Powered Paint: Nanotech Solar Ink

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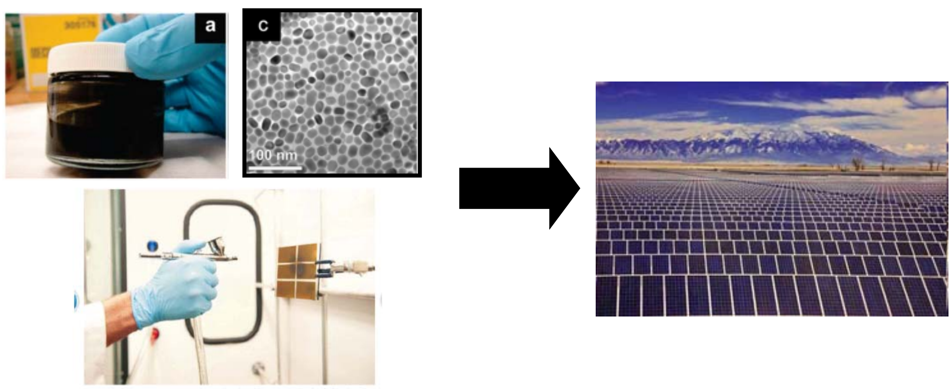


“Disruptive Solar”

- **Sustainable power competitive with fossil fuels (high efficiency & low cost)**
- **Portable light-weight power (efficiency is not necessarily the primary concern)**
- **“Multipurpose solar”—**
  examples: protective coatings & solar power
  fabrics & solar
  camouflage coatings & solar
  architectural/design & solar

To Lower the Cost of Solar Energy…

Change the way solar cells are made

Slow, high temperature vacuum processes

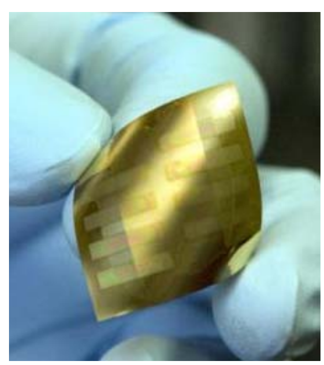
Print like newspaper

Photovoltaic Paints…?

To Lower the Cost of Solar Energy…

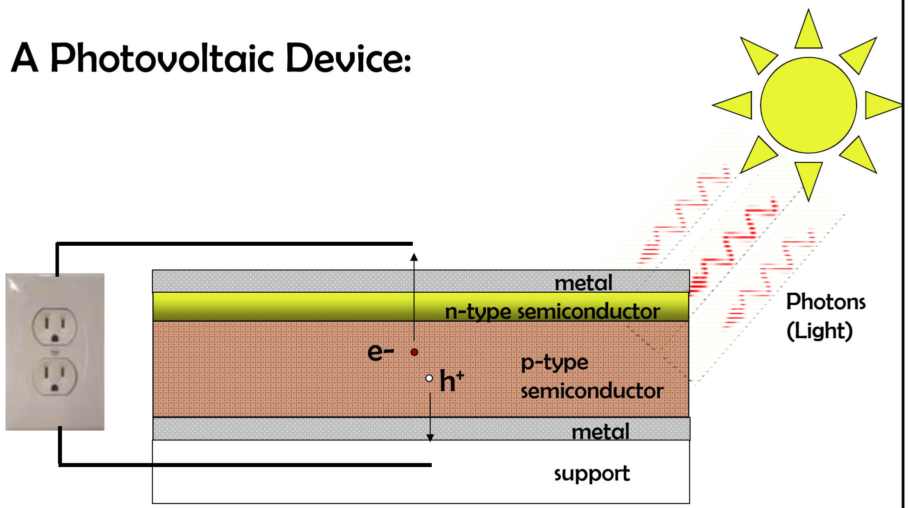
Change the way solar cells are made

Brittle and heavy



Light and flexible

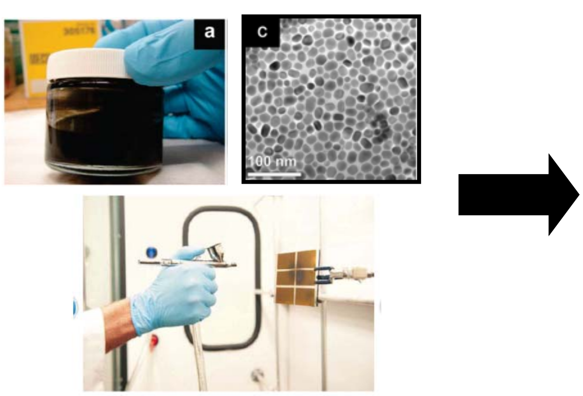
A Photovoltaic Device:



This is the basic design of every solar cell

Approach: Create a solvent-based ink that can be deposited under ambient conditions to obtain inorganic films for photovoltaic devices

Target processability of organics (moderate processing conditions; roll-to-roll high throughput; flexible lightweight substrates) with the stability of inorganic compounds.



Air-Stable All-Inorganic Nanocrystal Solar Cells Processed from Solution

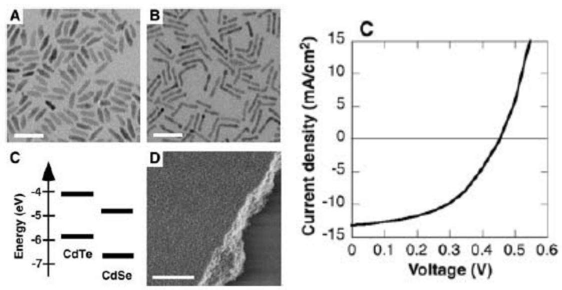
Ilan Gur,[1,3] Neil A. Fromer,[1] Michael L. Geier,[3] A. Paul Alivisatos[1,2*]

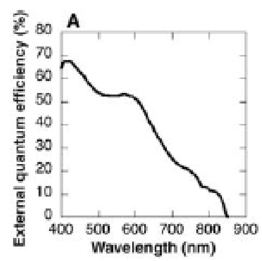
We introduce an ultrathin donor-acceptor solar cell composed entirely of inorganic nanocrystals spin-cast from solution. These devices are stable in air, and post-fabrication processing allows for power conversion efficiencies approaching 3% in initial tests. This demonstration elucidates a class of photovoltaic devices with potential for stable, low-cost power generation.

21 OCTOBER 2005 VOL 310 SCIENCE

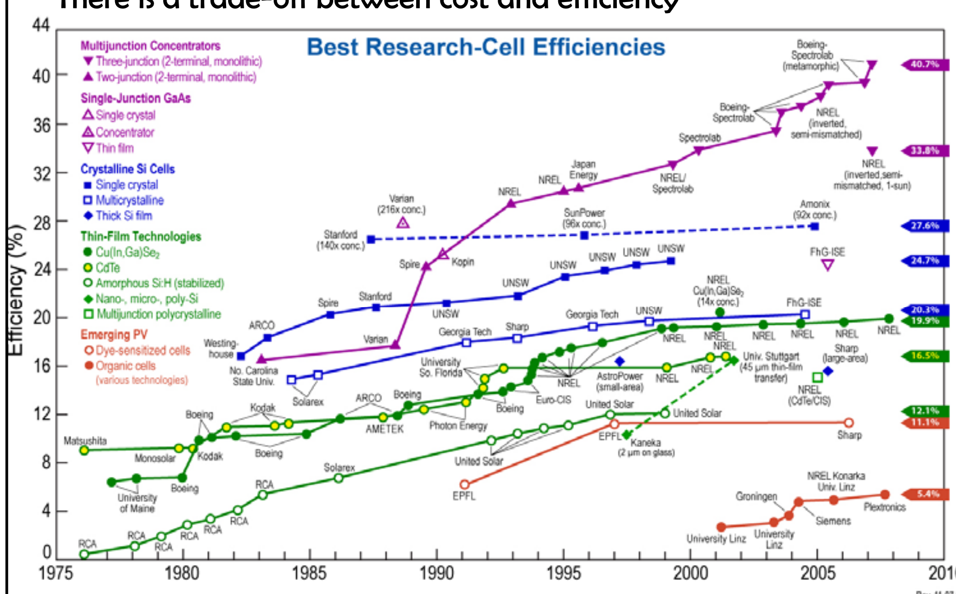
Are nanocrystal PVs a viable alternative to organic PVs?

3% efficiency
Sintered at high temp
CdSe/CdTe...Cd-based

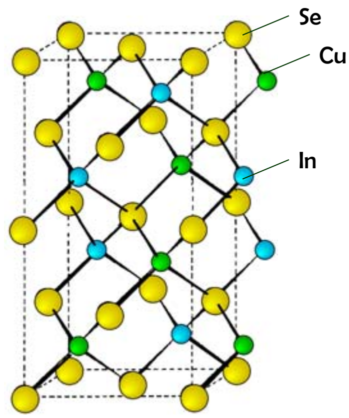




The Technology Challenge:
There is a trade-off between cost and efficiency



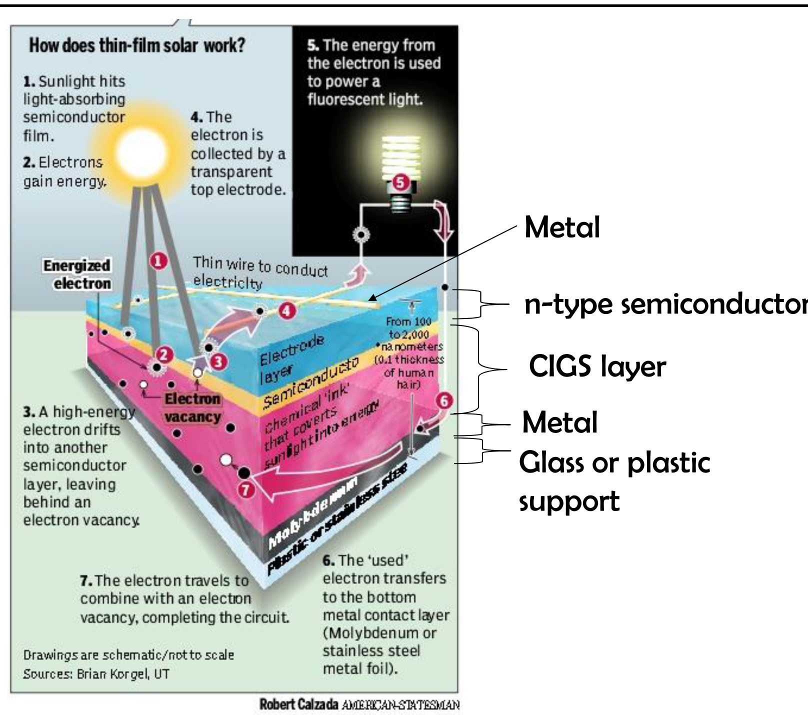
Copper indium gallium diselenide: CIGS

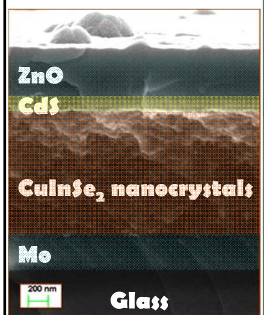


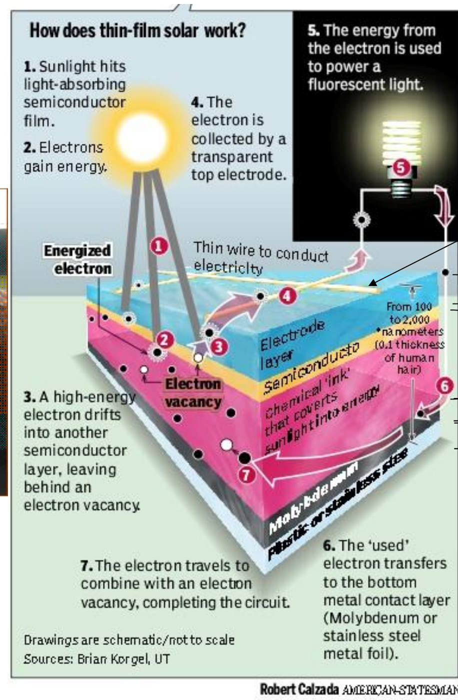
Chalcopyrite phase:
Isostructural with zinc blende with ordering of Cu and In atoms in the Se sublattice

Single junction vapor-deposited CIGS cells have reached >20% PCE; highly tolerant to grain boundaries & composition fluctuations

"Conventional" CIGS are made by vapor deposition of Cu,In,Ga layers followed by high temperature (>500°C) annealing under Se vapor







Metal

n-type semiconductor

Nanocrystal ink

Metal

Glass or plastic support

Synthesis

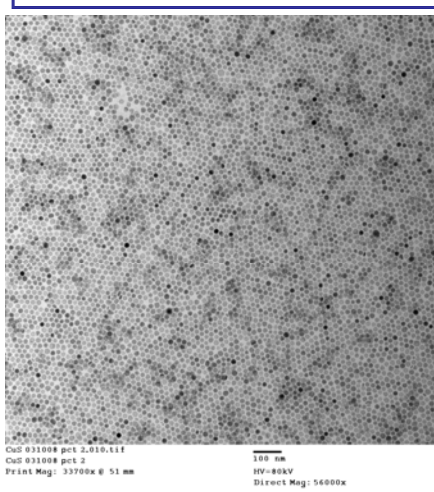
<u>Question in 2006</u>:
Is it even possible to combine three or four elements in a flask and obtain the desired composition and phase?

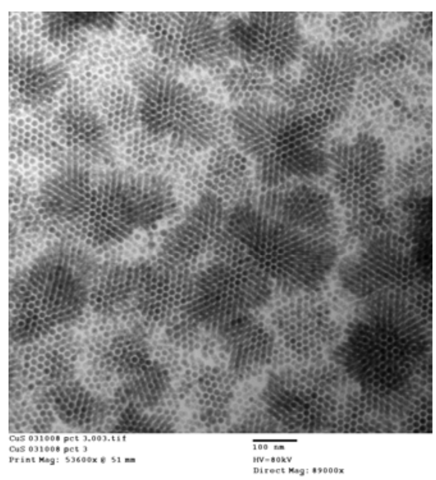
Approach to CIGS synthesis

- **In Sept. 2006, there was no known way to synthesize CIGS nanocrystals.**
- **There were methods for $CuInS_2$ nanocrystals reported, but these gave very low yields of material.**
- **We knew how to make copper sulfide nanocrystals, so we started there [Ghezelbash, Korgel, *Langmuir*, 2005]**
- **We first synthesized $CuInS_2$ nanocrystals, then extended that to $CuInSe_2$ nanocrystals**

CuS nanodisks

$Cu(acac)_2$ + S $\xrightarrow[\text{oleylamine/octenoic acid}]{\text{o-dichlorobenzene, 180°C}}$ CuS nanodisks



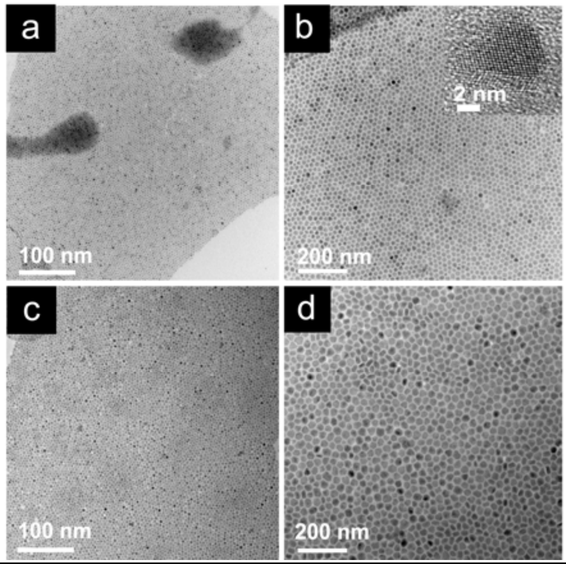


Made by Andrew Heitsch

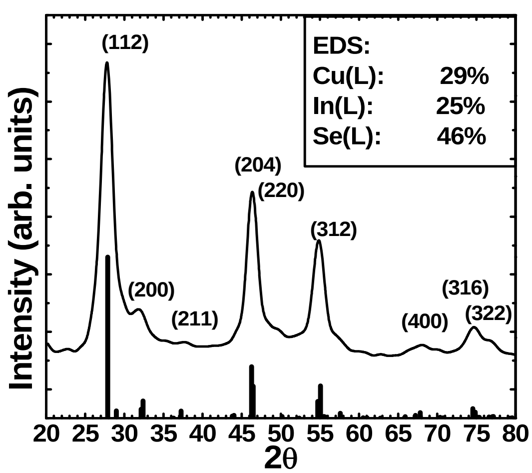
A. Ghezelbash, B. A. Korgel, "Nickel Sulfide and Copper Sulfide Nanocrystal Synthesis and Polymorphism," *Langmuir*, 21 (2005) 9451-9456.

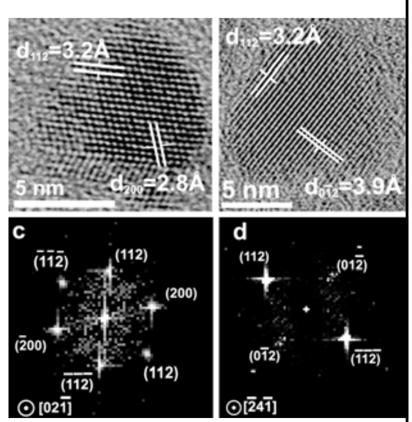
$CuInS_2$ nanocrystals

$Cu(acac)_2 + In(acac)_3 + 2S \xrightarrow[\text{oleylamine}]{\text{o-dichlorobenzene, 180°C}} CuInS_2$ nanocrystals



$CuInS_2$ nanocrystals

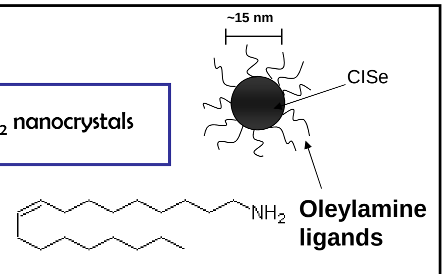


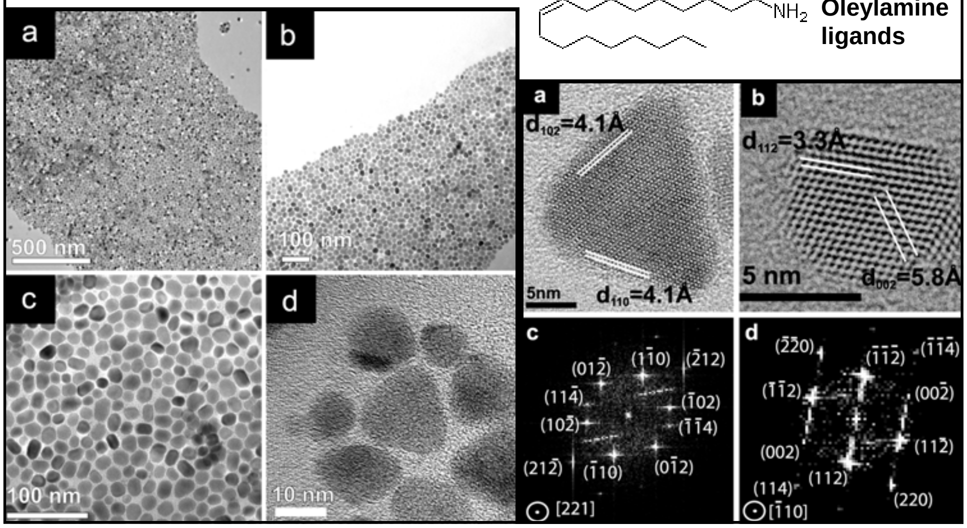


XRD pattern matches tetragonal (chalcopyrite) $CuInS_2$

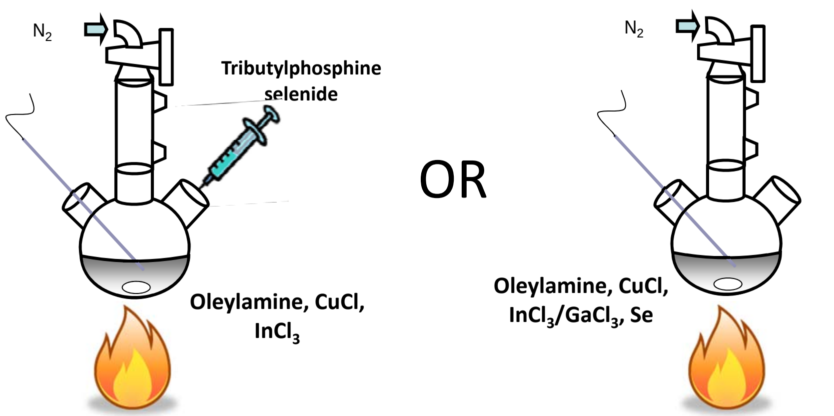
$CuInSe_2$ nanocrystals

$CuCl + InCl_3 + 2Se \xrightarrow{\text{oleylamine, 240°C}} CuInSe_2$ nanocrystals





CIGS Nanocrystal Synthesis



Heat to 180°C
Inject TBP:Se
React at 240°C for 15 min

Heat to 260°C for 30 min

Panthani, M.G.; Akhavan, V.; Goodfellow, B.; Schmidtke, J.P.; Dunn, L.; Dodabalapur, A.; Barbara, P.F.; Korgel, B.A., *JACS* **2008** 130(49), 16770-16777.

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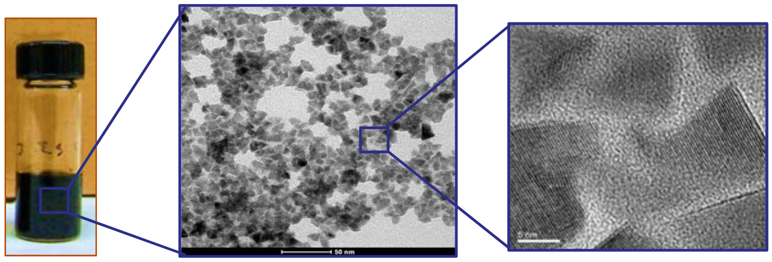
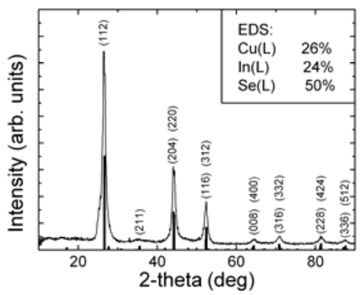
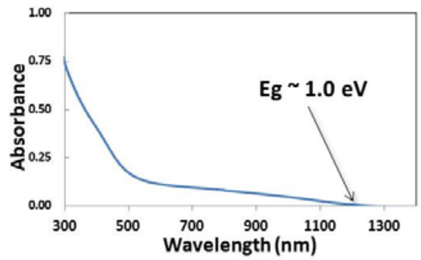
15 – 20 nm crystalline $CuInSe_2$ nanocrystals







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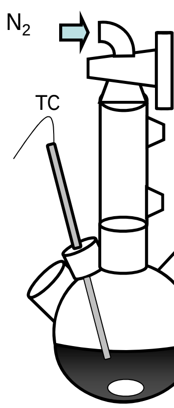
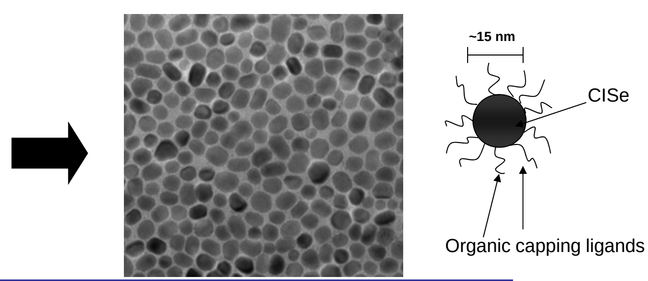
A nanocrystal ink:



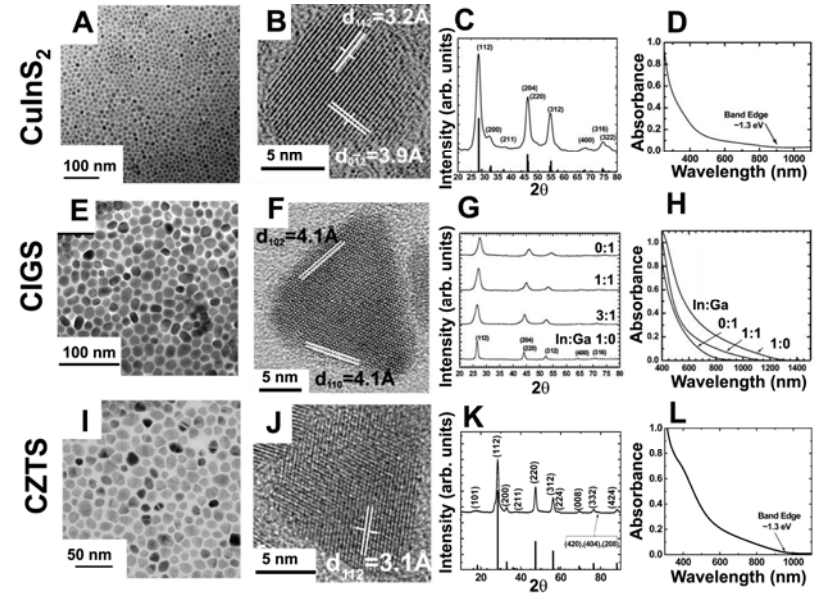
→Chemical synthesis of CIGS nanocrystals



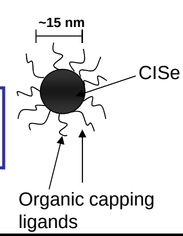
$CuCl + InCl_3 + 2Se \xrightarrow{\text{oleylamine, 240°C}} CuInSe_2$ nanocrystals

M. G. Panthani, V. Akhavan, B. Goodfellow, J. P. Schmidtke, L. Dunn, A. Dodabalapur, P. F. Barbara, B. A. Korgel, "Synthesis of $CuInS_2$, $CuInSe_2$ and $Cu(In_xGa_{1-x})Se_2$ (CIGS) Nanocrystal 'Inks' for Printable Photovoltaics," *J. Am. Chem. Soc.* 130 (2008) **16770-16777.**

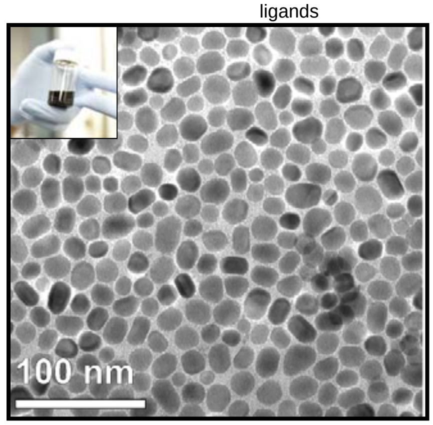
$CuCl + InCl_3 + 2Se \xrightarrow{\text{oleylamine, 240°C}} CuInSe_2$ nanocrystals



Chemical synthesis of CIGS nanocrystals

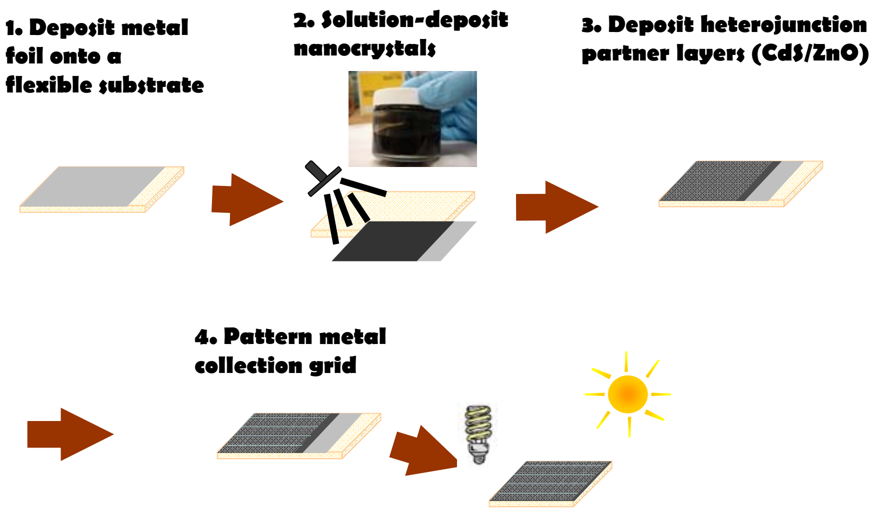


$CuCl + InCl_3 + 2Se \xrightarrow{\text{oleylamine, 240°C}} CuInSe_2$ nanocrystals



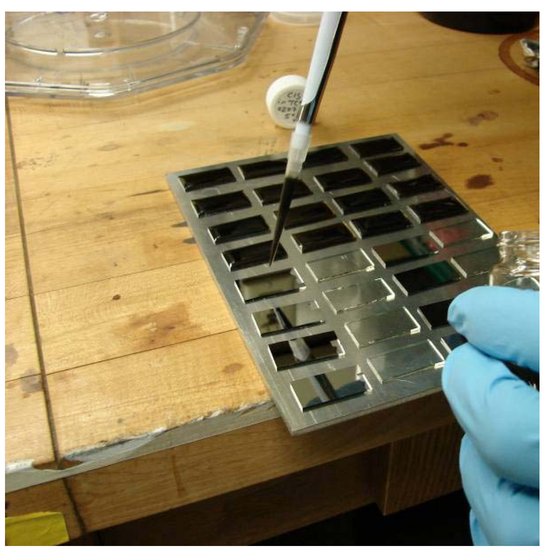
Dariya Reid (undergraduate chemical engineer)

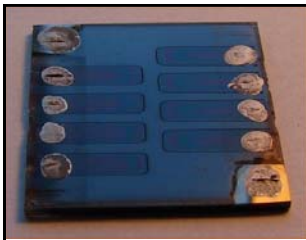
Nanocrystal PV Device Fabrication

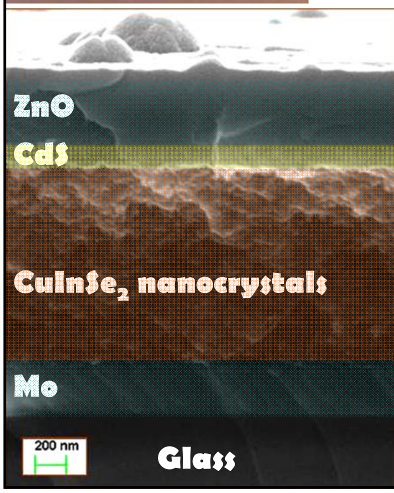


Nanocrystal Film Formation

For the solar cell, need uniform films of nanocrystals.

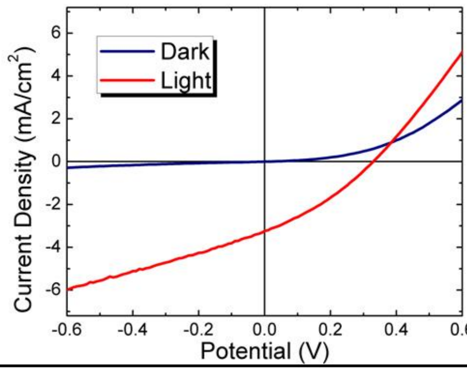


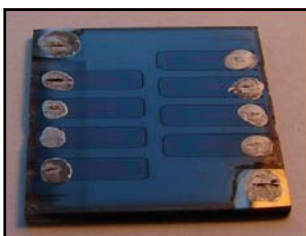




- Standard Cell

Efficiency	0.341%
V_{oc}	329 mV
J_{sc}	3.26 mA/cm²
Fill Factor	0.318



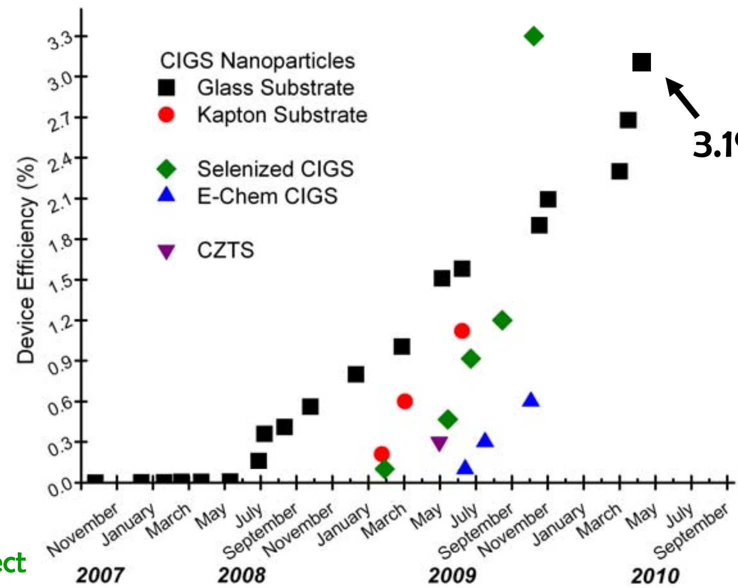


- Standard Cell

Efficiency	0.341%
V_{oc}	329 mV
J_{sc}	3.26 mA/cm²
Fill Factor	0.318

Mo work function is ~4.2 eV, resulting in a Schottky barrier at the Mo/CIS interface

Korgel group milestone chart for CIGS Nanocrystal PVs



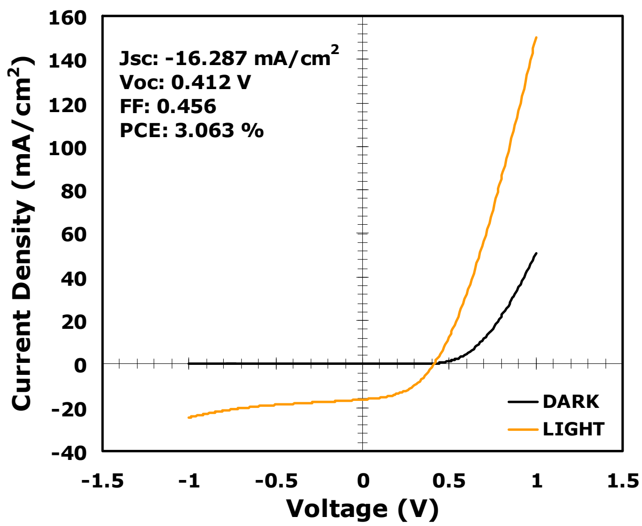
3.1%

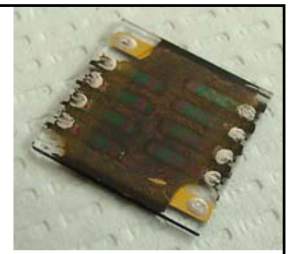
Project conception (Sept., 2006)

Nanocrystal Film Formation

For the solar cell, need uniform films of nanocrystals.

CIS Nanocrystal PV device

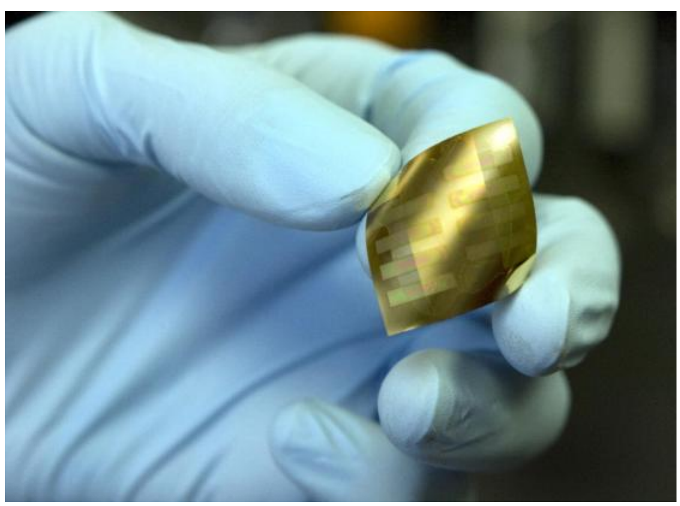




Efficiency of 3.1%

V. A. Akhavan, M. G. Panthani, B. W. Goodfellow, D. K. Reid, B. A. Korgel, "Thickness-limited performance of CuInSe2 nanocrystal photovoltaic devices," *Optics Express,* 18 (2010) A411-A420.

Flexible CIGS PVs



Energy Environ. Sci., 2010, **3**, 1600–1606
PAPER www.rsc.org/ees | Energy & Environmental Science

Spray-deposited $CuInSe_2$ nanocrystal photovoltaics

Vahid A. Akhavan,[ab] Brian W. Goodfellow,[ab] Matthew G. Panthani,[ab] Dariya K. Reid,[a] Danny J. Hellebusch,[a] Takuji Adachi[bc] and Brian A. Korgel[*ab]

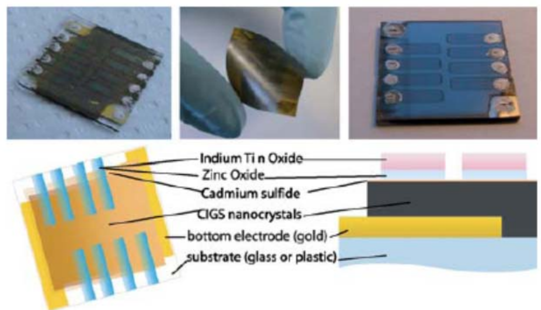
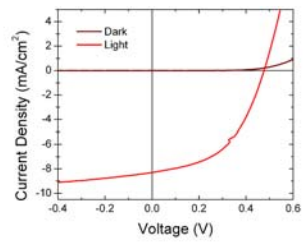


Fig. 3 (Top) Photographs of PVs fabricated by spray-depositing CIS nanocrystals on various substrates: (top left and right) glass and (top, middle) plastic (kapton). (Bottom) Illustration of the device layer structure as viewed from the top and from the side.

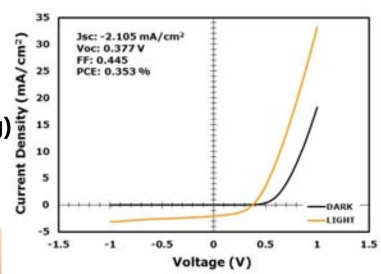


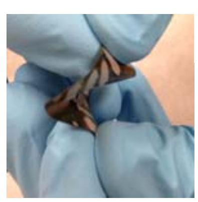
Voc = 476 mV
Jsc = 8.3 mA/cm^2
FF = 0.488
η = 1.9%

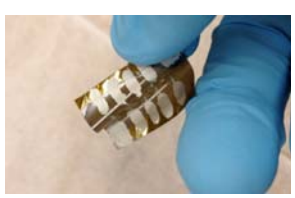
Efficiency of 2% on plastic

CIGS Nanocrystal Solar Cell Fabricated on Ultra-Light Ni-coated PET

Estimated Weight
31.4”x 61.4” Panel
Standard Si: 33 lbs (15 kg)
CIGS on PET/Ni: 0.5 lbs (.25 kg)







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Published on Web 08/17/2009

Synthesis of Cu_2ZnSnS_4 Nanocrystals for Use in Low-Cost Photovoltaics

Chet Steinhagen, Matthew G. Panthani, Vahid Akhavan, Brian Goodfellow, Bonil Koo, and Brian A. Korgel*

Department of Chemical Engineering, Center for Nano- and Molecular Science and Technology, and Texas Materials Institute, The University of Texas at Austin, Austin, Texas 78712-1062

Received July 16, 2009; E-mail: korgel@che.utexas.edu

J. AM. CHEM. SOC. 2009, *131*, 12554–12555

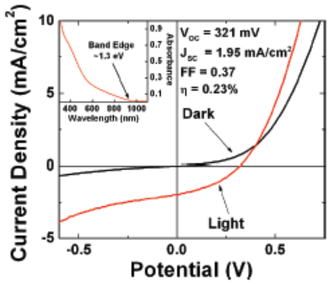
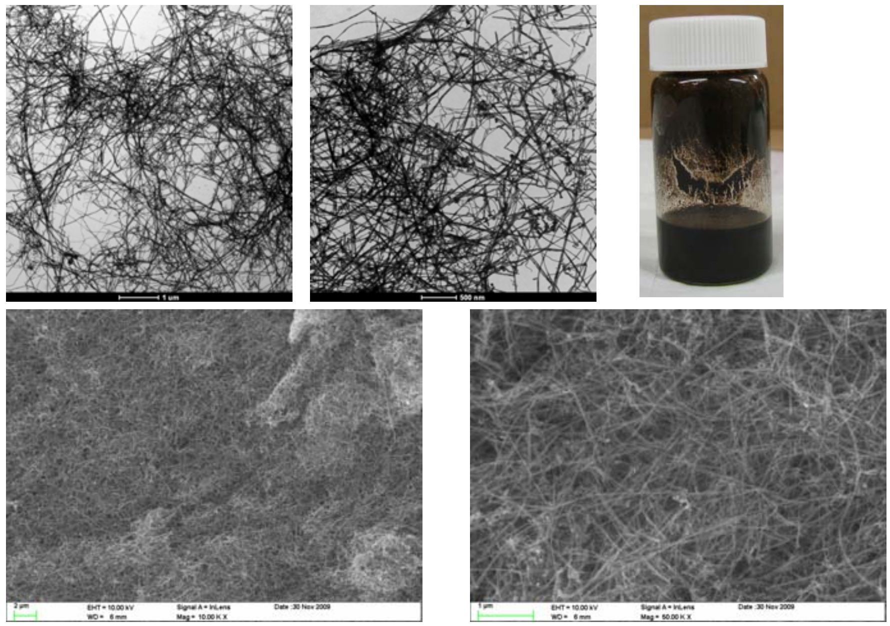


Figure 4. Current–voltage characteristics of a CZTS nanocrystal PV device. Inset: room-temperature UV–vis–NIR absorbance spectrum of CZTS nanocrystals dispersed in toluene. PV devices were tested on a Karl Suss probe station and an Agilent 4156C parameter analyzer. *I–V* data and power conversion efficiencies were obtained using a Keithley 2400 General Purpose Sourcemeter and a Xenon Lamp Solar Simulator (Newport) with an AM 1.5 filter.

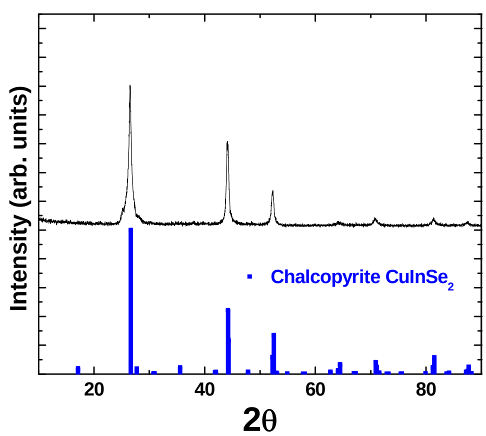
Reduce grain boundaries by synthesizing nanowires?

Bi-seeded $CuInSe_2$ Nanowires by SLS

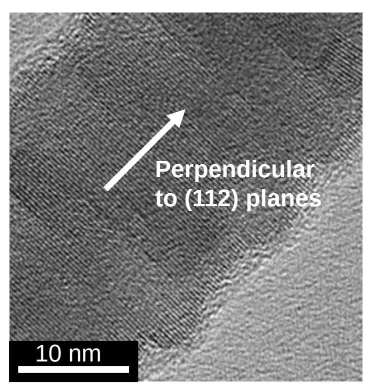


NW Characterization

XRD

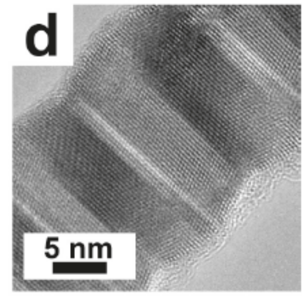


HRTEM

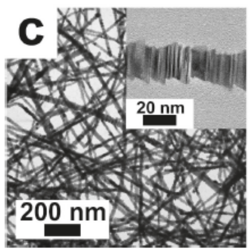


EDS analysis: $Cu_{1.0}In_{0.6}Se_{2.0}$

Wurtzite Phase $CuInSe_2$ Nanowires



twinning



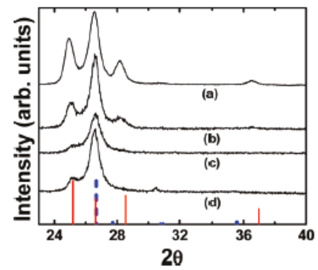
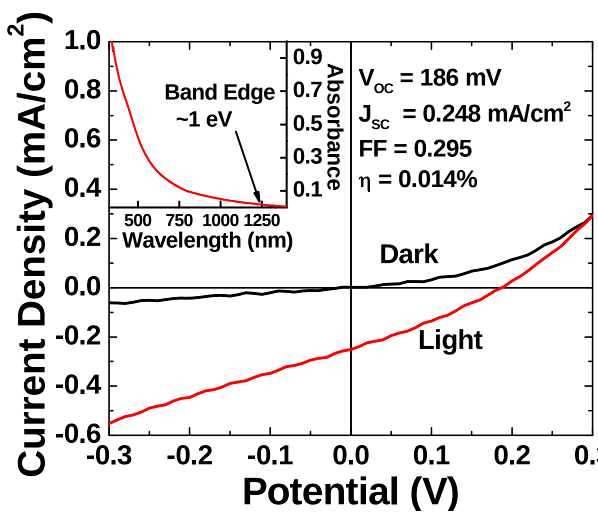


Figure 3. XRD patterns of CIS nanowires synthesized at 400 °C (a), 360 °C (b), 270 °C (c), and 360 °C with HDA (d). The dashed blue reference pattern corresponds to chalcopyrite CIS (JCPDS no. 97-006-8928), and the red reference pattern was simulated with CaRIne Crystallography 3.1 software using space group $P6_3mc$ and lattice parameters a = 4.08 Å and c = 6.69 Å.

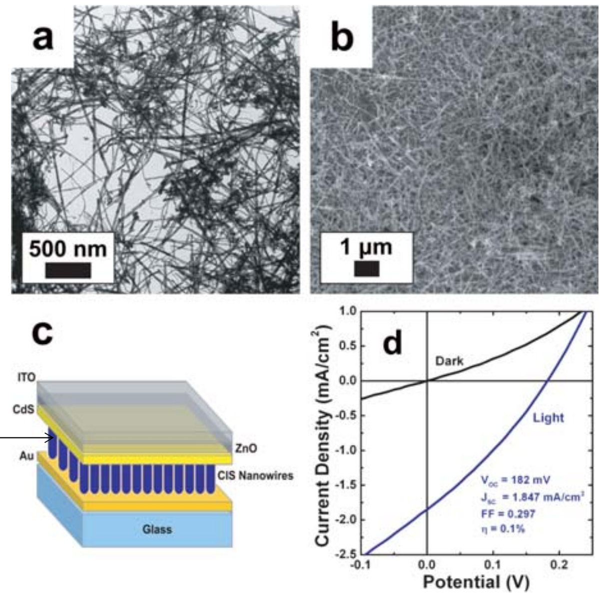
Proof of concept



Current voltage characteristics of a $CuInSe_2$ nanowire PV device. Inset: UV-vis-NIR absorbance spectrum of $CuInSe_2$ nanowires dispersed in toluene.

CIS Nanowires PV Device

An idealized device structure



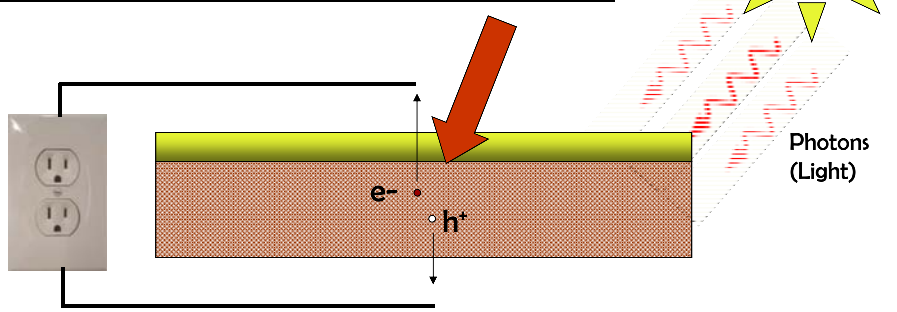
Device composed of a nanowire mat

Accomplished to date:

- Solar inks can be chemically synthesized
- Solar cells can be fabricated with solar inks
- Solar cells can be fabricated with solar inks on light-weight flexible substrates

How to achieve power conversion efficiencies of 10-20%?

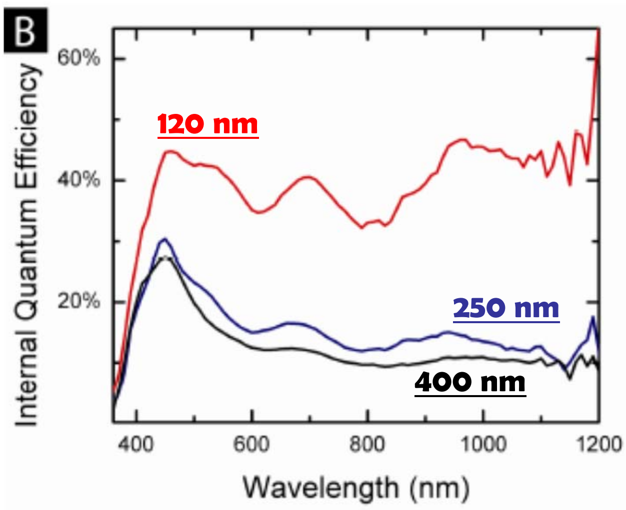
Extracting the photogenerated electrons and holes efficiently is currently the biggest challenge



The highest efficiency devices have very thin nanocrystal layers that do not absorb all of the light

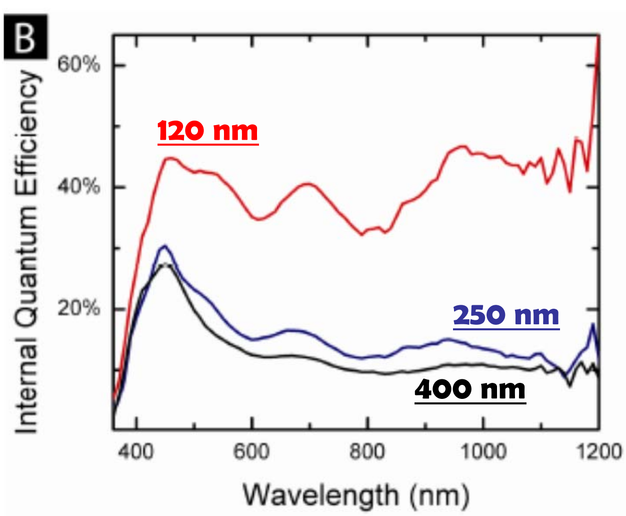
~200 nm thick layer of nanocrystals on glass disc

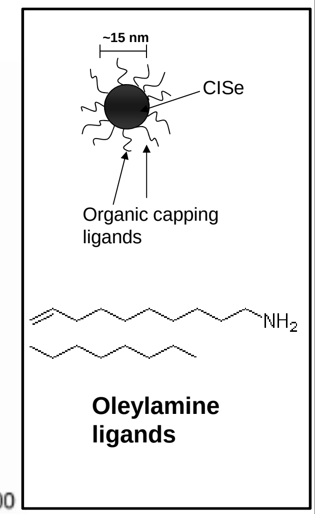
Thicker nanocrystal layers absorb more light, but lead to less efficient devices



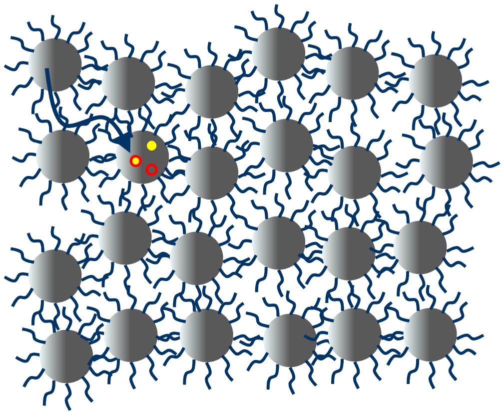
V. A. Akhavan, M. G. Panthani, B. W. Goodfellow, D. K. Reid, B. A. Korgel, "Thickness-limited performance of CuInSe2 nanocrystal photovoltaic devices," *Optics Express*, 18 (2010) A411-A420.

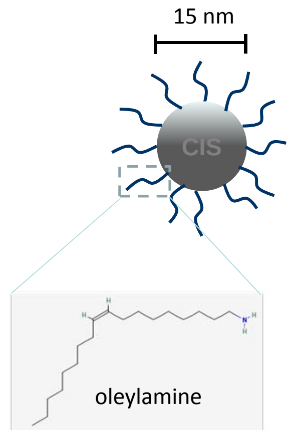
Thicker nanocrystal layers absorb more light, but are less efficient





V. A. Akhavan, M. G. Panthani, B. W. Goodfellow, D. K. Reid, B. A. Korgel, "Thickness-limited performance of CuInSe2 nanocrystal photovoltaic devices," *Optics Express*, 18 (2010) A411-A420.

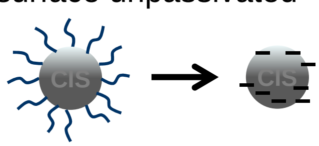




- Nanocrystals are coated with oleylamine
- Long chain hydrocarbon impedes carriertransport
- Improve charge transport by replacing oleylamine

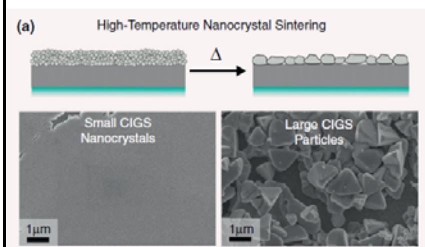
What to do with oleylamine?

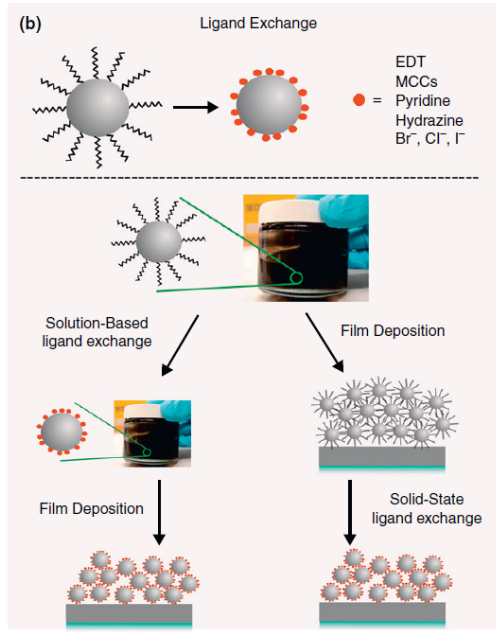
- Anneal?
  - Leaves surface unpassivated



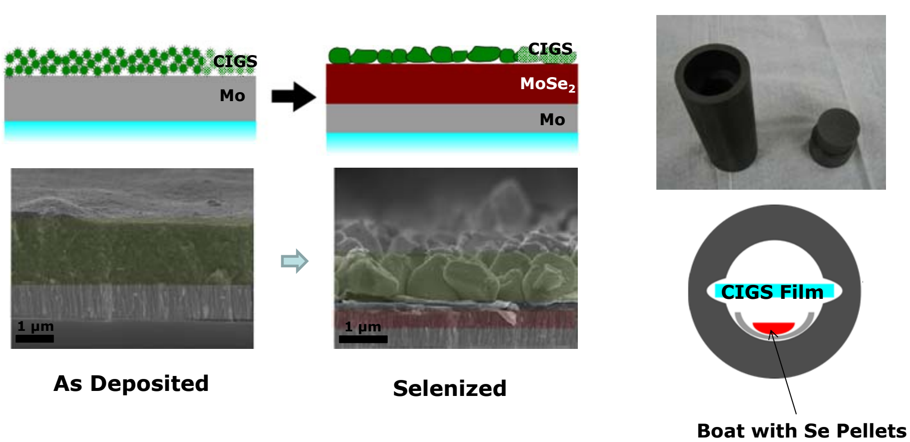
- Ligand exchange
  - Several attempts, but none have been successful
- Larger particles
  - Less boundaries for carriers
- Synthesize with shorter ligand
  - Shorter ligands are volatile, particles unstable

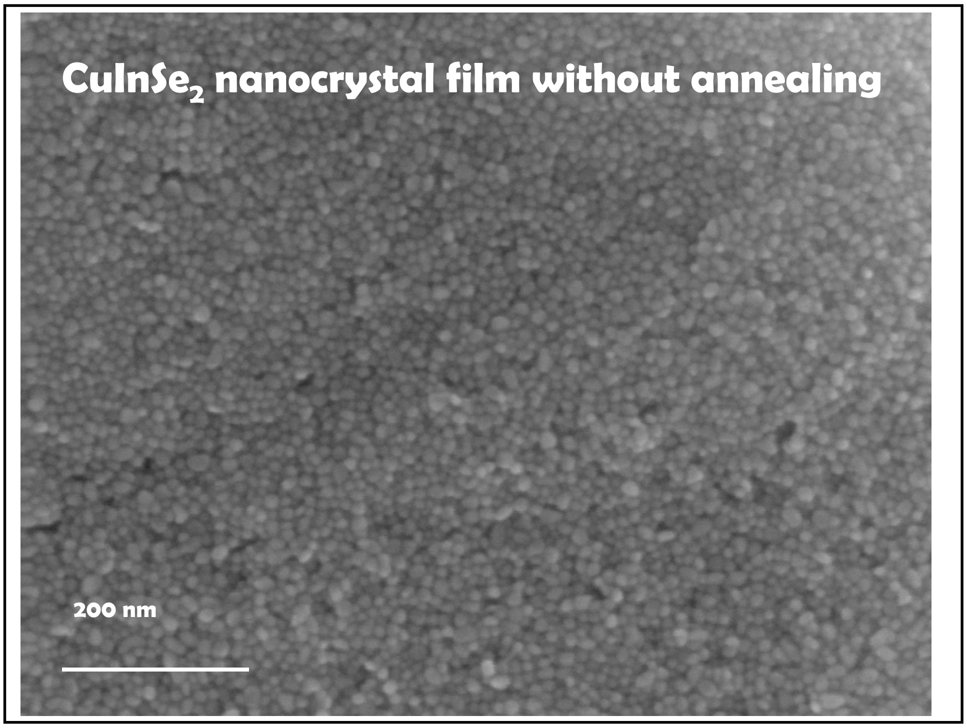
Improving transport?

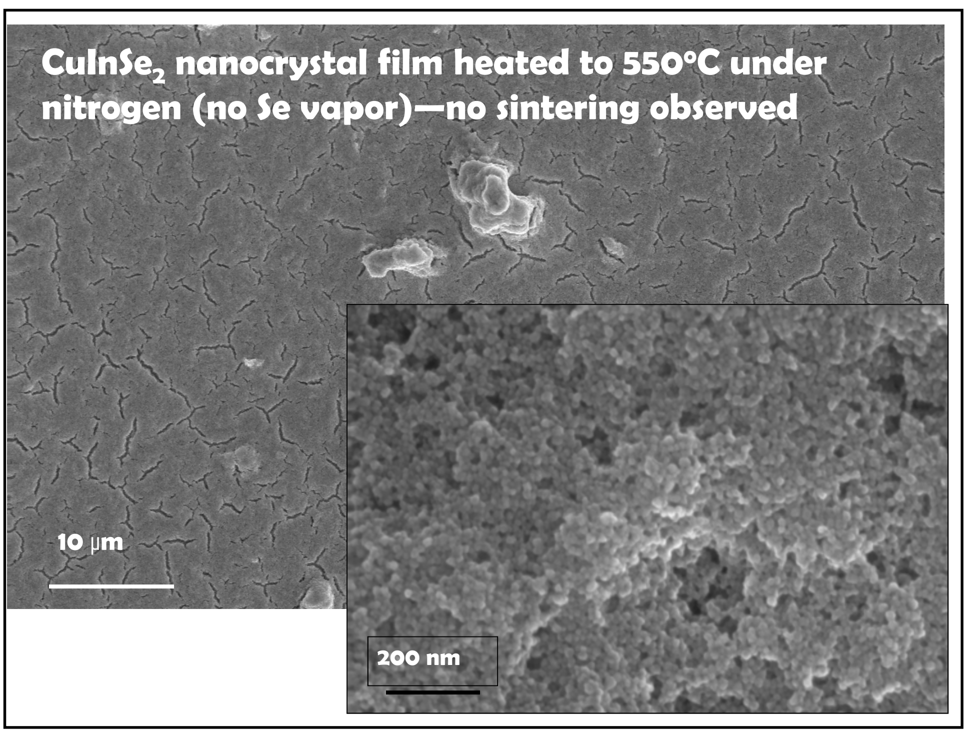




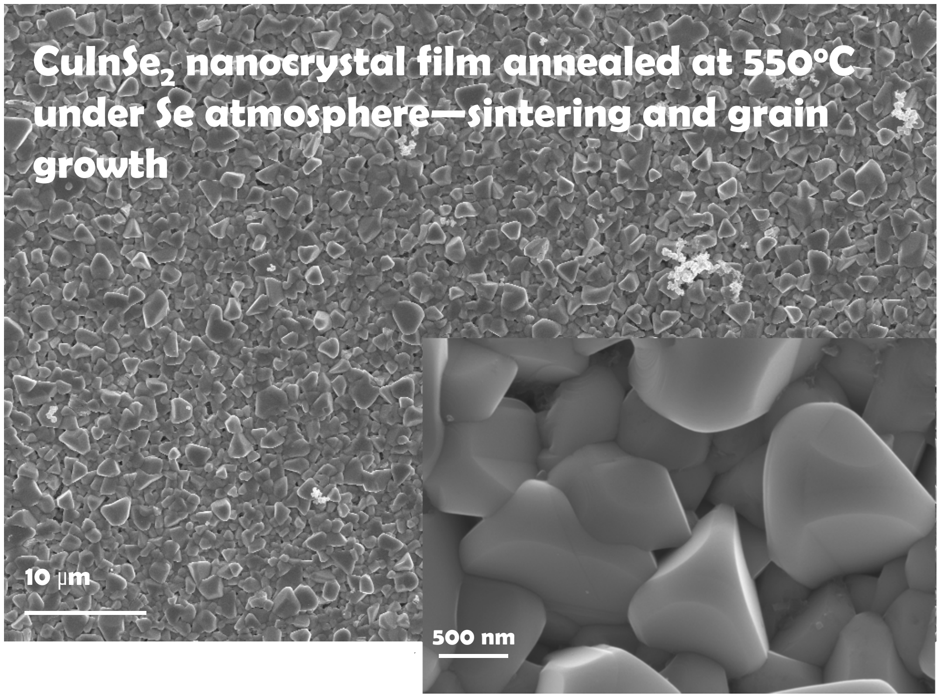
Selenization of CIGS Nanocrystals for High Efficiency PV's



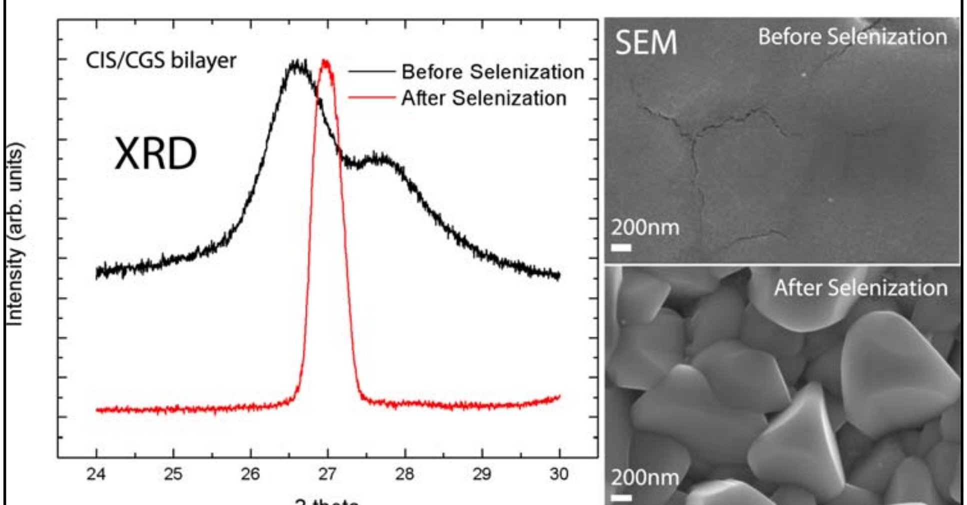

CuInSe2 nanocrystal film without annealing
200 nm


CuInSe2 nanocrystal film heated to 550°C under nitrogen (no Se vapor)—no sintering observed
10 μm
200 nm

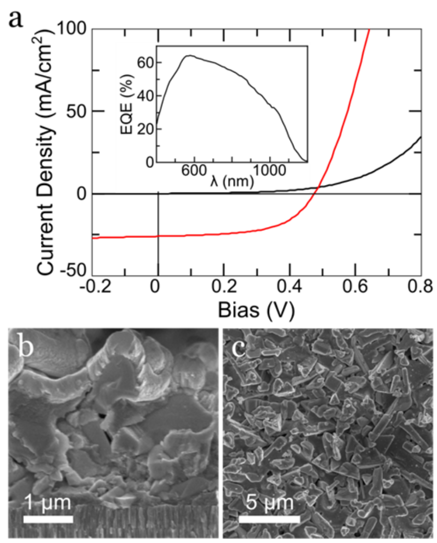
$CuInSe_2$ nanocrystal film annealed at 550°C under Se atmosphere—sintering and grain growth



Sintering requires high temperature (>450C) and Se vapor

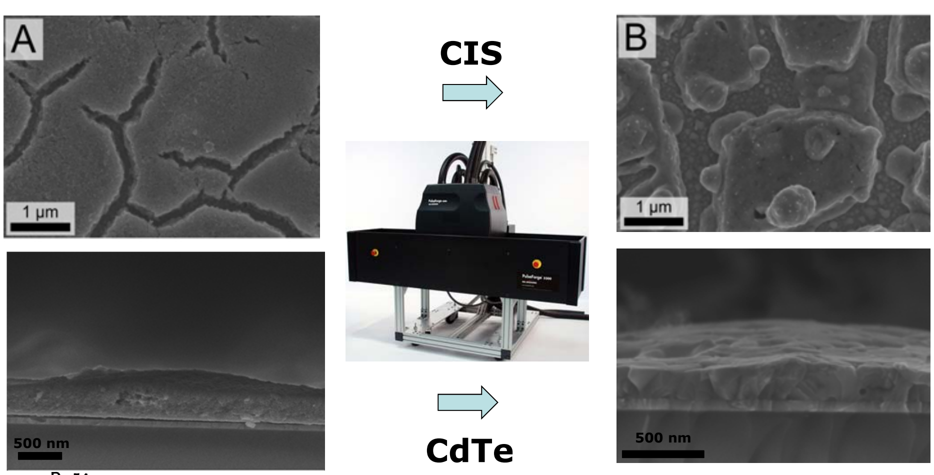


Selenization: Heating nanocrystal film to 525°C under Se vapor atmosphere



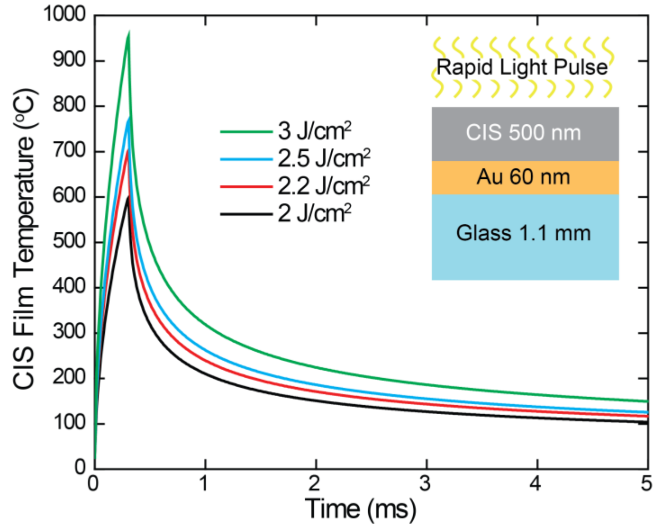
7.1% efficiency

Photonic Curing of CIS and CdTe Nanocrystal Films

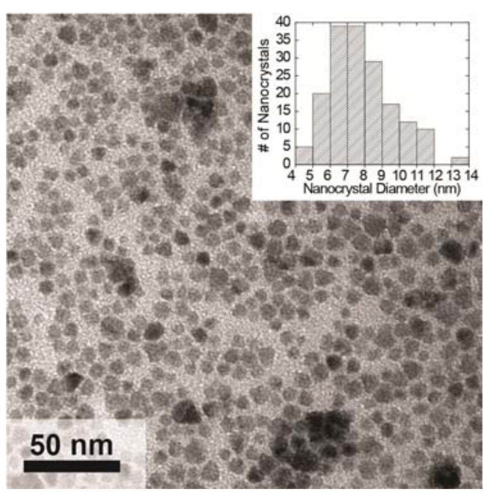


Pg 54

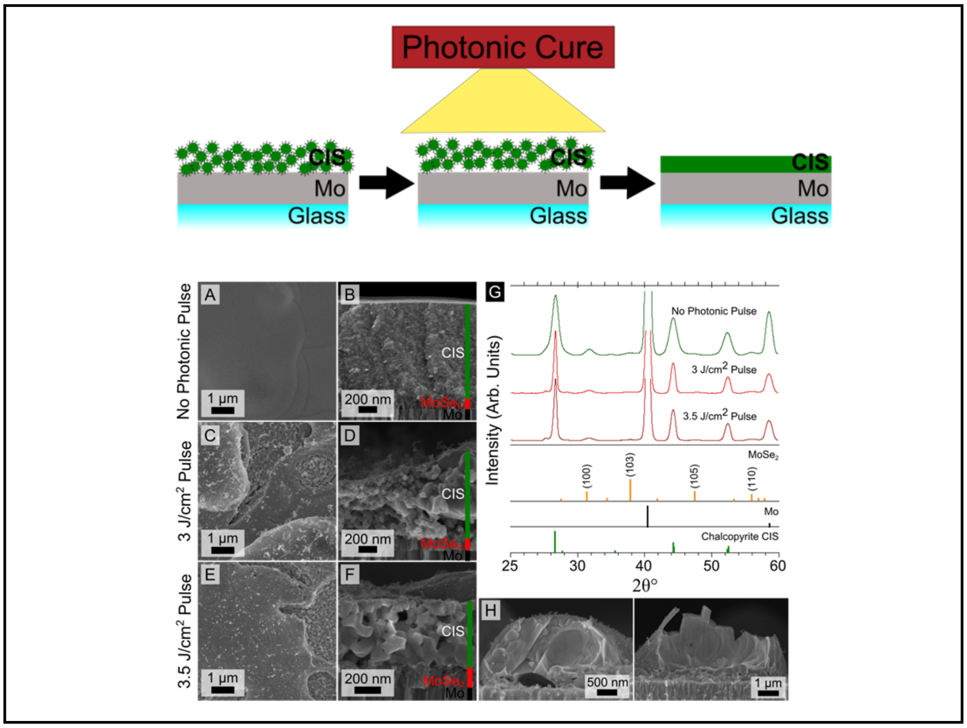
Temperature profile during photonic curing process

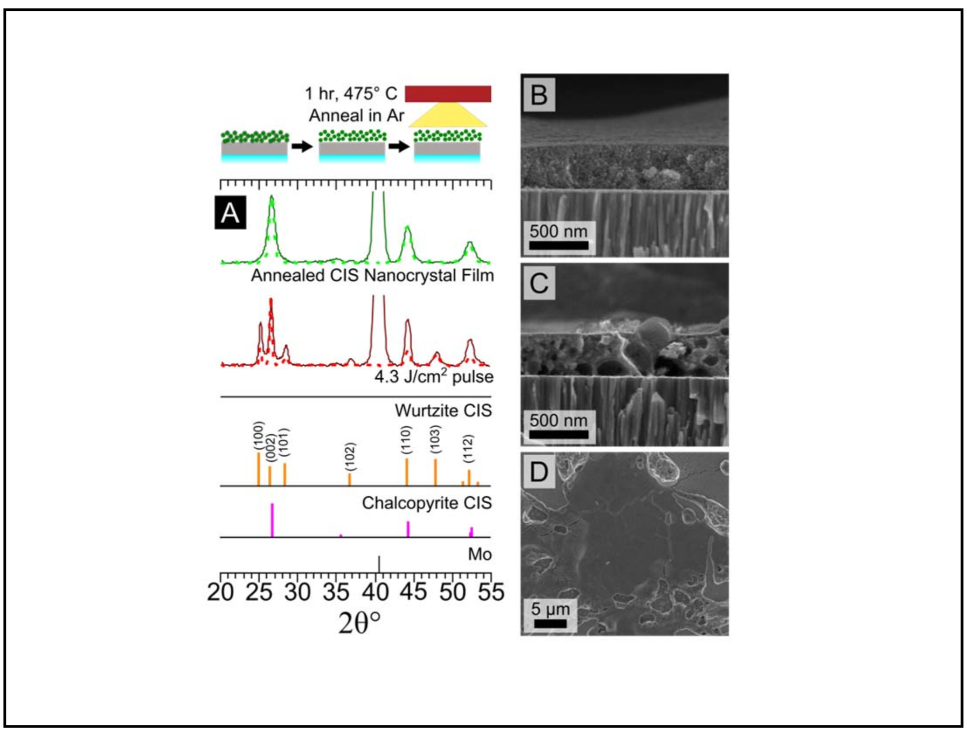


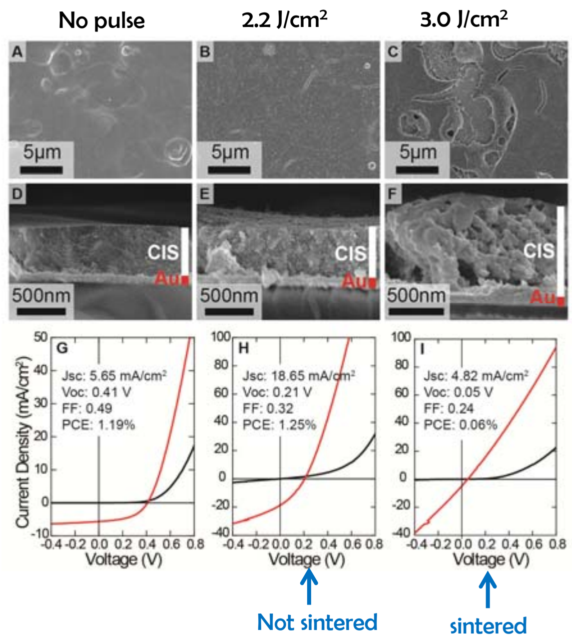
$CuInSe_2$



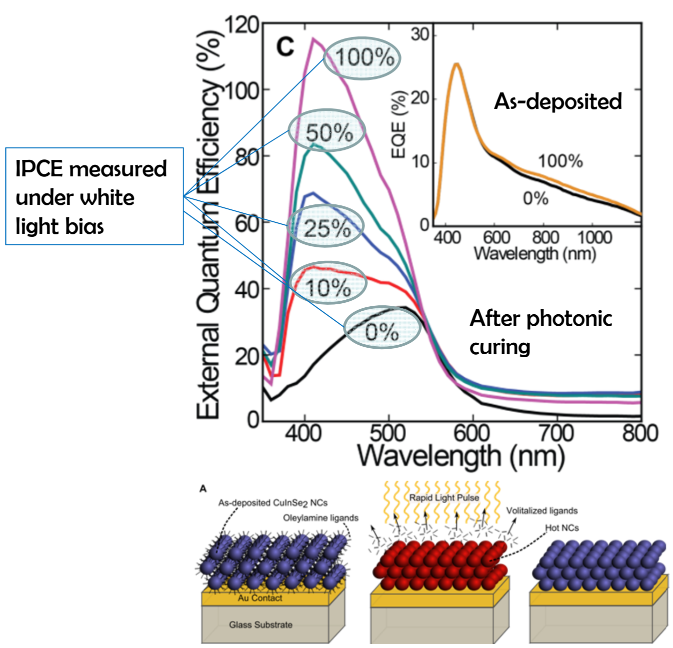
8.1 ± 2.1 nm in diameter


Photonic Cure
CIS
Mo
Glass
No Photonic Pulse
3 J/cm² Pulse
3.5 J/cm² Pulse
1 µm
200 nm
500 nm
MoSe₂
Intensity (Arb. Units)
No Photonic Pulse
3 J/cm² Pulse
3.5 J/cm² Pulse
Chalcopyrite CIS
2θ°

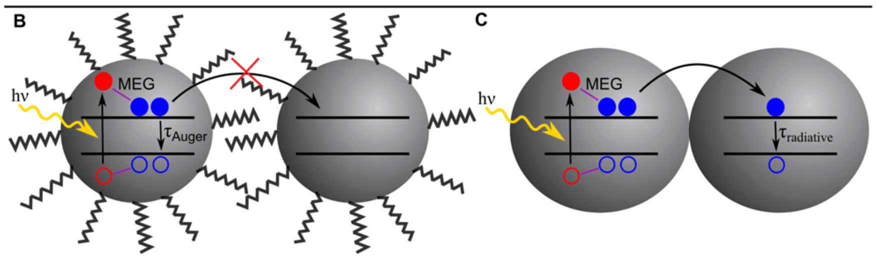

1 hr, 475° C
Anneal in Ar
Annealed CIS Nanocrystal Film
4.3 J/cm² pulse
Wurtzite CIS
(100) (002) (101) (102) (110) (103) (112)
Chalcopyrite CIS
Mo
20 25 30 35 40 45 50 55
2θ°
500 nm
5 µm



Internal quantum efficiency >100% under white light bias

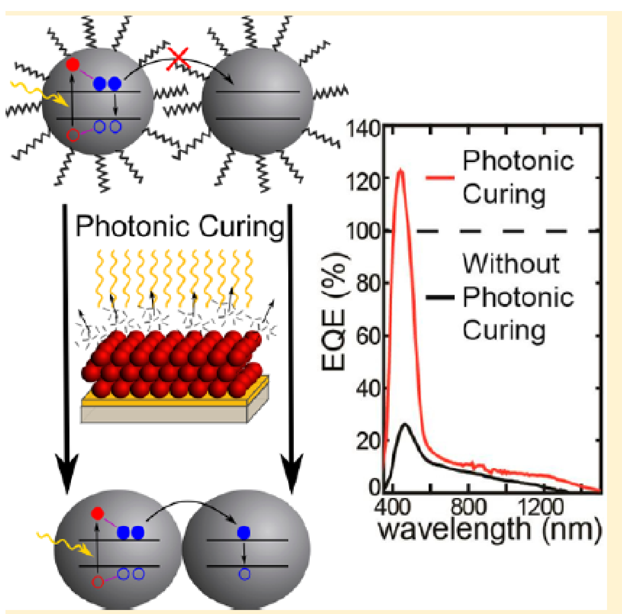


Multiple Exciton Solar Cells of $CuInSe_2$

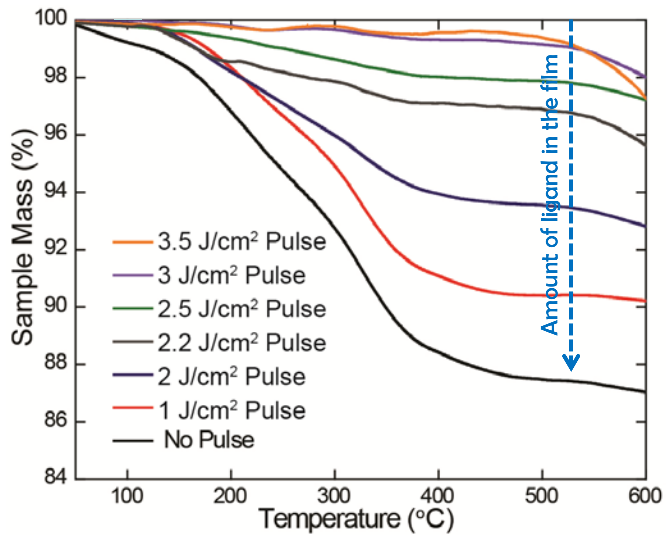


Achieving External Quantum Efficiency > 100%

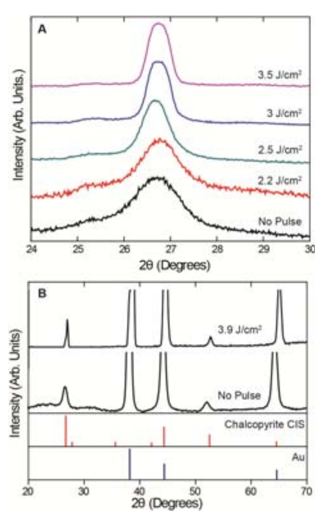
$\left(\frac{\text{\# of electron/hole extracted}}{\text{Incident photon}} \right)$



Thermal Gravimetric Analysis (TGA)

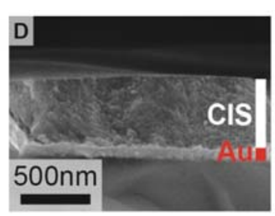


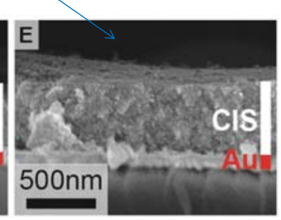
X-ray diffraction



Peak narrowing indicates sintering

No sintering in the film with MEG

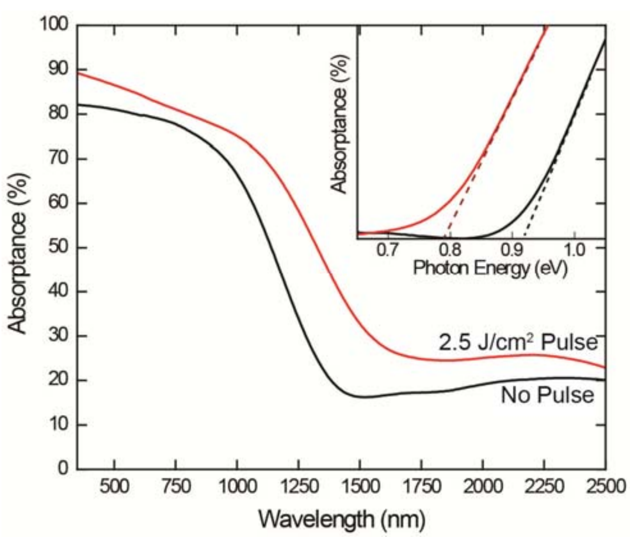




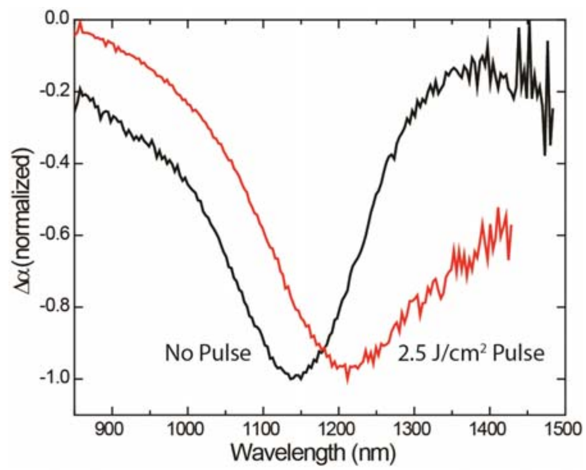
As-deposited

2.2 J/cm²

Check optically that MEG exists in the material

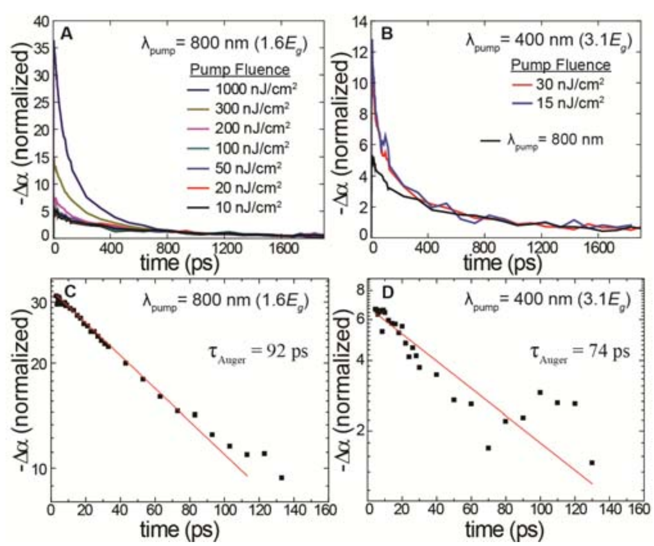


Transient absorption spectra



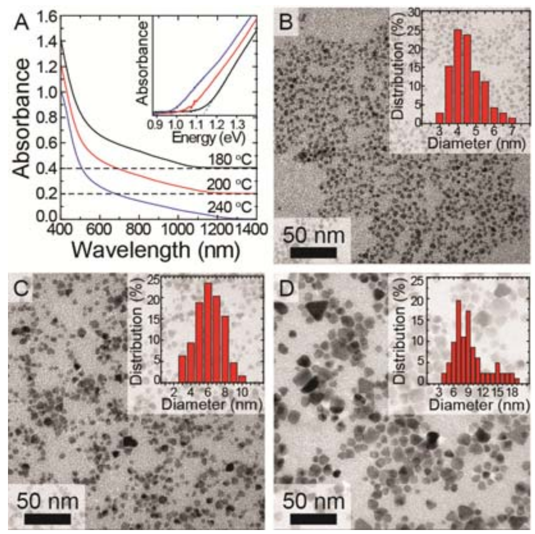
There is a bleach at the band edge

Confirmation of MEG in $CuInSe_2$ nanocrystal films

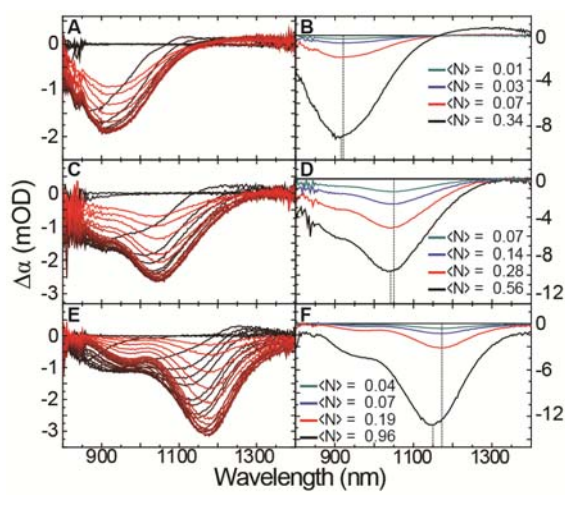


Stolle, et al. *J. Phys. Chem. Lett.* 2014.

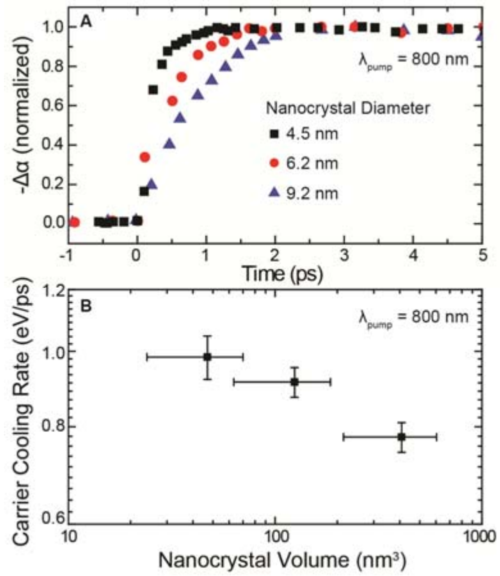
Three $CuInSe_2$ quantum dot sizes studied by TAS



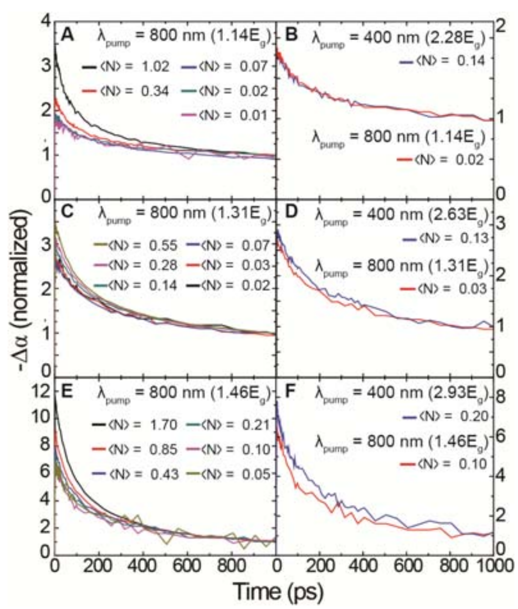
TAS: 800 nm pump (3 dif sizes)



Very short time TAS data (carrier cooling rates)



TAS kinetics as a function of nanocrystal size



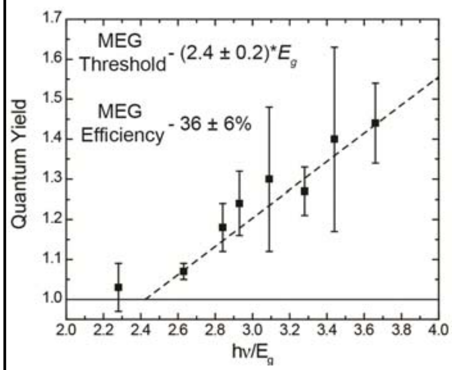


Table 1: MEG efficiency, MEG threshold, and bulk band gap for a variety of semiconductor nanocrystals found in the literature. Reported samples were stirred to avoid anomalous effects due to photocharging.[14,23]

Semiconductor Nanocrystal	MEG Efficiency (%)	MEG Threshold ($h\nu/E_g$)	Bulk Band Gap (eV)	Reference
$CuInSe_2$	36	2.4	1.0	--
PbS	40	3	0.5	24
PbSe	40	3	0.37	23
InAs	35	2	0.36	25
InP	30	2.1	1.27	7
CdSe/CdTe	53	2.7	0.91	26

1.36 excitons are generated at a pump energy of 3.4*optical gap

Shockley-Queisser Limit: 34% efficiency

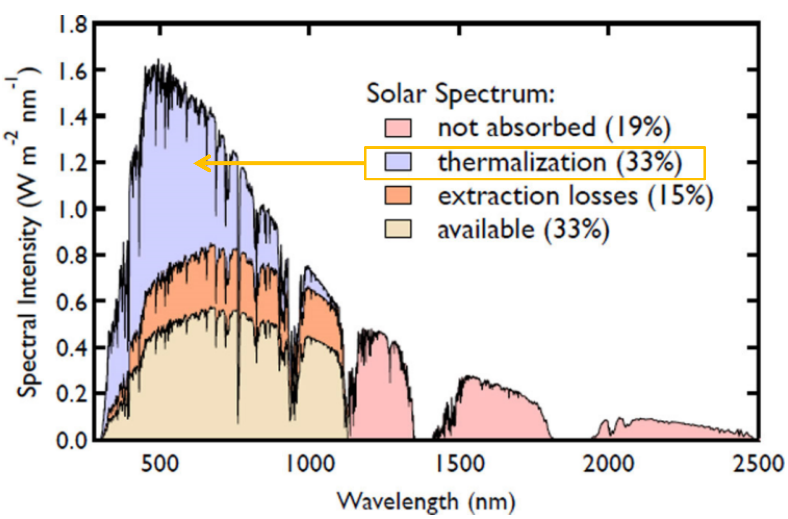
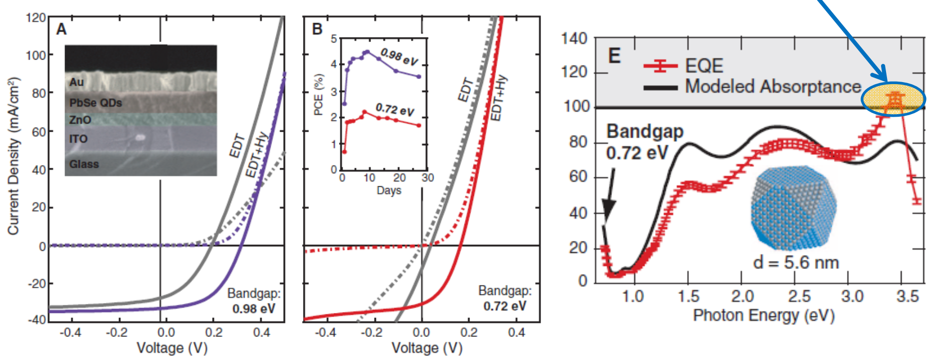


Image from Semonin, Beard, Nozik, SPIE Newsroom (2012)

Science **334**, 1530 (2011)

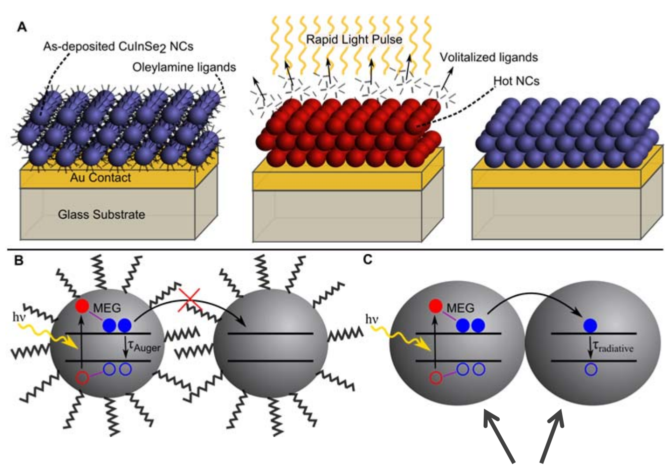
Peak External Photocurrent Quantum Efficiency Exceeding 100% via MEG in a Quantum Dot Solar Cell

Octavi E. Semonin,[1,2] Joseph M. Luther,[1] Sukgeun Choi,[1] Hsiang-Yu Chen,[1] Jianbo Gao,[1,3] Arthur J. Nozik,[1,4*] Matthew C. Beard[1*]



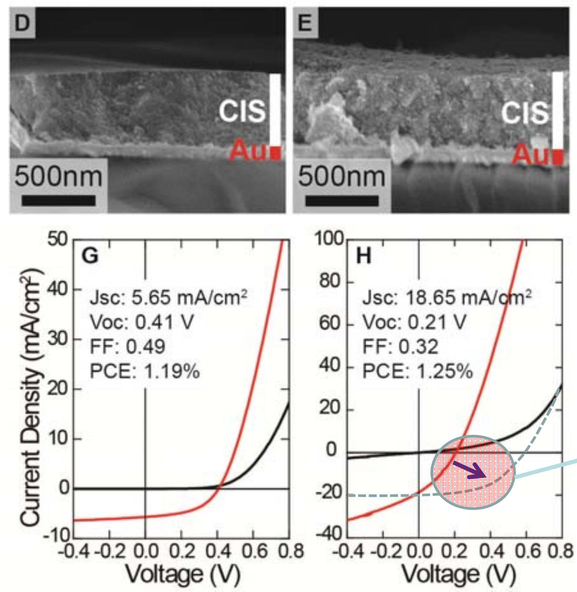
First report of EQE>100% in a functioning device

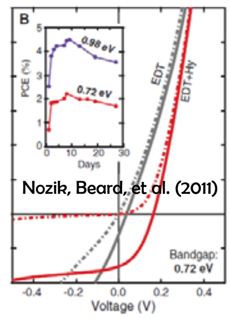
Multiple Exciton Generation and Extraction from a Nanocrystal Photovoltaic Device



Surface traps currently limit device efficiency;
Low open circuit voltage

Next step: Try to recover V_{oc} by passivating surface traps





Nozik, Beard, et al. (2011)

Next: Passivate the traps?
(a printed PV with 10% efficiency)

Printed Nanocrystal-Based Photovoltaics

- Nanocrystal inks: MEG occurs in $CuInSe_2$ nanocrystals
- Multiexciton extraction in PV devices appears to be relatively viable
- Is it possible to create multiexciton solar cells with high device efficiency?

Financial support : Robert A. Welch Foundation (F-1464), the Air Force Research Laboratory (FA-8650-07-2-5061) and the NSF Industry/University Cooperative Research Center on Next Generation Photovoltaics (IIP-1134849).

Special Acknowledgement to:

1st gen PV students→

Vahid Akhavan

Brian Goodfellow

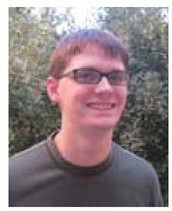
Matt Panthani

Danny Hellebusch

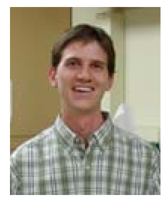
Dariya Reid

←Key undergraduate researchers

Next gen PV students→



Jackson Stolle



Taylor Harvey

Financial support : Robert A. Welch Foundation (F-1464), the Air Force Research Laboratory (FA-8650-07-2-5061) and the NSF Industry/University Cooperative Research Center on Next Generation Photovoltaics (IIP-1134849).