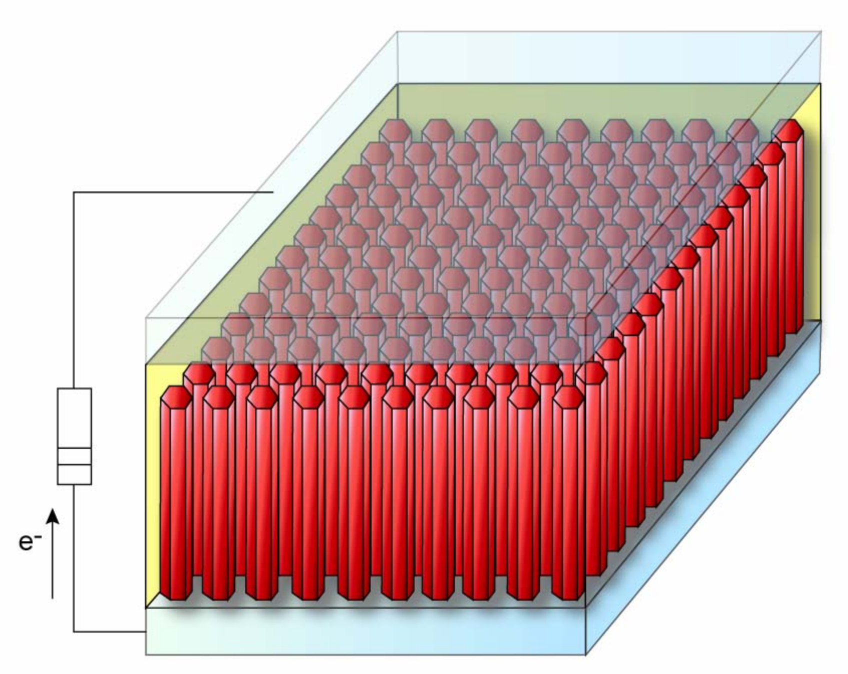
Nanowire Solar Cells



Peidong Yang
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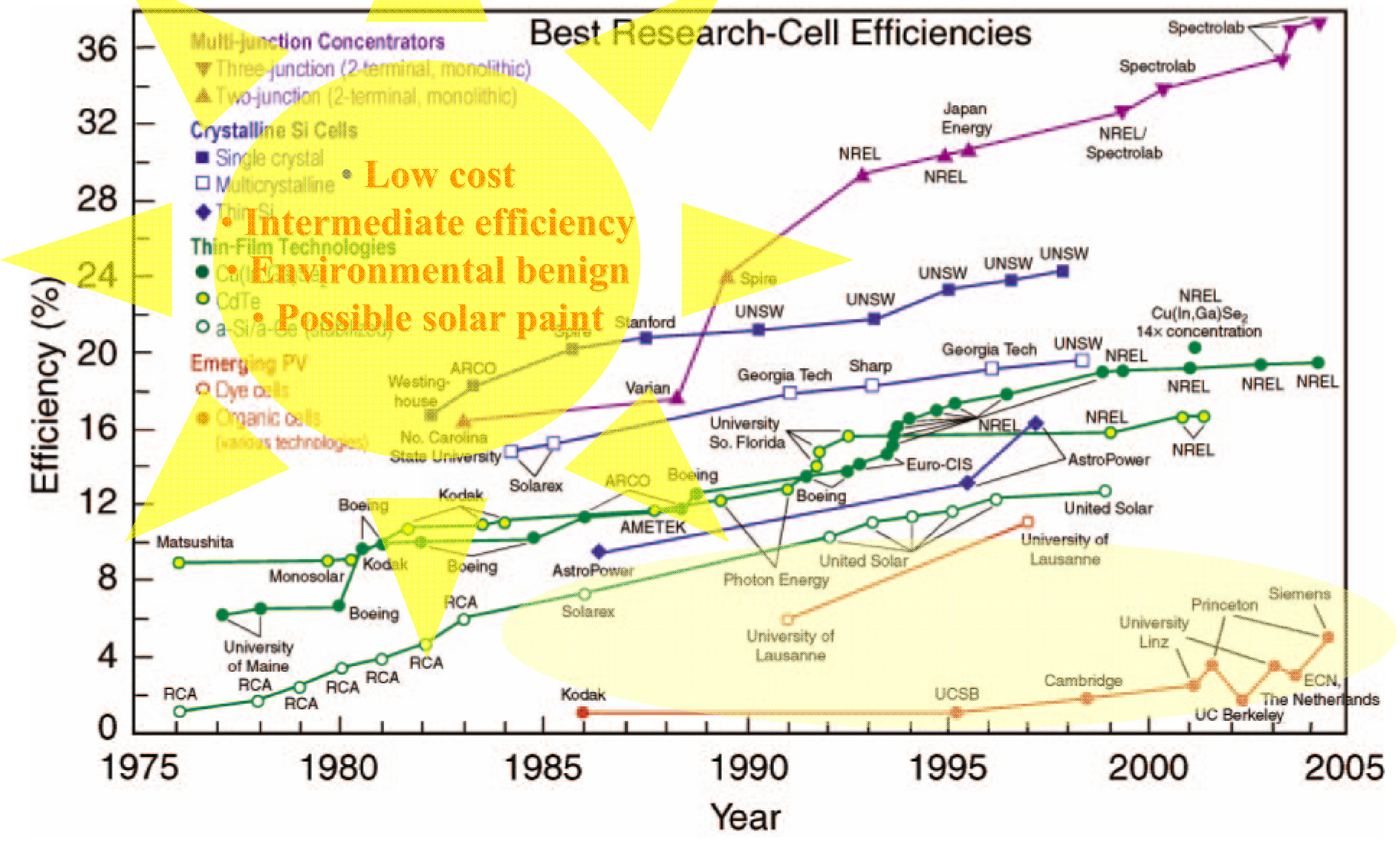
Lawrence Berkeley National Laboratory

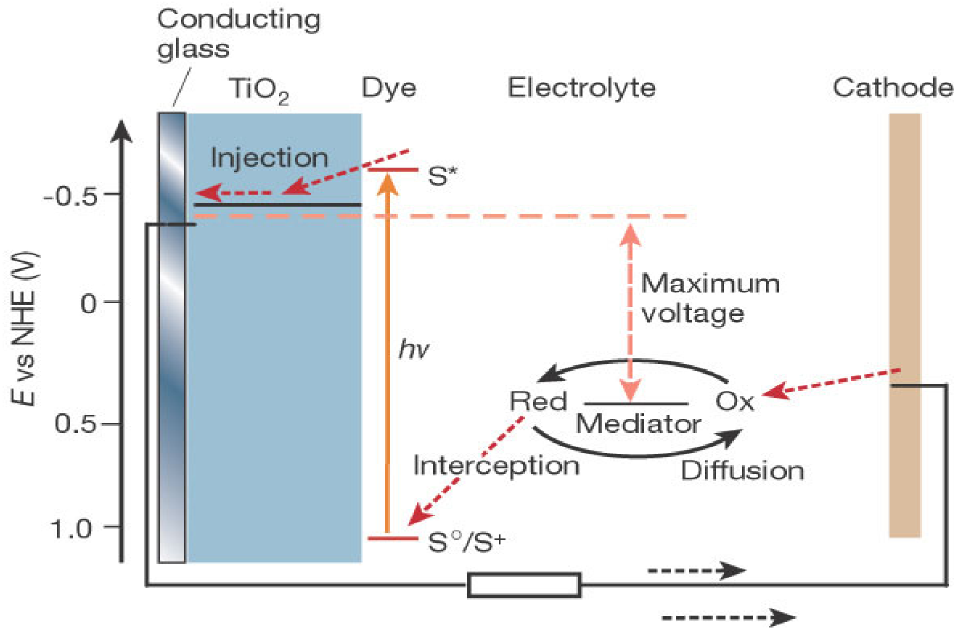
Emerging PV



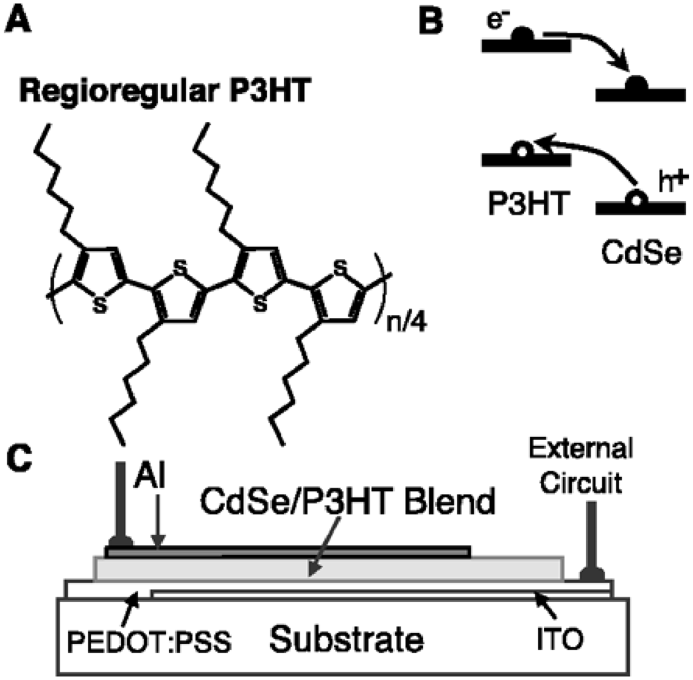
- Low cost
- Intermediate efficiency
- Environmental benign
- Possible solar paint

MRS Bulletin, Jan 2005

Emerging PV



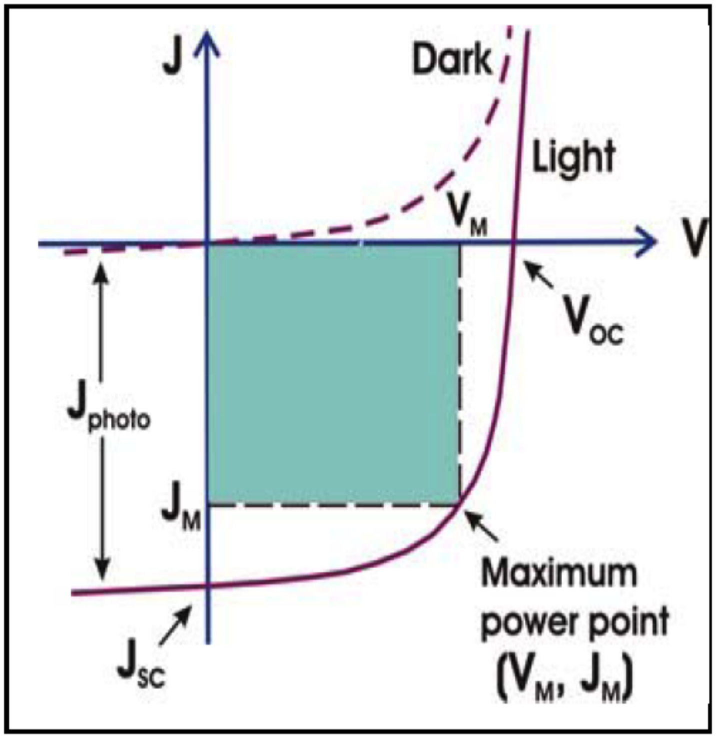
Grätzel, M. *Nature* 414, 2001.



Alivisatos et al. Science 2002, 295, 2425.

Why nanowires are important?

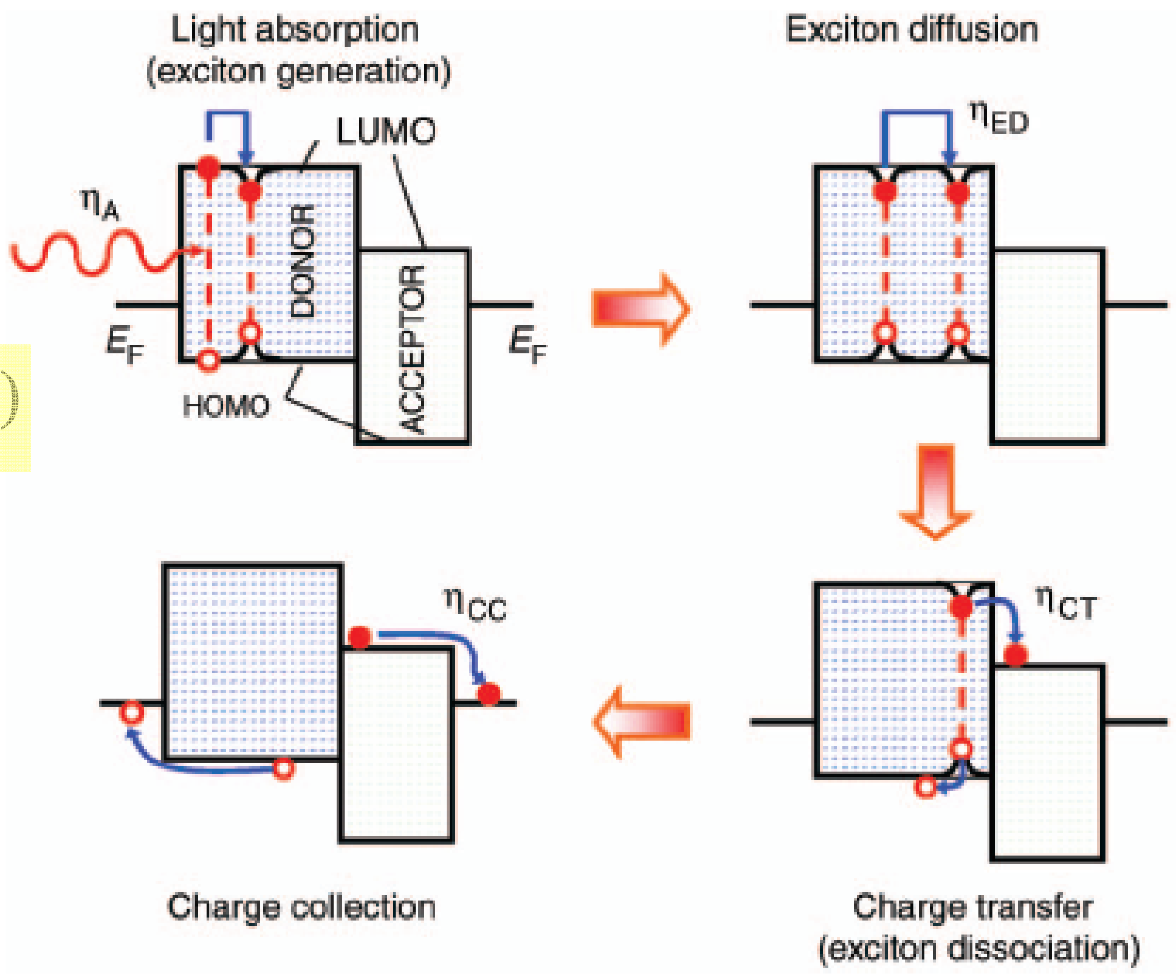
PV Performance Metrics



$$FF = \frac{J_M V_M}{J_{SC} V_{OC}}$$

$$Efficiency = \frac{P_{out}}{P_{in}} = \frac{FF \times V_{oc} \times J_{sc}}{P_{in}}$$

$$\eta_A = (1 - e^{-\alpha d})$$



$$\eta_{ED} = e^{-d/L_D}$$

$$\mathrm{IQE}(\lambda) = \eta_A(\lambda)\, \eta_{ED}\, \eta_{CT}\, \eta_{CC}$$

$$\eta_{PCE} = \frac{P_{out}}{P_{in}} = \frac{\mathrm{FF} \times V_{OC}}{P_{in}}\, q \int F(\lambda)\,\mathrm{IQE}(\lambda)\,d\lambda$$

S. Forrest. MRS Bulletin, Jan 2005

Emerging PV

- Use of solar at terawatt levels requires drop in $\$/W_p$

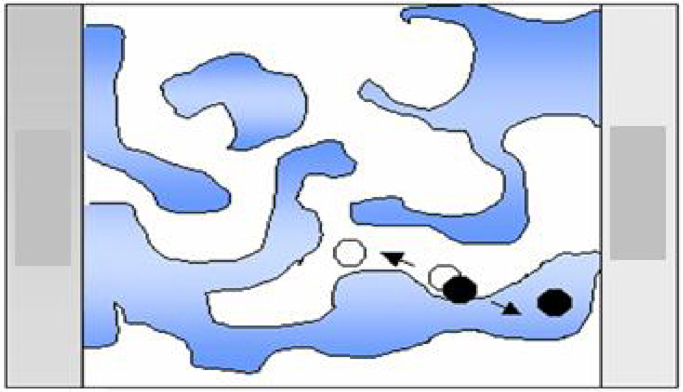
- 3N: New materials, New designs, New tricks

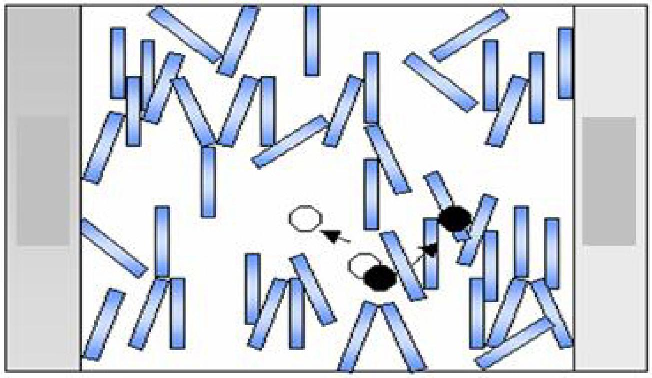
“dirty” semiconductors
organics
oxides
absorbers
biological subunits

dye-sensitized cells

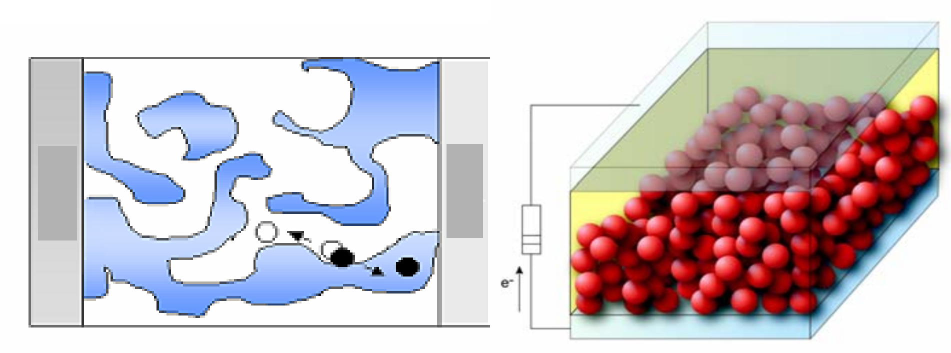
bulk heterojunction cells
(polymer, organic-inorganic)

quantum effects
carrier multiplication
frequency shifting
Interface engineering



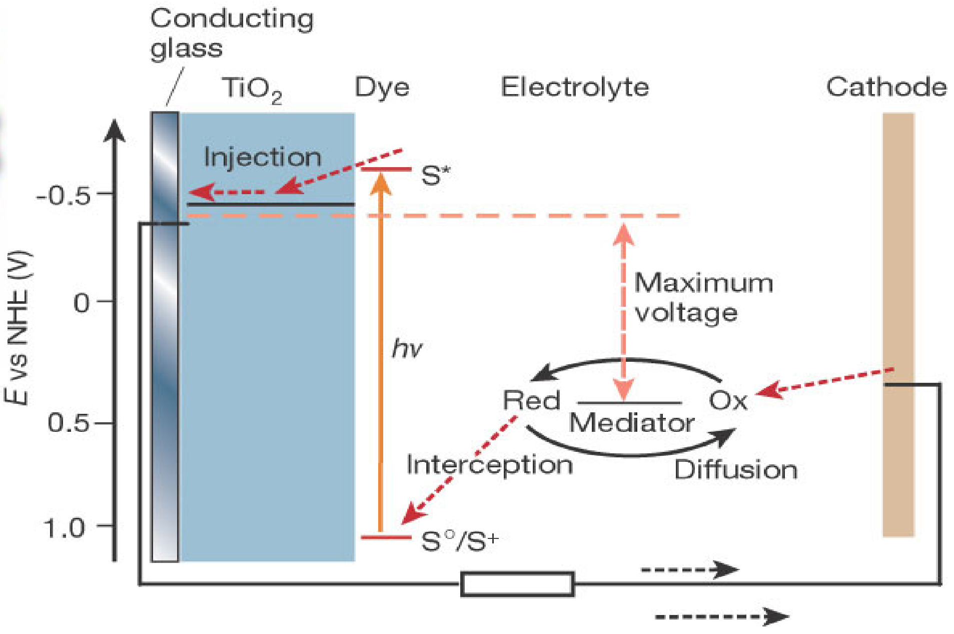


Dye-sensitized Photoelectrochemical Cell

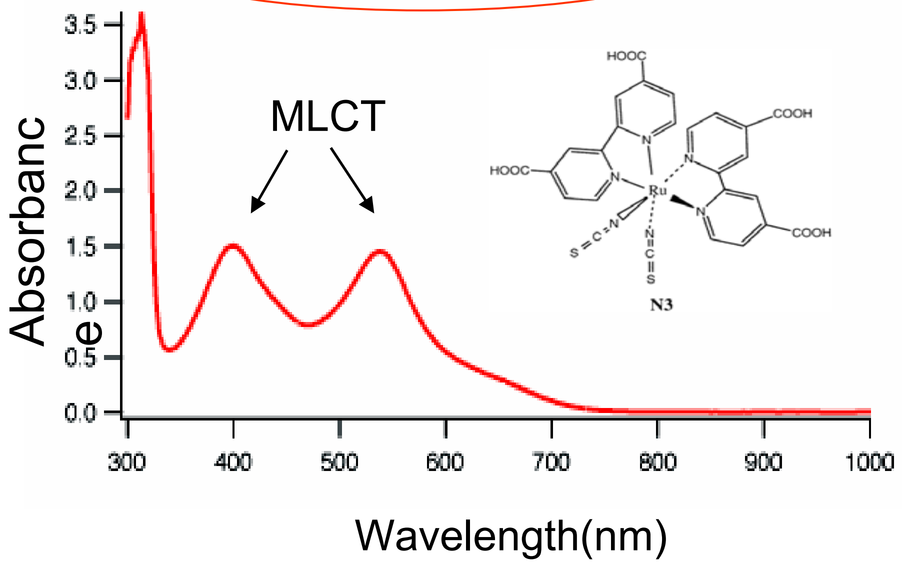


electron diffusivity: 10^{-4} cm^2/s

Poor charge collectors?



Grätzel, M. *Nature* 414, 2001.



Wavelength(nm)

DSC characteristics

- **surface area of 800 – 1000 cm^2 per cm^2**
- ***η* of 5 -10% with TiO$_2$ nanoparticles**
- **electron transport via trap-mediated diffusion**
- **Low efficiency at long wavelength**

The three ways to improve DSC efficiency

1) Find dyes that function efficiently across the visible and near-IR
2) Raise open-circuit voltage closer to its theoretical maximum
3) Increase the electron diffusion length in the oxide anode, $L_d = (D_e\tau)^{1/2}$

speed up electron transport

↓

adopt a nanowire geometry

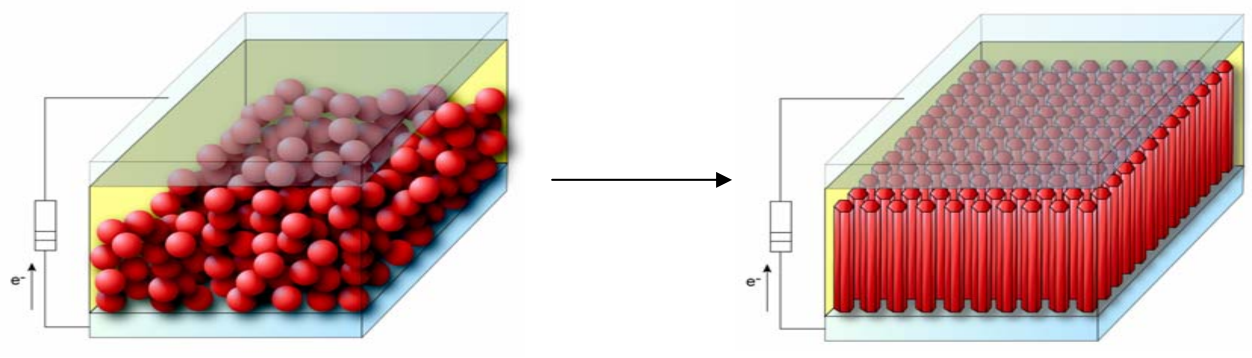
slow recombination

↓

engineer the active interface

Nanoparticle DSC	**Nanowire DSC**
random, polycrystalline network	oriented single-crystalline channels
slow diffusive transport	fast band conduction (field-assisted)
efficient for films ~10 μm thick	in principle, efficient for much thicker cells
high internal surface area	*smaller internal surface area*

Nanowire DSC: Design Principle

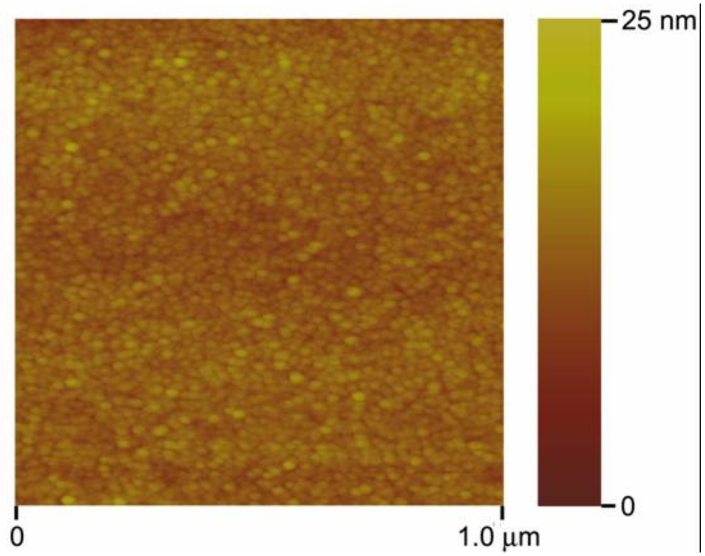


high nanowire density
long, thin nanowires

electrode	length (μm)	diameter (nm)	density (x10^{10} cm^{-2})	SA
nanoparticle	8 - 10	15 - 30	n/a	800 - 1000
ideal nanowire	20	60	3	1080
achieved NW	20	130	0.3	~200

Large-Scale Nanowire Array Synthesis

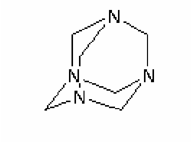
1st: dip-coat to get ZnO quantum dots **2nd: grow nanowires from QD seeds**

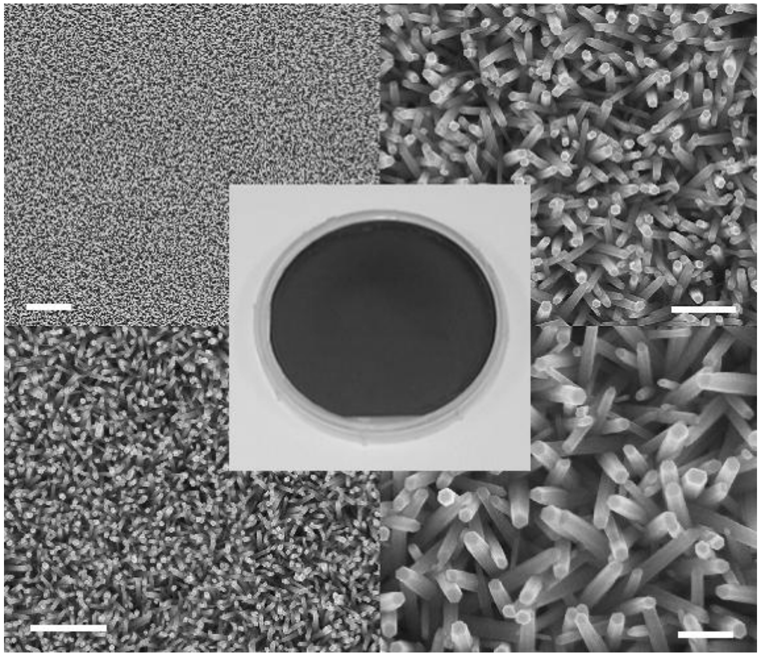


zinc salt hydrolysis, HMTA

→

60-90 °C



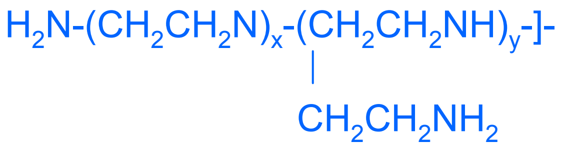


L. Greene et al. Angew Chem. Int. Ed. 42, 3031, 2003.

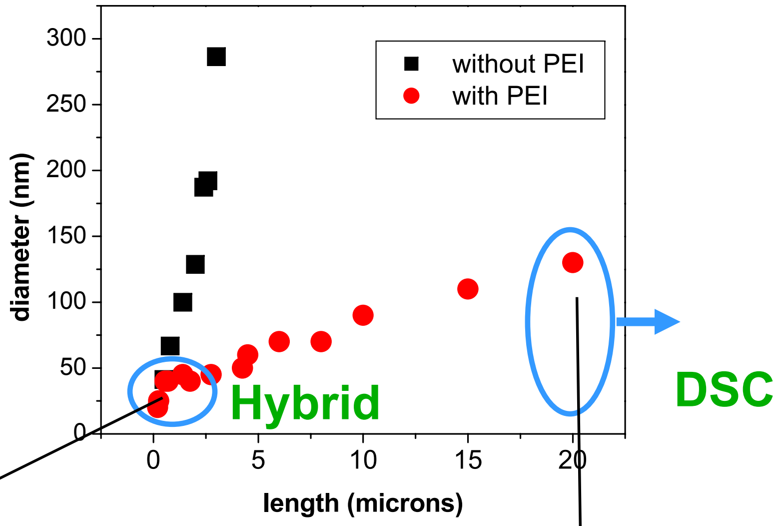
- **Nanowire densities of 1-40 billion cm^{-2}**
- **Single-crystalline wires in direct contact with the substrate**
- **Inexpensive and environmentally benign**
- **Compatible with arbitrary substrates of any size**

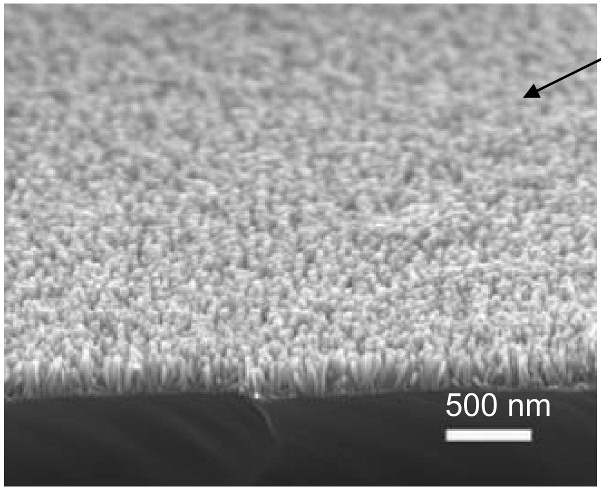
Control of Nanowire Aspect Ratio

Poly-ethylenimine (PEI):

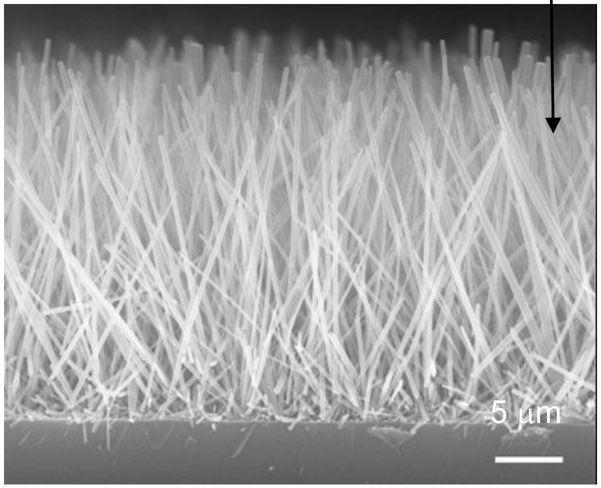


$H_2N\text{-}(CH_2CH_2N)_x\text{-}(CH_2CH_2NH)_y\text{-}]\text{-}$ with $CH_2CH_2NH_2$ attached to the N



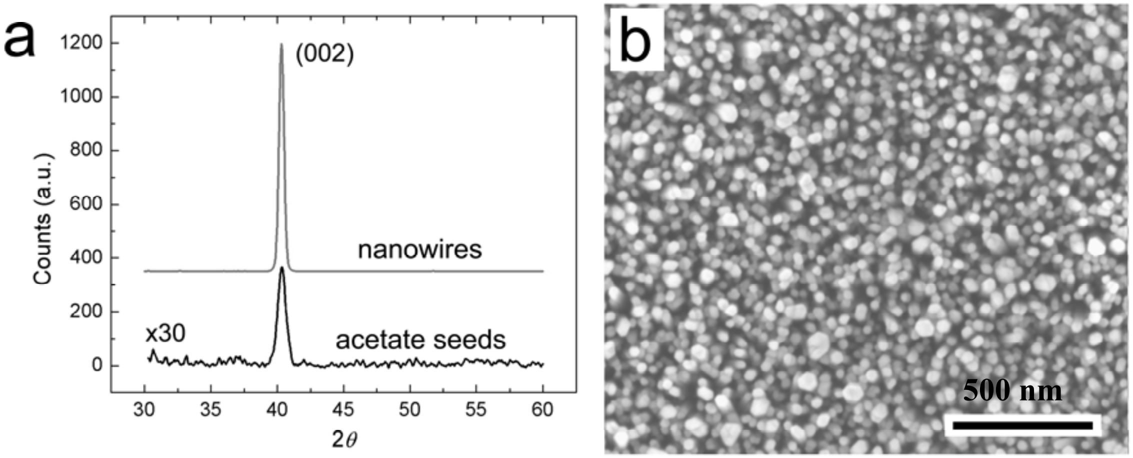


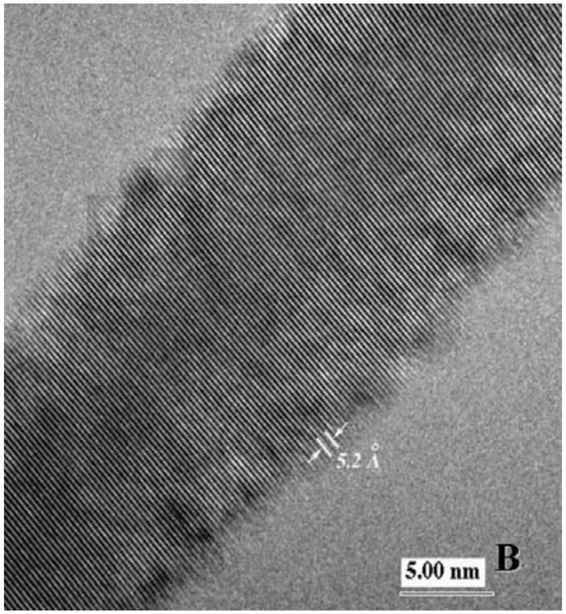
Hybrid: aspect ratio = 10

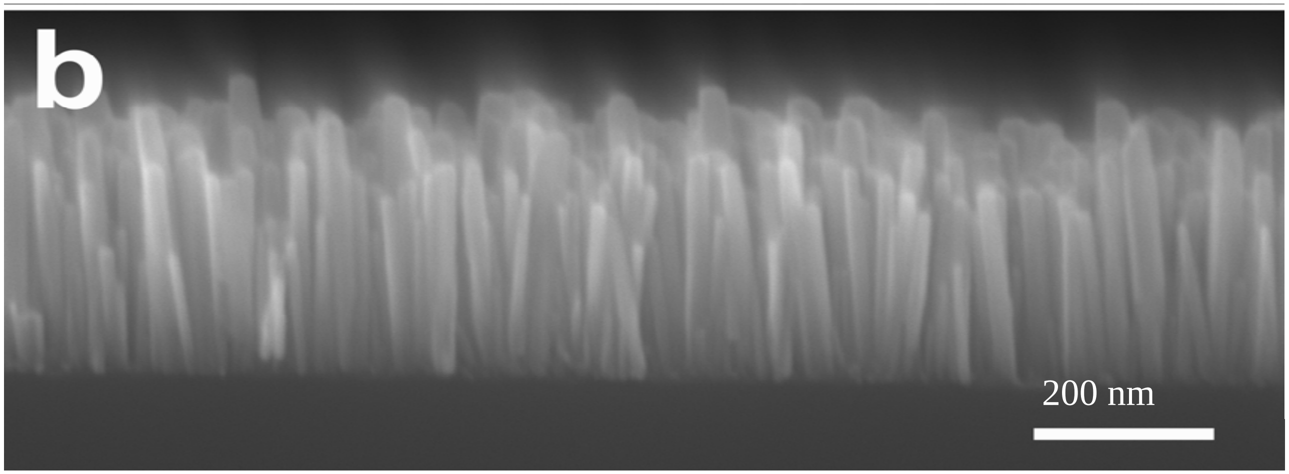


DSC: aspect ratio > 150

Alignment Control

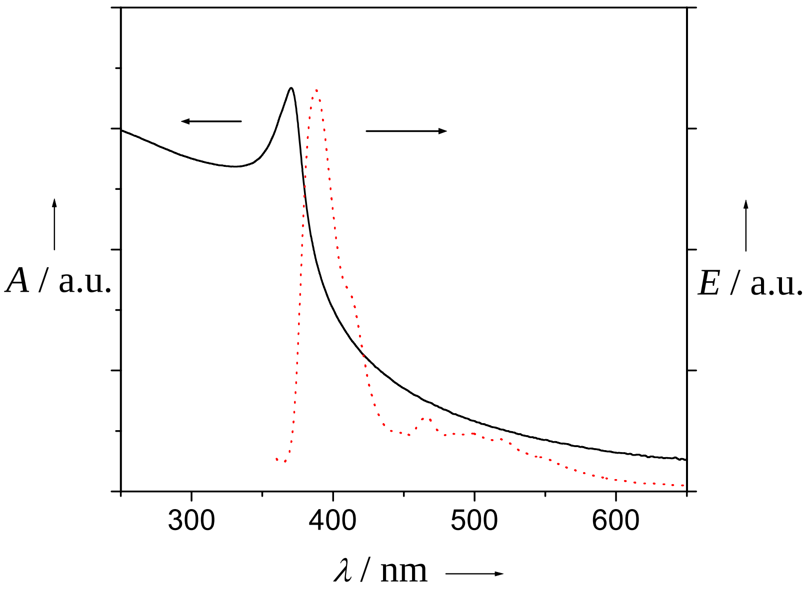


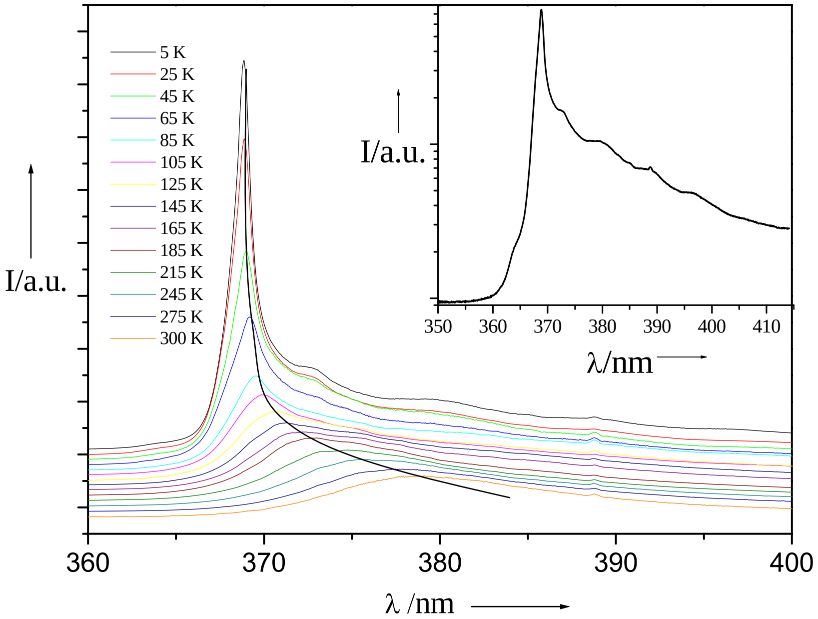




Greene, L.E., Law, M. et al. *Nano Letters* **5**, 1231 (2005).

High Optical Quality

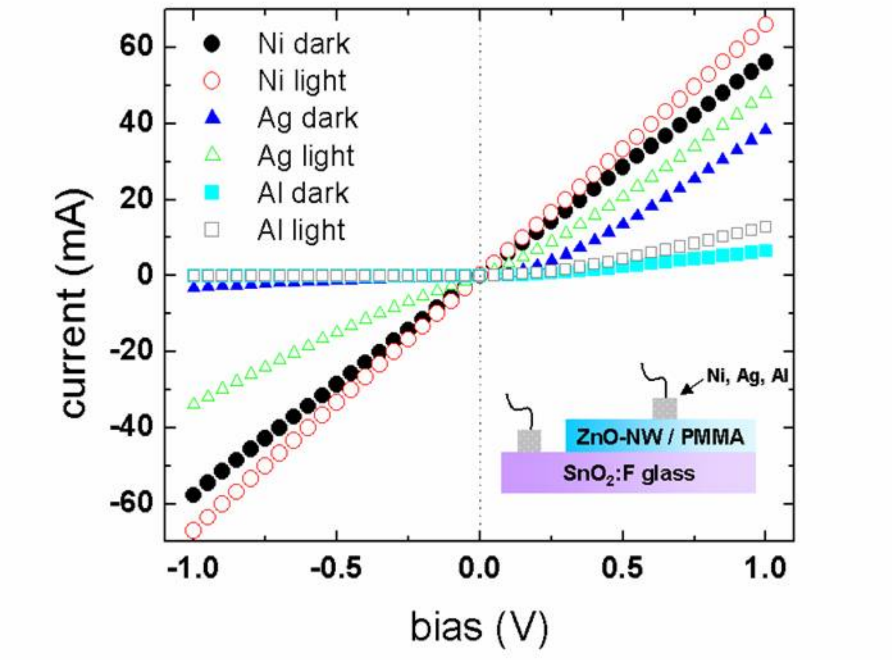




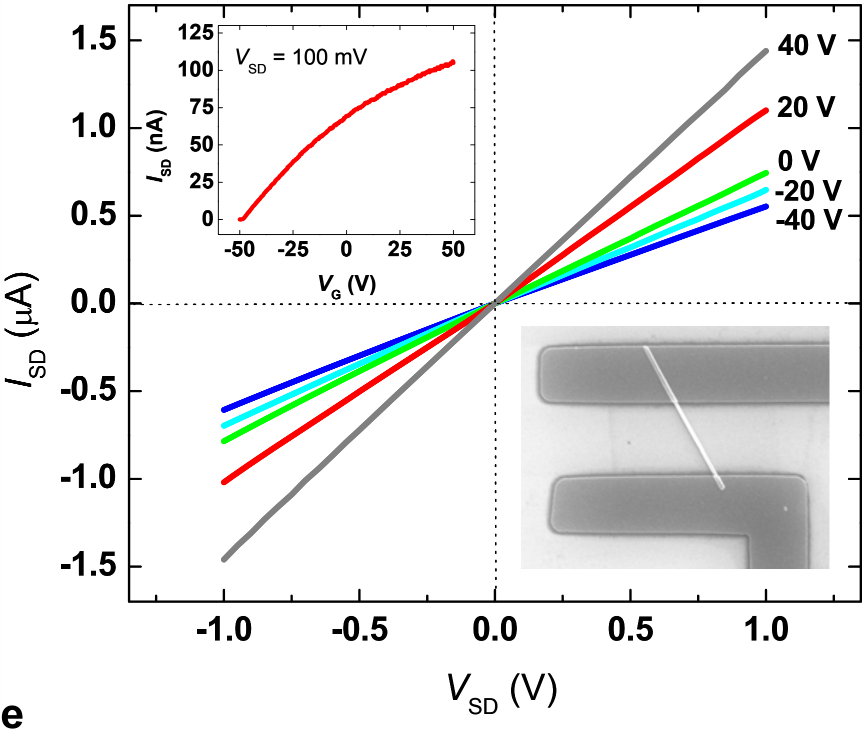
- TEM shows that the nanowires are single crystals
- Wire surfaces are clean (Raman, EELS) after 400 °C treatment

Characterization of Nanowire Arrays

Electrical: **Ohmic wire-substrate contacts**



FETs: Wires have high e$^-$ mobility

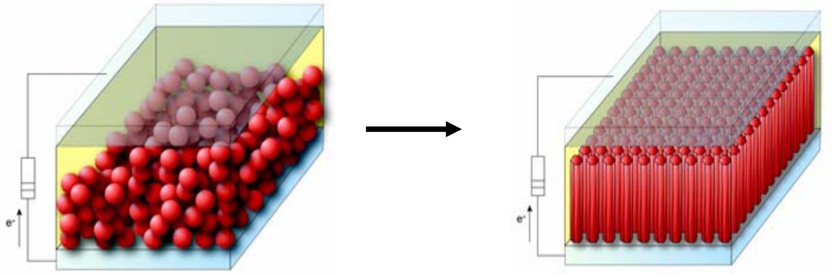


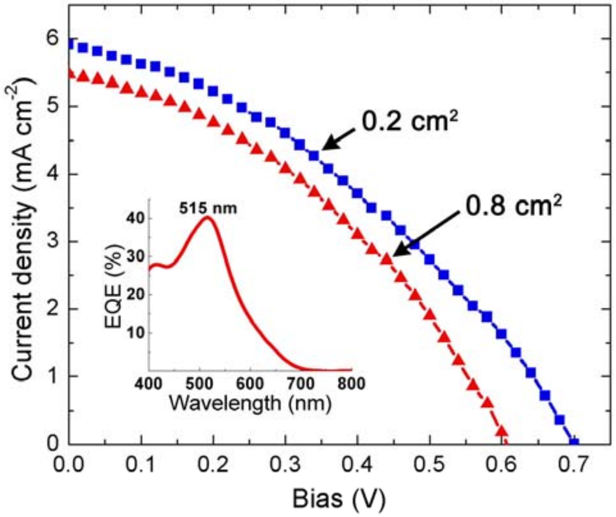
- **Individual wires are electrically conductive**

  ρ = 0.1 - 1 Ω cm
  mobility: 1-5 cm^{2}V^{-1}s^{-1}
  electron diffusitivity: D$_n$=0.05-0.5 cm^{2}s^{-1} [$D = k_B T\mu/e$]
  Ensure larger electron diffusion length, avoiding possible interfacial recombination

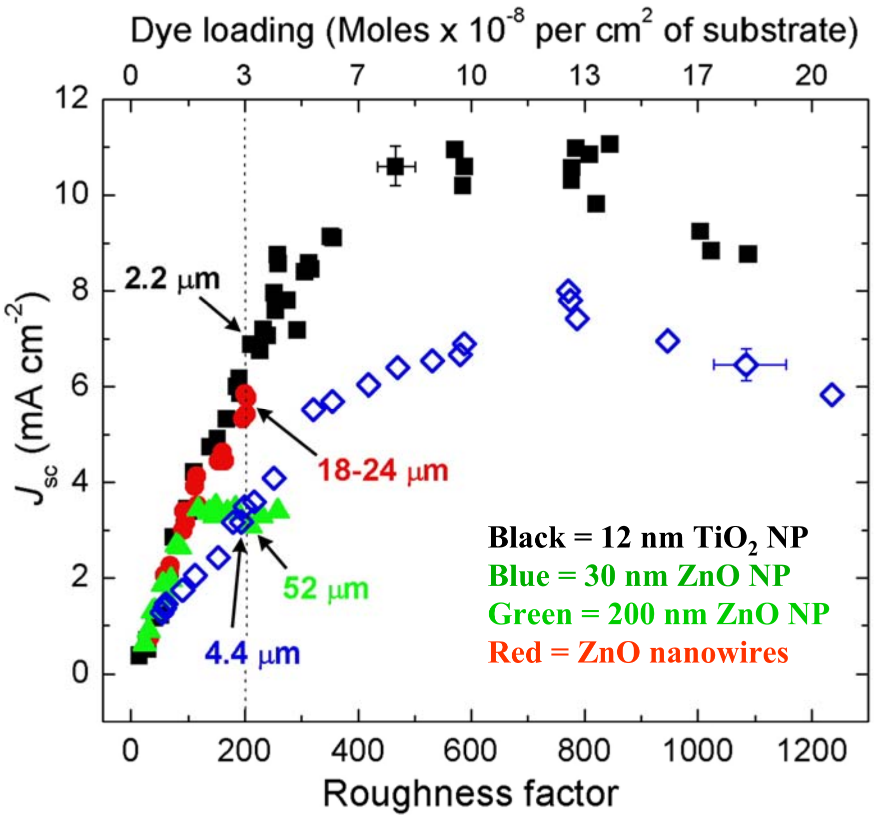
Law, M., Greene, L. et al.
Nature Mater. **4**, 455 (2005).

Nanowire based DSC





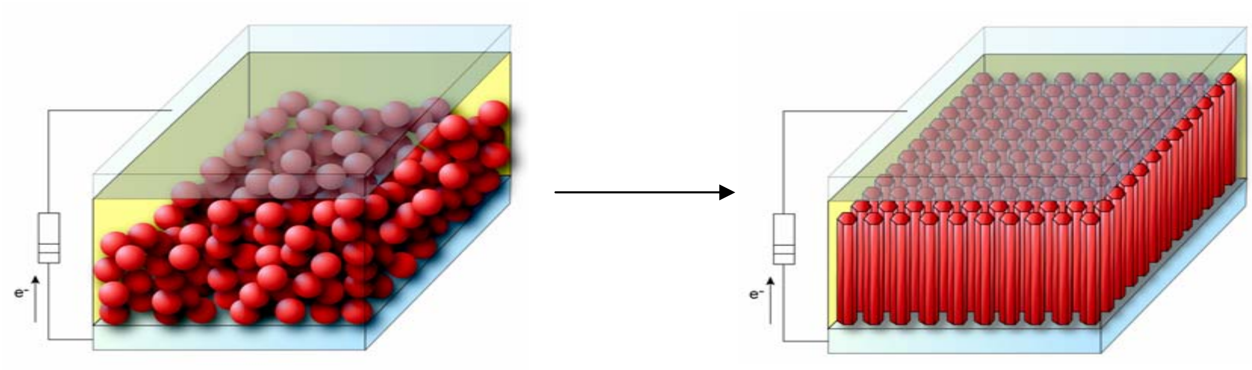
η_{PCE} = **1.5%** under AM 1.5 G conditions

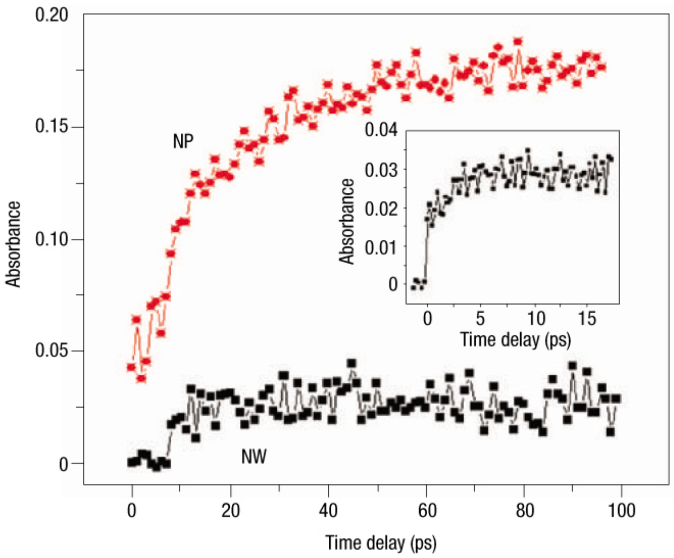


- NW cells are competitive with thin TiO_2 nanoparticle cells (η_{cc} ~ 100%)
- NW cells outperform ZnO nanoparticle cells

Law, M., Greene, L. et al. *Nature Mater.* **4**, 455 (2005).

Nanowire DSC





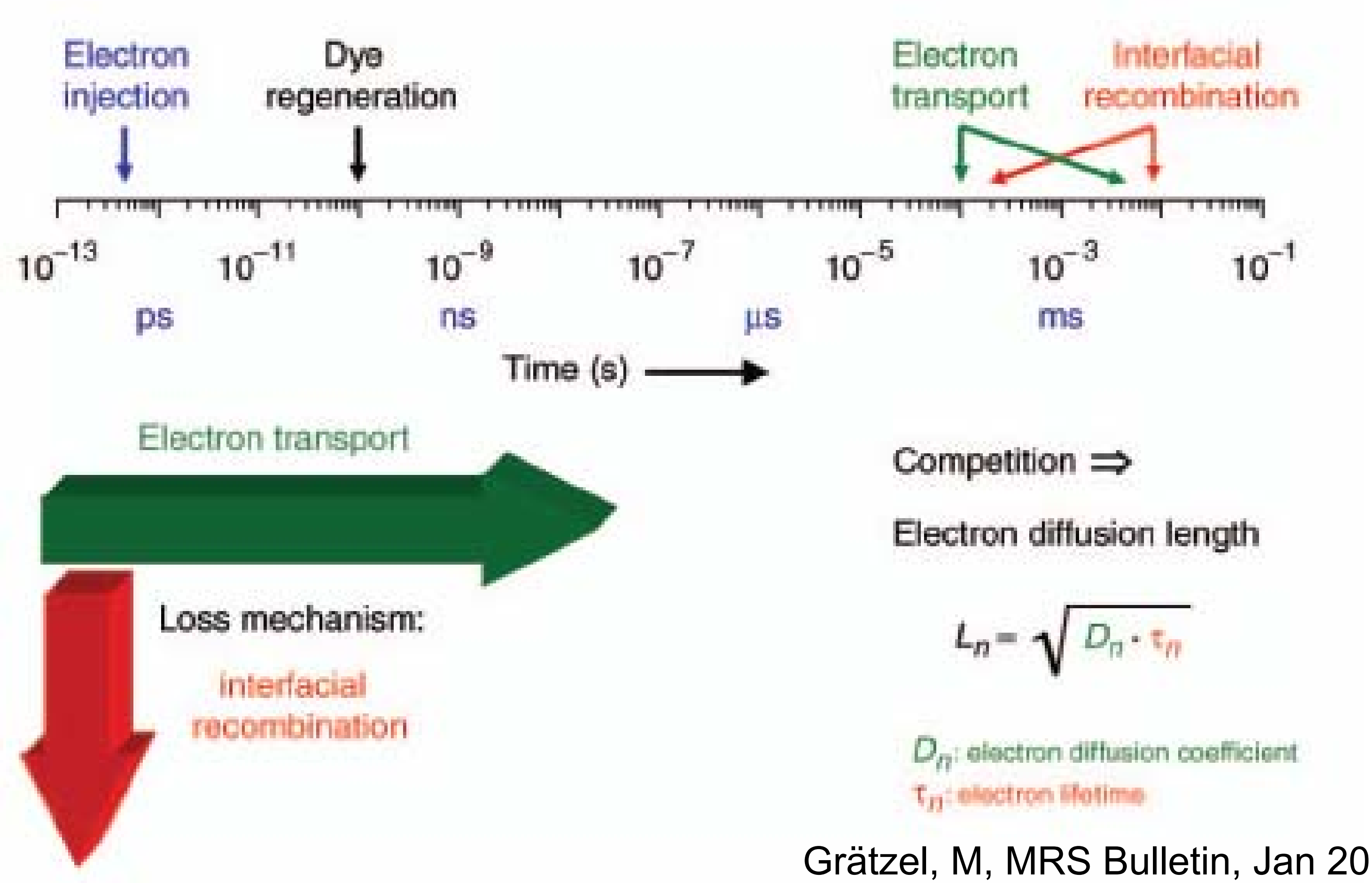
Faster electron injection in NW cell

Bi-exponential (<250fs, 3ps)

vs.

Tri-exponential (<250fs, 20ps, 200ps)

Time Scale for Electron Injection and Transport

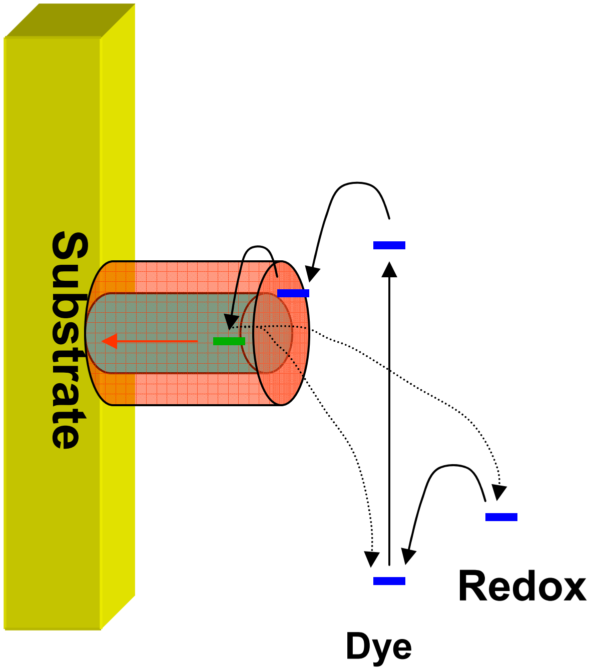


Grätzel, M, MRS Bulletin, Jan 2005

Engineer active interface to reduce recombination

Core-sheath Nanowire Cells

Overcoat the nanostructured electrode with an insulating or semiconducting oxide



Reduce recombination

- Physically separate electrons and holes
- Form a tunneling barrier
- Passivate recombination centers on oxide surface

Shift band edge to increase V_{oc}

- Use an oxide with a higher band edge energy
- Form dipole layer that bends band upwards

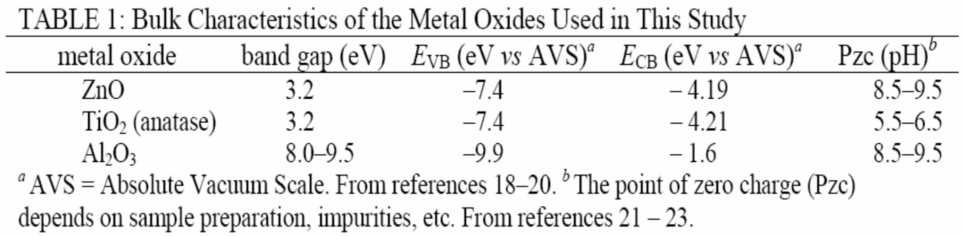


TABLE 1: Bulk Characteristics of the Metal Oxides Used in This Study

metal oxide	band gap (eV)	E_{VB} (eV *vs* AVS)[a]	E_{CB} (eV *vs* AVS)[a]	Pzc (pH)[b]
ZnO	3.2	−7.4	− 4.19	8.5–9.5
TiO_2 (anatase)	3.2	−7.4	− 4.21	5.5–6.5
Al_2O_3	8.0–9.5	−9.9	− 1.6	8.5–9.5

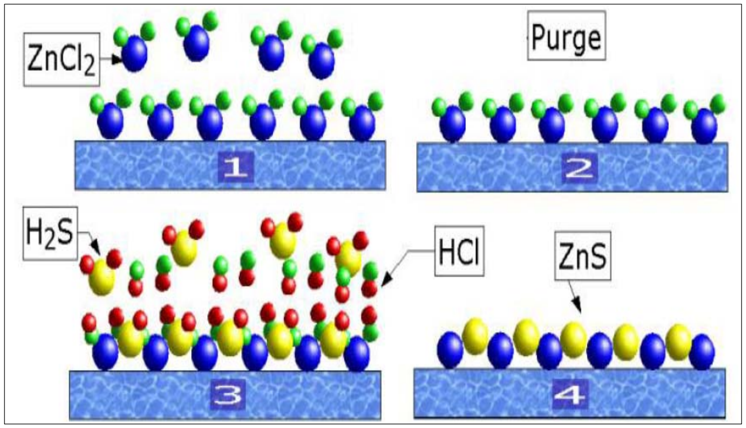
[a] AVS = Absolute Vacuum Scale. From references 18–20. [b] The point of zero charge (Pzc) depends on sample preparation, impurities, etc. From references 21 – 23.

Gregg, B. NREL.

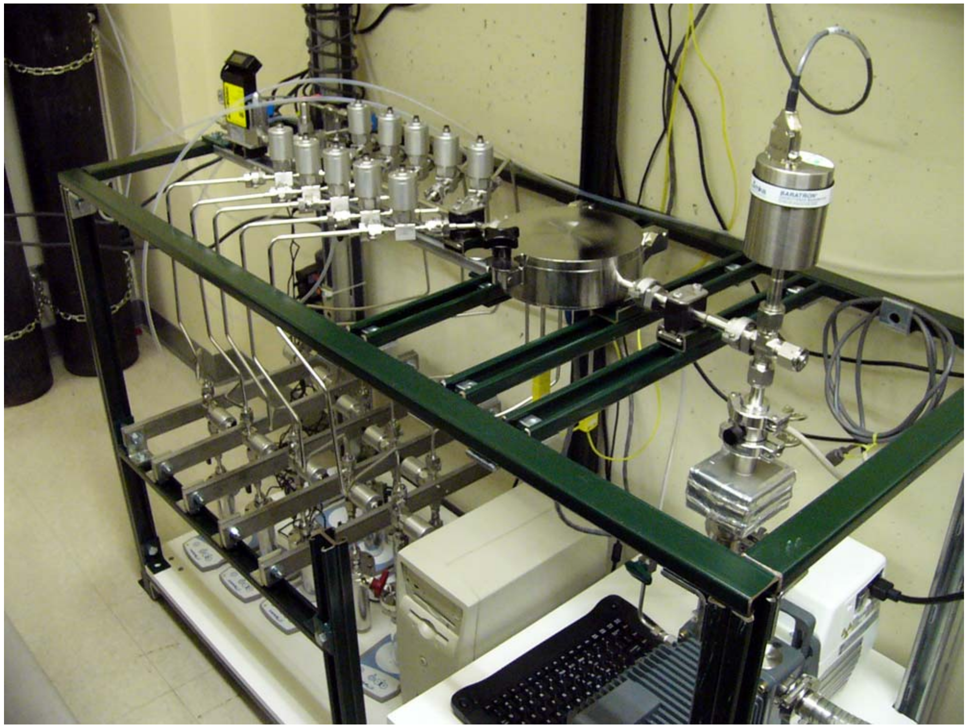
Atomic Layer Deposition (ALD)

Oxides: Al_2O_3, TiO_2, Ta_2O_5, Nb_2O_5, ZrO_2, HfO_2, SnO_2, ZnO, La_2O_3, Y_2O_3, CeO_2, Sc_2O_3, Er_2O_3, V_2O_5, SiO_2, In_2O_3, ...
Perovskites: $SrTiO_3$, $BaTiO_3$, $LiNbO_3$, $LaMnO_3$ …
Nitrides: AlN, TaN_x, NbN, TiN, MoN, ZrN, HfN, GaN, ... **Fluorides**: CaF_2, SrF_2, ZnF_2, ...
Metals: Pt, Ru, Ir, Pd, Cu, Fe, Co, Ni, ... **Carbides**: TiC, NbC, TaC, ...
Mixed structures: $AlTiN_x$, $AlTiO_x$, $AlHfO_x$, SiO2:Al, $HfSiO_x$, ... **Sulfides**: ZnS, SrS, CaS, PbS, ...
Nanolaminates: HfO_2/Ta_2O_5, $TiO2/Ta_2O_5$, TiO_2/Al_2O_3, ZnS/Al_2O_3, ATO (AlTiO) ...
Doping: ZnO:Al, ZnS:Mn, SrS:Ce, Al_2O_3:Er, ZrO_2:Y, ... rare earth metals (Ce3+, Tb3+ etc.) also co-doping

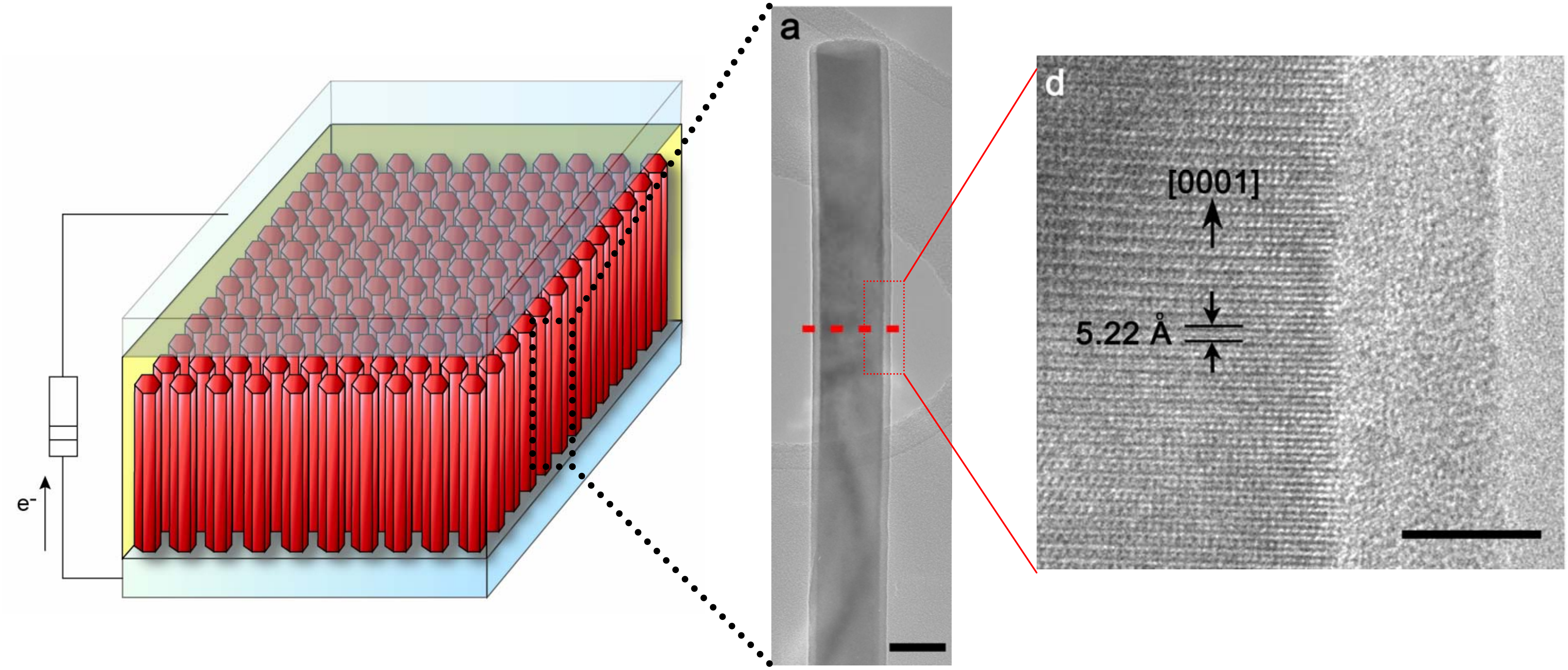
Example: ZnS



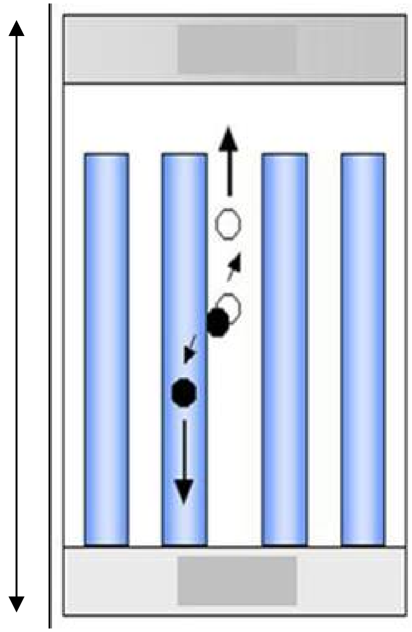
Planar Systems, Inc.

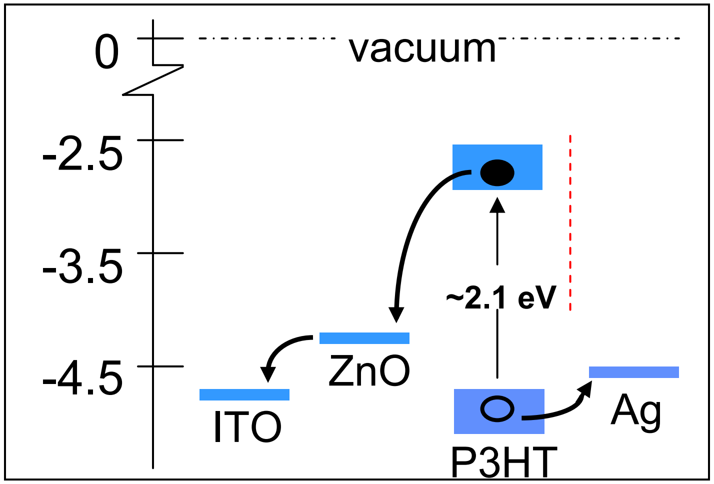


Core-sheath Nanowire Dye-sensitized Solar Cells

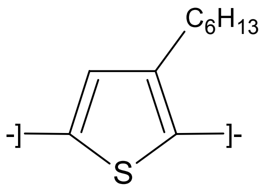


Nanowire-polymer Hybrid Cell

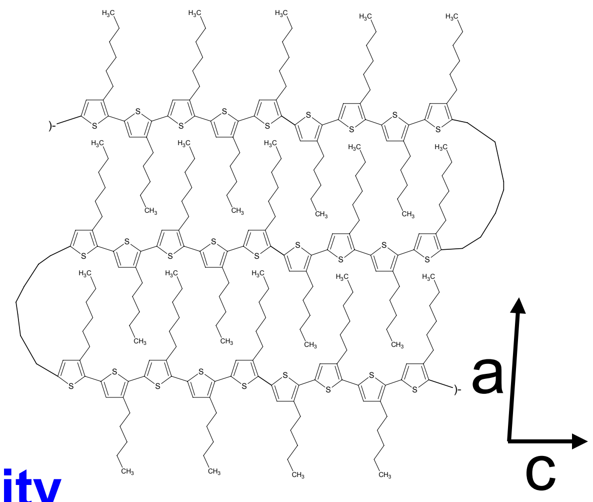


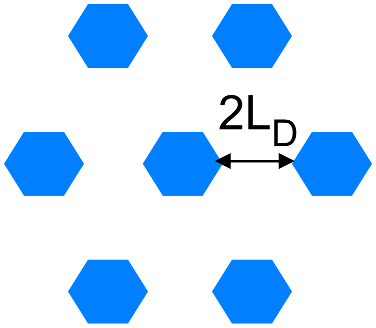


Poly(3-hexylthiophene)



$2L_D$ ~ 20 nm

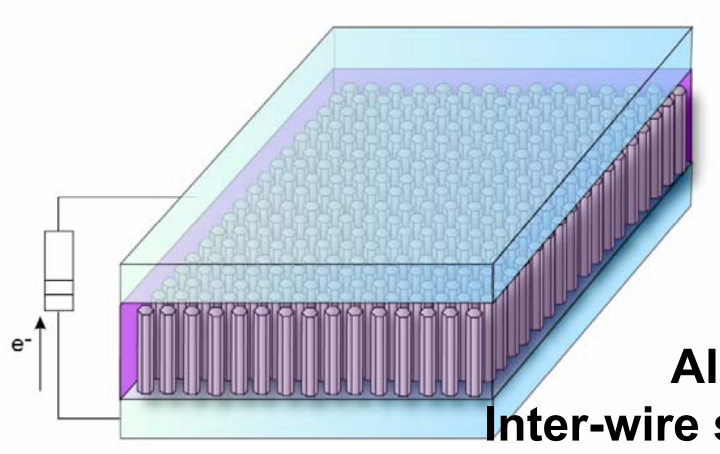


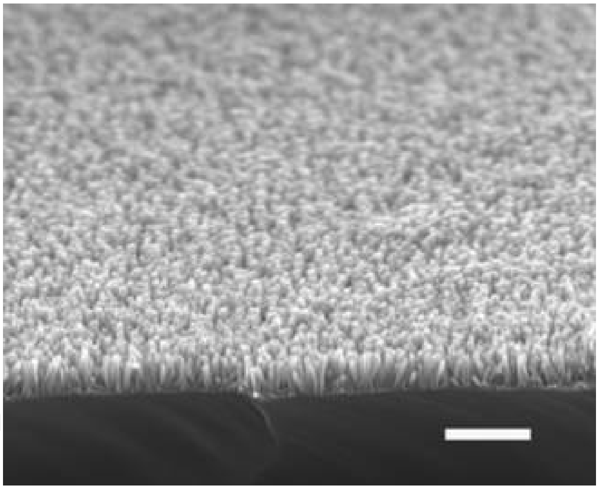


Target nanowire array

1) **ultrahigh nanowire density**
2) **short, thin nanowires**
3) **nanowires normal to substrate**

Nanowire-polymer Composite Film



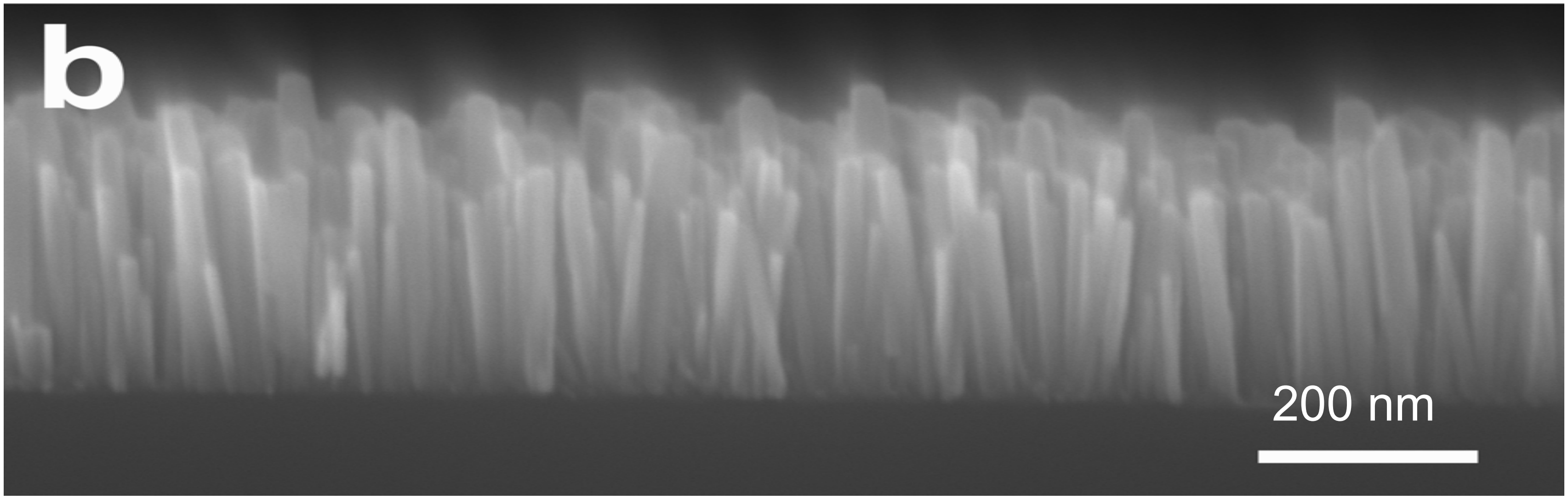


Aligned wires

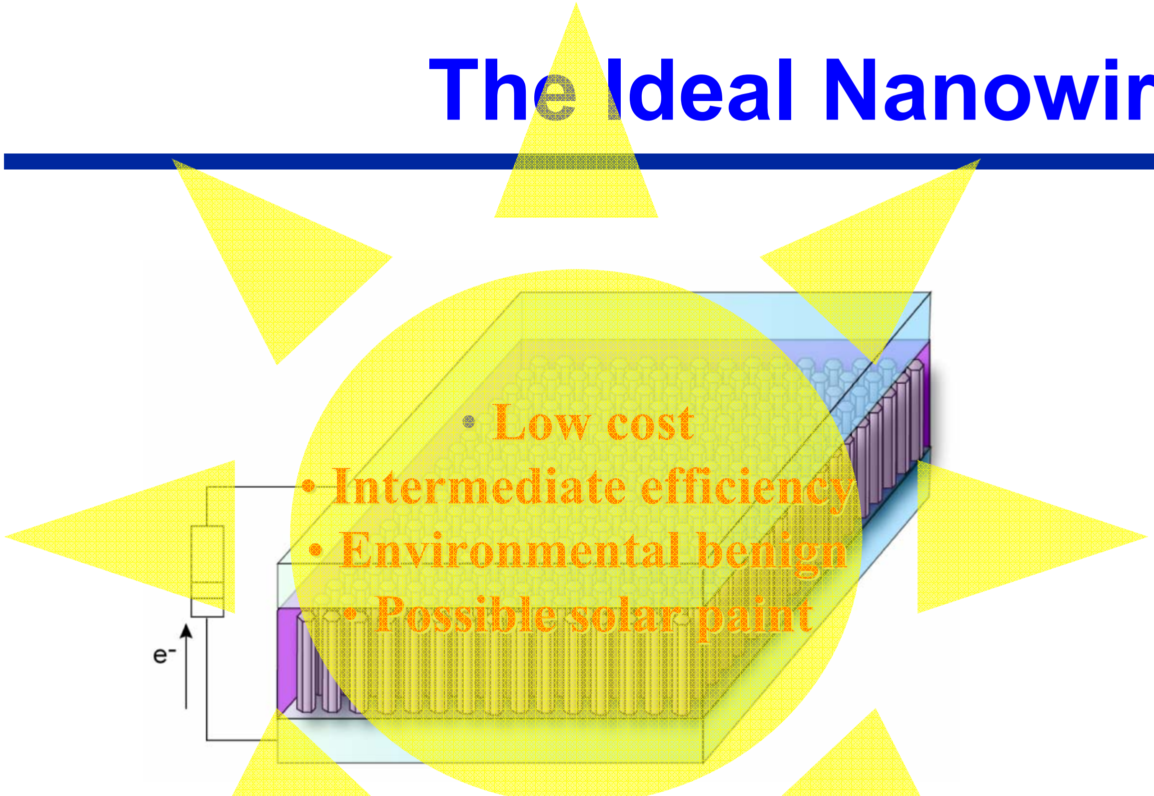
Inter-wire spacing is 10-50 nm

$2L_D$ for P3HT ~ 20 nm

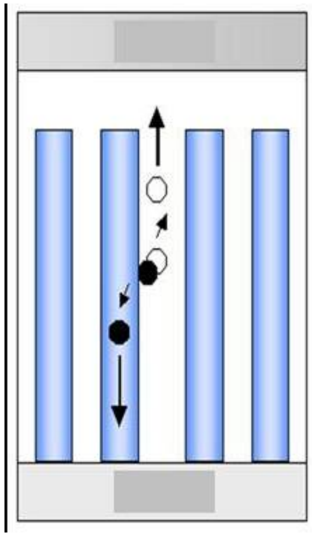
Thickness 200-300 nm

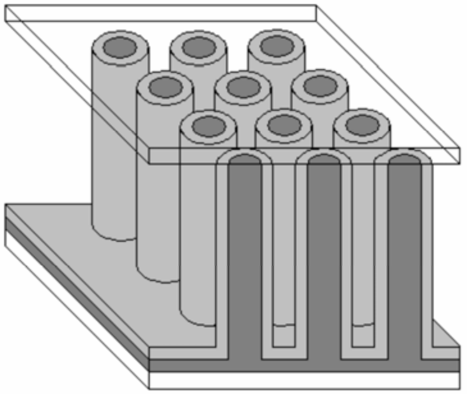


The Ideal Nanowire Cell



- Low cost
- Intermediate efficiency
- Environmental benign
- Possible solar paint





- Fully interdigitated donor-acceptor interface
- Acceptor wire array: high density, smaller band gap
- Donor: polymer/nanoparticles, maximize absorption
- Interface engineering: reduce recombination.
- Applicable to DSC, hybrid, and conventional semiconductor cells.

N. Lewis

Acknowledgement

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Dwaud Tan

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DOE

ITRI