Ultrafast Spectroscopy

Some Applications

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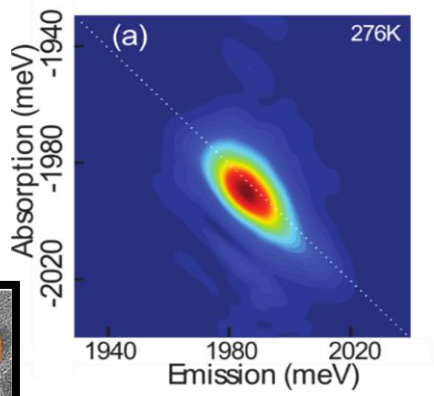
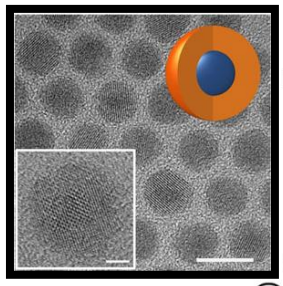
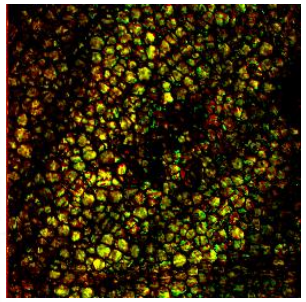
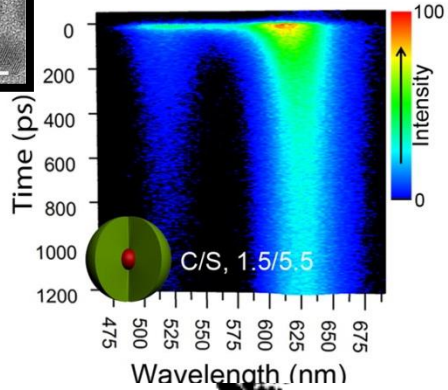
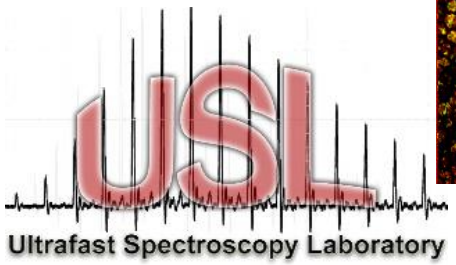
XV Jorge Andre Swieca School on Nonlinear and Quantum Optics











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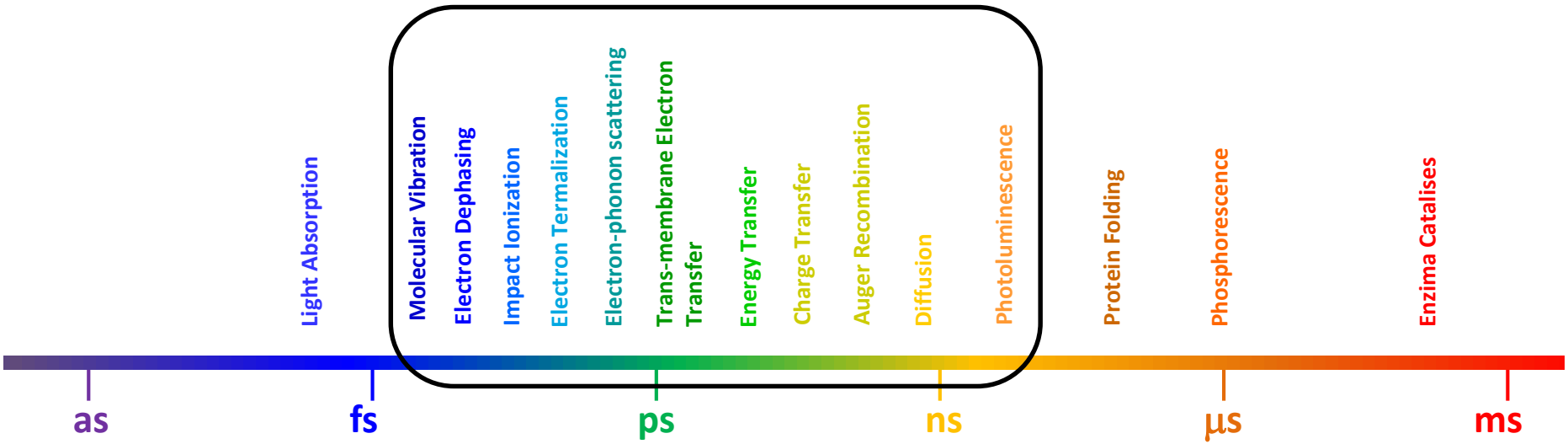
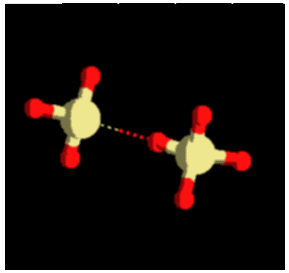
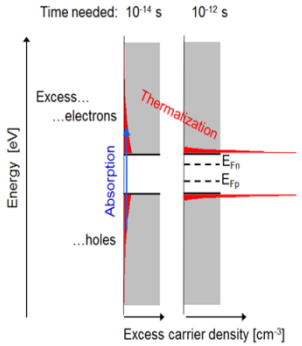
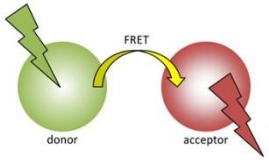
Time scale for natural occurring phenomena

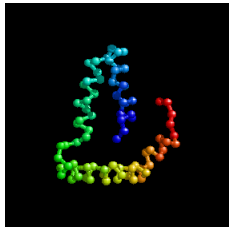
Ultrafast Spectroscopy Laboratory











To measure those fast processes we need something even faster

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THE JOURNAL OF PHYSICAL CHEMISTRY Letters

Perspective

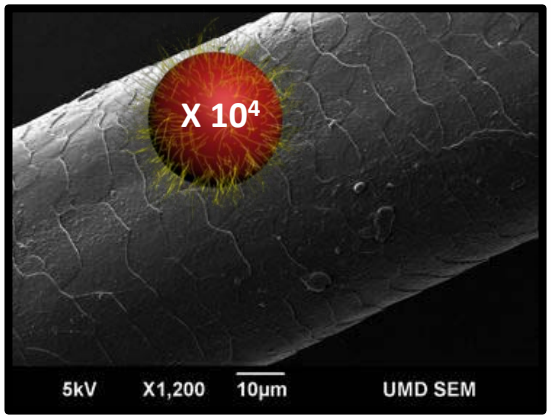
pubs.acs.org/JPCL

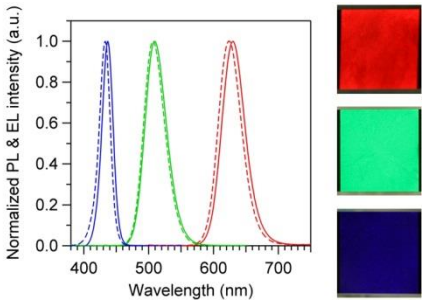
Contribution of Femtosecond Laser Spectroscopy to the Development of Advanced Optoelectronic Nanomaterials

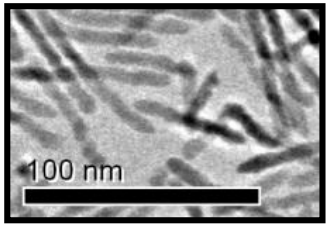
Chi-Hung Chuang and Clemens Burda*

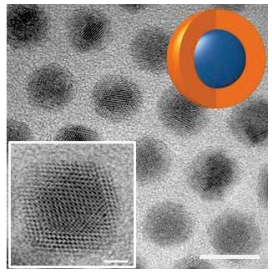
Center for Chemical Dynamics and Nanomaterials Research, Department of Chemistry, Case Western Reserve University, 10900 Euclid Avenue, Cleveland, Ohio 44106, United States

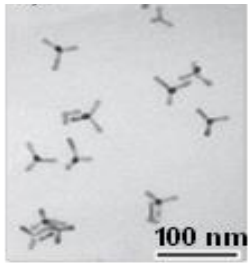
Semiconductor Colloidal Nanomaterials



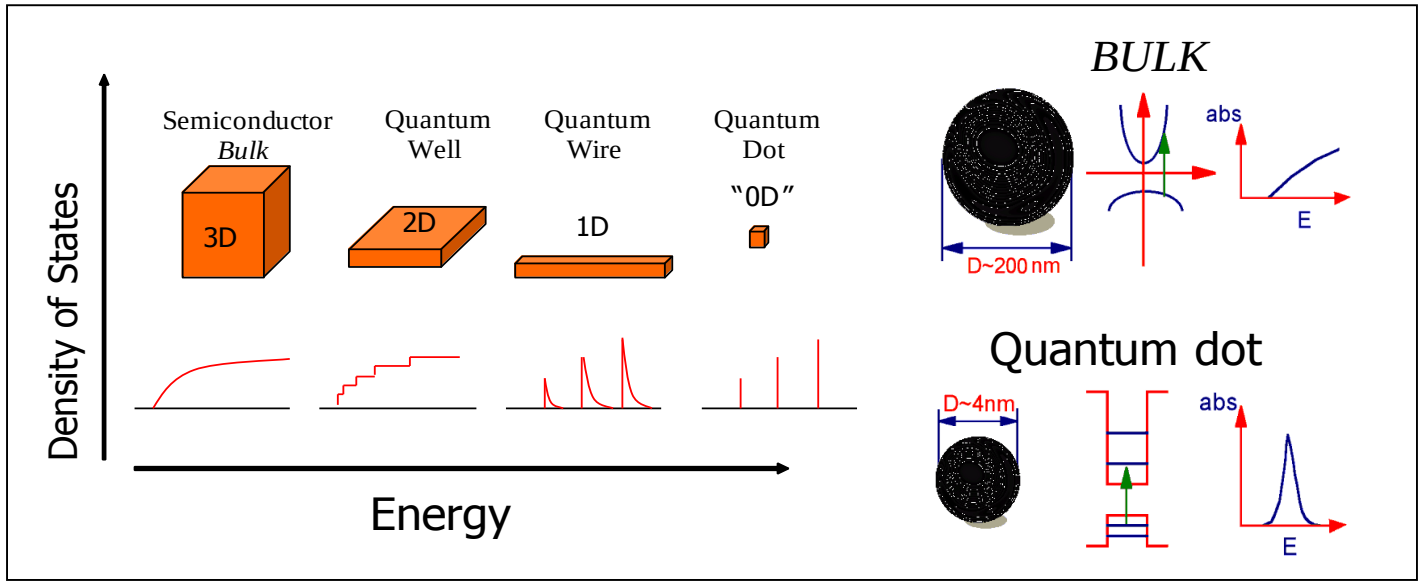






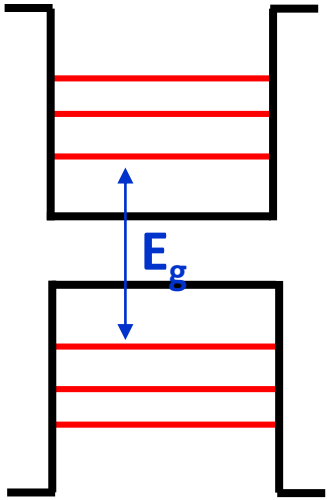


Semiconductor Colloidal Nanomaterials



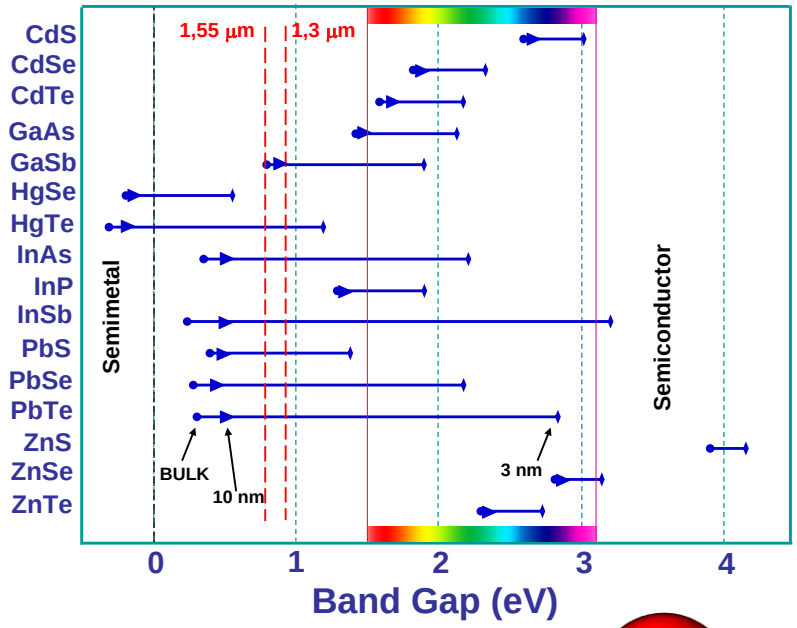
Lets think on the potential well problem

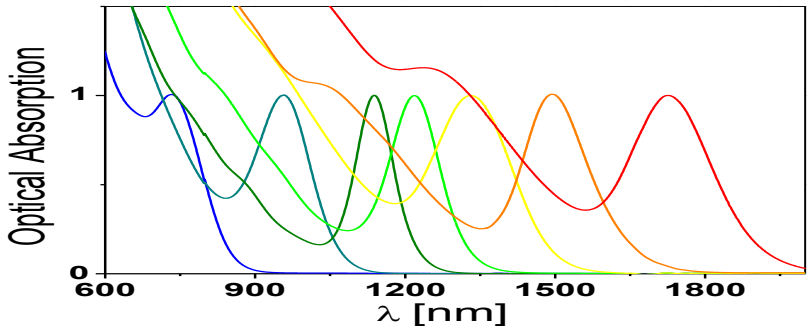
$$E_g = E_g^{Bulk} + \frac{\hbar^2 \xi_{nl}^2}{2m^* R^2}$$



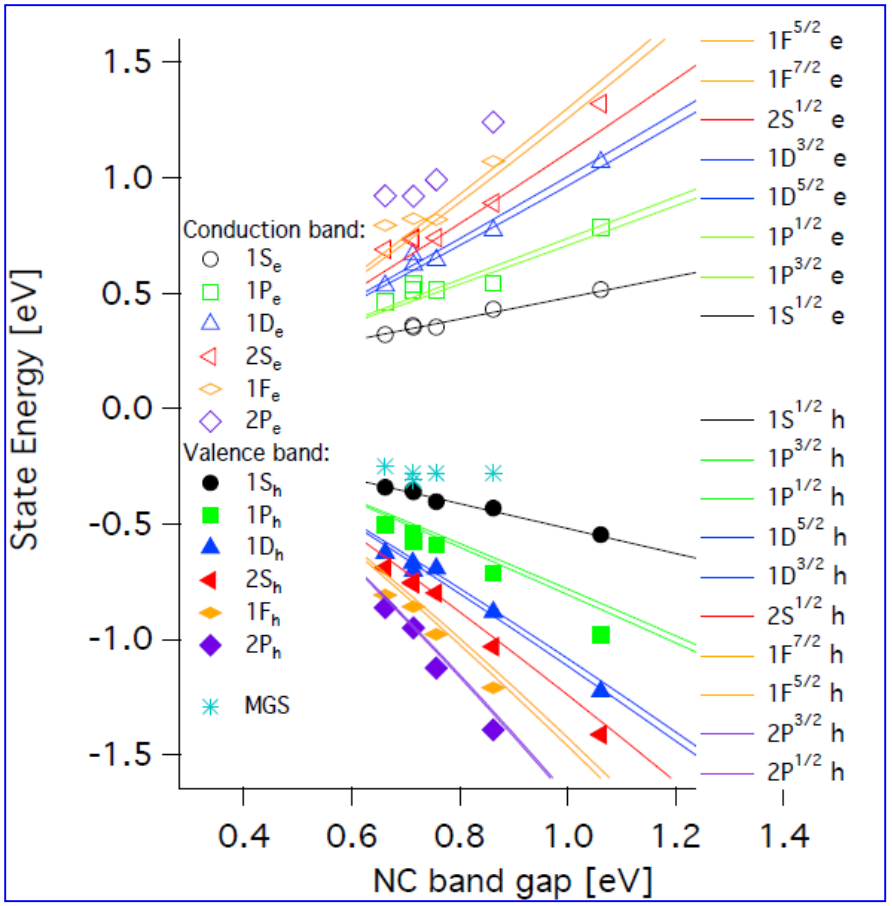
Changing the size, the band gap and intraband transition energies are tuned

Semiconductor Colloidal Nanomaterials





STS indentifies the states for PbS QDs

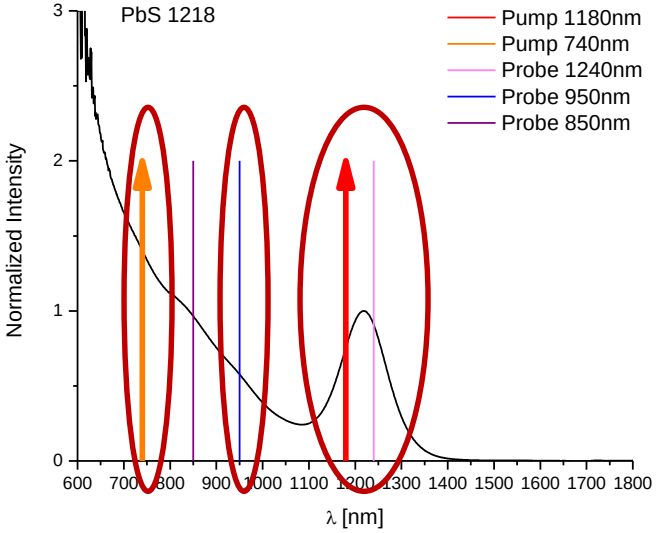


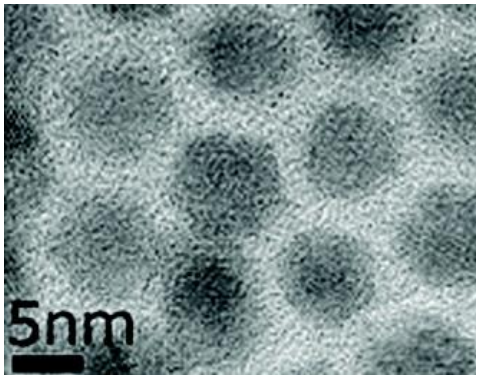
Diaconescu et.al. PRL 2013

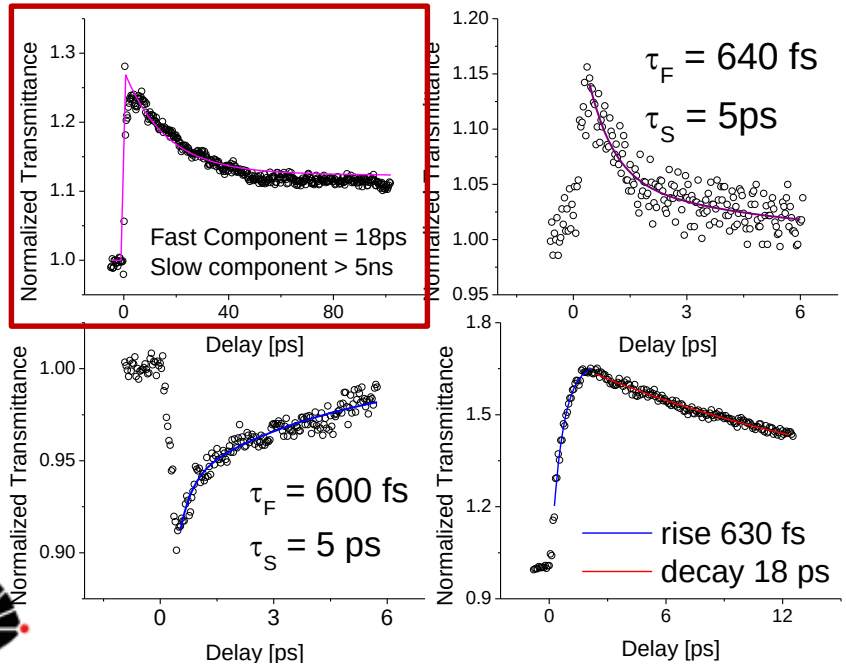
Semiconductor Colloidal Nanomaterials

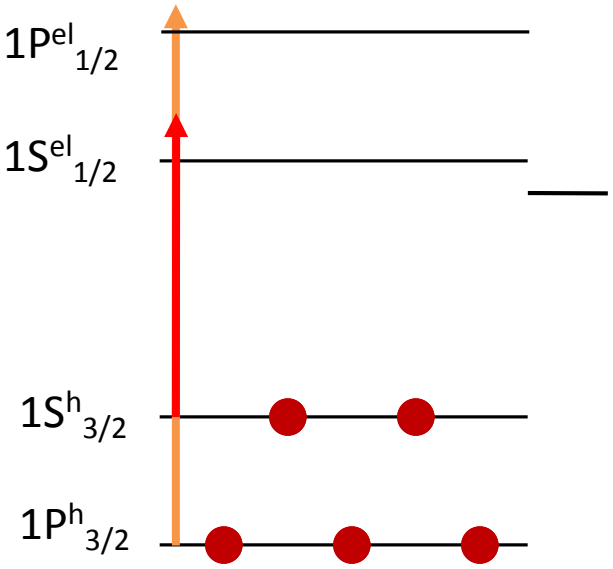
- Broad absorption
- Narrow emission (< 35 nm)
- Color tunability
- High PL QY (> 80 %)
- Solution processibility
- Momentum conservation requirements are relaxed ($\Delta x \Delta p \geq \hbar/2$)
- Possible phonon bottleneck due to relatively large intraband state spacing
- Stronger Coulomb interaction due to low dimensionality

Carrier Dynamics in PbS Quantum Dots - TA



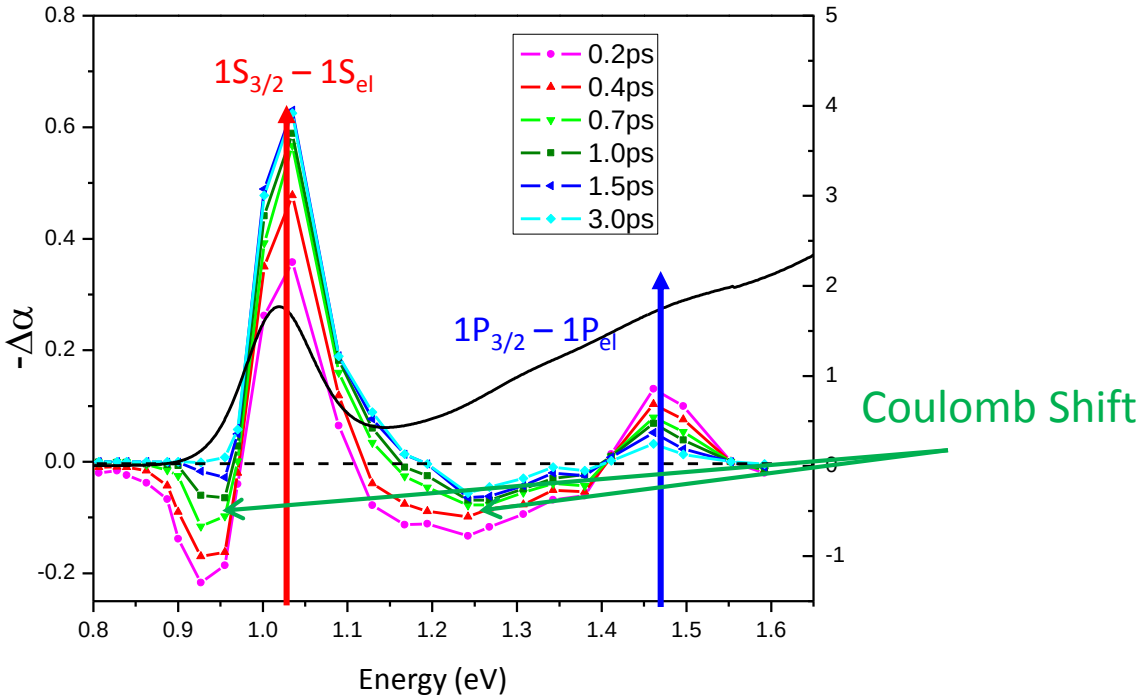


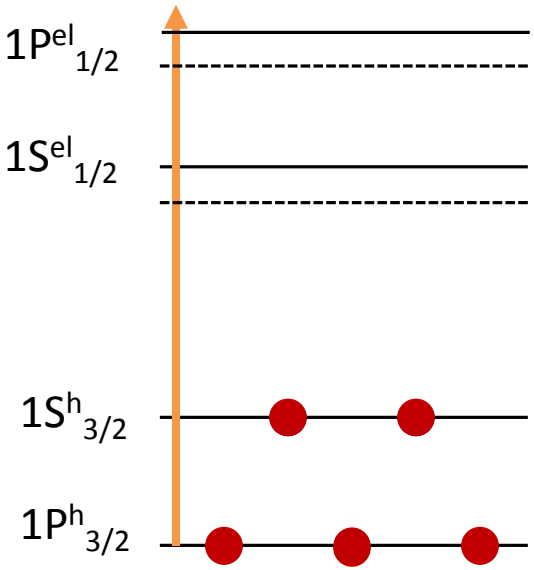




Nootz et.al. PRB 2011

Carrier Dynamics in PbS Quantum Dots - TA



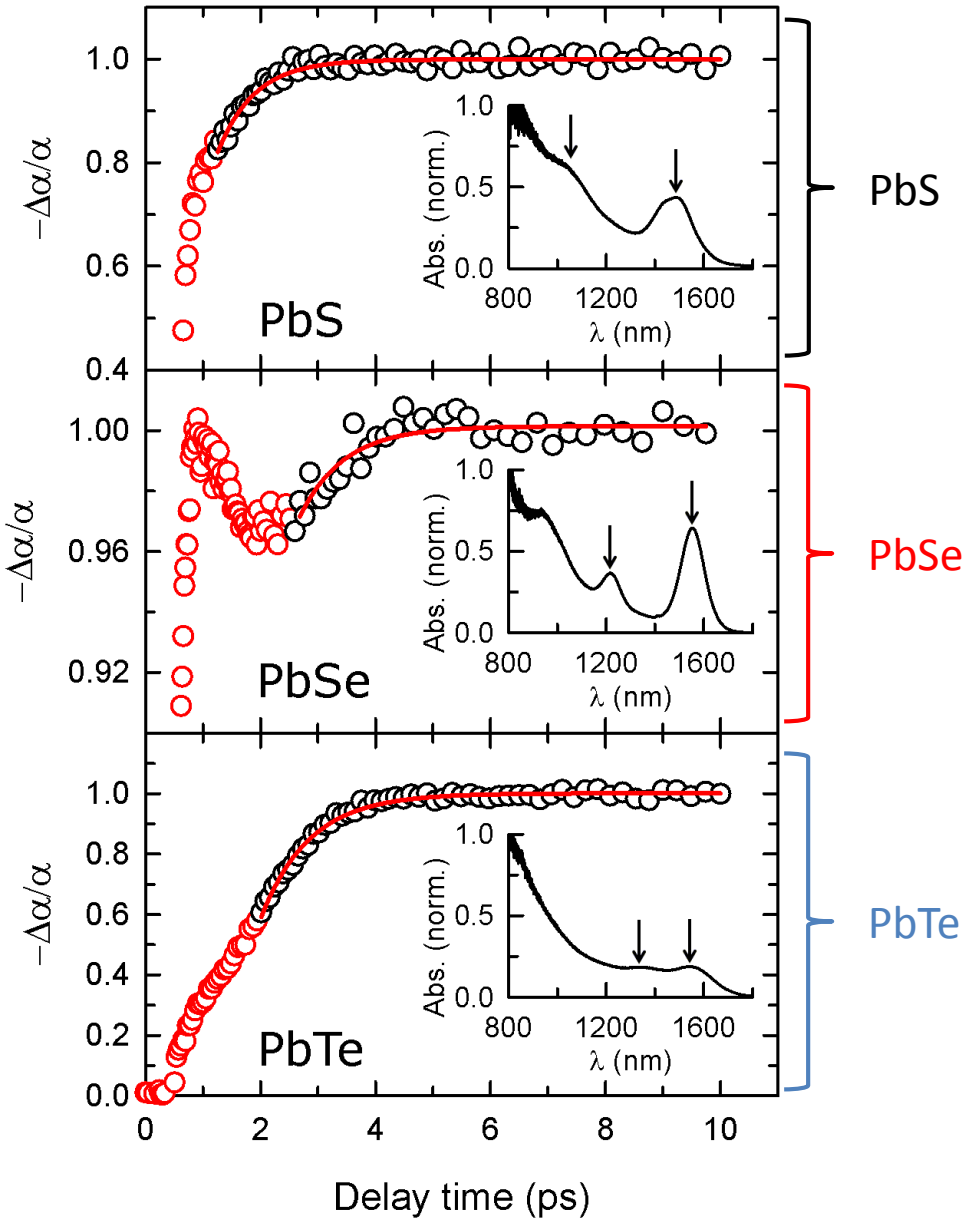


1. Electrons rapidly populates 1P level
2. Slowly, they decay to the 1S level
3. Exciton-exciton interaction generates Coulomb shift which decreases effective energy level

We can only understand the entire dynamics because we used multiple probe wavelengths

Nootz et.al. PRB 2011

Transient Absorption – Intraband Cooling



$$2\,k_{cool_{PbSe}} \approx k_{cool_{PbS}}$$

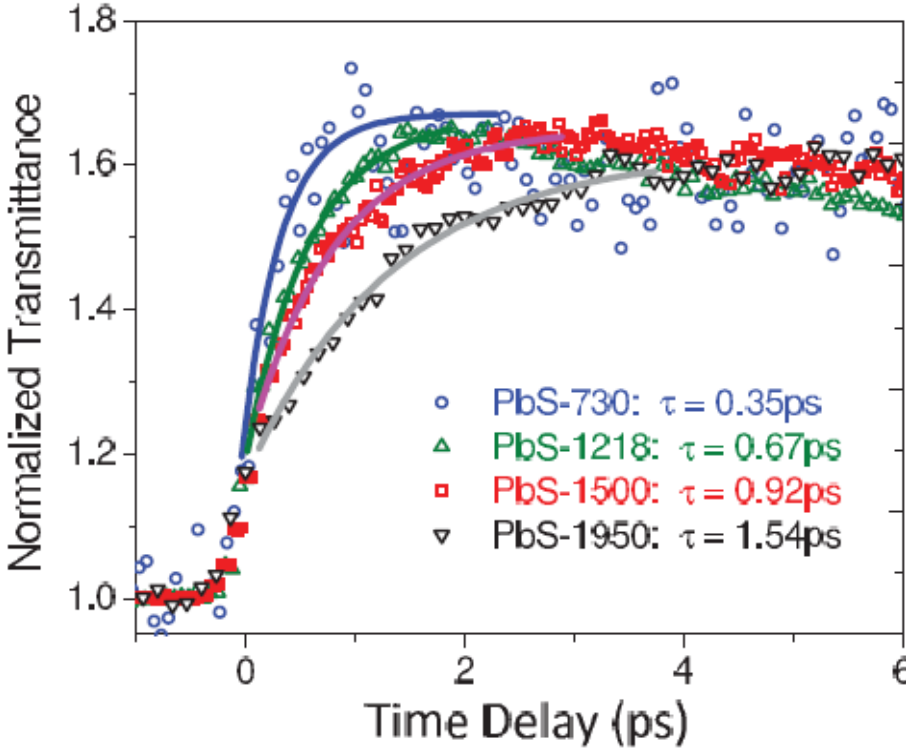
$$2\,k_{cool_{PbTe}} \approx k_{cool_{PbSe}}$$

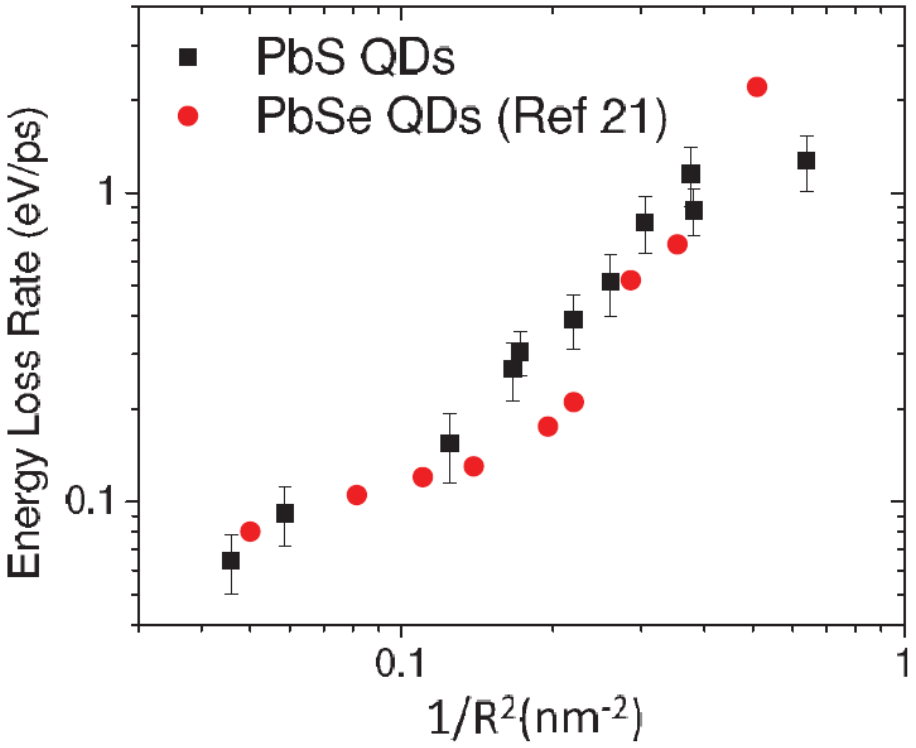
$$k_{cool_{PbS}} > k_{cool_{PbSe}} > k_{cool_{PbTe}}$$

Stewart et.al. JPCL (2013)

Transient Absorption – Intraband Cooling

QD Size Dependence – 1S Population



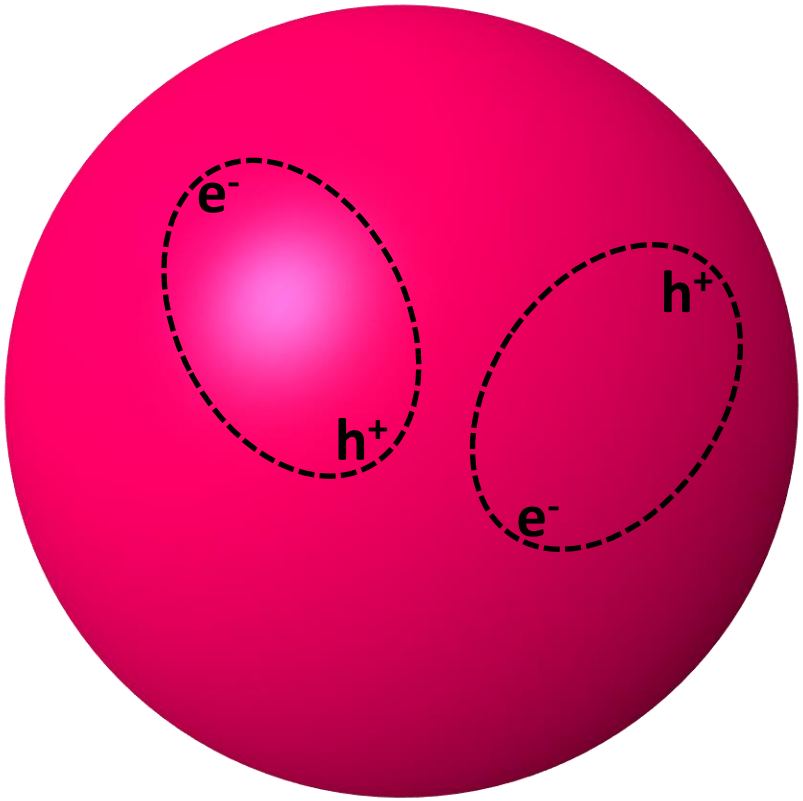


No bottleneck, the smaller the QD the faster the intraband cooling

PbS and PbSe have similar cooling rate – But note that PbS is faster

Nootz et.al. Phys. Rev. B (2011)

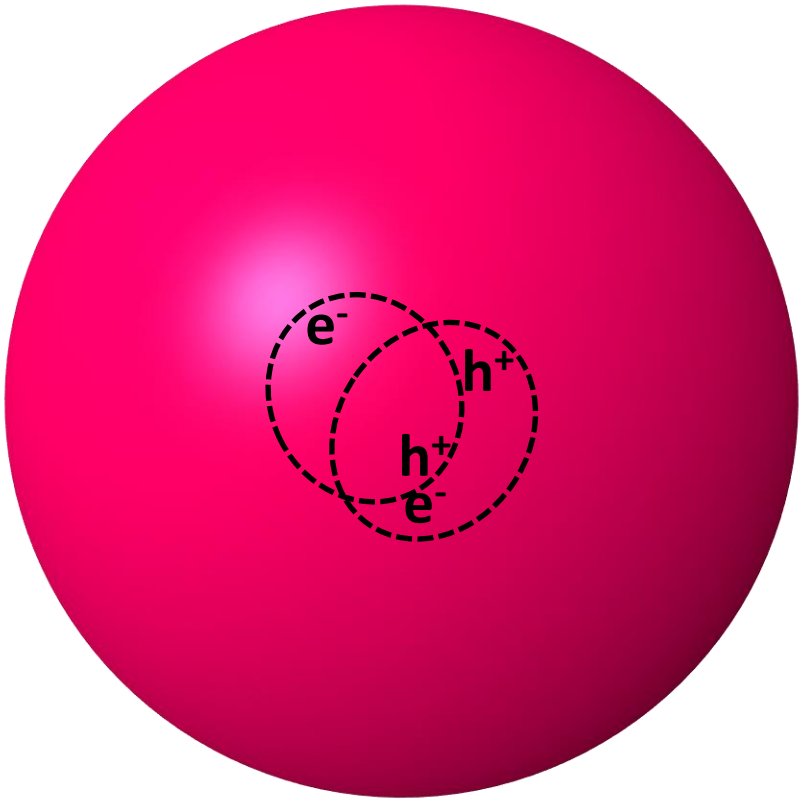
Multi-Exciton Interactions



$$E_g = E_g^{Bulk} + \frac{\hbar^2 \xi_{nl}^2}{2m^* R^2}$$

$$U_{Coulomb} \propto \frac{1}{R}$$

Multi-Exciton Interactions



$$E_g = E_g^{Bulk} + \frac{\hbar^2 \xi_{nl}^2}{2m^* R^2}$$

Excitons are too close to each other

⇩

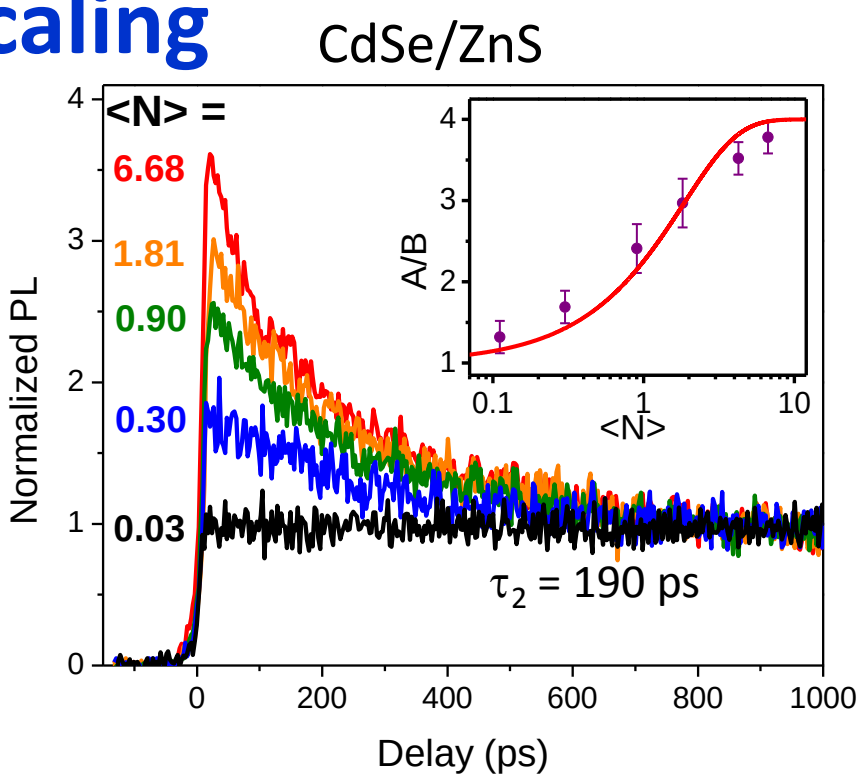
Multi-excitons strongly interact - Coulomb

⇩

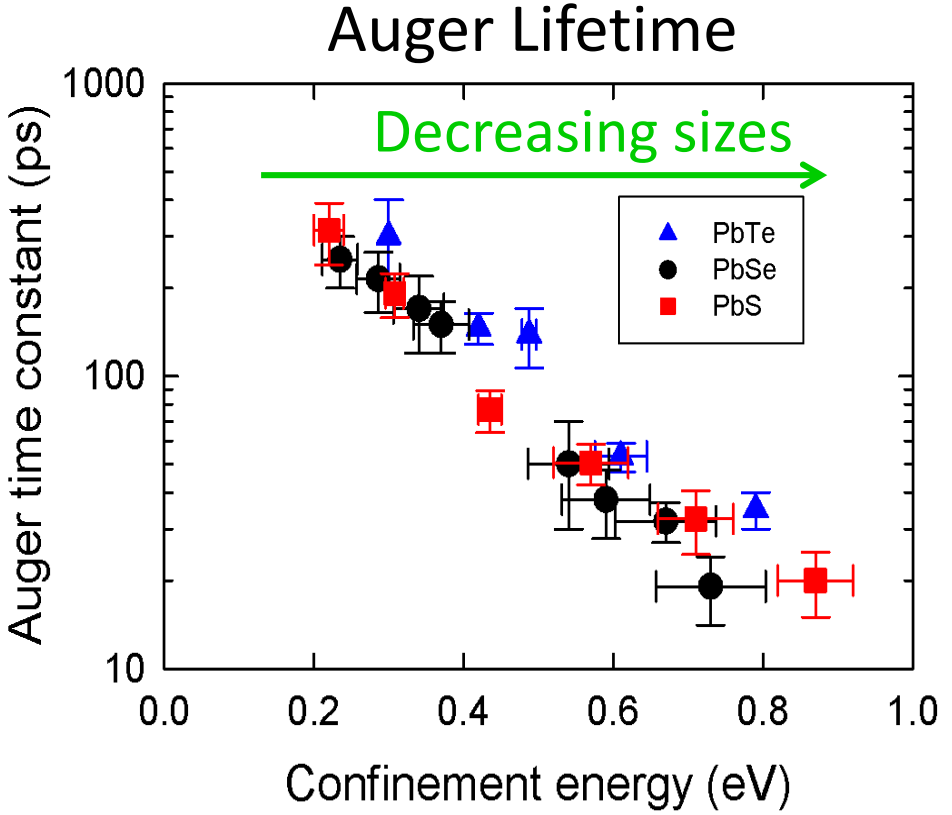
Auger Type of Interaction

$$U_{Coulomb} \propto \frac{1}{R}$$

Auger Recombination – QD Volume Scaling



Padilha et.al. Nano Lett. 2013

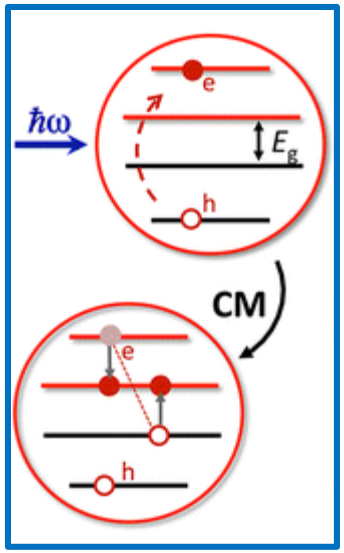


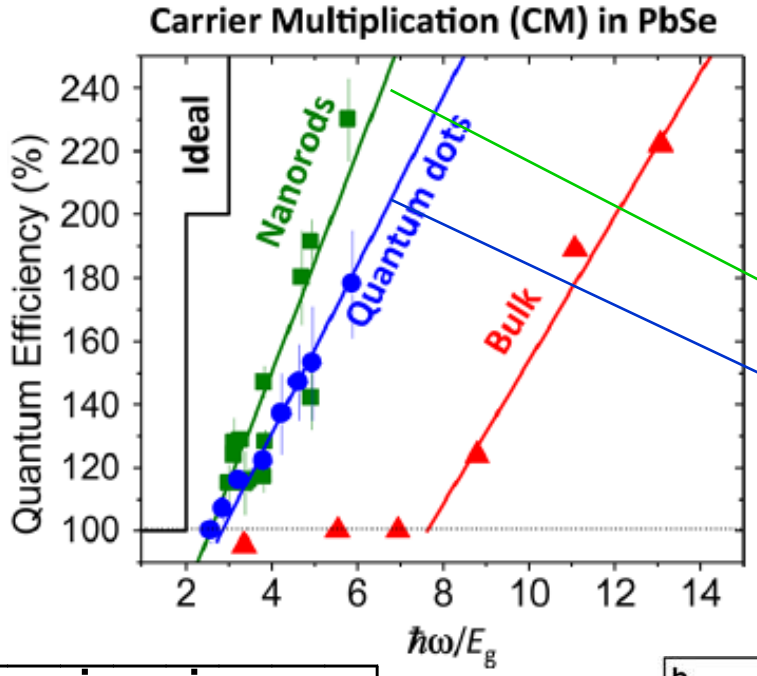
Padilha et.al. Acc. Chem. Res. 2013

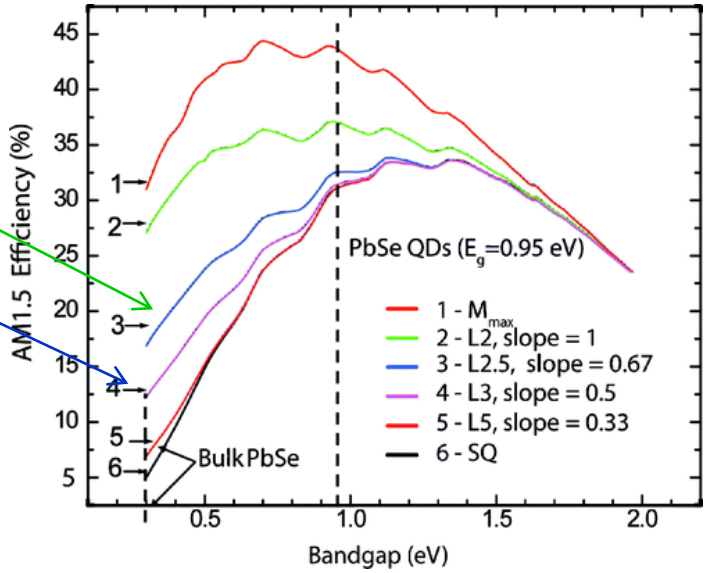
Coulomb interaction enhances with quantum confinement

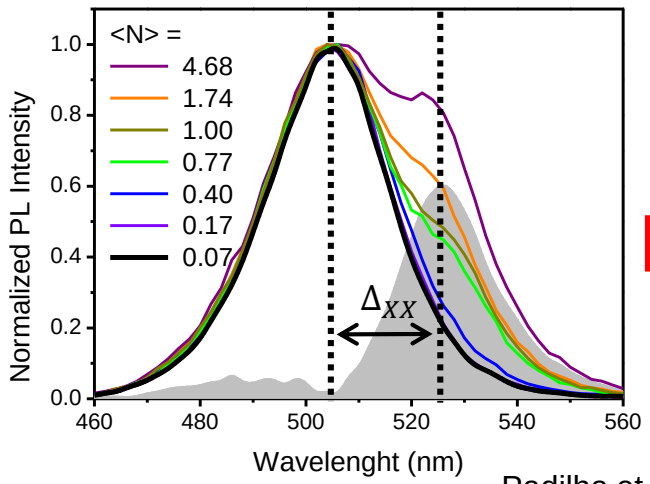
It is nearly material independent, and only depends on the degree of confinement (volume)

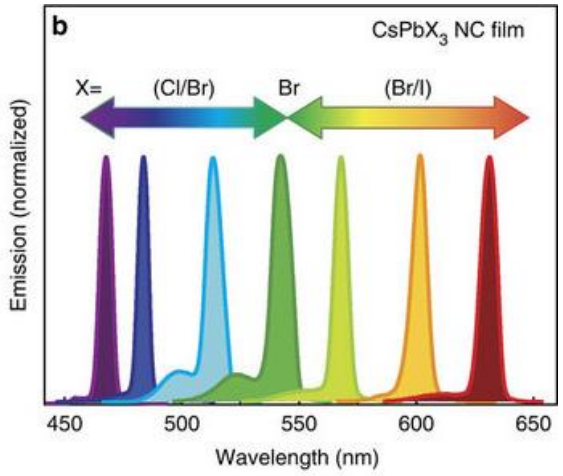
Coulomb Interaction – Good or Bad?





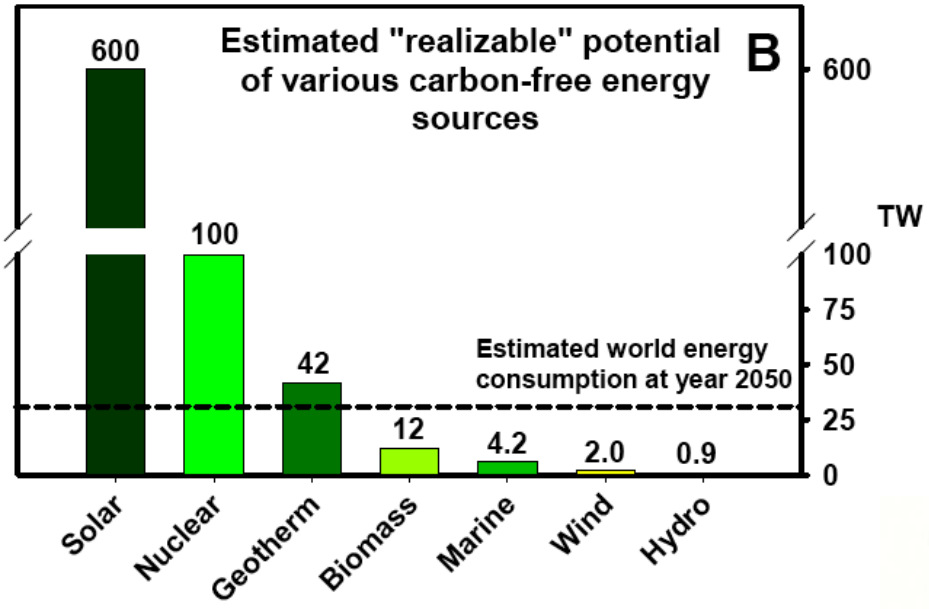






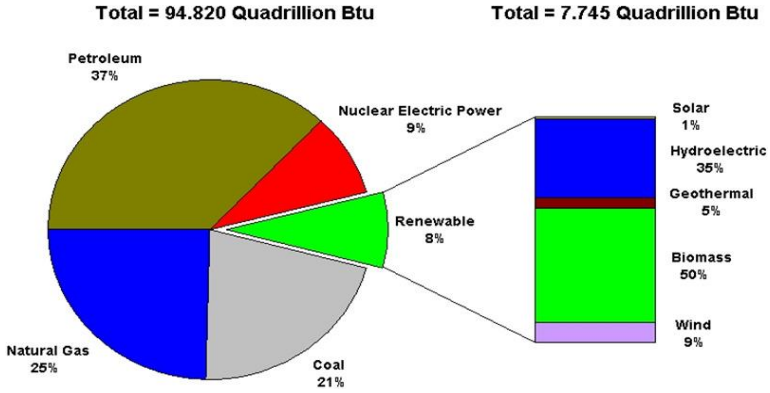
Padilha et al., Acc. Chem. Res., (2013)
Yakunin, et.al., Nat. Comm. (2015)

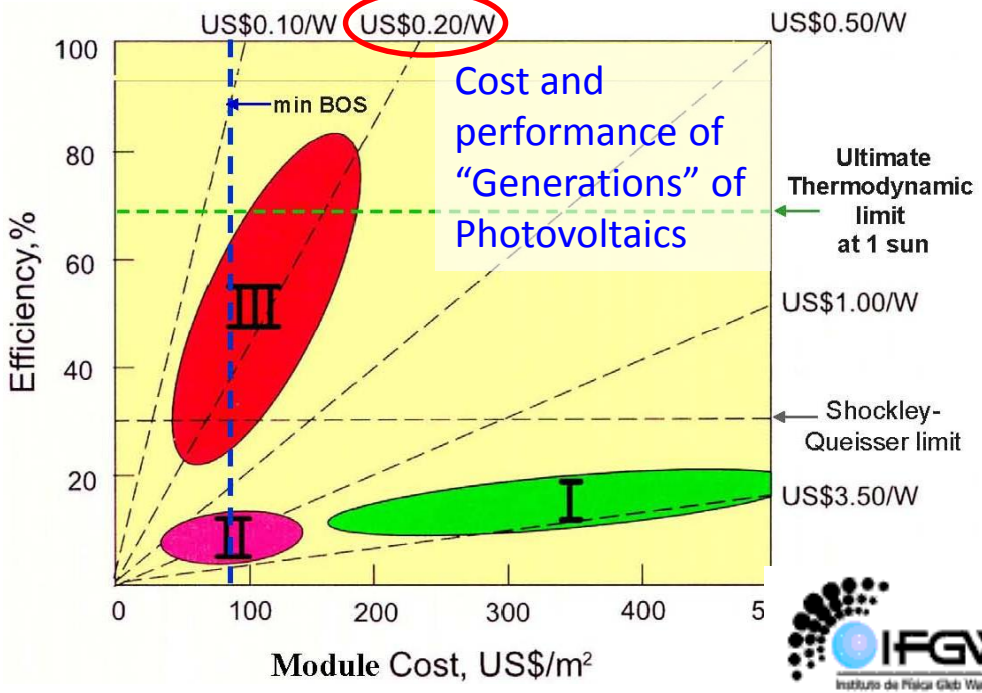
Energy: Crisis and Solutions



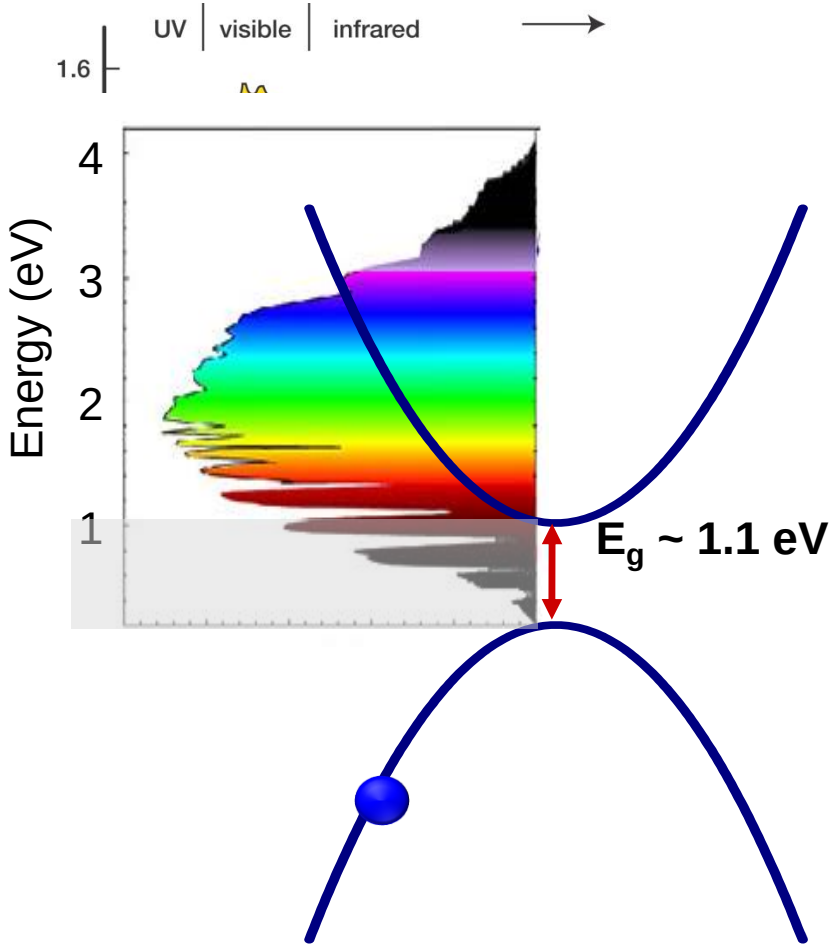
Solar has the most overall potential of all "carbon-free" energy sources, but is a tiny piece of the current energy puzzle due mainly to cost.

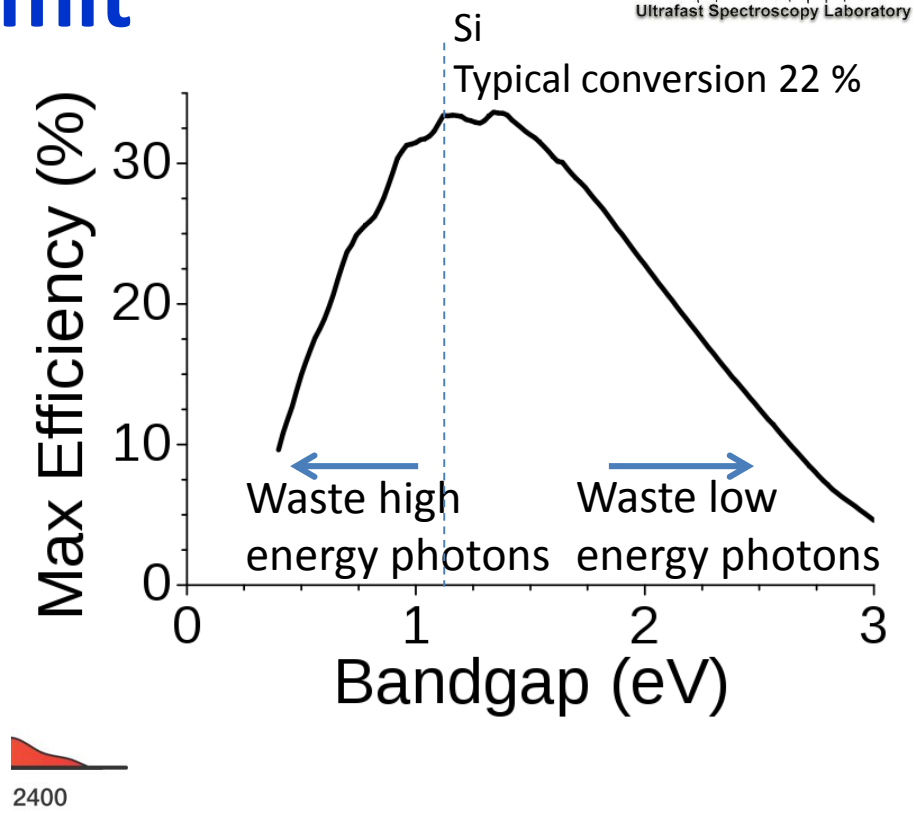
Current US energy consumption





The Shockley-Queisser Limit



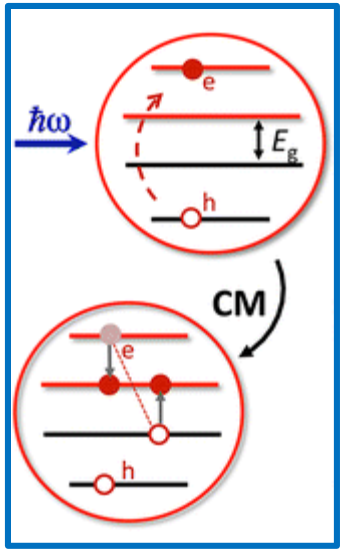


Generation III – make better use of the high and low energy photons

Generation III PV's – Paradigm Shift

One way is to make better use of the high energy photons

Carrier multiplication



Padilha et al., Acc. Chem. Res., (2013)

Highly excited carrier decay to the band edge by transferring the energy to a second electron on the valence band, creating a second exciton.

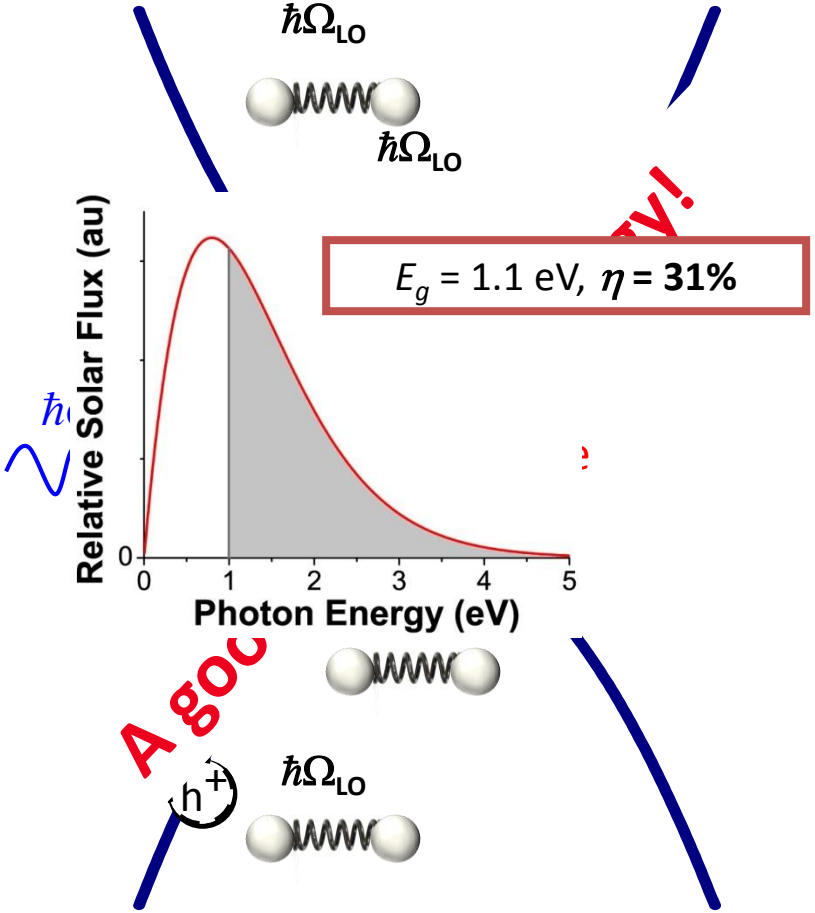
Coulomb interaction – same as Auger recombination.

Increases photocurrent but keep V_{oc} constant

Two Competing Processes

k_{cool}

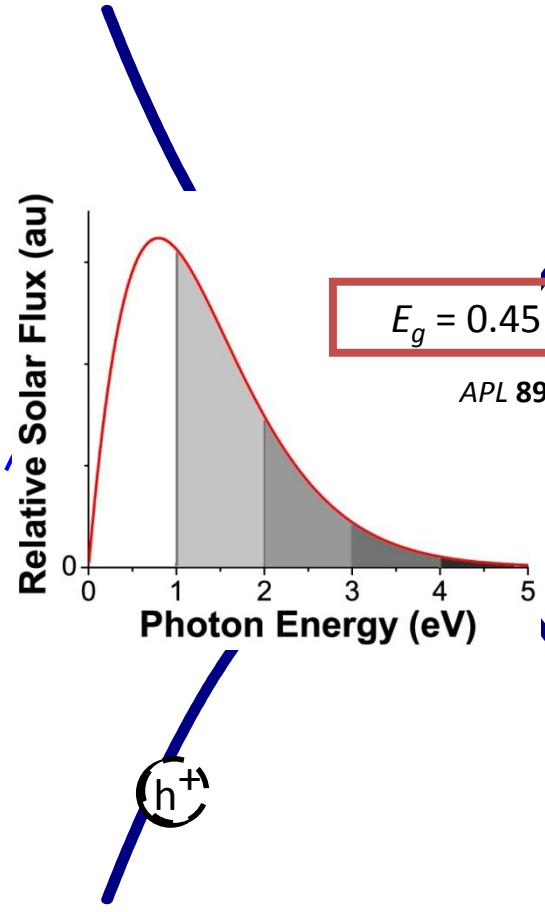
Phonon Emission



E_g = 1.1 eV, η = **31%**

Impact Ionization

k_{CM}

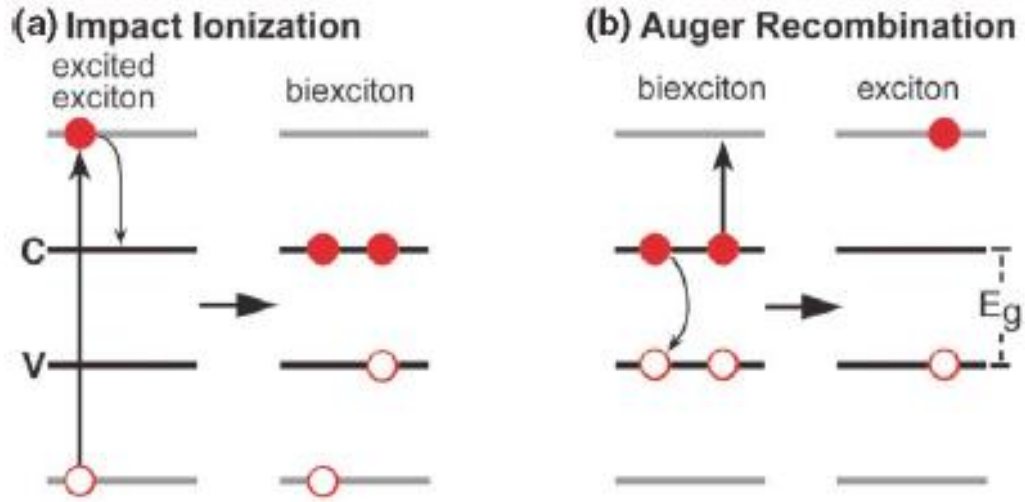


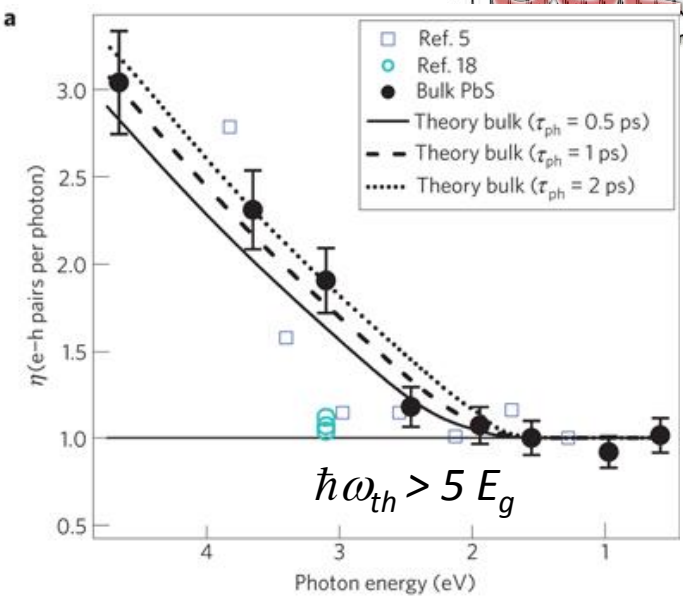
E_g = 0.45 eV, η = **42%**

APL **89**, 123118-123113 (2006).

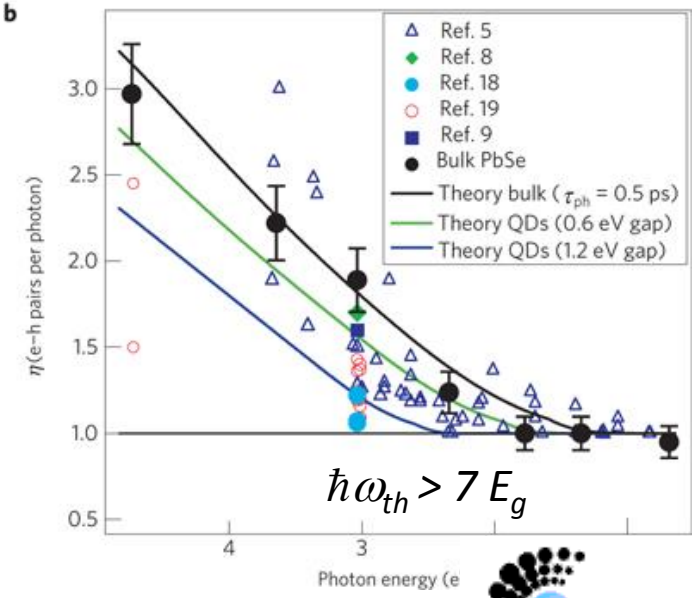
$$\varepsilon_{eh} \propto k_{cool}/k_{CM}$$

Carrier Multiplication



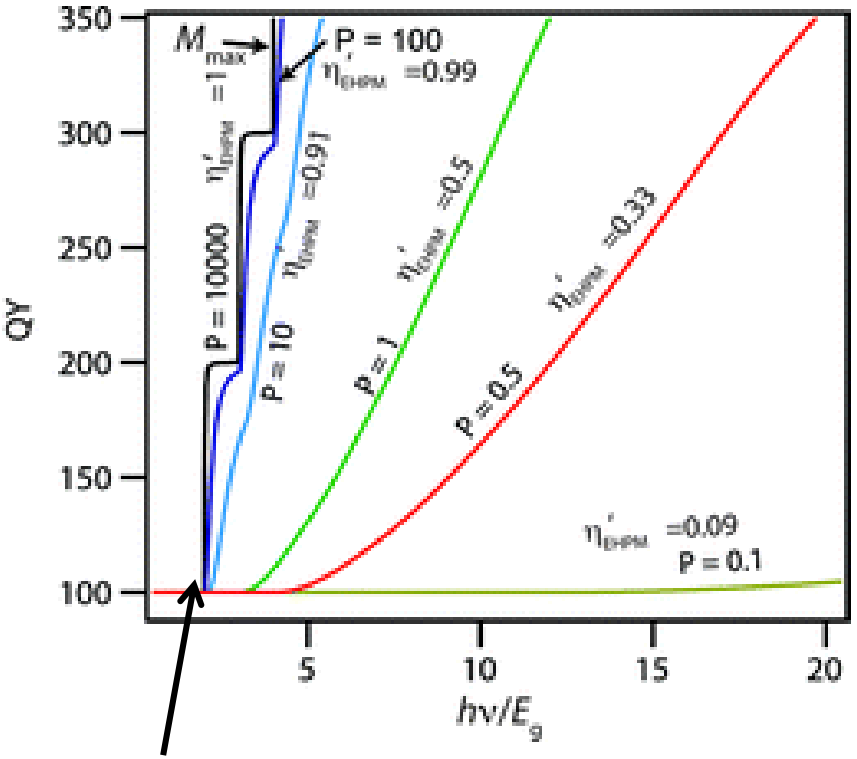


- In bulk it is a result of Impact Ionization – quite inefficient
- Limiting factors in bulk:
  - Energy and momentum conservation
  - Fast competing intraband relaxation processes

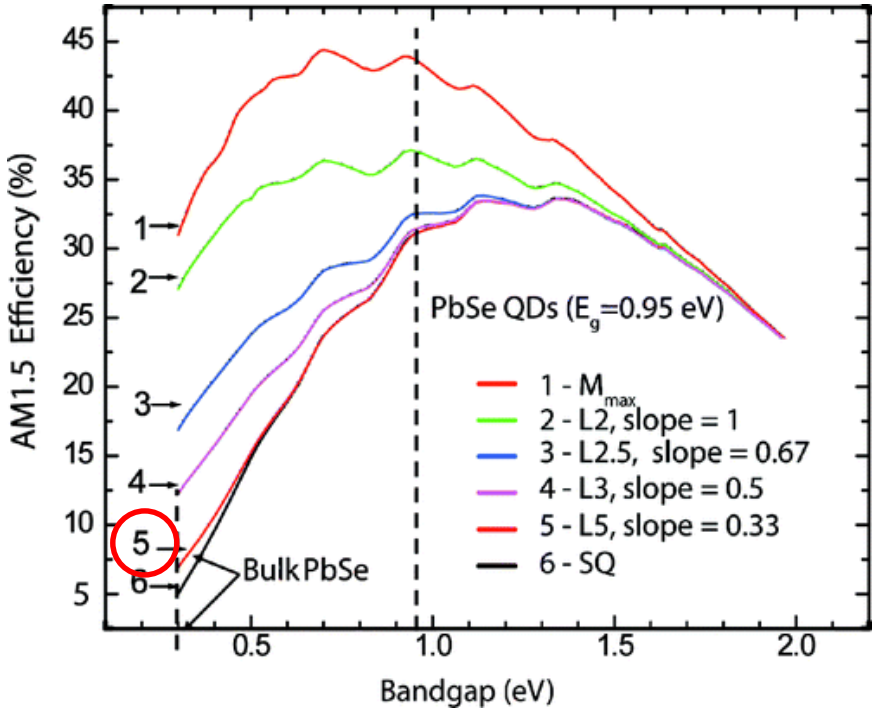


Pjipers et.al., Nat. Physics 5, 811 - 814 (2009)

PV Efficiency vs CM Efficiency



Ideal case $\hbar\omega_{th} = 2\ E_g$



$$\varepsilon_{eh} = \left(\frac{dQY}{d\hbar\omega}\right)^{-1}$$

$$\eta_{eh} = \frac{E_g}{\varepsilon_{eh}}$$

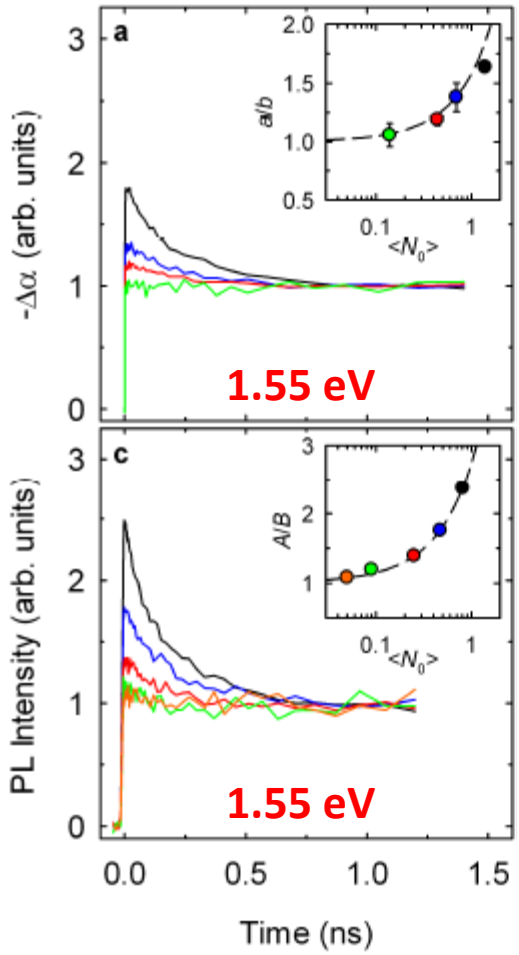
- It only makes a difference on solar power conversion efficiency near the theoretical limit!
- For bulk it is really far from working!
- How about nanomaterials?

Beard et.al. Nano Lett., 10, 3019–3027 (2010)

Measuring Carrier Multiplication in Nanoparticles

Multi-exciton signature is obtained from **Auger decay** from transient absorption (TA) or transient PL (trPL)

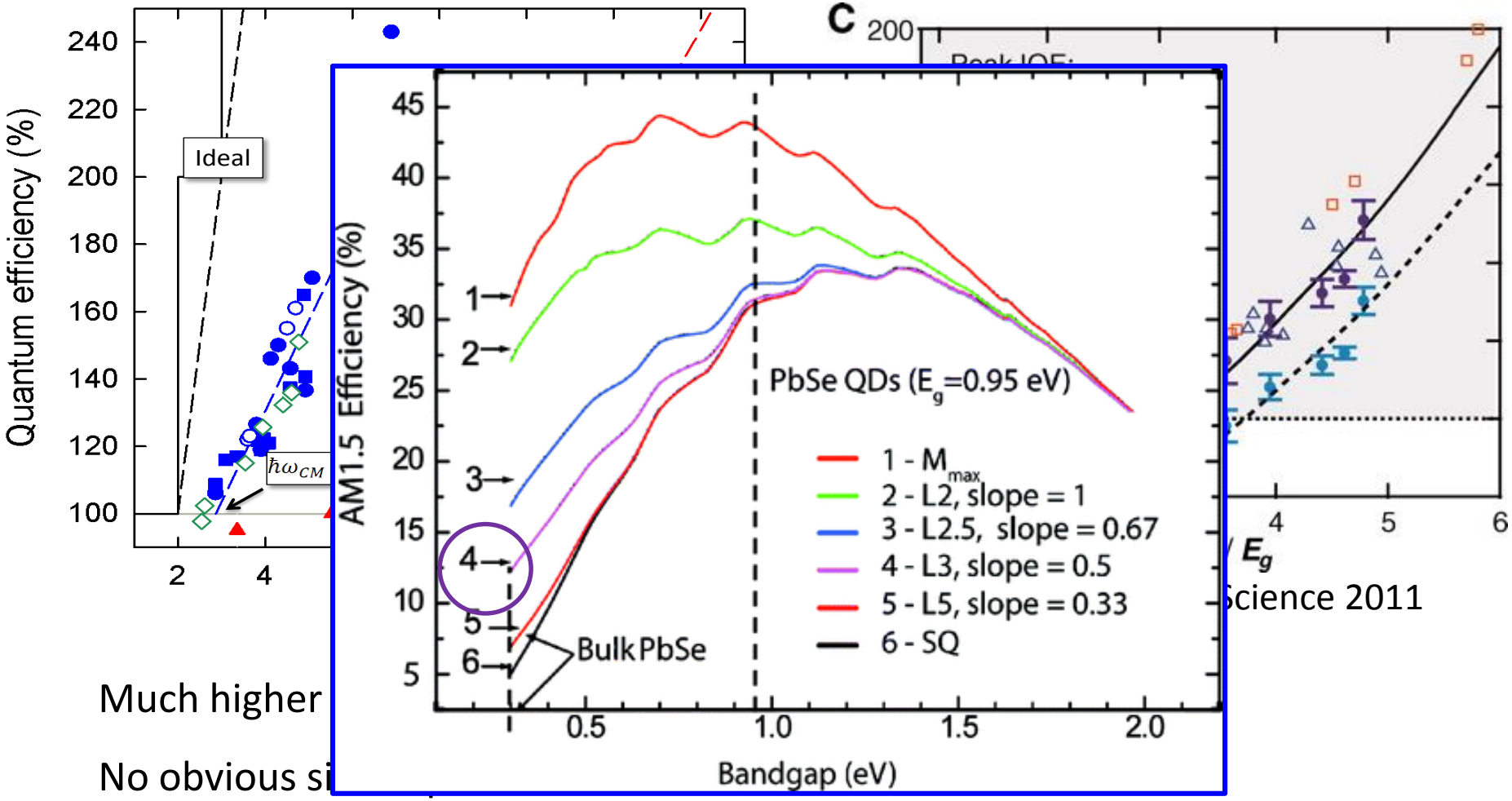
PbS QDs E_g = 0.71 eV



- Choose $\hbar\omega$ so that no CM is possible $\Delta\alpha \propto N$
- Use TA or trPL to measure Auger lifetimes $\text{QY} = {}^{A}/_{B}$
- Verify that the population follow a Poisson Distribution
- Once the baseline study is done, we change to spectral regions where CM is possible and repeat the experiment. $PL \propto N_e N_h$ $\text{QY} = {}^{({}^{A}/_{B}+2)}/_{3}$

Stewart et.al. Nano Lett. 2012

How Good is it in QDs?



Science 2011

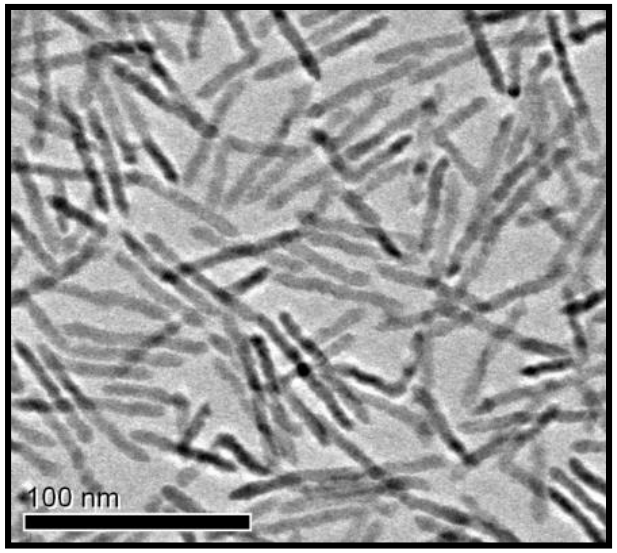
Much higher

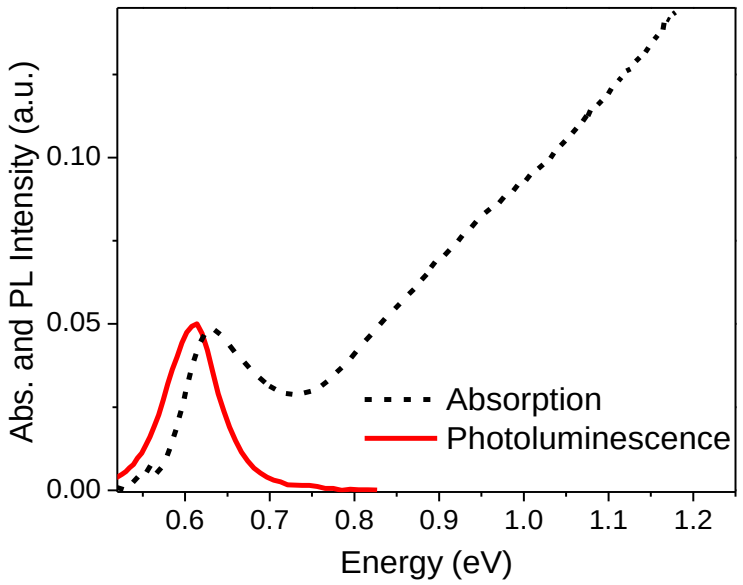
No obvious si

However, still too far from the ideal

Next step: understand the physical mechanism for CM in nanomaterials

Shape Effect: From QDs to NRs



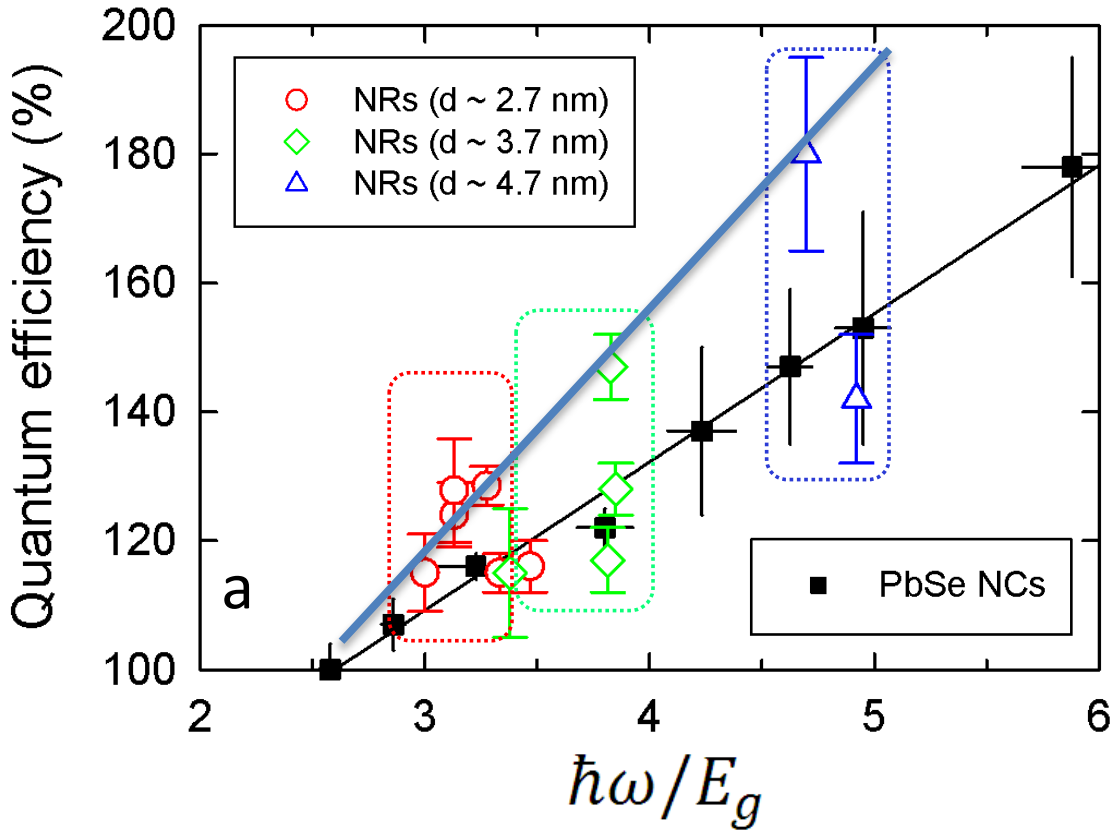


Length barely influences on the absorption and PL peak positions.

Excitons are confined in a 3D volume

Auger Recombination - Bimolecular

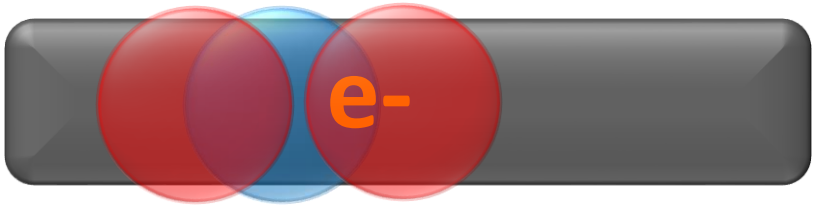
However, is the Coulomb Interaction the Same



CM may be higher, the same or even smaller for NRs than for QDs

Are Auger and CM rates really connected in this case?

Bimolecular type Auger recombination.



Effective Auger rate for the "Exciton Volume"

Padilha et.al. Nano Lett. 2013

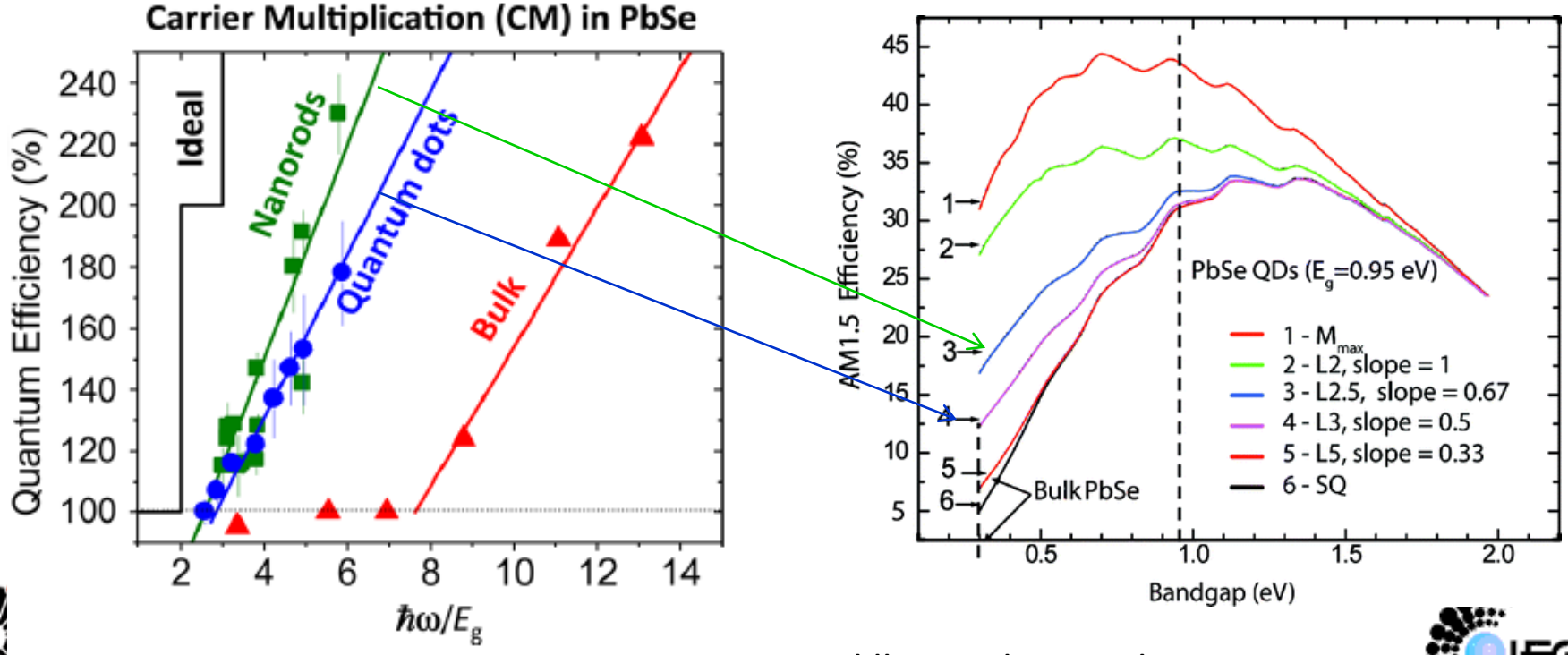
However, is the Coulomb Interaction the Same

Ultrafast Spectroscopy Laboratory

Enhanced Coulomb interaction enhances CM in NRs, but bimolecular Auger recombination slows down this process.

Elongated structure – if aligned, less hopping is necessary – better transport

Next new promising candidate for nanomaterial based solar cell.



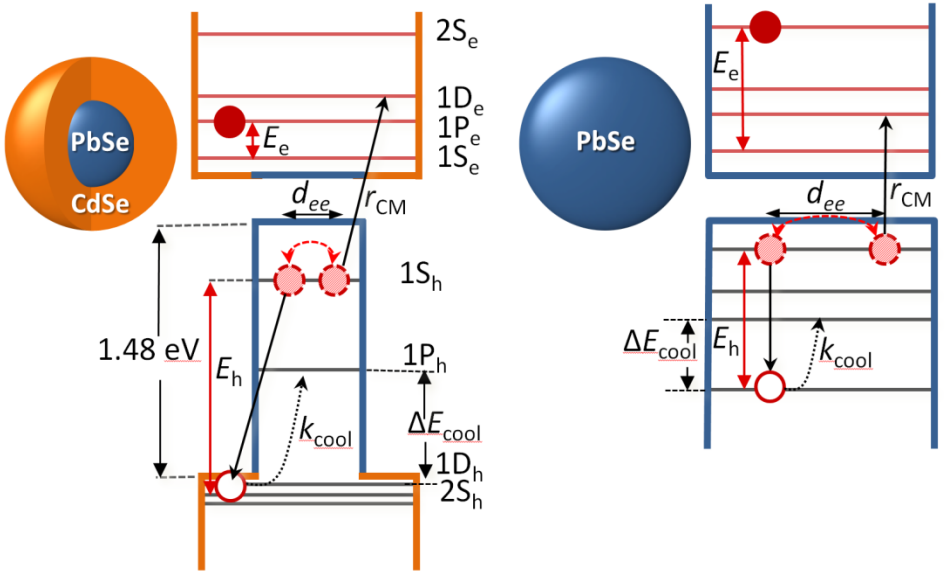
Padilha et.al. Acc. Chem. Res. 2013

UNICAMP

IFGW Instituto de Física Gleb Wataghin

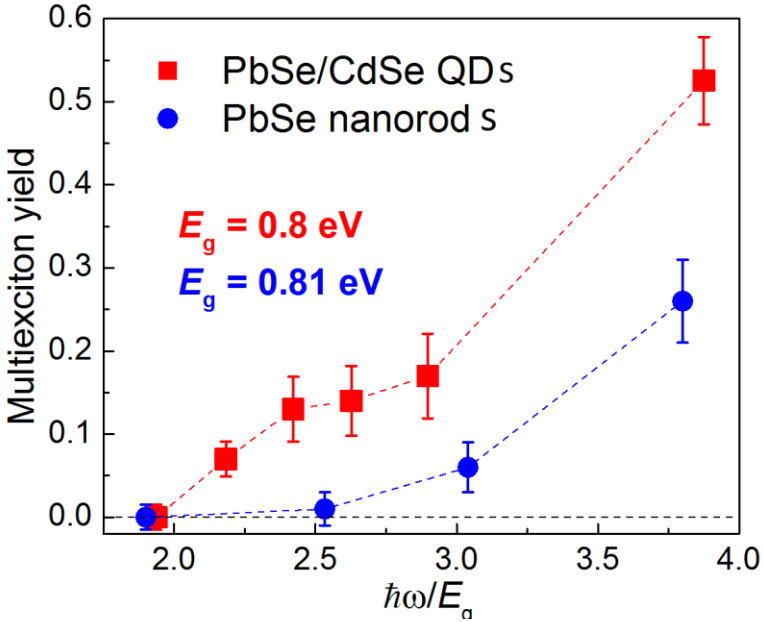
Engineering Quasi-Type-II Heterostructures

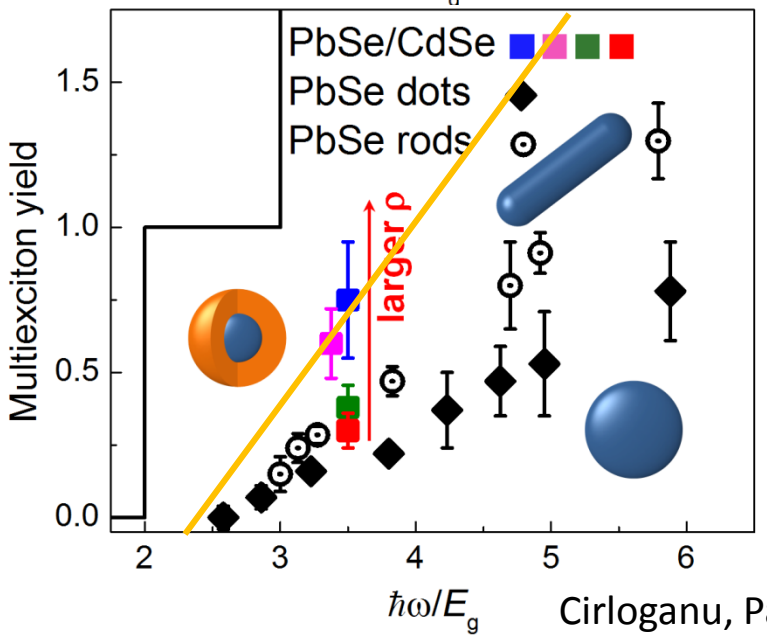
Increase CM efficiency by slowing down intraband cooling

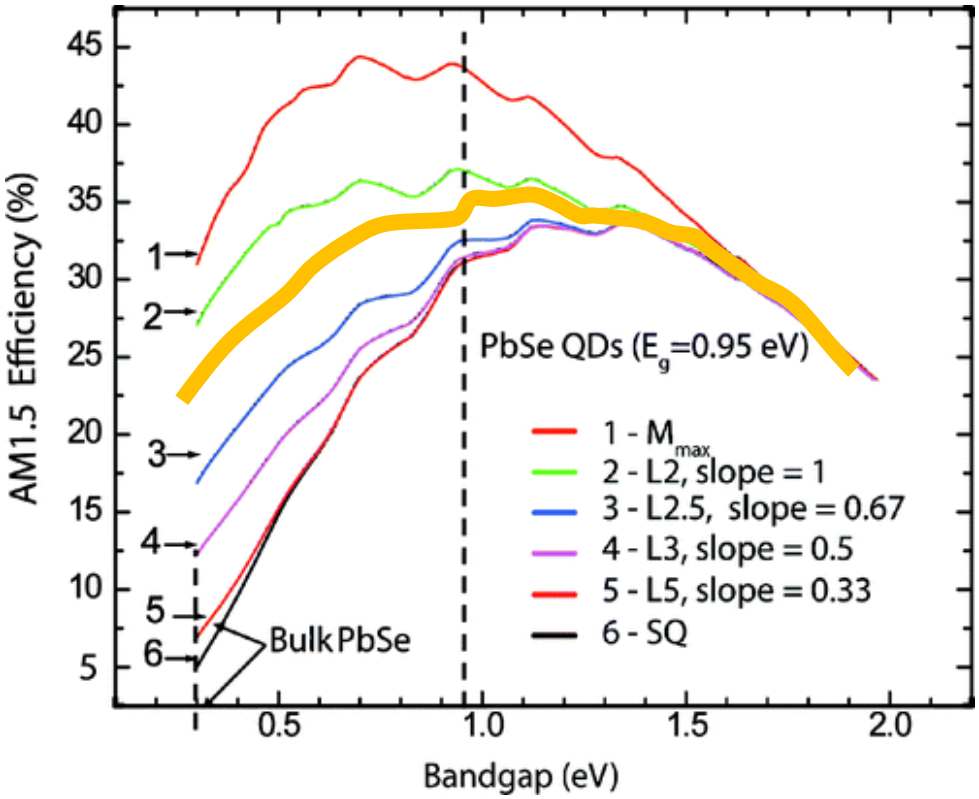


Cirloganu, Padilha et.al. Nat. Comm 2014

Engineering Quasi-Type-II Heterostructures







We have shown advances, but there is still a long way to go

Cirloganu, Padilha et.al. Nat. Comm 2014

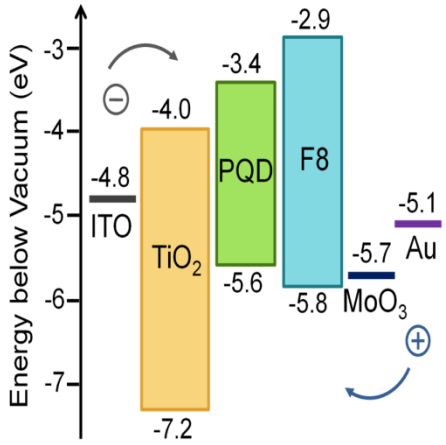
Cesium Lead Halide Perovskite QDs

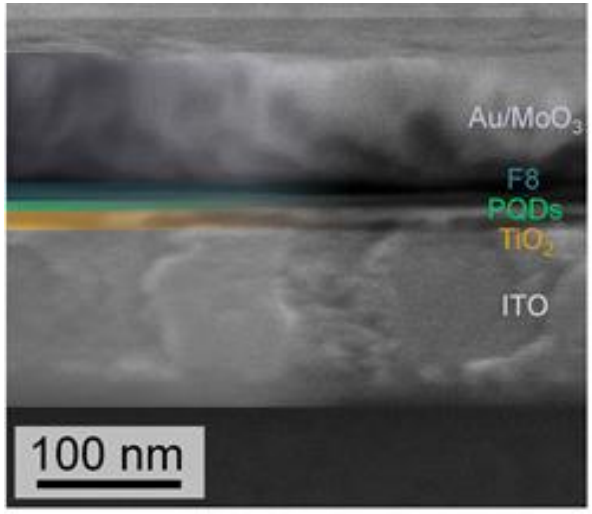
Ultrafast Spectroscopy Laboratory

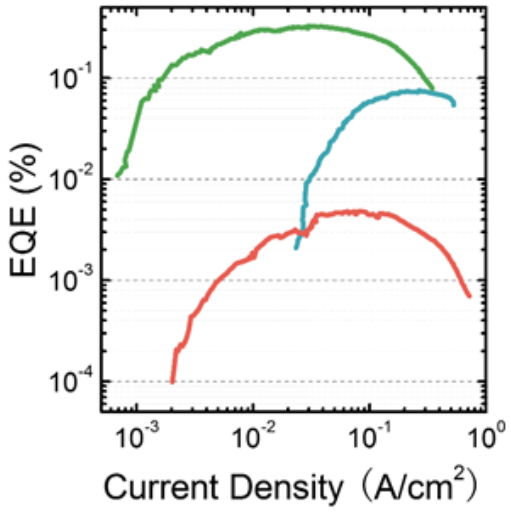
Perovskite based solar cell has the best increasing slope on efficiency out of any new solar cell technology – great electronic transport properties

Kovalenko's group shows that Cesium Lead Halide Perovskite QDs can be tunned thorugh the entire visible spectrum with high emission QY and narrow band.

Nevertheless, efficiency for LED's are way below what was hoped for.







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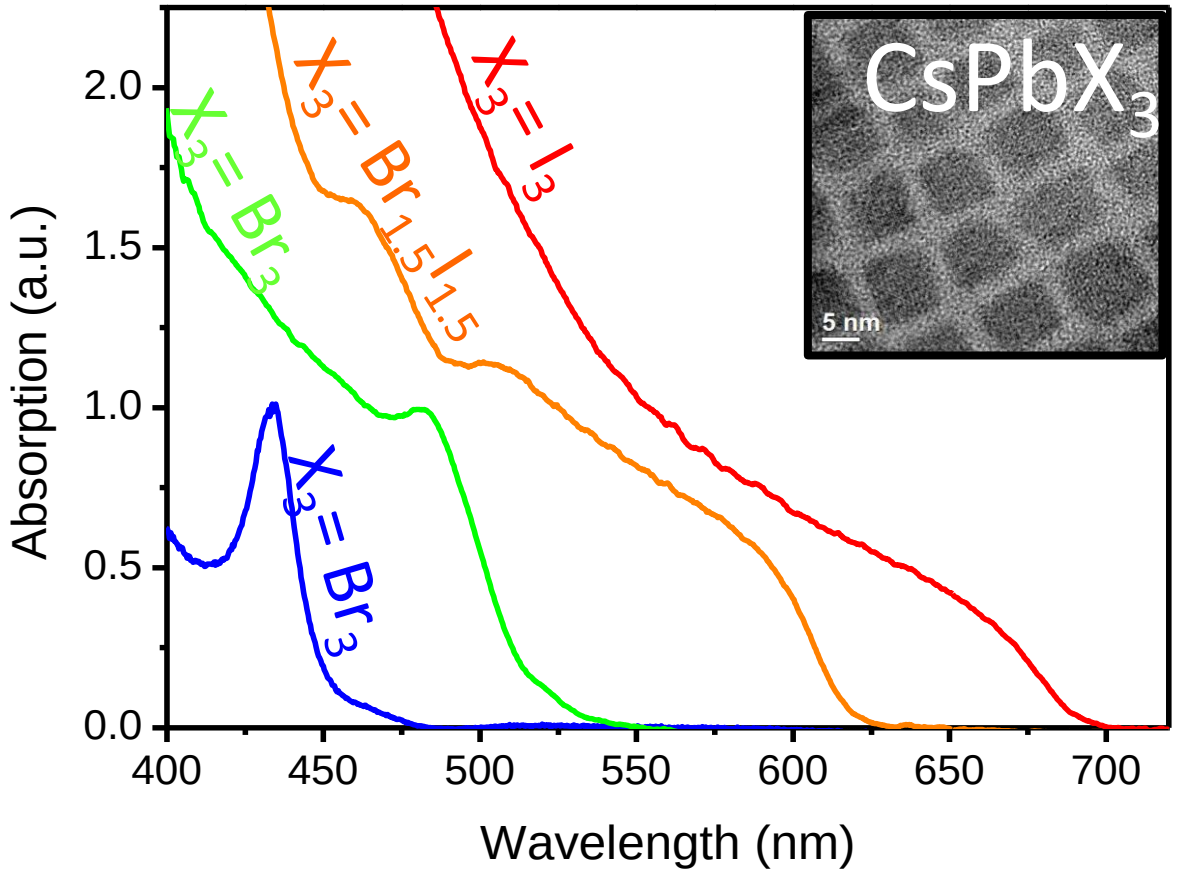
Yassitepe et.al. Submitted 2016

IFGW Instituto de Física Gleb Wataghin

Cesium Lead Halide Perovskite QDs

Ultrafast Spectroscopy Laboratory

Several bromide and iodide samples with volume changing by over one order of magnitude



Absorption band gap varying from

Bromide:
434 nm to 508 nm

Iodide:
640 nm to 685 nm

UNICAMP

Castaneda et.al. Submitted 2016

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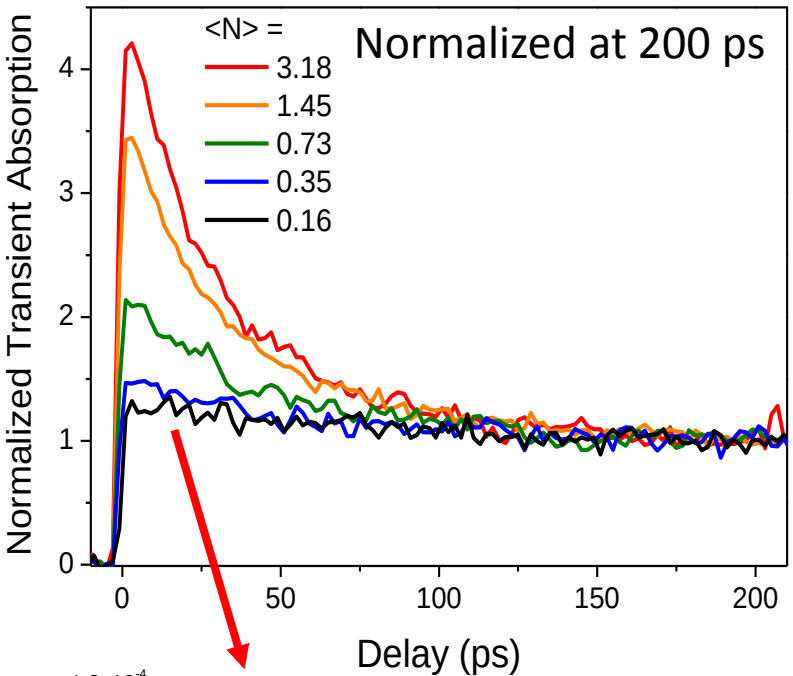
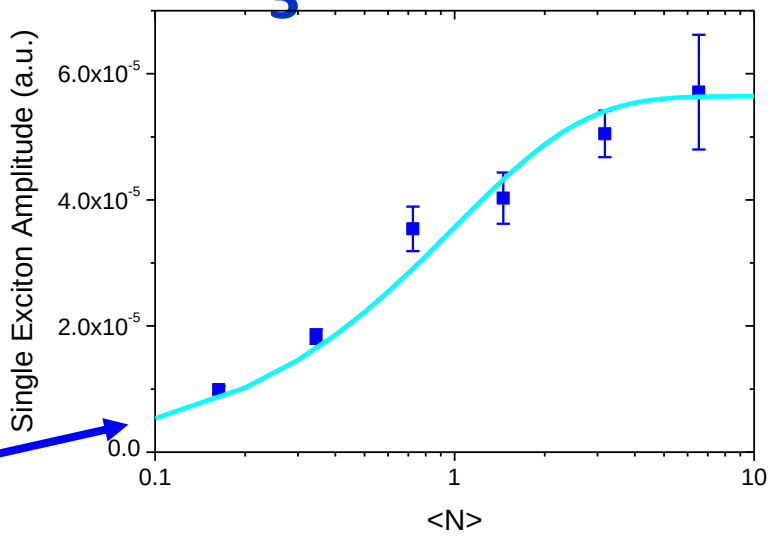
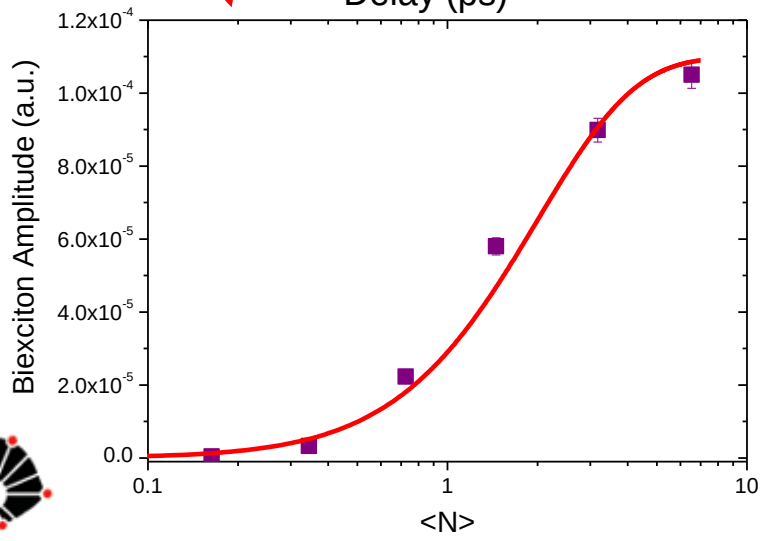
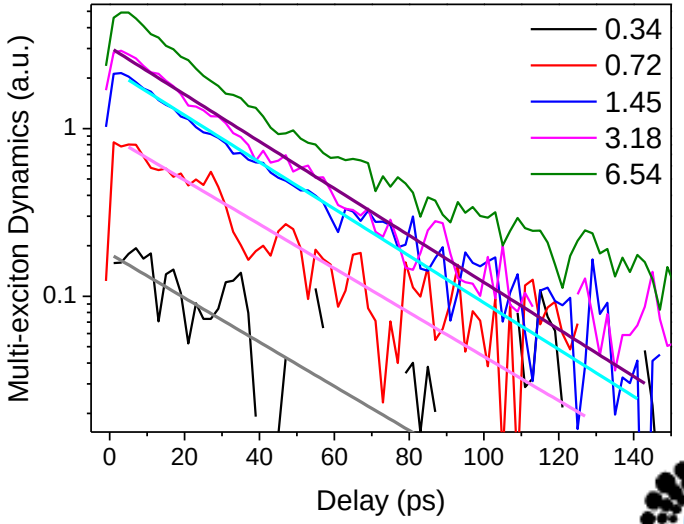
Transient Absorption – $CsPbBr_3$





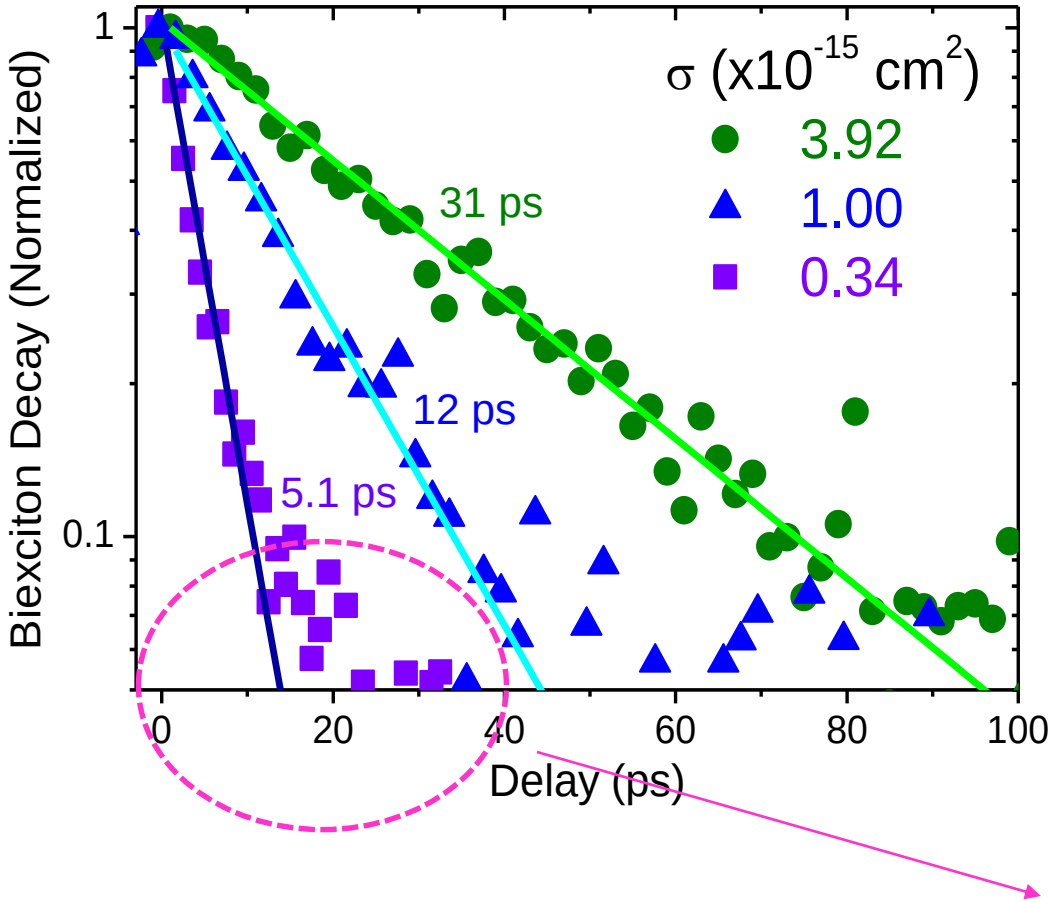
After subtracting the normalized low energy scan, all is left is a fast single decay of about 31 ps





Castaneda et.al. Submitted 2016

Transient Absorption – $CsPbBr_3$



Measuring the biexciton lifetime we observe that:

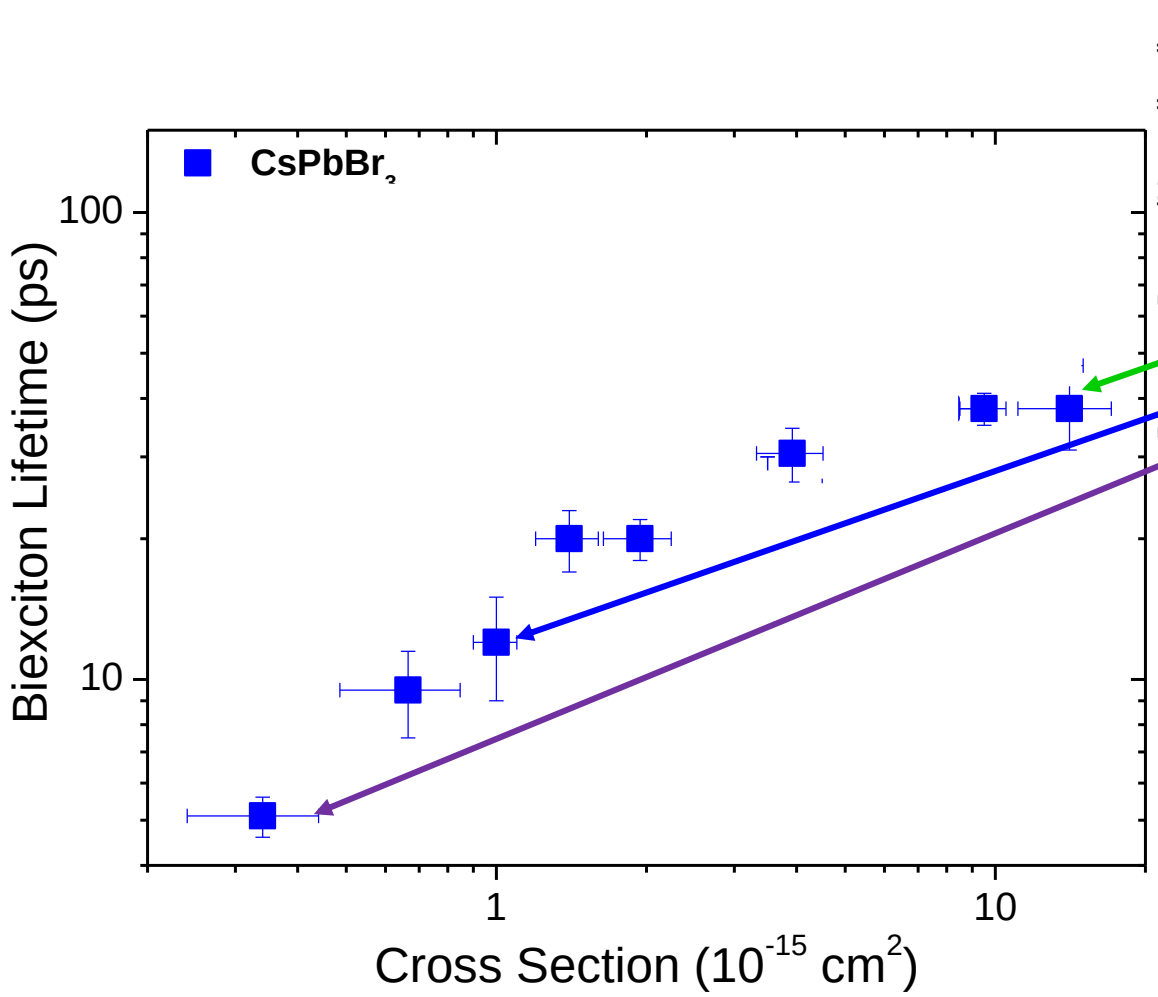
1) For cross section above ~ 2×10^{-15} cm^2 the size dependence of the lifetime is sublinear

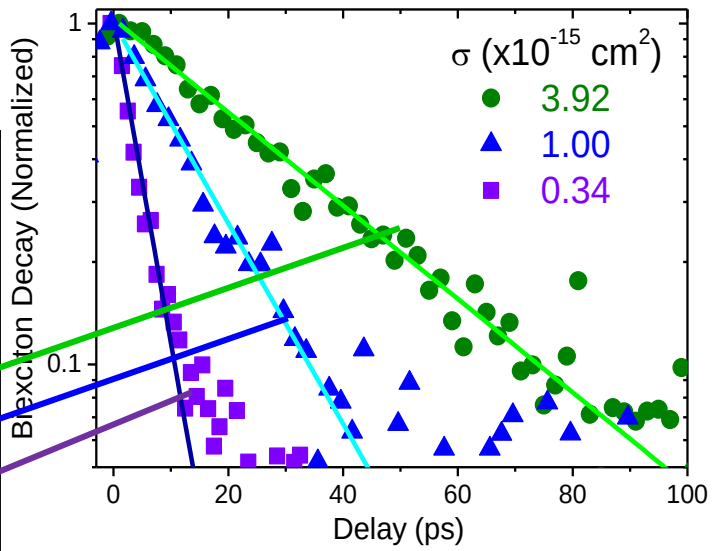
2) For smaller sizes, the dependence becomes linear!

3) Trion might be present, but it is not responsible for more than about 10% of the signal!

Castaneda et.al. Submitted 2016

Transient Absorption – $CsPbBr_3$



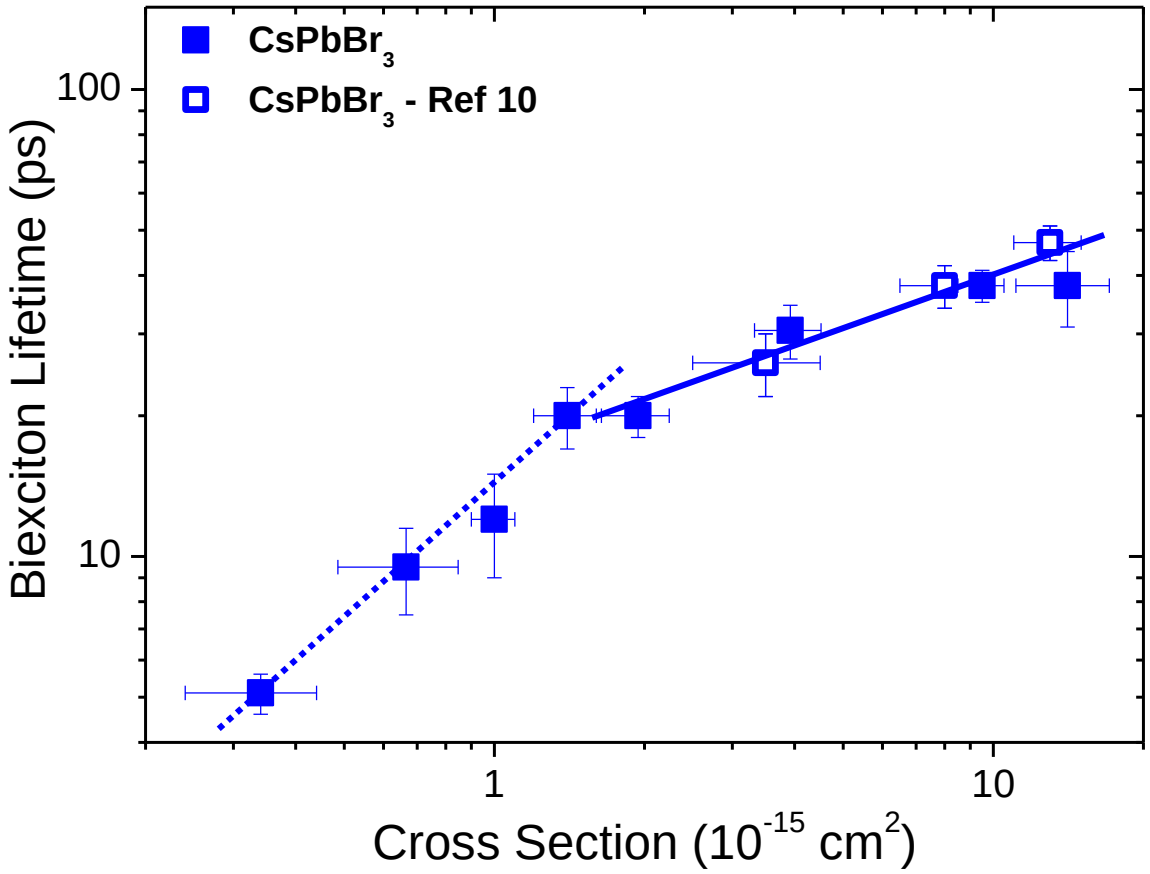


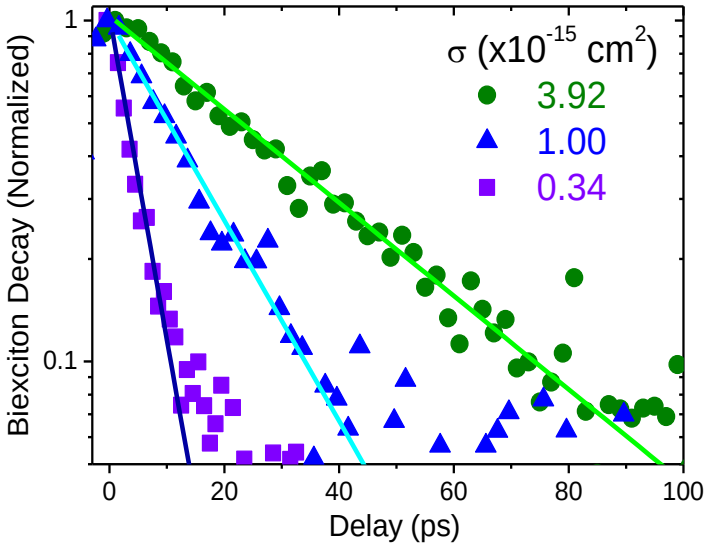
There is a clear change in slope for the size dependence of the biexciton lifetime

Good agreement between current and literature data

Castaneda et.al. Submitted 2016

Transient Absorption – $CsPbBr_3$





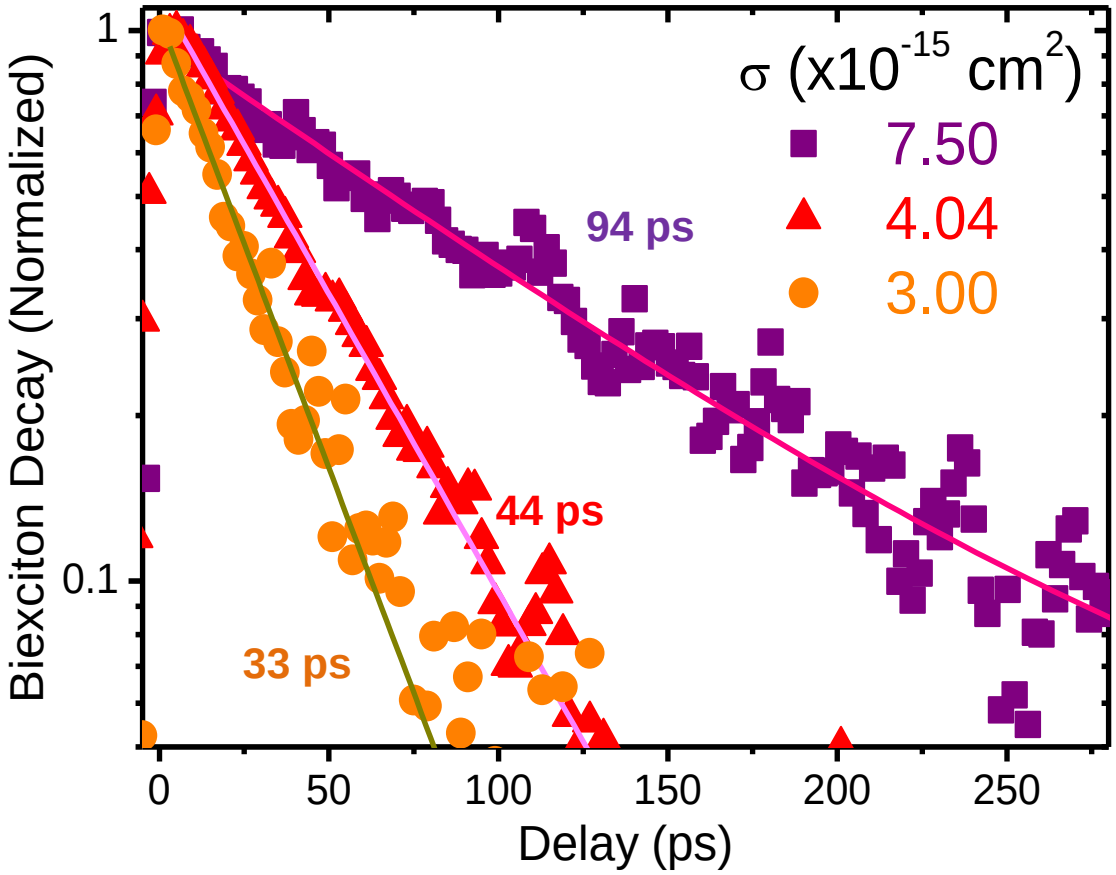
Dotted line is the power dependence fit for the 4 smallest PQDs and has a slope of 0.93

Full line is the power dependence fit for the largest PQDs and has a slope of 0.38

[10] Makarov et.al. Nano Lett. 2016

Castaneda et.al. Submitted 2016

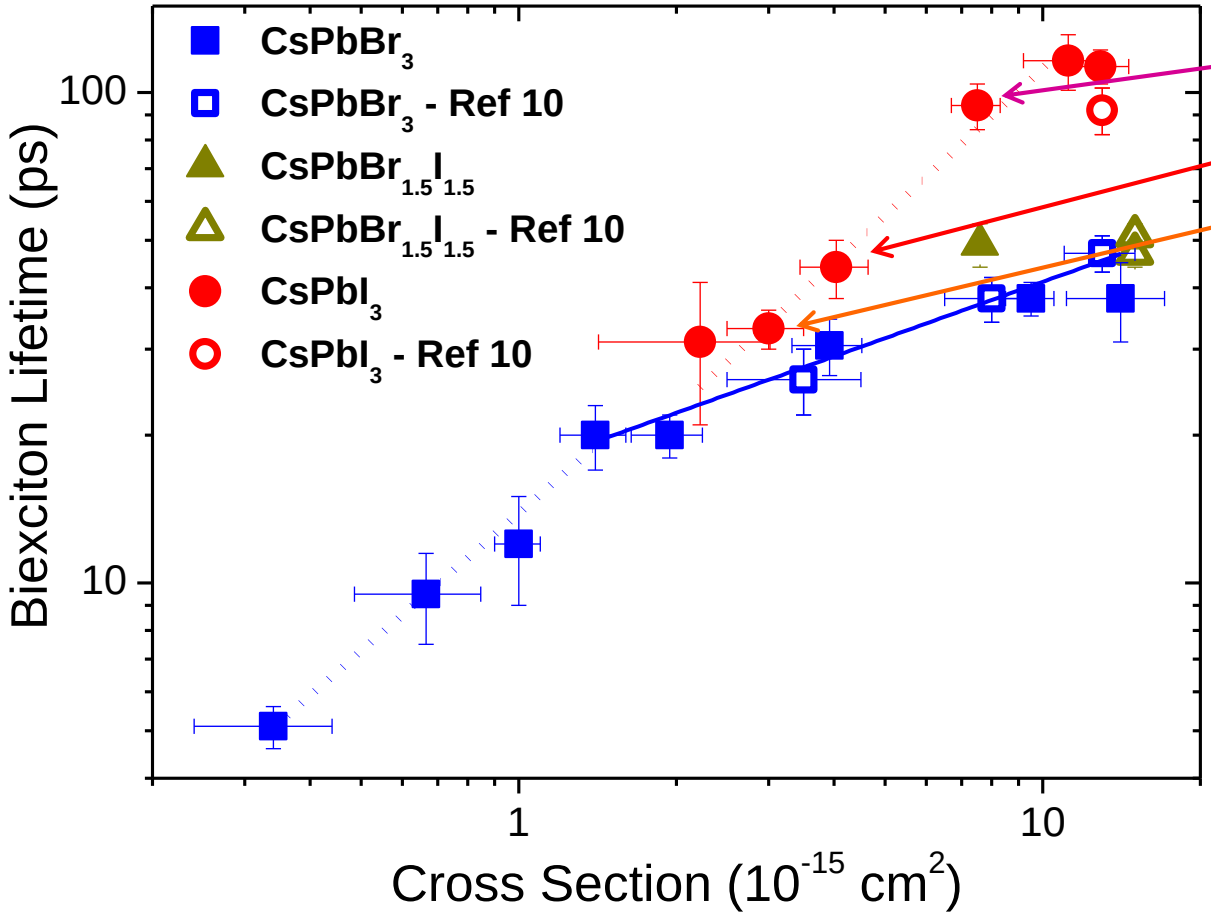
Transient Absorption – $CsPbI_3$

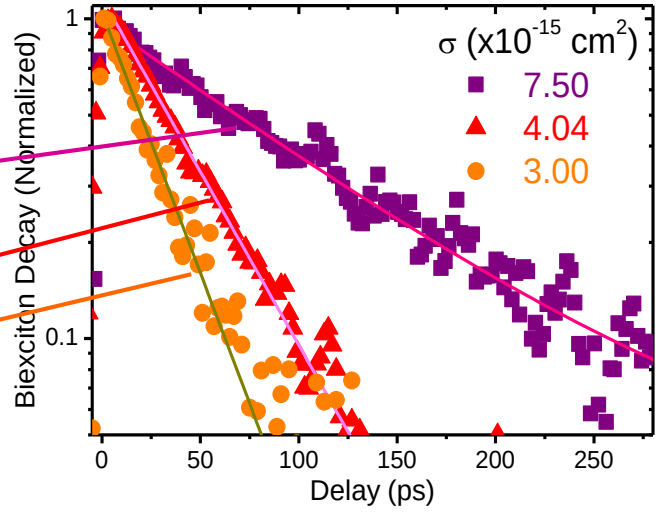


We observe strong size dependence even for large PQDs.

Castaneda et.al. Submitted 2016

Transient Absorption – $CsPbI_3$





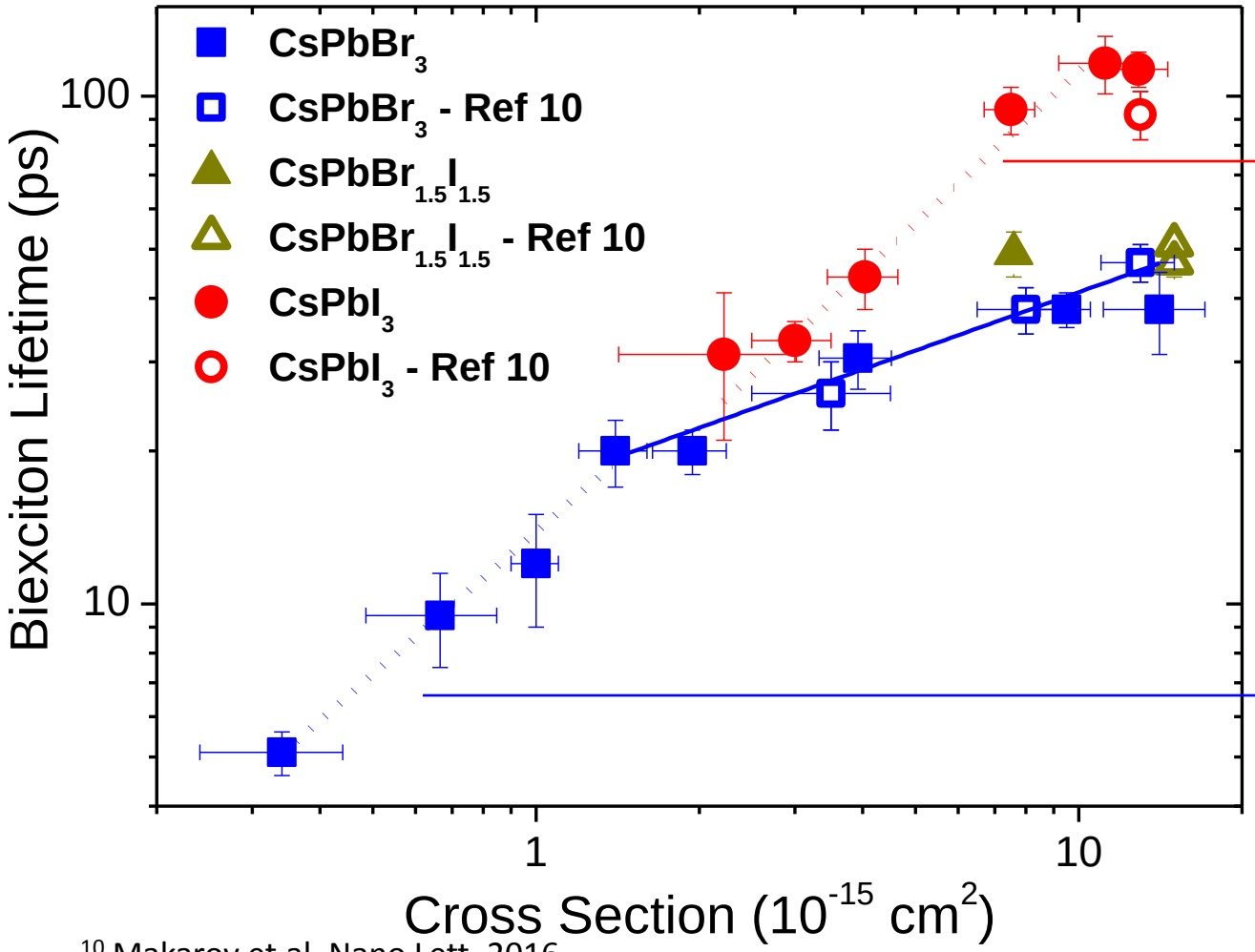
Slope for the iodide sample is near 1, indicating linear dependence.

Good agreement between current and literature data

[10] Makarov et.al. Nano Lett. 2016

Castaneda et.al. Submitted 2016

Perovskite – Biexciton Lifetime Summary



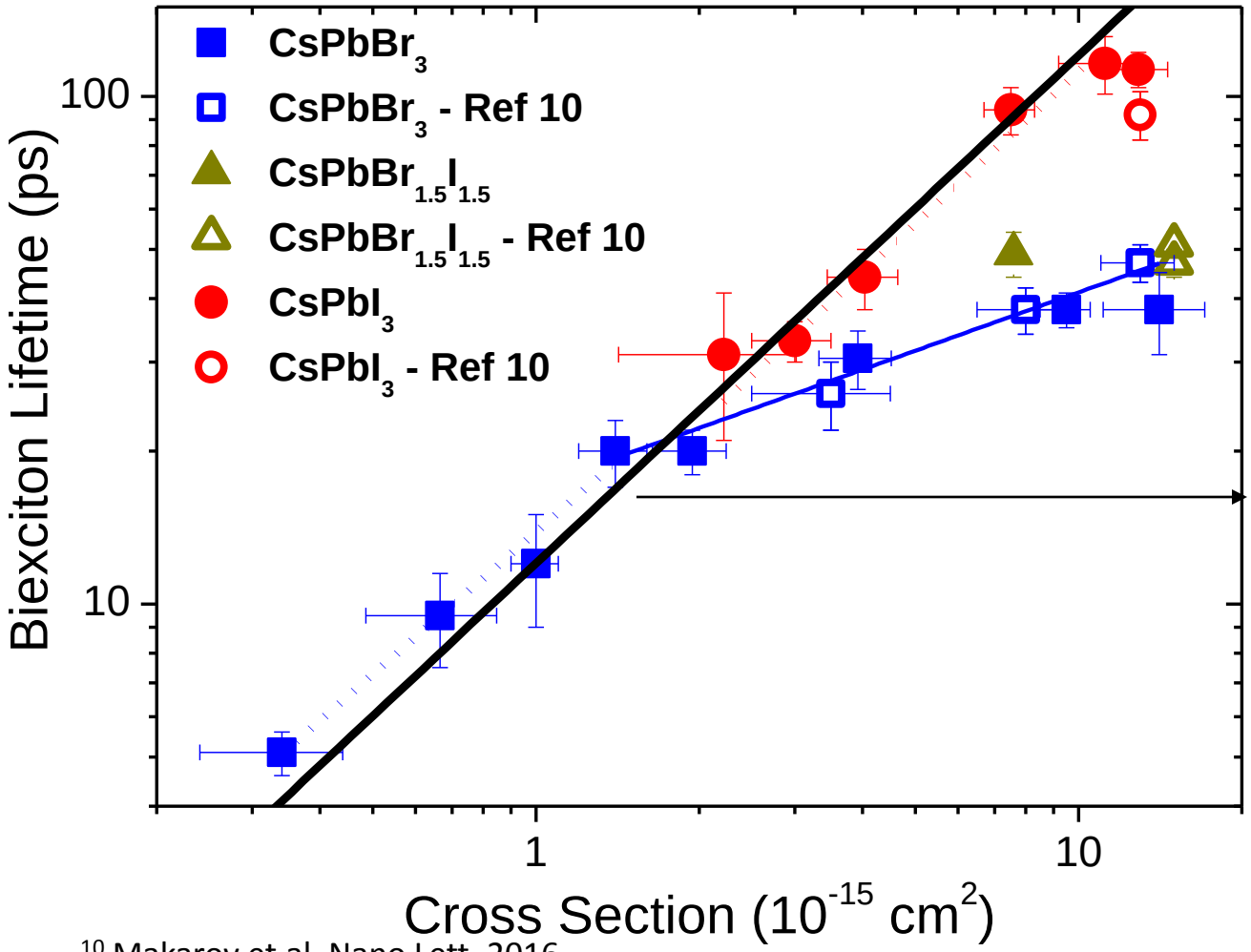
Linear dependence

Linear dependence

[10] Makarov et.al. Nano Lett. 2016

Castaneda et.al. Submitted 2016

Perovskite – Biexciton Lifetime Summary

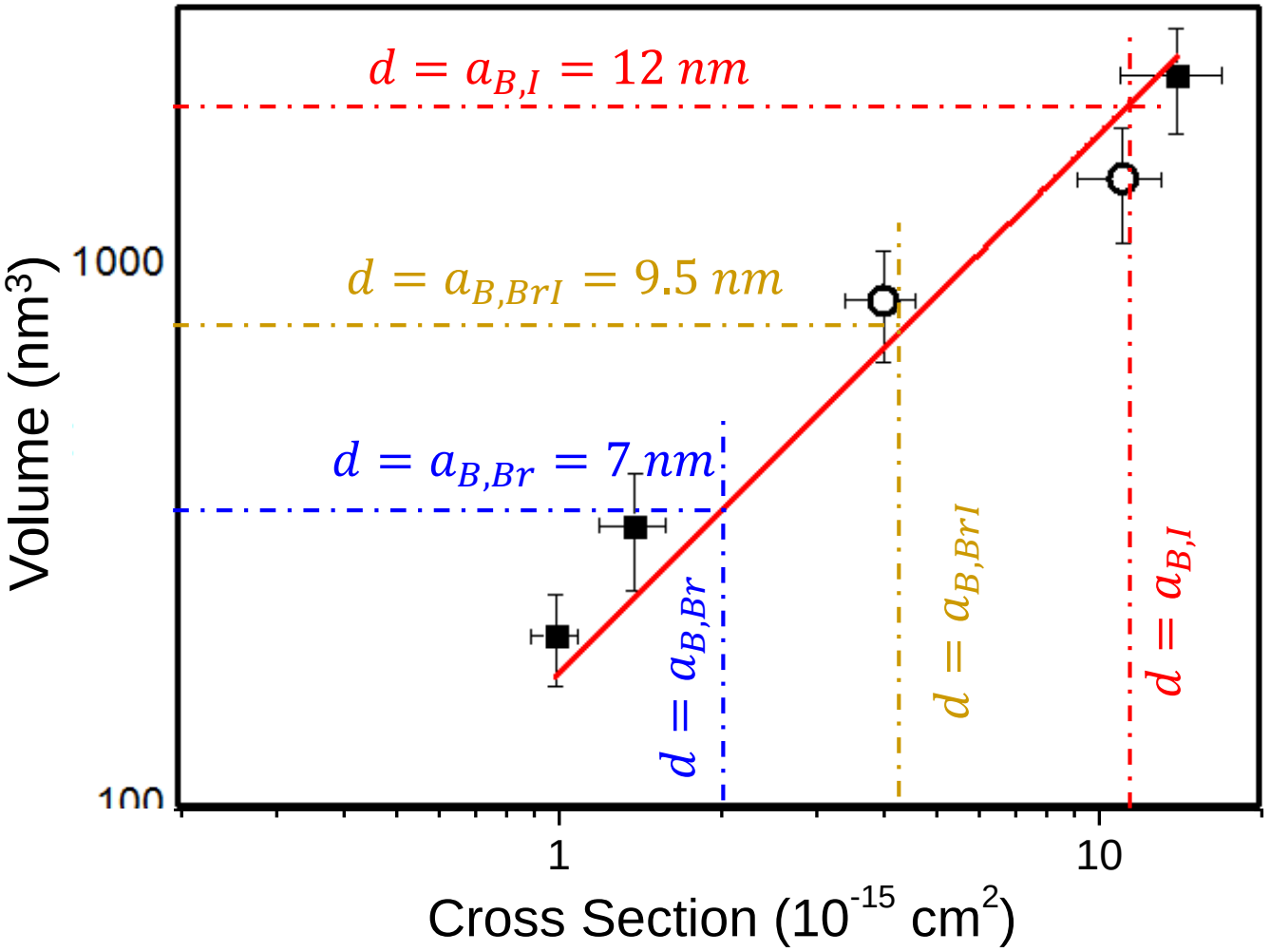


Single linear fit can accomodate all the data for iodine and small bromide

[10] Makarov et.al. Nano Lett. 2016

Castaneda et.al. Submitted 2016

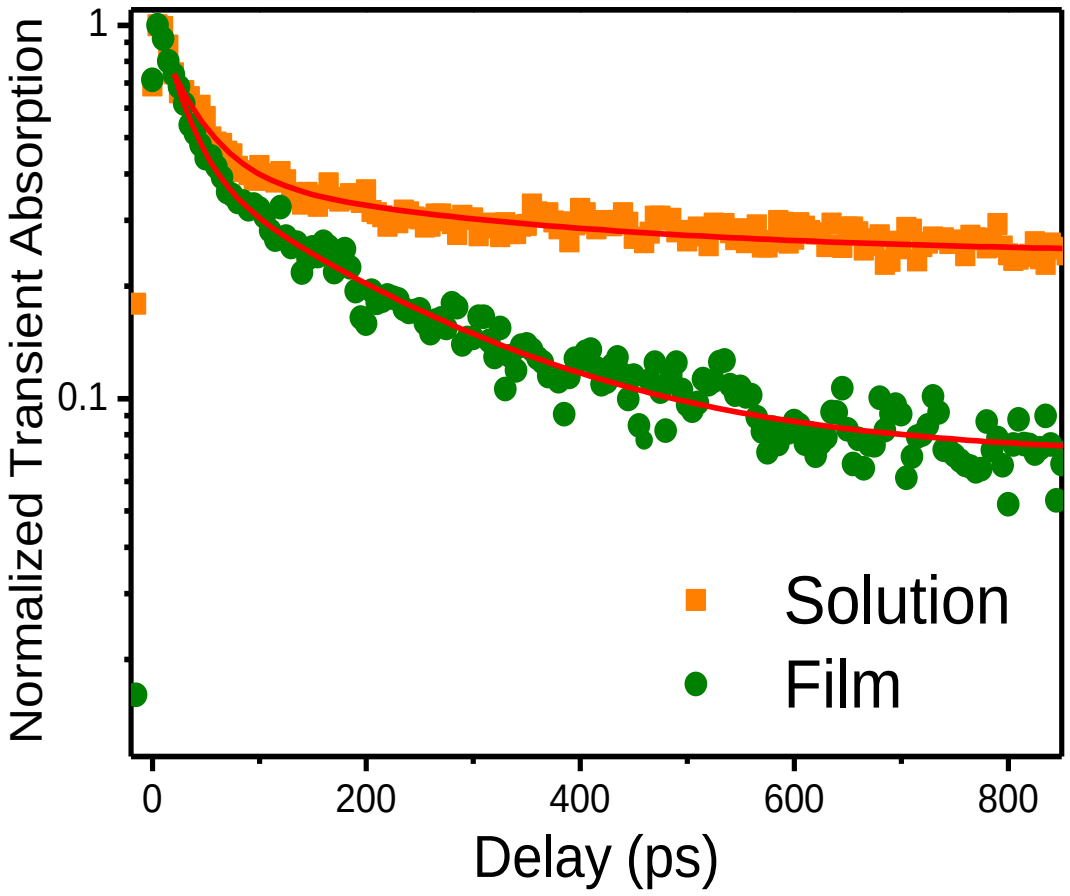
Perovskite – Biexciton Lifetime Summary



Data suggest that the break of the volume scaling occurs for PQDs larger than the Exciton Bohr radius

Castaneda et.al. Submitted 2016

Influence of Trion



Trion is also very fast in PQDs

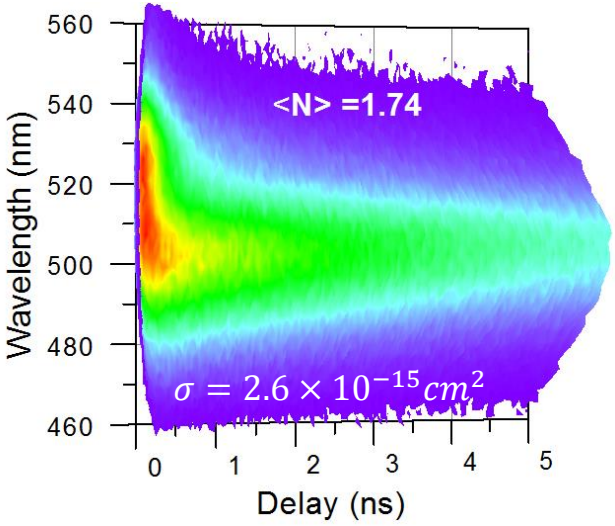
$$QY^* = \frac{2\tau_{X*}}{\tau_X} QY$$

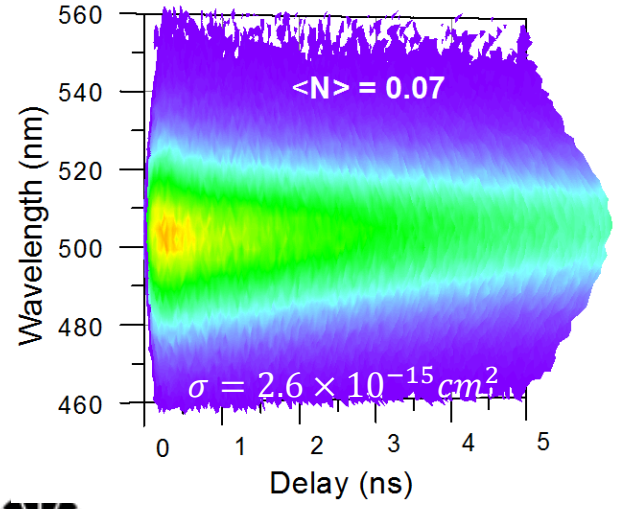
Assuming PL lifetime ~ 6 ns and QY of about 50%

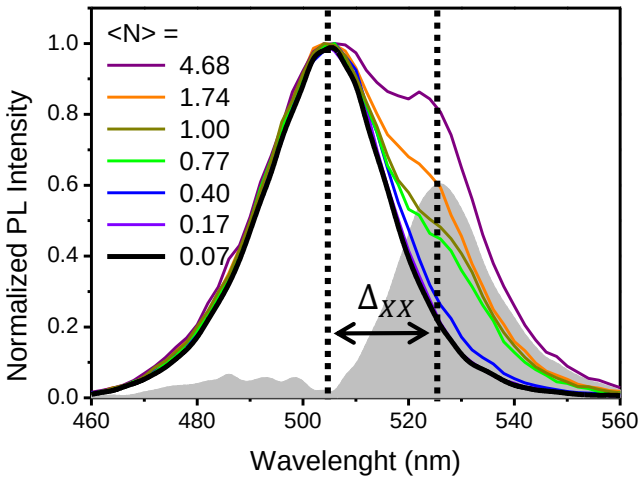
$$QY^* \cong 3\%$$

Castaneda et.al. Submitted 2016

Biexciton Binding Energy



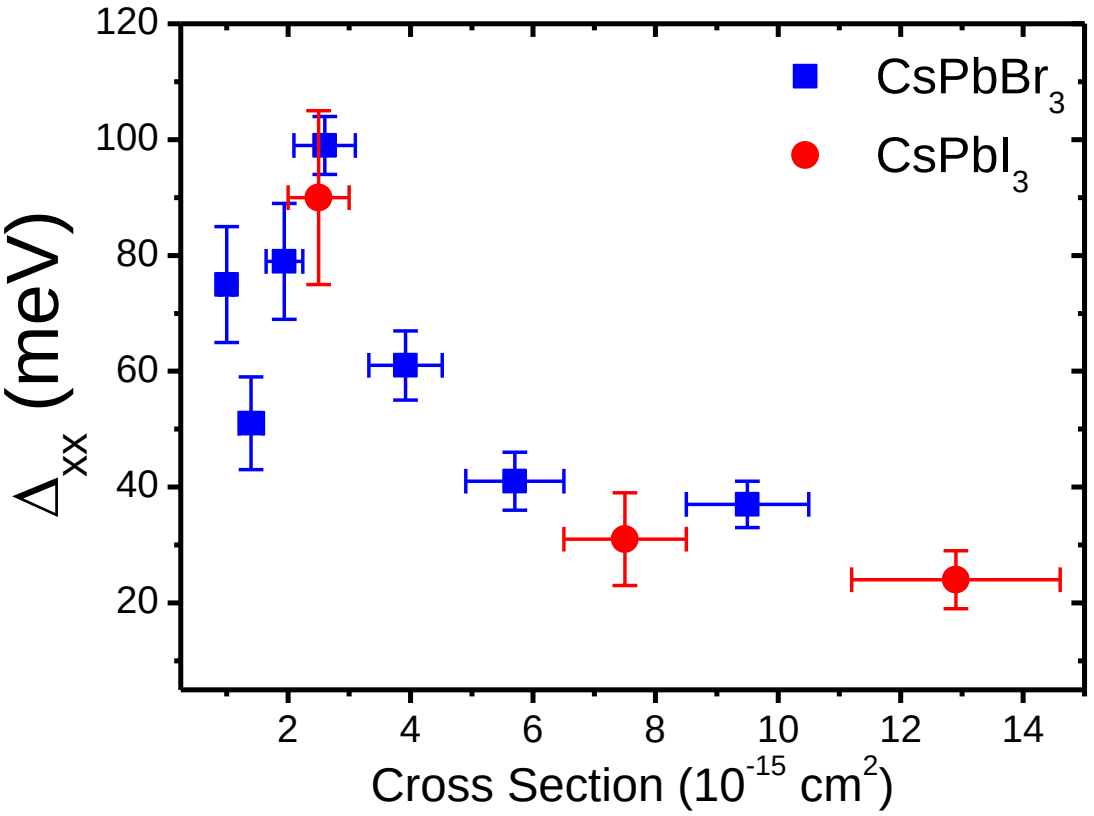




To quantify the shift we analyze the evolution of the low energy shoulder as the pump intensity increases

Castaneda et.al. Submitted 2016

Biexciton Binding Energy

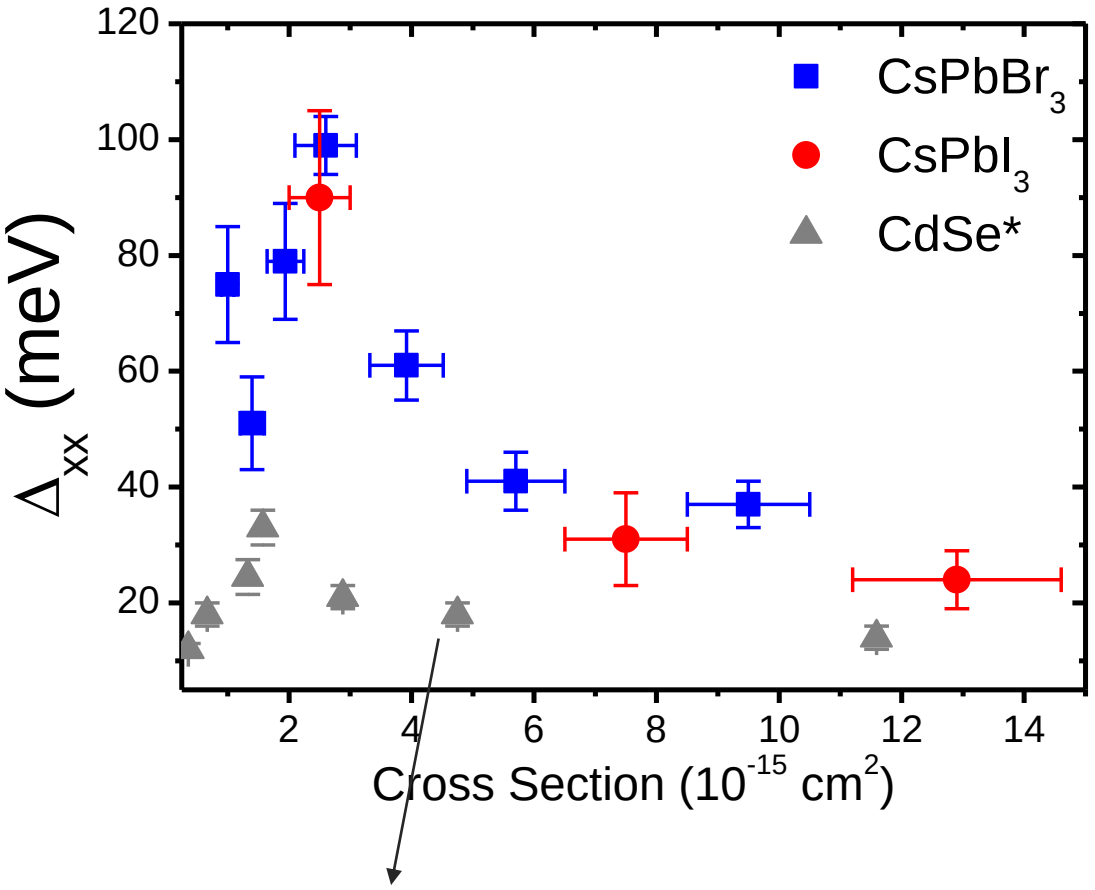


Mostly the binding energy increases as the QD is made smaller.

For very small bromide samples, this energy appears to start to decrease.

Castaneda et.al. Submitted 2016

Biexciton Binding Energy



Literature data for CdSe QDs

Similar behavior has been previously observed for CdSe QDs.

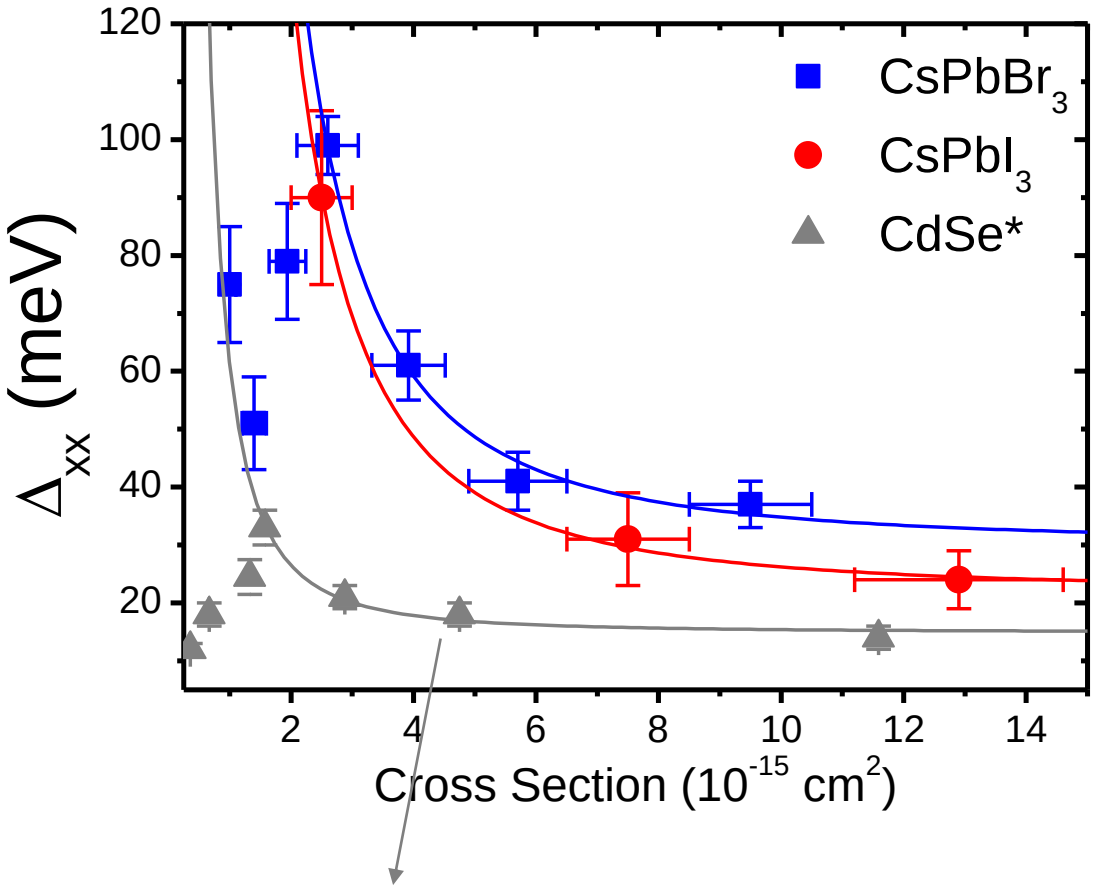
Binding energy is about 3x stronger in PQDs – Stronger Coulomb interaction!

Electron-electron and hole-hole Coulomb repulsion in small QDs could lead to such behavior.

*Achermann et.al. PRB 2003

Castaneda et.al. Submitted 2016

Biexciton Binding Energy



Literature data for CdSe QDs

Exciton binding energy in bromide perovskite (bulk) is nearly 40 meV, in iodide (bulk) it is 23 meV and in CdSe (bulk) is ~ 15 meV.

The data suggest that, at the limit for the very large PQDs, the **biexciton binding energy** is comparable to the **exciton binding energy in bulk**: Bromide (30 meV) and Iodide (21 meV)

*Achermann et.al. PRB 2003

Castaneda et.al. Submitted 2016

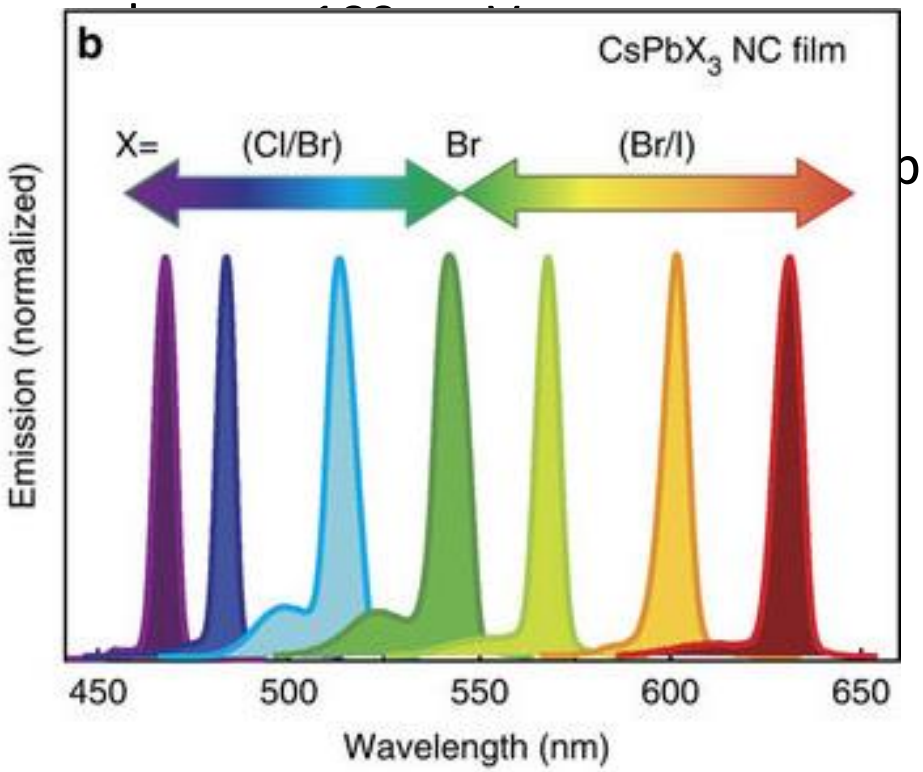
Conclusions and Perspectives

Very strong Coulomb interaction in PQDs – “Effective Volume” much smaller than the real volume.

Biexciton binding energy ca

Very fast multi-exciton inte

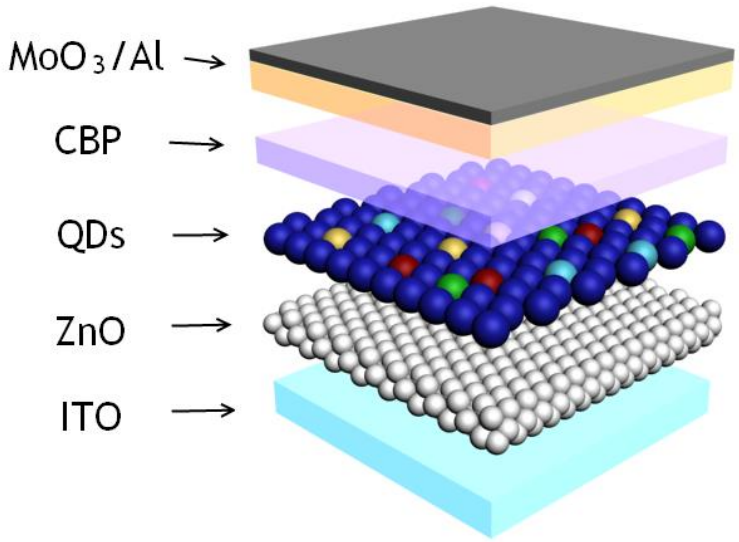
and further material develc

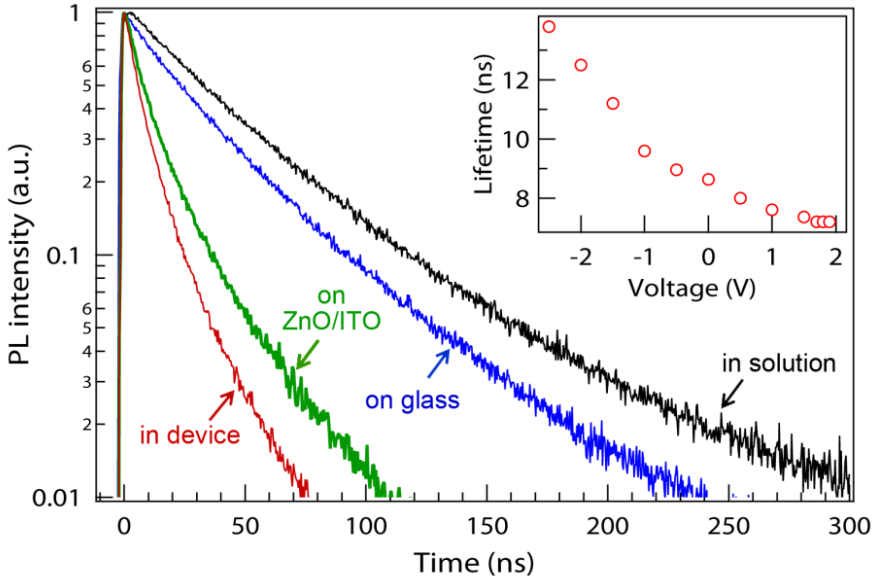


Yakunin, et.al., Nat. Comm. (2015)

Auger Recombination – A villain of QD based LED

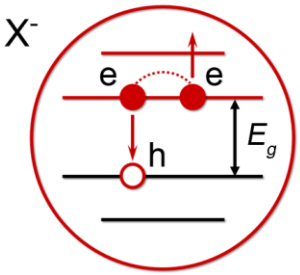
Device structure





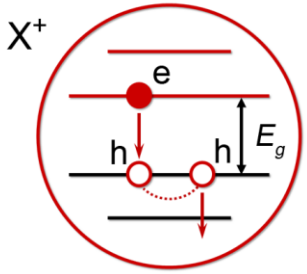
a

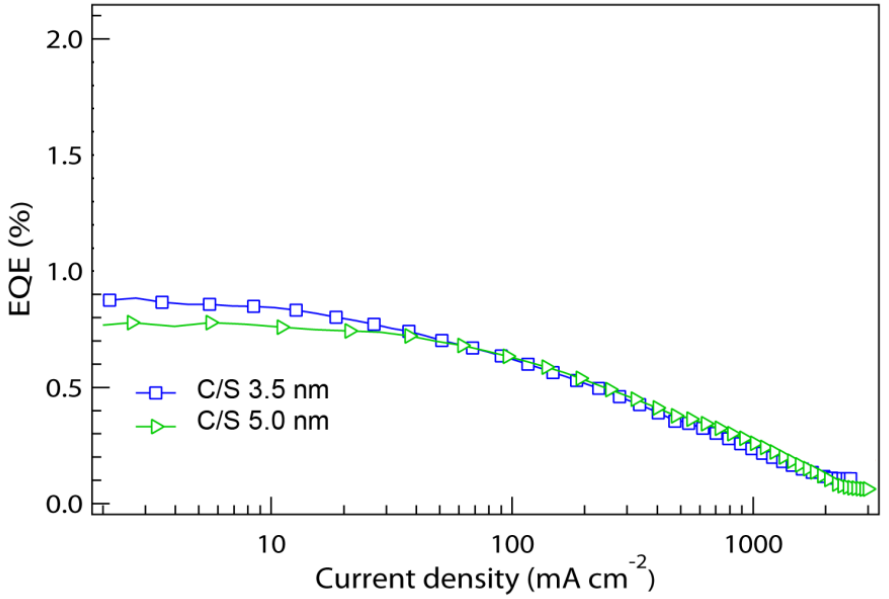
Auger recombination
in the presence of extra electron



b

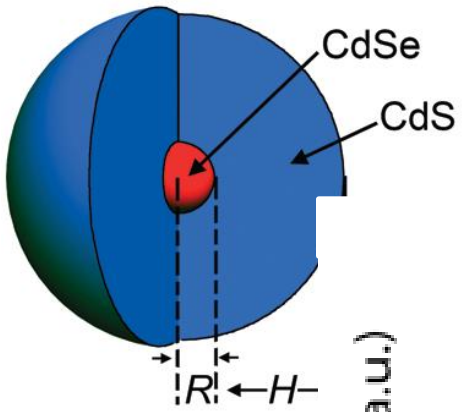
Auger recombination
in the presence of extra hole

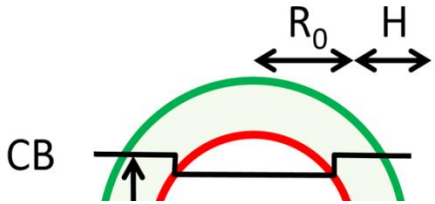


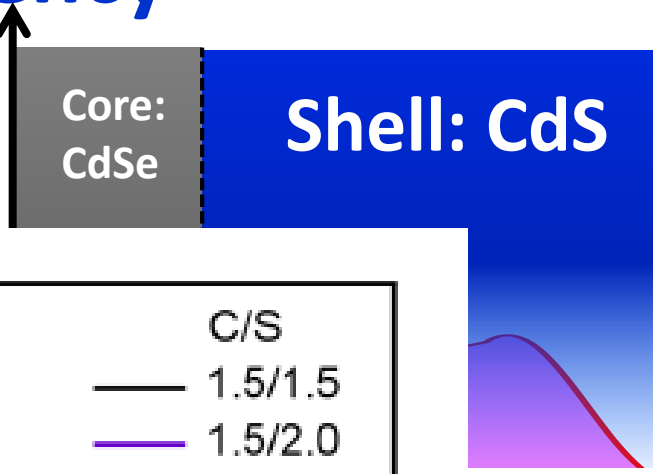


Bae, et.al, Nat. Comm. 2013

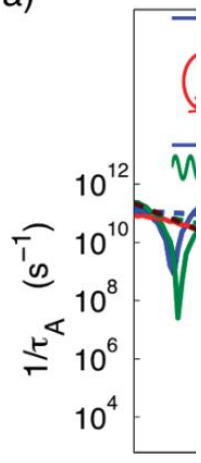
Ways to reduce Auger efficiency

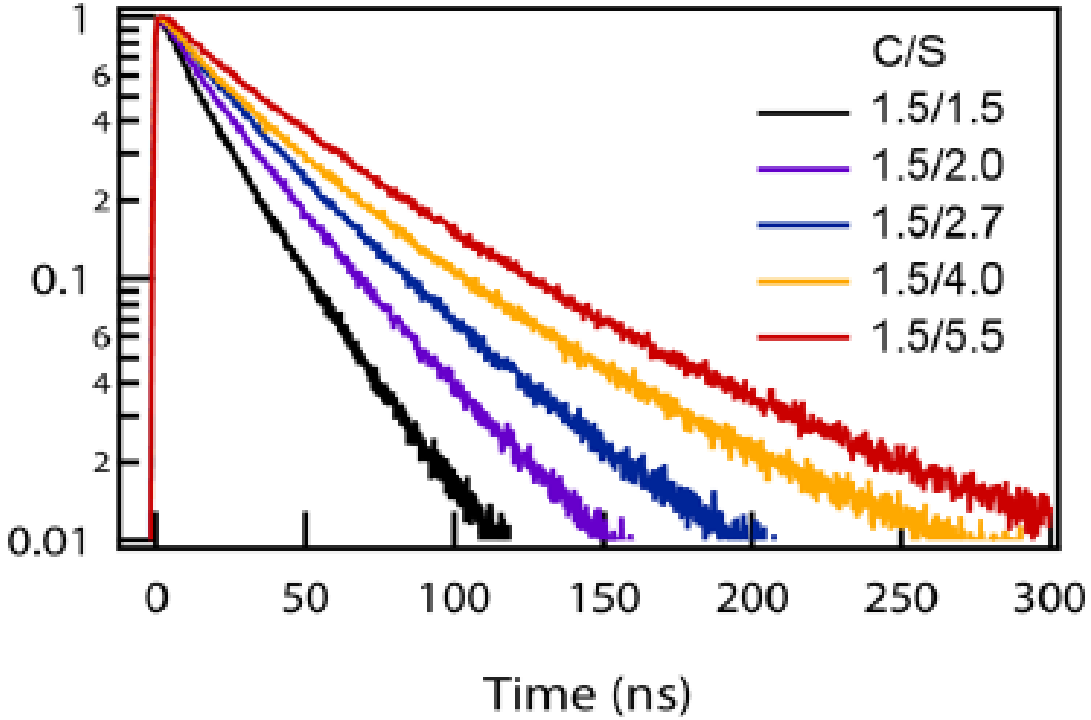






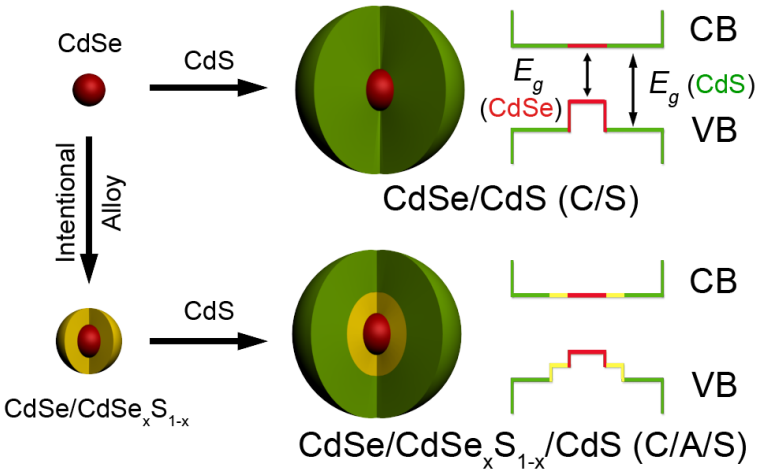
a)

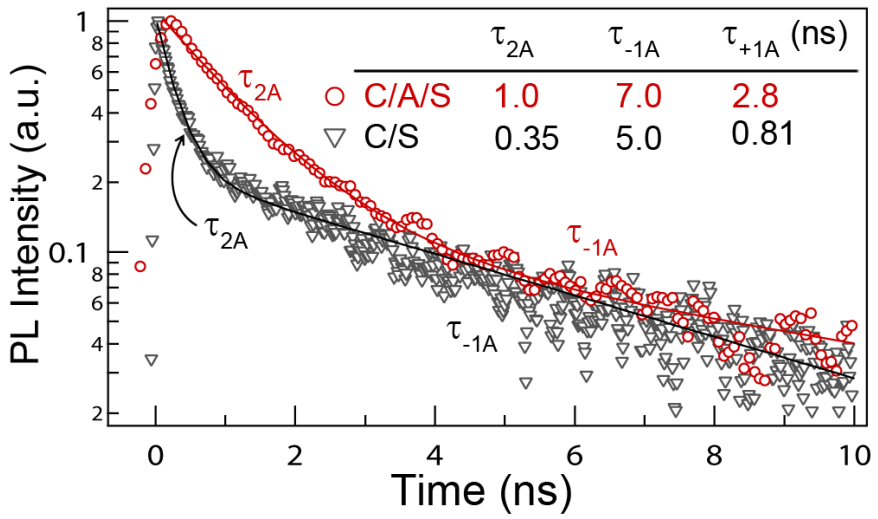


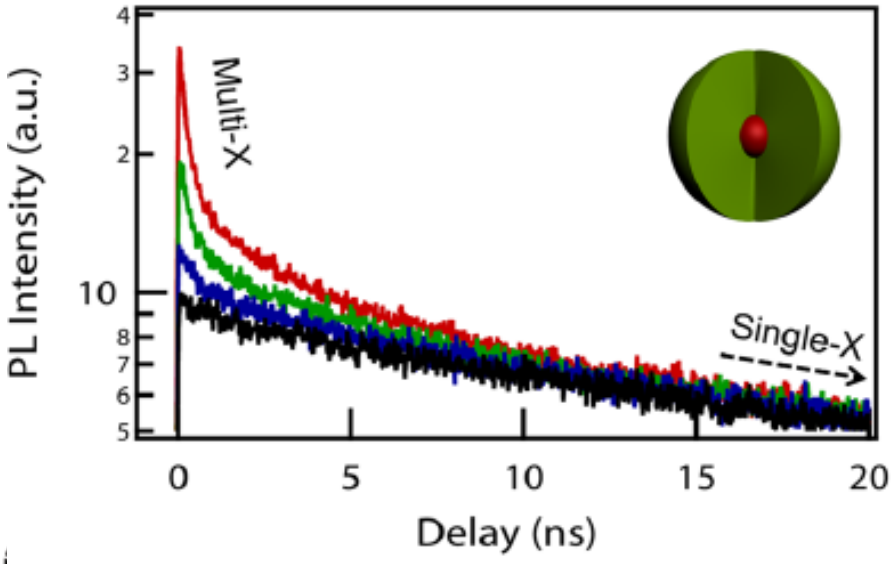


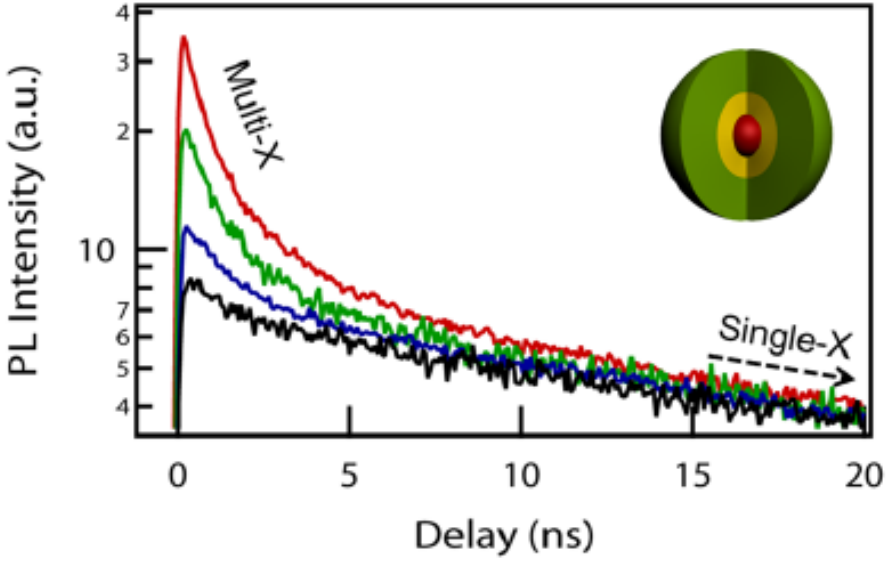
George E. Cragg *et al.*, *Nano Lett.* **2010**, *10*, 313.

Smoother Interface, Slower Auger





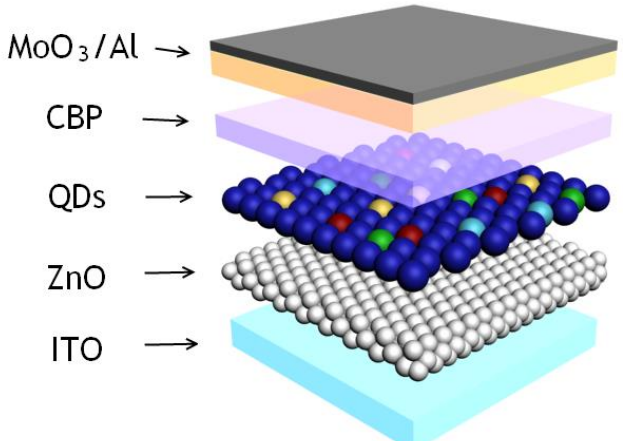


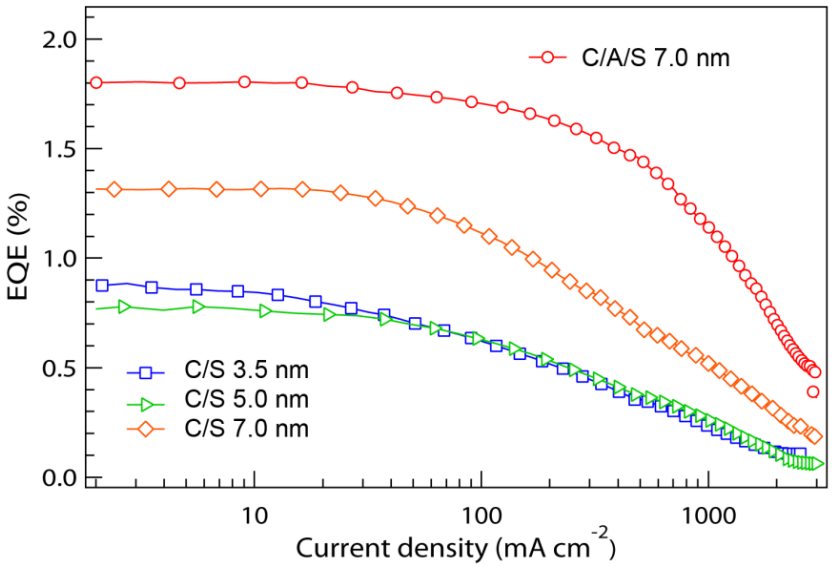


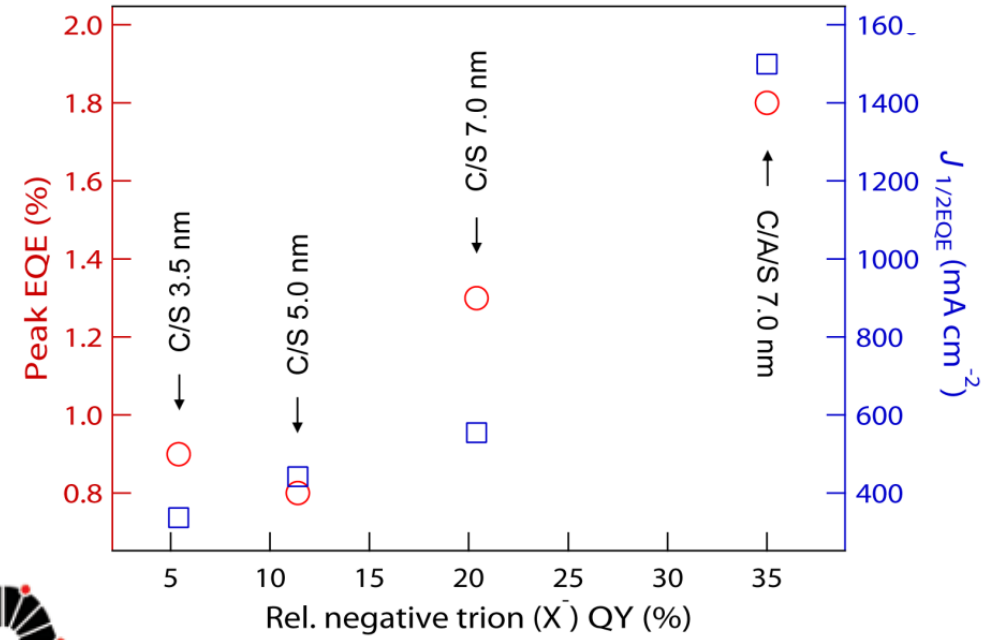
Bae, et.al, ACS Nano. 2012

QD based LED

Device structure



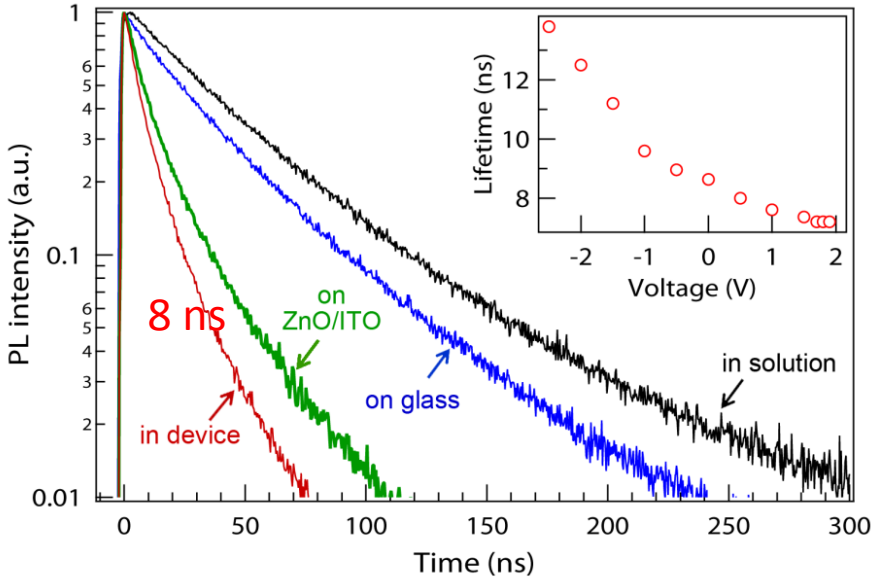


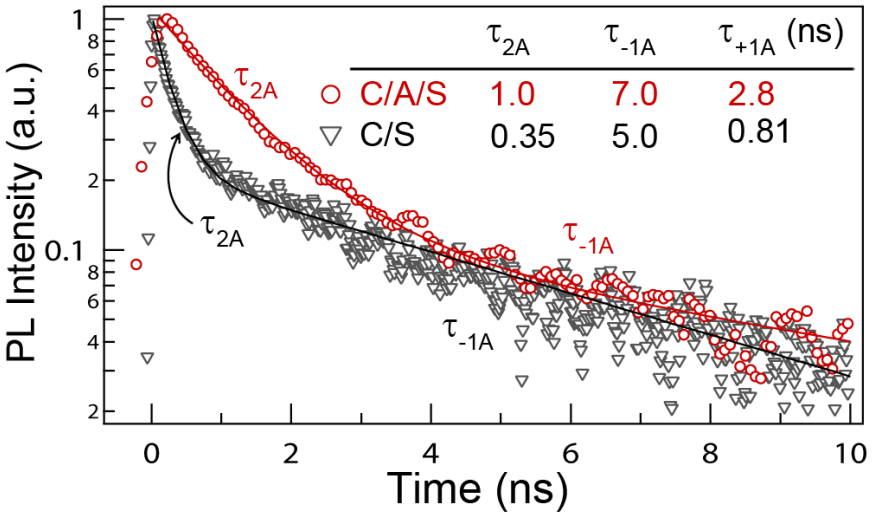


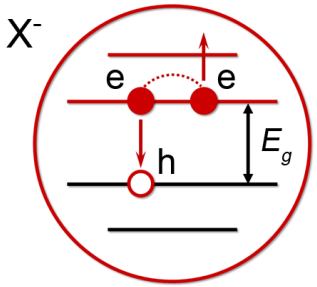
Slower Auger results in higher peak EQE and roll-off current

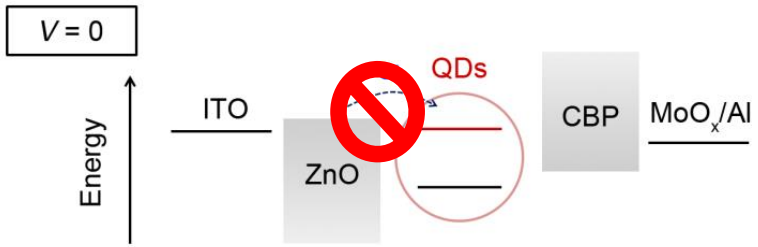
Bae et. al. Nature Comm 2013

QD based LED





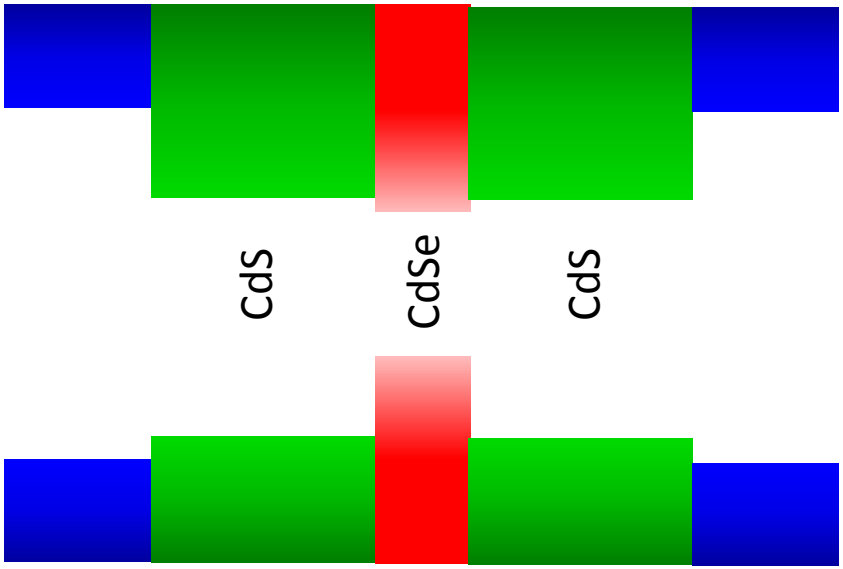




Bae et. al. Nature Comm 2013

QD based LED

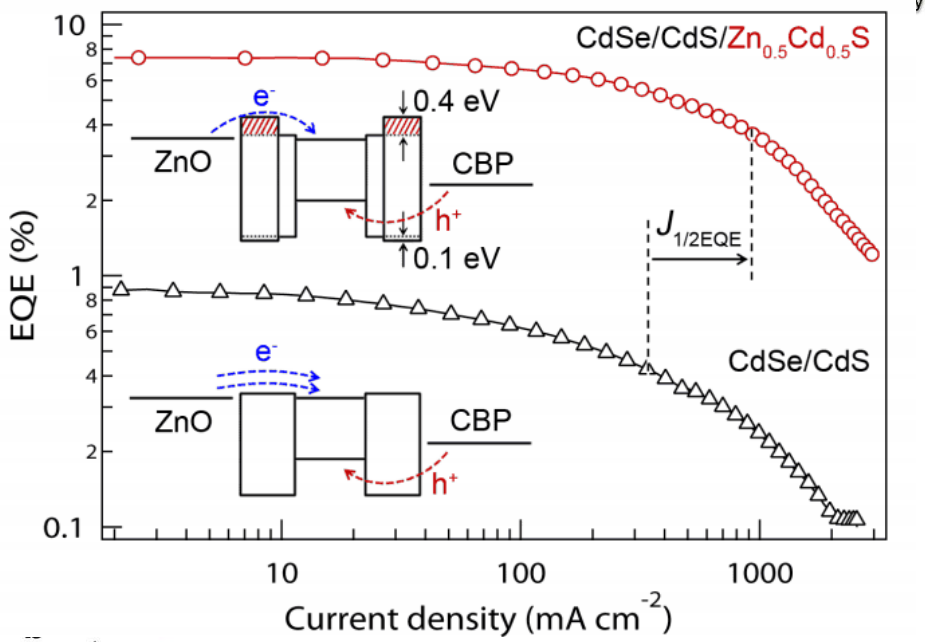
Using an extra CdZnS shell

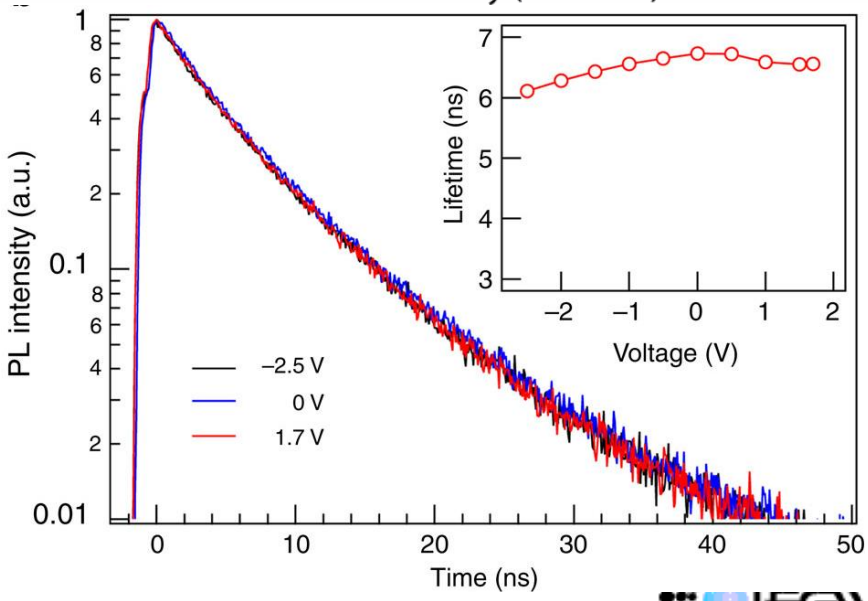


Maximum EQE increases by one order of magnitude

Roll-off current increases

PL is nearly independent on the bias





Bae et. al. Nature Comm 2013

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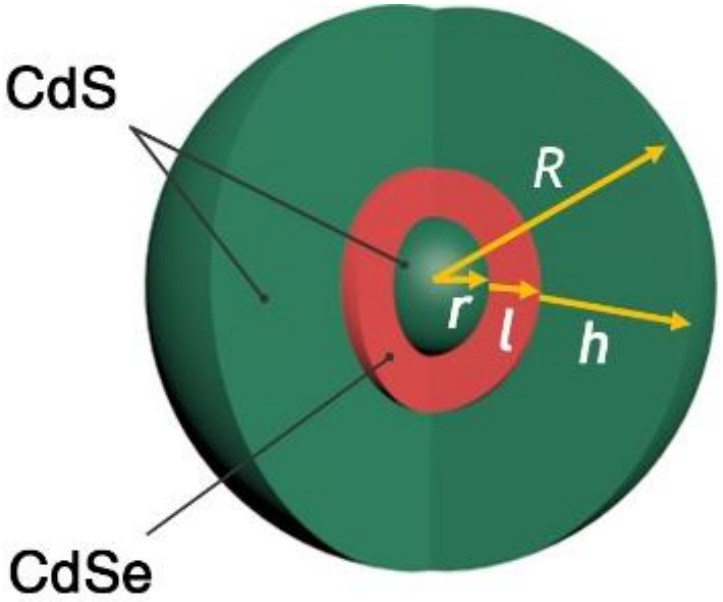
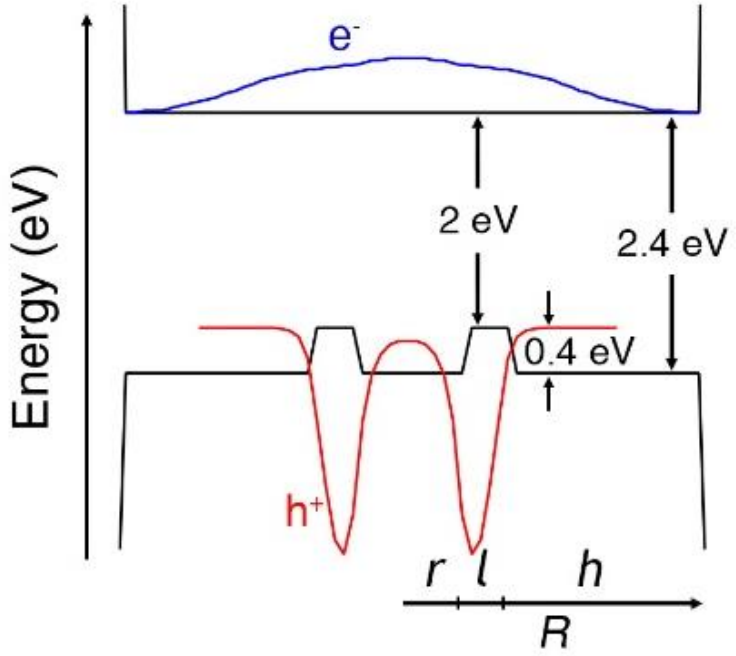
Controlling the Interaction at the Band-Edge

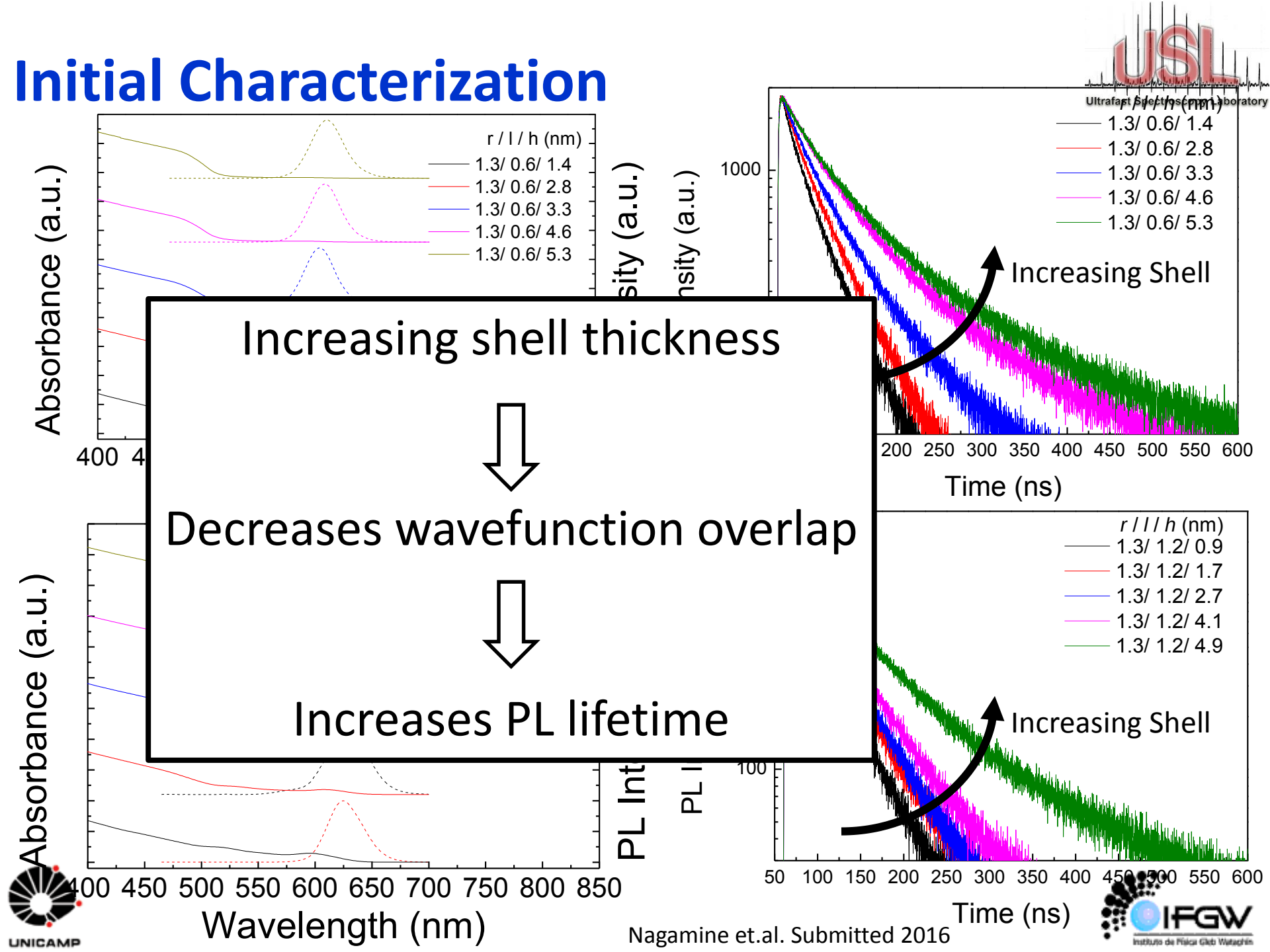
CdS/CdSe/CdS heterostructure (seed/SQW/shell)





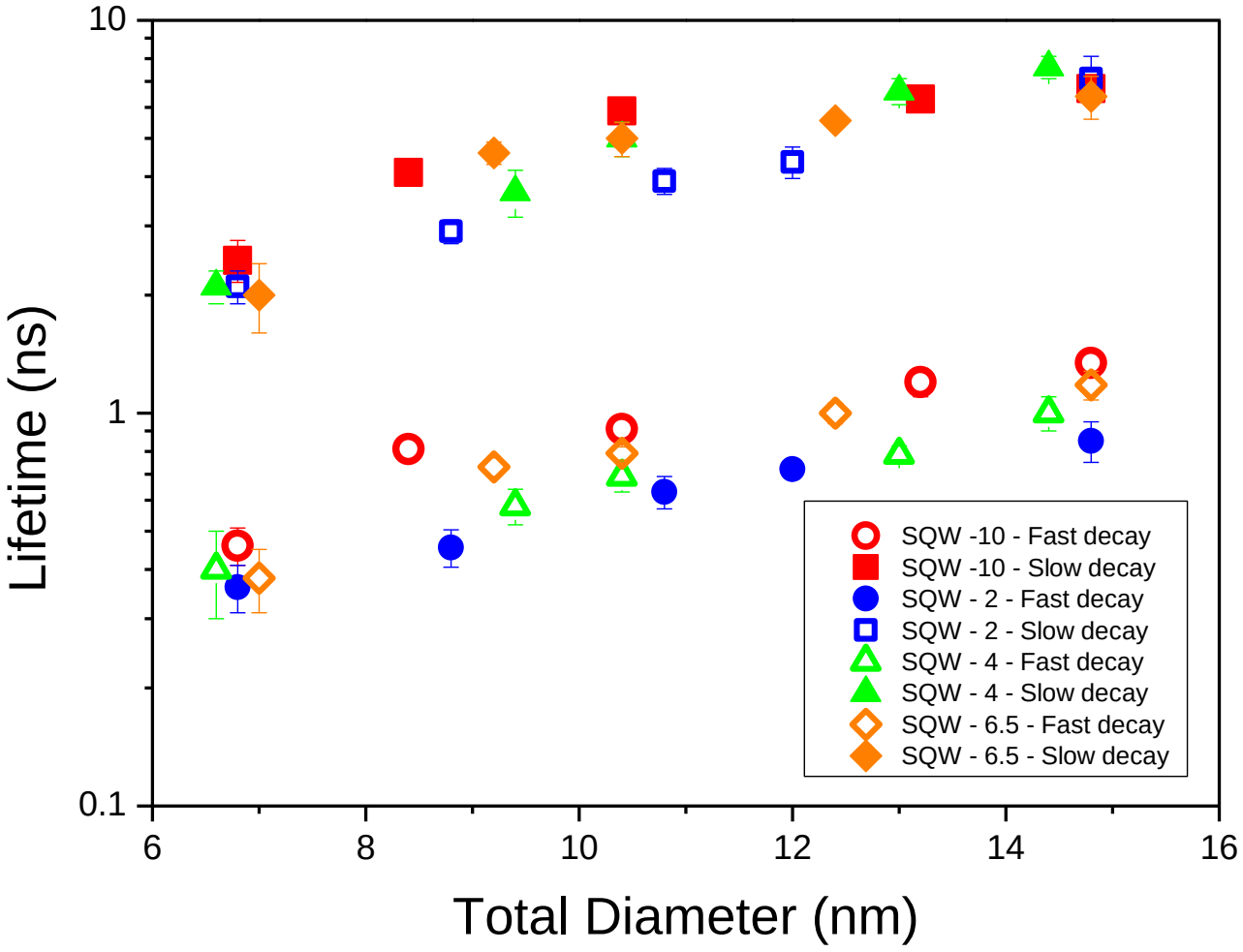
B.G. Jeong et. al. Submitted 2016

Initial Characterization



Nagamine et.al. Submitted 2016

Comparing Different Well and Shell Sizes

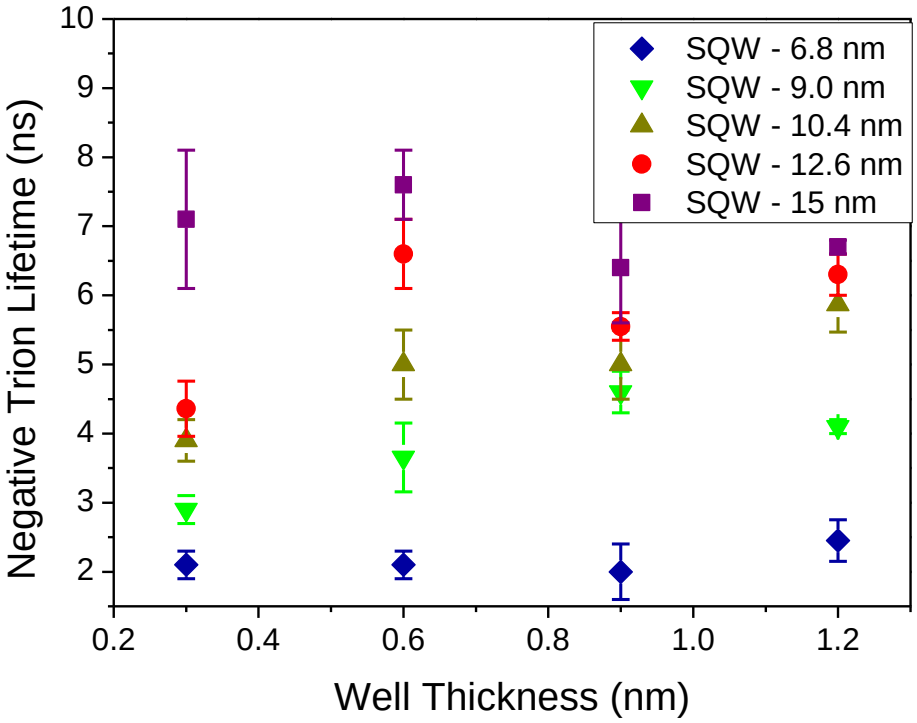


Fast decay → **positive trion** is strongly dependent on the well thickness.

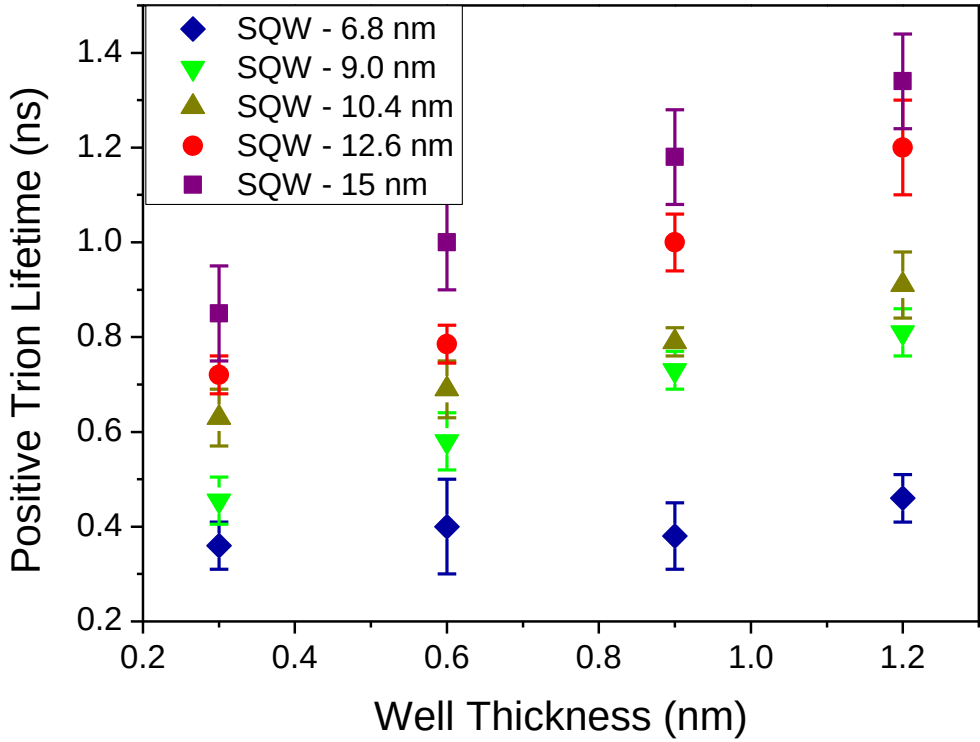
Slow decay → **negative trion**, it weakly depends on the well thickness.

Nagamine et.al. Submitted 2016

Comparing Different Well and Shell Sizes



For samples with similar volume, negative trion lifetime weakly varies

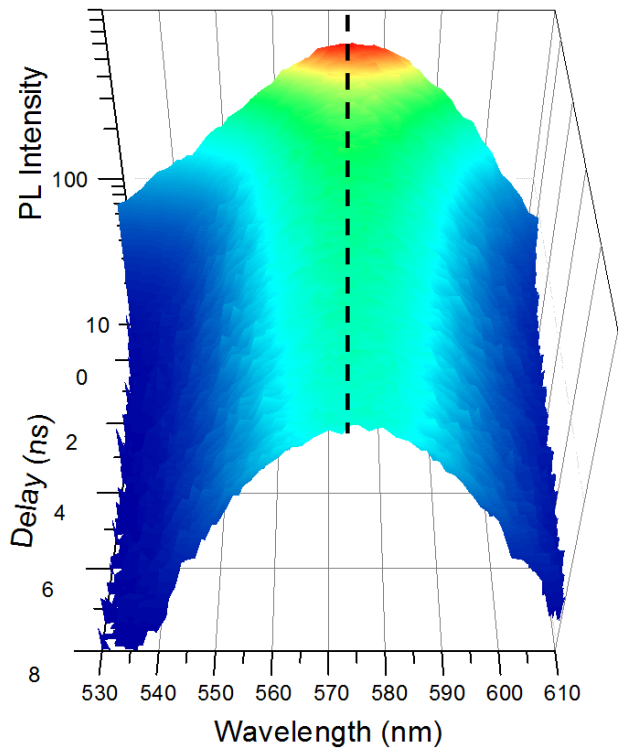


For the smaller SQW, it is possible that the positive trion is limited by the machine response

Nagamine et.al. Submitted 2016

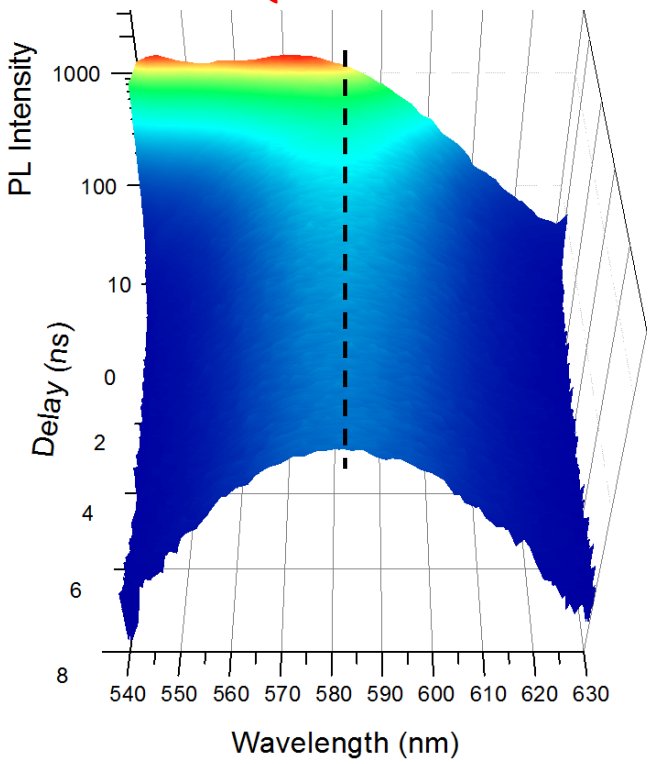
Time and Spectral Resolved PL SQW 2

SQW – 2 – 1



Initially, PL is shifted to low energy – red-shifted

SQW – 2 – 5

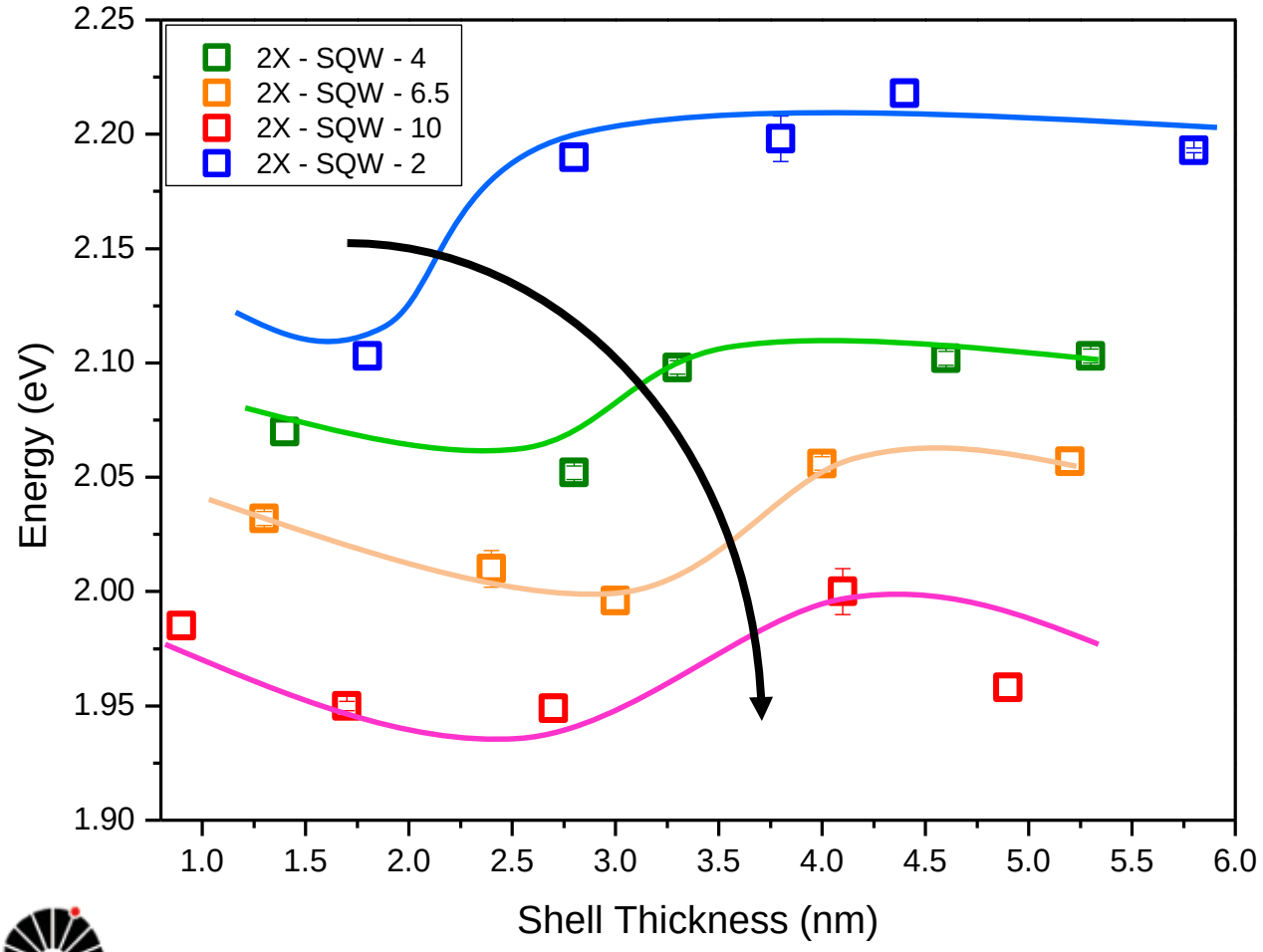


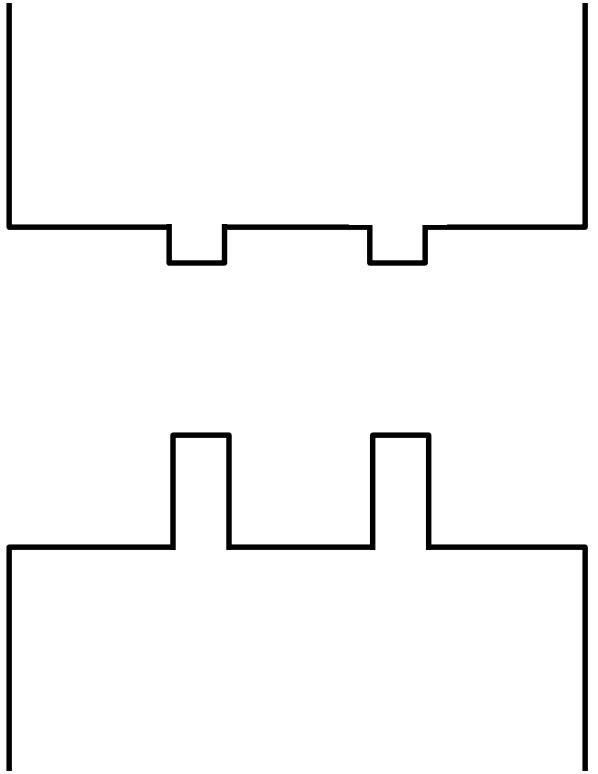
Initially, PL is shifted to high energy – blue-shift

Nagamine et.al. Submitted 2016

Going from Type-I to Type-II?

Looking only on the biexciton energy we can clearly see that there is a suddent increase as the shell gets thicker. Note also that for the thinner the well, the thinner the shell needs to be in order to have the energy shift.





Nagamine et.al. Submitted 2016

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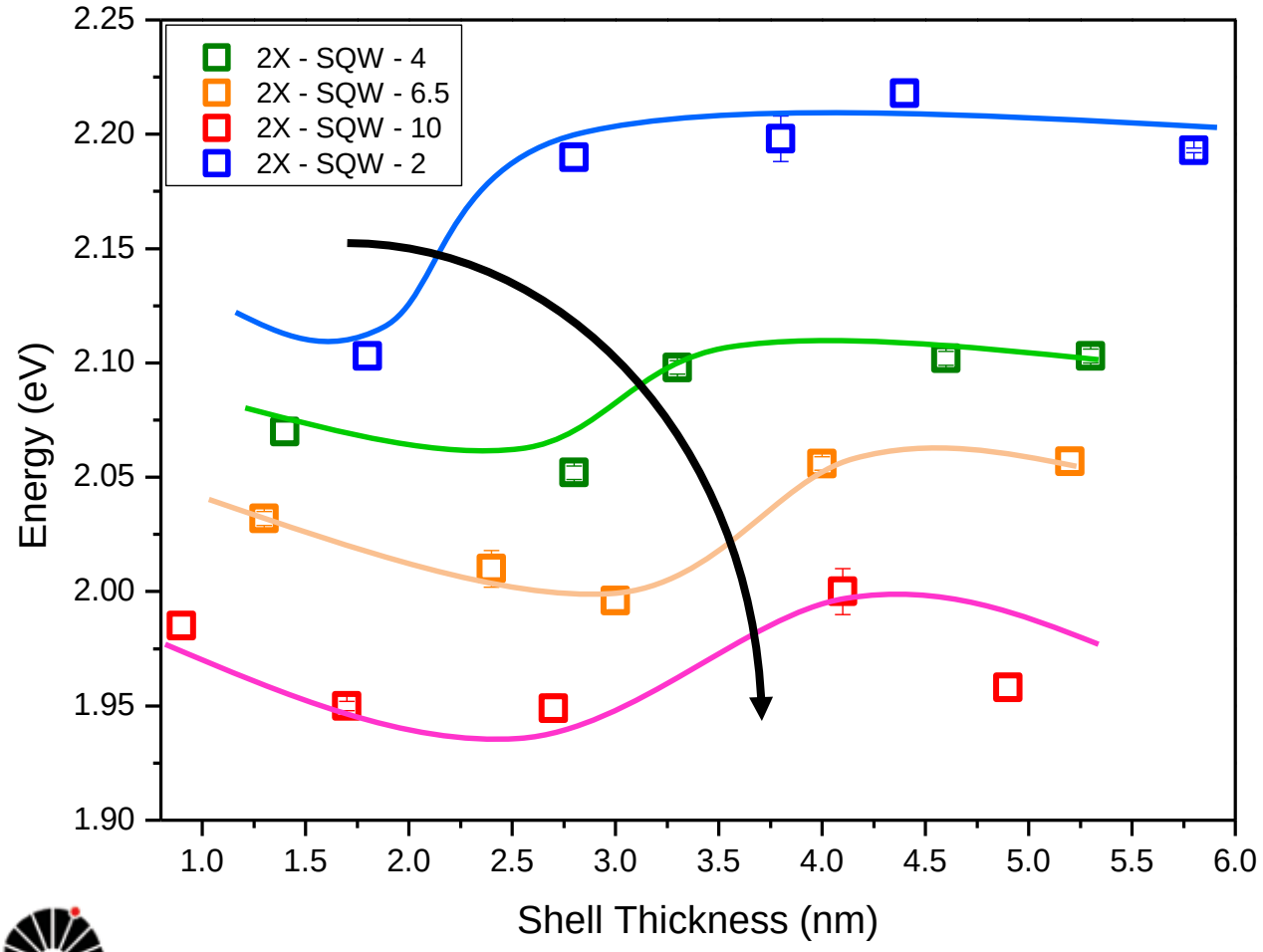
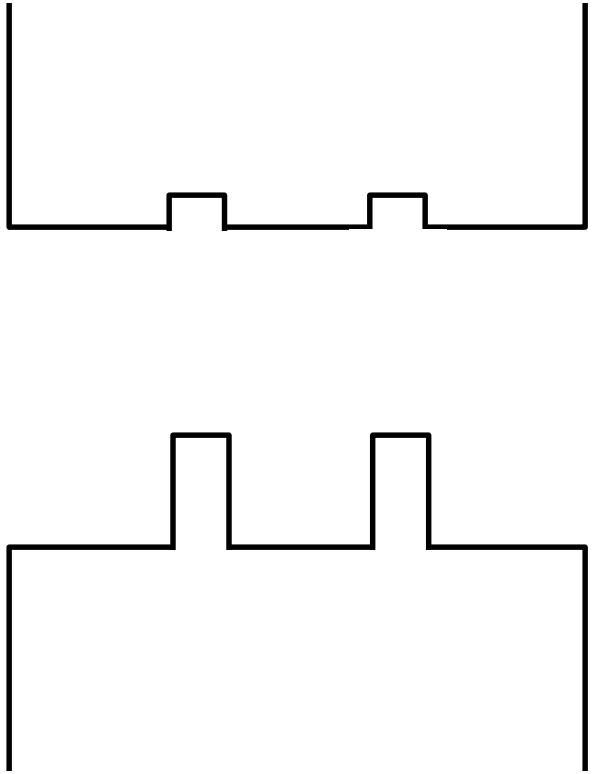
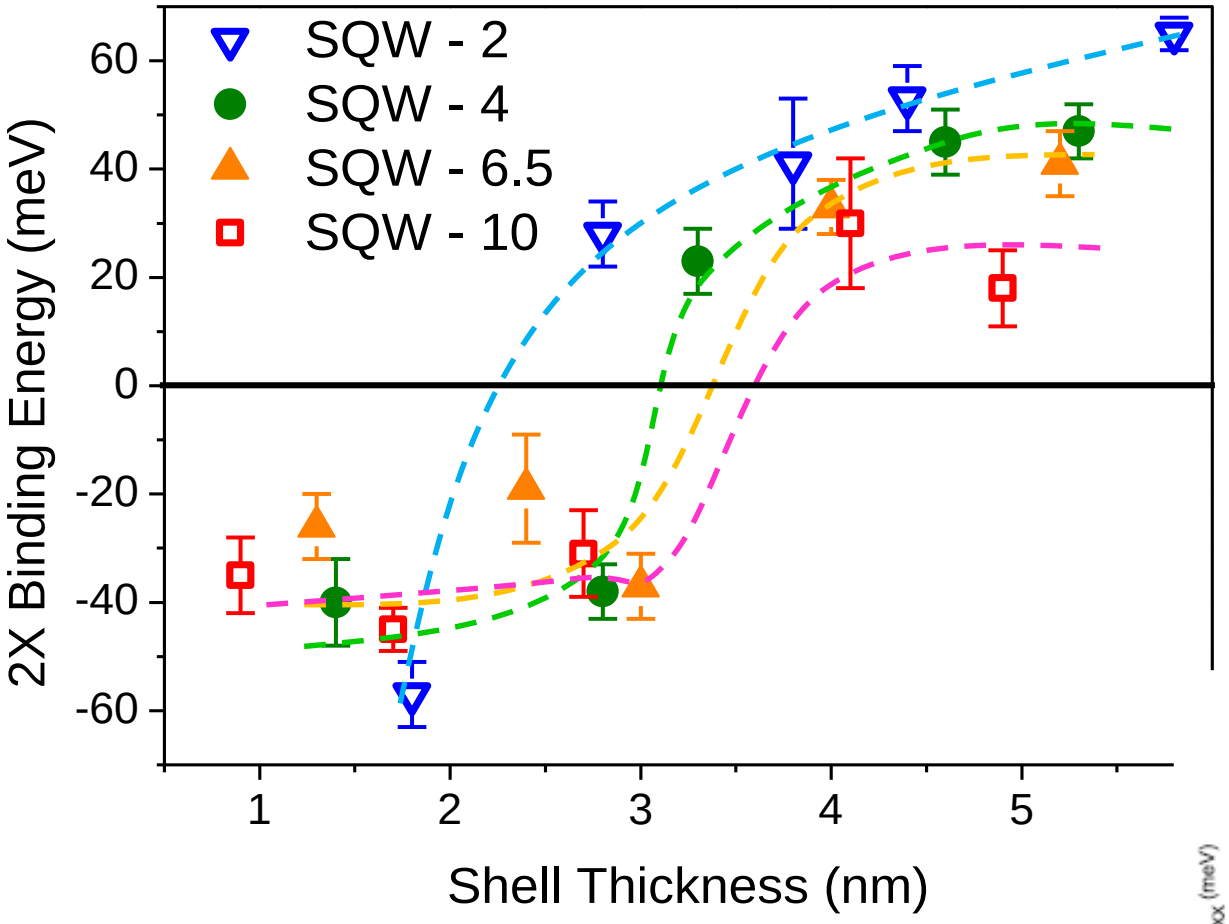




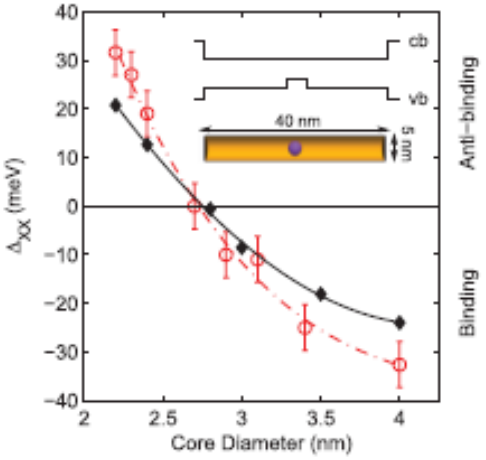
Nagamine et.al. Submitted 2016

Going from Type-I to Type-II?



Binding energy changes from an anti-binding to a binding regime as the shell thickness increase.

This behavior has already been observed in structures such as dot-in-rod and g-QDs, however, our data shows a **STEP-like** transition.

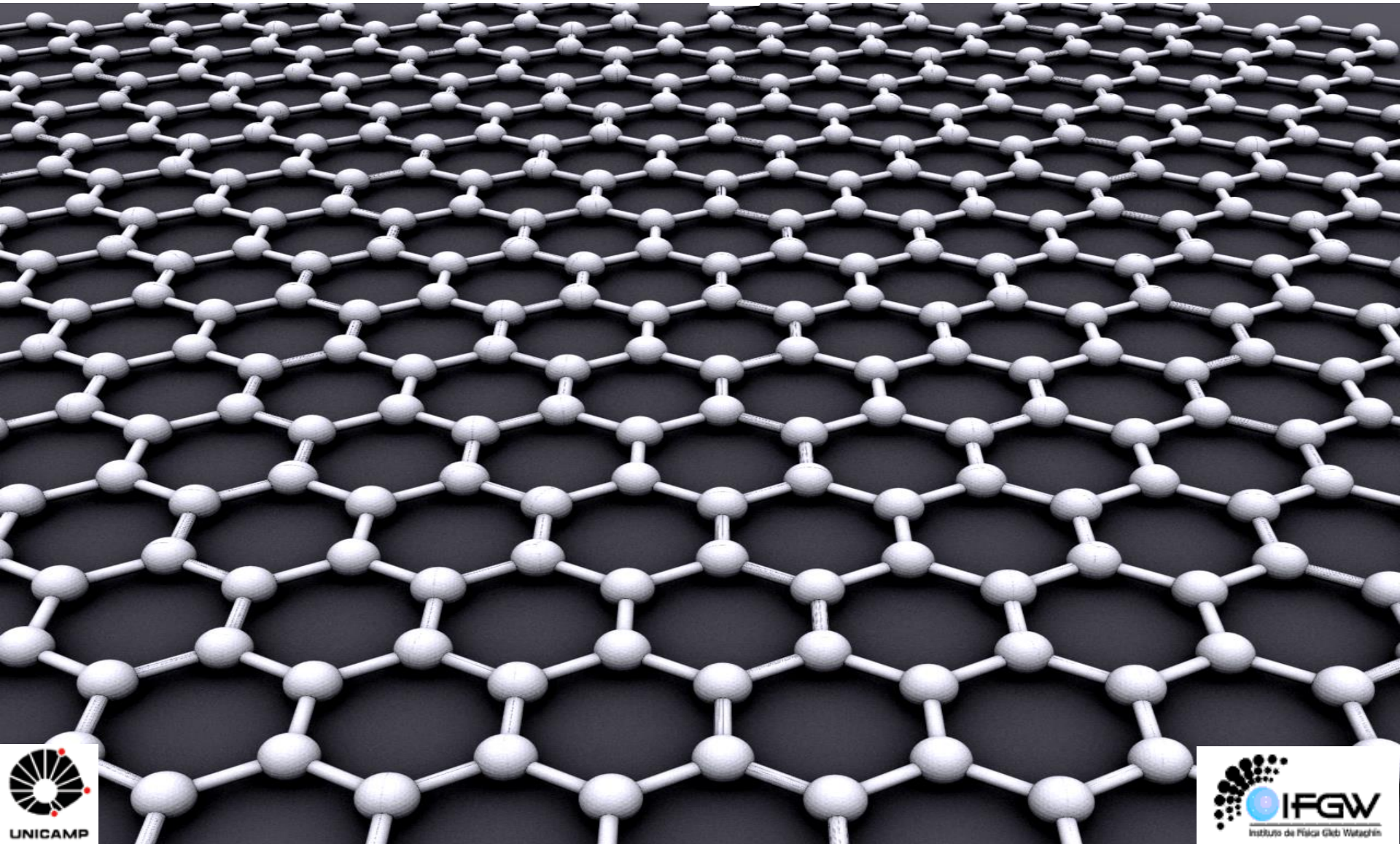


Sharp change from type-I to type-II

Nagamine et.al. Submitted 2016

McDonald, PRB 2012

Mapping the Ultrafast Dynamics in Graphene Monolayer



Ultrafast Spectroscopy Laboratory

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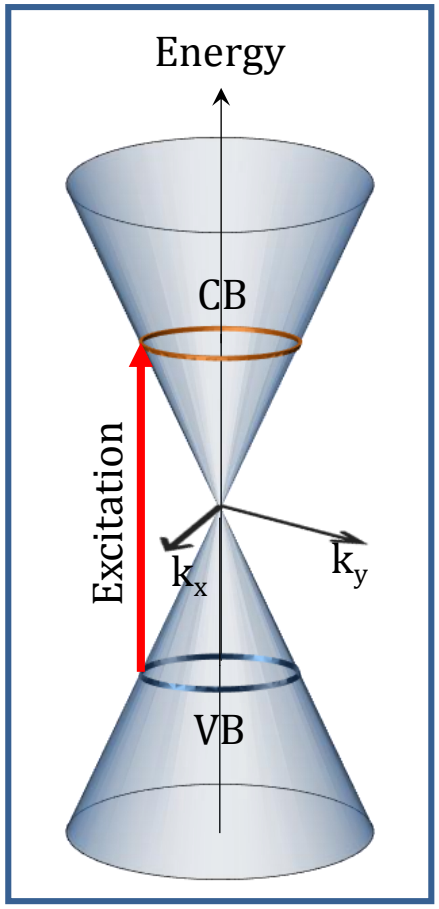
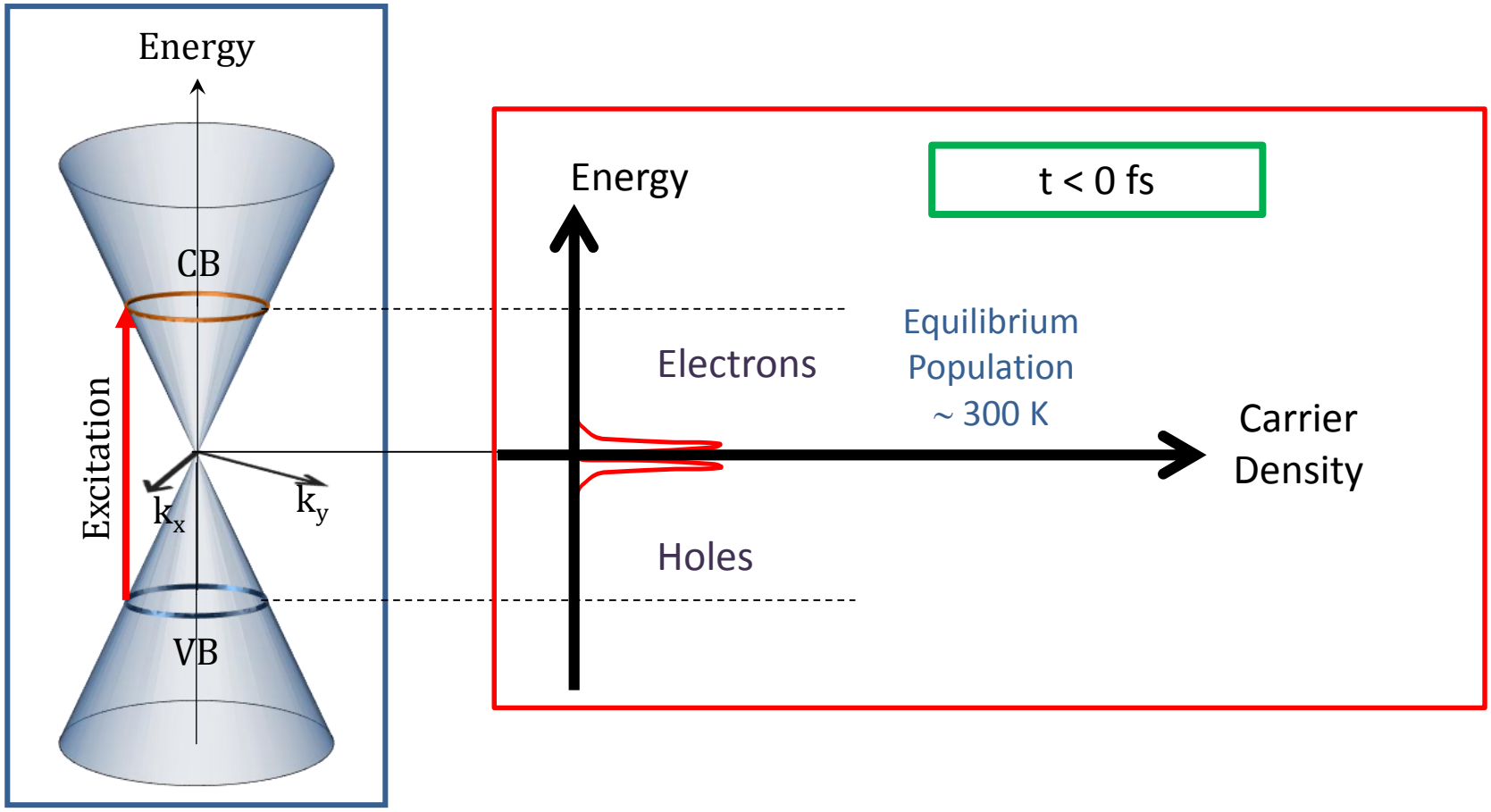
Mapping the Ultrafast Dynamics in Graphene Monolayer



Mapping the Ultrafast Dynamics in Graphene Monolayer



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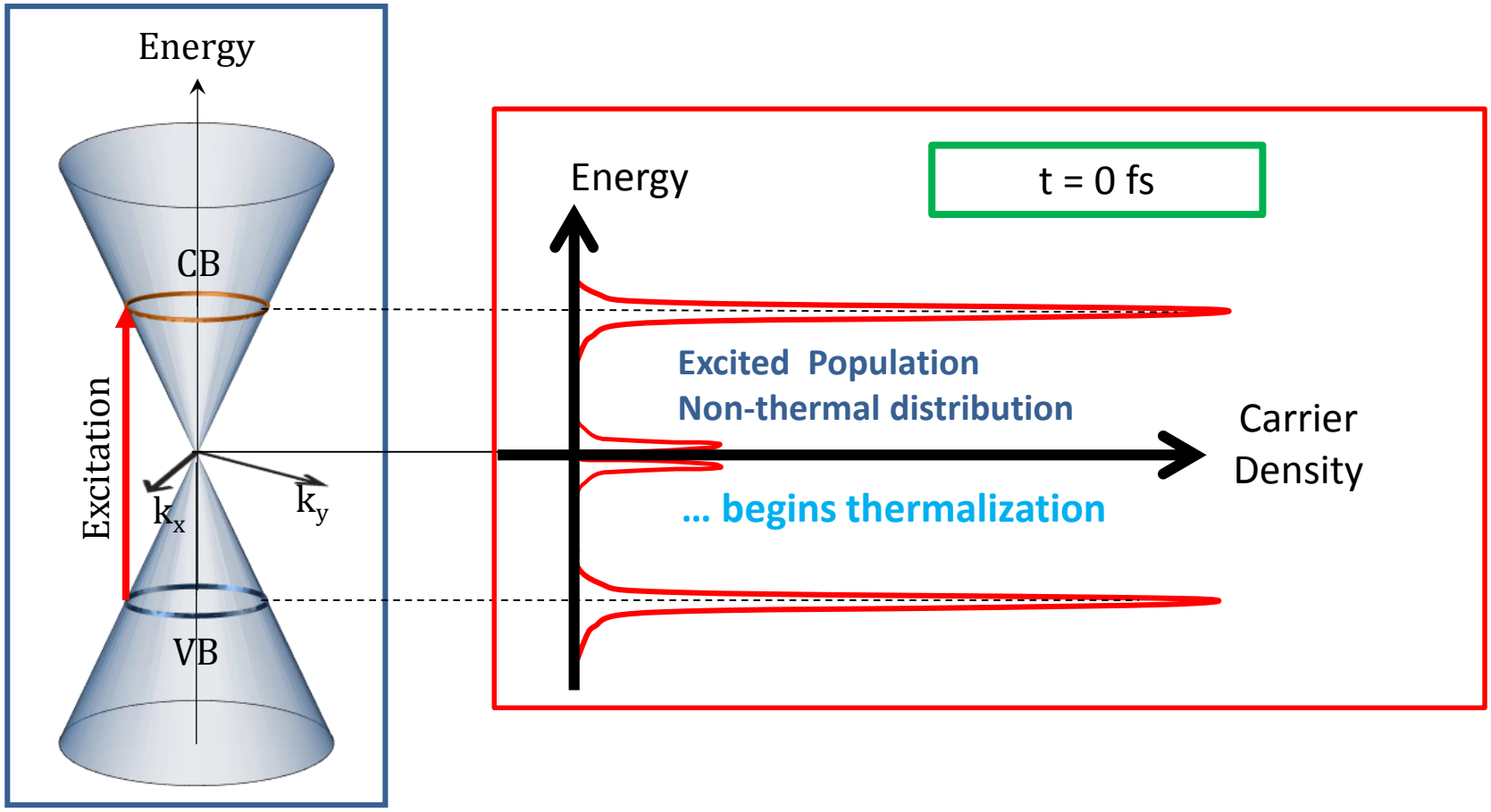

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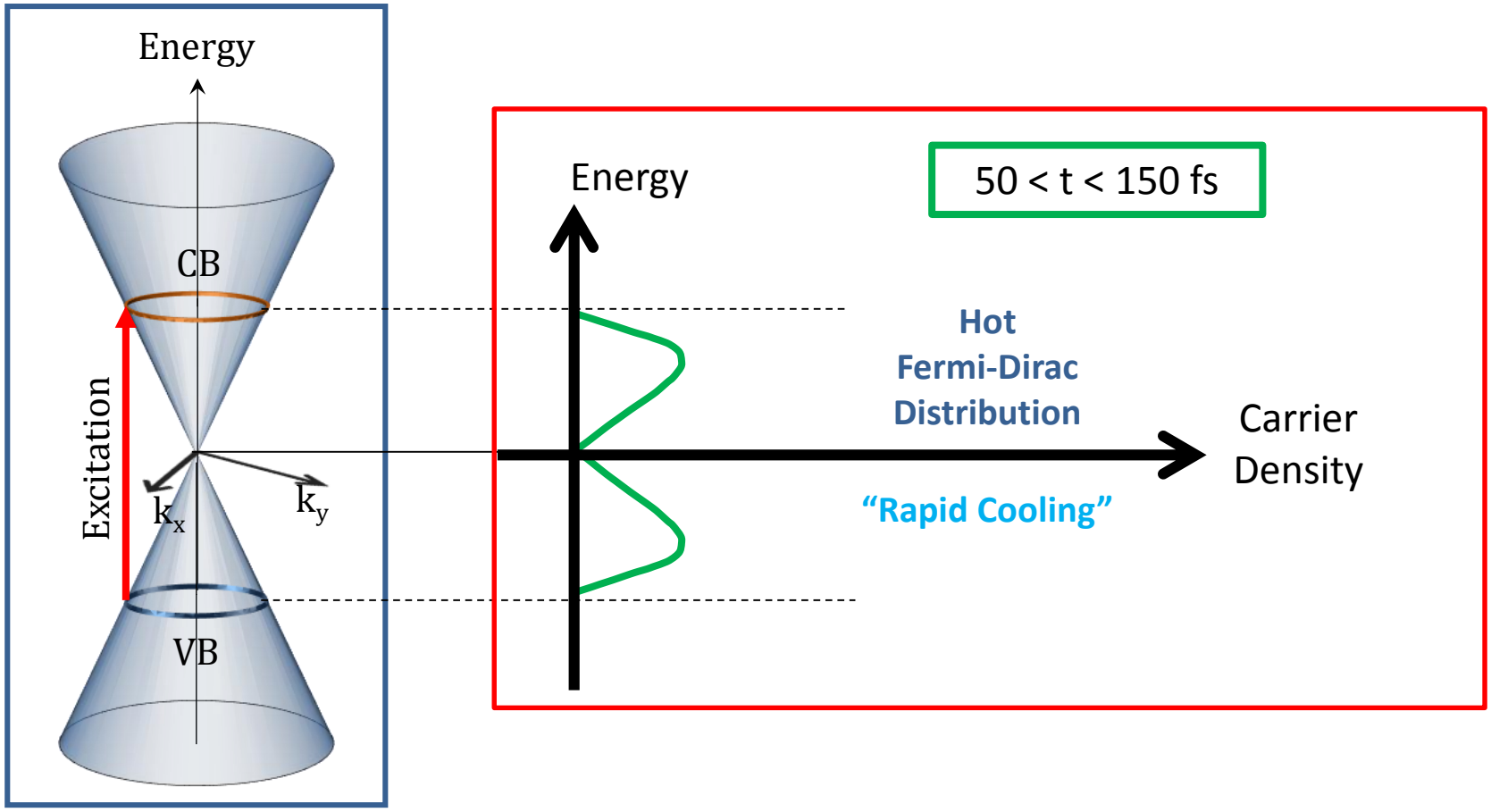

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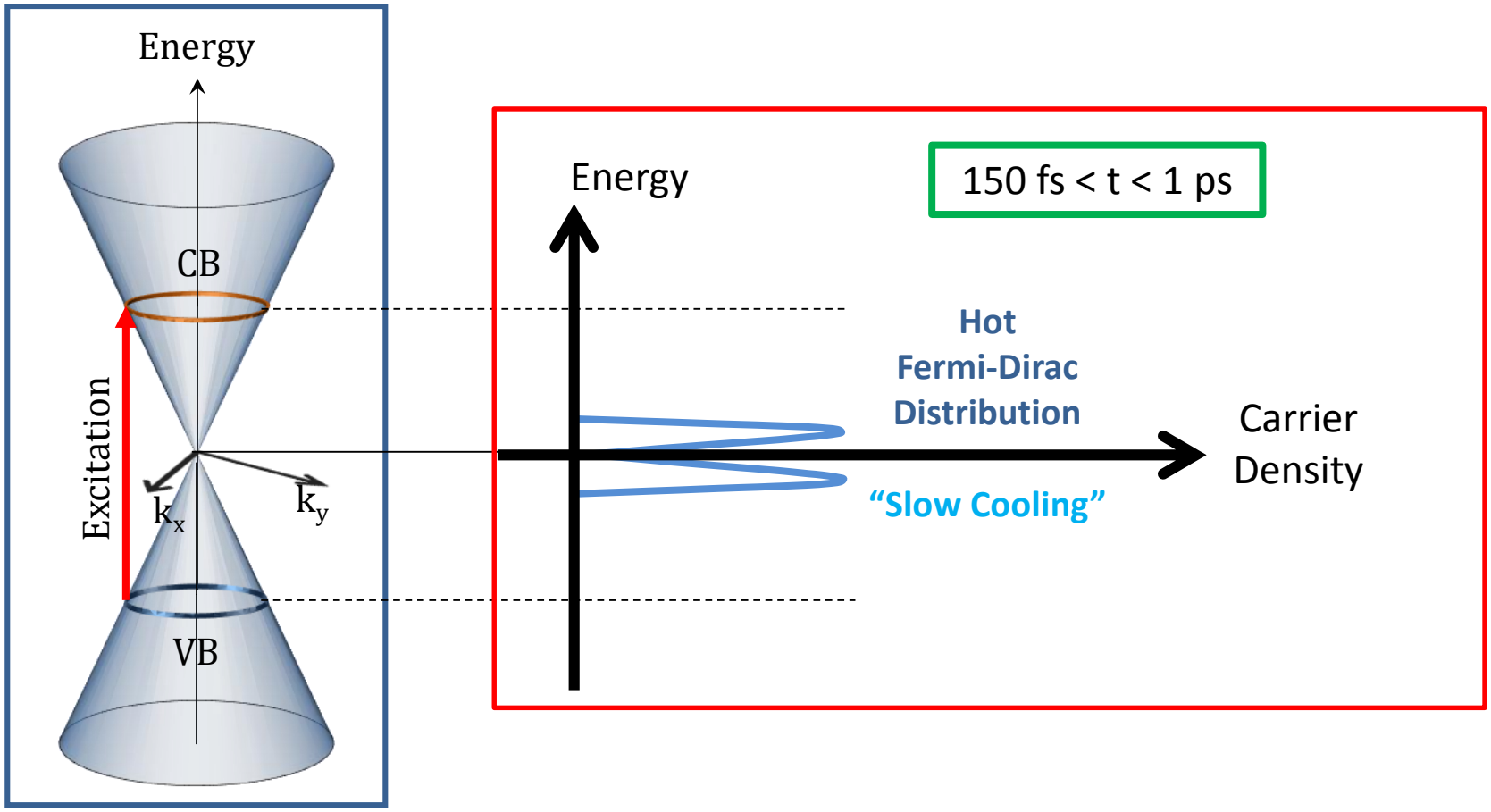
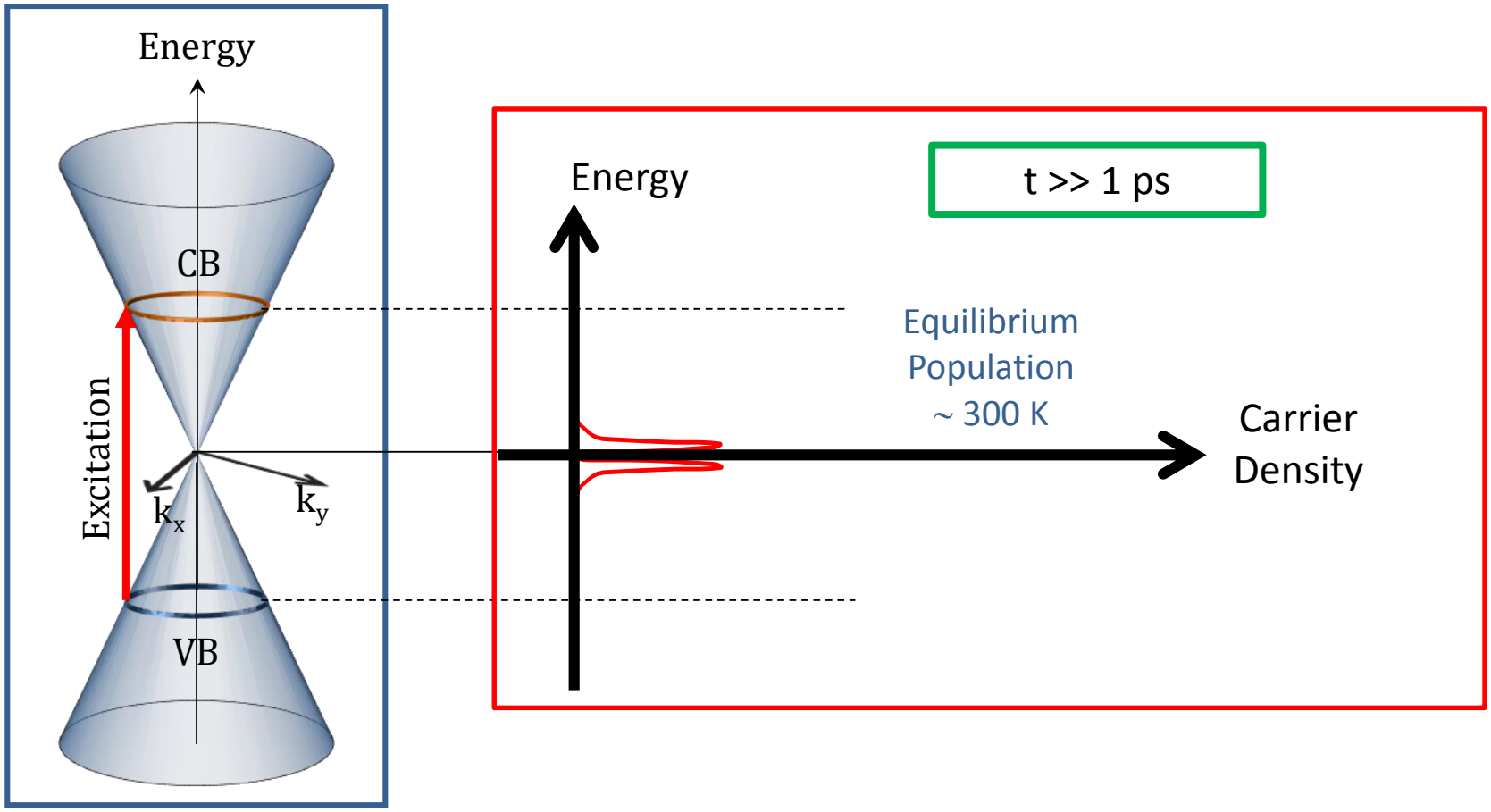


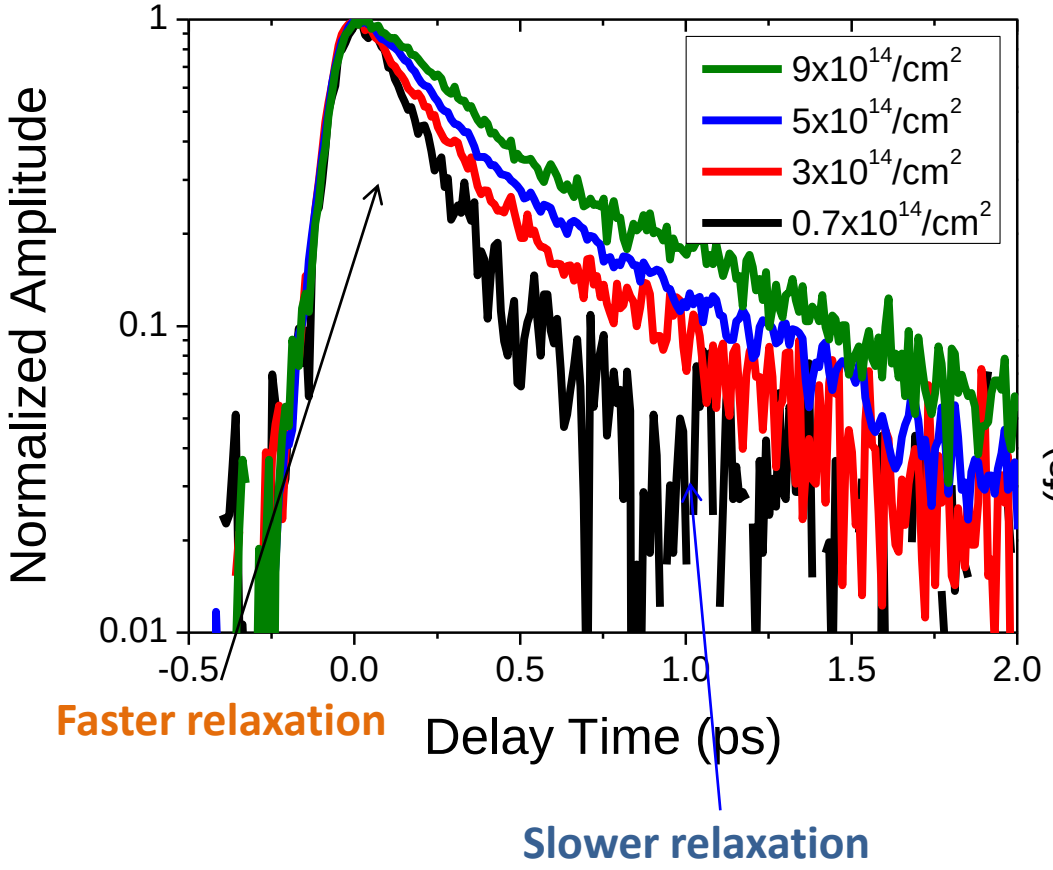
Mapping the Ultrafast Dynamics in Graphene Monolayer



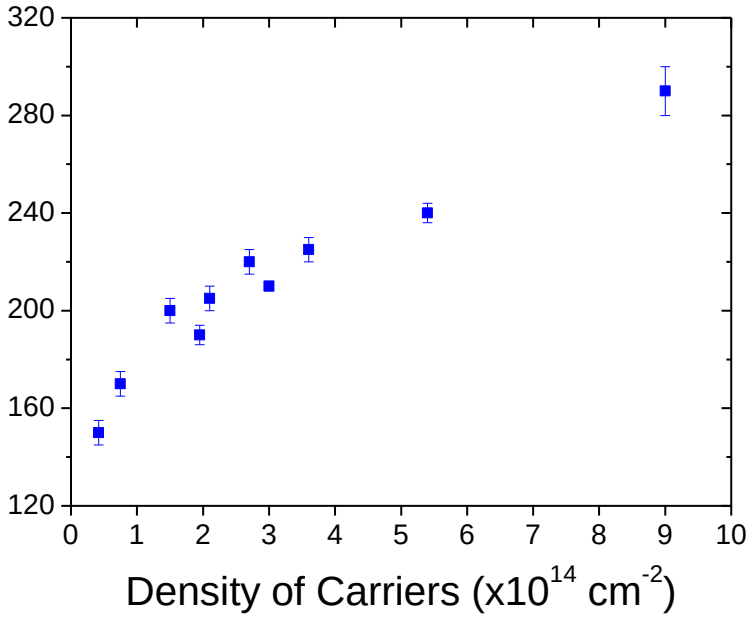
Mapping the Ultrafast Dynamics in Graphene Monolayer – Pump Dependence

Ultrafast Spectroscopy Laboratory

At 1.55 eV



Slow decay is constant ~ 1ps



J.A. Castañeda et.al. to be submitted (2016)

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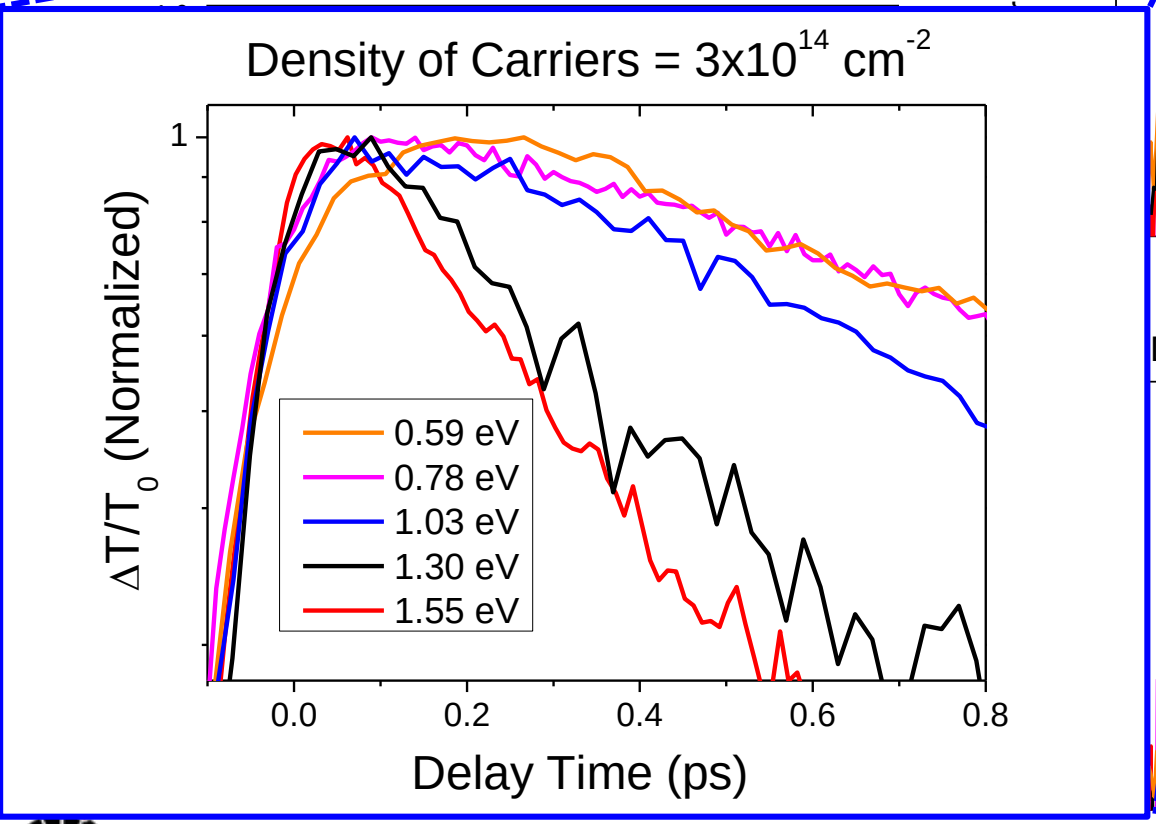
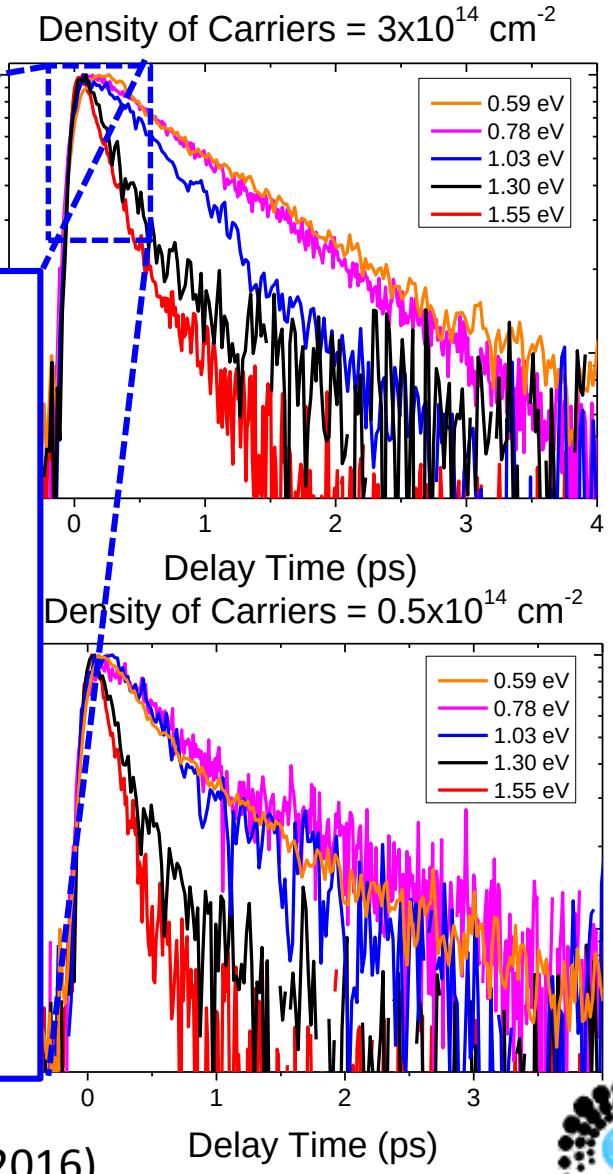
Mapping the Ultrafast Dynamics in Graphene Monolayer – Probe Dependence

Ultrafast Spectroscopy Laboratory

Ultrafast carrier dynamics were studied at several electron energy levels. **Optical pump at 1.55 eV.**





J.A. Castañeda et.al. to be submitted (2016)

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Mapping the Ultrafast Dynamics in Graphene Monolayer – Summary

Ultrafast Spectroscopy Laboratory

At high energy probe - two decay processes

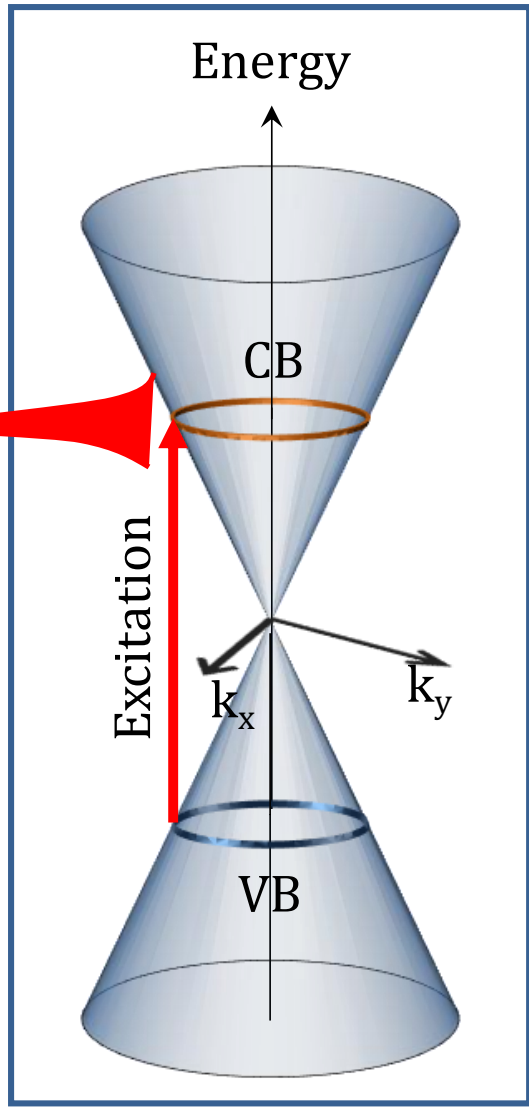
Fast decay – cooling of hot Fermi-Dirac distribution (optical phonons)

Slow decay – carrier-optical phonon decay (acoustic phonon)

At low energy probe – only slow decay

Slow growth of the TA signal at low probe energy – populates after fast decay

State saturation goes from 2.06 x 10^{14} cm^2 at 1.55 eV down to 0.54 x 10^{14} cm^2 at 0.59 eV



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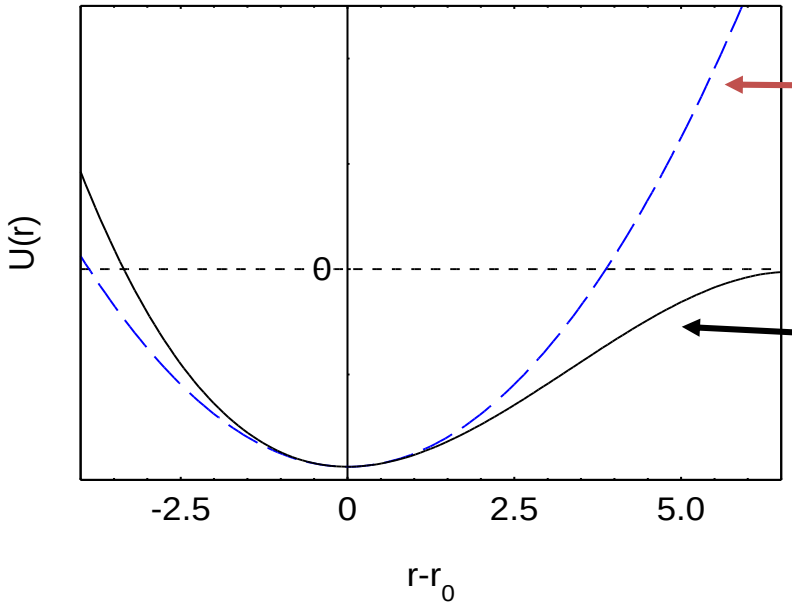
Going from Ultrafast to Nonlinear Spectroscopy

In real materials, electrons don't sit in parabolic potentials!



Parabolic potential

$U(r) \sim \frac{1}{2} Kr^2$

Nonparabolic potential

$U(r) \sim \frac{1}{2} Kr^2 + \frac{1}{3} ar^3 + \frac{1}{4} br^4 + \ldots$

$F(r) = -\partial U/\partial r \sim -Kr - ar^2 - br^3 - \ldots$

Leads to *nonlinear* dependence of P on E:

$$P(E) = \epsilon_0 \left(\chi^{(1)} E + \chi^{(2)} E^2 + \chi^{(3)} E^3 + \ldots \right)$$

Going from Ultrafast to Nonlinear Spectroscopy

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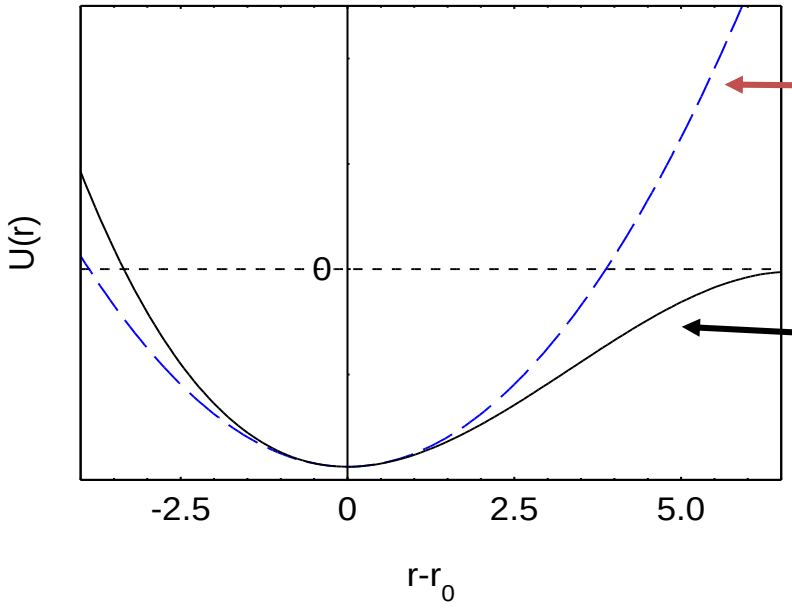

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$F(r) = -\partial U/\partial r \sim -Kr - ar^2 - br^3 - \ldots$

$\chi^{(3)}$ is lowest order nonlinearity for symmetric potential

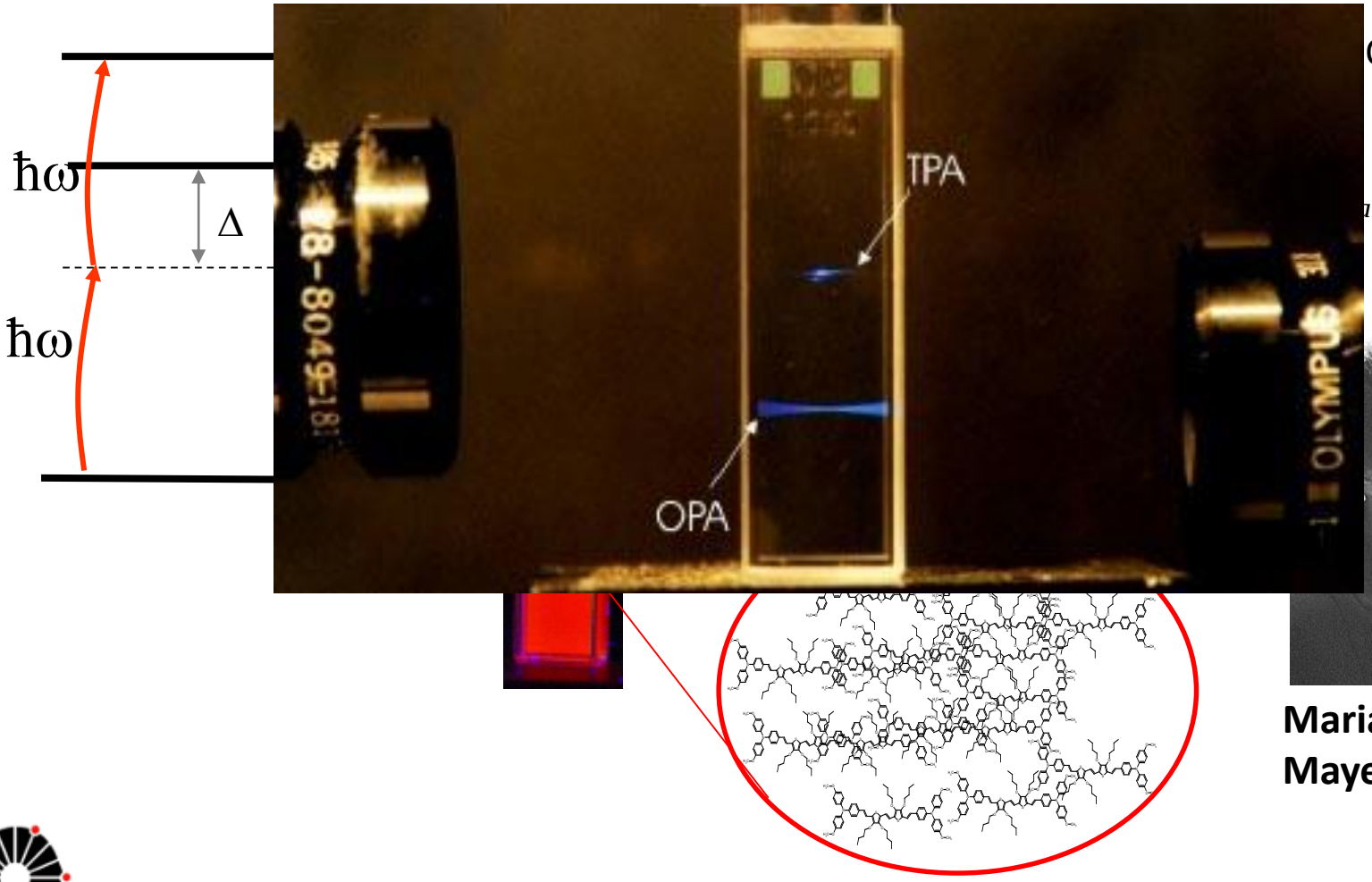
Leads to *nonlinear* dependence of P on E:

$$P(E) = \epsilon_0 \left(\chi^{(1)} E + \chi^{(2)} E^2 + \chi^{(3)} E^3 + \ldots \right)$$

Going from Ultrafast to Nonlinear Spectroscopy

$$\alpha(I) = \alpha_0 + \alpha_2 I$$

$\chi^{(3)}$ process - instantaneous



OMO-LUMO

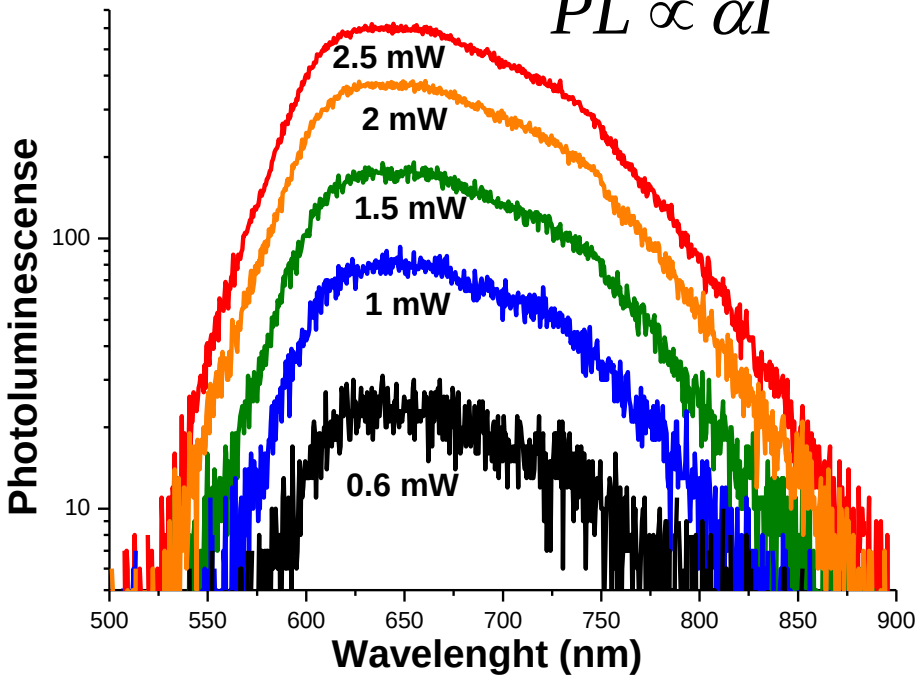
$_a, -\omega_a, \omega_a)\}$

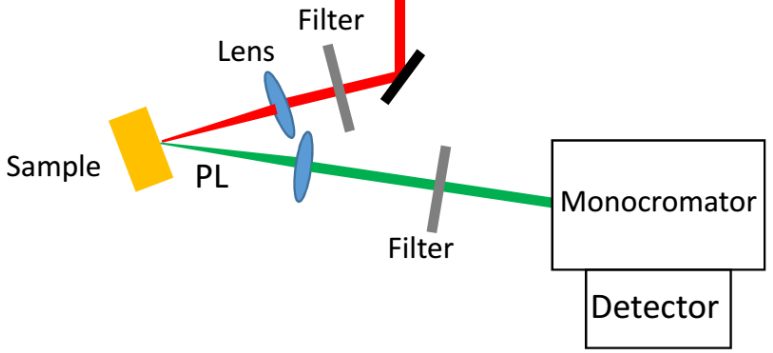
Maria Goeppert-Mayer

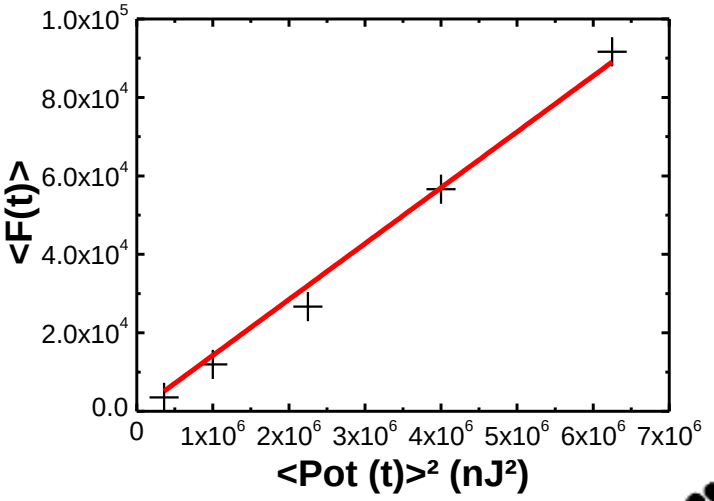
Ultrafast Lasers can reach the high intensity regime at low pulse energy

Two-photon excited fluorescence

$$PL \propto \alpha I$$







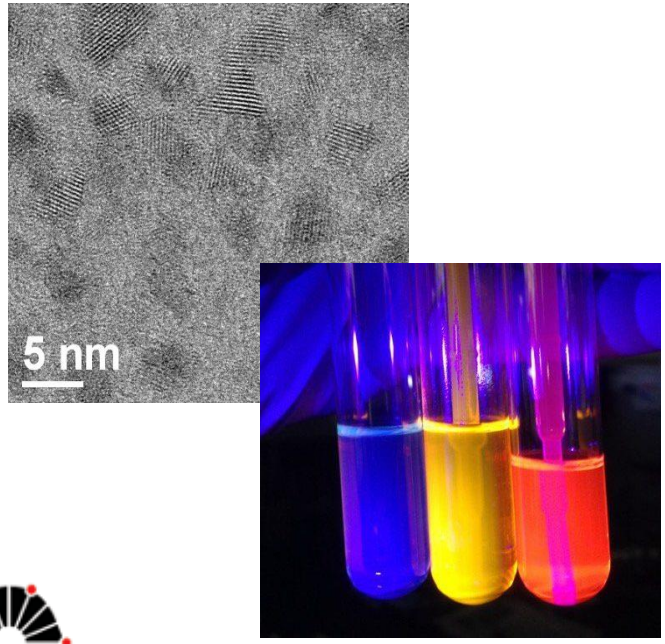
$CuInS_2$ QDs

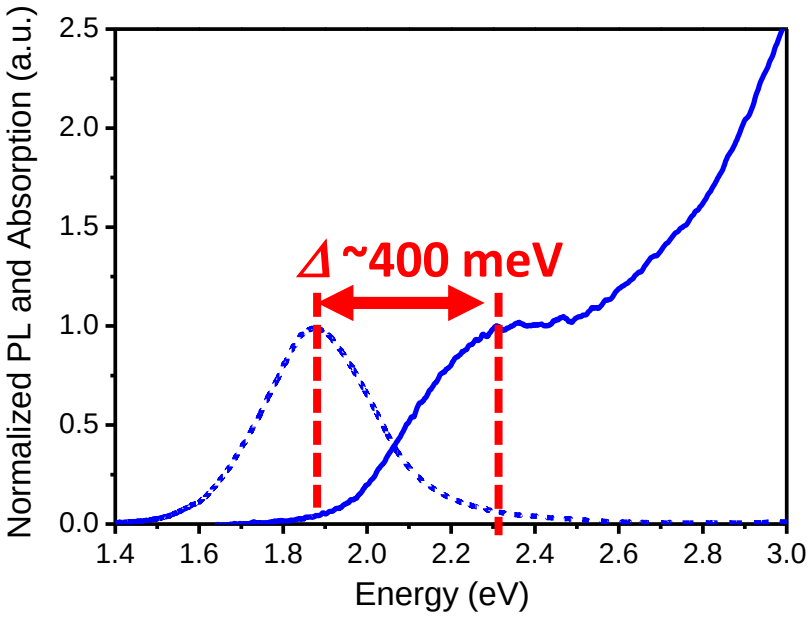
Band gap going from visible to near infra-red (500 – 1200 nm)

Low toxicit due to the absense of carcinogenic heavy metals

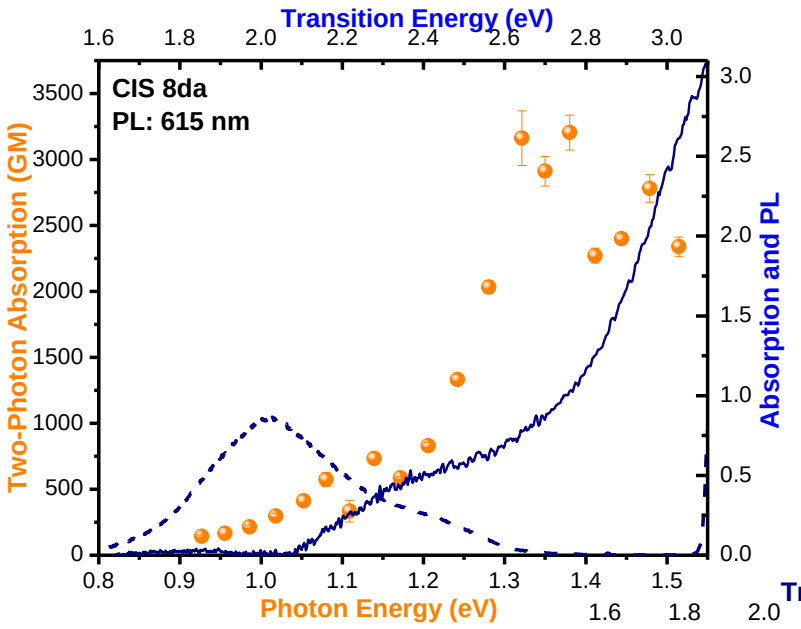
Unusually large Stoke Shift

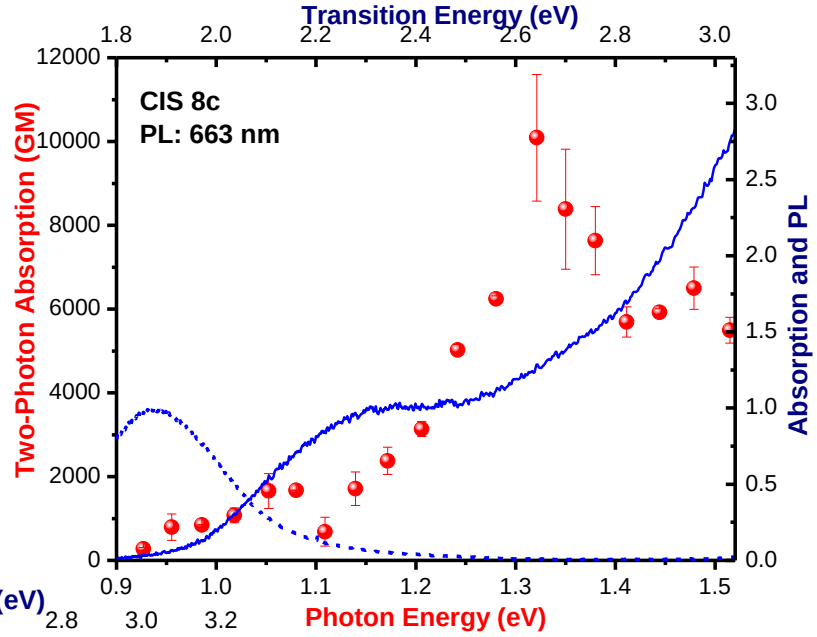
Highly desirable for technological aplications: next generation of photovoltaics, and fluorescent label for biological imaging

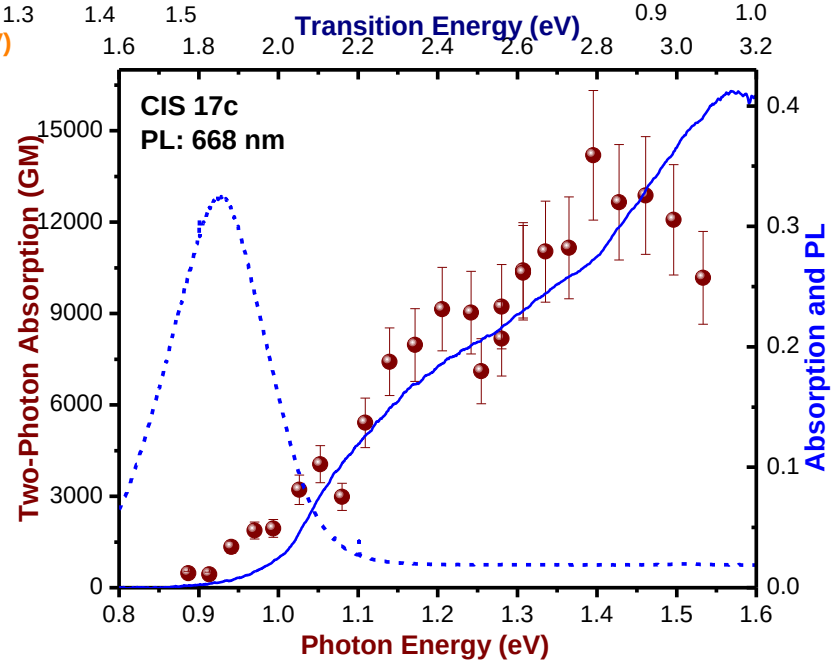




2PA in $CuInS_2$ QDs







Size dependente 2PA

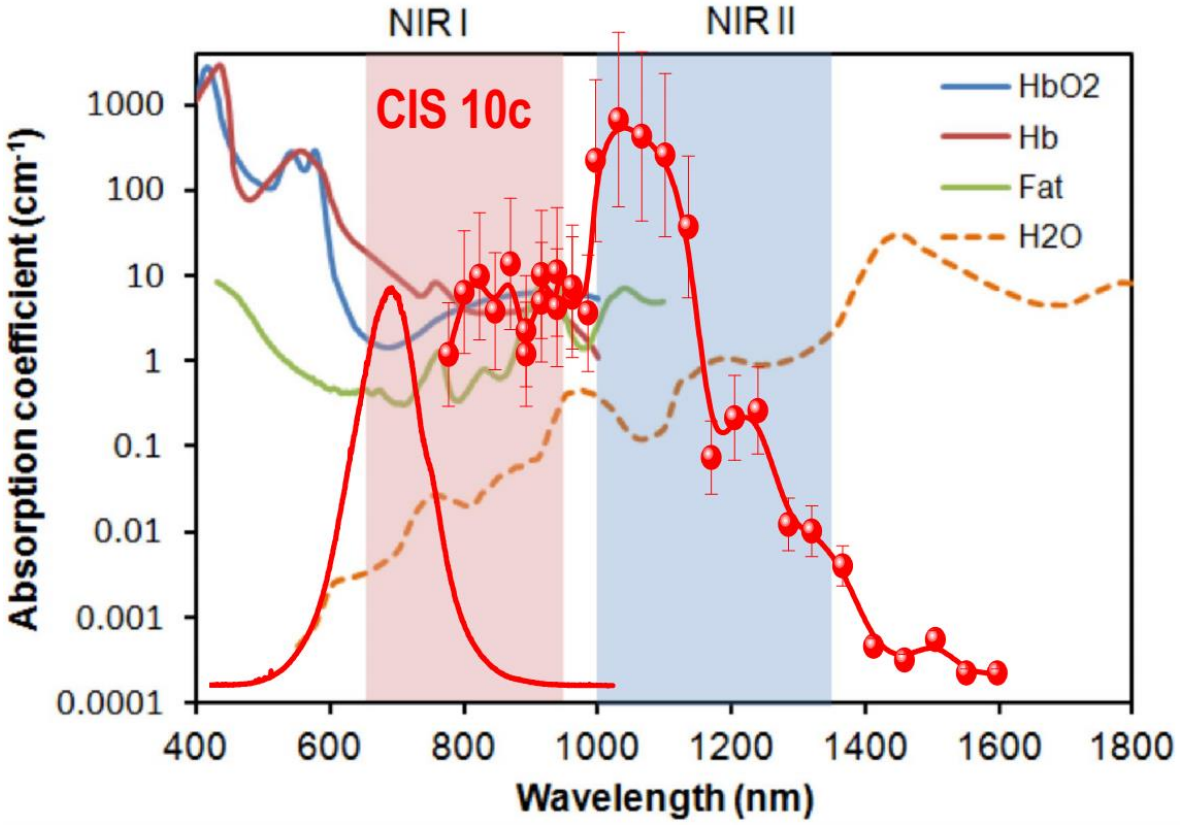
2PA cross-section as large as 15,000 GM

2PA in $CuInS_2$ QDs - Application

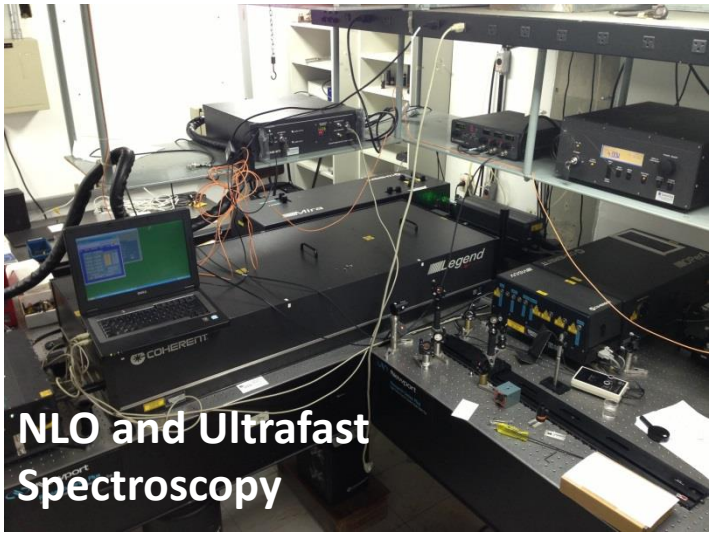
Large stoke shift avoid reabsorption

PL can be tuned to the first bio-window for transparency

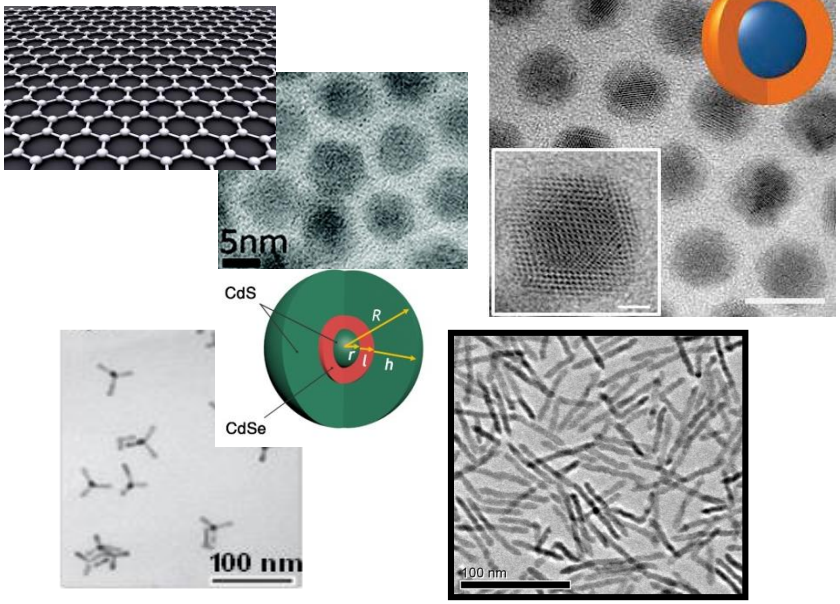
2PA can be tuned to the second bio-window for transparency



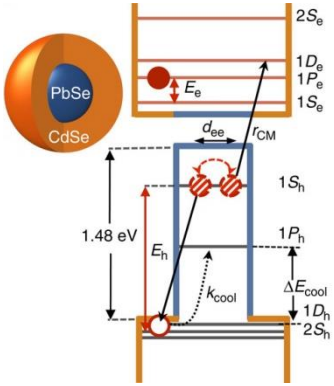
Finally…



Engineered Nanomaterials

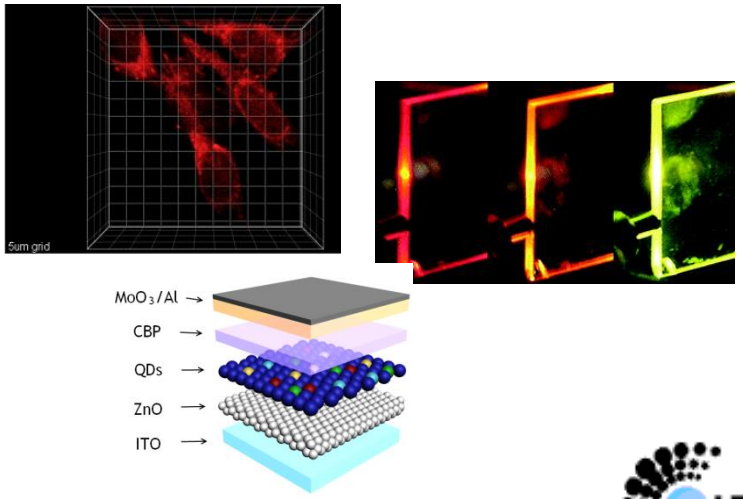


Novel Physical Phenomena



Controlled Coulomb Interaction;
Bimolecular Auger Recombination;
Intraband hole-blockage

Novel Applications



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