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Title: "Giant" nanocrystal quantum dots for light-emission applications

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"Giant" Nanocrystal Quantum Dots for Light-Emission Applications

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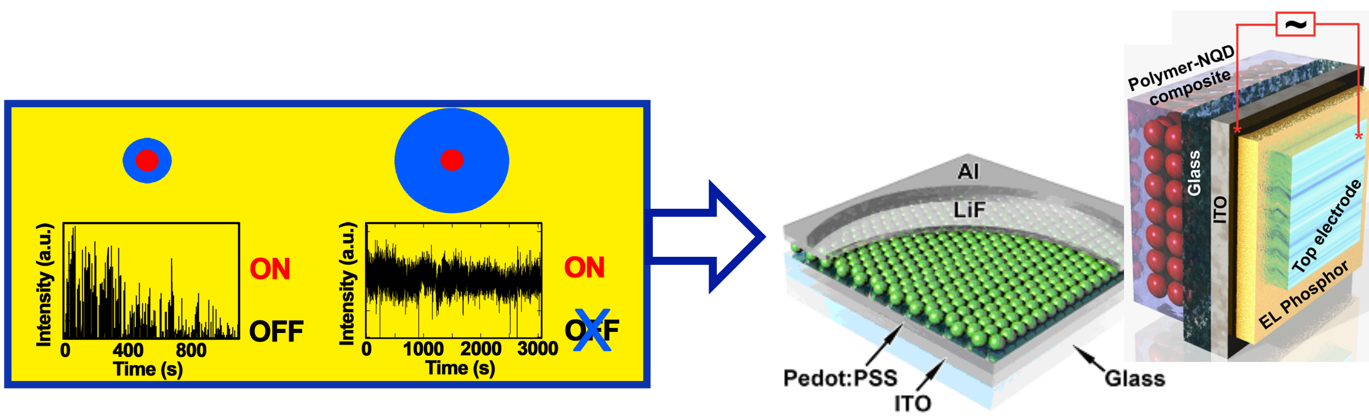
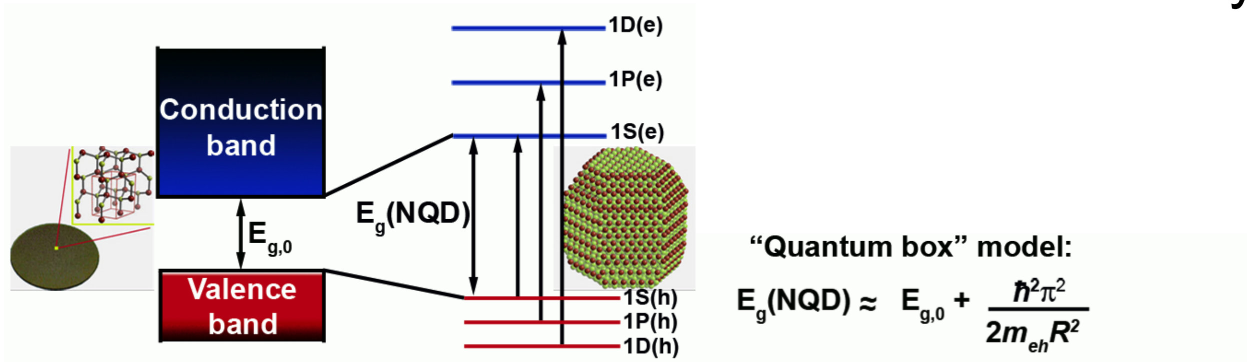
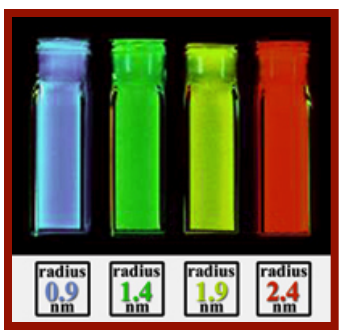


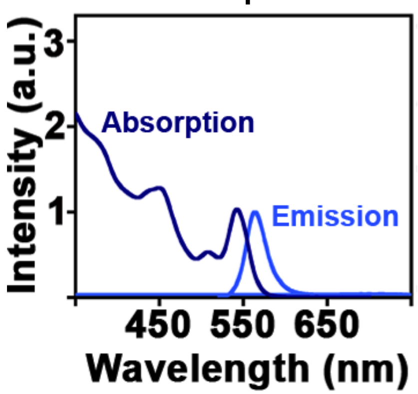
Quantum Dots (QDs): Functionality for Light-Emission Applications

- Quantum-confinement effects afford functionality

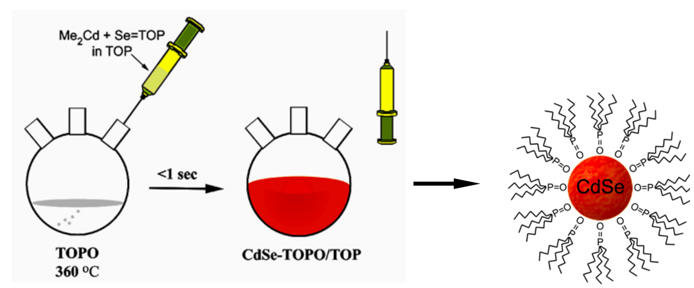


- Size-tunable bandgap / fluorescence
- Narrow & bright emission
- Broadband & efficient absorption



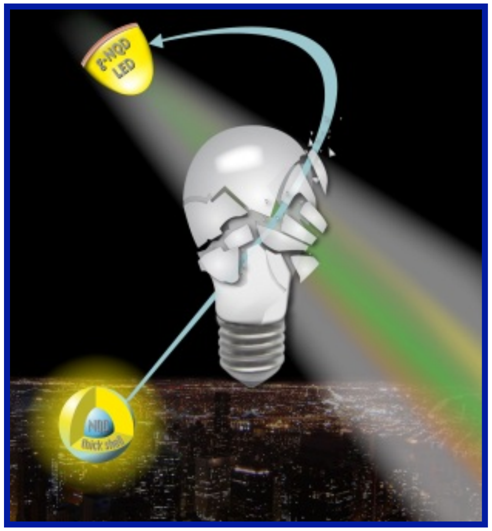


- Low-cost / scalable synthesis
- Solution processible
- High-quality: Low polydispersity (+/- 4%) & single-crystalline



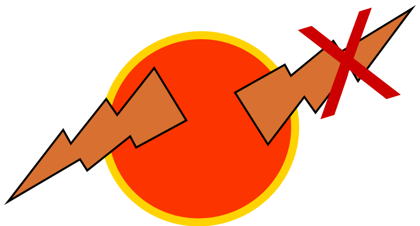
Quantum Dots:
Functionality for Light-Emission Applications

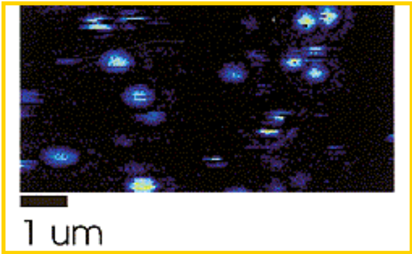
- Potential applications
  - ✓ Biological optical tags / reporters
  - ✓ Color-tunable lasing
  - ✓ Single-photon source
  - ✓ Light-emitting diodes (solid-state lighting)

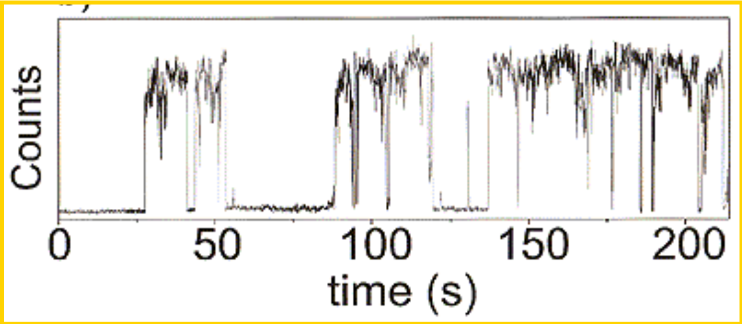


The darker side of QDs:
Blinking and non-radiative Auger recombination

- Quantum dot fluorescence intermittency



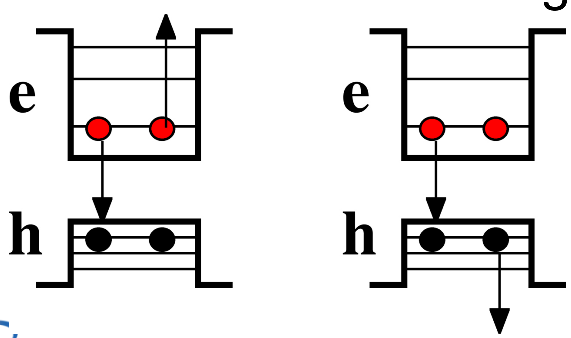




- Nirmal et al. *Nature* (1996) 802
- Efros *Nature Mater.* (2008) 612

> Conventional blinking model:
>
> - QDs randomly cycle through uncharged and charged states
> - In charged state, QD blinks 'off' due to Auger recombination

- Efficient non-radiative Auger recombination

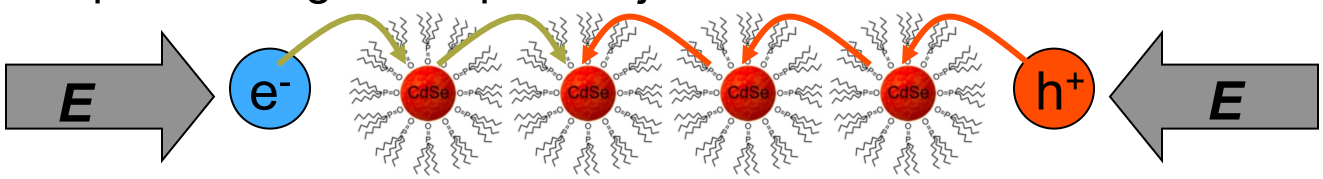


- Reduces optical gain lifetimes
- Reduces optical gain bandwidth
- Restricts time available to extract multiple excitons
- Limits ability to reliably extract single photons
- *Leads to non-radiative losses in LEDs (via charge build-up)*

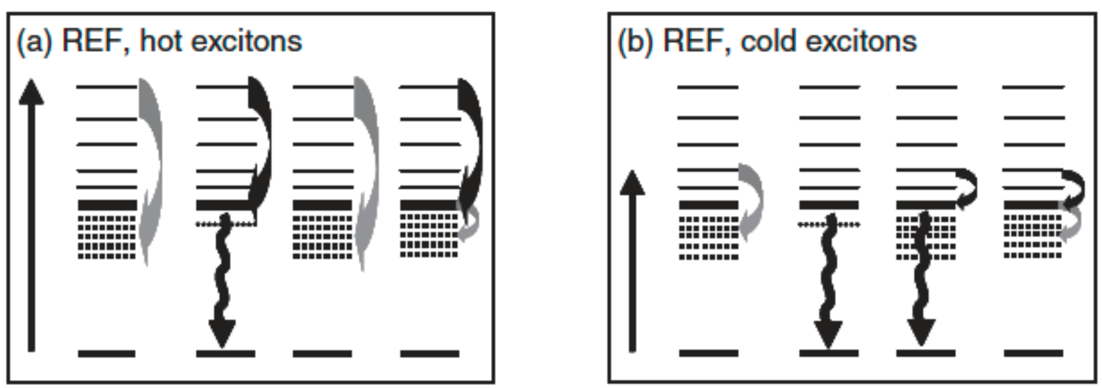
The darker side of QDs:
Traits that impede solid-state performance

Why are solid-state QD quantum yields an order-of-magnitude less than solution QD quantum yields?

- Optical properties depend on organic ligand layer
  - Damage to ligands diminishes NQD performance
  - Ligands can impede charge transport / injection



- Efficient QD-QD energy transfer in close-packed films
  - Excitons "funnel" to lowest-energy state, which can be a non-emitting trap state

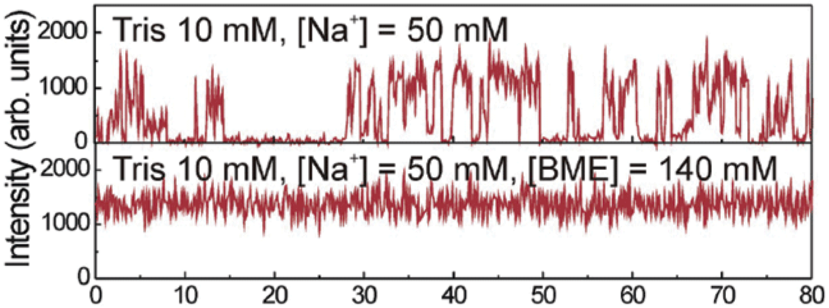


Trap levels

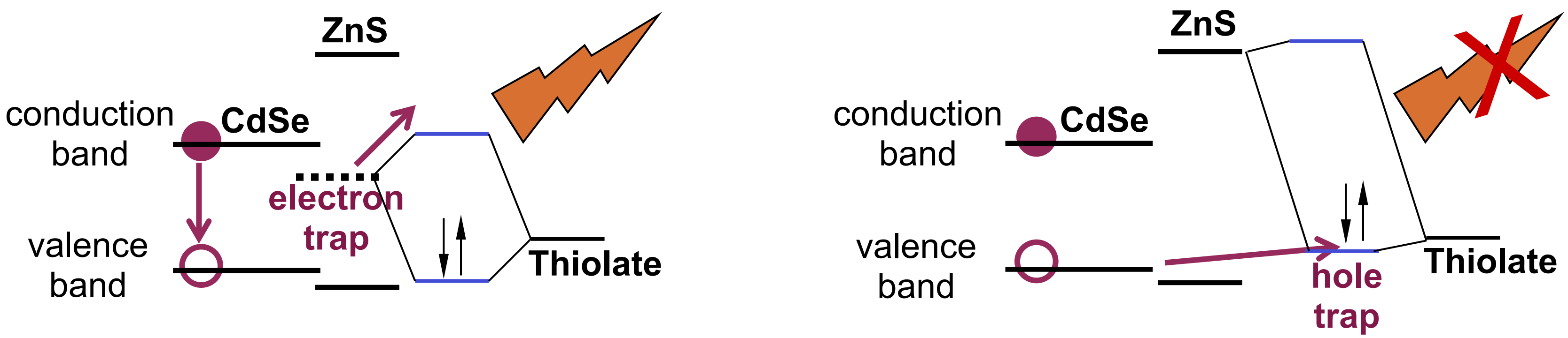
Adapted from Klar et al. Adv. Mater. 2005

QD blinking: The subject of intense investigation

- **Early attempts to suppress blinking used charge-mediators/ compensators to suppress charging**
  - Short-chain thiols: "BME"
  - Organic conjugated ligands
  - Propyl gallate ("antioxidant")
    - Hohng & Ha *JACS* 2004, *126*, 1324; Hammer et al. *JPC B* 2006, *110*, 14167; Fomenko & Nesbitt *Nano Lett.* 2008, *8*, 287



- **"Ligand" approach hard to reproduce and not robust**
  - Effects are concentration, time, pH dependent
  - Thiolate ion passivates electron traps at low concentrations (acidic pH)
  - Thiolate introduces hole traps at high concentrations (basic pH)



Conclusions from early work on QD blinking: Role of surface chemistry

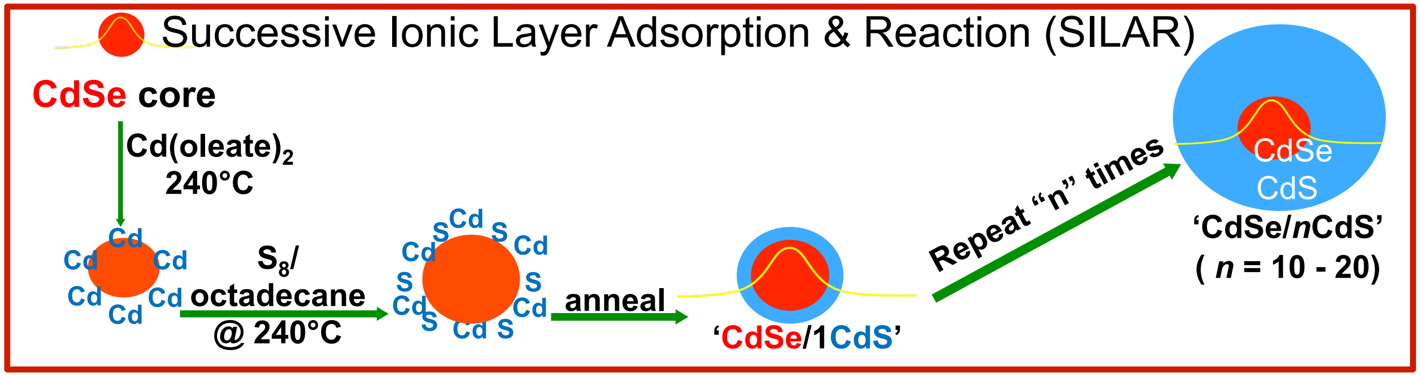
- Careful application of charge-donating ligands affords "window of opportunity" for photoluminescence enhancement
- However, control and long-term stability difficult to achieve
- Clearly, charging and/or surface trap states play a key role

What about an inorganic approach?

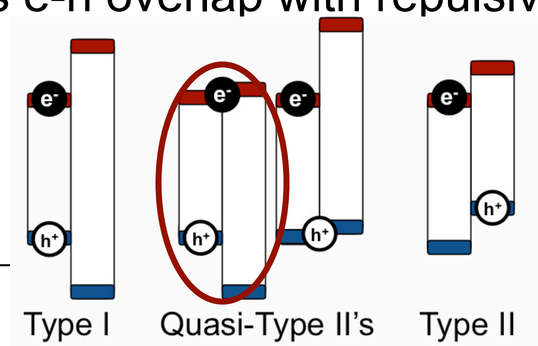
Jeong et al. J. Am. Chem. Soc. 2005,127, 10126-10127; Jeong, PhD Thesis 2006

Inorganic shell approach: *Is it possible to impact both charging/trapping and Auger recombination processes?*

- Epitaxial growth of wide-bandgap shell on a QD core improves PL efficiencies and stability
  - But, core/shell QDs still blink and still exhibit efficient Auger recombination
- Advanced 'shell engineering'
  - Thick shell to isolate carriers from surface / impede charge ejection



  - 'Type-II' core/shell band alignments: Partial or full electron-hole spatial separation reduces e-h overlap with repulsive Coulombic interactions possible

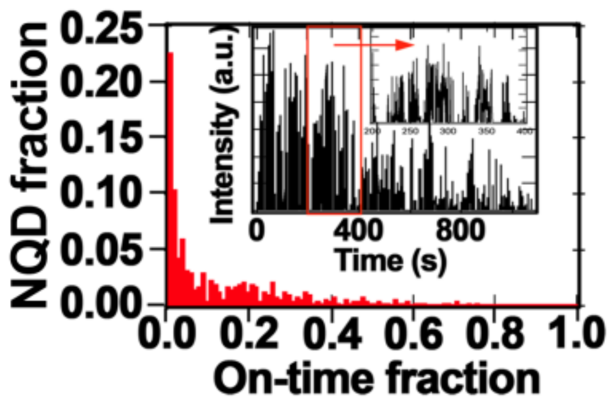


CdSe/CdS

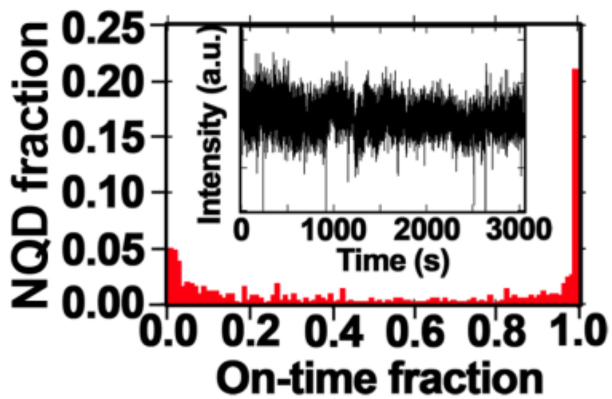
‘Giant’ quantum dots: New functional class of QD

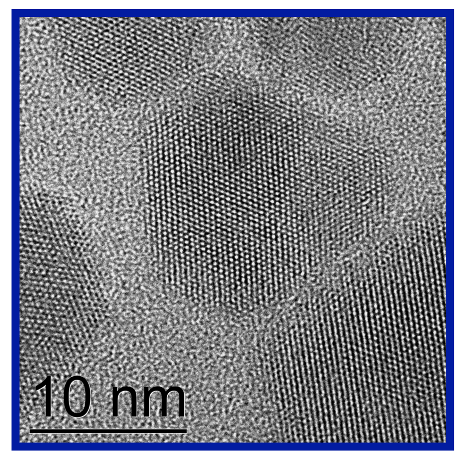
Single-dot-level optical stability: Suppressed blinking and photobleaching

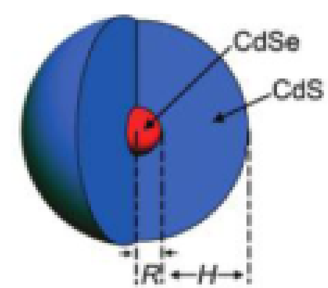
Conventional core/shell QD



‘Giant’ core/shell QD





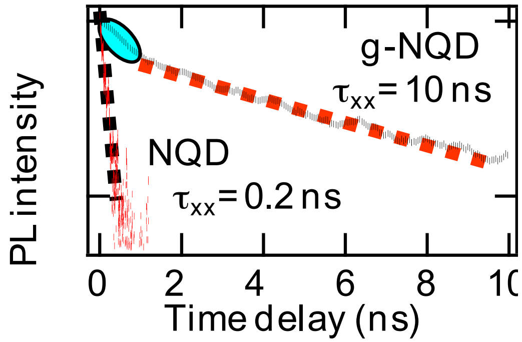


“Giant”: >10 monolayers of shell

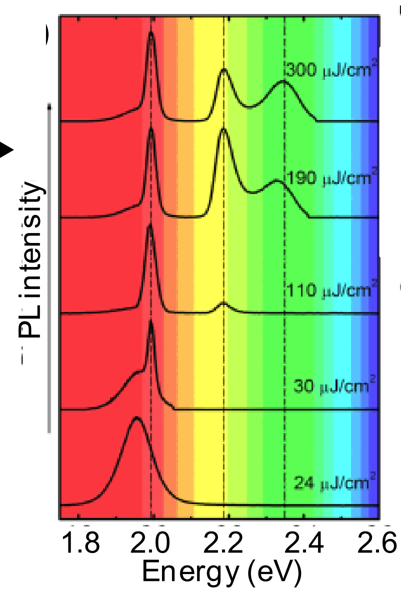
Blinking suppression:
Chen *et al. J. Am. Chem. Soc.* 2008
Vela *et al. J. Biophotonics* 2010
Hollingsworth et al. U.S. Patent 2011

‘Giant’ quantum dots: New functional class of QD

Evidence for suppressed Auger recombination

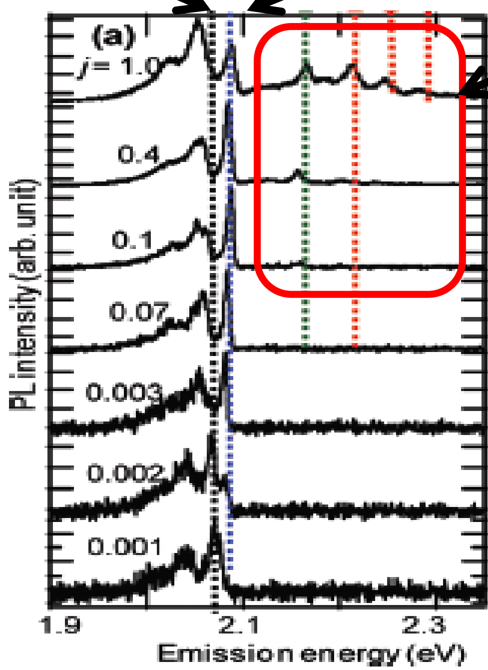


I.
Long-lived biexcitons



Optical amplification over a large bandwidth

exciton
bi-exciton
multi-exciton



II.
Efficient biexciton and multiexciton emission

Auger recombination:
García-Santamaría *et al. Nano Lett.* 2009
Htoon *et al. Nano Lett.* 2010
Park et al. *Phys. Rev. Lett.* 2011

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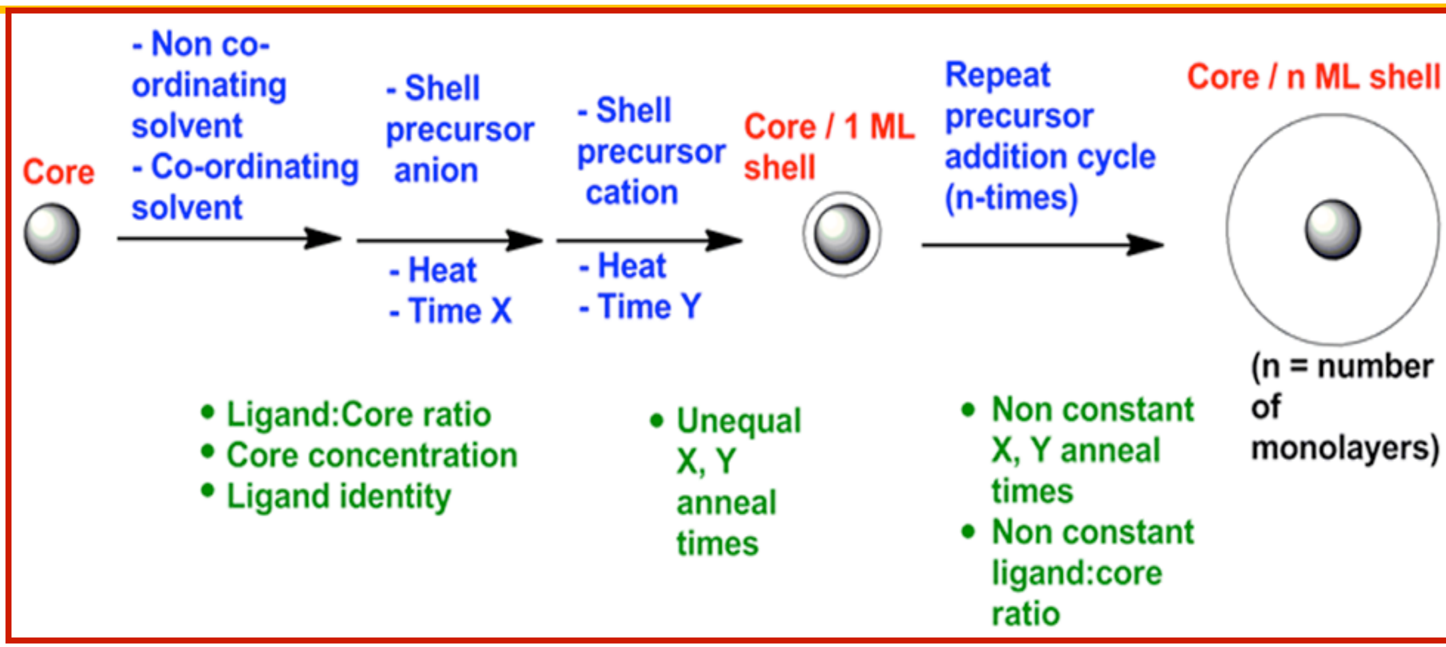
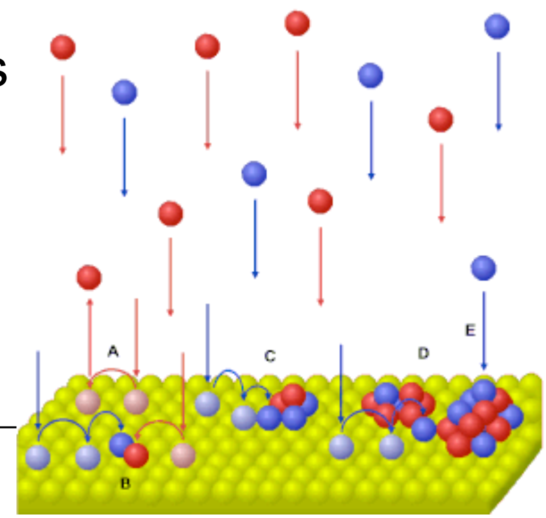
Process of thick-shell growth is complex: Numerous reaction parameters acting individually or in concert



- Correlate process conditions that control adatom addition at the solution-NQD interface with properties
  - Particle shape
  - Crystal structure
  - Photophysical properties/performance (QYs, blinking, lifetimes)

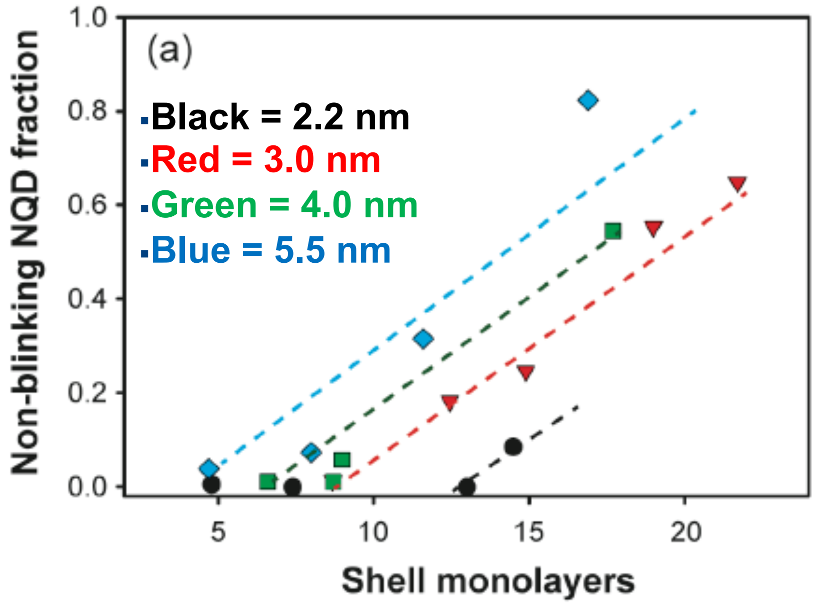


Los Alamos NATIONAL LABORATORY EST.1943

Ghosh *et al. J. Am. Chem. Soc. 2012, 134, 9634-9643*

Beyond shell thickness: Effect of core size

- Non-blinking fraction as a function of core size (2.2 to 5.5 nm) and shell thickness



- Universal behavior: Non-blinking fraction increases as a function of shell thickness
- Onset of blinking-suppression begins at different shell thicknesses for different core sizes
  - ✓ Largest cores exhibit earliest onset of non-blinking
  - ✓ Smallest cores reach transition at much thicker shells

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Ghosh *et al. J. Am. Chem. Soc. 2012, 134, 9634-9643*

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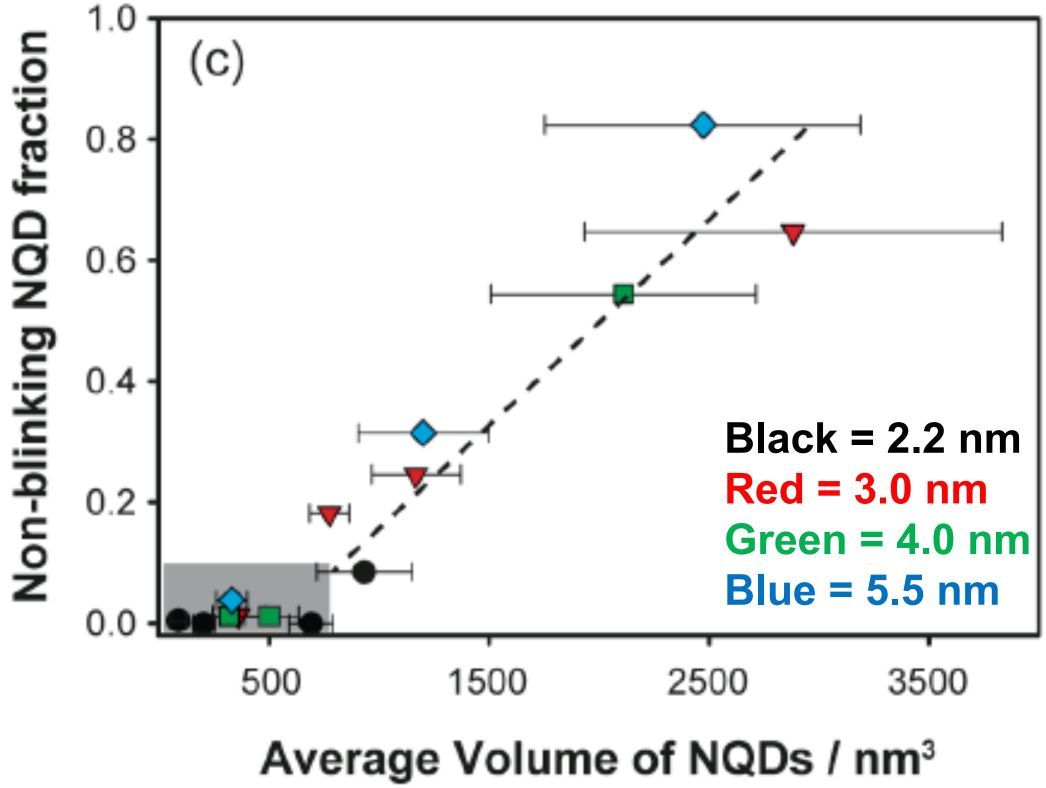
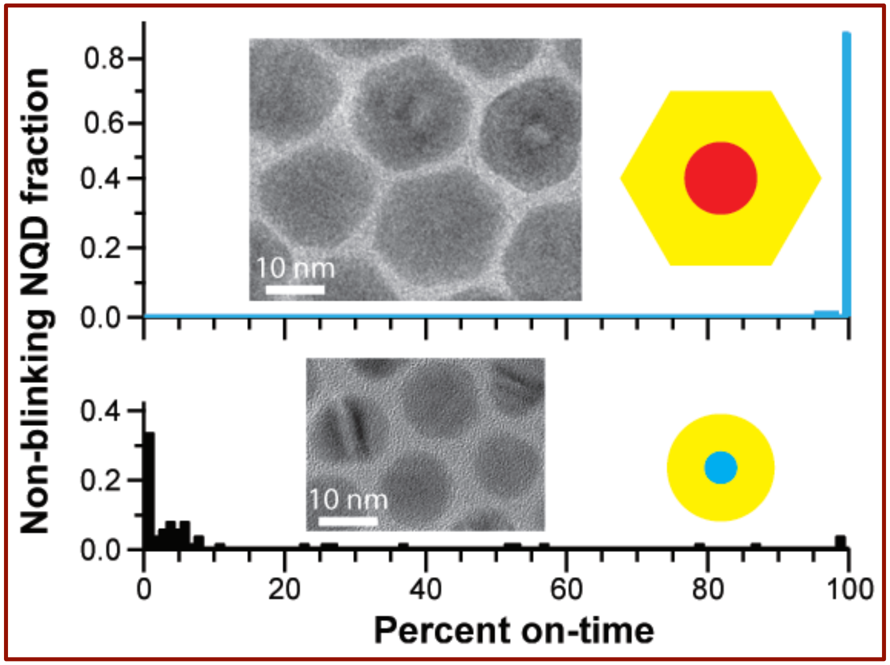
Understanding non-blinking behavior as a volume effect



- Non-blinking fraction trends explicitly with NQD volume
- "Volume threshold" at ~750 nm^3
  - By either a combination of a small core and thick shell or a large core and thinner shell

Ghosh *et al. J. Am. Chem. Soc. 2012, 134, 9634-9643*

Implications of core-size effect on blinking suppression



- Largest cores achieve fully suppressed blinking at thick shells (>85% of the NQDs are non-blinking)
- Smallest cores exhibit relatively little non-blinking behavior even after addition of ultra-thick CdS shells

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Ghosh *et al. J. Am. Chem. Soc. 2012, 134, 9634-9643*

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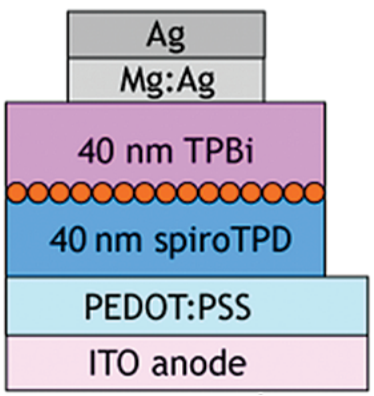
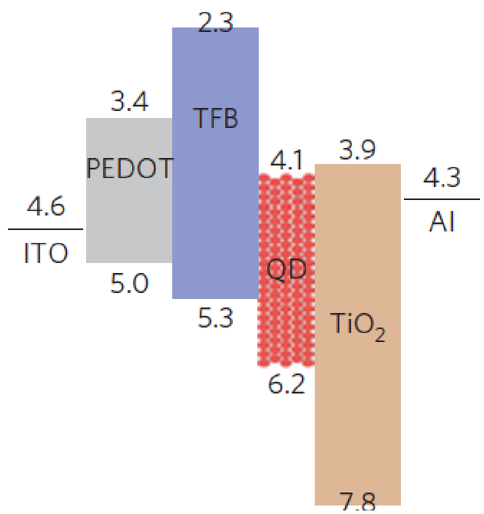
Applications: QD LEDs

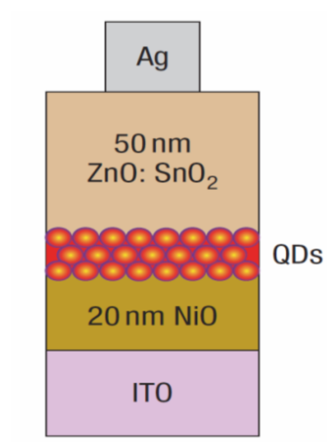
Conventional-QD light-emitting devices

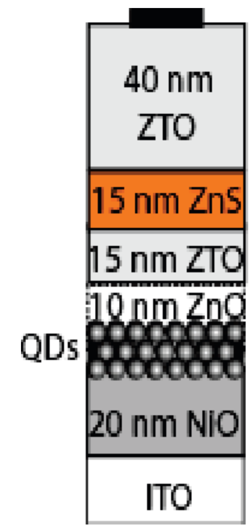
- Hybrid organic/inorganic devices





- “All” inorganic devices





- EQE’s up to ~3%
- Power efficiencies up to ~5 lmW^{-1}
- Now18%!

  - Kim et al. *Nat. Photonics* (2011) 176

- EQE’s up to 0.09% (left) and 0.2% (right)
- Now >1%

  - Caruge *et al. Nat. photonics* (2008) 247
  - Wood *et al. ACS Nano* (2009) 3581

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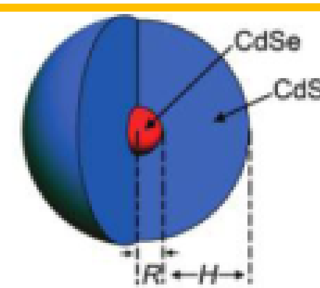
Applications: g-QD LEDs

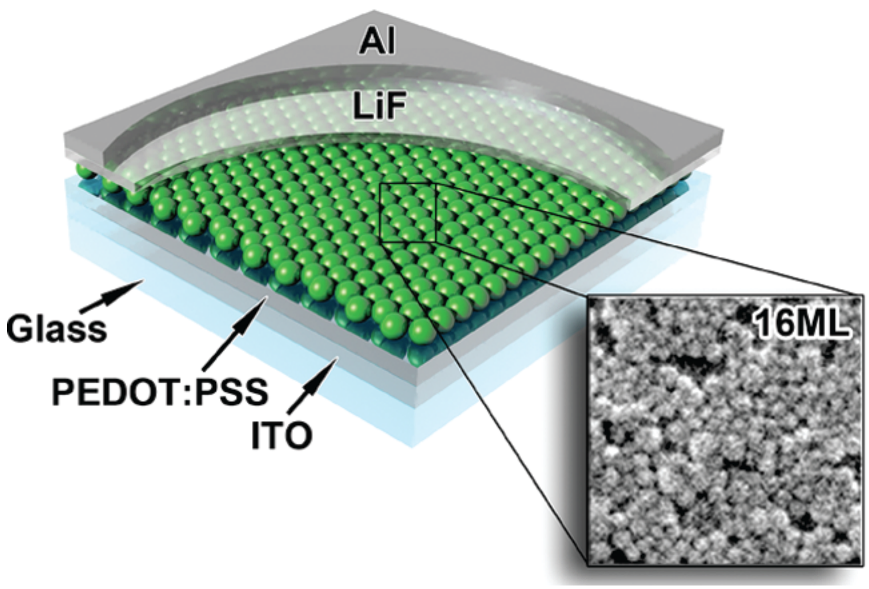
Possible challenges to g-QD LEDs

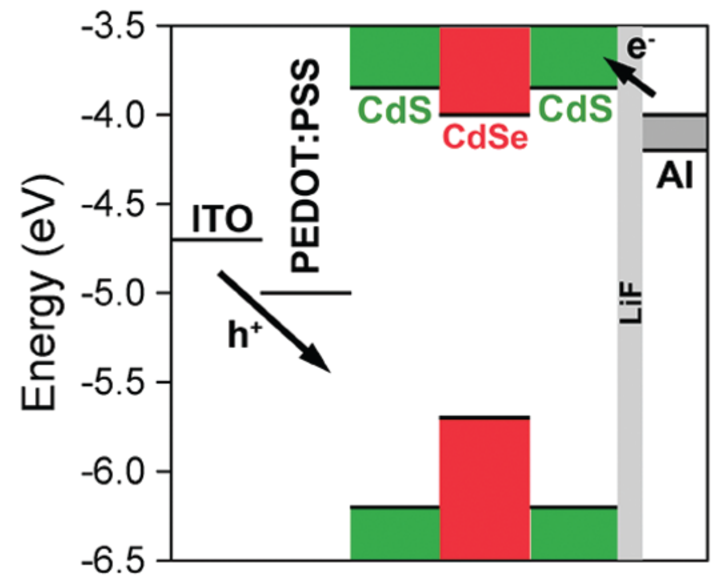
- g-QD quantum yields ~50-60%
- Large per-particle volume translates to low density of emitter centers
- The thick shell might impede charge injection



“Giant”: >10 monolayers of shell

Test-bed direct-charge-injection light-emitting diode



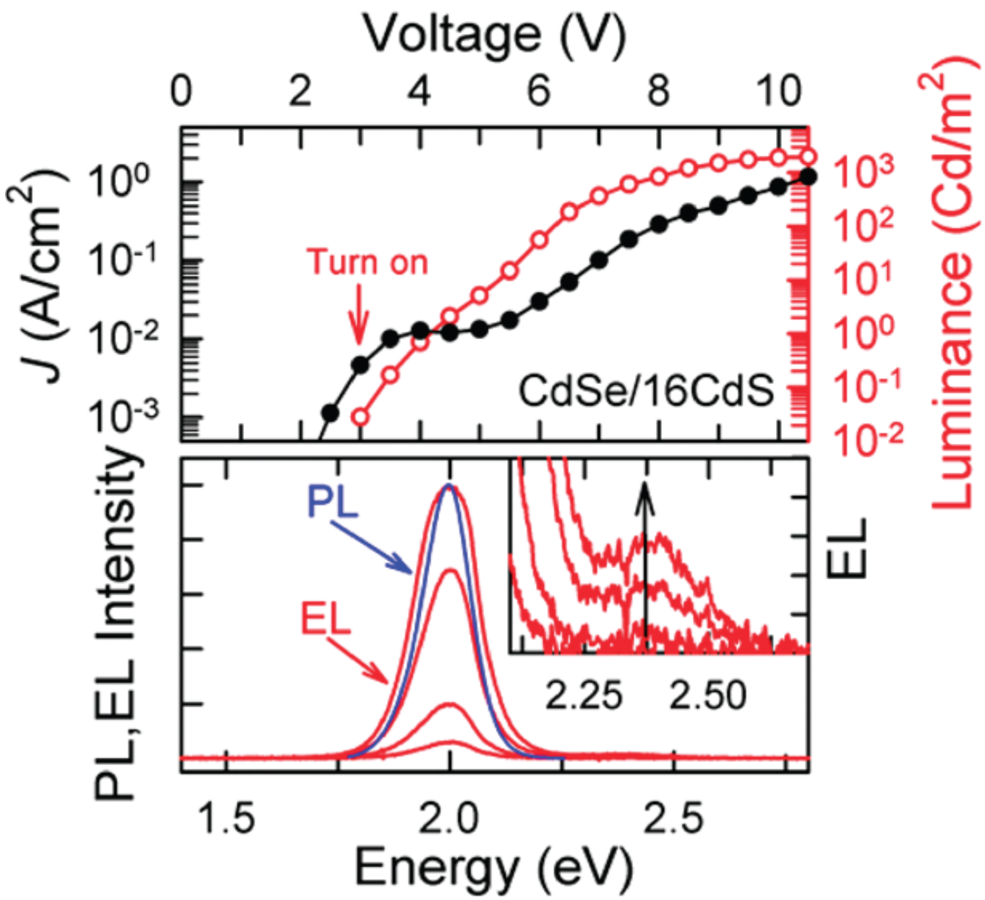


Band alignments vs. electrode work functions

Pal *et al. Nano Lett.* 2012, 12, 331-336

g-QD device outperforms similar QD device by two orders-of-magnitude!

- Performance comparable to more sophisticated “all-inorganic” QD LEDs



- Low EL turn-on voltage: 3.0 V
- ‘Standard video brightness’ (200 Cd/m^2) reached at 6.5 V and 180 mA/cm^2
- High maximum luminance ~2000 cd/m^2
- No deep-level trap emission even at high current densities
- Higher order excited states may be present due to Auger suppression!

Pal *et al. Nano Lett. 2012, 12, 331-336*

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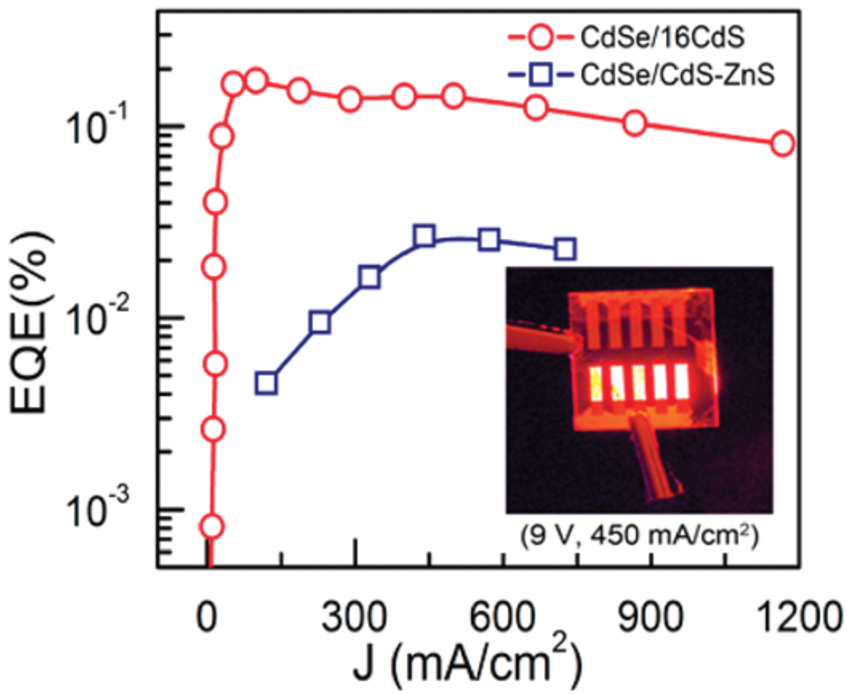
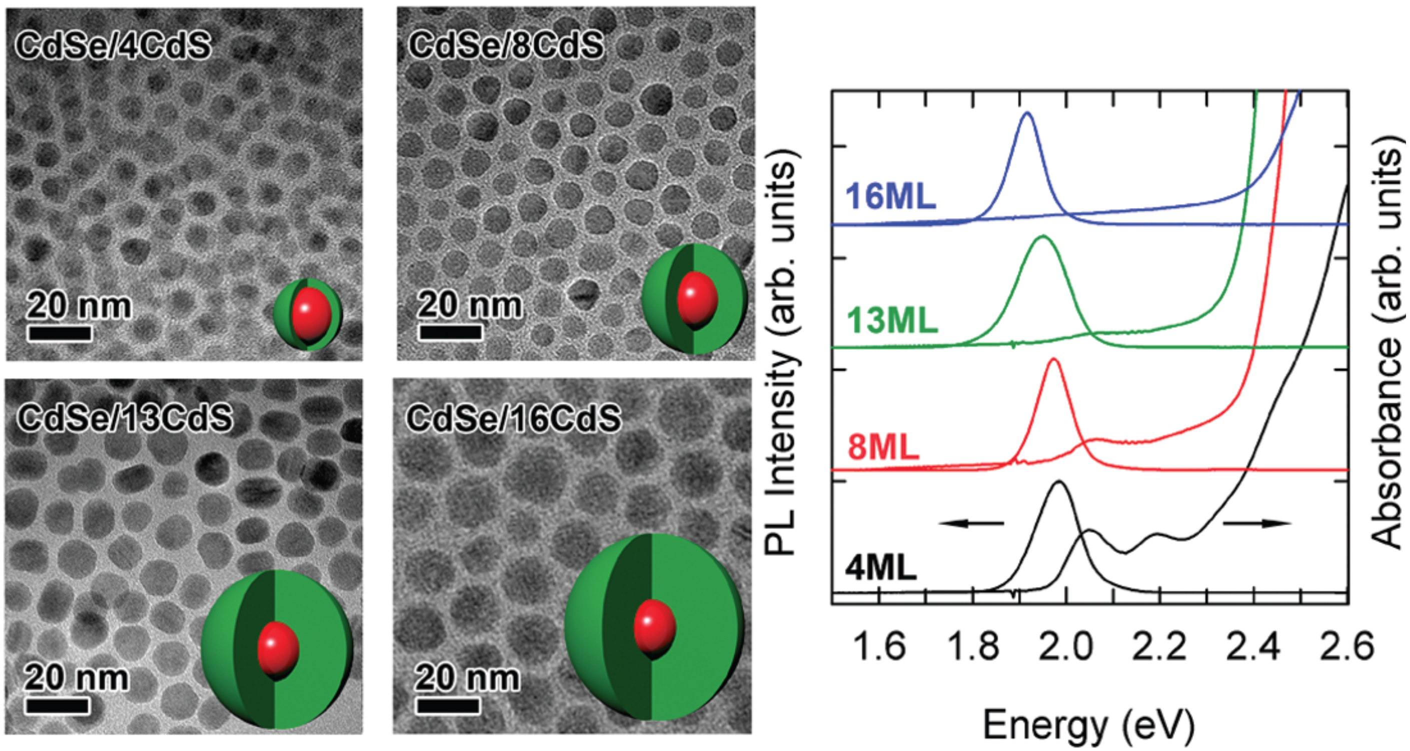


- Low EL turn-on voltage: 3.0 V
- 'Standard video brightness' (200 Cd/m^2) reached at 6.5 V and 180 mA/cm^2
- High maximum luminance ~2000 cd/m^2
- No deep-level trap emission even at high current densities
- Higher order excited states may be present due to Auger suppression!
- Max. EQE of 0.17% reached at 100 mA/cm^2 (7.0 V) – NOT intrinsic limit
- Stable in repeated testing for >1 month stored/tested in air

Pal *et al. Nano Lett.* *2012, 12, 331-336*

Directly probing the influence of shell thickness

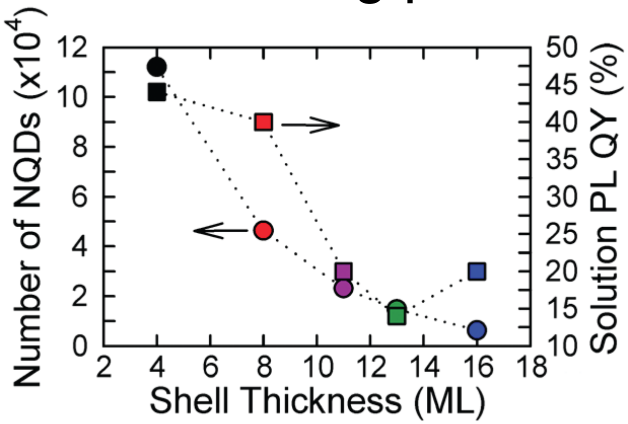
- Shell series (4CdS, 8CdS, 13CdS, 16CdS) compared



Pal *et al. Nano Lett. 2012, 12, 331-336*

QD LED performance as a function of shell thickness

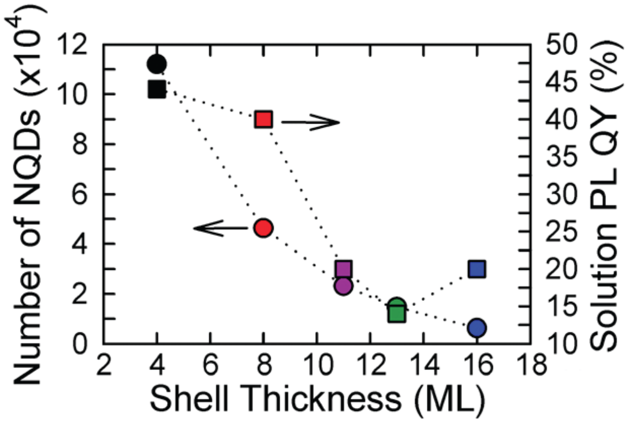
- The starting point

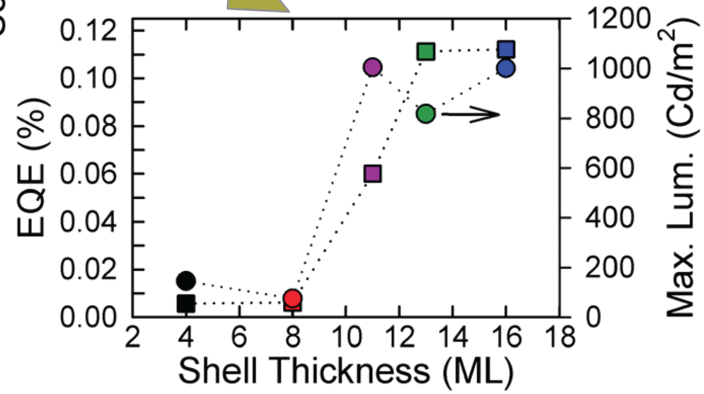


- g-QD solution-phase performance is poor compared to thinner-shell QDs
- Fewer g-QDs in a QD monolayer

QD LED performance as a function of shell thickness

- g-QD solid-state performance surpasses solution-phase behavior

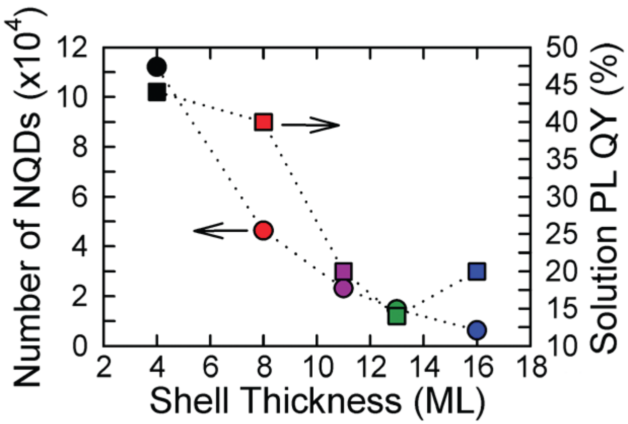


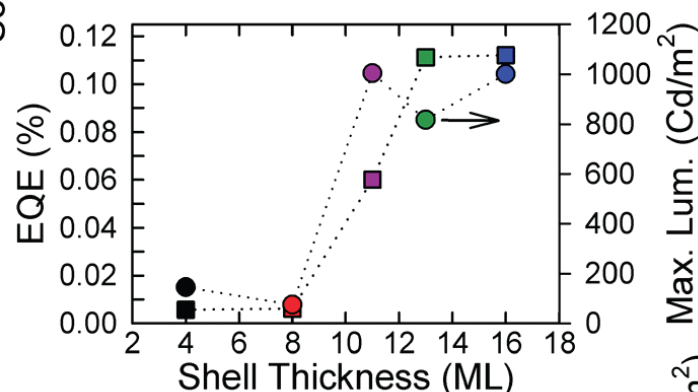


- EQE jumps for thick shells >10ML
- Shell thickness threshold for max. luminance, too

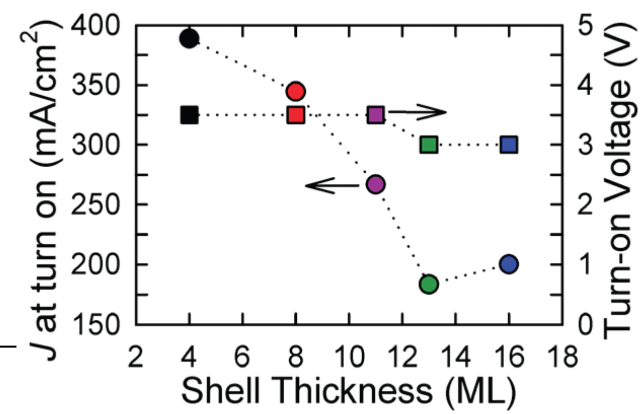
QD LED performance as a function of shell thickness

- g-QD solid-state performance surpasses solution-phase behavior



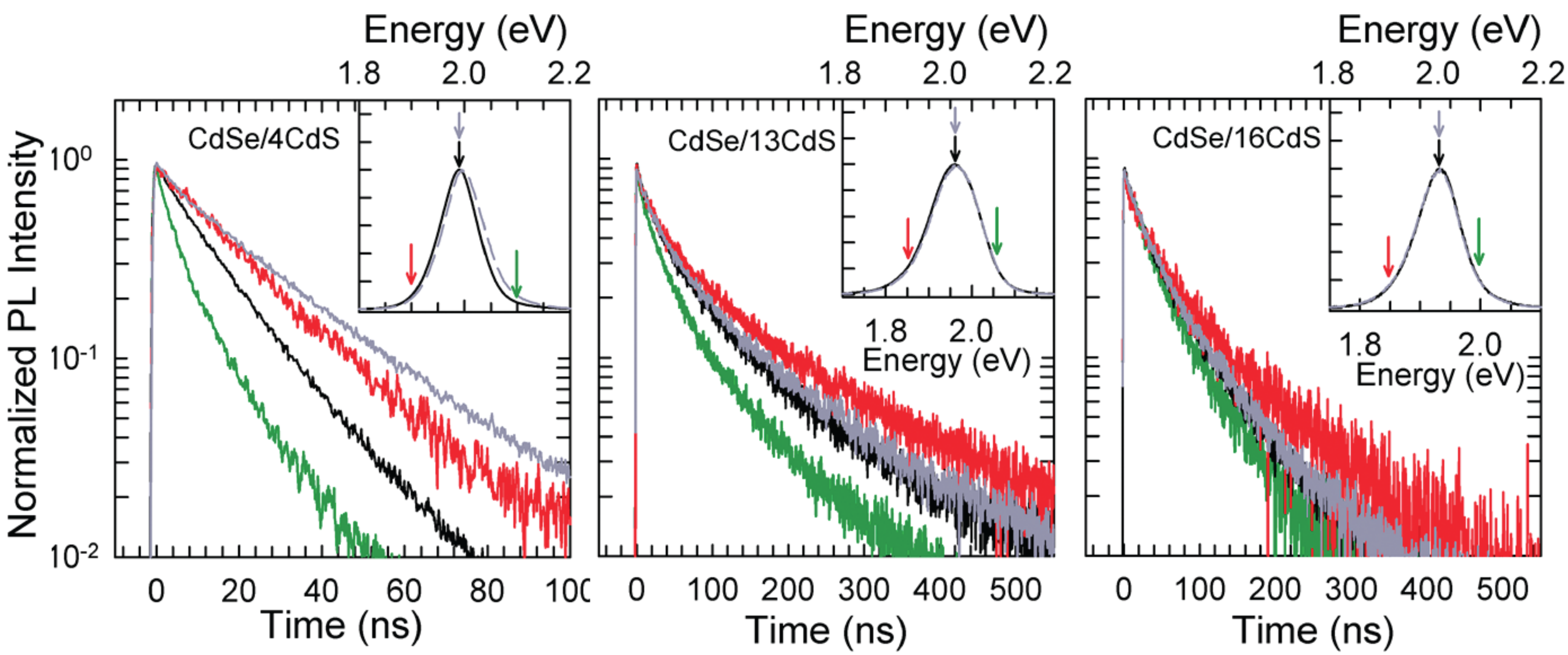


- Turn-on voltage: shell-thickness *independent*
- Reduced leakage current



Why do g-QDs outperform QDs in LEDs?

- g-QD luminescence is ligand-independent
- Auger recombination is suppressed; *charged excitons emit!*
- QD-QD energy transfer 'shut-down' at thick shells

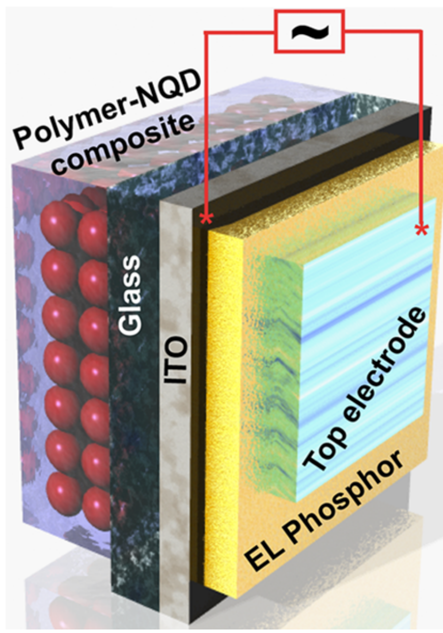


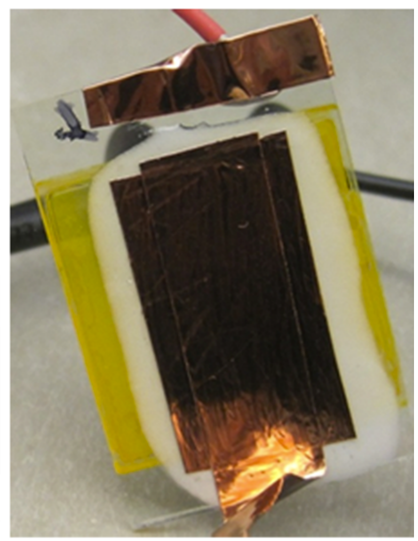
- Photoluminescence decay curves

Pal *et al. Nano Lett. 2012, 12, 331-336*

g-QDs as 'replacement' color-converting phosphors

- 'Test-bed' device architecture: so simple even a chemist can make it!
  - Commercial 'blue-emitting' electroluminescent (EL) phosphor: Cu/Cl-doped ZnS
  - EL phosphor sandwiched between indium tin oxide (ITO) bottom electrode and Cu tape top electrode
  - QD-polymer composite coated on backside of glass substrate



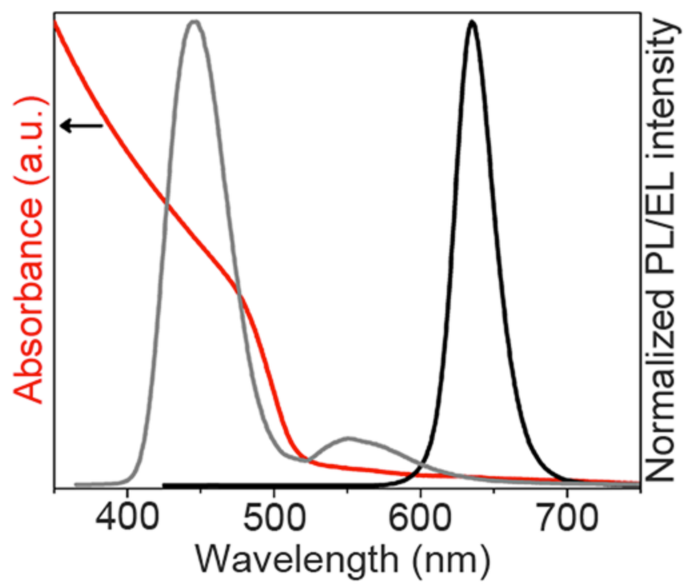


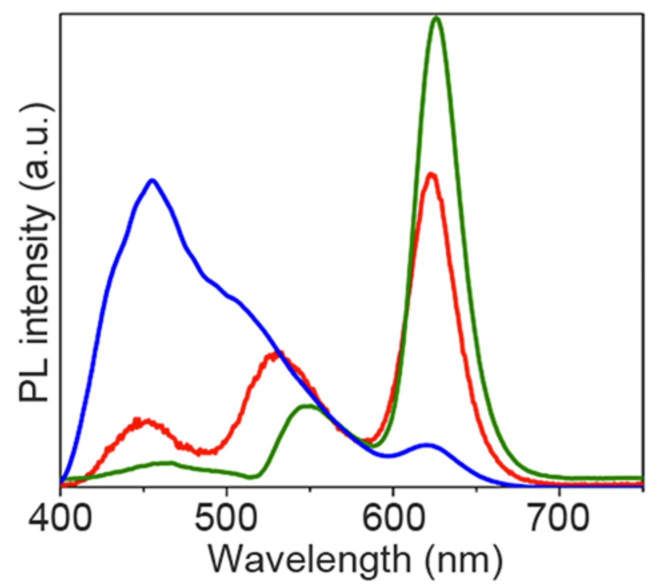
Kundu *et al. Nano Lett.* 2012, 12, 3031-3037

Key g-QD enabling characteristic: *Unique absorption profile*

- Large effective Stokes shift
- Absorption well matched to EL

- High down-conversion efficiency: 22% (green trace)
- High spectral purity: 84%
- 'Green-yellow' retained
- 30 Cd/m^2

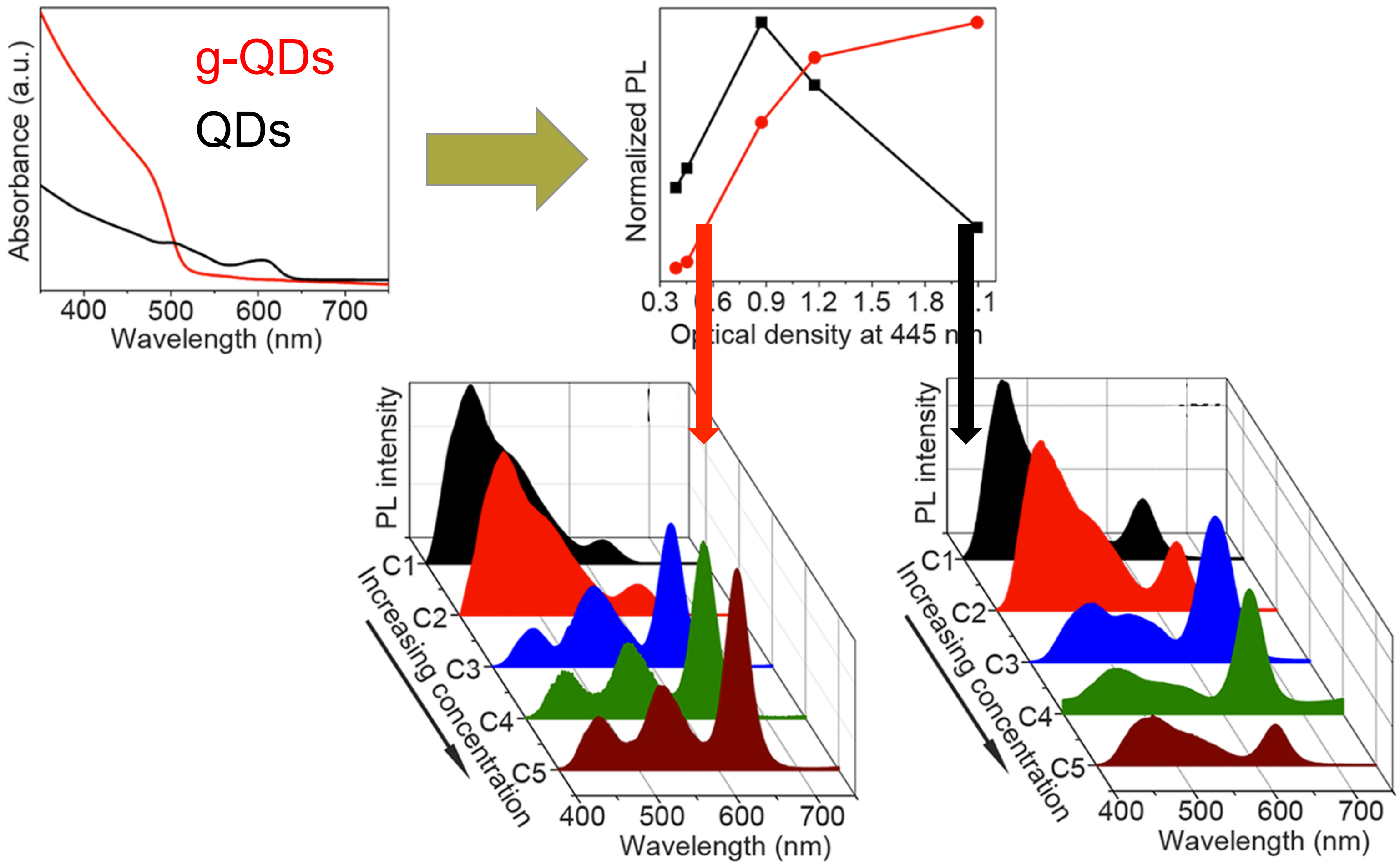




Kundu *et al. Nano Lett. 2012, 12, 3031-3037*

Key g-QD enabling characteristic:
Unique absorption profile

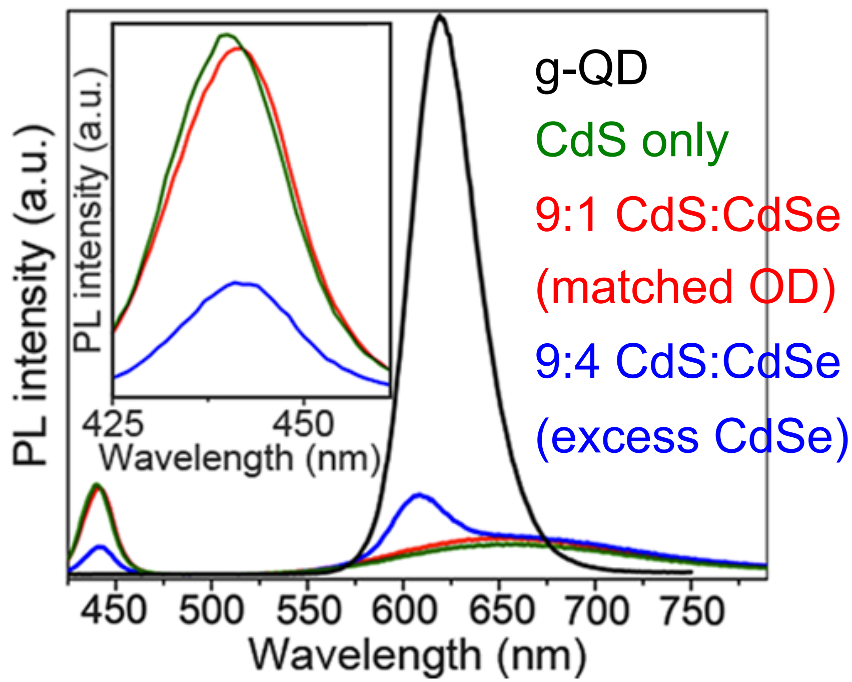
- g-NQDs can be packed at high densities without self-reabsorption losses



Kundu *et al. Nano Lett. 2012, 12, 3031-3037*

Key g-QD enabling characteristic:
Efficient shell→core energy relaxation

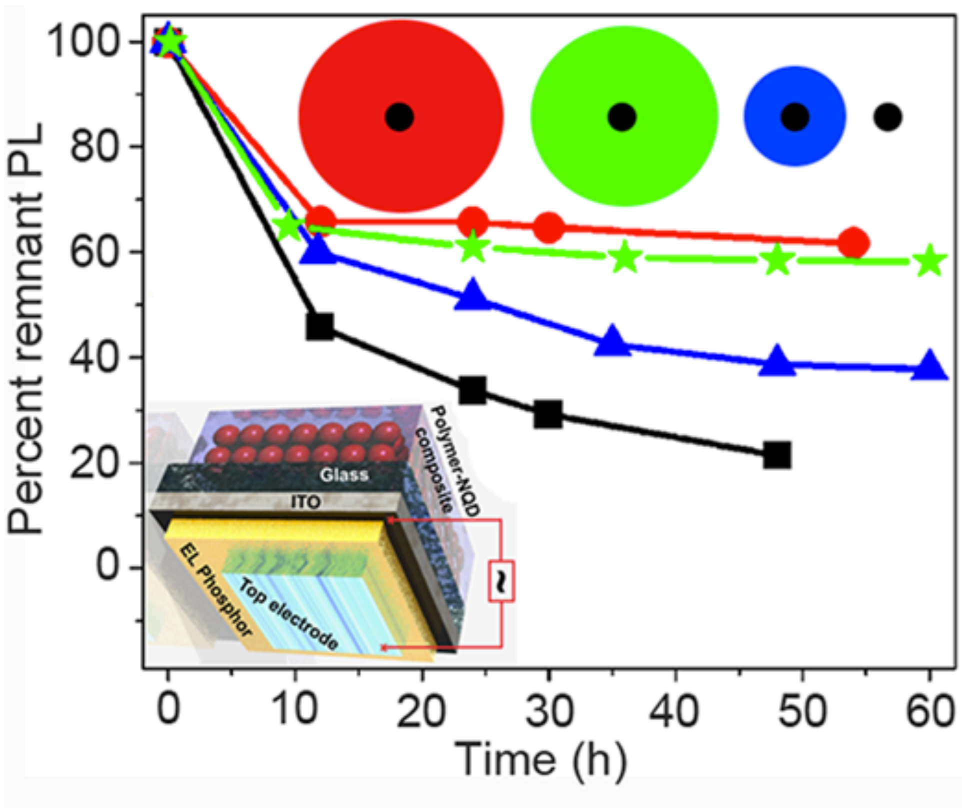
- In thick-shell QDs, precise engineering of nanoscale architecture affords independent control over absorption & emission properties
- Importantly, these functions remain intimately and efficiently coupled, allowing energy relaxation in g-NQDs to outcompete energy transfer in simple mixtures of absorbers/emitters



Kundu *et al. Nano Lett. 2012, 12, 3031-3037*

Key g-QD enabling characteristic: *Stability*

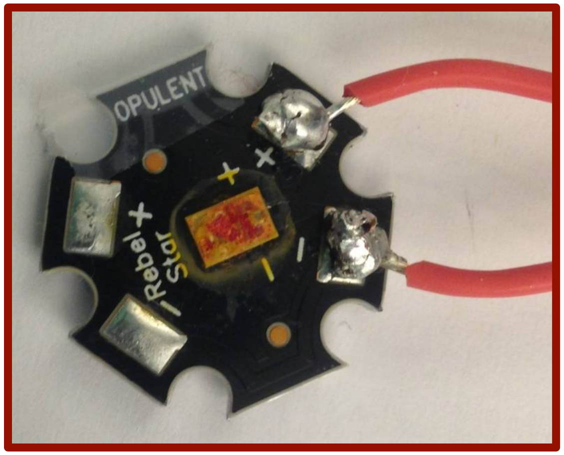
- Temporal device stability as a function of continuous biasing time



Transitioning proof-of-principle for g-QD down-conversion phosphors to high-power DC LEDs

NEW

- Characteristics of LED source: high luminous flux & temperature
  - Many conventional rare-earth phosphors characterized by long radiative lifetimes exhibit PL saturation
  - Many phosphors, including QD alternatives, are reversibly & irreversibly partially quenched by elevated temperature



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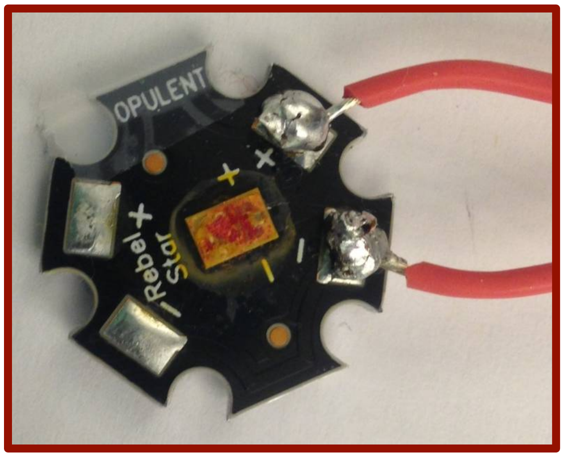

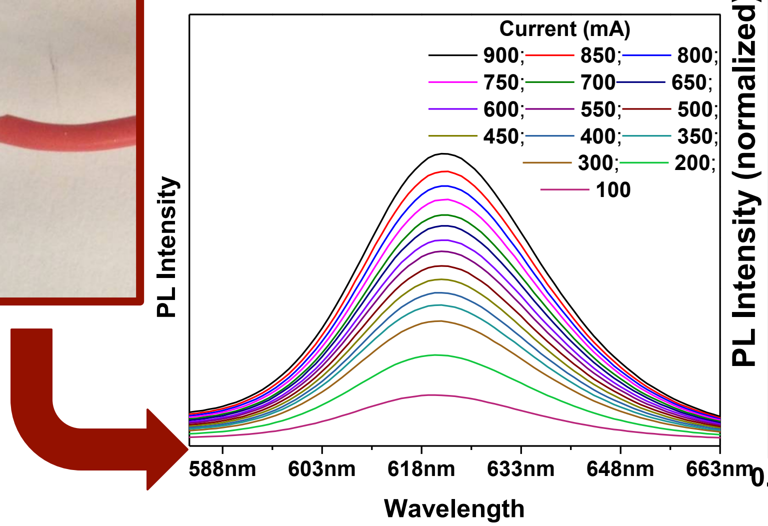

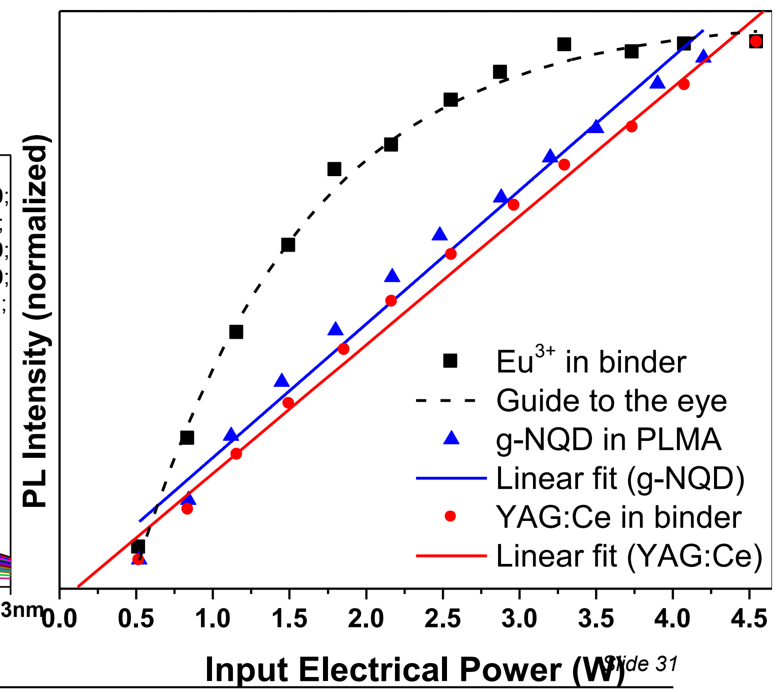

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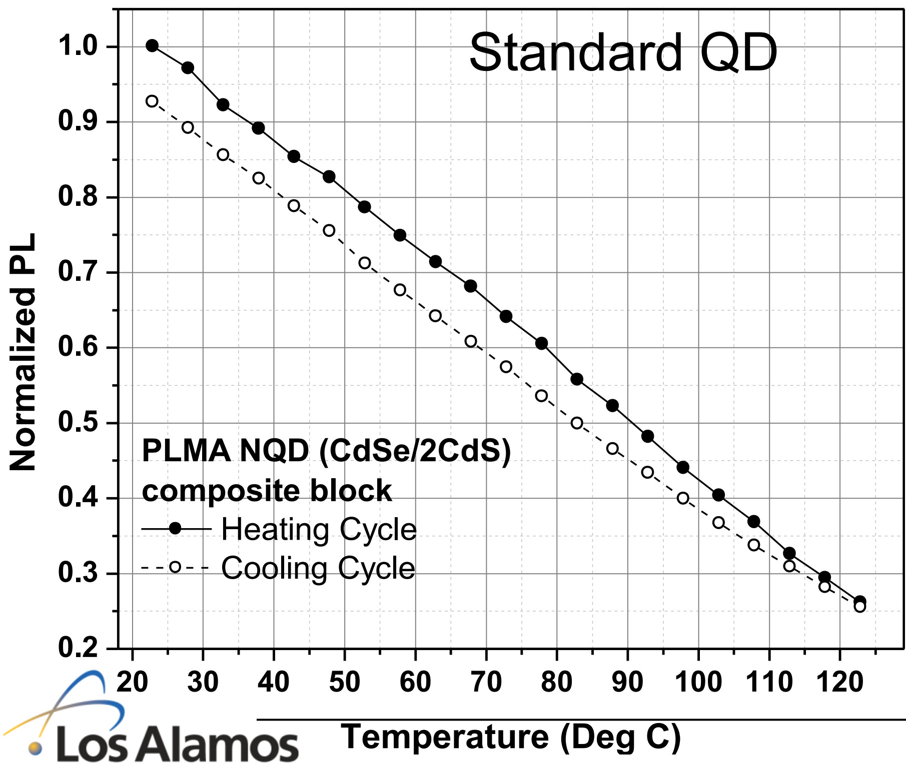

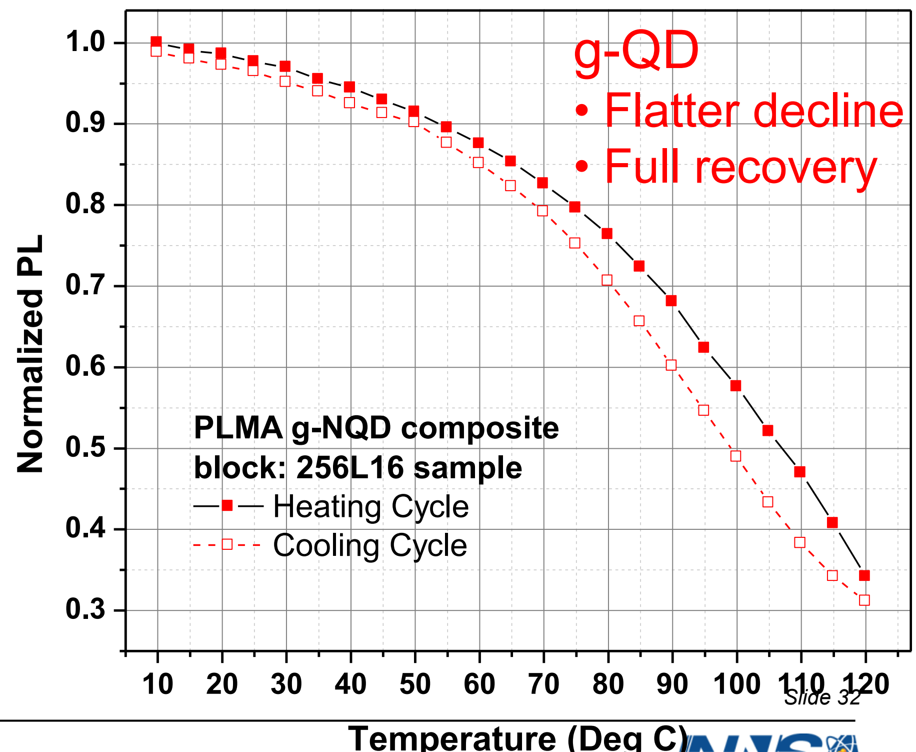

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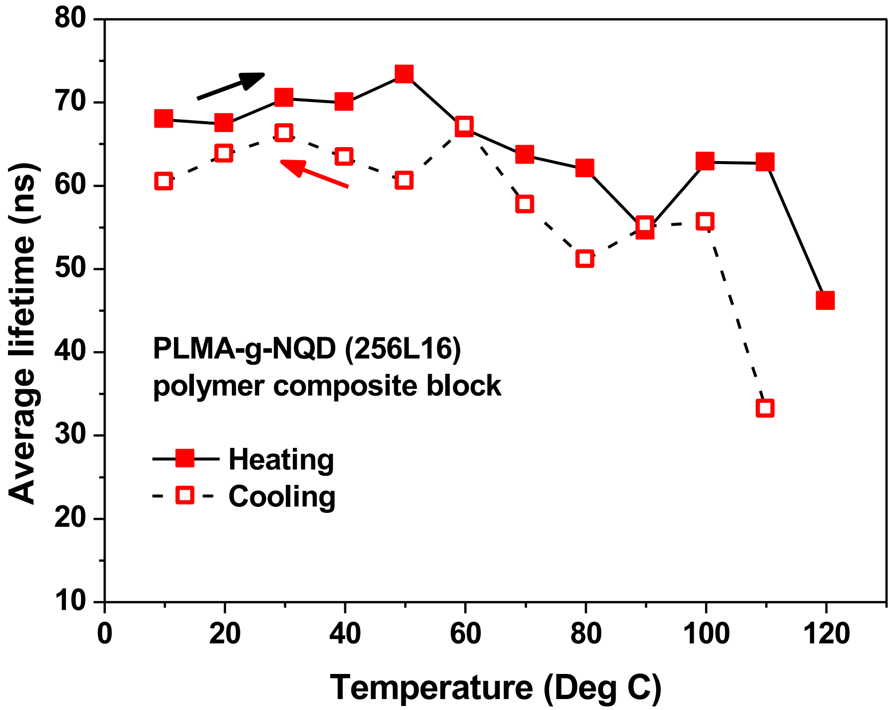

g-QD
- Lifetime changes reversible

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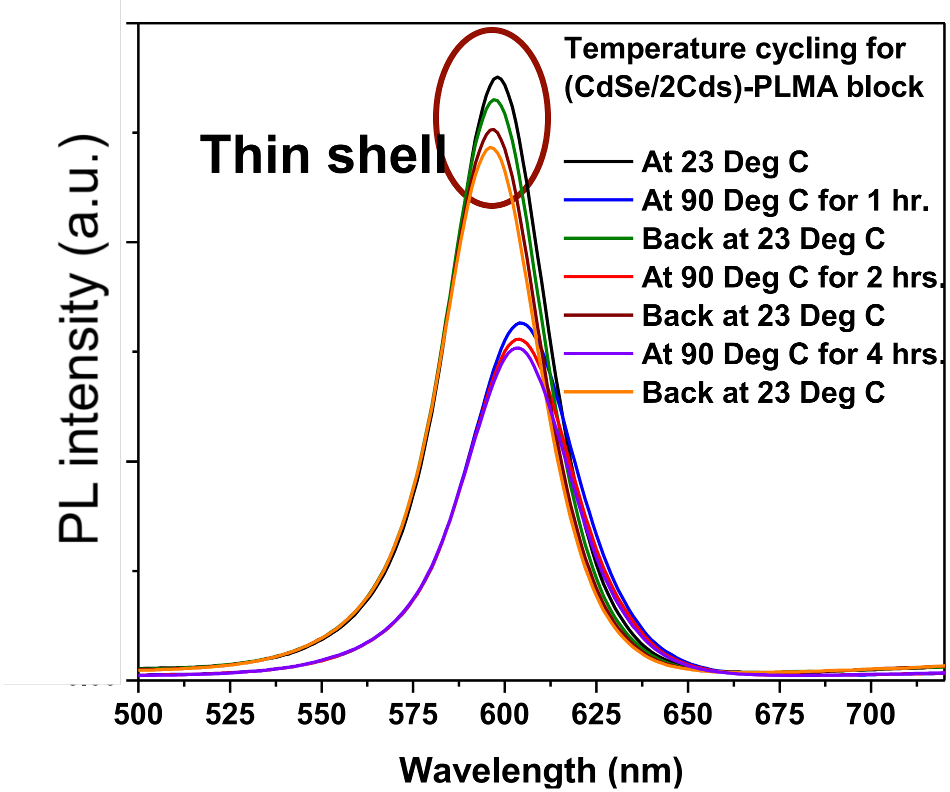
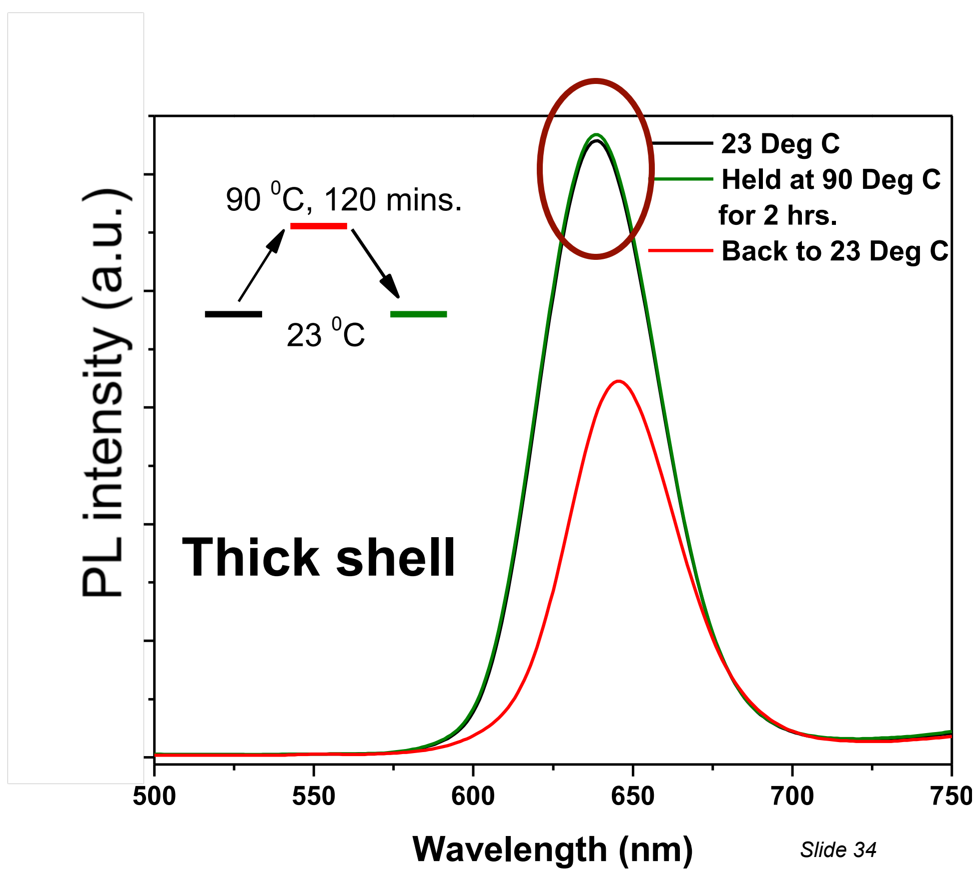
NEW

Effect of temperature cycling: 23 °C to 90 °C (hold) to 23 °C





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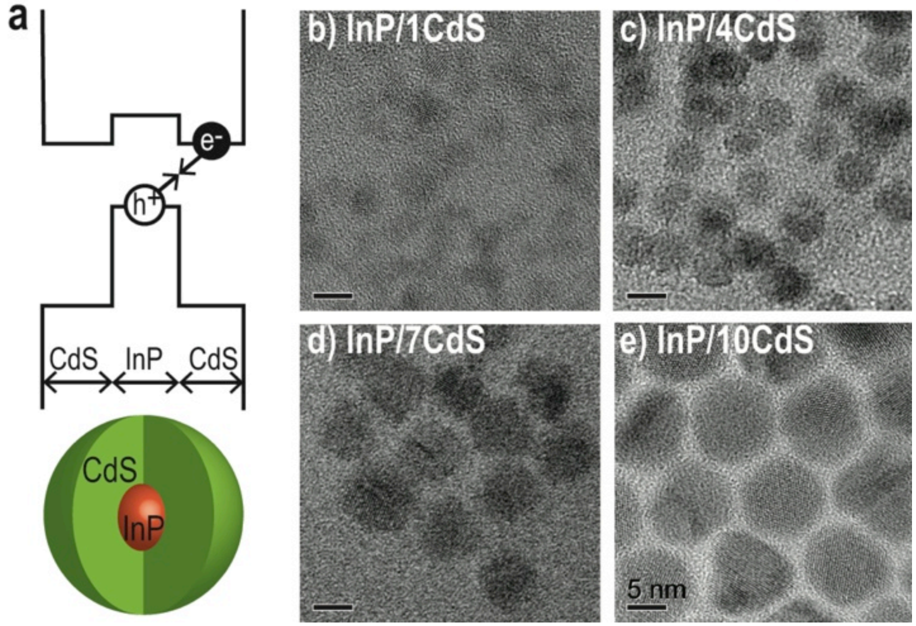
Limited examples of dual suppression of blinking and Auger recombination

- Alloyed CdZnSe/ZnSe system: Wang et al. Nature 2009
  - Suppressed Auger recombination via smoothing of the confinement potential
- Quasi type-II, thick-shell CdSe/CdS: Chen et al. J. Am. Chem. Soc. 2008 and Mahler et al. Nature. Mater. 2008
  - Suppressed ionization/charging via thick, protective shell
  - Suppressed Auger recombination via combined size, carrier-separation and (possibly) interface effects

Moving beyond CdSe:

InP-based core/shell heterostructuring also affords suppressed blinking and Auger recombination

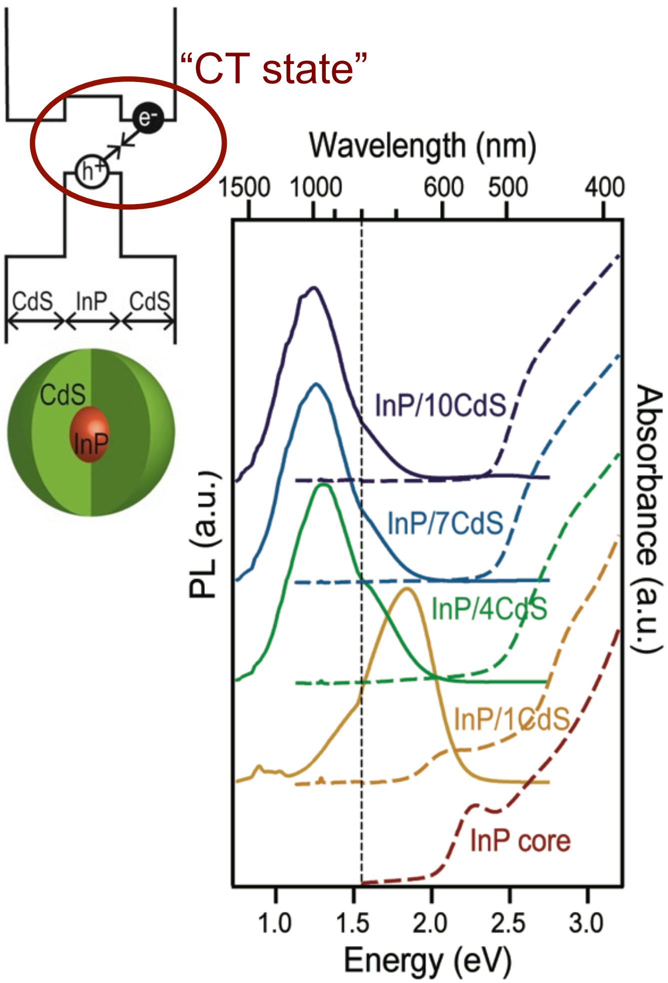
InP/CdS g-QDs: Addressing the effects of both electronic structure and shell thickness



- Distinguishing features of the InP/CdS core/shell system
  - Type II electronic structure: Fully charge-separated state
  - Synthetic challenge: InP amenable to high-temperature SILAR growth only after low-T application of first, protective monolayer
    - Susceptibility to surface oxidation
    - Tendency to etch at high-T in presence of acidic/basic ligands
  - Hexagonally faceted, wurtzite shells: Structurally equivalent to CdSe/CdS system

Dennis *et al. Nano Lett.* 2012, 12, 5545-5551

Spectral and dynamic signatures of the type-II heterojunction



- PL red shifts
- Abs broadens/red-shifts then dominated by shell for large "effective Stokes shift"

Dennis *et al. Nano Lett. 2012, 12, 5545-5551*

Unprecedented single-dot infrared-QD blinking studies

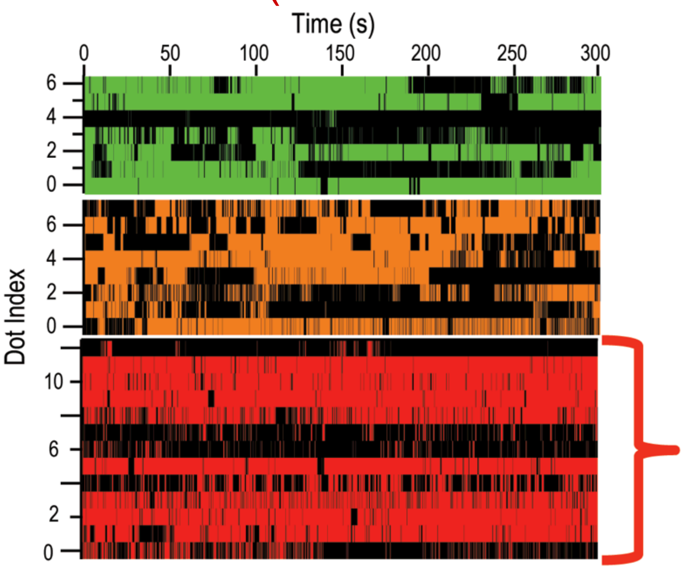
- Room-T blinking studies of type-II QDs previously unknown
  - Though well-known for quasi type-II CdSe/CdS and $CdTe/CdTe_xSe_y/CdSe$ QDs
  - Type II's photobleached
- Single example of single-dot emission from type I infrared emitting QD
  - Correa et al. Nano Lett. 2012 (Bawendi's lab)
  - Specialized superconducting nanowire single-photon detector required to surmount:
    - Materials instability issues
    - ~Long radiative lifetimes
- Our work: Standard sample-preparation and single-photon detection methods adequate

Effect of shell thickness and electronic structure on single-dot blinking behavior and photostability

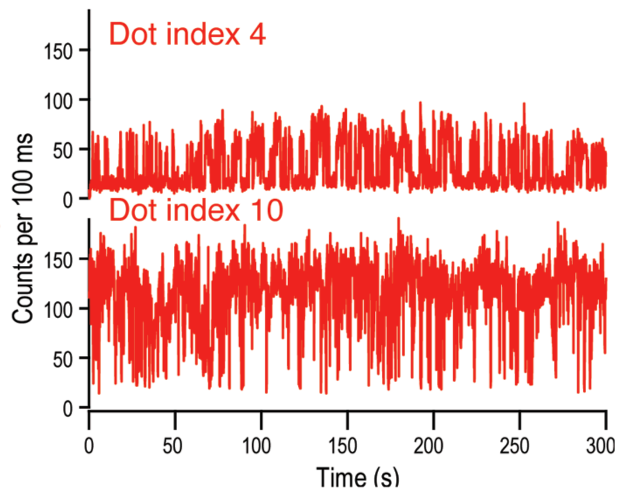
InP/1CdS (~15-20% dots: on-time % >80%)

InP/4CdS (~15-20% dots: on-time % >80%)

InP/10CdS (>60% dots: on-time % >80%; some 'non-blinking')



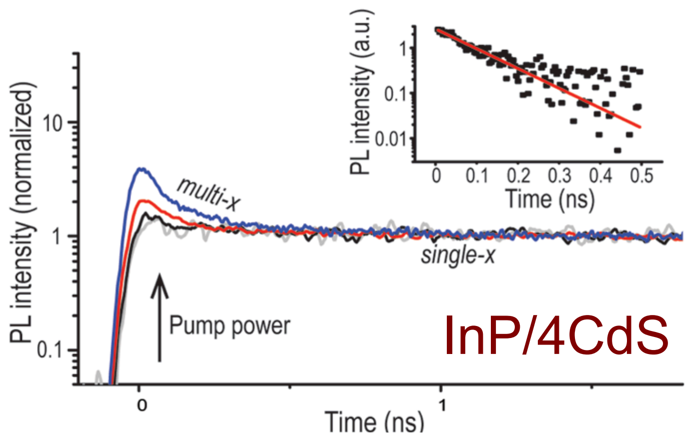
Black 'off' / Color 'on'

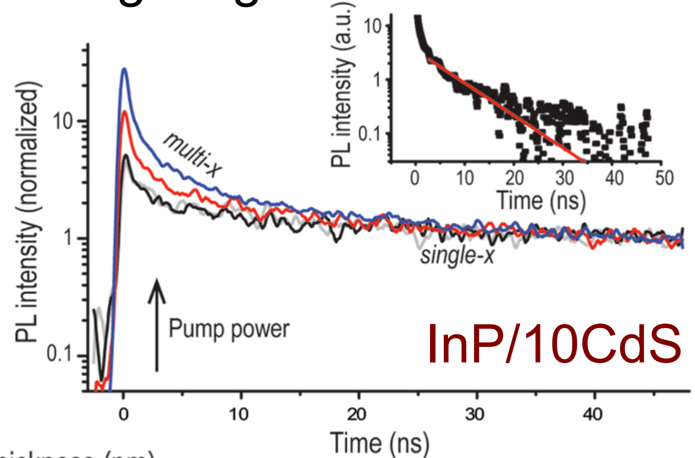


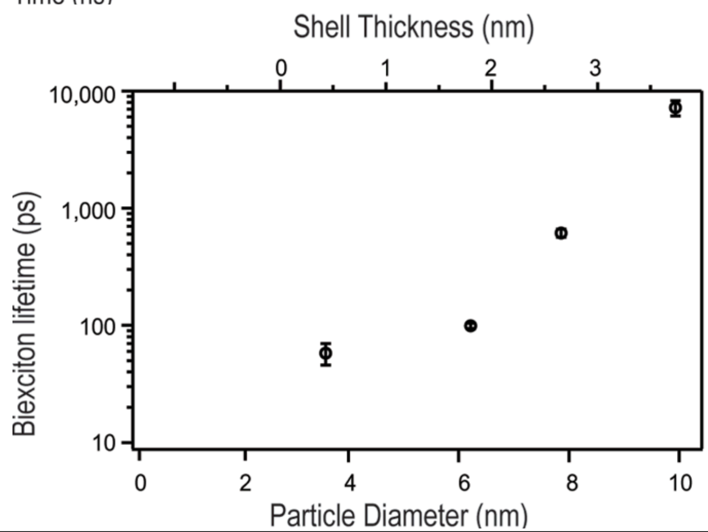
- Type-II bandgap alignment transitions the room-T, non-blinking excitonic emission into the near-IR for the first time
- Blinking less clearly shell-thickness dependent; Photobleaching more so

InP/CdS biexciton lifetimes trend with shell thickness

- Pump-intensity-dependent transient photoluminescence: traces converge at long times for thick-shell variants indicating long-lived multiexcitons





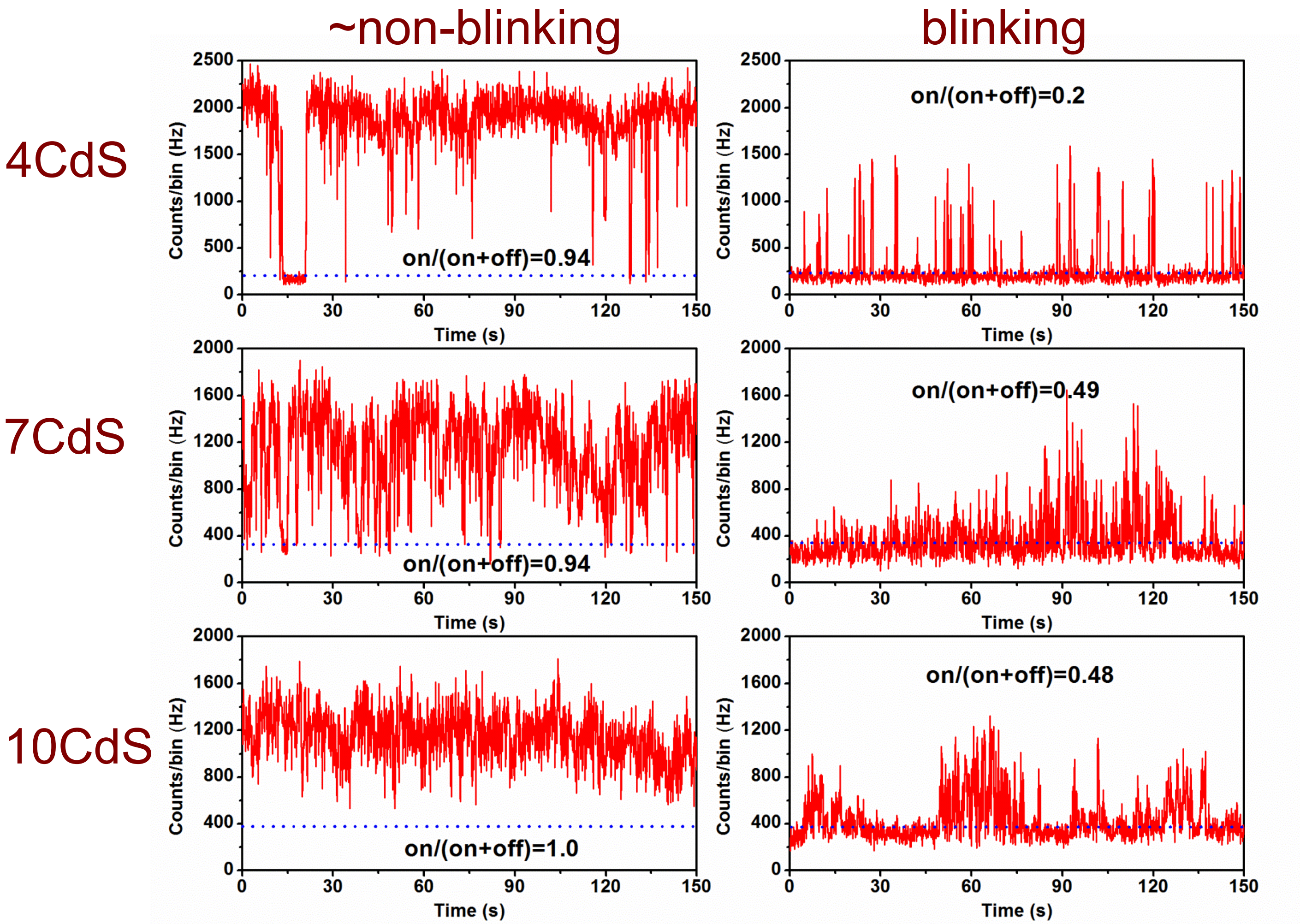


Dennis *et al. Nano Lett.* 2012, 12, 5545-5551

Examples of both non-blinking and blinking behavior for thin and thick-shell InP/CdS

NEW

- on/(on+off) ratios defined: “high” and “low” evident at each shell thickness

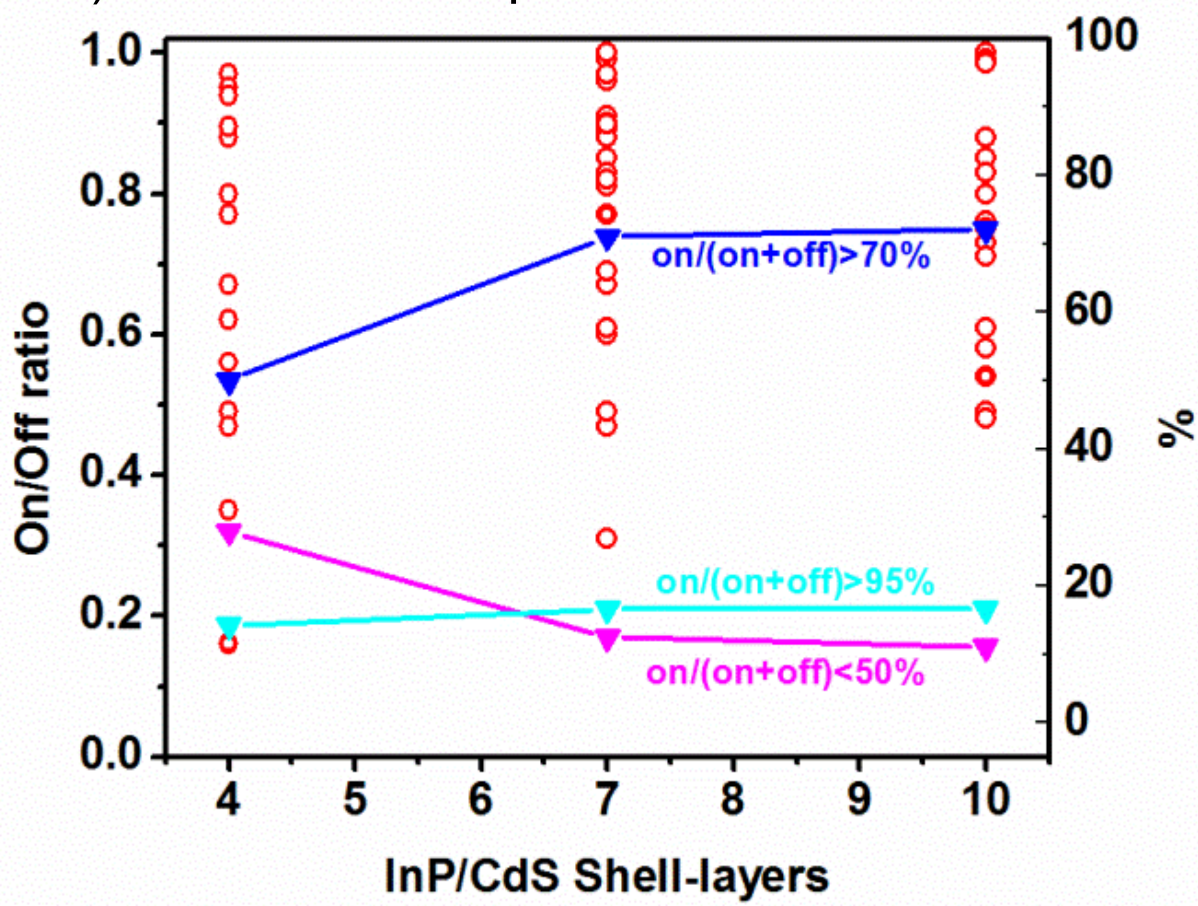


Manuscript in preparation with Han Htoon’s team

Detailed blinking statistics reveals nature of shell-thickness dependence in InP/CdS system

NEW

- Non-blinking percentage ~constant, *however…*
- High on/(on+off) ratios become more prevalent with increasing #CdS
- Low on/(on+off) ratios decline in prevalence



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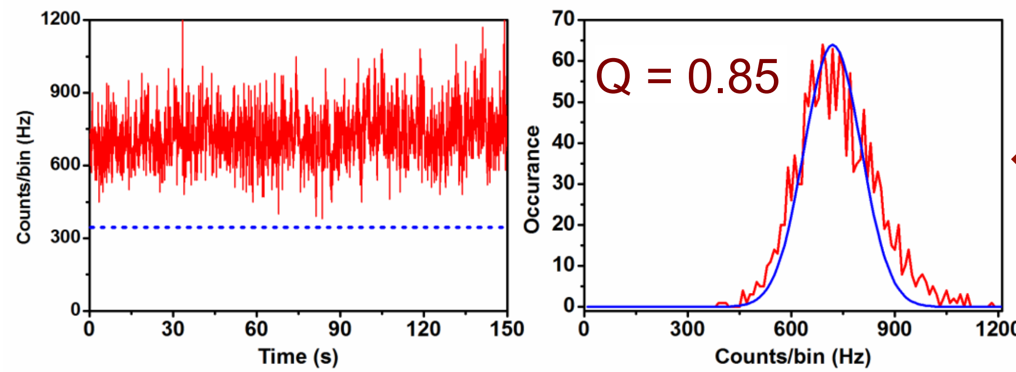
Mandel Q Parameter describes the degree of deviation from a Poissonian distribution of emission intensities

- Case 1: Perfect Poisson distribution

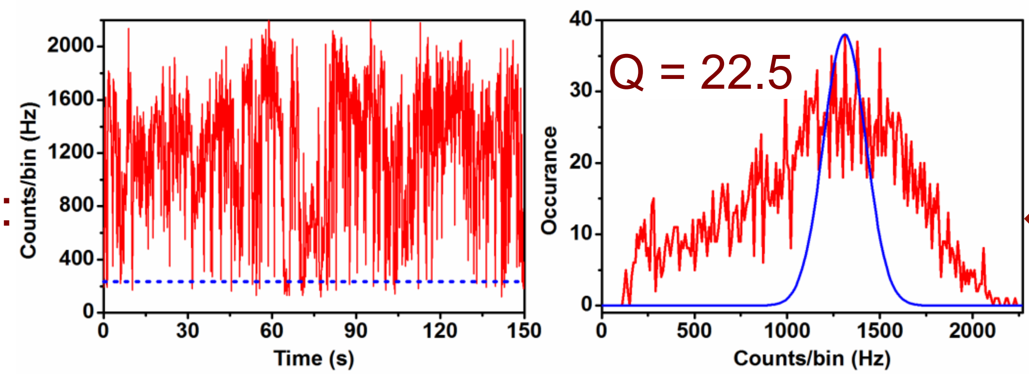
PL intensity trajectory: on/(on+off)>90%



Poissonian fits for intensity distribution of the trajectories

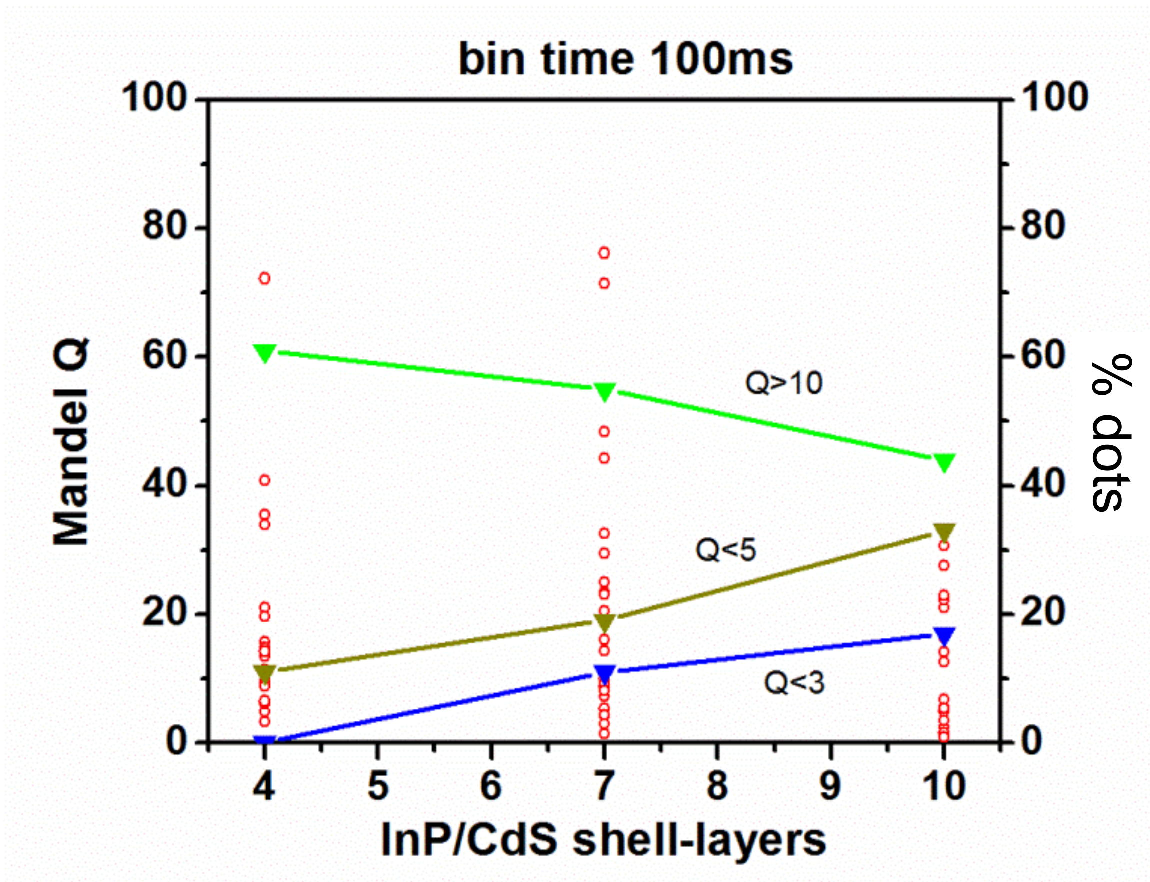
- Case 2: Large deviation from Poisson distribution

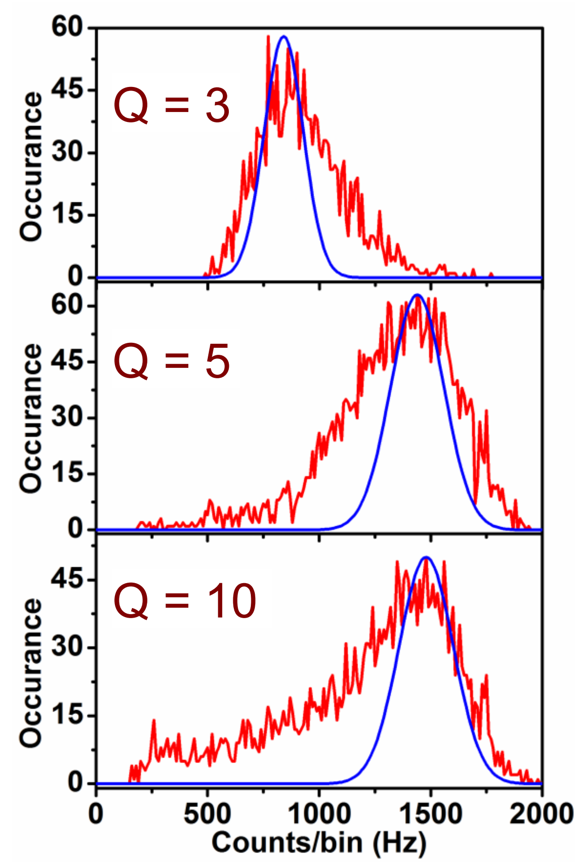
PL intensity trajectory: on/(on+off)>90%



Thicker shells appear to be converging to smaller Q's, i.e., tighter intensity distributions

NEW





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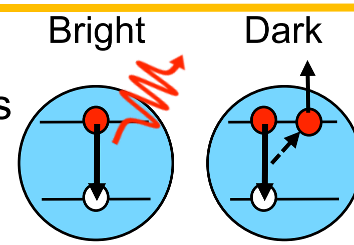
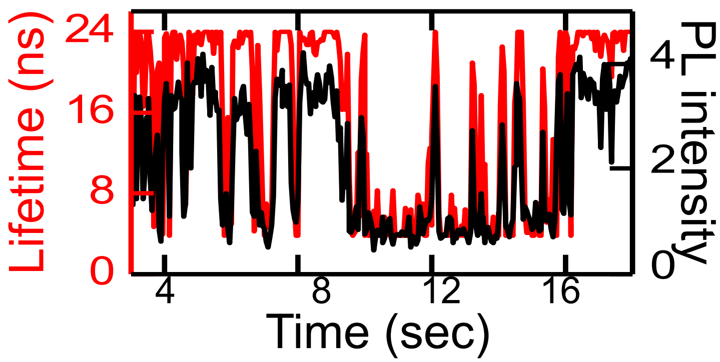
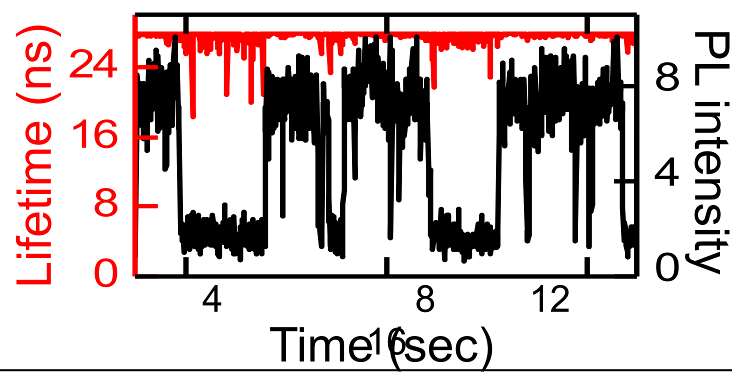
New way to think about blinking: Single-dot spectroelectrochemistry reveals two mechanisms

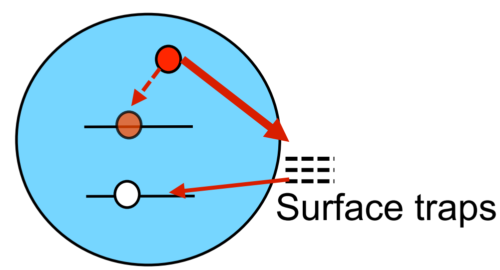
- Conventional blinking model: "Type A"
  - QDs randomly cycle through uncharged and charged states
  - QD blinks 'off' due to Auger quenching of charged exciton
  - PL intensities and lifetimes fluctuate together





- New blinking model: "Type B"
  - Trapping of hot electrons to surface states "darkens" PL





Excitonic emission "short-circuited"

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Galland *et al. Nature 2011, 479, 203-207*

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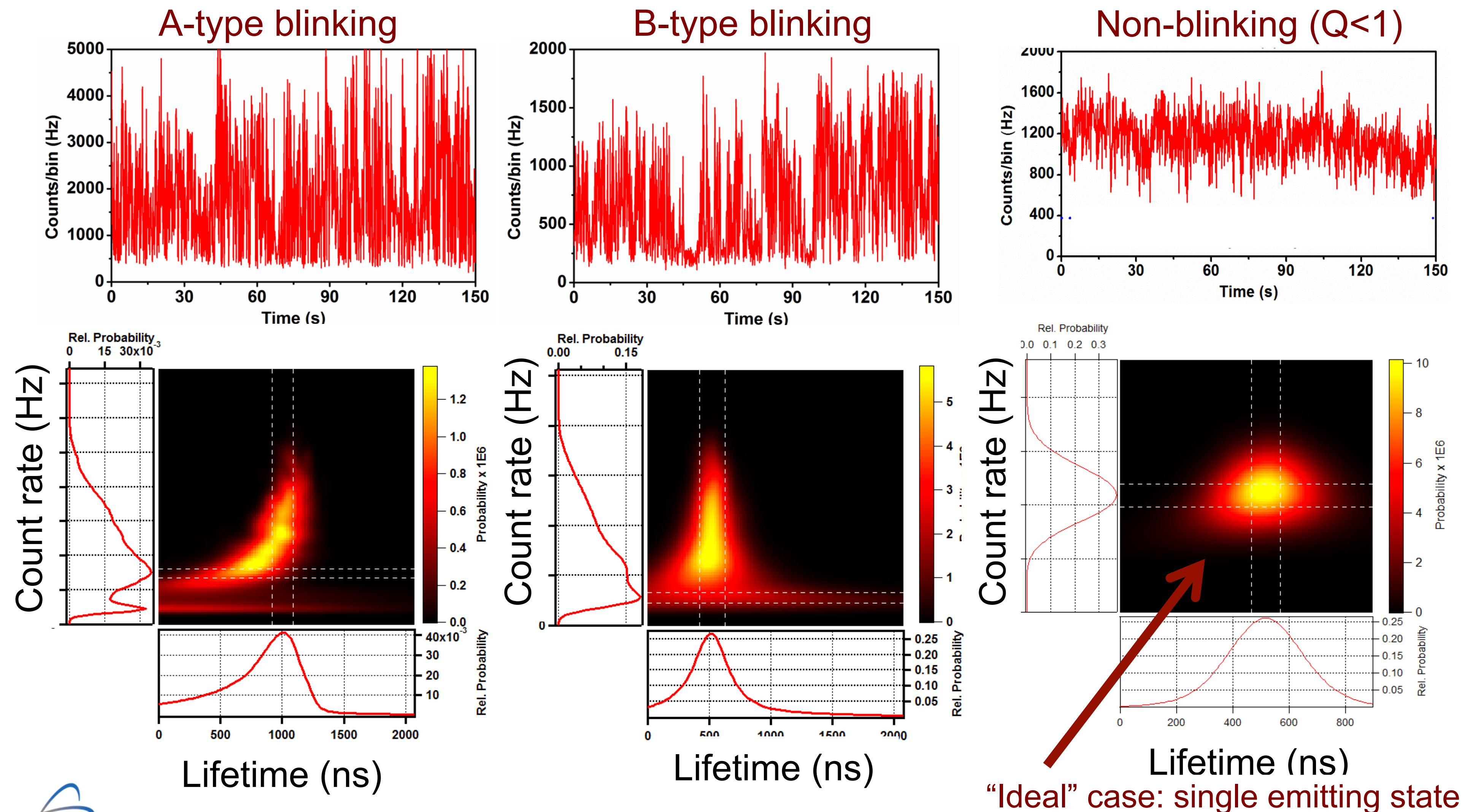
Fluorescence Lifetime Intensity Distributions (FLID): Correlated lifetime-intensity plots reveal more about "blinking" than intensity traces alone

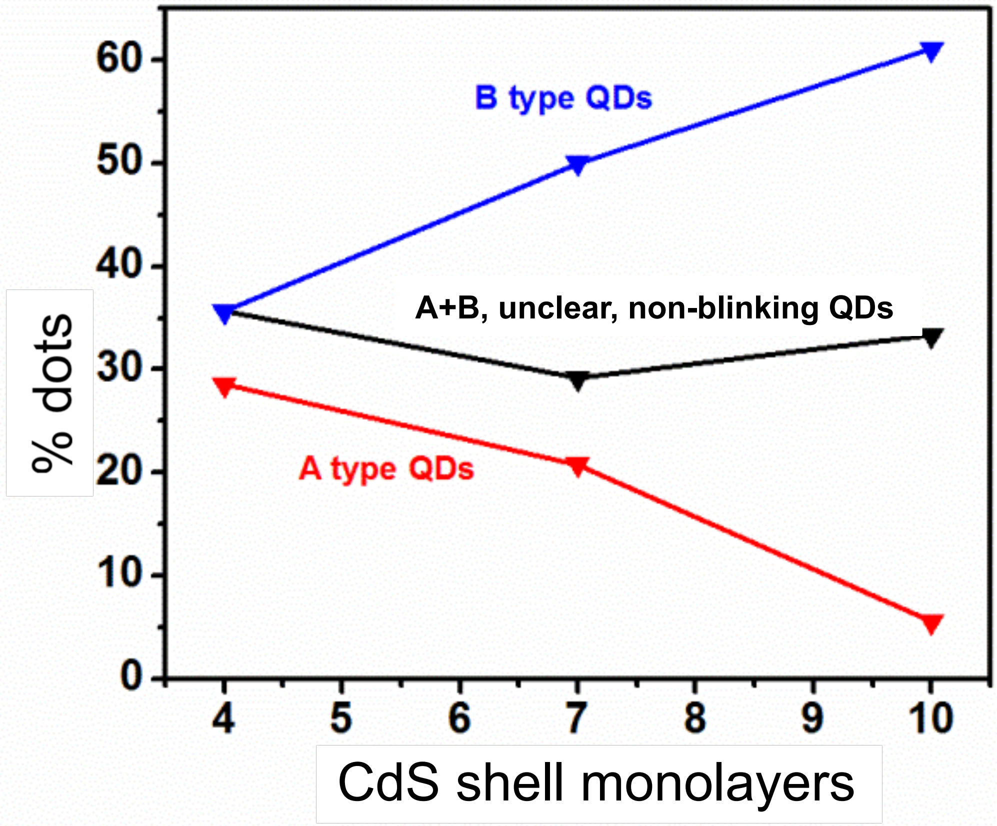
NEW



Manuscript in preparation with Han Htoon's team

Clear impact of shell thickness on blinking "type" in InP/CdS system

NEW

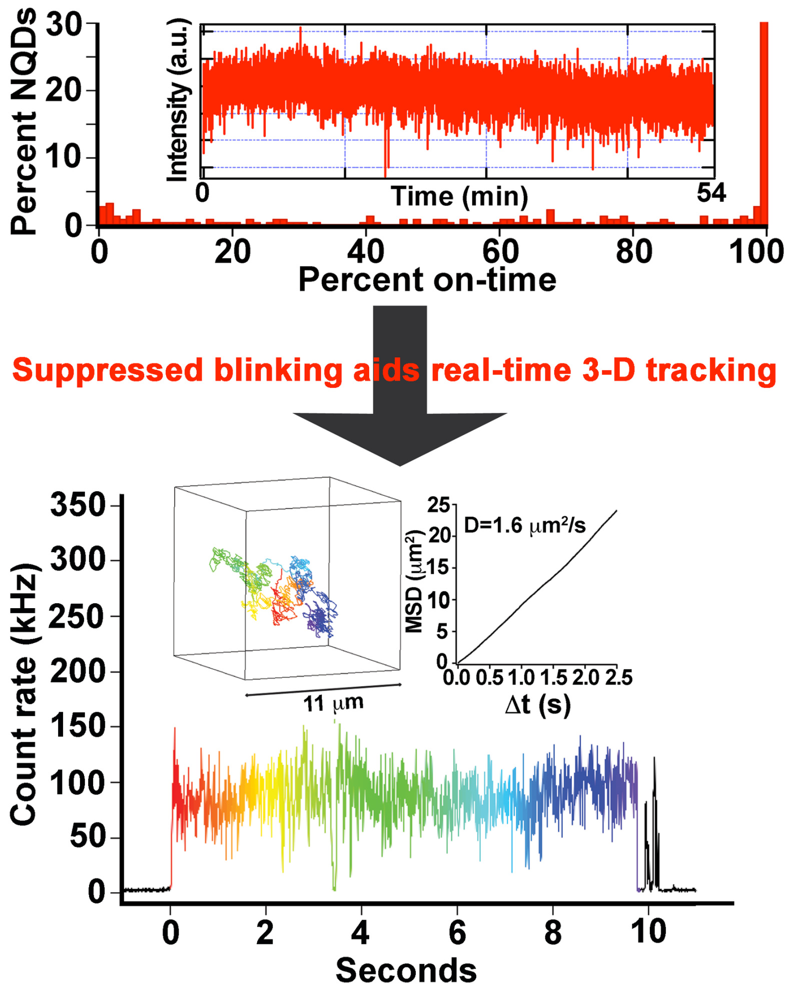


Comment: earlier onset of 'suppressed blinking' vs. CdSe/CdS system: *Apparent impact of transition to a fully type-II electronic structure*

- Decline in A-type blinking: consistent with our previous observation that Auger recombination efficiency decreases with increasing shell thickness
- Continued presence of B type blinking: implies even thicker shell is required

Other "light emission" applications of non-blinking g-QDs: 3D particle tracking

- With Jim Werner, R&D 100 Award Winner



<u>*Jim's work more broadly:*</u>

- *Three Dimensional Tracking of Individual Quantum Dots*, Lessard, G.A., P.M. Goodwin, and J.H. Werner, Applied Physics Letters. 91(22): p. 2224106 /1-3, (2007).
- *Time-Resolved Three-Dimensional Molecular Tracking in Live Cells*, Wells, N.P., G.A. Lessard, P.M. Goodwin, M.E. Phipps, P.J. Cutler, D.S. Lidke, B.S. Wilson, and J.H. Werner, Nano Letters. 10(11): p. 4732-4737, (2010).
- *Time-Resolved, Confocal Single Molecule Tracking of Individual Organic Dyes and Fluorescent Proteins in Three Dimensions*, Han, J.J., C. Kiss, A. Bradbury, and J.H. Werner, ACS Nano. (2012).

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From: Vela *et al. J. Biophotonics 2010, 3, 706-717*

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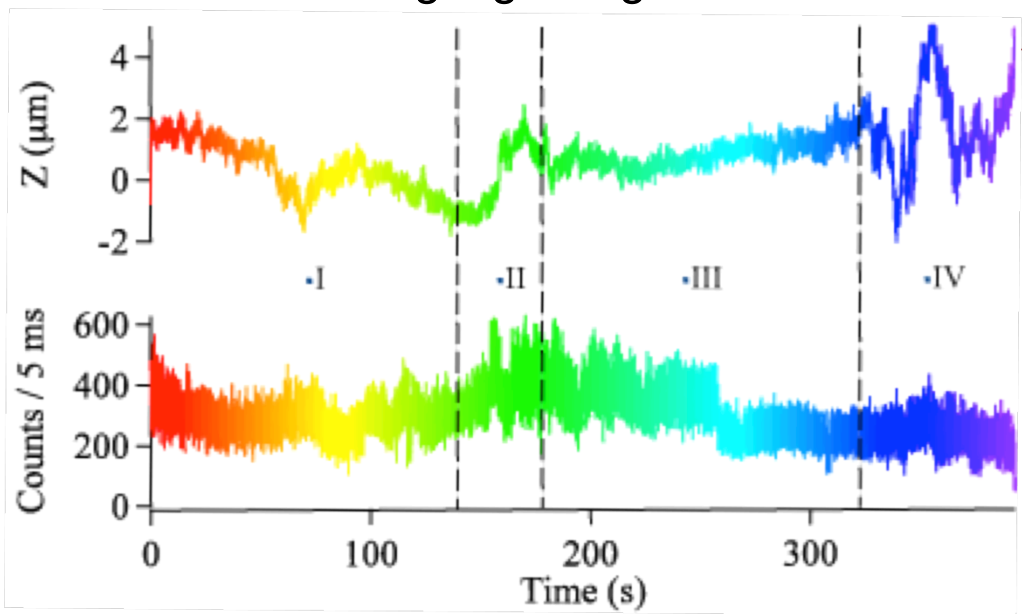
3D single-particle tracking in live mast cells:
20-fold increase in tracking duration!

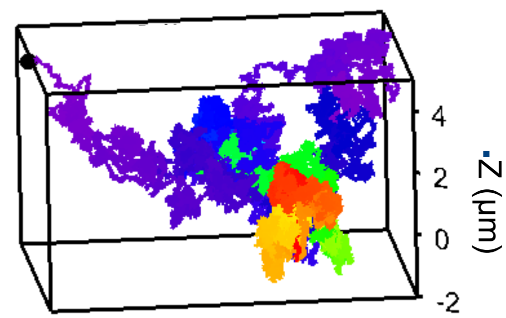
NEW

- Tracked single gQD-IgE for 6.5 min!

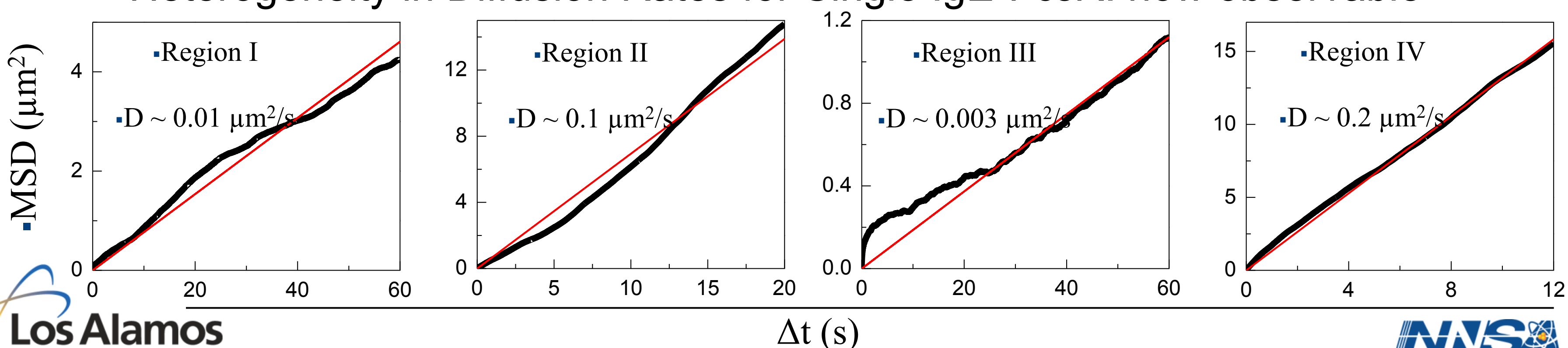


Average tracking duration

- g-QD-IgE = 111 ± 26 s
- Commercial $QDot_{655}$-IgE = 4.8 ± 1.3 s



- Heterogeneity in Diffusion Rates for Single IgE-FcεRI now observable



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Conclusions

- We addressed the long-standing QD 'blinking challenge'
- g-QDs nano-structural motif characterized by enabling traits
  - Suppressed Auger recombination
  - Suppressed charging and/or surface trapping
  - Stability independent of surface chemistry/chemical environment
  - Large effective Stokes shift (minimal self, green/yellow re-absorption)
  - Enhanced solid-state performance
  - Etc.
- Demonstrated application of g-QDs in proof-of-concept direct-charge-injection and down-conversion devices
- Extended g-QD 'approach' to new InP/CdS system
  - Suppressed blinking, photobleaching and Auger recombination
  - First near-infrared non-blinking QD
- New, 'sustainable' compositions are required = 'non-rare/non-toxic'
  - Simplify synthesis and enhance efficiency for rapid exploration: automation

Acknowledgements

Janardan Kundu: poster

Current LANL CINT g-QD team

- Han Htoon: Staff Scientist, Spectroscopy
- Jim Werner: Staff Scientist, 3D tracking
- Yagnaseni Ghosh: Chem PD
- Allison Dennis: Chem PD
- Janardan Kundu: Device fab/testing PD
- Aaron Keller: 3D particle tracking PD
- Bhola Nath Pal: Device fab/testing PD
- Ben Mangum: Spectroscopy PD

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U.S. DEPARTMENT OF ENERGY | Office of Science

LDRD

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(For more information: cint.lanl.gov)

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