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Novel Approach to the Preparation of Lead Chalcogenide Colloidal Quantum Dots and Properties Thereof †

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Abstract: In this work, we report the study of resizing of lead chalcogenide quantum dots both PbS and PbSe in the presence of oleylamine/oleic acid mixture. We demonstrated, that the resizing of lead chalcogenide nanocrystals could be performed in aprotic non-polar solvents. The kinetics of the shrinking could be followed by the measurement of absorption at 400 nm. The amount of resizing reagent namely oleylamine/oleic acid mixture influence the rate of reaction. This procedure could serve for the preparation of smaller lead chalcogenide quantum dots from a larger one.

Keywords: colloidal quantum dots; lead sulfide; lead selenide; resizing; solvent effect

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1. Introduction

The application of colloidal quantum dots (CQDs) for the production of low cost photodetectors offers a promising alternative to the expensive epitaxially-grown structures. Technologies based on near-/mid-IR CQDs are not so developed as a full-grown application of visible spectral range CQDs like CdSe. Lead chalcogenide colloidal quantum dots are promising nanomaterials exhibiting an excellent photosensitivity in the near-IR and mid-IR ranges. Bulk materials PbS and PbSe CQDs have band gaps 0.41 and 0.27 eV respectively.

In the past decades a lot of effort was put into the development of the efficient and scalable synthetic methods for the preparation of lead chalcogenide CQDs [1]. It is rather complicated to get broad range of nanocrystals sizes and the narrow size distribution by a single method even for the most developed material namely lead sulfide CQDs [2,3].

In our earlier studies, we developed several procedures for the preparation of SWIR PbS QDs. Application of dodecanthiol-1 as a reagent allows to slow down the formation of small nanocrystals and to get samples with first absorption peak at 760 nms. TEM revealed the mean size of obtained crystals about 2.5 nm. Synthesis of PbS QDs from PbO and oleylamine-sulfur solution allowed us to prepare the samples with a narrow size distribution and the first absorption peak in the range from 1700 to the 2050 nms.

Inspired by the demand on the simple general method for the preparation of broad size-spectrum of lead chalcogenides quantum dots we developed a new method. This procedure for the preparation of smaller PbS nanocrystals by resizing of larger one was developed in our lab by application of oleylamine/oleic acid mixture [4]. In this paper we report, the investigation of solvent effect on the resizing procedure. It was found that this transformation is much more general and both lead selenide and telluride nanocrystalls could be resized applying the same reagent. The combination of resizing approach with earlier developed synthetic methods allows to produce both lead sulfide and leas selenide colloidal quantum dots for near IR-applications.

For the applications of lead chalcogenides CQDs in photoelectric devices a preparation of photoconductive thin films are necessary [5]. Ligand exchange process in thin films of PbS CQDs was studied by FTIR spectroscopy applying HATR accessory. This approach allows to study the both efficiency and the rate of ligand exchange.

2. Materials and Methods

2.1. Materials

Chemicals

The following solvents and chemicals were used without additional purification: hexane (99% HPLC grade, Macron Fine Chemicals) and ethanol (96%, reagent grade, Khimmed). Oleylamine (OLA) (80–90%, Acros) and oleic acid were dried at 100 C at reduced pressure (5 mbar) for 1 h. PbS QDs and PbSe QDs for resizing studies were prepared by the methods reported earlier [4,6].

2.2. Methods

2.2.1. The Preparative Procedure for the Resizing of Lead Chalcogenide QDs

0.5 mL of OA/OLA 1:1 mixture was added to the solution of 10 mg PbS QDs in 5 mL of octane. The reaction mixture was stirred at room temperature for 3 h. After the reaction is complete, ethanol is added to this mixture. PbS QDs are isolated via centrifugation at 3000 rpm. Nanocrystals were redispersed in hexane and precipitated once more with ethanol. The washing step was performed for the three times. The product (5 mg, diameter) 8 nm was dried in air at room temperature

2.2.2. General Procedure for Resizing Study

0.1 mL of OA/OLA 1:1 mixture was added to the 2 mL lead chalcogenide QDs solution (5 mg/mL) in desired solvent the spectrophotometer 10 mm quartz cell. The reaction mixture was stored at room temperature for 2 h and spectra were recorded in certain time intervals.

3. Results and Discussion

Earlier, we demonstrated the resizing of lead sulfide quantum dots in the presence of oleylamine/oleic acid mixture. These two chemicals are common in the synthesis of colloidal nanoparticles It was demonstrated, that oleylammonium oleate formed by the reaction of oleic acid with oleylamine [4]. This compound is responsible for the dissolution of lead sulfide nanocrystal surface leading to the shrinking of the nanoparticles. The procedure for resizing has minimal requirements to the used equipment and could be performed even in the test tubes. For the analysis of reaction kinetics, the samples were taken and QDs were isolated by precipitation/redispersion with aliphatic alcohols.

In order, two analyze reaction kinetics more precisely the alternative procedure was developed. Size-distribution histograms based on the analysis of TEM images show that size-curved simply shift to the small sizes during the resizing process (Figure 1). It means that amount of nanoparticles and therefore concentration doesn't change during the reaction. According to the equation that is developed by Moreels et al. [8] for PbS nanoparticles molar extinction at 400 nm depends on the diameter of nanoparticles (d).

$$\varepsilon_{400} = (0.0233\ (0.0001)d^3\ cm^{-1}/\mu M$$

The absorption of colloidal solution at this wavelength changes according to the Beer–Lambert–Bouguer law and will be $D_{400} = \varepsilon_{400}*c*l$. It means, that the optical density at 400 nm will depend on the size of nanocrystals in colloidal solution during the resizing.

$$D_{400} \sim d^3$$

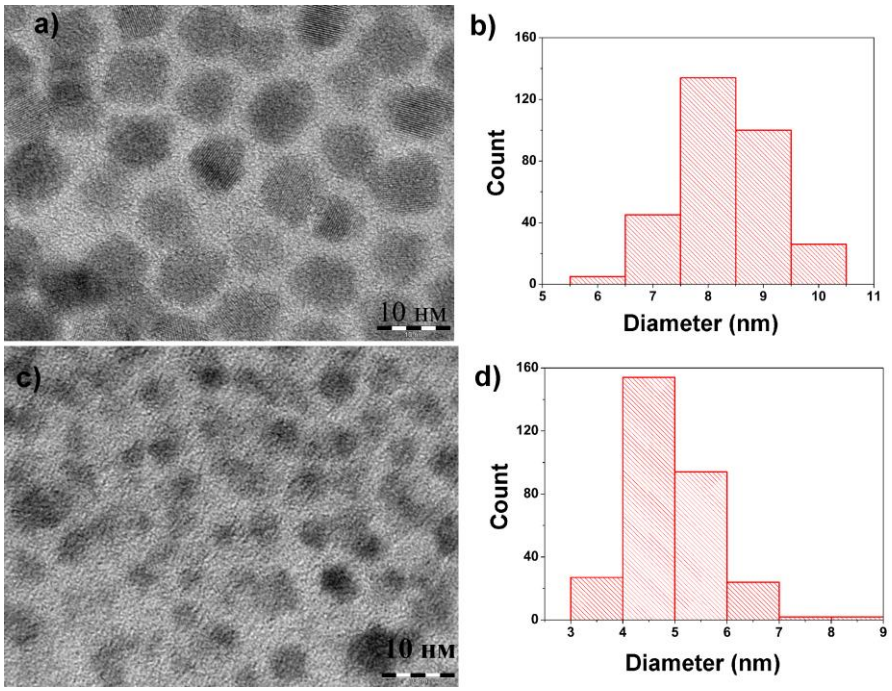

Figure 1. (**a**) TEM image of PbS QDs before resizing; (**b**) size-distribution of PbS QDs before resizing; (**c**) TEM image of PbS QDs after resizing; (**d**) size-distribution of PbS QDs after resizing.

This procedure allows to follow up the resizing directly in solvents these has strong absorption in near-IR like alkanes and olefins. Kinetic studies for both PbS and PbSe QDs could be performed directly in the cell of spectrophotometer.

It was found that reaction proceeds very fast within the first minute of experiment after an addition of oleylamine/oleic acid mixture leading to the significant drop of optical density. The exact drop of optical density depends on the amount of reagent applied and about 8% for 0.3 mL OA/OLA and 0.1 mL (Figure 2). Within next 30 min it proceeds linear with slope depended on the amount of reagent (Figure 3).

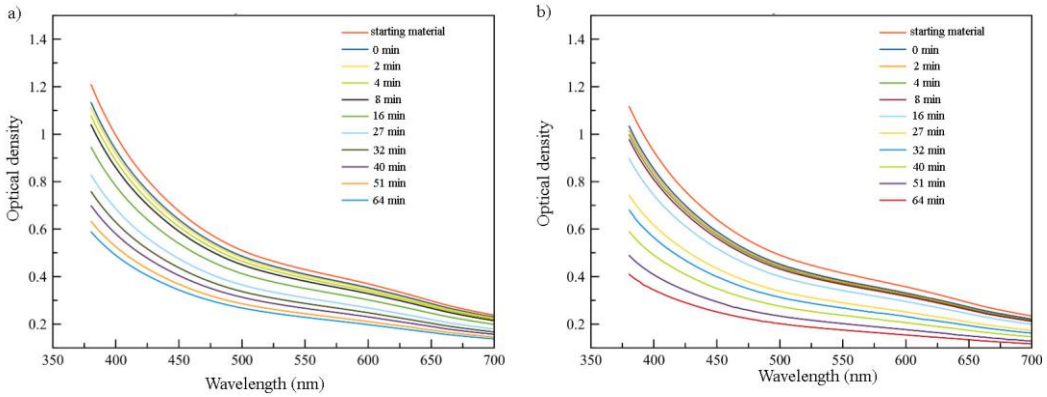

Figure 2. Development of the absorption spectra in UV-vis range (350–700 nm) in the presence of OA/OLA reagent: (**a**) 0.1 mL; (**b**) 0.3 mL.

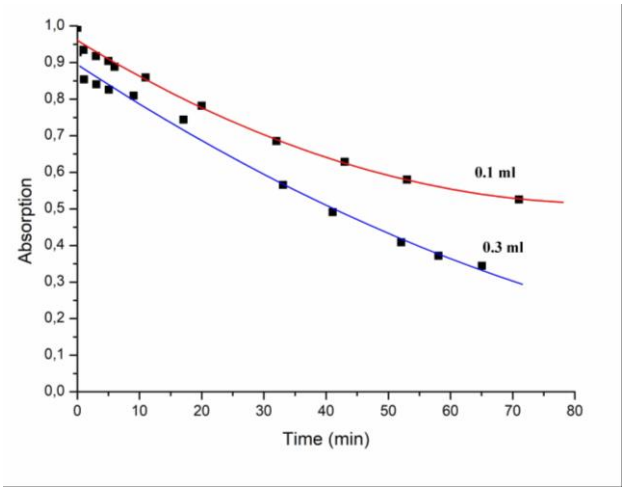

Figure 3. Development of optical density at 400 nm in the presence of OA/OLA reagent: (a) 0.1 mL; (b) 0.3 mL.

The solvent used makes significant impact on the rate of the transformation. Several aprotic non-polar solvents were used for this transformation. Resizing in octane was significantly faster than in hexane by the same amount of the reagent used. Transformation in CCl_4 is much slower than in hydrocarbons.

Resizing of lead selenide QDs proceeds very fast even with smallest amounts of OA/OLA mixture. With all tested concentrations of OA/OLA reagent in hexane reaction time was below 1 s. That exceeds time of absorption spectra recording and make the analysis of reactions kinetics in this case impossible. Resizing procedure for lead selenide could be performed by addition of certain amount of reagent followed by the immediate isolation of lead selenide nanocrystals.

For the further applications of lead chalcogenides CQDs a preparation of photoconductive thin films is necessary. Ligand exchange process in thin films of PbS CQDs was studied by FTIR spectroscopy applying HATR accessory [8]. This approach allows to study the both efficiency and the rate of ligand exchange.

4. Conclusions

Small size (below 3 nm) lead chalcogenide quantum dots could be prepared by direct synthesis or by the resizing of the larger nanocrystals. The resizing of lead sulfide is more general than it was found earlier and could be extended to other lead chalcogenides like PbSe. The transformation could be performed in the various non-polar solvents. This transformation could be followed by the changes of absorption at 400 nm. The rate of reaction depends on the amount of oleylamine/oleic acid mixture. Both PbS and PbSe lead chalcogenide quantum dots are available by resizing from a larger one.

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Conflicts of Interest: The authors declare no conflict of interest.

References

1. Shuklov, I.A.; Razumov, V.F. Lead chalcogenide quantum dots for photoelectric devices. *Russ. Chem. Rev*. **2020**, *89*, 379–391.
2. Cademartiri, L.; Montanari, E.; Calestani, G.; Migliori, A.; Guagliardi, A.; Ozin, G.A. Size-Dependent Extinction Coefficients of PbS Quantum Dots. *J. Am. Chem. Soc*. **2006**, *128*, 10337–10346. https://doi.org/10.1021/ja063166u.
3. Hines, M.A.; Scholes, G.D. Colloidal PbS Nanocrystals with Size-Tunable Near-Infrared Emission: Observation of Post-Synthesis Self-Narrowing of the Particle Size Distribution. *Adv. Mater.* **2003**, *15*, 1844–1849. https://doi.org/10.1002/adma.200305395.
4. Shuklov, I.A.; Toknova, V.F.; Lizunova, A.A.; Razumov, V.F. Controlled aging of PbS colloidal quantum dots under mild conditions. *Mater. Today Chem.* **2020**, *18*, 100357. https://doi.org/10.1016/j.mtchem.2020.100357.
5. Blachowicz, T.; Ehrmann, A. Recent Developments of Solar Cells from PbS Colloidal Quantum Dots. *Appl. Sci.* **2020**, *10*, 1743. https://doi.org/10.3390/app10051743.
6. Woo, J.Y.; Ko, J.-H.; Song, J.H.; Kim, K.; Choi, H.; Kim, Y.-H.; Lee, D.C.; Jeong, S. Ultrastable PbSe Nanocrystal Quantum Dots via in Situ Formation of Atomically Thin Halide Adlayers on PbSe(100). *J. Am. Chem. Soc*. **2014**, *136*, 8883–8886. https://doi.org/10.1021/ja503957r.
7. Mourdikoudis, S.; Menelaou, M.; Fiuza-Maneiro, N.; Zheng, G.; Wei, S.; Pérez-Juste, J.; Polavarapu, L.; Sofer, Z. Oleic acid/oleylamine ligand pair: A versatile combination in the synthesis of colloidal nanoparticles. *Nanoscale Horiz.* **2022**, *7*, 941–1015. https://doi.org/10.1039/D2NH00111J.
8. Shuklov, I.A.; Dyomkin, D.V.; Konavicheva, V.A.; Popov, V.S.; Razumov, V.F. Investigation of ligand exchange in thin films of PbS colloidal quantum dots with FTIR-spectroscopy. *Prikl. Fiz.* **2022**, 35–42. https://doi.org/10.51368/1996-0948-2022-6-35-42.