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Influence of the Surface Ligand Molecules Length on the Optical Properties and Photoconductivity of PbS Quantum Dot Condensates

M. A. Zvaigzne[a]*, A. E. Aleksandrov[a], P. S. Samokhvalov[a], I. L. Martynov[a], D. A. Lypenko[b], A. R. Tameev [b], V. R. Nikitenko[a], and A. A. Chistyakov[a]
[a] *National Research Nuclear University MEPhI, Moscow, 115409 Russia*
[b] *Frumkin Institute of Physical Chemistry and Electrochemistry, Russian Academy of Sciences, Moscow, 119071 Russia*
**e-mail: mariazvaigzne@gmail.com*

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Abstract—The influence of ligands—organic molecules on the quantum dot (QD) surface—on the optical properties of thin-layer condensates of lead sulfide QDs and the photoconductivity of diode structures based on them has been investigated. A decrease in the ligand length by a factor of 4 is shown to reduce significantly the luminescence-decay time and increase exponentially the conductivity.

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Currently, colloidal quantum dots (QDs) are promising material for optoelectronic devices [1–5] due to their unique optical properties and high photostability. Recently much interest has been paid to the QDs based on lead chalcogenides, which can absorb IR light [2–4] and, therefore, are promising for photovoltaic devices, IR photodetectors [5], and new-generation LEDs [6]. The analysis of QD films, which are condensed matter of new type, is urgent from both fundamental and applied points of view, because the properties of these films qualitatively differ from those of conventional solids and their unique characteristics are promising for various applications [7, 8]. Preparation of QD layers with a low defect concentration and efficient carrier transport is a key factor in designing highly efficient devices based on QD films. The chemical structure and the length of the ligand molecules coating the QD surface affect the aforementioned properties significantly [9, 10]. The choice of the surface ligand determines the spatial separation between neighboring QDs and the characteristics of the barrier for carrier tunneling; thus, it plays a critical role in fabricating QD layers with high carrier mobility and conductivity. The purpose of this Letter was to analyze the optical properties and photoconductivity of QD films in dependence of the characteristics of the used ligand molecules (in particular, their length).

The PbS QDs under study, with an average diameter of 4 nm, were synthesized by a method of colloidal chemistry. As a result of the synthesis, the QD surface was coated by a monolayer of oleic acid (OA) molecules. Hydrazine and 1,6-hexanedithiol (HDT) molecules, which are, respectively, four and two times shorter than an OA molecule, were used as new substituting ligands. While hydrazine is widely applied for replacing long-chain ligand molecules on the PbS QD surface, HDT is much less studied; it was used for the first time to form QD condensates. However, the presence of a thiol group (having a high affinity to sulfur molecules) in the composition of HDT makes the latter a promising ligand for PbS QDs, which can perform chemical cross-linking of QDs in the film.

The QD condensates were thin films obtained by spin coating. The ligand was replaced directly in the films. The films were prepared by droping a QD solution with OA (serving as ligand) in 50 μL toluene, with a concentration of 10 mg/mL, on a precleaned glass substrate and subsequent rotation for 30 s at an angular velocity of 1500 rpm. Then, 50 μL solution of another ligand (1 mol/L hydrazine in methanol, 0.1 mol/L HDT in acetonitrile) were deposited on the film surface with an automatic pipette and, after a 30 s exposure, the film was rotated for 30 s at 1500 rpm. To remove the excess molecules of new ligands from the film surface, a solvent (specific for each ligand) was deposited thereon, and the film was rotated again for 30 s at 1500 rpm. This procedure was repeated five times to obtain the desired thickness. The sample thickness, measured by a microinterferometer, ranged from 40 to 100 nm.

The result of replacing the initial ligand molecules with new ones was evaluated by analyzing the IR absorption spectra of QD films, recorded with a Varian 1000 FT-IR spectrophotometer.

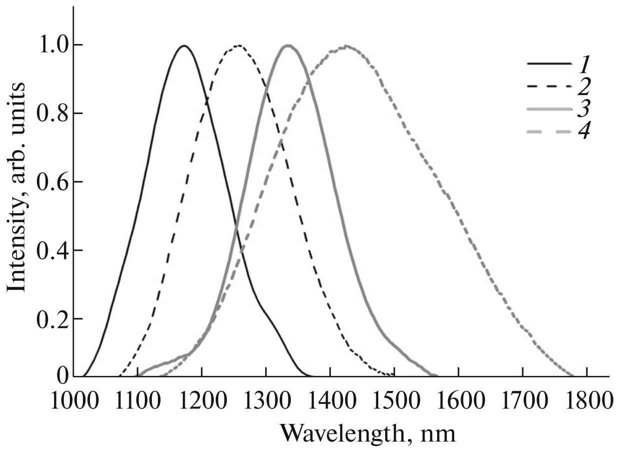

Fig. 1. Luminescence spectra of (*1*) QD solution with OA and (*2–4*) QD films with different surface ligands: (*2*) OA, (*3*) HDT, and (*4*) hydrazine.

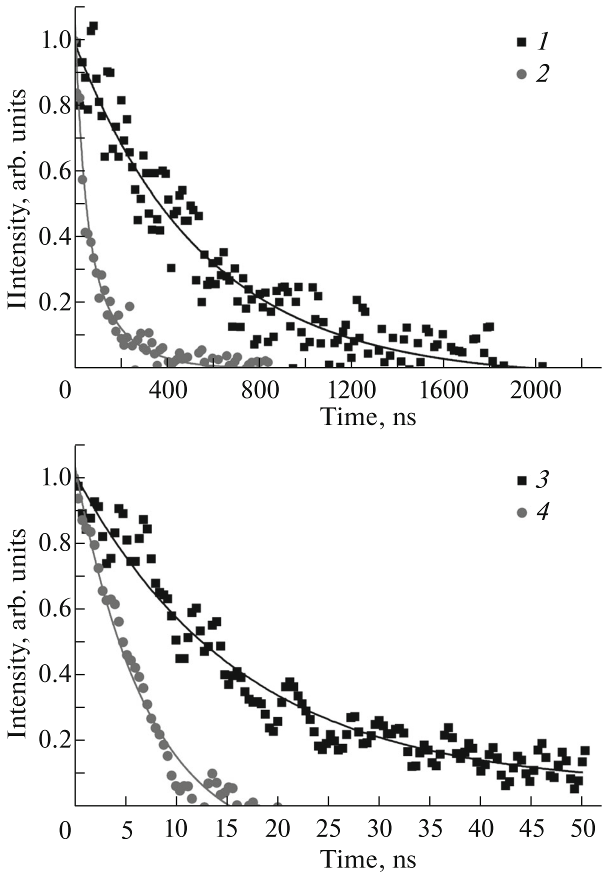

Fig. 2. Luminescence decay kinetics for (*1*) QD solution with AO and (*2–4*) QD films with different surface ligands: (*2*) AO, (*3*) HDT, and (*4*) hydrazine.

The luminescence and absorption spectra and the luminescence-decay kinetics were analyzed for all films and the QD solution. The absorption spectra were investigated using an Ocean Optics LS-1 halogen lamp with a wide spectral range as a light source; the luminescence was excited by a 908-nm semiconductor laser. In both cases, the spectra were recorded using an Avantes AvaSpec-NIR256-1.7 spectrometer. The luminescence spectrum of QD films was red-shifted with respect to the spectrum of the QD solution (Fig. 1), the shift becoming more pronounced when the substituting ligand was shorter that the initial one. In addition, the spectral width changed significantly, which is indicative of different degrees of homogeneity of the prepared samples (in particular, of aggregation of nanocrystals into clusters) [11, 12]. The QD films with HDT ligands exhibited the narrowest luminescence band, which may be caused by an efficient passivation of the QD surface, which prevented particles from aggregation. The first exciton absorption maximum remained invariable when passing from the solution to the condensed state.

The luminescence kinetics was analyzed using the second harmonic of a YAG:Nd^{3+} picosecond laser (wavelength 532 nm, pulse width 350 ps, pulse repetition rate 50 Hz, average power 3 mW). The signal was detected at the wavelengths of the luminescence peaks using a high-speed PIN photodiode. The luminescence-decay times were significantly shortened: from 570 and 160 ns for the solution and films with initial (OA) ligands, respectively, to 15 and 7 ns for the films with ligands replaced by HDT and hydrazine, respectively (Fig. 2). This may indicate the occurrence of an additional channel of nonradiative relaxation. An analysis of possible nonradiative mechanisms under our experimental conditions [13, 14] suggests that it is either resonance energy transfer between QDs of different sizes or carrier transport between QDs, which induces a photocurrent. However, the symmetry of the luminescence spectrum rather excludes resonant energy transfer.

Diode structures for investigating the film photoconductivity were prepared according to the following technique. A layer of PEDOT:PSS polymer was deposited on an ITO layer by spin coating at 2000 rpm. The layer was 30 nm thick. Deposition of QD layers on a polymer layer and ligand replacement were performed occurs in the same way as when forming films on glass. The next 30-nm-thick buffer ZnO layer was also deposited by spin coating at 2000 rpm. After forming all layers, several aluminum contacts were deposited on each structure through a mask by vacuum deposition, which allowed us to measure current–voltage (*I–V*) characteristics in different areas of the sample. A Keithley 6221 current source and a Keithley 194A HIGH SPEED voltmeter were used to this end. Figure 3 shows the *I–V* characteristics of the structures recorded both in darkness and under exposure to the Ocean Optics LS-1 tungsten halogen lamp of a wide spectral range. It can be seen that the current, being very low in the structures with unsubstituted ligands, exponentially rises with a decrease in the

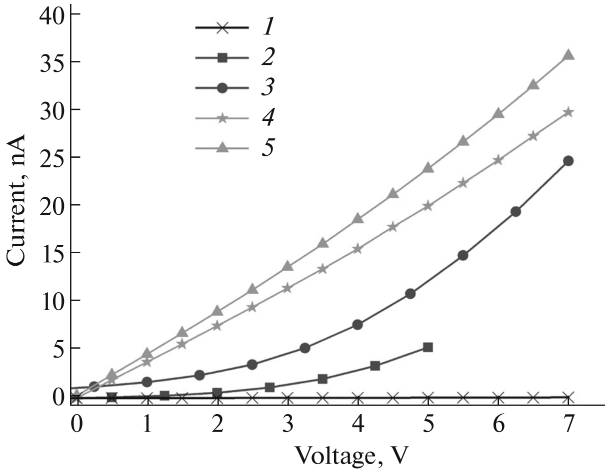

Fig. 3. *I*–*V* characteristics of QD film structures with different surface ligands: (*1*) AO, (*2*, *3*) HDT (measurements (*2*) in darkness and (*3*) in light), and (*4*, *5*) hydrazine (measurements (*4*) in darkness and (*5*) in light).

ligand length. In addition, light induces photocurrent in the structures. At voltages of less than 1 V, the *I*–*V* characteristic is almost linear. Assuming that the conductivity is controlled by the tunnel hopping of carriers between nanocrystals, so that the mobility contains an exponential factor $\exp(-2\gamma l)$ (γ is the inverse localization length of the wave functions, and l is the tunnel-hopping length (ligand length)), one can estimate l to be 0.4, 1.1, and 1.9 nm for hydrazine, HDT, and OA, respectively. These l values are in good agreement with the data in the literature [15].

The results of measuring the *I*–*V* characteristics of QD film structures, photoconductivity, and optical characteristics showed that the replacement of initial OA ligands (with relatively long molecules) with shorter ligand molecules, which are capable of chemical cross-linking of QDs, gives rise to efficient charge transfer between QDs. The photoconductivity is determined to a greater extent by the length of the ligand rather than its chemical nature or the degree of homogeneity of QD distribution in the film.

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