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OPTICAL PROPERTIES OF CdSe AND CdSe/ZnS QUANTUM DOTS

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Abstract

Original organic capping TOPO/TOP groups of CdSe and CdSe/ZnS quantum dots, from mother solution were replaced with 2-mercaptoethanol, which was chosen as model compound, in order to achieve water solubility. Obtained water dispersions of CdSe and CdSe/ZnS QDs were characterized by UV/Vis absorption and luminescence techniques. Luminescence measurements revealed that bare cores are very sensitive to surface capping, transfer to water diminished emission intensity. Core/shell, CdSe/ZnS, QDs are much more resistant to changes of the capping and solvent, and significant part of emission intensity was preserved in water.

Introduction

The organic ligand bound to the surface of colloidal quantum dots (QDs) plays a important role in determining their electronic and optical properties. A mixture of trioctylphosphine and trioctylphosphine oxide (TOP/TOPO) is the prototypical ligand system for most II-VI semiconductor systems, such as CdSe. These ligands provide colloidal stability in common organic solvents such as hexane and toluene.

Overcoating QDs with higher band gap inorganic materials has been shown to improve the photoluminescence quantum yields by passivating surface nonradiative recombination sites. Particles passivated with inorganic shell structures are more robust than organically passivated dots and have greater tolerance to processing conditions necessary for incorporation into solid state structures, transfer to water and further conjugation. Water solubility is increasingly recognized as a desirable characteristic as QDs are becoming the system of choice for PL biolabelling applications, and in many cases their greater stability is seeing as an important advantage in comparison to of their molecular counterparts (organic dyes) [1].

In this article, we report a study of the optical properties of CdSe and CdSe/ZnS QDs, that have been synthesized in noncoordinating organic solvent (TOPO/TOP) at high temperature, dispersed in nonpolar solvent and water. We show that capping of QDs with 2-mercaptoethanol readily produces stable water dispersions.

Experimental

All reagents were used without further purification.

Synthesis of CdSe QDs. Highly crystalline CdSe QDs were synthesized by method previously described by Peng and Peng [2]. Briefly, CdO, TOPO and HPA were loaded in 25 ml flask. The mixture was heated to 300 – 320 °C under Ar flow.

Selenium stock solution was injected in the mixture at 270 °C and left nanocrystals to grow for 4 minutes.

Synthesis of CdSe/ZnS core/shell QDs. Roughly, 0.1 μmol of CdSe QDs dispersed in hexane was transferred into reaction flask with dry TOPO and solvent was pumped out. Then, temperature of the solution was raised at 160°C, and precursors of Zn and S dissolved in TOP were added dropwise over a period of 5 minutes. The overcoated particles were stored in their mother solution during the night to ensure that the surface of the dots remained passivated with TOPO [3].

Extraction of QDs in water: Equal aliquots of CdSe or CdSe/ZnS QDS dispersed in hexane and 0.01 M aqueous solution of 2-mercaptoethanol (pH = 8-9) were mixed. Two separated layers were formed, hexane (colored) layer was at the top. After slight shaking, QDs were transferred in aqueous (bottom) layer, and it was used as is for optical measurements.

Optical characterization: Measurements of the absorption spectra were carried out on an Evolution 600 UV-Vis spectrophotometer (Thermo Scientific). The photoluminescence spectra were recorded on Perkin-Elmer LS-45 spectrofluorimeter. Quantum yields of emission were calculated using Tris[2,2'-bipyridyl]Ruthenium(II)chloride as standard.

Results and Discussion

The absorption and emission spectra of CdSe (triangles) and CdSe/ZnS (cycles) QDs are presented in Fig 1A and Fig 1B, respectively. As can be concluded from the position of the absorption peak, CdSe cores were from 3-4 nm in diameter. Exchange of capping agent and extraction in water didn't affect shape of absorption spectrum (Fig 1 A); CdSe QDs retain their original size. Unfortunately, extraction in water led to disappearance of characteristic emission peak at 560 nm (QY in chloroform was ~ 0.42 %).

Overcoating of CdSe QDs with shell of ZnS led to changes in shape and position of peak in absorption spectrum (Fig 1 A, cycles). Absorption peak moved from 543 nm to 553 nm and its FWHM increased, what indicated that particle sizes increased and their size distribution is wider in comparison to bare CdSe QDs. Changes in emission spectra (Fig. 1B, cycles) are more prominent. Emission intensity increased 10 times (QY= 4.2%) compared to bare CdSe and emission peak moved to 580 nm. Exchange of capping agent and extraction in water didn't affect shape of emission spectrum just its intensity. CdSe/ZnS QDs in water retain a measurable part of their original emission (QY= 0.55%). Once the QDs are dispersed in the water they can be used to detect different analytes as sensors, as a passive fluorescent labels (through conjugation with selective receptor molecules, antibodies) and design of simple multiplexed immunoassays, for FRET (fluorescence resonance energy transfer) and for labeling biological cells. Obtained results showed that 2-mercaptoethanol is suitable for transfer of core/shell QDs in water. Its functional groups allow excellent capping of the QD surface (SH group and ZnS) from one side, and polarity (OH) of its other side gives good water solubility.

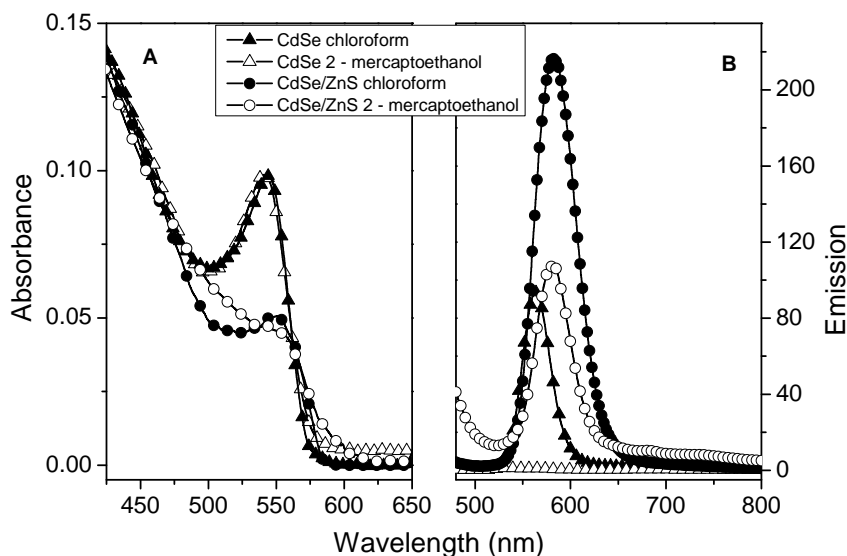


Fig. 1. Absorption (A) and emission (B) spectra of CdSe and CdSe/ZnS QDs dispersed in chloroform and water. $\lambda_{\text{exc}} = 450\text{nm}$.

Conclusion

The proposed synthetic method resulted in formation of CdSe QDs cores with diameters in the range from 3-4 nm. Addition of shell of ZnS over CdSe core didn't affect dimensions of core. CdSe/ZnS QDs have 10 times increased QY of emission in comparison to bare CdSe QDs. Extraction of QDs in water by exchange of capping agents, led to decrease of QY of emission of both bare CdSe and CdSe/ZnS QDs. Core/shell QDs dispersed in water sustained QY of emission large enough to be used for different bio-applications.

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