Dye Sensitized Solar Cells: R&D Issues

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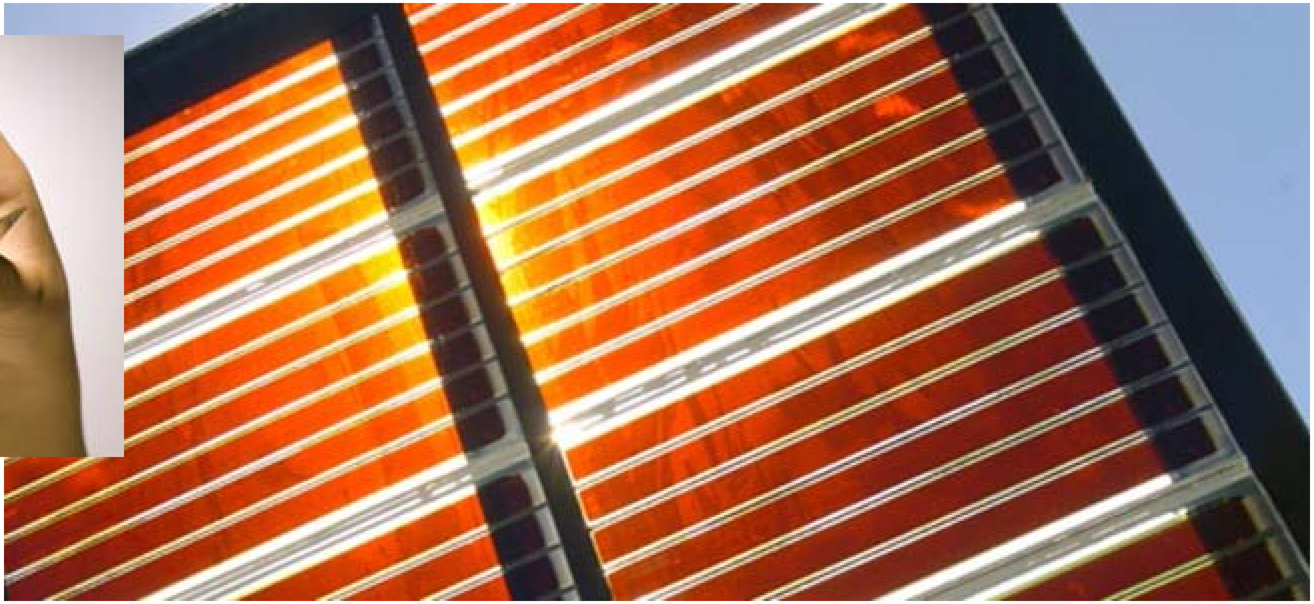
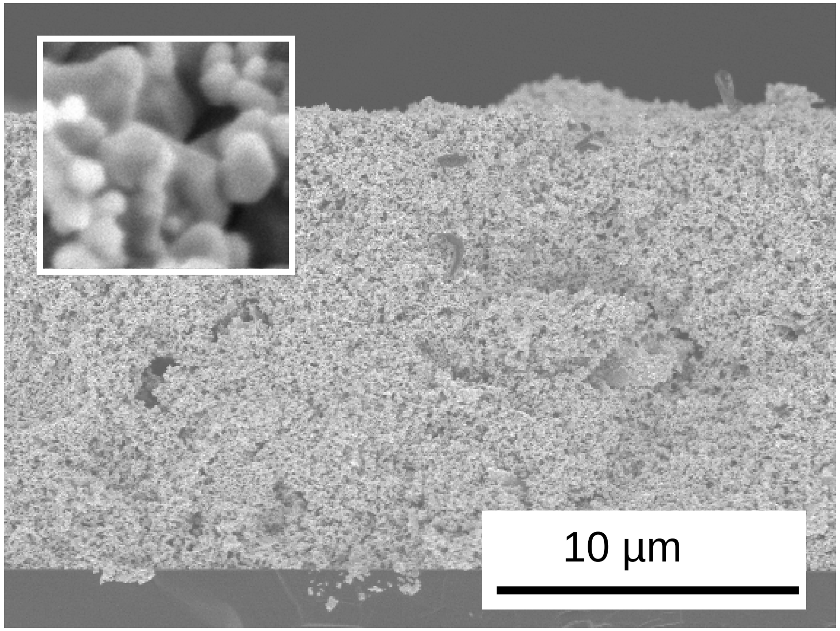
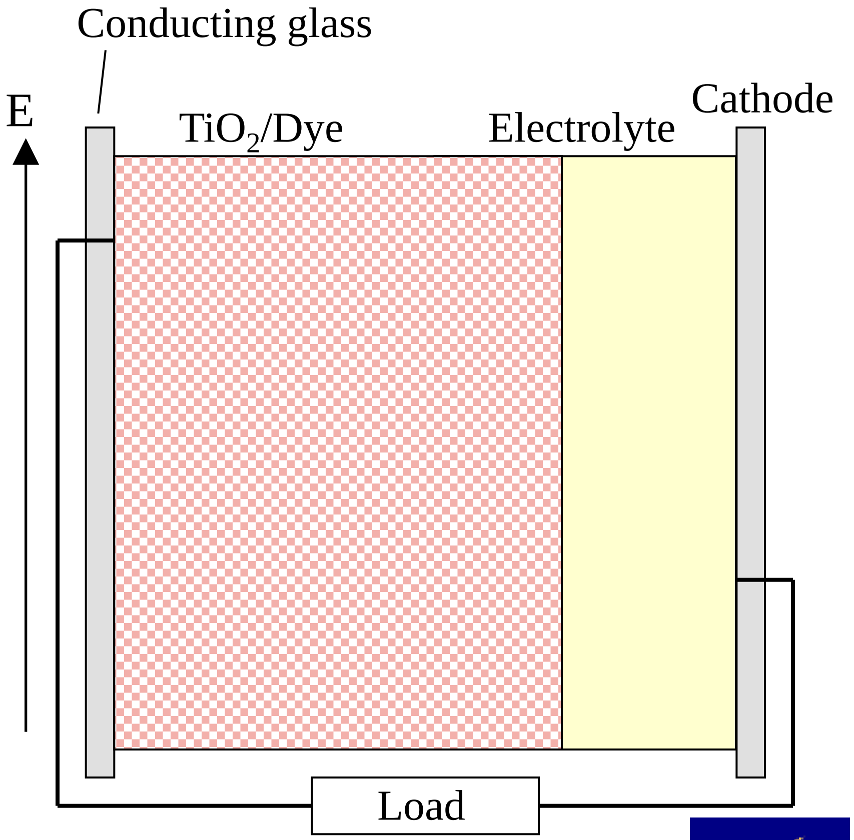


NSF PV Workshop
May 2010

Dye Sensitized Solar Cells

- TiO_2 sensitized with monolayer of dye for light harvesting.
- Semiconductor provides high surface area, good electron transport.
  - Nanocrystalline, mesoporous TiO_2 film on TCO/glass.
- Redox mediator completes circuit.
- Record efficiency 11.1%

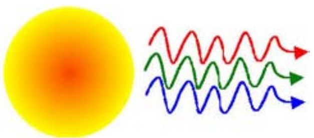


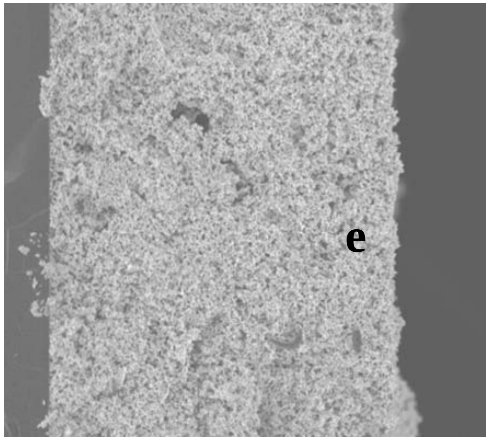


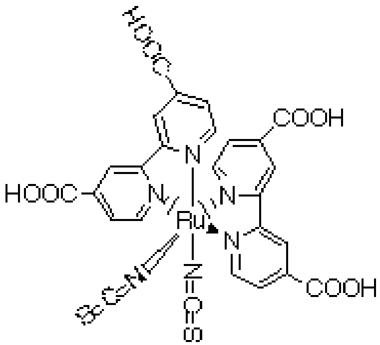
O'Regan and Gratzel, *Nature*, 1991.

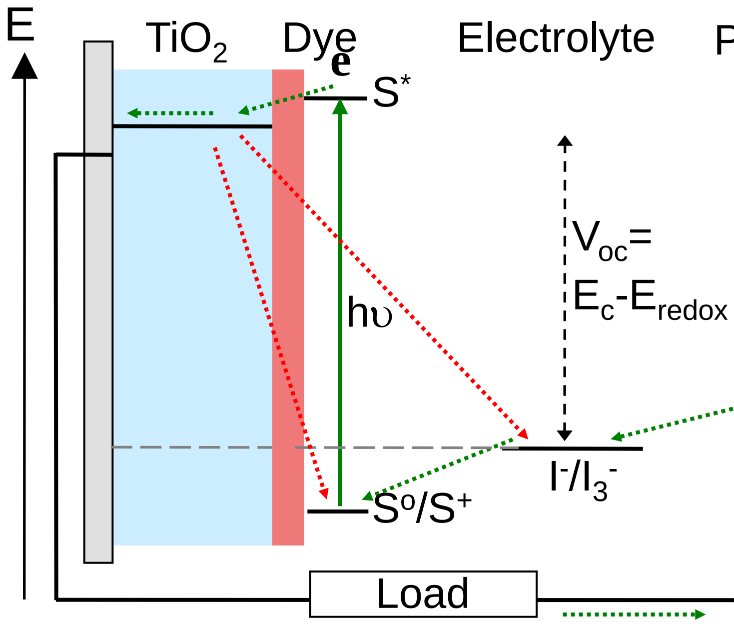
Gratzel, *Nature*, 2001.

Elementary Processes in DSSCs

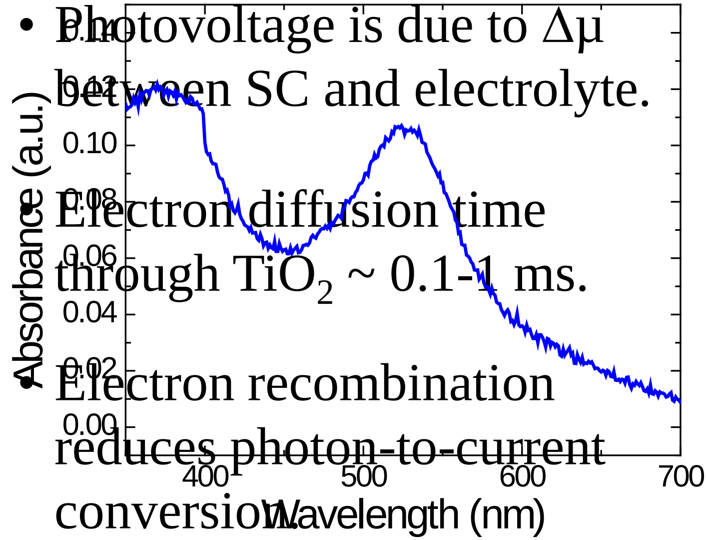






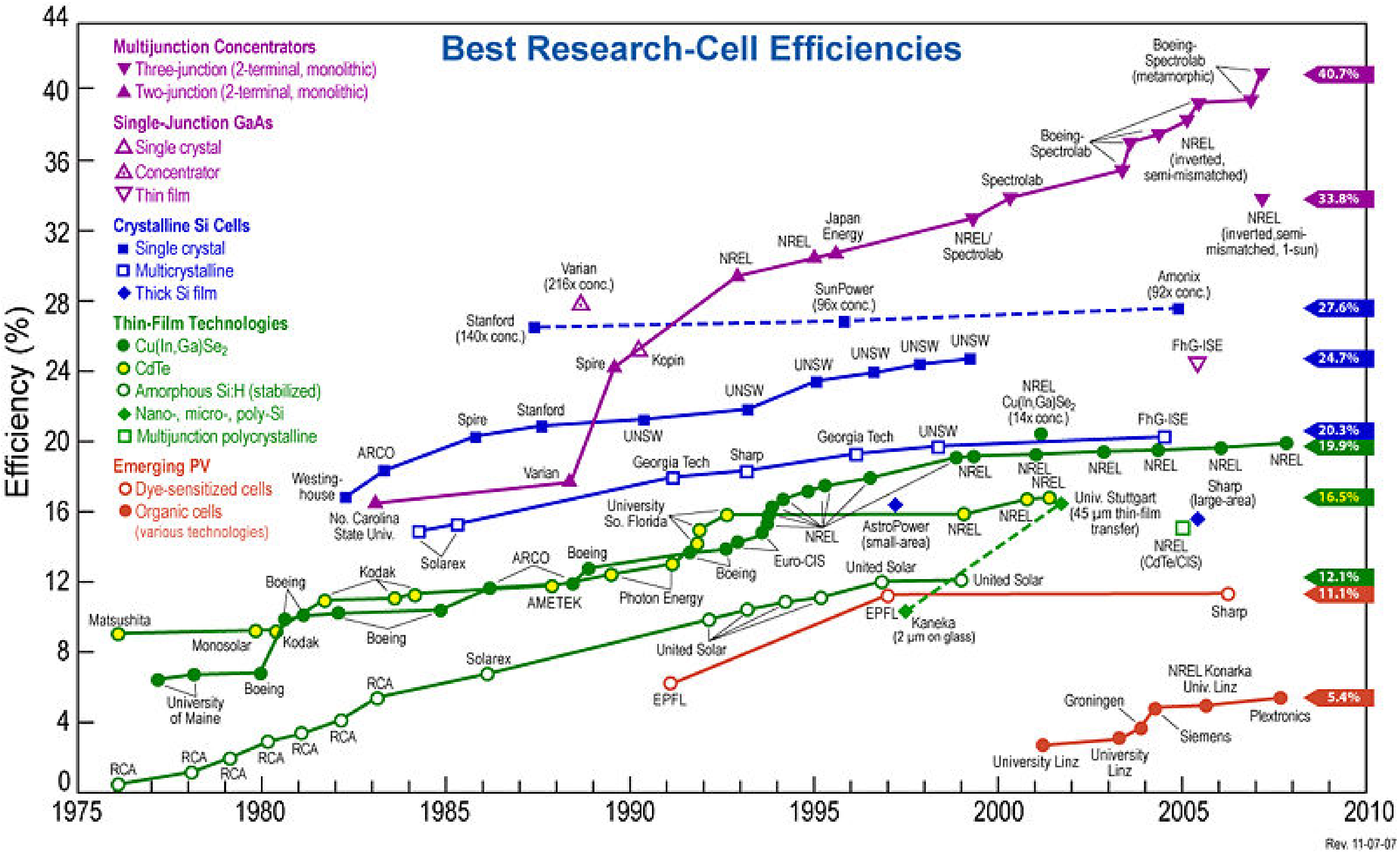


- Electron injection into TiO_2 is rapid, t ~ 0.1-1 ps.
- Injection quantum efficiency ~ 1.
- Photovoltage is due to Δμ between SC and electrolyte.
- Electron diffusion time through TiO_2 ~ 0.1-1 ms.
- Electron recombination reduces photon-to-current conversion.

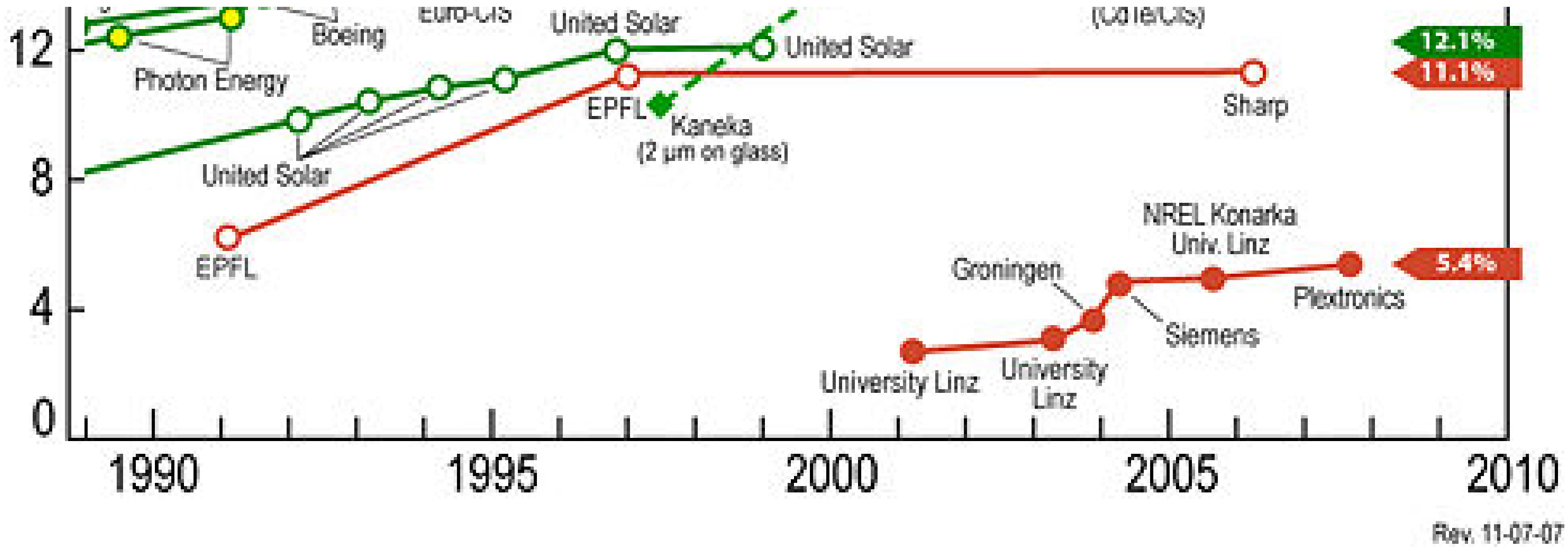


$$I_3^- + 2e^- \longrightarrow 3I^-$$

Efficiencies Over Time



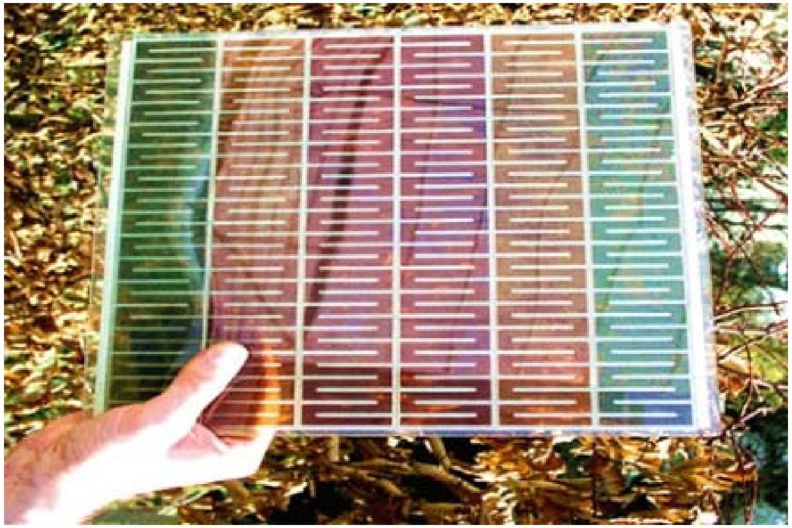
Efficiencies Over Time



- Champion research cell (as of Jan. 2010)- Sharp 11.1%
  - J_{sc} 22.0 mA/cm^2, V_{oc} 0.729 V, FF 65.2%
  - Gratzel has unconfirmed cell >12%
- Champion module: Sony 8.5% (17 cm^2)

Advantages of DSSCs

- Low cost
  - Inexpensive to manufacture, roll-to-roll processing possible
  - Low embodied energy (<1 yr payback)
- Non-toxic, earth-abundant materials (except Pt, Ru)
- Good performance in diverse light conditions: high angle of incidence, low intensity, partial shadowing
- Can be lightweight, flexible
- Can be semi-transparent, bifacial, selected colors

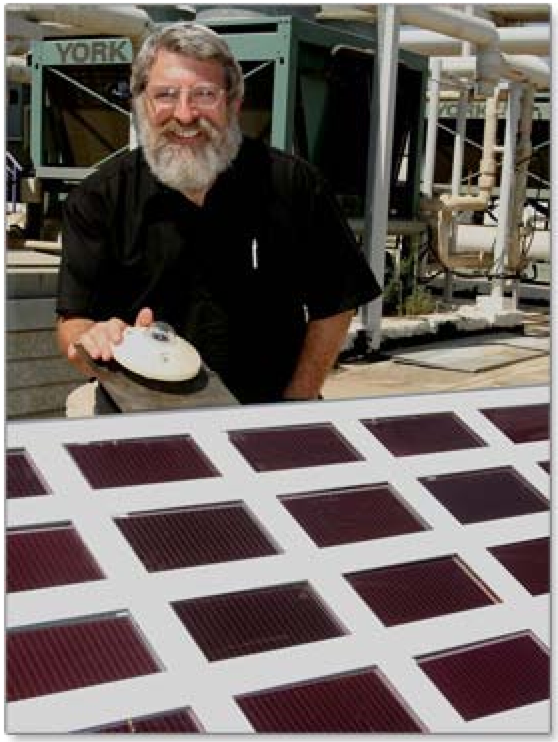


DSSC Commercialization

http://www.dyesol.com/conference09

- G24 Innovations
  - 120 MW plant, on flexible metal foil
  - First commercial product in 2009
- Dyesol (materials and processing tools)
- 3GSolar
- SolarPrint
- Samsung, Sharp, Sony, Toyota
- Many start-ups: TiSol, etc.

Rooftop



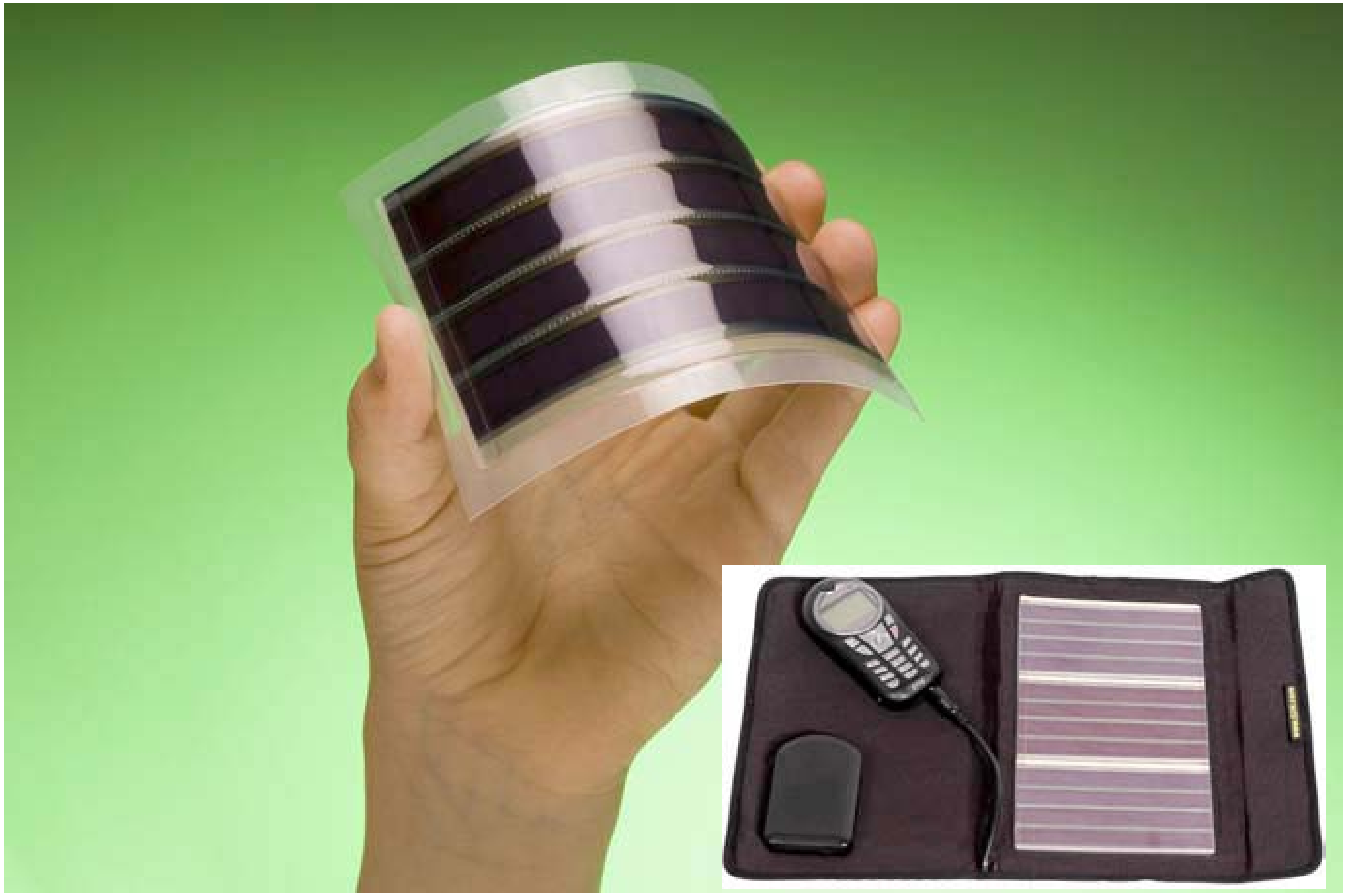
3G Solar (Israel)

Aisin Seiki / Toyota (Japan)

Building-Integrated PV

http://www.samsungsdi.com

Portable Electronics



G24 Innovations (Wales)

Indoor / Decorative

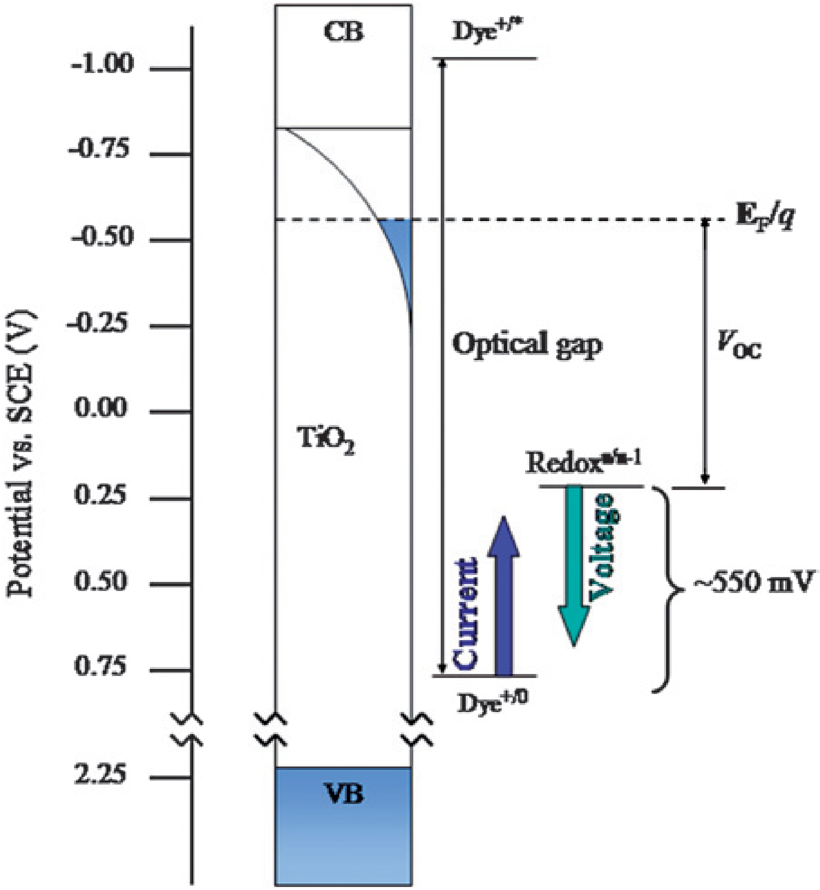
(c)AFP/Yoshikazu TSUNO
http://www.afpbb.com/article/environment-science-it/environment/2548884/3605307

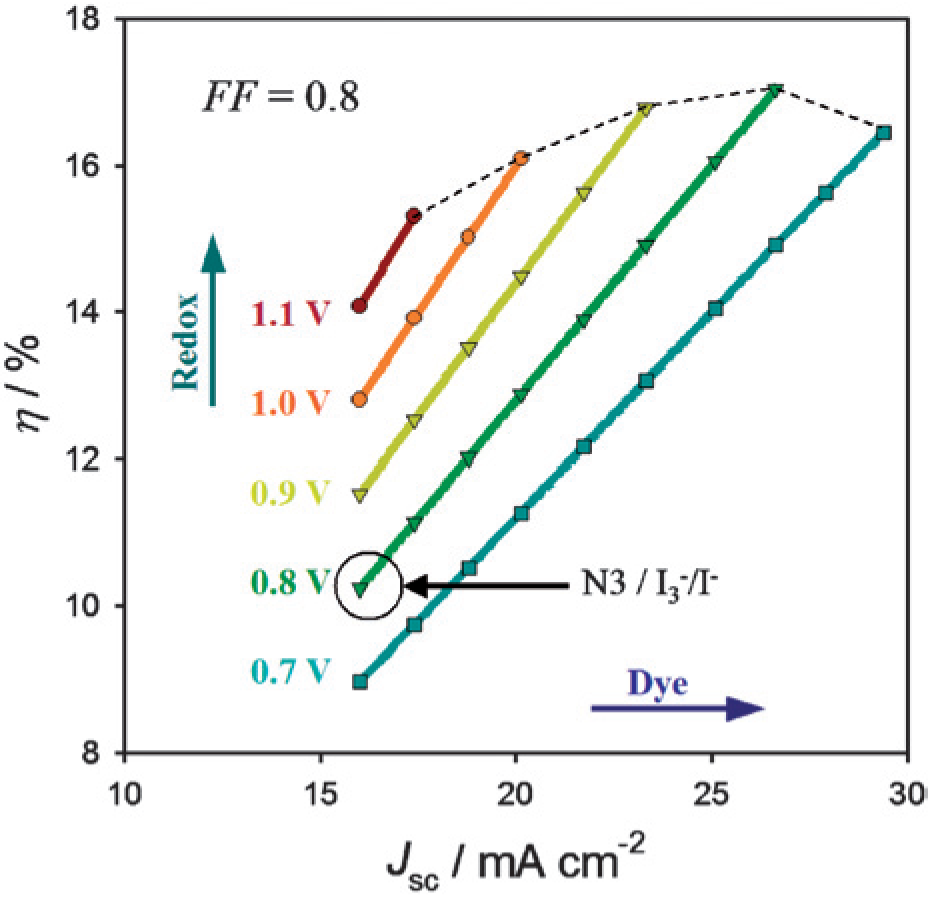
Aisin Seiki (Japan)

R&D Challenges for DSSCs

- Lab efficiencies <12% and stagnating
  - Low red and near-IR absorption
  - Low extinction coefficient requires high surface area
  - Only I^-/I_3^- redox couple has slow recombination kinetics, but it has unnecessarily large overpotential
- Stability and robustness
  - Liquid electrolyte is undesirable, but solid state hole conductors give lower efficiency
  - 10^8 turnovers of dye required for 20 year lifetime
  - I^-/I_3^- is corrosive

Margins to Increase Efficiency





Estimated efficiency of DSSCs employing dyes with increased spectral coverage in conjunction with redox shuttles with varying solution potentials. Efficiencies > 15% are, in principle, achievable in many configurations when there is minimal overpotential (ca. 200 mV) for dye regeneration (dotted line).
From Hamann, *Energy & Env. Sci.*, 2008, p. 66.

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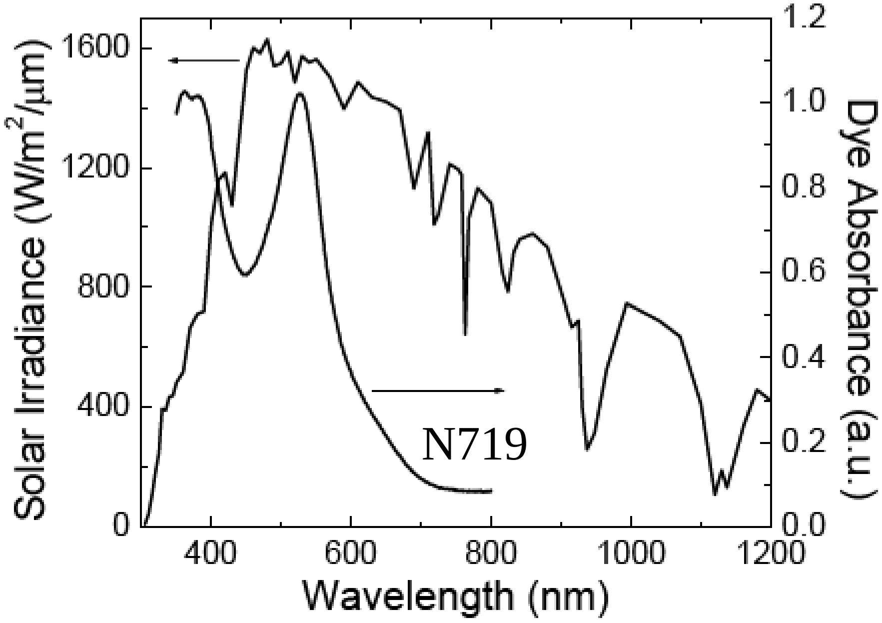
New Sensitizers

- Requirements for sensitizers:
  - Broad spectral coverage
  - High absorption cross-section (enables thinner devices)
  - Appropriate energetics to match oxide, redox
  - Fast kinetics for injection, regeneration
  - Stable for many (~10^8) turnovers



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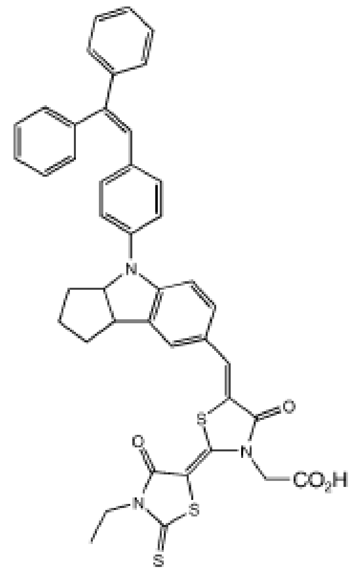
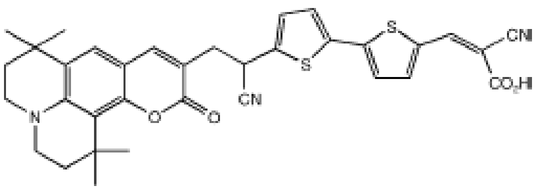
Alternative Sensitizers

- Strategies
  - Ligands to shift bands, broaden spectral coverage
  - Other classes of dyes
  - Donor-acceptor molecules
  - Porphyrin oligomers
  - Dye multilayers
  - Blends or tandem cells
  - Quantum dots

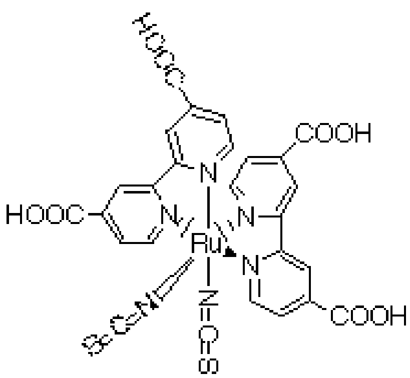
indoline



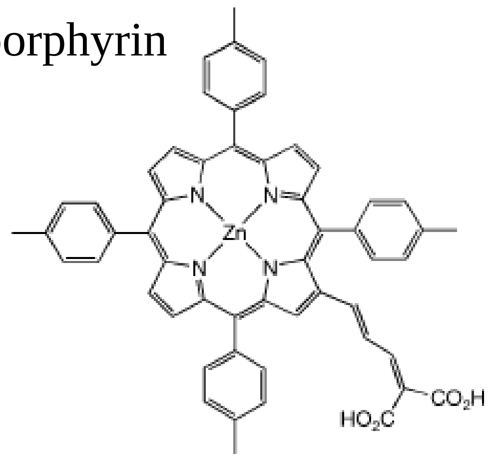
coumarin



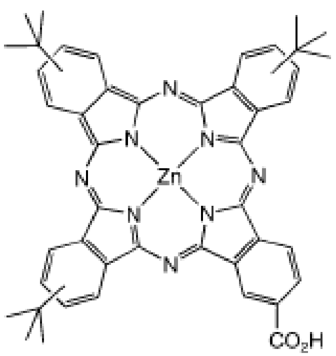
N3 (Ru bpy)



porphyrin



phthalocyanine



New Redox Couples

- Requirements:
  - Fast dye regeneration
  - Slow recombination with electrons from oxide (only I^-/I_3^- is slow enough for conventional cell)
  - Redox potential matched to dye HOMO (I^-/I_3^- has 500 mV overpotential, reducing V_{oc})
  - Stable and non-corrosive

- Alternatives:
  - Halogens: Br^-/Br_3^-
  - Pseudohalogens: $(SeCN)_2/SeCN^-$
  - Cobalt polypyridyl complexes
  - $Cu(dmp)_2^{2+/+}$ (dimethylphenanthroline)

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New Photoanodes

- Requirements:
  - Large surface area for dye loading
  - Sufficiently fast electron transport to the substrate compared to recombination (fast transport not necessary for conventional cell, but will be for other redox couples)
  - Open pore structure for dye sensitization and transport of redox couple
  - Transparent (but scattering can help), with appropriate band positions
  - For commercialization- scalable and inexpensive

- Alternatives:
  - Other oxides: ZnO, SnO_2, $SrTiO_3$
  - Other architectures
    - Aerogels: larger surface area, larger porosity, less robust
    - Nanowire/nanotube arrays: directed transport, but lower surface area

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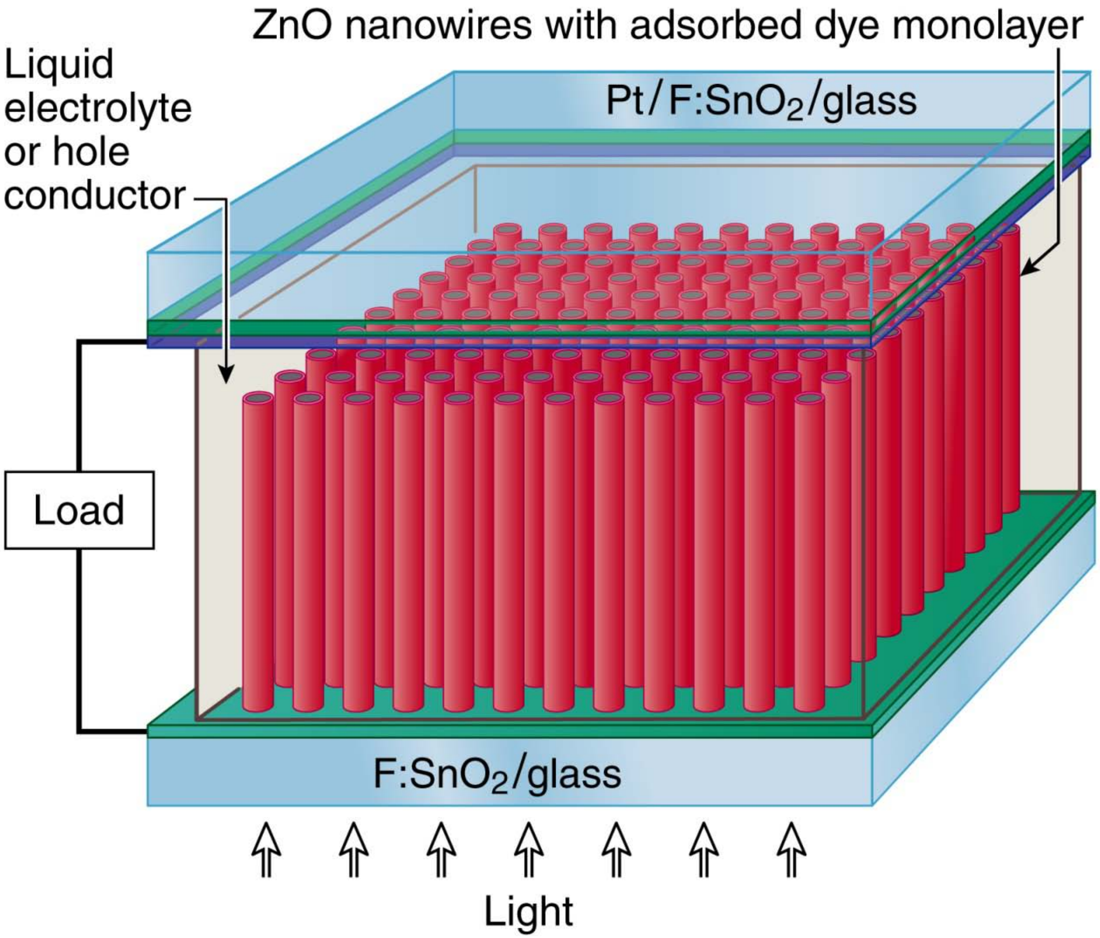
Advantages of Nanowire Arrays

- Nanowires provide a direct path to the substrate for fast charge transport.
- Faster transport can tolerate faster recombination- other redox couples can increase V_{oc} by ~300 mV.
- Aligned pores for facile pore filling and direct path for hole transport.



Baxter, *Nanotechnology*, 2006, S304.
Baxter, *Appl. Phys. Lett.*, 2005, 053114.

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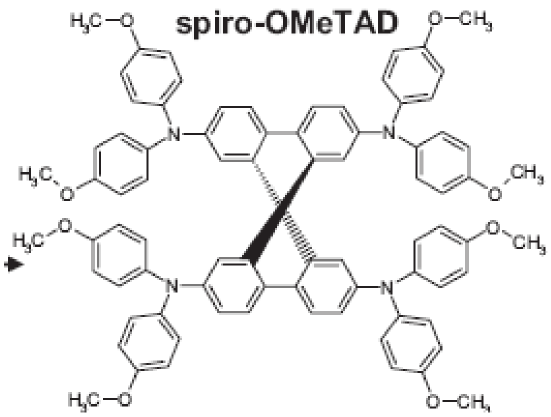
- Optimizing one material at a time has not resulted in significant increases in efficiency in the last 10-15 years.

- Multiple materials must be changed simultaneously to achieve large improvements.

Replacing the Liquid Electrolyte

- Solid state hole conductors are more robust, but efficiencies are lower.
- Difficulties in filling tortuous pore network limits thickness and efficiency.



- Possible alternatives:
  - Solid organic hole conductors: spiro-OMeTAD
    - Max η=4% with 2 μm thickness (Snaith, *Angew. Chem. Int. Ed.*, 2005, p. 6413)
  - Room temperature ionic liquids (molten salts)
    - Imidazolium iodide: η=8.2%, retained 93% performance after 1000 hrs light soak @ 60 ºC (Bai, *Nature Mat.*, 2008, p. 626)
  - Polymer electrolytes, gels
  - Inorganic p-type: CuSCN, CuI
    - Faster recombination than liquid

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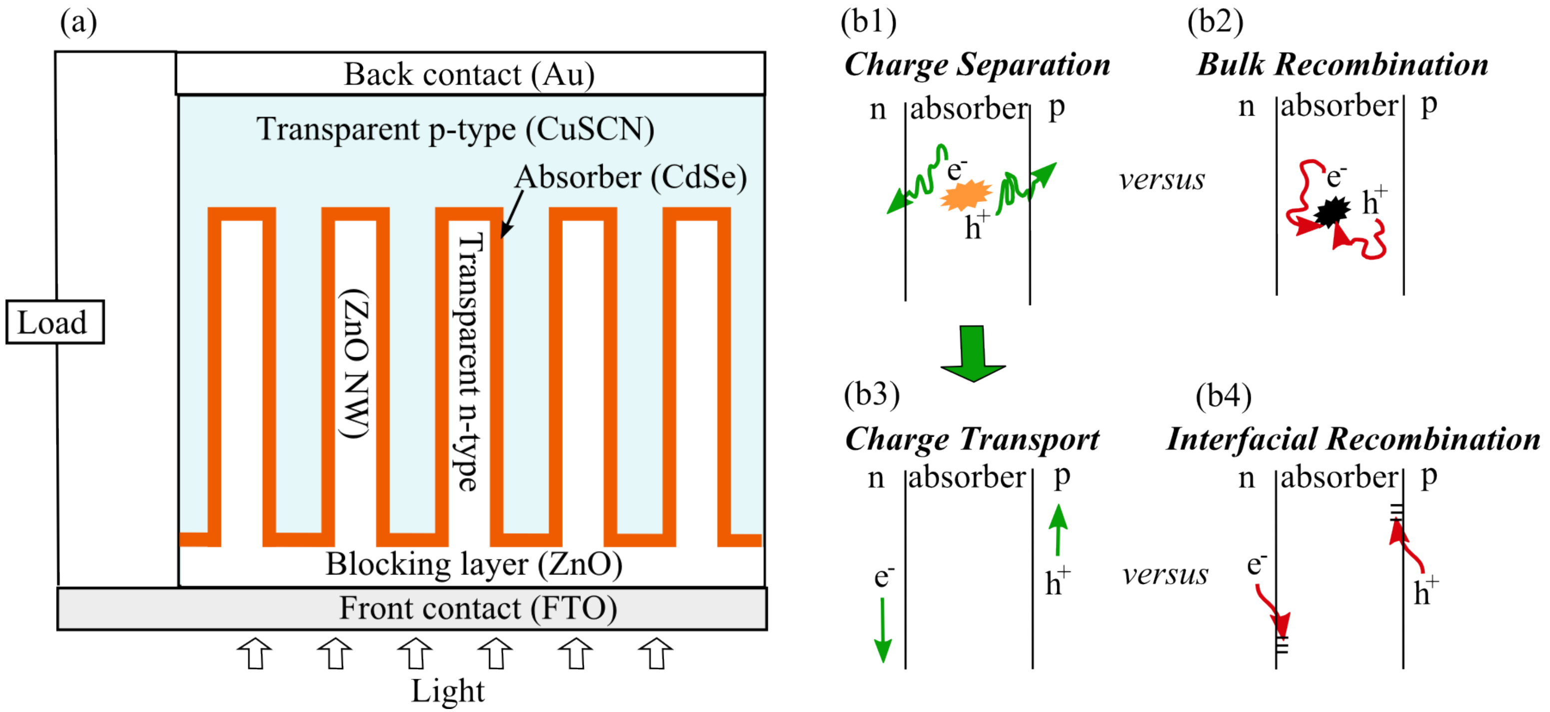
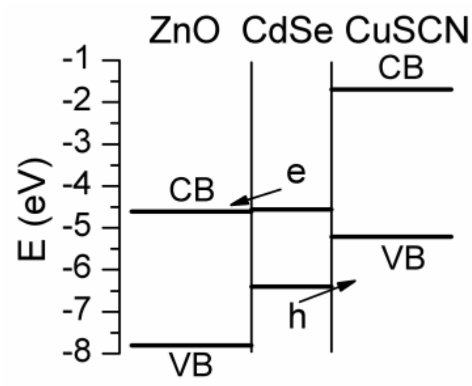
Extremely Thin Absorber Solar Cells



- High absorbance with smaller roughness factor than DSSCs.
- Improved robustness- all inorganic.
- Can offer more efficient charge separation and cheaper processing than planar thin film PV.



On-going work in Baxter Lab (NSF CAREER, CBET-0846464)

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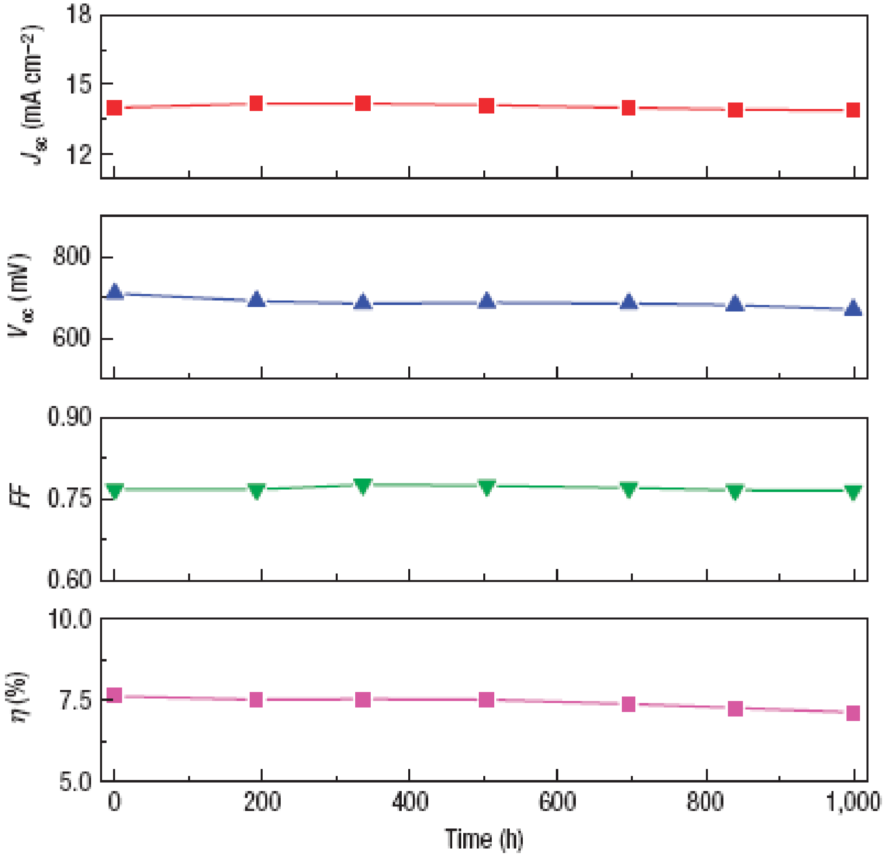
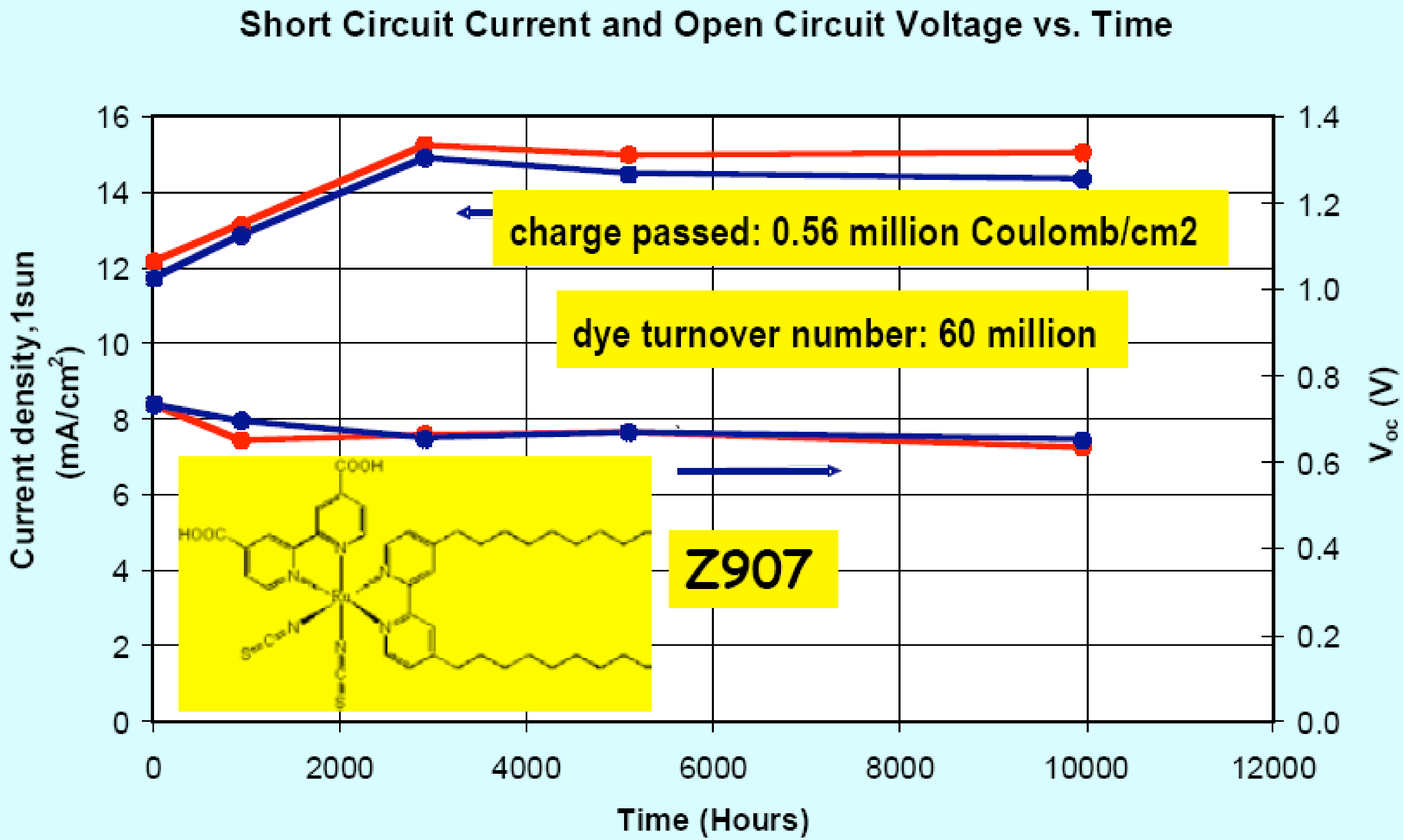
Lifetime Testing of DSSCs

- Requirements for outdoor use (required for Si, but not DSSCs so far)
  - UV plus 55 ºC, 1000 hours
  - 85 ºC, 1000 hours
  - Humidity and temperature cycling (sealing issues)



Ionic liquid DSSC
Bai, *Nature Mat*., 2008, p. 626.

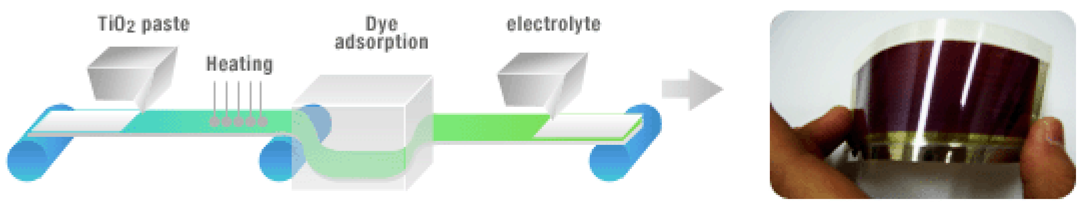
Z907 attains 10'000 hours stability in full sunlight (2-2008) Recently extended to 20'000 hours.



Courtesy: Dr.Ravi K. Harikisun, Dyesol Inc, Australia

Manufacturing

- Low cost, high throughput, robust processing
  - Roll to roll screen printing, inkjet printing etc.



www.samsungsdi.com

www.g24i.com

Summary of Directions for Research

- New combinations of materials to increase efficiency and stability
  - Multiple materials must be changed simultaneously
  - Mainly academic (so far, academics have emphasized efficiency over stability and lifetime)

- Low-cost, high-throughput manufacturing methods
  - Academic and industrial

- New ways to integrate DSSCs for new/emerging markets
  - Mainly industrial

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Useful References

- T.W. Hamann, R.A. Jensen, A.B.F. Martinson, H. Van Ryswyk, and J.T. Hupp. "Advancing beyond current generation dye-sensitized solar cells," *Energy and Environmental Science*. ***2008***, *1*.
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- J.B. Baxter, A.M. Walker, K. van Ommering, and E.S. Aydil. "Synthesis and Characterization of ZnO Nanowires and their Integration into Dye Sensitized Solar Cells," *Nanotechnology*. ***2006***, *17, S304-S312.*
- M. Gratzel. "Photoelectrochemical cells," *Nature*. ***2001,*** *414, 338-344.*
- H. Tributsch. "Dye sensitization solar cells: a critical assessment of the learning curve," *Coordination Chemistry Reviews.* ***2004***, *248, 1511-1530.*
- Y. Bai, Y.M. Cao, J. Zhang, M. Wang, R.Z. Li, P. Wang, S.M. Zakeeruddin, and M. Gratzel. "High-performance dye-sensitized solar cells based on solvent-free electrolytes produced from eutectic melts," *Nature Materials.* ***2008,*** *7, 626-630.*
- Slides from M. Gratzel’s invited talk available at http://www.energy.upenn.edu/solar09.html
- Websites of companies mentioned in earlier slides