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Phosphine-free synthesis of selenide colloidal quantum dots

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Abstract. Metal selenide colloidal quantum dots have promising properties for applications in many fields such as gas sensing, food quality control, car accessories for orientation under low-visibility conditions, Infrared detectors for spectrometers. The wide application of selenide nanoparticles is limited due to a number of reasons. High requirements to the equipment for preparation of these materials in an inert atmosphere as well as poor reproducibility of modern synthetic procedures are some of the major reasons for very limited application of the selenide quantum dots today. Preparation of mercury and lead selenide colloidal nanoparticles by standard phosphine based procedures are especially affected by these problems. In this paper we report the application of selenium precursor prepared by dissolution of elemental selenium by action of sodium borohydride in oleylamine in the synthesis of lead selenide and mercury selenide quantum dots. The optical properties of the obtained quantum dots are investigated. This reagent is more easily prepared and less affected by conditions as a common phosphine based precursors. The impact of the reaction conditions and isolation procedures on the size distribution is reported. The work-up procedures are developed.

Keywords: quantum dots, nanoparticles, selenides, hot-injection synthesis

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Синтез квантовых точек селенидов металлов с использованием безфосфиновых прекурсоров

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Аннотация. Коллоидные квантовые точки селенидов металлов, благодаря своим оптическим свойства, имеют потенциал для применений во многих областях, таких как сенсоры газов, системы контроля качества пищевых продуктов, системы для ориентации в условиях пониженной видимости, ИК-детекторы для спектрометров. Обширное применение наночастиц селенидов сдерживается рядом факторов. К таким факторам относится высокая стоимость оборудования для их получения в инертной атмосфере, а также плохая воспроизводимость существующих методик ссинтеза. Получение коллоидных наночастиц селенидов ртути и свинца с использованием стандартных прекурсоров на основе фосфинов особенно сильно страдают от вышеуказанных проблем.

В рамках данной статьи показана возможность применения прекурсоров селена, полученных растворением элементарного селена в присутствии боргидрида натрия, для получения коллоидных квантовых точек селенидов ртути и свинца. Для полученных наночастиц исследованы их оптические свойства. Данный реагент менее требователен к оборудованию и его легче использовать чем селениды фосфинов, используемые в настоящее время в качестве прекурсоров. Проведено исследование влияния условий синтеза и способа выделения на наночастицы.

Ключевые слова: квантовые точки, наночастицы, селениды, высокотемпературный коллоидный синтез

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Introduction

Metal chalcogenide colloidal quantum dots (CQDs) is promising materials for applications in many fields based on their physical properties. Cadmium selenide CQDs is already found application in QLED TVs. Very recently SWIR-video cameras based on PbS CQDs were commercialized by several firms. Many other applications like solar cells, bioimaging markers, lasers, gas sensors, food quality control, Infrared detectors for spectrometers are under development.

Selenide nanoparticles are interested for application in near-IR. PbSe has band gap 0.28 eV and exciton Bohr radius about 46 nm. These properties allow to obtain PbSe CQDs with a first absorption peak from 800 to 3200 nm [1]. Band gap of lead selenide CQDs and therefor optical properties could be estimated by following formula reported by Moreels et al

$$E_0 = 0.278 + \frac{1}{0.016d^2 + 0.209d + 0.45},$$

where d is diameter of nanocrystal in nanometers [2].

HgSe is a semimetal in bulk with bang gap 0 eV, HgSe has spectral tunability from 800 up to 12000 nm based on intra- or interband adsorption.

The wide application of selenide nanoparticles is limited due to a number of reasons. They are more air-sensitive and less developed than PbS CQDs [3–5]. High requirements to the equipment for preparation of these materials in an inert atmosphere as well as poor reproducibility of modern synthetic procedures are some of the major reasons for very limited application of the selenide quantum dots today.

Preparation of mercury and lead selenide colloidal nanoparticles with commonly used trioctylphosphine suffer from these problems. Herein we report the application of selenium precursor prepared by dissolution of elemental selenium by action of sodium borohydride in oleylamine in the synthesis of PbSe and HgSe quantum dots.

Results and Discussion

Synthesis of mercury selenide. Mercury precursor is prepared by dissolution of 20 mg mercury chloride in 6 ml of dry oleylamine in two-necked flask at 120 °C within 1 h in Ar-flow. Selenium-precursor is prepared in a Schlenk-tube from selenium powder (58 mg) and sodium borhydride (27 mg) in 6.5 ml of dry oleylamine. 1 ml of selenium-precursor is added swiftly to the solution of cooled mercury-precursor at 100 °C. Reaction time by vigorous stirring is 5 minutes. Reaction is quenched by adding 1 ml 1-dodecanethiol and immediate cooling with ice bath. Nanoparticles are purified by 2*x* redispersing in tetrachloroethylene and precipitation with methanol. Sample of HgSe are dispersed in tetrachloroethylene for storage and characterization.

Synthesis of lead selenide. Lead precursor is prepared by dissolution of 20 mg mercury chloride in 5 ml of dry oleylamine in two-necked flask at 150 °C within 1 h in Ar-flow. Selenium-precursor is prepared in a Schlenk-tube from selenium powder (40 mg) and sodium borhydride (19 mg) in 5 ml of dry oleylamine. 1 ml of selenium-precursor is added swiftly to the solution of cooled mercury-precursor at 150 °C. Reaction time by vigorous stirring is 5 minutes. Reaction is quenched by cooling with ice bath and adding cold toluene. Nanoparticles are purified by 2 *x* redispersing in toluene and precipitation with ethanol. Sample of PbSe are dispersed in tetrachloroethylene for storage and characterization.

Two selenium precursors could be prepared by dissolution of selenium in oleylamine (OLA). One by heating to the temperatures about 200 °C and the second one by addition of sodium borohydride [6–7].

We successfully applied OLA/$NaBH_4$/Se reagent for the preparation of both HgSe and PbSe CQDs. Mercury selenide CQDs prepared at 100 °C possess absorption peak about 5200 nm (Fig. 1). From the absorption spectra could be assumed intraband transition nature of this signal. The interband peak is not present in the absorption spectra. TEM analysis revealed spherical nanoparticles with a mean size of 23 nm.

The electron diffraction (SAED) pattern revealed a crystalline structure of studied material. The lattice dimension are typical for tiemannite (HgSe), which is isostructural to metacinnabar (β-HgS) (Fig. 1,*c*). first rings in SAED match up perfectly with the 111, 220, and 311 diffraction lines of the Fd3m structure of HgSe with $a = 6.08$ E.

Absorption spectrum in the near-IR/visible range doesn't possess any absorption peaks, these could be attributed as an excitonic peak. This pattern is common for HgSe nanocrystals with intraband absorption peaks. Band edge is about 1500 nm (Fig. 2).

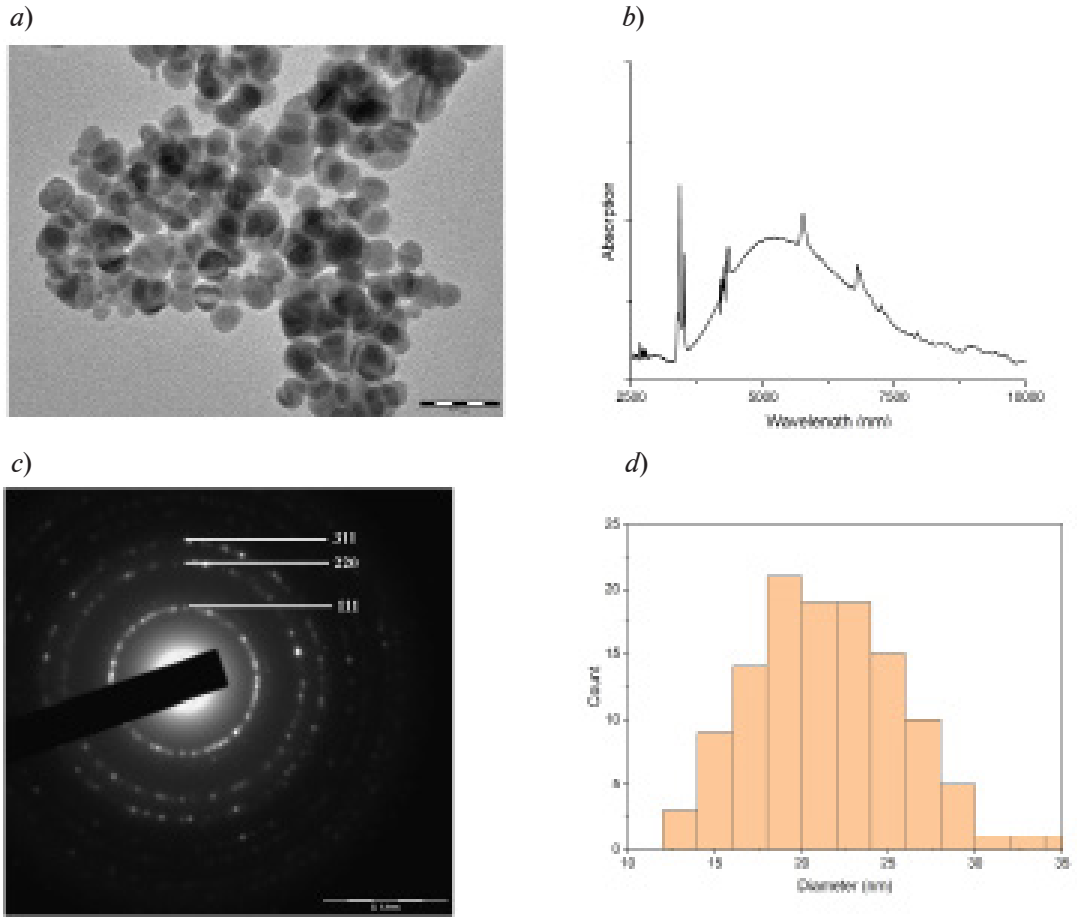

Fig. 1. HgSe CQDs: TEM image (*a*) and absorption spectrum (*b*) in 5000–1000 cm^{-1} range on the HATR Ge-plate , selected-area electron diffraction (SAED) pattern (*c*), size-distribution histogram (*d*)

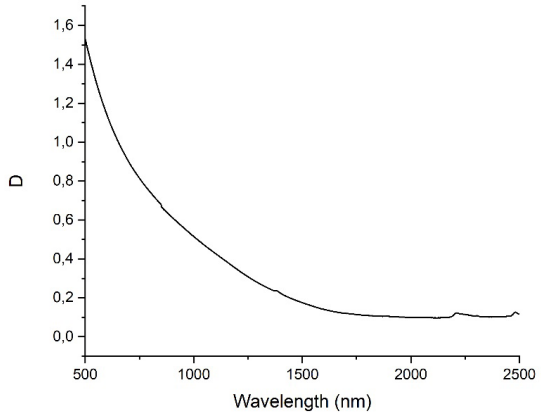

Fig. 2. HgSe CQDs absorption spectrum

Lead selenide CQDs require higher temperatures for synthesis. Reaction proceed at the temperature as high as 150 °C with this selenium precursor. Reaction rate of the PbSe CQDs is much higher then with trioctylphosphine selenide. The sample with a first absorption peak at 2100 nm could be obtained after 3 minutes of synthesis.

Conclusion

Selenium precursor prepared by dissolution of elemental selenium by action of sodium borohydride in oleylamine could be interesting alternative for the preparation of lead selenide and mercury selenide quantum dots. The obtained PbSe CQDs possess first absorption peak at 2200 nm. The obtained HgSe CQDs possess intraband absorption peak at 5000 nm.

REFERENCES

1. **Shuklov I.A., Razumov V.F.,** Lead chalcogenide quantum dots for photoelectric devices, Russian Chemical Reviews. 89 (2020) 379–391.

2. **Moreels I., Lambert K., De Muynck D., Vanhaecke F., Poelman D., Martins J.C., Allan G., Hens Z.,** Composition and Size-Dependent Extinction Coefficient of Colloidal PbSe Quantum Dots, Chem. Mater. 19 (25) (2007) 6101–6106.

3. **Ganeev R.A., Shuklov I.A., Zvyagin A.I., Dyomkin D.V., Smirnov M.S., Ovchinnikov O.V., Lizunova A.A., Perepukhov A.M., Popov V.S., Razumov V.F.,** Synthesis and low-order optical nonlinearities of colloidal HgSe quantum dots in the visible and near infrared ranges, Optics Express. 29 (11) (2021) 16710–16726.

4. **Ganeev R.A., Kim V.V., Shuklov I.A., Popov V.S., Lavrentyev N.A., Ponomarenko V.P., Mardini A.A., Dyomkin D.V., Milenkovič T., Bundulis A., et al.,** Third harmonic generation in the thin films containing quantum dots and exfoliated nanoparticles. Applied Physics B. 128 (2022) 202.

5. **Shuklov I.A., Toknova V.F., Lizunova A.A., Razumov V.F.,** Controlled aging of PbS colloidal quantum dots under mild conditions. Materials Today Chemistry. 18 (2020) 100357.

6. **Goubet N., Jagtap A., Livache C., Martinez B., Portalиs H., Xu X.Z., Lobo R.P.S.M., Dubertret B., Lhuillier E.,** Terahertz HgTe Nanocrystals: Beyond Confinement. Journal of the American Chemical Society. 140 (15) (2018) 5033–5036.

7. **Hou B., Benito-Alifonso D., Webster R., Cherns D., Galan M.C., Fermнн D.J.,** Rapid phosphine-free synthesis of CdSe quantum dots: promoting the generation of Se precursors using a radical initiator. Journal of Materials Chemistry A. 2 (2014) 6879–6886.

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