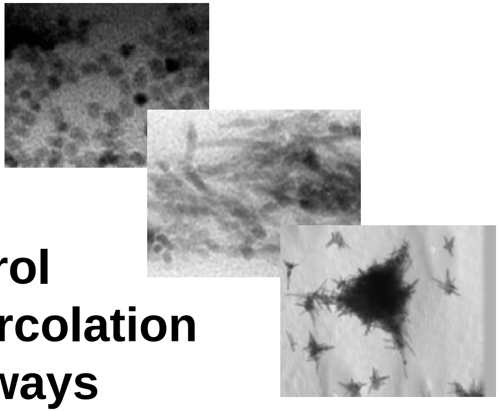
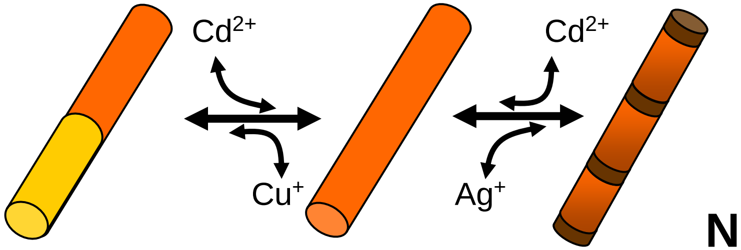
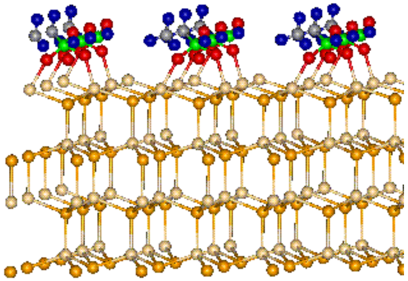
Nanocrystal-based solar cells



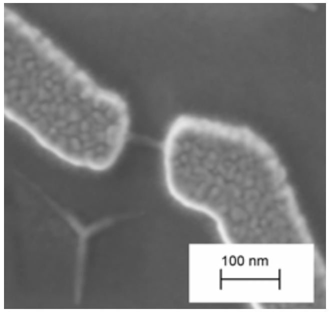
Control of percolation pathways



New nanoscale heterostructures for solar cells



Organic passivation and assembly



Model studies of single nanocrystals

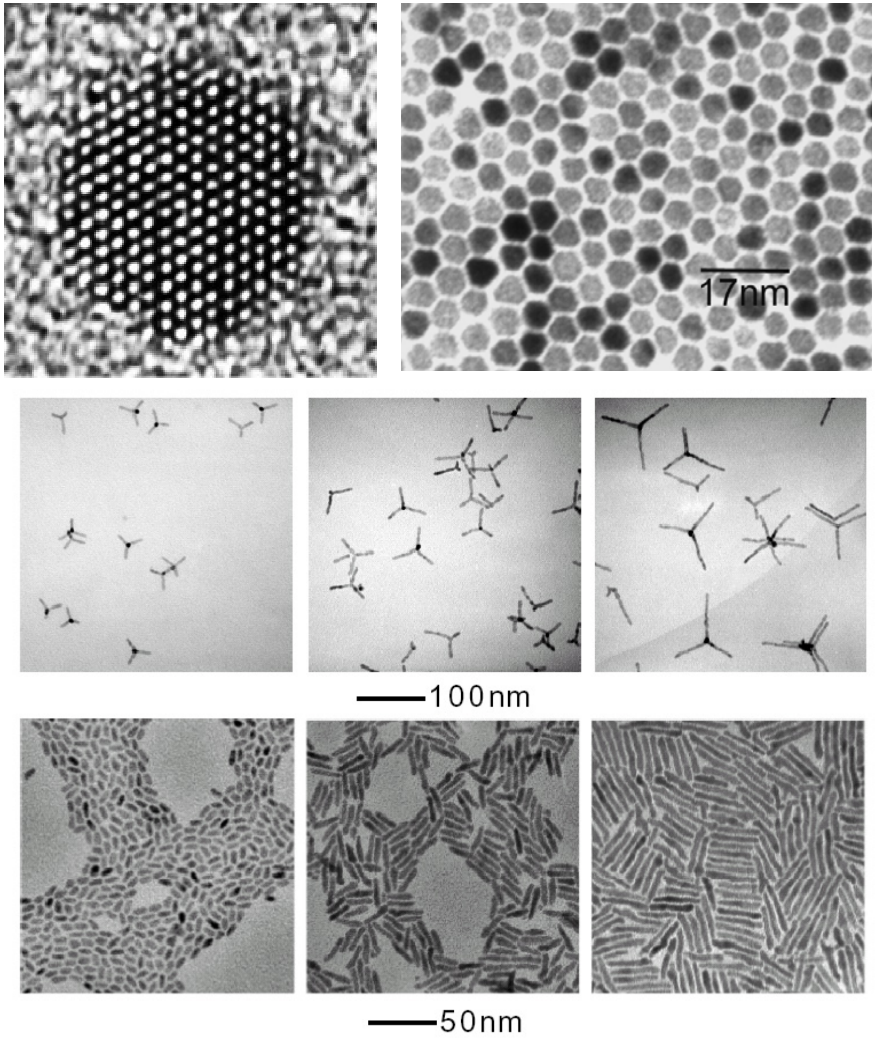
Paul Alivisatos
Larry and Diane Bock Professor of Nanotechnology, University of California, Berkeley
Materials Science Division, Lawrence Berkeley National Lab

Big crystals vs. nanocrystals for solar cells?

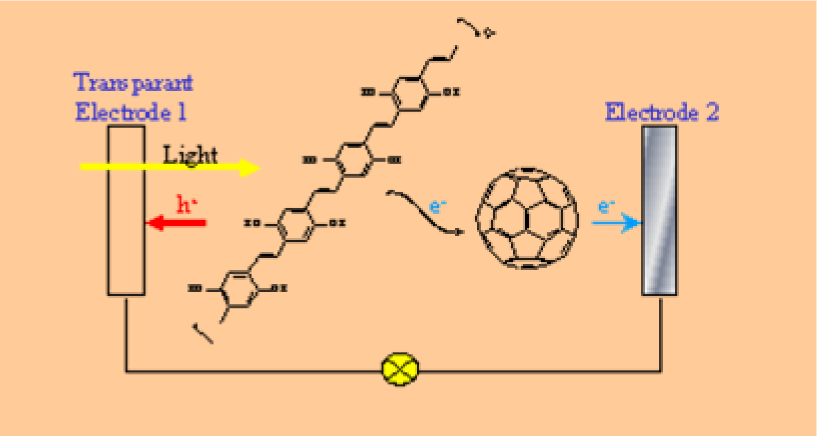
12 inches (330 mm)

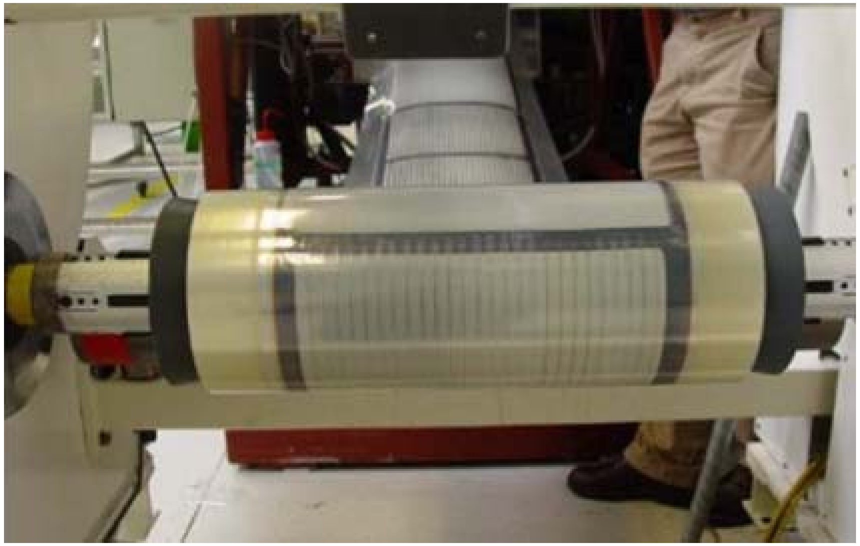
http://www.risoe.dk/rd/images/nua-ntd-Krystal.jpg

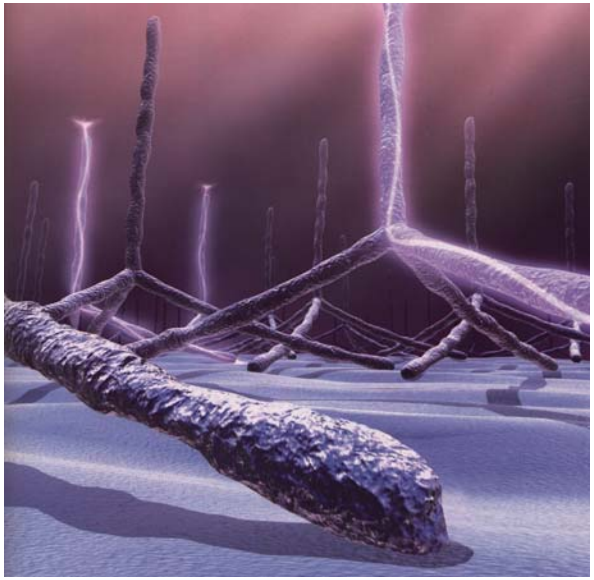
- Size: .000002- .000200 mm



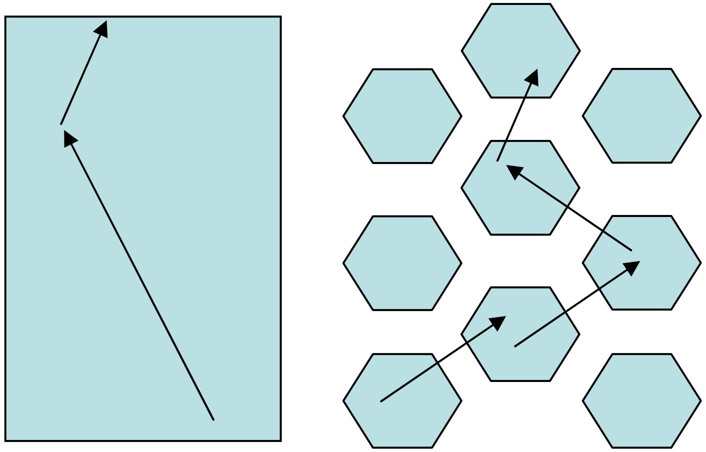
Mass production of high performance solar cells?







Some key issues with inorganic nanostructures for solar cells



DeBeer's Web site:
"Big diamonds are much rarer, so a diamond of double the weight costs around 4 times more. "

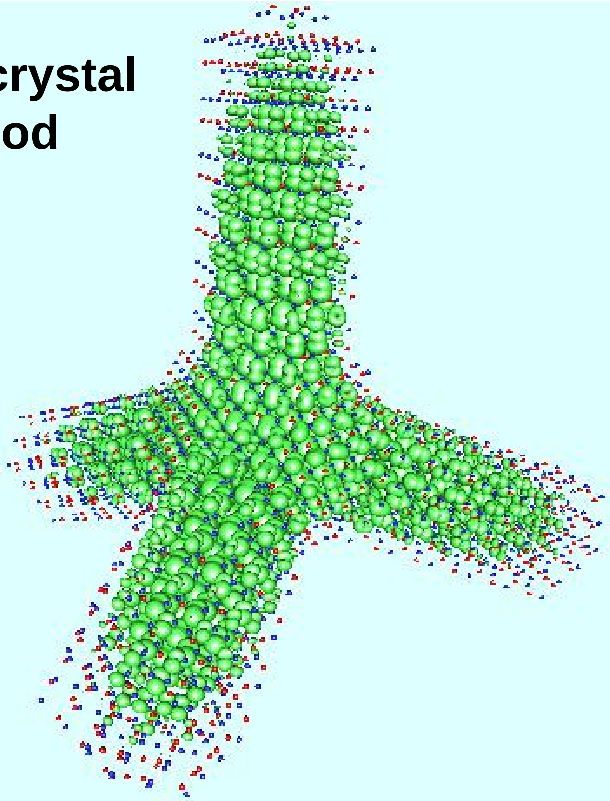
- Cost and time of fabrication limits solar cell use today
- Nanocrystals can be made as cheaply and in as large volume as plastics
- High surface area and charge trapping are the biggest problems
- A fundamental challenge for materials chemistry:

achieve adequate performance with assembly methods that can be scaled to large areas and high speed

How to "bury" the interfaces…

Crystals, Nanocrystals, Polymers - tension between delocalization, stability and control of electronic states

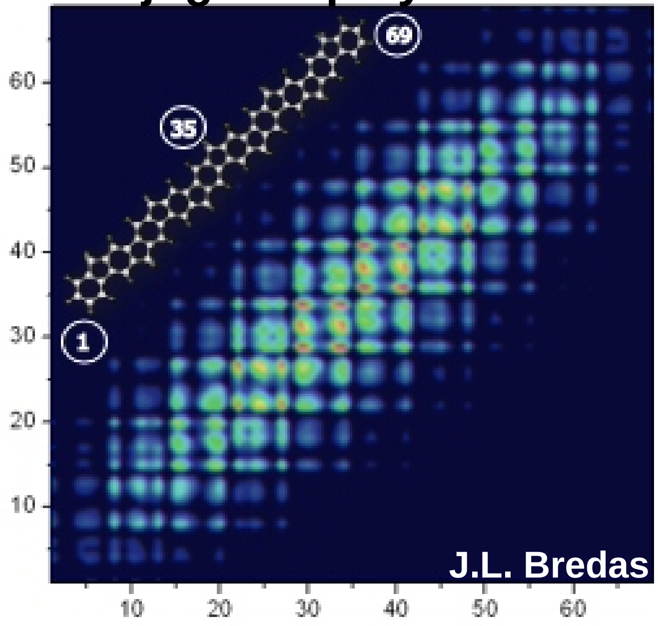
CdSe nanocrystal tetrapod



~1,000-10,000,000 atoms

L.W.Wang

Conjugated polymer



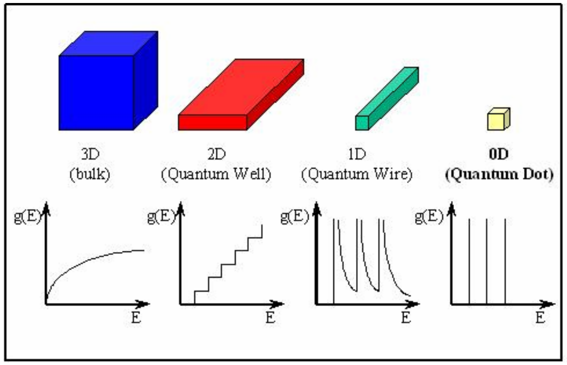
J.L. Bredas

~10-100 atoms

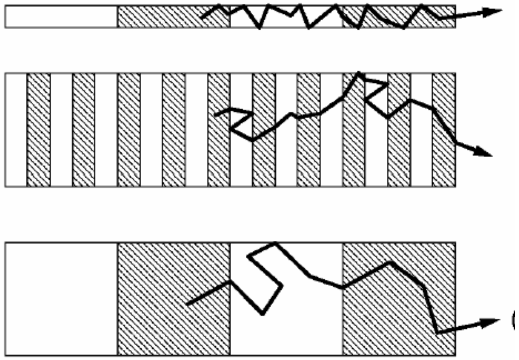
Exciton binding energy, Photochemical reactions

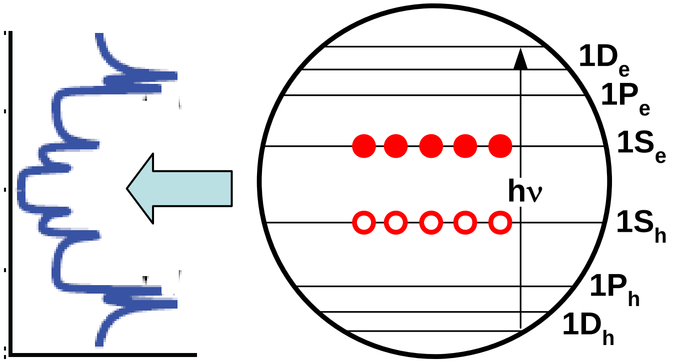
New physical phenomena in nanoscale PVs may enable high efficiency

electrons



phonons



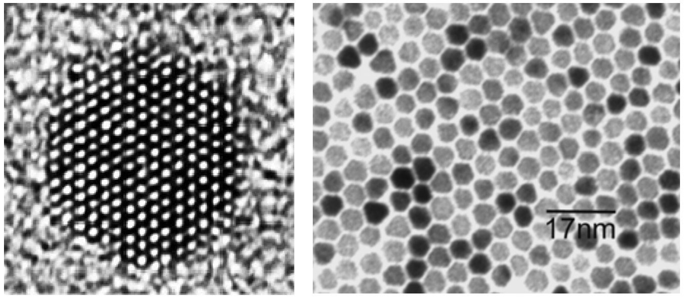


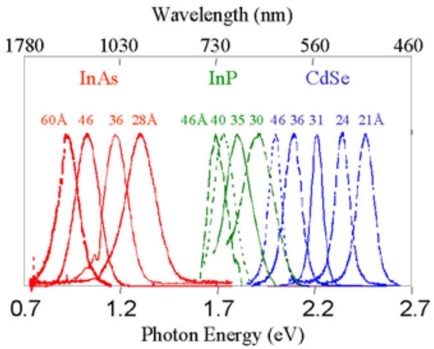
- Control of dissipation on the nanoscale
- Multi-exciton, hot electron, intermediate band gap concepts
- Novel quantum confinement based light absorbers
- Control of electrical transport within and between components

For nanocrystal PVs, we would settle for just solving the problem of transport

Dots, Rods, and Trees for Nanocrystal PVs

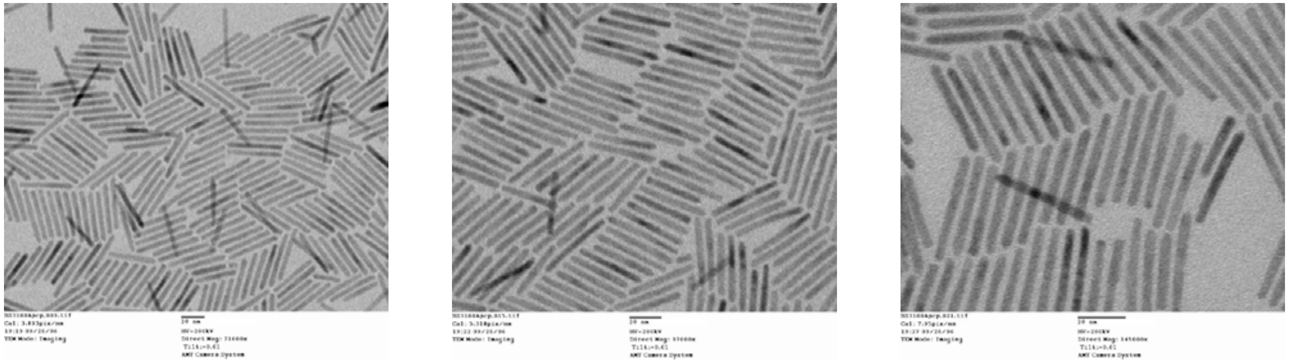
Dots





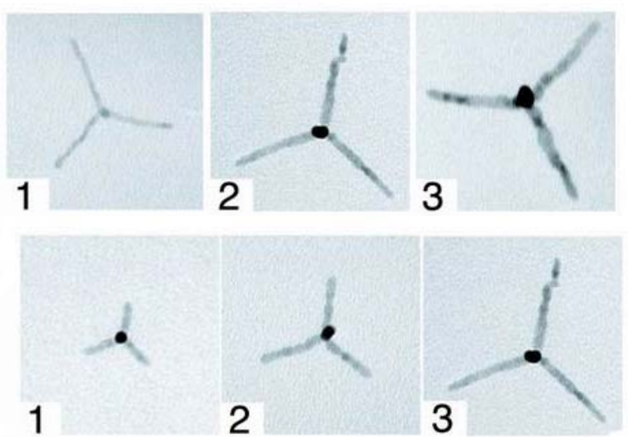
Science 271 933 (1996).

Rods

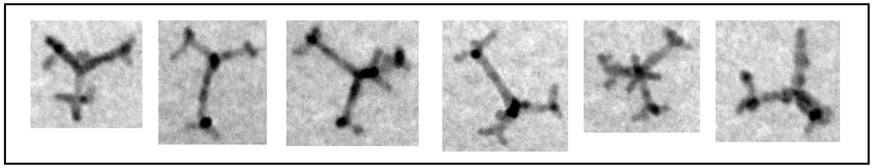


Nature **2000** *404*, 59-61.

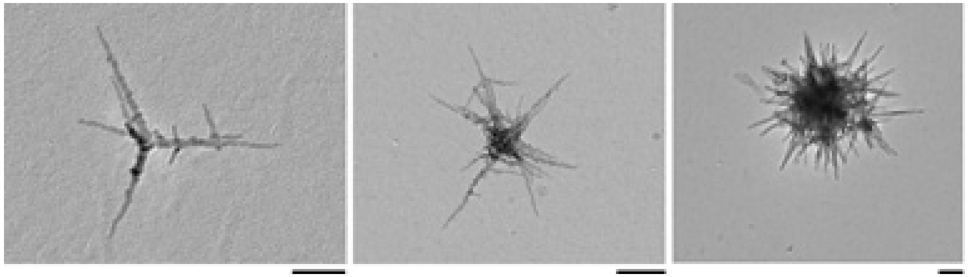
Branched



Nature Materials **2** 382 (2003).

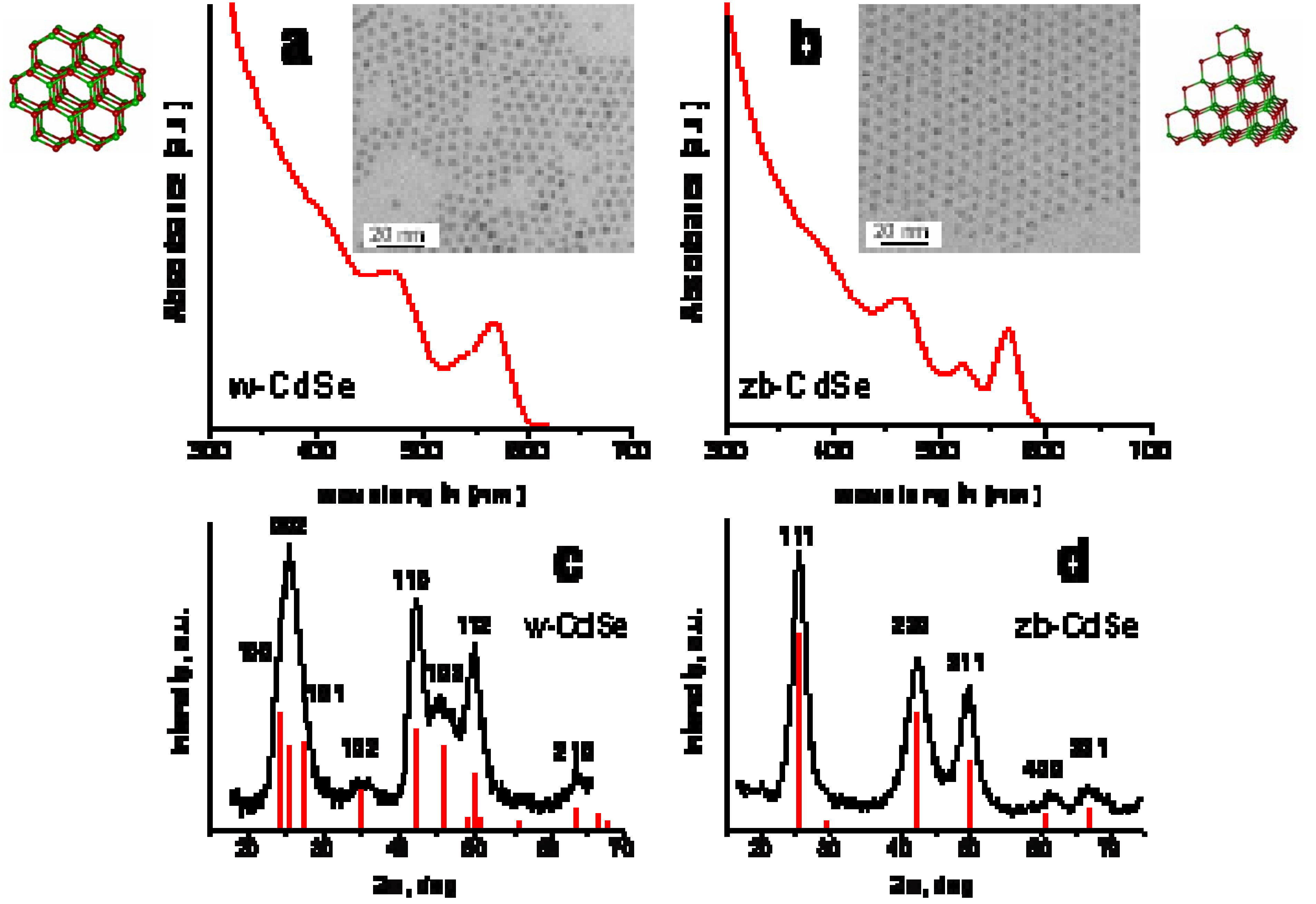


Nature **430** 190 (2004)

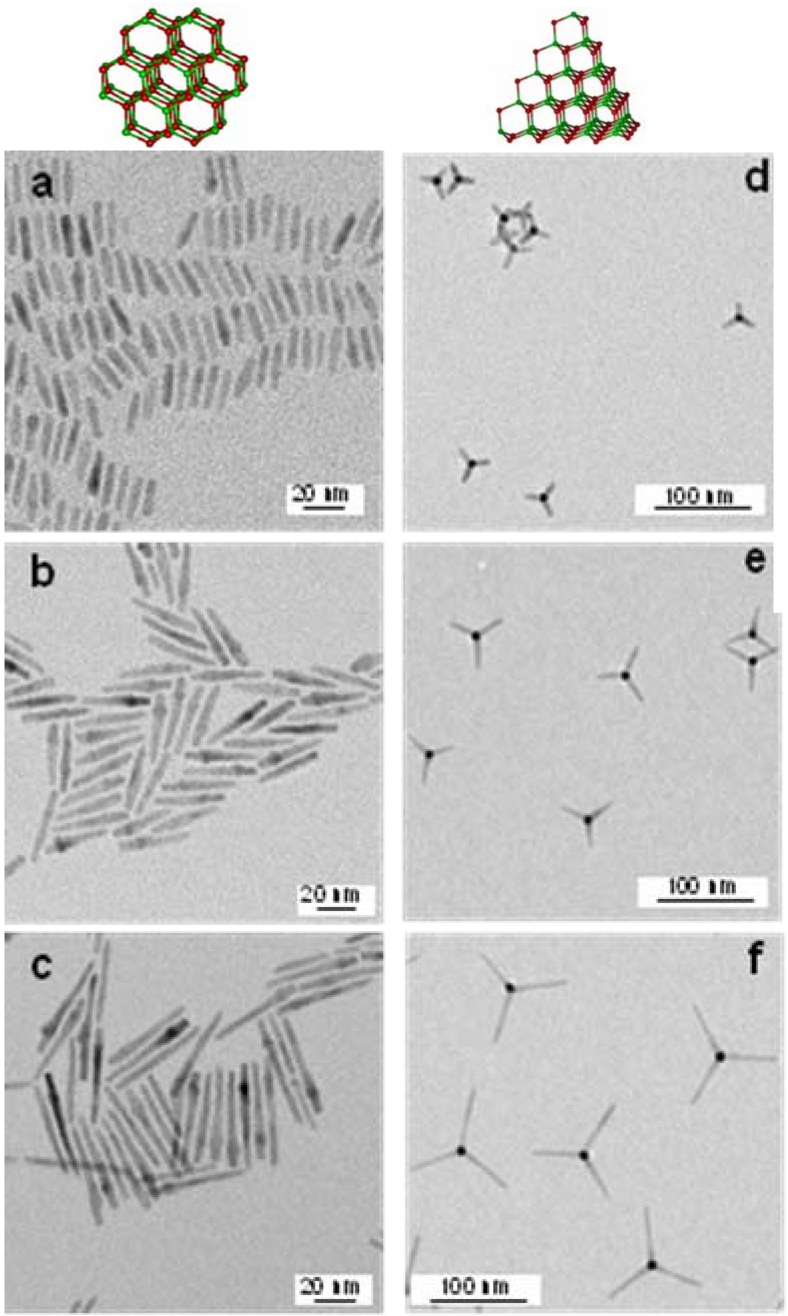


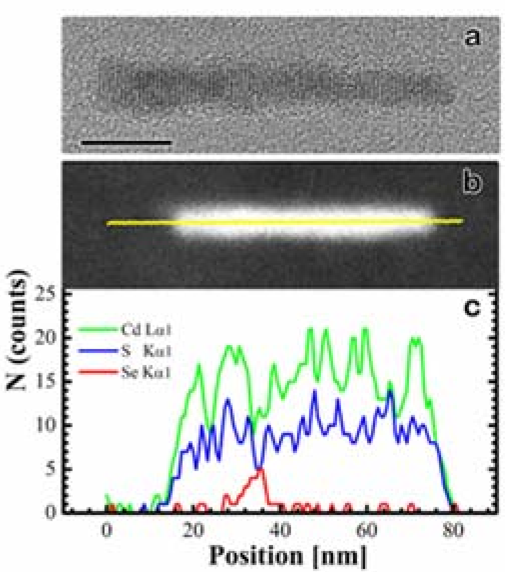
Nano Letters 5 2164 (2005).

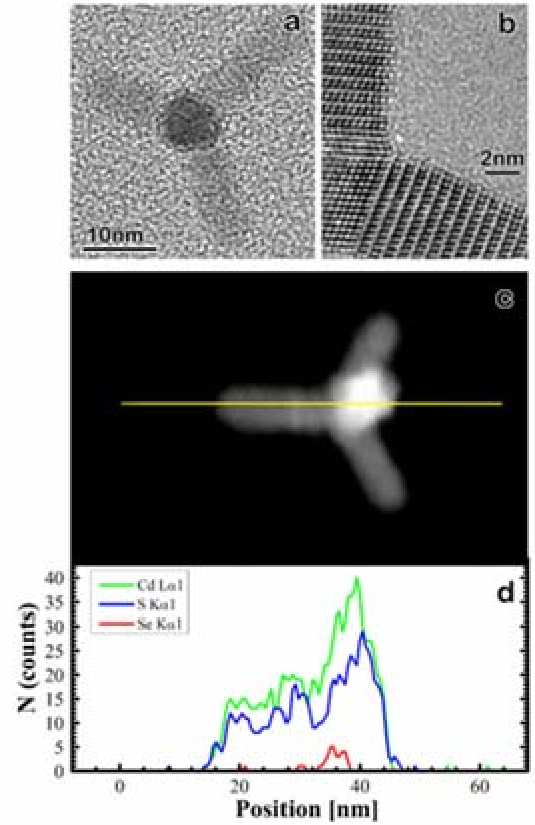
Seeded Growth from Wurtzite and Zincblende CdSe Seeds

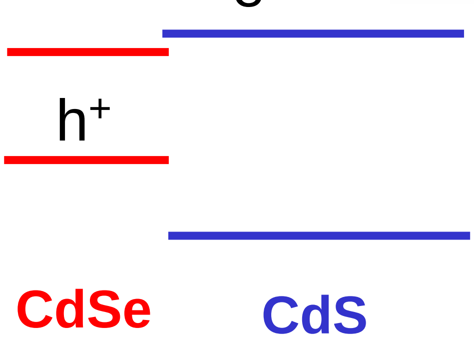


Seeded dot growth of rods and tetrapods








e^-

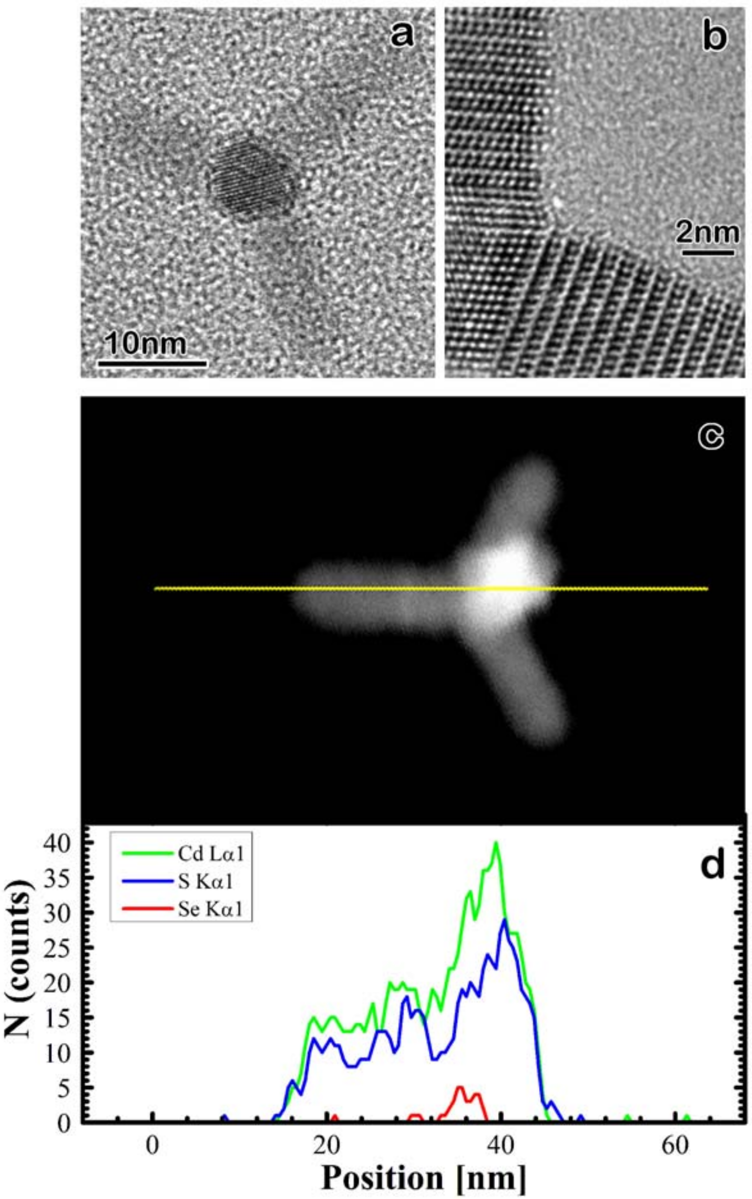
h^+

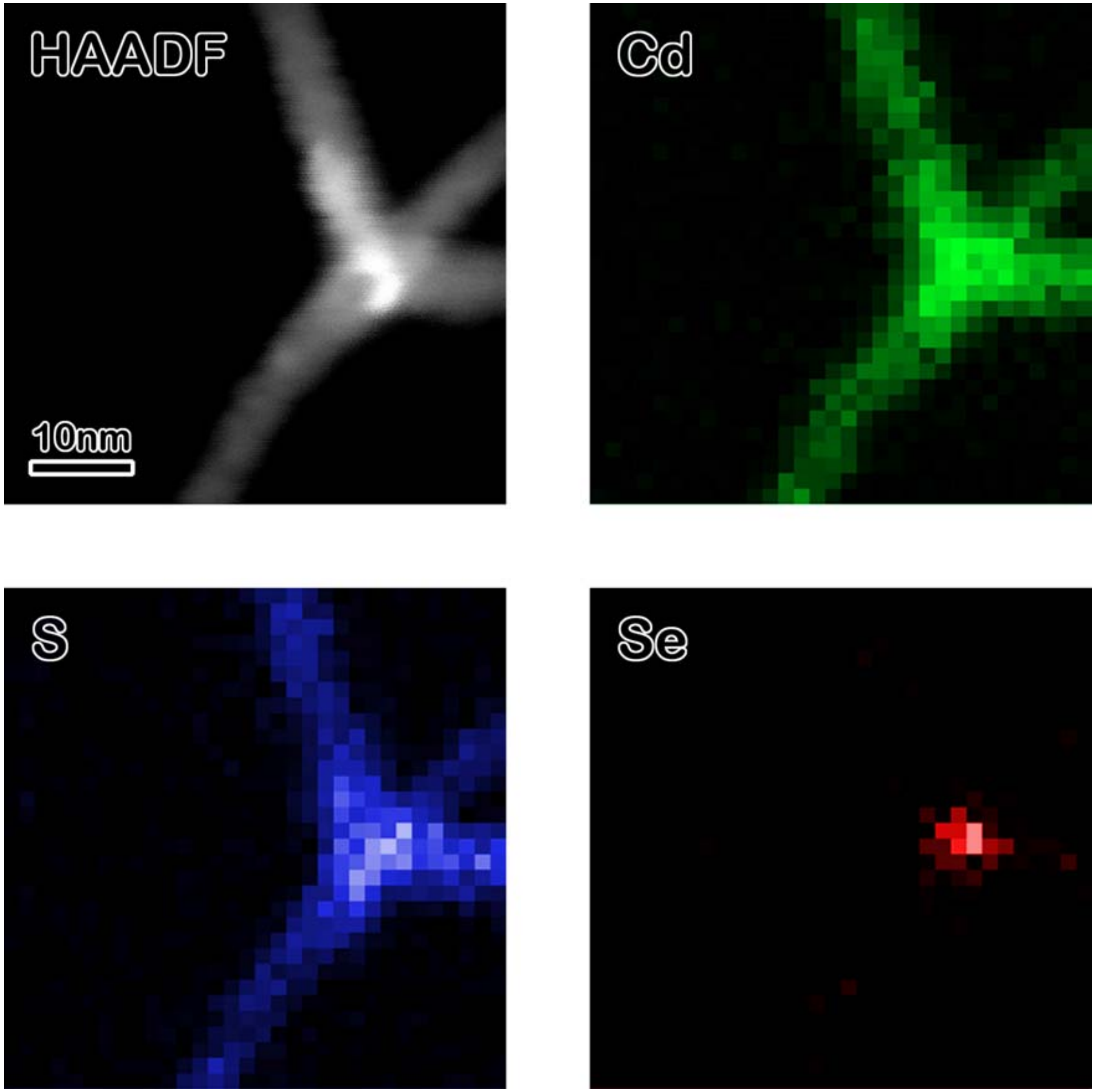
CdSe

CdS

Nano Letters (ASAP)

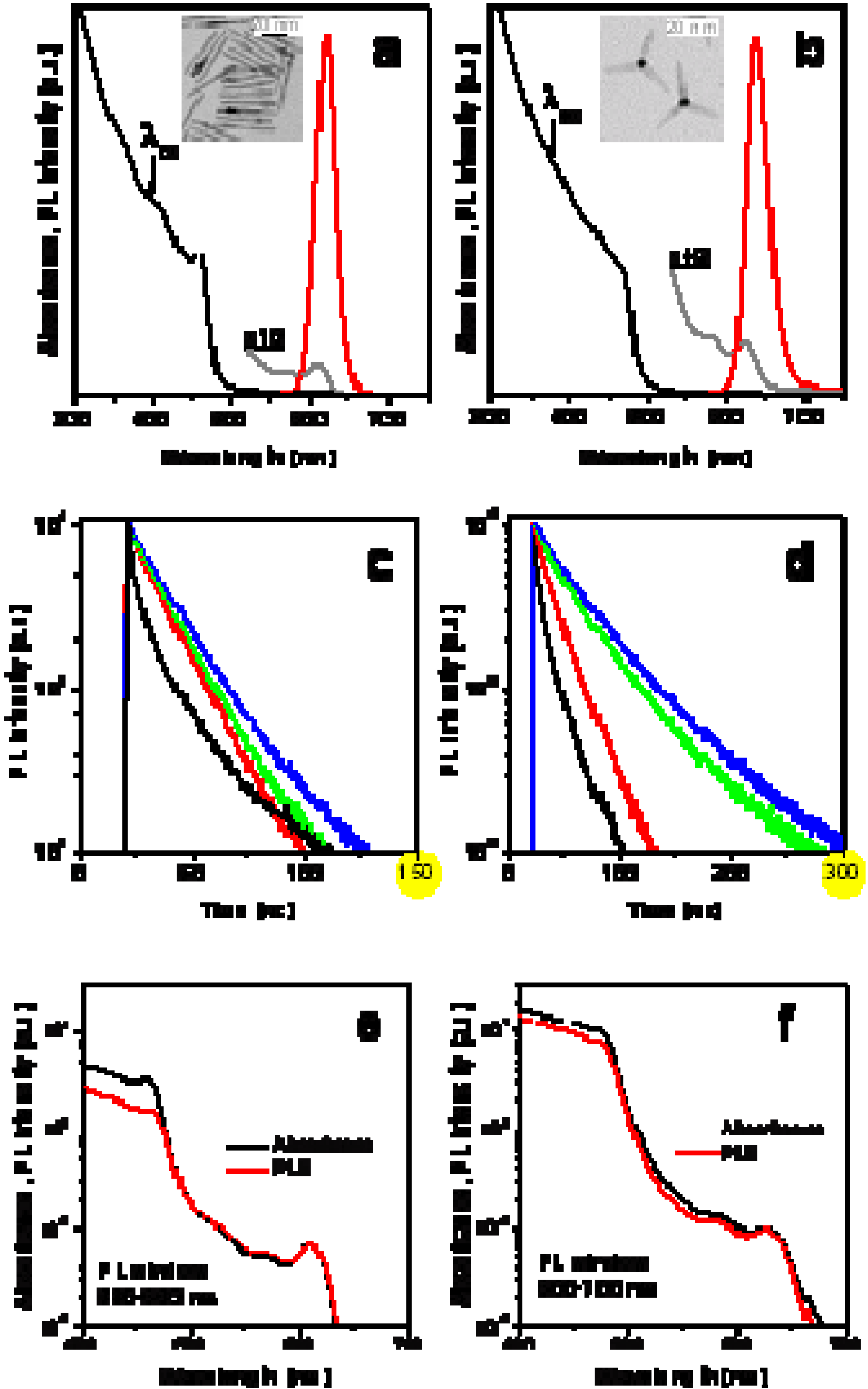
Structural and compositional analysis of the seeded tetrapods





Shaul Aloni

Optical properties
of seeded rods/tetrapods



Electron delocalizes into CdS regions

High quantum yields
(>80% for rods, >60% for tetrapods)

Near exponential decays

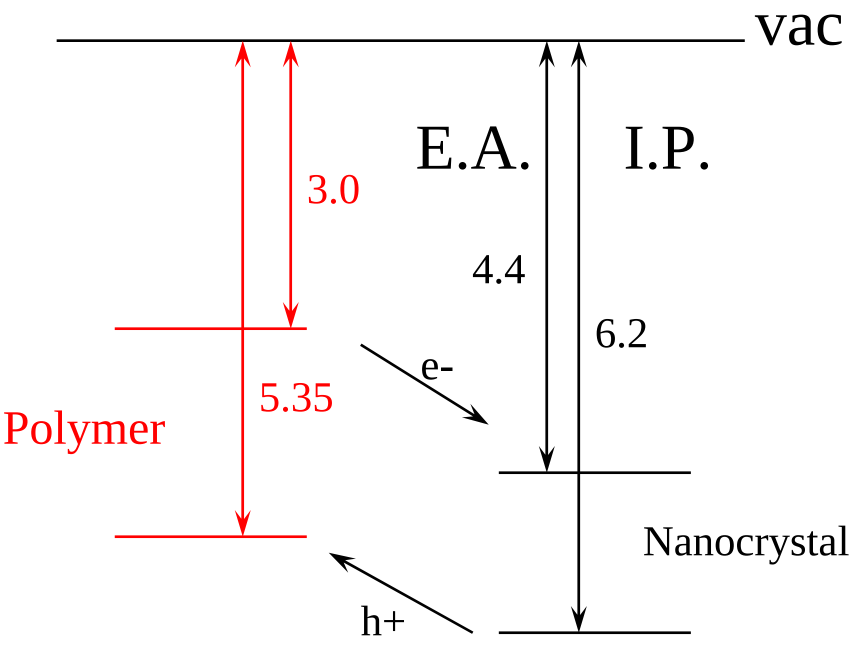
Longer arms -→ slower radiative rate

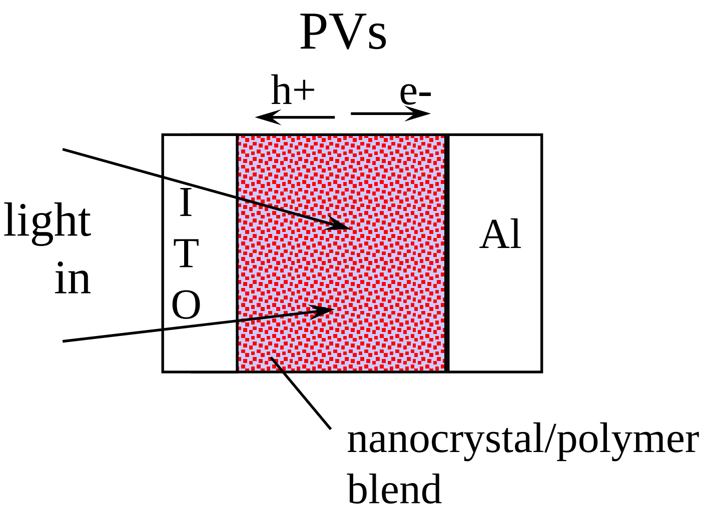
Absent symmetry breaking electrodes,
Photoexcited charges “fall”
into the central dot

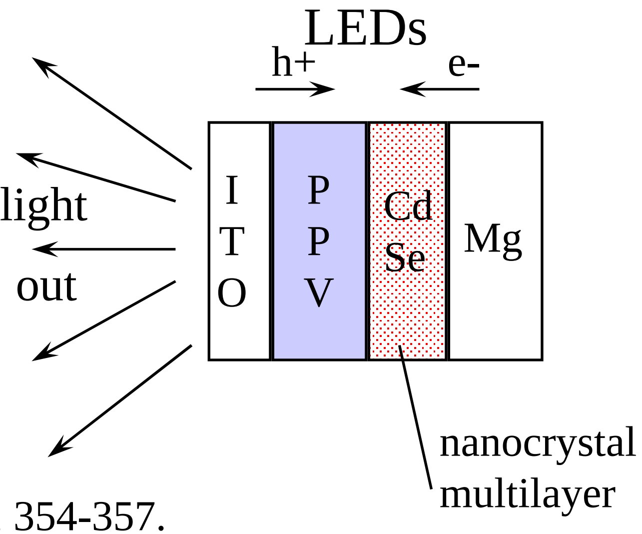
Absorbance as large as10^8 M-1cm-1

Nano Letters (ASAP)

Semiconductor Nanocrystals and Polymers
Band Offsets and Electrical Devices







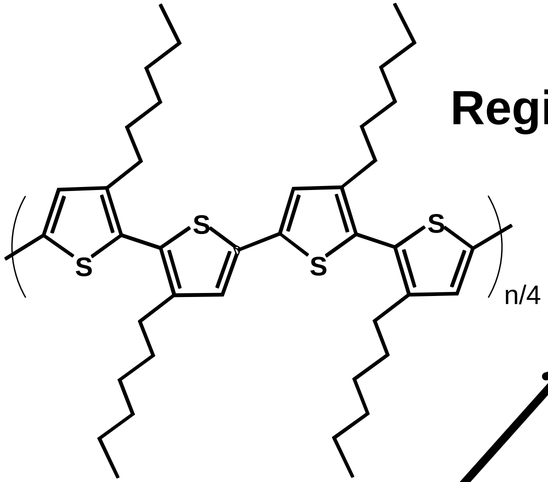
LEDs:

Colvin, V. L.; Schlamp, M. C.; Alivisatos, A. P., *Nature* **1994**, *370*, 354-357.

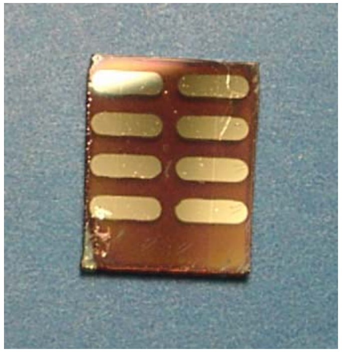
Schlamp, M. C.; Peng, X.; Alivisatos, A. P., *J. Appl. Phys.* **1997**, *82*, 5837-5842.

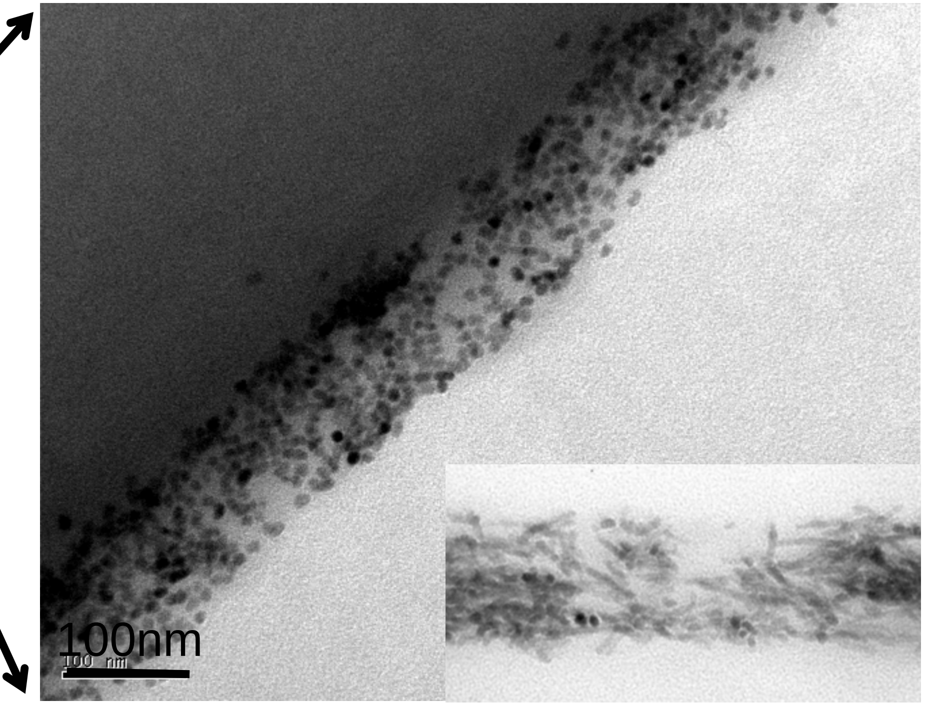
Charge separation in nanocrystal polymer blends *Phys. Rev. B* **54** 17628 (1996)

Nanocrystal/Polymer Solar Cells



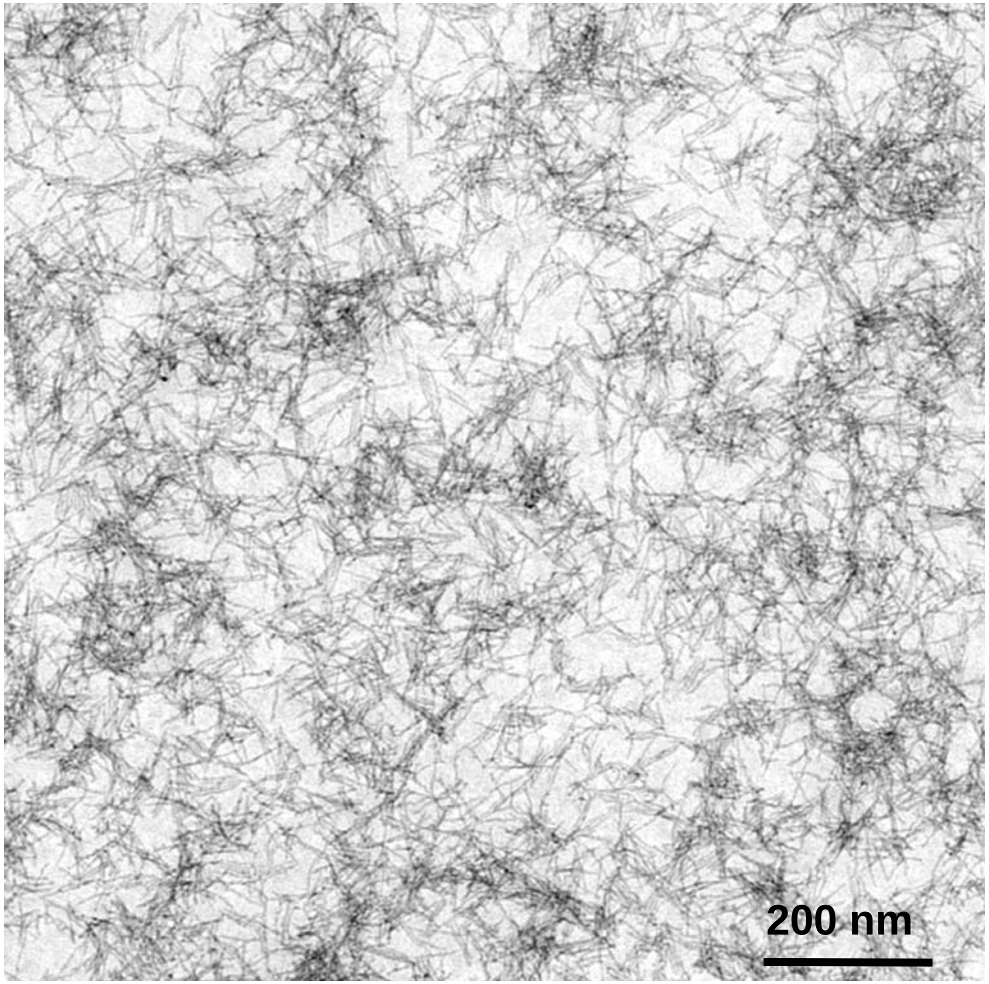
Regioregular P3HT





Huynh, W. U., J. J. Dittmer, Alivisatos (2002). "Hybrid nanorod-polymer solar cells." Science **295**(5564): 2425-2427.

CdSe nanorod/P3HT films

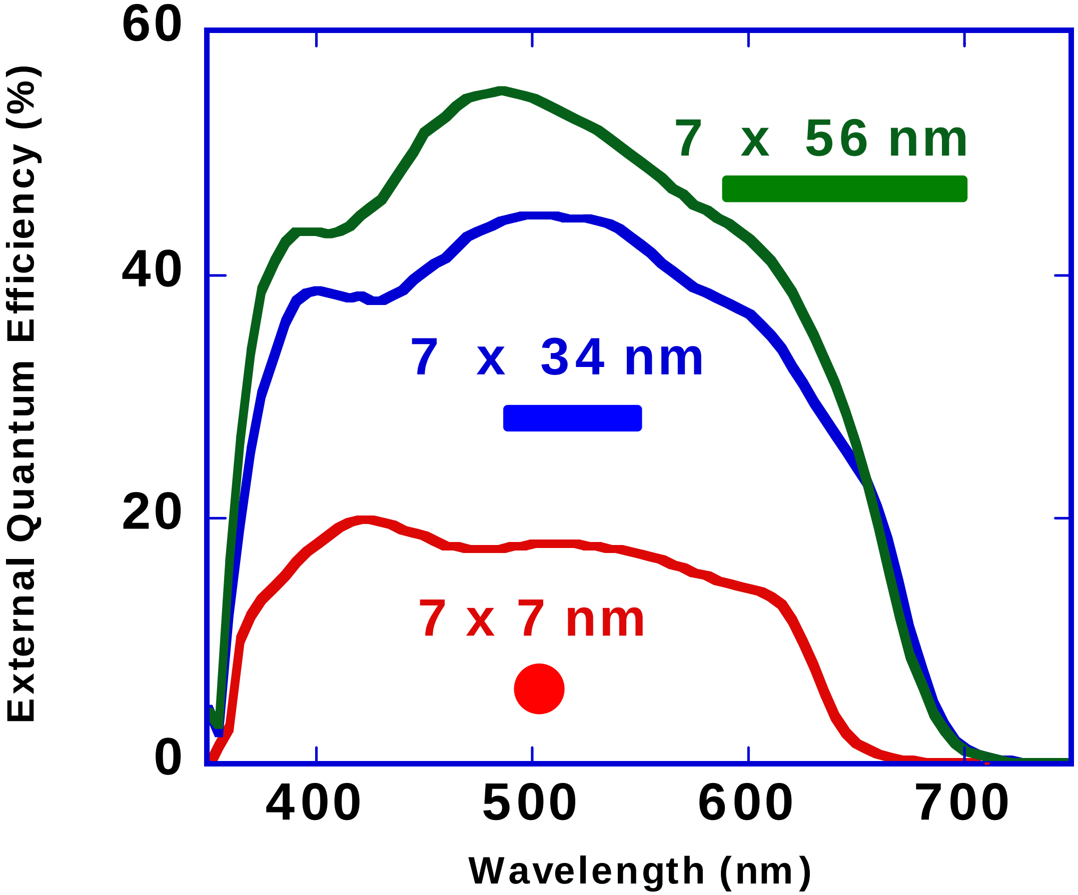


spin cast from 8% pyridine 92% chloroform solvent mixture

Huynh, W. U., J. J. Dittmer, W. C. Libby, G. L. Whiting and A. P. Alivisatos (2003).

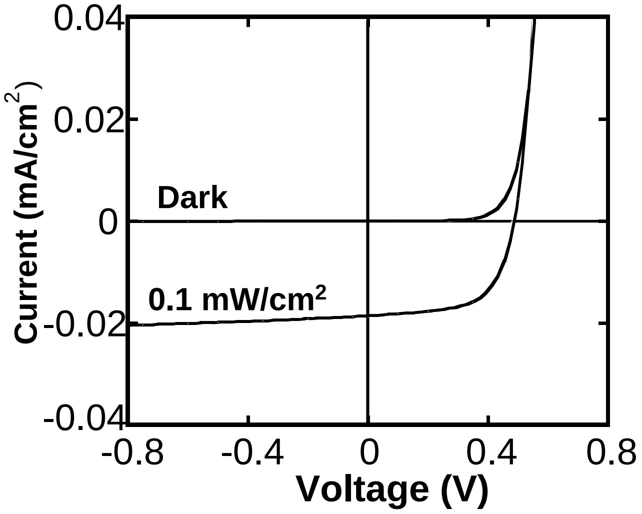
"Controlling the morphology of nanocrystal-polymer composites for solar cells." Advanced Functional Materials **13**(1): 73-79.

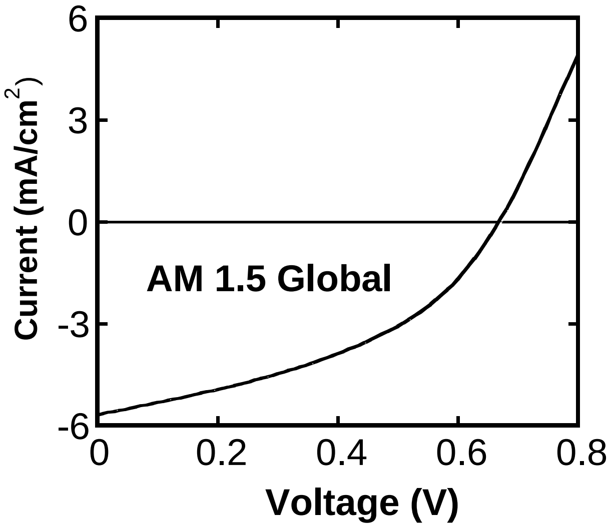
Shape and Performance

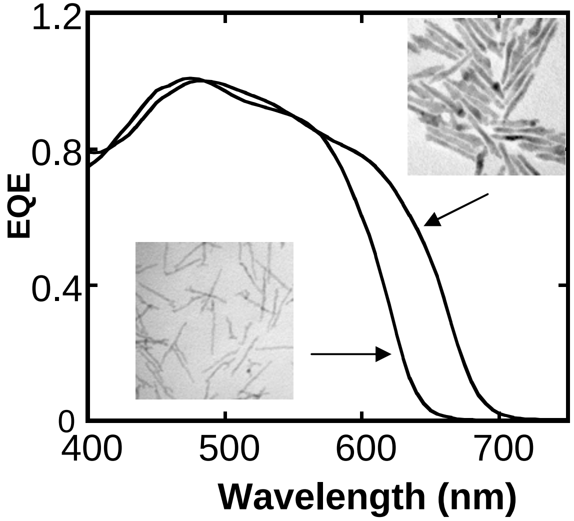


Measured at low intensity ~ 0.1 mW/cm^2

Plastic/Nanorod Solar Cell Power Efficiency







AM 1.5 Efficiency

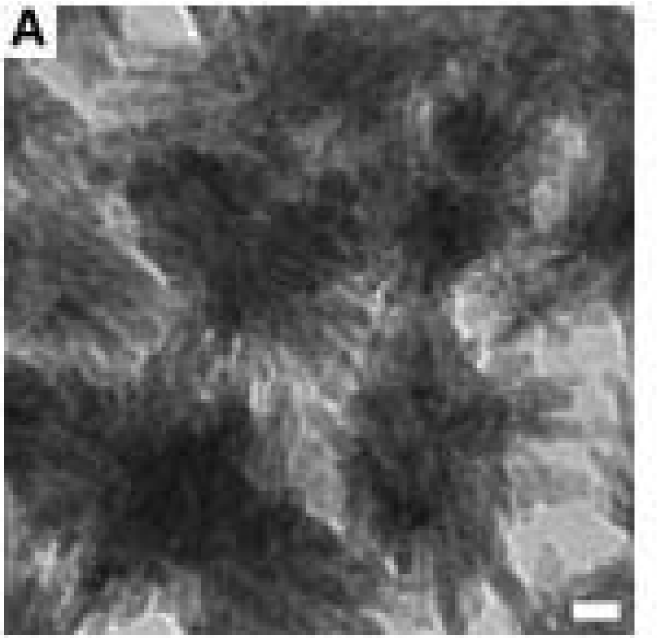
Power Conversion: **1.7%**

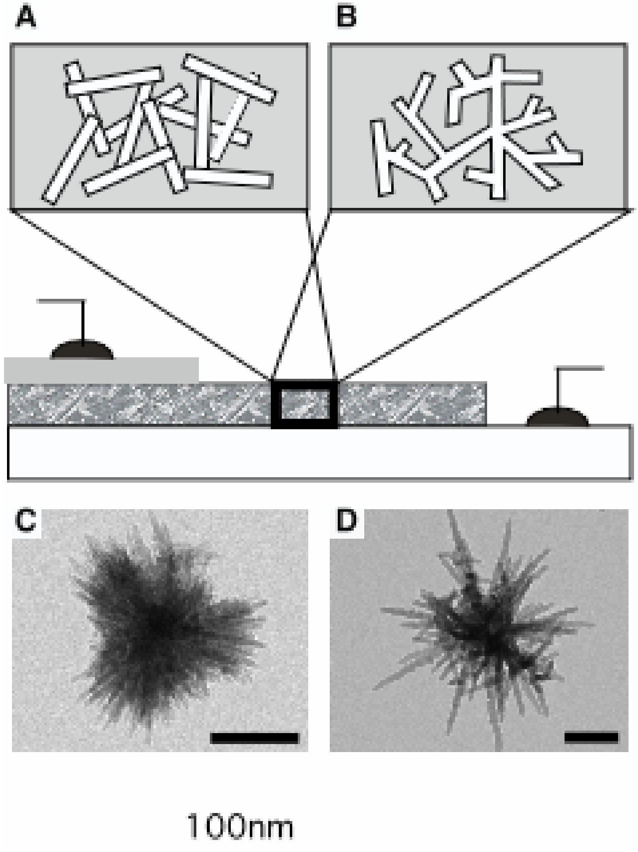
Short Circuit Current: 5.8 mA/cm^2

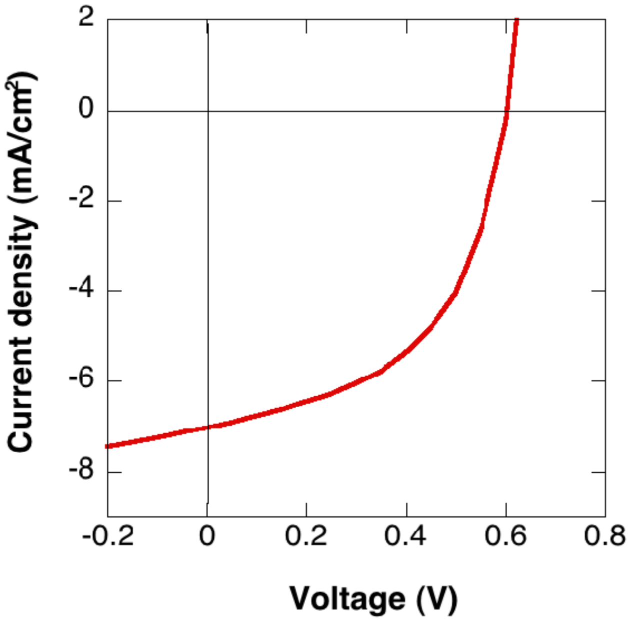
Fill Factor: 0.42

Voc : 0.67 V

Pre-formed percolation pathways with Hyperbranched Nanocrystals



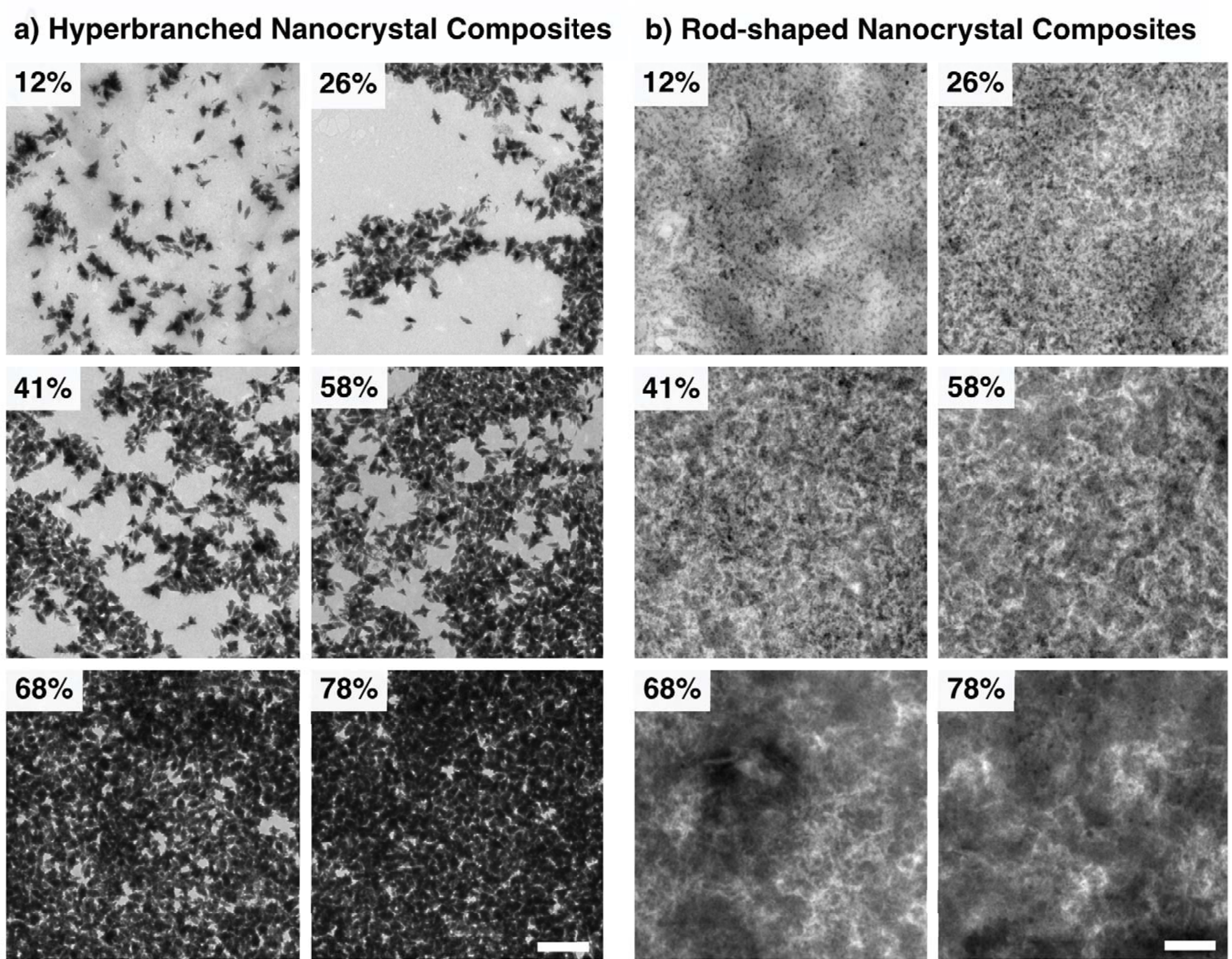




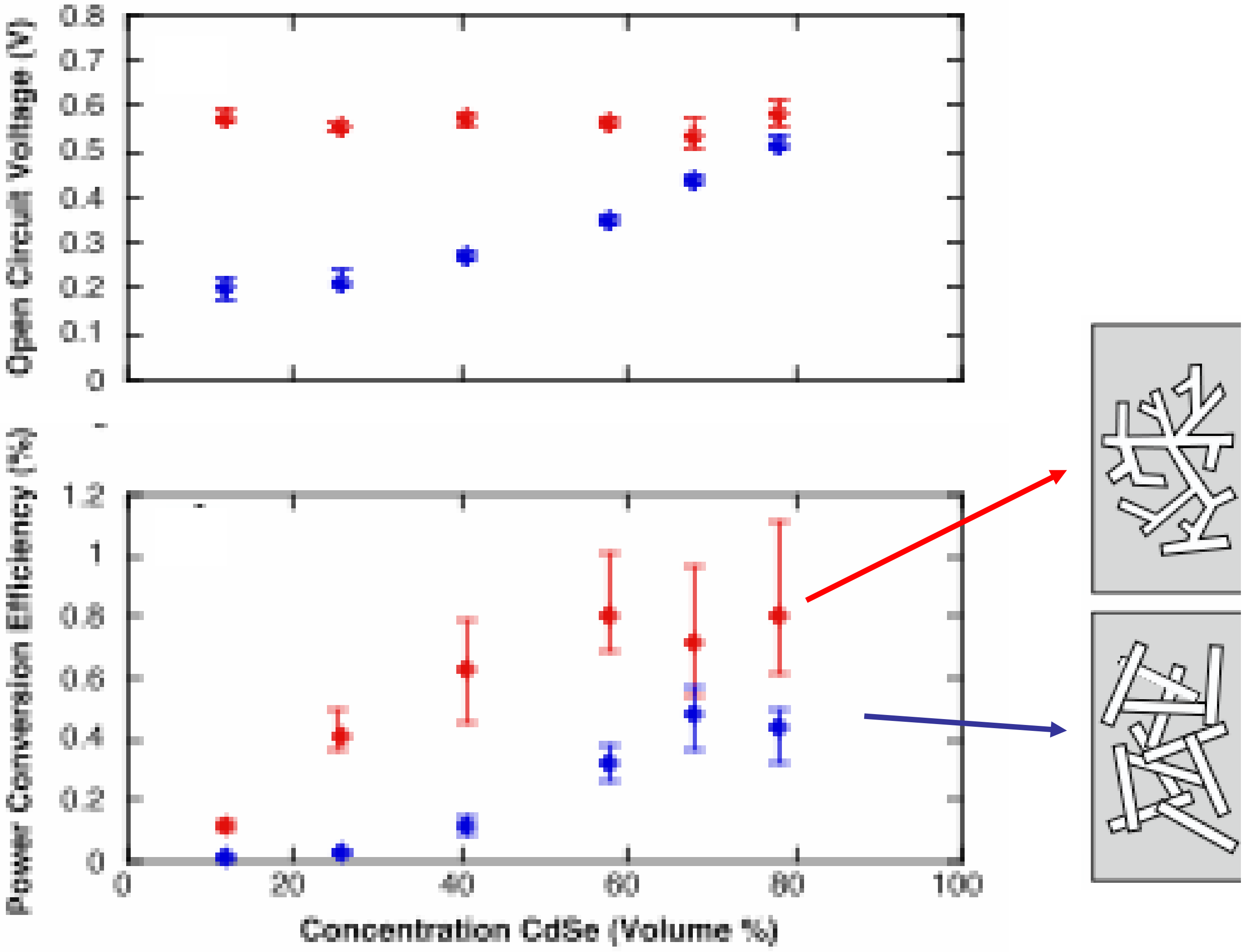
~2.5 % Power Efficiency

Gur, N. A. Fromer, C. P. Chen, A. G. Kanaras, and A. P. Alivisatos,
"Hybrid solar cells with prescribed nanoscale morphologies based
on hyperbranched semiconductor nanocrystals,"
Nano Letters 7 (2), 409 (2007).

Morphology of composites



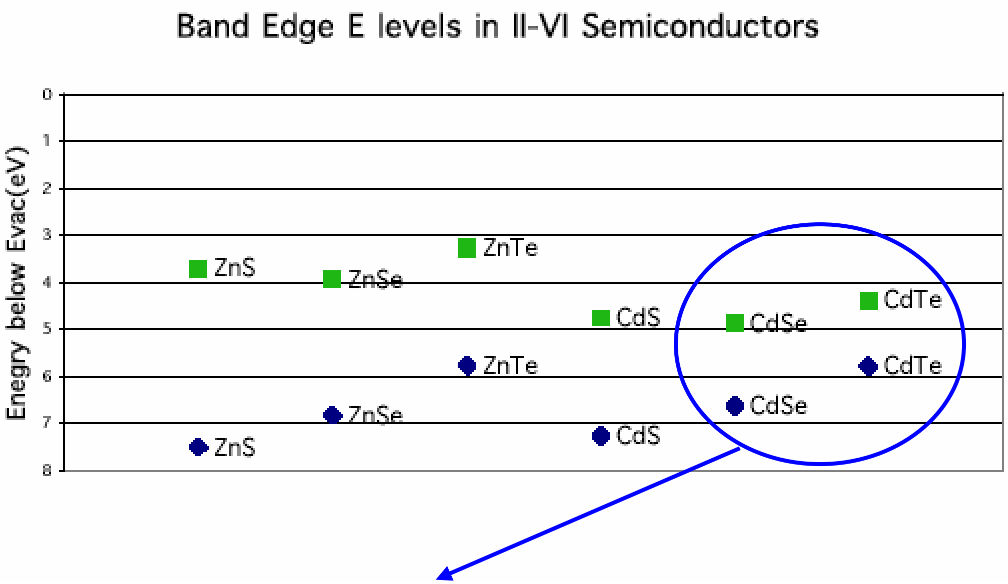
Percolation at all loading levels with hyperbranched particles



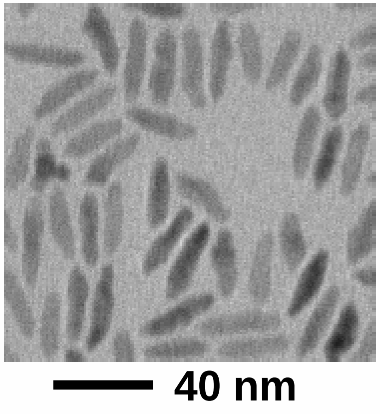
Processing is now very forgiving

Limitations of Hybrid Nanorod Polymer System

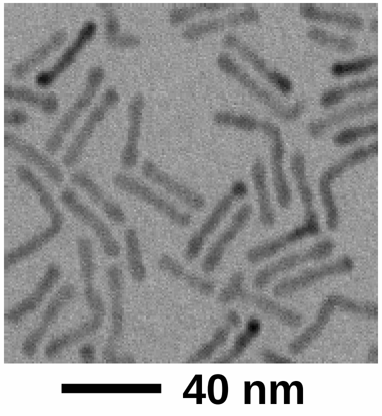
- TRANSPORT: Devices likely limited by low mobilities in organic component
- STABILITY: Organic materials potentially less stable than inorganic, under solar conditions



CdSe Rods



CdTe Rods



✓ Staggered Bands

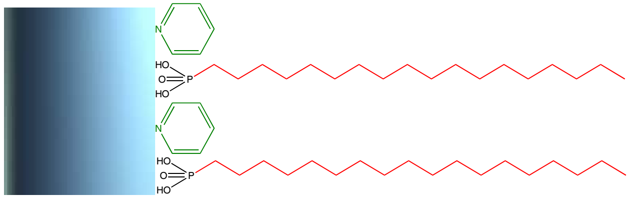
✓ Small Band Gaps

✓ Solution Synthesis Available

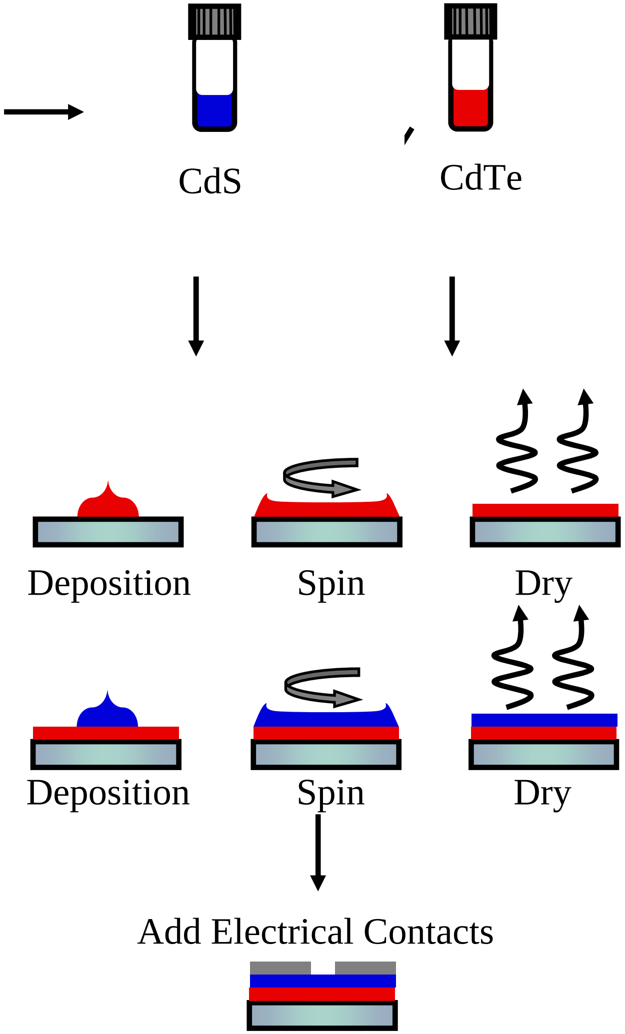
Next project: build an “donor-acceptor-type” solar cell composed entirely of inorganic colloidal nanocrystals

Gur, I., N. A. Fromer, M. L. Geier and A. P. Alivisatos (2005). "Air-stable all-inorganic nanocrystal solar cells processed from solution." Science 310(5747): 462-465.

Dual Nanocrystal Solar Cell Device Fabrication



Surfactant Exchange



CdS

CdTe

Deposition

Spin

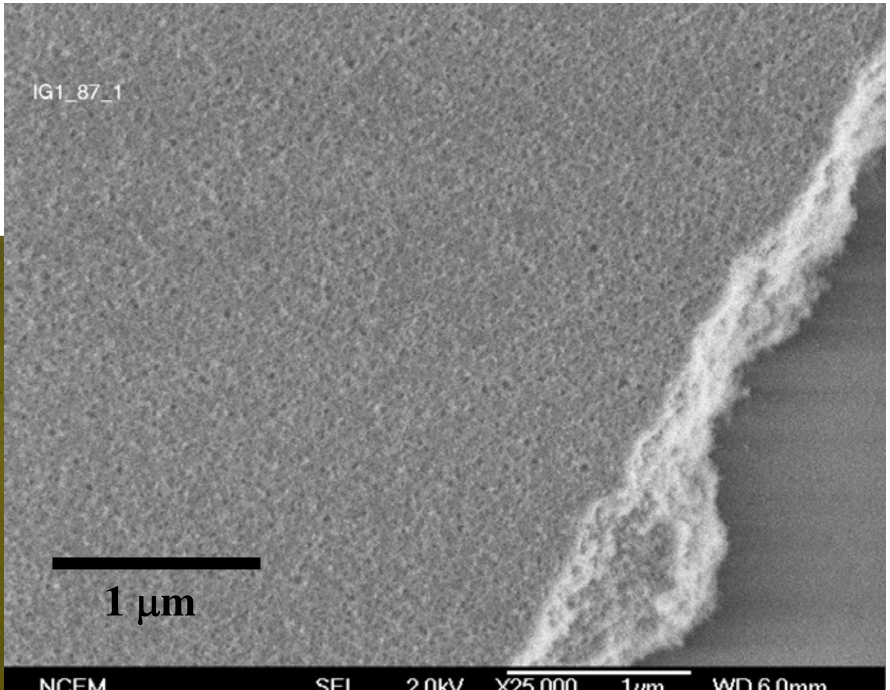
Dry

Deposition

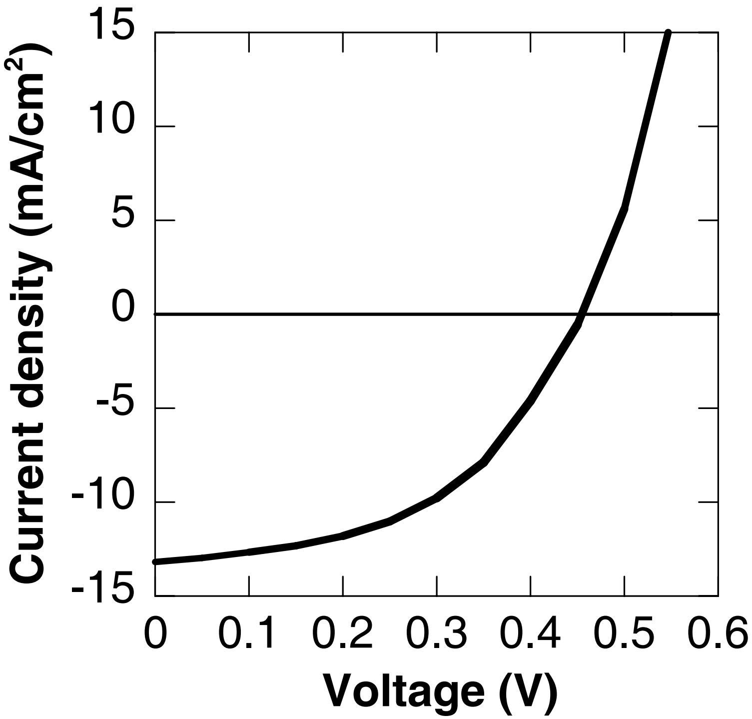
Spin

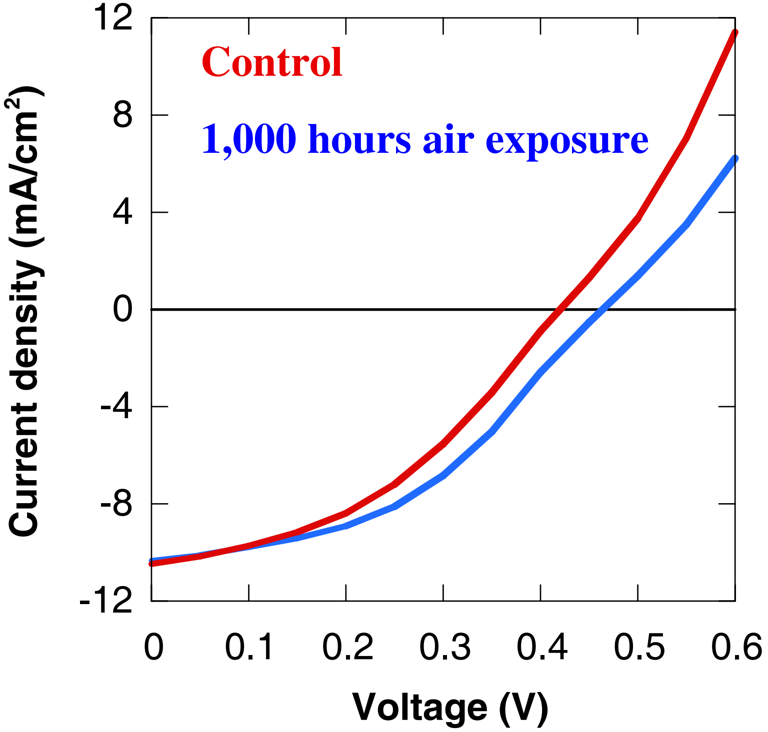
Dry

Add Electrical Contacts



Dual nanocrystal cell performance





Science 310 462 (2005).

V_{oc} = 0.45 V

I_{sc} = 13.2 mA/cm^2

FF = 0.49

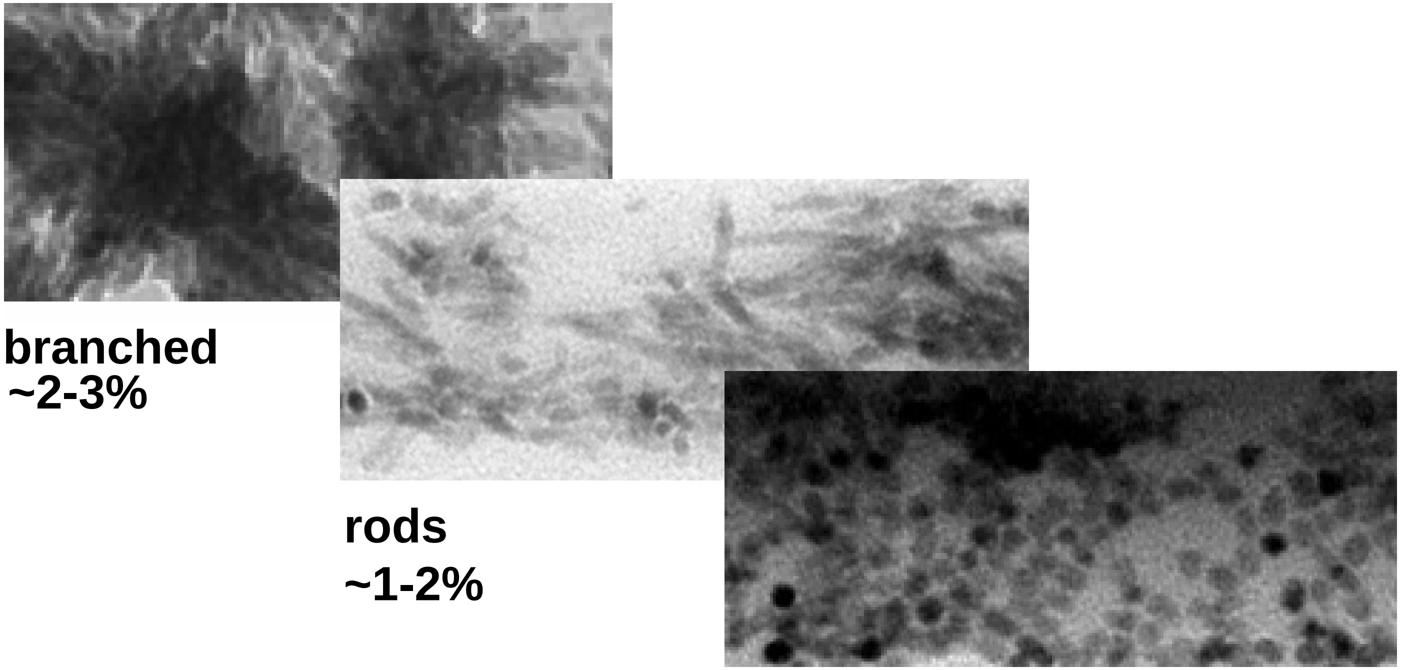
PCE = 2.9%

Nanocrystals have been sintered at 400C w/ $CdCl_2$
These results are limited by the selectivity of the contacts

Licensed by:

Solexant

Percolation pathway conclusion

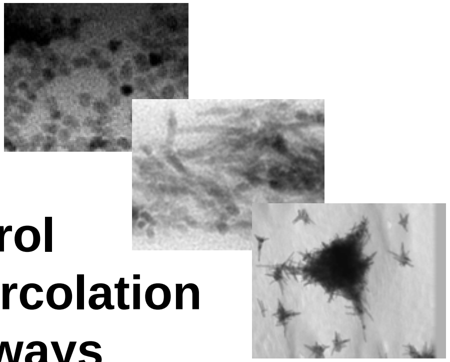


branched
~2-3%

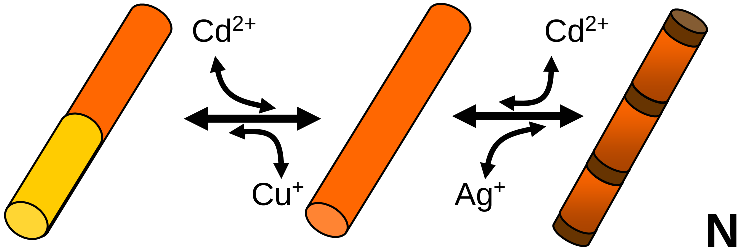
rods
~1-2%

dots
~0.1%

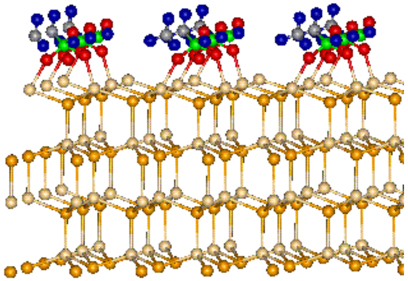
Can we *control* the pathway for charge transport while still using simple processing?



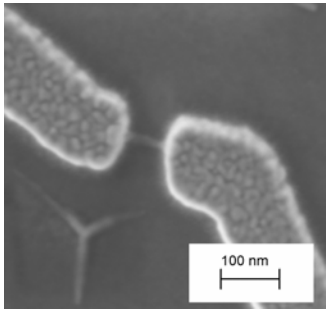
Control of percolation pathways



New nanoscale heterostructures for solar cells

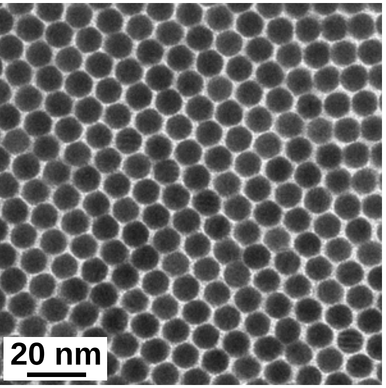


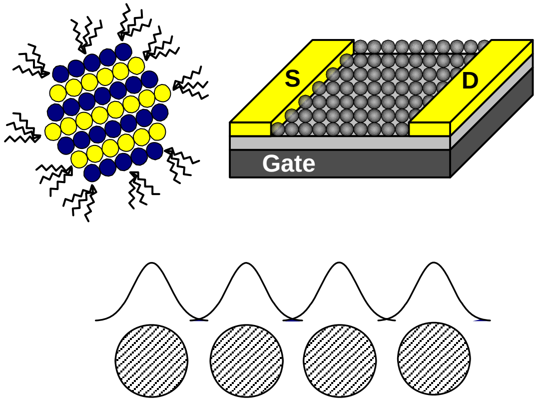
Organic passivation and assembly

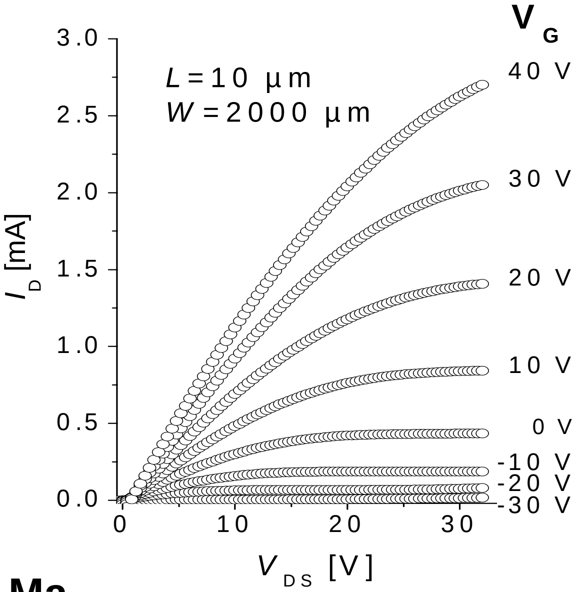


Model studies of single nanocrystals

New approaches to balance confinement and transport







Mobility:

e$^-$ 2.5 cm^{2}V^{-1}s^{-1}

h$^+$ 0.3 cm^{2}V^{-1}s^{-1}

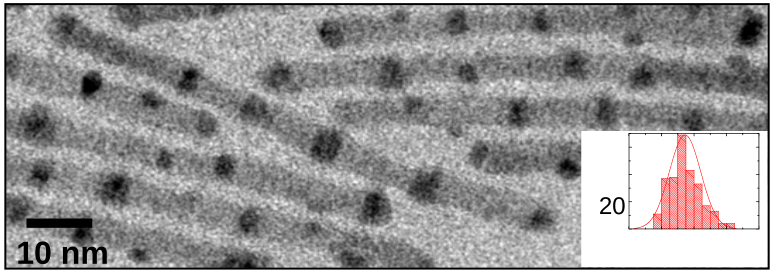
D. Talapin,
Science
310 86 (2005)

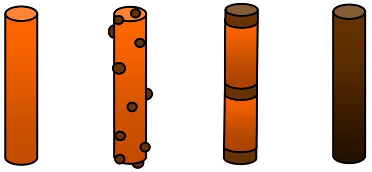
q dot superlattice
treated with hydrazine

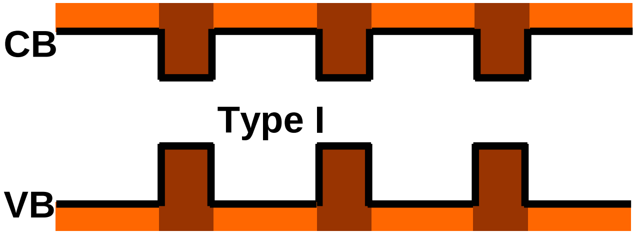
Wanli Ma

---

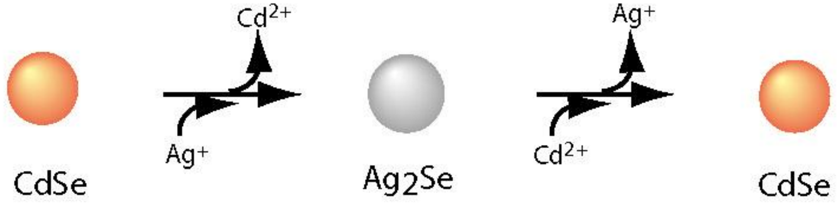
spontaneous formation
of q dots in a rod

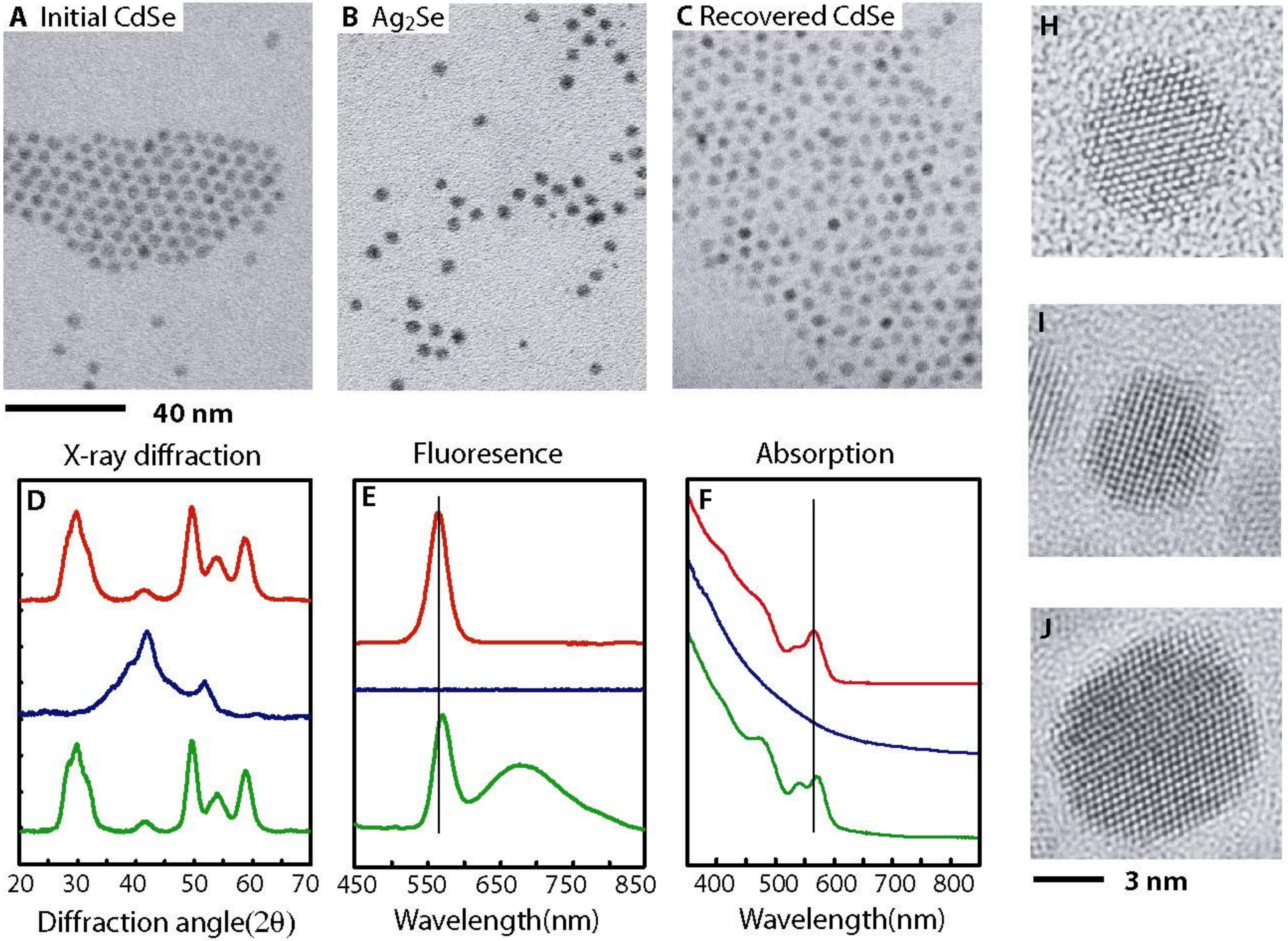






Cation Exchange is fully reversible





Son, Hughes, Yin, and Alivisatos Science 306 1009 (2004)

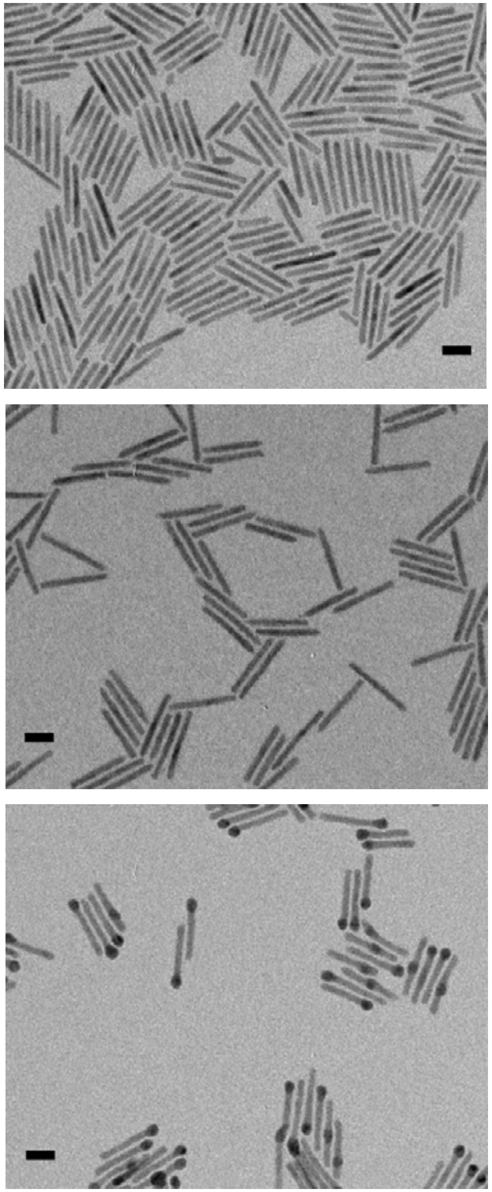
Cation Exchange with shape preservation

CdS

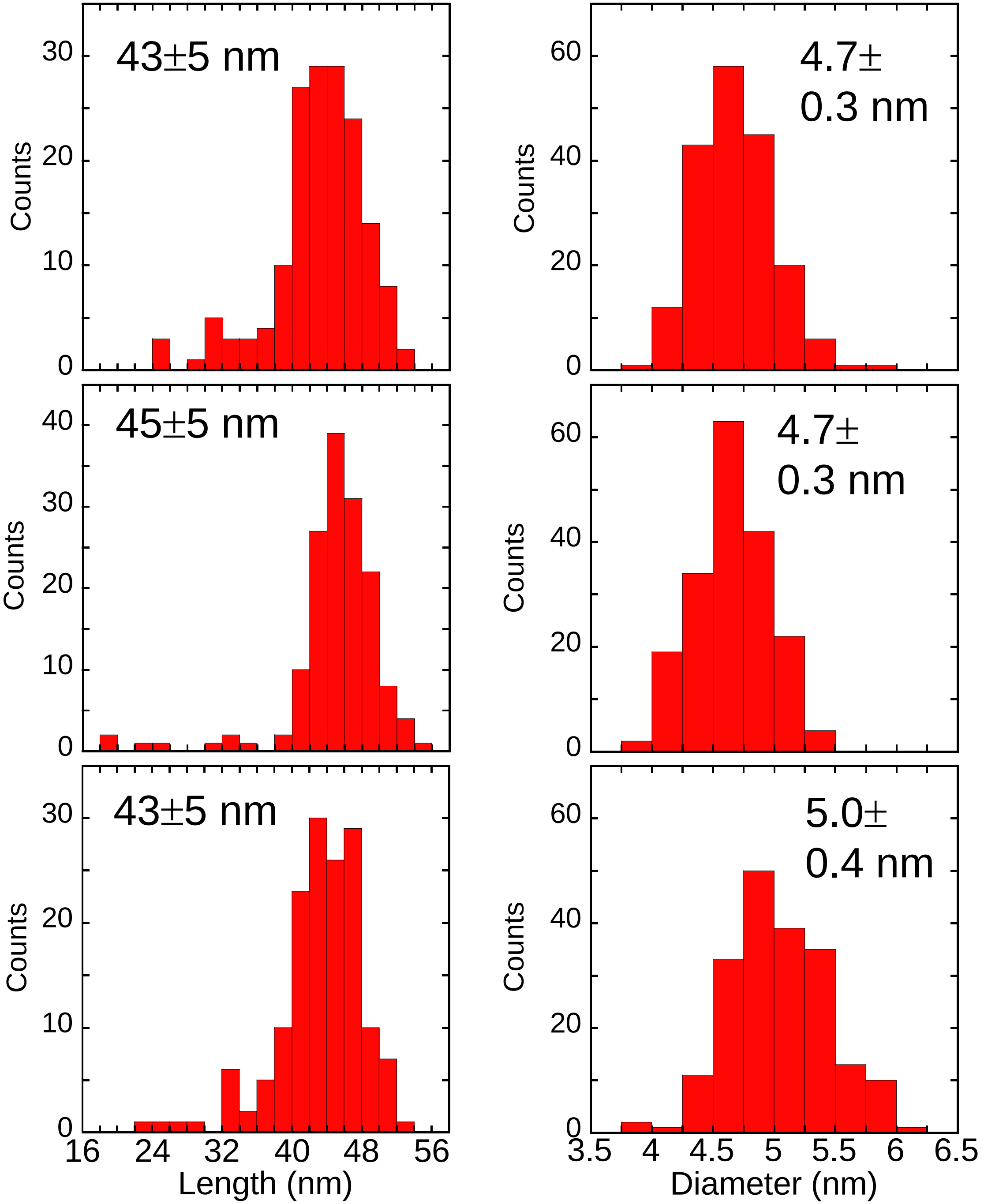
Cu_2S

Ag_2S

scale = 20 nm

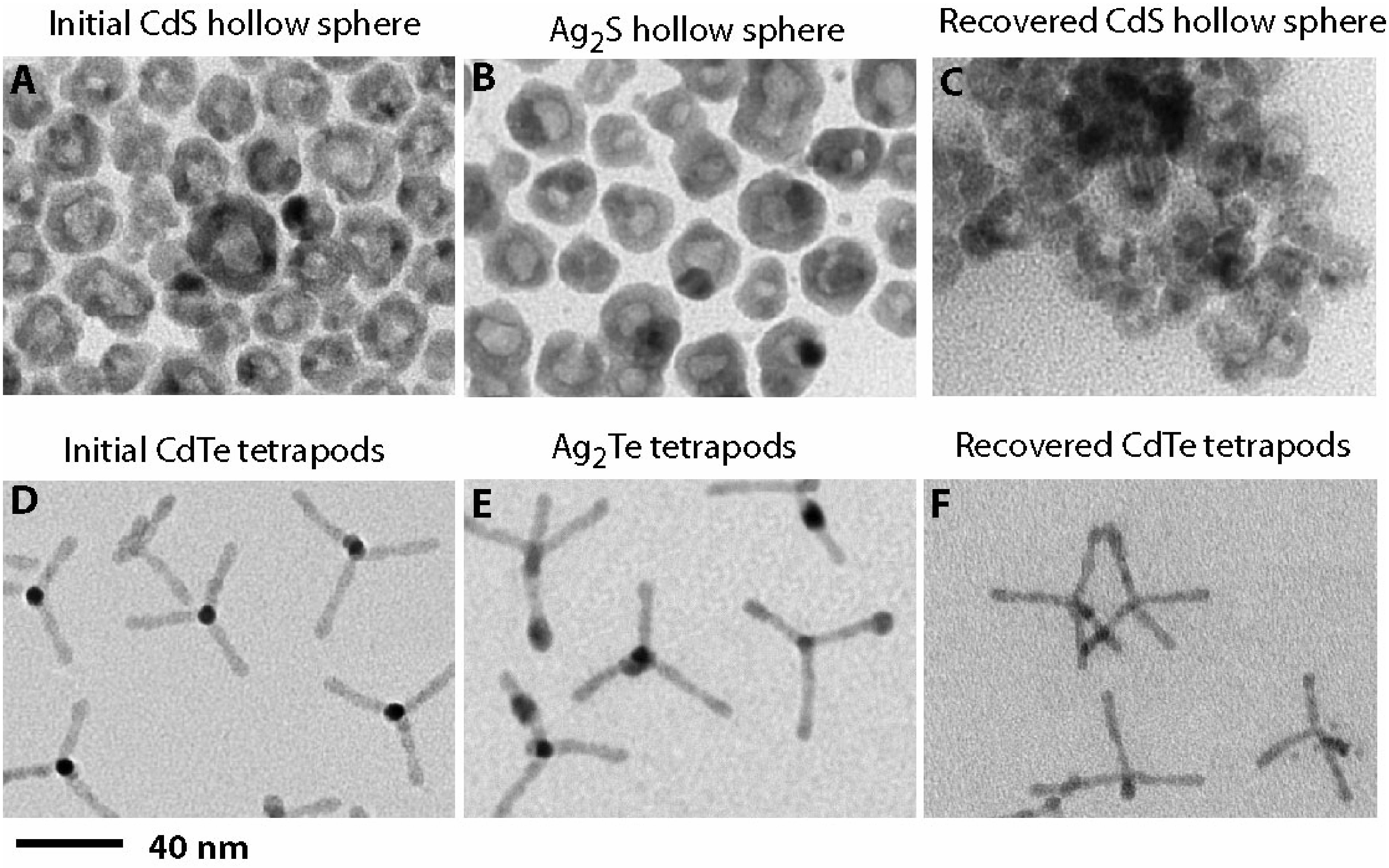


nanorod diameter distribution



Bryce Sadtler

Cation exchange cycles in complex nanostructures



Initial CdS hollow sphere

Ag_2S hollow sphere

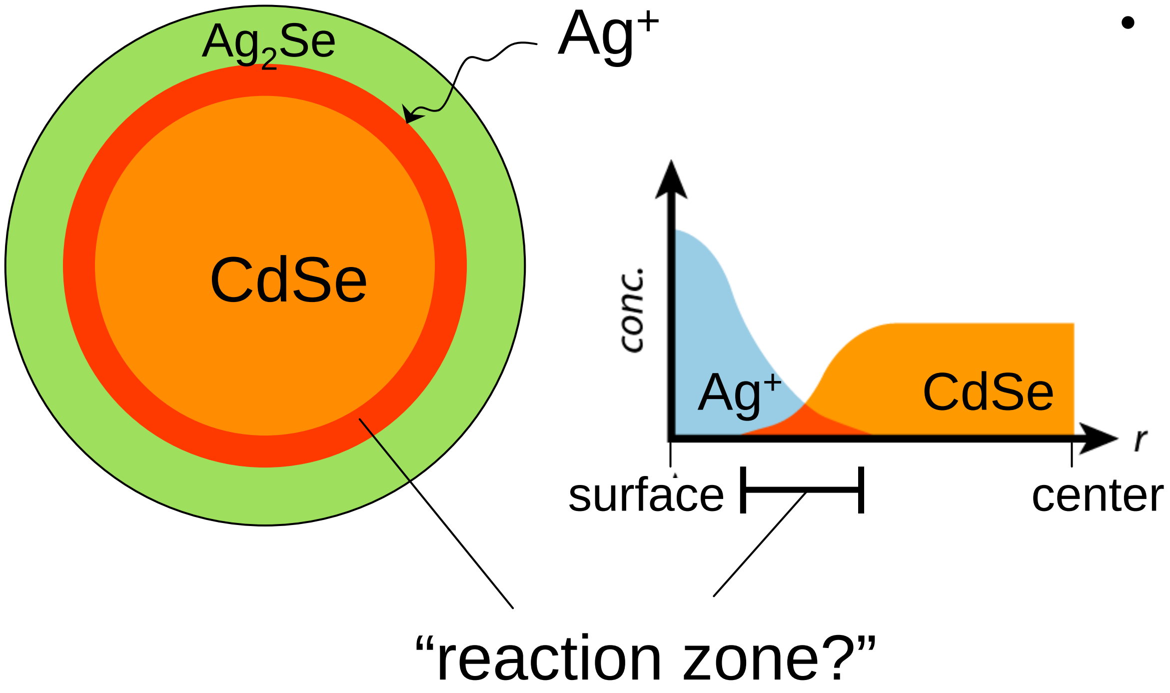
Recovered CdS hollow sphere

Initial CdTe tetrapods

Ag_2Te tetrapods

Recovered CdTe tetrapods

Time scale of cation exchange



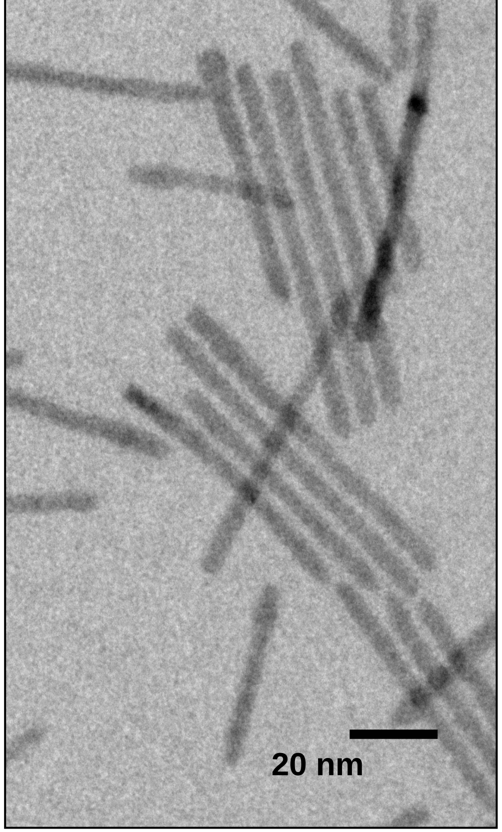
- A spherical diffusion model can be used to extract the *effective* diffusion constant of Ag^+ in $Ag_2Se/CdSe$.
  - $D_{eff} = 5 \times 10^{14}\ cm^2/s$

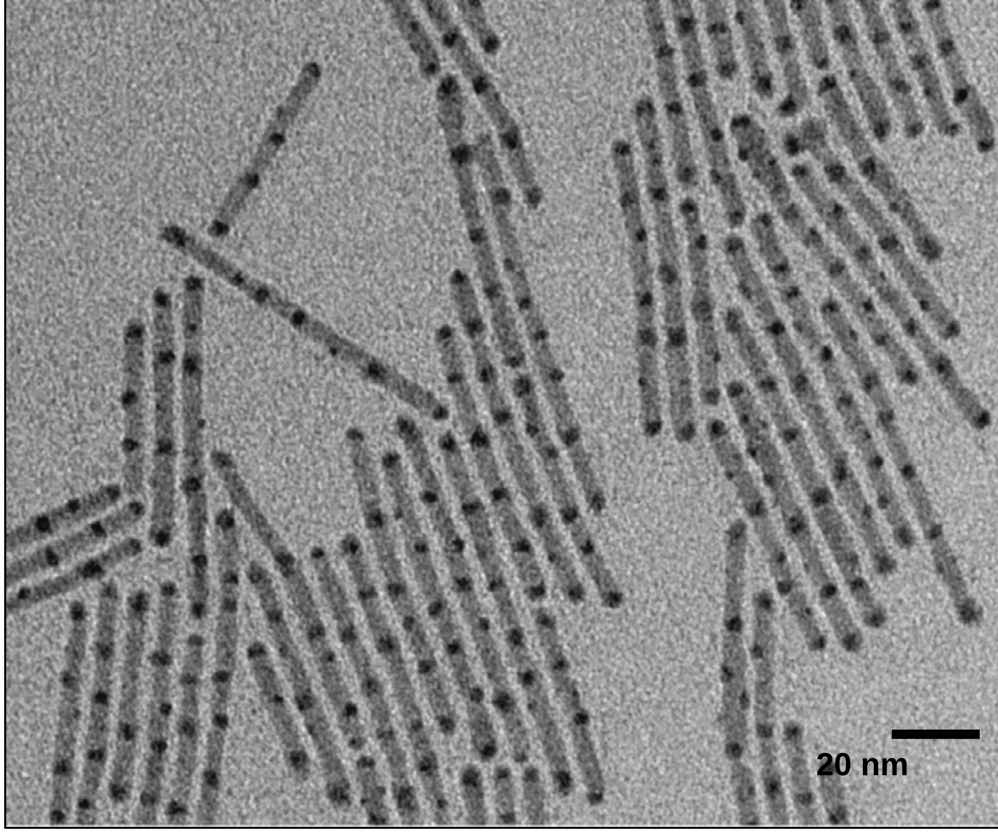
  agrees with literature.
  - $D = 3 \times 10^{14}\ cm^2/s$
  - $AgNO_3$ cation exchange on bulk CdSe (001) surface.
  - Leung *et al*, *J. Phys. Chem. 1991*, 95, 5918)

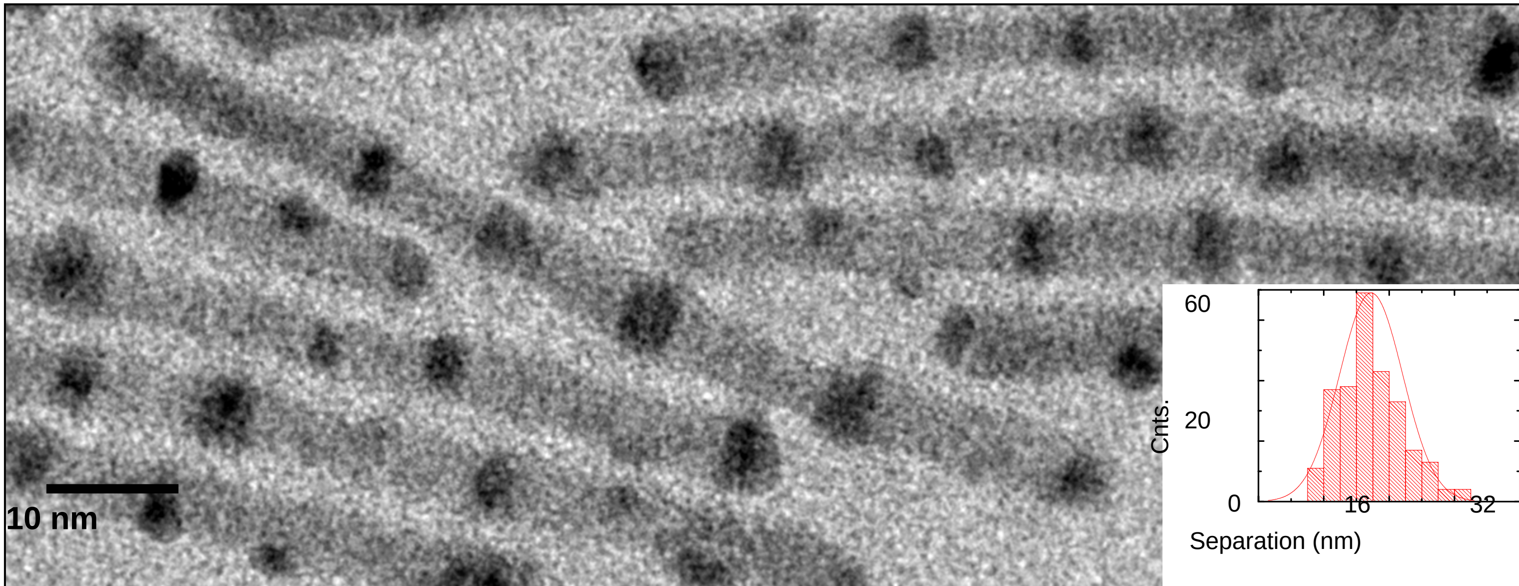
- $1/e = 66$ ms ~ 100 ms
- 4×10^7 collisions / second, between Ag^+, nanocrystals
- ~10^4 collisions result in 1 Ag_2Se molecule.
- Most reactions require 10^7-10^{11}

Partial Exchange?

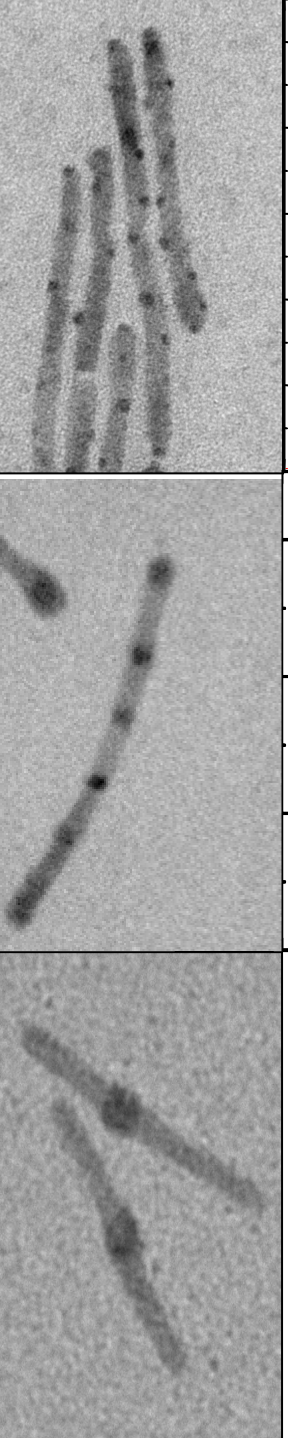
Partial cation exchange in nanorods

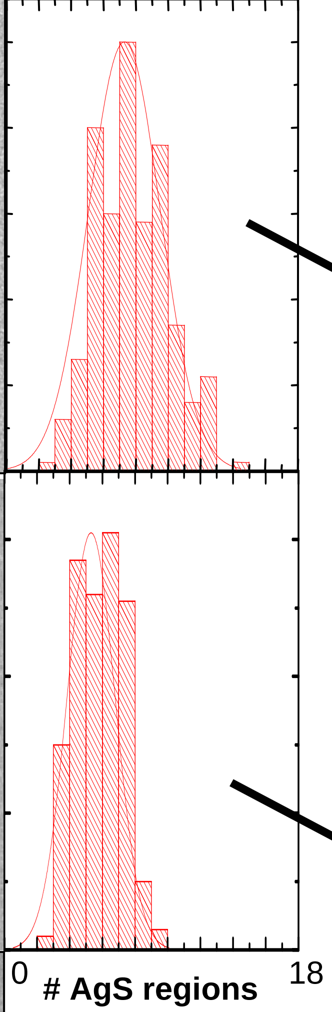


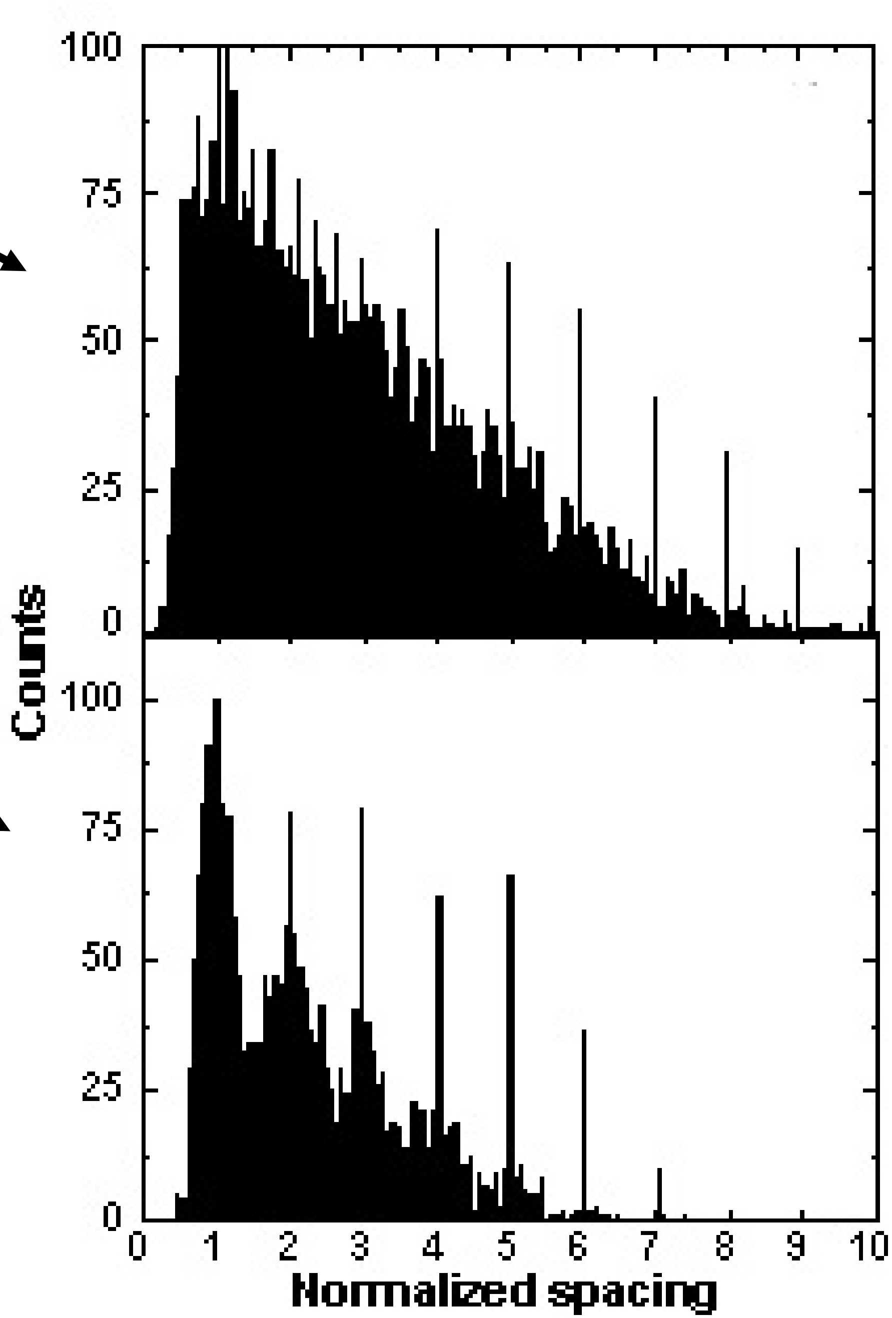




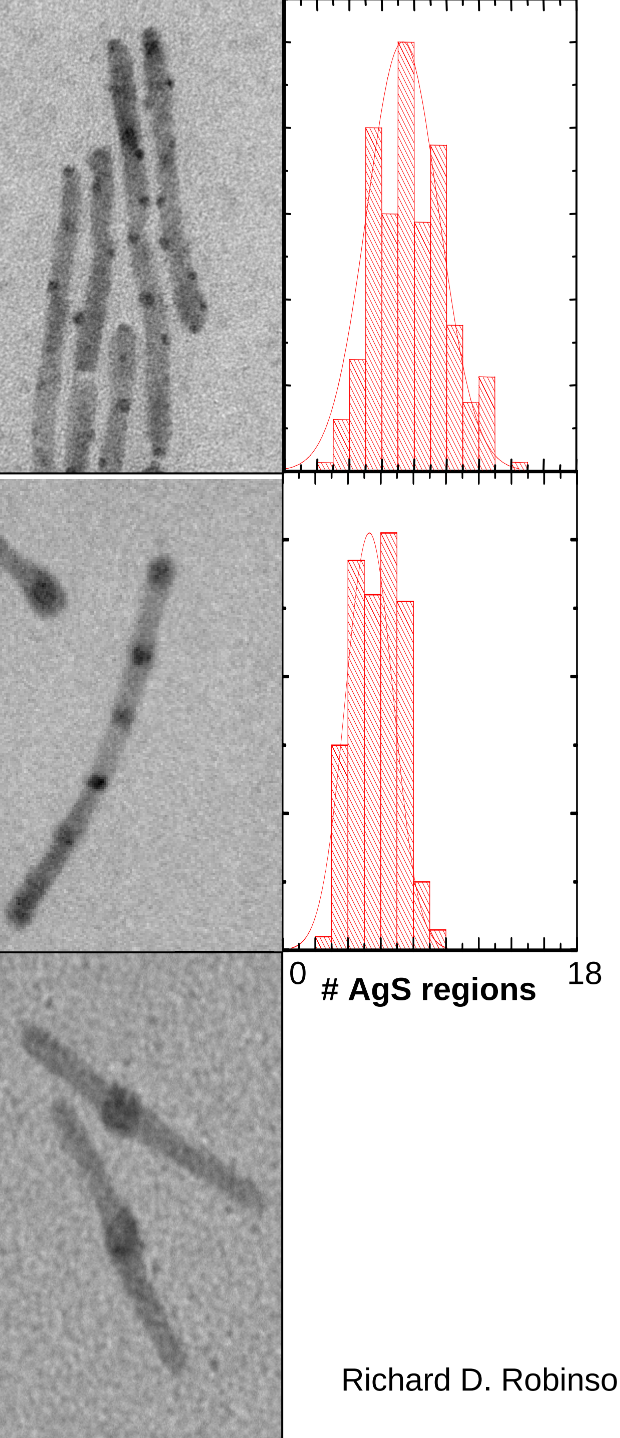
Evolution of the spaced dots in a rod

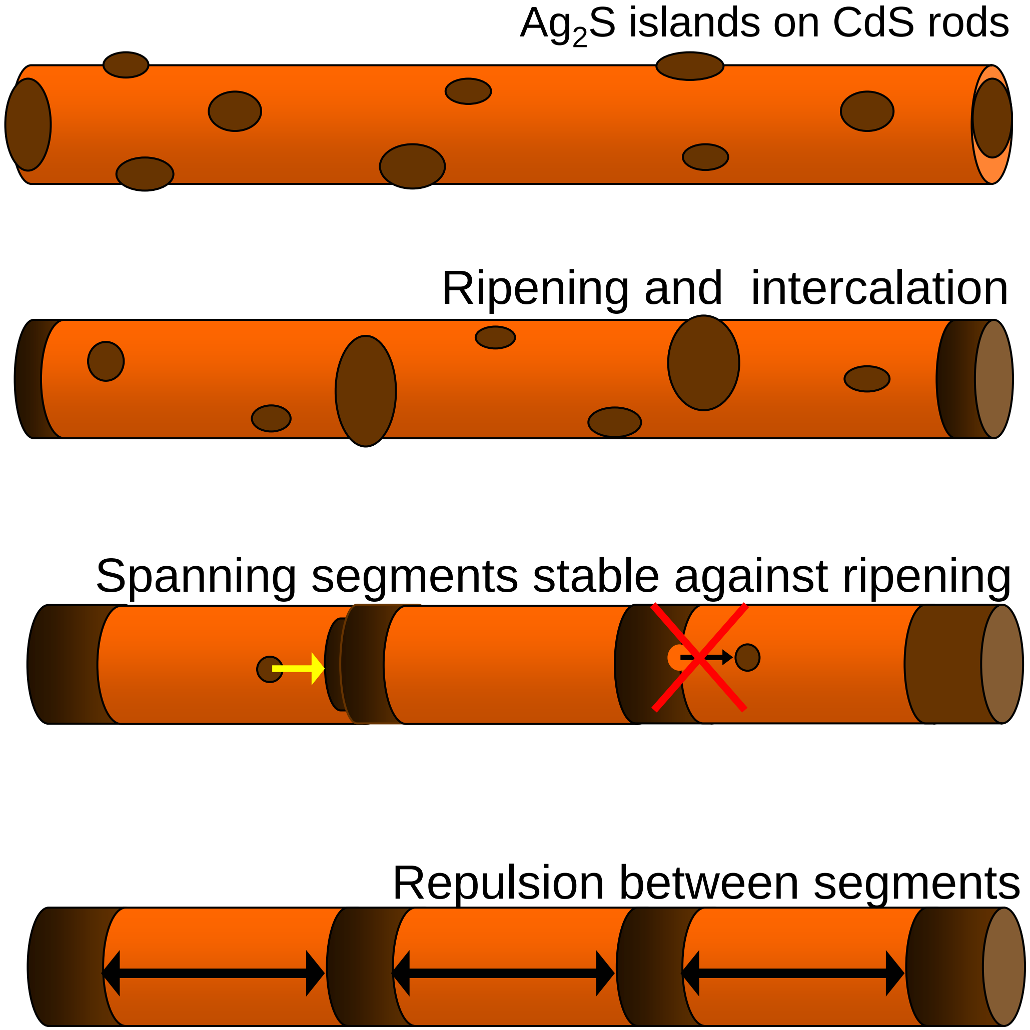






Evolution of the spaced dots in a rod





Ag$_2$S islands on CdS rods

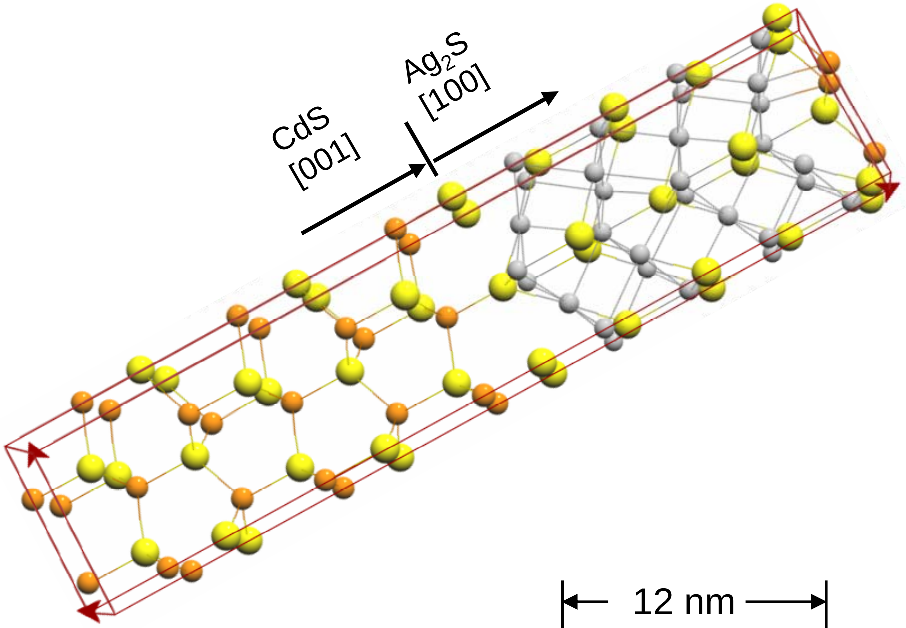
Ripening and intercalation

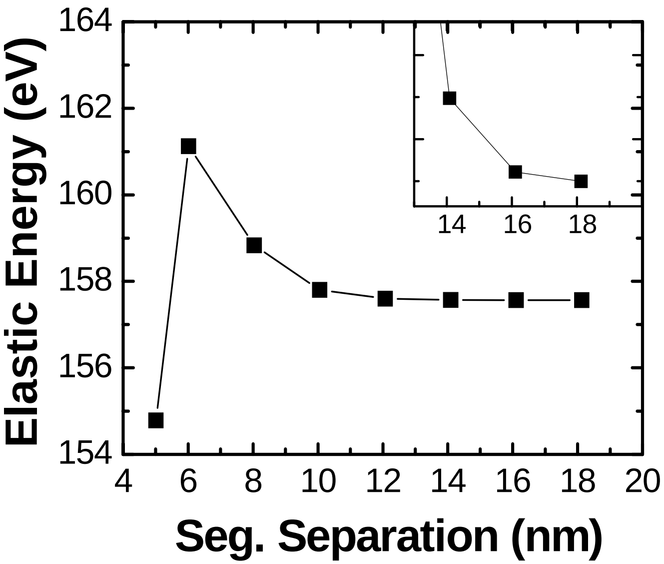
Spanning segments stable against ripening

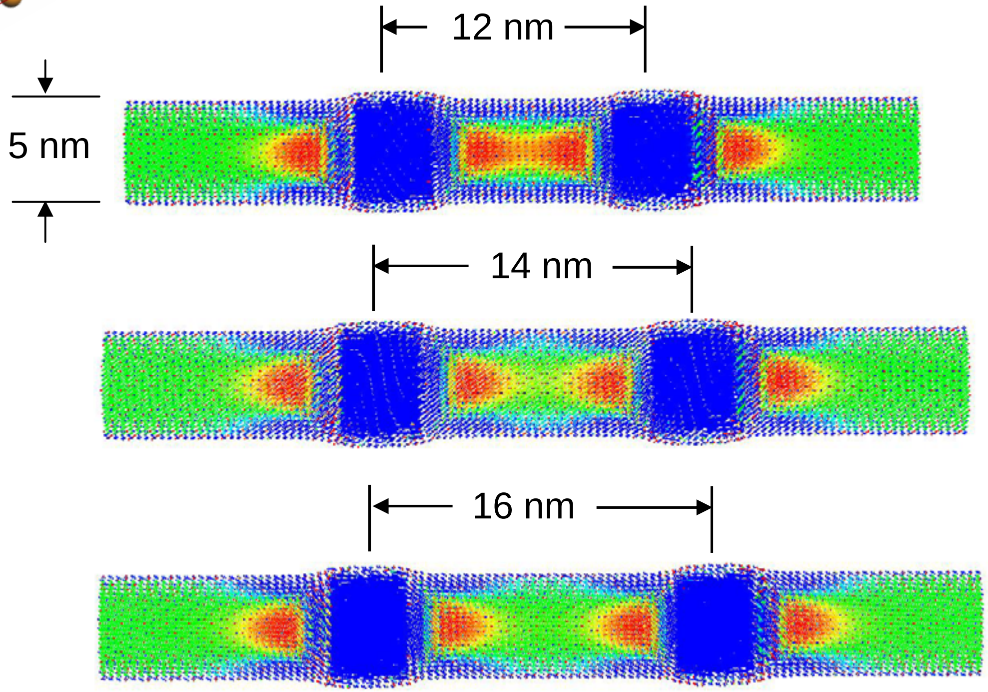
Repulsion between segments

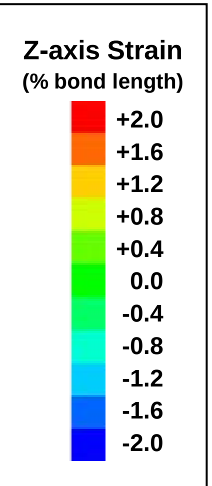
“Spontaneous Superlattice Formation in Nanorods through Partial Cation Exchange,”
Richard D. Robinson, Bryce Sadtler, Denis O. Demchenko, Can K. Erdonmez, Lin-Wang Wang, A. P. Alivisatos
Science **317,** 355 (2007)

Strain model explains spacings





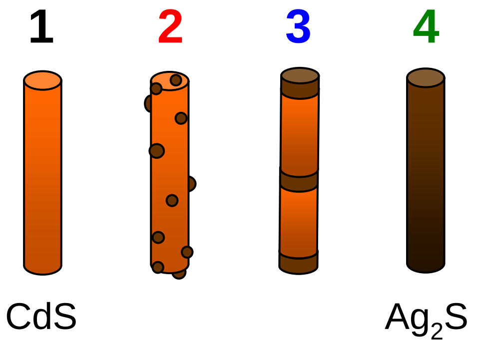


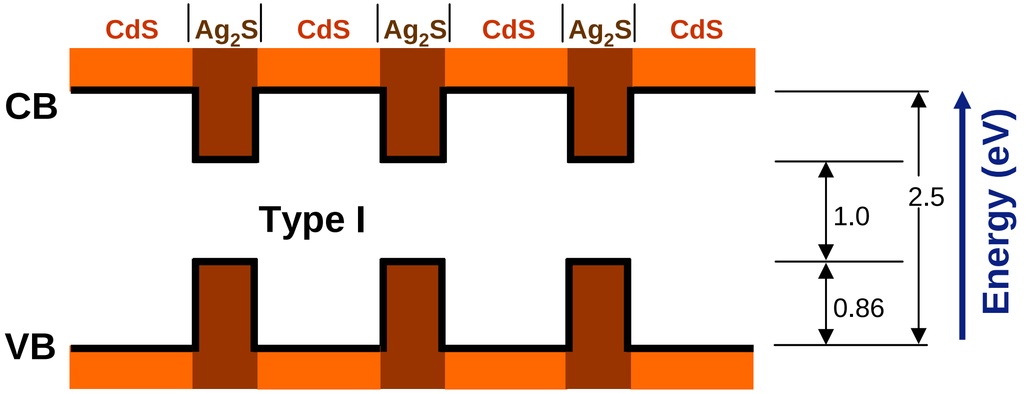


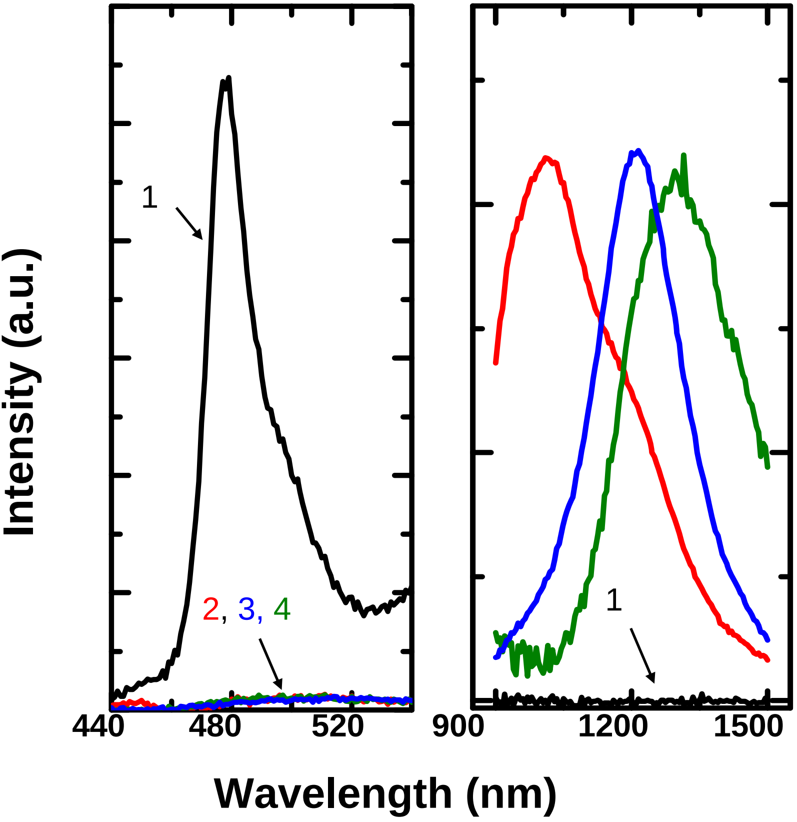
Can strain could be used to create a wider range of patterns within colloidal particles?

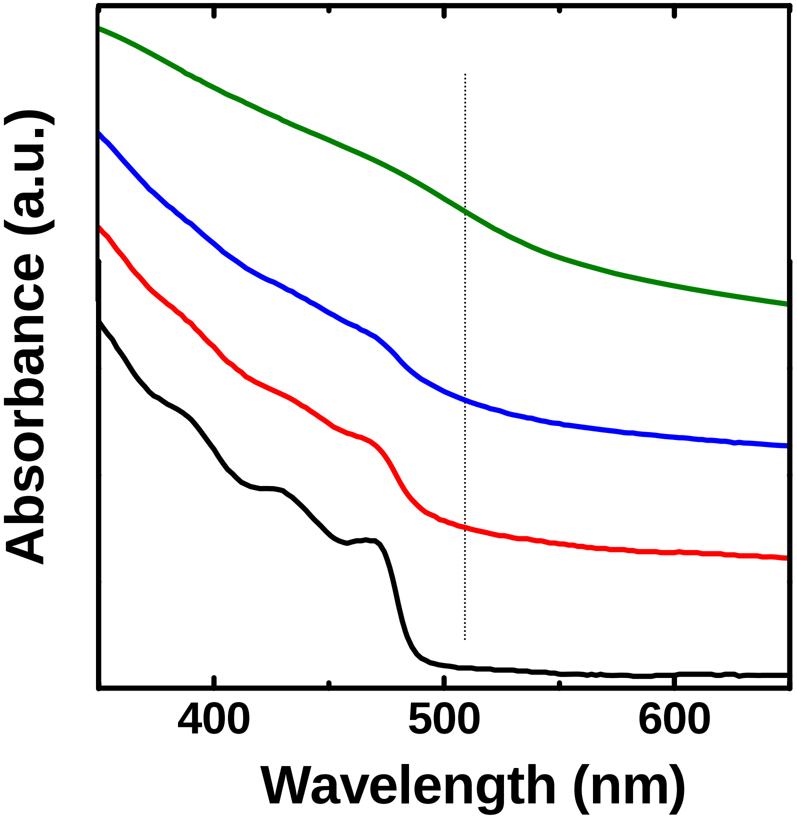
Dennis Demcenko
Lin-Wang Wang

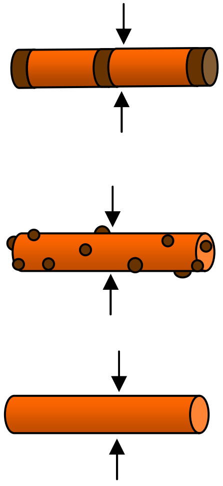
Optical properties and band offsets of partially exchanged rods





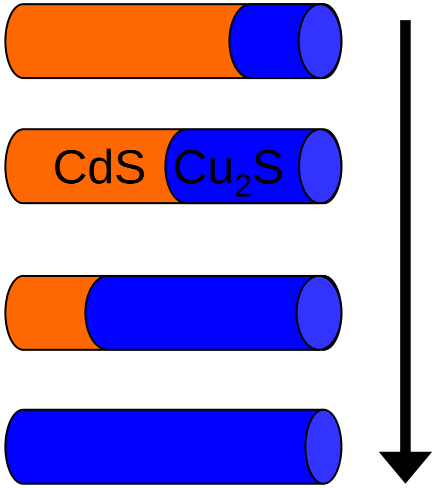


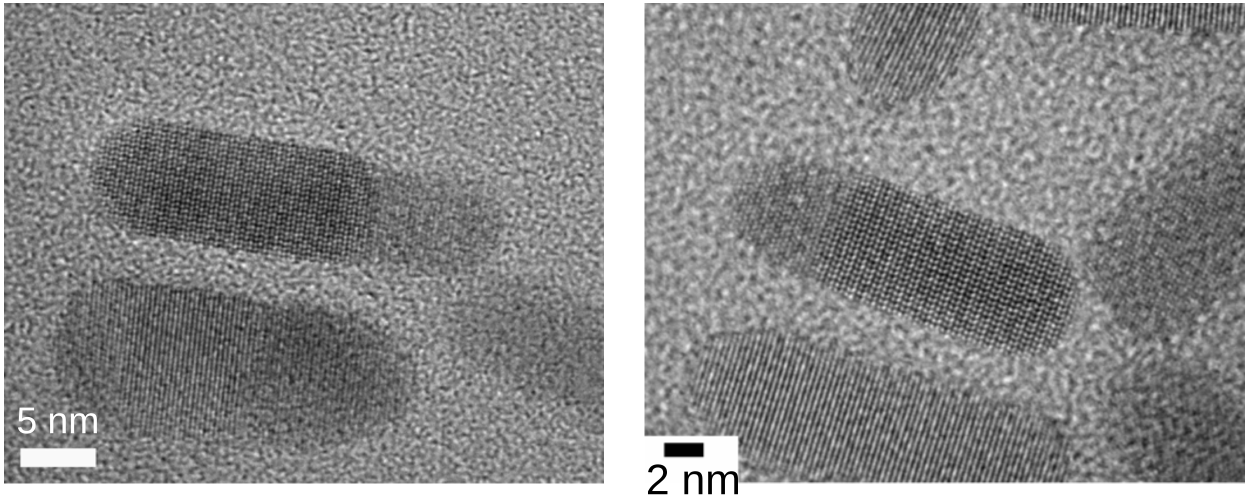




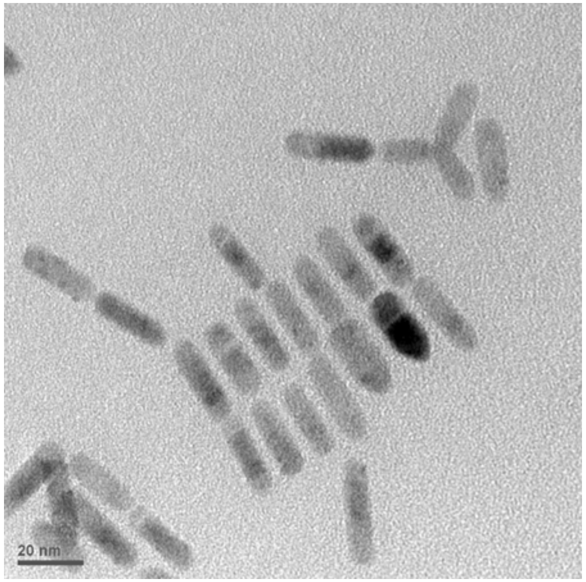
no diameter change

Partial exchange of copper – segmented rods

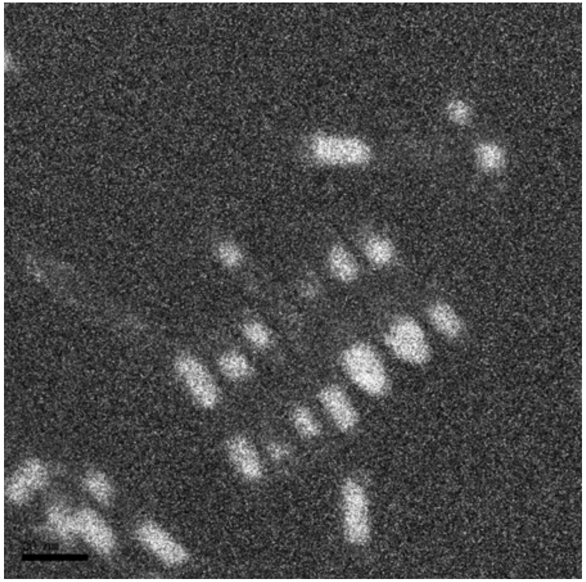




Brightfield image

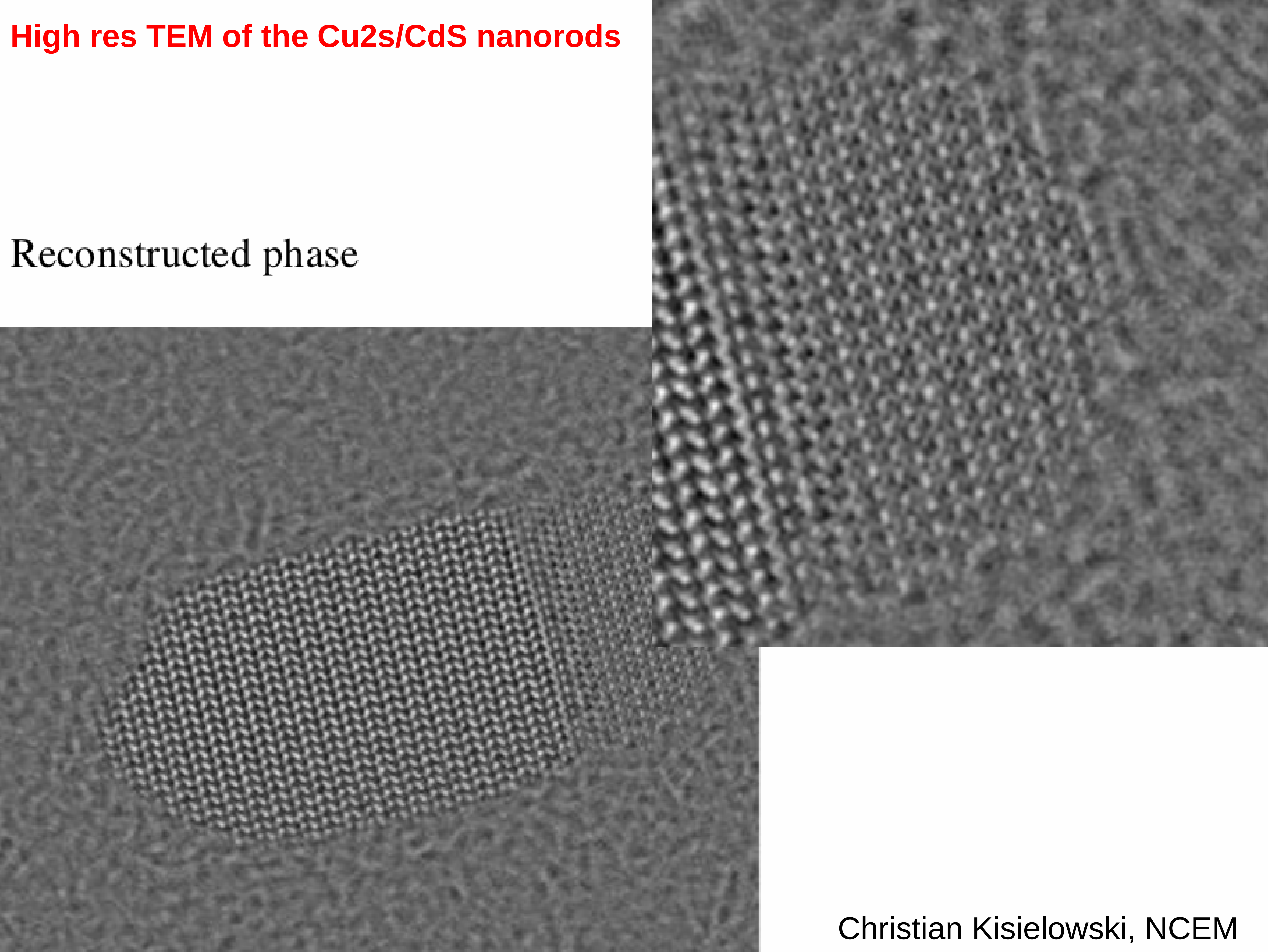


Cd energy-filtered image



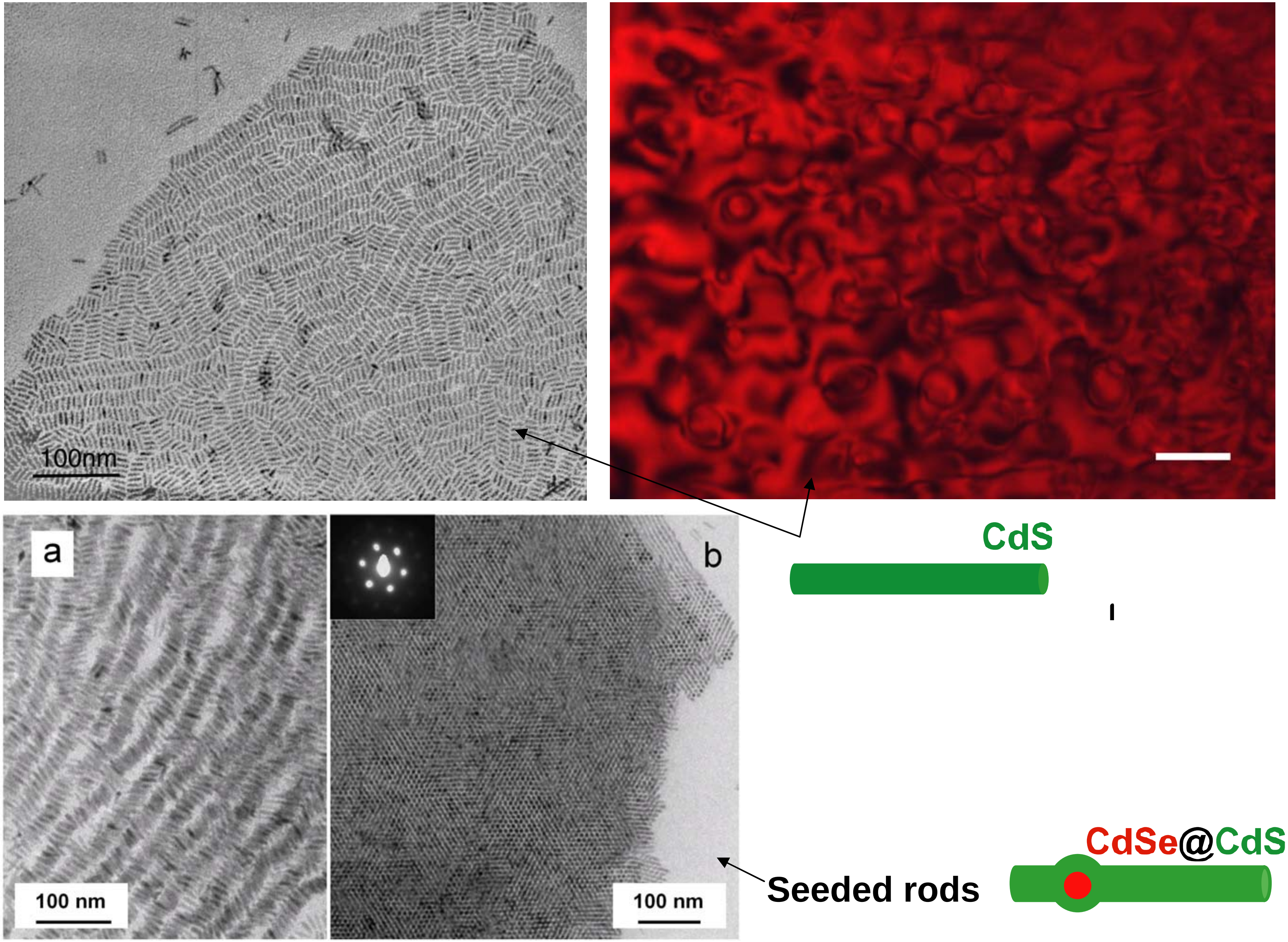
High res TEM of the Cu2s/CdS nanorods

Reconstructed phase



Christian Kisielowski, NCEM

Nanorod liquid crystals



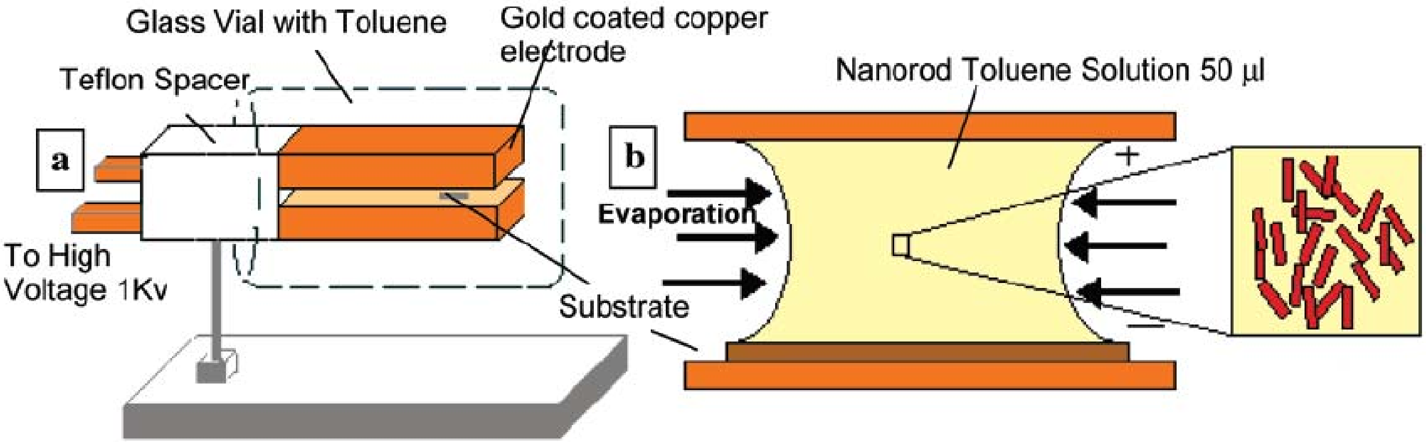
CdS

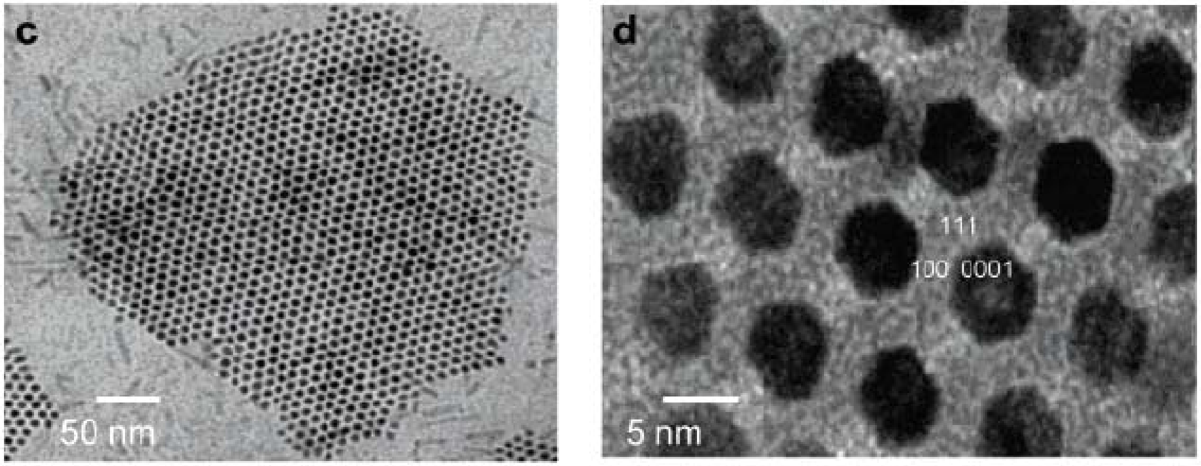
Seeded rods

CdSe@CdS

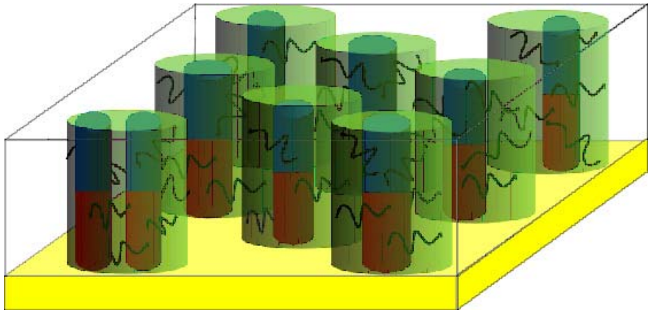
Liang-shi Li, Joost Walda, Liberato Manna, and A. Paul Alivisatos, Nano Letters 2002

Liquid crystal electric field asssembly of (striped and seeded) surfactant coated rods



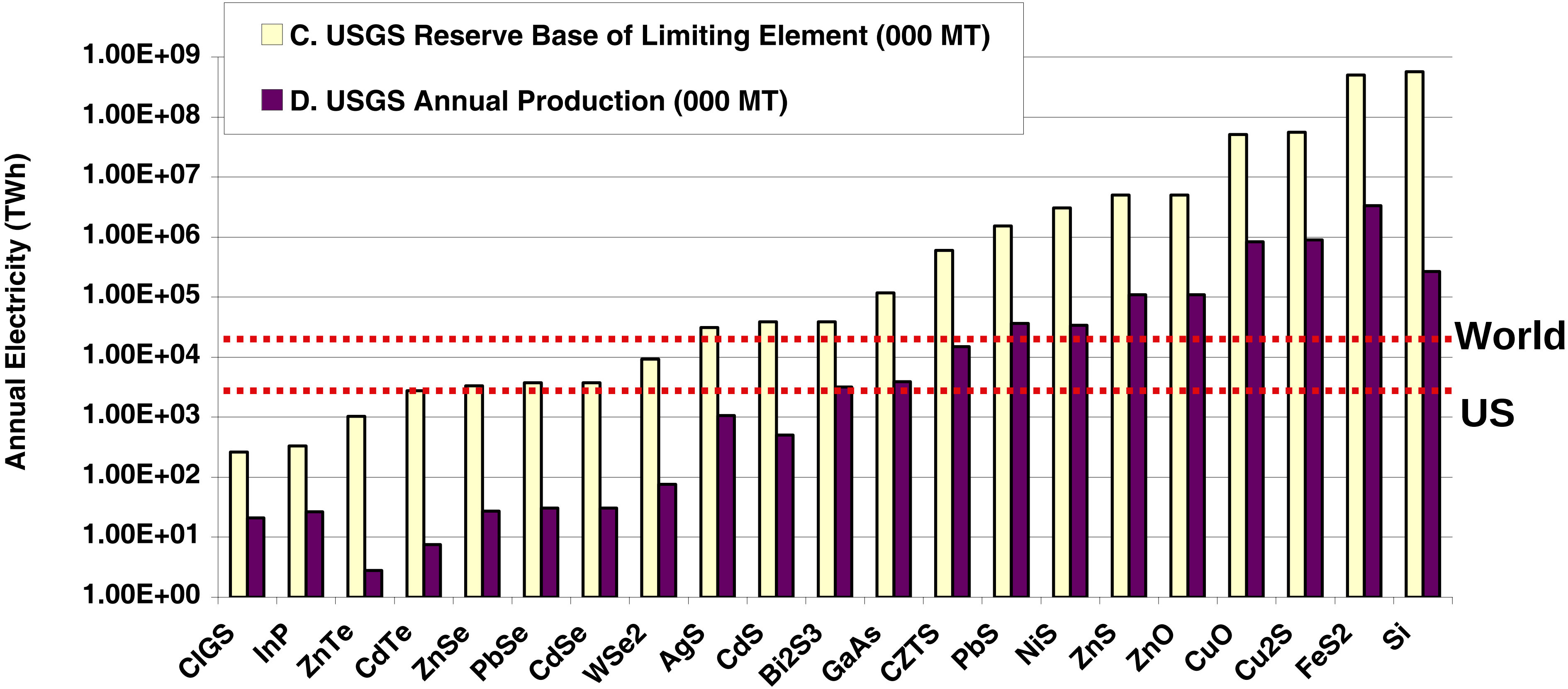


Could this be used to align the Cu2S/CdS segmented nanorods?



Nano Letters 6 (7): 1479-1482 Jul 12 2006

Environment-friendly, abundant nanocrystal systems for PVs



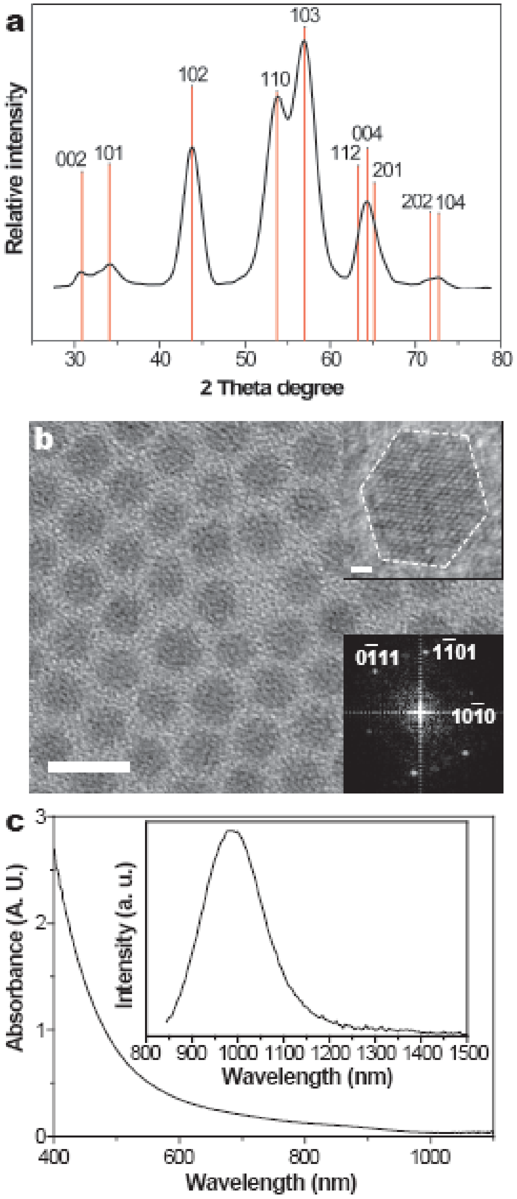
Assume 10% efficiency cells are made with all the available material

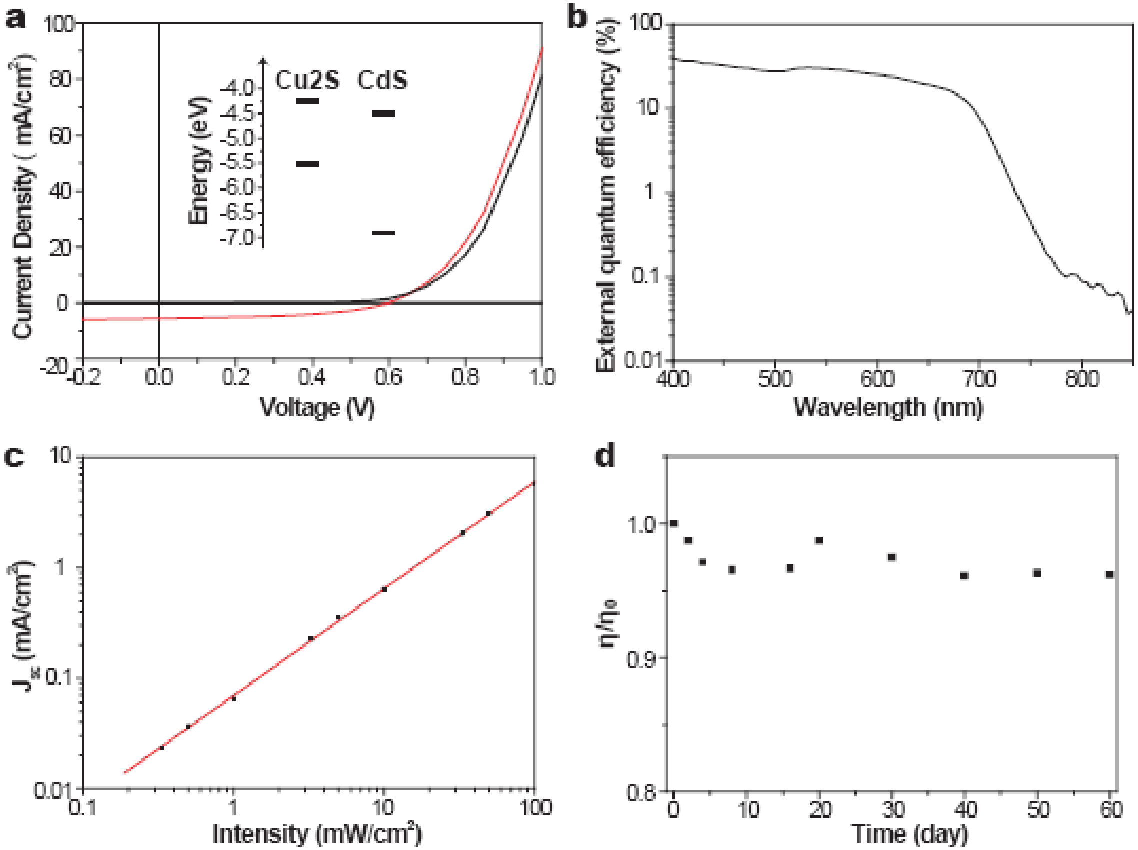
Materials previously rejected for bulk solar cells due to difficulty of doping both n and p or due to poor mobility may work well with nanocrystals

Cyrus Wadia

Cu_2S/CdS dual nanocrystal solution cast solar cell

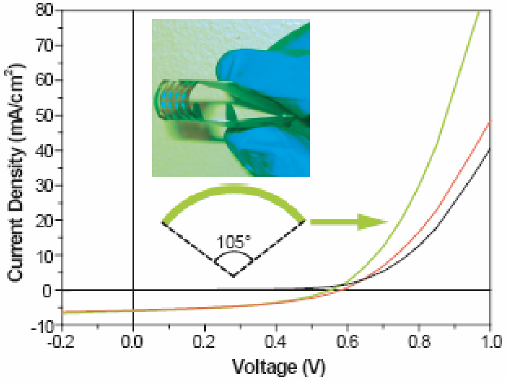
Cu_2S nanocrystals





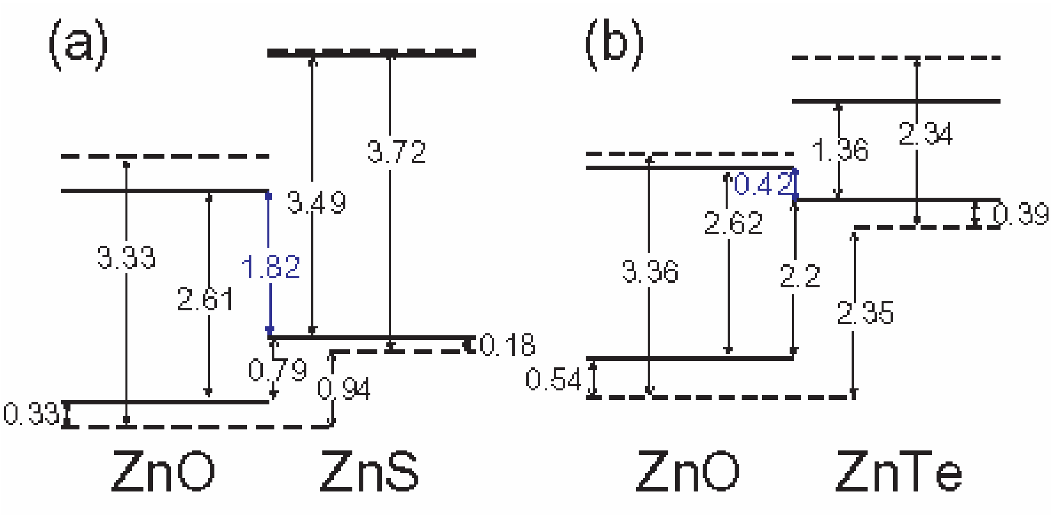
V_{oc} =0.6V
I_{sc}=5.6mA/cm^2
FF=0.475
%eff.= 1.6%

No sintering,
max T 150C

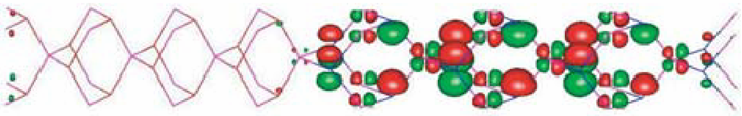


Cyrus Wadia, Yue Wu

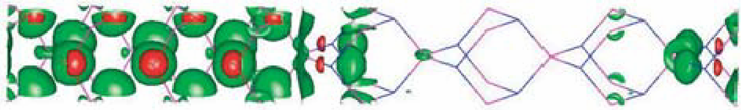
Nanostructuring expands the list of possible stable, abundant, and env. benign materials for PVs



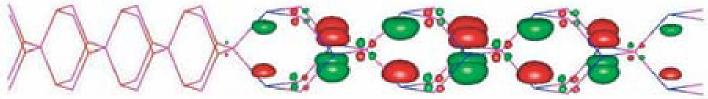
(a) ZnO/ZnS VBM



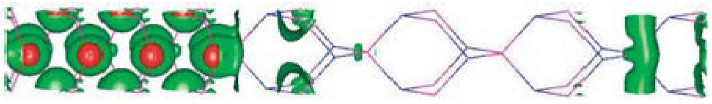
(b) ZnO/ZnS CBM



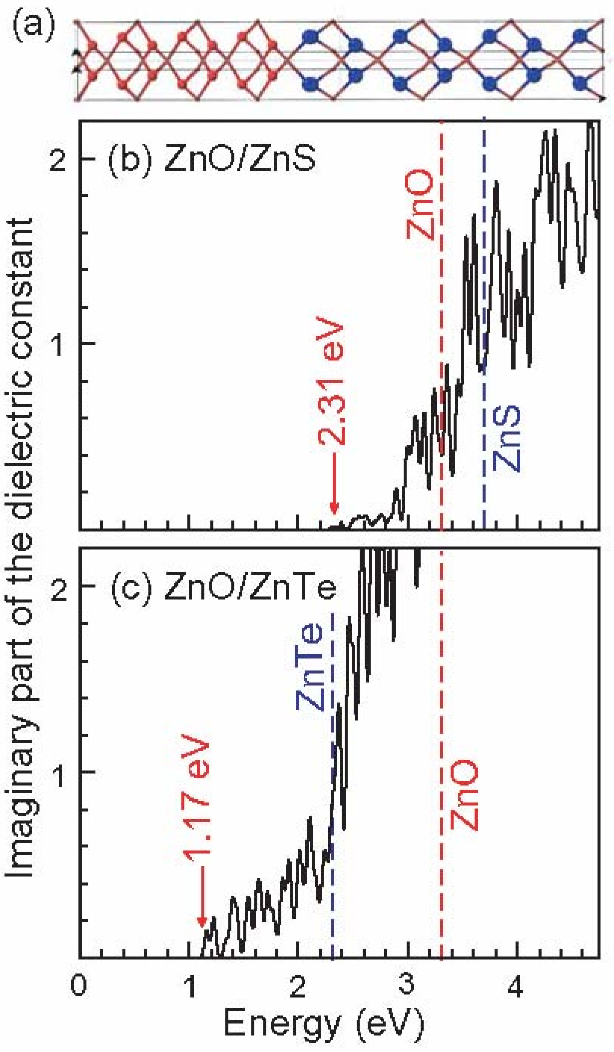
(c) ZnO/ZnTe VBM



(d) ZnO/ZnTe CBM

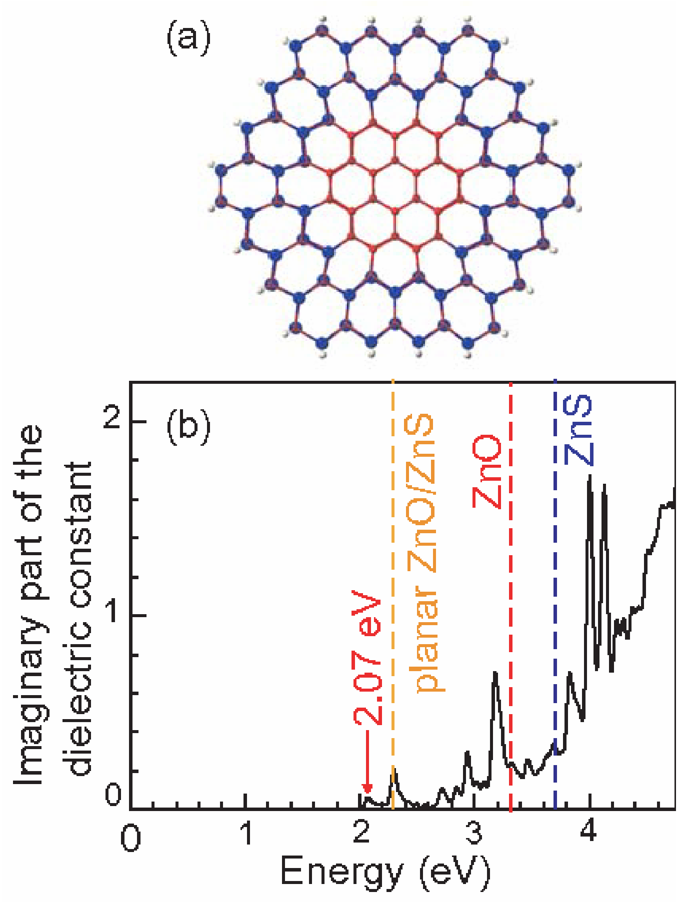


ZnO/ZnS, ZnO/ZnTe Superlattices

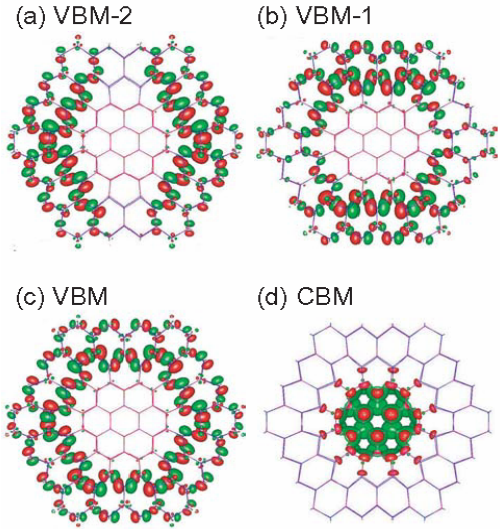


Nanostructuring expands the list of possible stable, abundant, and env. benign materials for PVs

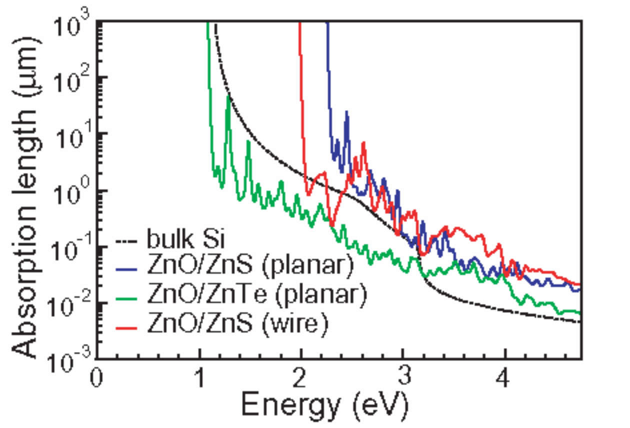
ZnO/ZnS core/shell wire



Band gap lower than 1d superlattices.

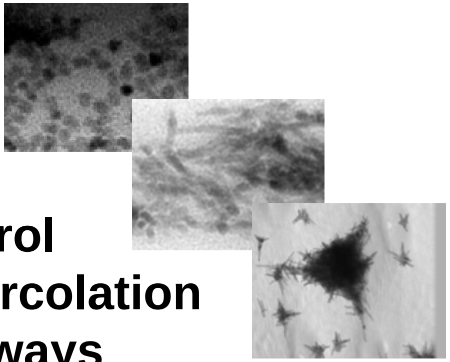


VBM-CBM transiton is forbidden due to state symmetry. This can prevent electron-hole recombination.

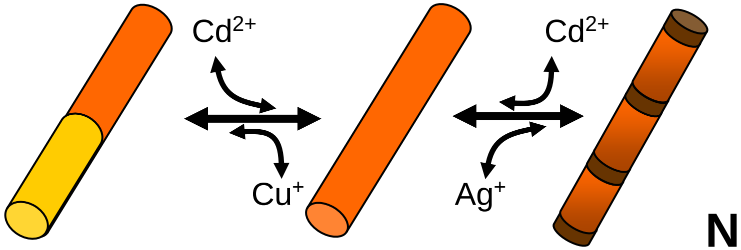


The absorption length is similar to bulk Si,

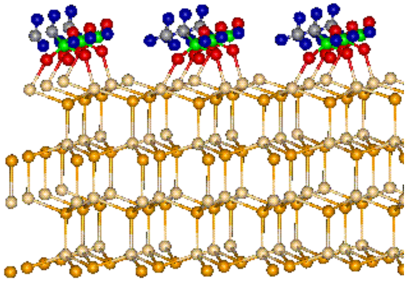
J. Schrier, D. O. Demchenko, L.W. Wang, A.P. Alivisatos, Nano Letters. 7, 2377 (2007).



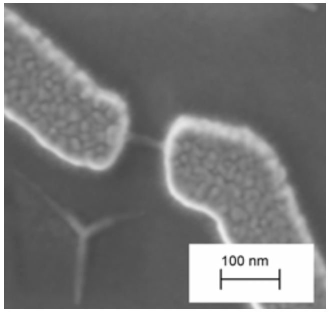
Control of percolation pathways



New nanoscale heterostructures for solar cells

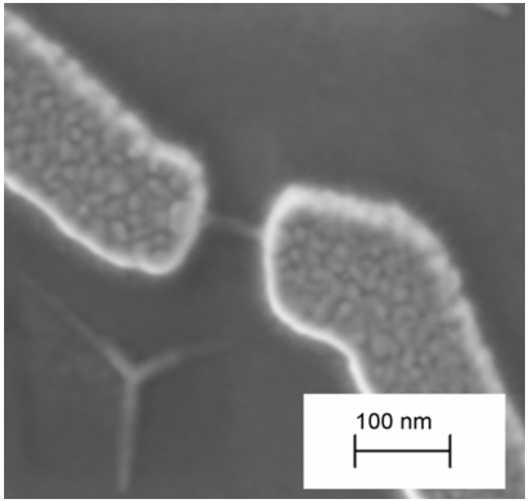


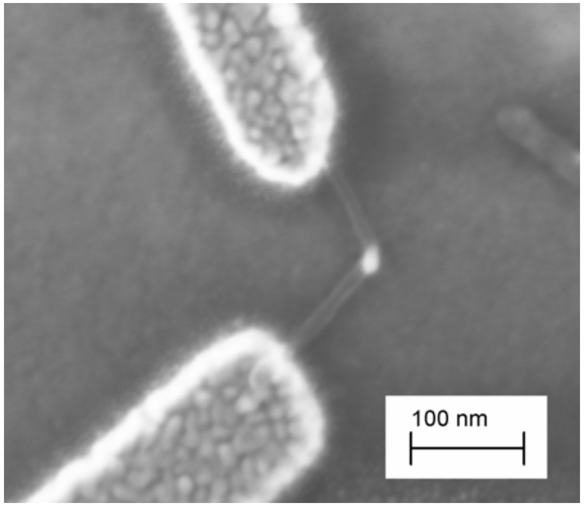
Organic passivation and assembly

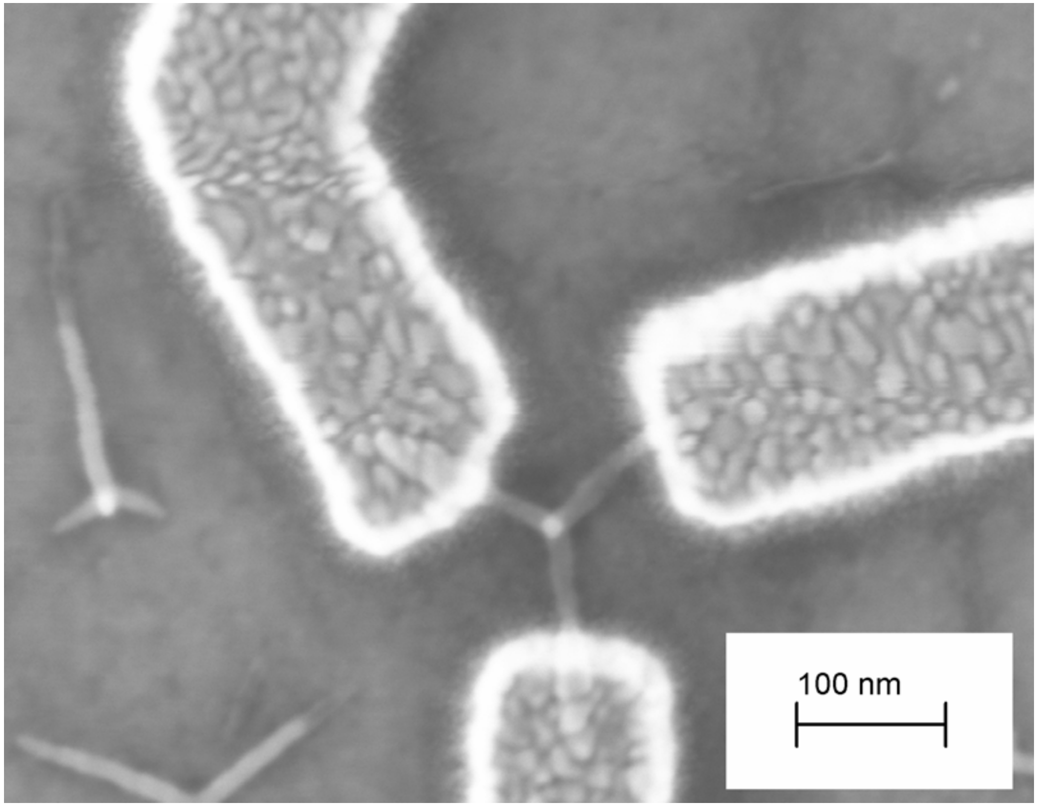


Model studies of single nanocrystals

Single rod/bipod/tetrapod single electron transistors

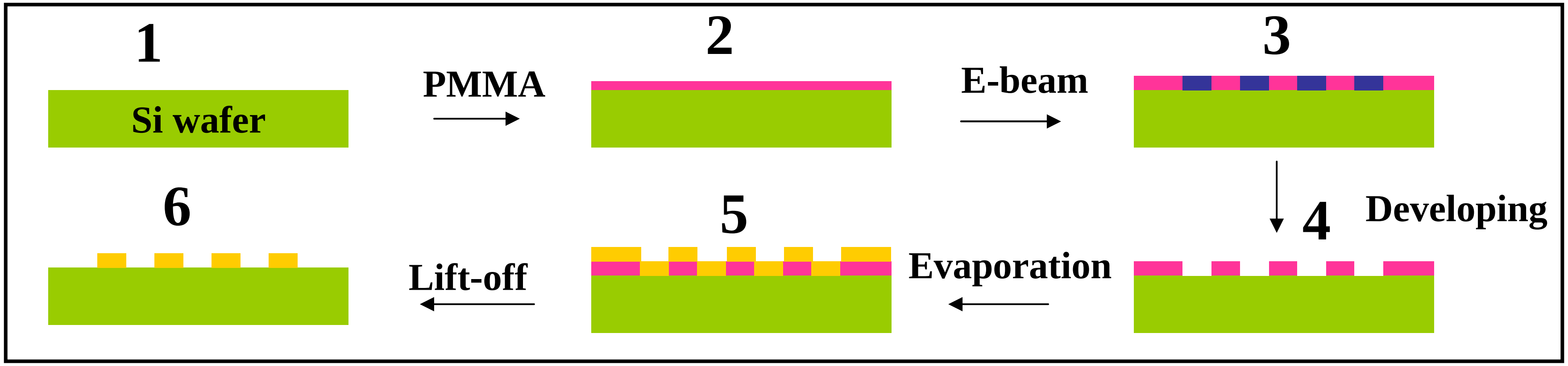






Yi Cui
Paul-Emile Trudeau
Matt Sheldon

E-beam, alignment, etch and contact


1

Si wafer

PMMA

2

E-beam

3

Developing

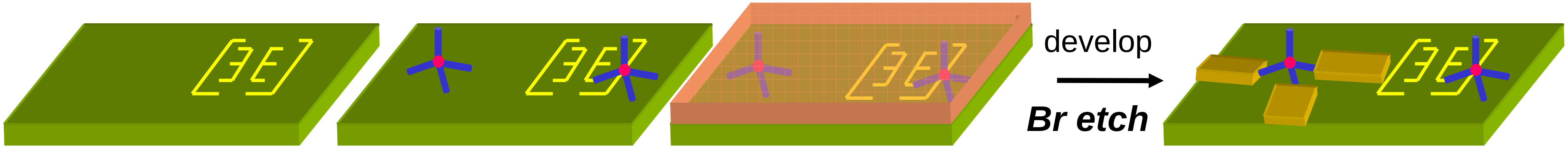
4

Evaporation

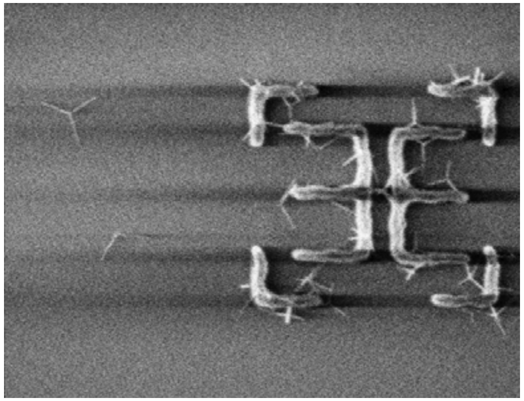
5

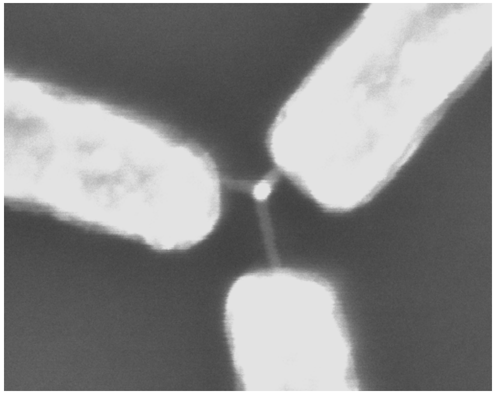
Lift-off

6


develop

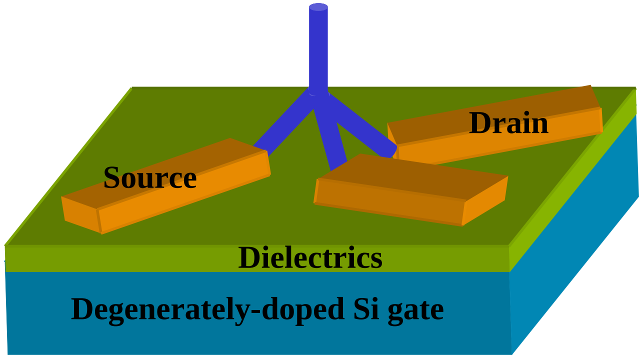
Br etch

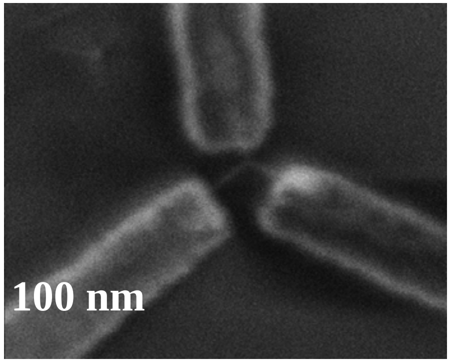




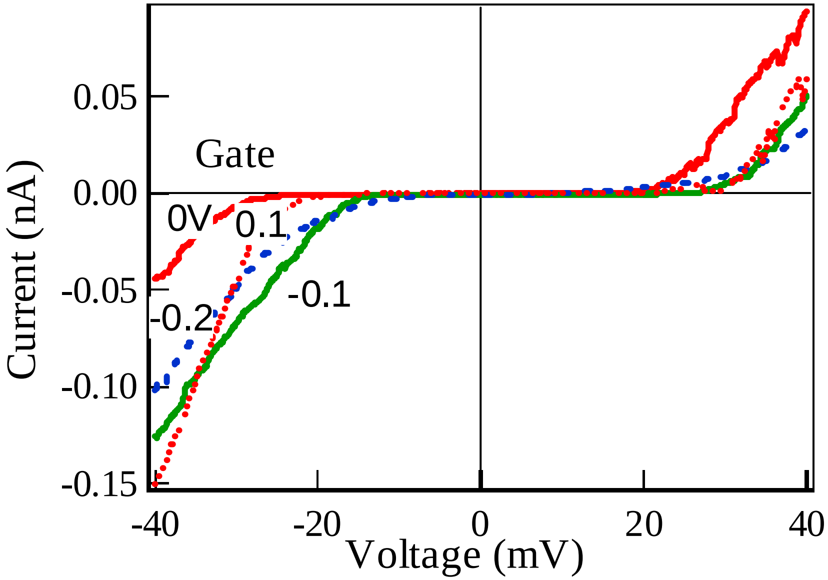
20 nm alignment accuracy in e-beam lithography.

Single electron charging





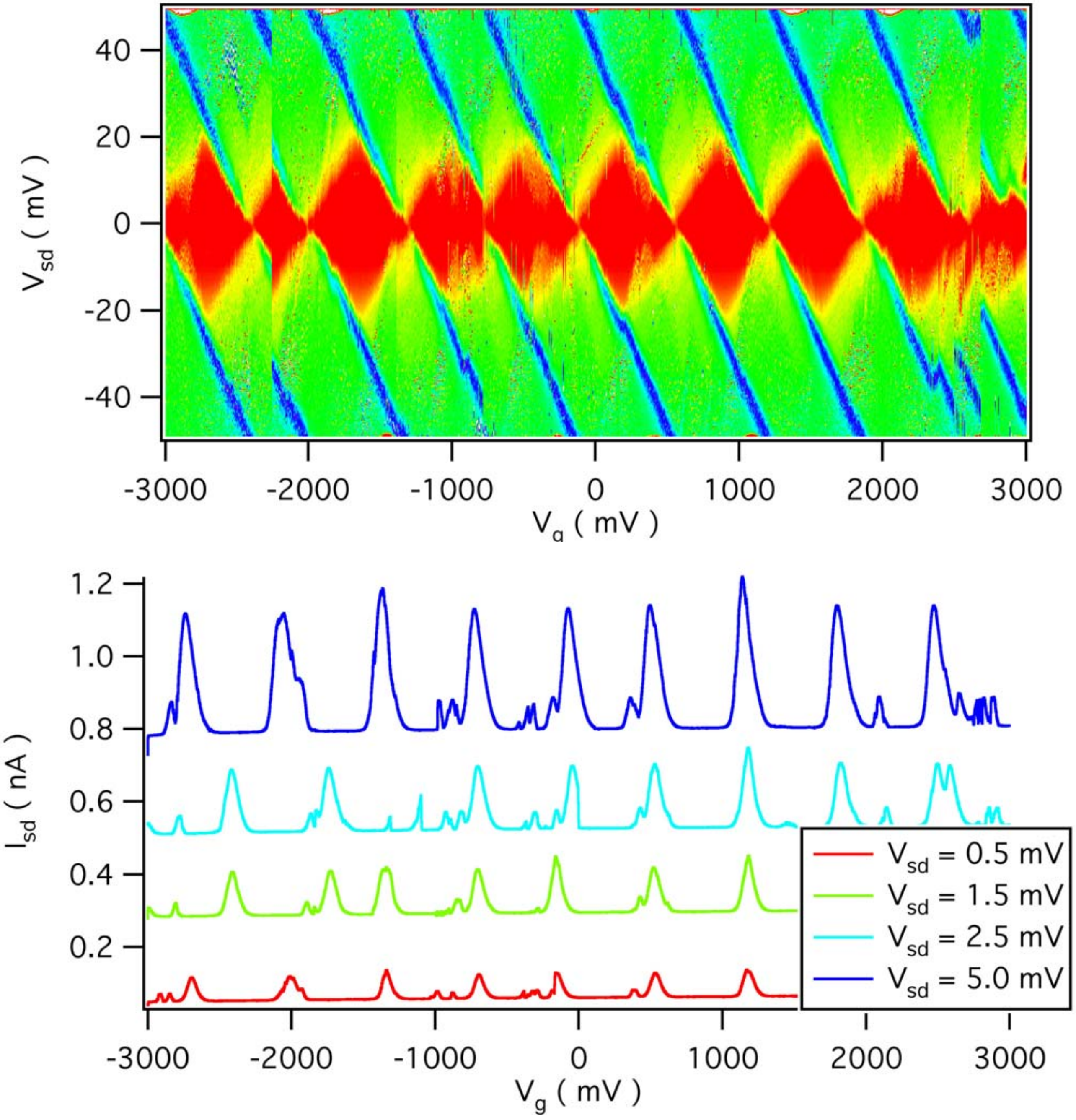
Temperature 5K



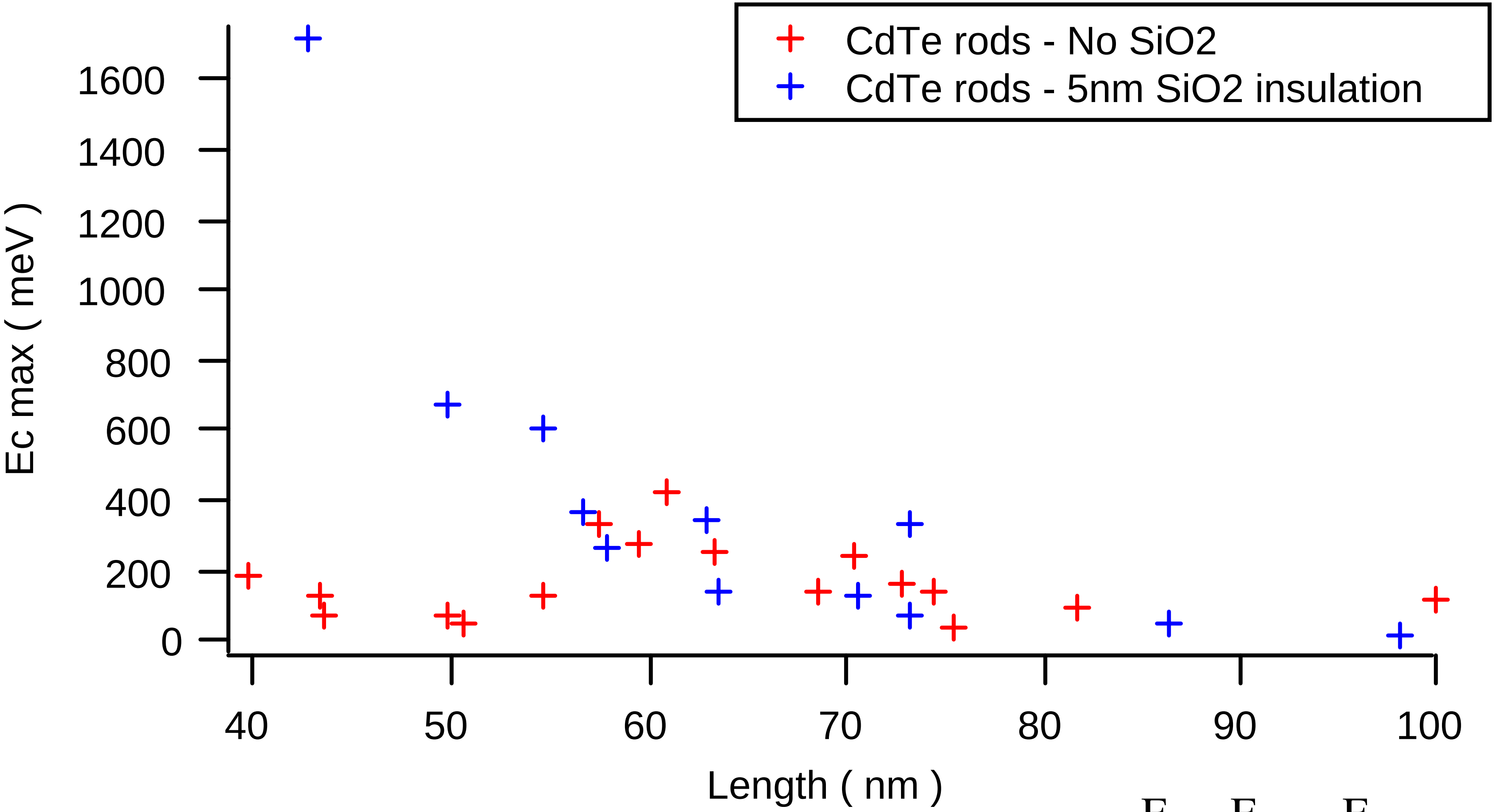
zero-conductance gap changeable by the gate voltage - the signature of single electron charging.

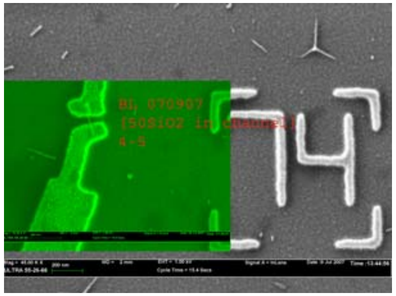
Cui, Y., U. Banin, M. T. Bjork and A. P. Alivisatos Nano Letters **5**(7): 1519-1523 (2005).
"Electrical transport through a single nanoscale semiconductor branch point."

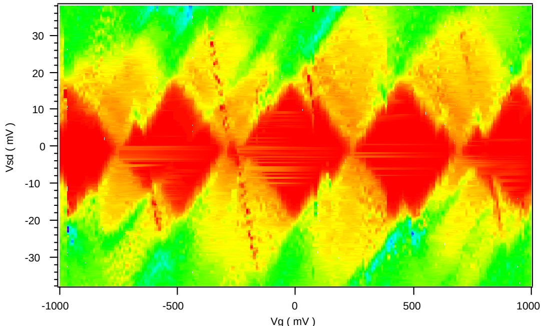
CdTe nanorod - tips etched with Bromine solution

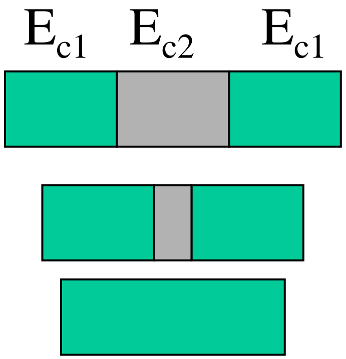


Electrical contacts and charging energy of individual nanorods

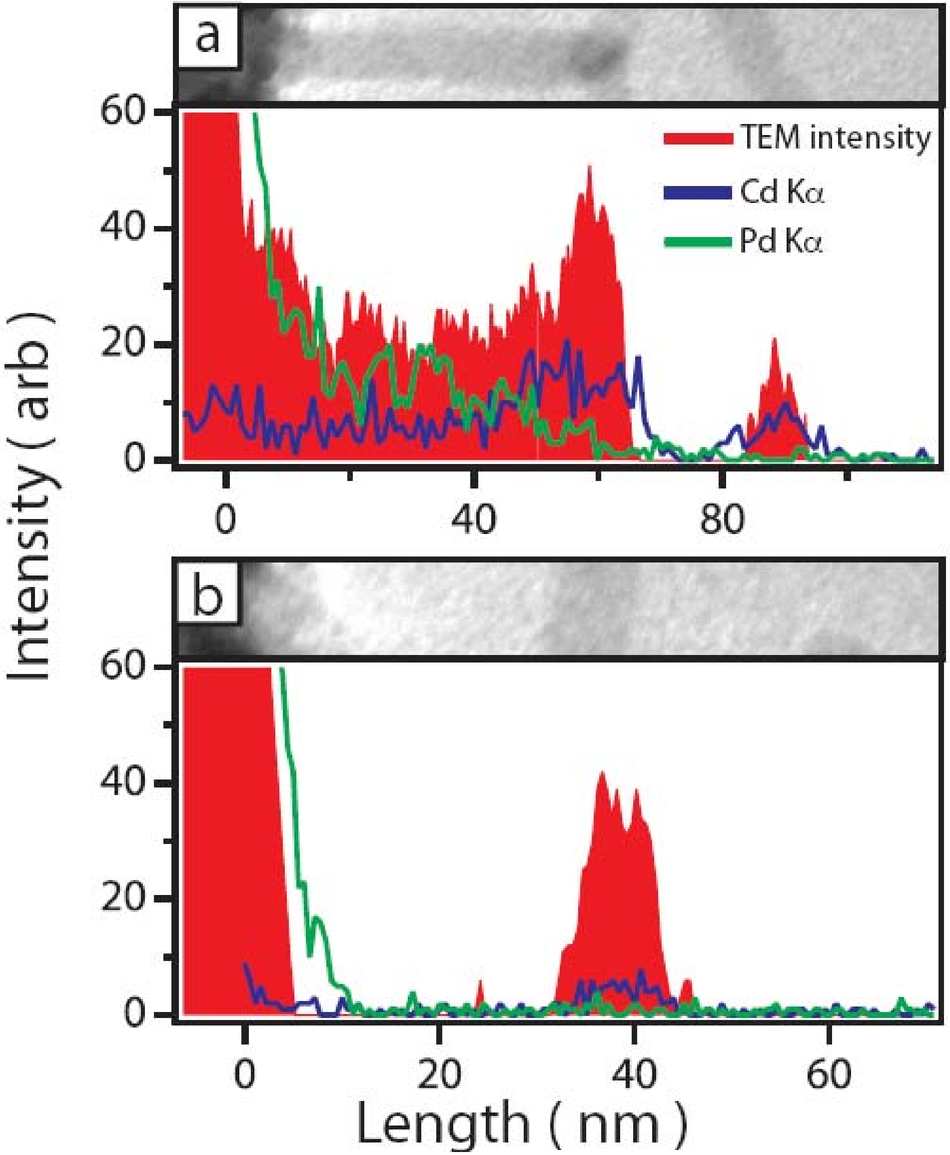






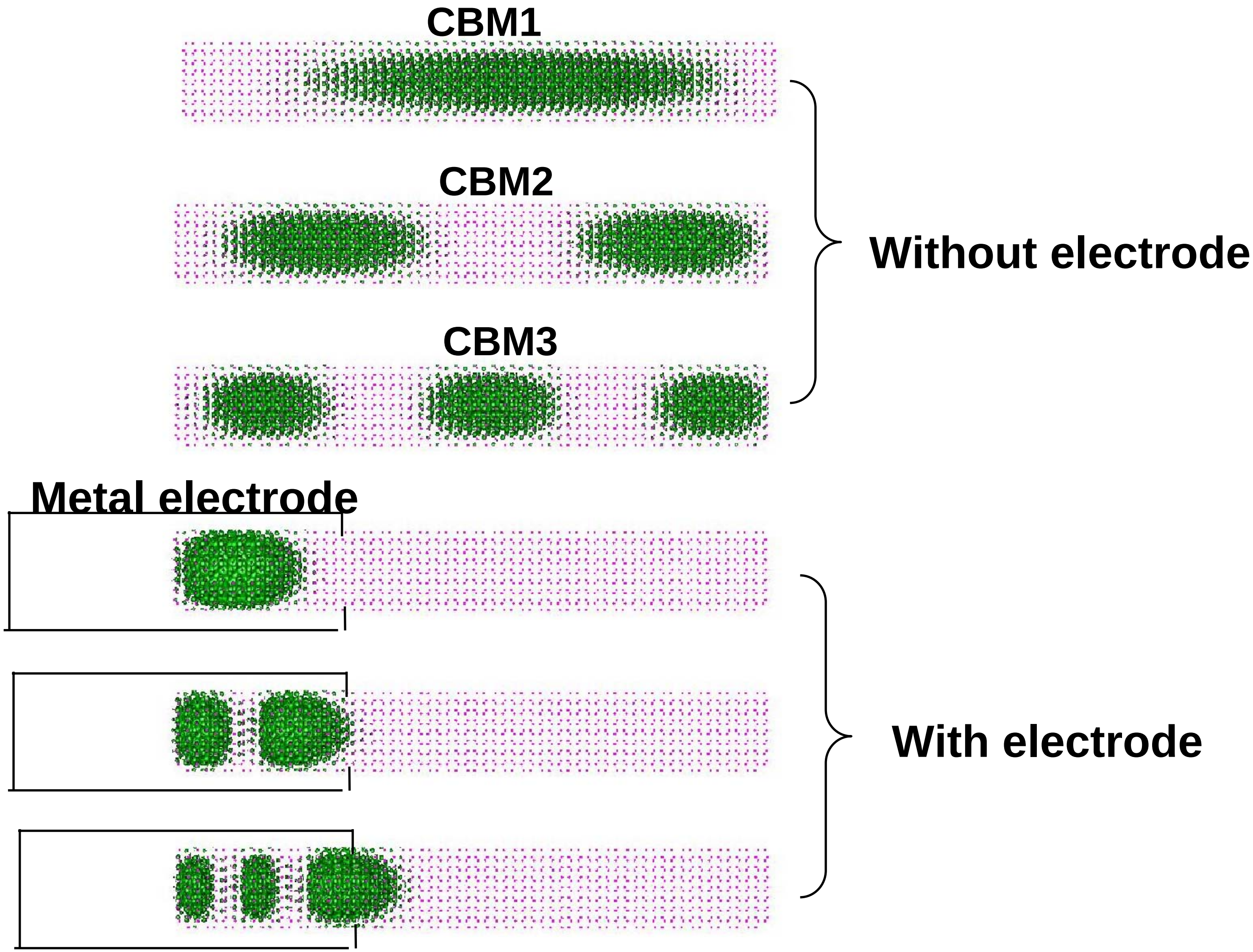


Pd reaction zone extends about 20 nm into the nanorod



Paul-Emile Trudeau
Matt Sheldon

Wavefunction localization due to the electrode



CBM1

CBM2

CBM3

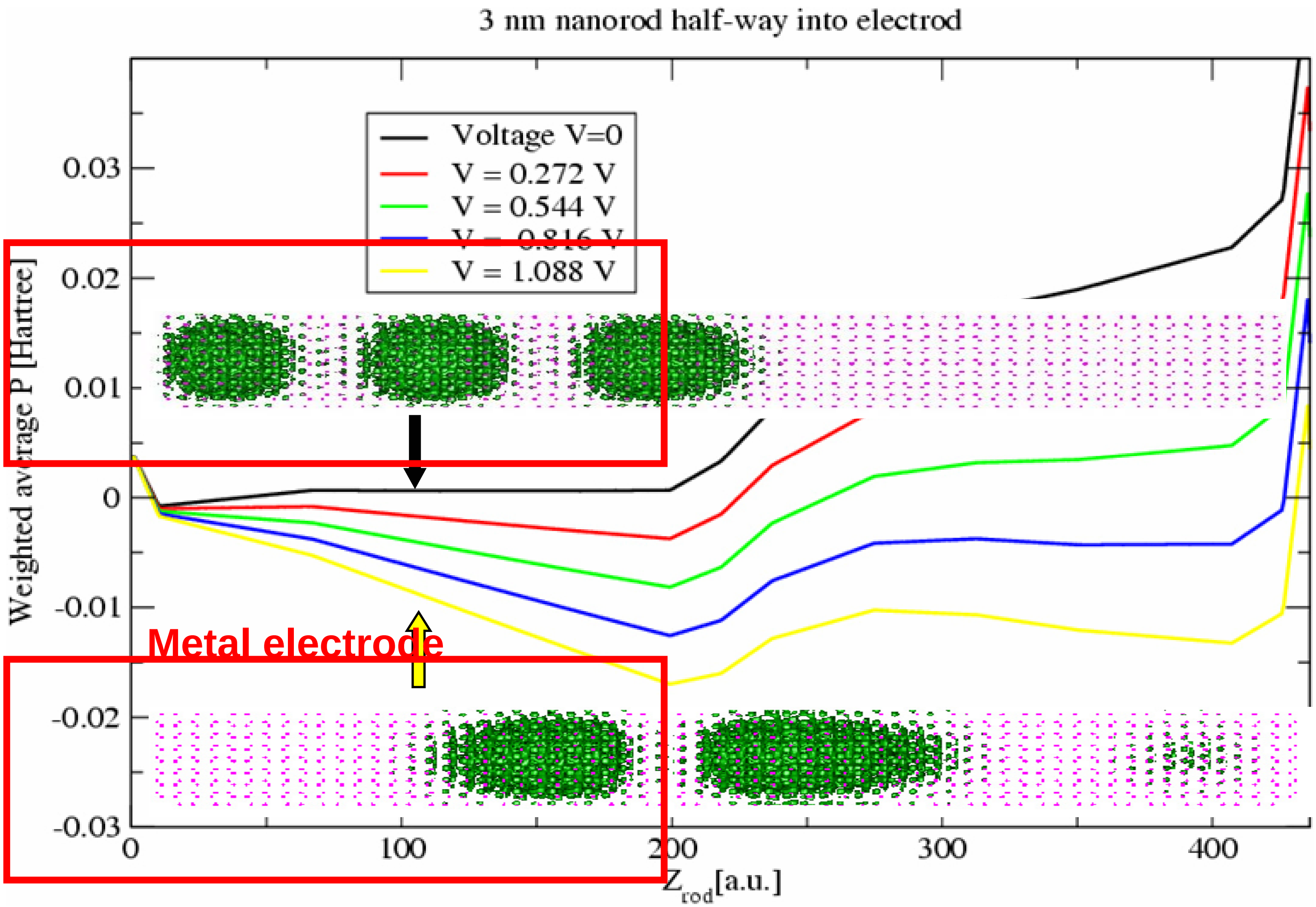
Without electrode

Metal electrode

With electrode

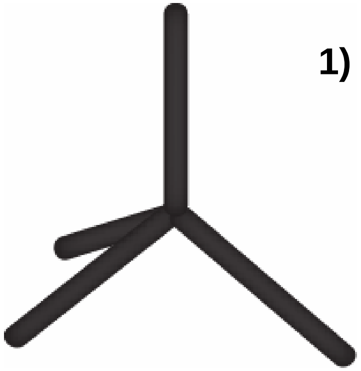
D. Demchenko, L.W. Wang, Nano Letters 7, 3219 (2007).

Using a bias voltage to overcome the localization

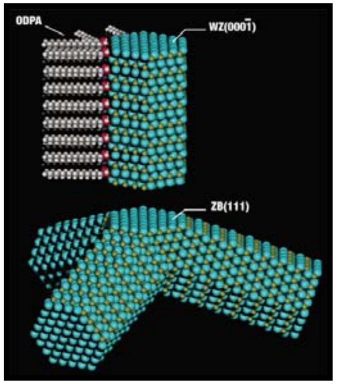


D. Demchenko, L.W. Wang, Nano Letters 7, 3219 (2007).

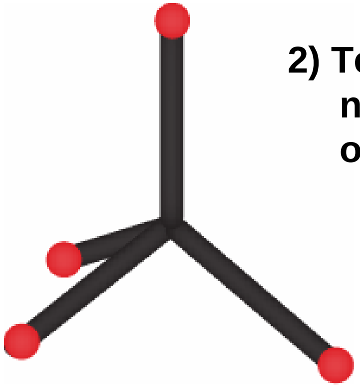
Growth of Au tips on Tetrapods



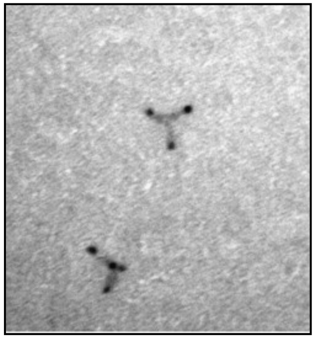
1) **Solution-phase synthesis of tetrapods**



Manna *et al.*, *Nature Mater.*, **2003**, *2*, 382.

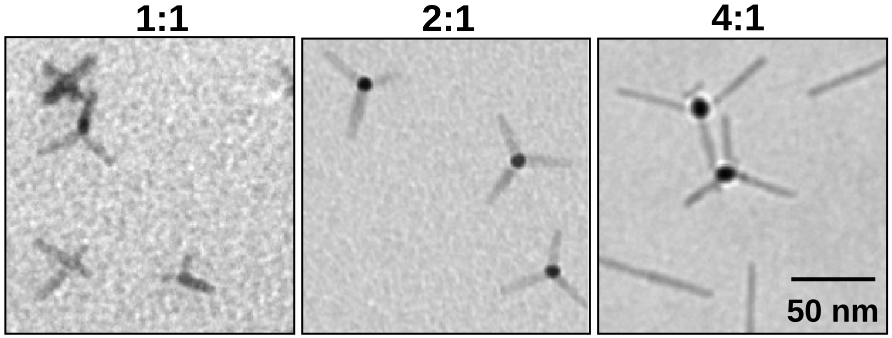


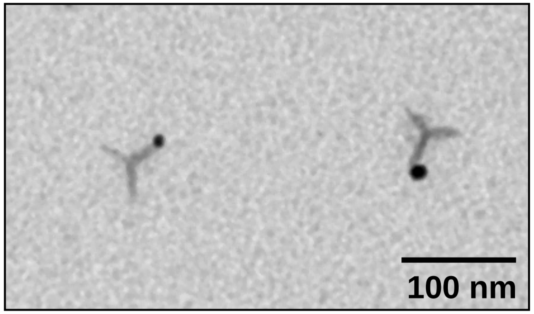
2) **Tetrapod tips provide nucleation sites for formation of gold nanoparticles**



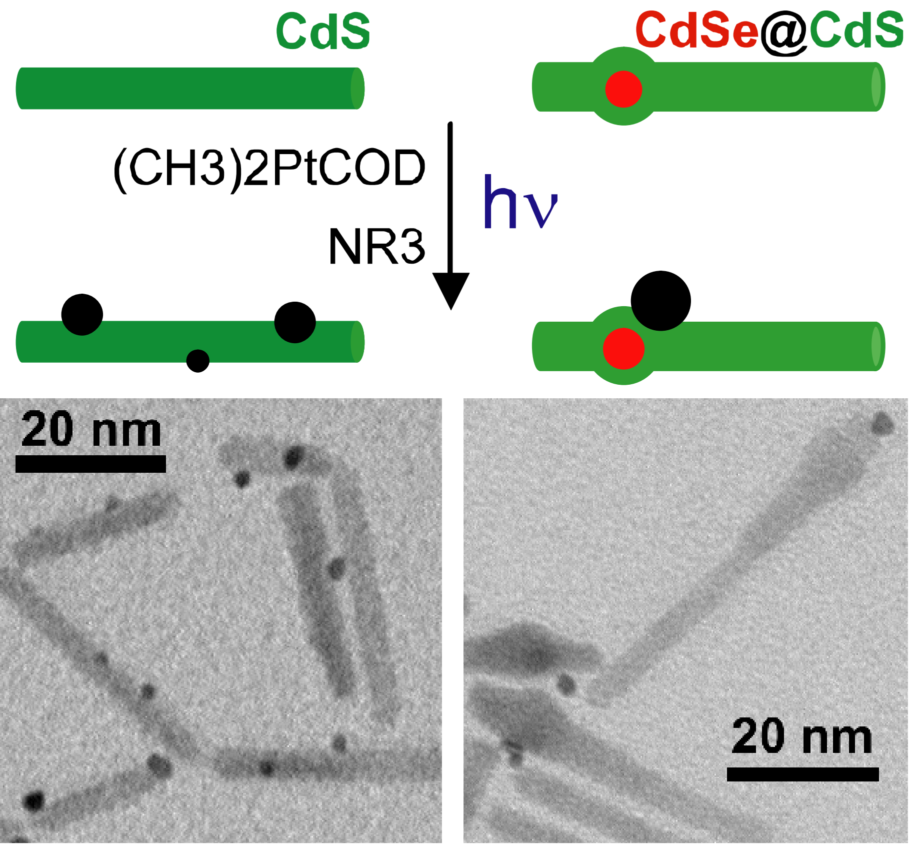
Mokari, Banin *et al.*, *Science*, **2004**, *304*, 1787.

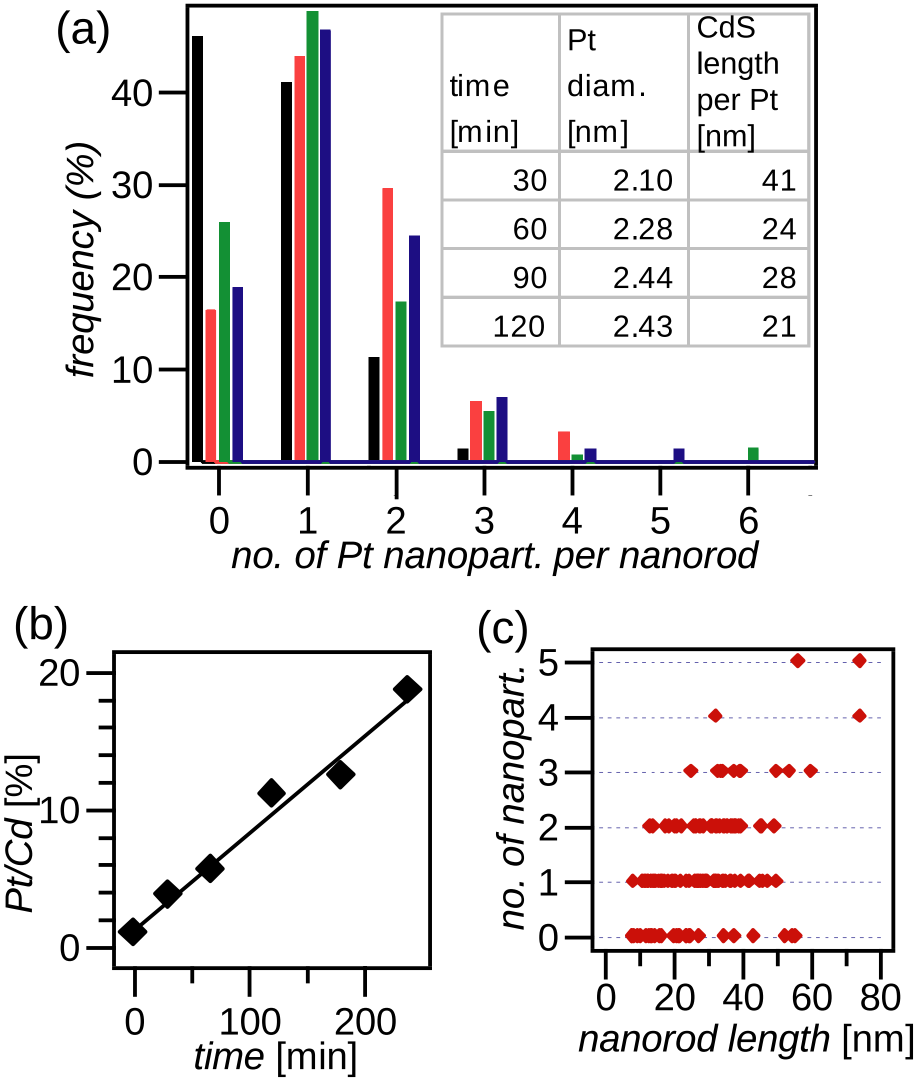
Cd/S ratio





Pt photodeposition on CdS and Cdse@CdS nanorods

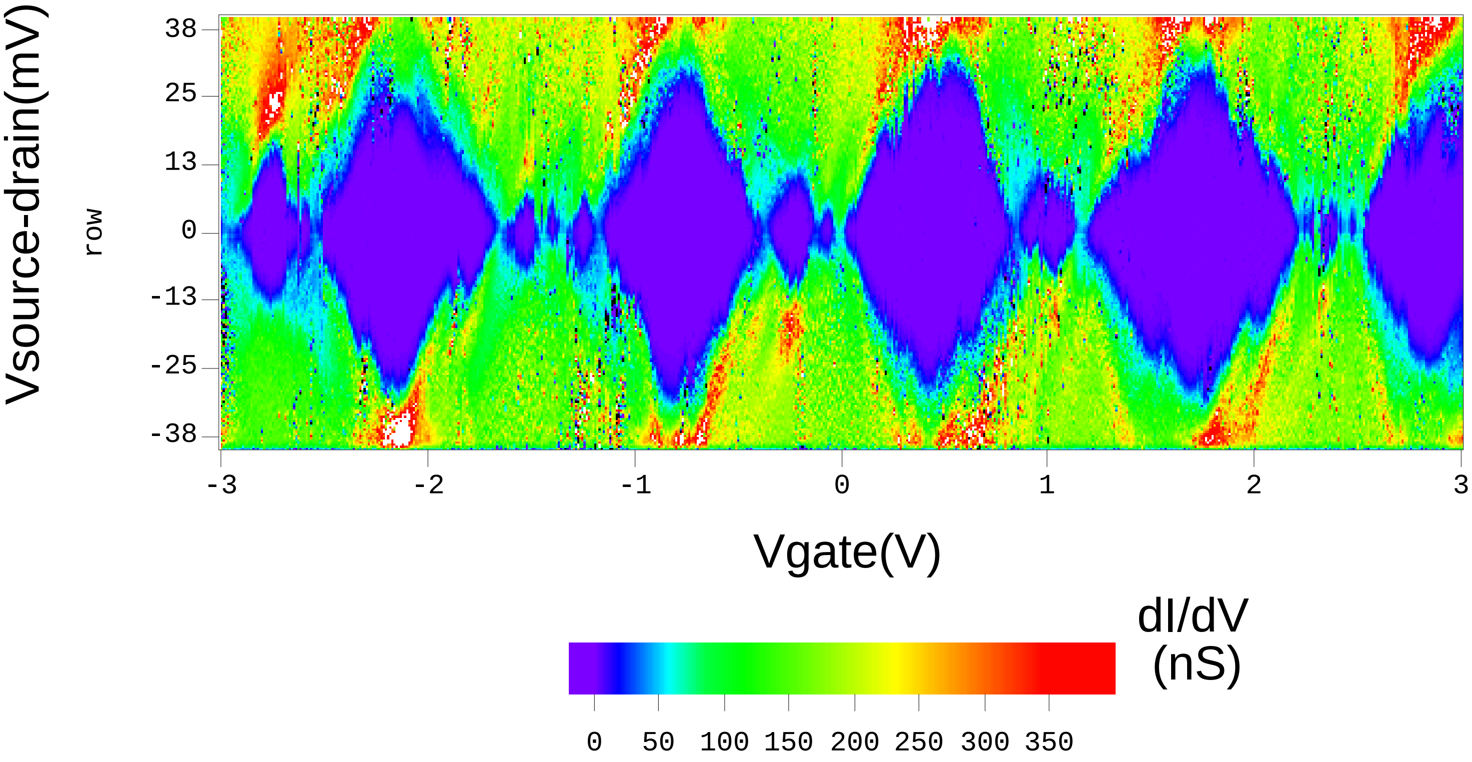


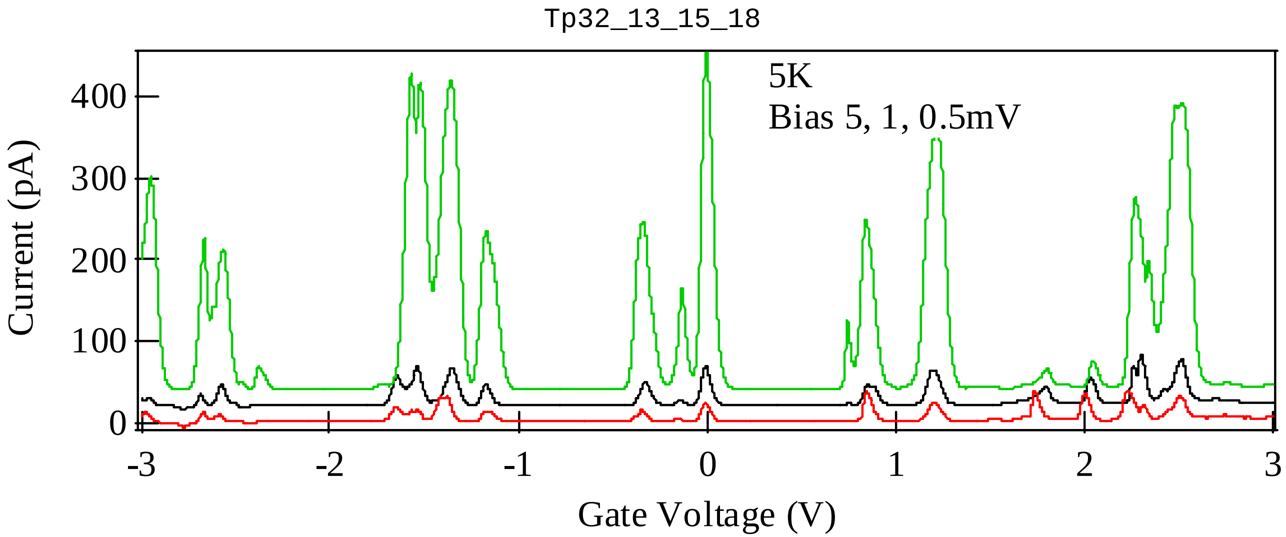


time [min]	Pt diam. [nm]	CdS length per Pt [nm]
30	2.10	41
60	2.28	24
90	2.44	28
120	2.43	21

Gordana Dukovic

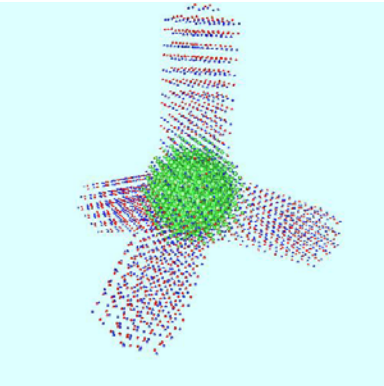
Tetrpaod SET: Strong Coupling Example



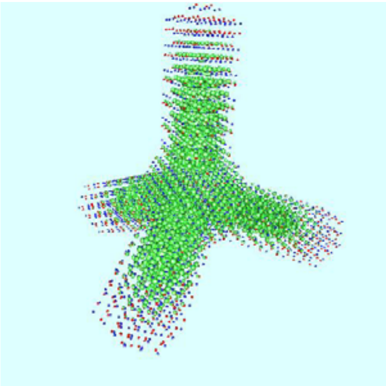


Electronic energy levels of tetrapods

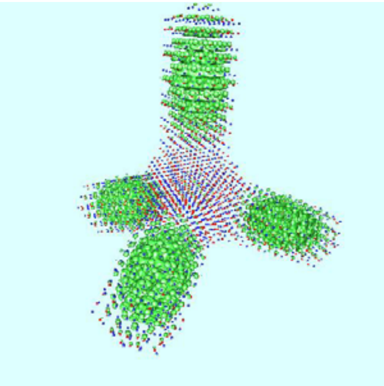
cb1



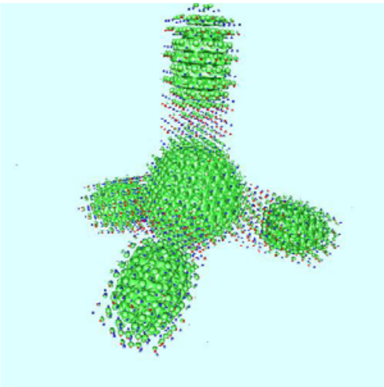
cb2



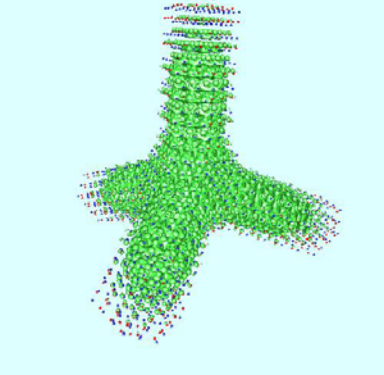
cb5



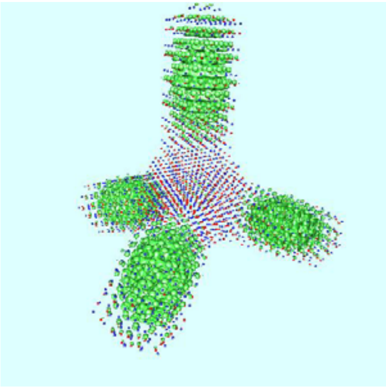
cb6



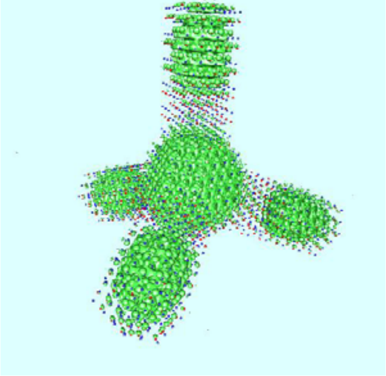
vb1,2



vb

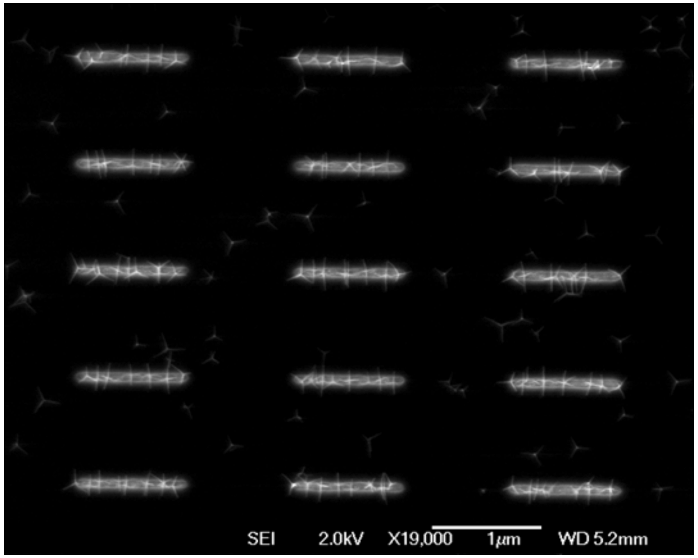


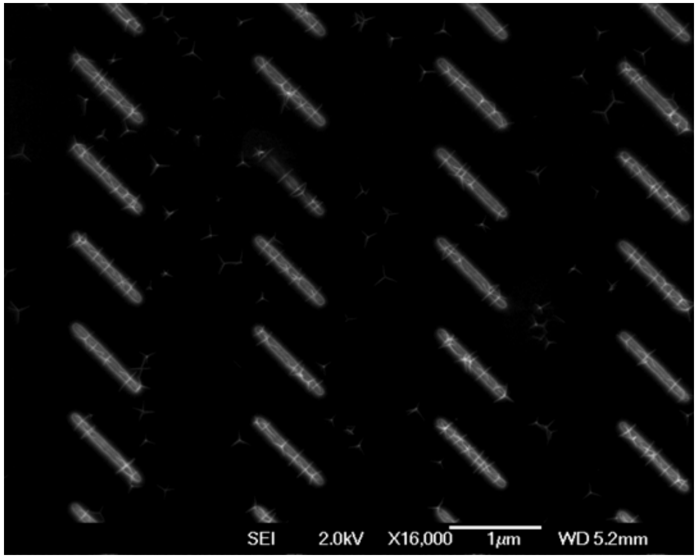
vb5,6

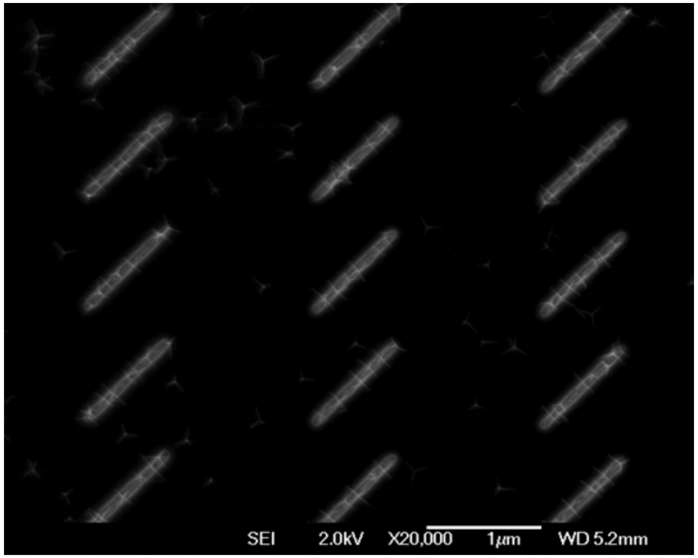


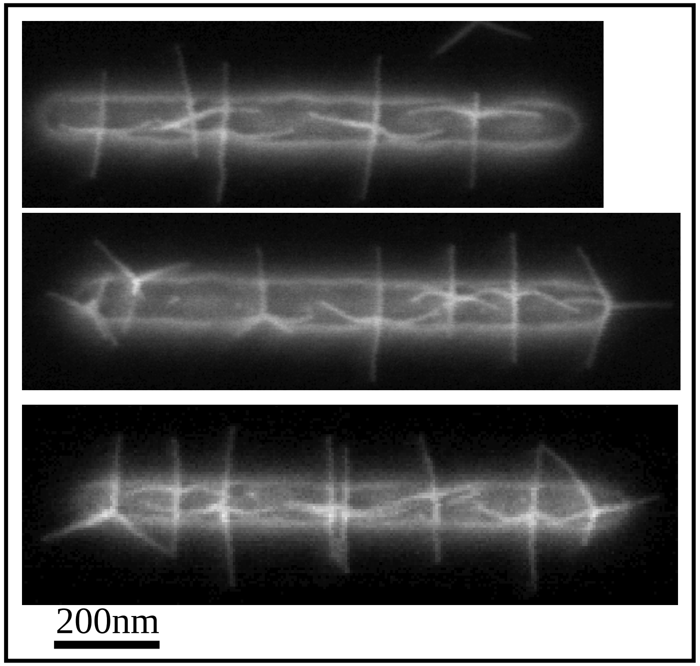
Li JB and Lin Wang Wang
Shape effects on electronic states of nanocrystals
Nano Letters 3 (10): 1357-1363 2003

Tetrapods pressed onto trench walls by capillary forces









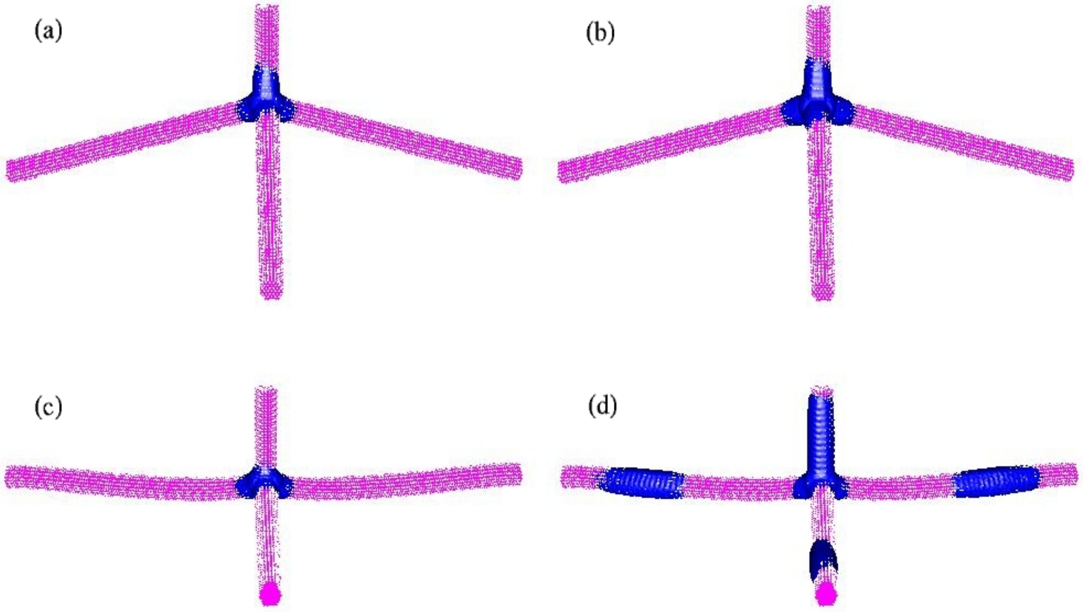
Y. Cui, Y., M. T. Björk, J. A. Liddle, C. Sönnichsen, B. Boussert and A. P. Alivisatos
"Integration of colloidal nanocrystals into lithographically patterned devices." Nano Letters **4**(6): 1093-1098 (2004).

Mechanically induced state crossing

Hole state **Electron state**

Free tetrapod

Pressed tetrapod

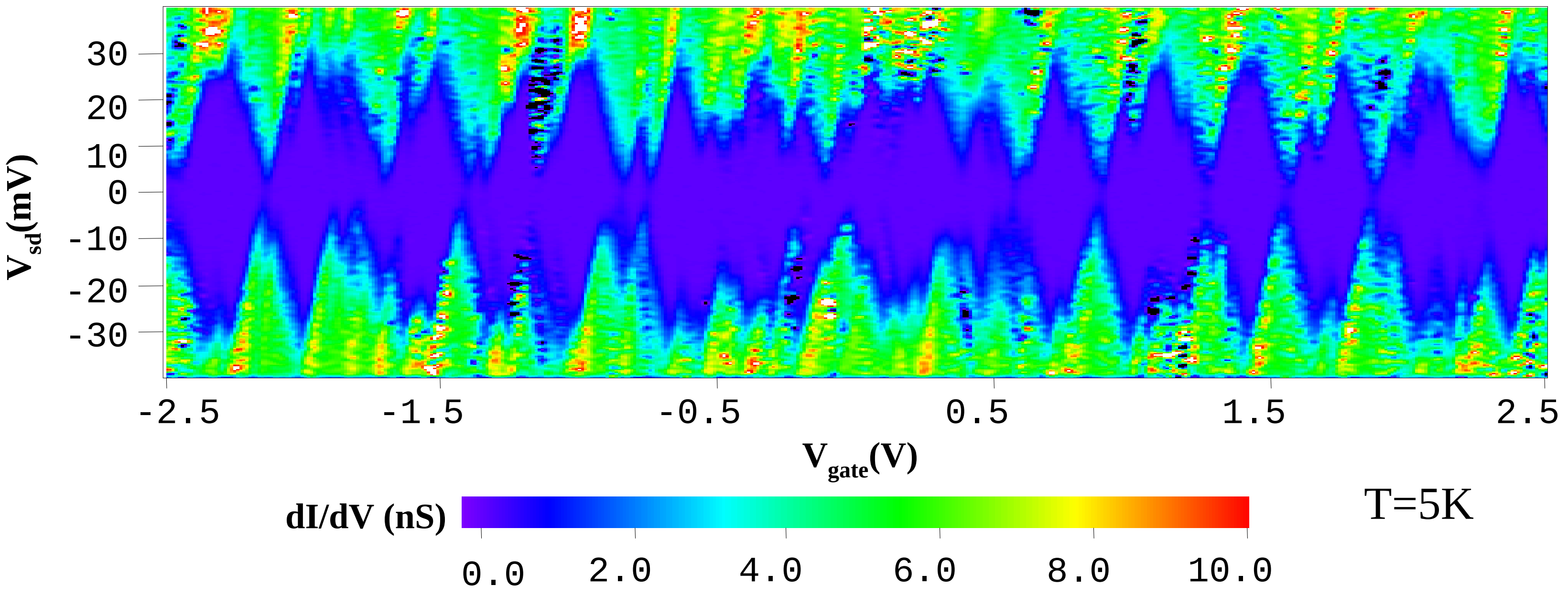


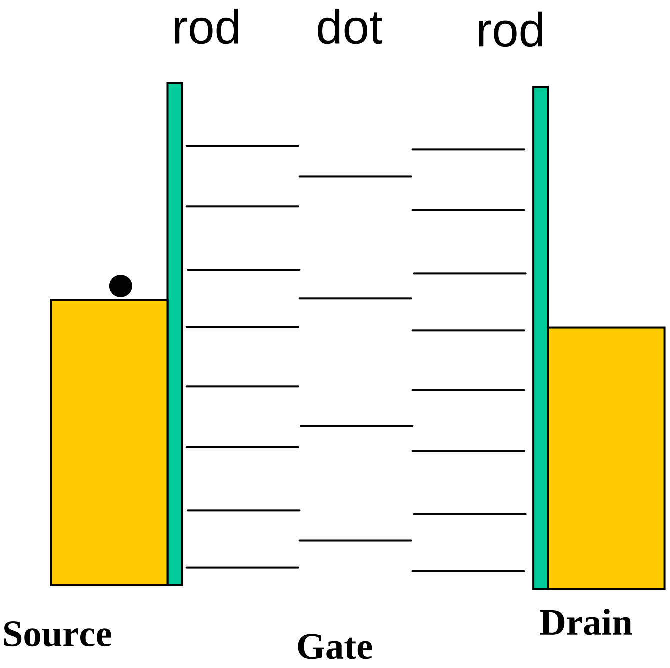
Empirical Pseudopotential Calculations with 25,000 atoms.

There is a state crossing for the electron state after press (mainly due to hydrostatic strain near the center). Should be detectable from single dot spectroscopy.

J. Schrier, B. Lee, L.W. Wang, J. Nanosci. Nanotech. (in press).

Signatures of a hopping case

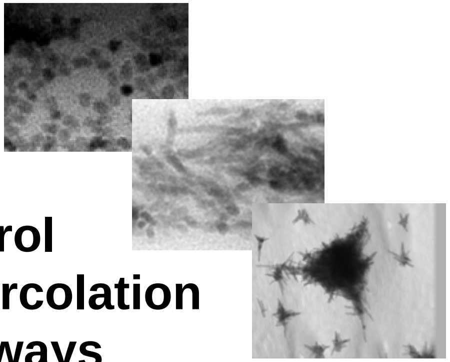




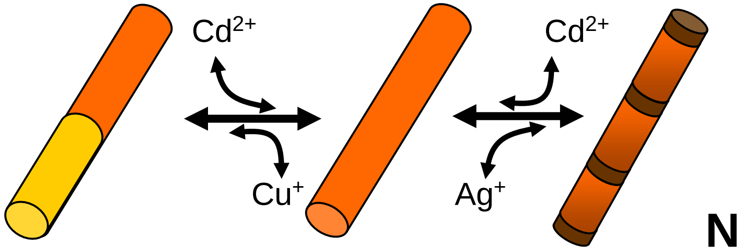
- **Sawtooth pattern: multi-dots**
- **Different Charging energy scales: 30 meV ~8 nm dots; 5 meV ~8 by 50 nm rods.**
- **Coulomb diamonds do NOT close at zero bias.**

(Nano Letters **5**(7): 1519-1523 (2005).

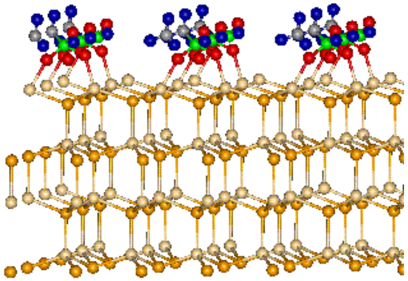
Nanocrystal-based solar cells



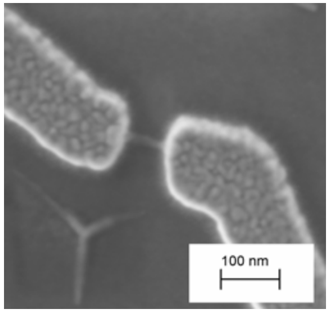
Control of percolation pathways



New nanoscale heterostructures for solar cells



Organic passivation and assembly



Model studies of single nanocrystals

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Materials Science Division, Lawrence Berkeley National Lab

Thank you

Vicki Colvin
Mike Schlamp
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Wendy Huynh
Janke Dittmer
Greg Whiting
Will Libby
Andreas Meisel
Liberato Manna
Erik Scher
Delia Milliron
Ilan Gur
Mike Geier

Antonis Kanaras
Neil Fromer
Richie Robinson
Bryce Sadtler
Dennis Demchenko
Lin Wang Wang
Cyrus Wadia
Yue Wu
Wanli Ma

US Department of Energy
(Darpa and Afosr)