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Conference Paper

Optical Properties of Core-Multishell Quantum Dots

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Abstract

During the past decade, colloidal semiconductor nanocrystals or quantum dots (QDs) have become not only a subject of interesting fundamental research, but also a product for real-life applications. Intense activities devoted to enhancement of QDs photoluminescence (PL) quantum yield (QY), starting from early attempts to deposit protective ZnS shells atop CdSe cores, have resulted in novel designs of core-shell QDs with 100% PL QY. In this work we present a detailed analysis of optical properties of core-"multishell" (MS) QDs, whose physical structure is specifically designed to attain maximum localization of excited charge carriers inside luminescent cores, and thereby to achieve 100% PL QY. We have produced samples of core-MS QDs having 3 to 7 shell monolayers, studied the evolution of optical transitions in such QDs during the process of shell deposition, and analyzed the effects of shell thickness on the optical properties of finally obtained QDs. Specifically, studies of PL lifetimes have revealed the possibility of alternative emission mechanism, based on delayed charge carrier transfer from excited outer CdS layer of the multishell into CdSe cores.

Keywords: quantum dots, core-shell, multishell, SILAR

1. Introduction

Colloidal quantum dots (QDs) have gained enormous success in optoelectronics, photovoltaics [1-3] and biomedical [4] applications. Several approaches to preparation of these fluorescent nanomaterials with a quantum yield close to 100% have been advanced in the past decade. One of the most prospective approach to 100%-emitting, non-blinking QDs with narrow emission band has been developed by Chen et al. [5]. The key feature of these QDs is their thick CdS shell, which allows sufficient screening of luminescent CdSe cores from the environment. Yet, such QDs are not desirable from the viewpoint of biomedical applications, since they have a relatively large physical

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size, typically more than 10 nm, and what is more important, an intrinsically toxic cadmium-containing shell. An alternative to these thick-shell QDs is the core-multishell (MS) concept of QD structure developed by our group, attracting significant attention [6-8]. The "core-MS" concept relies on strong confinement of charge carriers due to the strictly monolayer (ML) thickness of each shell layer ensuring the highest confinement potential created by each layer. Previously we demonstrated the synthesis and study of optical properties of the simplest core-MS QDs, having different core size but the same ZnS/CdS/ZnS structure of inorganic shell. In this study, we present detailed analysis of the optical properties of core-MS QDs where the total number of shell layers varied from 3 to 7 MLs.

2. Materials and Methods

2.1. Synthesis of core-multishell QDs

The QD samples were synthesized according to the previously reported method [6], using a modified SILAR [9] procedure. CdSe core nanocrystals were prepared by hot-injection technique using cadmium hexadecylphosphonate and trioctylphosphine selenide (TOPSe) as cadmium and selenium precursors, respectively. The injection of a cold solution of two-fold excess of TOPSe in trioctylphosphine (total volume 2.5 ml) to a hot solution of cadmium precursor in octadecene (ODE) was done at 240 °C in argon atmosphere under vigorous stirring. The reaction was allowed to proceed for 3 minutes, after what the solution was rapidly cooled down to 80 °C using a cold air flow. After the synthesis, the core nanocrystals were isolated from crude solution using methyl acetate as non-solvent, and purified from remaining precursors by means of gel permeation chromatography. For the latter procedure, BIO-RAD cross-linked polystyrene beads (SX-1) were used as a stationary media, and toluene was used as an eluent. After purification, CdSe cores were treated with oleylamine (OLA) and NaBH₄ to remove tightly-bound hexadecylphosphonate ligands and replace them with OLA. This procedure was found to be essential to achieve reproducible growth of multicomponent shells, since the presence of hexadecylphosphonate ligands hinders the surface reactions and prevents formation of a uniform shell.

After the purification and isolation, CdSe cores were dissolved in toluene, and an aliquot containing 100 nmol of them [10] was placed into shell deposition solution, a mixture of 3 ml ODE and 3 ml of OLA. Prior to deposition of shells, the quantities of metal and sulfur precursors needed for deposition of each shell monolayer were

calculated according to SILAR procedure and reduced by 30% to achieve a single monolayer thickness [6]. The deposition of shell monolayers was done at 170 °C using a home-built setup, which allows programmable injection of precursors and temperature control. Between the injection of precursors, a 10 minute pause was made to allow the reagents adsorb onto the surface and react with it. After the injection of the last portion of precursors was complete, the reaction was allowed to proceed for another 10 minutes and then stopped by an air flow. When the temperature of the reaction mixture was below 60°C, the obtained QDs were precipitated with methyl acetate, and then purified twice using hexane and methyl acetate as solvent and coagulant, respectively. Purified QDs were dissolved in hexane and kept in dark place before the experiments.

2.2. Instrumental methods

Absorbance and photoluminescence spectra were recorded using Agilent Cary 60 spectrophotometer and Agilent Cary Eclipse spectrofluorimeter, respectively. Aliquots from reaction mixture were diluted in hexane and measured in 10 mm light path quartz cuvettes. Measurement of PL quantum yield was done by a comparative method using Rhodamine 6G as a reference dye (solution in methanol with O.D. below 0.1 at 500 nm wavelength). Correction of media refractive indices was applied according to [11]. The luminescence kinetics were measured using the second harmonic of a YAG:Nd³⁺ laser with pulse width of 350 ps, pulse repetition rate 50 Hz as excitation source and Hamamatsu PMT detector.

3. Results and Discussion

The schematic representation of the core-MS QD's structure is given in Figure 1a. As can be seen, the simplest 3ML core-MS QDs consist of a 2.3 nm CdSe core covered with three consequent 1 ML-thick layers of ZnS, CdS and ZnS. This specific shell structure allows to create an interdigitating confinement potential, which forms a high potential barrier for enhanced localization of excited charge carriers inside the luminescent CdSe cores, and, therefore, allows to achieve nearly 100% PL QY [6]. In turn, 5- and 7ML core-MS QDs represent further "evolution" of 3ML core-MS QDs, having additional CdS/ZnS monolayer stacks. Therefore, the 5- and 7ML core-MS assure even more strong charge carrier confinement than in 3ML QDs, not only due to high magnitude of barrier potentials, but also by a large barrier length. During the synthesis of core-MS QDs, the deposition of the first CdS interlayer provoked a strong redshift of the

absorbance and photoluminescence maxima (Figure 1b), which is evidence of exciton wavefunction leakage into the shell. On the other hand, during the synthesis of 5- and 7ML QDs, the deposition of the second and third CdS interlayers did not lead to a noticeable redshift of either absorbance or PL bands, as can be seen from Figure 1b. This could be interpreted by assuming that the exciton wavefunctions are localized only in the inner shell space of the multishell structure, i.e., inside the first three ZnS-CdS-ZnS layers.

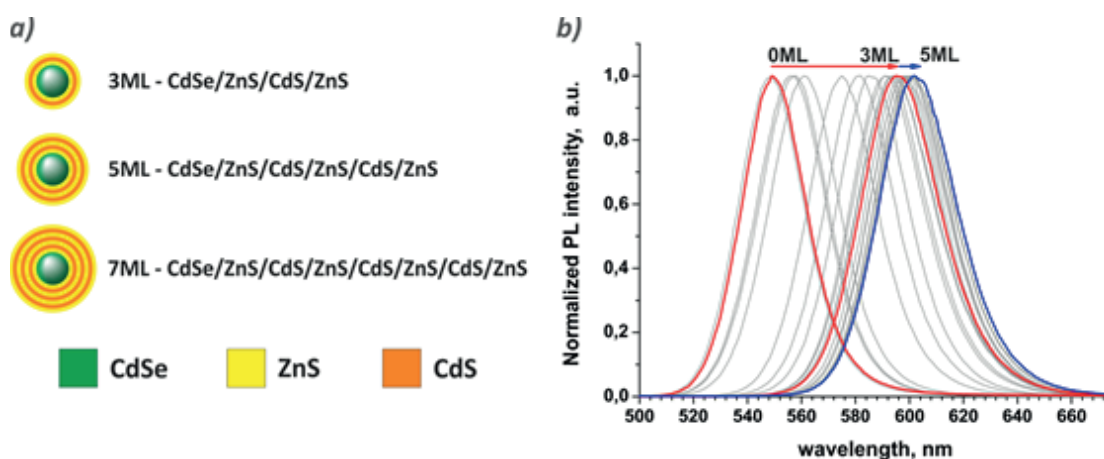


Figure 1: “Anatomy” (a) and evolution of PL spectra of core-MS QDs (b) during their synthesis.

The absorbance and PL spectra of the obtained core-MS QDs are presented in Figure 2. As can be seen, the 3-, 5- and 7ML QDs have practically the same emission profiles, while a step-wise rise of absorption below 450 nm can be seen when the thickness of the multishell is increased from 3 to 7ML. This can be rationalized by the fact that additional CdS layers have a strong absorption in spectral region below the bulk band gap of CdS (2.5 eV). On the other hand, the absorption profiles of all core-MS QDs above 500 nm are practically the same. These observations serve as another proof for localization of exciton wavefunctions inside the inner 3ML multishell substructure of 5- and 7ML samples, and successful formation of a multishell structure itself.

The study of PL kinetics (Figure 3) revealed another important feature of the studied core-MS QDs. The sample with a 3ML MS exhibited a single-exponential PL decay with a lifetime of 24 ns upon excitation at 532 nm. The PL decay curves of the samples with 5 and 7ML MSs upon 532 nm excitation could both be fitted by single-exponential functions with a lifetime of 29 ns, but the 7ML QDs have a more complex kinetic trace with a pronounced long-lived tail (Figure 3). Although the 5- and 7ML QDs had longer fluorescence lifetimes, their PL quantum yields were lower than that of the 3ML core-MS QDs. This difference in PL kinetics could be explained by the existence of an alternative excitation mechanism in thick-shell samples. We suppose that infra-dot

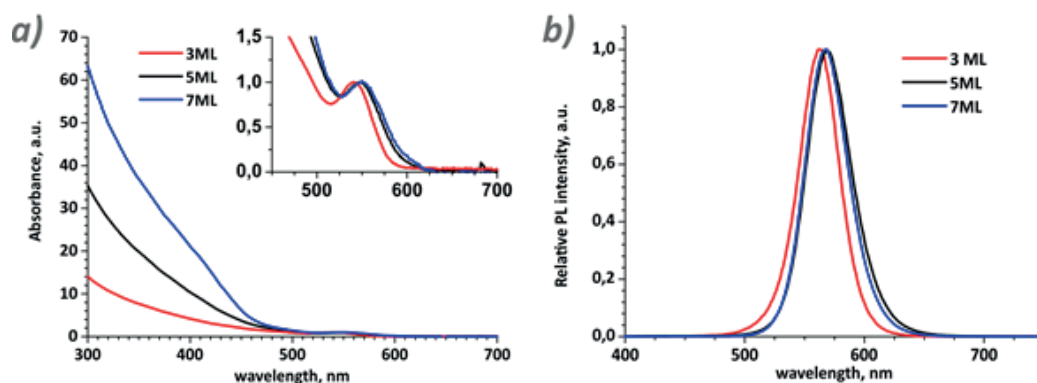


Figure 2: Absorbance (a) and fluorescence (b) spectra for core-MS QDs with 3 (red), 5 (black) and 7 (blue) MS MLs.

FRET excitation of the CdSe core by the outer CdS interlayer, or delayed transfer of charge carriers from the excited outer CdS layer might underlie this discrepancy. Since FRET mechanism is typically characterized by relatively short lifetimes of ns order [12], the latter charge transfer mechanism of long-lived PL can be considered as the better candidate to explain the observed phenomenon.

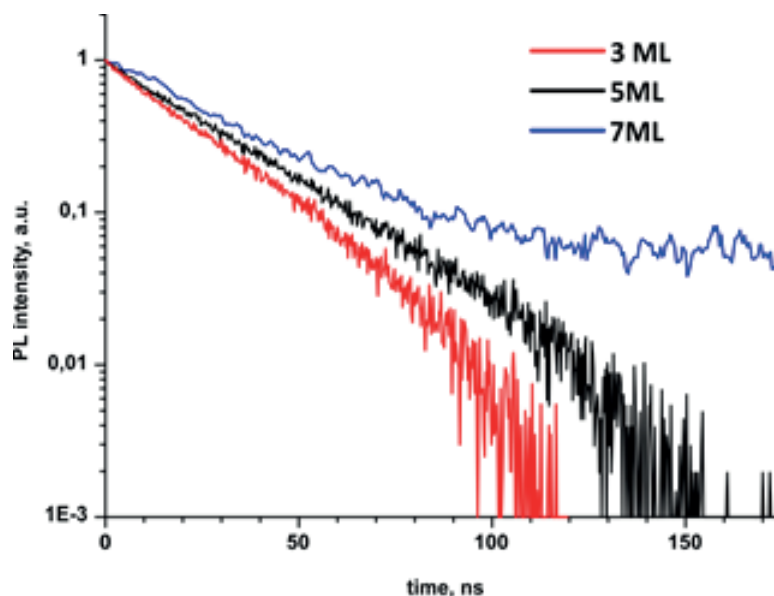


Figure 3: PL kinetics for core-MS QDs with 3 (red), 5 (black) and 7 (blue) MS MLs.

4. Conclusions

In this work we have synthesized and investigated core-MS QDs with 3, 5 and 7ML shell thickness. Although all three types of QDs have similar steady-state optical properties, the difference in PL kinetics of 7ML core-MS QDs from 3 and 5ML QDs allows to presume the existence of an alternative mechanism of 7ML QD's PL excitation. We believe that

the infra-dot transfer of excited carriers from excited outer CdS shell layer to the inner region of a core-MS QD, where the exciton wavefunctions are localized, could be the most reliable explanation for the observed long-lived tail in PL decay.

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