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Title:	Process-Dependent Properties in Colloidally Synthesized â€œGiantâ€• Core/Shell Nanocrystal Quantum Dots
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Intended for:	2012 MRS Spring Meeting, 2012-04-09 (San Francisco, California, United States) presentations to TT visitors.

Process-Dependent Properties in Colloidally Synthesized "Giant" Core/Shell Nanocrystal Quantum Dots

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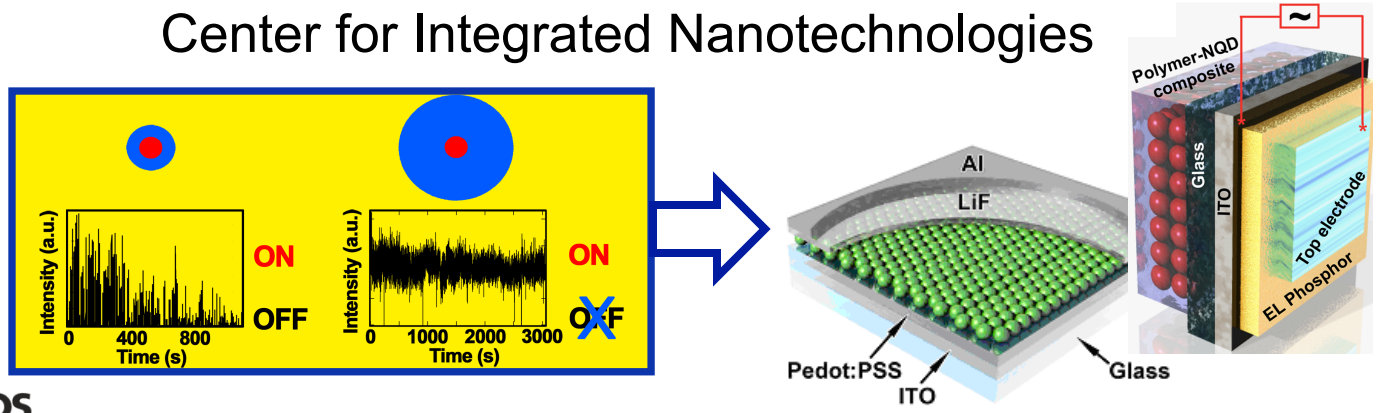
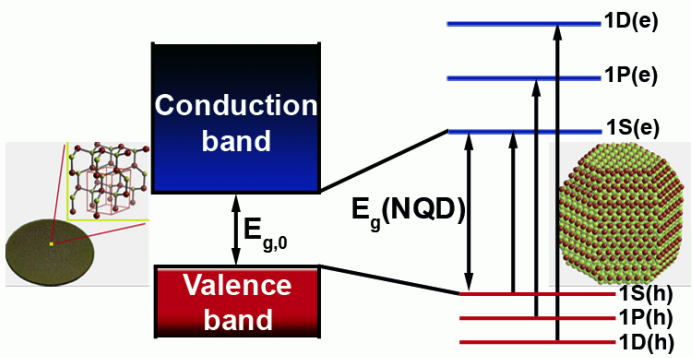
Center for Integrated Nanotechnologies



Semiconductor Nanocrystal Quantum Dots (NQDs): Why We Care

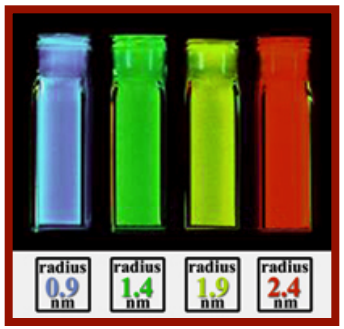
- Quantum-confinement effects afford functionality

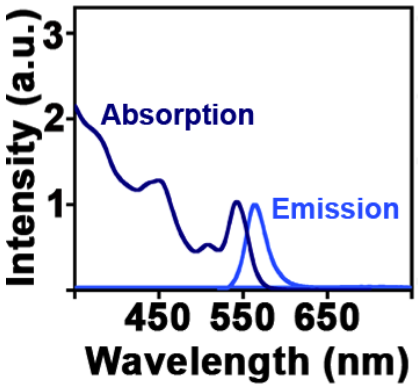


"Quantum box" model:

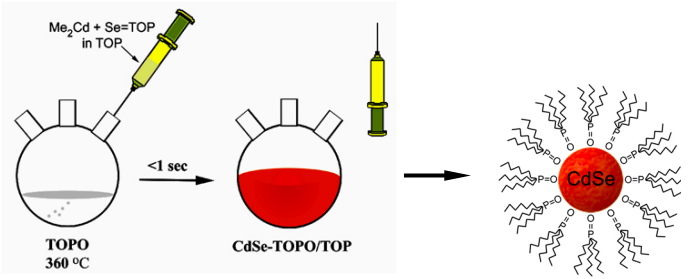
$$E_g(NQD) \approx E_{g,0} + \frac{\hbar^2\pi^2}{2m_{eh}R^2}$$

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





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



Semiconductor Nanocrystal Quantum Dots (NQDs): Why We Care

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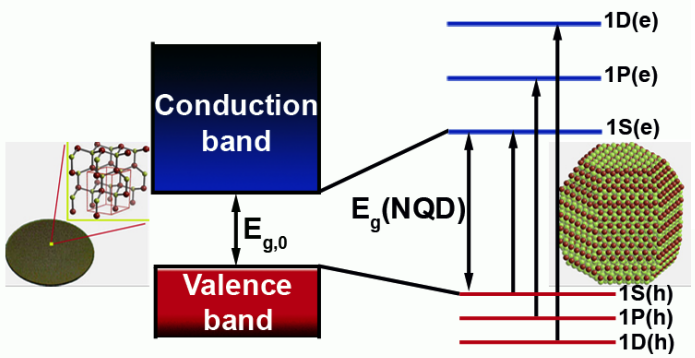


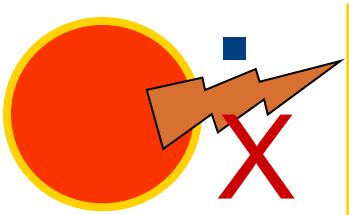
"Quantum box" model:

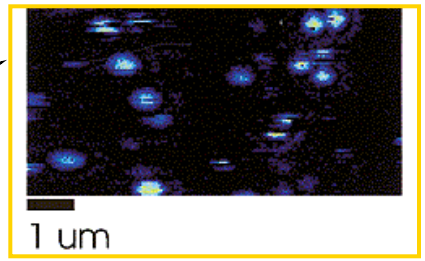
$$E_g(\text{NQD}) \approx E_{g,0} + \frac{\hbar^2\pi^2}{2m_{eh}R^2}$$

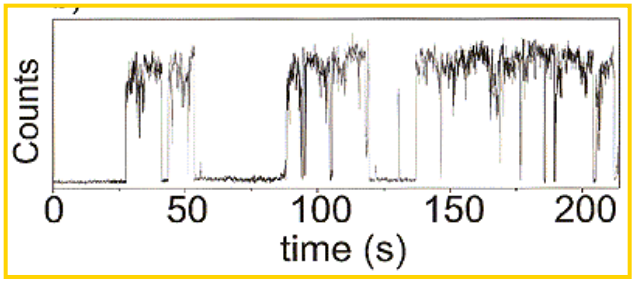
- Potential applications
  - ✓ Biological optical tags / reporters
  - ✓ Gen-III photovoltaics
  - ✓ Color-tunable lasing
  - ✓ Single-photon source
  - ✓ Light-emitting diodes (solid-state lighting)

The Darker Side of NQDs: Blinking, Non-radiative Auger recombination, Ligand Dependency

- Quantum dot fluorescence intermittency

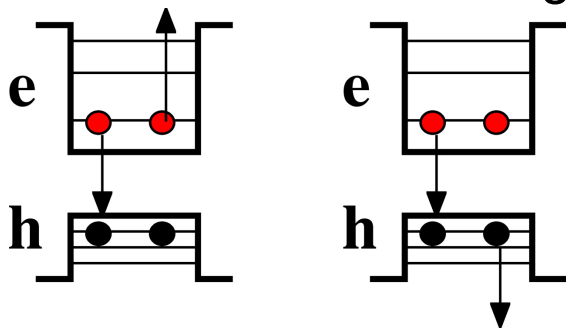






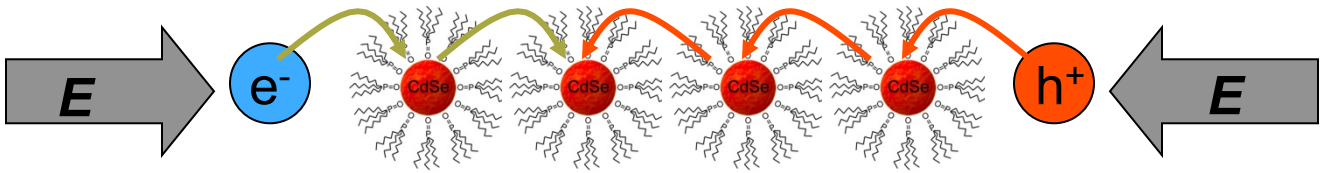
- Nirmal et al. *Nature* (1996) *8*02
- Efros *Nature Mater.* (2008) 612

- Efficient non-radiative Auger



- 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)*

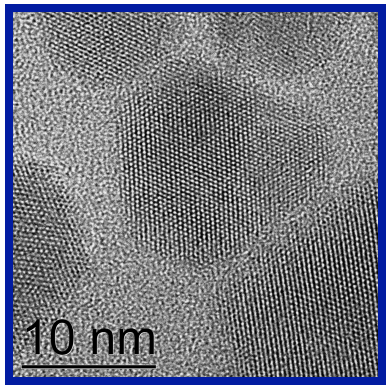
- Optical properties depend on passivating, organic ligand layer
  - Damage to ligands diminishes NQD performance
  - Ligands can impede charge transport / injection

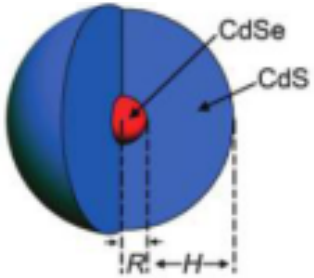


“Giant” Nanocrystal Quantum Dots (g-NQDs): New Class of NQD

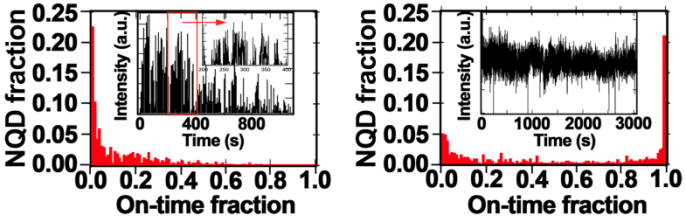
Unique photophysical properties

- Suppressed blinking
- Suppressed Auger (long-lived biexcitons; efficient multiexciton emission
- Non-photobleaching
- Ligand-independent emission
- Large Stokes shift (absorption-emission separation)

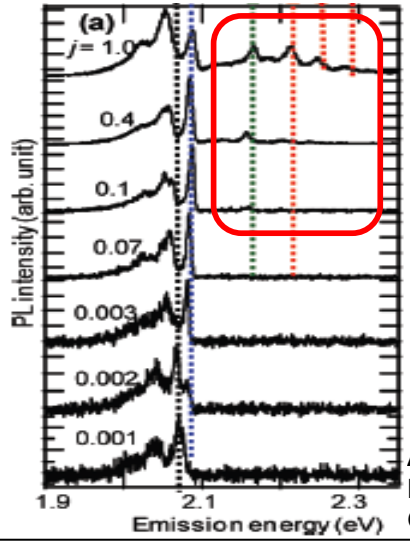




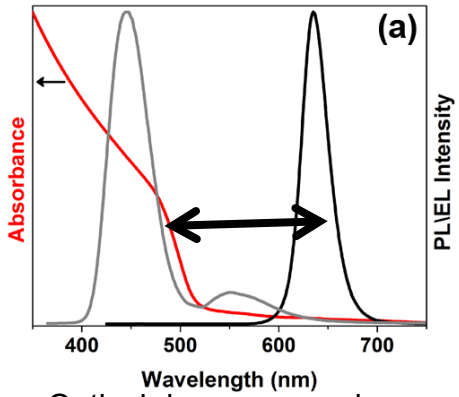
- “Giant”: >10 monolayers of shell



Blinking:
Chen *et al. J. Am. Chem. Soc.* 2008
Vela *et al. J. Biophotonics* 2010
Galland *et al. Nature* 2011
Ghosh *et al. J. Am. Chem. Soc.* 2012
Mahler *et al. Nat. Mater.* 2008 (<10 ML)



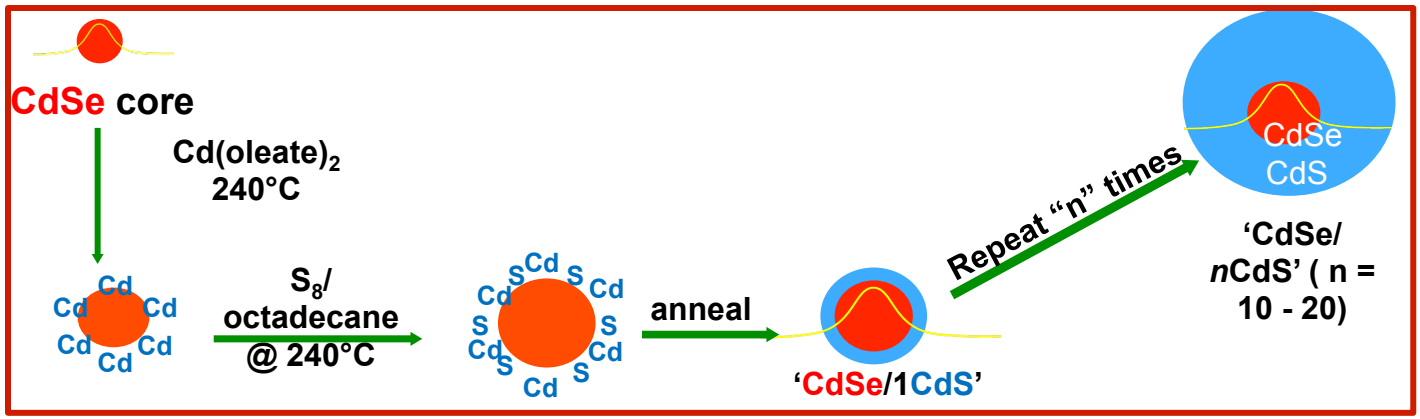
Auger:
Htoon et al. *Nano Lett.* 2009
García-Santamaría et al., *Nano Lett.* 2009



Optical down-conversion:
Kundu *et al. Nano Lett.* In Rev. 2012

Ultra thick-shell synthesis requires controlled approach to growth

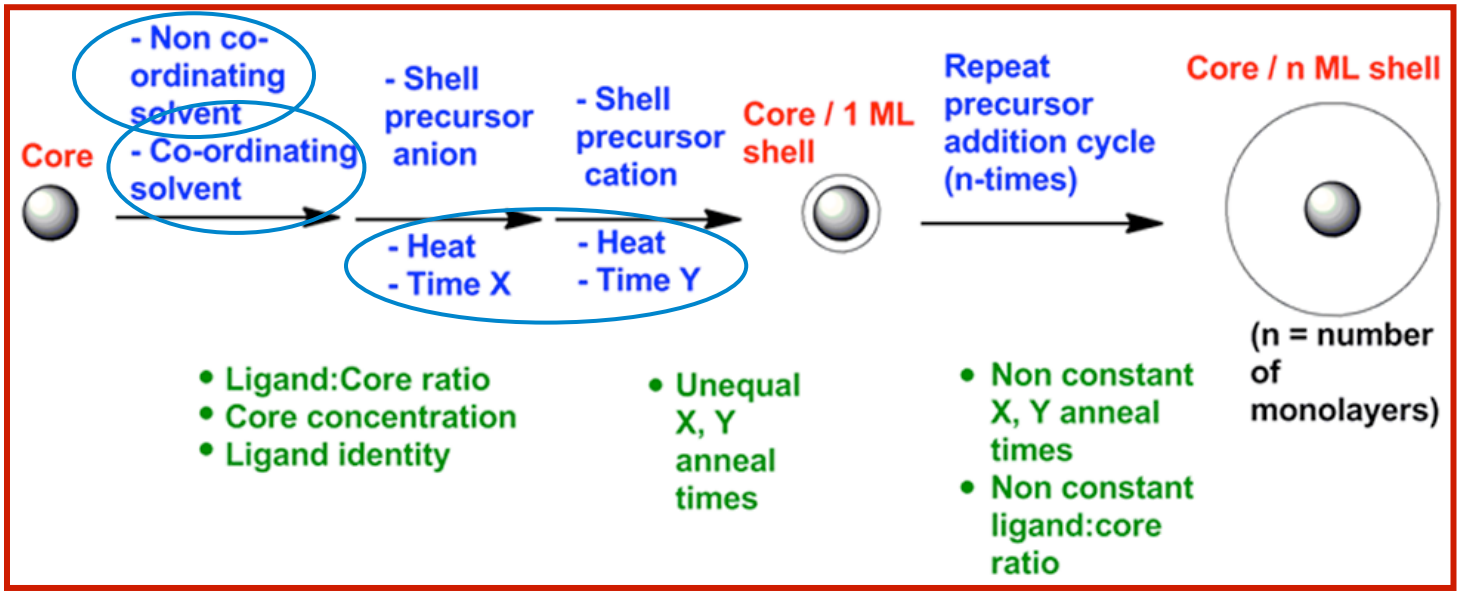
- Successive Ionic Layer Adsorption & Reaction (SILAR)



• Nevertheless, within-batch particle-size and shape variability does not equal that achieved for thin-shell systems or core-only NQDs

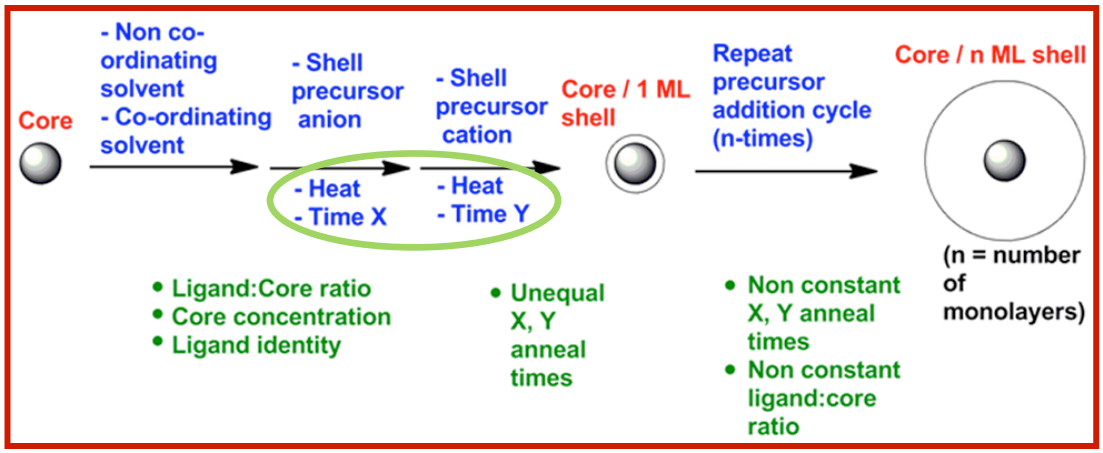
• Batch-to-batch reproducibility in structural and photophysical properties not ideal

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



- Correlate process conditions with g-NQD properties
  - Particle shape
  - Crystal structure
  - Photophysical properties/performance (QYs, blinking, lifetimes)

Conventional SILAR uses short "anneal" times: Is this adequate for thick-shell growth?

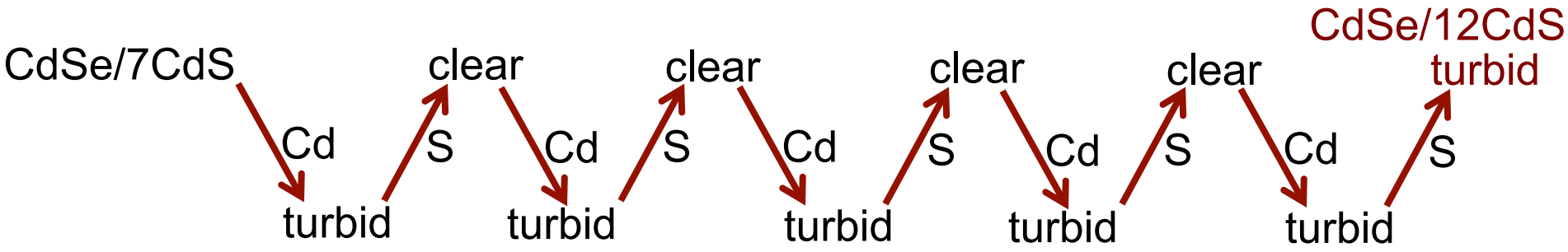


Anneal times	Quantum Yields in Emission (%)		
	At 5 MLs	At 11 MLs	At 15 MLs
Post S: 10 min Post Cd: 10 min	~20	~10	~5
Post S: 10 min Post Cd: 3 h	>45	~40	~15
Post S: 3 h Post Cd: 10 min	~35	~10	~6
Post S: 1 h Post Cd: 3 h	~70	~25	~20
Post S: 3 h Post Cd: 1 h	~25	~10	~5

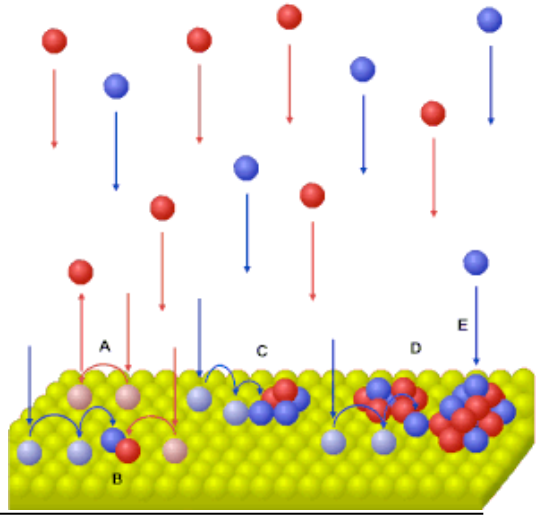
- Influence of reaction time
  - Conventional: 10 min per ionic layer addition
  - Thick shells add, but PL QY suffers
  - >5 monolayer shell thickness: longer anneal times improve QYs
  - Asymmetric distribution of anneal times: optimal
  - Longer anneal times post Cd addition: optimal

Peculiarity of thick-shell growth: NQD aggregation

- "Solubility cycling" occurs during thick-shell growth
  - Possible source of within- and across-batch variability

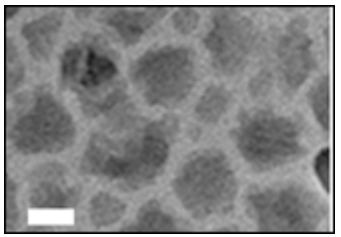


- Why do we care about reaction homogeneity?
  - May influences processes that govern Cd and S adatom addition
  - Solution-NQD interface processes of adsorption, desorption, and surface migration for minimization of defects
  - Ligand-mediated processes "interrupted" in NQD-aggregated state



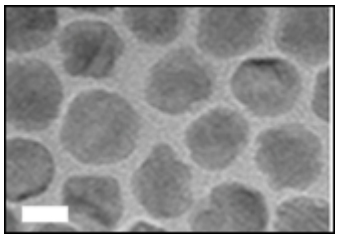
Impact of non-coordinating solvents on solubility cycling

- Standard octadecene solvent: turbidity onset at shell monolayer 7



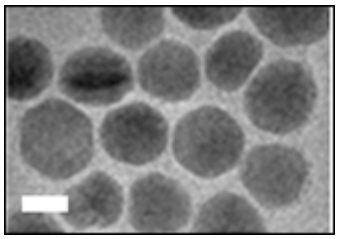
PL QY → Low

- Replacing octadecene with octadecane delays turbidity onset to ~shell monolayer 11



PL QY → Low

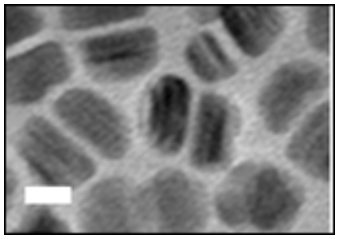
- Limited dilution with octadecane at later stages of growth improves size/shape uniformity



PL QY → Moderate to high

- Octadecane, limited dilution, and longer growth times afford good particle control and improved QYs

- Extreme dilution eliminates aggregation, but shape, crystal structure and QY suffer

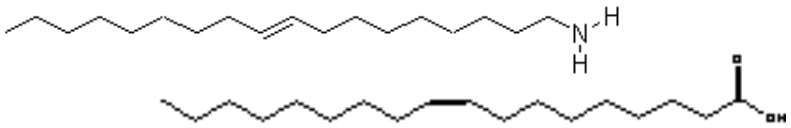


PL QY → Lowest

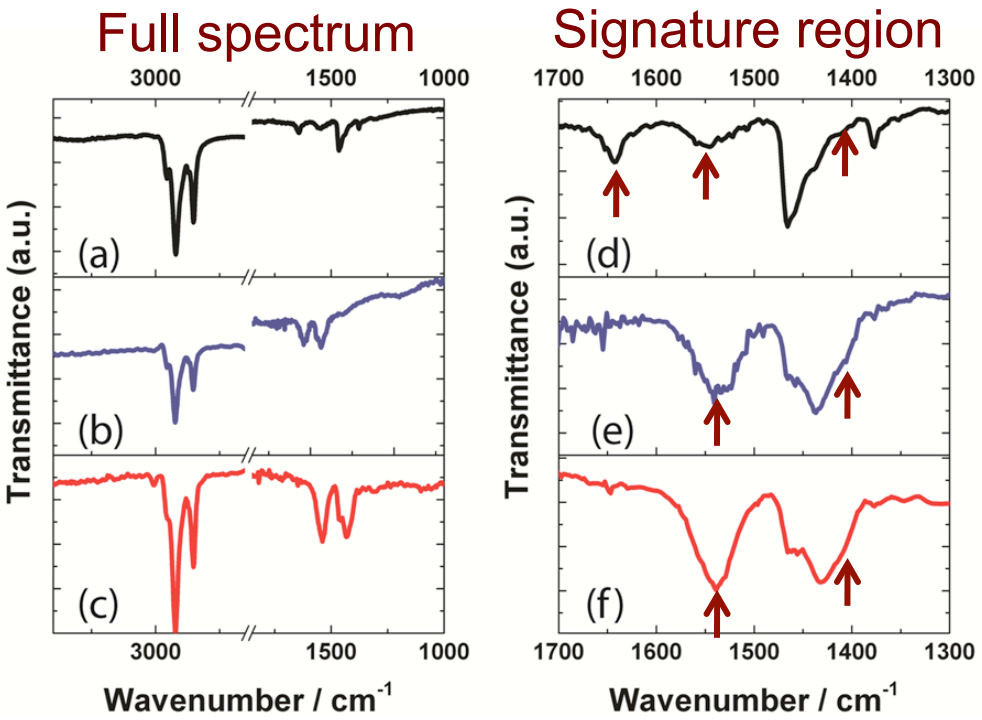
▪ Ghosh et al. In Revision *J. Am. Chem. Soc.* 2012

Impact of coordinating ligands on shell addition process and resulting NQD properties

- Cadmium-binding ligands: oleylamine and oleic acid
  - Amine can act as ligand or base
  - Amine present in excess throughout reaction
  - Oleic acid introduced with each Cd monolayer (Cd: OA = 1:4 or 1:10)



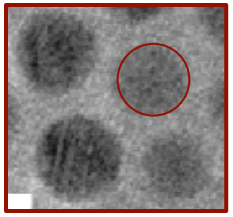
- FT-IR used to monitor ligand surface coverage
  - Lesser Cd:OA – amine dominates
  - Higher Cd:OA – oleate dominates
  - Oleylamine replaced with dioctylamine – oleate dominates



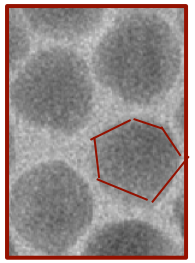
- **($\delta(NH_2)$ bending mode at ~1635 cm^{-1}**
- **$\nu_{as}(COO^-)$ & $\nu_s(COO^-)$ stretching modes: 1555 & 1408 cm^{-1}**

Impact of coordinating ligands on shell addition process and resulting NQD properties

- 1° amine-terminated g-NQDs are less faceted than oleate-terminated (~spherical vs. ~hexagonal)
  - QYs similar (mod-high)
  - Aggregation similar
  - Wurtzite dominates XRDs

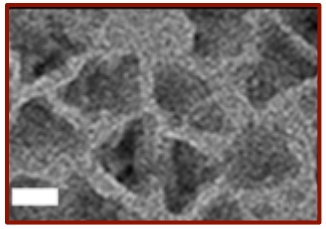


Amine-term.



Oleate-term.

- 2° amine reaction distinct
  - No aggregation/turbidity
  - Octahedral shape
  - No PL
  - Oleate-terminated; amine as base only



PL QY → None

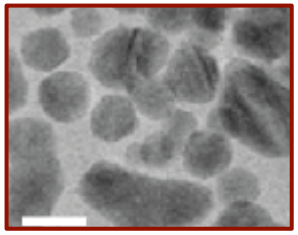
- No-amine reaction distinct
  - Early-onset aggregation (3rd monolayer)
  - Early-onset hexagonal faceting

} Correlated

Impact of reaction stoichiometry

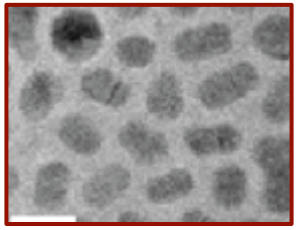
- Non-stoichiometric (excess) shell precursors (+1% and +10%)
  - Attempt to better support the dynamic equilibrium of adatom addition, re-dissolution and rearrangement
  - Aggregation reduces
  - But QYs decline
  - And shape non-spherical/irregular
- Constant/extreme excess of S precursor
  - All S added at start of reaction
  - Less & constant aggregation (non-cycling)
  - Poor QYs
  - Rods are kinetic shape by enhancing S precursor availability
  - Zinc-blende dominates
- 1% excess shell precursors plus excess oleic acid
  - Near-optimal properties: uniform hexagonal shapes and high QYs (50%)
  - Less-severe aggregation still occurs at thick shells

+ 10% Cd/S

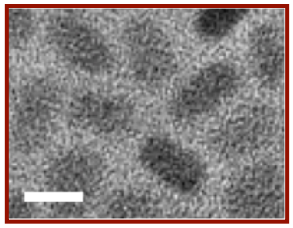


Very low PL QY

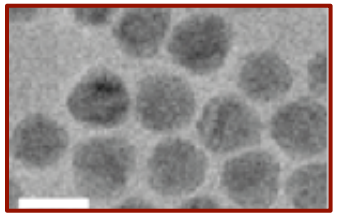
+ 1% Cd/S



Moderate PL QY



Non-SILAR S



Excess precursors and oleic acid

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What causes solubility cycling during thick-shell growth?

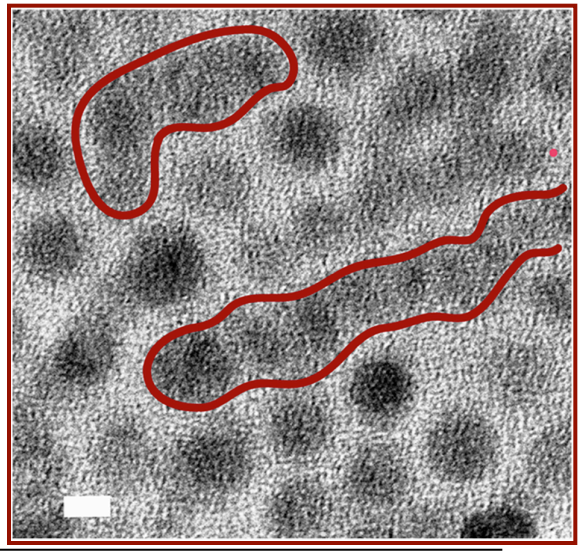
- Hypothesis 1: Surface-localized charges induce NQD-NQD aggregation
  - Not dipole-mediated, so independent of crystal structure
  - Evidence from literature: Oriented attachment observed for both hexagonal and cubic systems
  - However, in our case, we do not observe aggregation for (1) predominately zinc-blende core/shell g-NQDs nor for (2) wurtzite g-NQDs that adopt octahedral shape
- Hypothesis 2: Dipole-mediated interactions induce NQD-NQD aggregation
  - Anisotropic wurtzite crystal structure
  - As hexagonal faceting and NQD size increase, dipole moment becomes larger
  - Why cycling?
    - Perhaps S-dominated system experiences surface relaxation/reconstruction that decreases dipole strength
    - Vs. Cd-dominated system, which is well-supported by Cd-binding ligands, so NQD can adopt more perfectly wurtzite structure

What causes solubility cycling during thick-shell growth?

- ~~Hypothesis 1: Surface-localized charges induce NQD-NQD aggregation~~

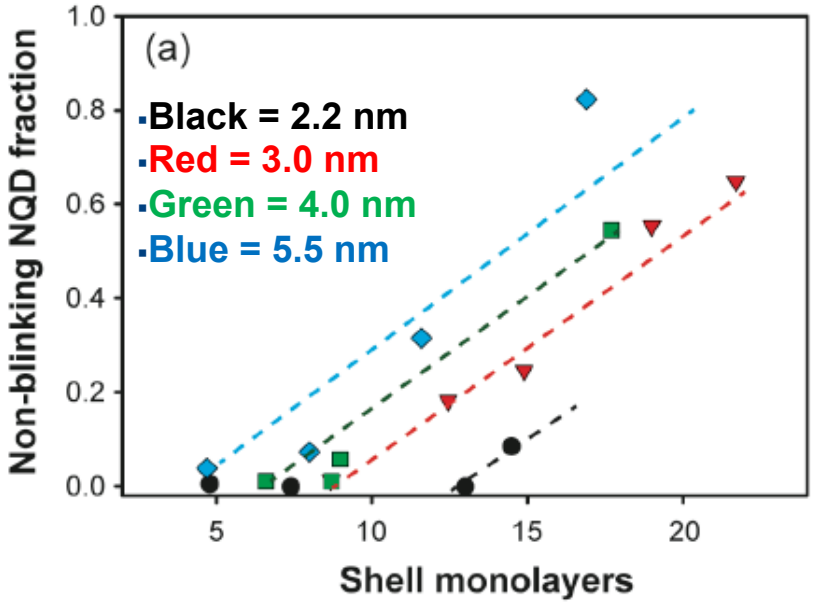
- Hypothesis 2: Dipole-mediated interactions induce NQD-NQD aggregation

- g-NQD-g-NQD associations can become "permanent"



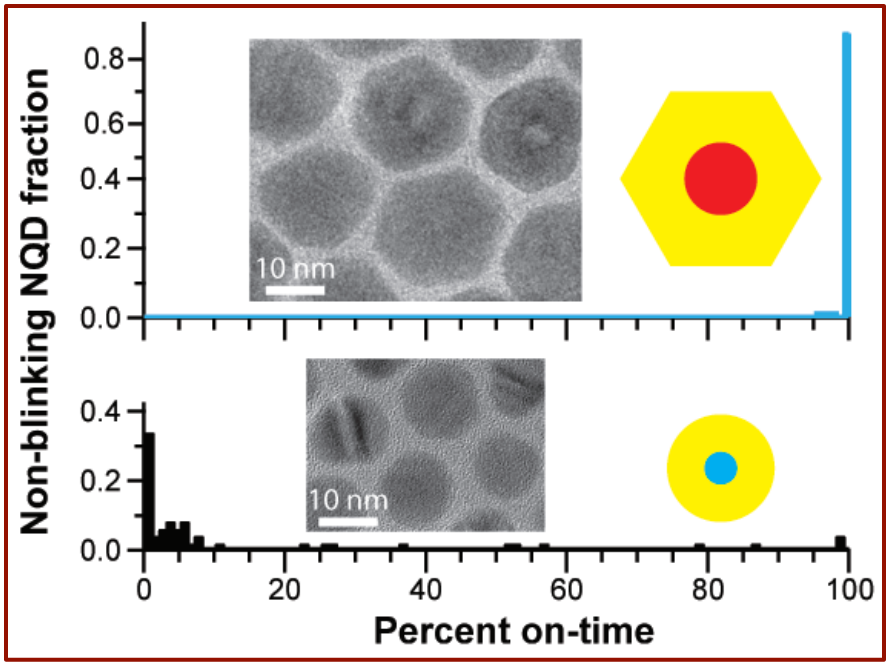
Beyond shell thickness: Effect of core size

- Here, we study blinking for core sizes from 2.2 to 5.5 nm



- 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

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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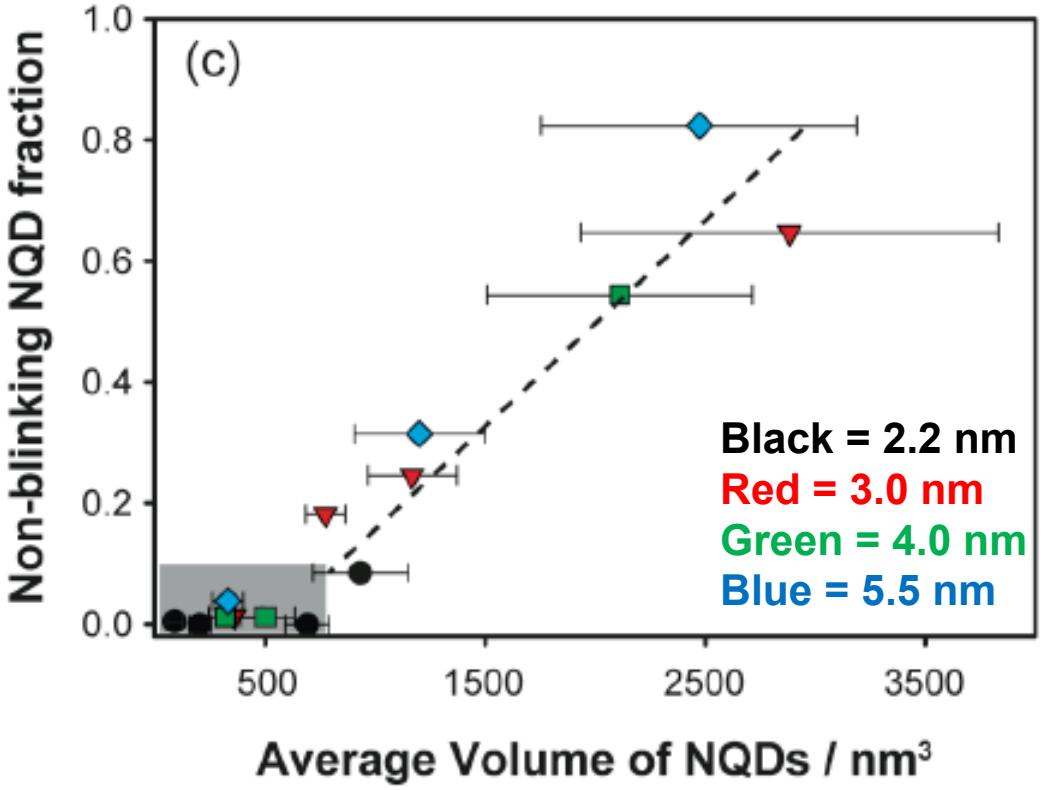
NNSA

Is non-blinking behavior a volume effect?



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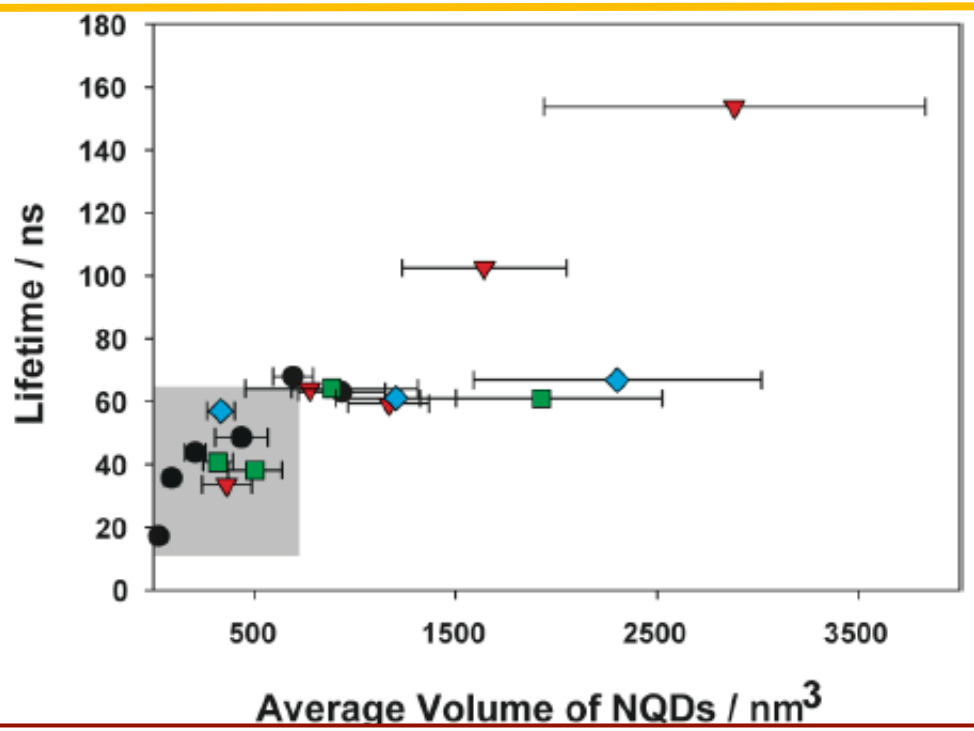
- Non-blinking fraction trends explicitly with NQD volume
- "Volume threshold" at ~750 nm^3
  - By either a combination of a small core and thick shell or a large core and thinner shell

Volume threshold for “non-blinking” radiative lifetime



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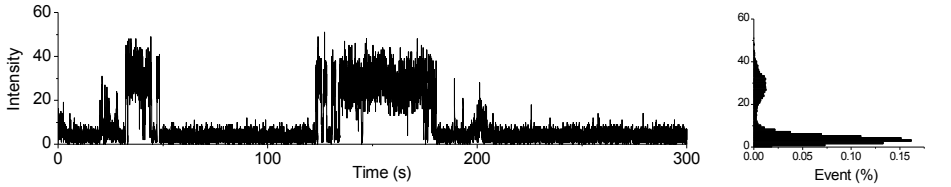
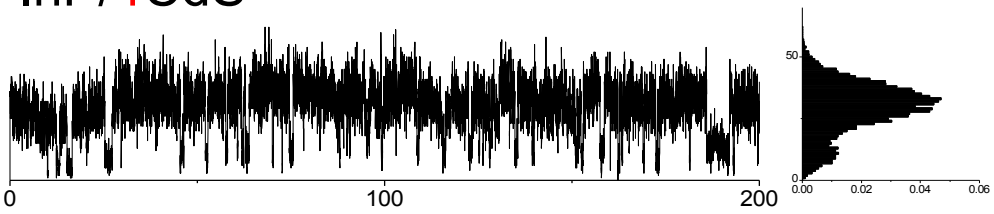
- Below ~750 nm^3, emission lifetimes range from ~20-50 ns
- Above ~750 nm^3, emission lifetimes are ~65 ns or greater
- Longer lifetimes are expected due to CdSe/CdS’s quasi-type II electronic structure, which leads to partial spatial separation of the carriers
- PL lifetimes of at least 65 ns are required for onset of non-blinking behavior

Materials-by-Design: Extending g-NQD approach to new system – InP/CdS

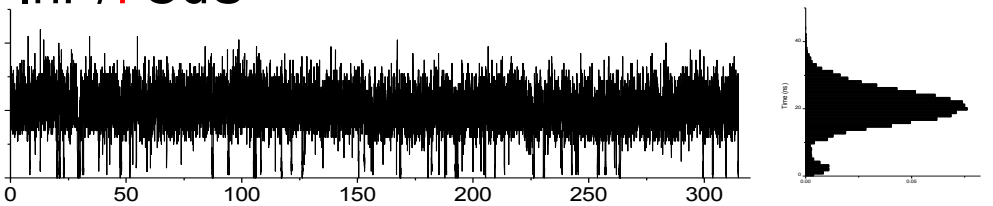
- InP/1CdS



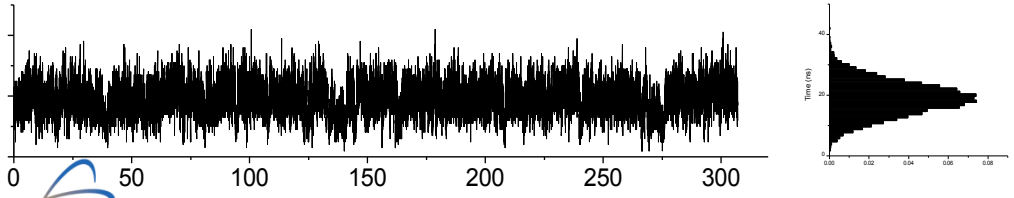
- InP/4CdS

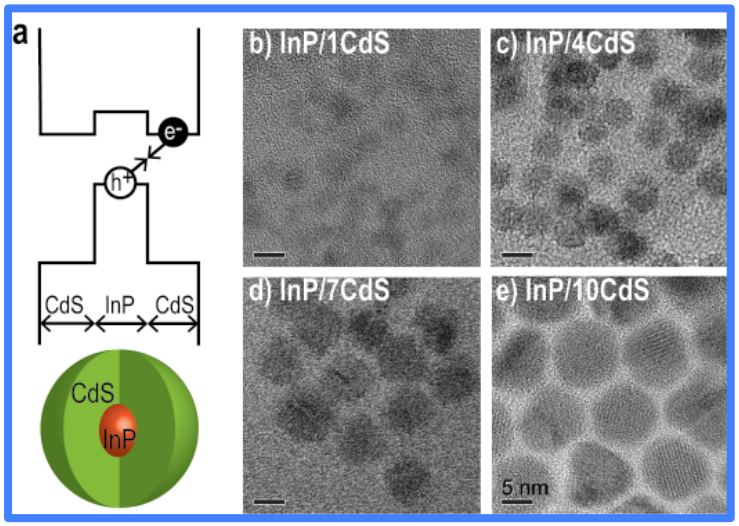


- InP/7CdS



- InP/10CdS

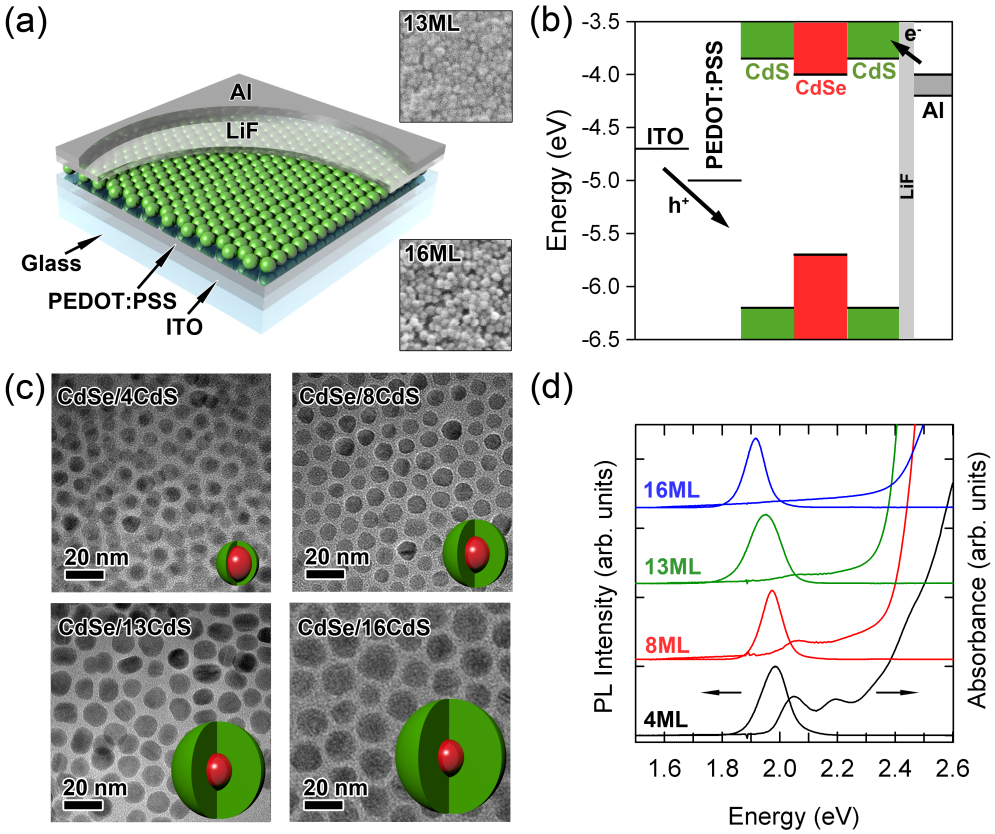




- Suppressed blinking
- Supporessed photobleaching
- Long biexciton lifetimes associated with Auger suppression

A little on “assembling” g-NQDs for useful purposes… Proof-of-concept direct-charge-injection device

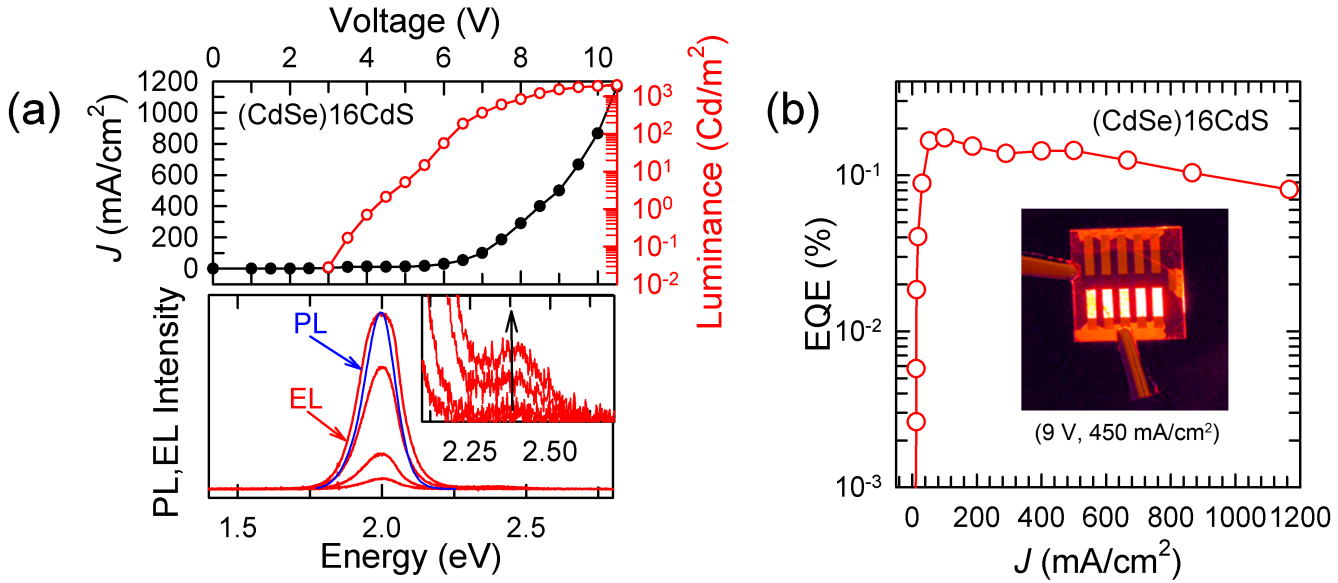
- Simple ‘test-bed’ device architecture



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

Thickest-shell g-NQDs affords best-performing device

- Comparable to more sophisticated literature “all-inorganic” NQD LED
- Two-orders-of-magnitude higher EQE vs. literature for similar device structure

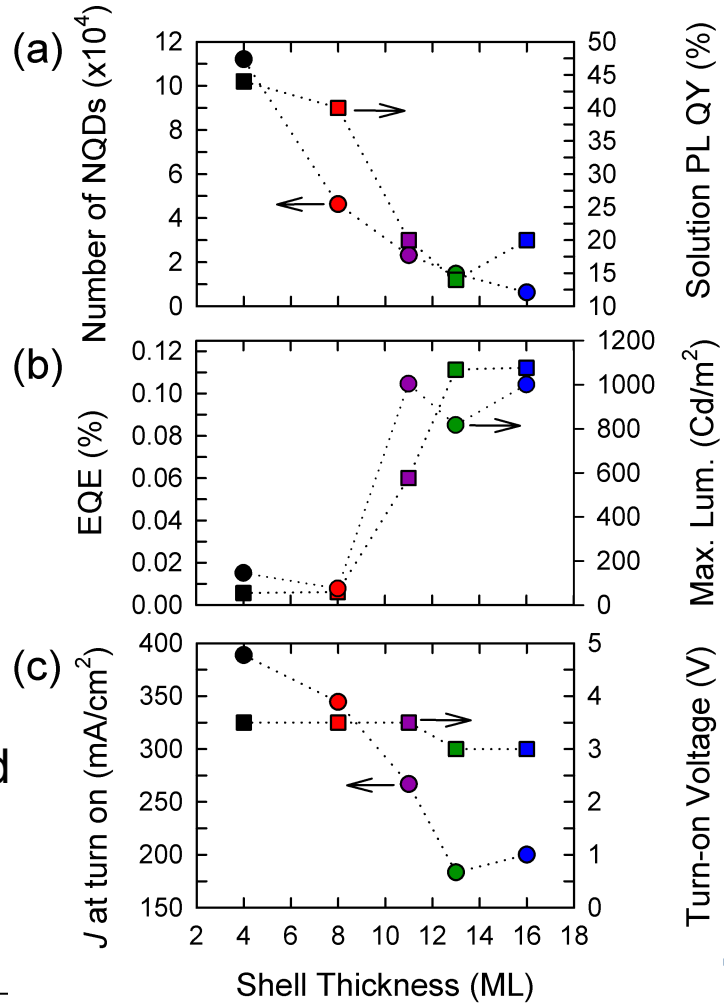


- EQE 0.16%
- Maximum luminance ~2000 cd/m^2
- Low EL turn-on voltage 3.0 V

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

NQD LED performance as a function of shell thickness

- g-NQD solid-state performance surpasses its solution-phase behavior

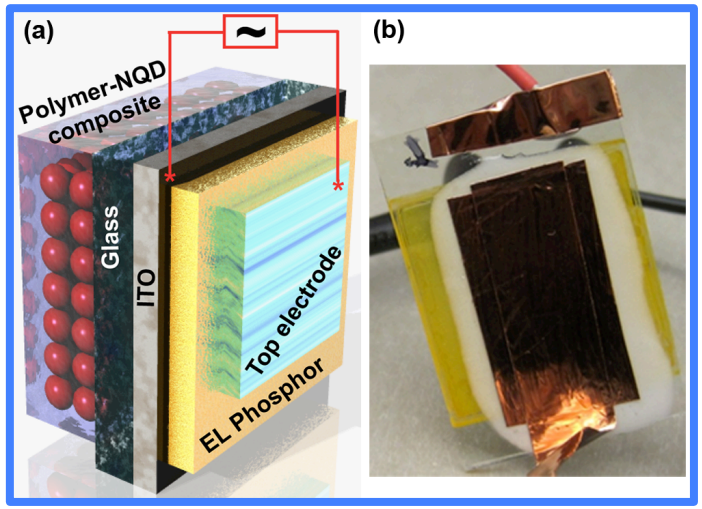


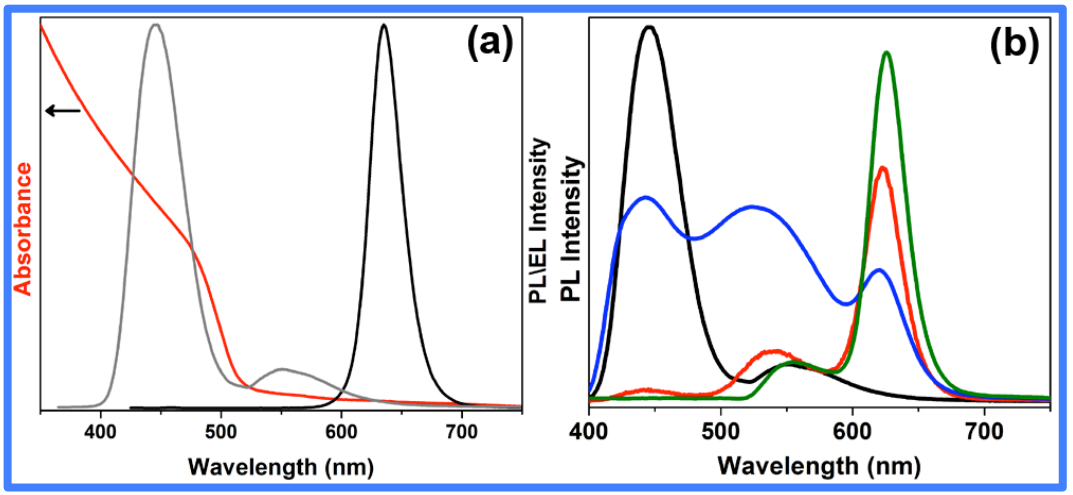
- Ligand effects minimized
- Auger suppressed
- Energy transfer suppressed

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

Proof-of-Concept Demonstration of g-NQDs as Color-Converting Phosphors

- Simple ‘test-bed’ device architecture



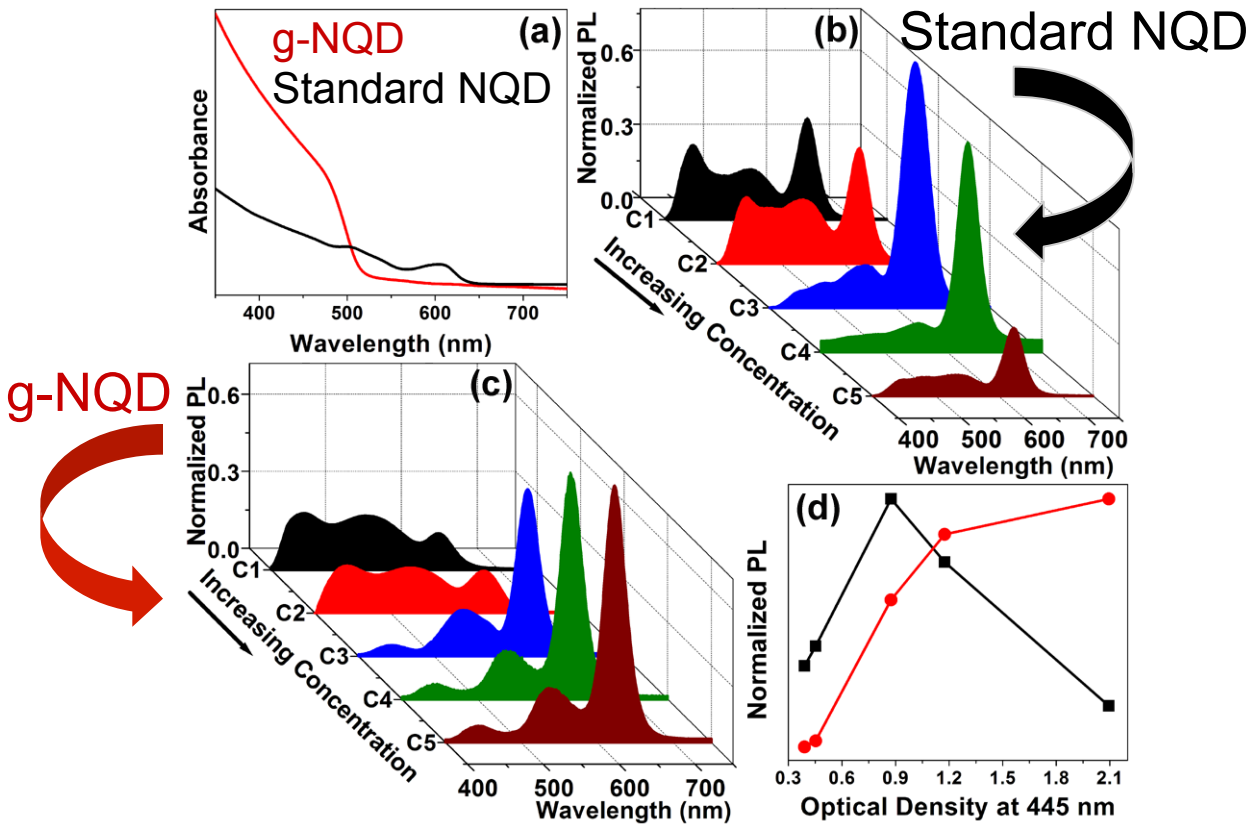


- green trace: 84% color purity (including green EL)
- 22% down-conversion efficiency

- Kundu *et al. Nano Lett.* In Revision 2012

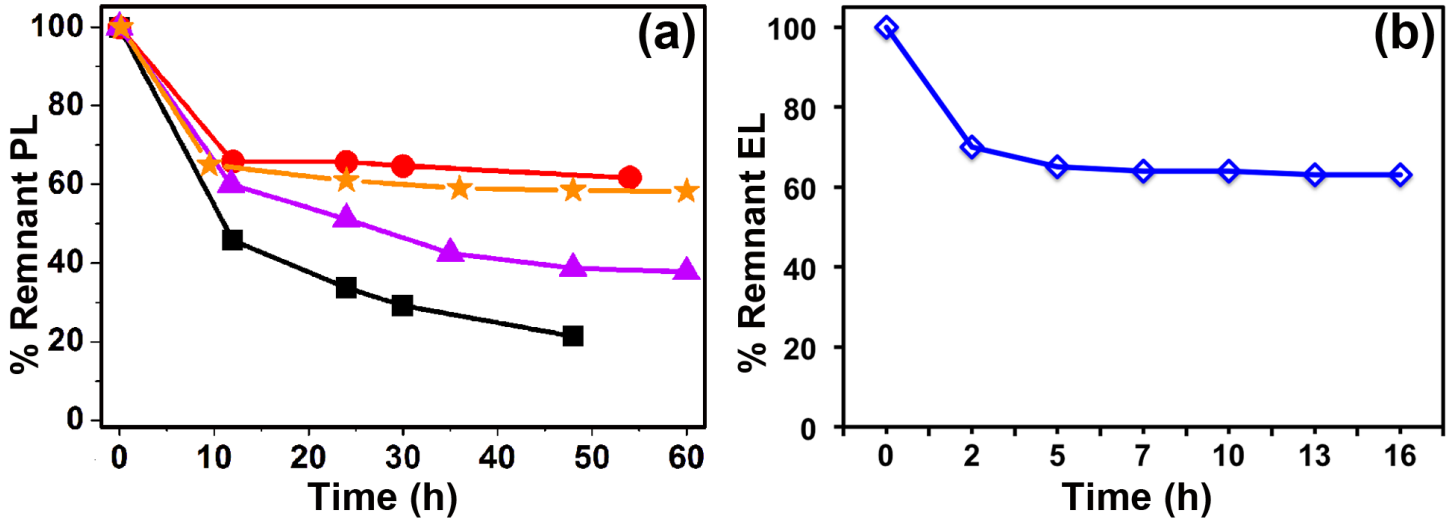
Key g-NQD attribute: Minimal self-reabsorption

- g-NQDs can be packed at high densities without signal loss



Key g-NQD attribute: Stability

- Temporal device stability: percent remnant PL intensity as a function of continuous biasing time



g-NQDs (16 shell)
g-NQDs (11 shell)
Standard core/shell NQD
Core-only NQD

EL phosphor

Conclusions

- Established new understanding of the constraining synthetic parameters for optimal monolayer-by-monolayer shell growth out to ~20 shell monolayers
  - Subtle differences in reaction time, solvent, ligand, and precursor:NQD ratio can dramatically affect morphology, crystal structure and optical properties
  - Optimal: Longer/asymetric reaction times, octadecane solvent, moderate dilution, small excess of precursor and ligand, primary amine (not secondary amine), full SILAR
- Structure:function correlated
- More purely wurtzite and hexagonally faceted g-NQDs exhibit improved blinking suppression and higher QYs, therefore, resulting "solubility cycling" may need to be tolerated
- A volume threshold of 750 nm^3 was observed for non-blinking behavior in the CdSe/CdS system
- A minimum PL lifetime (~65 ns) was also observed for non-blinking behavior, likely correlated with quasi-type II carrier separation
- g-NQDs can be assembled into light-emitting devices and demonstrate improved performance as a function of shell thickness

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Current LANL CINT g-NQD team

- Han Htoon: TSM, Spectroscopy
- Yagnaseni Ghosh: Chem PD
- Allison Dennis: Chem PD
- Janardan Kundu: Device fab/testing PD
- Bhola Nath Pal: Device fab/testing PD
- Ben Mangun: Spectroscopy PD
- Andrei Piryatinski: TSM, Theory

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NIGMS

LDRD

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Abstract

Due to their characteristic bright and stable photoluminescence, semiconductor nanocrystal quantum dots (NQDs) have attracted much interest as efficient light emitters for applications from single-particle tracking to solid-state lighting. Despite their numerous enabling traits, however, NQD optical properties are frustratingly sensitive to their chemical environment, exhibit fluorescence intermittency ("blinking"), and are susceptible to Auger recombination, an efficient nonradiative decay process. Previously, we showed for the first time that colloidal CdSe/CdS core/shell nanocrystal quantum dots (NQDs) comprising ultra-thick shells (number of shell monolayers, n, >10) grown by protracted successive ionic layer adsorption and reaction (SILAR) leads to remarkable photostability and significantly suppressed blinking behavior as a function of increasing shell thickness.[1,2] We have also shown that these so-called "giant" NQDs (g-NQDs) afford nearly complete suppression of non-radiative Auger recombination, revealed in our studies as long biexciton lifetimes and efficient multiexciton emission.[3,4] The unique behavior of this core/shell system prompted us to assess correlations between specific physicochemical properties—*beyond shell thickness*—and functionality. Here, we demonstrate the ability of particle shape/faceting, crystalline phase, and core size to determine ensemble and single-particle optical properties (quantum yield/brightness, blinking, radiative lifetimes). Significantly, we show how reaction process parameters (surface-stabilizing ligands, ligand:NQD ratio, choice of "inert" solvent, and modifications to the SILAR method itself) can be tuned to modify these function-dictating NQD physical properties, ultimately leading to an optimized synthetic approach that results in the complete suppression of blinking. We find that the resulting "guiding principles" can be applied to other NQD compositions, allowing us to achieve non-blinking behavior in the near-infrared. Lastly, in addition to realizing novel light-emission properties by refining nanoscale architectures at the single-NQD level, we also investigate collective properties by assembling our core/shell NQDs into larger scale arrays.

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- Garcia-Santamaria, F. *et al. Nano Lett.*, **2009**, 9, 3482.
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