Engineering CdSSe/CdS Core/Shell Quantum Dots for Use in Single-Protein Imaging

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Background

<u>What are Quantum Dots?</u>

- Semiconductor nanocrystals (2-15 nm) with size-tunable optical properties
- Larger QDs have a narrower band gap, resulting in lower-energy photon emissions ("red shift")
- Applications include solid state lighting, solar cells, and **single-protein imaging and tracking**

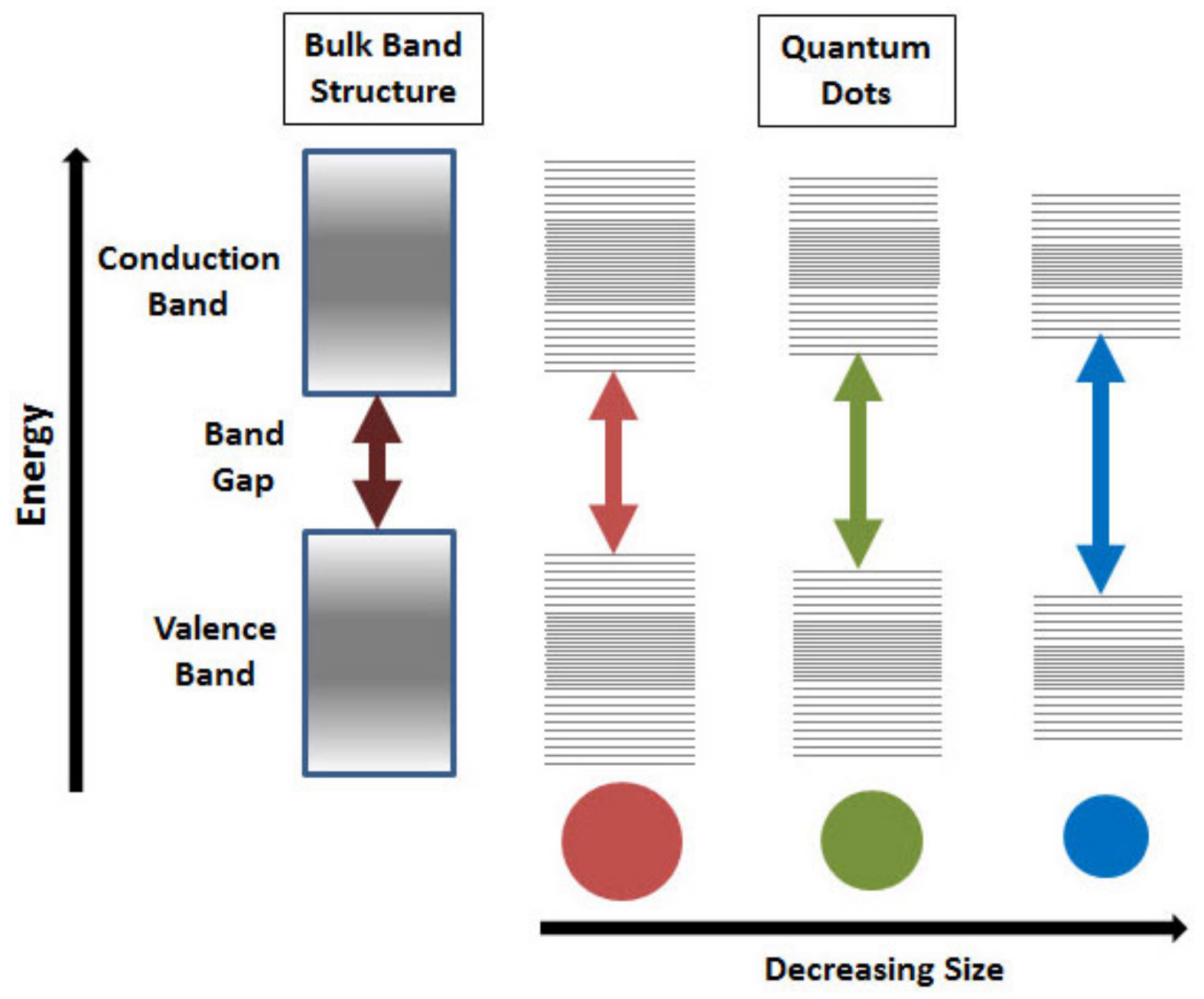


Figure 1: Quantum confinement in nanocrystals of different sizes [1]

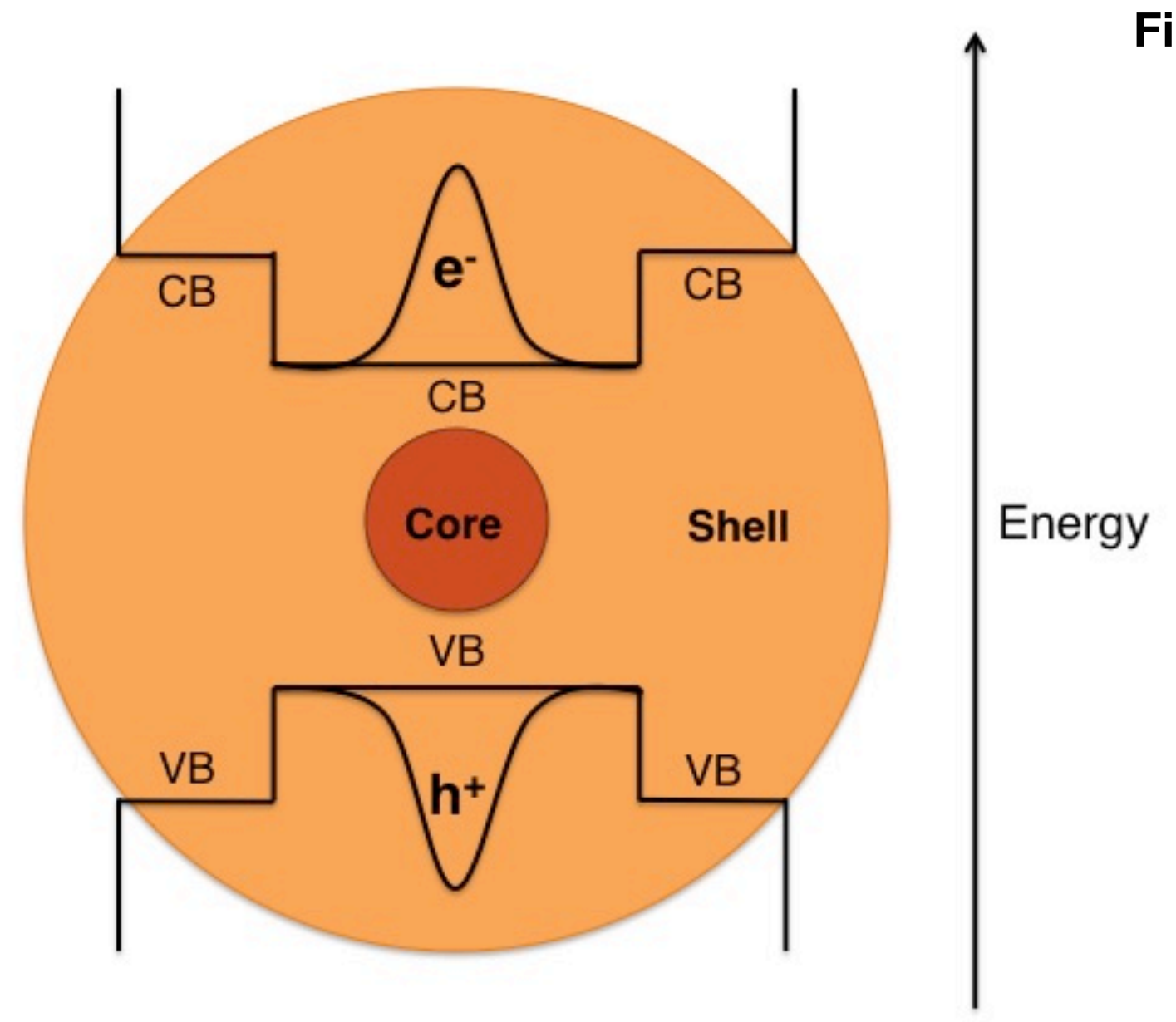


Figure 2: Quantum confinement of electron (e^-) and hole (h^+) wavefunctions between conduction (CB) and valence (VB) bands in a core/shell system

<u>Core/Shell Quantum Dots</u>

- Shelling QD cores with inorganic material (e.g. CdS) confines the **electron-hole pair** inside the QD
- Shelled cores have increased photostability and quantum yield

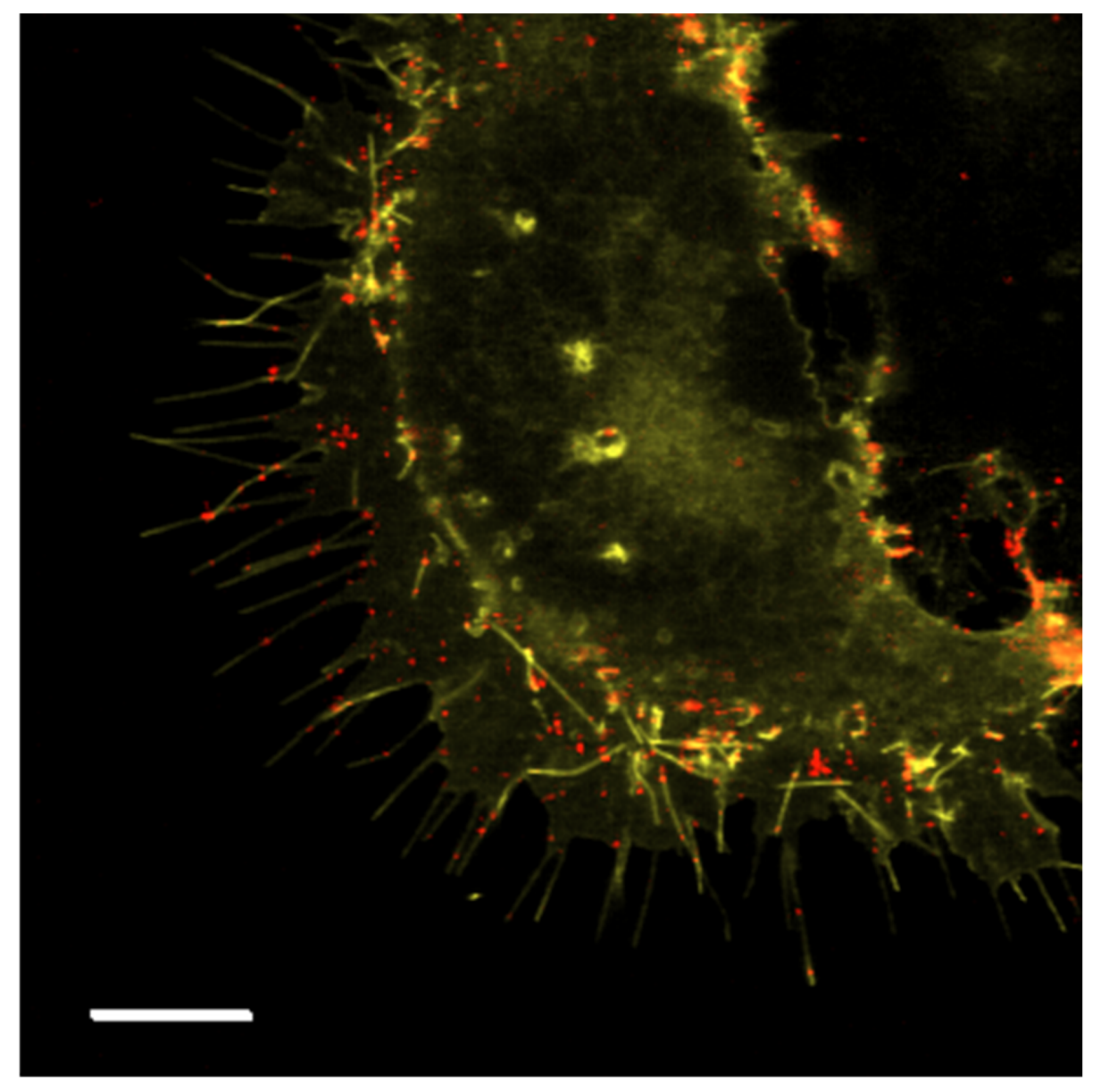


Figure 3: Laser-scanning confocal microscopy of a HEK293 cell (scale bar 10 µm) [2]
<u>Yellow</u>: Human dopamine transporter fused to yellow fluorescent protein at the N-terminus
<u>Red</u>: QDs (655 nm max emission)

<u>Ideal QDs for Biological Imaging</u>

- **Photostable**
  - "Non-blinking"
- **Bright**
  - High quantum yield
- **Narrow Emission Peak**
  - Small size-distribution

Research Goals

Engineer stable, bright, and size-uniform QDs for single-protein imaging by:

- Growing a CdS shell onto alloyed CdSSe cores

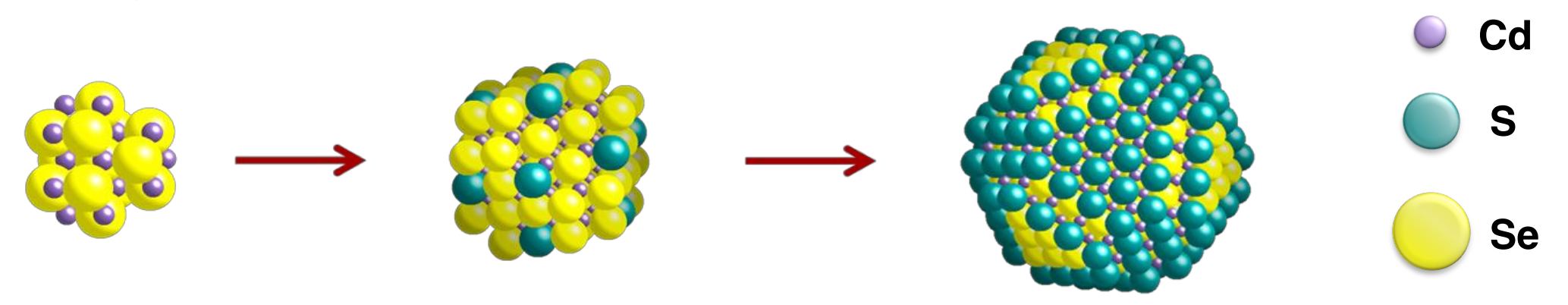
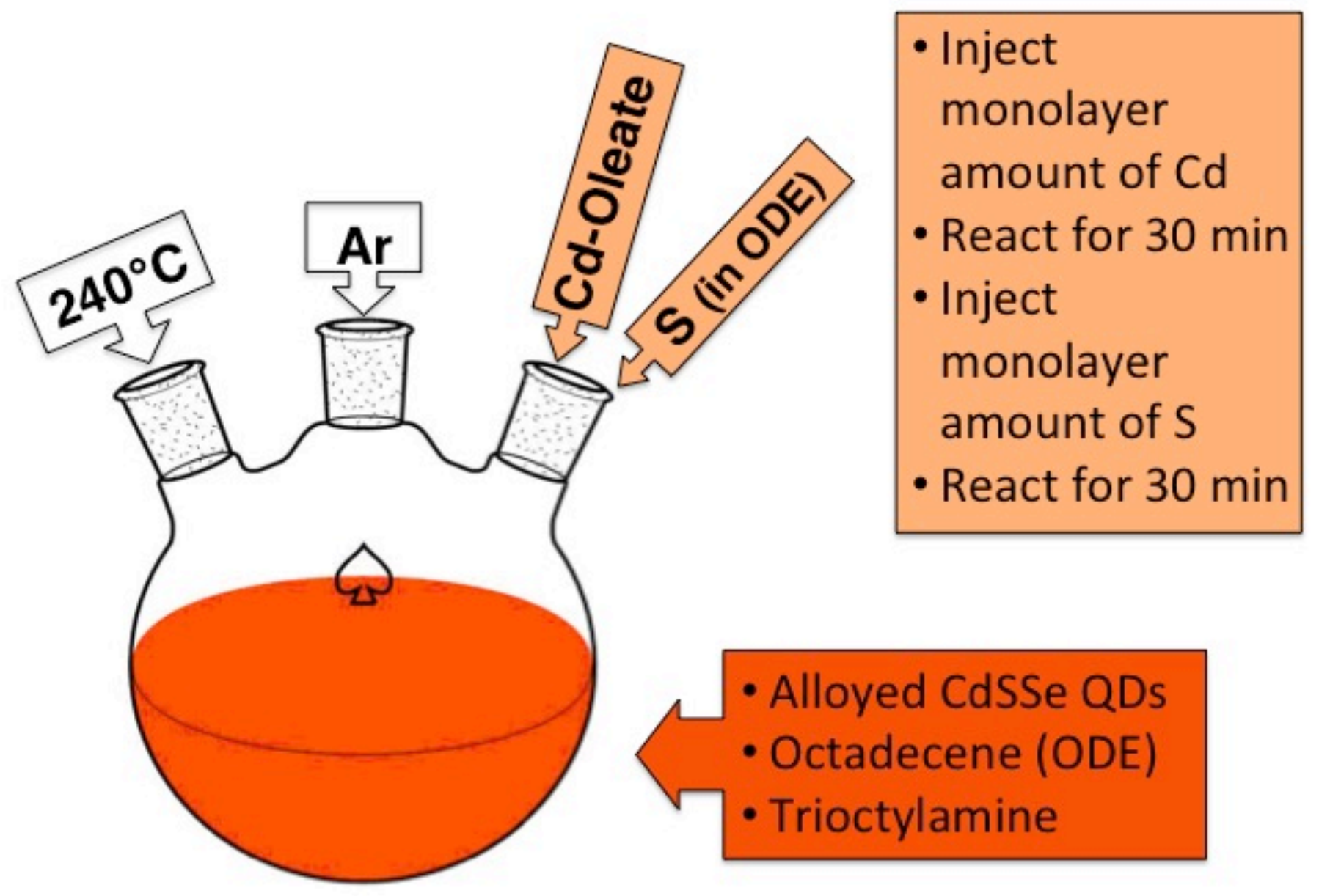


Figure 4: Reaction scheme for synthesis of CdSe-CdS core alloy [3]

- Studying photoluminescence and structural properties
- **Optimizing the quantum yield and size-distribution:**
  - Quantum yield is determined via fluorescence spectroscopy
  - Particle size obtained from transmission electron microscopy (TEM) images
- Two shelling procedures were performed and compared

Methods and Results

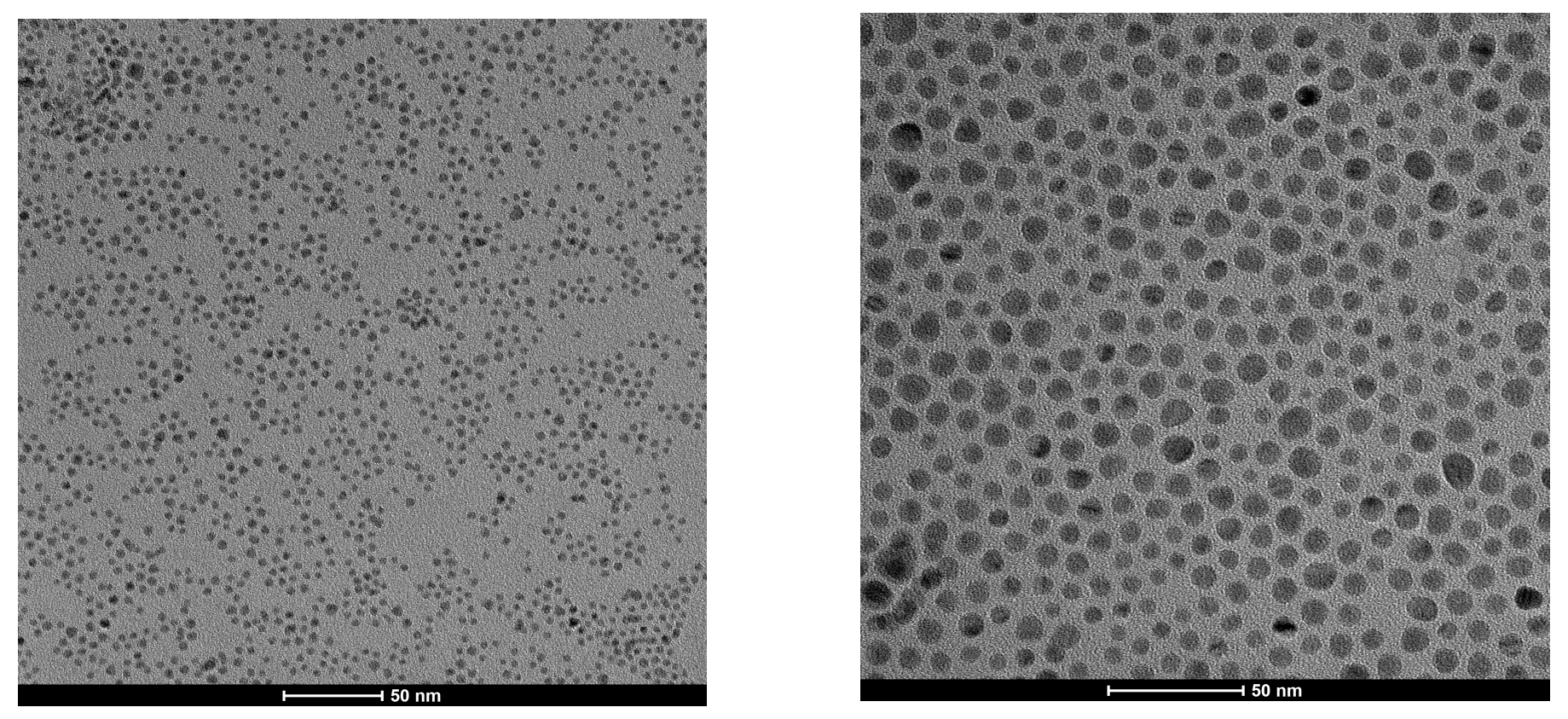
Successive Ion Layer Adsorption and Reaction (SILAR)



- Inject monolayer amount of Cd
- React for 30 min
- Inject monolayer amount of S
- React for 30 min

- Alloyed CdSSe QDs
- Octadecene (ODE)
- Trioctylamine

Figure 5: Reaction conditions for SILAR method



Cores
Avg. Diameter = 4.82 nm
FWHM = 0.76 nm

Shelled
Avg. Diameter = 8.73 nm
FWHM = 3.95 nm

Figure 6: TEM images for cores and SILAR-shelled QDs (scale bars 50 nm) [4]

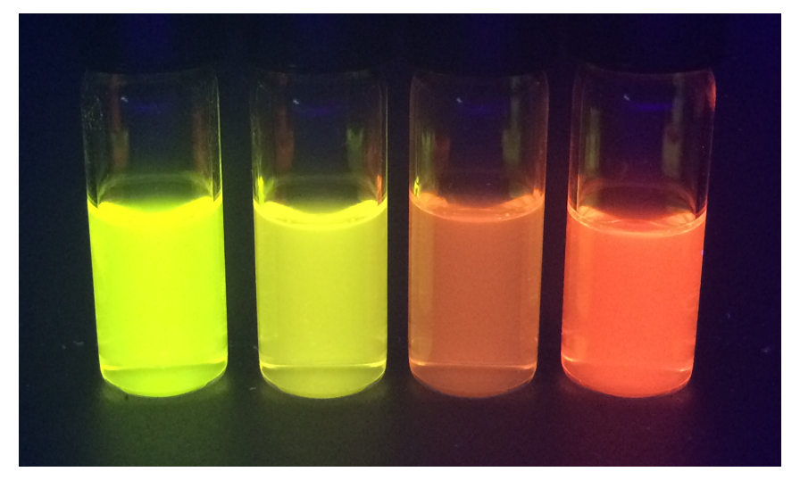


Figure 7: Red-shift of SILAR-shelled QDs under UV-light. From left to right: cores, 1 ML, 3 ML, 5 ML

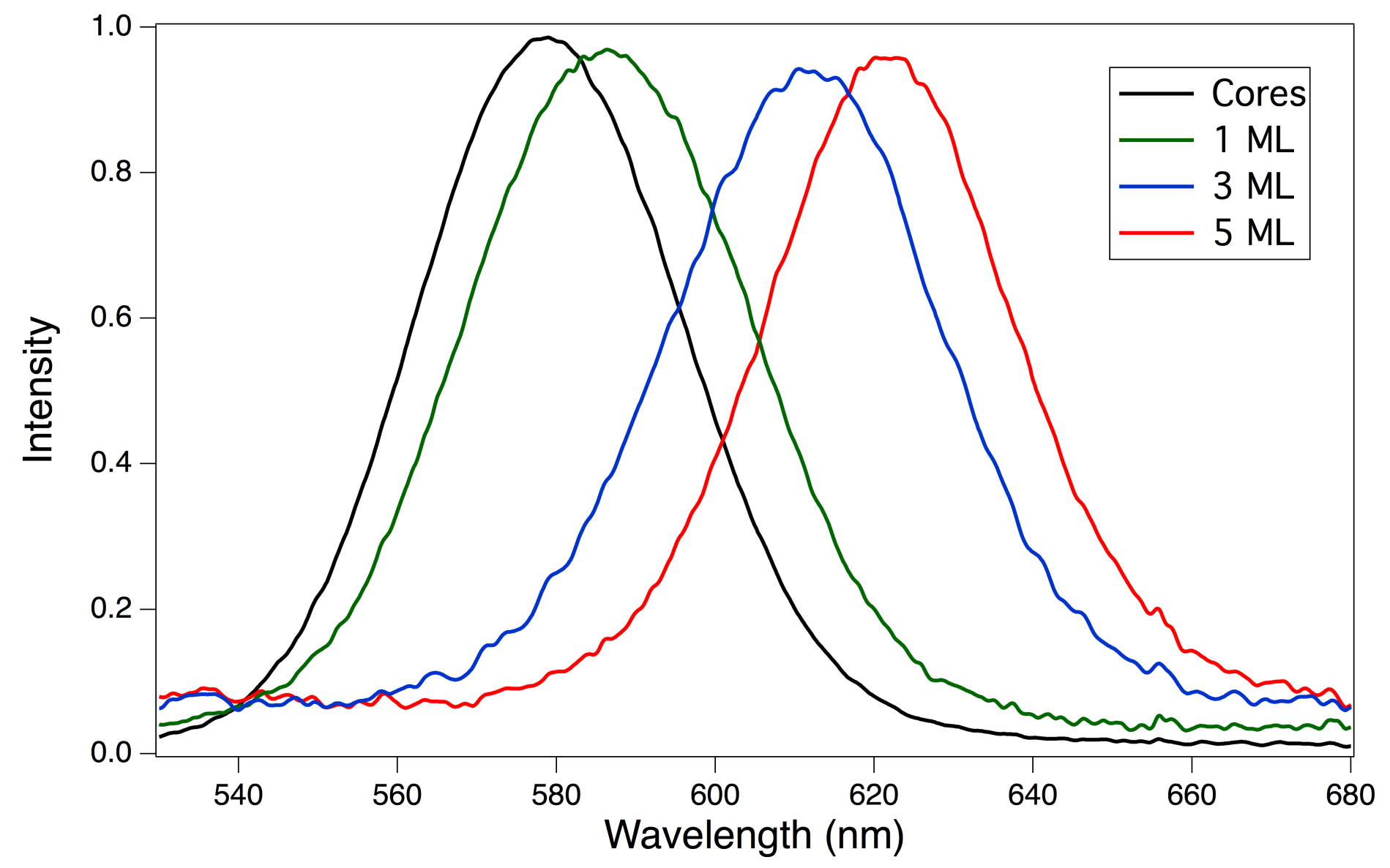
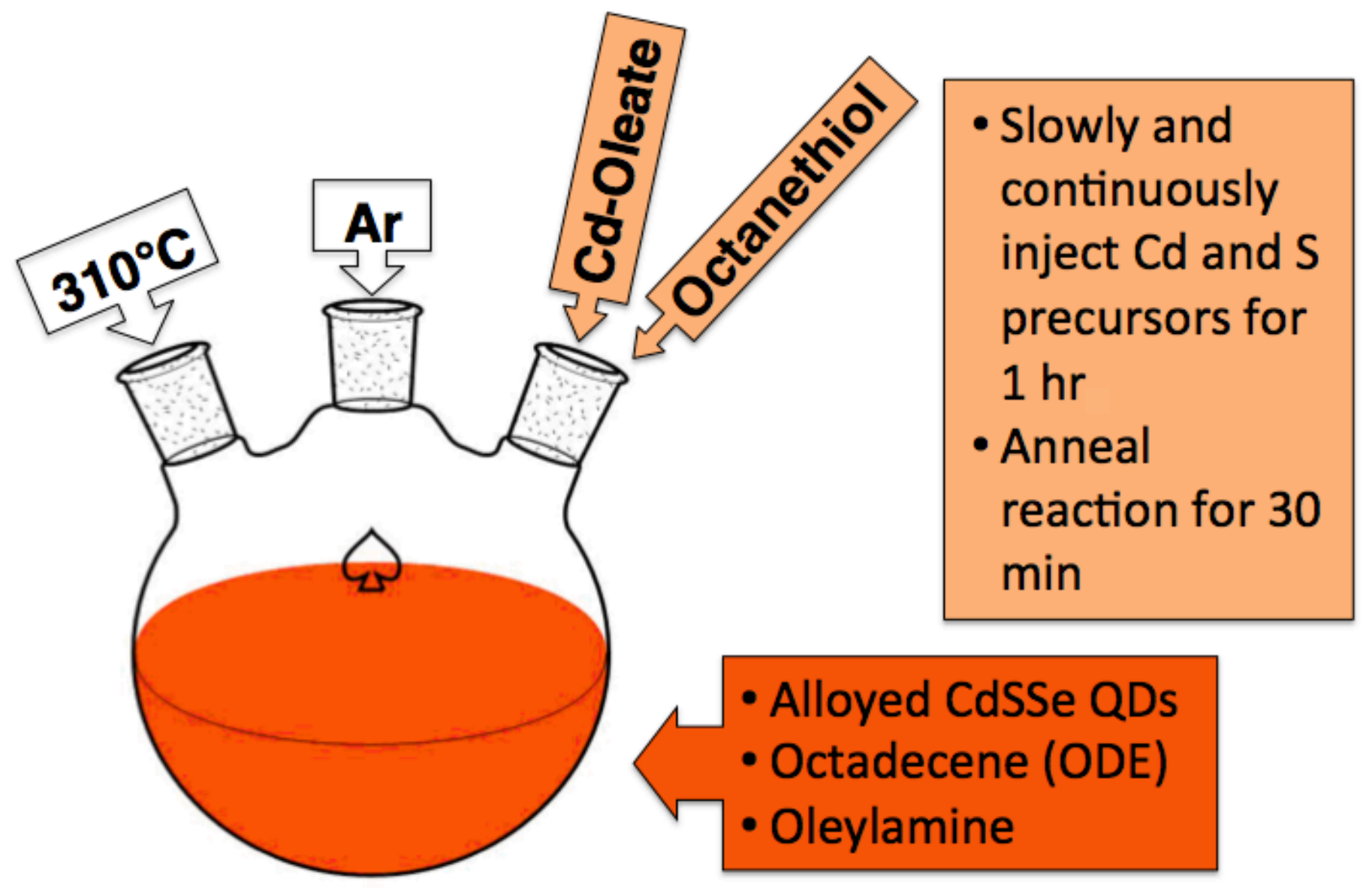


Figure 8: Normalized emission spectra for SILAR method

Table 1: Summary of results for SILAR method

Sample	Quantum Yield (%)	Max Emission (nm)	FWHM (nm)
Cores	74.3	579.16	39.58
1 ML	54.3	586.56	41.90
3 ML	17.4	611.38	40.95
5 ML	33.0	621.88	38.08

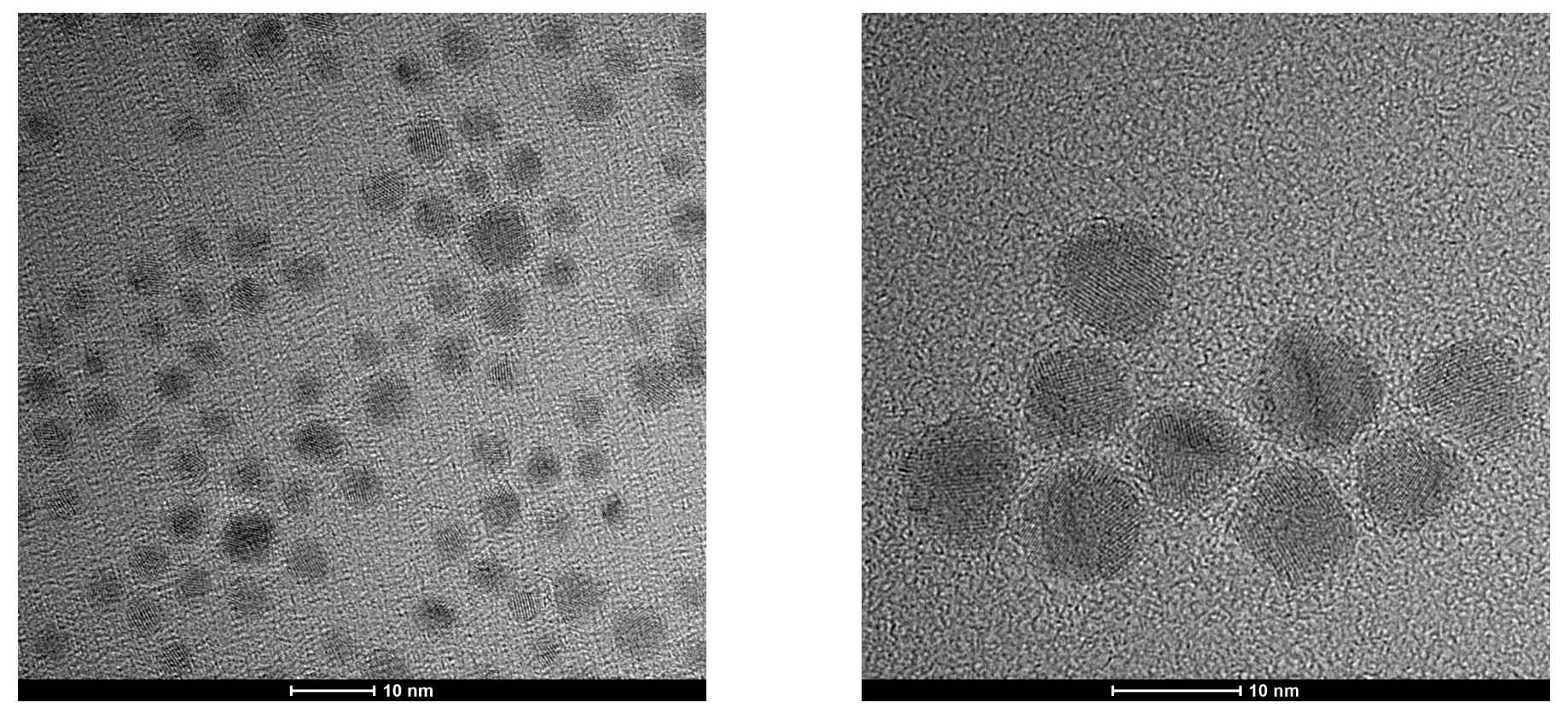
Continuous Precursor Infusion



- Slowly and continuously inject Cd and S precursors for 1 hr
- Anneal reaction for 30 min

- Alloyed CdSSe QDs
- Octadecene (ODE)
- Oleylamine

Figure 9: Reaction conditions for continuous infusion method



Cores
Avg. Diameter = 4.8 nm
FWHM = 0.76 nm

Shelled
Avg. Diameter = 9.5 nm
FWHM = 1.9 nm

Figure 10: TEM images for cores and continuous infusion-shelled QDs (scale bars 10 nm) [4]

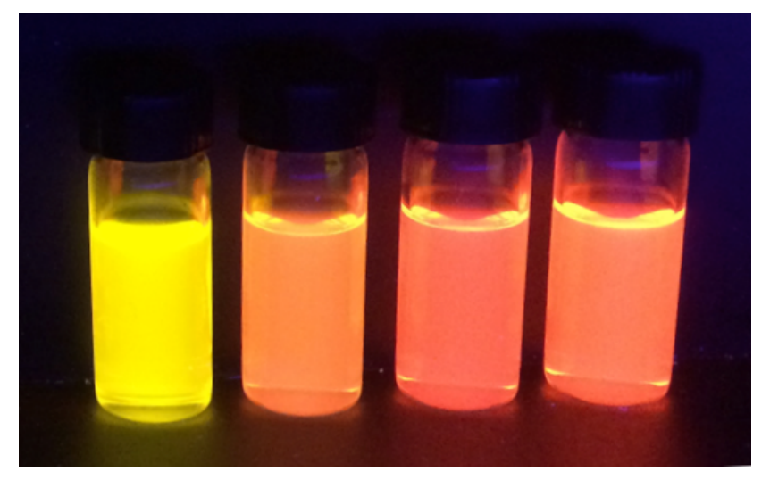


Figure 11: Red-shift of continuous infusion-shelled QDs under UV-light. From left to right: cores, 40 min, 75 min, 90 min

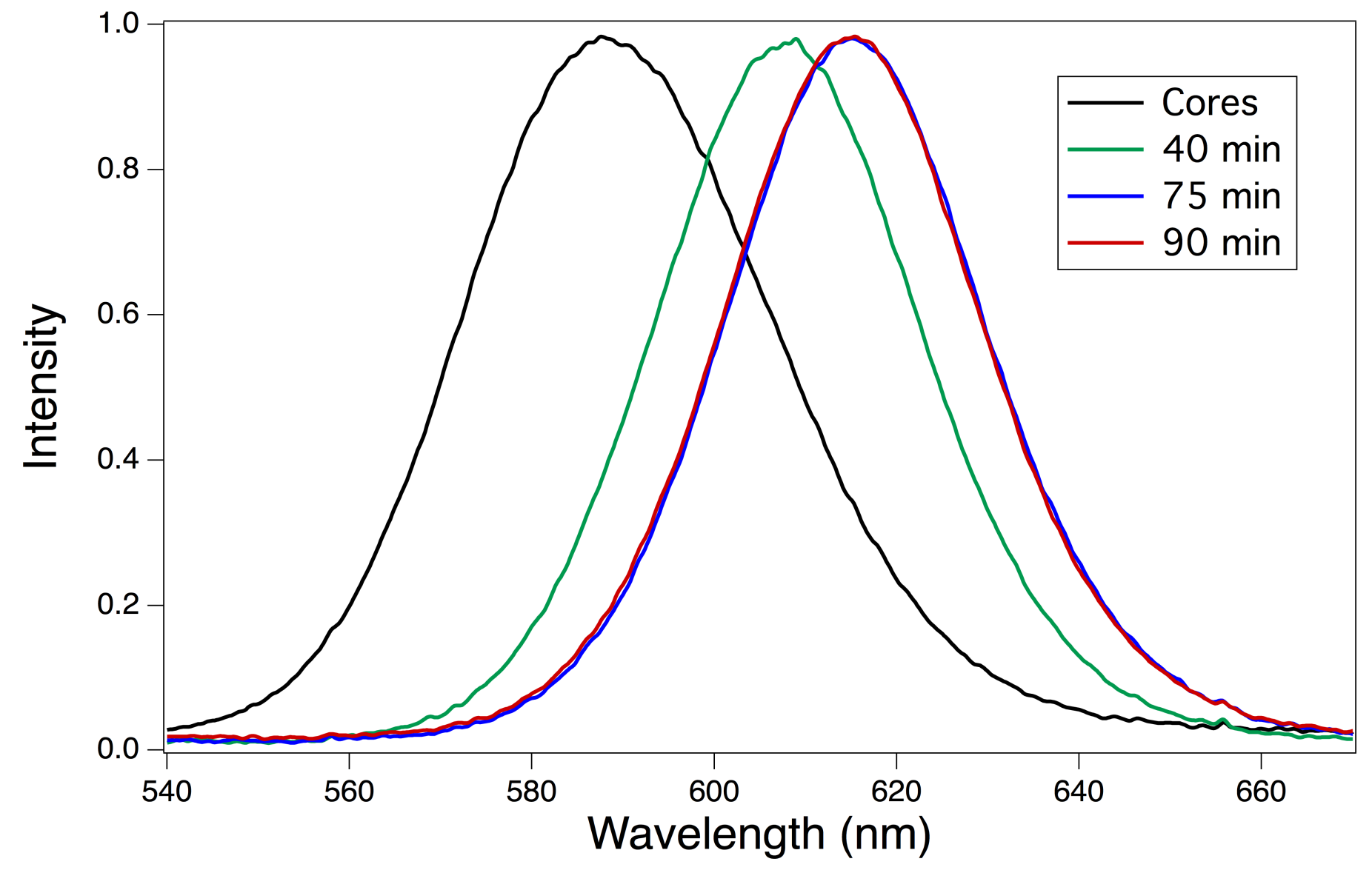


Figure 12: Normalized emission spectra for continuous infusion method

Table 2: Summary of results for continuous infusion method

Sample	Quantum Yield (%)	Max Emission (nm)	FWHM (nm)
Cores	74.3	589.59	40.09
40 min	54.0	608.09	34.97
75 min	45.9	615.50	34.53
90 min	62.0	615.15	34.51

Conclusions

SILAR Method

- Uneven size distribution
- Lower quantum yield
- Long reaction time

Continuous Infusion Method

- Narrower size distribution
- High quantum yield
- Shorter reaction time

<u>Applications in Biological Imaging</u>

- A thicker CdS shell:
  - Makes the QD more robust to biological ligand exchanges and conjugation
  - Protects the QD from a harsh biological environment
  - Confines the electron-hole pair inside the QD and retains optical properties

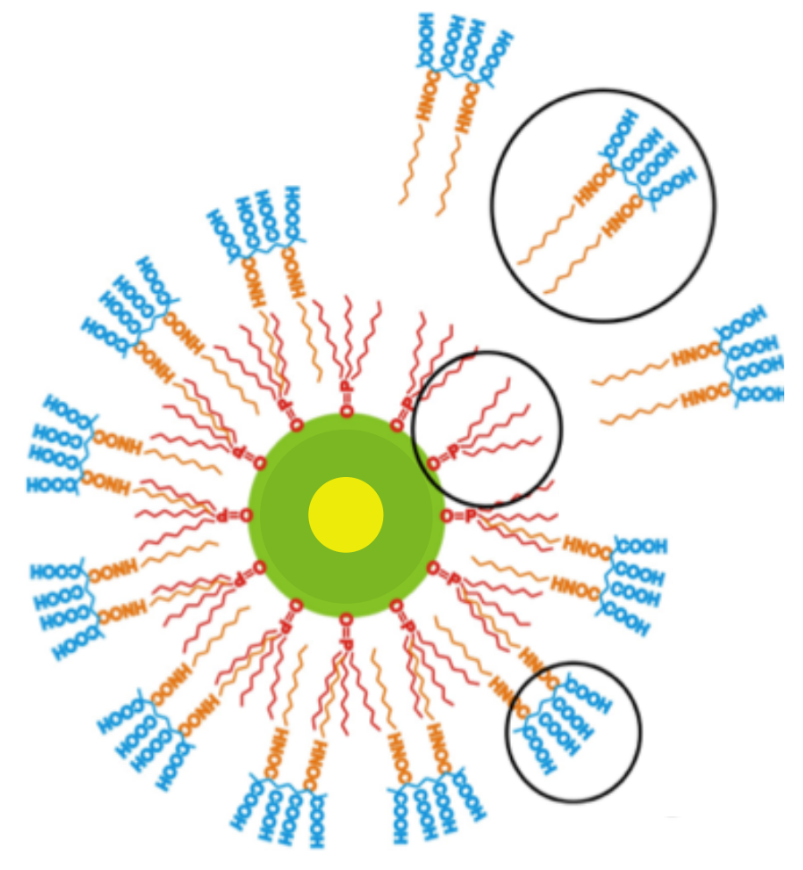


Figure 13: Core/Shell QD under ligand-exchange and biological conjugation for single-protein tracking [5]

Future Work

<u>Further optimize shelling procedure</u>

- Use syringe pumps for more consistent precursor injection
- Size-separate alloyed cores via column chromatography to produce better shelled-QD size distribution

<u>Study other optical properties</u>

- **Photostability**
  - "Blinking" and correlation to QD structure

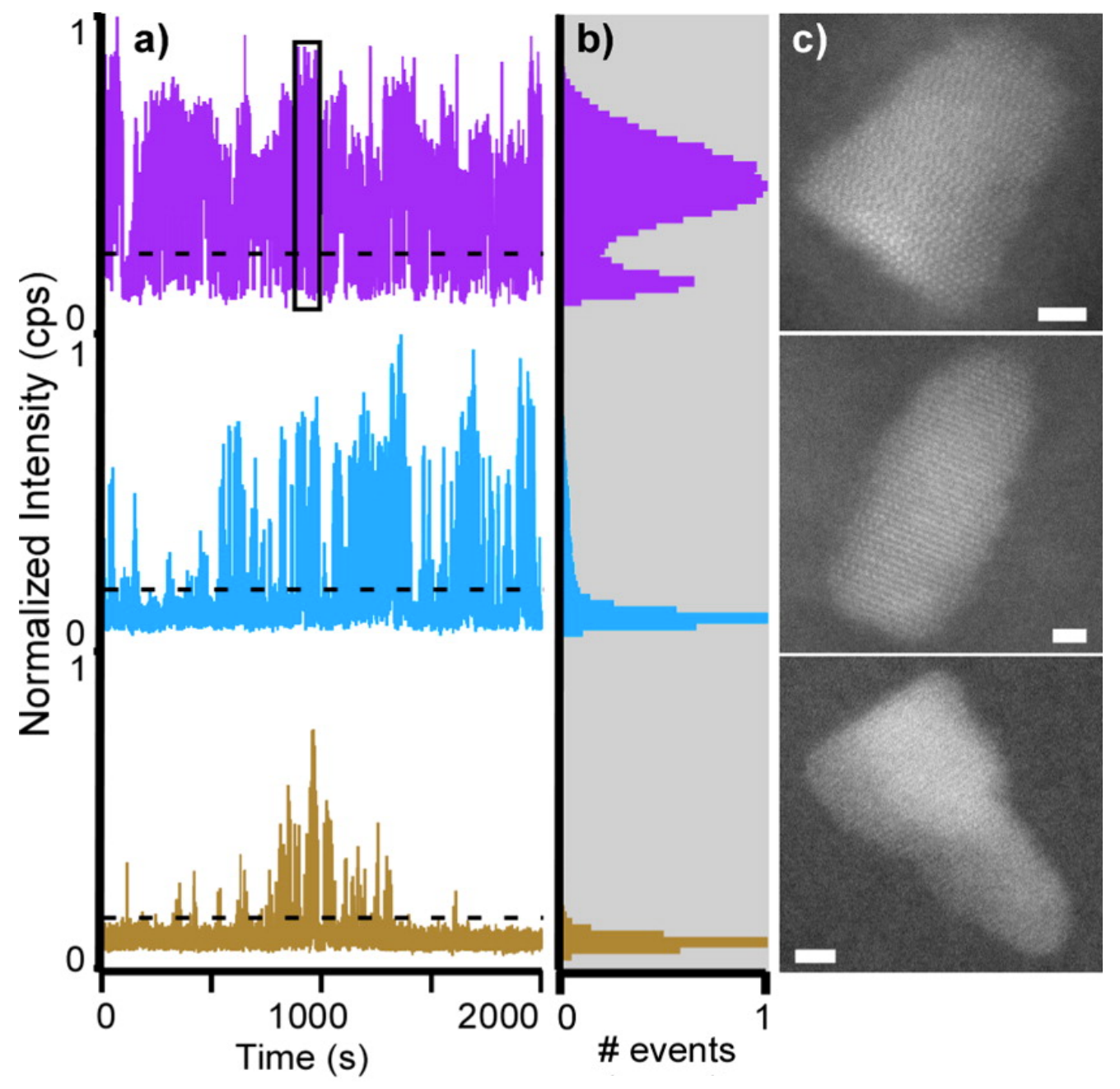


Figure 14: Correlation between photostability and QD structure [6]
a) Full fluorescence intensity
b) Corresponding histograms
c) TEM of individual QDs (scale bars 2 nm)

References

1. Image from http://www.sigmaaldrich.com/content/dam/sigma-aldrich/materials-science/nanomaterials/quantum-confinement-effect.jpg
2. Image courtesy of Dr. Oleg Kovtun
3. M.A. Harrison, *Isr. J. Chem*. **2012**, 52, 1063-1072
4. Images obtained by Kemar Reid
5. J.C. Chang, *J. Neurosci.* **2012**, 32(26), 8919-8929
6. N.J. Orfield, *ACS Nano.* **2015**, 9, 831-839

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