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Title: Bandgap Engineering of InP QDs Through Shell Thickness and Composition

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Bandgap engineering of InP nanocrystal quantum dots through shell thickness and composition

Fields as diverse as biological imaging and telecommunications utilize the unique photophysical and electronic properties of nanocrystal quantum dots (NQDs). The development of new NQD compositions promises material properties optimized for specific applications, while addressing material toxicity. Indium phosphide (InP) offers a “green” alternative to the traditional cadmium-based NQDs, but suffers from extreme susceptibility to oxidation. Coating InP cores with more stable shell materials significantly improves nanocrystal resistance to oxidation and photostability. We have investigated several new InP-based core-shell compositions, correlating our results with theoretical predictions of their optical and electronic properties. Specifically, we can tailor the InP core-shell QDs to a type-I, quasi-type-II, or type-II bandgap structure with emission wavelengths ranging from 500-1300 nm depending on the shell material used (ZnS, ZnSe, CdS, or CdSe) and the thickness of the shell. Single molecule microscopy assessments of photobleaching and blinking are used to correlate NQD properties with shell thickness.

Bandgap Engineering of InP QDs Through Shell Thickness and Composition

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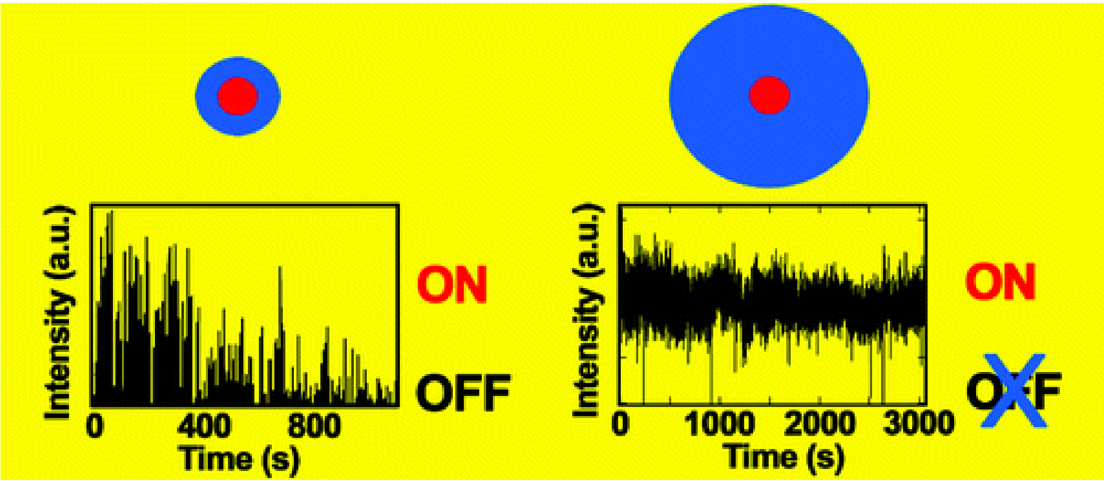
Previous Work

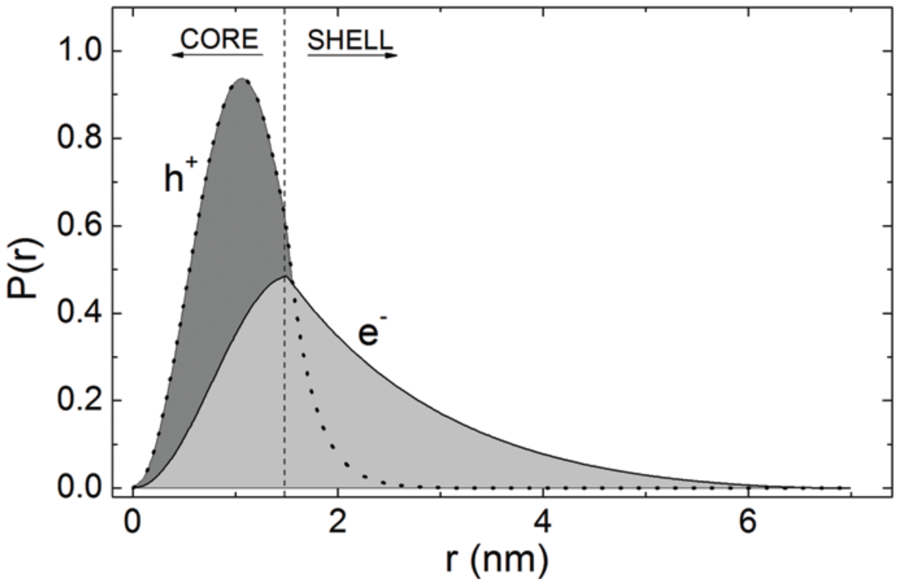
- **CdSe/CdS "giant" nanocrystal quantum dots (g-NQDs)**
  - Suppression (elimination) of blinking
  - Suppression of non-radiative Auger recombination
  - Improved chemical robustness



J. Am. Chem. Soc., **2008**, 130(15):5026-7; *Nano Lett.*, **2009**, 9(10): 3482-8; *J. Biophotonics*, **2010**, 3(10-11), 706-17; *Nano Lett.*, **2010**, 10(7):2401-7.

Why Study the Photophysics?

- **Unique material properties:**
  - Thick, protective shell
  - Large volume
  - Quasi-Type II electronic structure
    - Partial charge separation
  - Possible interfacial alloying

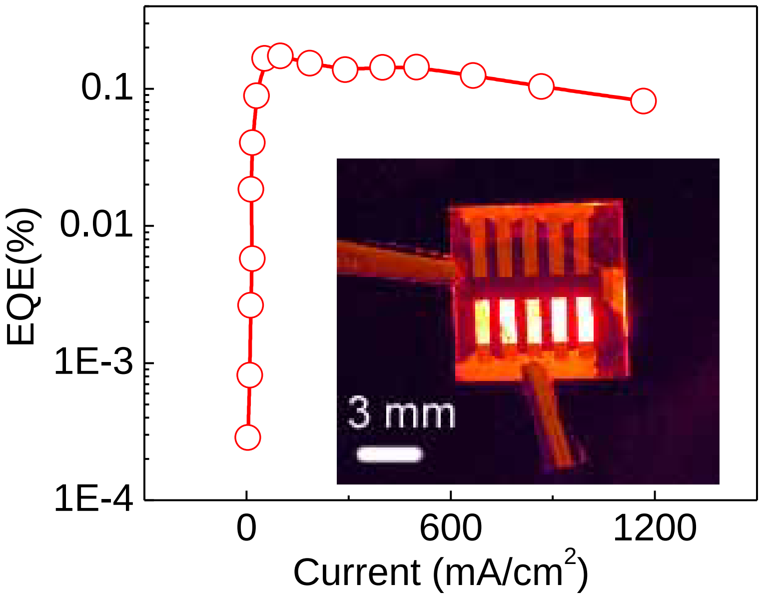


Spatial probability distribution of electron and hole in a CdSe/CdS g-NQD (core radius = 1.5 nm, shell = 5 nm thick).

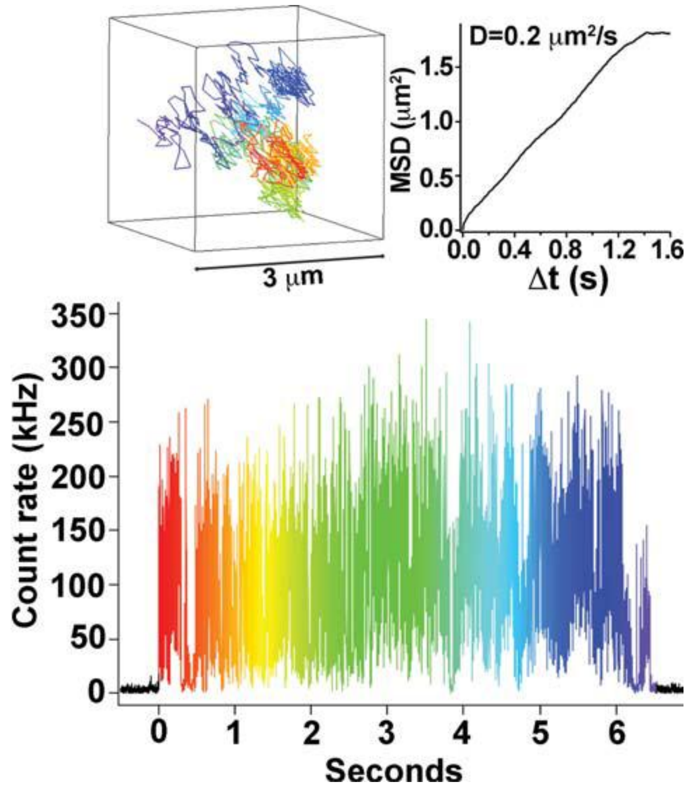
Nano Lett., **2009**, 9(10): 3482-8

Applications of g-NQDs

Solid State Lighting



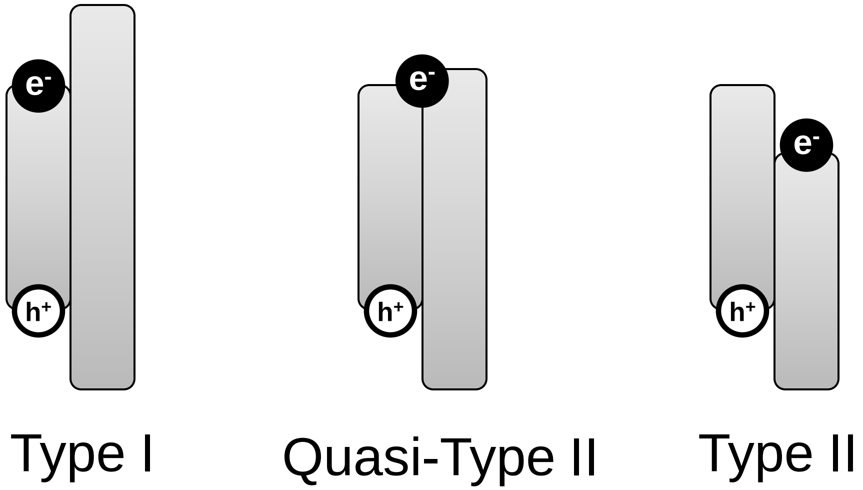
Single particle tracking



J. Biophotonics, **2010**, 3(10-11), 706-17

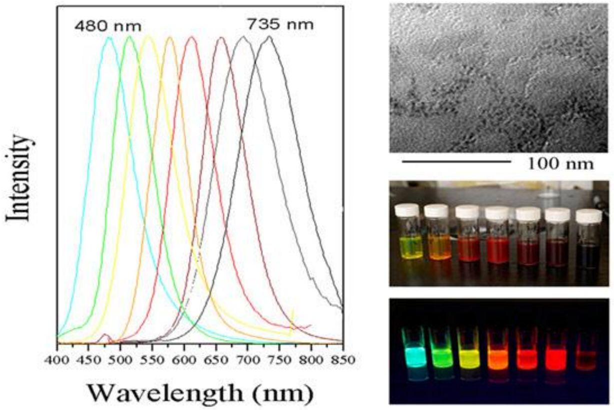
Developing Alternative gNQD Systems

- **Change core/shell composition**
  - Control of electronic structure
- **Investigate photophysical and structural properties**
  - Effect of bandgap alignment (electronic structure)
  - Volume effects
  - Interfacial (core/shell) effects
  - Effect of lattice strain
- **Resultant properties**
  - Tuning of PL emission?
  - Suppressed blinking?
  - Suppressed Auger?



InP Core

- Tunable from blue to NIR
- Multiple effective core preps
- InP as-synthesized typically non-emissive (without careful elimination of oxygen exposure)
- Bandgap emission emerges following surface etching or shelling



S. Xu, J. Ziegler, T. Nann, *J. Mater. Chem.* **2008**, *18*, 2653-2656;

Varying Shell Composition to Affect Core-Shell Properties

InP/ZnS

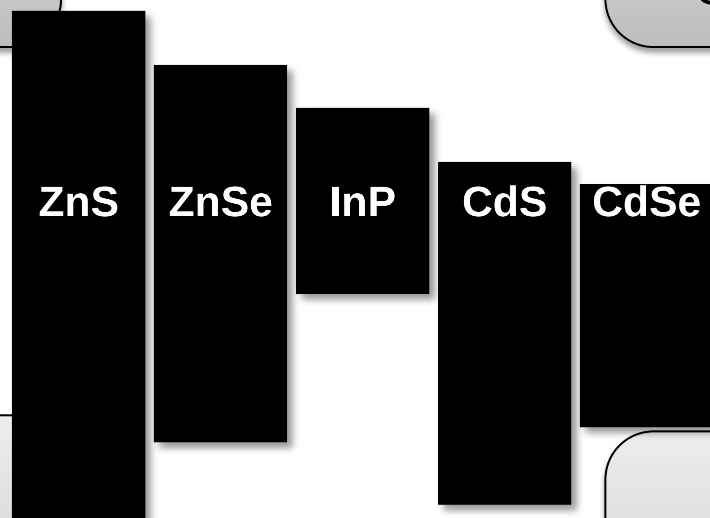
Large lattice mismatch

Type I bandgap structure

InP/CdS

Minimal lattice mismatch

Quasi-Type II to Type II



InP/ZnSe

Moderate lattice mismatch

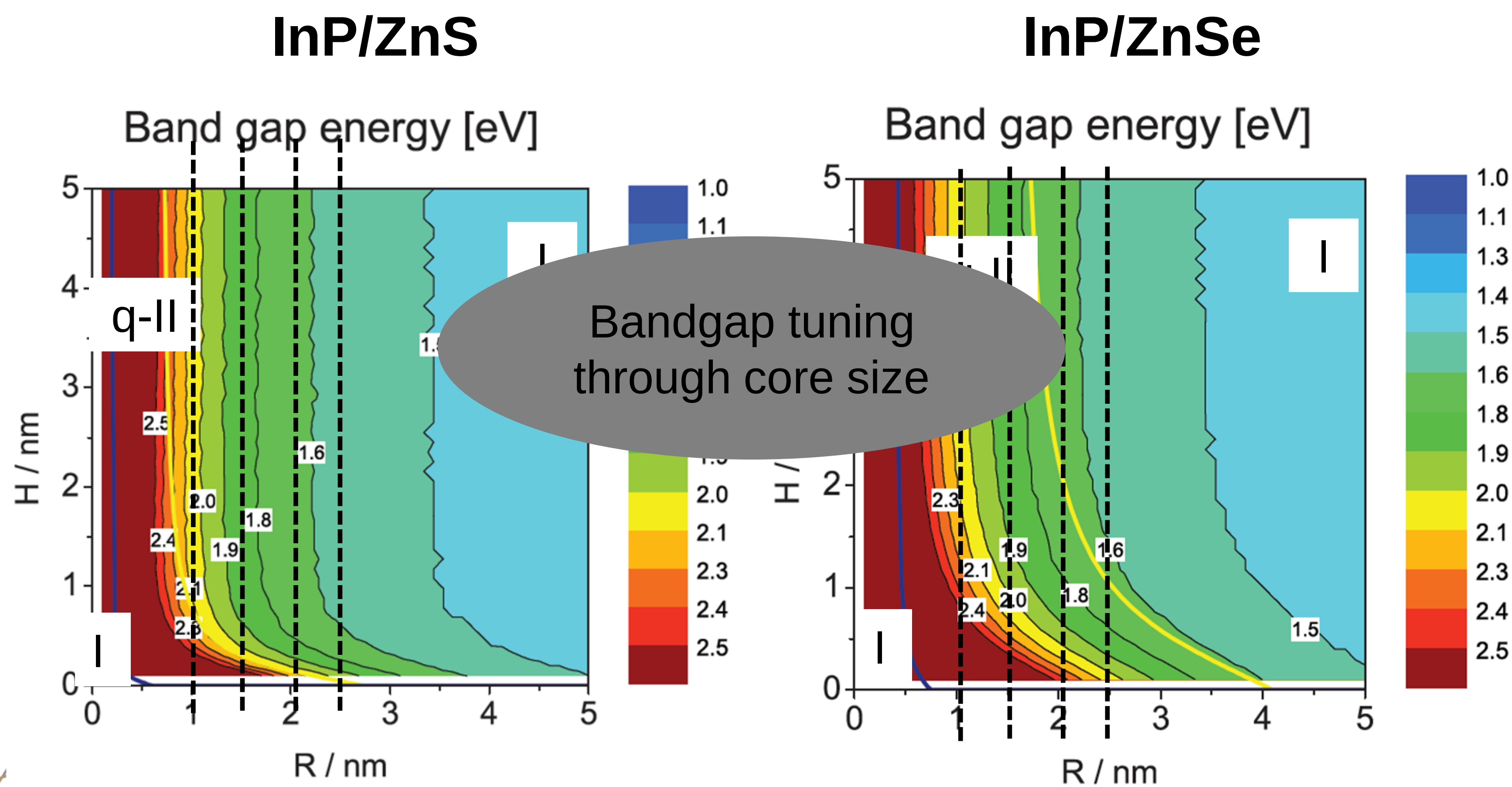
Quasi-Type II to Type I

InP/CdSe

Moderate lattice mismatch

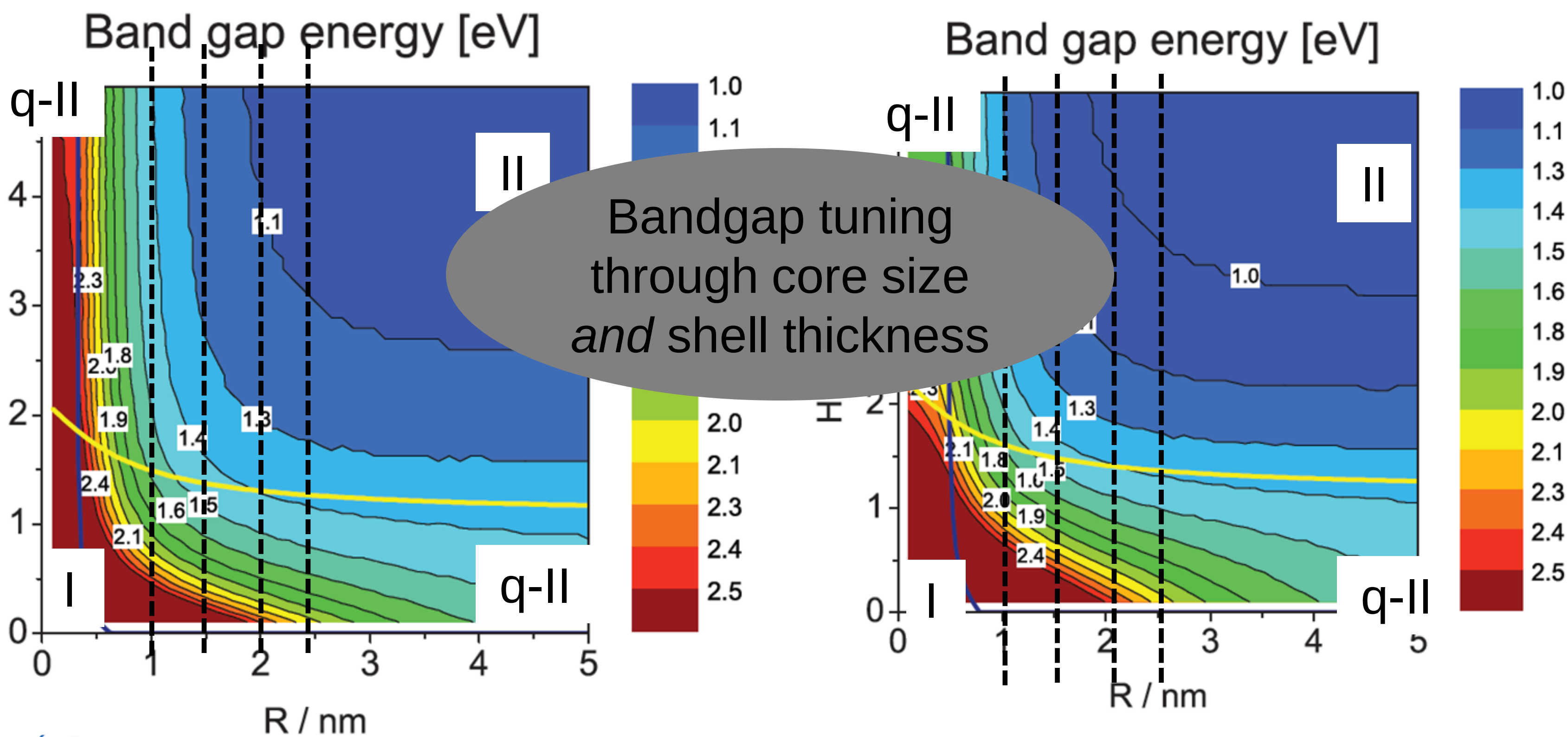
Quasi-Type II to Type II

Bandgap Energy Predictions: InP/ZnS and InP/ZnSe



Bandgap Energy Predictions: InP/CdS and InP/CdSe

InP/CdS | **InP/CdSe**

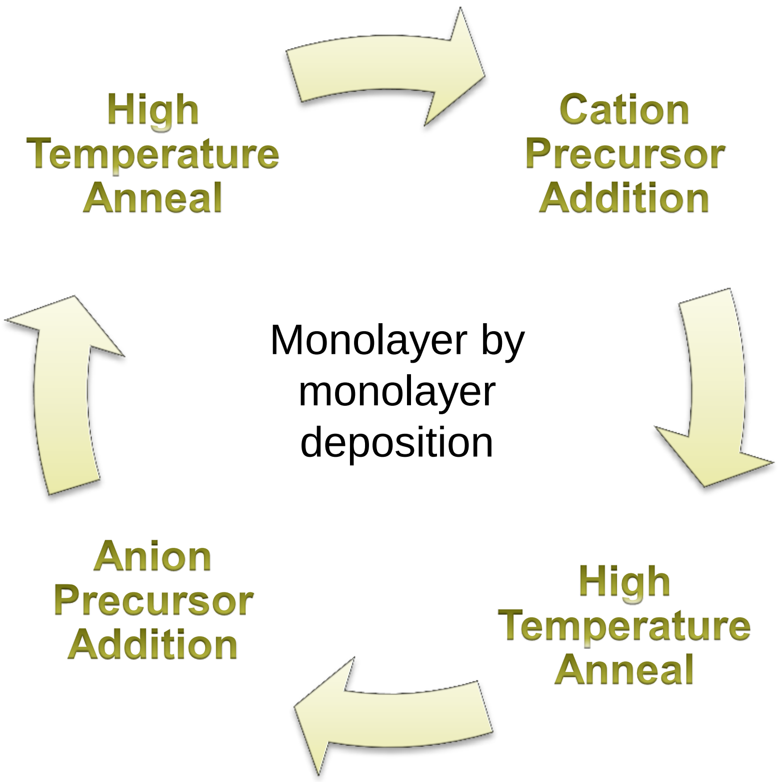


SILAR Shelling

Successive Ion Layer Adsorption and Reaction

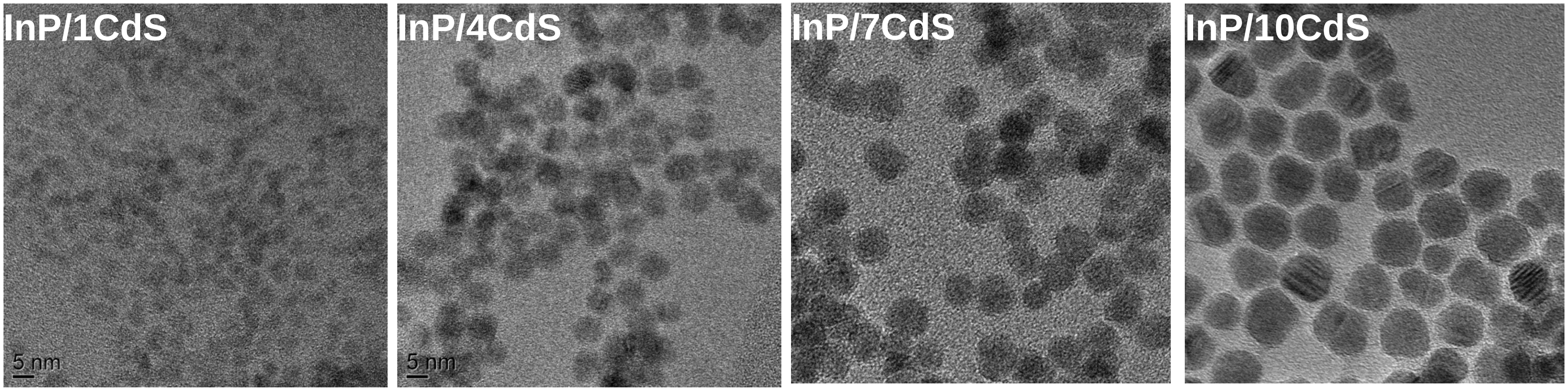
Variables:

- Ion precursors
  - Composition
  - Concentration
- Coordinating ligand
  - Composition
  - Concentration
- Annealing time
- Annealing temperature



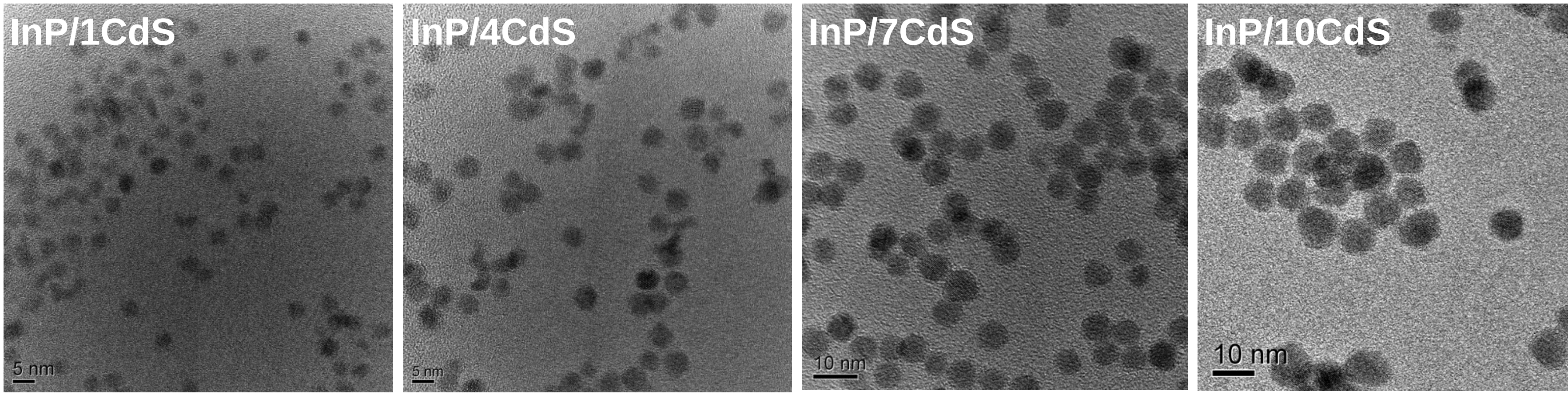
Li, et al., *J. Am. Chem. Soc.*, **2003**, *125* (41):12567–12575

Size Increase with Successive SILAR Depositions: InP/CdS



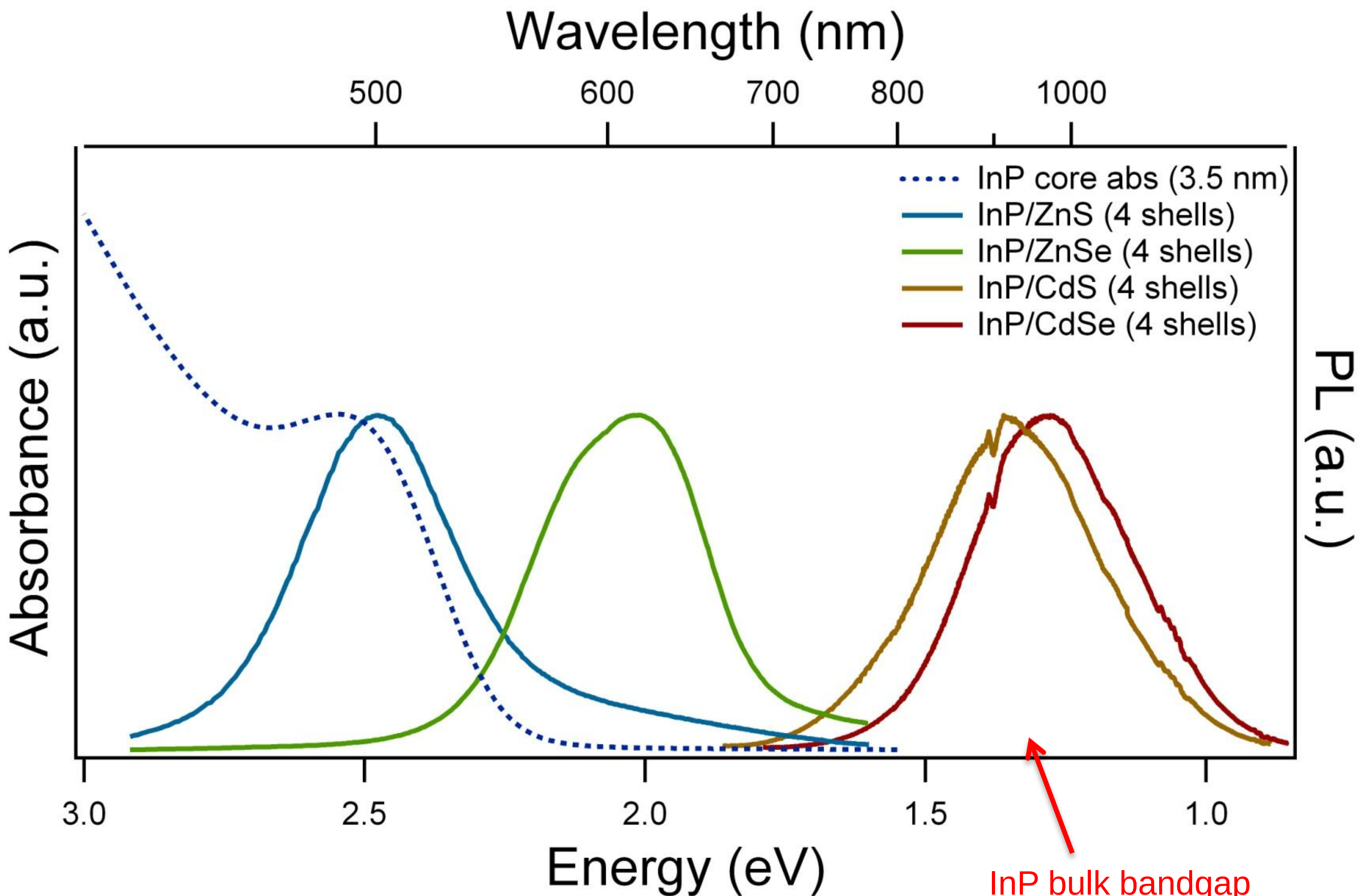
	Diameter (nm)	Shell thickness (nm)	Number of shell MLs
InP core	2.46		
InP/1CdS	3.28 ± 0.62 (19%)	1.21	1.2
InP/4CS	5.24 ± 0.56 (11%)	4.12	4.1
InP/7CdS	6.84 ± 0.68 (10%)	6.49	6.5
InP/10CdS	8.30 ± 0.72 (9%)	8.65	8.7

Size Increase with Successive SILAR Depositions

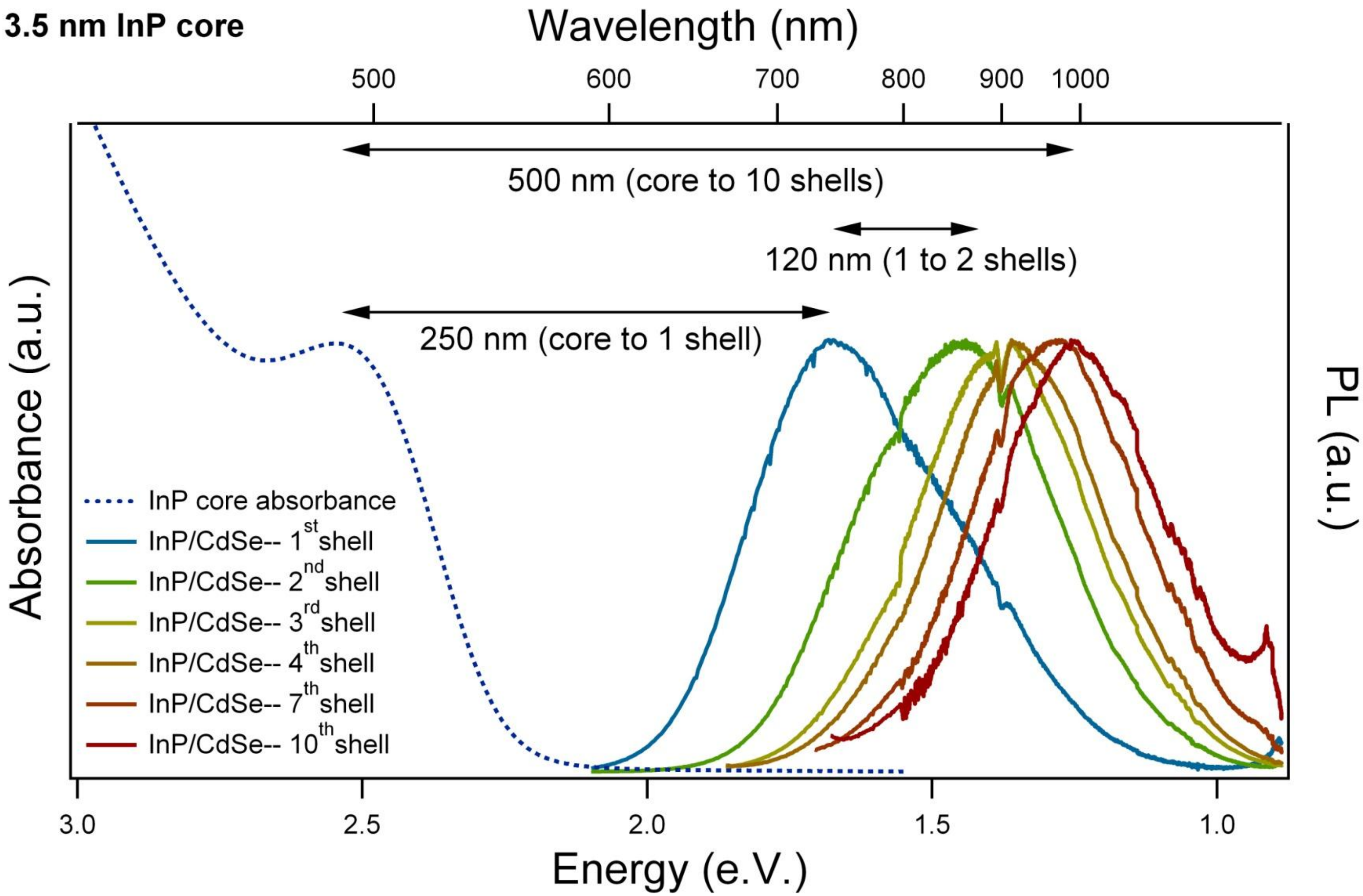


	Diameter (nm)	Shell thickness (nm)	Number of shell MLs
InP core	1.77		
InP/1CdSe	3.57 ± 0.35 (10%)	1.21	2.6
InP/4CSe	4.90 ± 0.59 (12%)	4.12	4.5
InP/7CdSe	6.19 ± 0.56 (9%)	6.49	6.3
InP/10CdSe	8.22 ± 0.77 (9%)	8.65	9.2

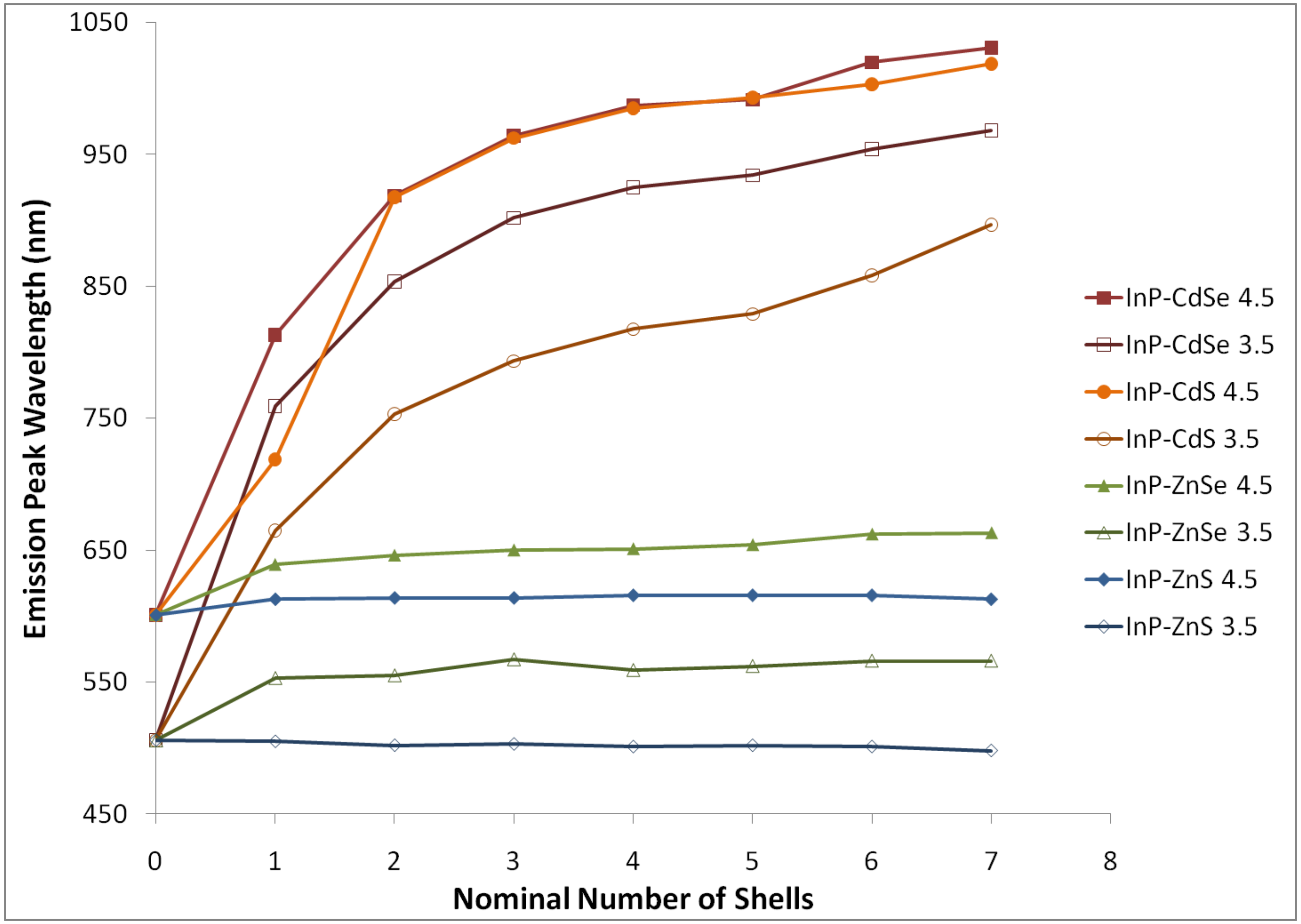
Tuning Emission with Shell Composition



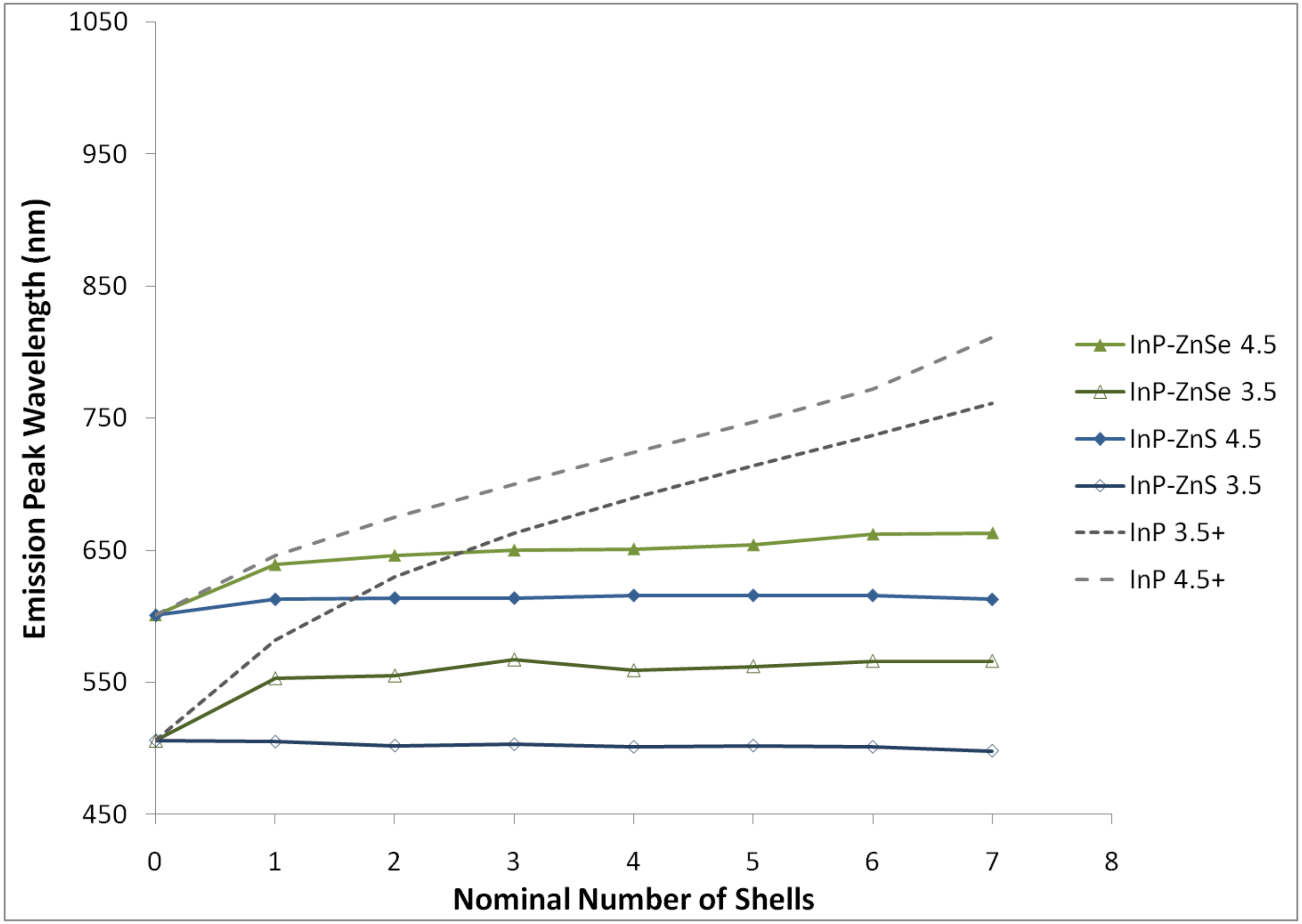
InP/CdSe:
Bandgap Tuning Through Shell Thickness



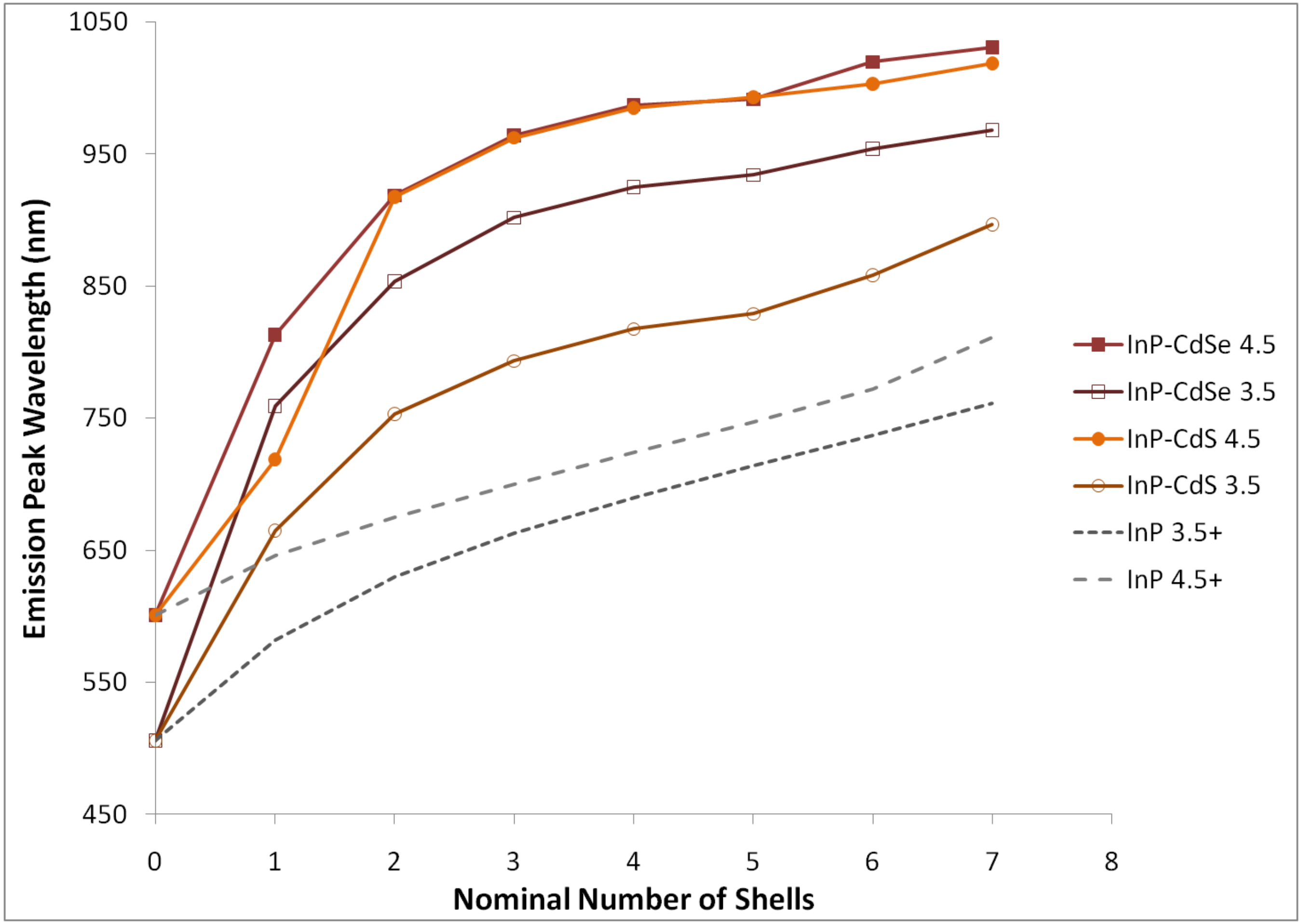
PL Red-shifting with Shell Addition



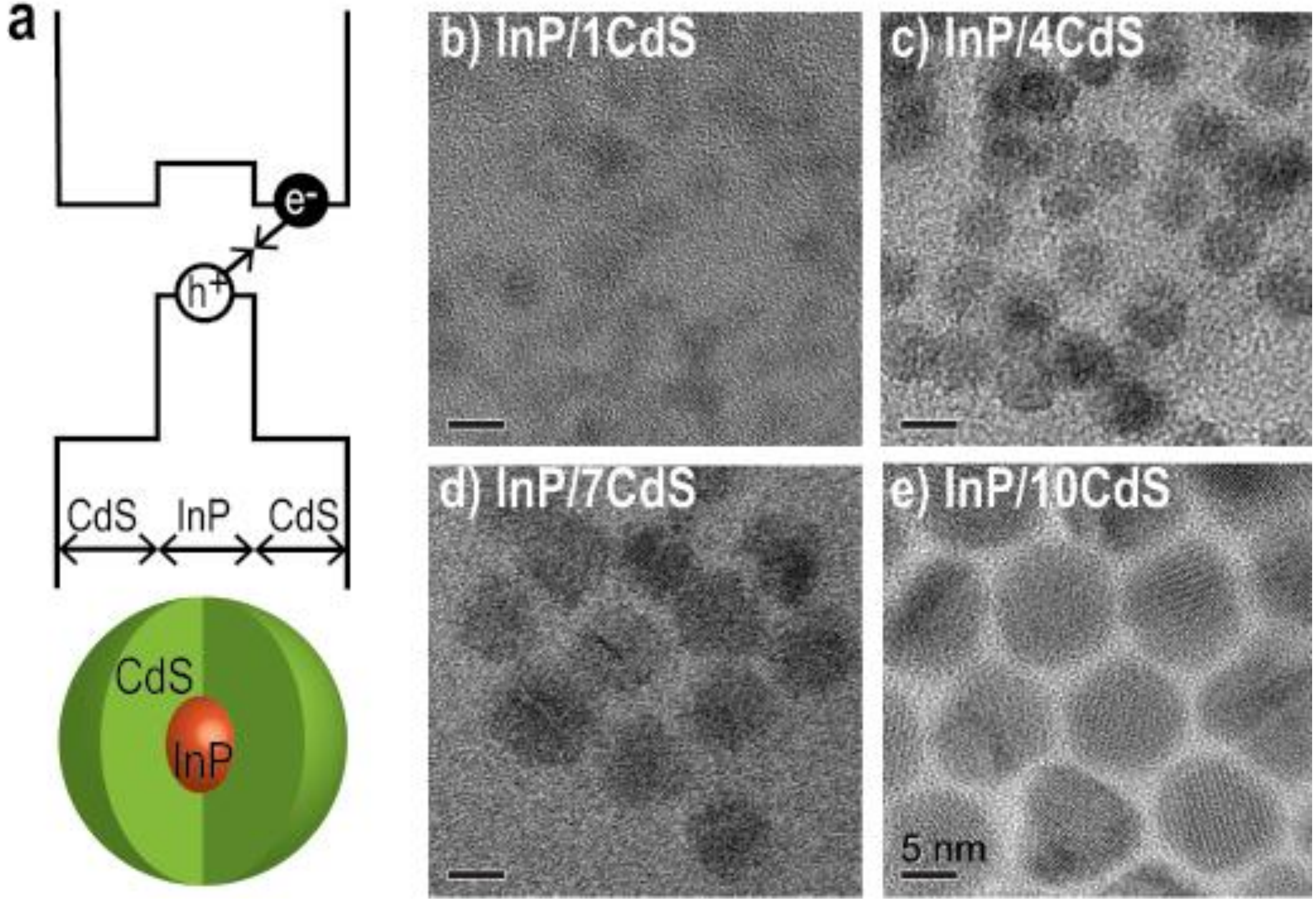
InP/Zn Systems Are Strongly Confined



InP/Cd Systems are Type II

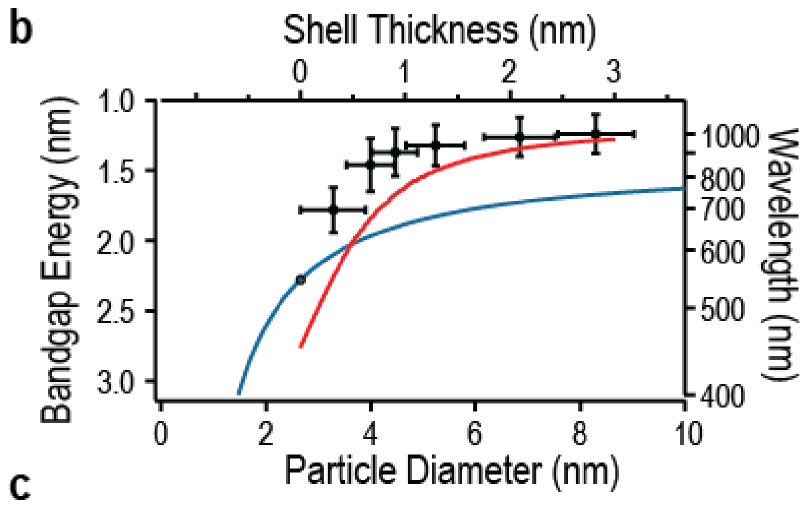


Closer Look at InP/CdS



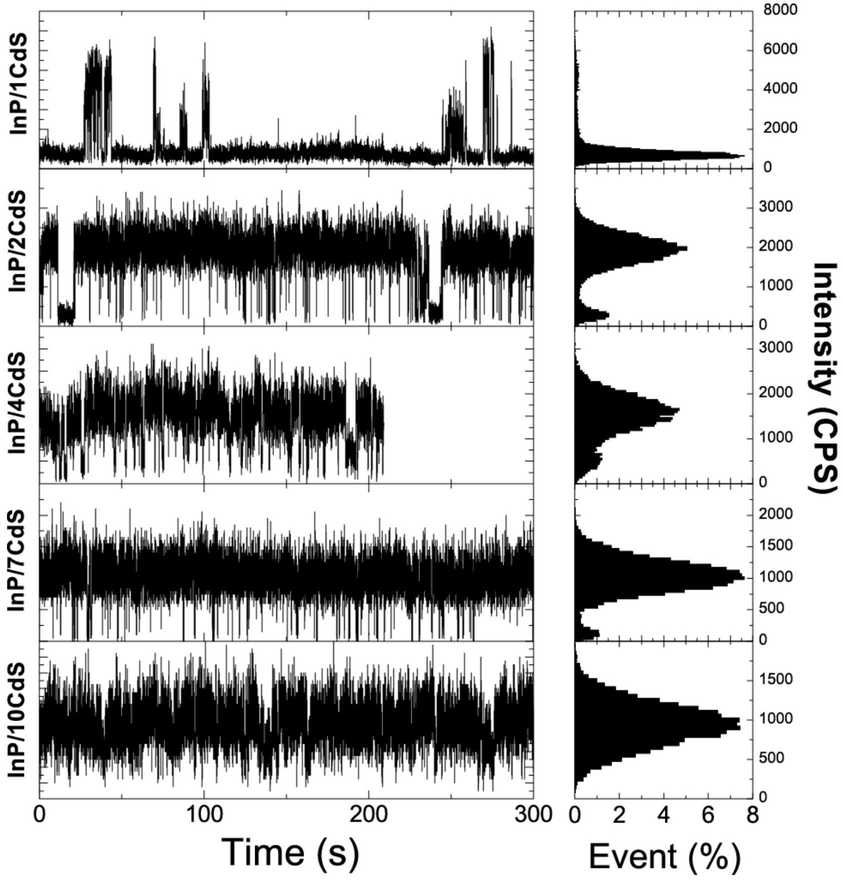
InP/CdS

- PL lifetime increases with shell thickness
- PL shifts non-linearly
- Lifetime increases linearly



- InP absorbance peak broadens with shelling
- CdS absorbance dominates at thick shells
- PL red-shifts quickly with first few shells, then steadies ~1 um

Blinking



Single-particle measurements, including blinking analysis to be presented in Ben Mangum's talk at 4:20.

Conclusions

- **New QD core-shell heterostructure chemistries**
- **Fresh opportunities to study electronic structure**
- **Bandgap engineering of InP QDs through**
  - Shell composition
  - Shell thickness
- **Emissions through the visible into the NIR**
- **On-going studies of single-particle photophysics on Type I and Type II systems**

Acknowledgements

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Number of CdS shell-addition cycles	Diameter (nm)[a]	Shell thickness (nm)	Number of shell MLs from TEM analysis	PL peak position nm/eV	PL FWHM nm/eV	Average lifetime (ns)	Biexciton lifetime (ps)
InP core	2.66	n/a	n/a	~600/2.1[b]	n/a	80-150[c]	n/a
InP/1CdS	3.28 ± 0.62 (19%)	0.31	0.89	696/1.78	124/0.32	213	58 ± 12
InP/2CdS	3.99 ± 0.45 (11%)	0.67	1.90	849/1.46	476/0.38	327	n/a
InP/3CdS	4.46 ± 0.44 (10%)	0.90	2.57	904/1.37	483/0.34	352	n/a
InP/4CdS	5.24 ± 0.56 (11%)	1.29	3.69	937/1.32	211/0.29	435	99 ± 5
InP/7CdS	6.84 ± 0.68 (10%)	2.09	5.97	982/1.26	220/0.28	652	612 ± 49
InP/10CdS	8.30 ± 0.72 (9%)	2.82	8.06	1000/1.24	229/0.28	714	7,212 ± 1,073