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Synthesis and DNA Functionalization of CdSe/CdS (Core/Shell) Quantum Dots

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Synthesis and DNA functionalization of CdSe/CdS Core/Shell Quantum Dots

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Abstract

In recent years, colloidal semiconductor nanocrystals, commonly known as quantum dots, have gained much attention in fields such as materials chemistry, bioengineering, chemical and biomedical engineering. These semiconductor nanocrystals display unique optical, electrical, and chemical properties unlike any bulk material or individual molecule. Areas of particular interest in the field of quantum dots include biofunctionalization. Advances in biology and medicine indicate successful bioconjugate functionalization of biomolecules such as peptides, antibodies, nucleic acids, or small-molecules for labeling and intracellular tracking. This research is focused on the multistep synthesis of CdSe/CdS core-shell nanoparticles as well as employment of two different solubilization methods—lipid encapsulation and ligand exchange with mercapto-carboxylic acids. The synthesis begins by synthesizing the CdSe core using CdO and Se as precursors. Two layers of CdS shells are then applied over the core with cadmium and sulfur. The quantum dot is then made water soluble by encapsulating the hydrophobic particle in a micelle using phospholipid encapsulation method or by using ligand-exchange method using 3-mercaptopropionic acid. Once water soluble, specific oligonucleotides (DNA) are then functionalized to the quantum dots.

Background

Quantum dots involve a multi-step synthesis to produce the core and shell of the fluorescent particle. For core synthesis, CdO and Se precursors are injected and mixed to yield a nanoparticle of desired size. The size and fluorescence emission wavelength of the nanocrystal is a function of the time and temperature of the reaction. To enhance particle fluorescence, CdS shells are applied over the core. Depending on the final destination of the hydrophobic particle, another step may be necessary to render it soluble in hydrophilic media, as is the case for biomolecular conjugation and biomedical imaging. To yield a water-soluble particle, two methods may be employed: lipid encapsulation with DSPE-PEG(2000) Maleimide (GMP) (Figure 1) or ligand exchange with 3-mercaptopropionic acid . Once a stable water-soluble quantum dot is produced, they may be functionalized to various small molecules, or biomolecules such as DNA, proteins, or antibodies.

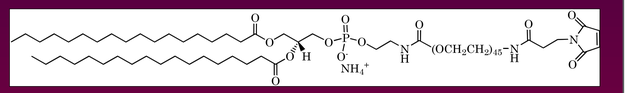

Figure 1: DSPE-PEG(2000) Maleimide (GMP) used in lipid encapsulation for water solubilization– 1,2-distearoyl-*sn*-glycero-3-phosphoethanolamine-N-[maleimide(polyethylene glycol)2000] (ammonium salt).

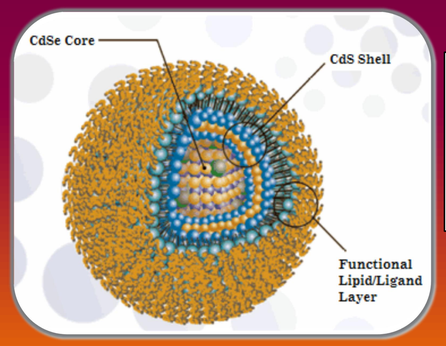

Figure 2: 3-D representation of CdSe core, CdS shell, and functional lipid/ligand water soluble layer. (Ref 5)

Acknowledgements

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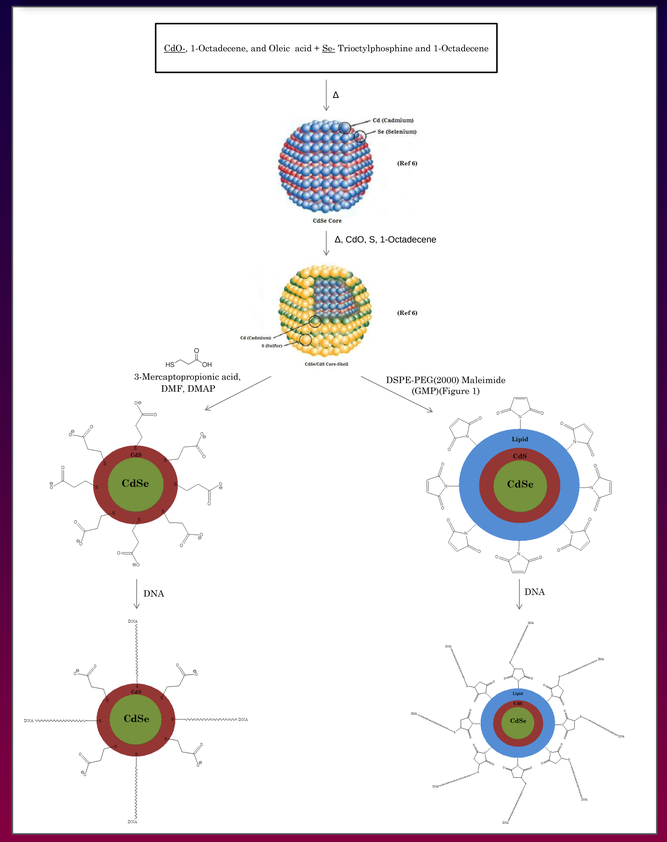
Materials & Methods



•**Step 1**– Core Synthesis: Selenium and trioctylphosphine dissolved in 1-Octadecene precursor and rapidly injected into cadmium oxide/oleic acid/1-octadecene precursor. Temperature is adjusted to yield desired size of nanocrystal.(Ref 4)

•**Step 2**– Shell Synthesis: Cadmium oxide/oleic acid and sulfur precursors are individually prepared in 1-Octadecene and added drop wise to the core solution.(Ref 4)

•**Step 3**– Water Solubilization: Hydrophobic core/shell particles can be made hydrophilic via encapsulation with DSPE-PEG(2000) Maleimide or ligand exchange with 3-Mercaptopropionic acid. Deprotonation of 3-Mercaptopropionic acid with DMAP creates a charged and hydrophilic particle.(Ref 1, 2, 3)

•**Step 4**– DNA Functionalization: DNA with a functional thiol can be functionalized directly to the maleimide moiety in the lipid procedure or by ligand exchange with 3-Mercaptopropionic acid.(Ref 1)

Results & Discussion

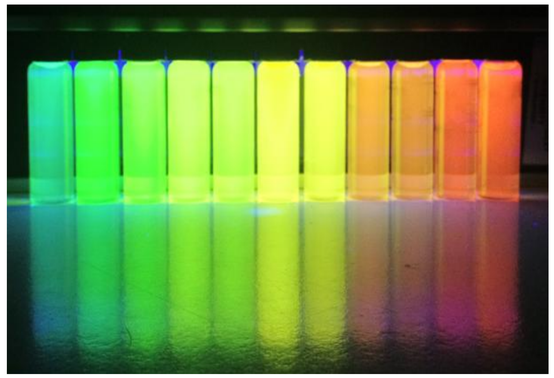


Figure 3: Full spectrum of CdSe/CdS core/shell quantum dot solutions from ~500-630 nm.

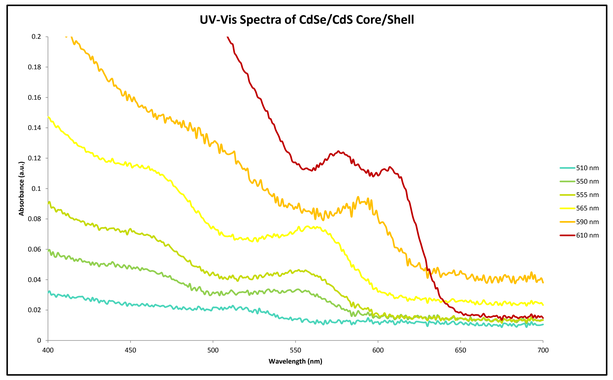


Figure 4: UV spectra scan of CdSe/CdS core/shell spectrum (Figure 2) displaying relationship of color to size.

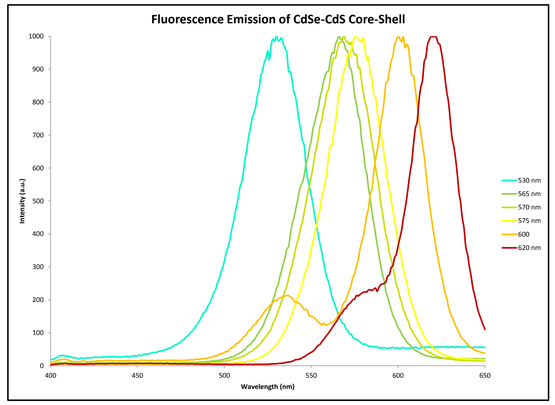


Figure 5. Fluorometry scan of CdSe/CdS core/shell spectrum (Figure 3) at excitation wavelength of 365 nm.

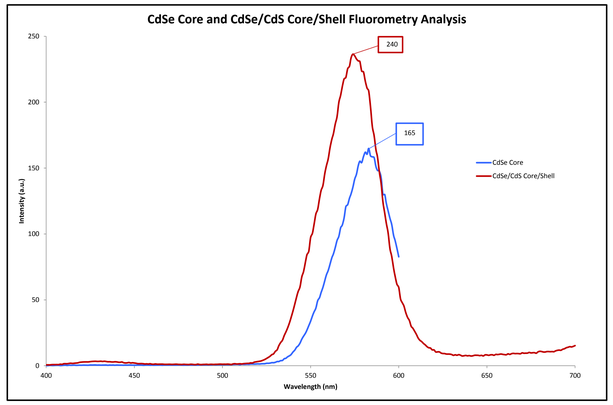


Figure 6. Fluorometry scan of individual core and core-shell particles at excitation wavelength of 365 nm.

Future Works

- Optimization of core and core/shell synthesis for specific temperature dependent particle diameter.
- Optimization of precursor concentrations for streamlined core and core/shell synthesis.
- Optimization of quantum dot water solubilization using both 3-Mecaptopropionic acid and phospholipids.
- Assembly of quantum dots using DNA origami as a template or co-assembly with metal nanoparticles for investigation of optical and electrical properties.

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