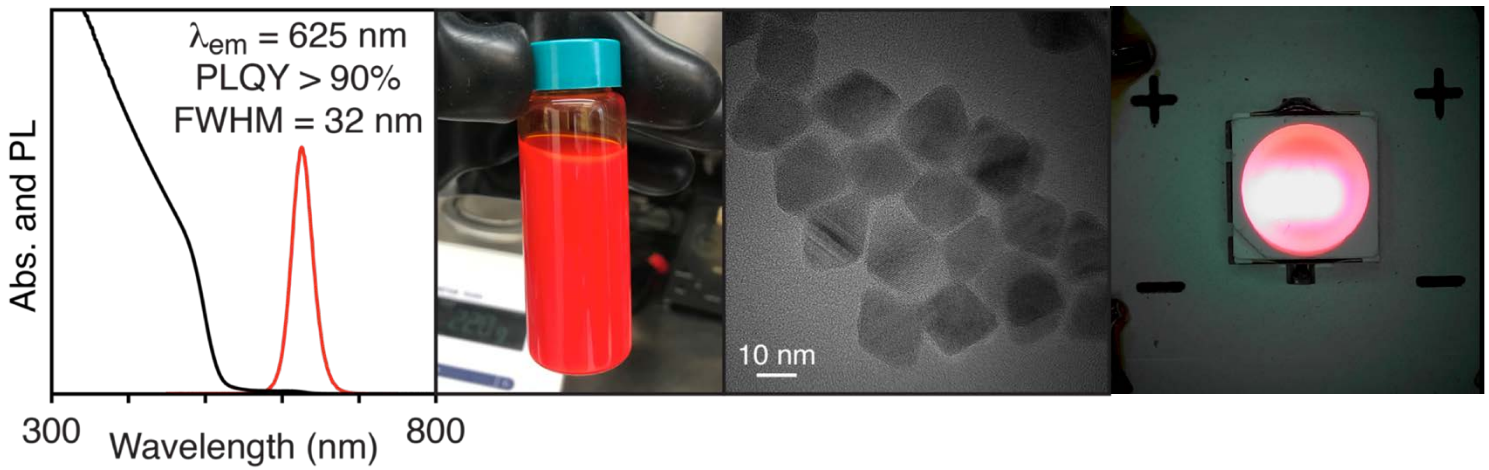
Graded Alloy Quantum Dots for Energy Efficient Solid State Lighting.



Columbia University, Osram Opto Semiconductors, Lawrence Berkeley National Laboratory
Jonathan S. Owen, Associate Professor of Chemistry
(212) 851-5879, jso2115@columbia.edu

Project Summary

Timeline:

Start date: 9/01/2016
Planned end date: 08/31/2018
Key Milestones

1. Meet and exceed industry standard performance using cost effective and scalable manufacturing process. Key performance metrics:

$\lambda_{max} = 625 \pm 5$ nm, PLQY > 95%, FWHM < 35 nm, at 150°C and 1 W/mm^2

Key Partners:

Columbia University	New York, NY
Osram Opto Semiconductors (Formerly Pacific Light Technologies)	Portland, OR
Lawrence Berkeley National Laboratory	Berkeley, CA

Budget:

Total Project $ to Date: Acquisition of Pacific Light Technologies has complicated financial reporting.

- Research program continues as planned.

Total Project $:

- DOE: $1,014,798
- Cost Share: $257,534

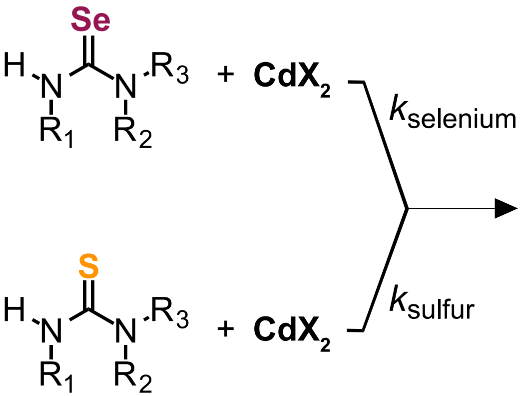
Project Outcome:

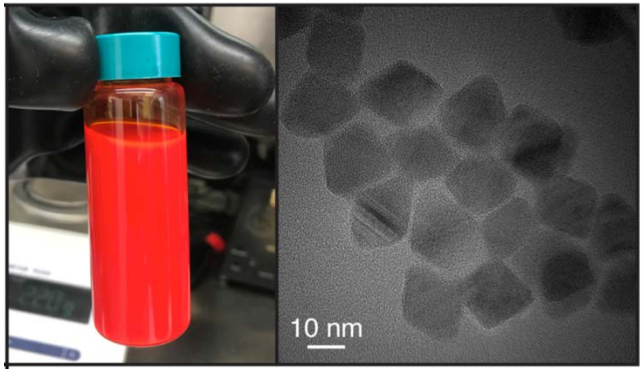
The target is to develop red emitting quantum dots that have sufficient stability on LED chips to withstand the flux, temperature, and reliability requirements of high-power LED operation.

Team

PI: Jonathan Owen
Columbia University

Precursor Libraries/Kinetics
Heterostructure Scale-up

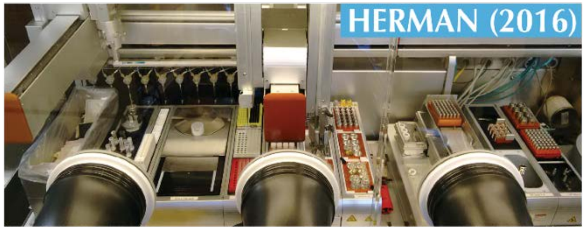




Owen *et al.*, *Science*, **2015**.

Dr. Emory Chan
Molecular Foundry,
Lawrence Berkeley
National Laboratory

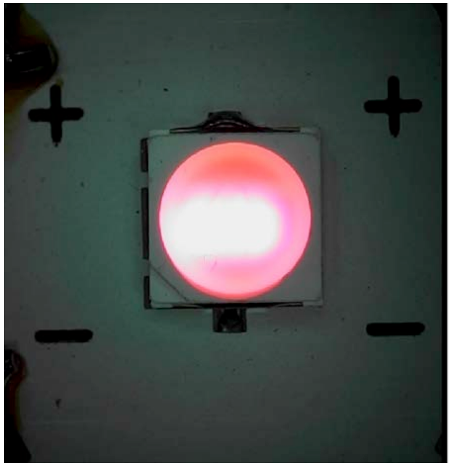
High Throughput
Screening Robotics



Chan *et al.*, *Nano Lett.*, **2010**.

Dr. Juanita Kurtin
Osram Opto
Semiconductors
(formerly Pacific
Light Technologies)

Device Fabrication and
High Throughput
Performance Testing



Kurtin *et al.*, *Phot. Res.*, **2017**.

Challenge

Problem Definition: Improved narrow band, red emitting down conversion phosphors are needed to increase the efficiency and improve the color rendering of solid state lighting.

Quantum Dots are leading candidates to achieve the performance goals outlined in the Solid State Lighting 2017 R&D Plan. (λ_{max} = 625 ± 5 nm, PLQY > 90%, FWHM < 35 nm, thermal stability > 90% at 150˚C.) **Stability under operation is the key challenge!**

1) Efficiency gains provided by narrow band red phosphors can reduce global energy consumption by as much as 1%.

2) Improved color rendering increases the user experience in retail applications (color of food, clothing, sporting events).

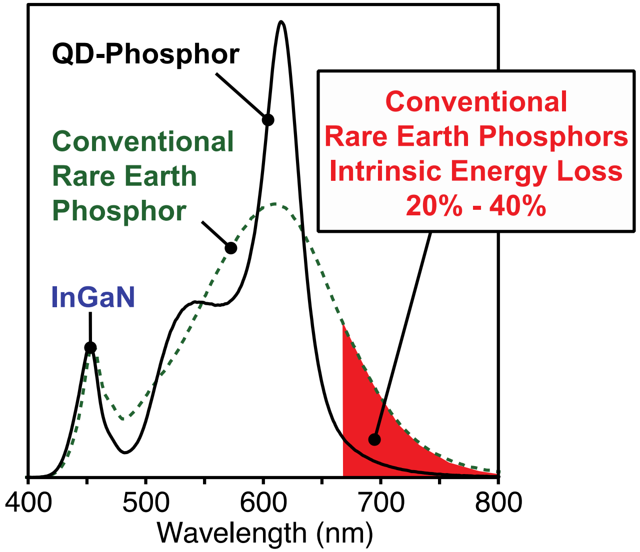
3) Spectral tunability can increase the productivity and lower the costs of indoor agriculture.

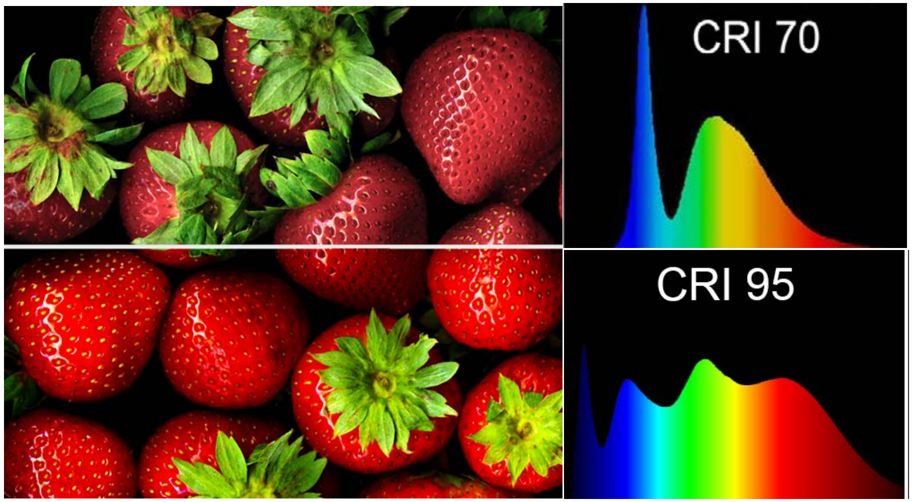
Impact

Improved narrow band, red emitting, down conversion phosphors can increase the luminous efficiency of solid state lighting packages while improving the color rendering index (CRI).

QDs improve the lumens per watt efficiency at 90 CRI (142 lm/W to 162 lm/W).

Solid State Lighting 2017 R&D Plan: 2020 Targets
λ_{max} = 625 ± 5 nm, PLQY > 95%, FWHM < 35 nm, at 150°C and 1 W/mm^2.



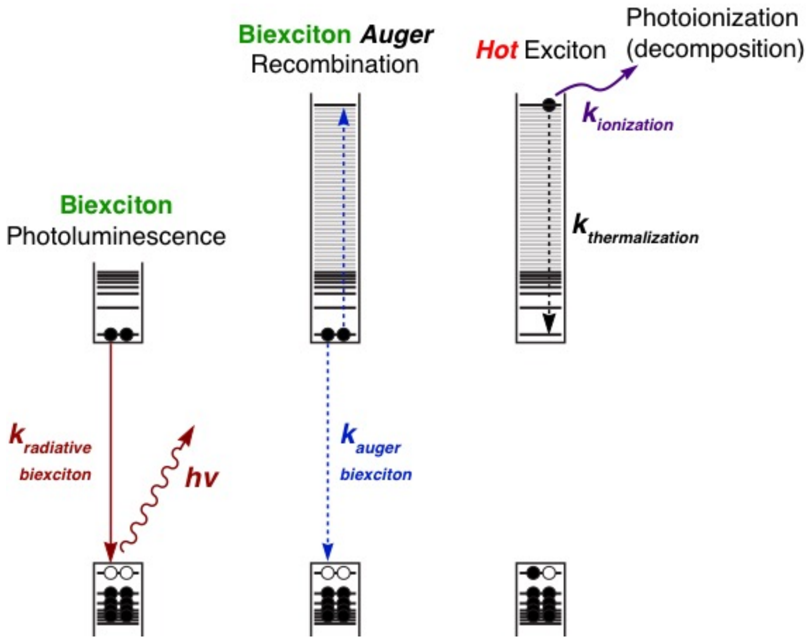


Improved synthesis reduces the labor and capital costs, scalability, and safety.

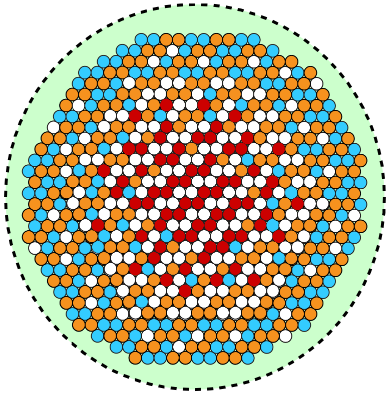
Approach: Improve QD Microstructure

Controlling the QD microstructure can address key performance challenges including photothermal quenching and reliability during LED operation.

-High intensity irradiation "on chip" leads to Auger recombination losses/decomposition.



Target QD Architecture



I. Alloy core ($CdSe_{1-x}S_x$)

II. Radially graded interfaces

III. Insulating ZnS shell

IV. Surface passivation

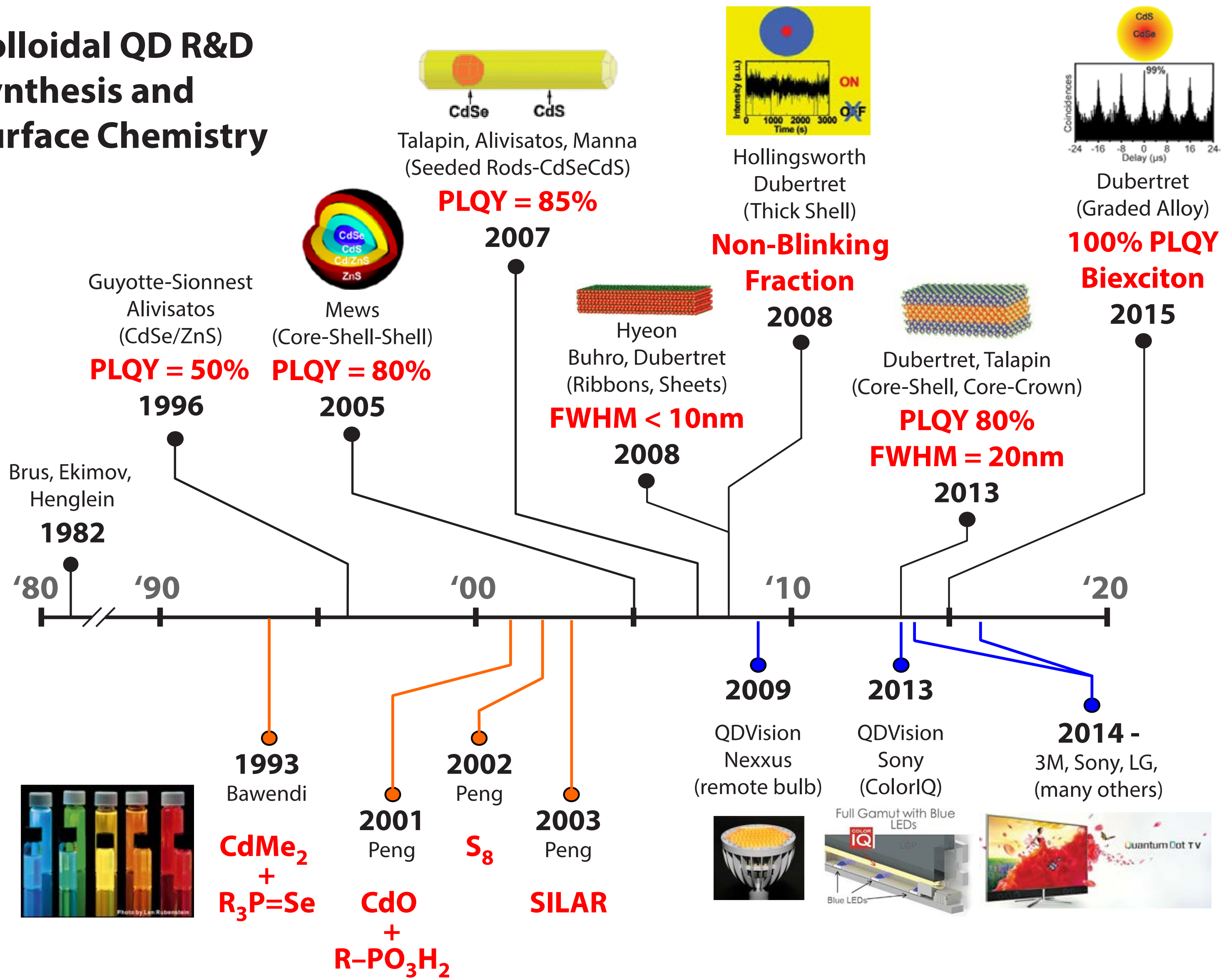
V. Ultrabarrier coating

soft confinement potential slows Auger recombination

- **Large QDs and graded CdSe/CdS** interface reduces Auger recombination.
- **Ultrabarrier coatings** provide environmental stability and reliability.

Approach: Slow Historical Improvements

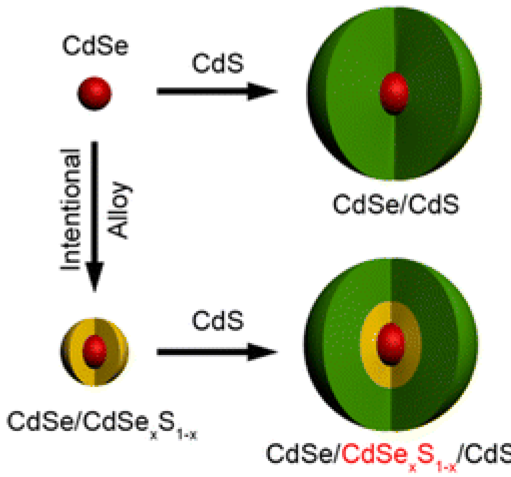
Colloidal QD R&D Synthesis and Surface Chemistry

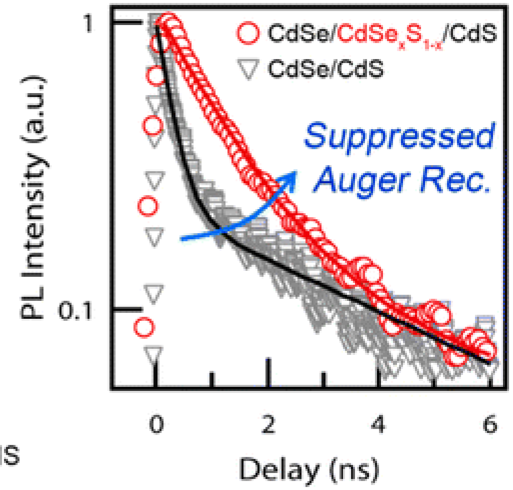


Approach: Graded Alloy Spherical Quantum Wells

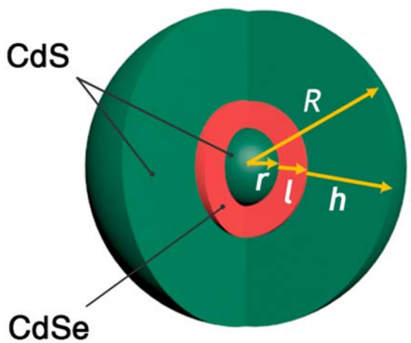
Large, Graded Alloys Suppress Auger Recombination

Dubertret, *Nano Lett.* **2015**.
Pietryga and Klimov, *ACS Nano* **2013**.
Klimov, Htoon *Phys. Rev. Lett.* **2011**.
Cragg and Efros, *Nano Lett.* **2010**.
Rabani and Baer, *Chem. Phys. Lett.*, **2010**.



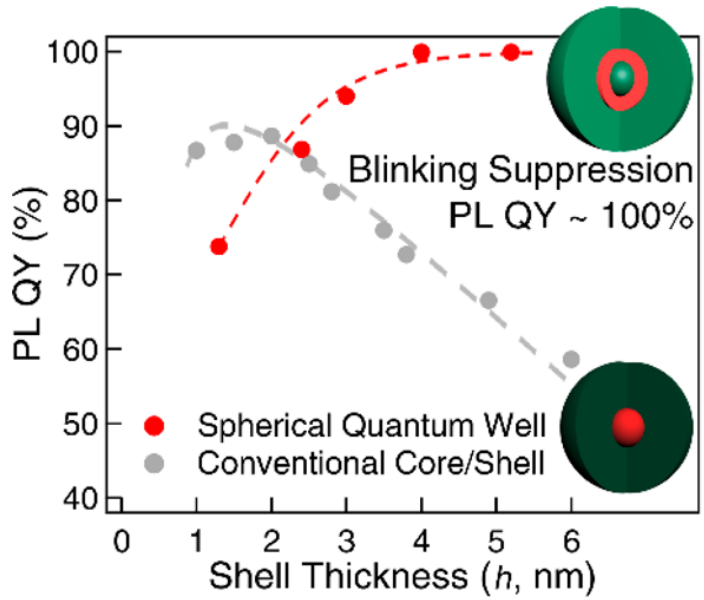


Spherical Quantum Well Architecture Reduces Strain and Defects



Critical thickness for misfit defects (h_c):

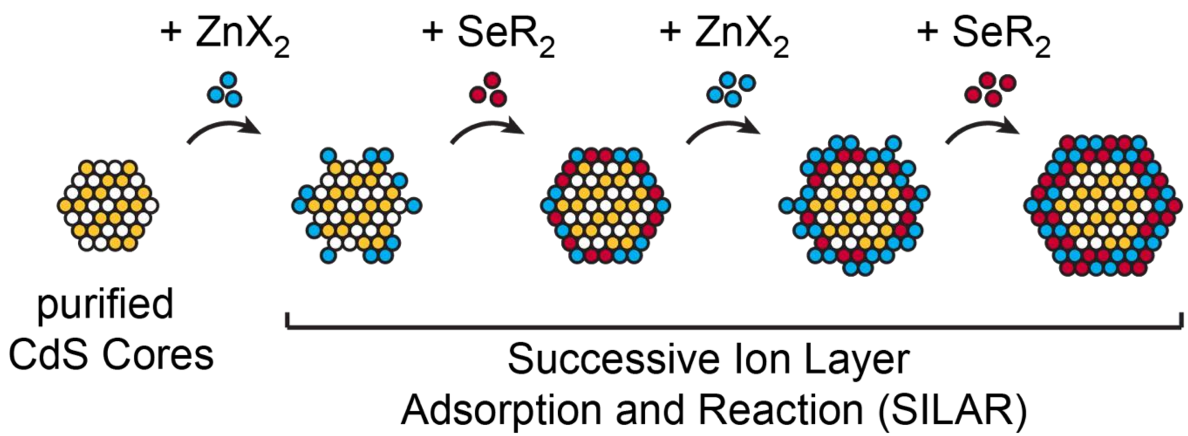
$$h_c = \frac{b}{2\pi f}\frac{(1-\nu\cos^2\alpha)}{(1+\nu)\cos\lambda}\left(\ln\frac{h_c}{b}+1\right)$$



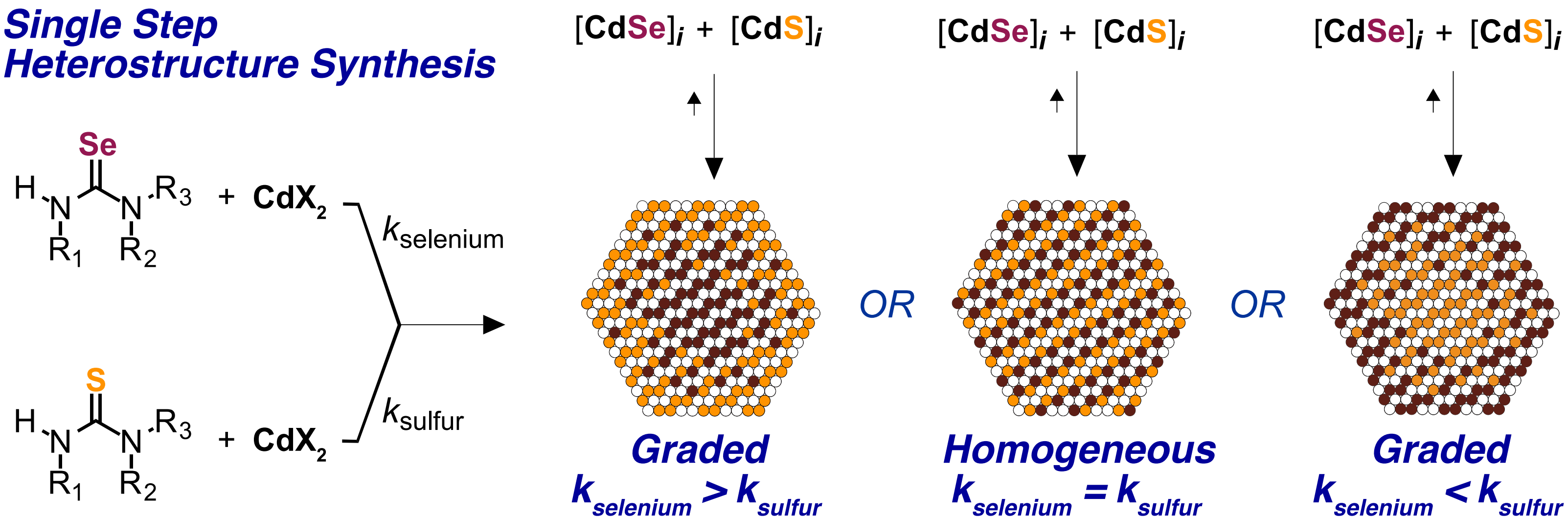
Jeong (Bae) et al. ACS Nano **2016**, *10*, 9297.
Matthews and Blakeslee, J. Cryst. Growth **1974**, *27*, 118-125.

Approach: Rapid Screening and Microstructure Control, Improve Manufacturability and Lower Cost

Layer-by-layer synthesis is difficult to optimize, notoriously irreproducible.

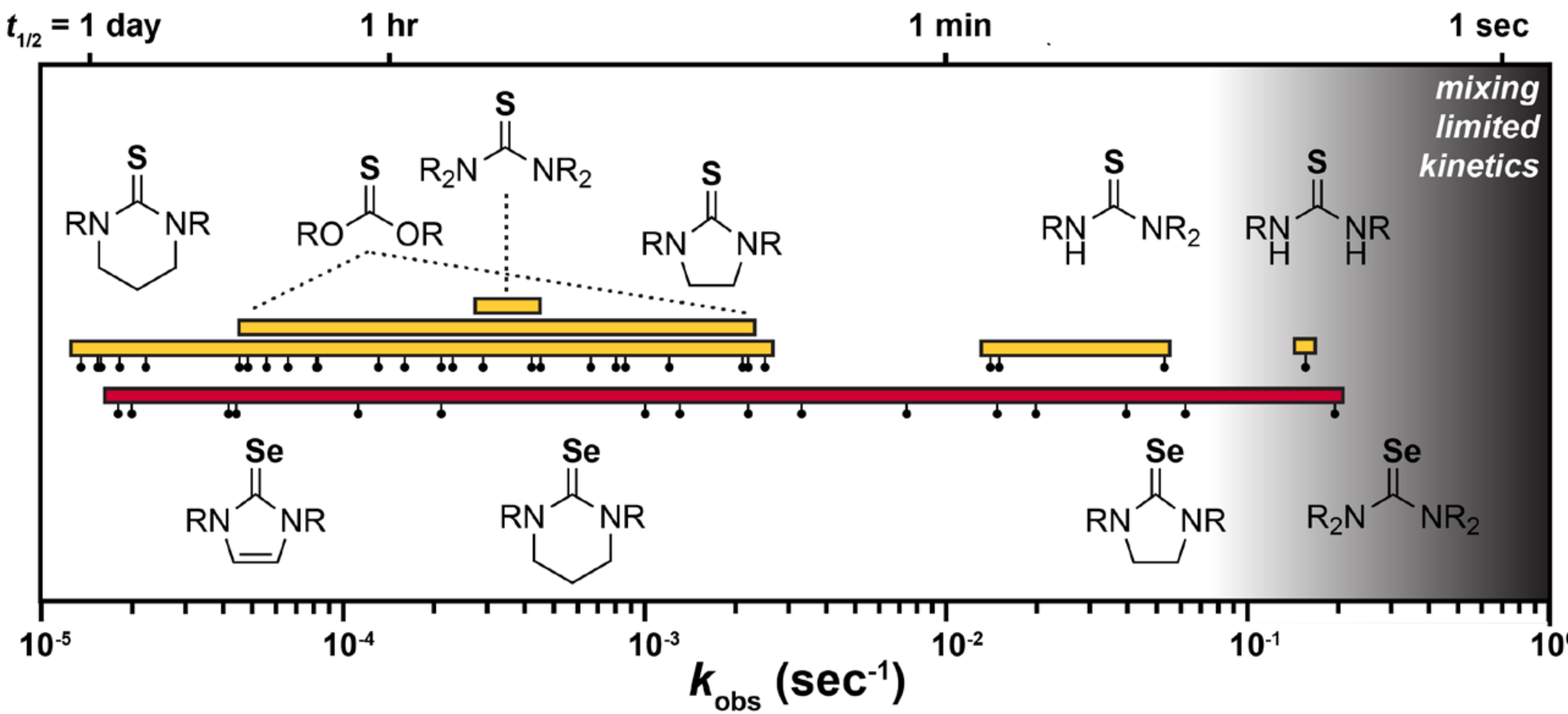


Single Step Heterostructure Synthesis



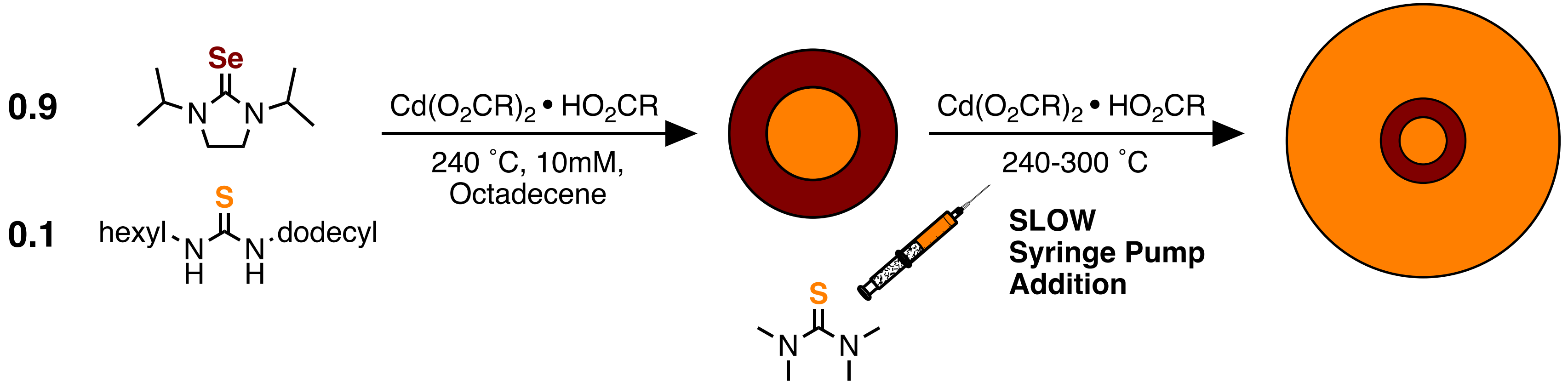
Progress: "Matched Pairs"

$$1.2\ \mathrm{Cd(oleate)_2} + 2.4\ \text{oleic acid} + \mathrm{ER_2} \xrightarrow[240\ ^\circ\mathrm{C},\ 10\ \mathrm{mM}]{\text{octadecene}/\mathrm{Ph_2O}} \mathrm{(CdE)_n(Cd(oleate)_2)_m}$$

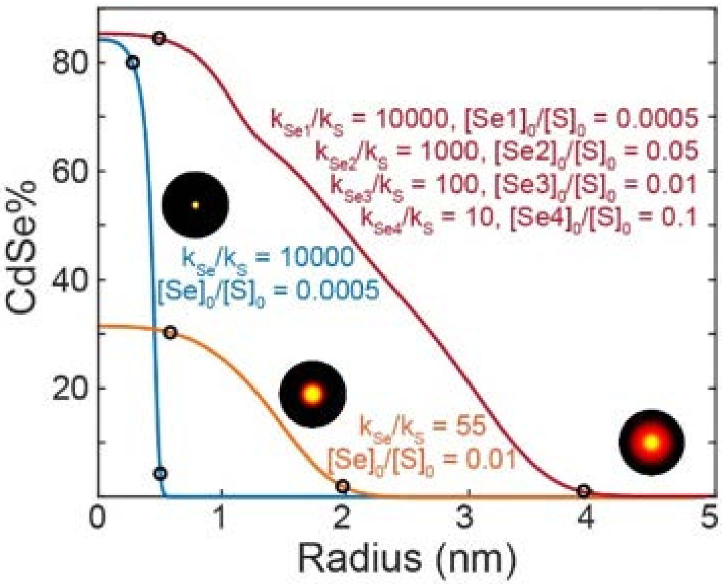


- Simulations suggest $k_{rel} < 10$ provides graded alloys

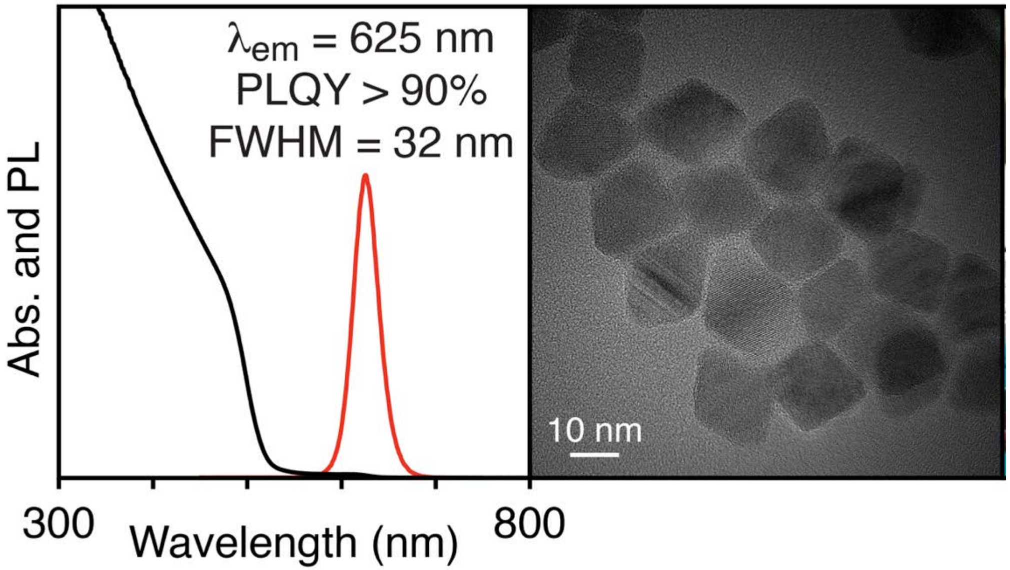
Progress: One Pot Synthesis



Simulations Guide Guide Precursor Selection

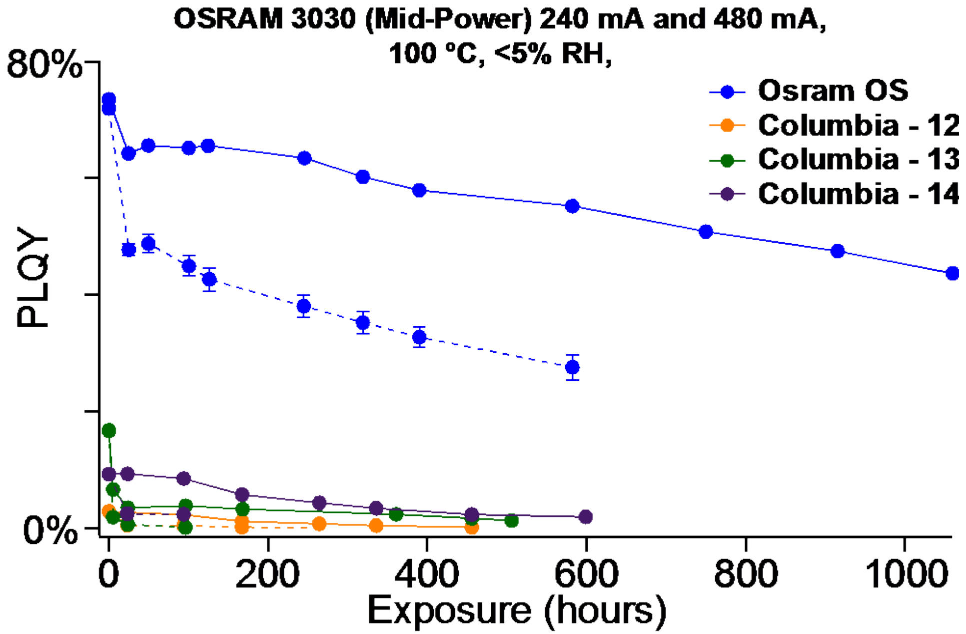


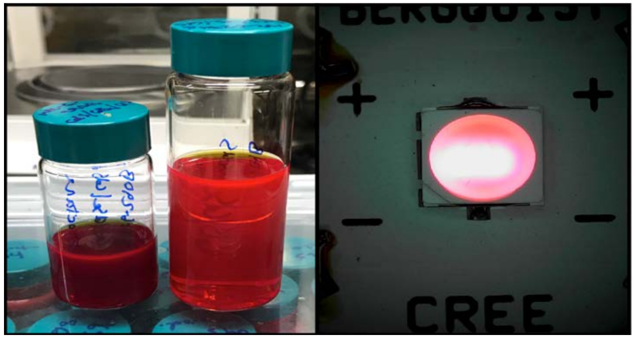
High PLQY (> 90%),Thick Shell QDs Year 1 Target

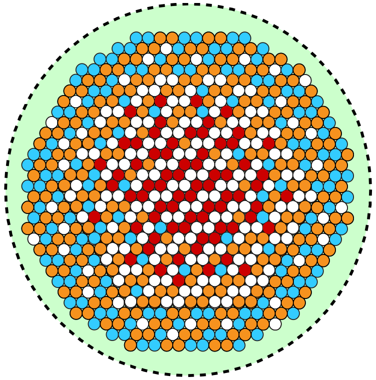


Progress: QDs + Encapsulation and Testing

No ZnS = little PLQY and No Reliability







I. Alloy core ($CdSe_{1-x}S_x$)

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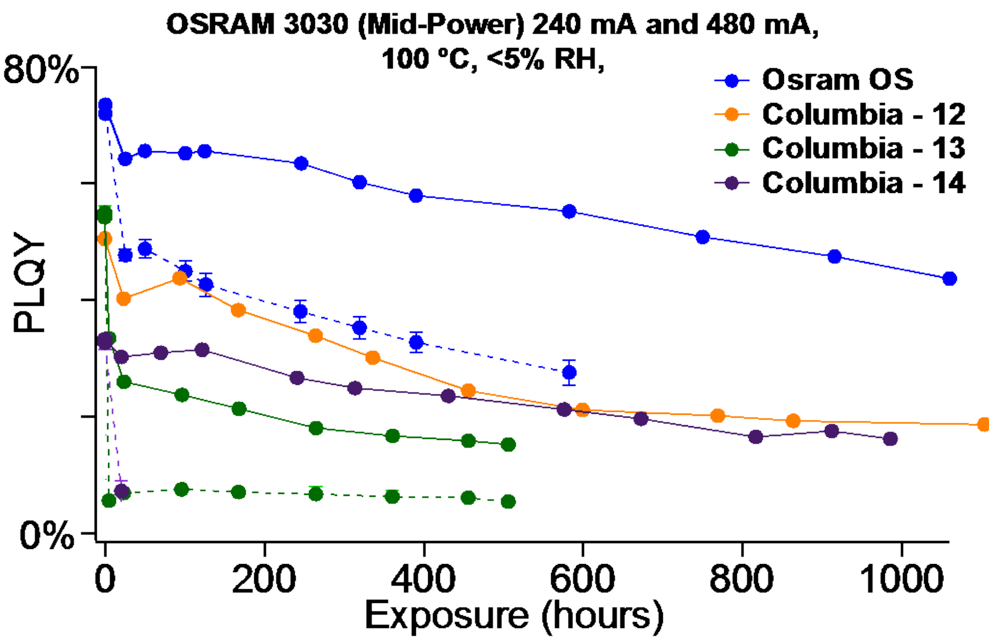
V. Ultrabarrier coating

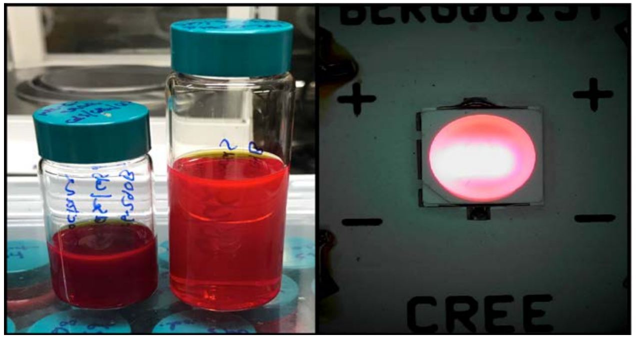
soft confinement potential slows Auger recombination

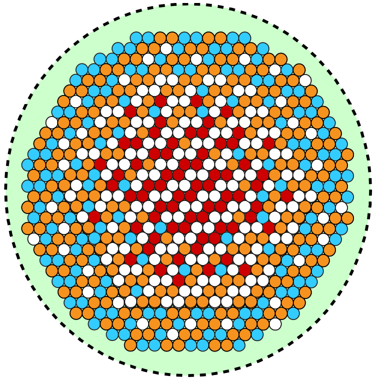
- >100 architectures screened to select narrow, red emitting QDs.
- 16 High performance QDs, encapsulated and evaluated on LED packages.
- Performance near industry state of the art (blue data, $15M and 10 years).
- ZnS Outerlayer is key to long-term reliability and PLQY during operation.

Progress: QDs/ZnS + Encapsulation and Testing

Improved ZnS = Improved Reliability







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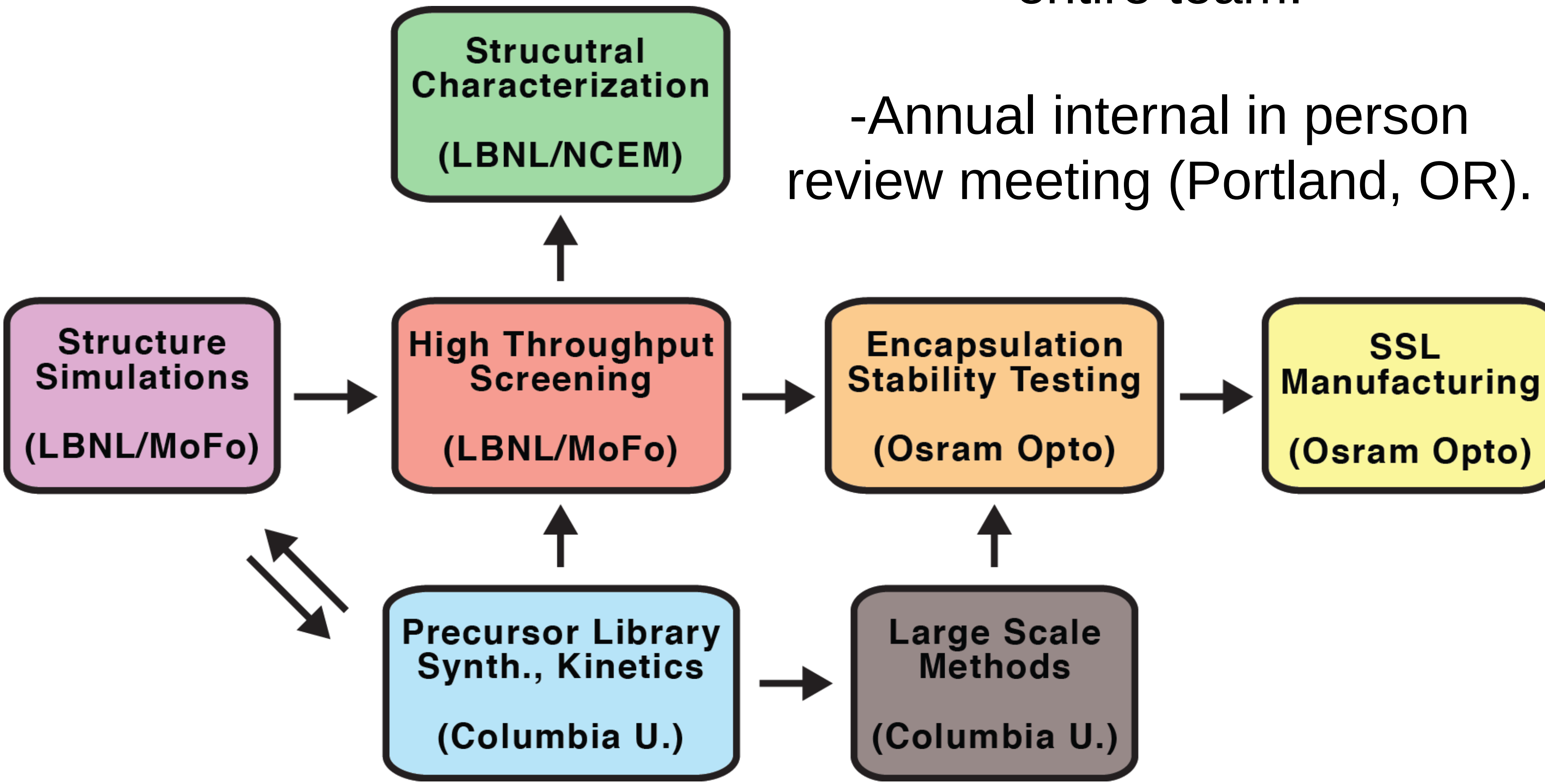
Stakeholder Engagement

-Biweekly conference calls of entire team.

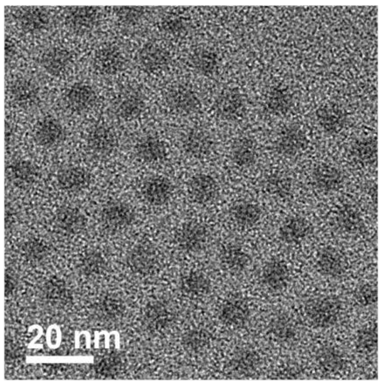
-Annual internal in person review meeting (Portland, OR).

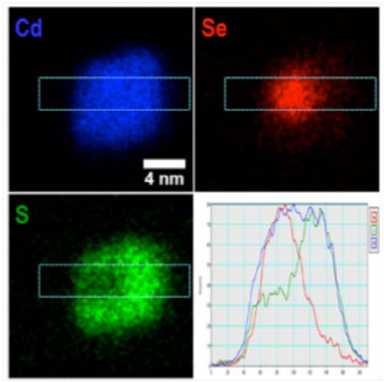


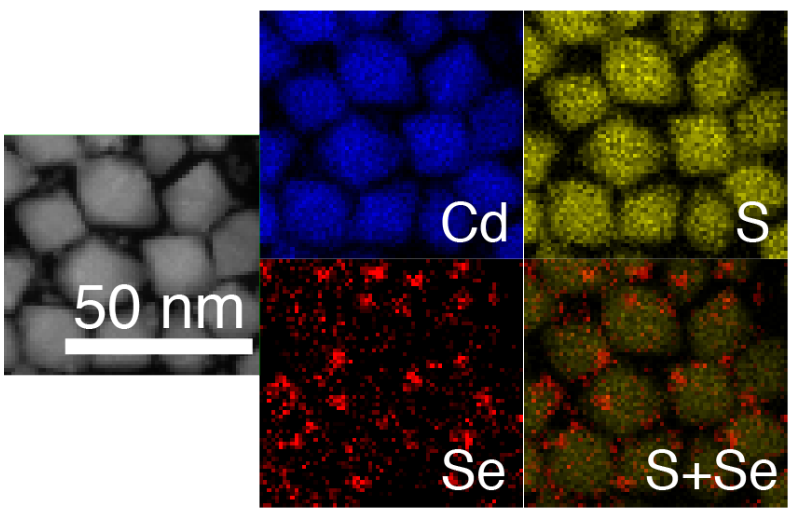
Remaining Project Work: Improve ZnS and MO_x

Anisotropic Shell Growth

Can we force CdSe region near the center of the CdS shell?

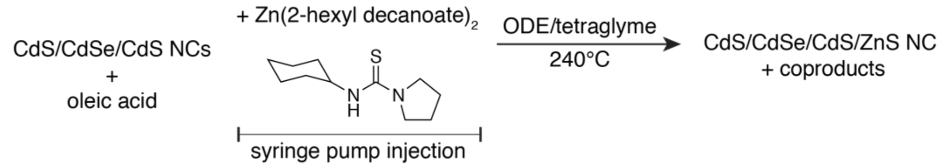


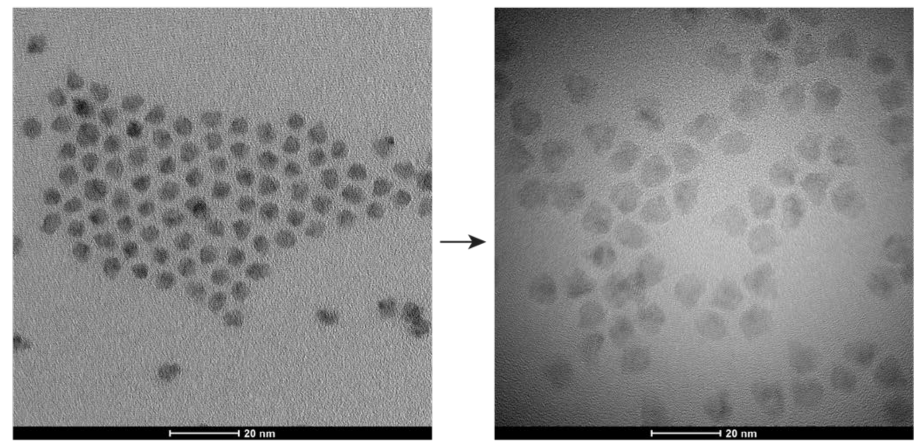




Improving ZnS Shell

Can we increase thickness and passivation?





Metal Oxide Encapsulation

Improved metal oxide ultra-barriers are critical for long-term reliability.

Thank You

Columbia University, Osram Opto Semiconductors, Lawrence Berkeley National Laboratory
Jonathan S. Owen, Associate Professor of Chemistry
(212) 851-5879, jso2115@Columbia.edu

REFERENCE SLIDES

Project Budget

Project Budget: Funds have been spent in the manner described in original budget justification. Budget period 1 and 2 are outlined below.
Variances: None.
Cost to Date: 75%
Additional Funding: Continuation funding pending at, NSF, Kairos Ventures, ARPA-e

Budget History					
Sept. 1, 2016 (past)		FY 2018 (current)		FY 2019 – Aug. 31, 2018 (planned)	
DOE	Cost-share	DOE	Cost-share	DOE	Cost-share
$535,081	$131,842	$479,717	$132,692		

Project Plan and Schedule

Milestone Summary Table				
Columbia University – Graded Alloy Quantum Dots For Energy Efficient Solid State Lighting				
Milestone	Description	Verification Process	Month	Complete?
Budget Period 1				
Technical	Encapsulation and film state testing; baseline PLQY at λ_{max} = 625 ± 10nm with FWHM < 100 nm @ 25 °C.	PLQY and thermal stability measurements at 1 and 10 W/cm^2 and 25–130˚C.	3	YES
Technical	Establish library of >20 S precursors and >10 Se precursors (1-5 g ea.). k_S, k_{Se} span >4 orders of magnitude.	^{1}H, ^{13}C NMR spectroscopy. k_S, k_{Se} by fitting temporal evolution of in situ absorbance or via NMR.	6	YES
Technical	HT tuning of composition of the core & V_{shell}/V_{core}. 10 compositions with d > 10 nm, λ_{max} = 625 ± 5 nm, PLQY > 40% , FWHM < 40 nm @ 25 °C.	HT screening microplate readers. d via TEM. Composition via simulations & STEM-EELS. PLQY in integrating sphere.	9	YES
Go/No Go	HT screening for large QDs (d > 25 nm). Criteria: Silicone film: λ_{max} = 625 ± 5nm, FWHM < 35 nm, PLQY > 75% @ 25 °C, thermal stability > 80% at 150˚C. HOTL reliability on chip: 30 W/cm^2 and 85 ˚C, < 10% decrease in PLQY over 1000 hours.	TEM, on-chip long-term stability testing.	12	Partially

Project Plan and Schedule

Milestone Summary Table				
Columbia University – Graded Alloy Quantum Dots For Energy Efficient Solid State Lighting				
Milestone	Description	Verification Process	Month	Complete?
Budget Period 2				
Technical	Identification of 3 matched pairs of S and Se precursors ($k_S/k_{Se} < 5$). k_S, k_{Se} span 2 orders of magnitude. Determination of kinetic rate law.	Kinetic analysis as described above. Rate law determined by fitting curves describing the rate vs. S or Se concentration.	15	Yes
Technical	HT optimization of GA-QD's tuning width of graded region & particle volume to meet DOE 2014 performance: $\lambda_{max} = 625 \pm 5$ nm, PLQY > 90%, FWHM < 35 nm, thermal stability > 90%.	Performance measurements taken as detailed above. Thermal stability at @ 150 °C, 100 W/cm^2.	18	Partially
Technical	HT optimization of green ($\lambda_{max} = 530 \pm 7$ nm) and amber (588 ± 7 nm) GA-QDs with PLQY > 90%, FWHM < 35 nm, thermal stability > 90%.	Spectral measurements taken as detailed above. Thermal stability at 100˚C and 25 W/cm^2.	21	No
Technical	GA $CdSe_xS_{1-x}/ZnS$ QDs at λ_{max} 625 ± 5nm, with PLQY > 93%, 93% thermal stability, FWHM < 30 nm, flux density saturation > 90%.	Flux density saturation measured in a spectrometer with a calibrated source. Thermal stability at 150˚C and 100 W/cm^2.	24	No
Technical	$InP@ZnTe_{1-x-y}Se_xS_y$ graded-shell QDs emitting at 625 ± 5nm, with PLQY > 85%, FWHM < 40nm, thermal stability > 90%.	Spectral measurements taken as detailed above. Thermal stability at 100˚C and 25 W/cm^2.	24	No