

SELF-ASSEMBLY OF PBS QUANTUM DOTS IN ORDERED SUPERSTRUCTURES

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Abstract

NIR-emitting colloidal quantum dots (QDs) attract much attention due to their unique properties in order to utilize in diverse areas of applications: from bio-sensing to solar cells fabrication. The self-assembly of QDs in a periodically ordered superstructures, such as superlattices and supercrystals, enables a formation of a new class of functional materials with remarkable optical, electronic, and vibrational properties. In this study we investigated the structures, obtained by self-assembly of lead sulfide (PbS) QDs of different sizes deposited on a mica substrate. The test samples were prepared by a method based on the evaporation of a saturated solution. The methods of X-ray structural analysis were used to describe the morphology of obtained ordered structures. It was found that the self-assembly of smaller QDs leads to formation of the superlattices, while the assembly of larger dots results in formation of three-dimensional structures. These superstructures possess the set of narrow peaks in the SAXS patterns similar to that obtained for conventional crystals. The positions of the scattering peaks were used for calculation of the crystal structure of the samples. It was shown that these structures have a primitive orthorhombic lattice with size of tens of micrometers. This work is of considerable interest for the development of photonic devices based on QDs superstructures, absorbing light in NIR-region.

Keywords: Lead sulfide, quantum dots, self-assembly, supercrystals

1. INTRODUCTION

Colloidal semiconductor nanocrystals, or quantum dots (QDs) - a monodisperse clusters with absolute dimensions smaller than the Bohr exciton radius [1]. Since the energy gap between the upper level of the holes and the lowest level of the electrons is determined not only by the chemical composition of the QD, but also by the QD diameter, the synthesis of QDs with precise control over size and chemical purity opens an opportunity to design a new class of functional materials with desirable parameters. Due to unique optoelectronic properties and long photostability of QDs, the structures based on them are very attracting for the utilization in diverse fields of applications [2, 3]. One of the most promising semiconductor materials for use in infrared devices is the class of colloidal QDs of lead chalcogenides, such as lead sulphide (PbS), with energy bands situated in the near infrared region of the spectrum (0.8-3 μm). PbS QDs possess unique properties, such as high extinction coefficient in IR-region, small and equal effective masses of electrons and holes [4], large values of the photoluminescence (PL) decay time [5], and others. Hence, materials based on the ordered structures from PbS QDs are promising for engineering and development of solar energy converters with improved parameters.

Nowadays to obtain the ordered structures from quantum dots a process of the QD self-organization on a substrate is used. Self-organization or self-assembly of particles is a spontaneous ordering of the particles into superstructures also called superlattices (SLs) and supercrystals (SCs) [2, 6, 7]. These structures have been already obtained from various kinds of nanoparticles [2]. Despite the intensive research, materials based on self-assembled structures are still far from their utilization. It has been found that such structures are extremely sensitive to a plurality of parameters, namely, QDs size and its distribution, the type of the solvent and ligands on the QD surface [6], etc. Thus, the investigation of the influence of various parameters on the process of QDs assembly on the substrates is of current interest.

In this work the influence of dot diameter on the process of self-organization of PbS QDs on mica slides is investigated.

2. EXPERIMENTAL

To determine the spatial structure of the supercrystals on the substrate, as well as to calculate the mean diameter of QDs the X-ray structural analysis was used [8]. For indexing peaks in obtained SAXS patterns program PDWin 3.0, developed by the “Burevestnik” was used. Lead sulfide colloidal quantum dots were obtained using a hot injection method of QDs synthesis [9]. Thus, the QD stock solutions in a tetrachlormethane (TCM) with dot concentration of about 10^{-6} M were obtained. The superstructures were obtained by the slow-evaporation method of stock solutions of QDs with mean diameters of 2.4, 4.4 and 6.0 nm. A thin layer of mica with Teflon ring was used as a cell. Volume of the stock solution in the cell was 300 ml.

3. RESULTS AND DISCUSSION

It has been found that at first stage of the solvent evaporation angular dependence of the SAXS intensity is classic angular dependence of the X-ray scattering intensity from isolated particles in the solution. These dependencies have been observed for all samples and described by Guinier formula [8]:

$$\ln\left(\frac{I}{I_0}\right) = \ln(N \cdot n^2 \cdot I_e) - 4\pi^2 \frac{R_0^2 \cdot \varepsilon^2}{3 \cdot \lambda^2} \quad (1)$$

where I_0 – intensity of the primary beam, N – particles amount in the system, n – number of electrons per particle, $\varepsilon = 2\theta$, I_e – Thomson intensity. Analysis of the angular distribution of the scattering intensity allows us to determine the size and shape of particles, as well as the spatial ordering of the structures obtained. With increase of the evaporation time a broad peak, caused by the interference between closely packed QDs, in the SAXS patterns appeared. Its position determines the distance between nanoparticles in superstructures, such as superlattices [10].

The further solvent evaporation has led to the formation of the 3D-ordered structures from QDs with diameters of 4.4 and 6.0 nm. After nearly 30 hours after the sample preparation in the SAXS patterns the set of narrow diffraction peaks have been observed. Obtained X-ray intensity angular dependencies are similar to such dependencies from the real atomic crystals. For the illustration, the angular dependence of the X-ray scattering intensity for superstructures formed from 4.4 nm QDs is shown in Figure 1.

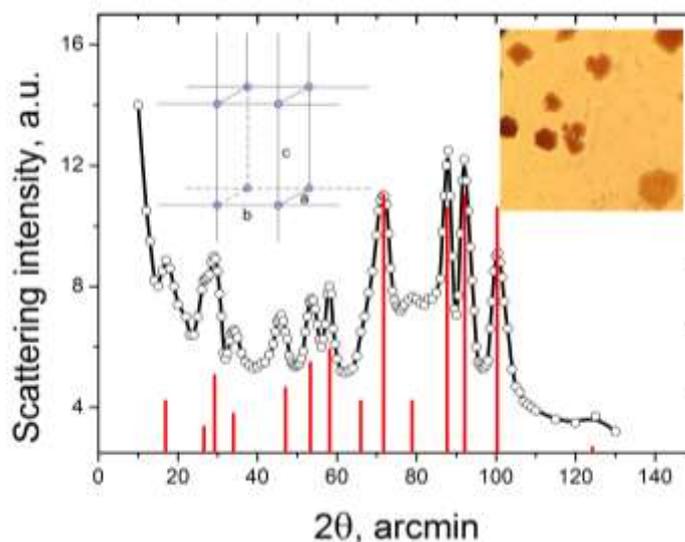


Fig. 1 SAXS pattern from 4.4 nm QDs supercrystals on mica slide. Inset: crystal lattice and microphotograph of obtained superstructures

The SAXS patterns for supercrystals from 4.4 nm and 6.0 nm quantum dots have been processed with use of the PDWin. As a result of diffraction peaks indexing the crystal lattice parameters of obtained superstructures are calculated. For instance, for the sample of the supercrystals from 4.4 nm QDs calculated peaks position and relative intensity are shown in Fig. 1 as red lines. It can be seen that they are completely consistent with the experimental data. It has been found that obtained superstructures represent an orthorhombic primitive lattice. The calculated lattice parameters for SCs from QDs with diameter of 4.4 nm are: $a = 21.1$ nm, $b = 36.2$ nm, $c = 62.5$ nm. The crystal lattice with these dimensions is shown on the inset in Fig.1. For SCs from 6.0 nm QDs the calculated lattice parameters are: $a = 18.5$ nm, $b = 30.1$ nm, $c = 40.9$ nm. Also the microphotography with use of confocal microscopy of the QDs superstructures have been obtained (see inset in Fig.1). In the microphotograph the structures with sharp edges located in the polymeric film are clearly visible. The PbS QDs superstructures have dimensions about tens of microns.

At the same time, the sample, containing the 2.4 nm QDs, after 30 hours of the solvent evaporation remained in the liquid phase. When the TCM was completely dried no set of diffraction peaks in the SAXS pattern have been observed. Thus, the superstructure obtained from smaller QDs represents only the 2D-ordered structure, i.e. superlattice. The distance between nanoparticles have been calculated as in [10] and is of 4.9 nm.

4. CONCLUSION

The data obtained from experiment allow us to conclude that the self-organized structures of the lead sulfide quantum dots, obtained by the slow evaporation of the solvent from the stock QD solution, represent the ordered superstructures. The smaller QDs assemble in the superlattices with a value of the spatial period close to the dot size. At the same time, the self-assembly of large nanocrystals results in the formation of 3-D superstructures. Such structures possess a set of narrow diffraction peaks similar to SAXS patterns of real crystals. A deeper understanding of the QDs self-organization process in the 2D- and 3D-structures requires further investigation. The establishment of the influence of various parameters on morphology of the superstructures, obtained by the nanocrystals self-assembly, is of considerable interest for the development of solar cells based on thin layers of PbS quantum dots, absorbing light in near-IR region of the spectrum.

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LITERATURE

- [1] Rogach, A. L., Eychmüller, A., Hickey, S. G., Kershaw, S. V. Infrared-Emitting Colloidal Nanocrystals: Synthesis, Assembly, Spectroscopy, and Applications. *Small*, 2007, V. 3, No. 4, pp. 536-557.
- [2] Collier, C. P., Vossmeier, T., Heath, J. R. Nanocrystal superlattices. *Annual Review of Physical Chemistry*, 1998, V. 49, No. 1, pp. 371-404.
- [3] Algar, W. R., Tavares, A. J., Krull, U. J. Beyond labels: A review of the application of quantum dots as integrated components of assays, bioprobes, and biosensors utilizing optical transduction. *Analytica chimica acta*, 2010, V. 673, No. 1, pp. 1-25.
- [4] Giansante, C. et al. Colloidal Arenethiolate-Capped PbS Quantum Dots: Optoelectronic Properties, Self-Assembly, and Application in Solution-Cast Photovoltaics. *The Journal of Physical Chemistry C*, 2013, V. 117, No 25, pp. 13305-13317.

- [5] Ushakova, E.V., Litvin, A.P., Parfenov, P. S., Fedorov, A. V., Artemyev, M., Prudnikau, A. V., Rukhlenko, I. D., Baranov, A. V. Anomalous Size-Dependent Decay of Low-Energy Luminescence from PbS Quantum Dots in Colloidal Solution. *ACS Nano*, 2012, V.6, No. 10, pp. 8913-8921.
- [6] Scheele, M. et al. PbS Nanoparticles Capped with Tetrathiafulvalenetetracarboxylate: Utilizing Energy Level Alignment for Efficient Carrier Transport. *ACS Nano*, 2014, V. 8, No. 3, pp. 2532-2540.
- [7] Quan, Z. et al. Solvent-mediated self-assembly of nanocubesuperlattices. *Journal of the American Chemical Society*, 2014, V. 136, No. 4, pp. 1352-1359.
- [8] Glatter, O., Kratky, O. *Small angle X-ray scattering*. London: Academic press, 1982. 515 p.
- [9] de Mello Donegá, C., Liljeroth, P., Vanmaekelbergh, D. Physicochemical Evaluation of the Hot-Injection Method, a Synthesis Route for Monodisperse Nanocrystals. *Small*, 2005, V. 1, No. 12, pp. 1152-1162.
- [10] Ushakova, E. V., Golubkov, V. V., Litvin, A. P., Parfenov, P. S., Cherevkov, S. A., Fedorov, A. V., Baranov, A. V. Self-organization of lead sulfide quantum dots of different sizes. *SPIE Photonics Europe. International Society for Optics and Photonics*, 2014, pp. 912625-912625.