DoE SSL R&D Workshop
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Nashville, TN

peter@palomakiconsuting.com
www.PalomakiConsulting.com
www.linkedin.com/in/ppalomaki
@nanopalomaki

Quantum Dot Downconverters for SSL

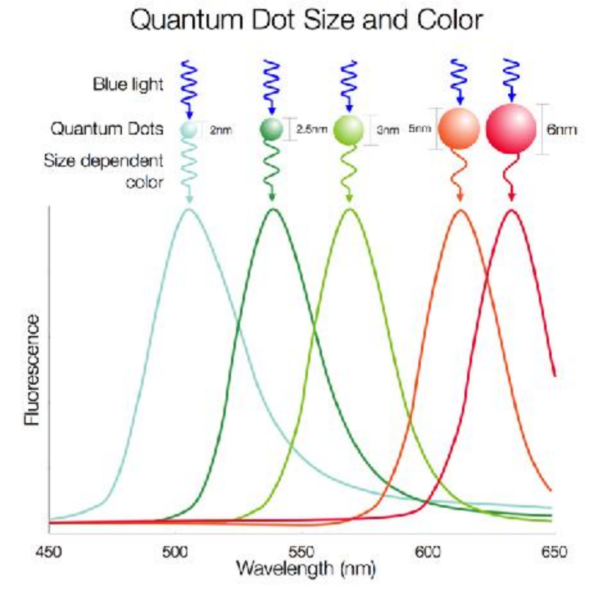
PETER PALOMAKI

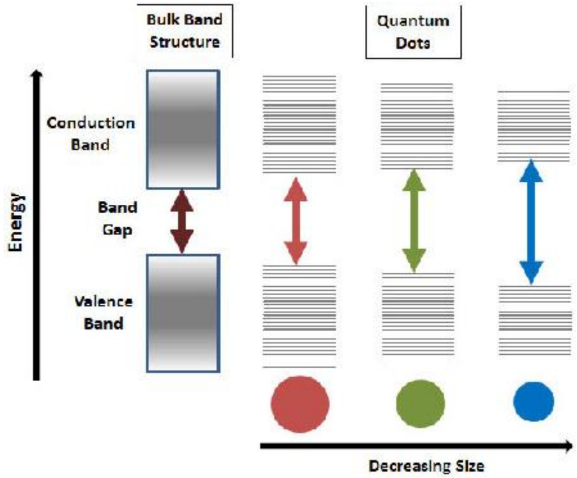
PALOMAKI CONSULTING

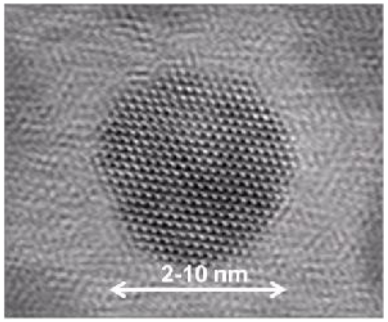
What are Quantum Dots?

A quick refresher

- Quantum confined semiconducting nanocrystals
  - Made of inorganic semiconductor material
  - Commonly “grown” using colloidal synthetic chemistry
  - Electron and hole confinement results in unique optical properties
- Highly efficient (and *tunable*) downconverter
  - Absorbs high energy photons (UV-blue)
  - Emits lower energy photos (Vis-IR)



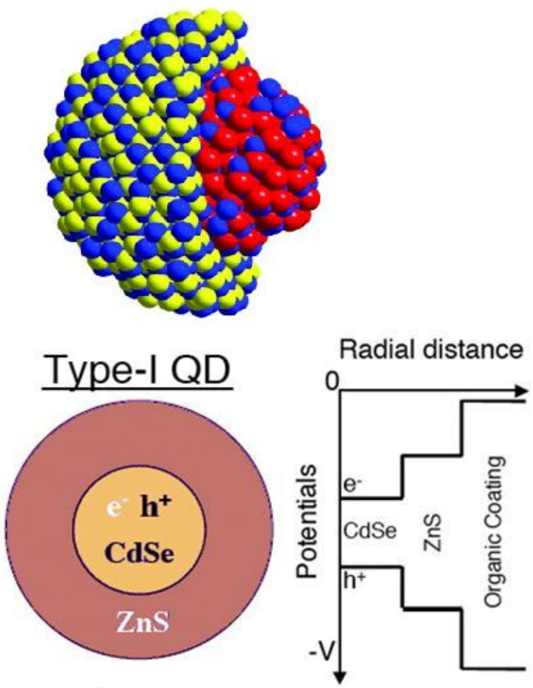




Quantum Dot structure

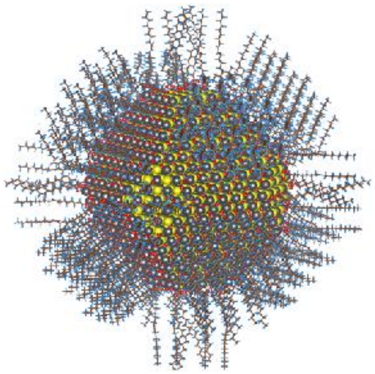
Inorganic Core/Shell with organic ligand

Inorganic core/shell dictates optical properties

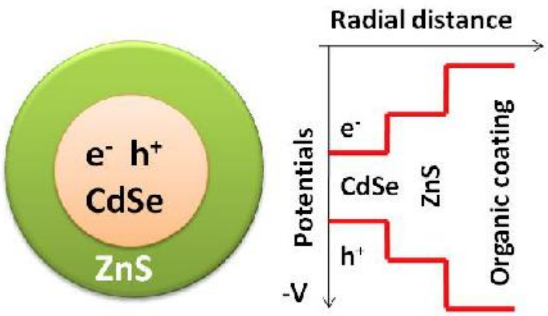


Bawendi group, MIT

Organic ligands dictate interactions with environment



Science 344, 1380 (2014)



Khalil Ebrahim Jasim (2015). Quantum Dots Solar Cells, Solar Cells - New Approaches and Reviews

- Shell confines electron/hole pair to the core
  - efficient radiative recombination = high quantum efficiency
- Shell helps to eliminates imperfections at the CdSe surface
- Ligands dictate interaction with environment – VERY IMPORTANT

Colloidal QD History

We've come a long way…

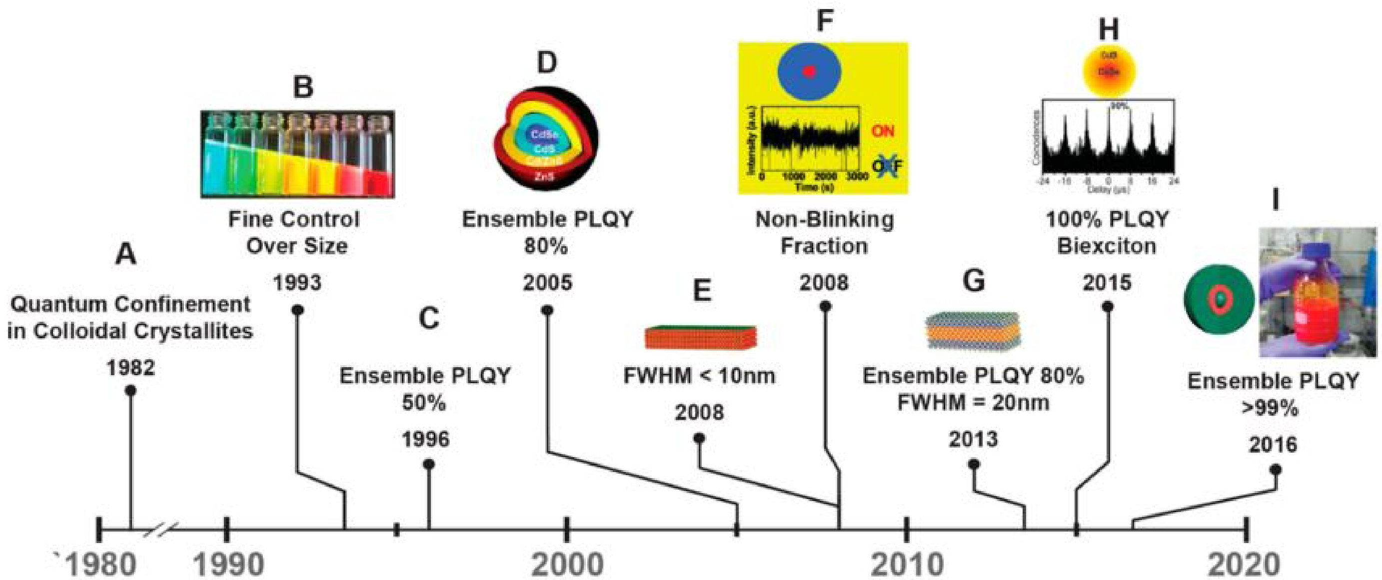


Figure 3. Colloidal qdot research timeline illustrating evolution of nanostructure and luminescence performance. (A) Liquid colloidal quantum dots first described.[2] (B) High-temperature synthesis of qdots with narrow size distributions and size-dependent photoluminescence.[11] (C) Core/shell CdSe/ZnS qdots with 50% luminous efficiency.[12] (D) Multi-shell architecture CdSe/CdS/$Cd_{1-x}Zn_xS$/ZnS.[32] (E) Atomically thin nanoplatelets with narrow luminescence.[37] (F) "Giant" shell CdSe/CdS qdot.[30] (G) Shelling of nanoplatelets produces narrow band luminescence with 80% luminous efficiency.[38] (H) Graded alloy CdSe/$CdSe_{1-x}S_x$/CdS with high luminous efficiency of bi-excitons.[37] (I) Gram-scale synthesis of spherical quantum well CdS/CdSe/CdS with low internal defects and thick shell provides near-unity luminous quantum efficiency from the ensemble.[33]

Owen & Brus, *J. Am. Chem. Soc.*, **2017**, *139* (32), pp 10939–10943

First synthesis of InP (NREL, Nozik)
J. Phys. Chem. 1994, 98, 4966–4969.

InP Review (Reiss)
Chem. Mater. 2016, 28, 2491−2506

Commercial history and current market

Display market has driven most advancements – lifetime achieved through encapsulation

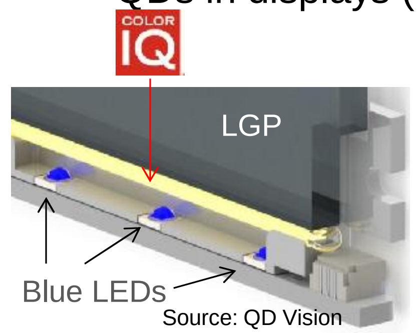
QD Christmas Lights

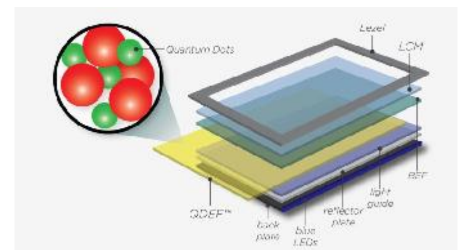
Evident Technologies (2009)

QD "warm" LED

Nexus/QD Vision (2009)

QDs in displays (edge and film)

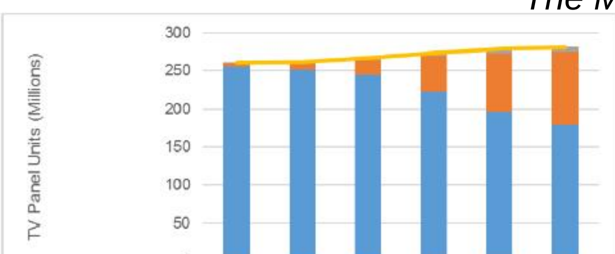




Source: Nanosys

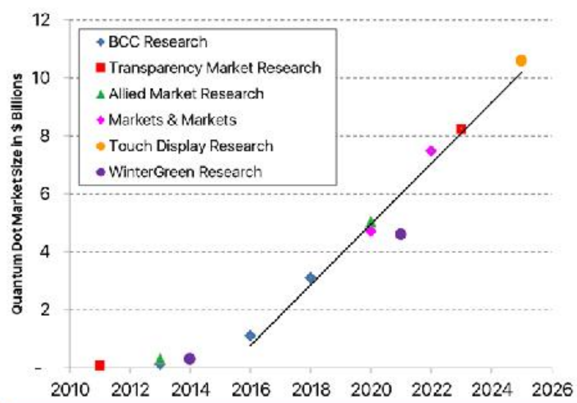
QD Vision, Nanosys, Samsung, (2013-present)

The Market is BIG



	2016	2017	2018	2019	2020	2021
OLED	0.9	1.7	2.6	3.2	5.6	6.8
LCD Quantum Dot	4	9	20	47	76	95
LCD Conventional	256	251	245	223	197	180
Total TV Panels	261	262	268	273	279	282

Source: Display Supply Chain Consultants (DSCC)



All successful technology (to-date) has required protection from atmosphere to achieve sufficient lifetime (~20-30k hrs)

QDs on LED will require self-stable QDs with no macroscopic encapsulation

QD benefits for lighting

FWHM - Tunable Spectrum - Small Size - Rapid Decay

FWHM

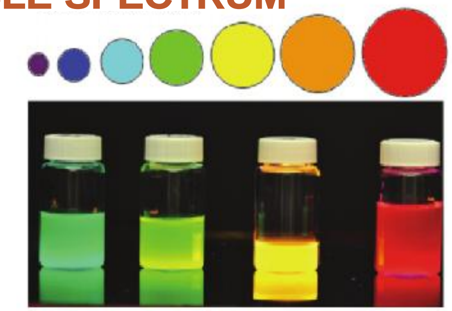
Table 1. Simulated FWHM Dependence for LE at 3000 K and 90 CRI

Photonics Research 5 (2) April 2017

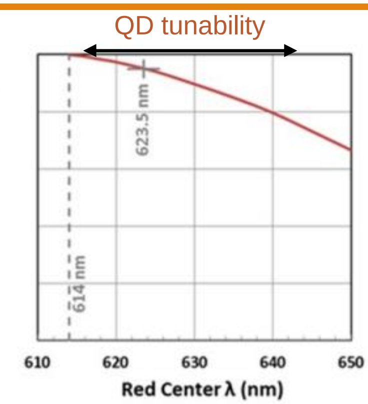
3000K,90CRI		Gaussian Green FWHM (nm)				
		30	50	70	90	110
Gaussian Red FWHM (nm)	30		117%	118%	116%	113%
	50		114%	113%	111%	109%
	70	110%	109%	107%	106%	105%
	90	105%	104%	102%	101%	100%

QDs can result in >10% efficiency gains compared to phosphors at high CRI

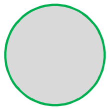
TUNABLE SPECTRUM



Nano Rev. 2010 1:5161

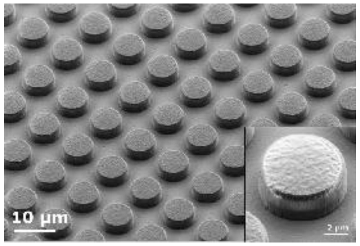


QDs emission tunability based on size and composition allows for maximization of efficiency and flexibility in color point



Phosphor particle (25 um)

QD (X1000)



LETI 10 um pitch microLEDs

SMALL SIZE

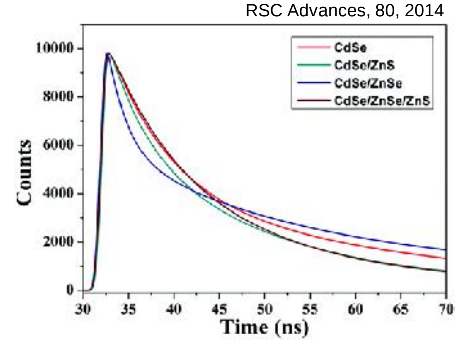
- Reduced settling
- Reduced scattering
- Printable

QDs can be combined with different form factors (OLED, micro-LEDs) due to small size (5-10 nm)

RAPID DECAY

Rapid radiative recombination means more turnovers, lower multi-photon absorption, and lower material requirement
(depends on abs coef.)

RSC Advances, 80, 2014



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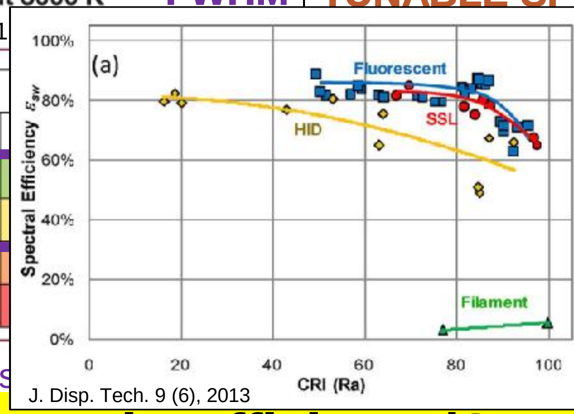
FWHM



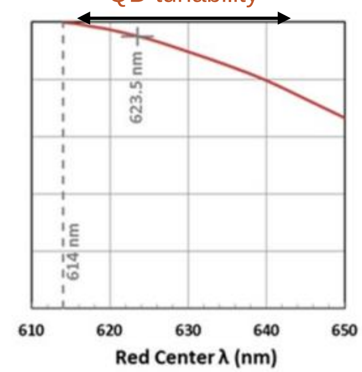
J. Disp. Tech. 9 (6), 2013

QDs can result in >10% efficiency gains to phosphors at high CRI

TUNABLE SPECTRUM

0 1:5161

QD tunability



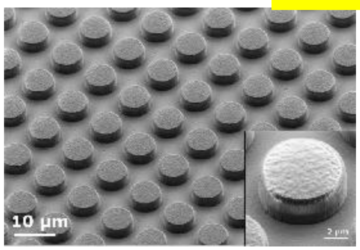
n tunability based on size and composition allows and flexibility in color point

Reduces the efficiency/CRI tradeoff!

SMALL SIZE

Phosphor particle (25 um)

QD (X1000)



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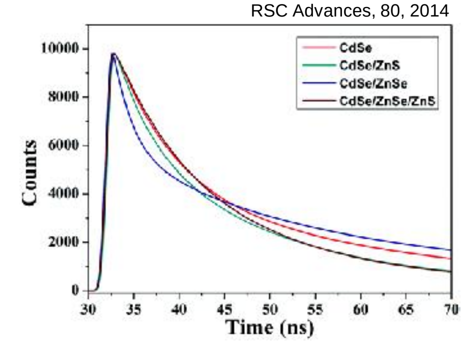
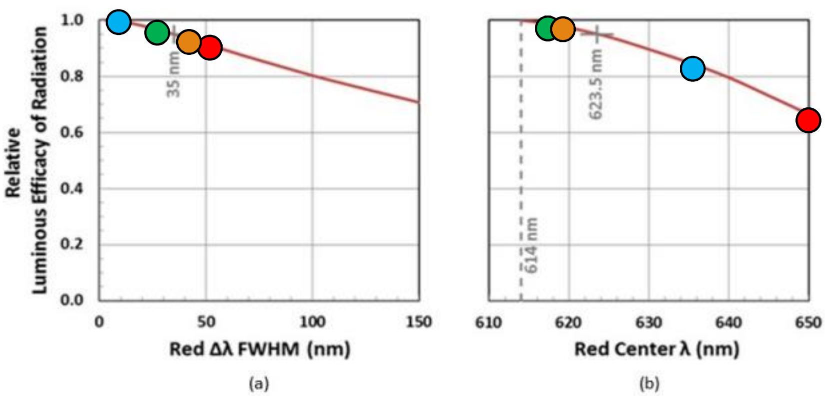


Red down-converter comparison

SLA vs PFS/KSF vs QDs

	Target (DoE 2025)	$Sr[LiAl_3N_4]:Eu^{2+}$ (1) 🔴	$K_2SiF_6:Mn^{4+}$ (2,3) 🔵	CdSe QD 🟢	InP QD (5) 🟠
FWHM (nm)	30	50	<4 (5 peaks)	<30	40
λ_{max} (nm)	615-635	650	613, 631, 636, 648	**Tunable**	**Tunable**
QE at 25C (%)	95	76	>90	>90	~70
Thermal Quench (150/25 C, %)	96	95	95	50-90	<50
Stokes shift (nm)		88	>150	Tunable (~20-100)[4]	~25 nm
Stability on LED	Excellent	Good	Good	Fair	Poor

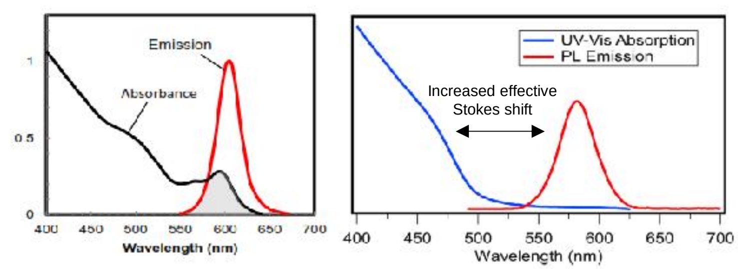
1. Nature Materials **13**, 891–896 (2014)
2. SID 2015, 46 (1), 927–930
3. ECS Journal of Solid State Science and Technology, 2 (2) 3059-3070 (2013)
4. Nano Lett. **2014**, 14 (7), 4097
5. ACS Nano, 8 (1) 977–985, 2014



Note:
Relative white light LER as the (a) FWHM linewidth of the red phosphor increases, for a given red center wavelength of λ = 614 nm, and (b) red center wavelength increases, for a given FWHM linewidth of Δλ = 7 nm. In both cases, the blue and green linewidths were fixed at 20 nm and 50 nm FWHM, but their center wavelengths were allowed to vary so as to optimize LER while maintaining Ra = 80 and R9 > 0. The 95% efficiency points are indicated: FWHM of 35 nm and center wavelength of 623.5 nm.

DoE SSL Roadmap 2016

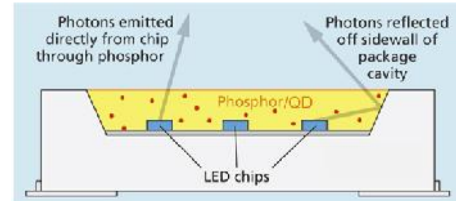
Stokes shift engineering of CdSe QDs (a problem for InP)



Courtesy of Juanita Kurtin (PLT), QD Forum 2017

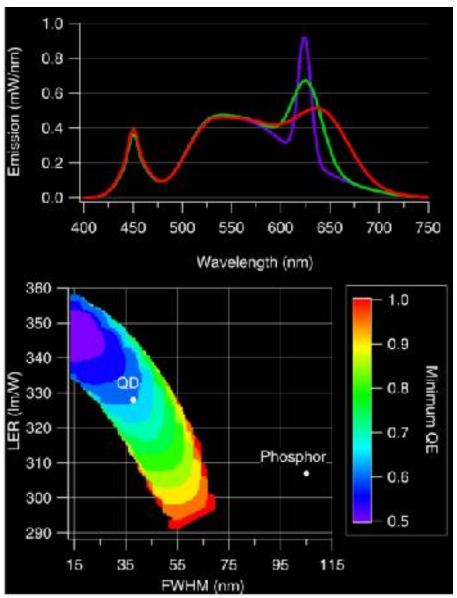
Recent success on-chip

Stable red QD on mid-power LED



Pacific Light Technologies LUMILEDS

- CdSe (red) with on-chip focus for lighting or display
- Demonstration of long lasting QD on chip solution
- ~~Not commercially available (yet)~~ *Released!*

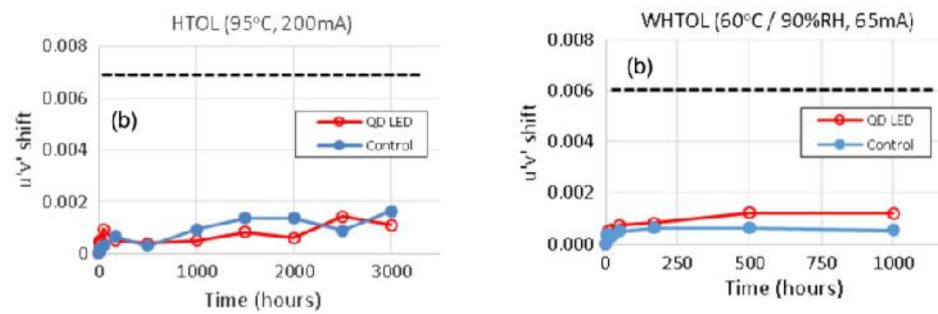


Modeling of red QD/green phosphor LED. 4000k, R9 > 50, CRI > 90

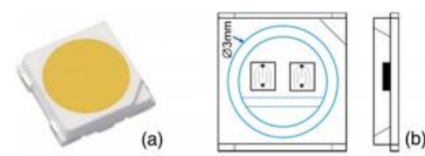
Table 2. External Testing Results of a QD Based LED and a pcLED Module on Printed Circuit Board

Sample	Current (mA)	CCT (K)	CRI	R9	Luminous Flux (lm)	Efficacy (lm/W)
QD based pcLED module A	225	2966	89	52	497	160
Phosphor based pcLED module B	225	3061	89	45	439	142
	258	3057	89	44	495	137

Photonics Research 5 (2) April 2017



"The LED stability with 20 W/cm² of incident blue light and QD temperatures over 110°C have passed 3000 h and continue to show no degradation."



LUXEON 3535L HE plus (mid power LED)

Works well in mid-power LED package, not in high power (yet)

Challenges

(Opportunities)

And some examples

Opportunity #1: Alternatives to CdSe

Description: Explore new, high-efficiency wavelength conversion materials for the purposes of creating warm white LEDs, with a particular emphasis on improving spectral efficiency with high color quality and improved thermal stability and longevity to enable use of materials in high-brightness LED packages. Downconverters that are non-toxic and do not contain scarce materials are encouraged. 1

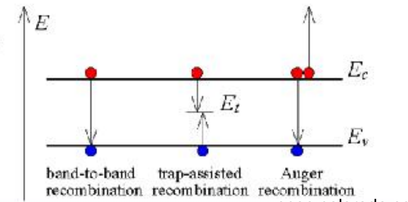
	Target[1]	CdSe	InP	Perovskite	CuInSeS	ZnSe:M	Si	III-N (visible)
Colors	G+ R	Both	Both	Both	Both	Both	R only	
Quantum Yield (%)	95%	>90%	65-90%	>70%	>70%	<50%	50%	?
FWHM (nm)	30 nm	25-30	38-50	15-40	>90	>60	>50	
450 nm Abs	Excellent	Good	Good	Good	Poor	Poor	Poor	
Air/blue light stability	Excellent	Good	Moderate	Poor	Good	?	Poor?	
Scalable	Yes	Yes	Yes	Yes	Yes	Yes	?	
		High Performance, tunable abs	No Cd, moderate performance	Simple to make, no Cd, very narrow	No Cd, inexpensive, large stokes shift	No Cd, familiar chemistry	No Cd, stable, abundant	Stable? Continuous alloying possible?
		Cd	Pyrophoric precursor, high cost, availability of Indium	Contains Pb, poor stability, no shell, small stokes shift	Broad emission, poor blue abs	Broad emission, poor blue abs	Indirect bandgap, poor blue abs, broad emission	Hard to make colloidally with good PL

**An incomplete list of potential visible QD emitters

1) DoE SSL 2017 Suggested Research Topics

Opportunity #2: Improve efficiency

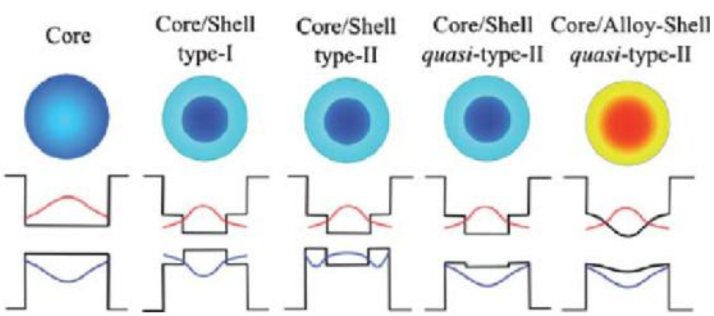
Reduce non-radiative recombination



ecee.colorado.edu

Defects/traps

- Often at surfaces/interfaces
- Graded alloy shells
- Custom ligand chemistry to keep surface atoms intact
- Reduce interaction of e^-/h^+ wavefunction with surface (improve confinement)

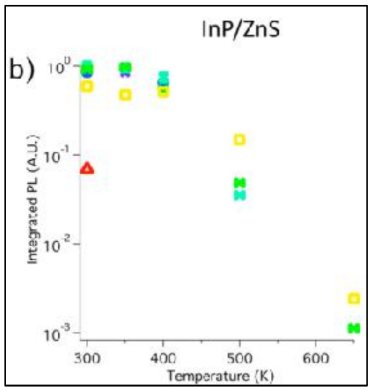


Nanoscale, 2013, 5, 7724–7745

QE loss at temp

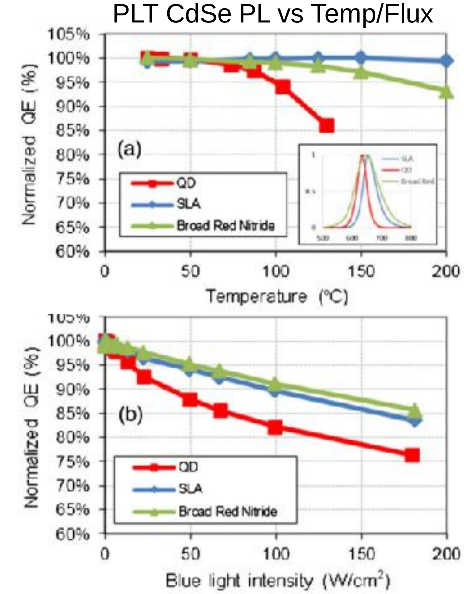
- Thermally assisted trapping
- QD design and interfaces have major impact – exactly how is not well-understood

InP PL drop at high temp (log scale)



ACS Nano, 8 (1) 977–985, 2014

PLT CdSe PL vs Temp/Flux



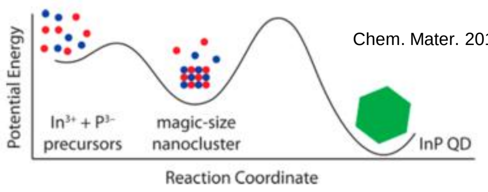
Photonics Research 5 (2) April 2017

Opportunity #3: Reduce FWHM

Needed for all non-Cd QDs (except perovskites)

InP

- precursor conversion not well-controlled
- Progress has come from better materials design (addition of Zn, gradient alloy shells, etc).

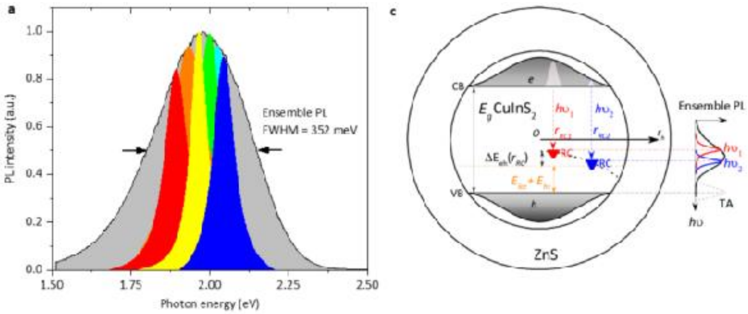


Chem. Mater. 2015, 27, 1432−1441

QDs with dopant-induced emission centers

- Must control location of dopant atoms – not easy to do

Single dot FWHM is good, ensemble is bad ($CuInS_2$/ZnS)

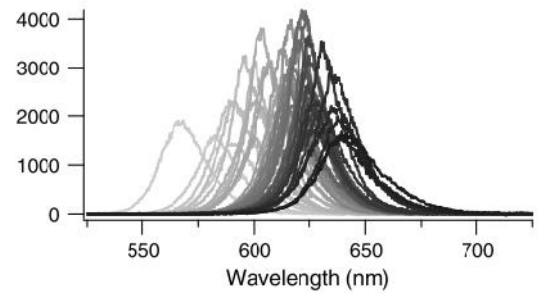


Nano Lett., **2017**, *17* (3), pp 1787–1795

Size uniformity (scalable)

- Core size distribution
- Shell quality/distribution
- Temp/concentration uniformity in reactor

Single particle measurements (CdSe)



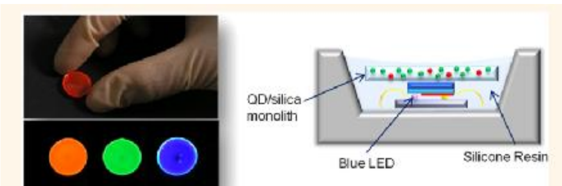
Photonics Research 5 (2) April 2017

Opportunity #4: Stability

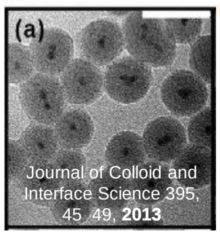
Without macroscopic encapsulation

Nano/micro encapsulation

- organic and inorganic



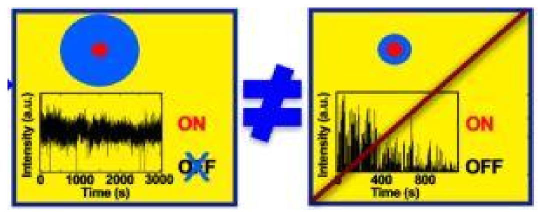
ACS Nano 7(2), 1472–1477, **2013**

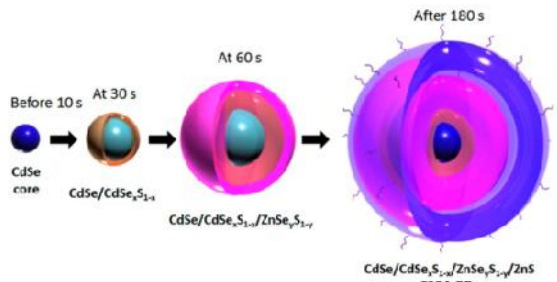


Journal of Colloid and Interface Science 395, 45 49, **2013**

QD design

- Graded alloy interfaces
  - Thick (giant) shell





Langmuir, **2017**, *33* (15), pp 3711–3719

Additives

- Dispersion/surface stabilization is important

QDs on LEDs

- **It's not a pipe dream anymore**
- **Display industry has driven most QD progress (required encapsulation)**

Reasons QDs are great for SSL

High CRI & High LER:
- **Tunable Spectrum**
- **Narrow FWHM**

Small Size

Rapid PL Decay

Research opportunities/areas for improvement

Eliminate Cd

Improve Efficiency

Reduce FWHM (for non-Cd)

Improve Stability

Questions

DoE 2025 targets

Where is work required for QDs to reach targets?

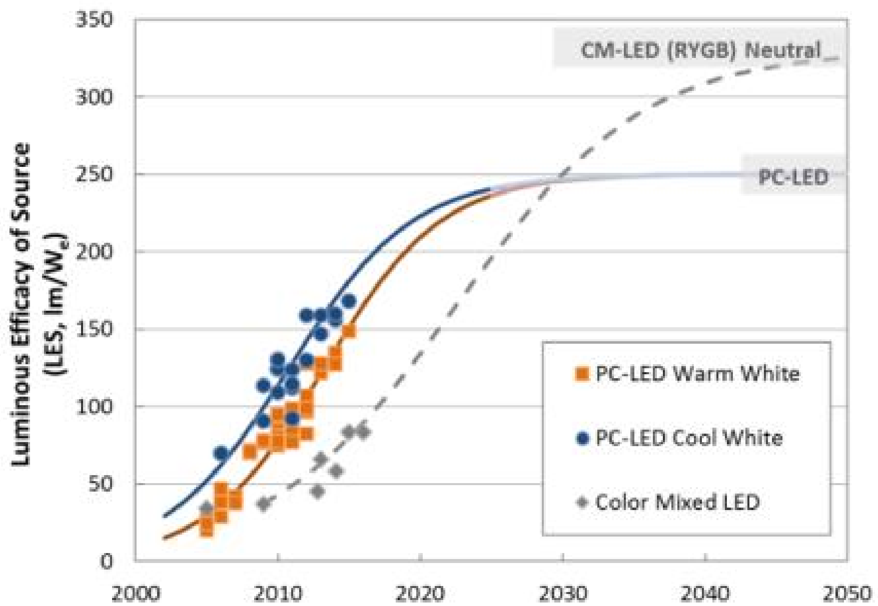
Easy

Moderate

Hard

Table 5 Downconverters

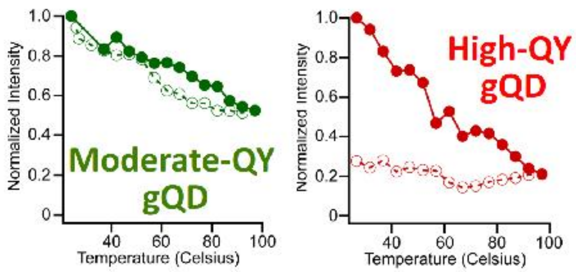
Downconverters			
Description: Explore new, high-efficiency wavelength conversion materials for the purposes of creating warm white LEDs, with a particular emphasis on improving spectral efficiency with high color quality and improved thermal stability and longevity to enable use of materials in high-brightness LED packages. Downconverters that are non-toxic and do not contain scarce materials are encouraged.			
Metrics	**2016 Status**	**Interim 2020 Targets**	**2025 Targets**
Quantum yield (QY) at 25°C across the visible spectrum	98% (Green) 90% (Red)	99% (Green) 95% (Red)	99% (Green) 95% (Red)
Thermal stability – Relative QY at 150°C vs. 25°C	90%	95%	96%
Spectral FWHM	100 nm (Red/Green)	30 nm (Red) 70 nm (Green)	30 nm (across visible spectrum)
Color shift over time (when integrated into pc-LED)	Δu'v' < 0.007 at 6,000 hours	Δu'v' < 0.002 over life	Δu'v' < 0.002 over life
Flux density saturation – Relative QY at 1 W/mm² (optical flux) vs. peak QY	-	95%	96%



Suggested Research Directions

1. QE temperature stability (all materials)

- Fundamental study required
- Function of composition/thickness?
- Function of crystallinity?
- What other factors impact?



Hollingsworth, LANL

3. Stability (all materials)

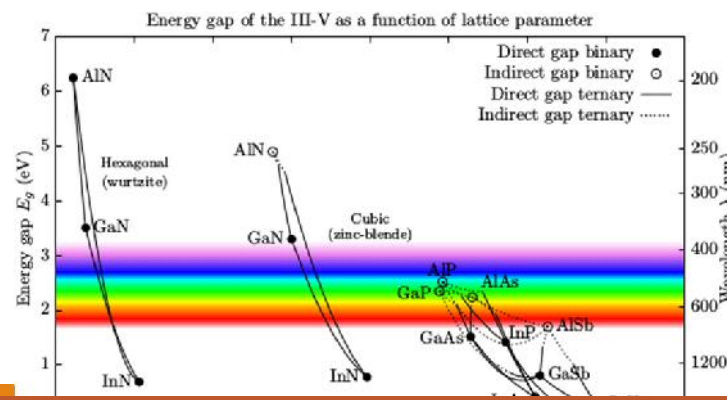
- Encapsulation
- QD Design
- Mechanism of degradation

2. Improve optical properties for non-Cd systems

- Innovations in shell design to induce larger stokes shift/increase blue abs
- Reduce FWHM by synthetic improvements – approach atomistic control

4. Improved synthetic methods for III-N QDs

- A largely untapped area
- Potential for emission across the visible
- Potential for more stable QDs



http://mcaroba.dyndns.org/wiki/index.php/Group-III_nitrides