Influence of the length of organic molecules of ligands on the PbS QD solids optical properties

Y V Goltyapin\(^1\), M A Zvaigzne\(^1\), A A Chistyakov\(^1\), V R Nikitenko\(^1\), P S Samokhvalov\(^1\), I L Martynov\(^1\) and A R Tameev\(^2\)

\(^1\)National Research Nuclear University MEPhI (Moscow Engineering Physics Institute), Moscow, 115409, Russia
\(^2\)A.N. Frumkin Institute of Physical Chemistry and Electrochemistry of the Russian Academy of Sciences, 31-bld.4 Leninsky Prospect, Moscow 119071, Russia

Abstract. The quantum dot (QD) solids are promising materials for use in electronics. We studied the effect of variations in the length of organic ligands on the optical properties of PbS QD solids from the measurements of photoluminescence spectra and decay kinetics. The decay is becoming exponentially faster along with the decrease of the length of ligand molecules, which is consistent with the decay of excitons by hopping of charge carriers.

1. Introduction
In recent years, the great attention is devoted to the optical and electrical phenomena in the so-called QD-solids. This term means a new type of a condensed matter, which is formed by “artificial atoms” – metallic or semiconducting nanoparticles. QD solids are very promising for electronics, in particular related to photovoltaics [1] and electroluminescence [5,6], because one can manage the optical and electronic properties due to quantum confinement effect. Charge transport is an important process for the operation of electronic devices [7,8]. Although great activity was developed in order to obtain well-ordered structures (superlattices), positional and hence energetic disorder of electronic (hole) states remain a very important factor, in particular, due to scatter in a size of QDs [7]. Another important source is a disorder in a non-ideal structure of shell around every QD, which is formed by surface-active organic molecules (ligands). These shells are considered typically as spacers, separating different QDs hence supporting the quantum confinement, but the function of ligands in QD solids is not completely clear [9]. The disorder in combination with the weakness of electronic coupling of different QDs can provide localization of all electronic (hole) states in a QD-solid [11], reminiscent to organic semiconductors [2,8]. The nature of transport in semiconductor QD solids is still under debates. It was considered as band-like process via extended states [1], while the hopping nature of transport also was supported [2,7,8]. The latter case seems to be very probable in a rather disordered QD-solids [2,8]. In this work, we replaced ligands in a PbS QD-film and analyzed the influence of variations in the length of molecules of ligands on the photoluminescence spectra and decay kinetics.

2. Experimental
In this work, QDs PbS synthesized by the colloidal chemistry method were used, and they have a typical diameter of 4 nm. The surface of QDs was covered with a monolayer of molecules of oleic acid (OA) as a result of the synthesis. The initial ligands were replaced by new ligands, such as hydrazine, and 1.6-hexanediethiol (HDT). The lengths of new surface molecules, respectively, are 4 and 2 times...
smaller in comparison with the OA molecule. Hydrazine is widely used to replace long-chain ligand molecules on the surface of PbS QDs. In turn, HDT is still poorly researched and is used for the first time, to our best knowledge, as a surface molecule for the formation of condensates of quantum dots. The presence of a thiol group in the composition of the HDT suggests that it will be used in the "role" of the ligand for QDs PbS, due to the high affinity for sulfur molecules, which allows chemically to "sew" the QDs in the film. QD-solids with the initial ligands were thin films obtained by the spin-coating method. The replacement for new ligands was carried out directly in the process of the film preparation. A solution of QD (with OA as a ligand) in toluene with a volume of 50 μl and a concentration of 10 mg / ml was applied to a pre-cleaned glass substrate, which was then rotated for 30 seconds at an angular rate of 1500 rpm in a spin-coating setup. After that, 50 μl of the solution of the molecules of the new ligand (for hydrazine, 1 mole / L in methanol, for HDT 0.1 g / liter in acetonitrile) was applied to the resulting film using an automatic pipette, and after 30 seconds of exposure the film was rotated 30 seconds at an angular speed of 1500 rpm again. The described procedure was repeated 5 times to obtain the required thickness. The thickness of the obtained samples, 40-100 nm, was measured with a microinterferometer.

Control of replacement of surface molecules was carried out by analyzing the IR absorption spectra, obtained with the Varian IR spectrophotometer "Scimitar1000 FT-IR" for QD films. For all samples of the films and the QDs solution, the luminescence and absorption spectra were measured, as well as the luminescence decay kinetics. For research of the absorption spectra, we used the halogen lamp Ocean Optics LS-1 for a wide spectral range, a semiconductor laser with a radiation wavelength of 908 nm was used to excite the luminescence. The spectra were recorded with the AvaSpec AvaSpec-NIR256-1.7 spectrometer.

For the research of the kinetics of luminescence, the second harmonic of the picosecond YAG: Nd3+ laser was used (532 nm wavelength, pulse duration 50 ps, pulse repetition frequency 50 Hz, average power 3 mW). The signal was recorded at the wavelengths of the luminescence maxima with the help of a high-speed PIN photodiode.

3. Results

As follows from Figure 1, a red shift of the luminescence spectra of the QD films was observed in the respect to the solution, which became more pronounced when the ligand was changed to a shorter one. The position of the first exciton absorption maximum remained unchanged after the transition from the solution to the condensed state. In addition, the width of the luminescence spectra varied. If the transition from a solution of QD with OA as a ligand to a film occurs, the spectrum was broadened and amounted to Δλ = 195 ± 8 nm. If the original ligands were replaced with HDT in the film, the luminescence spectrum narrowed to Δλ = 159 ± 8 nm, and if it was replaced by hydrazine, it significantly broadened and amounted to Δλ = 320 ± 8 nm.
When measuring the kinetics of luminescence decay, the typical biexponential time dependence of decay kinetics [9] was observed in QD-films with initial ligands (OA):

\[ I(t) = A_1 e^{-t/\tau_1} + A_2 e^{-t/\tau_2}, \]

where \( \tau_1 \) and \( \tau_2 \) represent the fast-decay and the slow-decay component, respectively; \( A_1 \) and \( A_2 \) are their amplitudes. We obtained \( \tau_1 = 40 \) ns and \( \tau_2 = 160 \) ns, while in a solution decay kinetics is monoexponential with the decay time \( \tau_0 = 570 \) ns, see Figure 2.

A significant decrease in the decay time of luminescence was observed in the films with replaced ligands, namely 15 and 7 ns for the case of ligands HDT and hydrazine, respectively. Probably, monoexponential kinetics is observed.

4. Discussion

The width of the luminescence spectrum is directly related to the spreading of QDs over the size inside the film. The spreading could be apparently increased by an aggregation of QDs. One can assume that an aggregation is sufficient after replacing HDT ligands with hydrazine, reflected on the increased width of the spectrum, see the Figure 1, while in a QD film with a HDT, the particles are fairly uniformly distributed over the sample.
The observed redshift in the photoluminescence peaks of QDs, see the Figure 1, can be mainly due to four possible causes [12]:

a) increase in the size of QDs, that is not occurs in this case;

b) stronger electronic coupling between neighboring QDs with shorter ligands, which reduces the quantum confinement and increases the probability of charge transfer over the manifold of size-distributed QDs; an electron (a hole) is transferred most probably from a nanoparticle with a wider energy gap to a nanoparticle with a smaller energy gap at initial time interval;

c) the Förster-type resonant transfer of an exciton; this process of energy transfer will lead to the formation of an asymmetric spectrum due to the extinction of photoluminescence from the high-energy side [12]; however, the symmetry of the luminescence spectra is observed from Figure 1, precluding the exciton transfer;

d) charge transfer between QD and surface ligands; one has to note, that the charge transfer between QD and the surface ligand is not a noticeable process in the PbS QD films [13].

Therefore, one can assume that a stronger coupling of electrons and respective facilitation of charged transfer to neighbor QDs is the main factor, contributing to the redshift, observed in the luminescence of QD films with replaced ligands. This fact allows us to assume an appearance of an additional channel of nonradiative relaxation after replacing of initial ligands to the shorter ones. An analysis of the possible mechanisms of nonradiative processes under the conditions of our experiment [14,15] suggests that this is either resonant energy transfer between QDs of various sizes (excluded, as was mentioned above), or transfer of charge carriers between QDs. The transfer rate increases exponentially along with the decrease of a length of a ligand molecule, leading to the sharp increase of a photocurrent [16]. Despite the aggregation of QDs and the non-uniform spatial distribution of particles inside the film with hydrazine, the luminescence kinetics for these samples are the shortest, indicating a higher probability of the charge transfer process compared to other films. Consequently, the main factor affecting the transfer efficiency is the ligand length, which determines the distance between neighboring QDs, rather than the chemical structure or uniformity of QDs distribution within the sample.

In order to analyze evolution of characteristic times of luminescence decay along with transition from a solution to QD-film and from longer to shorter ligands in QD-films, we describe kinetics of charge carriers and excitons by the following set of equations:

\[
\frac{dE}{dt} = \frac{E}{\tau_d} - k_m P^2 \quad \text{(2)}
\]

\[
\frac{dP}{dt} = -E \left( \frac{1}{\tau_0} + \frac{1}{\tau_d} \right) + k_m P^2 \quad \text{(3)}
\]

where \(E\) and \(P\) are concentrations of excitons (which is proportional to luminescence intensity) and charge carriers (holes and electrons), respectively; \(\tau_0\) is a recombination time in solution (i.e. lifetime of excitons in isolated QD); and \(\tau_d\) is a transfer time of a carrier to the neighbor QD. Eq. 2 assumes that charge carriers appear due to decay of excitations, and disappear due to formation of excitons after the meeting with opposite charge, see the second term with the rate constant \(k_m\) (generation is supposed to be spatially uniform, hence transport term is absent). Eq. (3) means that decay of excitons results from production of charge pairs and recombination, the rate of the latter is the same as in solution. Biexponential character of the luminescence decay, see Eq. (1), provides that \(E\) is a solution of a differential equation \(\ddot{E} + 2\beta \dot{E} + \omega^2 E = 0\), \(\beta^2 - \omega^2 \geq 0\), where \(\beta\) and \(\omega\) are some constants.

Comparing this equation and Eq. (3) after differentiation in time, one require \(\omega^2 E \approx -2k_m P \dot{P}\). Analysis of the system (2), (3) under this approximation yields

\[
\frac{1}{\tau_1} + \frac{1}{\tau_2} = \frac{1}{\tau_d} + \frac{1}{\tau_0} \quad \text{(4)}
\]

Substitution of measured values of \(\tau_0, \tau_1, \tau_2\) for the case of ligands OA leads to the conclusion, that \(\tau_d \approx \tau_1\) (more precisely, \(\tau_d \leq \tau_1\)). Eq. (4) is consistent with experimental result \(\tau_0 > \tau_2\).

Since \(\tau_1 = \tau_2\) for the case of ligands HDT and hydrazine, and \(\tau_0 \gg \tau_d\), eq. (4) yields...
\[ \tau_d \approx \frac{\tau_1}{2} \]  \tag{5}  

for these ligands. Providing hopping nature of charge separation, we assume

\[ \tau_d = t_0 \exp(2\gamma l) \]  \tag{6}  

where \( \gamma \) is an inverse localization radius, \( l \) is the length of a ligand molecule, and \( t_0 \) is an attempt-to-jump time. Substitution of \( \tau_d \) values from Eqs (4), (5) to Eq. (6), and \( l \approx 2, 1 \) and 0.5 nm for OA, HDT and hydrazine, respectively, yields \( \gamma_{opt}^{-1} \approx 1.2 \) nm. One has to note, that the estimation of the same value from steady-state conductivity measurements \[16\] results in considerably smaller value, \( \gamma_{cond}^{-1} \approx 0.4 \) nm, which is more consistent with the hopping nature of charge transfer. One has to remind, however, that the measurements of luminescence decay shows the transient process in a disordered media on a short time scale. Charge transport should be involved in this process in an extremely non-equilibrium (dispersive) mode, while conductivity measurements reveals it in quasi-equilibrium mode. In the first case, an average hopping frequency should be much larger, because the fastest jumps realized on a short time scale after the generation pulse. This means that the 1) hopping distances are considerably scattered (position disorder); 2) the shortest distances are involved in hopping on a short time scale, and 3) thermally activated (hence delayed) hopping is a rate-limiting step in a quasi-equilibrium mode, due to energetic disorder. Thus, \( \gamma_{opt}^{-1} \approx 1.2 \) nm seems to be an apparent value, rather the shorter lengths \( l \) should be considered.

5. Conclusion

Using PbS QD solids, we demonstrated that the shorter the length of ligand molecules the faster the rate of luminescence decay. This length is considered as a measure of the mean inter-QD distance in QD solid. We propose that the reason of the correlation is the increase of an additional channel of exciton’s decay, namely the exciton dissociation by means of hopping of a charge carrier to the neighbor QD. This result agrees well with the recently reported conclusion that photocurrent increases exponentially with decreasing ligand length \[5\].

6. Acknowledgements

The work was supported by “improving the competitiveness” program of the National Research Nuclear University “MEPhI”. Preparation of QD solids was supported by the Russian Foundation for Basic Research, grant no. 17-02-09623 (O. M).

7. References

[1] Choi J H, Fafarman A T, Oh S J et al 2012 *Nano Lett.* **12** 2631

[2] Chistyakov A A, Zvaigzne M A, Nikitenko V R et al 2017 *J. Phys. Chem. Lett.* **8**

[3] Pathak D, Wagner A, Aoki T, Nunzi J M 2015 *Synth. Met.* **200** 102

[4] Kramer I J, Sargent E H 2014 *Chem. Rev.* **114** 863

[5] Dayneko S, Linkov P et al 2016 *Materials Today: Proceedings* **3** 211

[6] Dayneko S, Lyapin V, Linkov P et al 2014 *Proc. SPIE* **9270** 927009

[7] Guyot-Sionnest P 2012 *J. Phys. Chem. Lett.* **3** 1169

[8] Luther J M, Law M, Qing Song, Craig L et al 2008 *ACS Nano* **2** 271

[9] Zarghami M H, Liu Y, Gibbs M et al 2010 *ACS Nano* **4** 2475

[10] Zvaigzne M A, Alexandrov A E, Samokhvalov P S et al 2017 *Tech. Phys. Lett.* **44**