Photoluminescence quantum yield of CdSe-ZnS/CdS/ZnS core-multishell quantum dots approaches 100% due to enhancement of charge carrier confinement

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ABSTRACT

Quantum dots (QDs) with the highest possible photoluminescence quantum yields are necessary for modern nanotechnology applications to biosensing and optoelectronics. To date, core-shell QDs are the best. We suggest and demonstrate a novel approach to enhancement of charge-carrier confinement in the core of CdSe QDs by creating a ZnS/CdS/ZnS shell with staggered potential barrier. The CdS interlayer breaks the ZnS-shell structure continuity, which allows combining the benefits of a single ZnS-monolayer inner shell, creating the highest possible confinement potential, with a sufficient overall shell thickness and suitability for common surface modification techniques. This approach allows the preparation of CdSe-ZnS/CdS/ZnS QDs with photoluminescence quantum yields approaching 100% and small photoluminescence peak width.

Keywords: quantum dots, core-shell, confinement potential engineering, quantum yield

1. INTRODUCTION

Semiconductor quantum dots (QDs) have become the point of much research and industrial interest in the past decade. For biological applications, it is important to have semiconductor QDs with narrow emission lines, a high quantum yield (QY) close to that of standard organic dyes, and a high photostability and chemical stability. In QDs, the electron and hole are confined in a small nanocrystal space; hence, radiative recombination becomes the major relaxation pathway. At the same time, surface defects and the organic ligands that stabilize QDs in surrounding media may interfere with relaxation process and decrease photoluminescence (PL) QY of the ensemble. That is why, in general, the PL QY of bare CdSe quantum dots does not exceed 30-40%.

The negative effects of defect states and passivating ligands are commonly eliminated upon coating of QD cores with an inorganic shell made of a material with a higher band gap. Though many materials are possible candidates for the role of passivating QD shells, group II-VI semiconductors, namely ZnS, CdS, and ZnSe have proven to be the best. Coating of CdSe cores with an ABVII shell may greatly enhance the photoluminescence QY, yet the goal of preparation of 100%-emitting QDs is still a challenge.

Recently, several methods were developed for synthesis of QDs with a nearly 100% PL QY. Among them are methods using 1-octanethiol as a novel sulfur source, phosphate-free protocols, and others. The common feature of these methods is that a relatively thick shell should be grown atop CdSe cores to obtain 100%-emitting QDs that will be stable after purification and ligand exchange procedures. Here, we suggest an alternative procedure for obtaining highly luminescent QDs based on charge carrier confinement engineering. Specifically, we propose a novel core-multishell CdSe/ZnS/CdS/ZnS QD structure, which benefits from both high confinement potential of the first monolayer-thick ZnS layer and overall moderate shell thickness sufficient for reliable protection of excited carriers from the environment but not greatly increasing the QD diameter.

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2. MATERIALS AND METHODS

2.1. Materials

Cadmium oxide (powder, 99.5%), zinc oxide (powder, 99.99% trace metals basis), 1-octadecene (ODE, technical grade, 90%), oleylamine (OLA, technical grade, 70%), selenium (powder, 100 mesh, 99.5%), thiourea (ACS reagent, ≥99.0%) tri-n-octylphosphine (TOP, technical grade, 97%), tri-n-octylphosphine oxide (TOPO, reagent grade, 99%), 2-ethyhexanoic acid (2-EHA, 99%), tri-n-octylamine (TOA, 98%), triethylene glycol dimethyl ether (TEGDME, ReagentPlus, 99%), and anhydrous solvents (chloroform, hexane, methanol and 2-propanol) were purchased from Sigma-Aldrich; n-hexadecylphosphonic acid (97%) was purchased from PlasmaChem GmbH. All chemicals were used as received without any purification.

2.2. Synthesis of core CdSe quantum dots

Core CdSe quantum dots were prepared using a modified procedure reported in\(^5\). Briefly, 1 mmol of cadmium oxide, 0.5 mmol of 2-hexadecylphosphonic acid, 2 mmol of 2-ethylhexanoic acid, 2 ml of tri-n-octylamine, and 8 ml of ODE were placed into a 25 ml three-necked reaction flask. The flask was heated to 120°C and evacuated at 10 mbar for 10 minutes. Then, under argon atmosphere, the cadmium oxide was dissolved at 220°C. After complete dissolution of CdO, the reaction mixture was cooled down to 120°C and evacuated again to remove residual water. The selenium precursor was prepared by dissolution of 2 mmol of Se powder in 2 ml of TOP and 0.5 ml of ODE under an argon flow without external heating. Selenium solution was swiftly injected into the cadmium precursor solution at 240°C, kept in argon atmosphere under vigorous stirring. The reaction was monitored by UV-Vis spectroscopy and was stopped after 5 minutes by intensely cooling with an air flow. The obtained QDs were isolated from the crude solution by precipitation with 2-propanol, and then were purified by two successive dissolution/precipitation cycles using chloroform/methanol as a solvent/coagulant combination, respectively.

2.3. Growth of shells

*Preparation of precursor stock solutions.* Zinc and cadmium stock solutions were prepared by dissolving 25 mmol of the corresponding oxide in 52 mmol of 2-EHA diluted with 20 ml of TEGDME. Oxide dissolution was conducted at 220°C under vigorous stirring until clear solutions were obtained. The sulfur stock solution was prepared by dissolving 34 mmol of thiourea in 40 ml of TEGDME under sonication. All solutions were leveled with TEGDME to obtain final precursor concentrations of 0.85 M.

Shell coating was done according to the SILAR procedure\(^6\) with quantities of reagents reduced to 80%\(^7\) of those calculated using a spherical QD model to avoid excess precursor accumulation in the reaction mixture. Determination of the core size and core QD concentration was performed by the UV-Vis spectroscopy method using the dependences of the first excitonic absorption peak position on the QD size and its intensity on the QD extinction coefficient presented in\(^8\). Purified CdSe cores were dissolved in hexane, and a portion containing 100 mmol of them was transferred into a mixture of 3 ml ODE and 3 ml OLA. Hexane was further removed by mild heating under a reduced pressure, and, finally, the mixture was degassed at 90°C during 20 minutes. Under argon atmosphere, 1 mmol of TOP was injected into the flask, and the core solution was allowed to settle for 15 minutes prior to the beginning of shell growth.

Successive injection of precursors was performed in the thermal cycling mode. Injections were made at 100°C, then the temperature of the reaction mixture was ramped to 170°C within 5 minutes, and the solution was kept at this temperature for 5 more minutes to complete the adsorption and reaction. The first cycle was started with the zinc or cadmium precursor, and 0.5 mmol of TOP was added to the reaction mixture prior to each injection of the sulfur precursor to stabilize QDs obtained in the succeeding cycle when thiourea is injected. The growth of the shell was monitored using UV-Vis spectrophotometry and PL measurements.

After completion of shell growth, the resulting QDs were isolated from the crude solution by precipitation with 2-propanol, and then were purified in two successive dissolution/precipitation cycles using chloroform and methanol as the solvent and coagulant, respectively. Finally, the product was dissolved in chloroform, and 1 mmol of TOPO was added to this solution to change surface ligands from oleylamine to TOPO for long-term storage and further processing.
2.4. Characterization techniques

The UV-Vis spectra were recorded using an Agilent Cary 60 spectrophotometer. Photoluminescence was measured using an Agilent Cary Eclipse spectrofluorimeter. The PL QYs of the QD samples dissolved in anhydrous chloroform were determined using different organic dyes with known QYs: fluorescein in 0.1 M NaOH solution (90%) and rhodamine 6G in methanol (95%). All optical densities at the measurement wavelengths were kept below 0.1 to ensure elimination of emission reabsorption. PL QYs were calculated according to the following equation\(^7\):

\[
QY_{QD} = \frac{P_{QD}}{P_{dye}} \cdot \frac{OD_{dye}}{OD_{QD}} \cdot \frac{n_{dye}^2}{n_{QD}^2} \cdot QY_{dye}
\]

where \(P_{QD}\) is the PL peak area, \(OD_{dye}\) is the optical density at the measurement wavelength (460 and 500 nm for fluorescein and rhodamine 6G, respectively), \(n_d\) is the refractive index of the media at the measurement wavelength, and \(QY_{dye}\) is the PL QY of the reference dye. Images of quantum dots were taken on a JEOL JEM-2100F transmission electron microscope operating at 200 kV in the STEM and HRTEM modes.

3. RESULTS AND DISCUSSION

During shell coating of CdSe cores, one can notice that, in the beginning of ZnS shell growth, the PL QY of the sample may approach 100%. Yet, when these CdSe/thin ZnS QDs are isolated and purified, the QY sufficiently drops and may decrease to 5-10% after ligand exchange to thiols for the purpose of phase transfer. After a few more shell monolayers are grown atop cores, the ensemble QY slowly falls from nearly 100% to 60-70%, but, in this case, the PL is not quenched during postsynthetic processing. We suppose that the reason for this effect is the change in the confinement potential of the shell. Specifically, the thinnest possible 1 ML shell of ZnS has the largest band gap and, therefore, creates the highest confinement potential for excited charge carriers. When the thickness of the shell is increased, the conduction and valence bands move toward their bulk energies, resulting in a decrease in the effective energy barrier. On the other hand, the increased shell thickness physically enlarges the tunneling length necessary for electron or hole interaction with the external medium, which confines the photogenerated carriers inside the photoluminescent core. CdS and ZnS are the most common materials for shell growth over CdSe cores. Zinc sulfide creates a stronger confinement potential for both electrons and holes (Figure 1a), but it has a relatively large lattice mismatch with CdSe, which is suggested to be the reason for the QY falling due to a large interfacial strain when a thick shell is grown\(^6,7\). CdS creates a smaller interfacial strain, but its potential barriers are weaker compared to ZnS. An approach combining the benefits of both the high potential barriers of ZnS and lattice compatibility of CdS was proposed in\(^8\), where a thin layer of CdS was coated atop CdSe cores, and then a second shell of ZnS was grown over CdSe/CdS QDs. In this case, a PL QY of 70-80% can be achieved.

We suggest another approach, which allows to strongly lock the electron-hole pair in the luminescent CdSe core. Our hypothesis is that the shell itself undergoes a strong quantum confinement effect, and the least possible shell thickness should create the maximum potential barrier for photexcited charge carriers. These high barriers should considerably increase the probability of radiative recombination of the exciton and hinder any charge transfer processes. On the other hand, the shell should be sufficiently thick to protect the luminescent QD core from the environment. Therefore, a mere increase in the shell thickness will not be enough to preserve the initially high confinement potential. A solution to this problem may be found in introducing a miscible thin interlayer between the first shell monolayer and its residual external part in order to break the high-bandgap shell crystal continuity. Such an interlayer will create a high and abrupt potential barrier at the core-shell interface and also serve as a „padding“ for further thick shell growth. Experimentally, this novel nanostructure may be engineered in the form of a CdSe/ZnS/CdS/ZnS core-multishell QD, which we demonstrate below.
To test our hypothesis, we synthesized a series of core-shell QDs from one batch of CdSe cores. High-quality cores were synthesized according to the protocol adapted from using phosphonate anions to stabilize growing QDs and restrict their rapid growth. We chose relatively small 2.3 nm CdSe cores with the first excitonic transition at 489 nm as an object of interest because, in this case, the quality of the shell and its confinement potential should have the highest possible effect on the photoluminescence properties of the resulting QDs due to the high band gap and the maximum deviation of the band levels from their bulk values. The optical properties of the CdSe cores used in this study are presented in Figure 1b. Employing the SILAR procedure, which allows exact control over the number of shell monolayers grown, we synthesized core-shell QD samples with three different shell types: CdSe/ZnS(3 ML), CdSe/CdS(1 ML)/ZnS(2 ML), and CdSe/ZnS(1 ML)/CdS(1 ML)/ZnS(1 ML). Since all samples have the same shell monolayer number grown under the same synthetic conditions, the shell structure and its confinement potential are the key parameters determining the optical properties of the QDs. The absorption and emission spectra of the three obtained samples are given in Figures 2a, 2b. The samples containing CdS layers in the shell exhibit a large spectral shift of both the PL and first excitonic absorption peaks to the red region as compared to the CdSe/ZnS samples. Interestingly, when the first shell monolayer is CdS, the excitonic transition in the absorption spectrum becomes smeared. We assume that the weak barrier potential created by cadmium sulfide is the reason for this effect, because, in both samples having ZnS as the first monolayer of the shell, the excitonic transitions are clearly resolved. Therefore, application of a CdS interlayer inside the ZnS shell may be used as a method of extension of tuning the PL window of fixed-size CdSe cores without degradation of the spectral purity.

A dark-field STEM image of the core-multishell sample is presented in Figure 2c. The QDs have no pronounced regular shape, yet their local arrangement in a hexagonal lattice pattern gives evidence for a high size uniformity. The mean diameter was determined to be 4.6 nm with a standard deviation of 0.4 nm (measured over >100 QDs), so the shell thickness can be estimated as 1.15 nm, which is close to the predicted 0.95 nm, the sum of wurtzite phase single CdS and double ZnS monolayer thicknesses along (001) directions. An inset in Figure 2c shows a HRTEM image of a single CdSe/multishell QD. Visible lattice fringes give evidence for conformal growth of the complex shell, despite the expected high strains caused by the combination of materials chosen.

In Figure 3, the evolution of the PL QY during the shell growth of three different samples is shown. Application of the CdS shell causes a large PL redshift; therefore, when these layers were grown, we changed the PL QY reference from fluorescein to rhodamine 6G in order to keep the excitation wavelength close to the first excitonic transition. As expected, the CdSe/ZnS QDs exhibited a slow degradation of the initially high PL QY with an increase in the shell thickness. In contrast, the PL QY of the CdSe/CdS/ZnS and CdSe/multishell samples did not fall during shell growth, yet the difference in the type of the very first shell monolayer and its band levels leads to quite a different PL QY of the obtained core-shell QDs.
Figure 2. The (a) absorption and (b) emission spectra of the three studied samples. (c) A DF-STEM image of CdSe/ZnS/CdS/ZnS core-multishell quantum dots; a HRTEM image of a single quantum dot is given in the inset. (d) Schematic representation of a core-multishell quantum dot structure and its energy diagram.

The optical properties of all three QD batches are summarized in Table 1. The listed values show that the suggested concept of enhancement of carriers confinement is reasonable, because the CdSe/multishell QDs have not only the highest PL QY, but also the minimal PL emission peak width, what is important for multiplexed diagnostic applications. Noteworthy, it can be seen that changing of the shell structure can be employed as a method to tune the QD emission properties in a wide spectral range.

Figure 3. Evolution of the photoluminescence quantum yield during shell growth of the three samples studied. Points labeled with asterisks denote measurements using rhodamine 6G as a reference; other points were measured against fluorescein.
Table 1. Absorption and photoluminescence properties of the three core-shell QD samples synthesized.

<table>
<thead>
<tr>
<th>Sample type</th>
<th>Excitonic absorption maximum, nm / PL emission maximum, nm / PL emission width, nm</th>
<th>PL QY, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>CdSe/ZnS (3 ML)</td>
<td>502 / 527 / 41</td>
<td>60(^a)</td>
</tr>
<tr>
<td>CdSe/CdS (1 ML)/ZnS (2 ML)</td>
<td>540 / 575 / 52</td>
<td>68(^a)</td>
</tr>
<tr>
<td>CdSe)/ZnS (1 ML)/CdS (1 ML)/ZnS (1 ML)</td>
<td>541 / 563 / 39</td>
<td>97(^a)</td>
</tr>
</tbody>
</table>

\(^a\) measured using fluorescein as a reference
\(^b\) measured using rhodamine 6G as a reference

4. CONCLUSIONS

We propose an approach ensuring strong charge carrier confinement in photoluminescent cores of CdSe-ZnS/CdS/ZnS core-multishell QDs. Unlike CdSe/CdS/ZnS or alloyed-shell QDs, where CdS serves to reduce the lattice strain at the core-shell interface, the multishell QDs contain a CdS interlayer in the ZnS shell introduced to break its continuity. This allows combining the advantages of the maximal potential barrier created by a single monolayer of the internal ZnS shell with an excellent protection of the core and suitability of the external ZnS shell layer for the QD-surface modification protocols generally used for QD solubilization and functionalization with capture molecules.

Using an adapted SILAR procedure, we have synthesized an extended series of CdSe-based core-shell QDs with various shell-layer combinations. We have found that CdSe/ZnS/CdS/ZnS QDs have a higher photoluminescence quantum yield (approaching 100\%) and a smaller FWHM than CdSe/ZnS and CdSe/CdS/ZnS QDs.

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