Investigating the electronic coupling of quantum dot-ligand interaction

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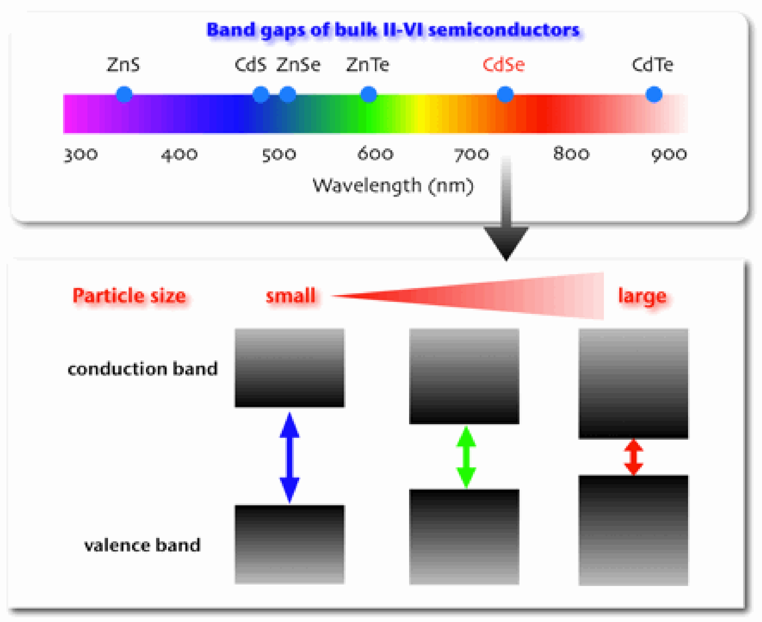
Introduction

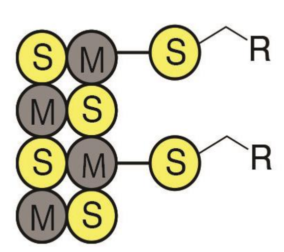
- Quantum dots are nanosized (1-100 nm) particles of semiconductors that show size dependent optical properties
- The band gap can be adjusted via size control to manipulate the wavelengths that are emitted due to fluorescence
- This property makes quantum dots useful in solid-state lighting, LED, biological probes, and solar energy capture



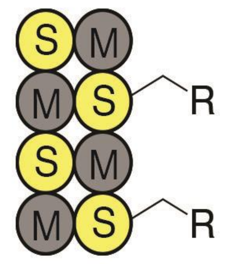
http://www.scl.kyoto-u.ac.jp/~teranisi/research/Opt-e.html

Crystal Bound Ligands

- The Macdonald group has discovered a new crystal-bound thiol ligand system
- This system is more robust as the head group is bound to sites with higher coordination than usual ligands on nanoparticles



Surface-bound ligand



Crystal-bound ligand

[1]Turo, M. J., Macdonald, J. E. *ACS Nano*, **2014**, submitted

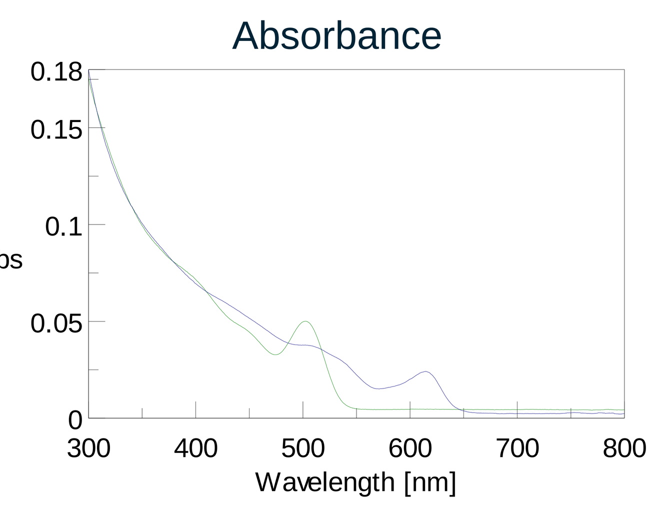
What is the nature of the electronic effects of crystal-bound ligands?

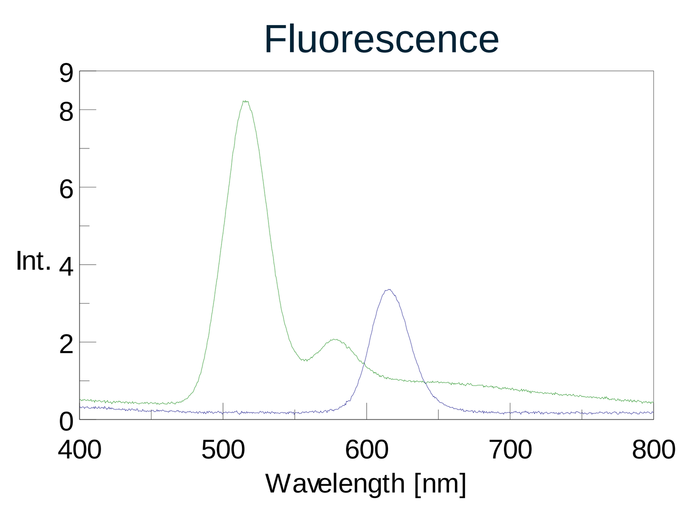
- In this project we use CdSe@ZnS quantum dots as a probe to understand the opto-electronic effects of crystal-bound thiols
- These particles are highly fluorescent and the emission intensity and wavelength of absorption and emission are very sensitive to particle surface chemistry

Seed Synthesis

The sizes of the CdSe seeds are easily customizable due to a variety of factors

- ❑ The temperature at which the Se:TOP solution is injected
- ❑ The concentration of the Se:TOP solution
- ❑ The length of time of the reaction
- ❑ The amount of supplementary injections (if necessary)

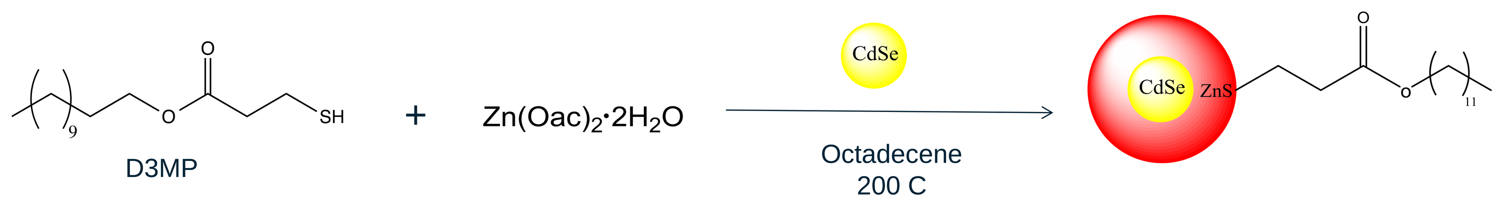


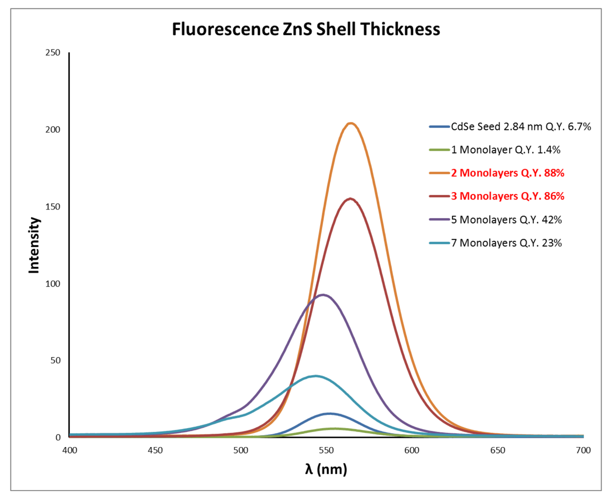


Absorbance and fluorescence of CdSe nanoparticle sizes of 2.37 nm (green line) and 5.23 nm (blue line). There is a red shift in absorbance and fluorescence from smaller to larger seeds.

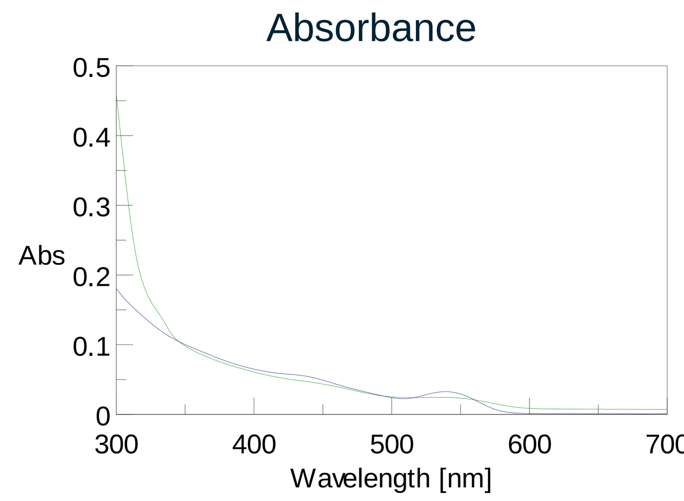
Shell Synthesis

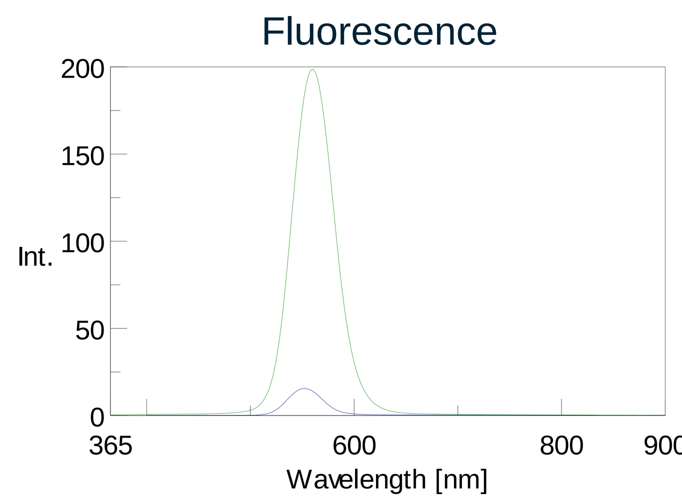
- The second reaction involves the growth of the ZnS shell with crystal-bound thiols
- We used dodeceyl-3-mercaptopropionate (D3MP) as the ligand of choice for two reasons
    1. It has a long chain which helps stabilize the quantum dots in solution
    2. The long chain can be cleaved to make the quantum dots water soluble





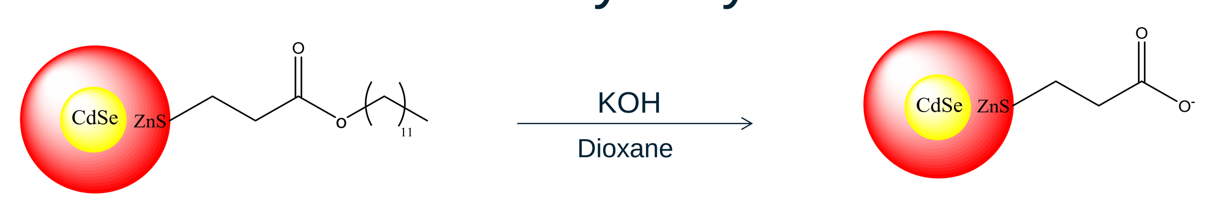
- We were able to carefully control the size of the shell by changing the amount of Zinc acetate.
- Thicker ZnS shells caused the quantum yield to increase, though a threshold was reached where shelling became counterproductive





Quantum Yield increased from 6.7% without shelling (blue line) to 94.5% (green line) with shelling

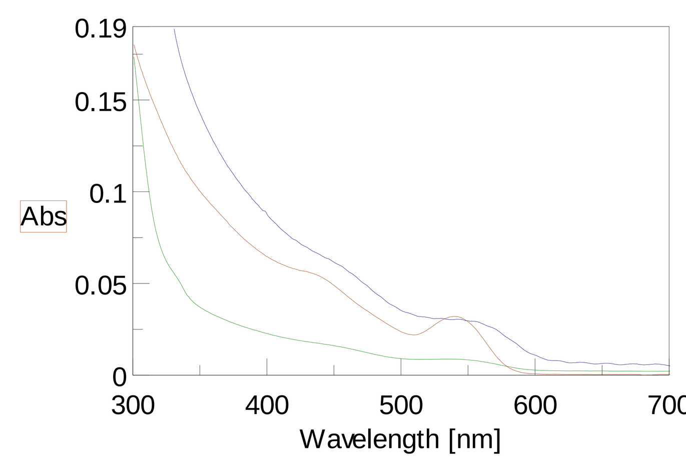
Shell Hydrolysis

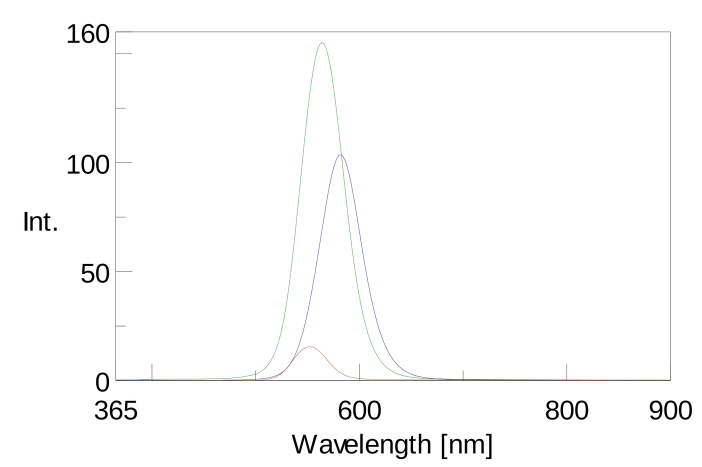


CdSe@ZnS with D3MP

CdSe@Zns w/hydrolyzed ligand

- After the CdSe@ZnS core-shell nanoparticles were made they were hydrolyzed using base catalyzed hydrolysis
- Although the quantum yield dropped after hydrolysis, it still remained higher than the initial seeds due to surface passivation
- The use of quantum dots in some applications -including biomedical ones- can only be possible if the nanoparticles are dissolved in water

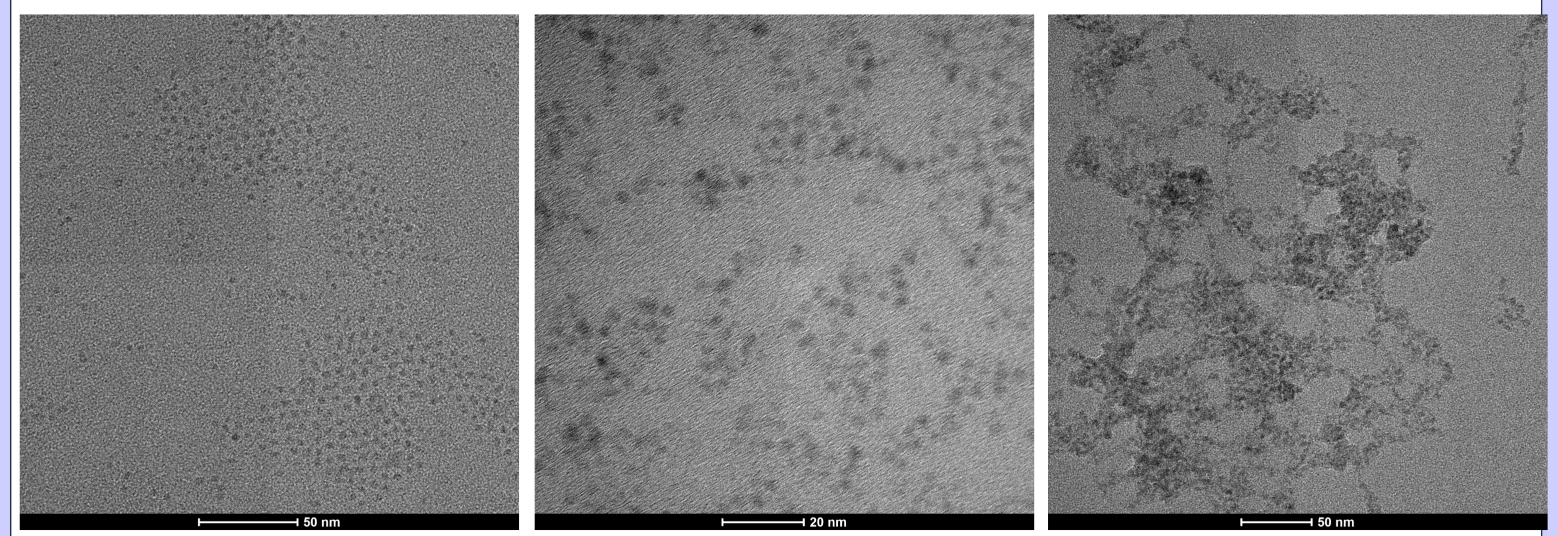




ZnS core-shell nanoparticles, and the hydrolyzed core-shells
Quantum yields of seed, core-shell, and hydrolyzed core shell: 6.7%, 85.7%, 30.77%
We notice the hydrolysis step causes a red shift in the absorbance and fluorescence

Transmission Electron Microscopy

Images of the seeds, shells, and hydrolyzed nanoparticles



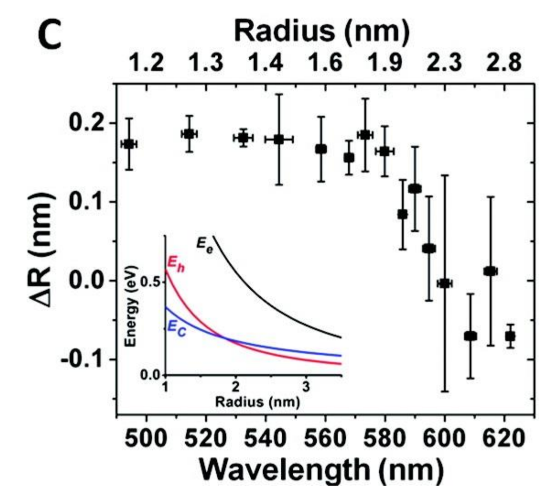
Seed   Core-Shell   Hydrolyzed Core-Shell

Discussion

A red shift means the ligands are causing the particle to appear larger to either the electron or the hole

$$\Delta E = E_{gap} + \frac{h^2}{8r^2}\left(\frac{1}{m_e^*} + \frac{1}{m_h^*}\right) - \frac{1.8e^2}{\varepsilon\varepsilon_o r}$$

Brus equation



The Weiss group used the Brus equation and compared the red shift caused by dithiocarbonate ligands to figure out if it was the hole being delocalized and not the electron

Frederick, M. T., Amin, V. A., Cass, L. C., and Weiss, E.A. *Nano Lett.*, **2011**, *11* (12), pp 5455–5460

Future Directions

- We plan to finish preparing a series of series of CdSe@ZnS with crystal-bound D3MP. The ester will be hydrolyzed and the size of the red shift measured
- Using the sizing data we plan on inputting it into the Brus' quantum confinement equation to find more of the ligands electronic effects
- This information will be applied to synthetic designs in photocatalytic and photovoltaic systems

Acknowledgements

- TN-SCORE grant– NSF EPS-1004083
- The Macdonald Group
- The Vanderbilt Institute of Nanoscale Science and Engineering