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Large-scale Synthesis of Monodisperse PbS Quantum Dots

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Abstract

PbS quantum dots (QDs) are a promising material for designing of modern solar energy convertors. Yet, their reproducible synthesis is still intractable, since typical methods do not allow controlling the growth of PbS nanocrystals due to the high reaction rates. Here we propose the two-step synthetic procedure, which allows controlling precisely nanocrystal growth on the second stage. The first step allows obtaining small PbS QDs by the standard hot injection method, which are then slowly grown to a desired size on the second stage. By use of this method, we were able to obtain gram-scale batches of PbS QDs with high reproducibility of the photoluminescence properties of the synthesis product.

Keywords: PbS quantum dots, nanoparticles growth, infrared luminescence

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1. Introduction

During the past decade quantum dots (QDs) attracted much attention due to their unique properties [1]. The unprecedented width of the absorption spectra, high extinction coefficients and long-term stability of QDs have made them an integral part of modern solar energy conversion technologies, specifically solar cells [2] and photocatalysis [3]. One of the possibilities to enhance the efficiency of solar energy conversion is to increase the fraction of absorbed solar light, what can be achieved by using QDs with intense absorption in the infrared region (IR-QDs) in charge generation and separation active photovoltaic layer of solar cell. For this purpose, PbS QDs have been widely applied in recent years [4].

In this work we have developed a procedure for large scale (several grams of QDs per single run) synthesis of PbS QDs which have highly reproducible properties. The peculiarity of the synthesis of PbS QDs lies in the following: due to the extremely high reactivity of precursors typically used for the synthesis, formation of PbS nanocrystals occurs at a tremendous rate, what makes the control of the optical properties of the final product by stopping the reaction at the specific time moment almost impossible. In order to overcome this difficulty, we propose a one-pot two step synthesis method for PbS QDs. In the first stage, a monodisperse PbS QD ensemble is obtained by a conventional reaction, while in the second stage these small QDs are overgrown to a given size by slow and controllable addition of extra precursors.

2. Materials and methods

2.1. Materials

Lead oxide(<99.9%), oleic acid(OA,<98%), 1-octade (ODE,<98%), bis(trimethylsilyl) sulphide (BTMS, <99%) and toluene (98%), were purchased from Sigma-Aldrich, methyl acetate (99%) was purchased from Acros Organics, all chemicals were used as received without any purification.

2.2. QDs synthesis

The lead precursor solution in the form of lead (II) oleate is prepared by the following procedure. 3.2 mmol of PbO, 12.8 mmol of OA 32 ml of ODE are placed into the three-neck round bottom flask, and the mixture is heated to 250 °C in an argon atmosphere until all lead oxide is dissolved to a clear yellow-colored solution. The solution is then cooled down to 100 °C and degassed under 20 mbar in order to remove residual water. Sulfur precursor for the first stage of the synthesis was obtained by dissolution of 1.6 mmol of bis(trimethylsilyl) sulphide (BTMS) in 6.7 ml ODE in argon atmosphere. Sulfur precursor for the second stage is obtained by the similar procedure, but with a higher dilution: 4.8 mmol of BTMS is dissolved in 19 ml ODE and kept in argon atmosphere.

On the first stage of the synthesis sulfur precursor solution was sharply injected into the vigorously stirred lead precursor solution at 150°C, and then the mixture was kept under constant stirring for 1.5 minutes and rapidly cooled down to 50°C in order to stop the reaction. After that, additional portion (2.4 mmol) of lead precursor was slowly injected to QDs solution obtained on the previous stage. Then the reaction

mixture was slowly heated to 100°C, and the second type of sulfur precursor was slowly added to the reaction mixture using a syringe pump under the continuous stirring. The growth of QDs was monitored by recording photoluminescence (PL) spectra (Avantes AvaSpec-NIR256-1.7) after specific amount of precursors were added, and was stopped by intense cooling with air flow when QDs the desired size. The obtained QDs were purified from unreacted precursors and solvents by double cycles of QDs precipitation and redissolution using methyl acetate and toluene as coagulant and solvent, respectively. After purification, QDs were stored as a concentrated solution in toluene.

3. Results and discussion

The main peculiarity of the growth process of PbS QDs is a high speed of the reaction, and hence, the difficulty in the control of their properties. Traditional one-stage hot-injection method of QDs synthesis does not allow obtaining a batch of PbS nanocrystals with a specific size by varying the duration of reaction. To overcome this problem, we offer a two-stage synthesis method. The main idea of our procedure is to split the synthesis into two stages. On the first stage we obtain particles of the least possible size by a traditional hot-injection at a relatively high temperature and precursor supersaturation. On the second stage, the obtained small nanocrystals undergo slow growth in mild precursor saturation at a relatively low temperature, what allows to prevent the formation of the new PbS nuclei and to control the growth rate.

In a typical synthesis of QDs, two parallel processes occur: crystallization and nanoparticle dissolution to precursors. Critical radius is the size of the particle at which the second process if overwhelmed by the first and nanoparticles become stable. The value of the critical radius is defined by equation (1) [5], where r_{crit} is critical radius, S - supersaturation of the solution, γ – surface energy of the particles, and ν – molar volume.

$$r_{\text{crit}} = \frac{2\gamma\nu}{k_B T \ln S} \tag{1}$$

The aim of the first stage of the two-stage synthesis is to obtain nanoparticles with least possible size, and hence we have to decrease the value of the critical radius. This can be achieved by the reducing of the surface energy or increasing of the supersaturation and temperature. In order to decrease the surface energy of the nanocrystals we used oleic acid as the anion that can passivate lead cations on the surface of growing QDs and protect them from aggregation. In order to increase the supersaturation we

do the rapid injection of the sulfur precursor to the reaction mixture, what causes high local supersaturation, leading to formation of large amount of PbS nuclei with narrow size distribution. An excessive increase in the reaction temperature will cause the particle growth to be so fast that it cannot be controlled, what leads to poor reproducibility of the results. Therefore, when choosing the reaction temperature, we chose a compromise value of 150°C, at which a stable and reproducible quality of the resultant PbS nanocrystals can be achieved.

The second stage of the synthesis is the overgrowth of the PbS nuclei to the desired size. In order to make such overgrowth more reproducible it's necessary to carry out the growth reaction at a low rate. It's well known that the growth of the nanoparticles depends on the two factors: diffusion of the precursors from the solution to the nanoparticle surface and reaction of the former with the surface atoms. The rate of both processes has a direct dependence on the reaction temperature. Decreasing the temperature can cause lowering of both the diffusion coefficient of precursors and rate constant and hence decrease the overall reaction rate. Therefore, the temperature chosen for the second stage of the synthesis was rather small - 100°C. Reduction of the BTMS concentration in the second precursor solution and low injection rate, compared to the first stage, lead to the reduction of the precursor concentration gradient and decrease of the diffusion rate. All these parameters in combination allow obtaining PbS QD ensembles with a narrow size distribution.

According to the method described above, a batch of PbS QDs was synthesized. Photoluminescence spectra of PbS QDs at different stages of the synthesis are presented in Figure 1. The PbS nuclei obtained after the first stage of synthesis have the maximum in the PL spectrum centered at 1282 nm. The other traces in Figure 1 demonstrate the evolution of PL spectra of PbS QDs during their growth on the second stage of the synthesis. Thus, the spectra having peaks at 1458 nm, 1548 nm, and 1597 nm correspond to addition of 1/3, 2/3 and the whole portion of the sulfur precursor, respectively. The results shown are highly reproducible, the error in position of the PL maximum did not exceed 50 nm at each stage in three syntheses conducted according to our procedure. The nonlinearity of the redshift of the position of the PL maximum is due to the fact its spectral position has direct correlation with the diameter of QD, which in turn is in cubic dependence on the amount of added precursor. This synthesis method is scalable and can be adapted for large-scale production. Thus, starting from a 3.2 mmol loading of lead precursor we managed to obtain more than 2 grams of purified PbS QDs per one synthesis.

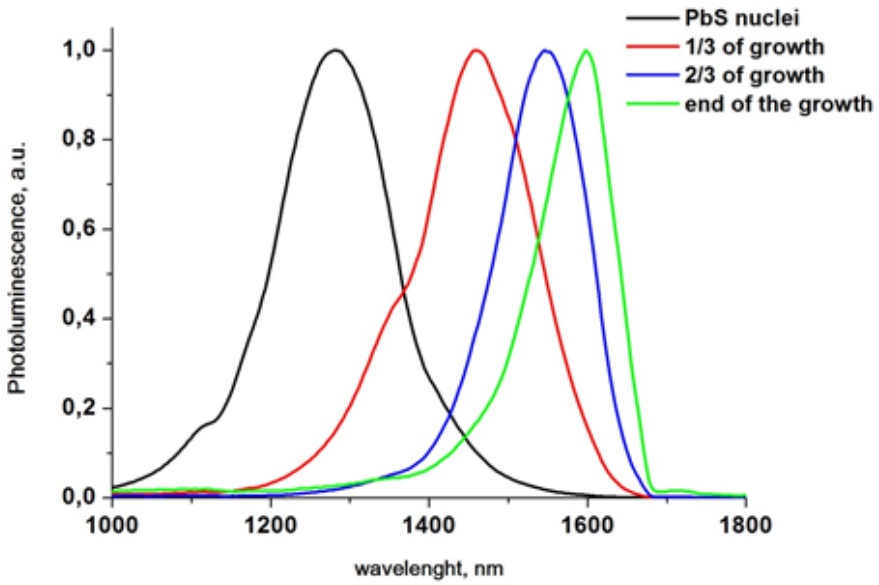

Figure 1: Photoluminescence spectra of PbS QDs at different stages of the synthesis.

4. Conclusions

A two-stage, reproducible method for the synthesis of PbS QDs emitting in the short wavelength IR region has been developed. Our synthetic procedure involves the stages of rapid formation of PbS nuclei and their slow growth to the desired size. Based on the theory of nanoparticle growth we propose the optimal experimental conditions for both stages. The proposed method is highly reproducible and allows obtaining gram-scale monodisperse batches of PbS QDs per one synthesis.

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