Carrier Dynamics and Multiple Exciton Generation in Nanocrystals: Applications to 3rd Generation Solar Photon Conversion

A.J. Nozik
National Renewable Energy Laboratory
University of Colorado, Boulder

Randy Ellingson	**Exciton dynamics, MEG**
Matt Beard	**THz spectroscopy, MEG**
Justin Johnson(PD)	**SF,Exciton dynamics,MEG**
Kelly Knutsen (PD)	**Exciton dynamics, MEG (Si)**
Joseph Luther (GS)	**MEG photocurrent, QD arrays**
Jim Murphy (GS)	**THz Spectroscopy, QD arrays**
Pingrong Yu	**MEG Solar Cells**
Mark Hanna	**Thermodynamic Efficiencies**
Sasha Efros (NRL)	**Theory of MEG**
Andrew Shabaev (NRL)	**Theory of MEG**
Josef Michl (UCB)	**Singlet Fission (SF)**
Mark Ratner (NWU)	**Singlet Fission (Theory)**

Funding: U.S. DOE Office of Science, Div Basic Energy Sciences, Division of Chemical Sciences

Consequences of Size Quantization

- Large blue shift of absorption edge
- Discrete energy levels/structured absorption and photoluminescence spectra
- Dramatic variation of optical and electronic properties
- Enhanced photoredox properties for photogenerated electrons and holes
- Greatly enhanced exciton absorption at 300 K
- Conversion of indirect semiconductors to direct semiconductors or vice versa
- Greatly enhanced oscillator strength per unit volume (absorption coefficient

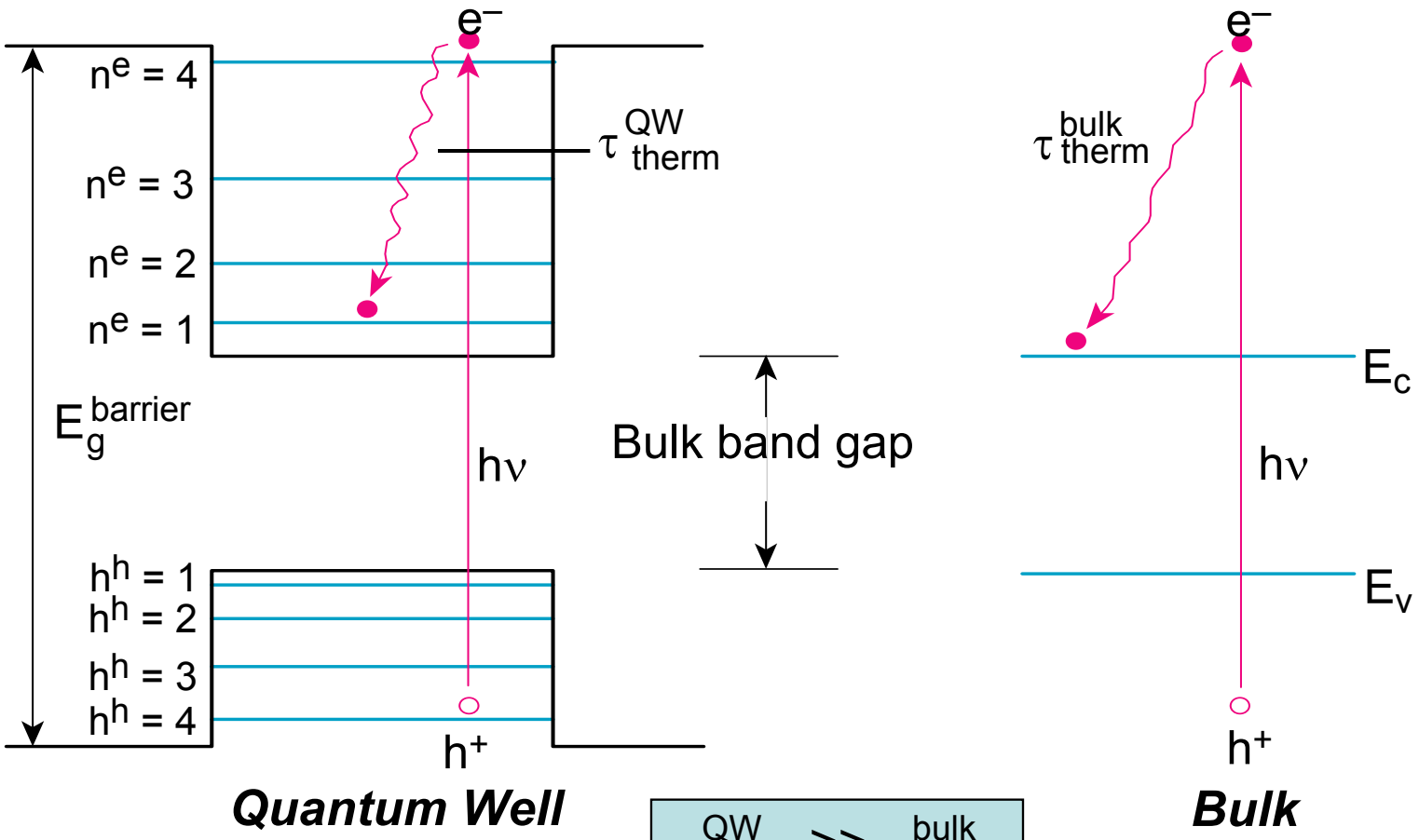
- Greatly modified pressure dependence of phase changes and direct to indirect transitions
- Greatly enhanced non-linear optical properties
- Efficient anti-Stokes luminescence

Effects on Dynamics:

- **Slowed relaxation and cooling (~10X) of photogenerated hot electrons and holes (excitons)**
- **Conservation of crystal momentum relaxed**
- **Enhanced Auger processes (invoked to explain PL blinking, breaking phonon bottleneck, and multiple exciton generation)**

QUANTIZATION EFFECTS

- Auger processes enhanced
- Hot exciton cooling slowed (compared to MEG)
- Crystal momentum not a good quantum number



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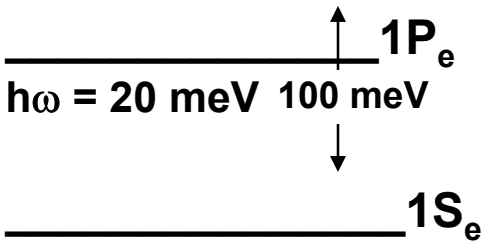
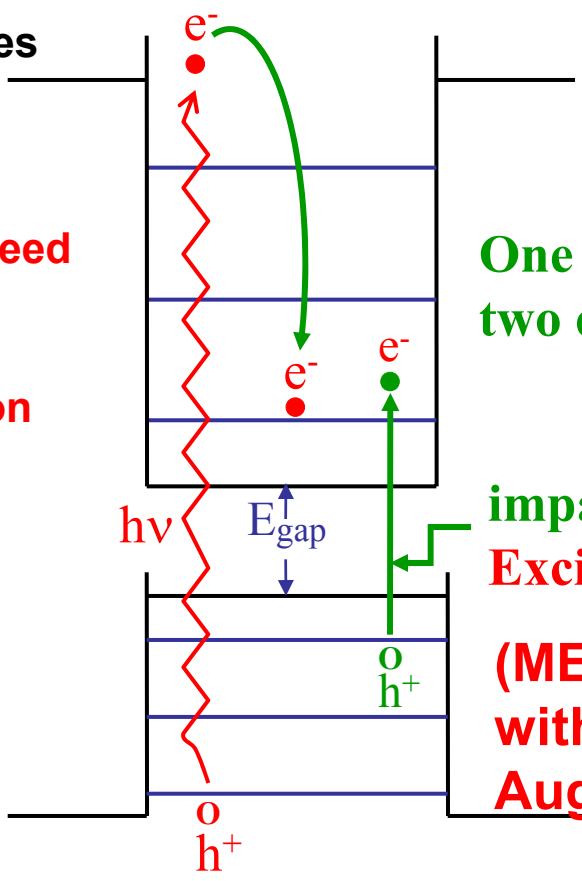
Enhanced Photovoltaic Efficiency in Quantum Dot Solar Cells by Multiple Exciton Generation

MEG is an inverse Auger process; Auger processes are enhanced in QDs:
$\langle 2P_e|v(r_1,r_2)|1S_e1S_e1S_h\rangle$

- **crystal momentum need not be conserved (not a good quantum number)**
- **Carrier thermalization is suppressed (phonon bottleneck)**





Quantum Dot

One photon yields two e^-–h^+ pairs

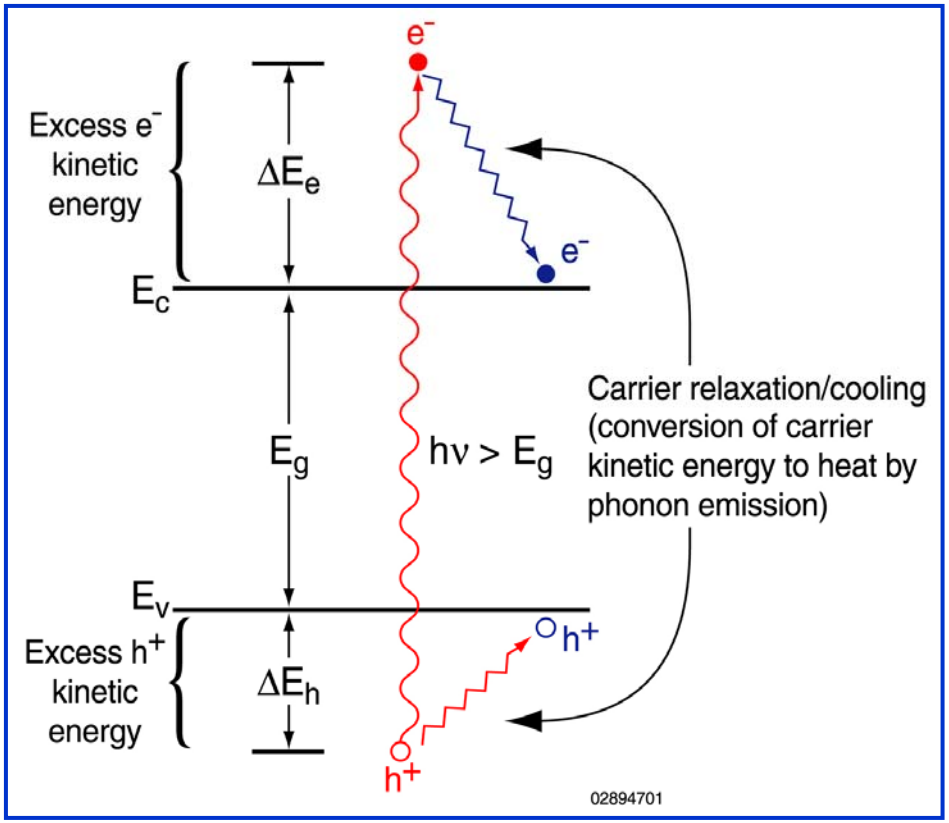
impact ionization (now called Multiple Exciton Generation (MEG)

(MEG can compete successfully with phonon emission and forward Auger processes)

A.J. Nozik, *Ann. Rev. Phys. Chem*. 52, 193, 2001; Physica E14,115, 2002; and in "*Next Generation Photovoltaics*", Marti& Luque, Eds, AIP, 2003;

Efficiency of Solar Photon Conversion

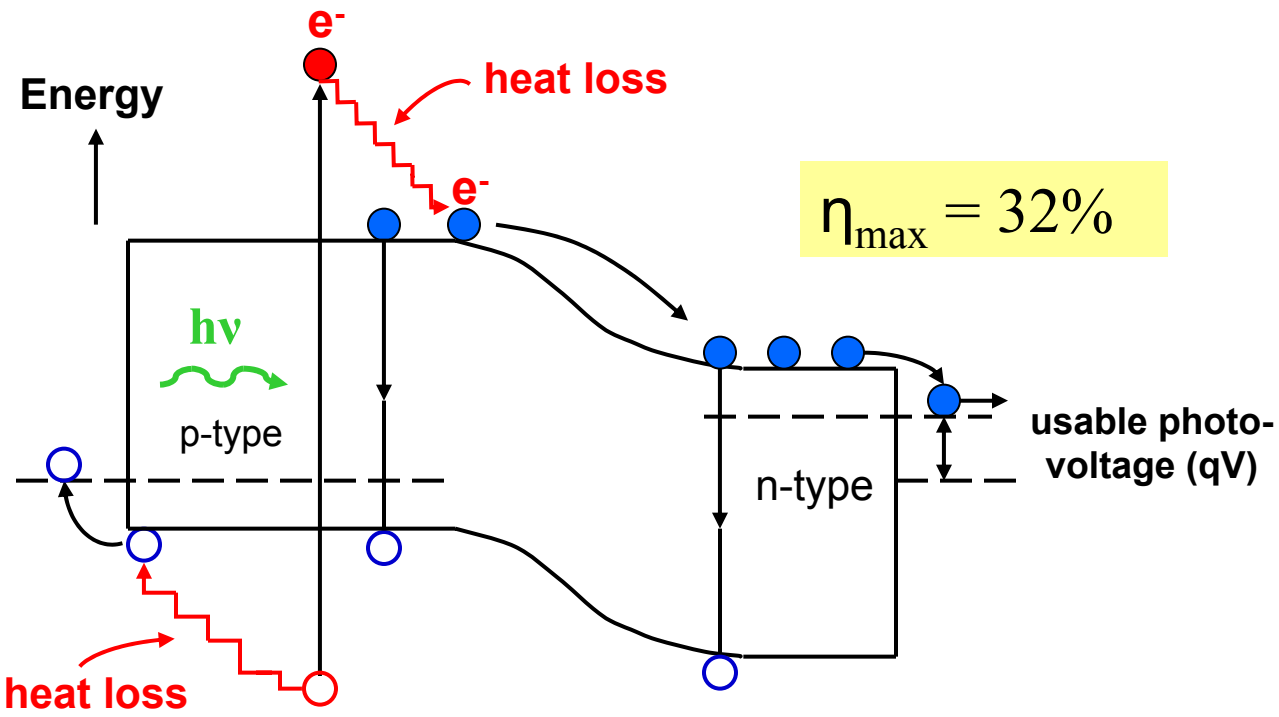
Main Process Limiting Conversion Efficiency (> 50% loss)



Hot e⁻ Relaxation

SOLAR ELECTRICITY

Conventional PV Cell



$\eta_{max} = 32\%$

1 e^- - h^+ pair/photon

Photovoltaic Cells

I. **1st Generation**
   - Single crystal Si
   - Poly-grain Si

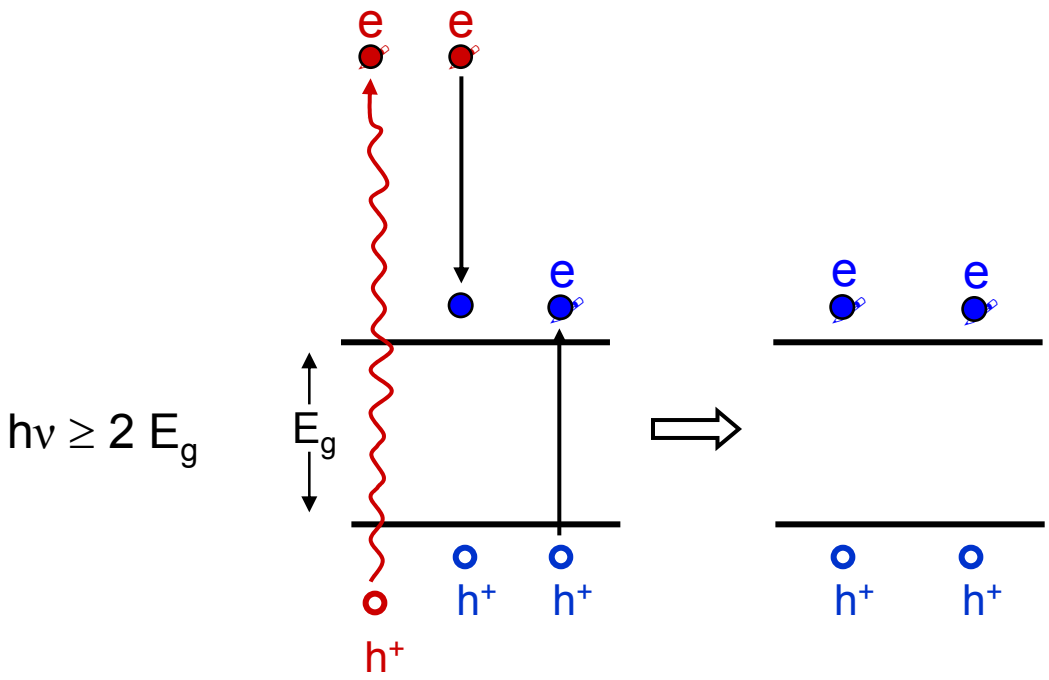
II. **2nd Generation (Polycrystalline Thin Film)**
   - Amorphous Si
   - Thin film Si
   - $CuInSe_2$
   - CdTe
   - Dye-sensitized Photochemical Cell

III. **3rd Generation (n_{theor}>32% Queisser-Shockley limit and low cost)**
   - *(High efficiency multi-gap tandem cells(here now but expensive))*
   - **Multiple Exciton Generation (MEG) solar cells**
   - **Quantum Dot Solar Cells**
   - **Singlet Fission Solar Cells**
   - Hot electron converters
   - Intermediate Band PV
   - Photon management (upconversion and down conversion)
   - Thermophotovoltaics/thermophotonics

See: M. Green, "Third Generation Photovoltaics". Springer, 2003, and Marti and A. Luque, "Next Generaton Photovoltaics", Inst. Of Physics Series in Optics and Optoelectronics, 2002

Another Way

Photocurrent Multiplication by Impact Ionization (I.I.)



1 photon yields 2 (or more) e^- - h^+ pairs

(I.I. previously observed in bulk Si, Ge, InSb, PbS, and PbSe > 30 years ago—mainly with applied electric field (avalanche photodiodes)—BUT NOT USEFUL FOR PV BULK MATERIALS

Detailed Balance Efficiency Calculations

Detailed balance model

-All photons above the bandgap are absorbed.
-Photons less than the bandgap not absorbed.
-Only loss if radiative recombination.
-All photogenerated carriers are collected.

QY for carrier generation:
QY=0 E<Eg
QY = M MxEg<E<(M+1)Eg for M <Mmax, where Mmax=4/Eg

Photogenerated current:

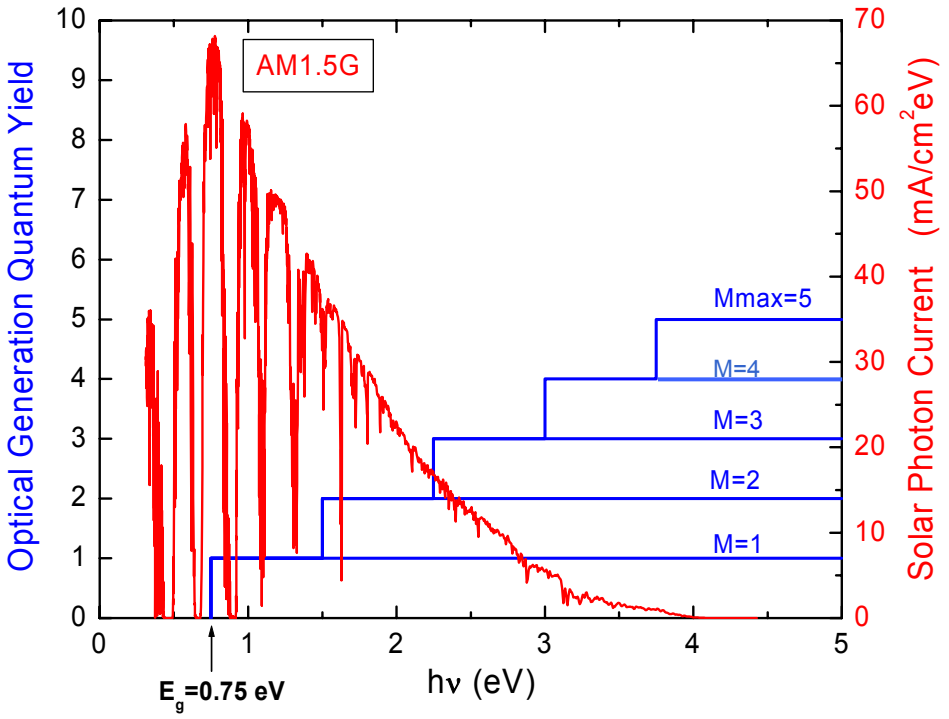
$$Jg = q\,C\int QY(E)\Gamma(E)dE$$

Recombination current:

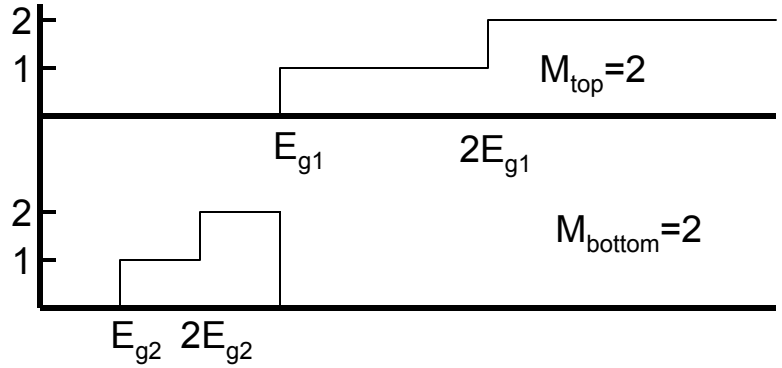
$$J_R(V,E_g) = qg\int_{E_g}^{\infty} \frac{QY(E)E^2}{\exp\left(\frac{E-qQY(E)V}{kT}\right)-1}\,dE$$

IV curve: $J(V)=J_g - J_R(V)$

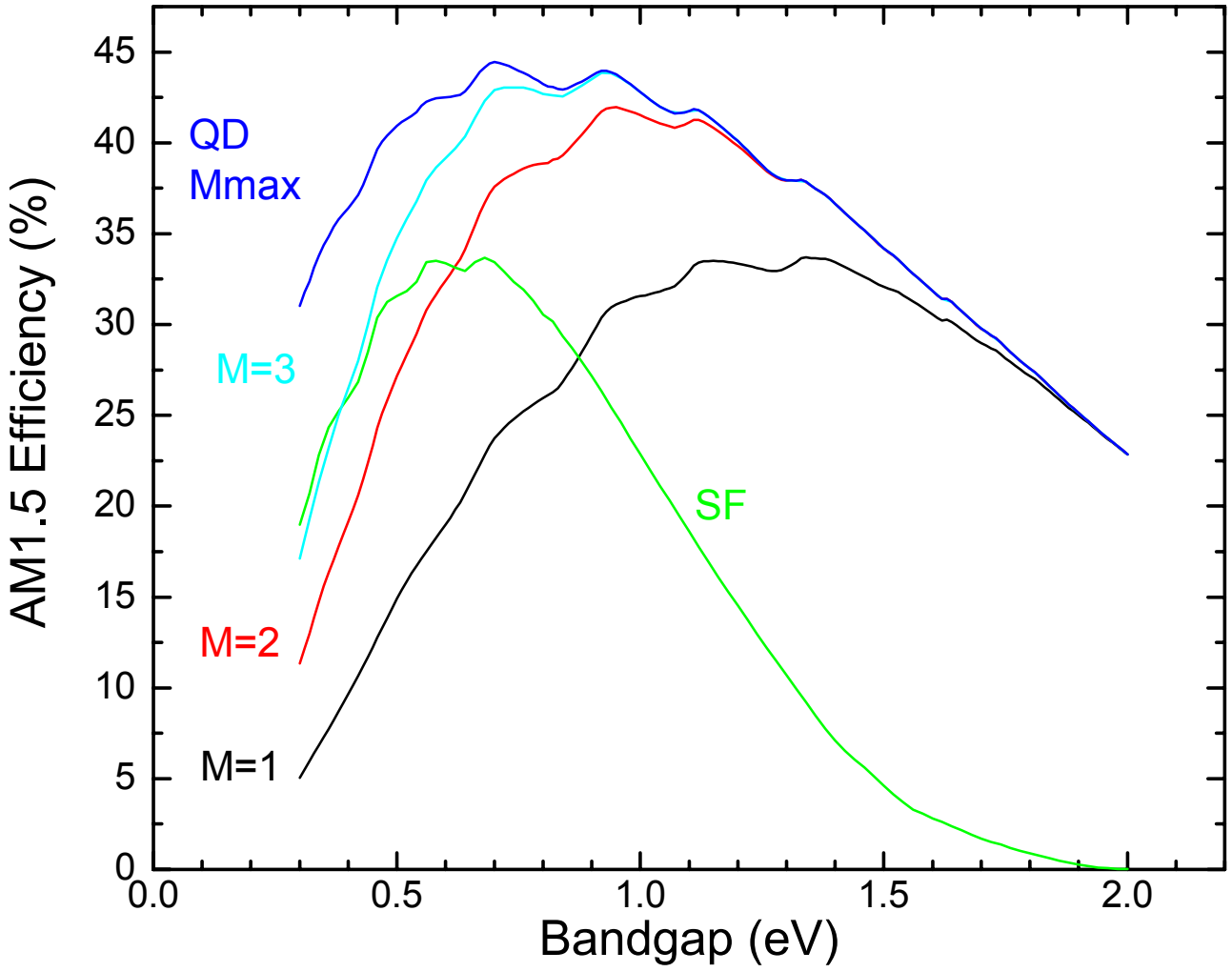
Series connected Tandem Cell:
$J(V) = J_1(V_1) = J_2(V_2)$ and $V = V_1+V_2$.



QY for a tandem MEG cell

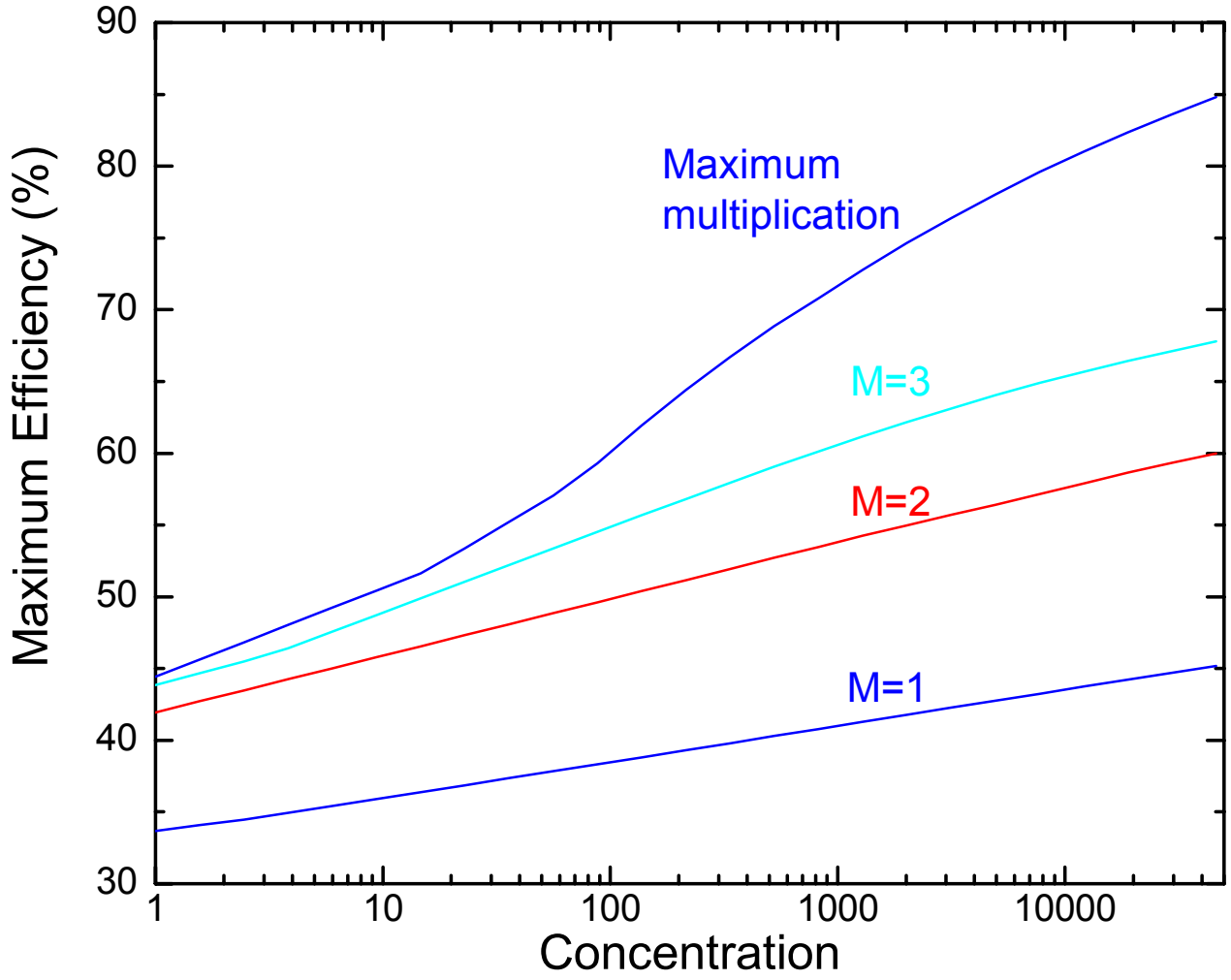


Limiting Efficiency for Unconcentrated AM1.5G Spectrum (Single Bandgap)



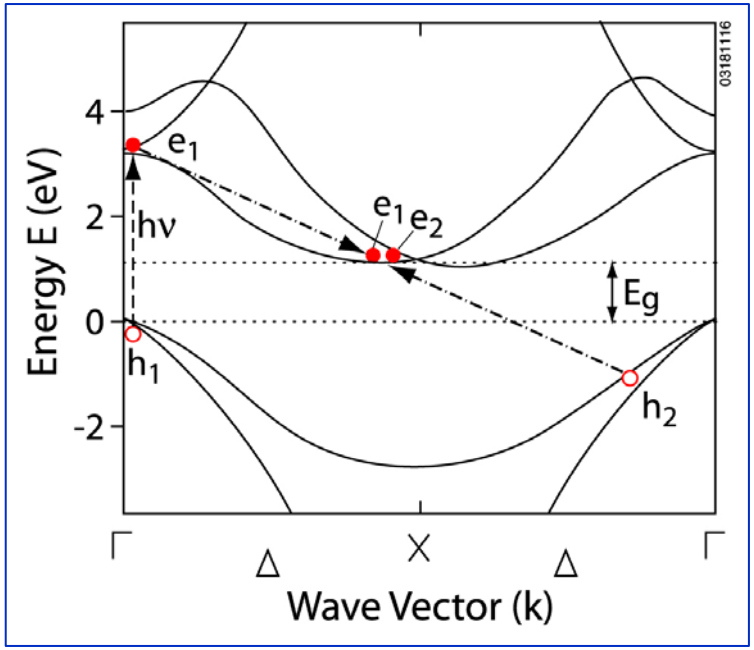
Hanna and Nozik, JAP 100, 74510 (2006)

RATE OF EFFICIENCY INCREASE WITH SOLAR CONCENTRATION



Single gap MEG cell efficiency increases at a faster rate under solar concentration than a normal semiconductor cell with no carrier multiplication (M=1).

Bulk Si



Queisser, et al. 1994

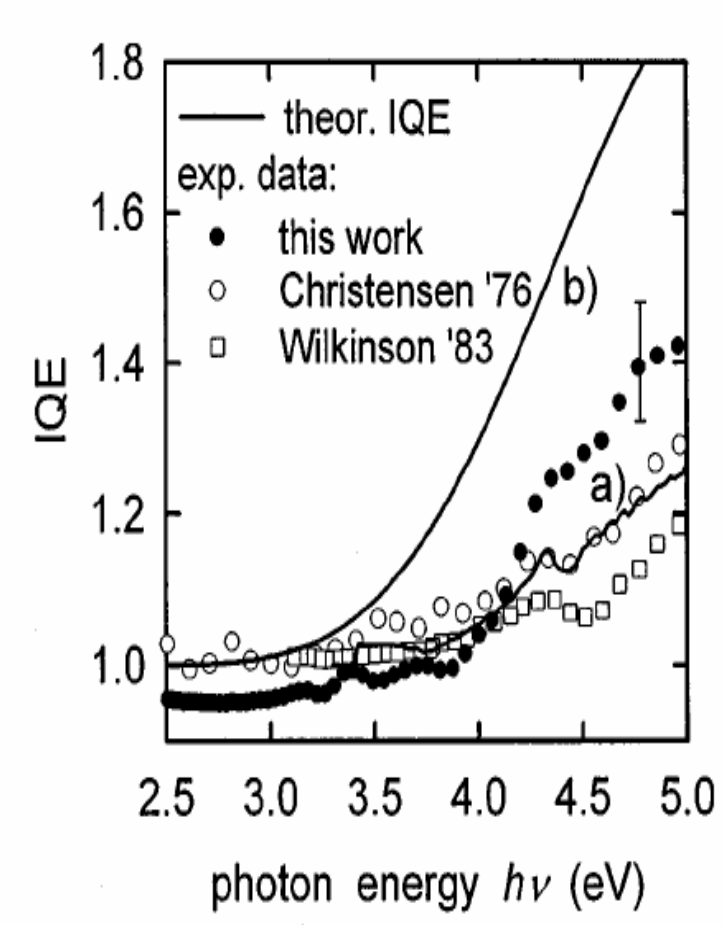
Conservation of energy E and momentum hk/(2π) is fulfilled if the two dash-dotted arrows add vectorially to zero.

QDs: ***Requirement for conservation of momentum is relaxed. Threshold should be lower.***

Quantum yield & IQE measurements

Si

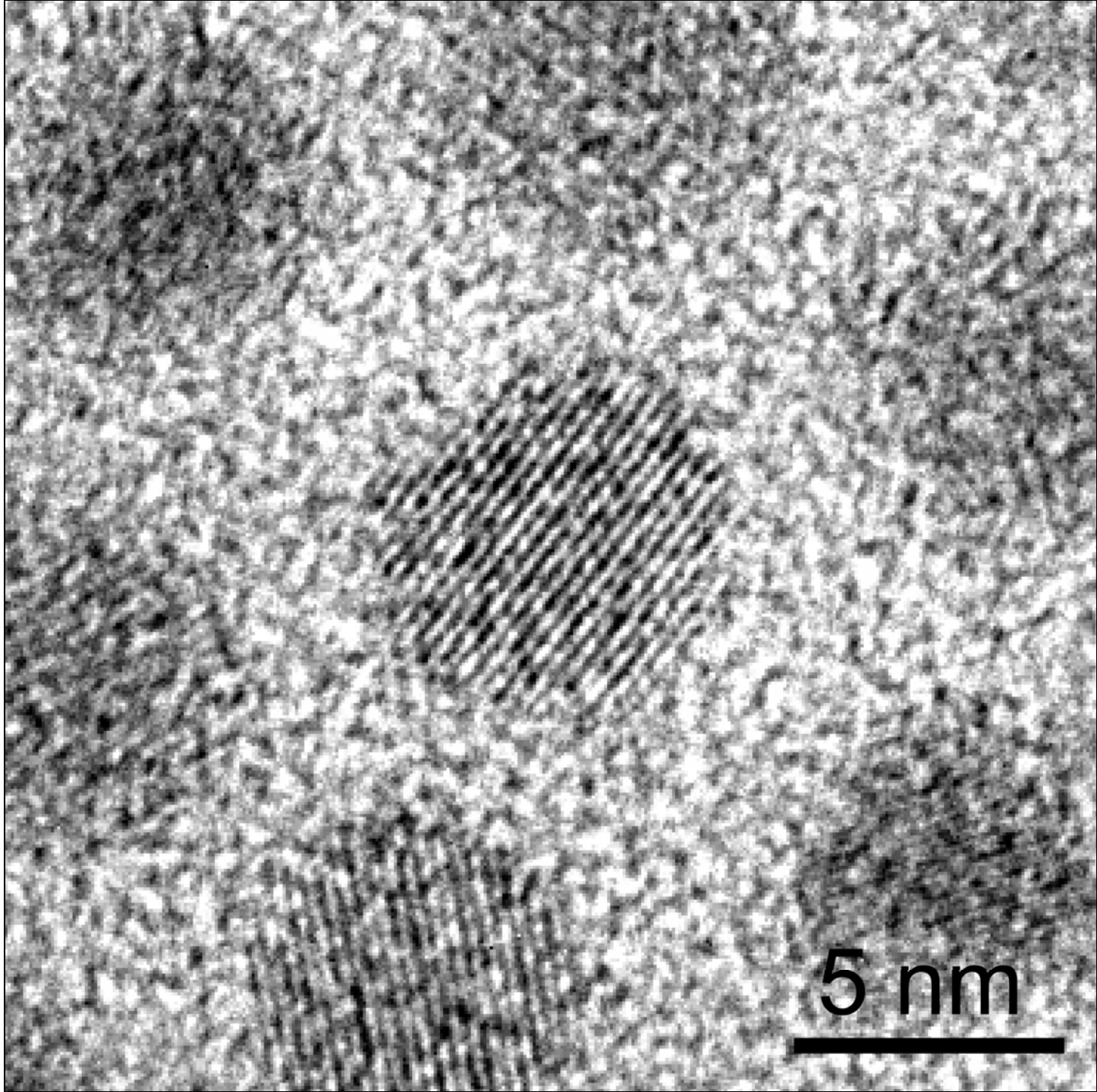
Because of the need to conserve momentum, and because the rate of impact ionization is much slower than the rate of phonon emission at low electron energies, impact ionization is an inefficient process in bulk semiconductors in the visible and near IR, and for Si requires UV photons.



Transmission Electron Micro-graph (TEM) of PbSe Quantum Dots (also called (Nanocrystals)

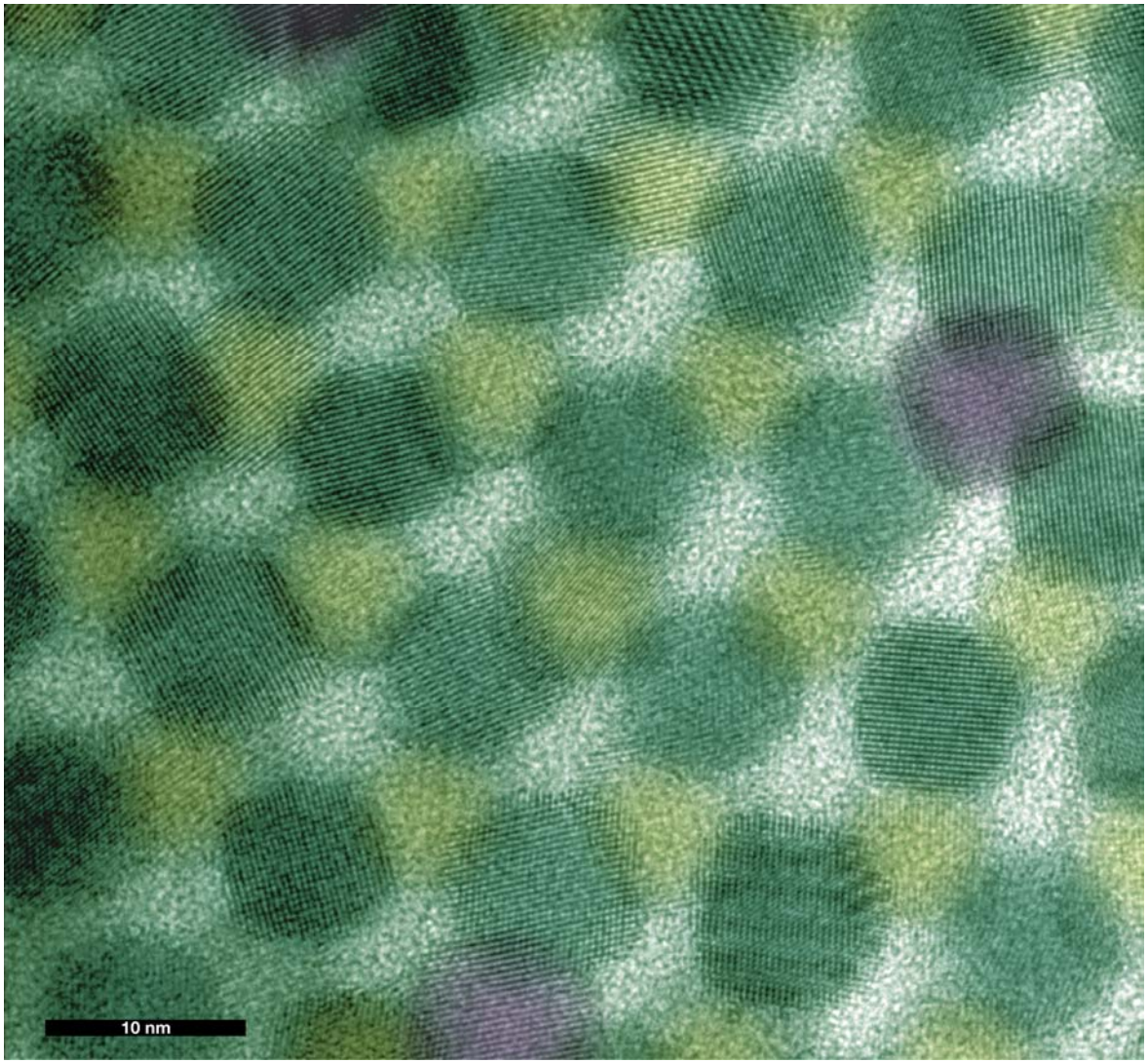
5 nanometers
5 x 10^{-9} m
0.000005 mm

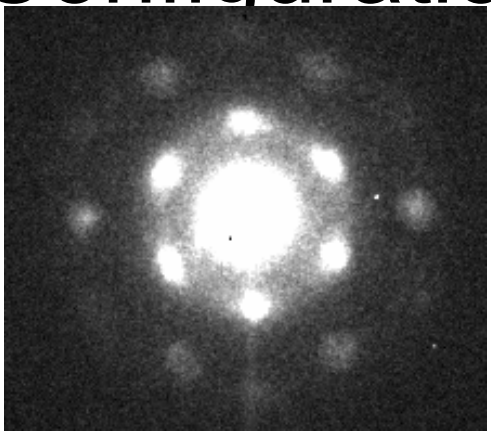
20 rows of atoms, ~ 6000 atoms, in these QDs



TEM From Andrew Norman

PbTe Arrays in HCP Configuration





PbTe NCs

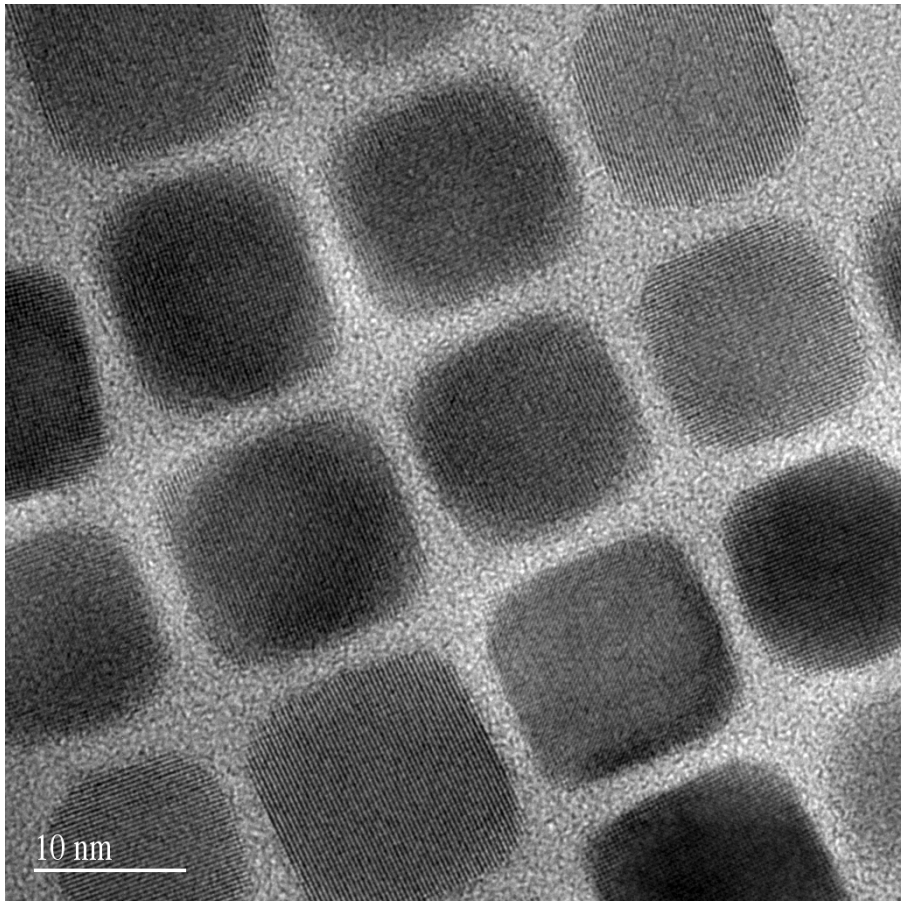
- New Synthetic Routes
- First optical characterization
  - -absorption spectra
  - -Photoluminescence
  - -multiple exciton generation
- Sphere to Cube Transition
- Comparison of Lead Salt Properties

Murphy, J. E. et al. "PbTe Colloidal Nanocrystals: Synthesis, Characterization, and Multiple Exciton Generation." *J. Am. Chem. Soc.* ***128****, 3241–3247 (2006).*

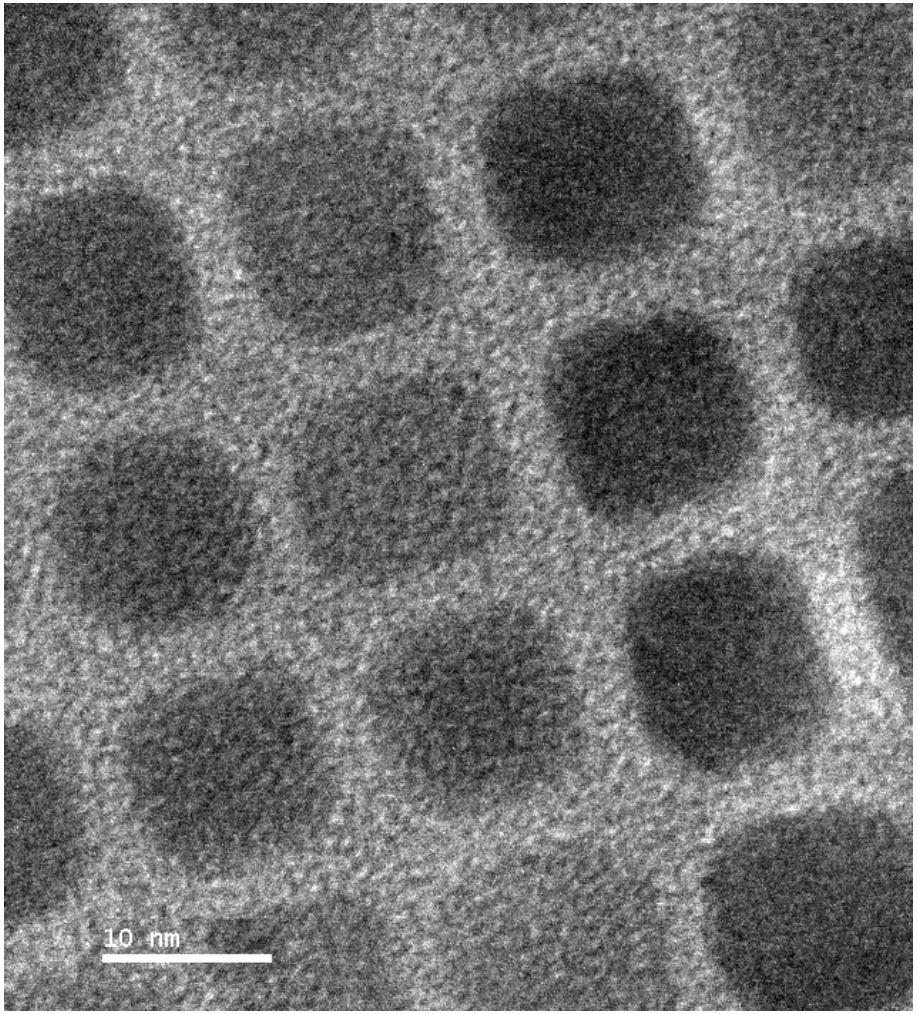
TEM: Andrew Norman

Arrays of Cubic-shaped Lead Salt NCs

PbSe



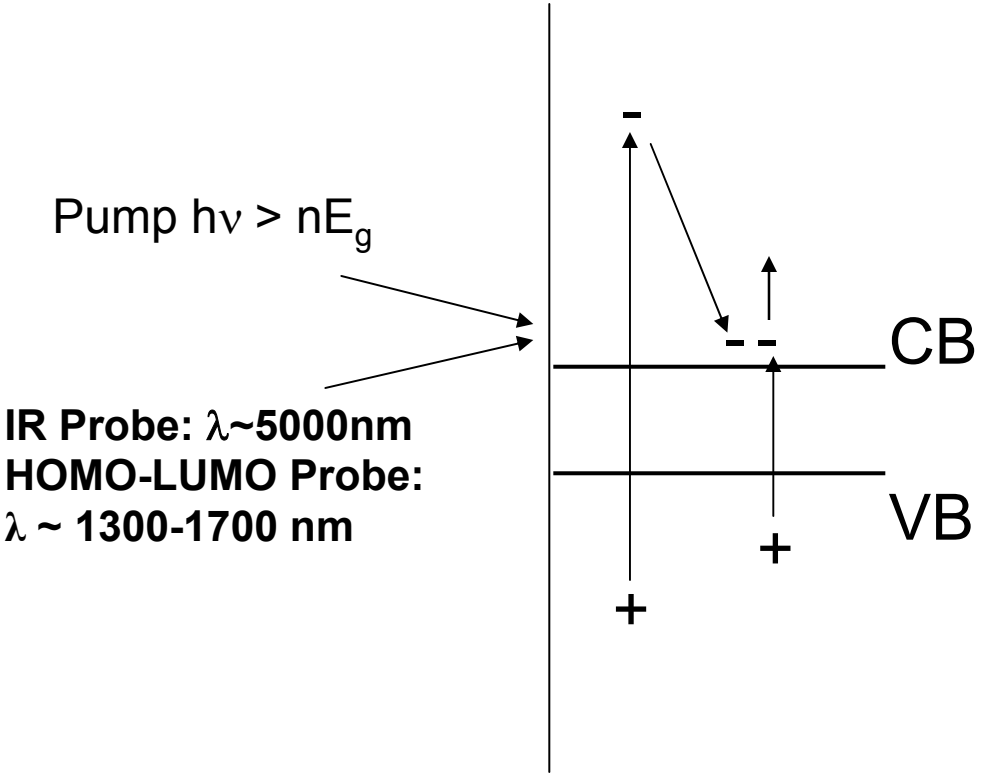
PbTe



TEM: Andrew Norman

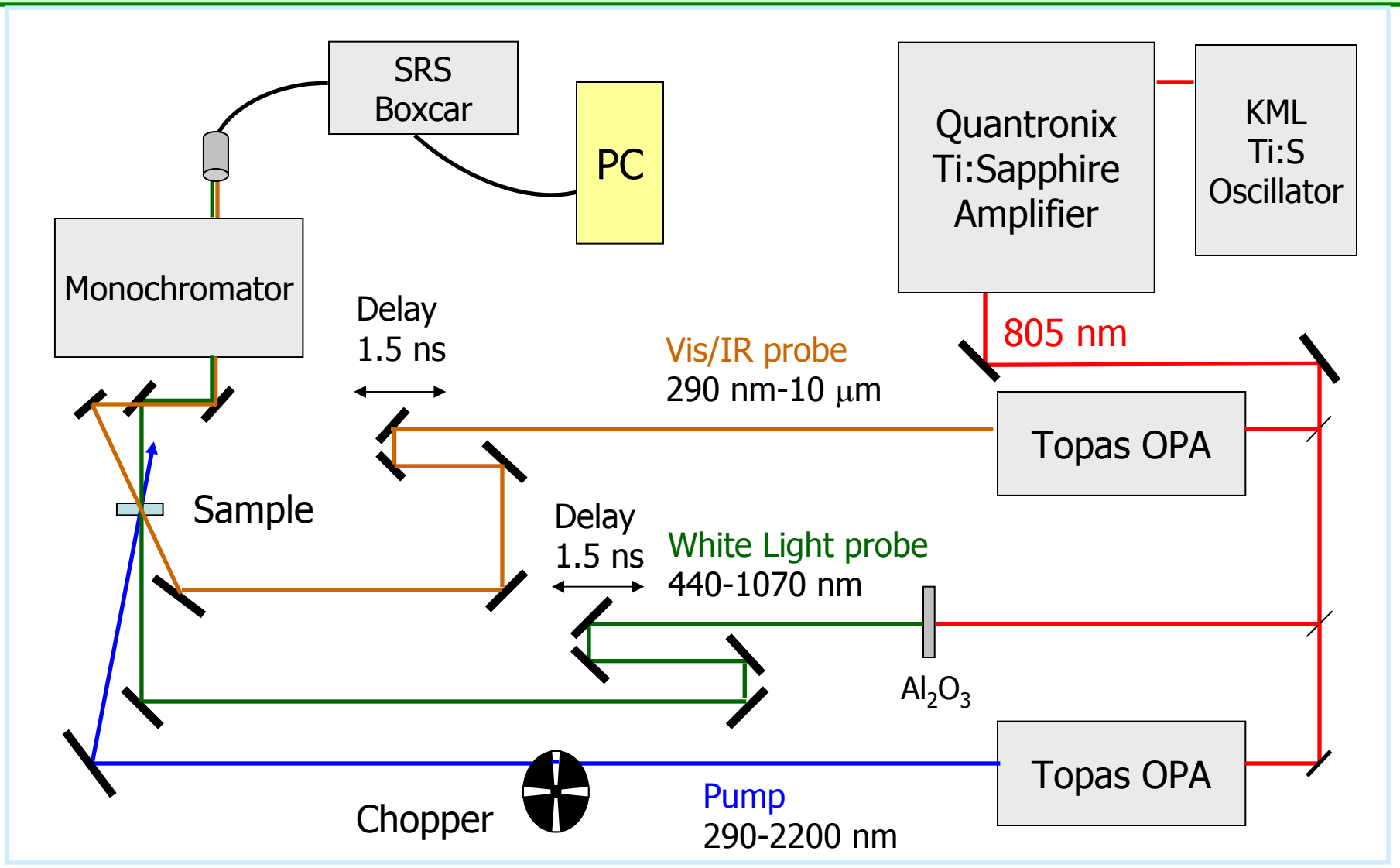
MEG DYNAMICS

Determine the photogenerated carrier density (QY) and thus MEG dynamics by: (a) measuring the free carrier absorption (IR probe) and exciton bleach (HOMO-LUMO probe); (b) measuring dynamics of multi-exciton decay vs single exciton decay, and the rise time of exciton bleaching and induced exciton absorption



$\Delta\alpha$ α e-h pair (exciton) density; 1S bleach decay dynamics = f(multiexciton density); 1S bleach dynamics and induced exciton absorption determine carrier cooling rate and carrier multiplication rate

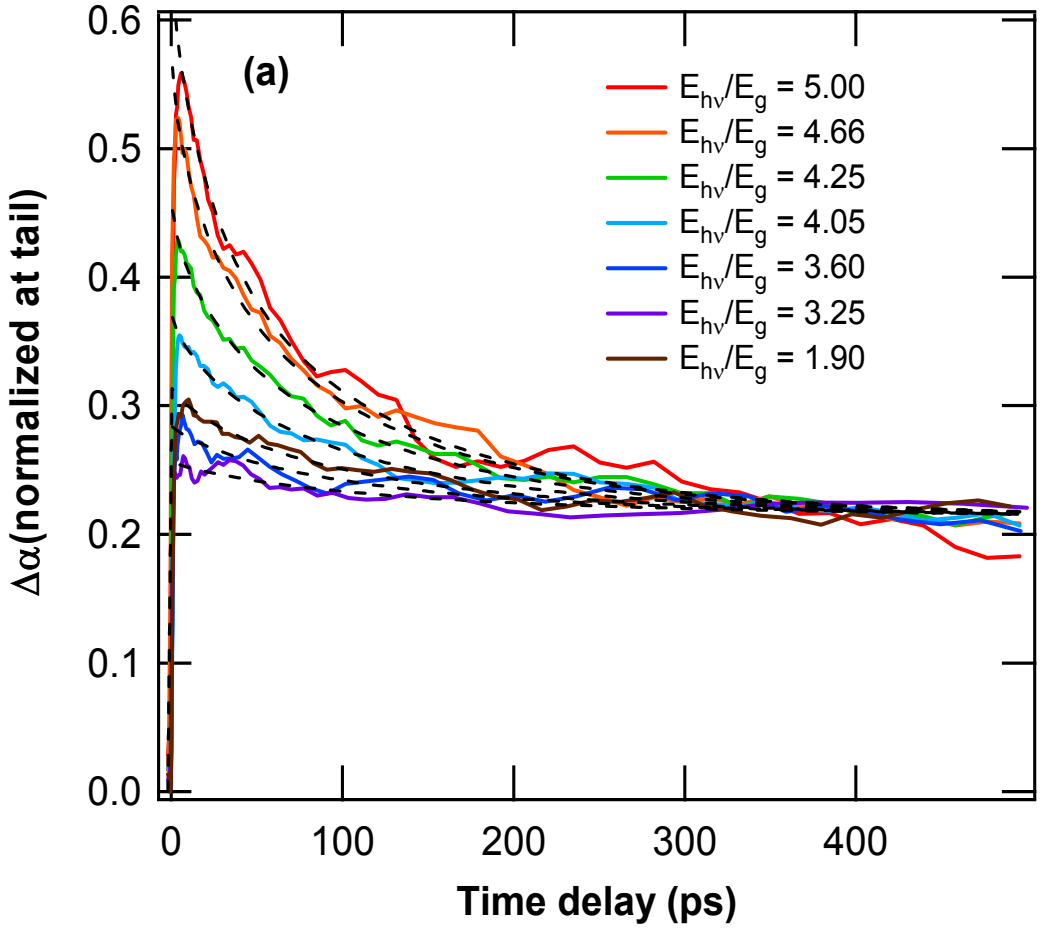
Transient absorption experimental setup



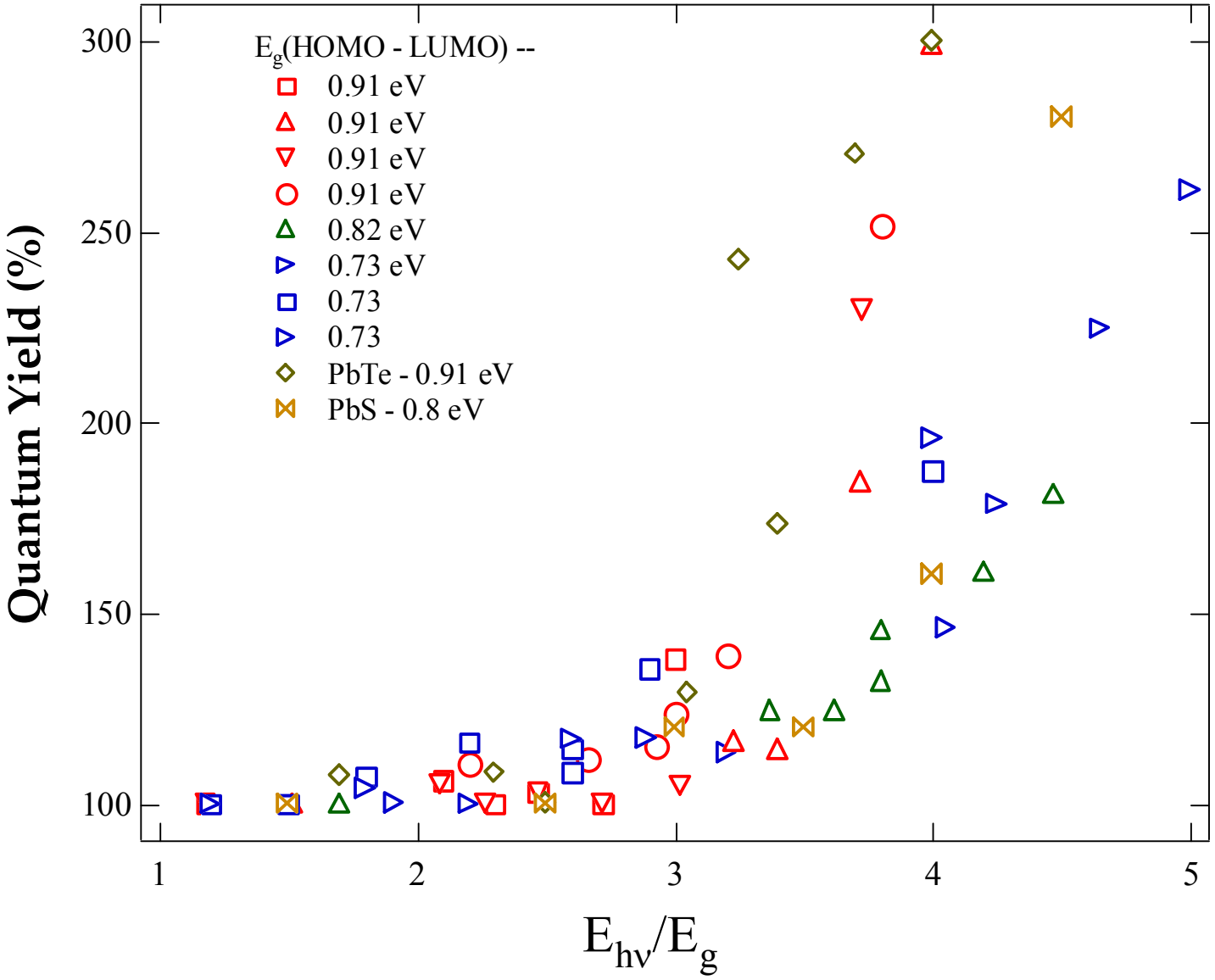
Experimental Verification of Greatly Enhanced e^--h^+ multiplication (we term Multiple Exciton Generation (MEG)) in Quantum Dots

- R.D. Schaller and V.I. Klimov, Phys. Rev. Letts, 92, 186601 (May), 2004 (PbSe QDs)
- R.J. Ellingson, M. Beard, J. Johnson, P. Yu, O.Micic, A. Shabaev, A. Efros, A.J. Nozik, Nano Letters 5, 865, 2005 (PbSe and PbS QDs; 300% QY (3 e^-/photon) at 4 times Eg)
- Recently, MEG also found in PbTe (NREL, JACS, 128, 3241, 2006) and CdSe (LANL, APL, 2005); 7 e^-/photon in PbSe! (LANL, NanoLetts, 6, 424, 2006); InAs (Van Maekelbergh, Banin, et. Al., J. Phys. Chem. C (2007)); and Si (NREL, 2007)

Exciton dynamics for different pump energies with mid-IR intraband probe (5 μ)

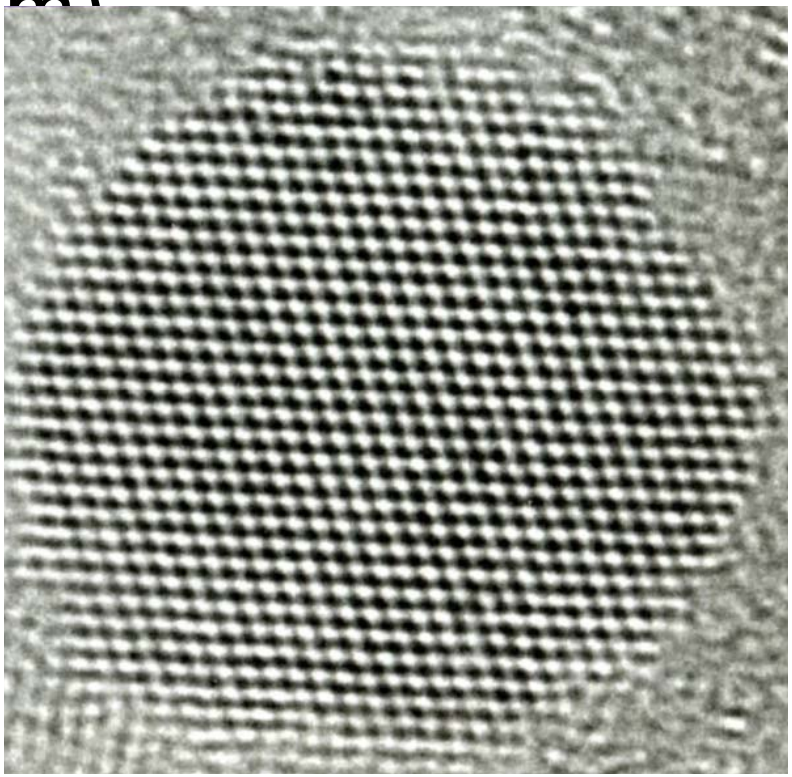


MEG in PbX; X = Se, S, Te
(QY > 200% means 3 e-/photon are created; QY = 300% means all dots have 3 e-)



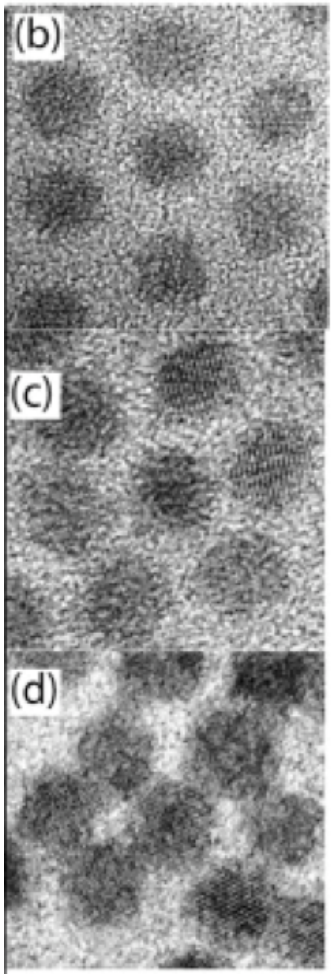
Silicon Nanocrystals

- Particles 3-10 nm diameter
- Bulk bandgap 1.12 eV (~1100 nm);
- Si NC bandgaps 1.22-1.6 eV (1016 – 775 nm)



TEM image courtesy of Innovalight, Inc.

Amine soak properties

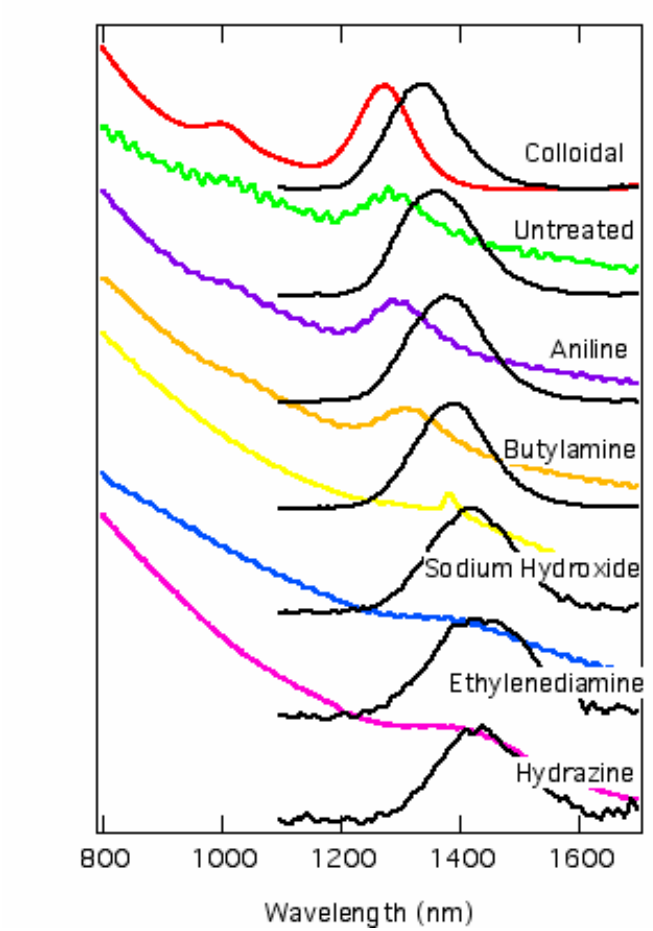


oleate

aniline

ethylenediamine

ligand	d (nm)	ϵ_{ligand}	mobility ($cm^2\ V^{-1}\ s^{-1}$)
butlyamine	0.4	5.4	7.4
hydrazine	0.25	53	29.4
NaOH	0.1	1	35
ethylenediamine	0.4	16	47



Murphy, Beard, Nozik, JPC B 2006

PROPOSED NEW PHYSICS BASED ON MODEL INVOLVING:

COHERENT SUPERPOSITION OF MULTI-EXCITON STATES IN SEMICONDUCTOR NANOCRYSTALS

Shabaev, Efros, Nozik, Nano Lett. 6, 2856 (2006)

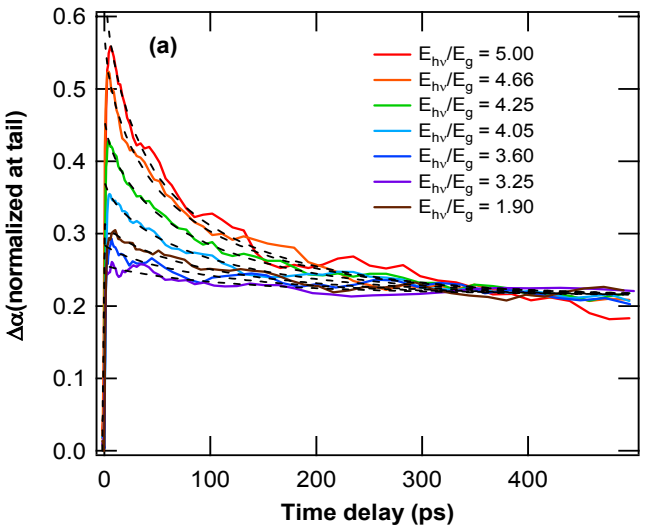
Other proposed models to explain MEG:

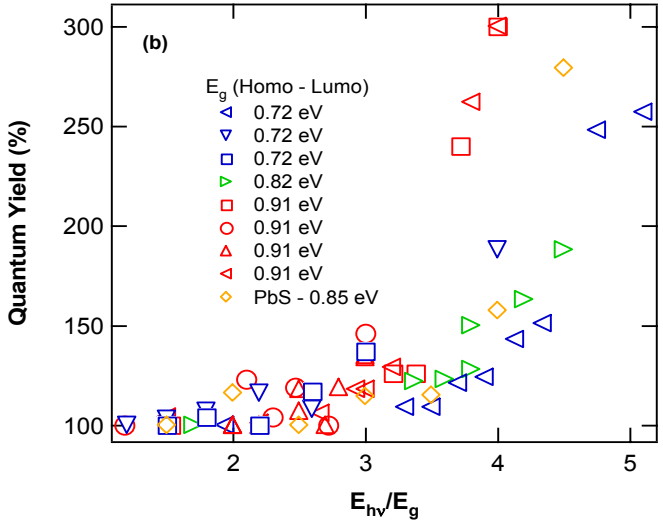
R.D. Schaller, V.M. Agranovich, and V.I. Klimov, *Nature Phys.* **1** (2005) p. 189.

A. Franceschetti, J.M. An, and A. Zunger, *Nano Lett.* **6** (2006) p. 2191.

Multi-Exciton Generation by One Photon

Efficient Multi-Exciton Generation in PbSe



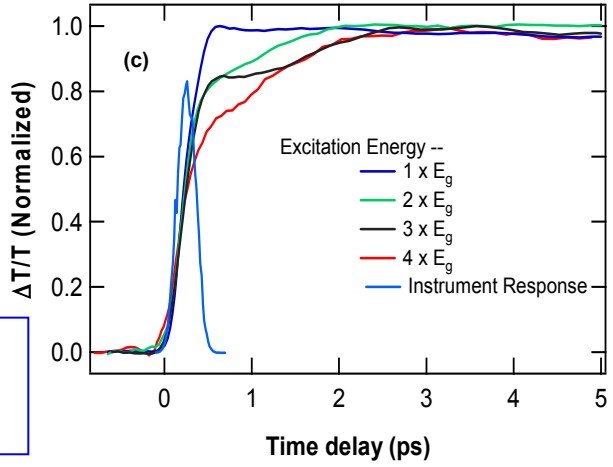


R.Ellingson, et.al. NanoLetters TBP

What is the reason of such high efficiency? - Impact Ionization?

Puzzle:

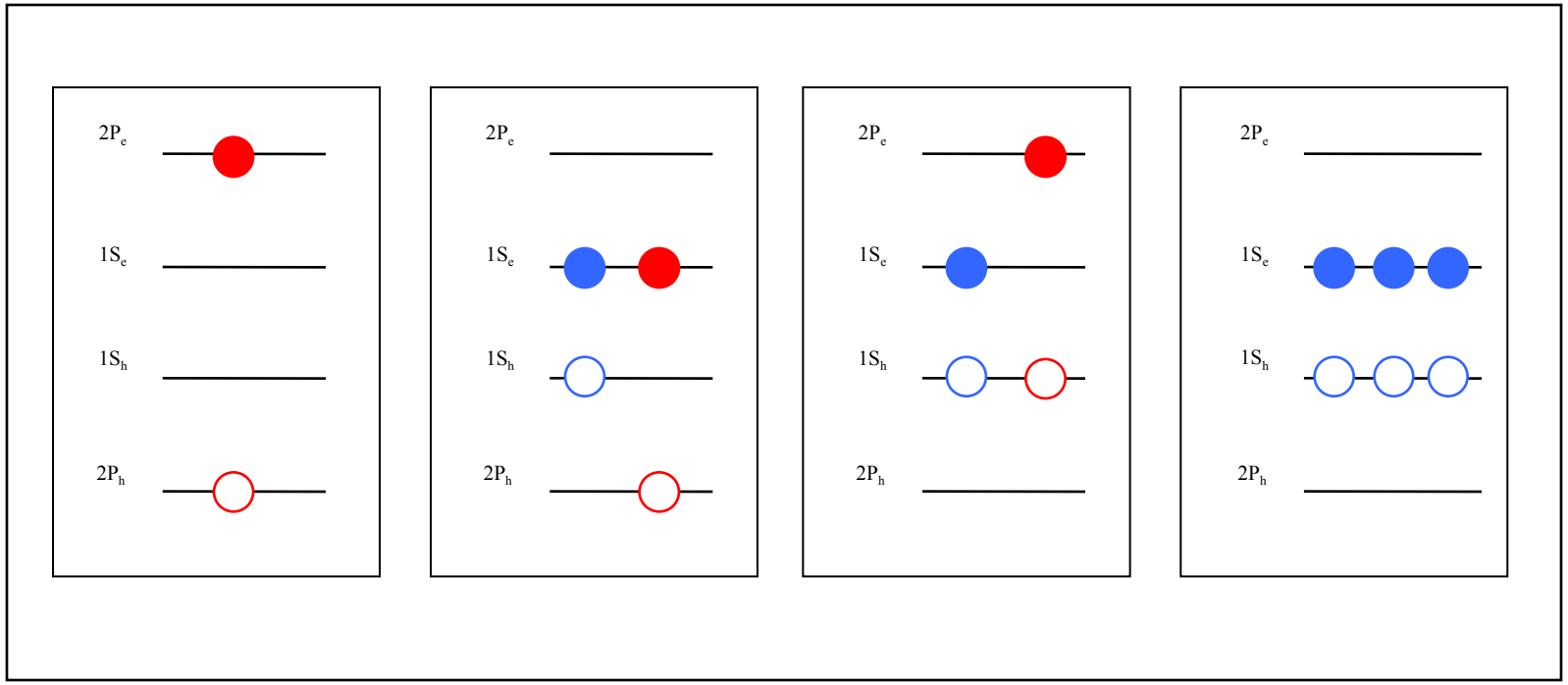
- Decay time ~100 ps (Auger process)
- Rise time ~ < 2-3 ps (Inverse Auger process)



Instantaneous creation of a coherent superposition of several electron-hole pairs by a single photon

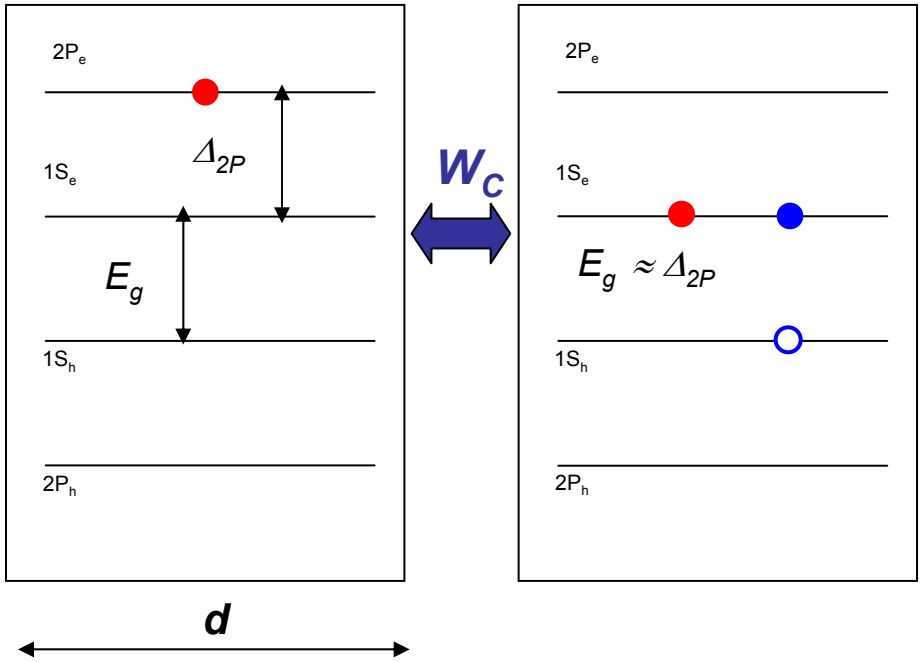
NEW MODEL FOR MEG

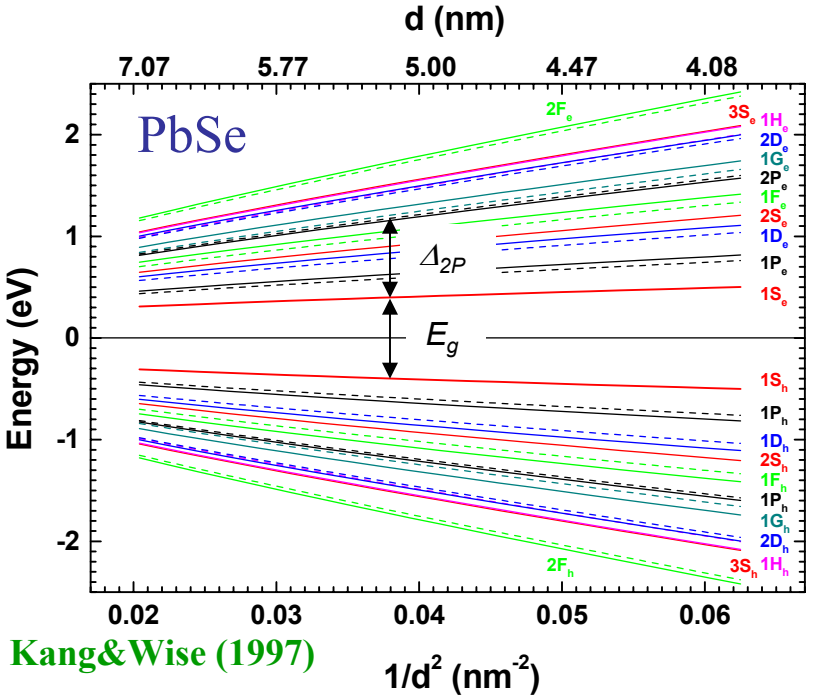
Coherent Superposition of Multi-Excitonic States in PbSe QDs

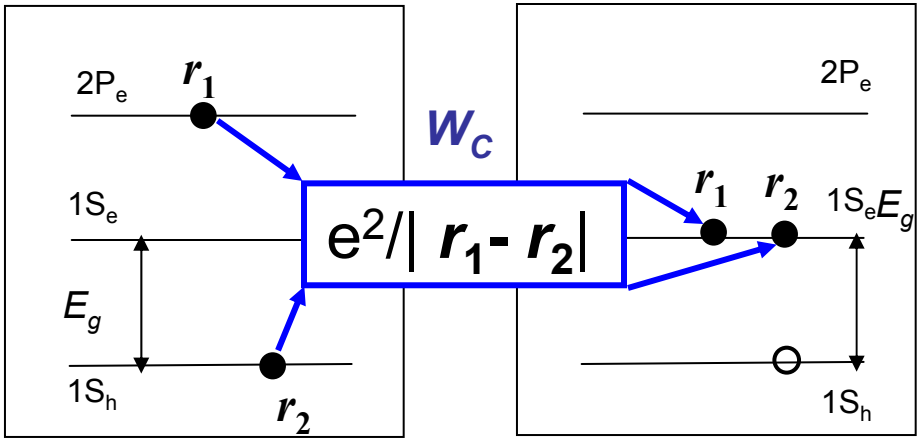


States with Energy Larger than Energy Gap

Electron in NC occupying $2P_e$ state:







Two states are degenerate and coupled:

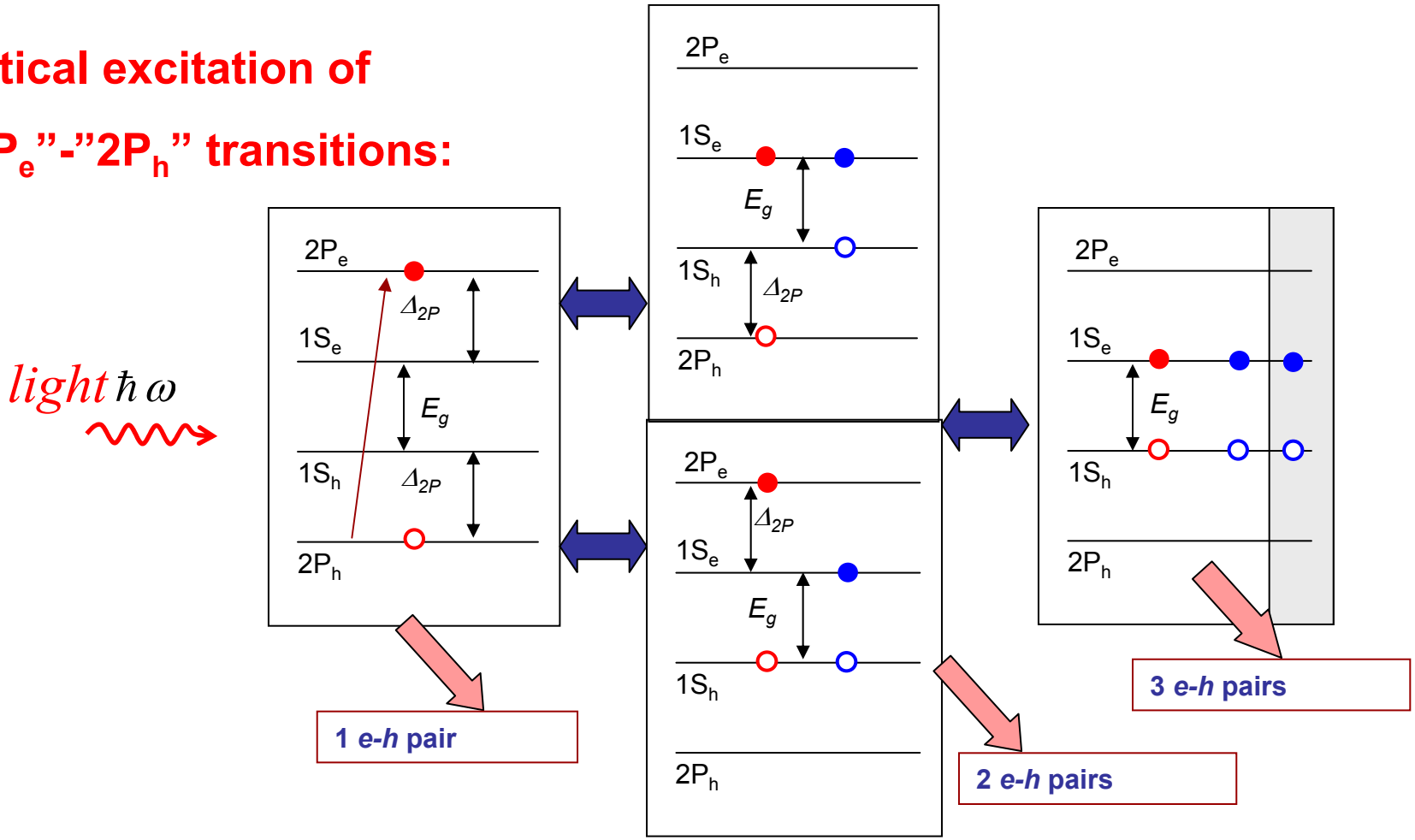
$W_C = \langle 2P_e | v(r_1,r_2) | 1S_e\, 1S_e\, 1S_h \rangle$

$\neq 0$

Coherent Superposition of Multi-Exciton States

Optical excitation of

"$2P_e$"-"$2P_h$" transitions:



The efficiency of the multi-exciton generation depends on the relaxation mechanism.

There is high probability that the state relaxes to the two *e-h* pair state.

Density matrix

Theoretical description requires:

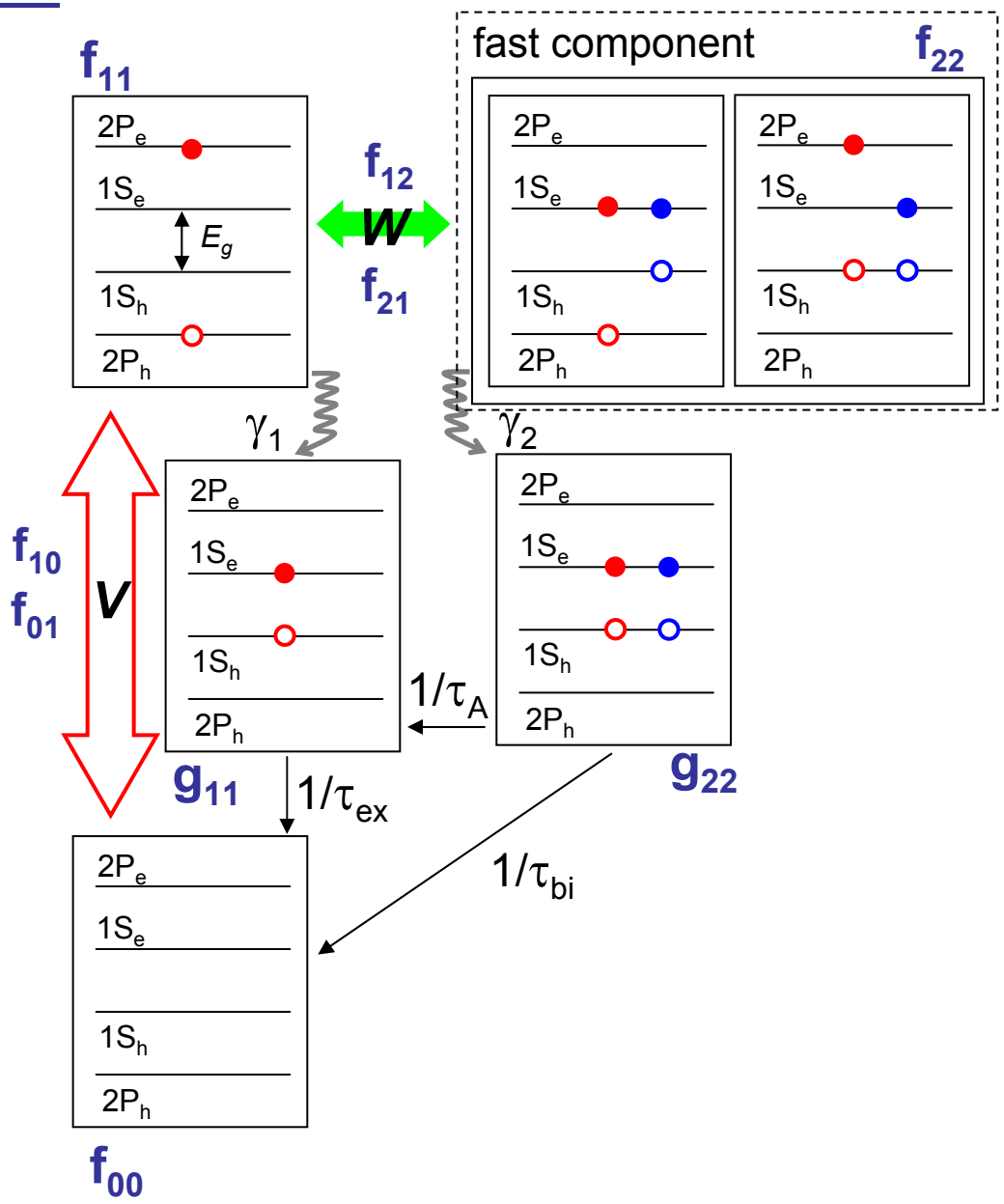
time dependent density matrix for:

- **Short pulse excitation**
- **Different relaxation mechanisms**

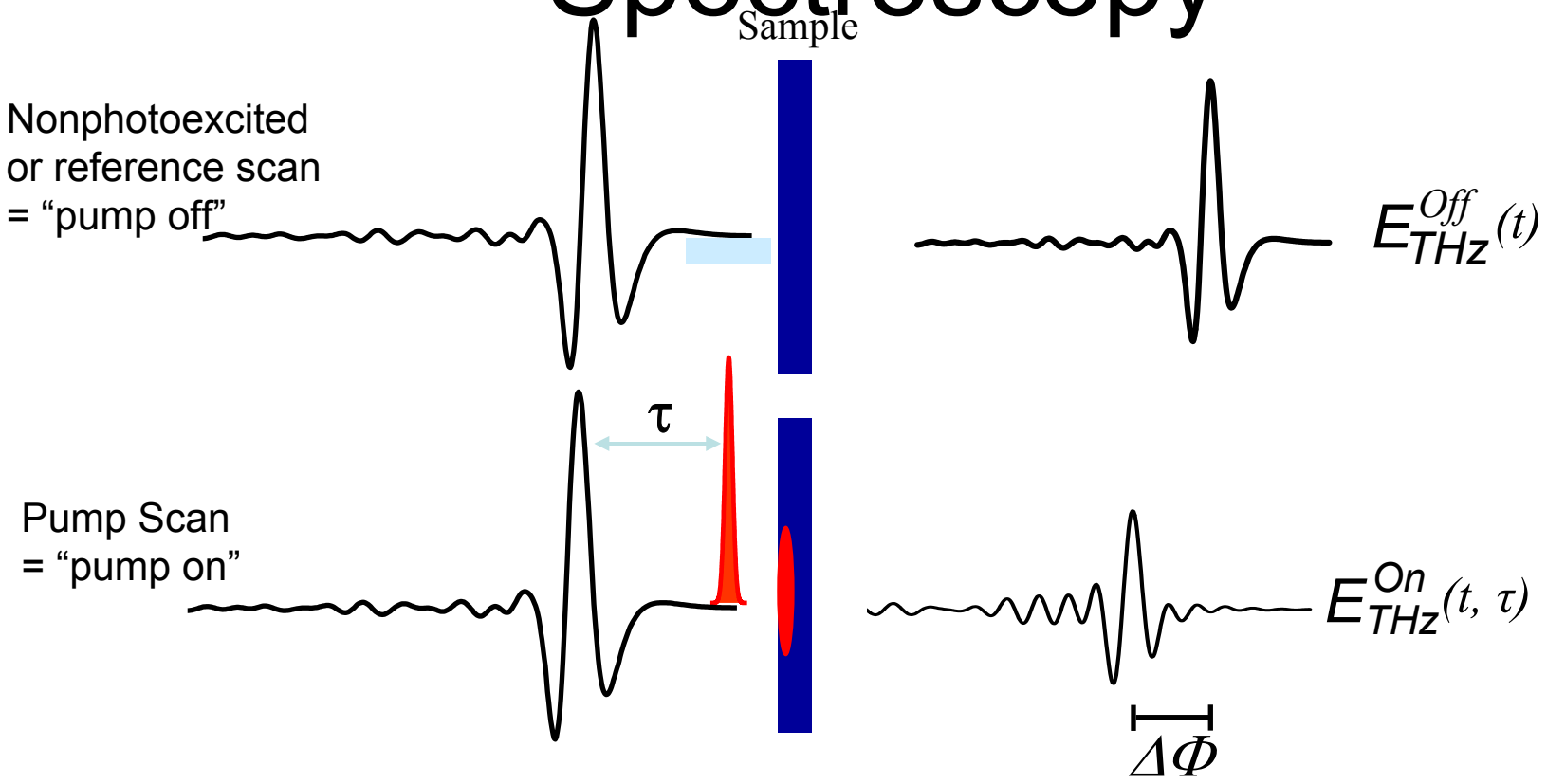
$$\frac{\partial \rho}{\partial t} = \frac{i}{\hbar}[\rho H]$$

Dynamics for times: $\Delta t << \tau_A << \tau_r$

(Shabaev, Efros, Nozik, Nano Lett. 6, 2856 (2006)



Time Resolved THz Spectroscopy

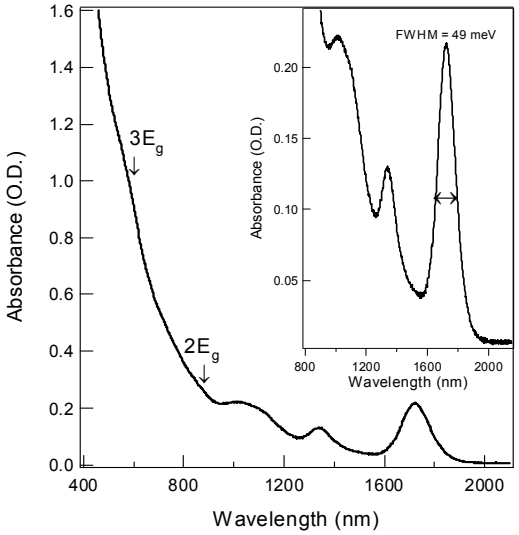


$$\frac{\Delta E_{THz}(t,\tau)}{E_{THz}^{Off}(t)} \cong \frac{-\sigma(\tau)x}{2cn\varepsilon_o}$$

- Measure transient THz frequency average conductivity
- Subpicosecond resolution
- Mechanistic information
- No electrical contacts

Film Treatments

Treatment	*d(nm)*	ε_S	n_{ave}	μ ($cm^2V^{-1}s^{-1}$)
Oleic Acid	1.8	2	1.57	---
Aniline	0.8	2	2.2	---
Butlyamine	0.4	5.4	2.46	7.4
ethylenediamine	0.4	16	2.62	47.0
hydrazine	0.25	52	2.69	29.4
NaOH	0.1	1	2.4	35.0

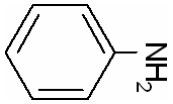


Oleate Cap

$CH_3(CH_2)_7HC{=}CH(CH_2)_7COOH$

D ~ 1.8 nm

Aniline Cap

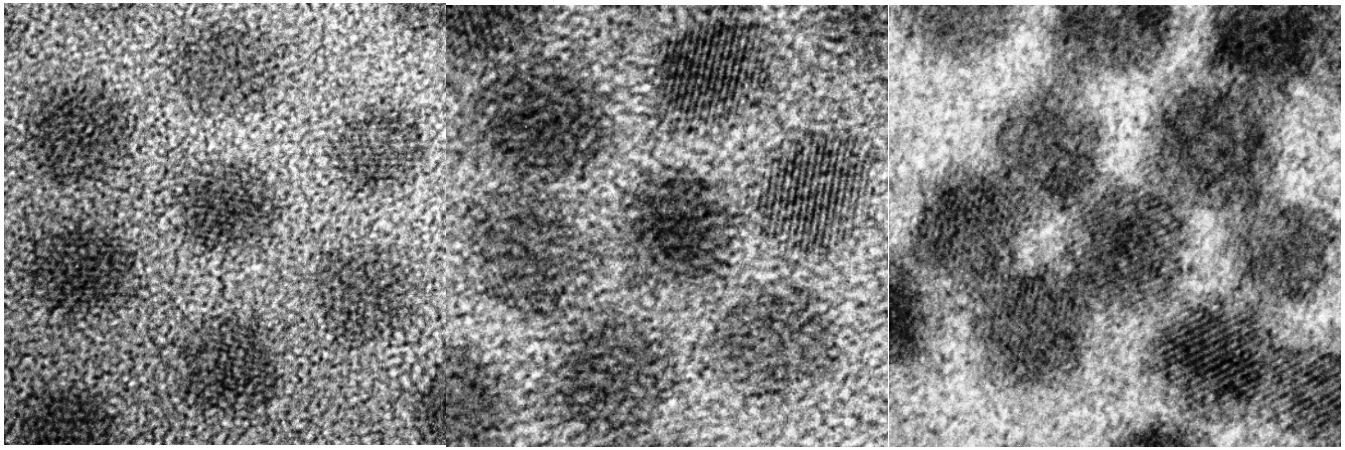


D ~ 0.8 nm

Ethylenediamine

$H_2NCH_2CH_2NH_2$

D = < 0.4 nm



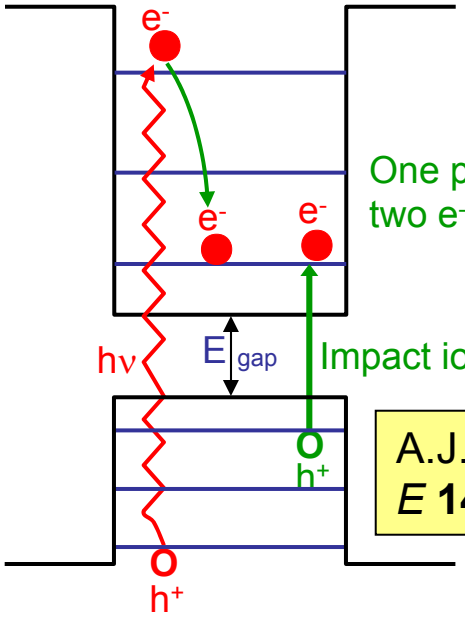
Quantum Dot Solar Cells

Potential Major Advantages of Using Quantum Dots

- Enhanced photocurrent multiplication by MEG (Inverse Auger Process
- Hot electron transport through minibands in QD arrays
- Slowed Cooling of High Energy (Hot) Electrons (phonon bottleneck)

Enhanced Photovoltaic Efficiency in Quantum Dot Solar Cells by Inverse Auger Effect (Impact Ionization)

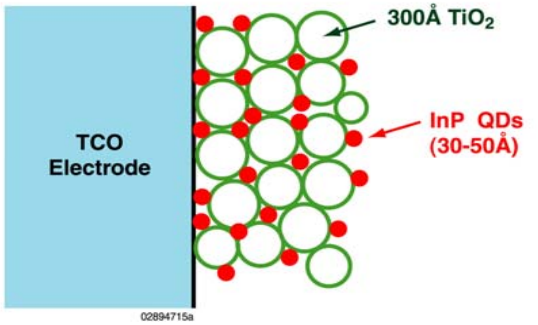
Quantum Dot Solar Cells

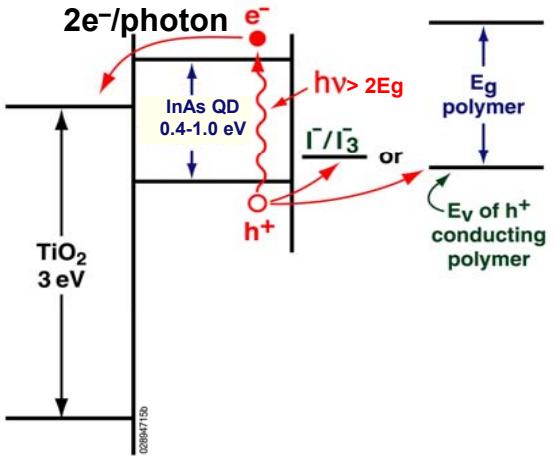


One photon yields two e^-–h^+ pairs

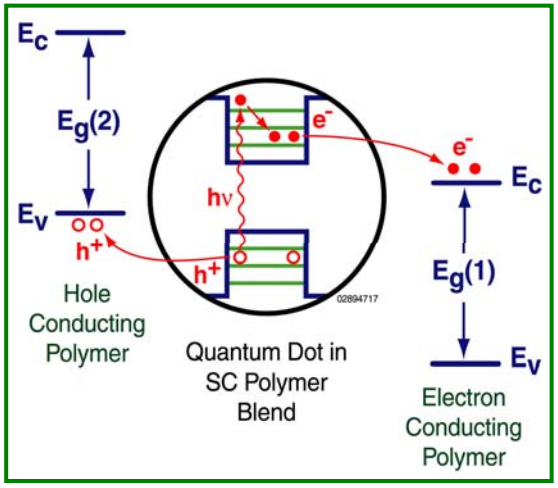
A.J. Nozik, *Physica E* **14**, 115 (2002);

QD-Sensitized Nanocrystalline TiO_2 Solar Cell

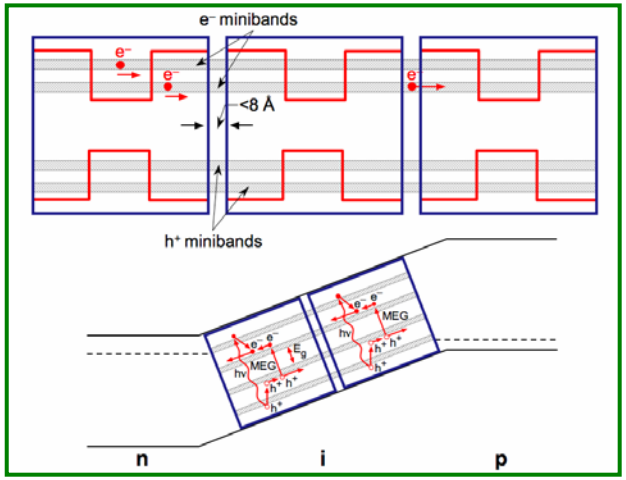




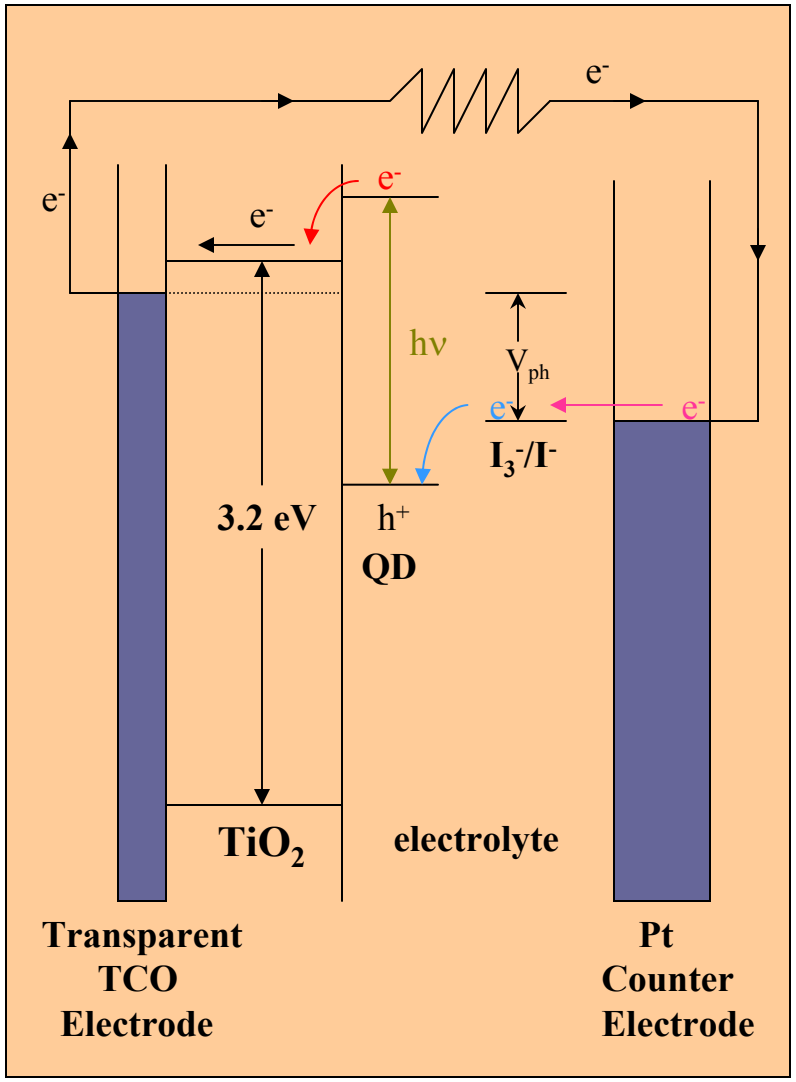
QD-Conducting Polymer Blend Solar Cell

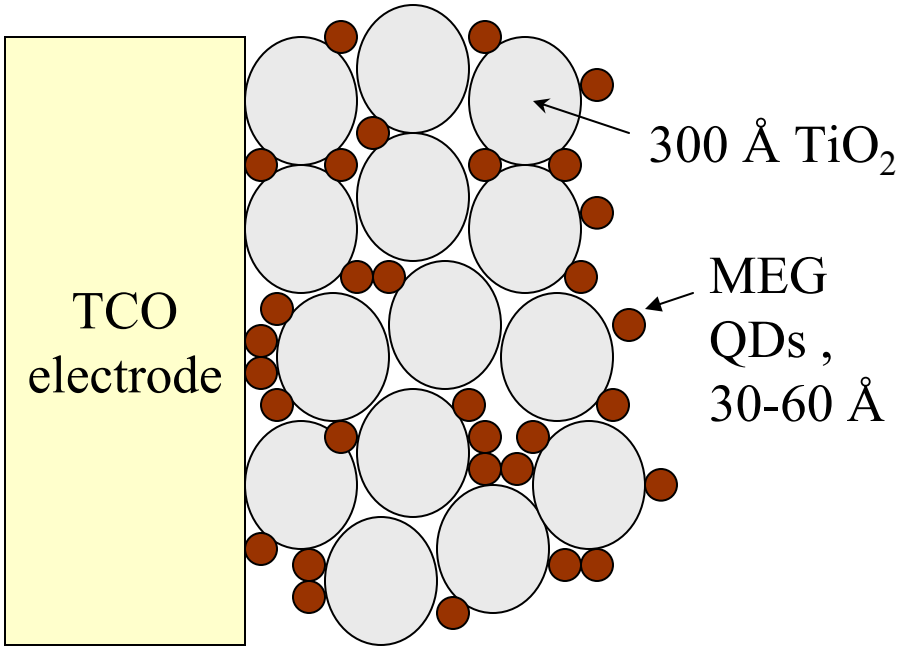


p-i-n QD Array Solar Cell



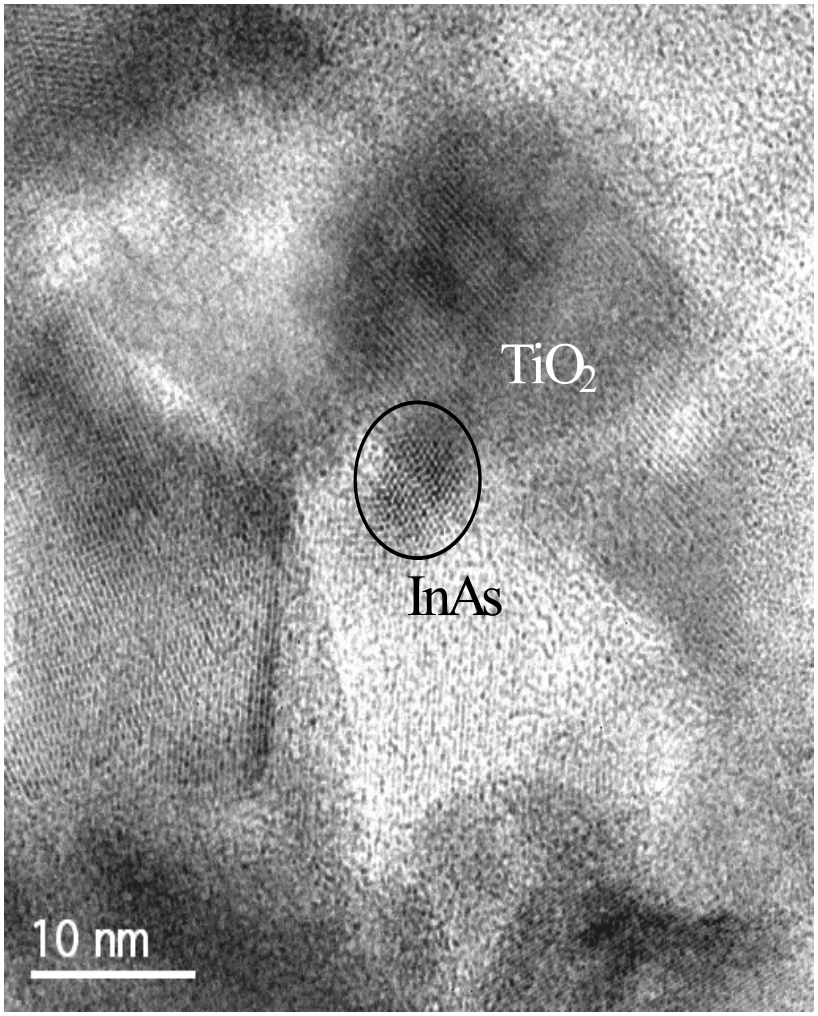
Quantum Dot Sensitized TiO_2 Solar Cell

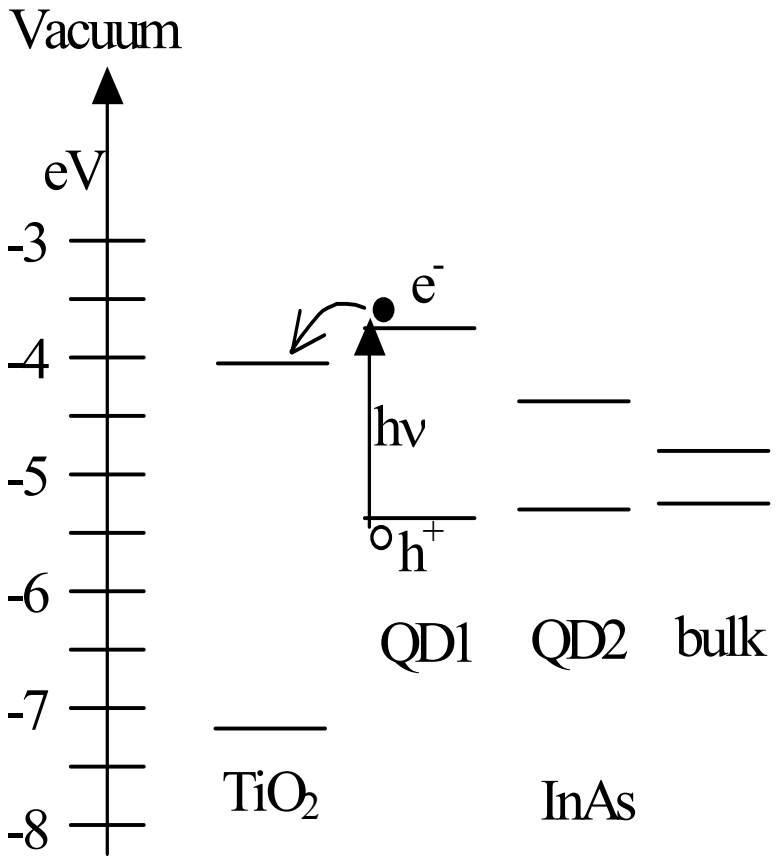




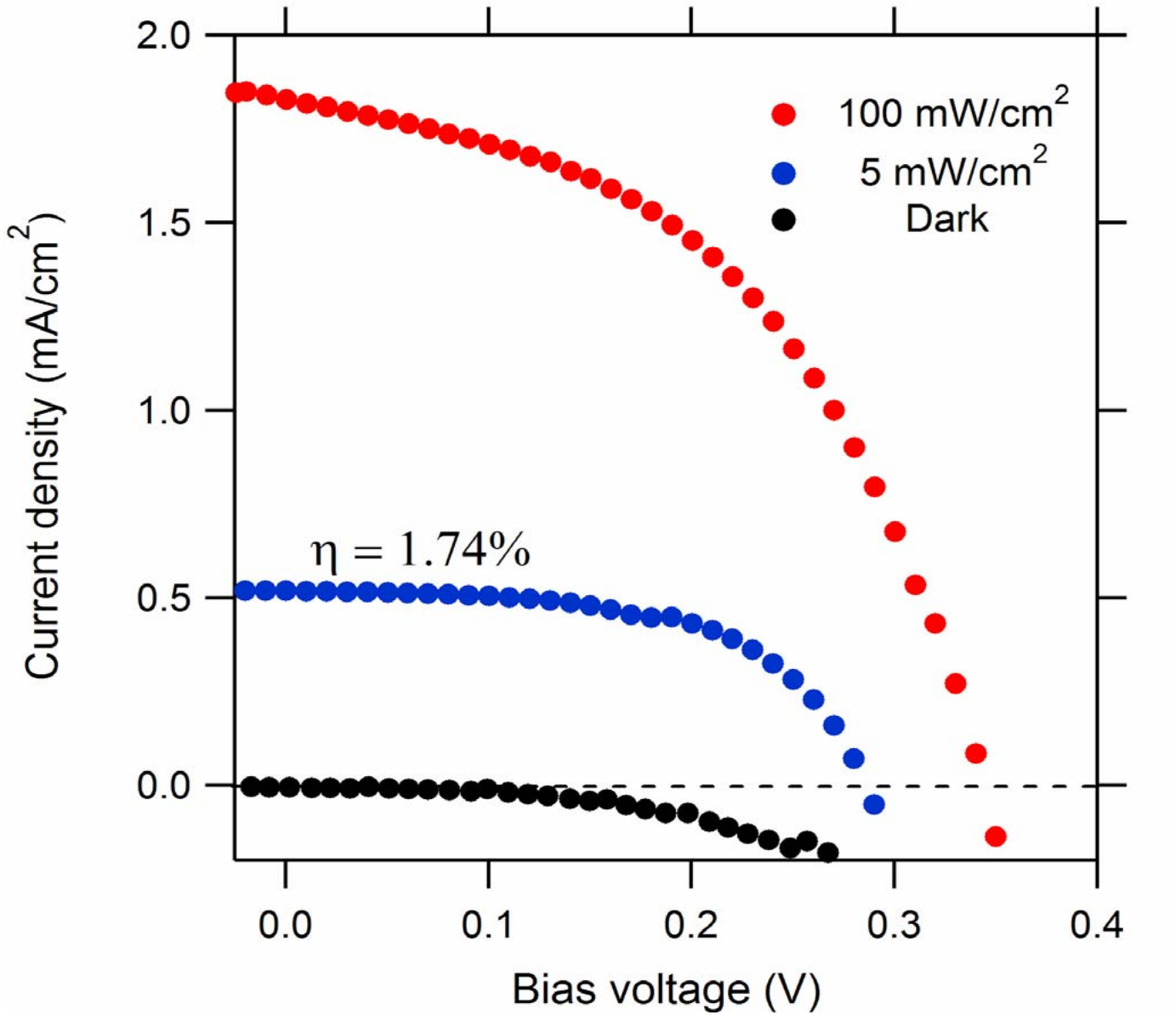
-Analogous to dye-sensitized TiO_2 solar cells
  -10 to 20 μm film of NC TiO_2 (10-30 nm)
  -Ru dyes ⇒ Efficiency ~ 11%
-Advantages of QD's as sensitizers:
  -possibility of slowed hot e^- cooling
  -possibility of impact ionization
  -tunable absorption

InAs QD Solar Cell Based on NC TiO_2

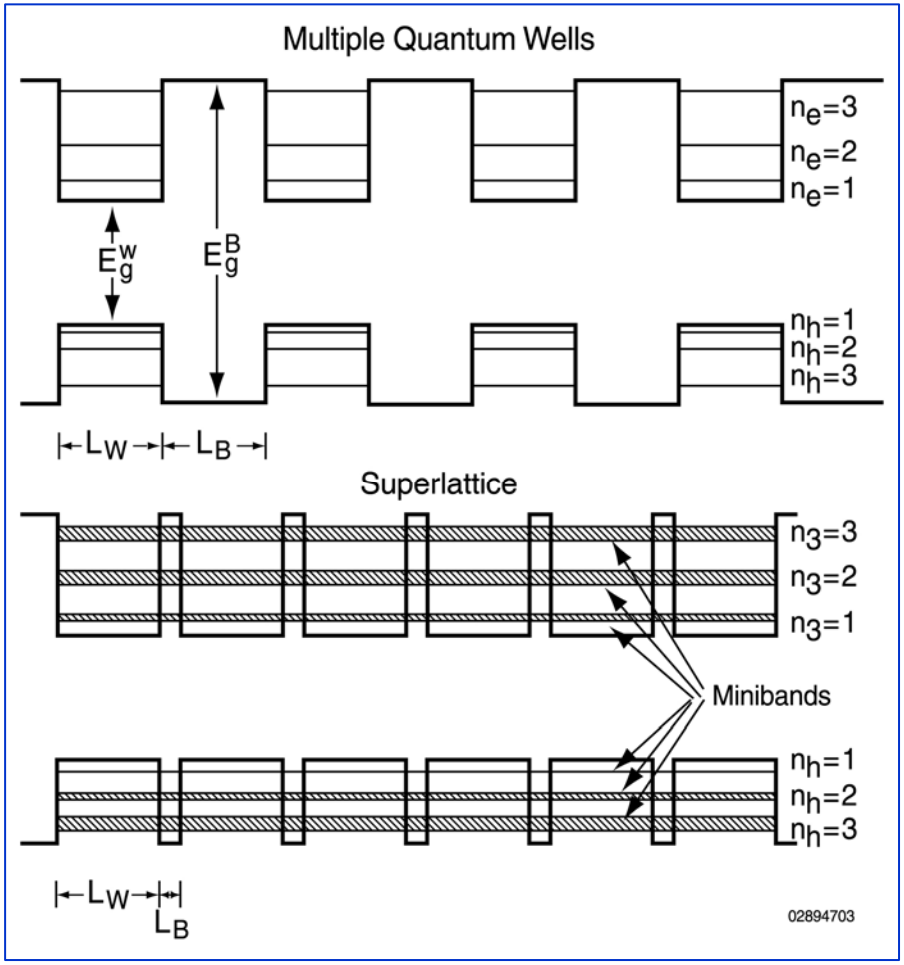




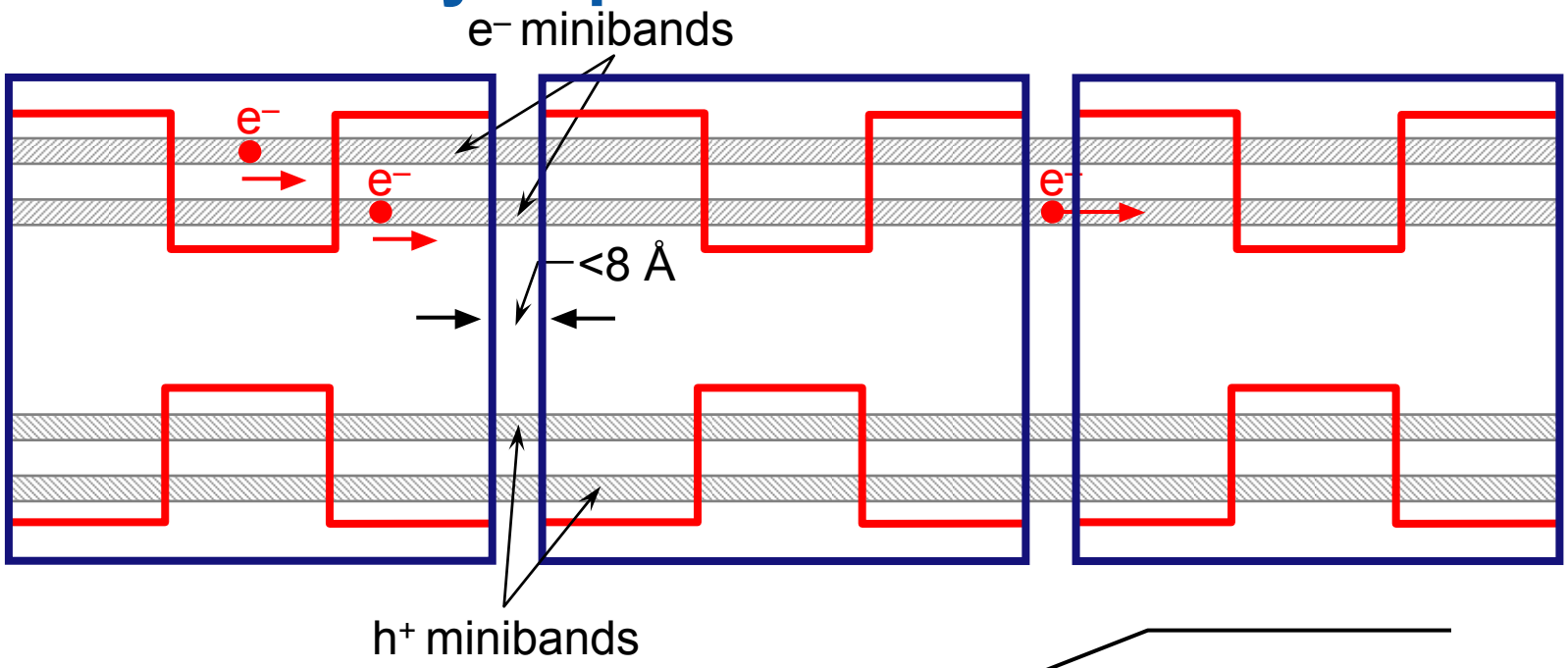
J-V Characteristic for 3.4 nm InAs QD Sensitized Solar Cell

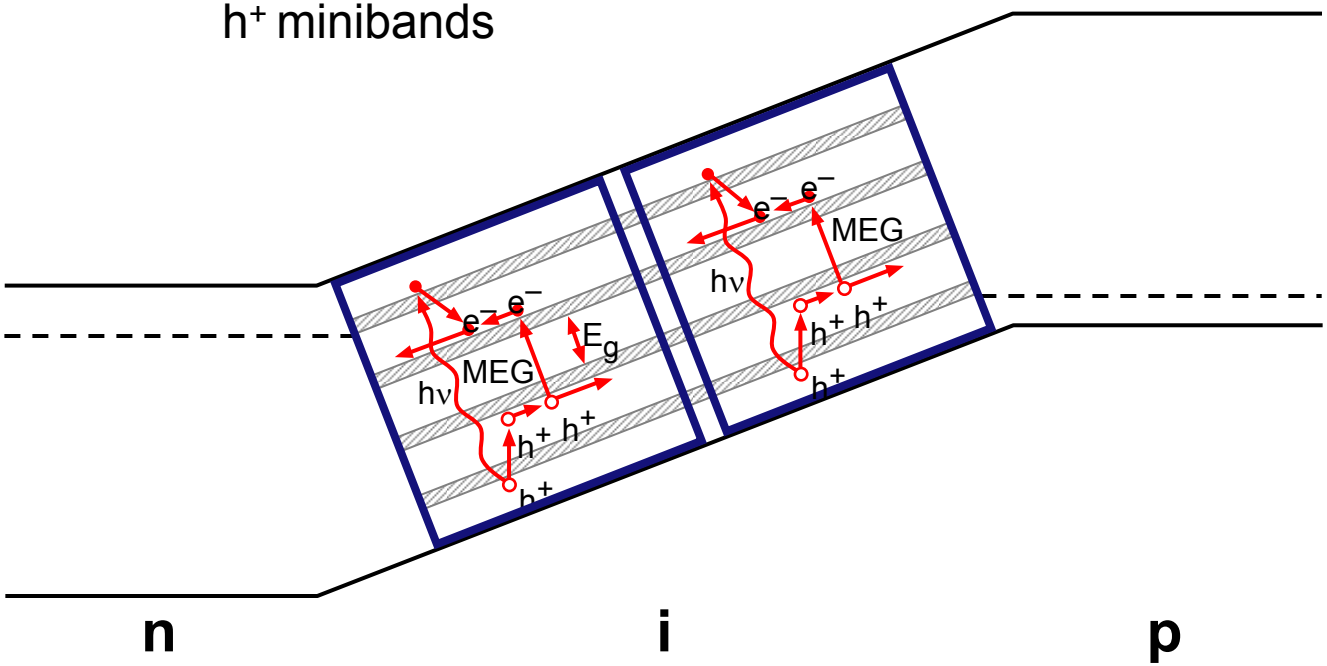


Miniband Formation in 1-D Confined Quantum Films

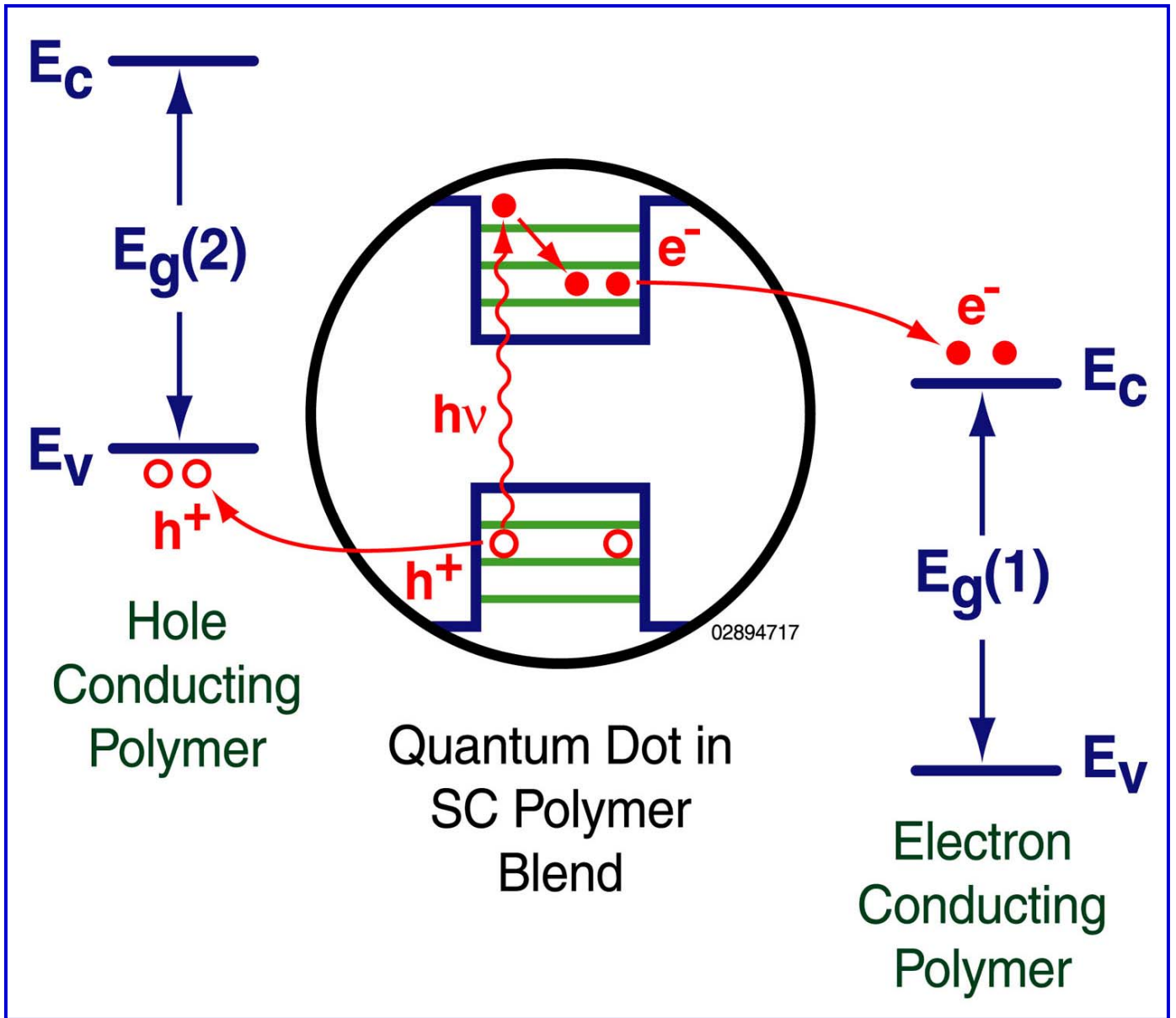


QD Array in p-i-n Photon Conversion Cell





PV Cell Based on QDs Dispersed in n-and p-type Organic Conducting Polymers



Summary/Conclusions

- *Size quantization in semiconductors may greatly affect the relaxation dynamics of photoinduced carriers. These include:*
  - *slowed hot electron relaxation (partial phonon bottleneck)*
  - *enhanced Auger process (MEG)*

- *The theoretical and measured energy threshold for impact ionization in bulk semiconductors (e.g. Si, InAs, GaAs) is 4-5 times the band gap. Much lower thresholds are predicted for QDs because of the relaxation of the need to conserve momentum. The rate of exciton multiplication is also expected to be much faster in QDs (Auger processes α $1/d^6$)*

- *Very efficient exciton multiplication experimentally observed in PbSe, PbTe, PbS, InAs, and Si QDs; the threshold photon energy is 2Eg. Up to 3 electrons per photon (300% QY) have been observed at sufficiently high photon energies ($\geq 4E_g$). A new model based on coherent superposition of multiexcitonic states is introduced to explain these results. <u>Two excitons/photon yield over 90% of the efficiency benefit of carrier multiplication.</u>*

- *Singlet fission is the molecular analog of MEG and also could yield enhanced solar photon conversion efficiencies. It had been observed in dimeric diphenylisobenzofurane. Single gap cells with carrier multiplication with MEG yield the same improvement for PV as 2-gap tandem PV cells. A tandem cell with SF and/or MEG is required to improve maximum efficiency for H2O splitting. Higher efficiency in SF cells for PV require a tandem cell configuration.*

Summary/Conclusions - Continued

- Various configurations of Quantum Dot Solar Cells are suggested that could yield high conversion efficiencies:
  1. Nanocrystalline TiO2 sensitized with QDs
  2. QD arrays exhibiting 3-D miniband formation
  3. QDs embedded in a polymeric blend of electron- and hole-conducting polymers.
  4. SF molecular chromophores in a tandem cell for PV and photoelectrolysis
- ***THE DYNAMICS OF HOT ELECTRON and EXCITED MOLECULE COOLING, FORWARD AND INVERSE AUGER RECOMBINATION (MEG), AND ELECTRON TRANSFER CAN BE MODIFIED IN QD AND SF SYSTEMS TO POTENTIALLY ALLOW VERY EFFICIENT SOLAR PHOTON CONVERSION VIA EFFICIENT MULTIPLE EXCITON GENERATION***