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Synthesis of colloidal quantum dots of lead sulfide in decene-1 as a solvent

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A new approach to the synthesis of lead sulfide colloidal quantum dots is proposed, in which decene-1 is used for the first time as a solvent for the synthesis of nanocrystals. PbS CQDs with a long-wavelength exciton absorption peak in the range from 1.17 to 1.53 µm were obtained. The influence of temperature and reaction time on the spectral characteristics of the obtained PbS quantum dots was studied.

Keywords: lead sulfide; high-temperature colloidal synthesis; precursor; quantum dots.

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Introduction

Colloidal quantum dots have been the subject of intensive research over the past decades to create cheap and readily available solar cells, photodetectors, lasers, and LEDs. The ability to easily tune the spectral range and the availability of applying solutions of these nanomaterials make them particularly interesting for applications in electronics, in particular for the creation of photodetectors [1]. The combination of a large Bohr exciton radius in the bulk material (18 nm) and a band gap of 0.41 eV makes PbS CQDs particularly attractive [2]. This allows changing the position of the maximum of the exciton absorption peak in the range from 800 nm to 2100 nm with a change in the average size of nanoparticles from 2 to 10 nm. Thus, changing the range of spectral sensitivity in photodetectors based on them.

The first industrial samples of megapixel format matrix photodetectors were created in recent years using PbS CQDs [3]. The simplicity of the technology provides new possibilities for reducing the cost of matrix photodetectors and expanding their possible applications.

The synthesis of colloidal nanocrystals currently uses a standard set of high-boiling solvents and reagents that have proven themselves well in terms of efficiency and reproducibility, as well as low cost. One such reagent is octadecene-1. This long-chain alkene is often used in the syntheses of colloidal quantum dots such as PbS, CdSe, and InP as a high-boiling non-coordinating solvent [4–6]. Less frequently, octadecene-1 is used as a reagent for the preparation of chalcogen precursors: sulfur [7] or selenium [8]. In modern conditions, there is a

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need to find an affordable Russian analogue of this reagent. An important factor for use in the synthesis of nanocrystals is also the possibility of using such substances not only after maximum purification, but also in a commercially available form. It is known that the purity of reagents can greatly influence the results of nanocrystal synthesis. E.g., impurities in trioctylphosphine critically affect the nucleation of CdSe [9]. Impurities in oleylamine have a major impact on the solubility of lead halides and, as a result, on the quality of PbS nanocrystals obtained in this solvent [10].

One of the possible candidates for replacing octadecene-1 is decene-1. This substance is available in the “pure” grade from a number of Russian manufacturers. Compared to octadecene-1, it has a lower boiling point of 171 °C, which allows it to be used in the synthesis of lead chalcogenides.

In the context of studies on the production and study of the properties of PbS CQDs, carried out in our laboratory, we were attracted by the possibility of finding an alternative to octadecene-1 [11–14]. In this work, the production of colloidal quantum dots of lead sulfide was investigated using decene-1 as a solvent for the lead precursor and, accordingly, in the synthesis of lead sulfide CQDs. For the use of this reagent in the synthesis of nanocrystals, it is important both to be able to use it with the highest degree of purity and to use it in a commercially available form.

Experimental section

Reagents

The following chemicals were used in the synthesis of PbS CQDs without further purification: lead oxide (99.99 %, Lanhit), sulfur (special purity grade, Reakhim), oleic acid (90 %, Vekton), 1-octadec (90 %, Aldrich), decene-1 (“Ch”, Vekton), n-hexane (99 % HPLC grade, Macron Fine Chemicals), ethanol (reagen tgrade, Khimmed), and oleylamine (80–90 %, Acros), which was pre-dried under reduced pressure and at 90 °C.

Measurement methods

The following methods and measurement tools were used to study the properties of nanoparticles: TEM (JEM-2100, JEOL), spectrophotometer (JASCO V-770, JACSO), gas chromatograph (Chromatec 5000.2, VR-1 column, 60 m), IR Fourier spectrometer (Spectrum 100, PerkinElmer) with a HATR Accessory (ATR), equipped with a Ge prism (angle of incidence 45°, number of reflections 25).

Discussion of the results

Decene-1, like octadecene-1, is an alkene with a terminal double bond. In industry, it is obtained by oligomerization of ethylene or cracking of high-boiling fractions of oil followed by distillation [15]. Decene-1 is an important starting material in the production of poly-alpha-olefins used in the automotive and aviation industries as lubricating oils, which determines its availability and low cost [16]. Impurities in decene-1 depend on the method of its production. They can be saturated and unsaturated hydrocarbons. Gas chromatography showed the content of the main substance, decene-1, to be about 98 %. The commercial decene-1 used also contains at least two impurities, each with a content of about 1 mol% (Fig. 1*a*). ^{1}NMR spectroscopy also showed the presence of aldehydes and aromatic derivatives of benzene in commercial decene-1 at concentrations of the order of tenths of a percent (Fig. 1*a*).

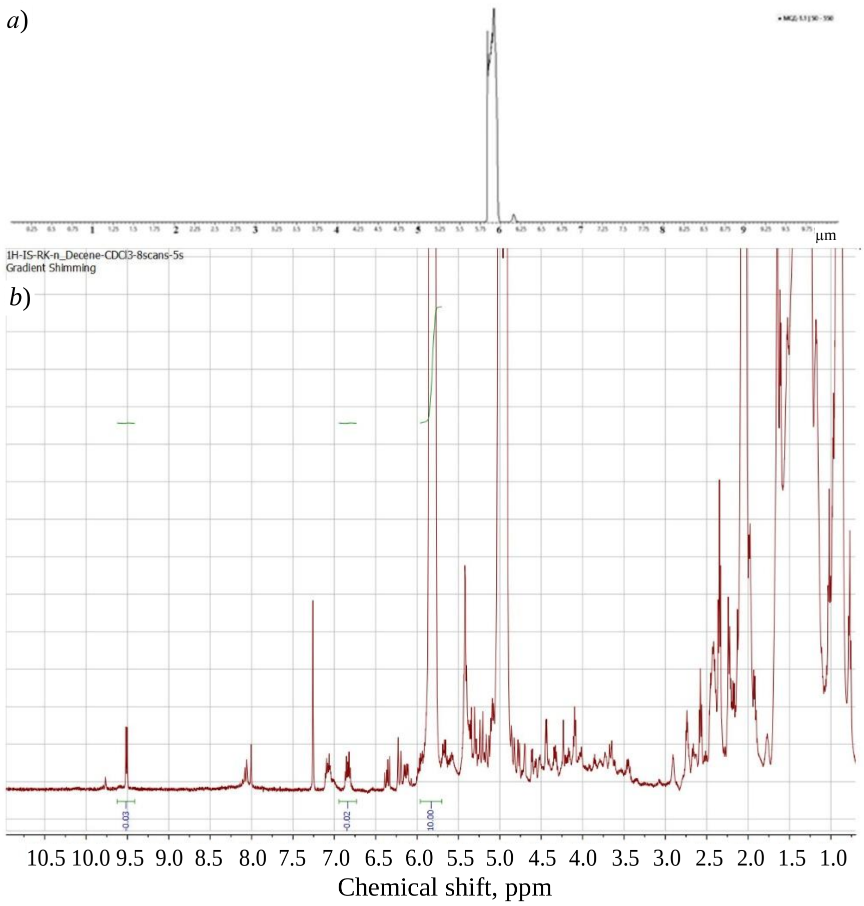


Fig. 1. a) – GC-Chromatogram and b) enlarged ^{1}NMR spectrum of decene-1 used in the synthesis

The authors established that the synthesis of lead sulfide CQDs is possible in commercial decene-1 produced in Russia using a method similar to that previously published by us [13]. It was found that replacing octadecene-1 with decene-1 does not result in a change in particle size when using the same reaction conditions, i.e., temperature, synthesis time and concentrations of the remaining reagents. When synthesizing at 120 °C, samples were obtained with practically identical positions of the exciton peak at 1530 nm with FWHM 171 nm in decene-1 and 1525 nm with FWHM 170 in octadecene-1 (Fig. 2). The distribution of nanoparticle sizes according to spectroscopic data also did not change: FWHM 171 in decene-1 and FWHM 170 in octadecene-1. Moreover, even without additional purification, decene-1 does not inhibit the nucleation and growth of lead sulfide nanocrystals.

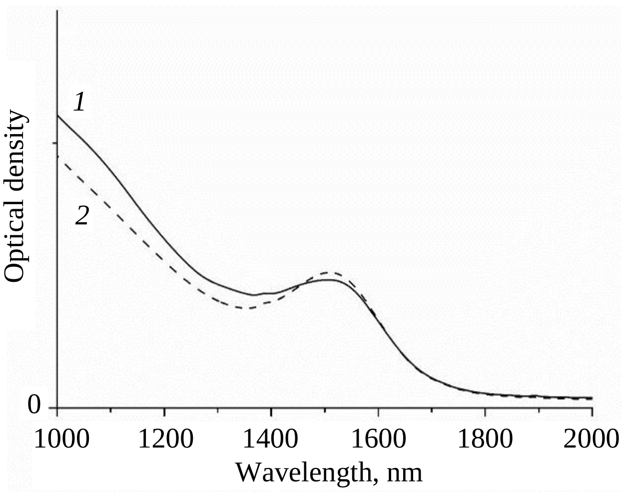


Fig. 2. Absorption spectra of PbS CQD samples obtained in decene-1 (1) and octadecene-1 (2) at 120 °C

By varying the synthesis temperature from 80 °C to 120 °C, it is possible to obtain particles with the position of the exciton absorption peak maximum from 1170 nm at 80 °C to 1530 nm at 120 °C (Fig. 3). The spectrum of nanoparticles obtained at 100 and 120 °C shows a pronounced exciton peak with FWHM of 173 and 171 nm. In the sample obtained at 80 °C, the exciton peak is weakly expressed.

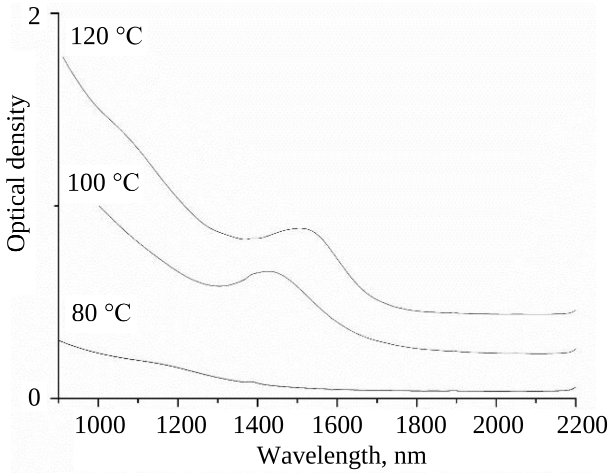


Fig. 3. Absorption spectra of PbS CQD samples obtained in decene-1 at different temperatures: 1 – 80 °C; 2 – 100 °C; 3 – 120 °C

For the reaction carried out at 100 °, the kinetics was investigated (Fig. 4). As for the similar system based on lead oxide in oleic acid in octadecene, the greatest growth is observed in the first two minutes of synthesis and the first sample has the first exciton absorption peak at 1350 nm. Samples at 8 and 15 minutes showed a slight increase to 1440 and 1480 nm, respectively. The observed exciton absorption peak of the 15 min sample is more pronounced compared to earlier samples with FWHM 180 nm.

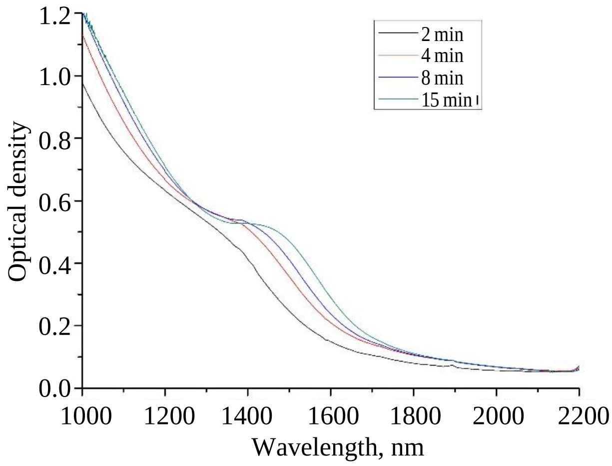
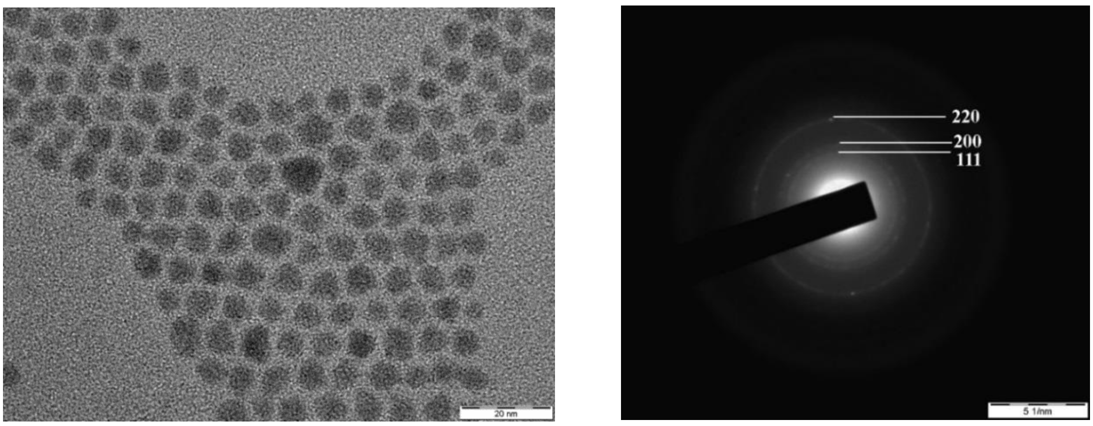


Fig. 4. Absorption spectra of PbS CQD samples collected during synthesis at a temperature of 100 °C at the following time points: 1 – 2 min; 2 – 4 min; 3 – 8 min; 4 – 15 min after mixing the reagents

PbS nanoparticles obtained by this method at a temperature of 100 °C have a spherical shape. To determine the crystalline phase of nanocrystals, the selected area electron diffraction (SAED) method was used (Fig. 5*a*, *b*). In the SAED electron diffraction pattern, reflections from the planes (111), (200) and (220) are observed, characteristic of the cubic syngony, confirming the structure of galena [17]. These PbS CQDs have an average diameter of 5.5 nm according to TEM data, which is in good agreement with the measured absorption spectra and the size calculation using the relationship between the transition energy and the nanoparticle diameter [18]:

$$E_0 = 0,41 + \frac{1}{0,0252d^2 + 0,283d}$$



a) *b*)

Fig. 5. TEM image and SAED electron diffraction pattern of PbS quantum dots obtained at 120 °C

Measurement of the Fourier-transform IR spectra of a thin film of PbS CQDs obtained by evaporating the solvent from the film of PbS CQD sol on Ge crystals of the ATR attachment showed (Fig. 6) that the most intense signals of asymmetric and symmetric vibrations of CH_2 groups are observed at 2923 cm^{-1} and 2854 cm^{-1}. The signals of medium intensity at 1525 cm^{-1} and 1403 cm^{-1} correspond to asymmetric and symmetric vibrations of the carboxylate anion COO^- of oleic acid from the ligand shell. The presence of two carboxyl anion peaks in the spectrum of quantum dots indicates bidentate coordination of oleate on the surface of PbS CQDs. Thus, the Fourier IR spectroscopy data confirm the presence of oleic acid in the ligand shell of the PbS CQD nanoparticles and its coordination.

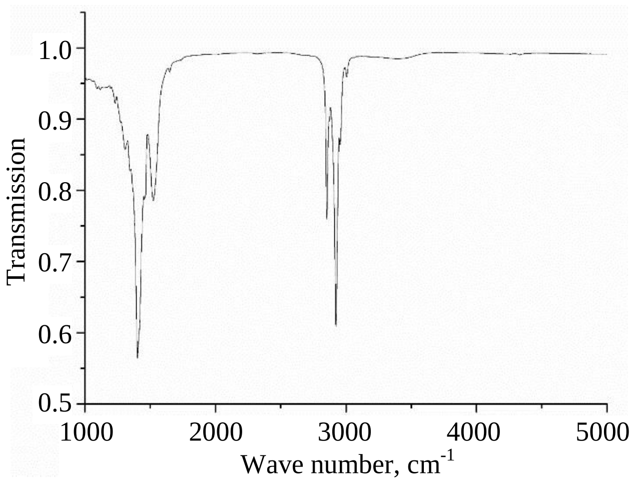


Fig. 6. ATR-FTIR spectrum of PbS CQD thin film

Conclusion

In this work, it was shown for the first time that decene-1 can be used to obtain nanoparticles and, in particular, PbS CQDs as a solvent. It was established that commercial pure grade decene-1 of Russian production, containing aromatic hydrocarbons as impurities, is suitable. Using our method, it is possible to obtain PbS CQD samples with the first exciton peak in the wavelength range from 1170 to 1530 nm. It has been shown that it is possible to vary the sizes of the obtained PbS CQDs by varying the reaction temperature, while the size distribution does not change significantly with temperature. Using Fourier-transform IR spectroscopy, the composition of the ligand shell of the obtained CQDs was shown.

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REFERENCES

1. Ponomarenko V. P., Popov V. S., Shuklov I. A., Ivanov V. V. and Razumov V. F., Russ. Chem. Rev. **93**, RCR5113 (2024).

2. Shuklov I. A. and Razumov V. F., Russ. Chem. Rev. **89**, 379 (2020).

3. Hinds S., Klem E., Gregory C., Hilton A., Hames G. and Violette K., Infrared Technology and Applications XLVI. SPIE **11407**, 11–19 (2020).

4. Bullen C. R. and Mulvaney P., Nano Letters **4** (12), 2303–2307 (2004).

5. Antanovich A., Prudnikau A. and Artemyev M., The Journal of Physical Chemistry C **118** (36), 21104–21109 (2014).

6. Lucey D. W., MacRae D. J., Furis M., Sahoo Y., Cartwright A. N. and Prasad P. N., Chemistry of Materials **17** (14), 3754–3762 (2005).

7. Li Z., Ji Y., Xie R., Grisham S. Y. and Peng X., Journal of the American Chemical Society **133** (43), 17248–17256 (2011).

8. Chen O., Chen X., Yang Y., Lynch J., Wu H., Zhuang J. and Cao Y. C., Angewandte Chemie International Edition **47** (45), 8638–8641 (2008).

9. Evans C. M., Evans M. E. and Krauss T. D., Journal of the American Chemical Society **132** (32), 10973–10975 (2010).

10. Baranov D., Lynch M. J., Curtis A. C., Carollo A. R., Douglass C. R., Mateo-Tejada A. M. and Jonas D. M., Chemistry of Materials **31** (4), 1223–1230 (2019).

11. Ganeev R. A., Shuklov I. A., Zvyagin A. I., Dyomkin D. V., Bocharova S. I.,

Popov V. S., Toknova V. F., Lizunova A. A., Ovchinnikov O. V. and Razumov V. F., Optical Materials **121**, 111499 (2021).

12. Shuklov I. A., Toknova V. F., Lizunova A. A. and Razumov V. F., Materials Today Chemistry **18**, 100357 (2020).

13. Shuklov I. A., Toknova V. F., Demkin D. V., Lapushkin G. I., Nikolenko L. M., Lizunova A. A., Brichkin S. B., Vasilets V. N. and Razumov V. F., High Energy Chemistry **54** (3), 183–188 (2020).

14. Shuklov I. A., Dyomkin D. V., Konavicheva V. A., Popov V. S. and Razumov V. F., J. Commun. Technol. Electron. **68** (2), S184–S189 (2023).

15. Ullmann's encyclopedia of industrial chemistry. Elvers B.: Verlag Chemie Hoboken, NJ, 1991.

16. Brennan J. A., Industrial & Engineering Chemistry Product Research and Development **19** (1), 2–6 (1980).

17. Beygi H., Sajjadi S. A., Babakhani A., Young J. F., van Veggel F. C. J. M., Appl. Surf. Sci. **457**, 1–10 (2018).

18. Moreels I., Lambert K., Smeets D., De Muynck D., Nollet T., Martins J. C., Vanhaecke F., Vantomme A., Delerue C., Allan G. and Hens Z., ACS Nano **3**, 3023.1 (2009).