Graded Alloy Quantum Dots:
Energy Efficient Down Conversion on LED Packages

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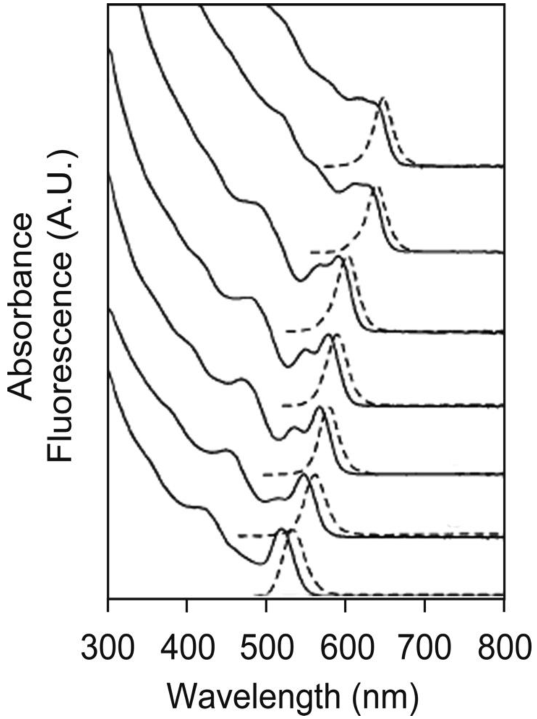
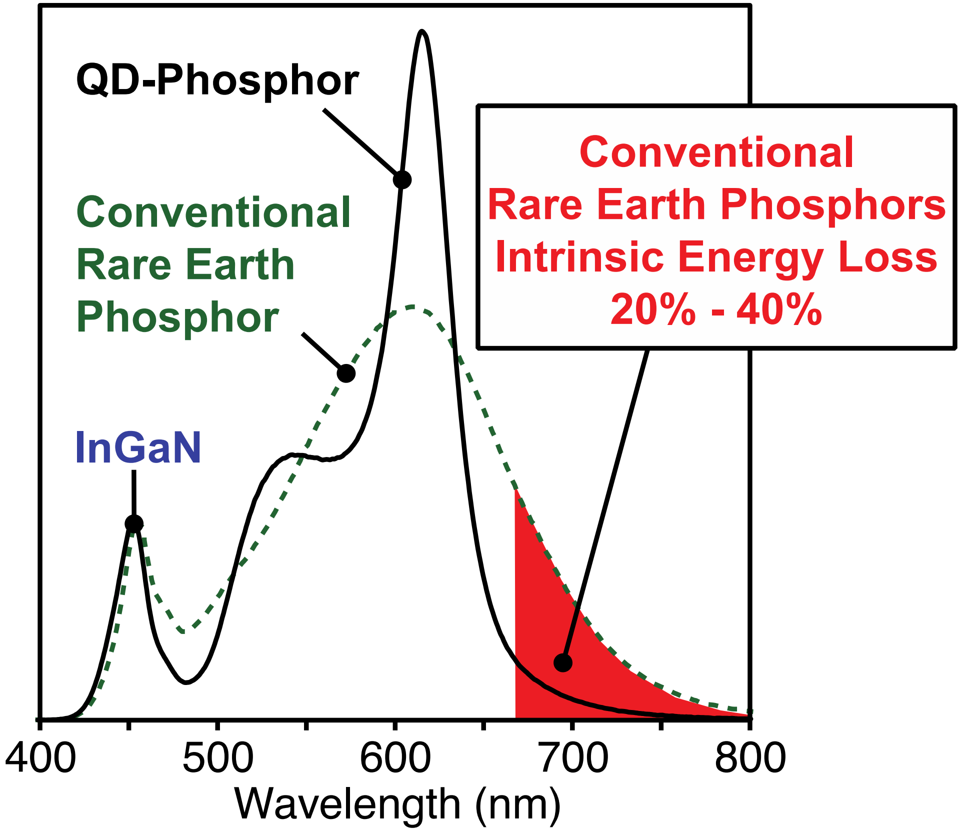
Quantum Dot Down Converters in Solid State Lighting

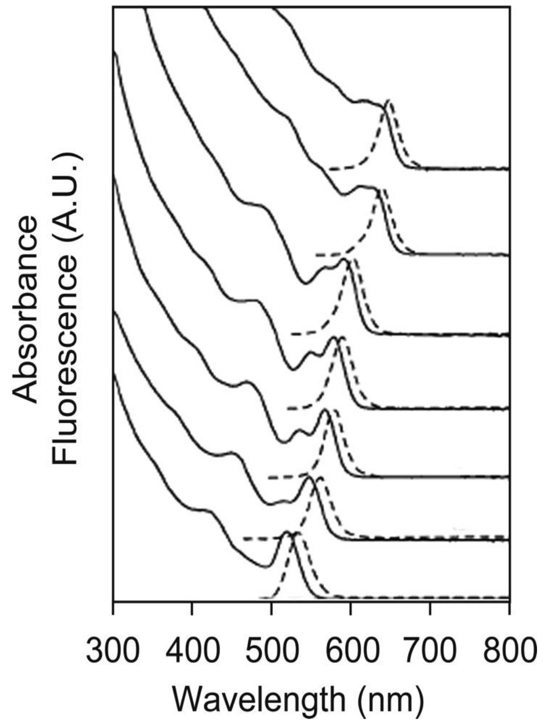


Critical Need: High Efficiency, Stable, Narrow Red and Amber Down Converters



Solid State Lighting R&D Plan, **2015**, U.S. Department of Energy, Office of Energy Efficiency and Renewable Energy, Solid State Lighting Program.

Quantum Dot Down Converters in Solid State Lighting



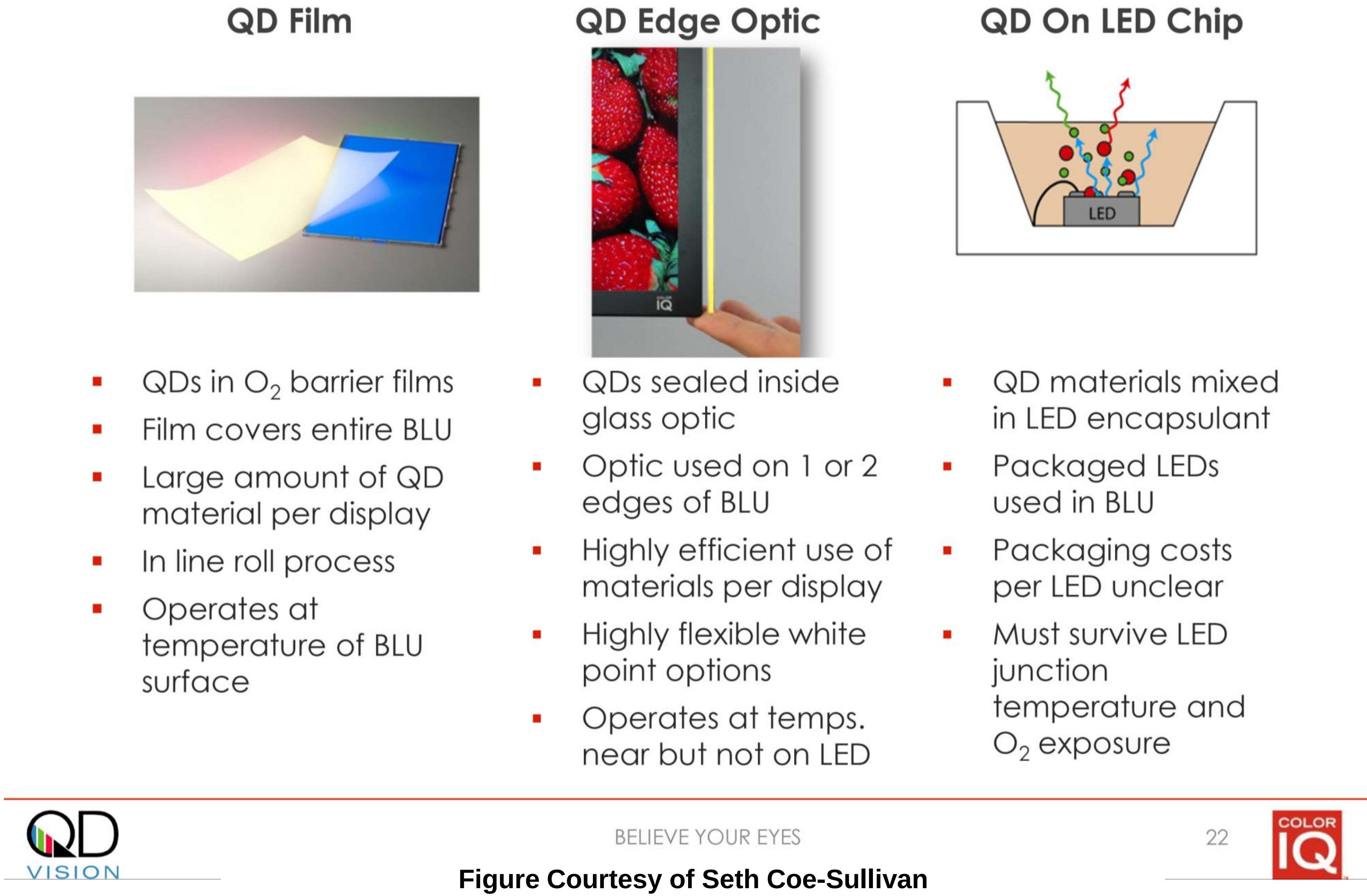
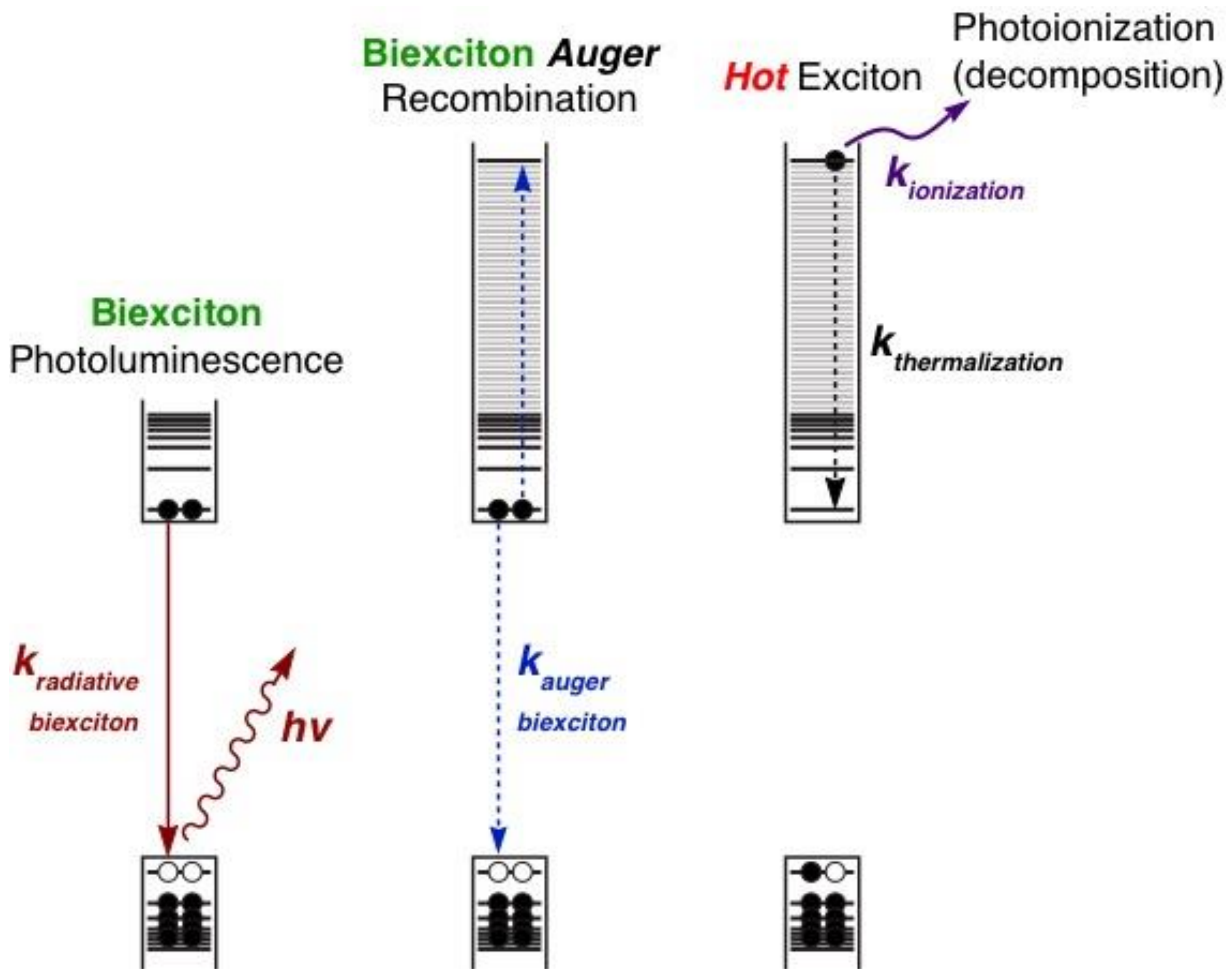


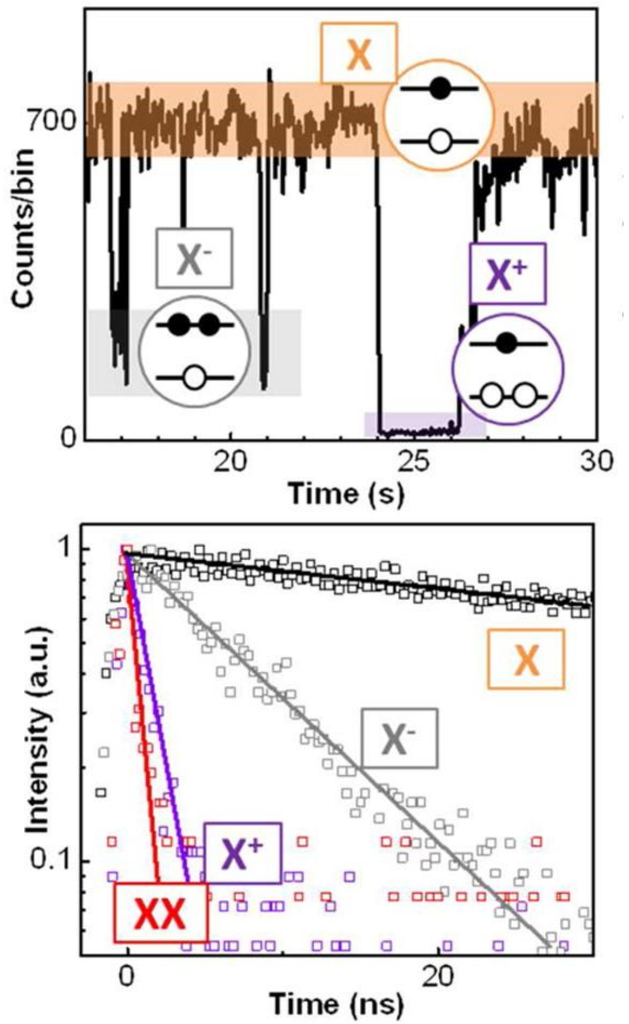
Figure Courtesy of Seth Coe-Sullivan

Multiexciton Auger Recombination Causes Photoionization



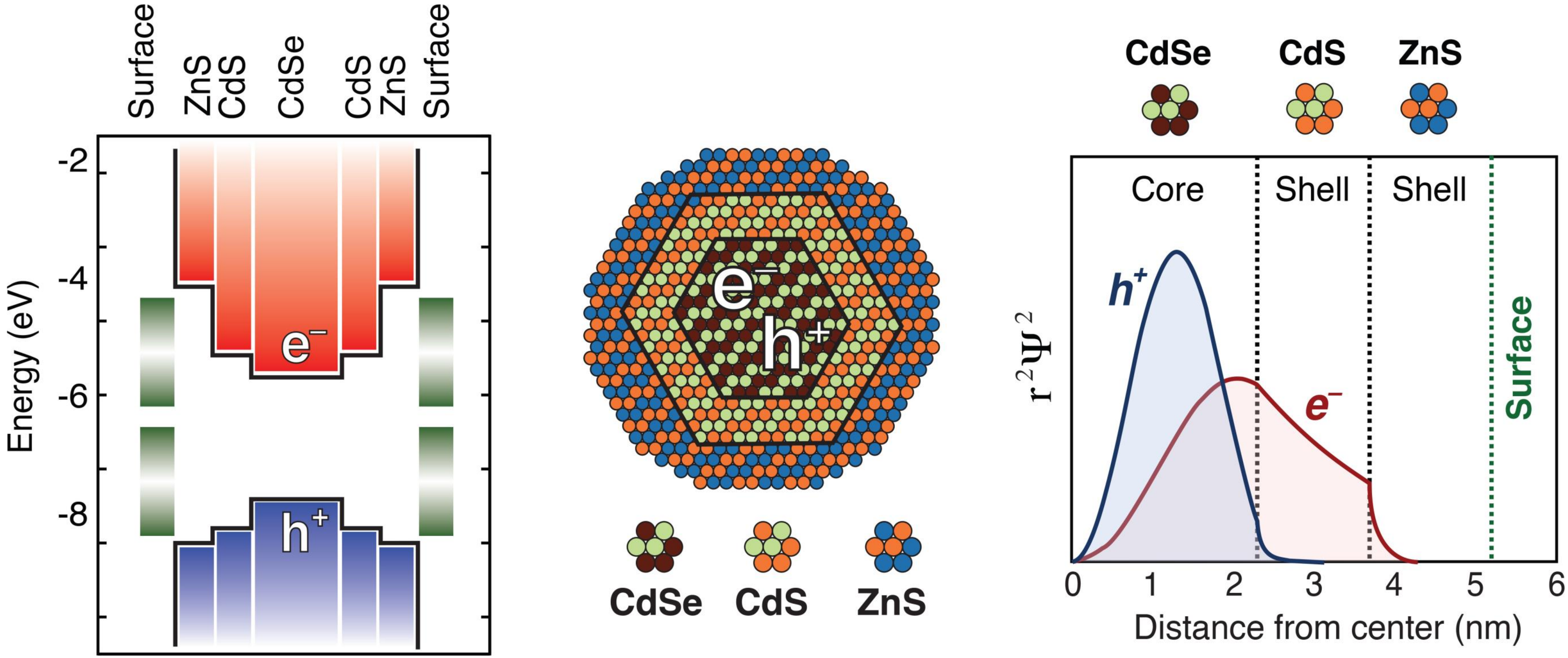
Bawendi, *Chem. Soc. Rev.*, **2014**, *43*, 1287

QD Charging Causes "Blinking"



Klimov, *ACS Nano*, **2014**, *8(7)*, 7288.

Core-Shell Nanocrystals Isolate Excitons From Surfaces



Energy level landscape localizes excited electron and hole within the crystal core

Photoluminescence quantum yields remain sensitive to surface structure

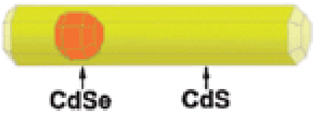
Colloidal QD R&D Timeline

'80 — '90 — '00 — '10 — '20

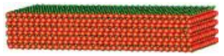
Brus, Ekimov, Henglein
1982

Guyot-Sionnest
Alivisatos
(CdSe/ZnS)
PLQY = 50%
1996

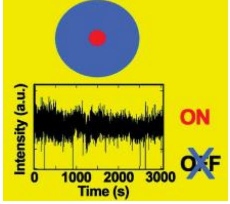
Mews
(Core-Shell-Shell)
PLQY = 80%
2005



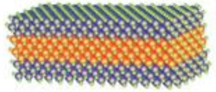
Talapin, Alivisatos, Manna
(Seeded Rods-CdSeCdS)
PLQY = 85%
2007



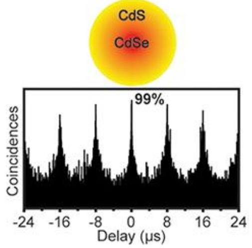
Hyeon
Buhro, Dubertret
(Ribbons, Sheets)
FWHM < 10nm
2008



Hollingsworth
Dubertret
(Thick Shell)
Non-Blinking Fraction
2008



Dubertret, Talapin
(Core-Shell, Core-Crown)
PLQY 80%
FWHM = 20nm
2013



Dubertret
(Graded Alloy)
100% PLQY
Biexciton
2015

Large Graded Alloy QDs:

(1) Reduce interfacial strain

(2) Slow Auger

(3) Reduce blinking, increase PLQY

1993
Bawendi
$CdMe_2$ + $R_3P{=}Se$

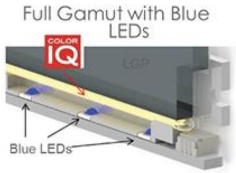
2001
Peng
CdO + $R{-}PO_3H_2$

2002
Peng
S_8

2003
Peng
SILAR

2009
QDVision
Nexxus
(remote bulb)

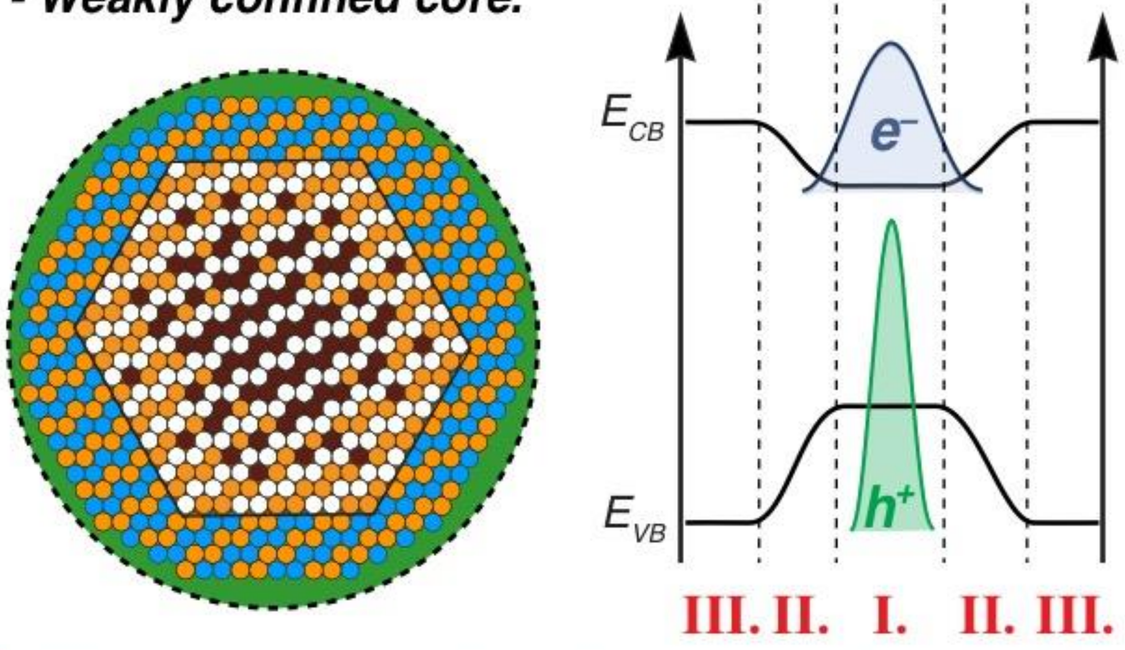
2013
QDVision
Sony
(ColorIQ)



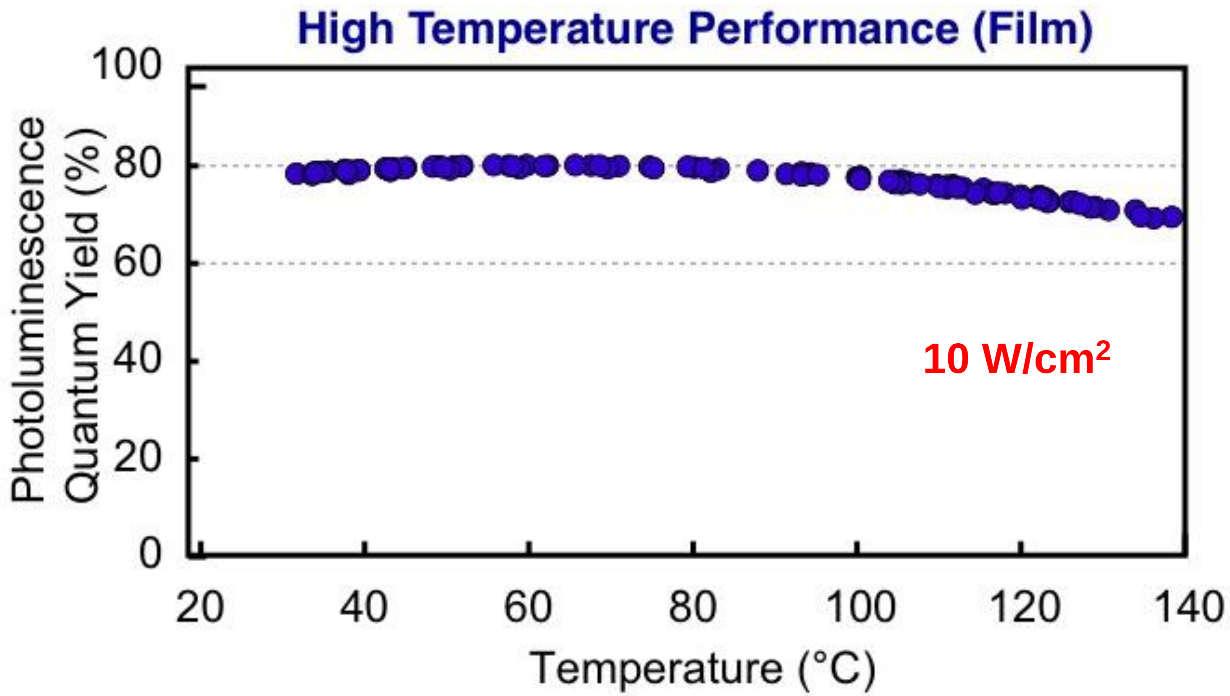
2014
Nanosys
(many others)

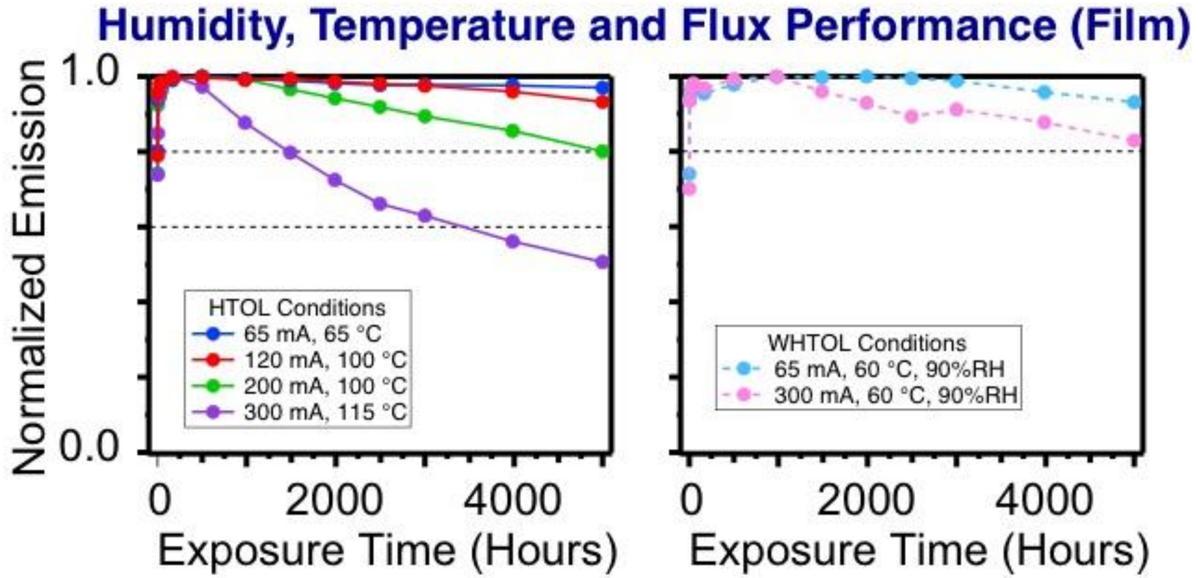
On Chip Performance: Pacific Light Technologies

- *Atomically smooth, graded interface.*
- *Weakly confined core.*

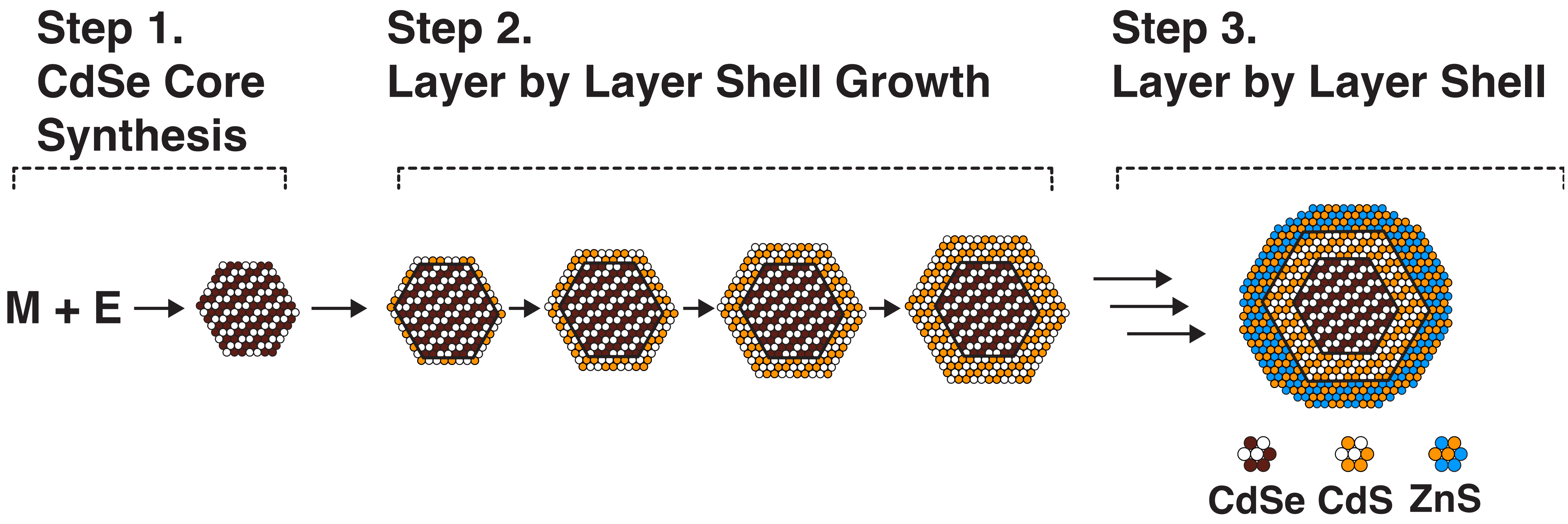


I. Alloy core - narrow linewidth, synthetic reliability
II. Graded interfacial alloy - increased flux stability
III. Insulating shell - low photoionization
IV. PLT Ultrabarrier - thermally robust





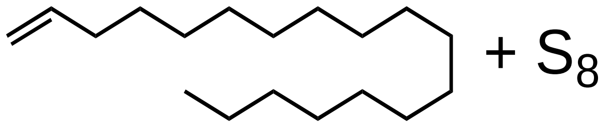
Current Synthetic Methods Use a Long Linear Sequence



- **difficult to control** precursor reactivity leads to **irreproducibility**
- **linear sequence compounds irreproducibility**
- managed with engineering controls, **little knowledge of underpinning chemical reactions**.
- Nanosys: “tons of QD material annually” (http://www.nbclearn.com/nanotechnology)

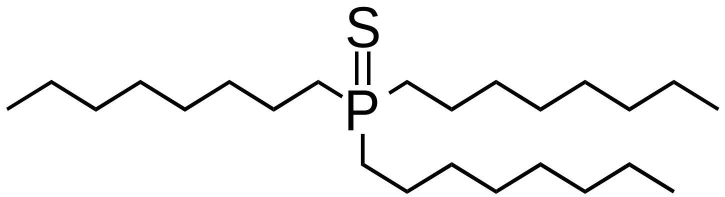
Properties of Common Sulfur Precursors

Inexpensive
Moderate reactivity, but ill-defined
Undesirable by products, low yields



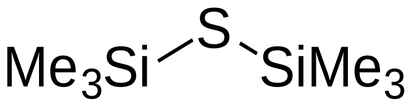
$212 / mole
$13 / mole

Pyrophoric
Impurities are reactive



$263 / mole

Extreme reactivity (mixing limited)
Toxic and air sensitive!

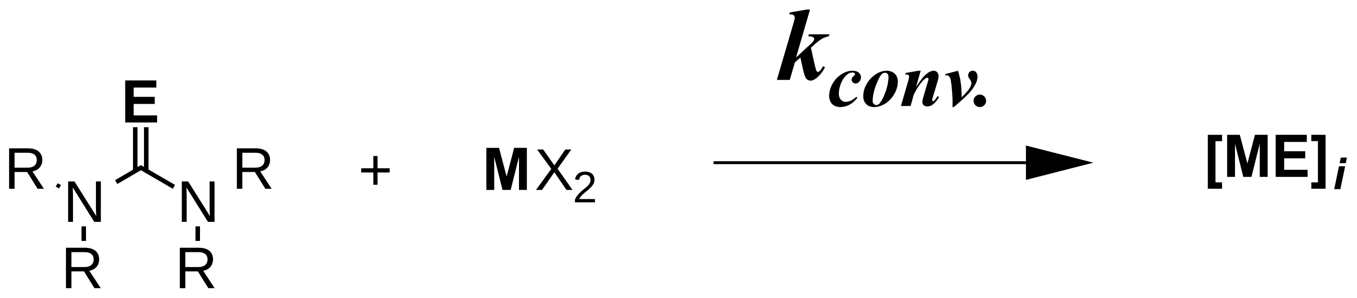


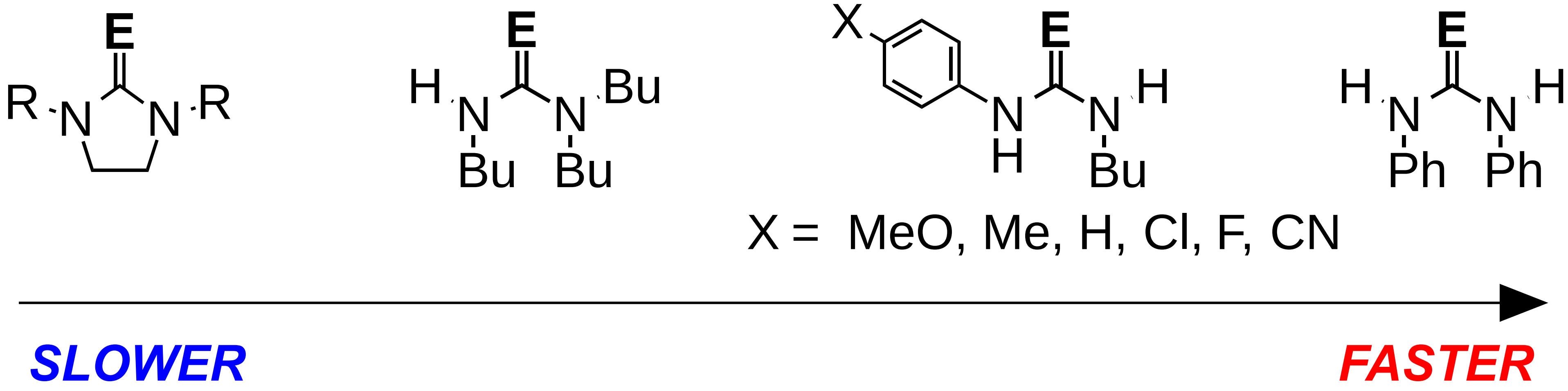
$2,912 / mole

Poorly defined conversion byproducts contaminate QDs and complicate surfaces

Garcia-Rodriguez, Hendricks, Cossairt, Liu, Owen *Chem. Mater.*, **2013**, *25*(30), 1233-1249.

Conversion Kinetics are Sensitive to Chalcogenourea Structure





- $CuZnSnS_4$, $CuInSe_2$, CdSe@CdS, PbS, PbSe, CdSe, CdS, ZnSe, ZnS

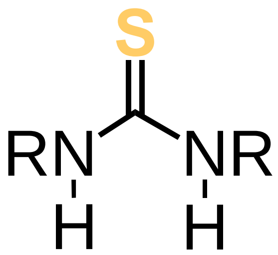
Hendricks, Campos, Cleveland, Jen-La Plante, Owen, *Science*, **2015**.

Precise Control Over QD Formation Kinetics and Size at 100% Yield

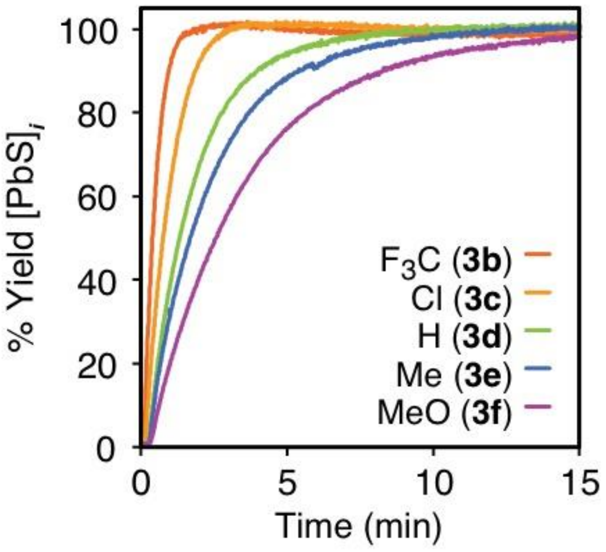
ABSORPTION KINETICS

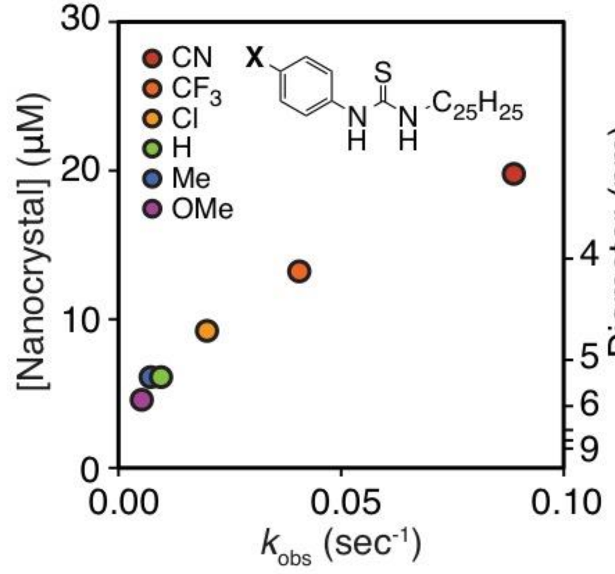
PRECISE CONTROL OVER NUCLEATION

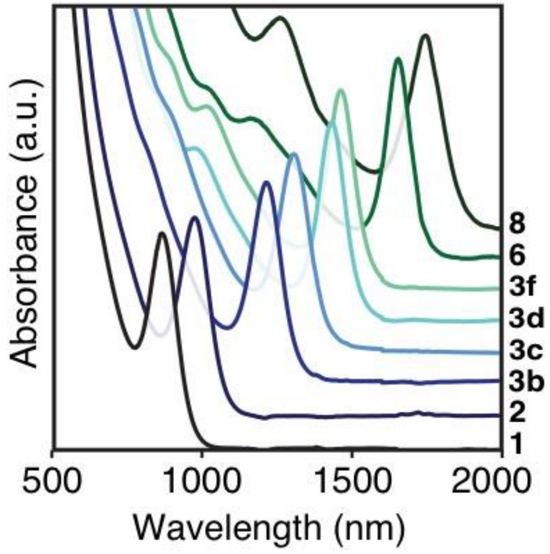
WIDE RANGE OF SIZES NARROW POLYDISPERSITY

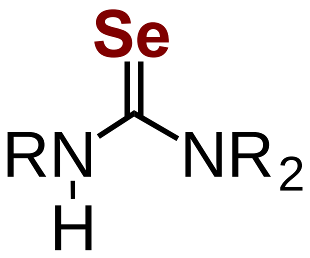


Owen et al., *Science*, **2015**

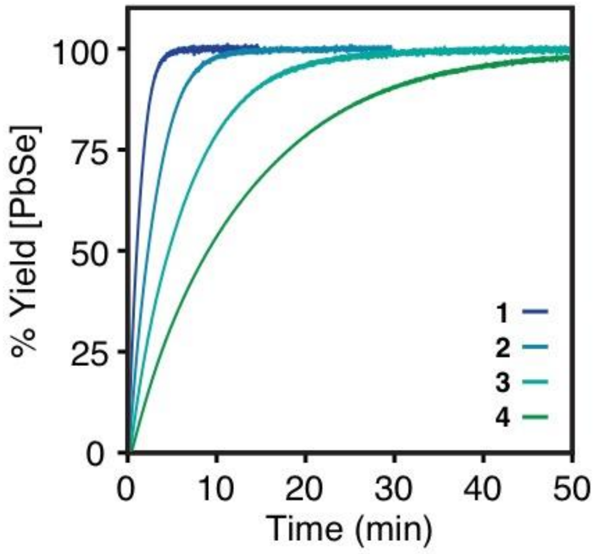


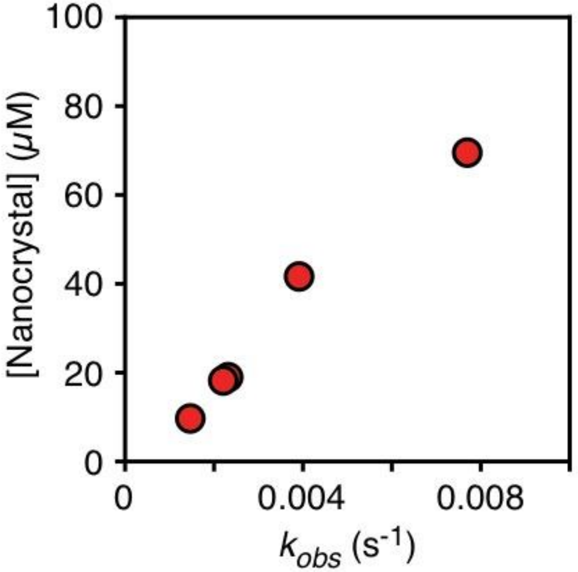


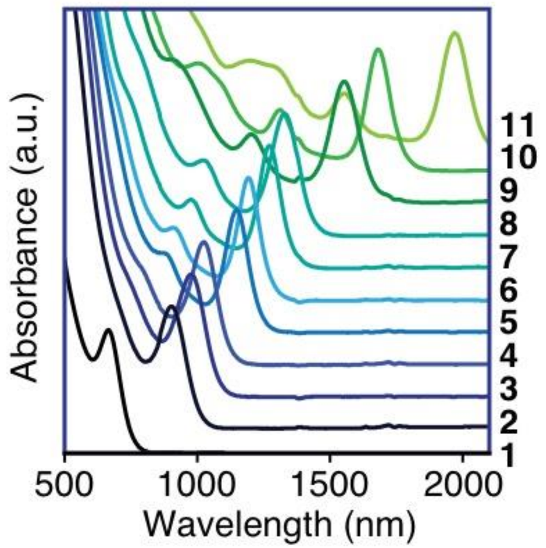




Owen et al., *JACS*, **2017**

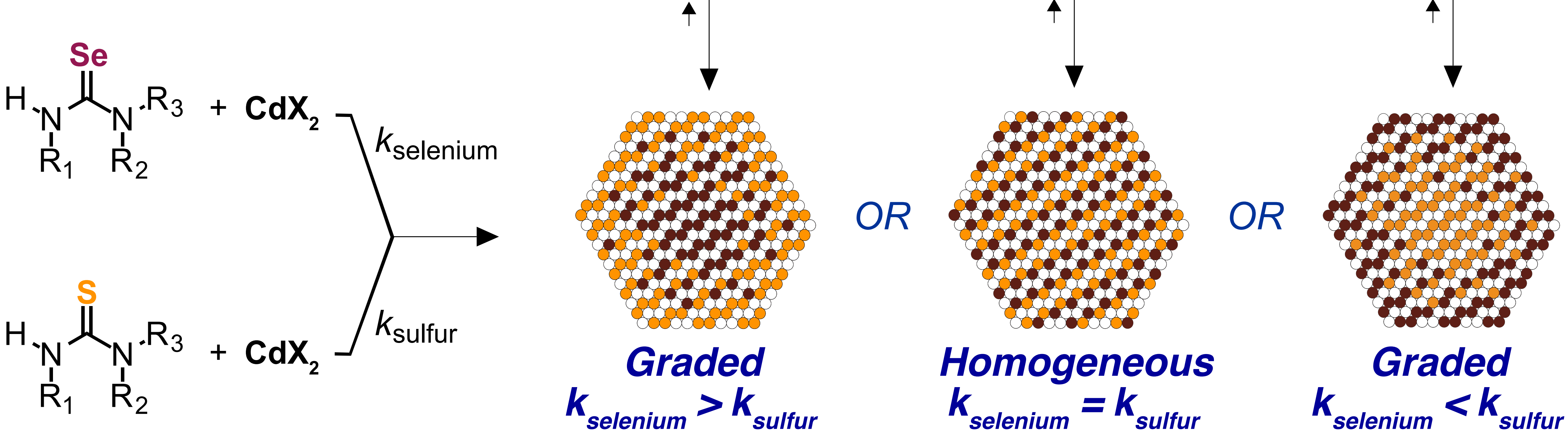






Predictive Fine Control Over QD Se/S Alloys in One Synthetic Step

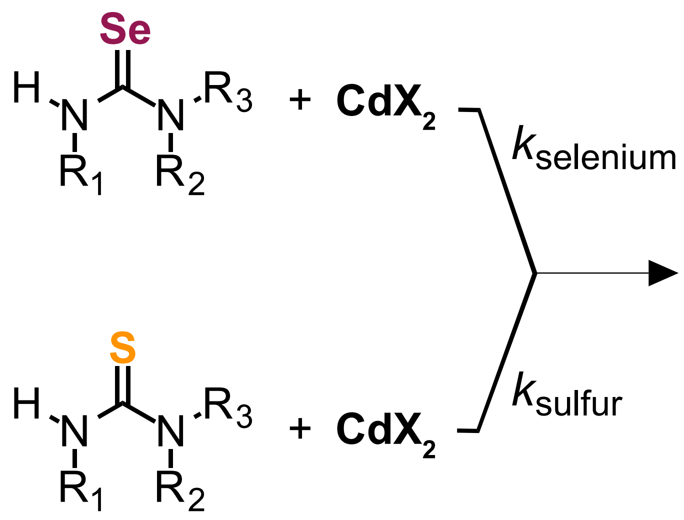
Single Step Heterostructure Synthesis

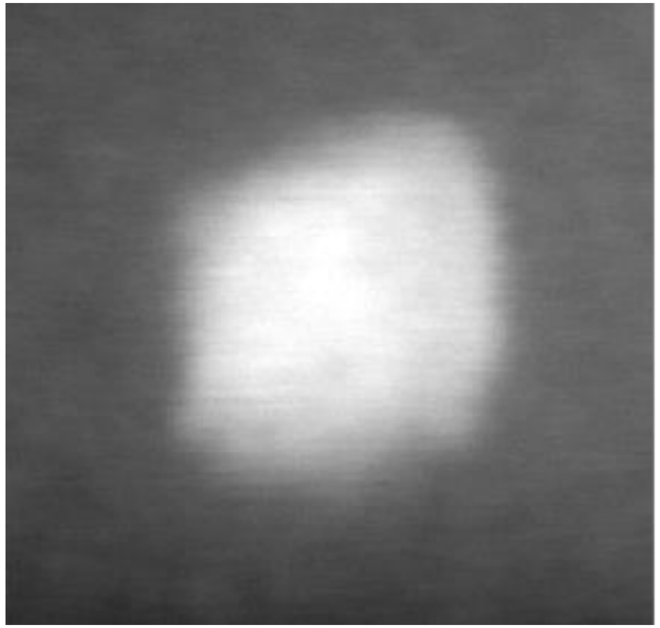


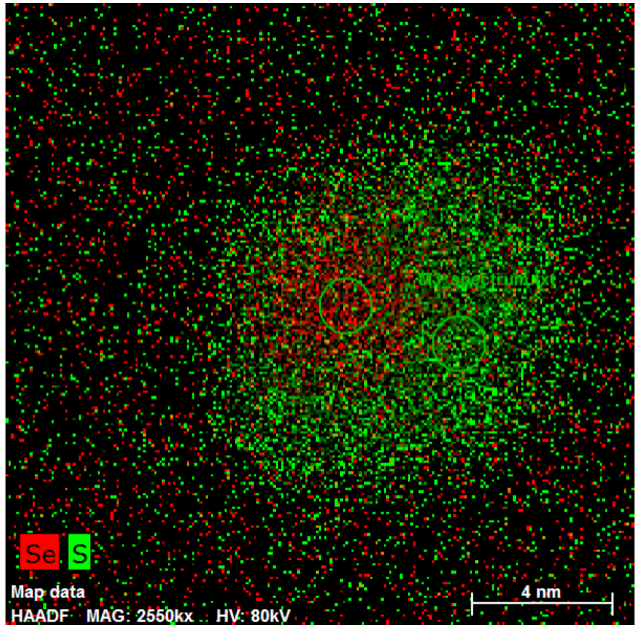
Fewer manufacturing steps
Alloy composition tunes color (rather than size) improving reliability
Urea conversion provides high chemical yield and well-defined coproducts

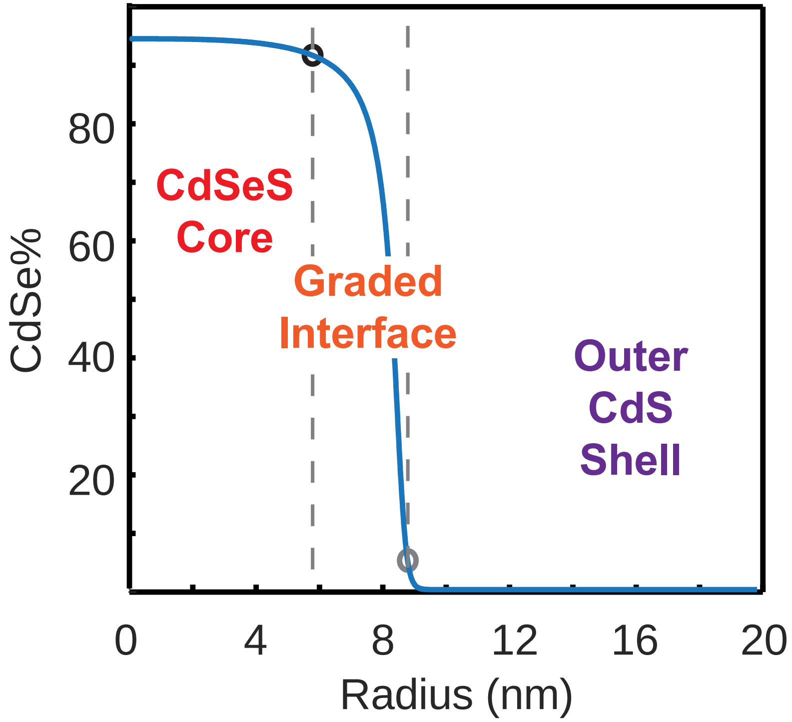
Owen and Alivisatos, *JACS*, **2007.** Owen and Alivisatos, *JACS*, **2010.** Owen, *et al. Science*, **2015**.

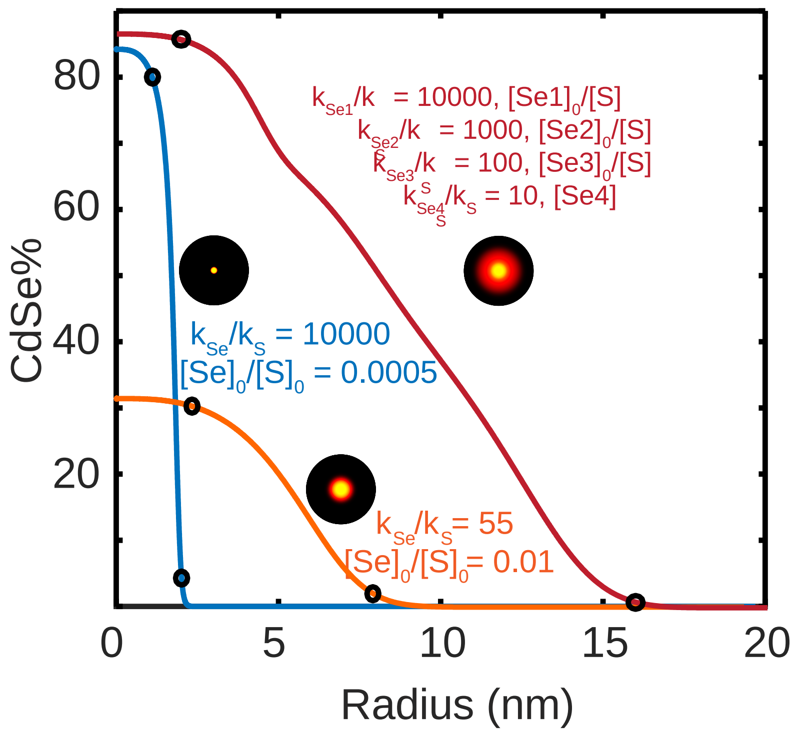
Single Step Heterostructure Synthesis

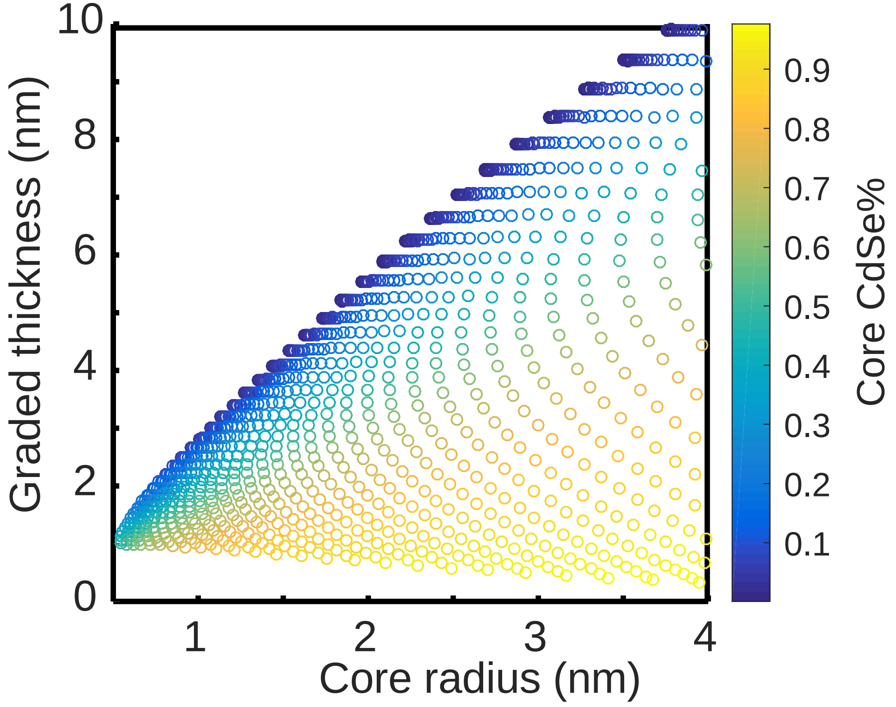




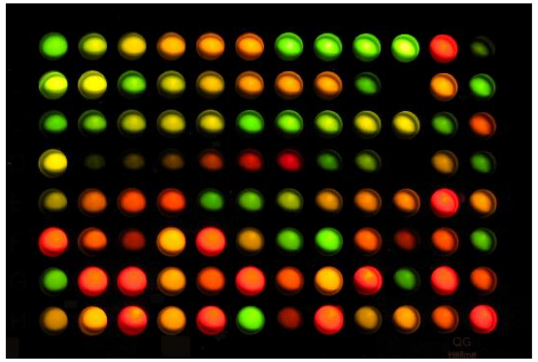




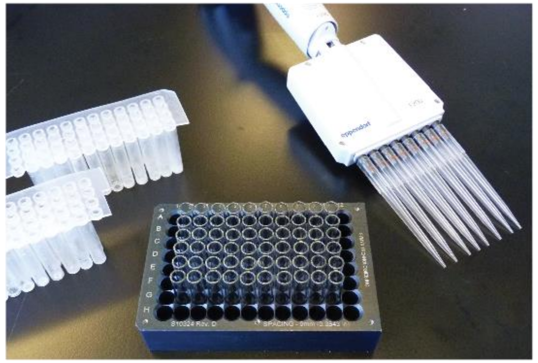




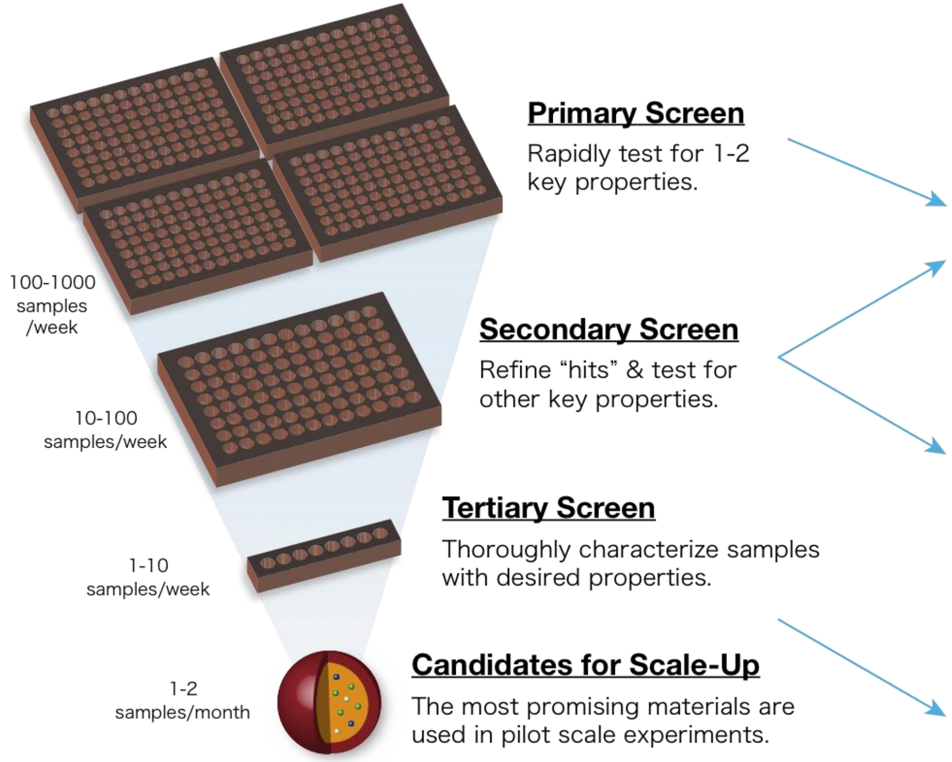
High Throughput Experimentation
The Molecular Foundry, Lawrence Berkeley National Lab



Photoluminescence of QDs in 96 Well Plate



96 Well High Temperature (350 ˚C) Reactor



Chan, Cohen, Milliron, Owen, *Nano Letters* **2010**, 10, 1874-1885.

THANK YOU