DE-EE0009692

Cd-free Quantum Dot Building Blocks for Human Centric Lighting

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Introduction

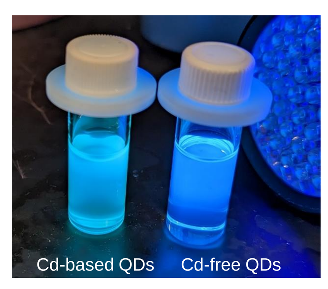
Human Centric Lighting

- Improve well-being by making lighting centered around the human experience

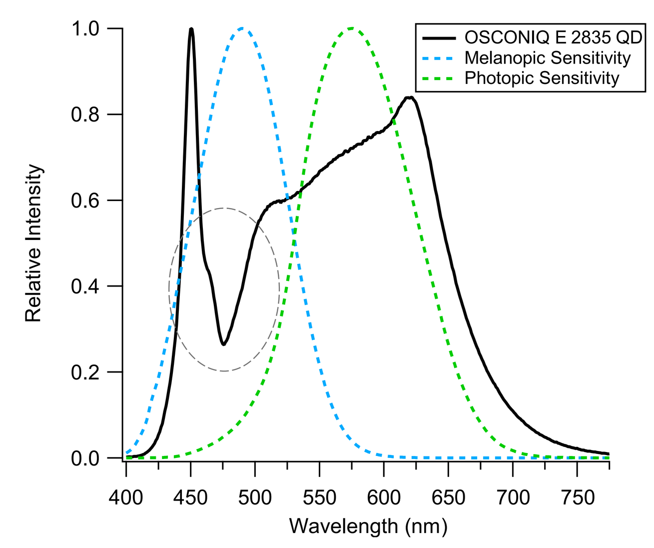
WELL Building Standard:
L01 Light exposure
L02 Visual lighting design
L03 Circadian lighting design
L04 Electric light glare control
L05 Daylight design strategies
L06 Daylight simulation
L07 Visual balance
L08 Electric light quality
L09 Occupant lighting control

Melanopic Response

- Cyan-enhanced and full-spectrum HCL lighting solutions consider human well-being by engineering light quality to mimic daylight and maintain circadian rhythms
- MDER: Melanopic Daylight Efficacy Ratio
  - A comparison of melanopic response of engineered light vs. natural sunlight
  - 4000K lighting has a MDER of ~0.7



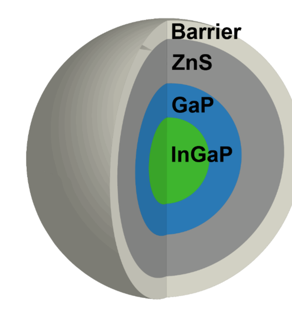
Cyan QDs in solution



- Typical LED spectra are severely lacking in cyan light content
- MDER can be greatly improved by filling the gap in the cyan spectral region

Filling the Cyan Gap

- Quantum dot (QD) downconverters have narrow emission bands that can fill spectral gaps more effectively than traditional phosphors
  - ➢ Engineer new QD materials tuned for HCL applications
  - ➢ Develop cadmium-free nanomaterials for commercialization
  - ➢ Optimize semiconductor layers for band alignment and metal oxide coating for stability



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

Project Targets

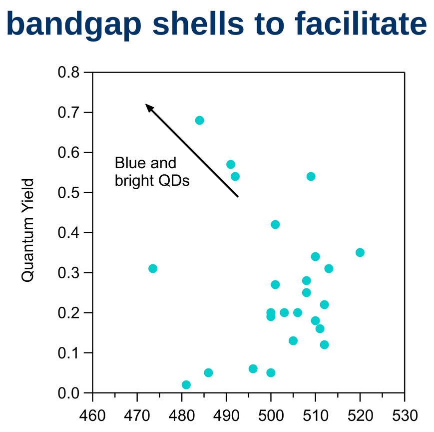
- Final Device Goals: CRI 90, CCT = 4000K, 210 lm/W
- Achieve the final device goals by developing new QD nanomaterials:
  - → Make them "green"
    - Develop a new class of heavy-metal-free materials
  - → Make them cyan
    - Tune the wavelength through quantum size effects
  - → Make them bright
    - Improve 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

Results

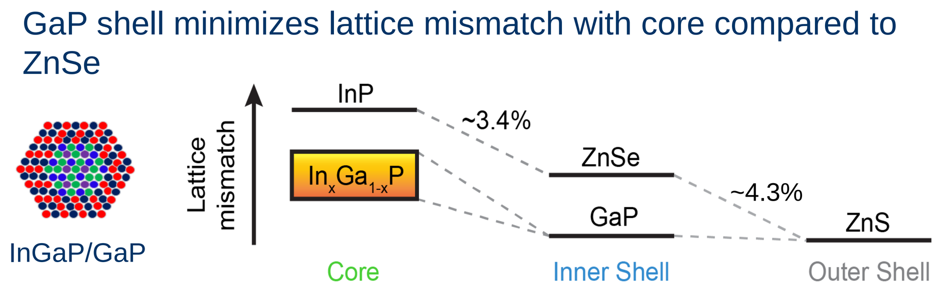
Task 1: Synthesis of down-converters

InP and InGaP cores require larger bandgap shells to facilitate emission and confer stability

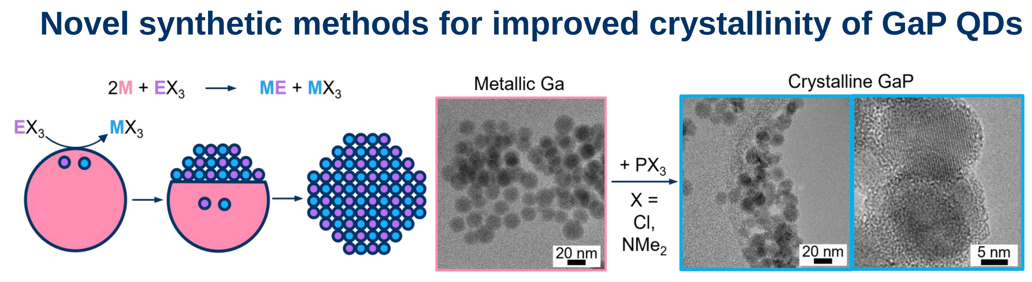
- Cyan QDs have a high surface area-to-volume ratio and are sensitive to shelling chemistry
- Red QDs absorb light from phosphors and cyan-emitting QDs
  - ➢ High conversion efficiency is especially important for blue particles

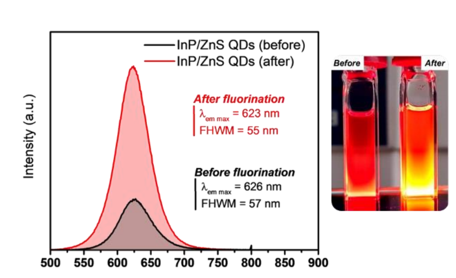


- GaP shell minimizes lattice mismatch with core compared to ZnSe

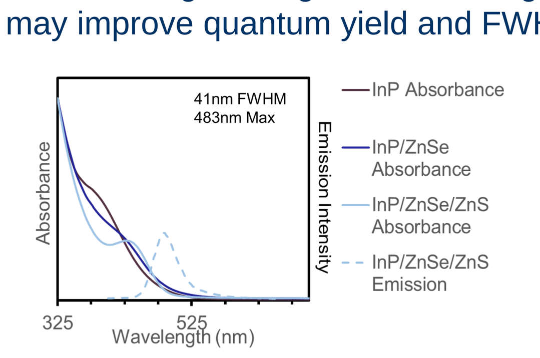


Novel synthetic methods for improved crystallinity of GaP QDs

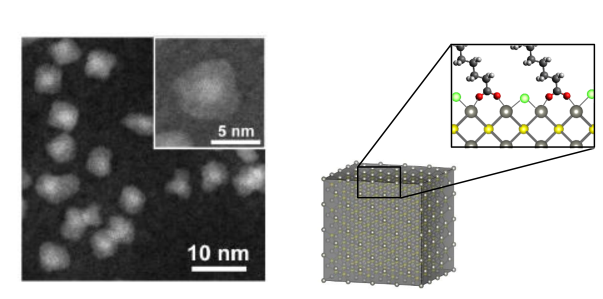




- Interface engineering before shelling may improve quantum yield and FWHM



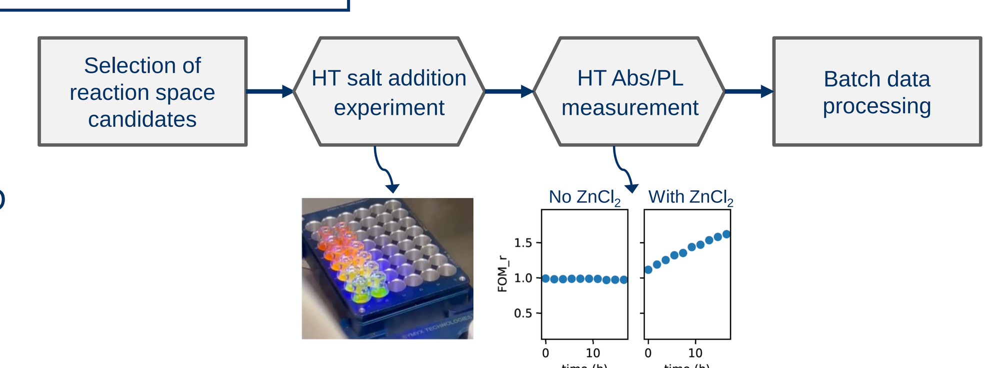
- Zinc chalcogenide shelling can relieve strain and improve passivation, yielding narrow band emission material



- Stability can be conferred by increasing ZnS shell thickness or tailoring organic ligand identity and composition

Task 2: QD surface passivation

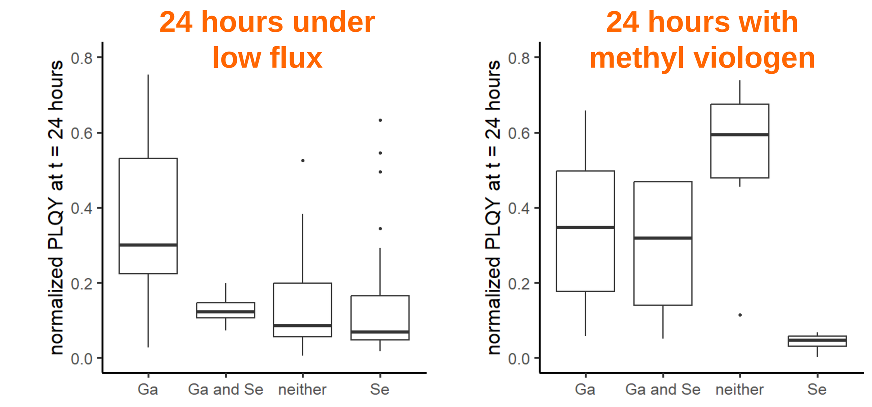
High-throughput screening yields insight into the stability of the QD surface



- The robot HERMAN screened the addition of various zinc salts for improving PL at QD surfaces
- Barrier and silicone coatings will also be tested with the robotic workflow

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

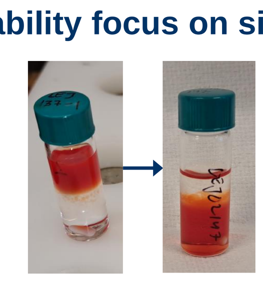
- Tests are designed to interrogate the quenching mechanism for GaP and ZnSe shells
- QD emission is greatly quenched by low flux blue light and methyl viologen
- These data can aid in selection of the inner shell composition and guide the synthesis of stable particles

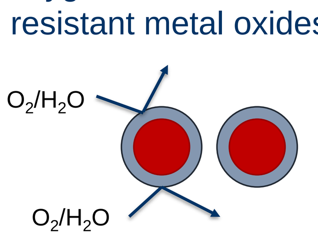


Task 3: Novel barrier coatings

Approaches to improve stability focus on single-particle encapsulation

- Hydroxyapatite forms a phosphate barrier that will be further surrounded by oxygen- and moisture-resistant metal oxides



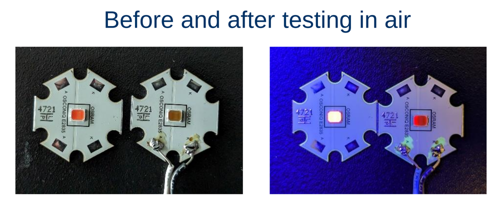


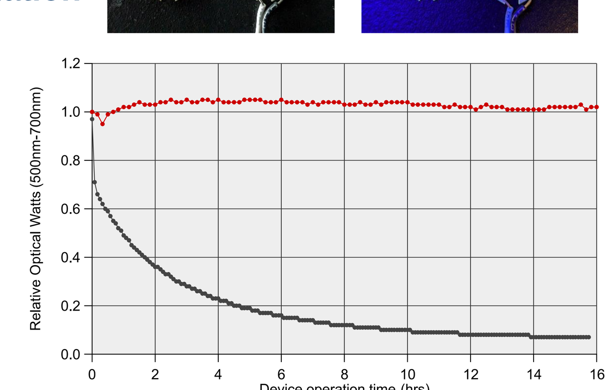
Initial step in depositing hydroxyapatite

- Solubility of QDs changes with phosphate barrier

- Encapsulation with metal oxides is critical for QD survival on-chip
- Rapid device degradation during operation in air shows O_2 quenches QDs

Before and after testing in air



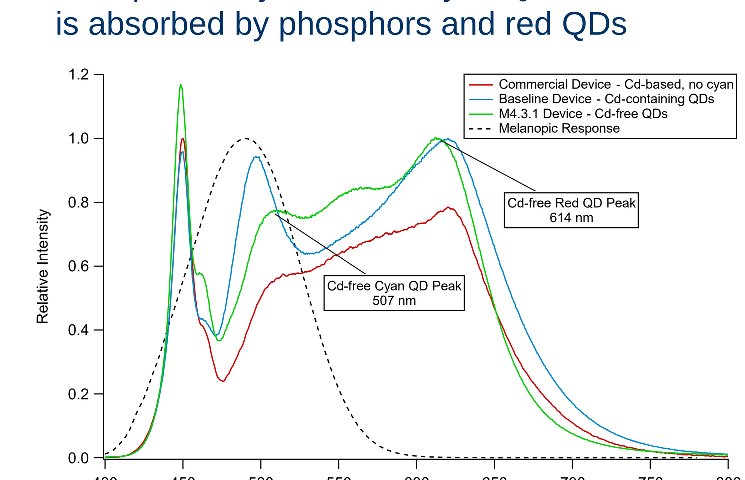


Task 4: Cyan-enhanced QD LED devices

Cd-free HCL device brightness increased by 10% over Cd-containing device at CRI 90, 4000K, and MDER > 0.7

- 450 nm pump wavelength was calculated to be optimal
- QD emission peaks red-shift on-chip, so optimal wavelengths need to be about 20 nm blue-shifted of target
- The quantum yield of the cyan QD is crucial, as the blue emission is absorbed by phosphors and red QDs

Cd-free QDs in Device		
Material	InP/ZnS	InP/ZnSe/ZnS
Color	Cyan	Red
PLQY	68%	49%
Centroid	488	617
Peak	485	613
FWHM	47	50

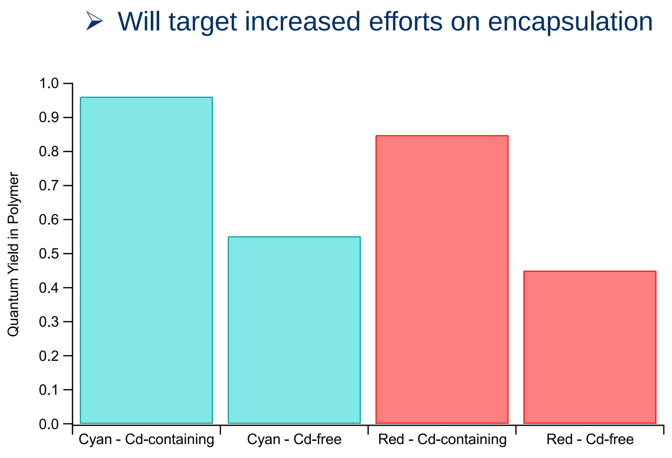


	Baseline Cd-containing Device	Cd-free HCL Device	M4.3.1 Targets	% Increase over Baseline Device
Lumens	21.78	24.33	-	11.7%
lm/W	123.5	138.5	160	12.1%
LER	301	332	-	10.3%
CCT	4030	4261	4000	-
CRI	92	91	> 90	-
MDER	0.76	0.71	> 0.7	-

Planned Work for Project Year 2

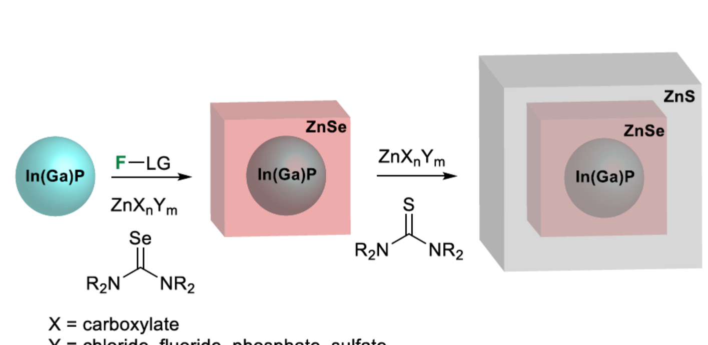
Improve QD stability in silicone polymer

- Cd-free QDs need big improvements to stability when transferred from solution to polymer
  - ➢ Will target increased efforts on encapsulation



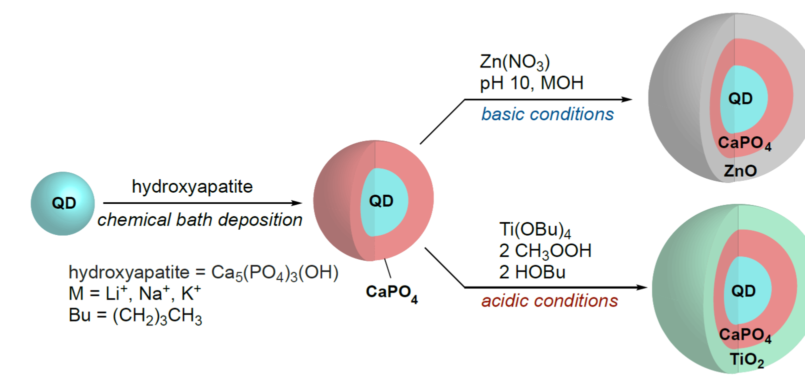
Investigate chemically stable facets

- Different crystal facets have different reactivities, ligand binding strengths, and thus stabilities
  - ➢ Focus will be added to making cube-shaped structures that display highly stable facets



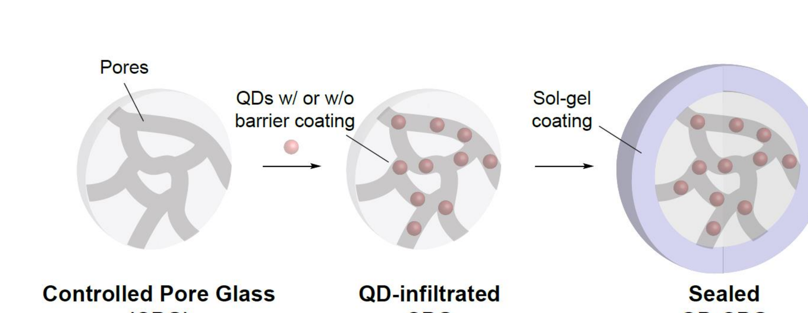
Develop novel barrier coatings

- Ideal barrier coatings are low in organic content and have good moisture and temperature stability
  - ➢ Hydroxyapatite meets these criteria so we will continue efforts on encapsulating QDs with this material



Seal QDs in controlled porous glass

- QDs can be protected further by housing them in porous glass structures that can subsequently be sealed because QDs cannot withstand glass sintering temperatures
  - ➢ To survive challenging LED conditions and bolster device reliability, QDs may be added to porous glass



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