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Fine-tuning of Silica Coating Procedure for Preparation of Biocompatible and Bright Pbs/Sio2 Qds

Zvaigzne M.A.[1], Martynov I.L.[1], Voronin V.S.[1], Bozrova S.V.[1], Vokhmincev K.V.[1], Goncharov S.A.[1], Dovzhenko D.S.[1], Korenkova A.V.[1], Samokhvalov P.S.[1], Nabiev I.R.[1,2], and Chistyakov A.A.[1]

[1]National Research Nuclear University MEPhI (Moscow Engineering Physics Institute), Kashirskoe shosse 31, Moscow, 115409, Russia
[2]Laboratoire de Recherche en Nanosciences, LRN-EA4682, Université de Reims Champagne-Ardenne, Reims, France

Abstract

Near-infrared semiconductor PbS quantum dots (QDs) with emission in biological transparency window are promising material for *in vivo* biolabelling and deep-tissue imaging of biological specimen. Among various approaches that render initially hydrophobic and toxic QDs biocompatible, the growth of a silica shell on the QD surface represents an efficient method to minimize QD toxicity. Nevertheless, it is important to preserve QDs emission properties after the silica coating procedure. Here we report on the optimal parameters of this procedure which allow to obtain a stable silica shell and maintain the optical properties of initial PbS QDs. Furthermore, we show that PbS QDs with the optimal SiO_2 shell retain their luminescence quantum yield even after condensation into a solid film. Thus, our procedure can become a basis in development of bright, receptor-targeted NIR fluorescent probes for *in vivo* tumor imaging.

Keywords: quantum dot, SiO2 shell, bioimaging

Corresponding Author:
Zvaigzne M.A.
mariazvaigzne@gmail.com

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1. Introduction

In the past decade, a variety of vivid applications of quantum dots (QDs) as *in vitro* and *in vivo* bioimaging probes has been demonstrated [1, 2]. Since the human body has so-called "transparency windows" in the near infrared (NIR) region of optical spectrum, PbS QDs fluorescing in the NIR-region attracted a lot of attention as promising *in vivo* labels. However, the intrinsic toxicity of lead and photoluminescence (PL) instability of PbS QDs prevent their direct utility in biological experiments. One of the approaches used to render QDs biocompatible is coating of a QD with silica shell [3]. Yet, the PL quantum yield (QY) of QDs after the silanization procedure can be significantly reduced.

Thus, the problem of reliable maintaining high PL QY and initial optical properties of the PbS-cores after their coating with the SiO2-shell is in-demand. Here, we investigated the effect of reaction parameters on the QY and PL spectra of silica-coated PbS QDs. The method for silica coating reported in [4] was taken as a basis and adapted in order to reduce the amount of sodium bis(2-ethylhexyl) sulfosuccinate (AOT) surfactant, high content of which is undesirable by virtue of its destructive effect on the living cells. As AOT is a necessary component that reversibly caps the growing silica layer on the surface of QD, and prevents coalescence of the neighboring nanoparticles in solution, it may not be excluded but should be minimized to the quantity sufficient for stable passivation of the QD surface during the silica coating procedure.

2. Materials and Methods

PbS QDs used in this study were obtained by colloidal synthesis using lead oleate and bis(trimethylsilil)sulfide according to the method reported in [5]. Initially, quantum dots were dissolved in toluene and covered with an oleic acid as a surface ligand. For the silanization procedure 10 mg of QDs were purified from the excess of ligand molecules by dissolution–precipitation using acetone as a coagulating agent, and then redissolved in 4.5 ml of cyclohexane. Then 15µl of (3-aminopropyl)triethoxysilane (APTES) was added and the solution was stirred for 5 min at 550 RPM. After that 12 ml of AOT solution in cyclohexane (9.5 mg/ml) were added to the flask, and the resulting solution was stirred for 30 min at 1500 RPM. Further on, different amounts (Table 1) of 26% NH_4OH solution and tetraethyl orthosilicate (TEOS) were added to the reaction solution drop-by-drop and finally the solution was stirred for 24h at 1500 RPM to complete the reaction.

Table 1: Amounts of reagents added to the reaction mixture during silica coating procedure.

Sample	Reagents ratio to original procedure	V_{NH4OH}, µl	V_{TEOS}, µl
S_1	1/4	70	50
S_2	1/8	35	25
S_3	1/12	23	16,5

After that silica-coated QDs were dried in ambient atmosphere. After drying, these QDs were readily soluble in both polar and nonpolar media, including water. For optical studies, silica-coated QDs were redissolved in toluene to a concentration of 1 mg/ml. QD films were fabricated on glass substrates by spin-coating.

The luminescence spectra of the QD solutions were measured using an Avantes AvaSpec-NIR256-1.7 spectrometer and a 908-nm laser as an excitation source. The luminescence kinetics were measured using the second harmonic of a YAG:Nd3+ laser with pulse width of 350 ps and pulse repetition rate 50 Hz and a high-speed PIN photodiode as a detector.

3. Results

Our preliminary experiments have shown that it is possible to considerably reduce, down to 40 times, the amount of AOT surfactant in the silica coating procedure of PbS QDs reported in the original procedure [4] and, as a result, to obtain stable solutions of SiO2-coated QDs. Yet, after such alteration of the procedure, we were unable to obtain reproducible characteristics of the resulting product. Therefore, we have varied the quantities of other components of the reaction, namely TEOS and NH_4OH, to achieve the best optical performance of silica-coated PbS QDs. We have found that the eight-fold reduction in the quantity of these components (sample S_2) results in the highest luminescence intensity of silica-coated QD solutions. The quantum yield of this sample increased by 1.2 times when compared with the sample S_1. It is worth noting that the proposed modification of synthesis procedure did not provoke widening or shift of luminescence spectra of PbS/SiO2 QDs. At the same time, for the sample S_3 we observe a sharp drop of the luminescence intensity and broadening of the spectrum. This result is most likely due to incomplete formation of silica shell due to the lack of silica-forming components in the reaction solution. The luminescence spectra of the QD solutions after completion of silica shell formation and drying with are shown in Figure 1.

In order to study the susceptibility of silica-coated PbS QD's luminescence to external factors that could lead to its quenching, we have prepared compact films made of bare and PbS/SiO2 QDs and compared the PL kinetics in forms of solid film and solution. It is known that when QDs form a condensed structure, their PL is significantly quenched due to formation of non-radiative de-excitation channels by Ferster Resonance Energy Transfer (FRET) between small and large QDs in inhomogenous ensemble [6]. The results obtained in this experiment are shown in Figure 2.

Since PL quantum yield is proportional to the PL lifetimes, it can be concluded that coating of PbS QDs with SiO_2 prevents the drop of the quantum yield in the transition from solution to a solid film, as it can be observed for bare QDs. In this case, we believe that this phenomenon is associated with absence of close contacts between

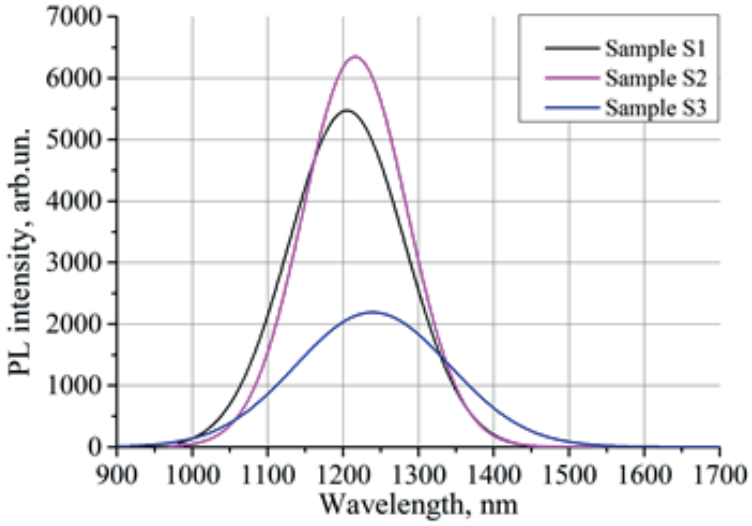

Figure 1: Photoluminescence spectra of samples S1-S3 in toluene.

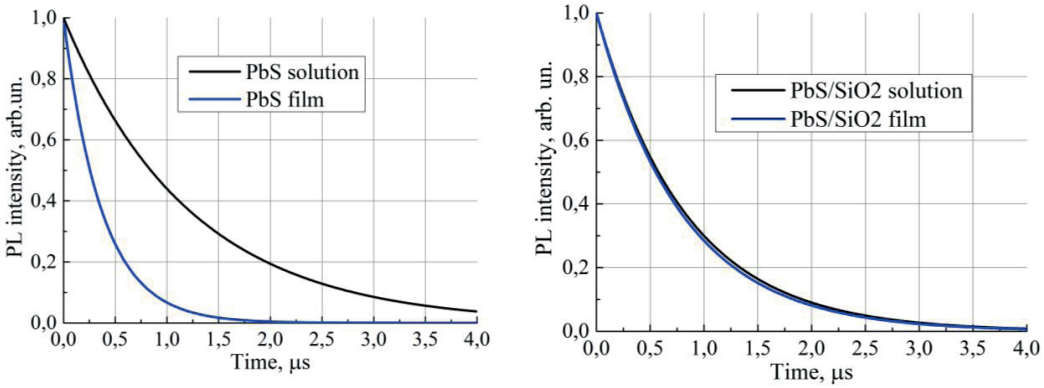

Figure 2: PL decay kinetics for bare PbS QDs (left) and PbS/SiO2 QDs (right) in the forms of solution (black) or solid film (blue).

luminescent PbS cores of neighboring QDs in the film, which leads to a significant decrease in the probabilities of FRET, and as well good passivation of defects on the QDs surface.

4. Summary

Our findings show that the luminescence efficiency of silica-coated QDs strongly depends on the parameters of the coating procedure. It is possible to make a proper choice of precursor amounts and reaction parameters to minimize the content of AOT surfactant, making further QDs bioadaptation more safe, while maintaining high PL quantum yield and stable shape of QDs PL spectrum. Therefore, the developed

procedure could be the very first stage in development of highly luminescent NIR nanoprobes suitable for *in vivo* imaging or diagnosis applications.

Acknowledgments

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