quanta increases.

References

1. Slooff L.H., Bende E.E., Burgers A.R., Budel T., Pravettoni M., Kenny R.P., Dunlop E.D., Büchtemann A. A luminescent solar concentrator with 7.1% power conversion efficiency. *phys. status solidi* (RRL). 2008. **2**, No 6. P. 257–259. https://doi.org/10.1002/pssr.200802186.
2. Bergren M.R., Makarov N.S., Ramasamy K., Jackson A., Guglielmetti R., McDaniel H. High-performance $CuInS_2$ quantum dot laminated glass luminescent solar concentrators for windows. *ACS Energy Lett*. 2018. **3**. P. 520–525. https://doi.org/10.1021/ascenergylett.7b01346.
3. Shkrebtii A.I., Sachenko A.V., Sokolovskyi I.O., Kostylyov V.P., Kulish M.R. Impact of semiconductor quantum dots bandgap on reabsorption in luminescent concentrator. *Semiconductor Physics, Quantum Electronics & Optoelectronics*. 2018. **21**, No 1. P. 58–64. https://doi.org/10.15407/spqeo21.01.058.
4. Kitai A. *Luminescent Materials and Applications*. John Wiley & Sons Ltd, 2008. https://doi.org/10.1002/9780470985687.
5. Flügge S. *Practical Quantum Mechanics*. I. Springer–Verlag, Berlin, New York, 1999. https://doi.org/10.1007/978-3-642-61995-3.

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