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Progress Towards Stable, Cadmium-Free Quantum Dot Down-Converters

Department of Energy, Solid-State Lighting Workshop 2022

Nanosys | Ilan Jen-La Plante | 02.01.2022

Existing challenges for solid-state lighting

Problem Definition:

- Solid state lighting has greatly reduced energy consumption compared to older lighting technologies, but still lags the theoretical maximum for luminous efficacy.
- Color-mixed direct LED emission offers the highest potential efficacy, but due to material challenges, this technology has not yet surpassed phosphor-converted LEDs.
- The future of solid-state lighting technology requires precisely tunable emission spectra to improve light quality, while simultaneously increasing luminous efficiency.

Impacts of Lighting Quality

Color Perception

Philips CRI comparison

Health and Productivity

Zumtobel Ernst & Young whitepaper

Safety

Cree outdoor lighting case study

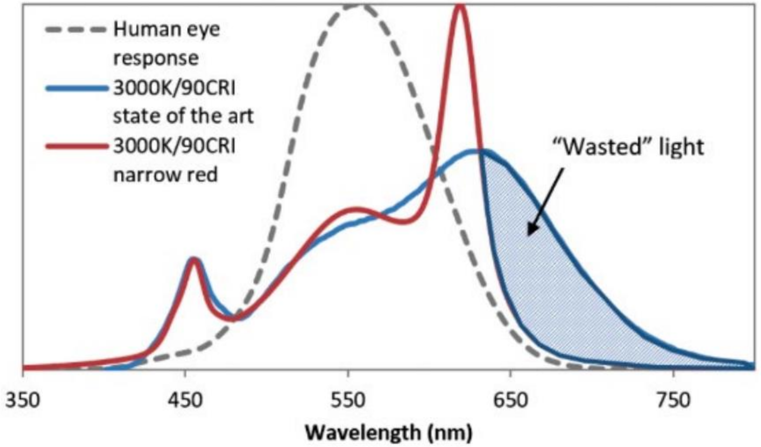
Proposed solution:

- For phosphor-converted LEDs, developing a narrow, efficient, and tunable downconverter could produce high quality light at improved luminous efficacy with incredible flexibility across multiple lighting applications.

Advantages of Quantum Dot down-converters

Nanosys QD examples

Quantum Dots (QDs) offer narrow, efficient, and tunable emission properties, but improvements in operational stability are required for use in LEDs.



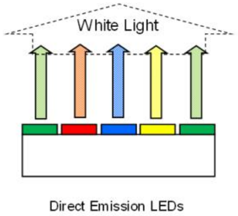
DOE, EERE, 2019 Lighting R&D Opportunities

- Red QDs (40 nm) used in combination with a conventional green phosphor material can improve LED conversion efficiency by up to 15% (2700 K) over commercial pc-LEDs. K. T. Shimizu et al., *Photonics Research,* vol. 5, no. 2, pp. A1-A6, 2017.
- Using conservative estimates, a mid-range improvement of 10% results in a payback of less than one year for incorporation of red QDs downconverters in an LED.
- Existing commercial products harness the narrow emission linewidths of QDs to improve LED efficacy at high CRI (>90) but rely on cadmium-containing QDs and thus further efficacy gains are limited by restrictions on heavy metal content.

Developing stable, cadmium-free quantum dot downconverters would enable greater gains in LED efficacy without compromising regulatory standards.

Comparison to existing and competing technologies

Direct electroluminescence



Pros:
Theoretical maximum light production efficiency due to elimination of downconversion energy losses.

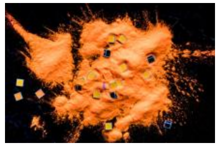
Cons:
Color-mixed (CM)-LEDs require efficient emission across all emission wavelengths; green and amber emitters have poor demonstrated efficiency.

Inorganic phosphor down-converters

Pros:
Low-cost material with good stability in high-flux excitation environments.
Some recent examples of narrow, red emission have been demonstrated.

Cons:
Opportunities remain to improve operational stability under high-T/high-flux conditions.
There are no current solutions for wavelength tuning in narrow phosphor emitters preventing use in green or amber downconversion applications.

Cadmium-based Quantum Dots



Osram OSCONIQ® S 3030

Pros:
Demonstrated product readiness meeting required stability targets, tunable PWL, and narrow FWHM

Cons:
Regulations on total Cd concentration in consumer products limits use and adoption

Compared to competing technologies, heavy-metal-free Quantum Dots offer significant benefit as emitter materials.

- These benefits include 1) narrow emission wavelengths with conversion efficiencies of 90-100%, 2) highly tunable emission wavelengths can be mixed to maximize spectral efficiency, 3) demonstrated stability (>30,000 hours) under display conditions or environmental stress tests, and 4) elemental compositions not under regulatory restriction.

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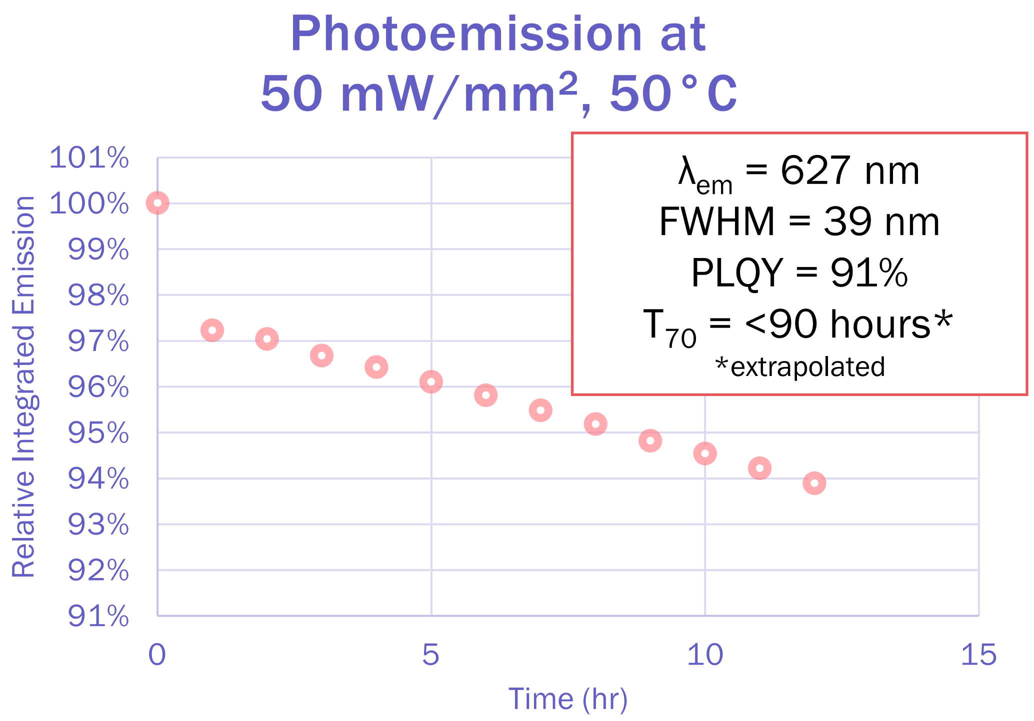
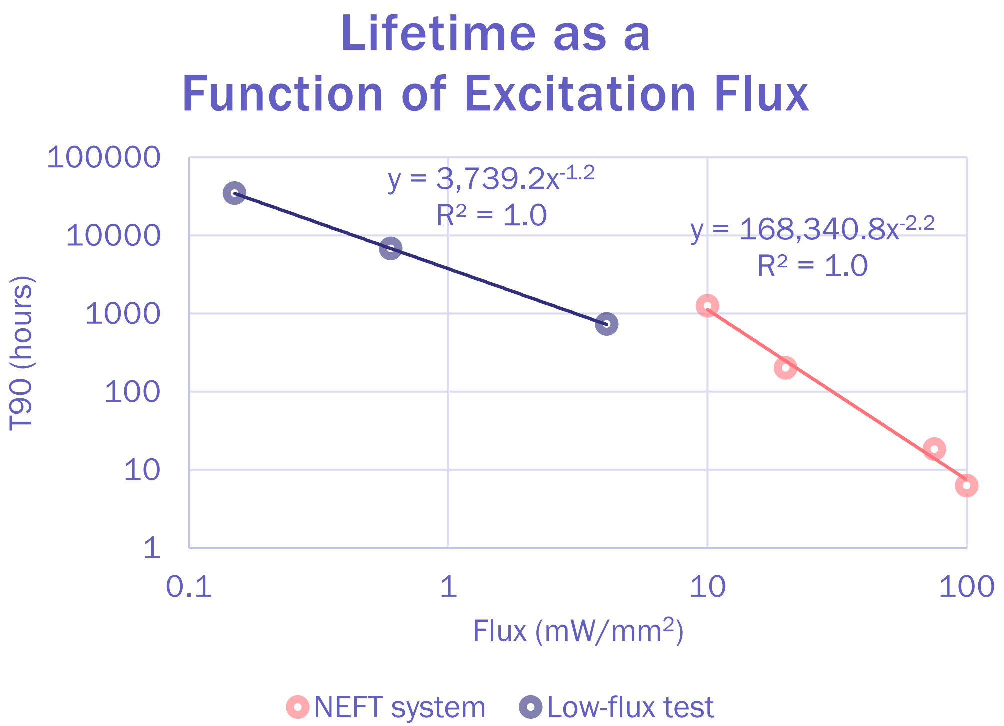
Quantum Dot lifetimes under elevated temperature and excitation flux





- Initial baseline measurements of heavy-metal-free QD lifetime as a function of time are insufficient to meet the demands of solid-state lighting
- The super-linearity of QD degradation rate as a function of excitation flux implicates biexciton formation as a critical pathway in permanent QD emission loss

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Research approach

Currently working on DOE-funded project (DE-EERE0009164: Stable Cadmium-Free Quantum Dot Optical Down-Converters for Solid-State Lighting) to improve QD stability to meet lighting product specifications

Project Management
Quantum Dot Synthesis
Optical Physics, Engineering, and Testing

Photophysical Characterization
Atomic-level Structural Characterization

Synthetic Control of QD Structure → Confirmation of QD Structure

Correlation of QD Photophysics and Performance

Synthesis
Minimize Auger recombination
Control Auger excitation branching ratio
Improve excited state confinement.

Structural Characterization
Composition analysis by ICP, FTIR, NMR, XRD, XPS, TGA, TEM, STEM-EDS, and Raman spectroscopy.

Control of QD Structure by Synthetic Modifications

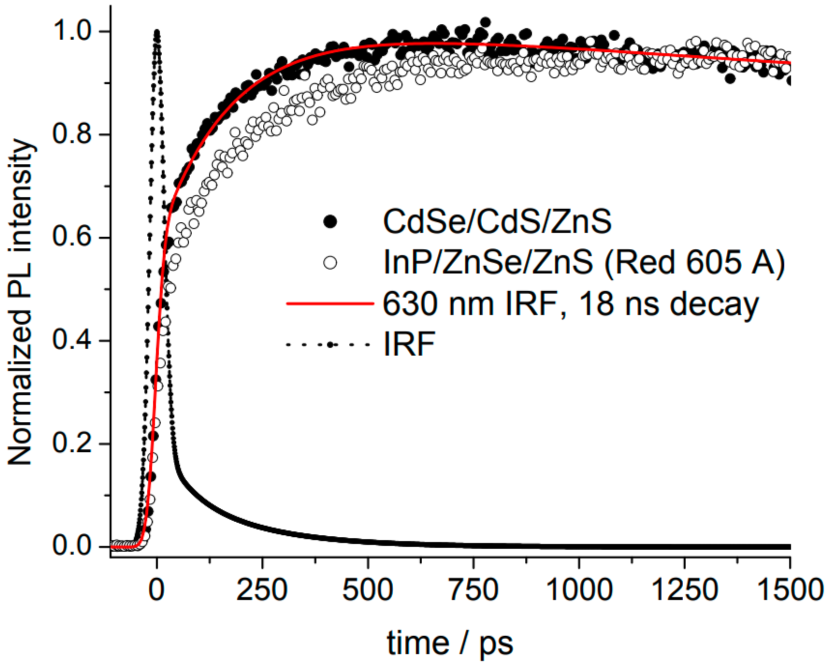
Best QDs

Photophysical Characterization
Measure Auger dynamics using transient absorption spectroscopy and time-resolved photoluminescence spectroscopy of negatively charged QDs.
Measure PL dynamics using time-resolved emission and photoluminescence spectroscopy.

Performance Testing
Measure static QY at 0.0001 to 1 W/mm^2 and temperatures of RT to 150°C.
Measure QD power retention lifetime across same temperature and flux range as above.

Identify properties that improve performance

Observations of photoluminescence risetimes



Extremely Slow Trap-Mediated Hole Relaxation in Room-Temperature InP/ZnSe/ZnS Quantum Dots,
Anh T. Nguyen, Ilan Jen-La Plante, Christian Ippen, Ruiqing Ma, and David F. Kelley,
J. Phys. Chem. C **2021**, 125, 7, 4110-4118.

InP/ZnSe/ZnS QDs exhibit slow photoluminescence (PL) risetimes on the order of 50-500 ps; this is a phenomenon not previously observed in CdSe/CdS/ZnS QDs.

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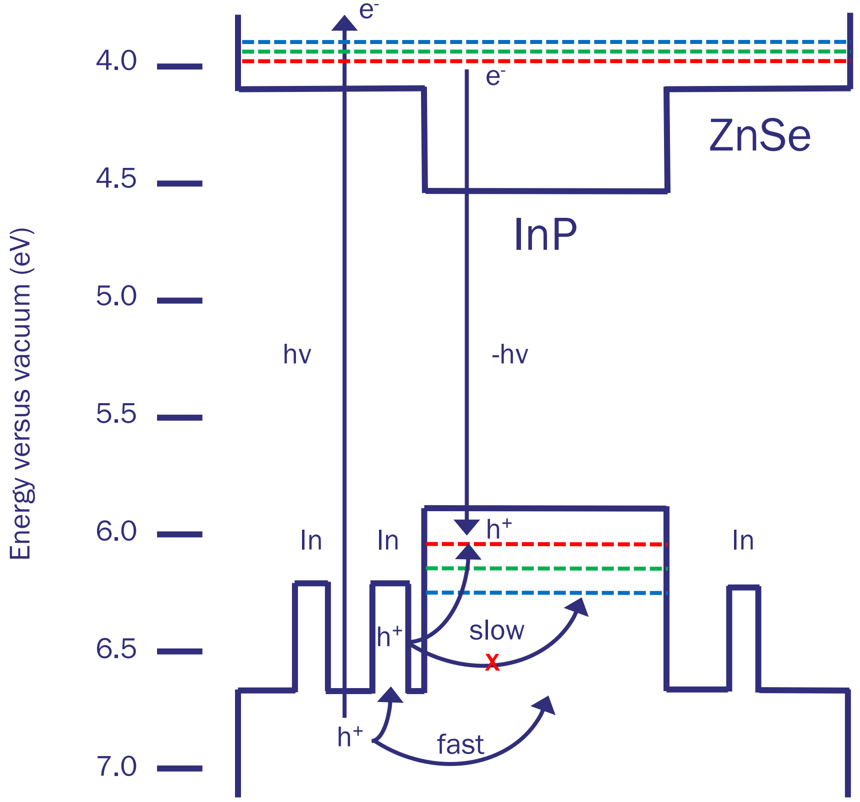
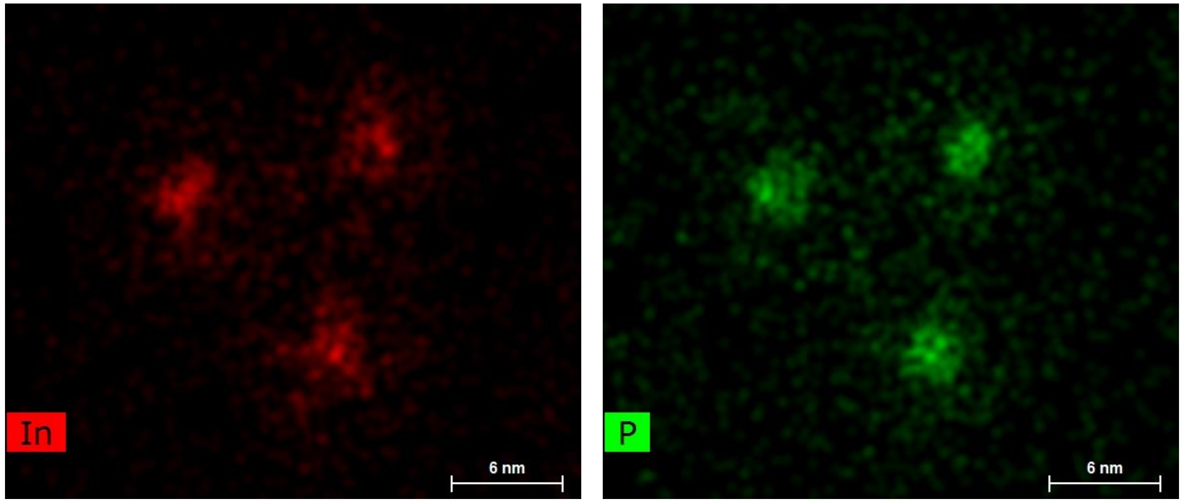
Photoluminescence risetime model



Elemental mapping by STEM-EDS



Non-stoichiometric In confirmed by elemental ratios (ICP), mapping (STEM-EDS), and Raman spectroscopy

Resonance Raman Study of Shell Morphology in InP/ZnSe/ZnS Core/Shell/Shell Nanocrystals
Paul Cavanaugh, Ilan Jen-La Plante, Christian Ippen, Ruiqing Ma, David F. Kelley, Anne Myers Kelley
J. Phys. Chem. C **2021**, 125, 19, 10549-10557

We have developed a model to explain this behavior based on transient hole trapping on non-stoichiometric In sites where absorption by the ZnSe shell results in delayed localization to the core band edge and subsequent emission

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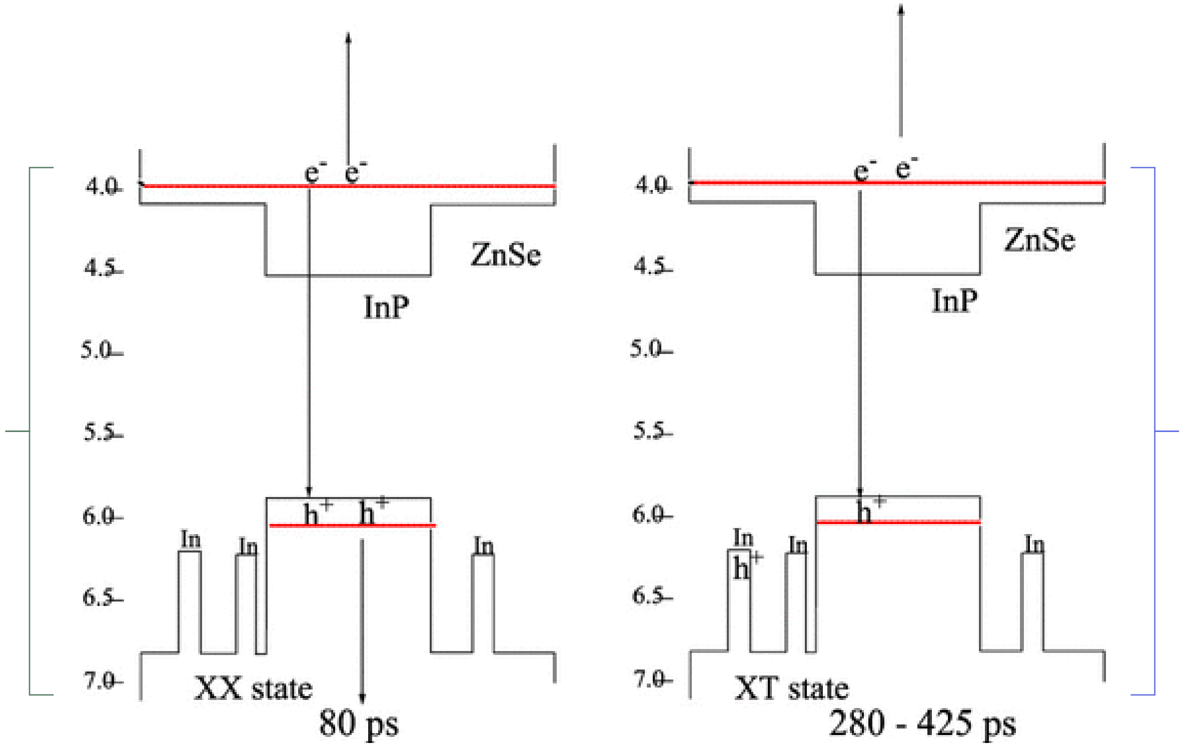
Impact to Auger branching ratios

- Hole trapping on In sites results in a multiexciton state that behaves similarly to a negative trion resulting in a slower average Auger rate and an increase in the Auger electron excitation fraction

The XX biexciton state
- Occurs when there are two conduction band electrons and two valance band holes
- Has an average Auger lifetime of 80 ps



The XT multiexciton state
- Occurs when there are two conduction band electrons, one valance band hole, and one hole trapped in the ZnSe shell (on an In-associated site)
- Has an average Auger lifetime of 280-425 ps

Auger Dynamics in InP/ZnSe/ZnS Quantum Dots Having Pure and Doped Shells
Anh T. Nguyen, Paul Cavanaugh, Ilan Jen-La Plante, Christian Ippen, Ruiqing Ma, and David F. Kelley
J. Phys. Chem. C **2021**, 125, 28, 15405–15414

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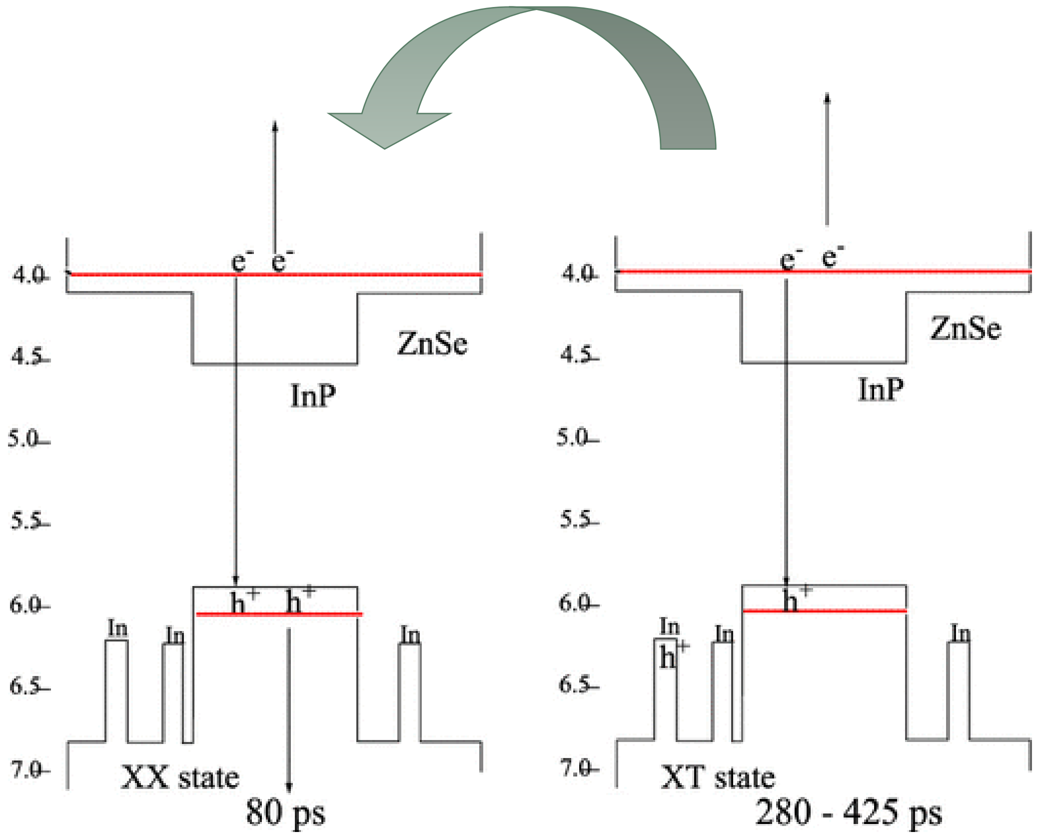
Hole trapping is a transient phenomenon



- In an XT multiexciton state, absorbance in the ZnSe shell results in a trapped hole on a In-associated site
- The trapped hole can tunnel to the InP valence band edge reverting to a standard XX biexciton state

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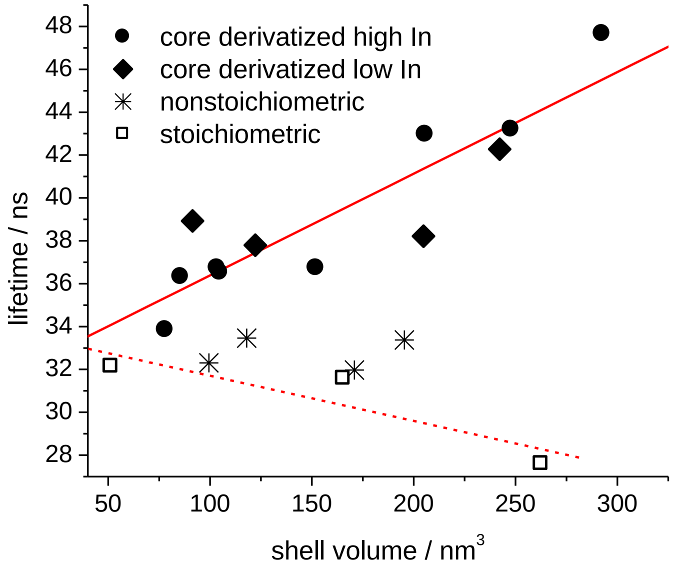
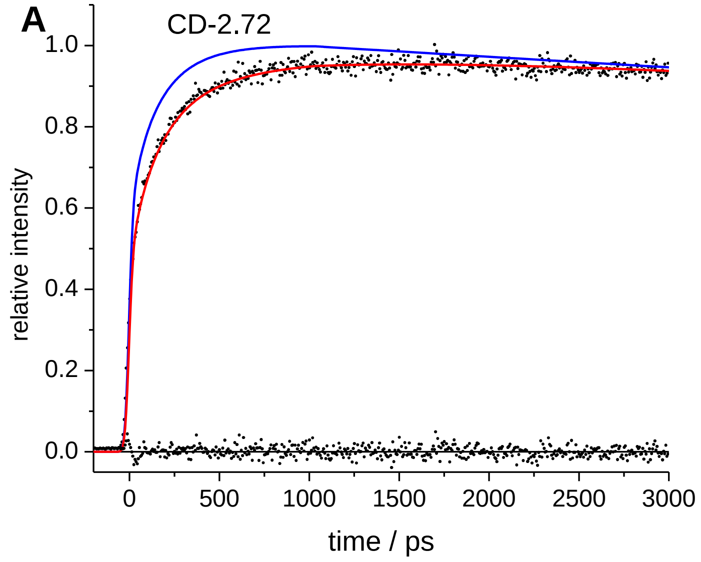
Core/shell interface composition impacts trapping likelihood

Radiative lifetime



Photoluminescence risetime



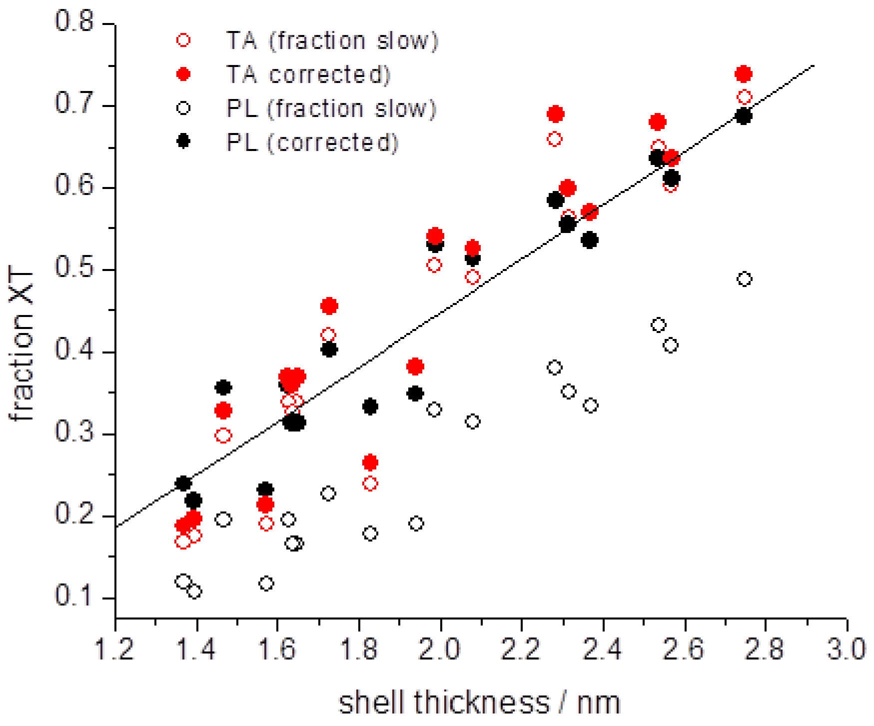
Radiative dynamics and delayed emission in pure and doped InP/ZnSe/ZnS quantum dots

Paul Cavanaugh, Haochen Sun, Ilan Jen-La Plante, Maria J. Bautista, Christian Ippen, Ruiqing Ma, Anne Myers Kelley, and David F. Kelley

J. Chem. Phys. **2021**, just accepted

Composition control of the InP/ZnSe core/shell interface can promote the XT state leading to increased transient hole trapping as seen via long radiative lifetimes and slow photoluminescent risetimes

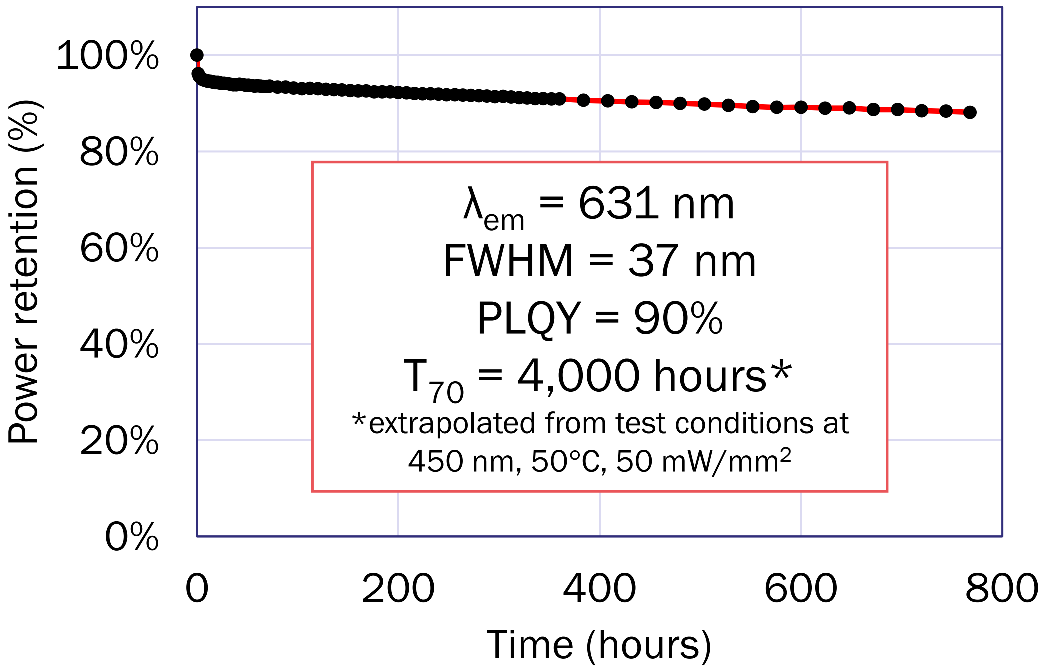
Transient hole trapping is maximized in thicker ZnSe shells



Biexciton and trion dynamics in InP/ZnSe/ZnS quantum dots
Haochen Sun, Paul Cavanaugh, Ilan Jen-La Plante, Maria J. Bautista, Christian Ippen, Ruiqing Ma, and David F. Kelley
submitted

For In-associated holes traps within the first ~2 monolayers of the ZnSe shell, the hole wavefunction is coupled with the InP valance band preventing the formation of the XT state.

Maximizing the less damaging Auger electron excitation process improves QD lifetime under high-flux excitation



- QD composition was controlled to maximize the degree of transient hole trapping thereby promoting Auger electron excitation (over Auger hole excitation) when a multiexciton Auger process does occur
- InP/ZnSe/ZnS core/shell structural modifications made as a result of these findings have led to some of our longest lifetime samples representing a >50X improvement in T_{70} since the project start

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Acknowledgments and technical project team

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Ilan Jen-La Plante Ruiqing Ma Ernest Lee Jason Tillman Maria Bautista Xudong Wang Kethry Soares Nick Brockman	David Kelley Anne Myers Kelley Anh Nguyen Paul Cavanaugh Haochen Sun	Work supported by the U.S. Department of Energy's Office of Energy Efficiency and Renewable Energy under the Award Number DE-EE0009164


THANK YOU
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