Cadmium-Free Quantum Dot Building Blocks for Human Centric Lighting, DE-EE0009692

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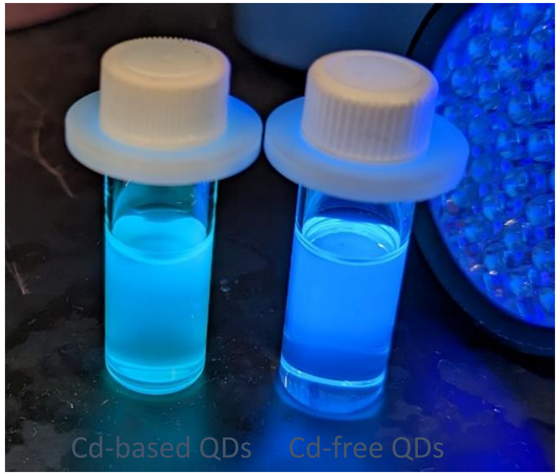
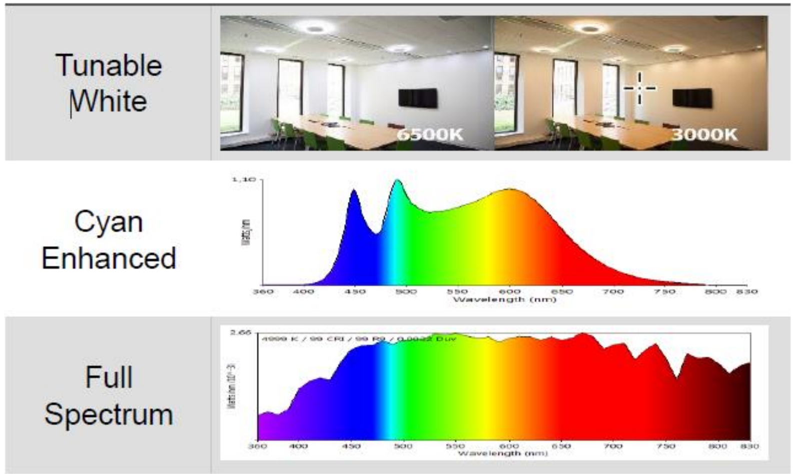
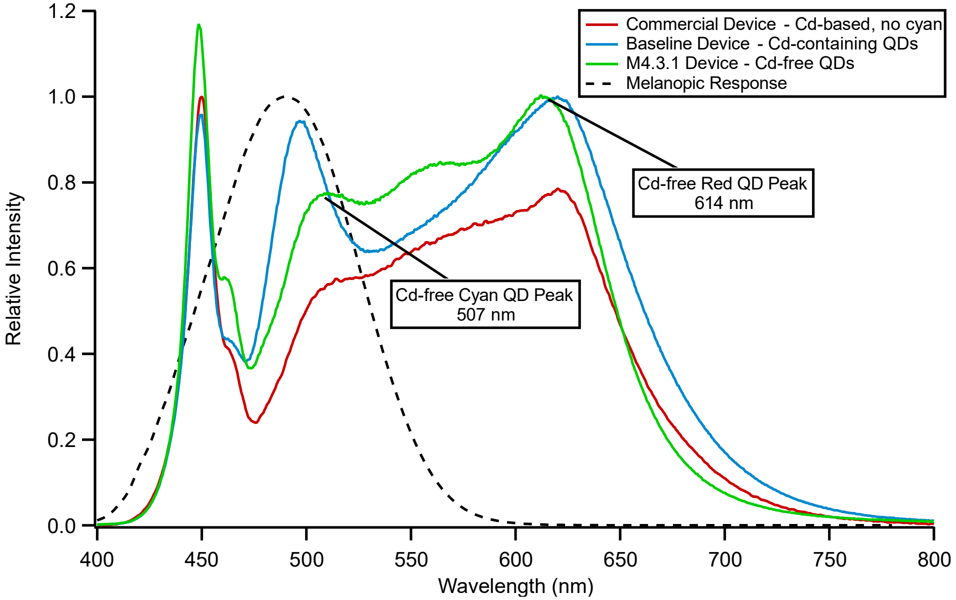
Co-PI: Jonathon S. Owen, Columbia University
Co-PI (FFRDC): Emory Chan, Molecular Foundry, Lawrence Berkeley, National Lab

U.S. DEPARTMENT OF ENERGY
Energy Efficiency & Renewable Energy

Project Manager: Amy Falcon (Joel Chaddock)







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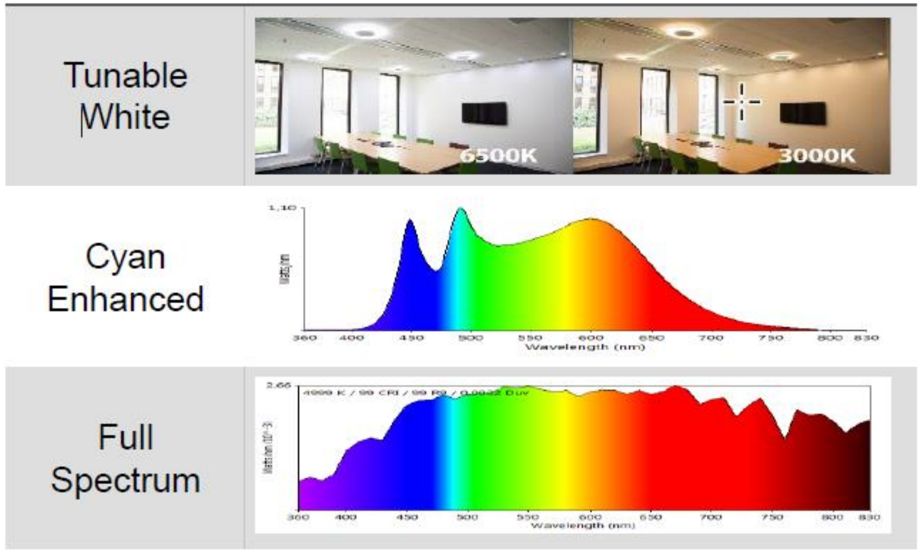
OSRAM Opto Semiconductors

Columbia University

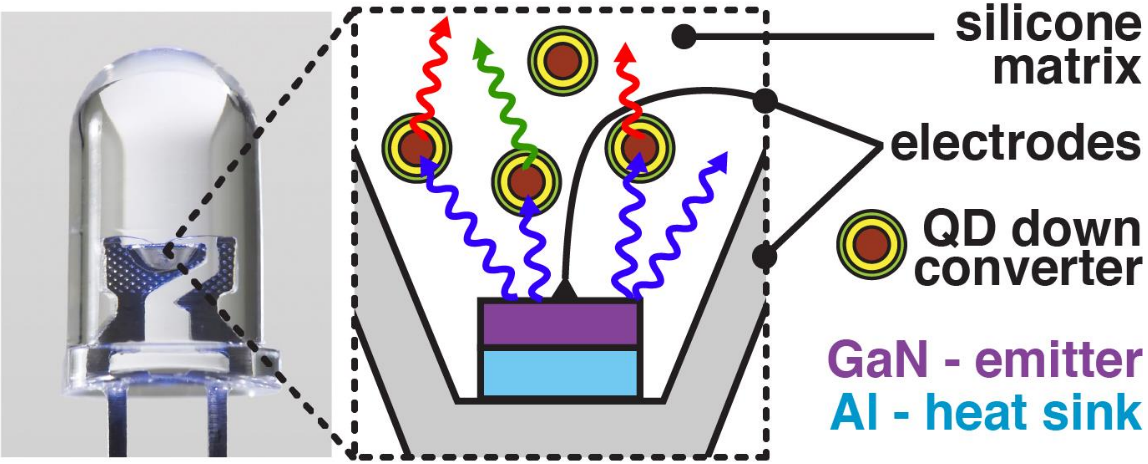
Molecular Foundry

Objective

At a high level, this project at completion will have demonstrated a cyan-enhanced 4000K (MDER>0.7, CRI > 90) white down-converted on-chip device with high efficacy (210 lm/W). This efficacy and these color metrics will be achieved using quantum dot and phosphor hybrid solutions based on cadmium-free quantum dots. This will require generation of a cyan dot as well as a red dot capable of withstanding challenging on-chip conditions. It will also require choice of an optimum commercially viable LED emitter chip and solution development to optimize color quality and efficiency.



Overall, the most significant challenge we face is the inherently poor *chemical* stability of nano-III-V structures. This instability makes it difficult to passivate the particles with larger bandgap epitaxial layers. More importantly, it currently prevents application of a stabilizing amorphous oxide layer. We will focus on control of QD morphology and faceting to generate hardened QDs that will be compatible with oxide passivation.



Budget Summary

	BP 1		BP 2		BP 3		Total	
	Federal Share	Cost Share	Federal Share	Cost Share	Federal Share	Cost Share	Federal Share	Cost Share
Prime Applicant	$255,185	$265,335	$255,185	$265,335	$0	$0	$546,370	$530,670
Columbia	$481,060	$25,000	$481,663	$25,000	$0	$0	$962,723	$50,000
LBNL	$190,173	$0	$196,598	$0	$0	$0	$386,771	$0
Total	**$926,418**	**$290,335**	**$933,446**	**$290,335**	**$0**	**$0**	**$1,895,864**	**$580,670**
Cost Share %		24%		24%		0%		23%

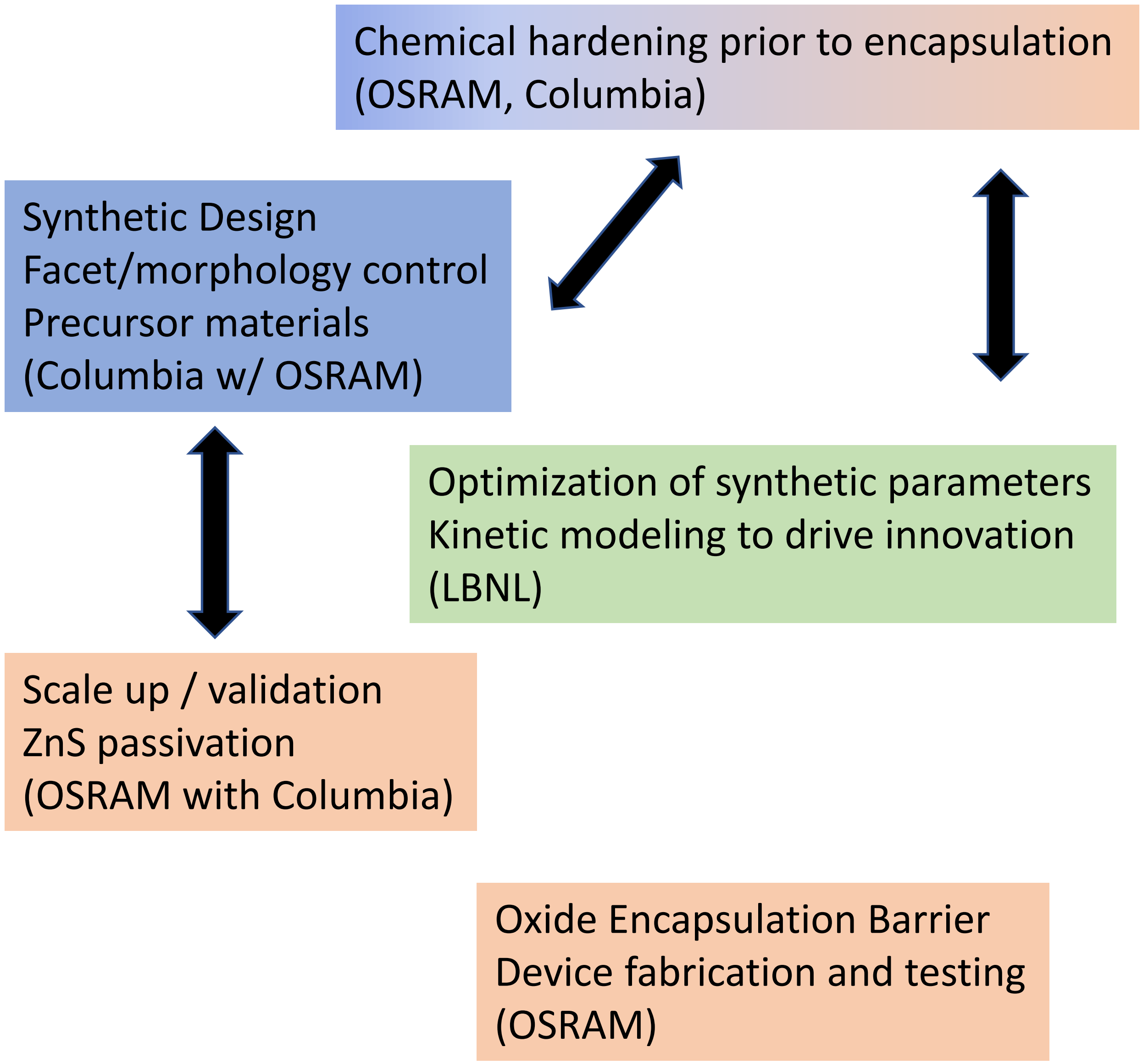
Project Partners

Dr. Joseph Treadway – OSRAM Opto Semiconductors
- Particle passivation (ZnS, oxide)
- LED solution development
- Device fabrication and optical testing

Dr. Jon Owen – Columbia University
- Synthetic design and practice, kinetics, mechanism
- Particle faceting and epitaxy
- Microscopy, X-ray techniques – particle characterization

Dr. Emory Chan – Lawrence Berkeley National Lab
- High-throughput robotic screening and chemical optimization
- Kinetic modeling
- TEM

The DOE of course



Best-in-class LEDs and smart indoor lighting solutions

- Intelligent and innovative LEDs, spectral and ambient light sensors that form the backbone for human-centric lighting (HCL)
- HCL to optimize daylight patterns, manage circadian rhythms, improve productivity and performance, mental and emotional well-being
- Smart lighting managers to create more cost-effective, accurate and tunable lighting
- Spectral and ambient light sensors add competence to room monitoring systems increasing the comfort and well-being

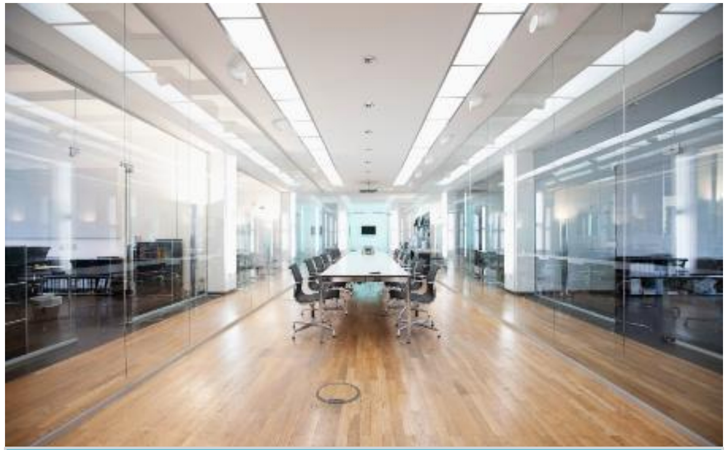
What is Human-Centric Lighting?

Ideally, we address the needs of different customers at the component level

- HCL looks beyond efficacy, at the visual and non-visual effects of light on people in a given setting
- Designed to produce or suppress certain physiobiological effects
- Produces the right spectrum light for the setting and/or group of people

Hospital

Light for Children – Class room



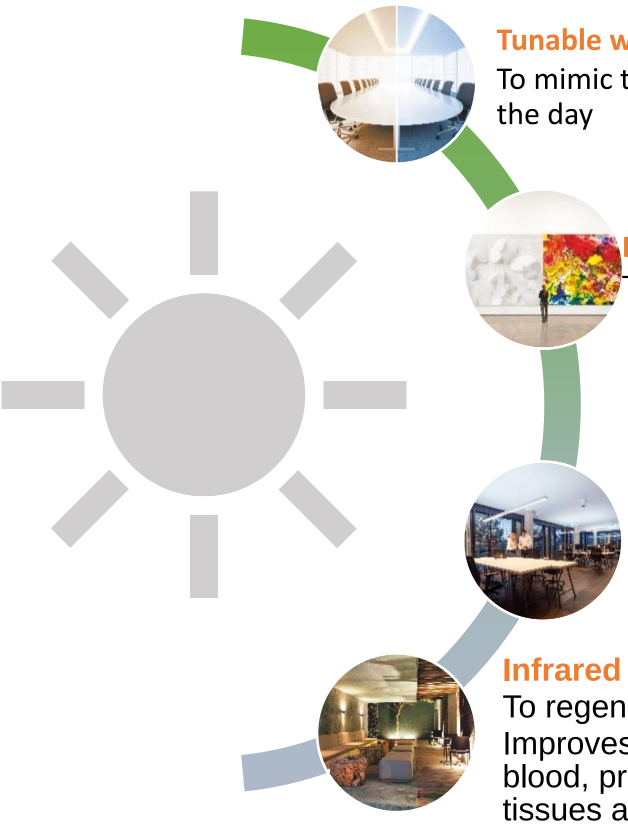
Light for Adults – Office

Light for Elders – AMD

Strategic Roadmap for Human-Centric Lighting

Innovative LED components to enable all aspects of Human Centric Lighting

Human centric lighting is the art of creating lighting that mimics the natural daylight that drives our bodily functions



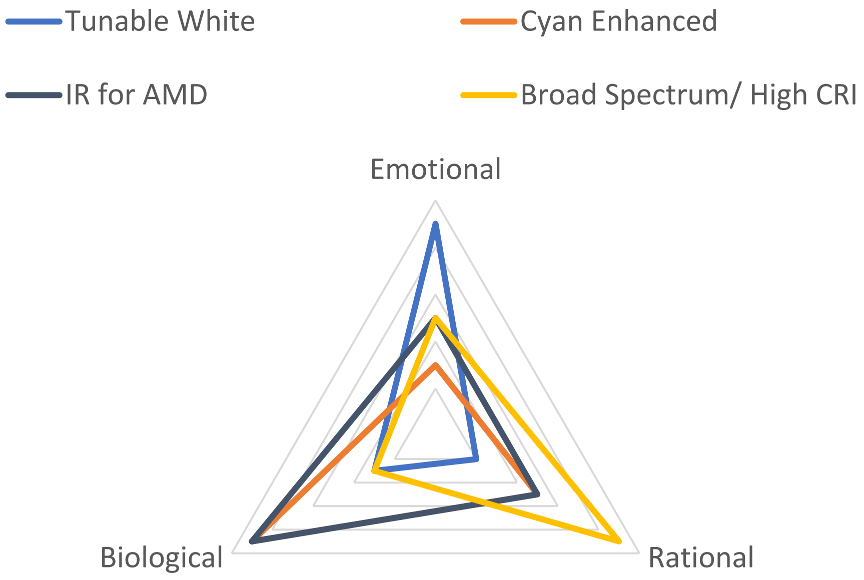
Tunable white
To mimic the sunlight color temp along the day

Broad Spectrum, High CRI
To replicate the sunlight spectrum

Cyan Enhanced
To trigger alertness

Infrared
To regenerate or repair cells themselves. Improves the circulation of oxygen-rich blood, promoting faster healing of deep tissues and relieving pain.

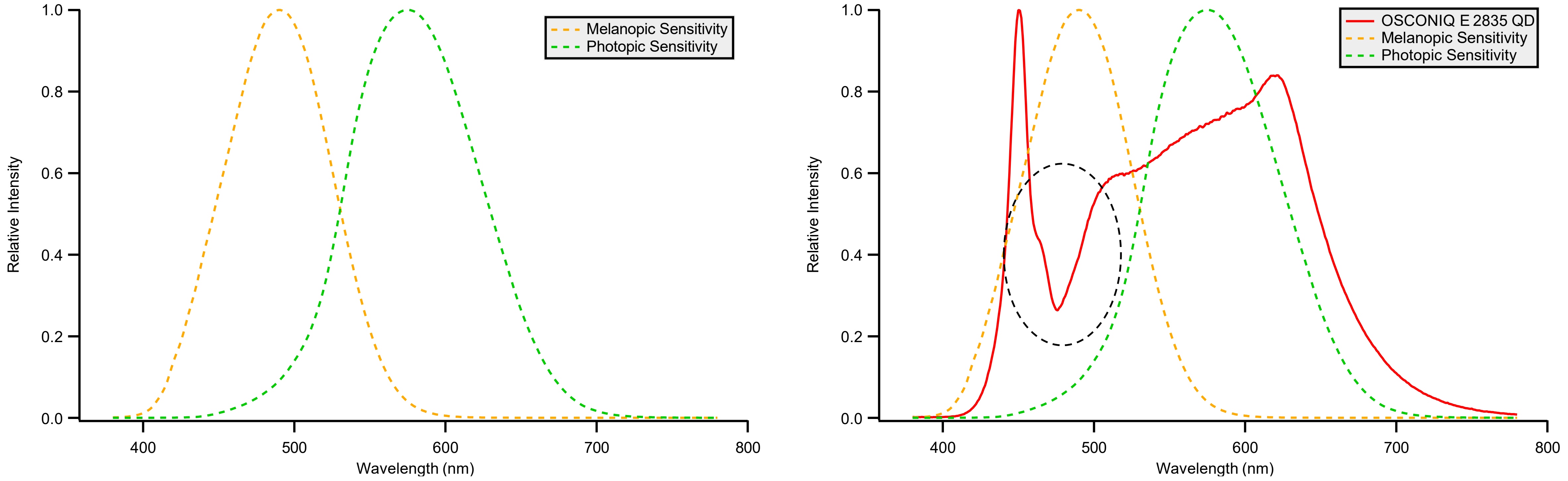
Dimensions of Human Centric Lighting



- **Emotional** – Consumers have a positive feeling e.g. tunable white towards warm white in the living room.
- **Rational** – Professionals have a positive perception e.g., high CRI values, high efficacy
- **Biological** – real biological effects which can be evaluated by action spectra e.g. CIE S 026 ipRGC-Influenced Responses to Light or IR light

HCL: Targeting the Melanopic Response

- **Photopic curve** is related to the luminous sensitivity of the eye
- **Melanopic action spectrum** is related to the sensitivity of the intrinsically-photosensitive retinal ganglion cells (ipRGC), specific to the generation of melatonin
- **The focus for LED development** has been mainly to get the **highest efficacy**, which is tuning to the photopic curve
  - ➢ This has led to the so-called “cyan gap”, with a low melanopic daylight ratio

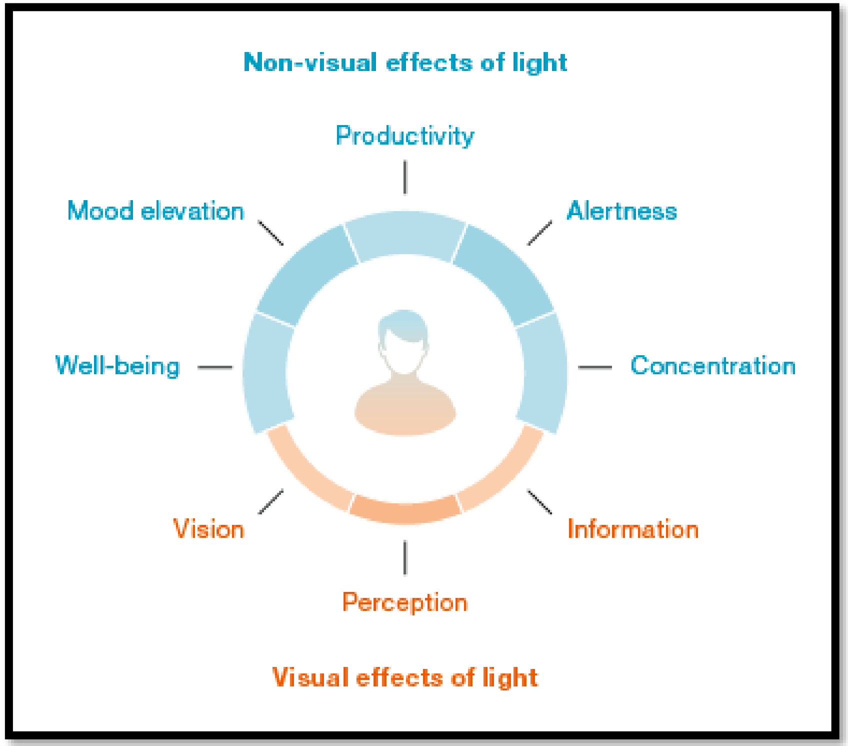


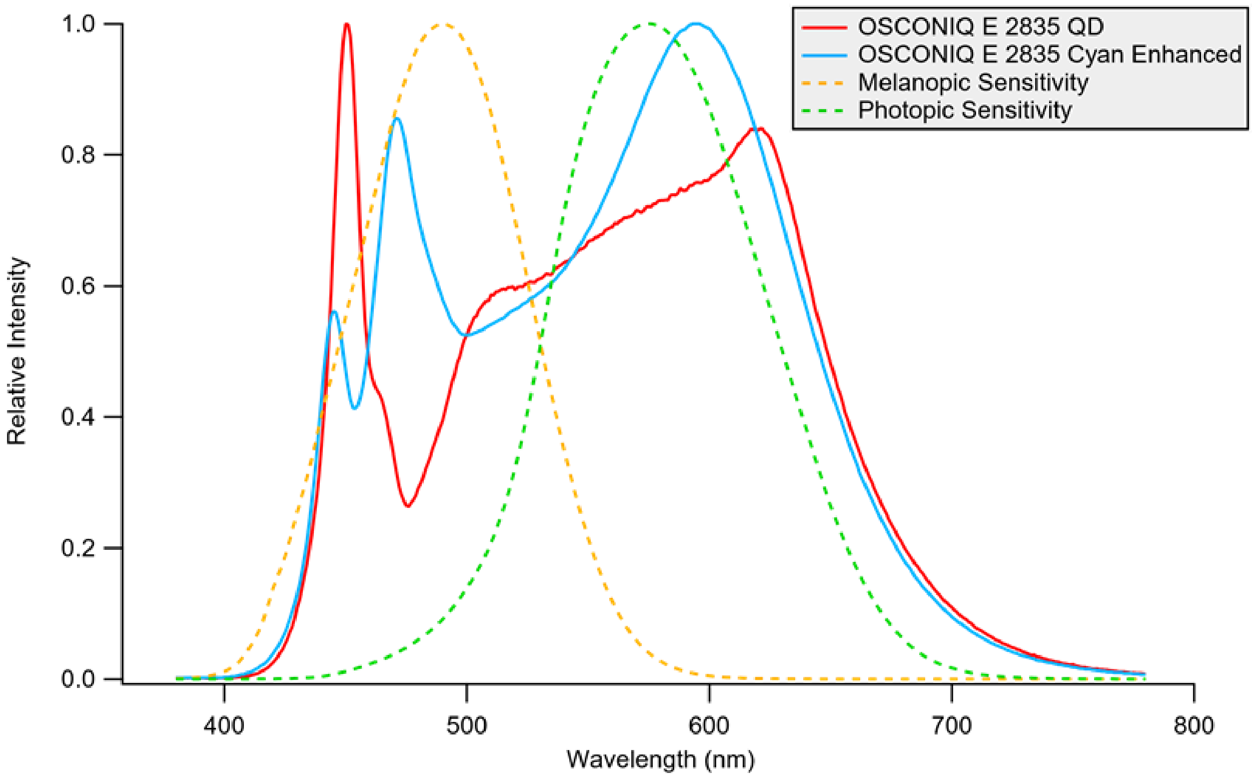
HCL: Targeting the Melanopic Response

Lighting to support circadian rhythm

- **Healthier & higher performing humans (school, workplace, etc)**
  - Cyan enhanced: Energizing, high melanopic ratio spectrum to improve productivity and efficiency during work hours
  - Full spectrum, CCT tunable: Broad spectrum High CRI to provide a near-to-daylight environment

WELL Building Standard:
L01 Light exposure
L02 Visual lighting design
L03 Circadian lighting design
L04 Electric light glare control
L05 Daylight design strategies
L06 Daylight simulation
L07 Visual balance
L08 Electric light quality
L09 Occupant lighting control





Project Targets

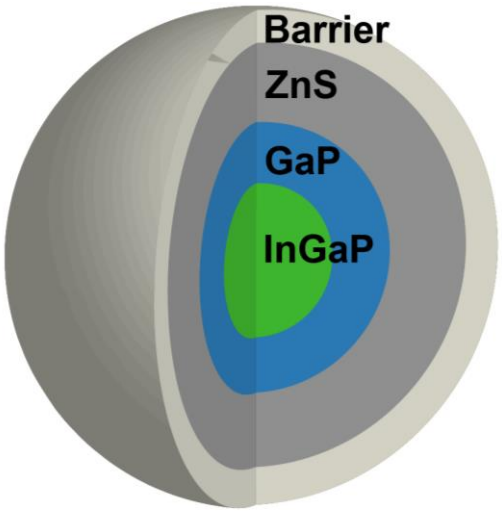
- Final Device Goals: CRI 90, CCT = 4000K, 210 lm/W
- Achieve the final device goals by developing new QD nanomaterials:

→ Make them „Green“
  - Develop a new class of heavy-metal free materials

→ Make them Cyan
  - Tune the wavelength through quantum size effects

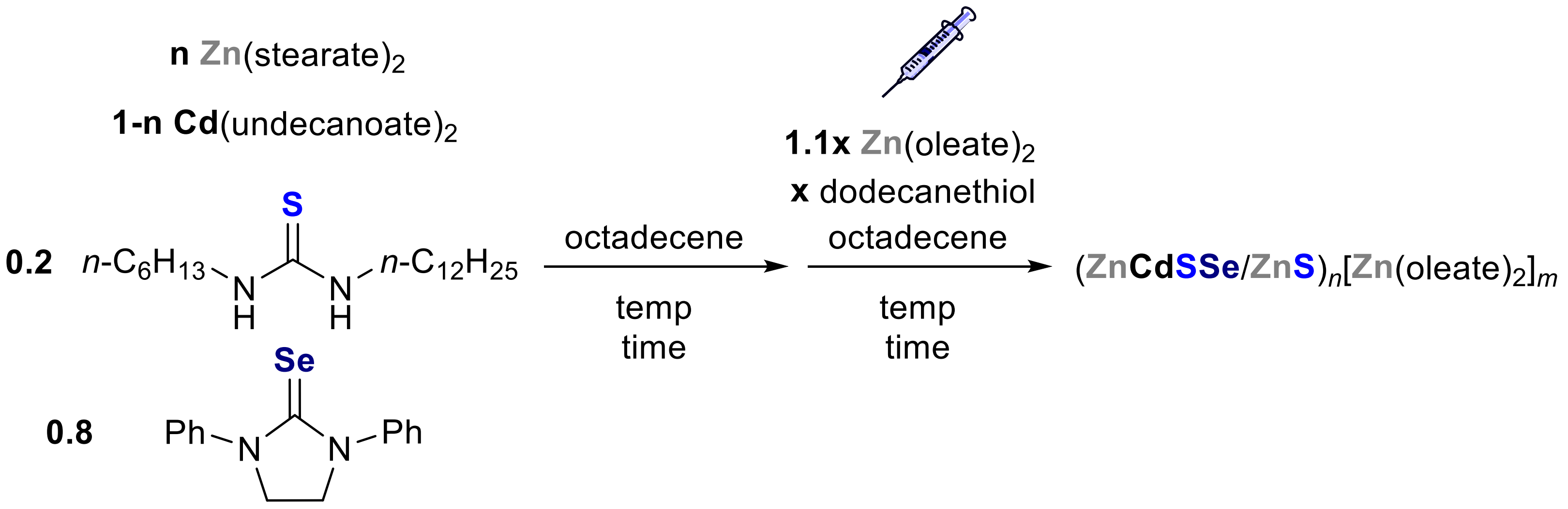
→ Make them bright
  - Optimize crystal structure and ligand chemistries to achieve high conversion efficiencies

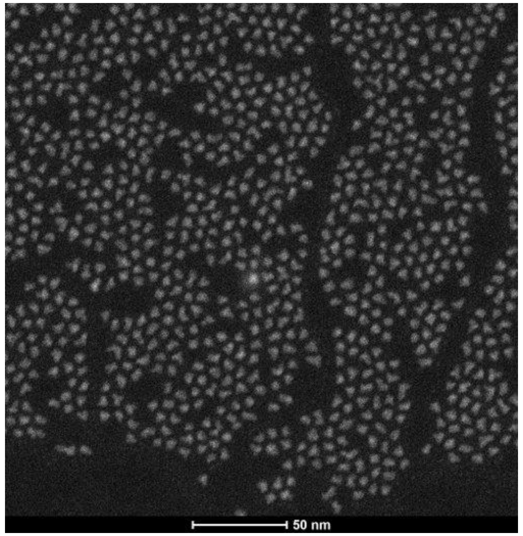
→ Make them stable
  - Apply barrier layers around each QD to allow for on-chip operation

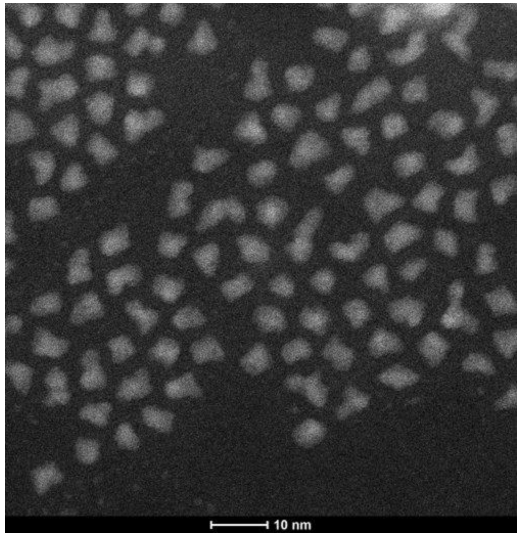


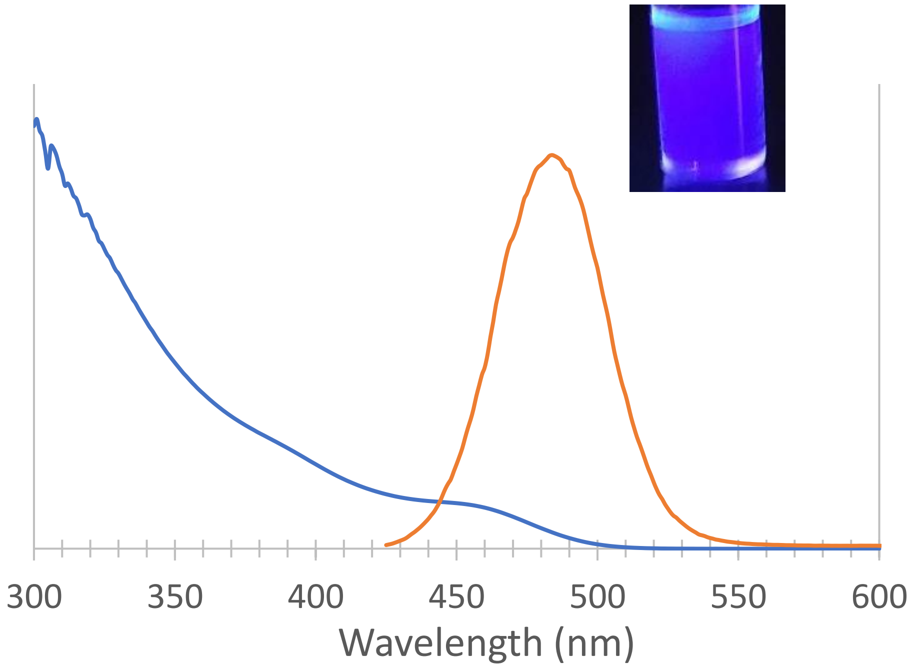
Layer	Materials	Focus
Core	InP or InGaP	Absorption & Emission
Shell	GaP, InGaP, or ZnSe	Protection & Ideally Absorption
Passivation	ZnS	Air Stability & Reliability
Barrier	Metal Oxides	Reliability

Baseline Proof-of-Principle for QD HCL Device: A Cadmium-Lite Half-Step

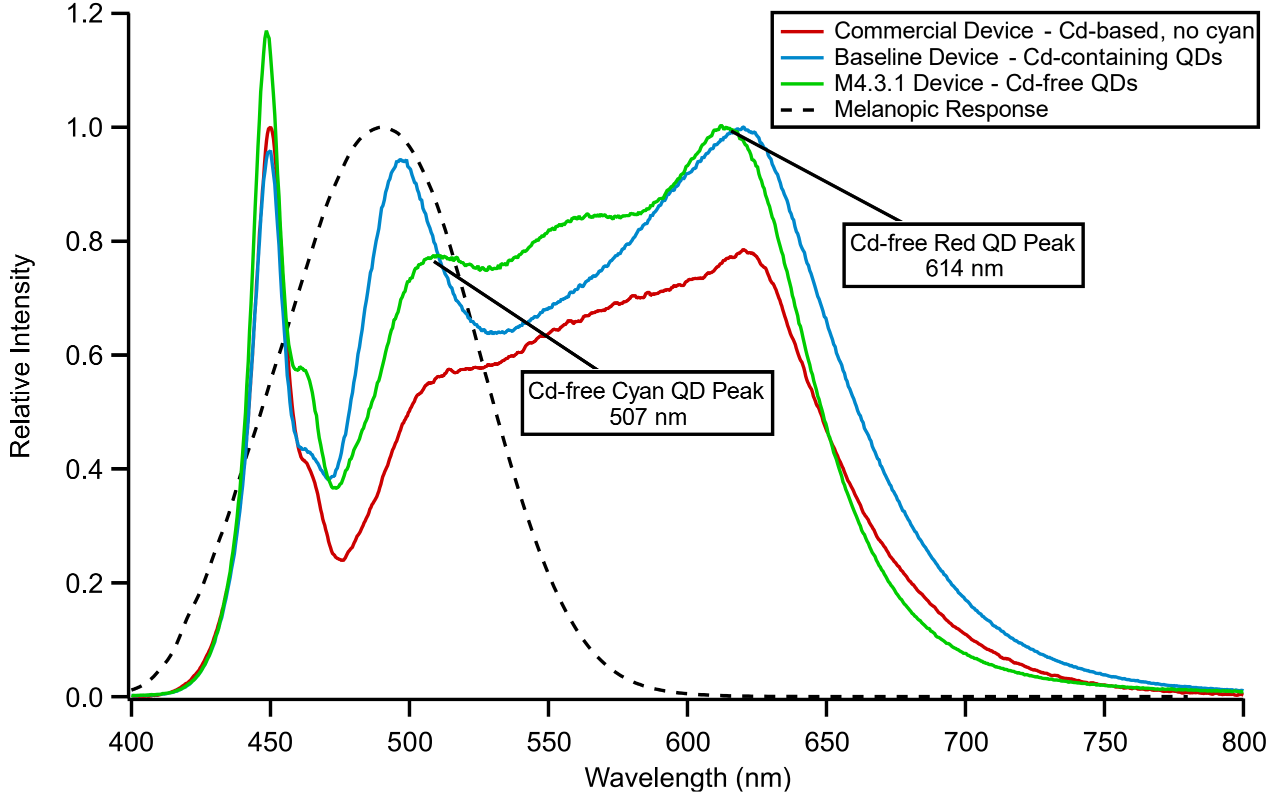








Baseline Proof-of-Principle for QD HCL Device: A Cadmium-Lite Half-Step

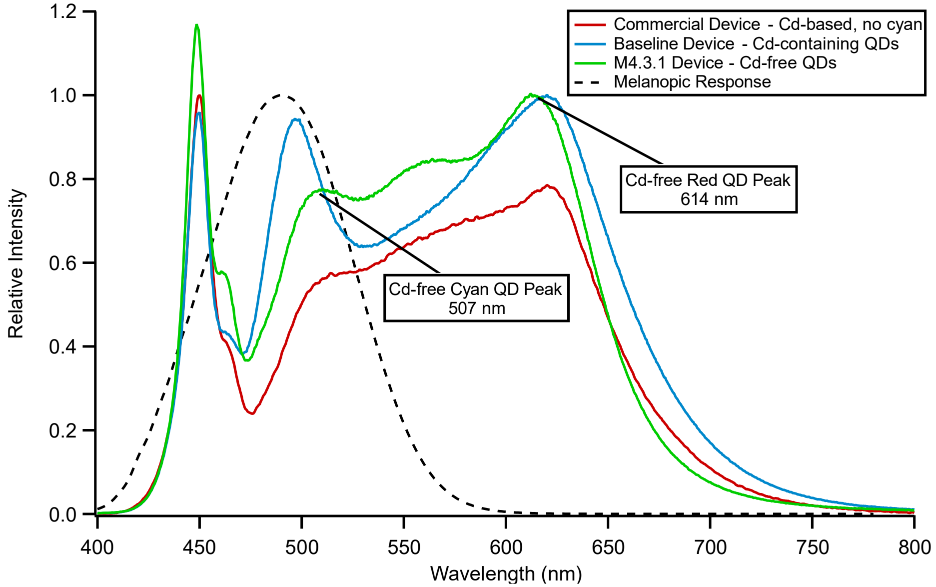


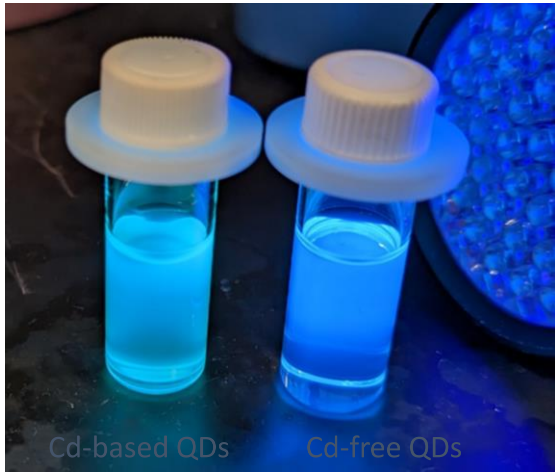
	Baseline Cd-containing Device	M4.3.1 Targets
Lumens	21.78	-
lm/W	123.5	160
LER	301	-
CCT	4030	4000
CRI	92	> 90
MDER	0.76	> 0.7

Key Learnings:

- Efficacy, MDER, and R9(!) unusually dependent fine details of blue line-shape and QY
- Surprisingly, extensive work has shown there is no value to switching from a 450 LED to a shorter-wavelength source (green phosphors)

Go/No-Go Milestone: A Fully Cd-Free Cyan-Enhanced Device





Cd-based QDs Cd-free QDs

Key Learnings:

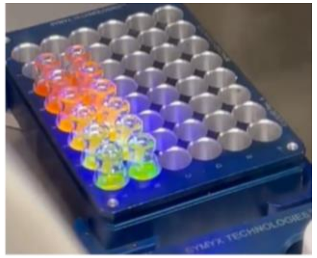
- LED light passes through cyan dots on the way to other phosphors/dots so PLQY retention during silicone polymerization is critical!
- While not quite meeting the milestone, these results are arguably better than the commercial offering at 157 lm/W at CRI 80

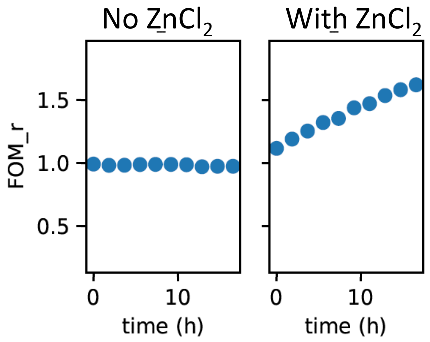
	Baseline Cd-containing Device	Cd-free HCL Device	M4.3.1 Targets	% Increase over baseline device
Lumens	21.78	24.33	-	11.7%
lm/W	123.5	138.5	160	12.1%
LER	301	332	-	10.3%
CCT	4030	4261	4000	-
CRI	92	91	> 90	-
MDER	0.76	0.71	> 0.7	-

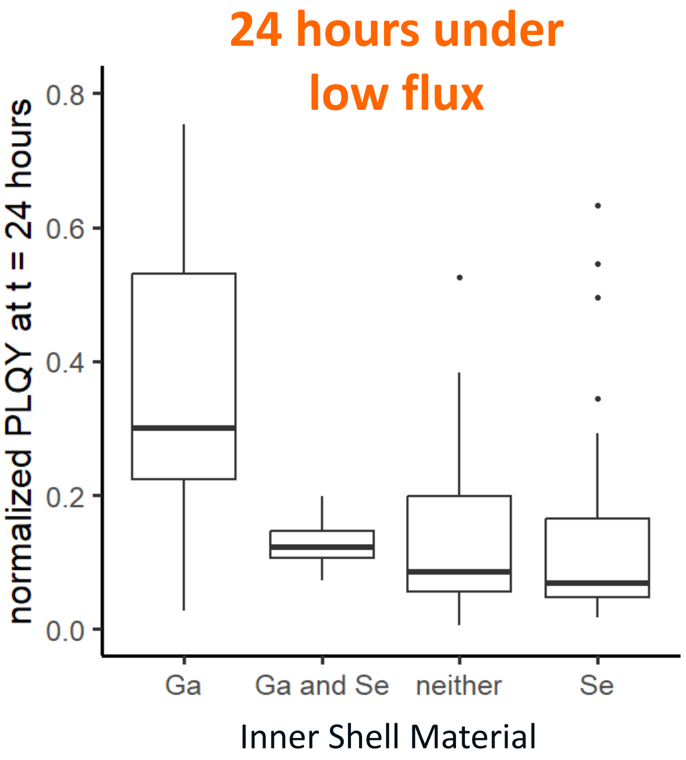
Optimizing Towards More Resilient Materials

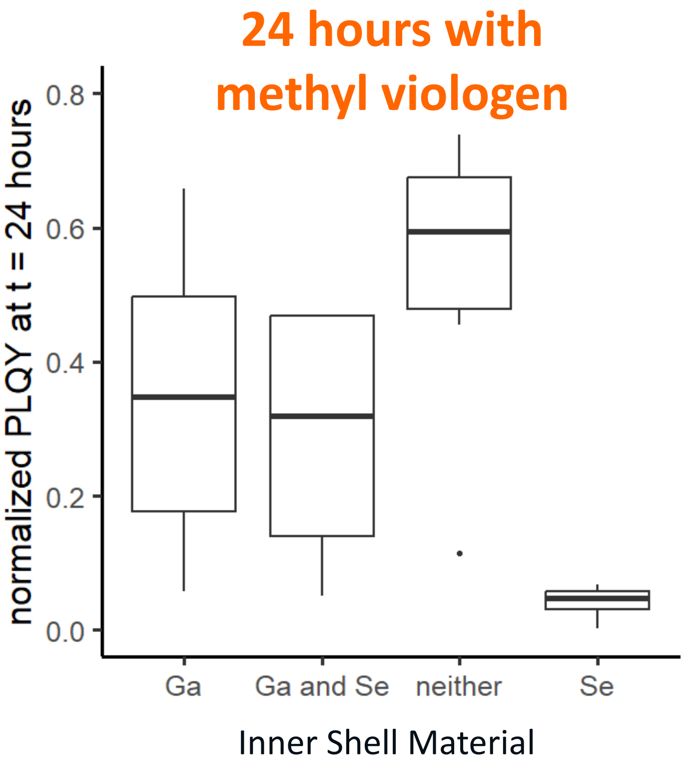
Workflow for chemical and photo-induced quenching of QD emission has been developed

- Tests are designed to interrogate the quenching mechanism for GaP and ZnSe shells
- QD emission is greatly quenched by low flux blue light and methyl viologen
- These data may aid in selection of promising inner shell composition and guide the synthesis of stable particles
- HT Robotic data focuses on optimizing leads

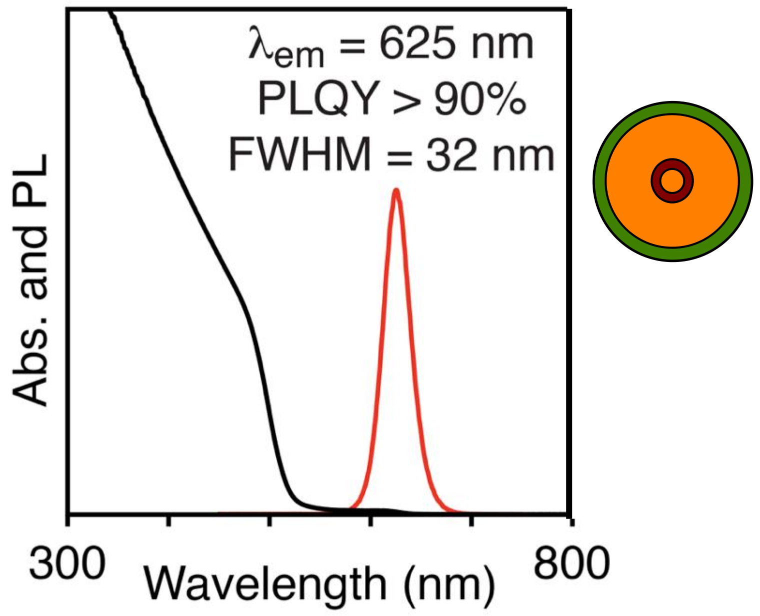


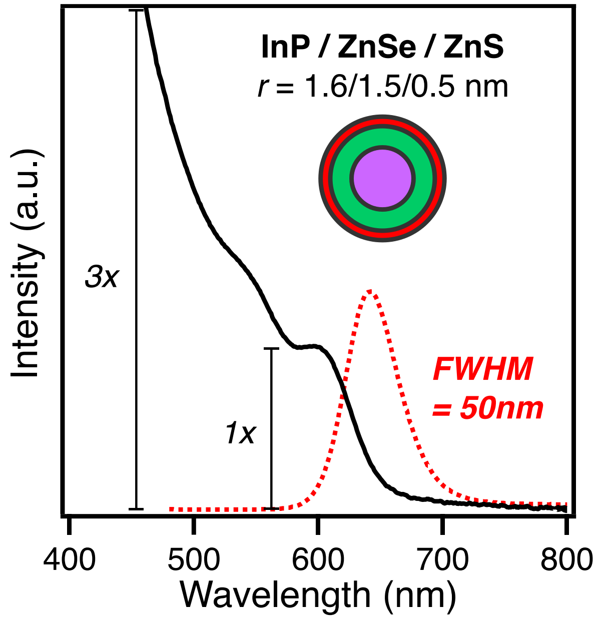






ZnSe is an Important Inner Shell but GaP Offers Advantages





CdS shell layer provides absorptivity at 450nm (95:5 S:Se shown above).

Shell thickness increases chemical robustness, reduces Auger recombination, and lengthens luminescence lifetime.

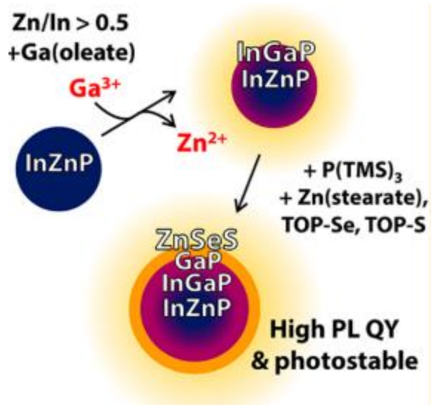
Poor absorptivity and reabsorption of red and of green is a major drawback.

GaP layers would increase absorption at 450 nm, and better passivate InP layer.

Fundamentally new synthetic methods to grade InP/GaP interfaces are needed.

GaP Strategies

Ga(oleate)$_3$ from GaCl$_3$ and TMS-P

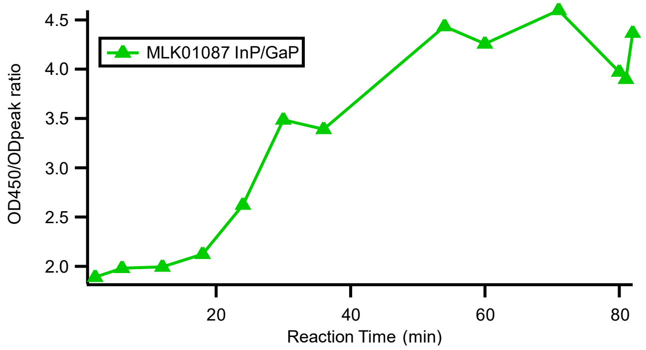


Pietra et al. *Chem. Mater*, **2017**, *29*, 5192.

Difficulty reproducing this promising literature approach. Still a contender for simultaneous formation of InGaP and InGaP/GaP

Ga(oleate)$_3$ from Ga(acac)$_3$ and TMS-P

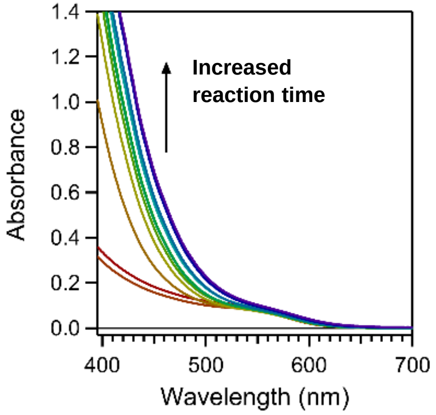
ACC04191 Red InP → (Vac, 120 °C, 60 min, ODE) → (+TMS-P, Ga(oleate)$_3$, 60 min, RT->290 C) → InP/GaP

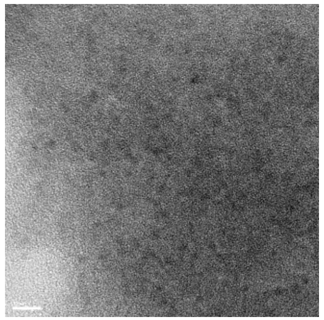


Approach fully developed in-house shows promise in increasing blue absorption, but lacks adequate analytics

Ga-halides and TMS-P

$$\text{InGaP} + 10\ \text{GaI}_3 + 5\ \text{ZnI}_2 + 9.1\ (\text{CH}_3\text{Si})_3\text{P} \xrightarrow[\text{TOP}]{300\ ^\circ\text{C}} \text{InGaP/GaP QDs}$$



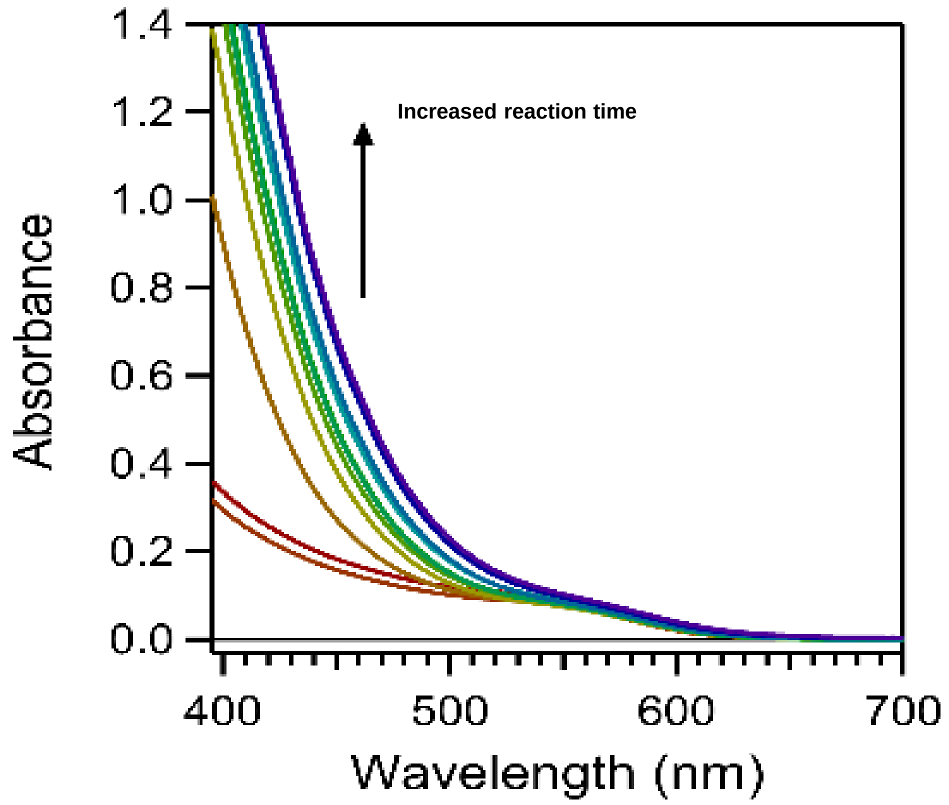


First unequivocal example of GaP shells. Elemental analysis and TEM confirm 4 monolayers

Results from GaP-containing Core-Shell Structures

Sample	Core Diameter (nm)	GaP Thickness (nm)	ML GaP	InP/GaP Diameter (nm)	Total Diameter (nm)
InP	3.2	-	-	-	-
InP/GaP/ZnS	3.2	1.1	4.1	5.4	5.6
InP/GaP	3.2	1.9	6.8	6.9	-
InP/GaP/ZnS	3.2	1.8	6.6	6.8	7.4

$$InGaP + 10\ GaI_3 + 5\ ZnI_2 + 9.1\ (CH_3Si)_3P \xrightarrow[\text{TOP}]{300\ °C} \text{InGaP/GaP QDs}$$



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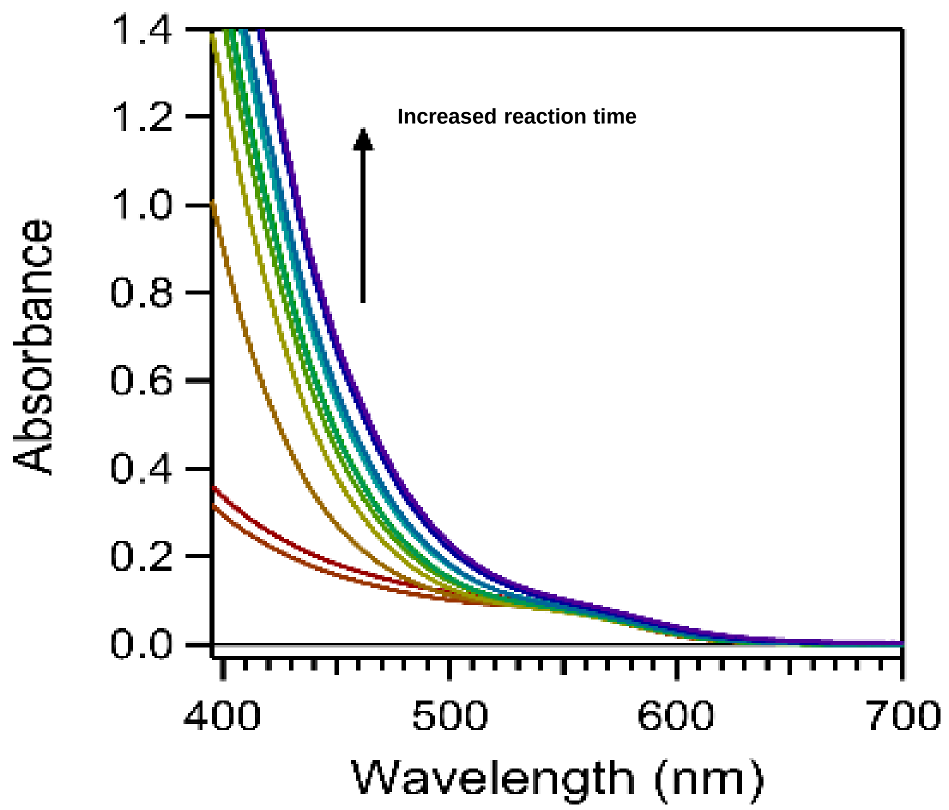
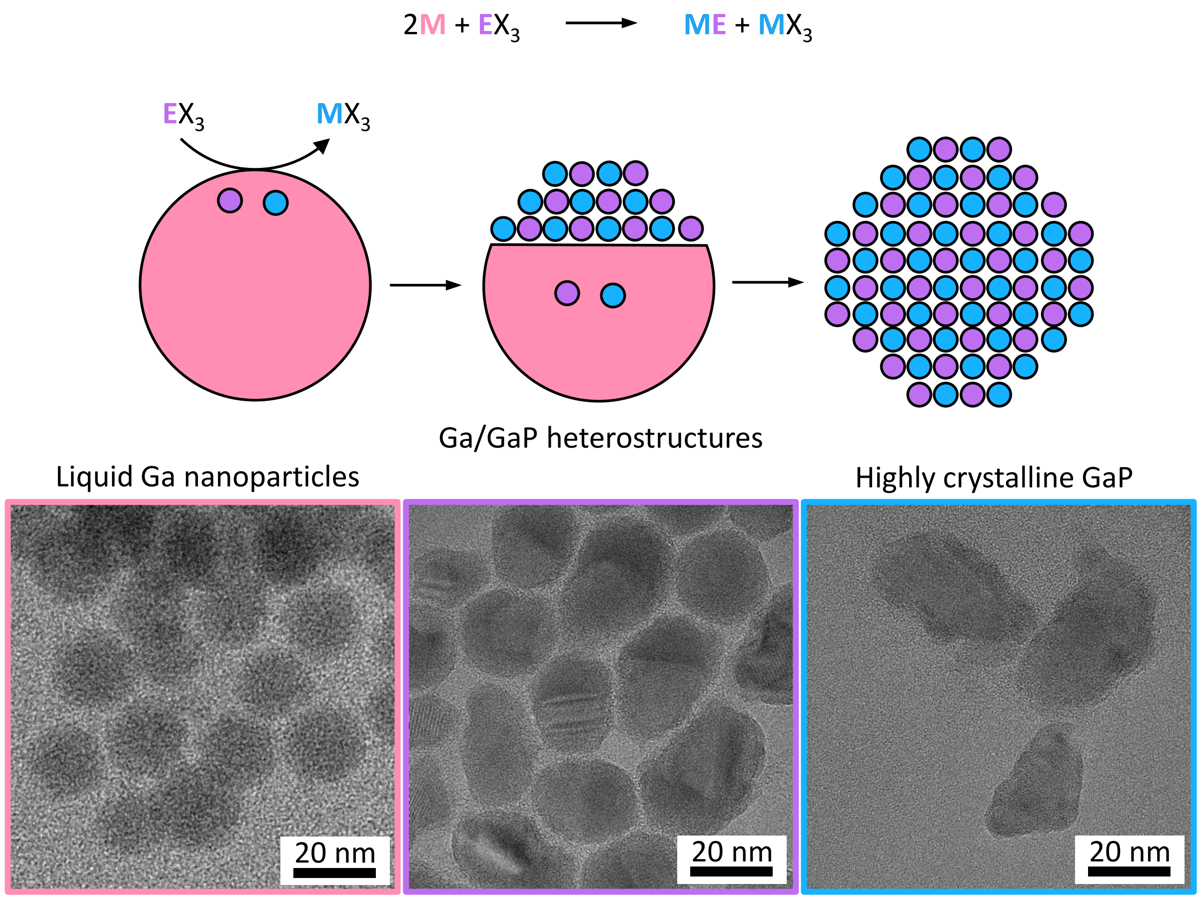
InP/GaP	3.2	1.9	6.8	6.9	-
InP/GaP/ZnS	3.2	1.8	6.6	6.8	7.4

Quantum yields range from 0 – 5% !!

$$InGaP + 10\ GaI_3 + 5\ ZnI_2 + 9.1\ (CH_3Si)_3P \xrightarrow[\text{TOP}]{300\ °C} InGaP/GaP\ QDs$$

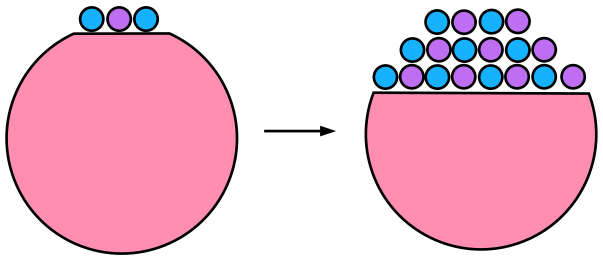


Crystalline GaP (!) from nano-Gallium Droplets (!!!)



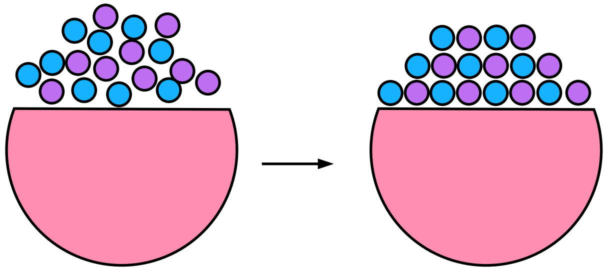
Crystallization through a liquid metal intermediate circumvents the formation of amorphous materials commonly produced in molecular syntheses of III-V semiconductors.

Facilitates nucleation and growth



Lowers energy barrier to nucleation and growth of covalent materials by solvating precursors in a highly polarizable medium and then directing layer-by-layer crystallization.

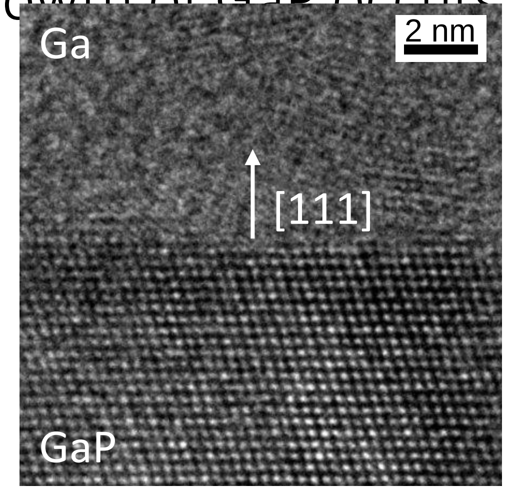
Achieves microscopic reversibility



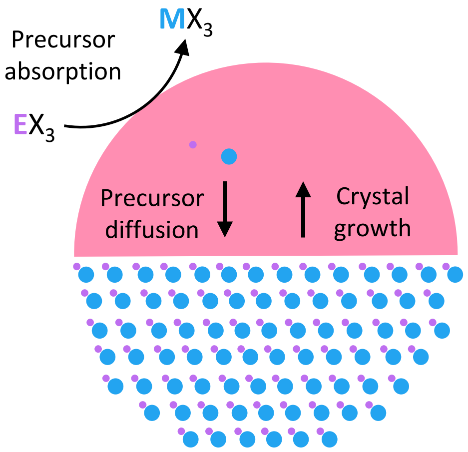
Highly polarizable liquid metal interfaces facilitates rapid bond breaking and making in covalent systems.

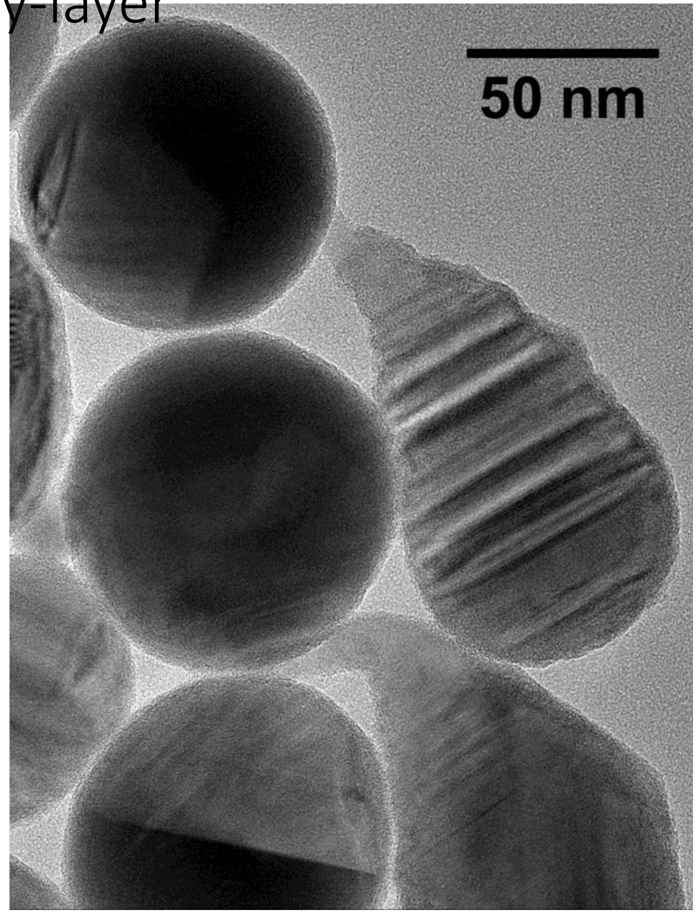
Growth of GaP Occurs Layer-by-Layer

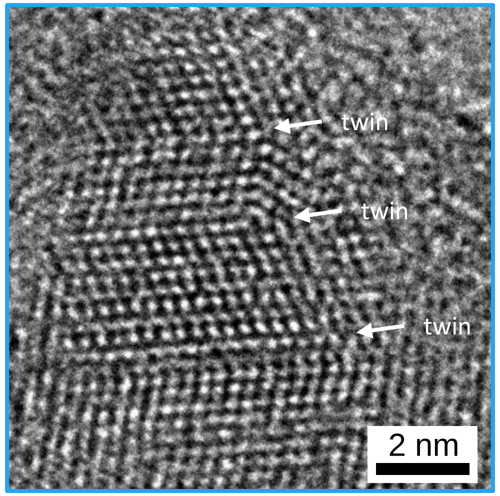
Growth of GaP occurs layer-by-layer

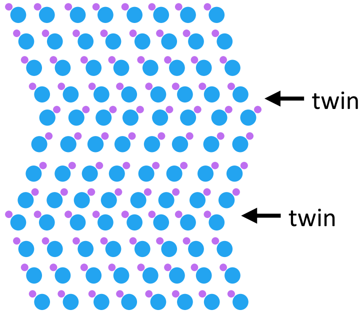


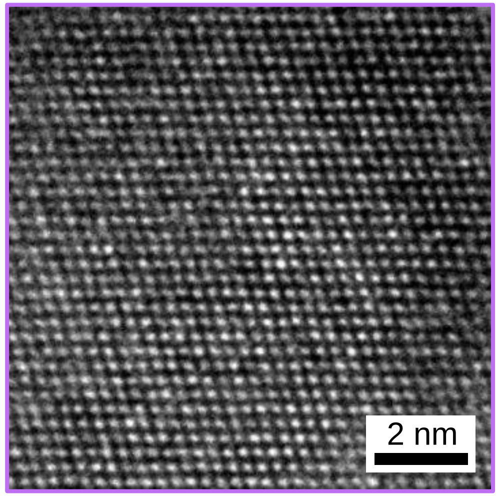
$2M + EX_3 \longrightarrow ME + MX_3$

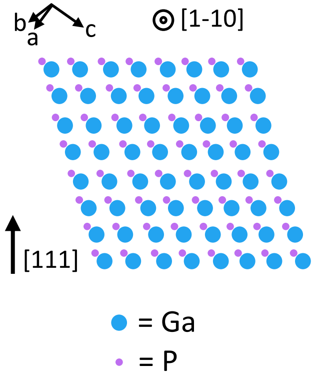






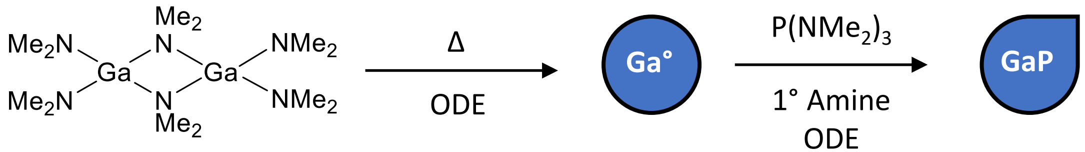






The synthesis produces a mixture of nanocrystals that are nearly single-crystalline or have some planar twin defects.

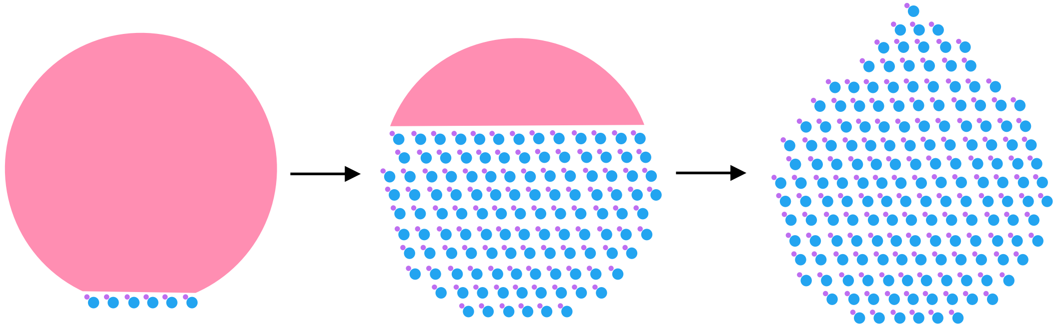
Injection of Primary Amine Halts Gallium Growth



In 15 eq $HN(Oct)_2$ to Ga

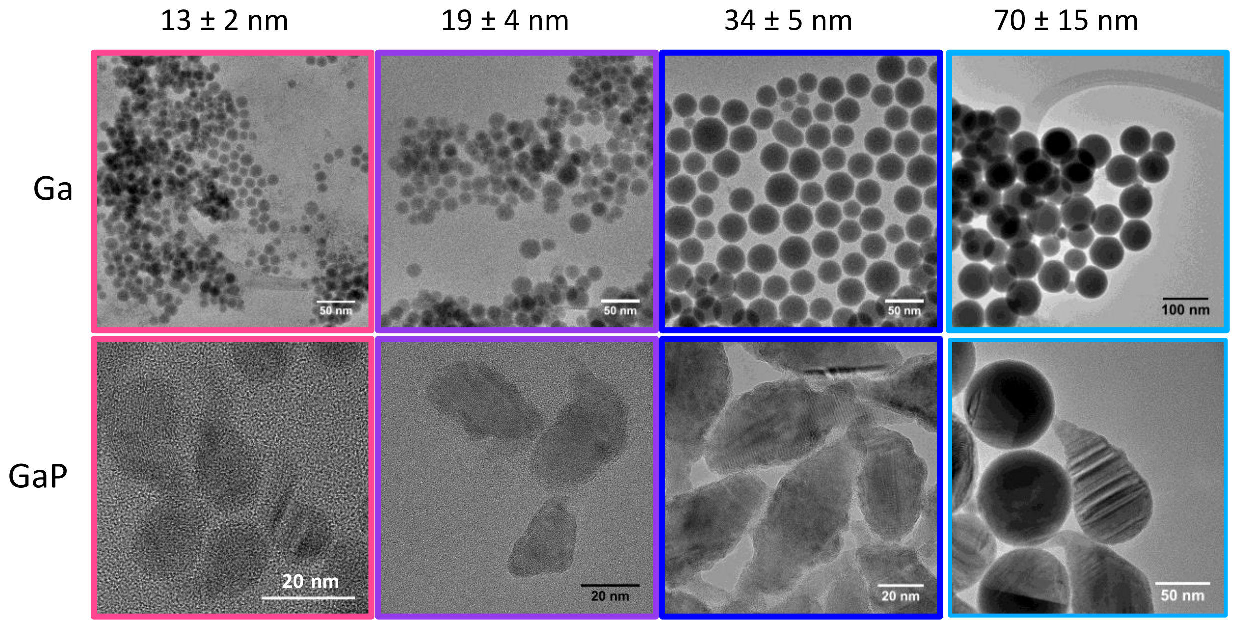
Injection of primary amine sequesters unreacted gallium by the formation of unreactive aminogallanes!

The addition of primary amine dictates nanocrystal shape



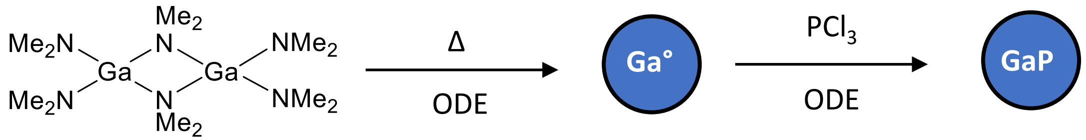
Phosphidation only occurs with available gallium metal resulting in teardrop-shaped nanocrystals rather than wires, which are commonly formed during SLS growth.

The addition of primary amine dictates nanocrystal size

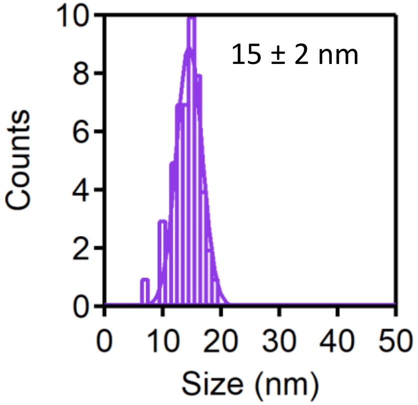


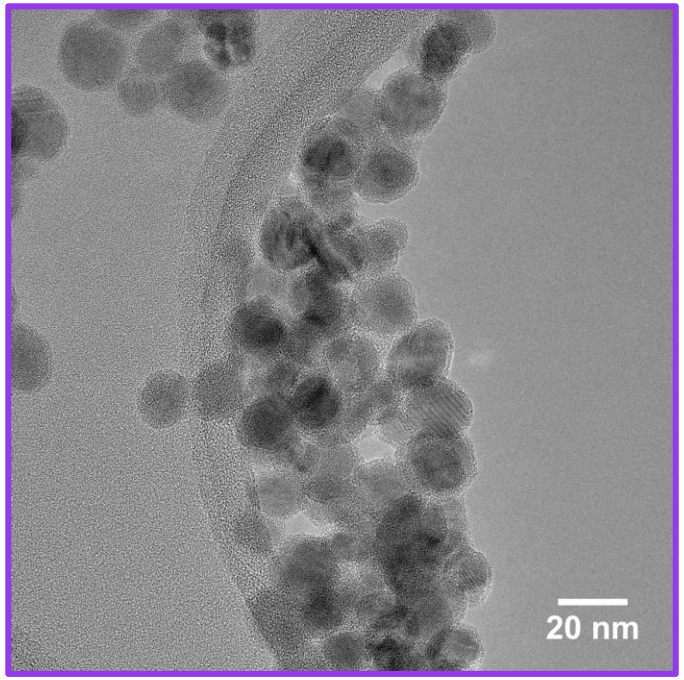
The width of GaP is consistent with the radius of metallic gallium at the time of injection.

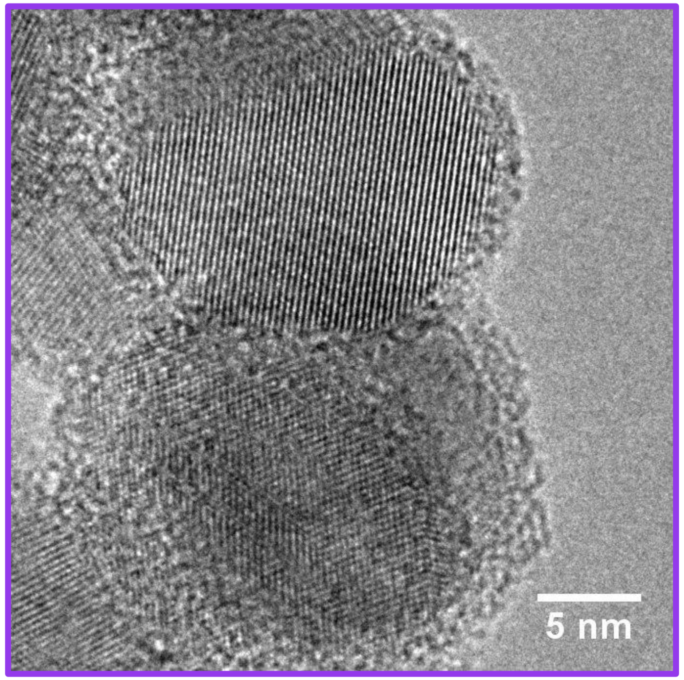
Spherical Nanocrystals Formed with Stronger Oxidant PCl_3



In 3 eq $HN(Oct)_2$ to Ga

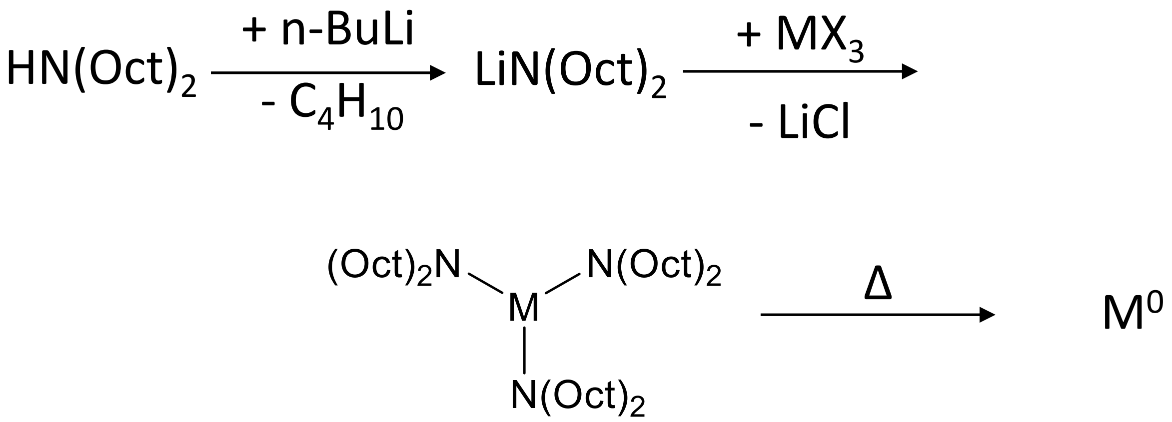


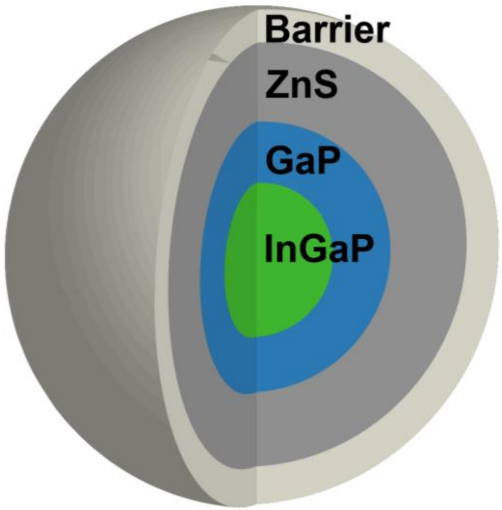




- Phosphidation is complete just 30 seconds after PCl_3 injection (compared to roughly 1 hr for $P(NMe_2)_3$.
  - Color change from black to yellow/orange observed. Particles are crystalline by TEM.
- Particles are round rather than teardrop shaped.
- Resulting GaP much smaller than anticipated Ga size (35 nm).
  - Possible etching from PCl_3?
- Increased aggregation due to lack of surface ligands.

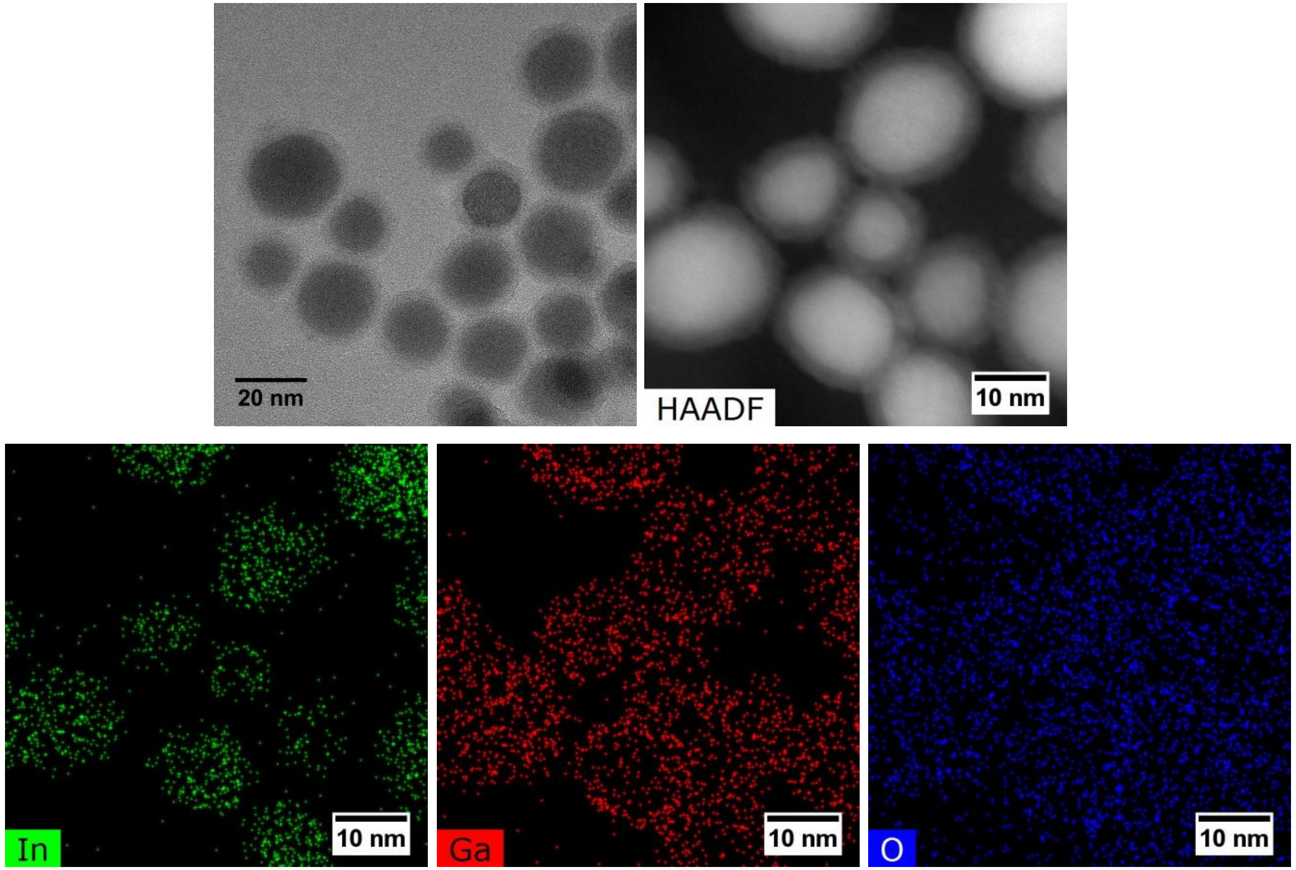
Taking the Technology to the Next Step: In/Ga Alloyed Seeds





Inspiration from: He et al. *Chem. Mater.* 2015, 27, 2, 635–647

Synthesis: 1:1 $GaCl_3/InI_3$

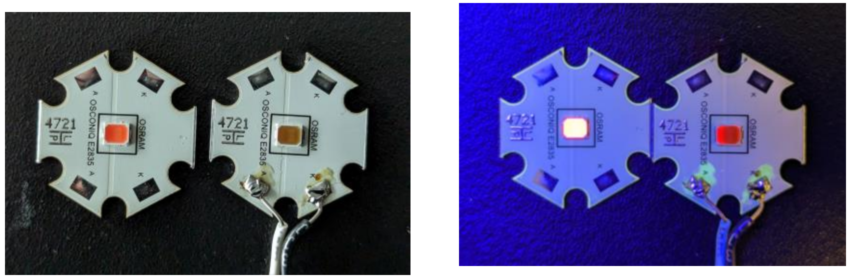


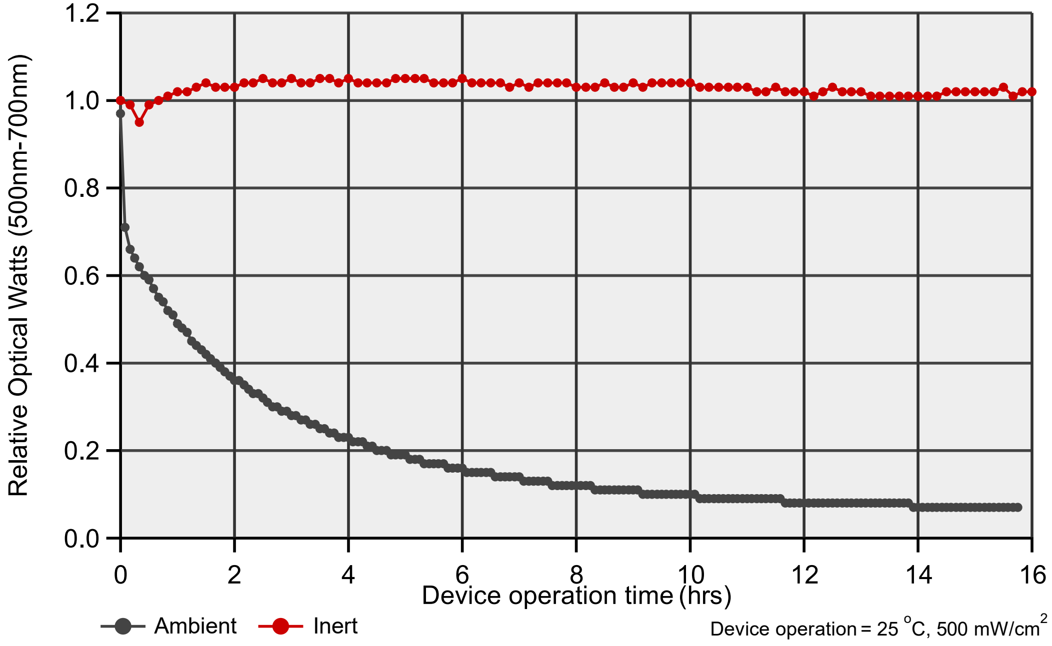
Gallium metal has a lower redox potential than indium, which results in a gallium-rich oxide shell when exposed to air.

Oxygen is Still a Big Problem Even with Optimized Materials

- Rapid degradation in air shows that oxygen quenches QDs
- Further passivation is required both at the core-shell and encapsulant stages
- Initial device PLQY for non-cadmium dots has increased from ~3% with outside materials to >50% with new in-house dots
- This high PLQY must be maintained over the operating lifetime of the devices
- Encapsulation with metal oxides is critical for QD survival on-chip

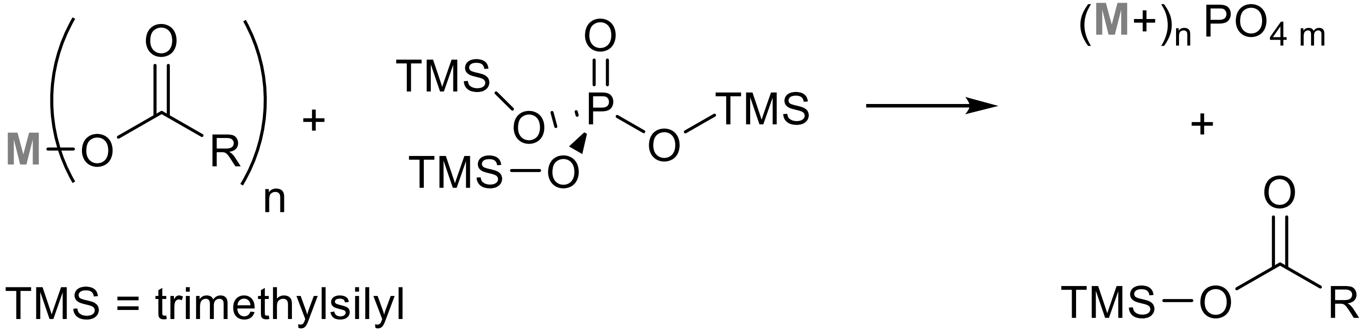
Before and after testing





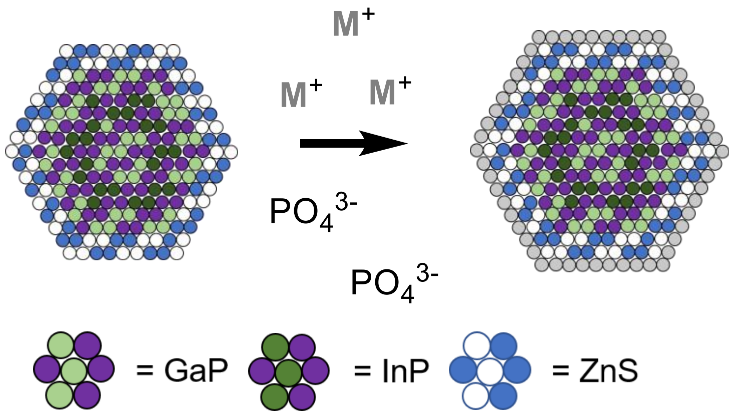
Future Directions:

Metal phosphate shelling



TMS = trimethylsilyl

M^+ = Li, Na, Mg, Ca, Zn, Cd, Al, etc.

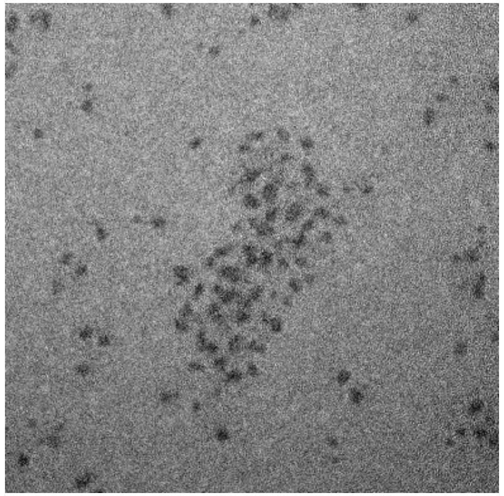


Metal phosphates must be identified the improve PLQY and allow silicone encapsulation. The metal phosphate could prove sufficient (especially those with M^{2+} and M^{3+} ions), or may act as a buffer layer prior to silicone encapsulation.

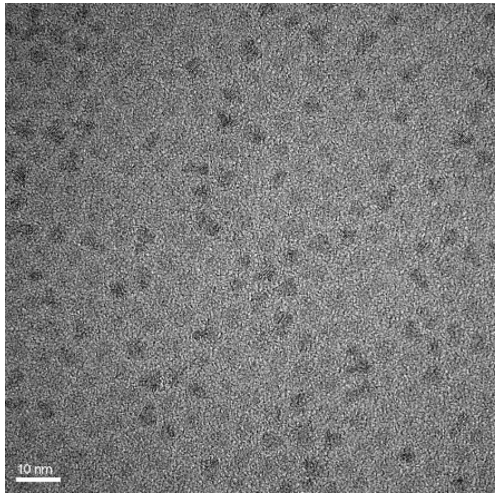
Layer-by-layer and syringe pump methods are targeted.

Basic science of metal and phosphate adsorption on QDs to identify isoelectric points and PLQY dependence on adsorption isotherms.

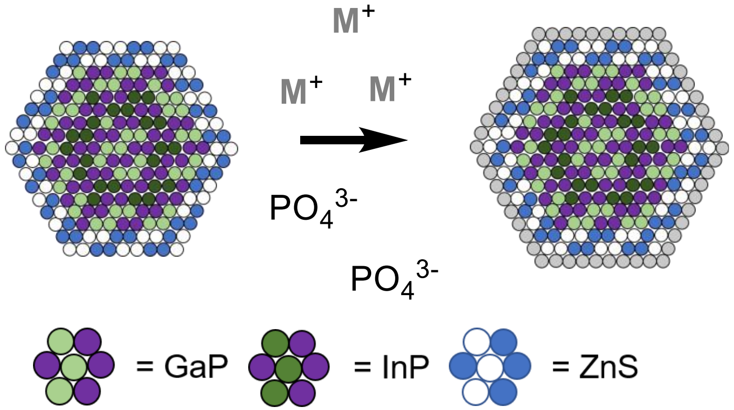
Future Directions:



InGaP

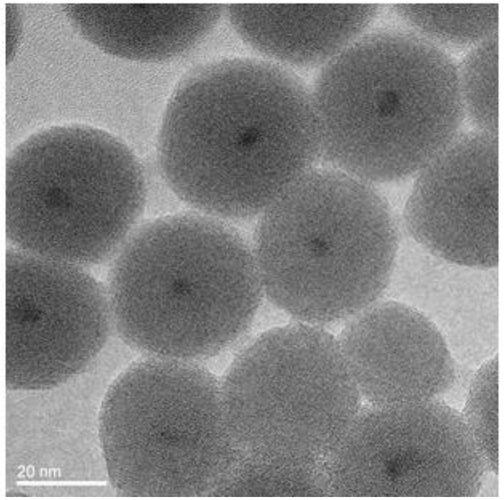


InGaP/ZnS

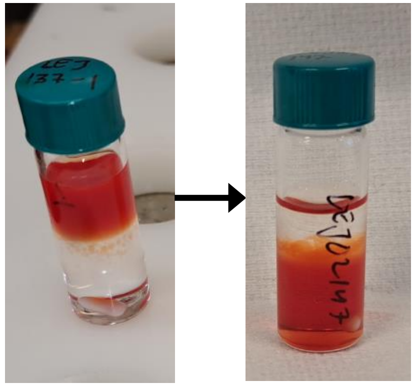


Transfer from non-polar to polar solvent as quantum dots become coated with poly-phosphate

III-V quantum dots encapsulated in thick silica-aluminate encapsulant



InGaP/ZnS+oxide



Year 1 Progress towards Milestones

Milestone	SOPO Task/ Subtask Number	Planned Completion Date	Verification Method	% Completion	Comments
CdZnSeS/ZnS (cyan)	Task 1/ Subtask 1.1	3/31/2022	1 g, 475 ± 15 nm, FWHM < 35 nm emitter, PLQY > 90%	90	Did not make 1 g per batch, PLQY ~75%
Determine proper LED light source	Task 4/ Subtask 4.1	3/31/2022	Demonstrate cyan-enhanced white light LED with CdZnSeS/ZnS QD and establish baseline HCL values	100	123 lm/W
Determine optimal LED pump wavelength	Task 4/ Subtask 4.1	6/30/2022	Consider cost and long-term potential of LED source verses efficacy and color quality of white solution	100	450 nm
InGaP/GaP/Zn(Se)S/ZnS (cyan)	Task 1/ Subtask 1.2	9/30/2022	0.1 g, 475 ± 15 nm, FWHM < 40 nm, PLQY > 85%	90	PLQY ~60%
InGaP/GaP/Zn(Se)S/ZnS (red)	Task 1/ Subtask 1.3	12/31/2022	1 g, 625 ± 10 nm, FWHM < 40 nm emitter, PLQY > 85%	80	FWHM ~50 nm, PLQY ~80%
Facet Control During InGaP/(ZnSe)ZnS core-shell Synthesis	Task 2/ Subtask 2.1	12/31/2022	Successful initial HERMAN screening run w/ Zn salts	80	Facet control should use HERMAN
Demonstrate and quantify PLQY stability InGaP/GaP/ZnS QDs	Task 2/ Subtask 2.3	12/31/2022	Solution/shelf stability- PLQY retention as a function of challenge condition, eg. pH	100	Developed chemical and flux challenges
Tune QD size, composition for high absorption	Task 4/ Subtask 4.1	12/31/2022	(ODoptimal / ODpeak) > 4	25	Low GaP work; no increase in Abs
Demonstrate cyan-enhanced capability of Cd-free QDs	Task 4/ Subtask 4.3	12/31/2022	CRI Ra = 90, CCT = 4000, MDER (D65) > 0.7	100	Achieved HCL device
Demonstrate cyan-enhanced capability of Cd-free QDs	Go/No-Go	12/31/2022	CRI Ra = 90, CCT = 4000, MDER (D65) > 0.7, 160 lm/W, solution PLQY > 60% for cyan and red QDs	90	139 lm/W

Year 2 Upcoming Milestones

MILESTONE SUMMARY FOR BUDGET PERIOD 2				
Milestone Number	**Milestone**	**SOPO Task/ Subtask Number**	**Planned Completion Date**	**Verification Method**
M3.1.1	Optimize chemical bath deposition of hydroxyapatite onto InGaP/ZnS QDs to establish baseline PLQY. Grow >5 nm of hydroxyapatite onto QDs	Task 3/ Subtask 3.1	3/31/23	Standardized optical testing protocol. X-ray diffraction. TEM.
M3.3.1	Novel barrier coated Cd-Free QD system with a PLQY > 50 % Measured in film at $10 W/cm^2$, 120 °C	Task 3/ Subtask 3.3	6/30/23	Standardized optical testing protocol.
M4.2.1	Barrier-coated QD Stability Studies: PLQY Maintenance > 50% of baseline at 500 hrs LED HTOL & WHTOL Reliability	Task 4/ Subtask 4.2	6/30/23	Real time monitoring of changes in efficacy and color metrics in test LED devices under industry-standardized conditions
DP1	Report best surface chemistry for novel barrier coating	-	6/30/23	Comparison of optical brightness and reliability for candidate processes
DP2	Opt to pursue porous glass encapsulation based on PLQY and reliability data	-	6/30/23	Comparison of optical brightness and reliability for candidate processes
M3.2.1	Demonstrate next gen capabilities of metal-oxide encapsulation of QDs HTOL and WHTOL 1000-hour reliability challenges by 50% over manufacturing baseline methods.	Task 3/ Subtask 3.2	9/30/23	Real time monitoring of changes in efficacy and color metrics in test LED devices under industry-standardized conditions
M3.3.2	Novel barrier coated Cd-Free QD system with a PLQY > 90% Measured in film at $10 W/cm^2$, 120 °C	Task 3/ Subtask 3.3	9/30/23	Standardized optical testing protocol.
M4.2.2	Barrier-coated QD Stability Studies: PLQY Maintenance > 100% of baseline at 1000 hrs LED HTOL & WHTOL Reliability	Task 4/ Subtask 4.2	12/31/23	Real time monitoring of changes in efficacy and color metrics in test LED devices under industry-standardized conditions
M4.3.2	Demonstrate full spectrum capability by building LEDs with Cd-free of PLQY > 90% for red and cyan QDs	Task 4/ Subtask 4.3	12/31/23	CRI Ra = 95, CCT = 4000, MDER (D65) > 0.7
M4.3.3	Demonstrate CRI 90, 4000K device with red, Cd-free QDs	Task 4/ Subtask 4.3	12/31/23	CRI Ra = 90, CCT = 4000, MDER (D65) > 0.7, 210 lm/W

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