Power from the Sun, the Advent of Mesoscopic Solar Cells

"Towards a Sustainable Low Carbon Society"
International Symposium, Hokkkaido University
Sapporo, Japan, June 23 2008

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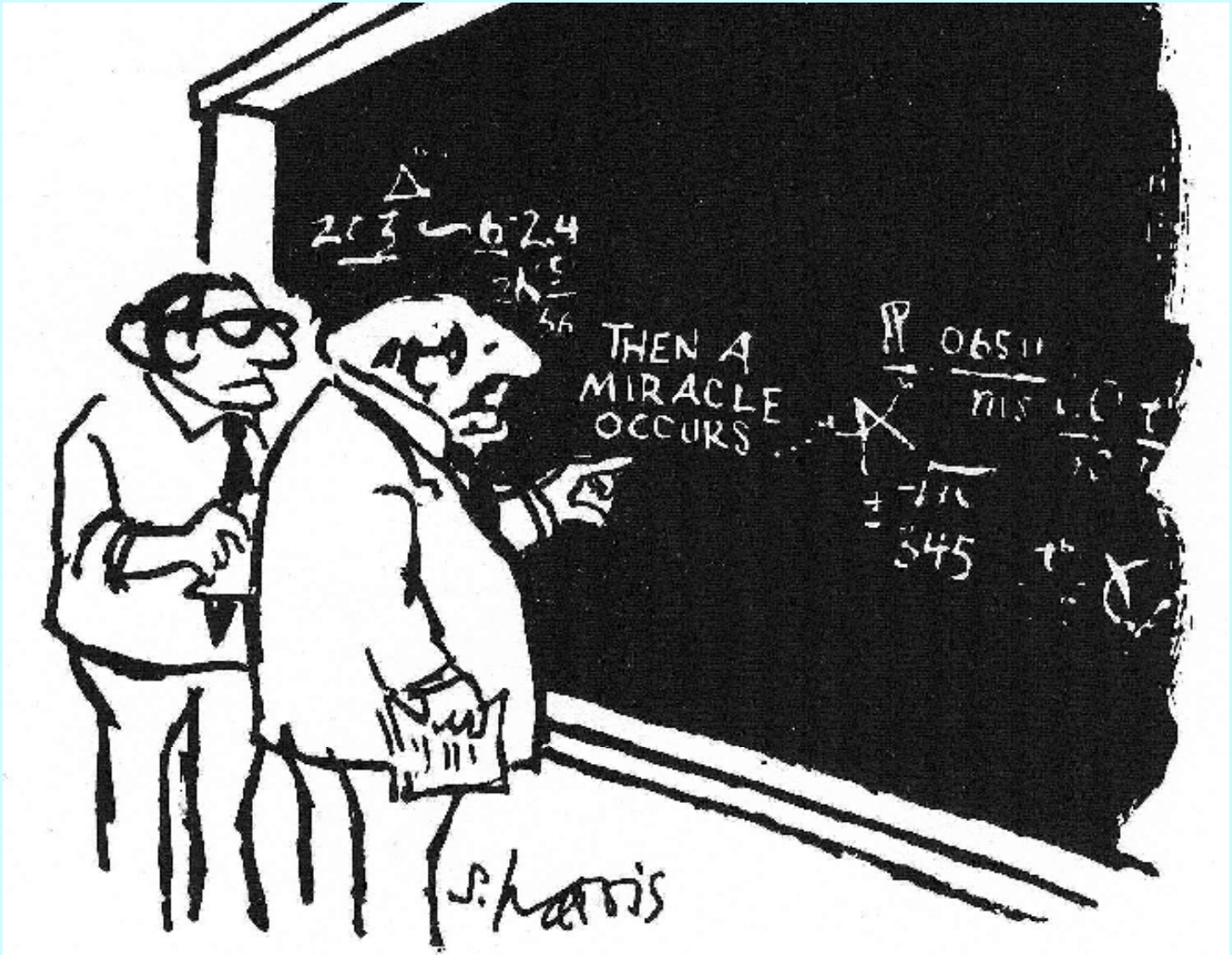
THE SOLAR CHALLENGE

- With a projected global population of 12 billion by 2050 coupled with moderate economic growth, the total global energy consumption is estimated to be ~28 TW. Current global use is ~11 TW.

- To cap CO_2 at 550 ppm (twice the pre-industrial level), most of this additional energy needs to come from carbon-free sources.

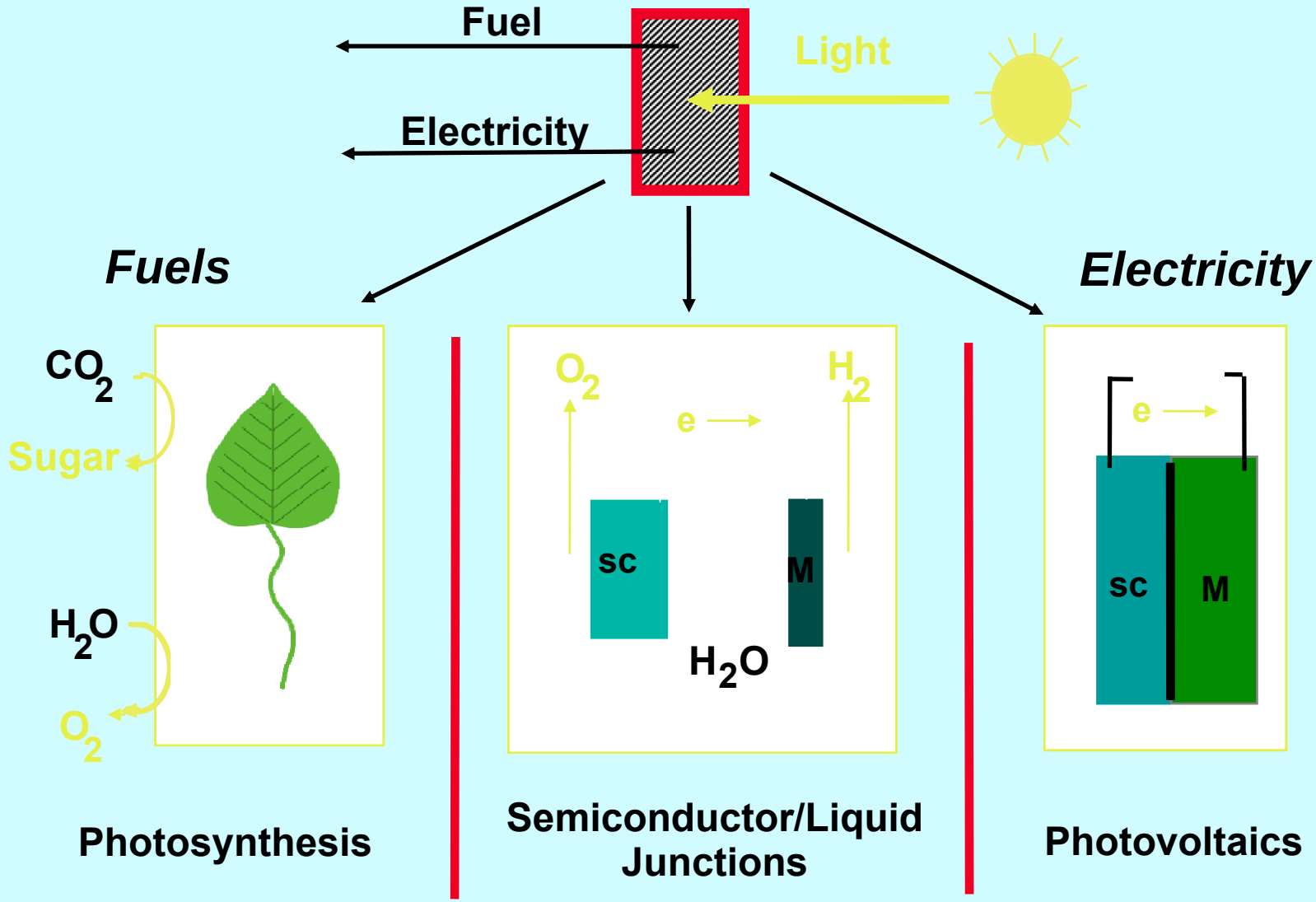
- Solar energy is the largest non-carbon-based energy source (100,000 TW).

- However, it has to be converted at reasonably low cost.



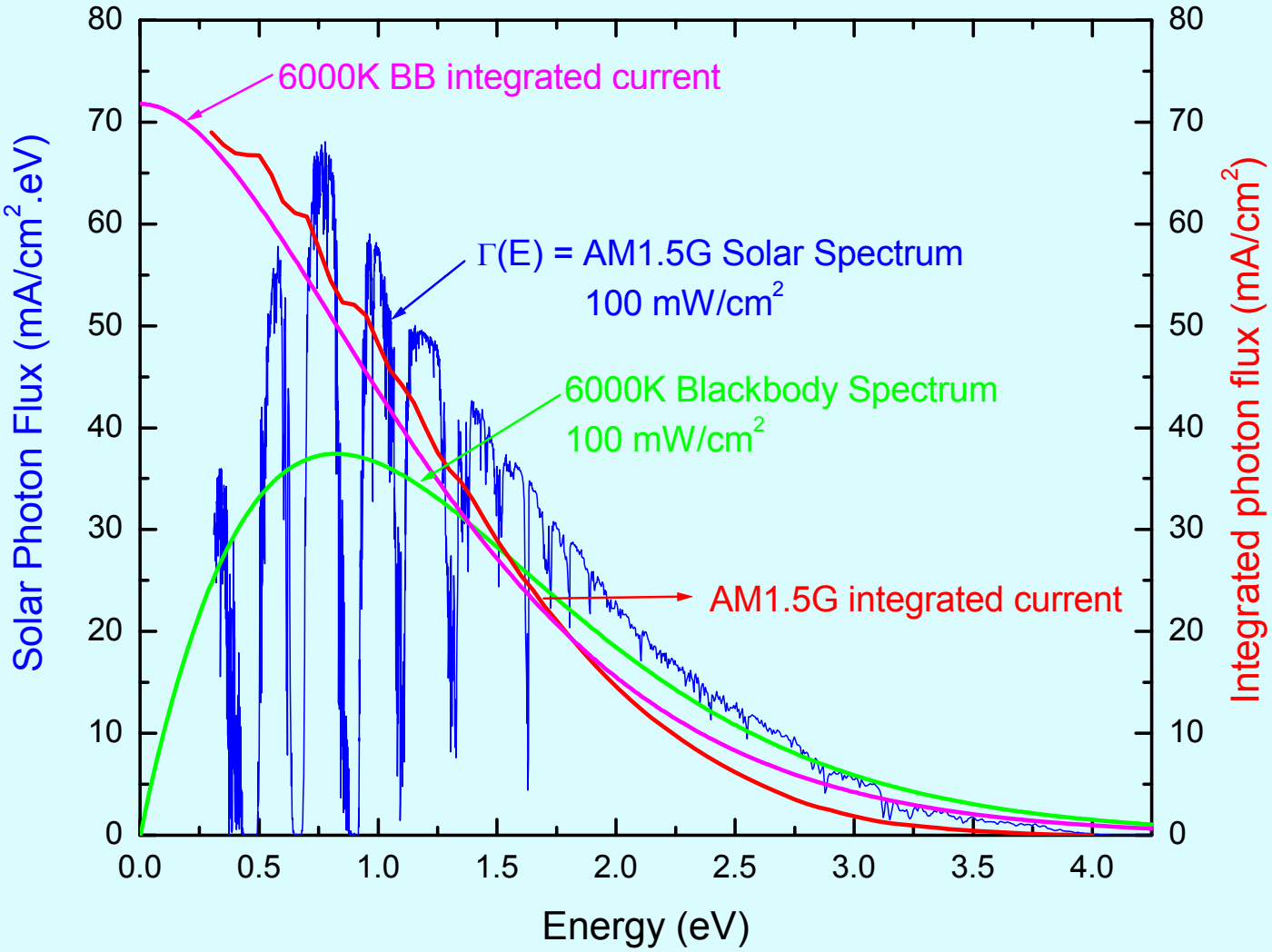
"I think you should be more explicit here in step two."

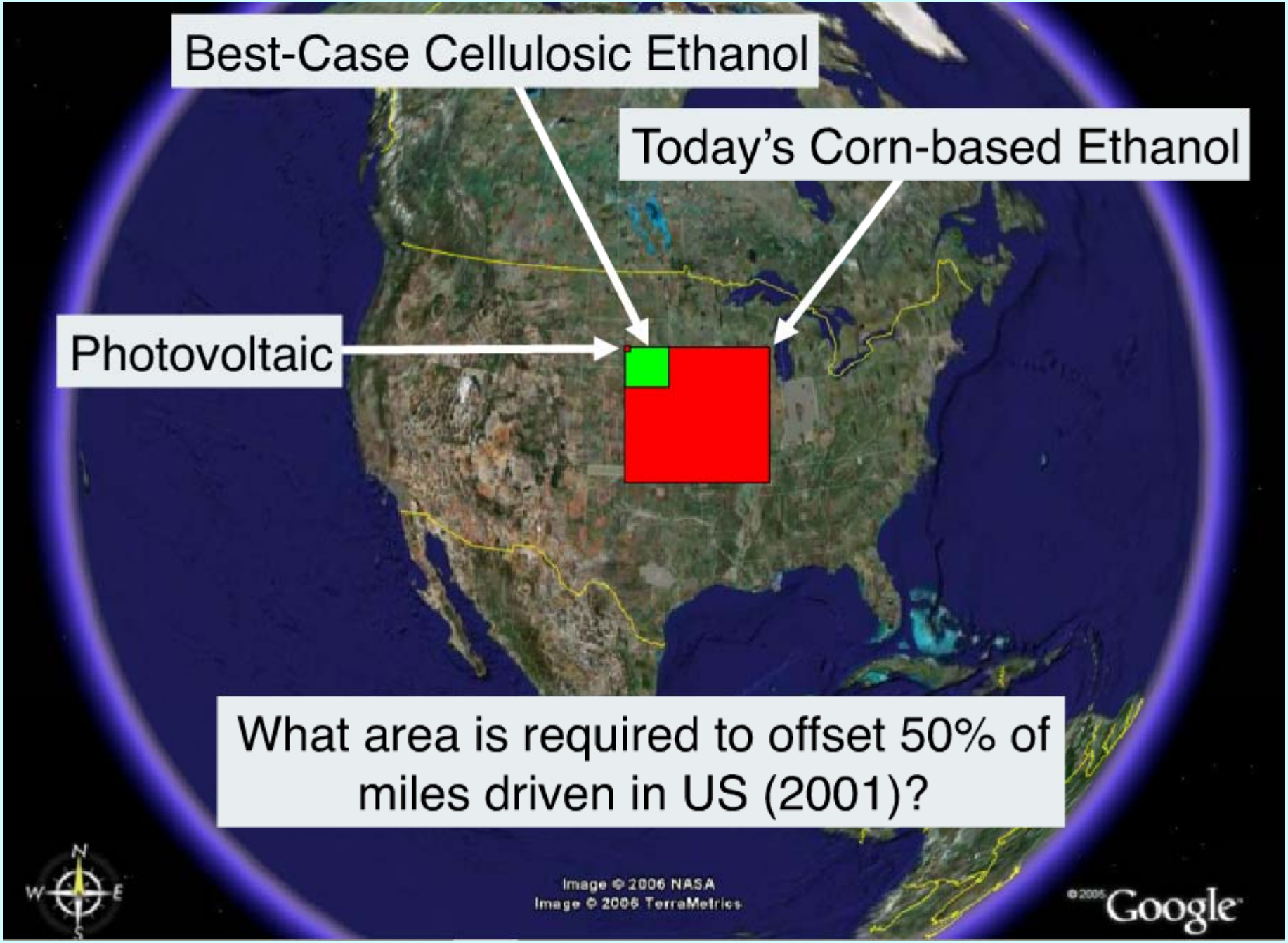
Quantum Energy Conversion Strategies



THE SOLAR RESOURCE

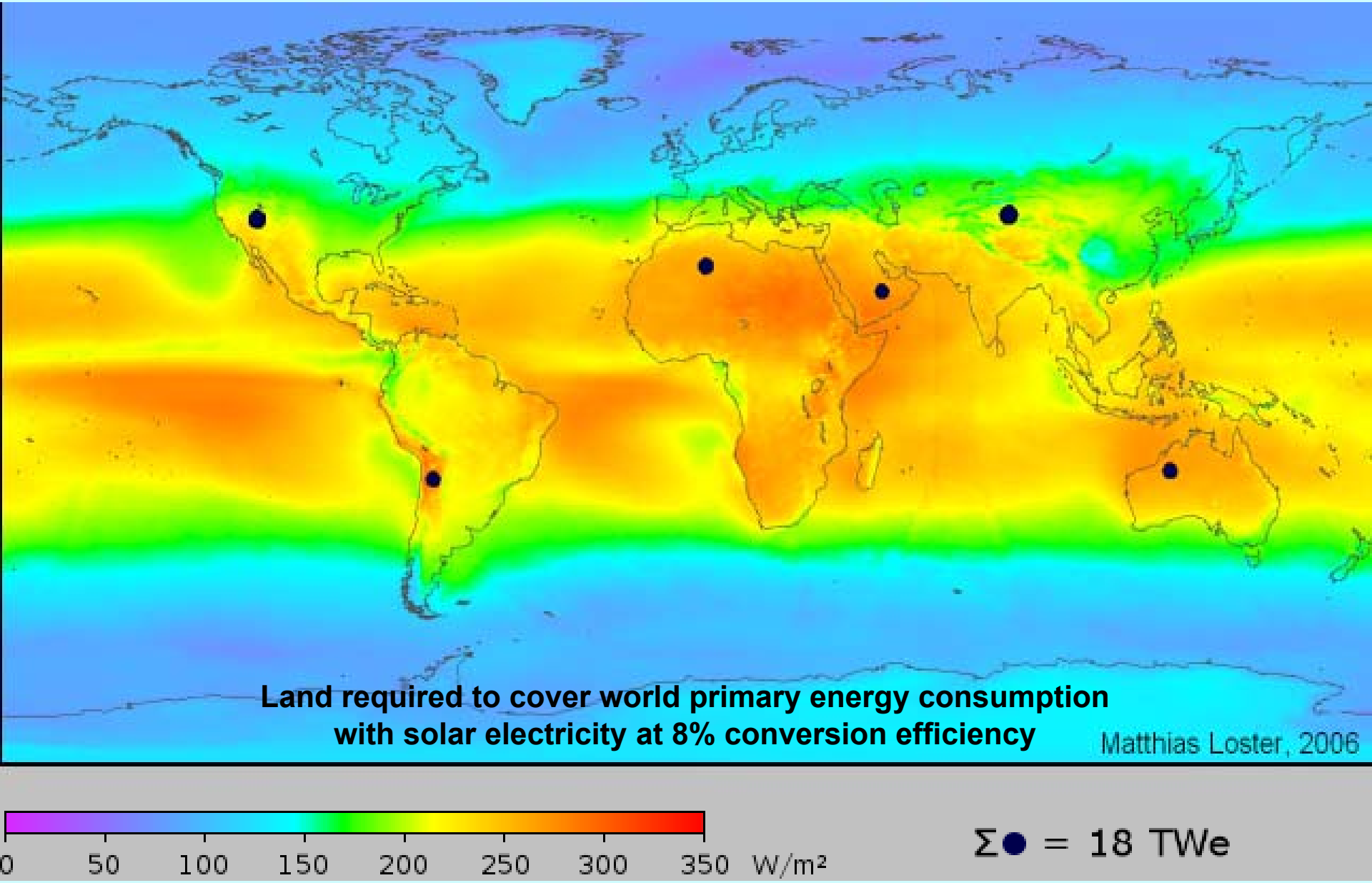
Solar Spectrum and Available Photocurrent





http://www.teslamotors.com/blog1/wp-content/uploads/2006/09/converted.swf

There is enough dessert land to harvest solar power



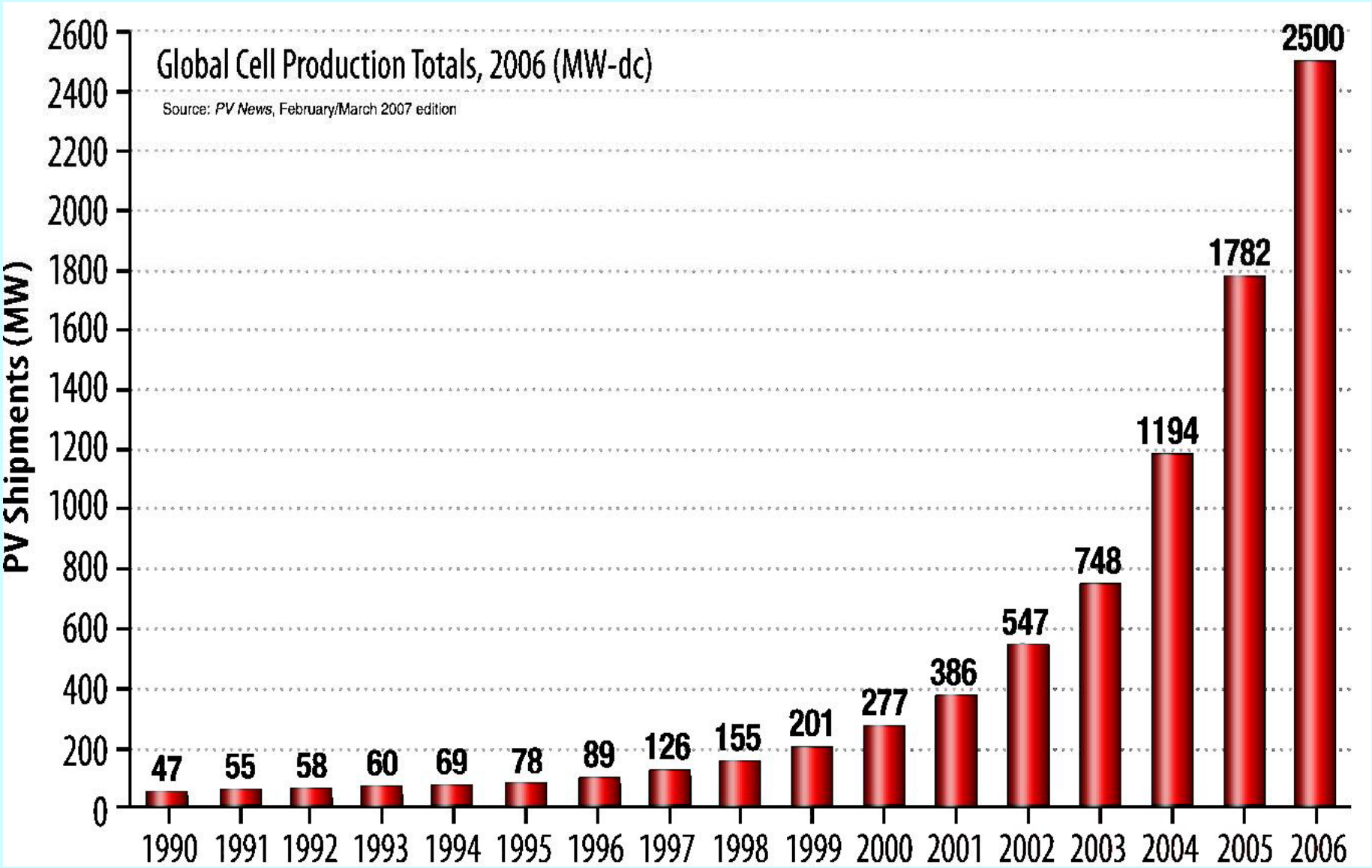
solar irradiation averaged over the year (horizontal surface)

http://www.ez2c.de/ml/solar_land_area/

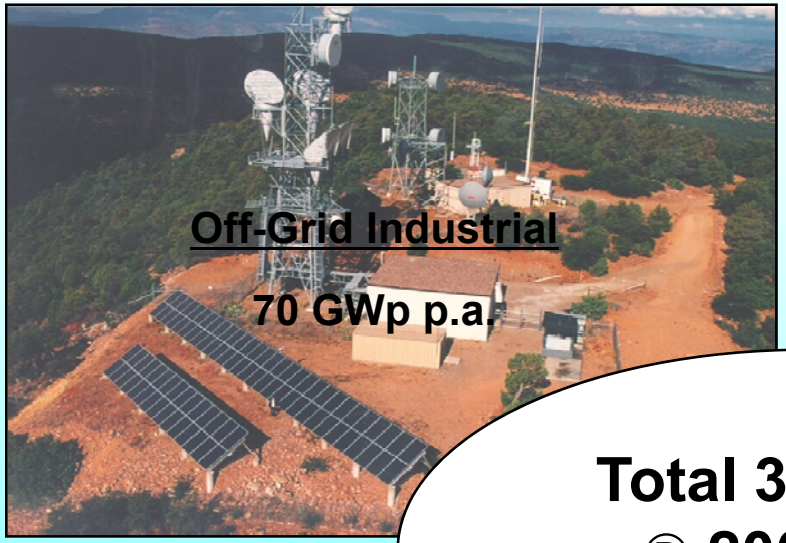
Outline

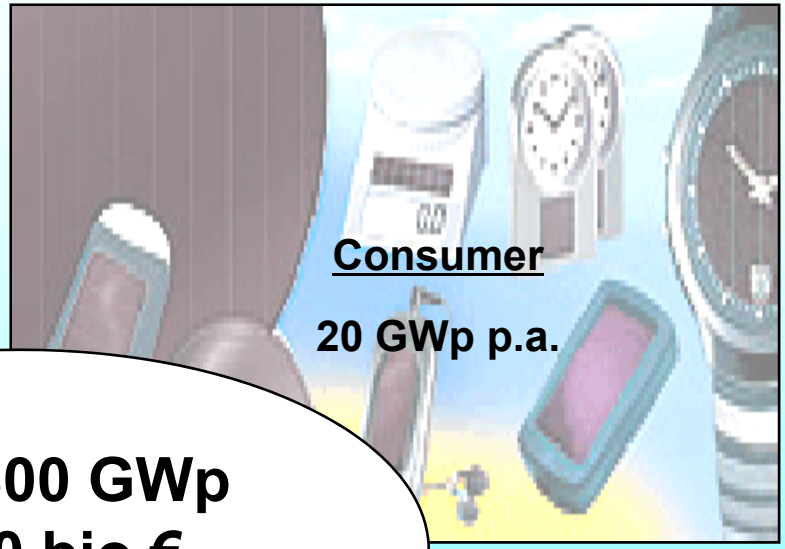
- Electric power generation by mesoscopic photovoltaic cells
- Tandem cells for solar hydrogen generation from water and carbon dioxide fixation

The yearly shipments of PV cells are growing exponentially

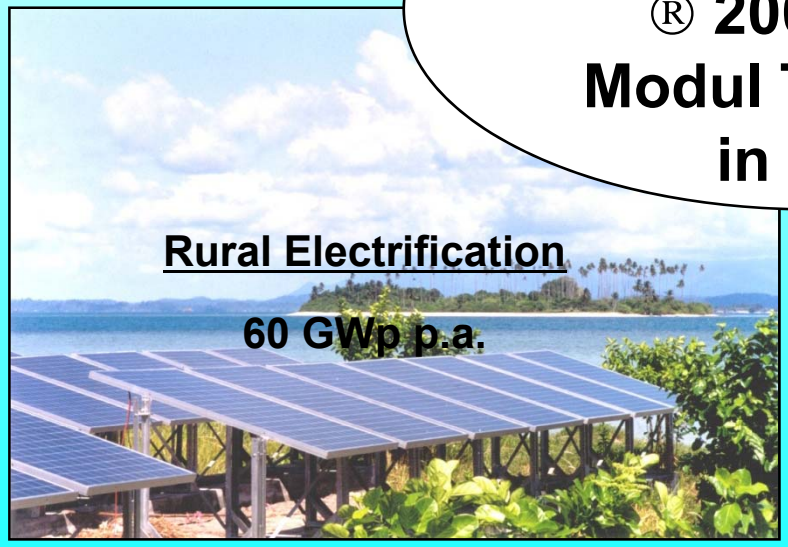


The market size in 2030 for the four main PV segments is projected to be 200 bio €



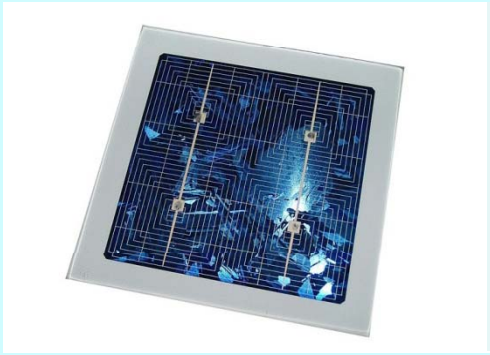


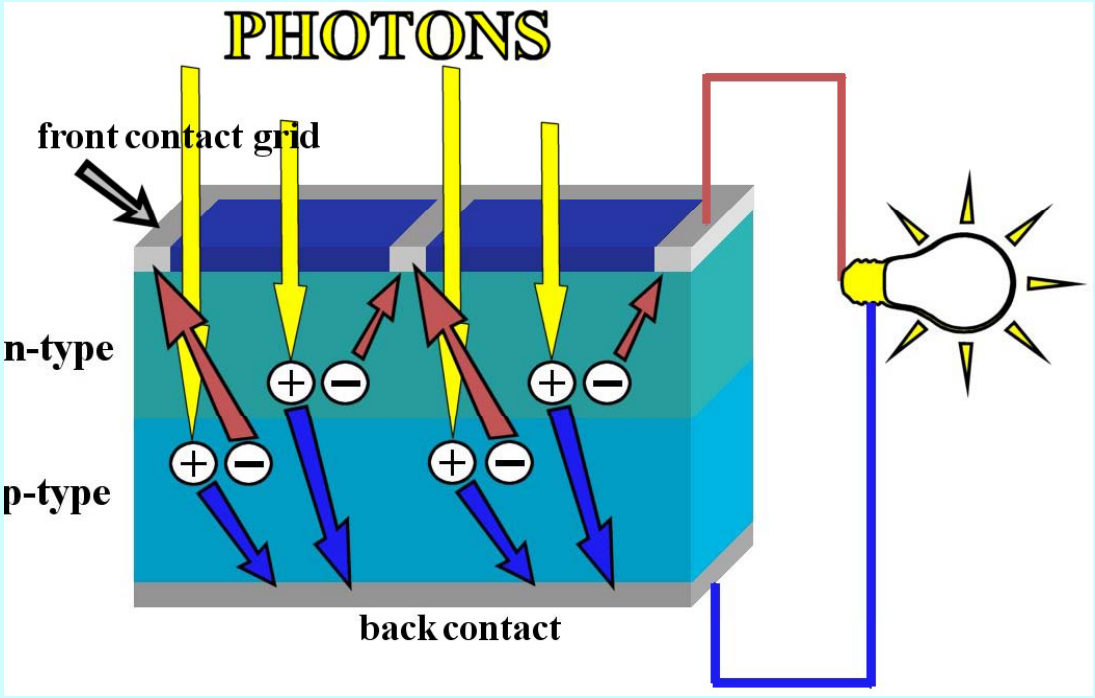
Total 300 GWp
® 200 bio €
Modul Turnover
in 2030



Courtesy Dr. Winfried Hoffman, CEO, RWE, SCHOTT Solar GmbH

Silicon solar cells dominate the market

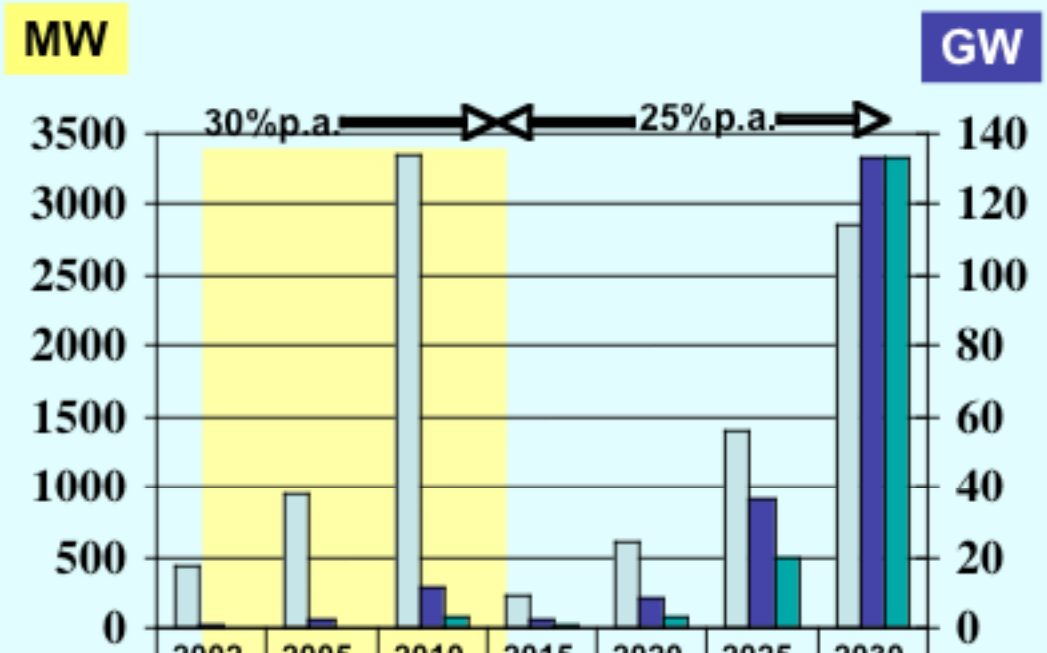




Production Forecasts of Solar Modules Call for Contributions from Different Technologies

2010 (Forecast)

Jp	1.200
EU	1.000
US	500
SOA	500
ROW	500
Σ	3.700

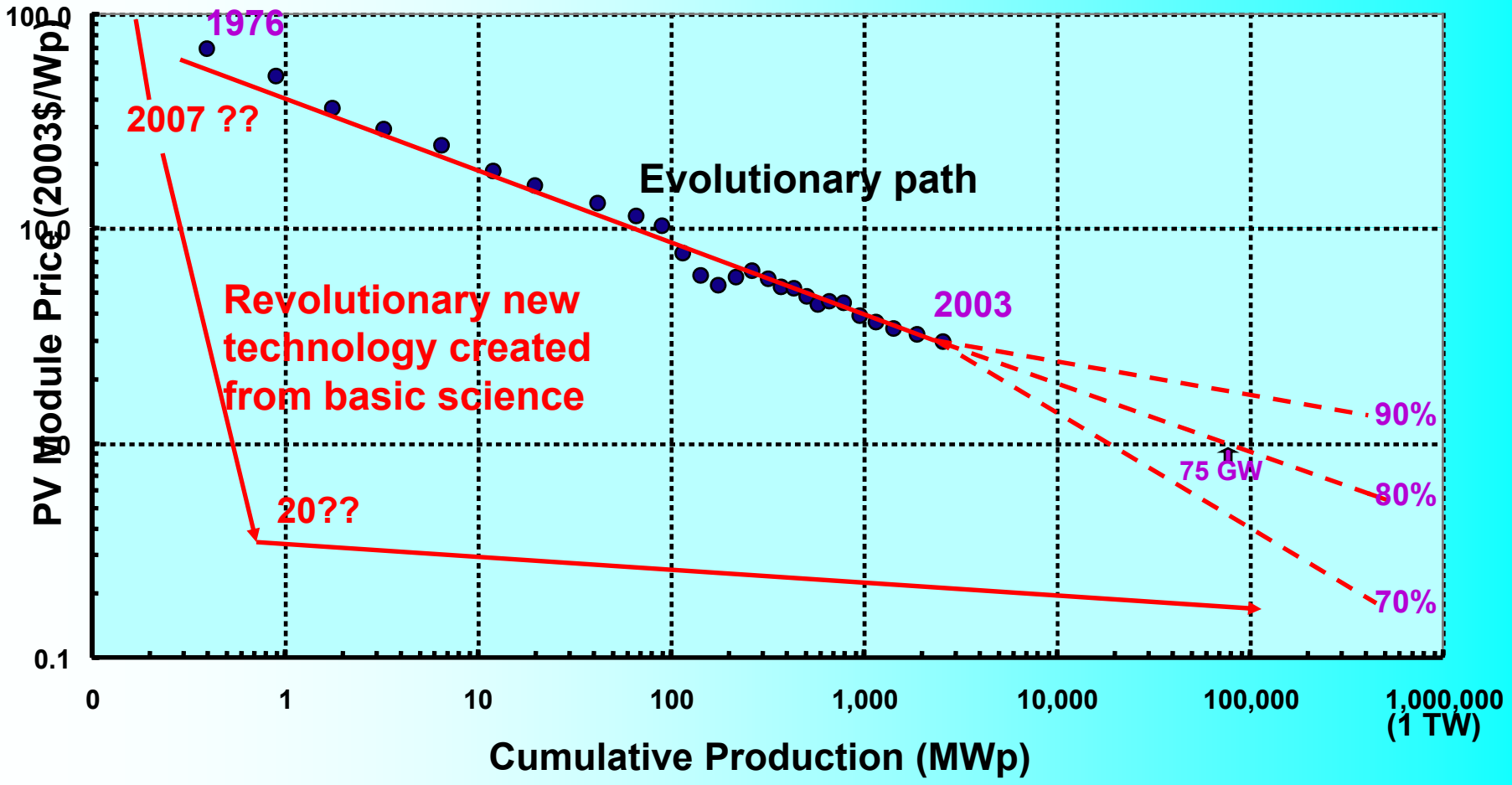


	2002	2005	2010	2015	2020	2025	2030
c-Si	430	950	3340				
thin film	20	50	290				
"New Concepts"			70				
c-Si				9	24	56	114
thin film				2	8	36	133
"New Concepts"				1	3	20	133

c-Si
thin film
"New Concepts"

Courtesy Dr. Winfried Hoffman, CEO, RWE, SCHOTT Solar GmbH

Disruptive PV technology approach required to meet cost targets



From T. Surek, JCG, 2005

A new paradigm :

Mesoscopic solar cells based on interpenetrating network (bulk) junctions

Dye sensitized nanocrystalline solar cells lead the new PV generation

LETTERS TO NATURE

A low-cost, high-efficiency solar cell based on dye-sensitized colloidal TiO_2 films

Brian O'Regan* & Michael Grätzel†

Institute of Physical Chemistry, Swiss Federal Institute of Technology, CH-1015 Lausanne, Switzerland

THE large-scale use of photovoltaic devices for electricity generation is prohibitively expensive at present: generation from existing commercial devices costs about ten times more than conventional methods[1]. Here we describe a photovoltaic cell, created from low- to medium-purity materials through low-cost processes, which exhibits a commercially realistic energy-conversion efficiency. The device is based on a 10-μm-thick, optically transparent film of titanium dioxide particles a few nanometres in size, coated with a monolayer of a charge-transfer dye to sensitize the film for light harvesting. Because of the high surface area of the semiconductor film and the ideal spectral characteristics of the dye, the device harvests a high proportion of the incident solar energy flux (46%) and shows exceptionally high efficiencies for the conversion of incident photons to electrical current (more than 80%). The overall light-to-electric energy conversion yield is 7.1–7.9% in simulated solar light and 12% in diffuse daylight. The large current densities (greater than 12 mA cm^{-2}) and exceptional stability (sustaining at least five million turnovers without decomposition), as well as the low cost, make practical applications feasible.

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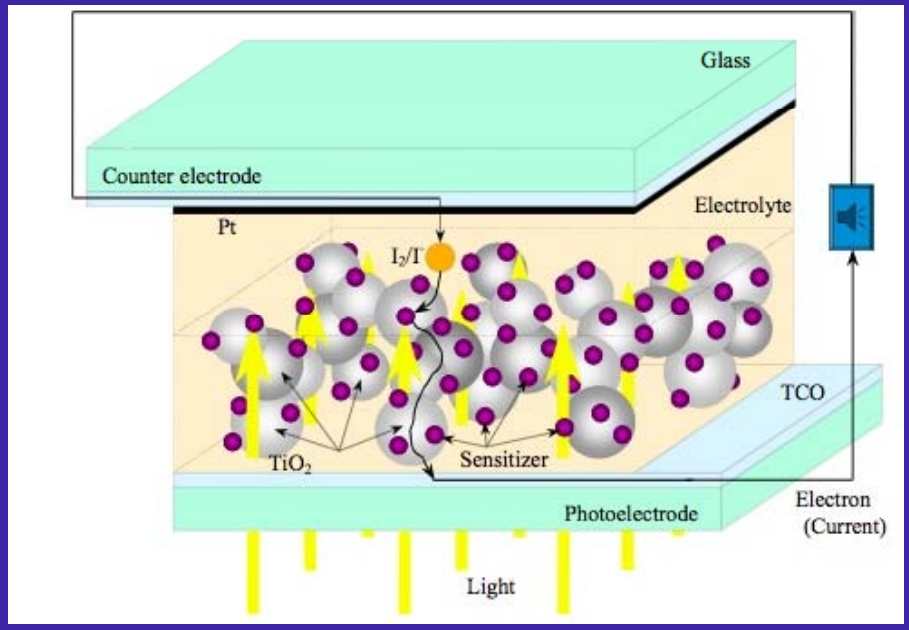
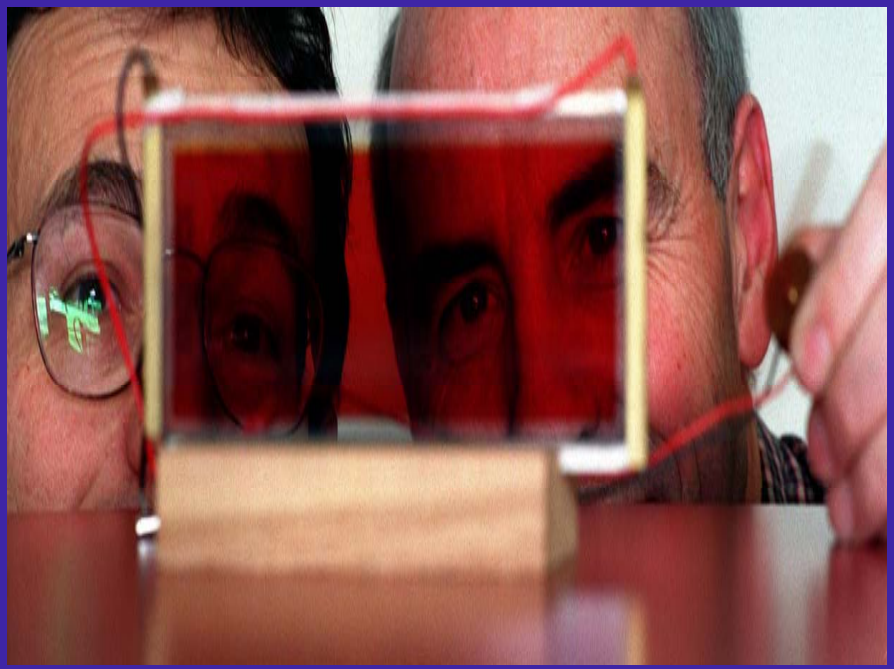
† To whom correspondence should be addressed.



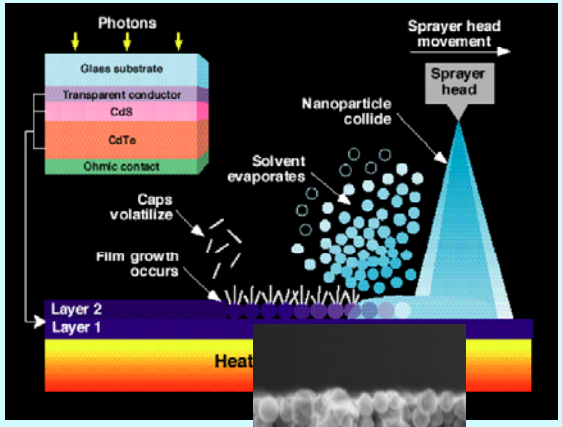


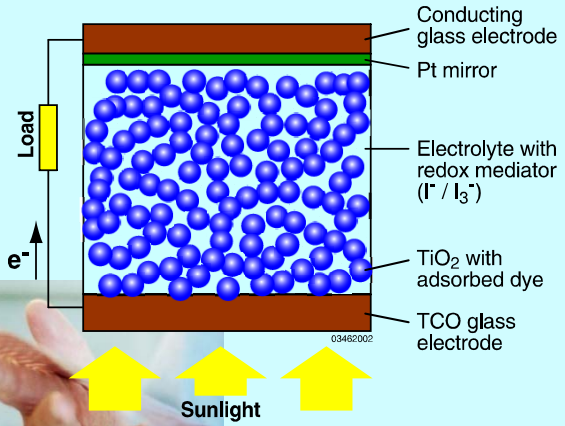
Bifacial light collection by dye sensitized solar cells offers practical advantages

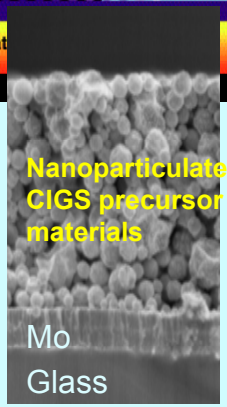
Mesoscopic PV Technologies

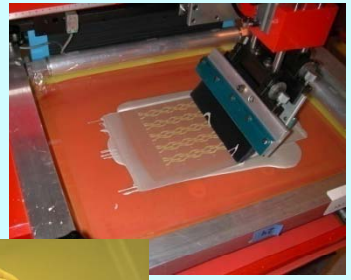
From T. Surek

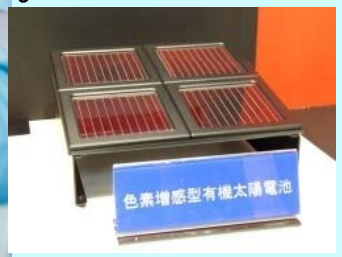
- Opportunities for innovation– ultra low cost, ultra high efficiencies, new materials, new chemistry,new physics
  - Photoelectrochemistry
  - Excitonic cells (dye cells, semiconducting polymers, molecular semiconductors)
  - Quantum dot cells; hot-carrier and impurity band cells; photon tailoring

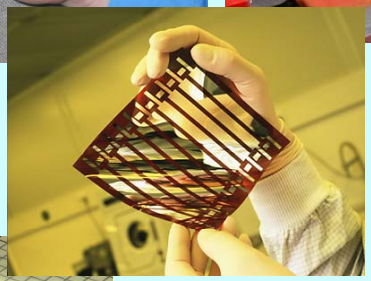


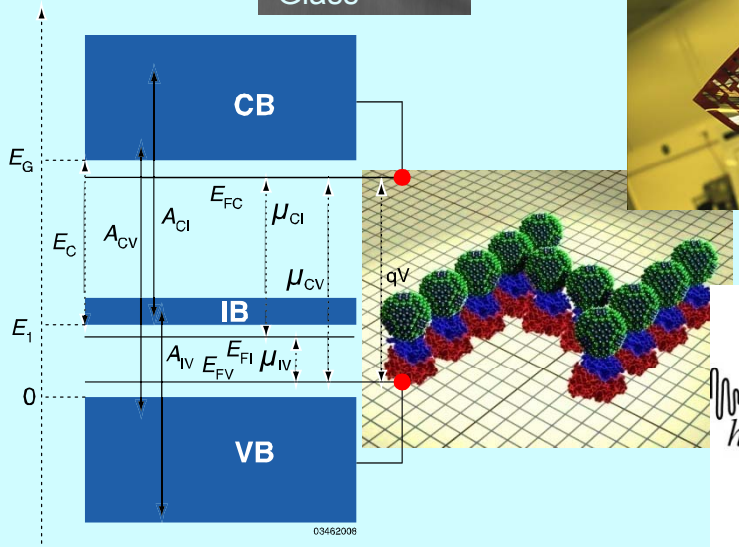


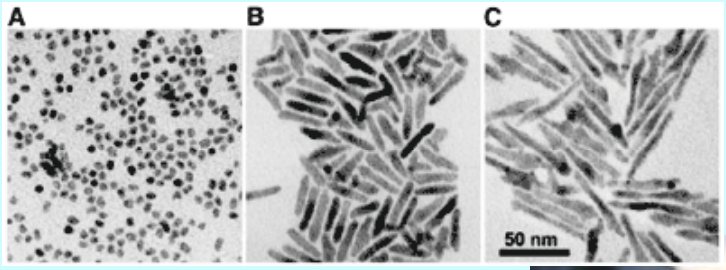


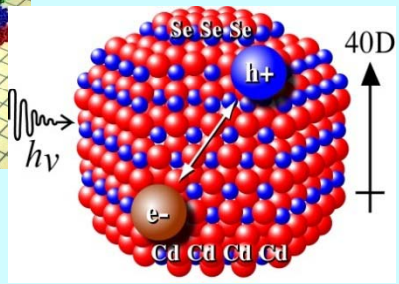


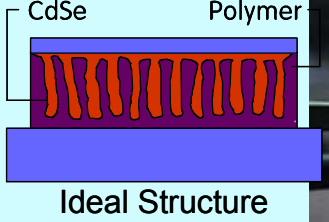




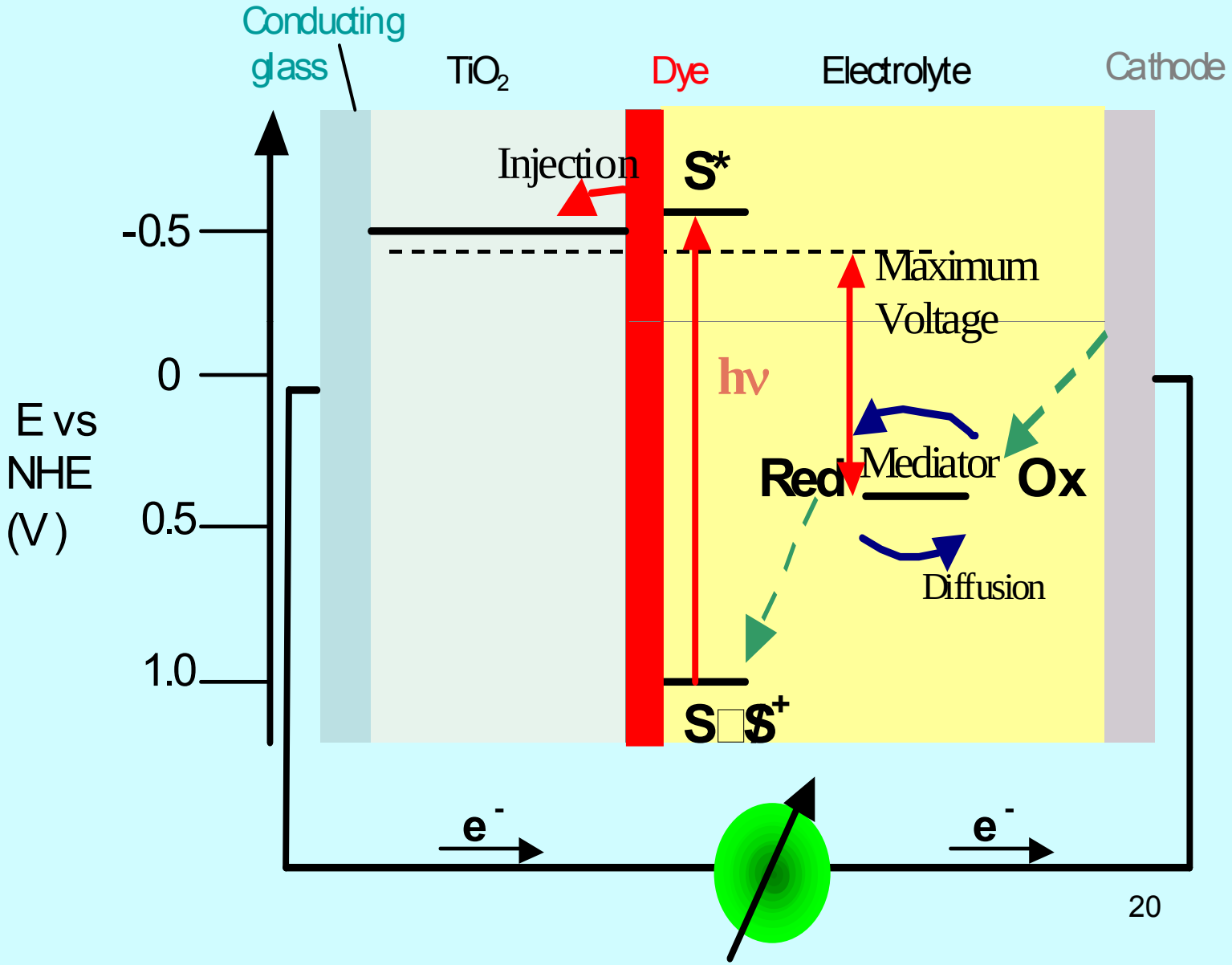




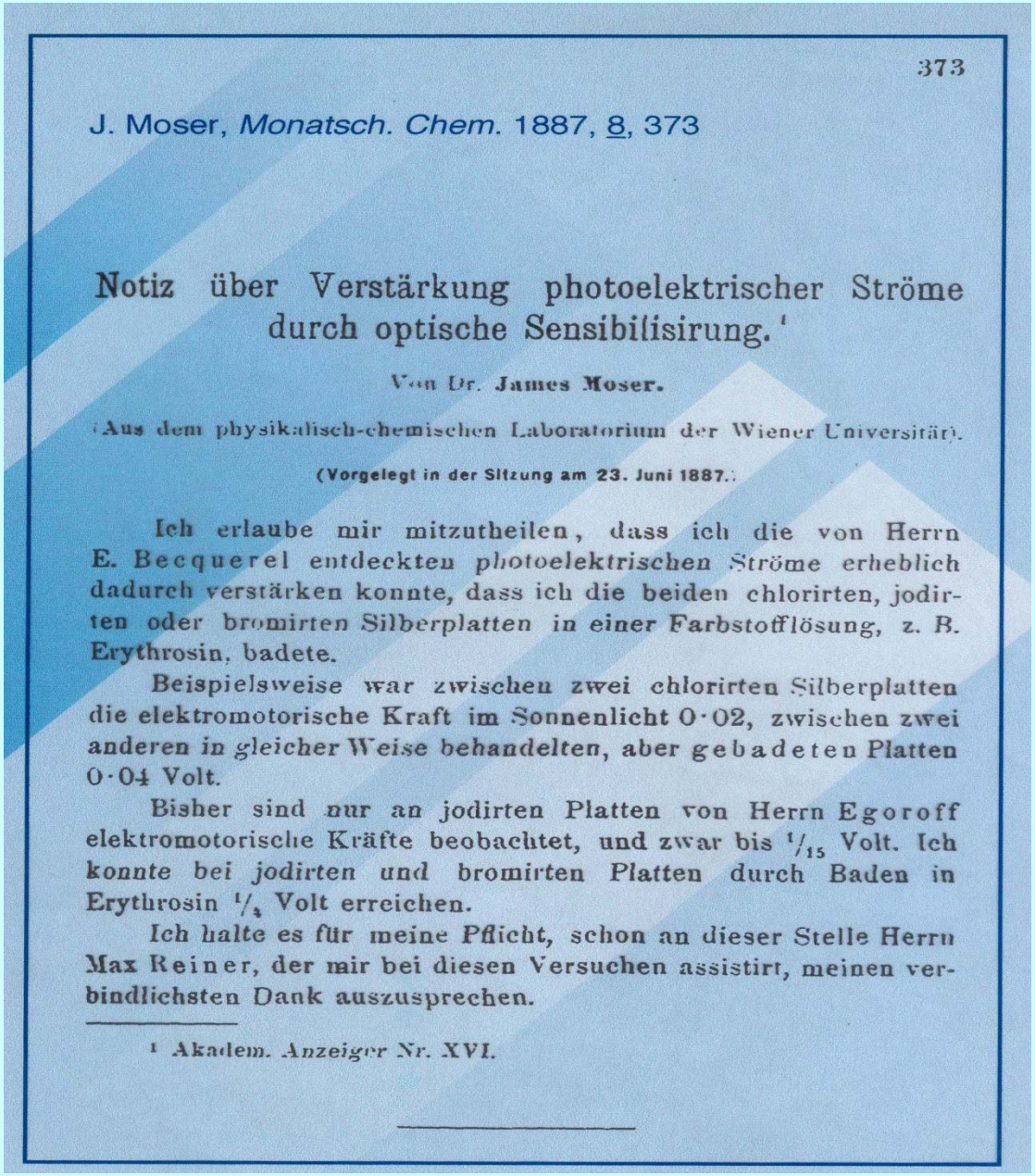




The dye sensitized solar cell (DSC) is the only photovoltaic cell using a molecular light harvester, generating charge carriers after photo-excitation



Sensitization of silver bromide by eosin was discovered in 1887



J. Moser, *Monatsch. Chem.* 1887, 8, 373

Notiz über Verstärkung photoelektrischer Ströme durch optische Sensibilisirung.[1]

Von Dr. James Moser.

(Aus dem physikalisch-chemischen Laboratorium der Wiener Universität).

(Vorgelegt in der Sitzung am 23. Juni 1887.)

Ich erlaube mir mitzutheilen, dass ich die von Herrn E. Becquerel entdeckten *photoelektrischen Ströme* erheblich dadurch verstärken konnte, dass ich die beiden chlorirten, jodirten oder bromirten Silberplatten *in einer Farbstofflösung*, z. B. Erythrosin, badete.

Beispielsweise war zwischen zwei chlorirten Silberplatten die elektromotorische Kraft im Sonnenlicht 0·02, zwischen zwei anderen *in gleicher Weise behandelten*, aber gebadeten Platten 0·04 Volt.

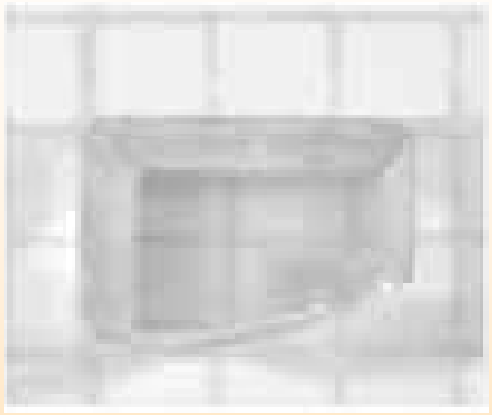
Bisher sind nur an jodirten Platten von Herrn Egoroff elektromotorische Kräfte beobachtet, und zwar bis $^1/_{15}$ Volt. Ich konnte bei jodirten und bromirten Platten durch Baden in Erythrosin $^1/_4$ Volt erreichen.

Ich halte es für meine Pflicht, schon an dieser Stelle Herrn Max Reiner, der mir bei diesen Versuchen assistirt, meinen verbindlichsten Dank auszusprechen.

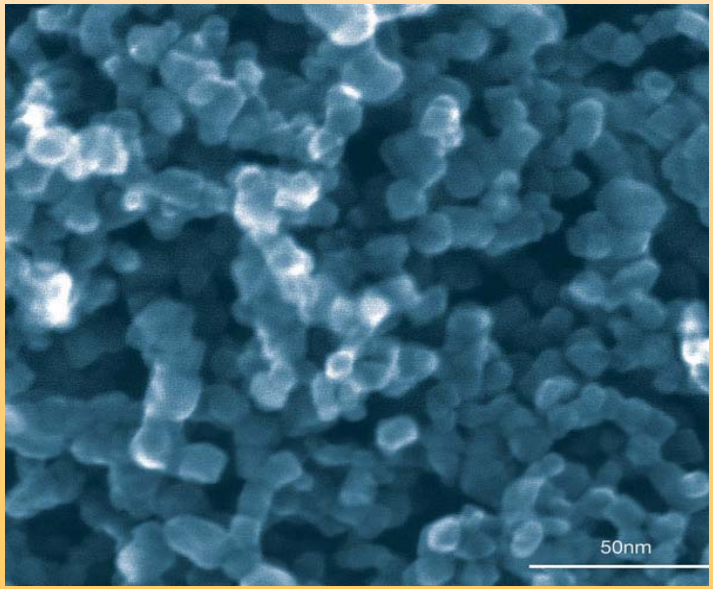
[1] Akadem. Anzeiger Nr. XVI.

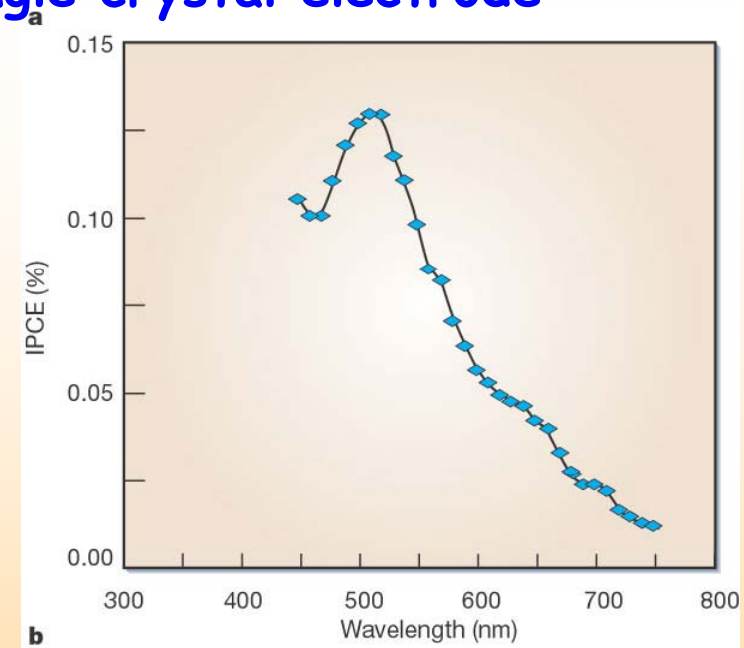
A dye sensitized nanocrystaline film generates over 1000 times more photocurrent than a single crystal electrode

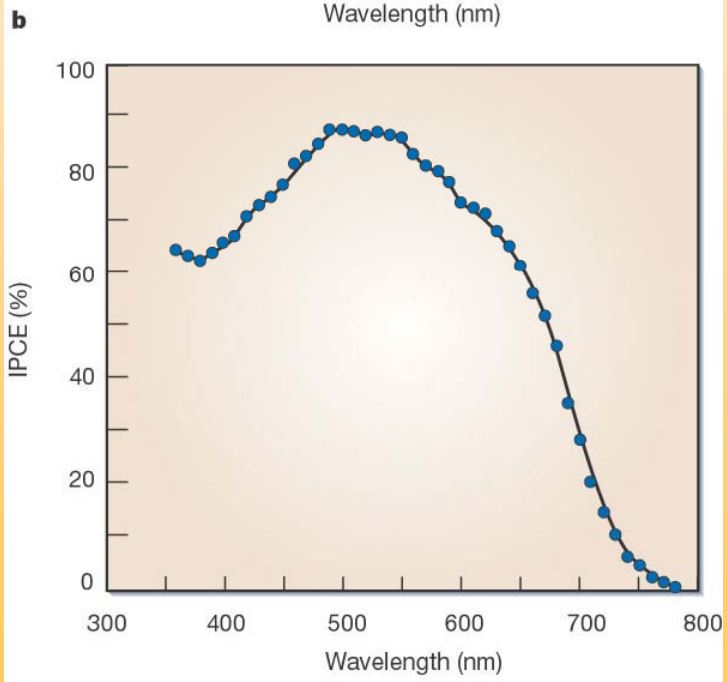
single crystal of anatase



Nanocrystalline anatase film







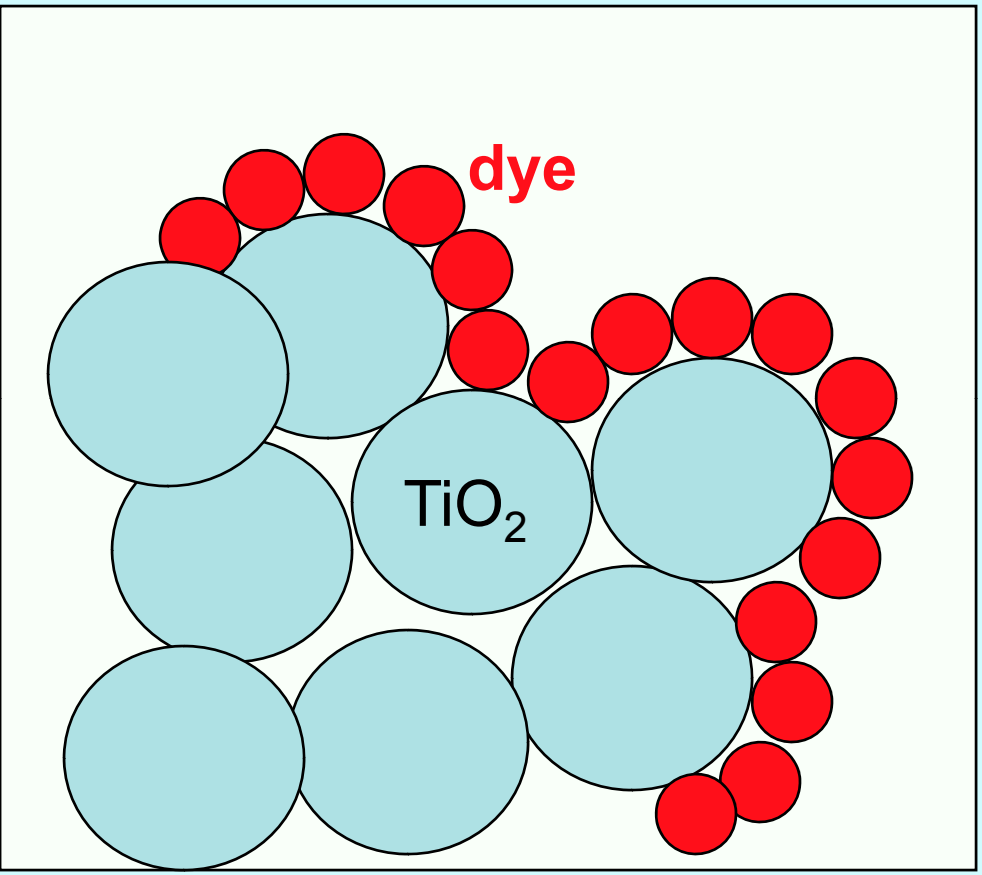
Dye sensitized nanocrystals achieve quantitative conversion of photons into electric current

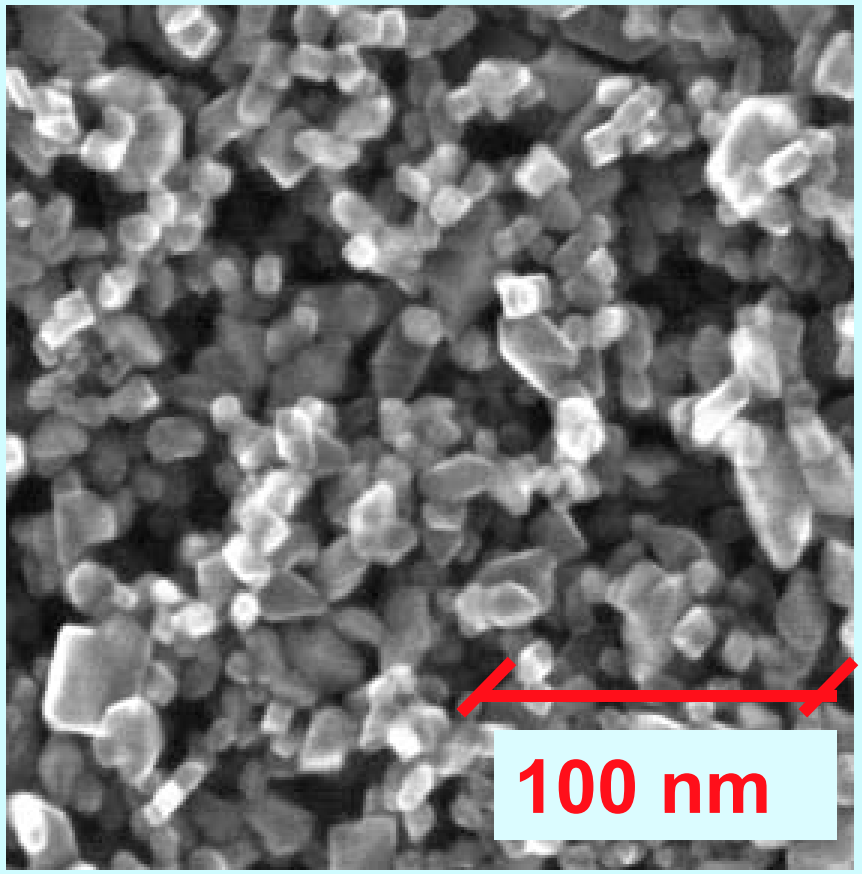
The incident photon to electrical current conversion efficiency (external quantum efficiency) can reach close to 100 %

$$\eta = \eta_{abs} * \Phi_{ini} * \eta_{coll}$$

A key question is how electrons are quantitively collected from the disordered network of nanoparticles.

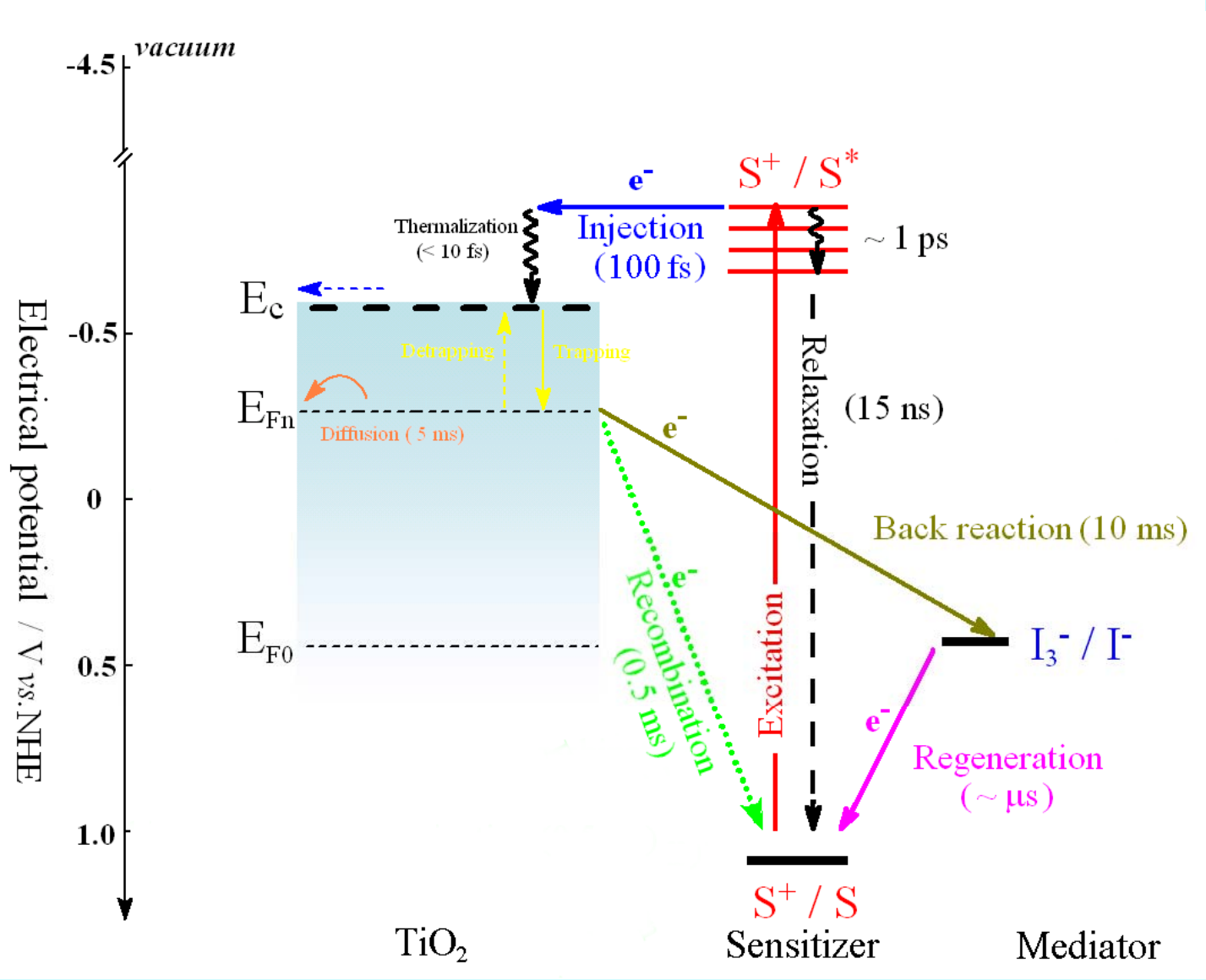
The collection of photo-generated electrons by the nanoparticle array is quantitative





The electrons ad holes move in different phases and are separated by a phase boundary retarding their recombination

Photo-induced interfacial charge separation occurs within femtoseconds



The electron diffusion length exceeds largely the film thickness

$$L_n = \sqrt{D\tau}$$

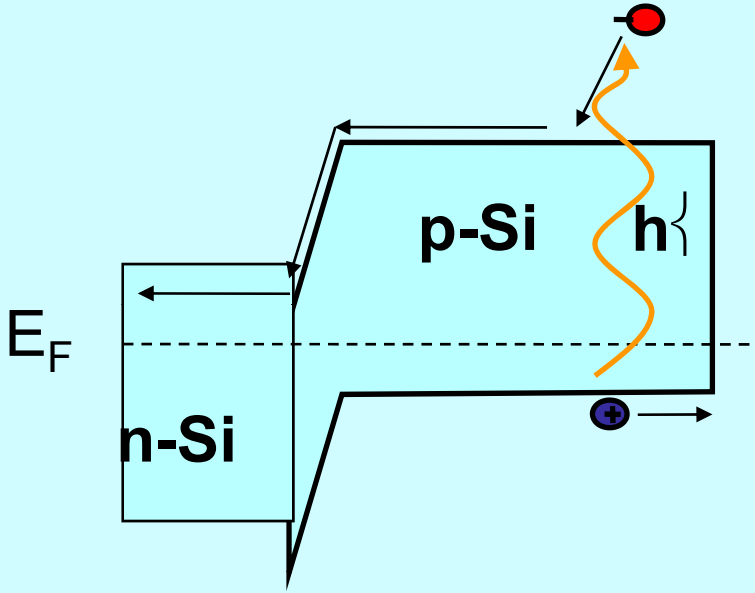
Typical values for high performance (η >10%) cells at V_{mpp}:

$D = 10^{-4}\ cm^2/s$, τ = 1 s, <u>L = 100 μm</u>

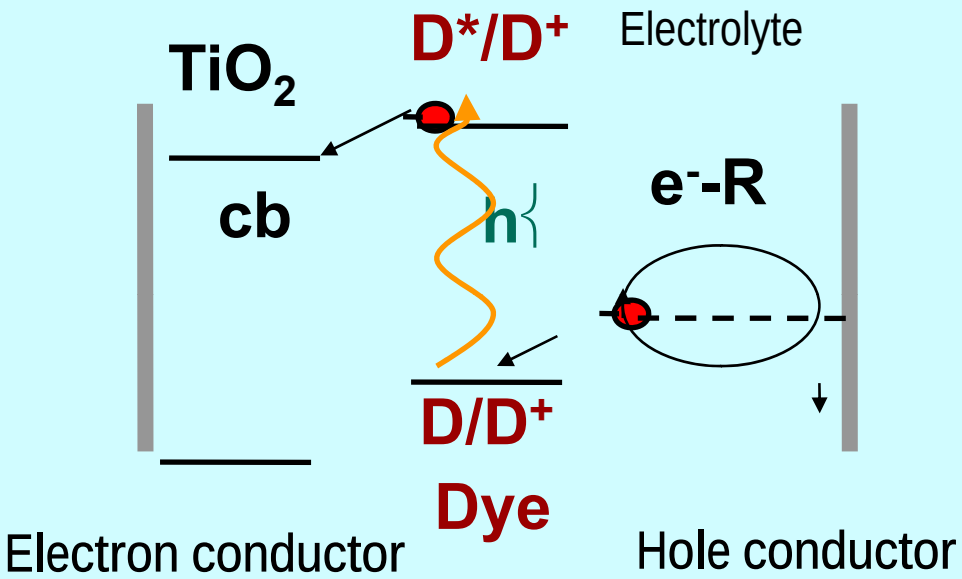
The film thickness is <u>less than 30 micrometer</u>

Dye sensitized solar cells separate light absorption from carrier transport

p-n junction photovoltaic cells



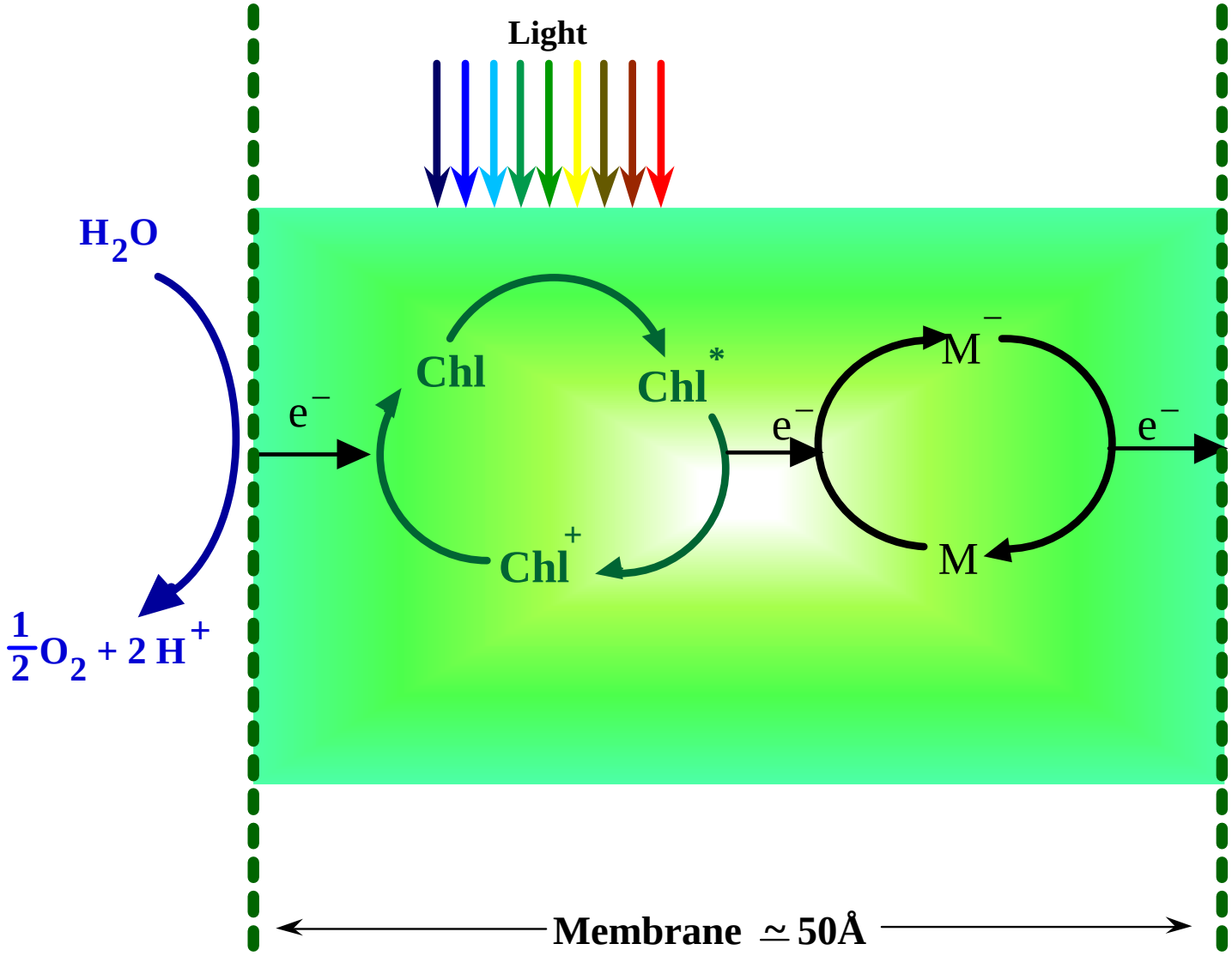
dye sensited solar cells DSC



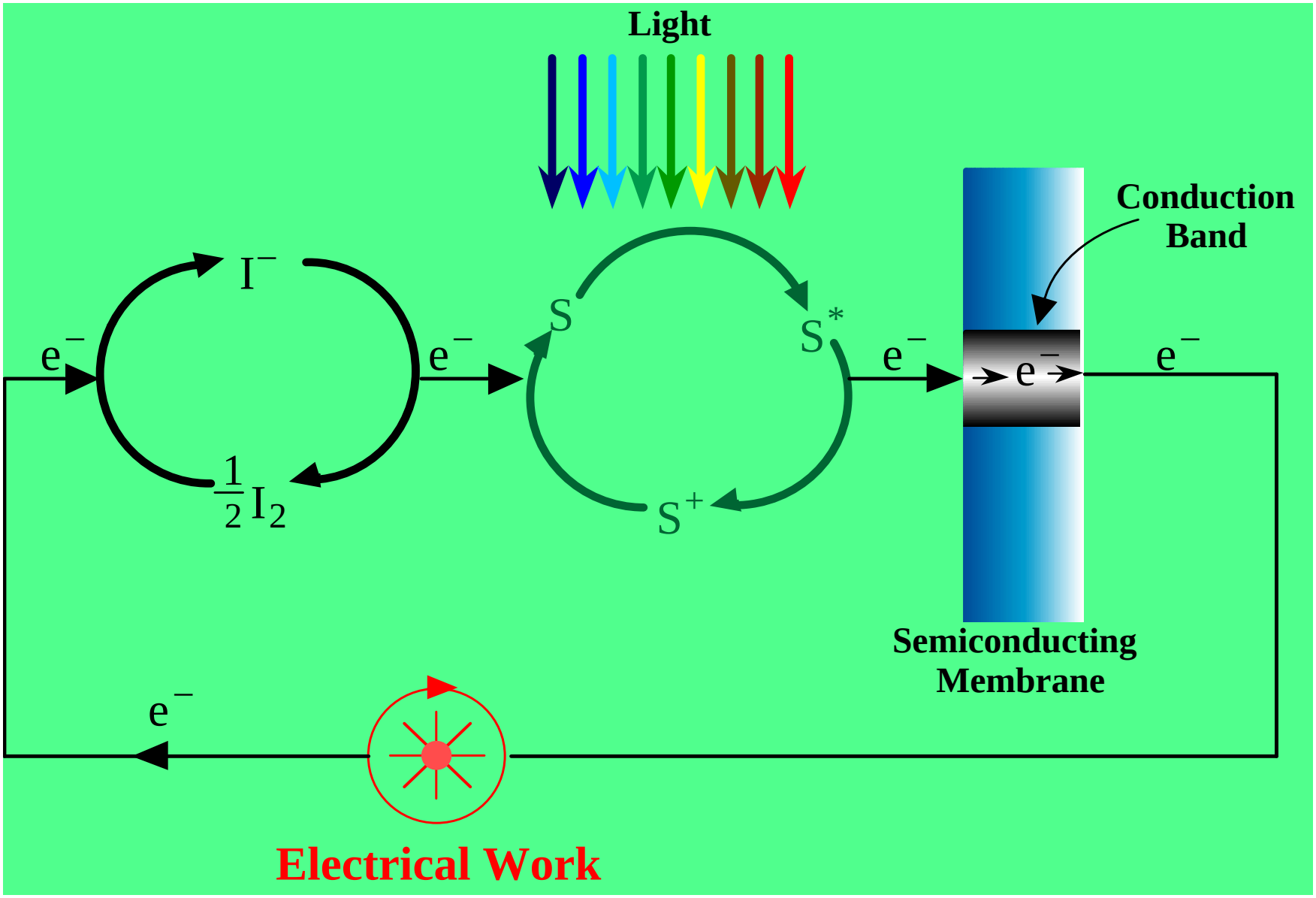
Charge separation by electric field at the p-n junction

Charge separation by kinetic competition as in photosynthesis

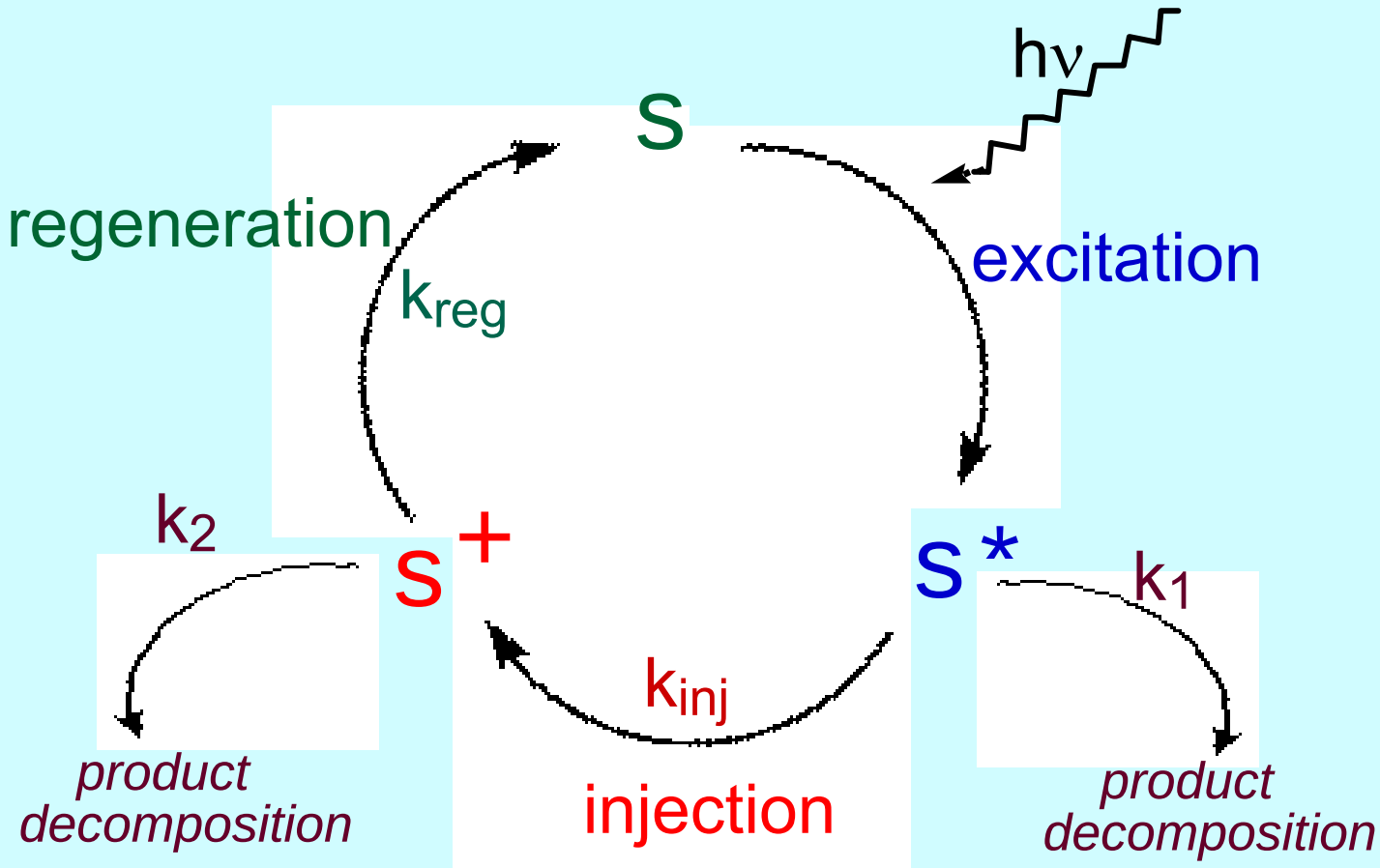
The light driven electron pump in green leaves drives transmembrane charge separation



The DSC mimics natural photosynthesis

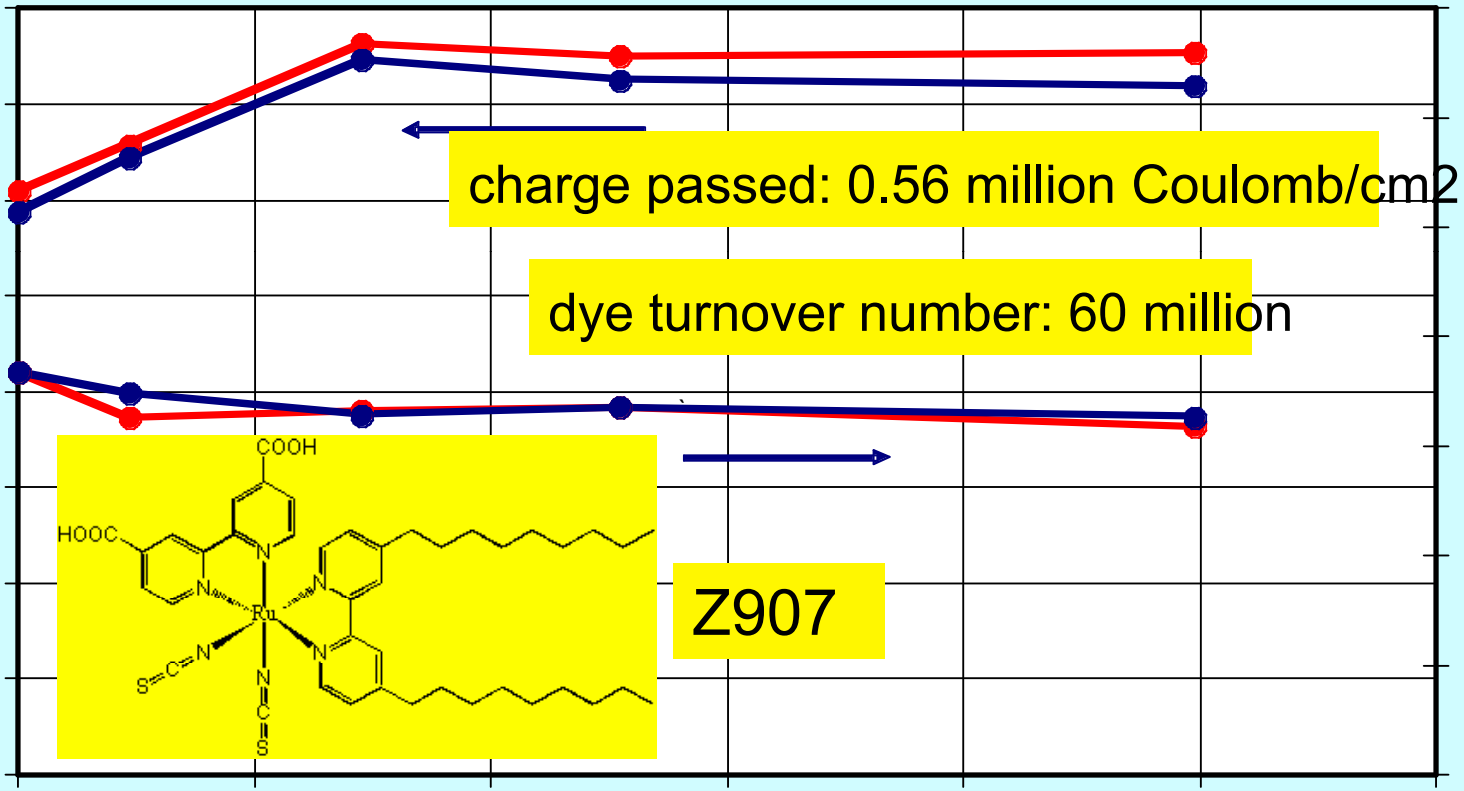


The sensitizer has to sustain 100 million cycles during 20 years of outdoor cell operation



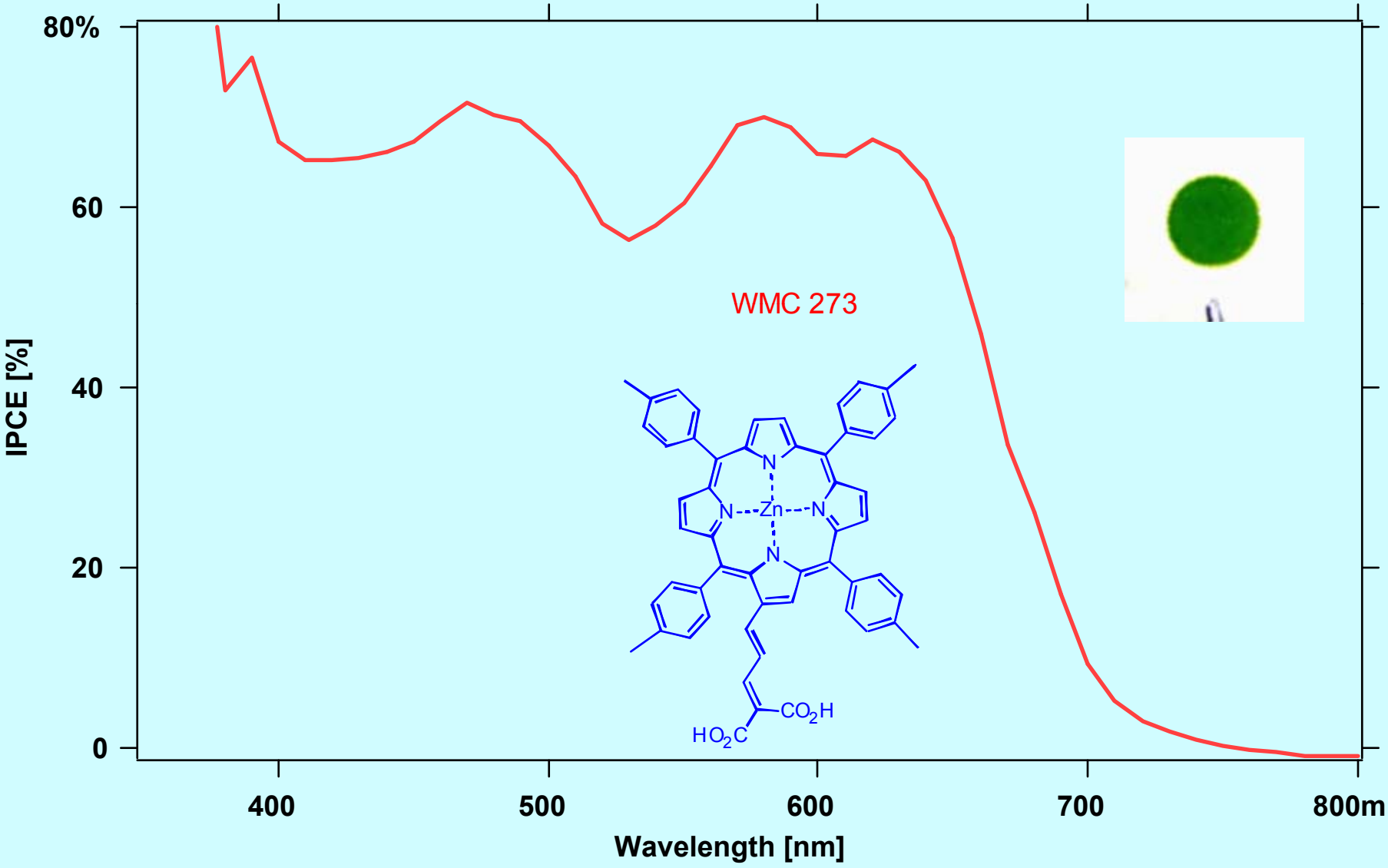
To reach 100 million turnovers branching ratios of k_{Inj}/k_1 and $k_{reg}/k_2 > 10^8$ are required

Z907 attains 10'000 hours stability in full sunlight (ca 15 years outdoor)



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

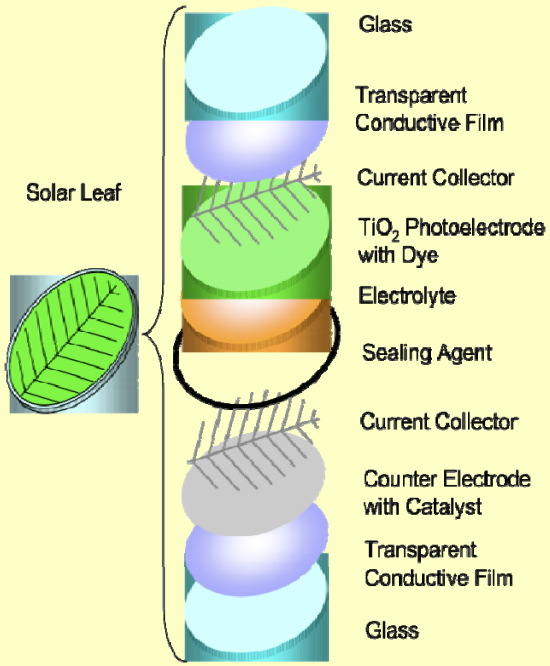
green solar cells mimic the green leave



In collaboration with Professor David Officer, Univ.Wollongon,Australia

Artificial Plant with Leaves exhibited at EXPO 2005

Butterflies flutter and stop using the electricity generated by this plant under the intermittent lightings.

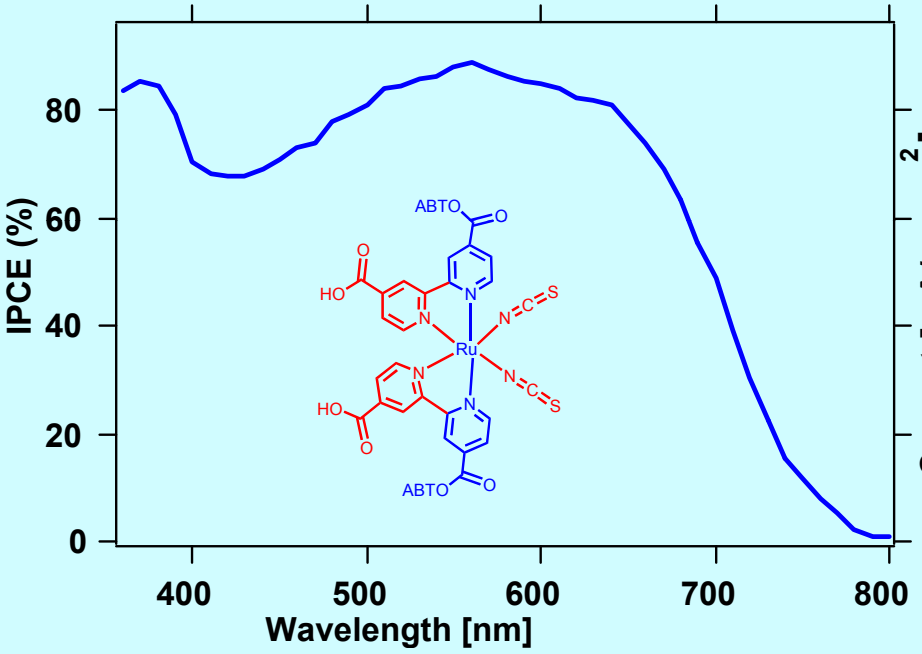


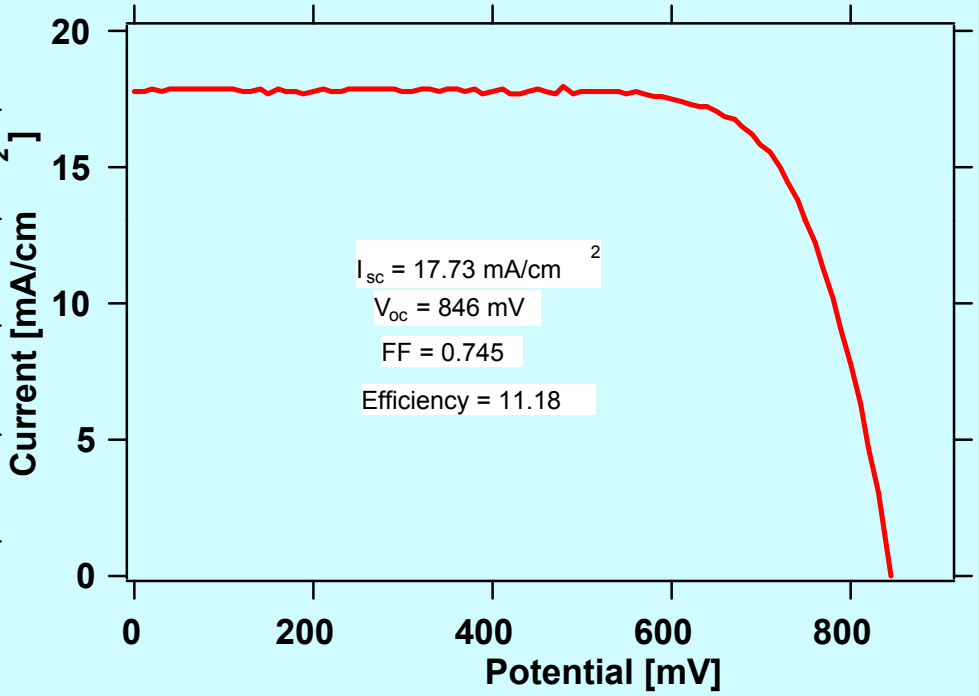
Leaf-shaped transparent DSC with four colors

The solar to electric power conversion efficiency of the DSC in full AM 1.5 sun light validated by accredited PV calibration laboratories has presently reached over 11 %.

Chiba, Y., Islam, A.; Watanabe, Y; Komiya, R.; Koide, N.; Han, L..
Dye-sensitized solar cells with conversion efficiency of 11.1%.
Japanese Journal of Applied Physics, Part 2: Letters & Express Letters (2006), 45(24-28),

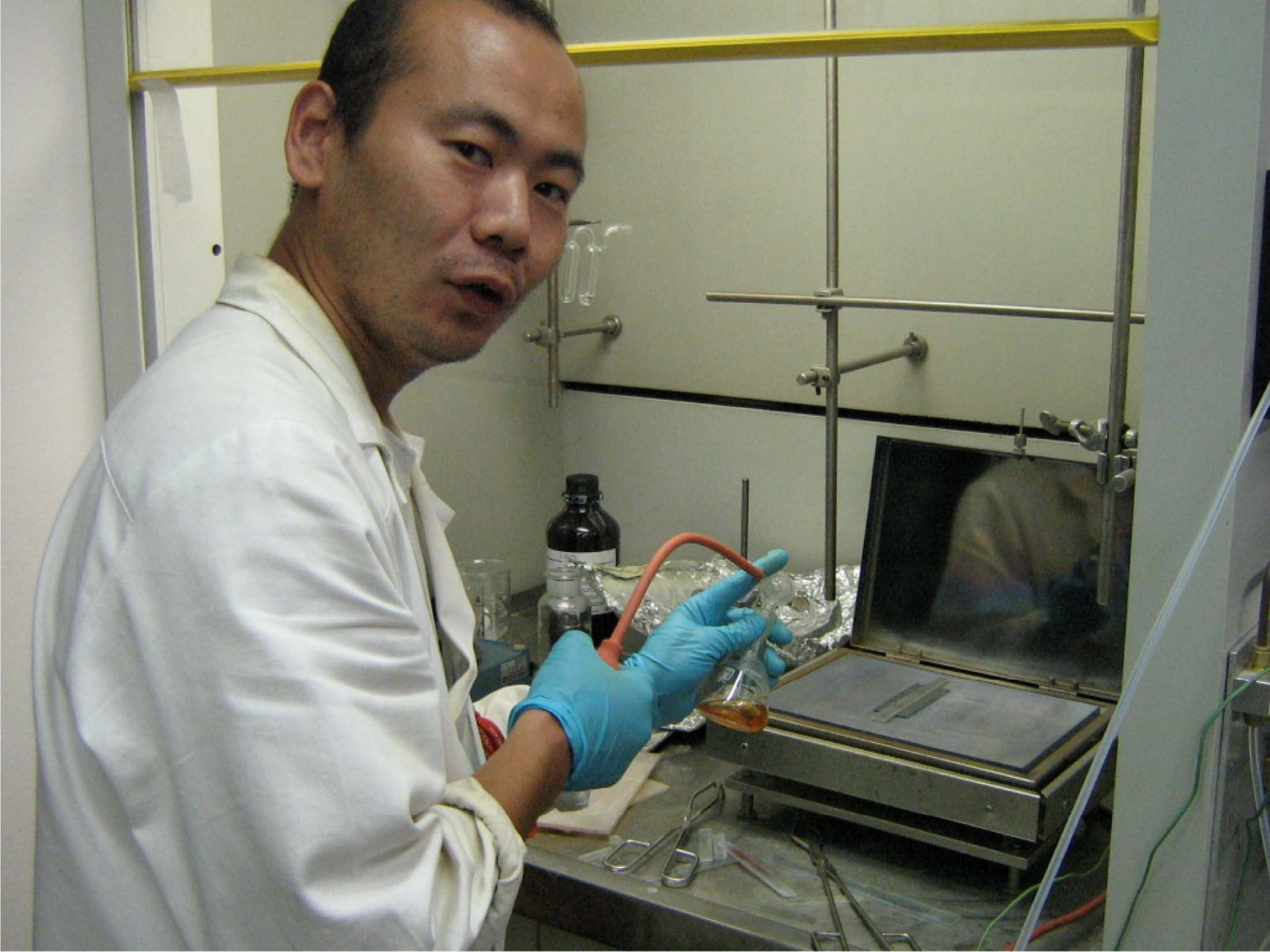
Champion cells reach over 11 percent conversion efficiency However their near IR response is insufficient





$$\eta = i_{ph} V_{oc} ff / I_s$$

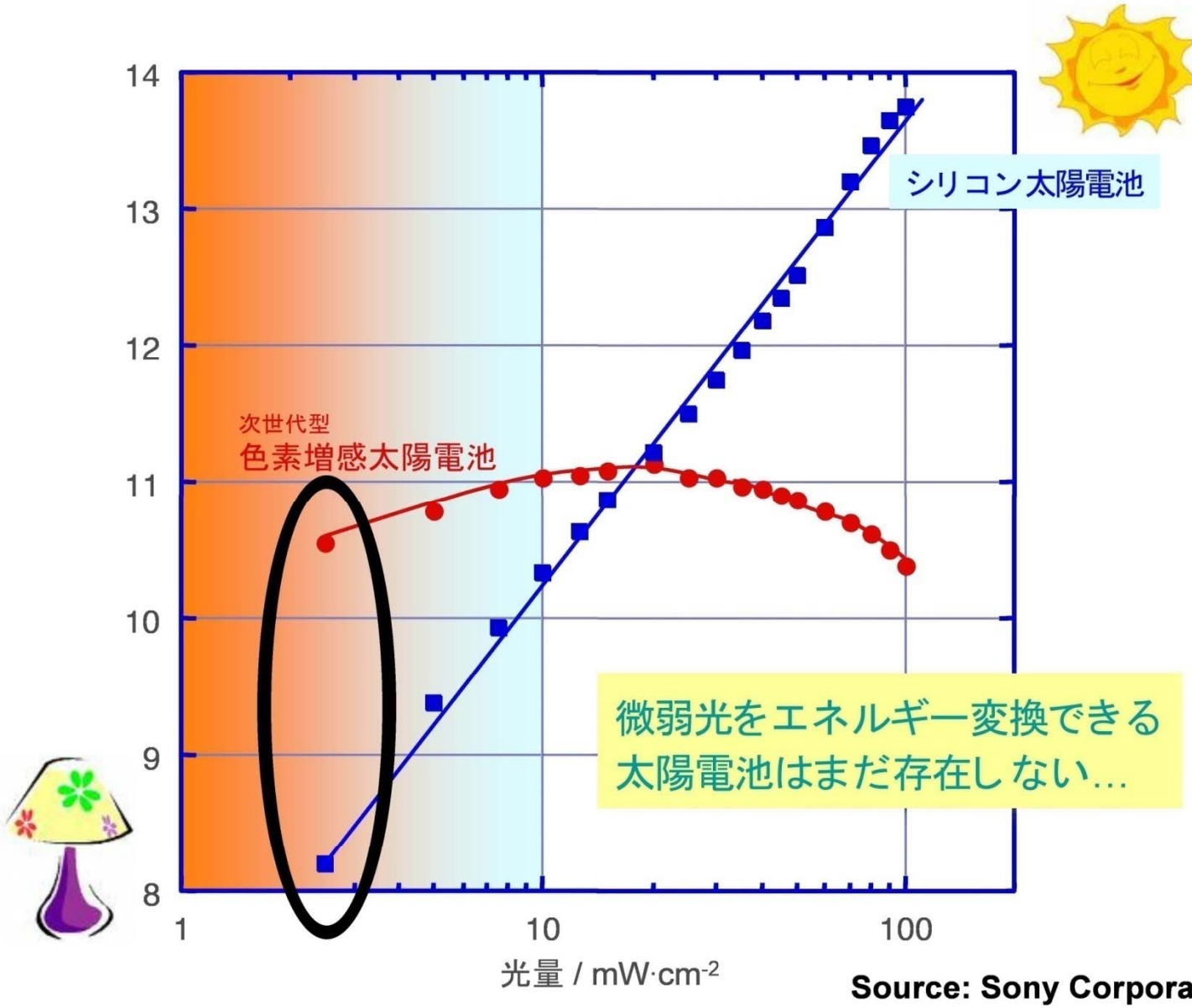
Nazeeruddin, Mohammad K.; De Angelis, Filippo; Fantacci, Simona; Selloni, Annabella; Viscardi, Guido; Liska, Paul; Ito, Seigo; Takeru, Bessho; Graetzel, Michael. JACS (2005), 127(48), 16835-16847.



Sony press release published in last Sunday's (May 25,2008) Nikkei edition

特徴 **Dye sensitized solar cells outperform silicon at lower light levels**

屋内希薄光エネルギーの利用



Source: Sony Corporation (2007)

ITRI eyes dye-sensitized solar cells

STAFF WRITER, WITH CNA Saturday, Jun 14, 2008, Page 11

The Industrial Technology Research Institute (ITRI, 工研院) is working on improving production technologies related to dye-sensitized solar cells, hoping to mass produce the low-cost component in three to five years, sources at the Hsinchu-based institution said yesterday. ITRI's prototype dye-sensitized solar cells are being presented to the public at the three-day Taiwan Nano 2008 Exhibition in Taipei. The first dye-sensitized solar cell was developed in 1991 by two Swiss-based scientists, Michael Graetzel and Brian O'Regan at the Ecole Polytechnique Federale de Lausanne. The cells use titanium dioxide-laced dye material to capture photons. The energy in the particlescan then be converted to electrical energy.

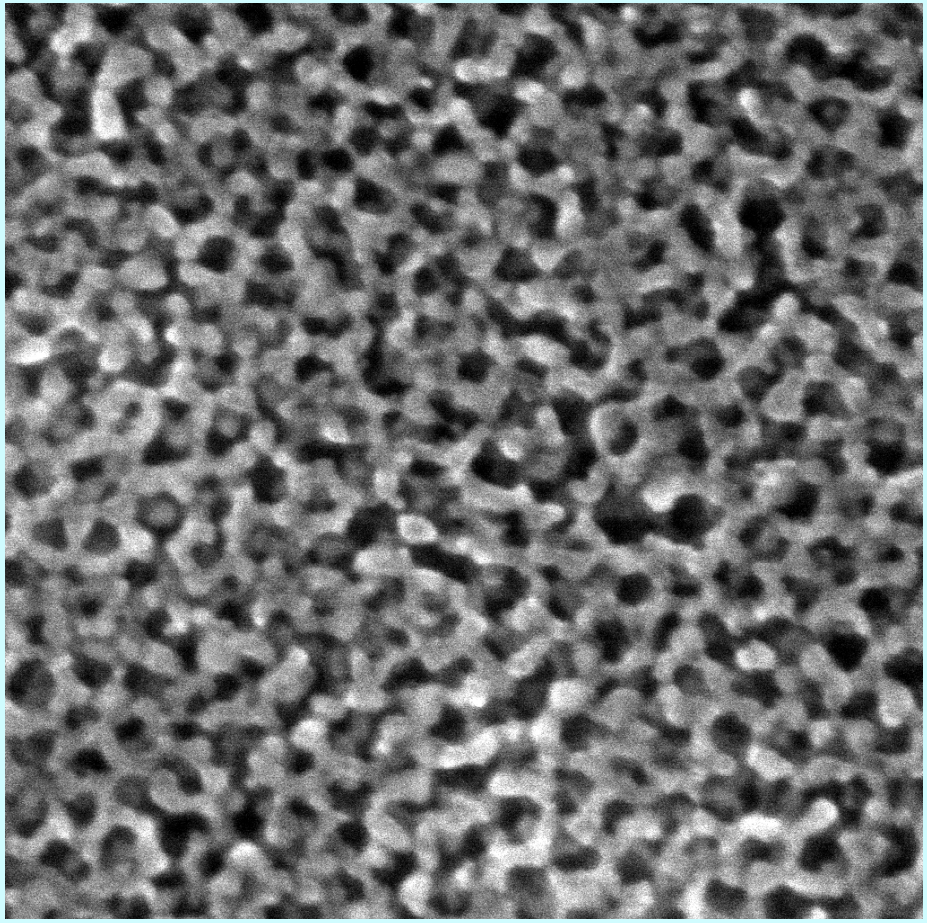
These solar cells, which combine nanocrystal technology and nano thin films, are efficient in

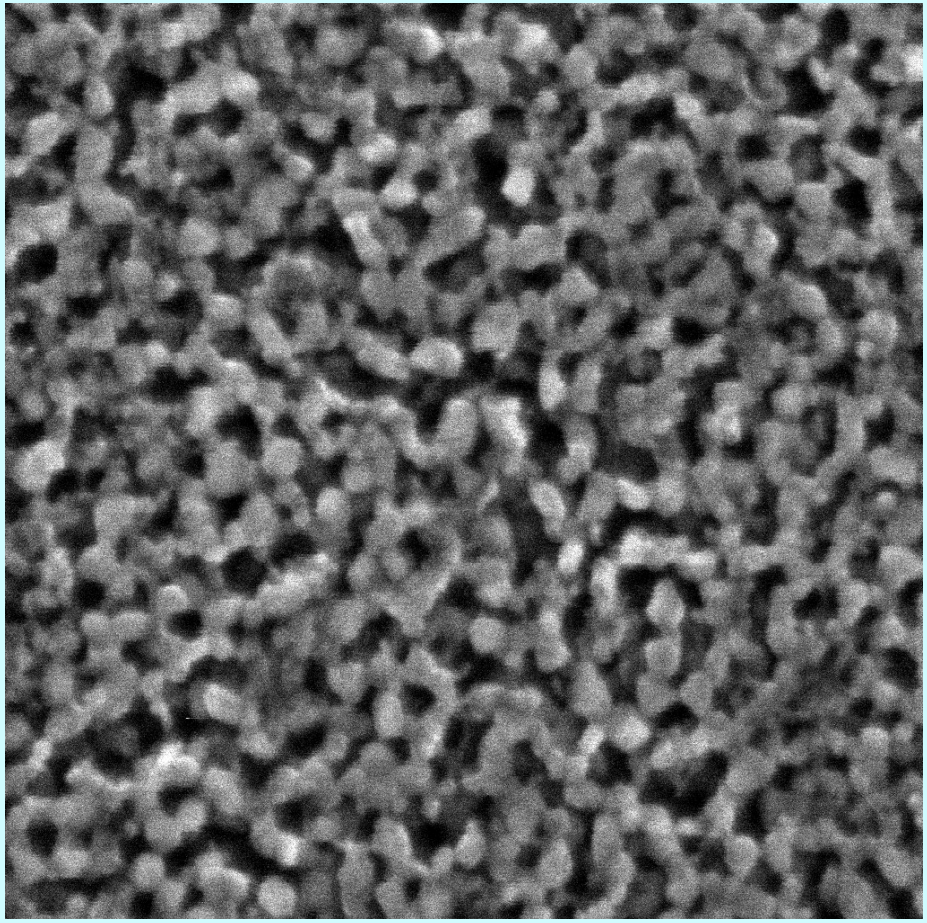
Ongoing research

- Advanced nanostructures
- Light induced charge separation
- new sensitizers
- new redox mediators
- Solid state heterojunctions
- Quantum dot cells
- tandem devices
- solar photolysis of water

Ordered mesoporous TiO2 films produced by Stucky's Pluronics templating method

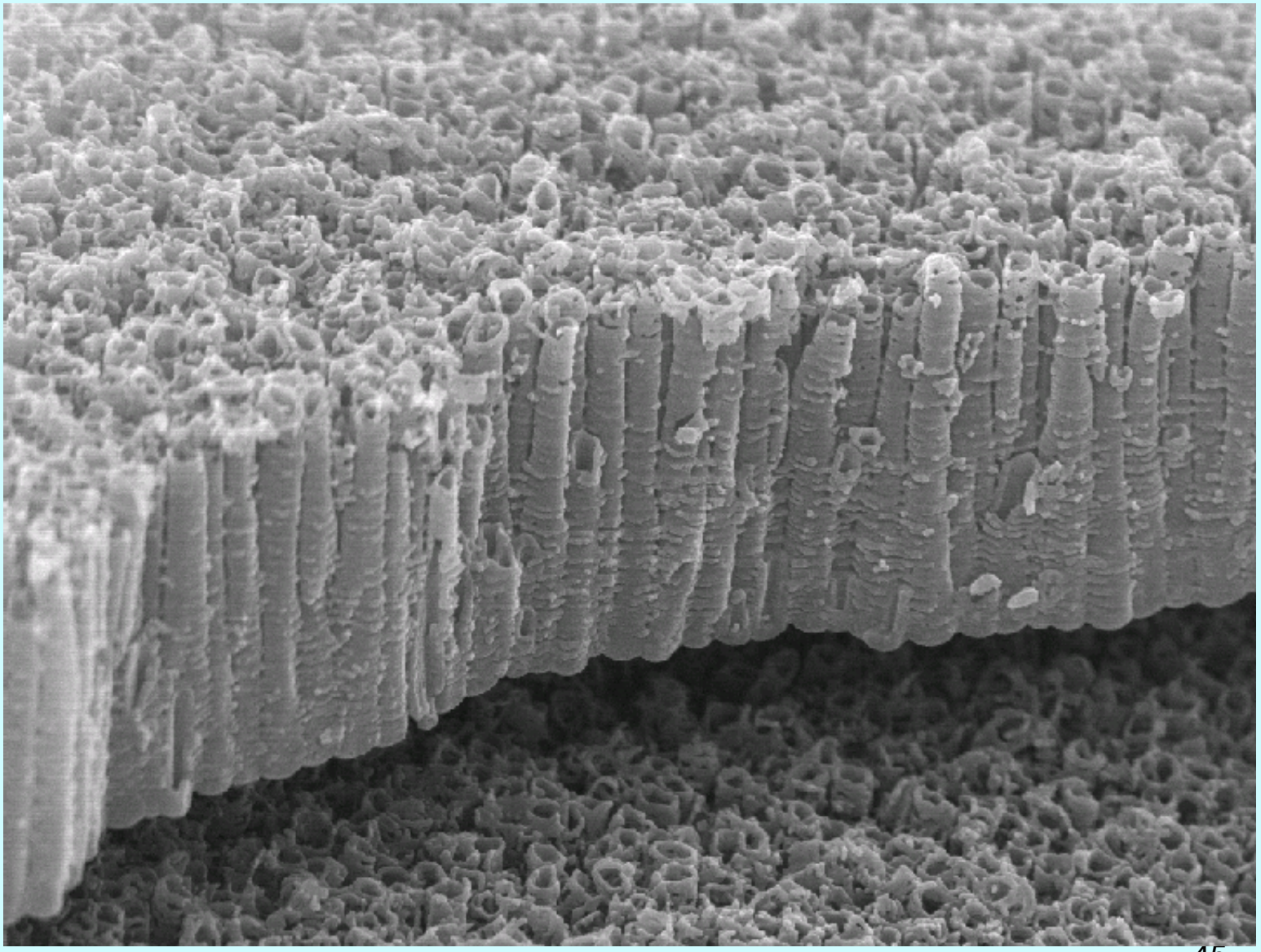
Yang, Peidong; Zhao, Dongyuan; Margolese, David I.; Chmelka, Bradley F.; Stucky, Galen D.. Nature (London) (1998), 396(6707), 152-155





L. Kavan, J. Rathousky, M. Graetzel, V. Shklover, and A. Zukal
J. Phys. Chem. B, 104, No. 50, 12012-12020 (2000).
DSC applications: M. Zukalova, A. Zukal, L.Kavan,M.K Nazeeruddin, P. Liska, M.Graetzel, Nano Letters, 5, p. 1789-1792 (2005).

TiO_2 Nanotubes



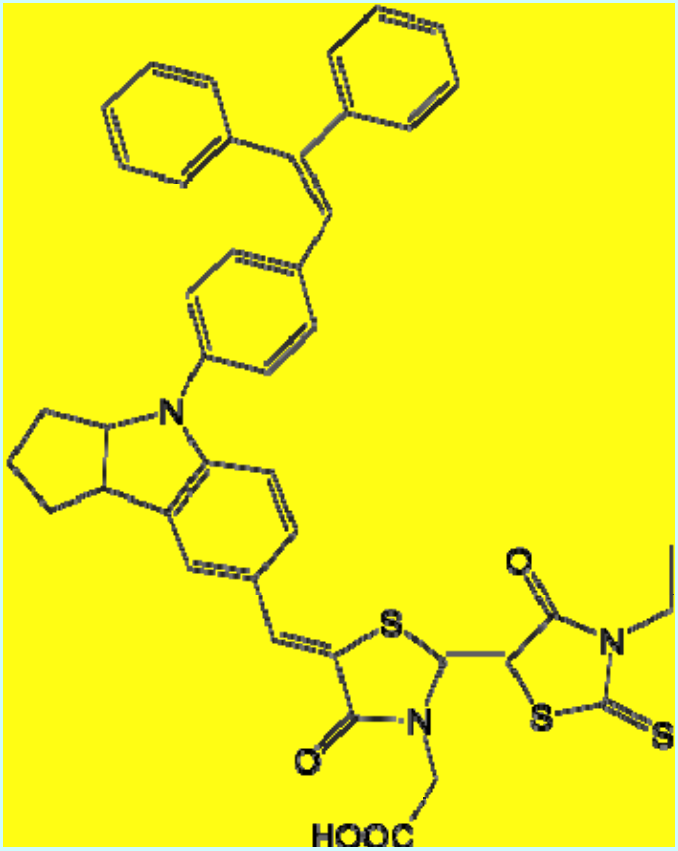
Q. Cai, M. Paulose, O. K. Varghese, C. A. Grimes, *J. Mater. Res.* 20 (2005) 230

Ongoing research

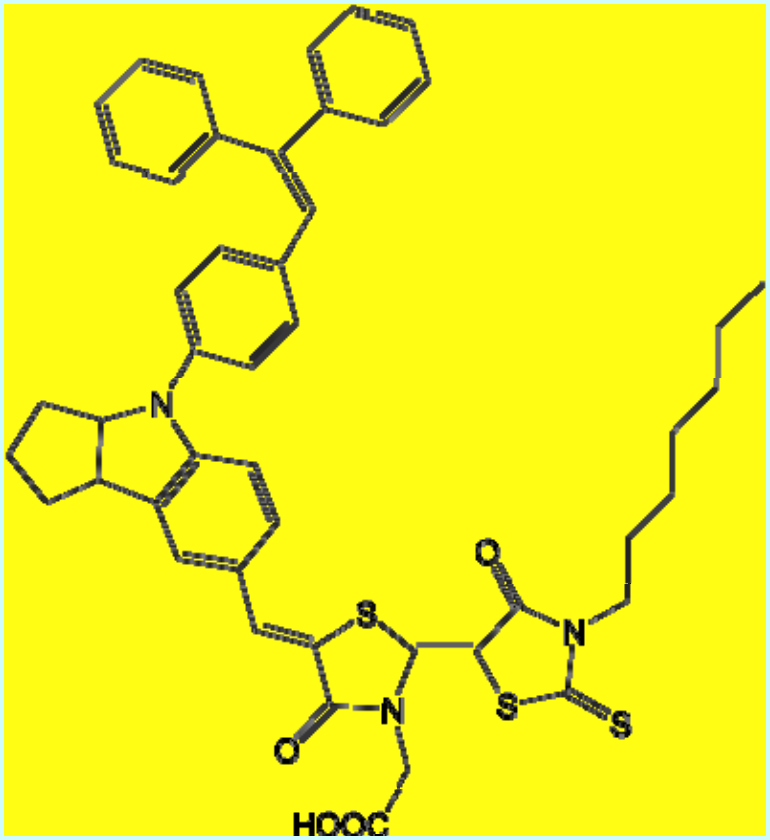
- Advanced nanostructures
- Light induced charge separation
- new sensitizers
- new redox mediators
- Solid state heterojunctions
- Quantum dot cells
- tandem devices
- solar photolysis of water

However organic dyes are catching up

Molecular structures of D149 and D205

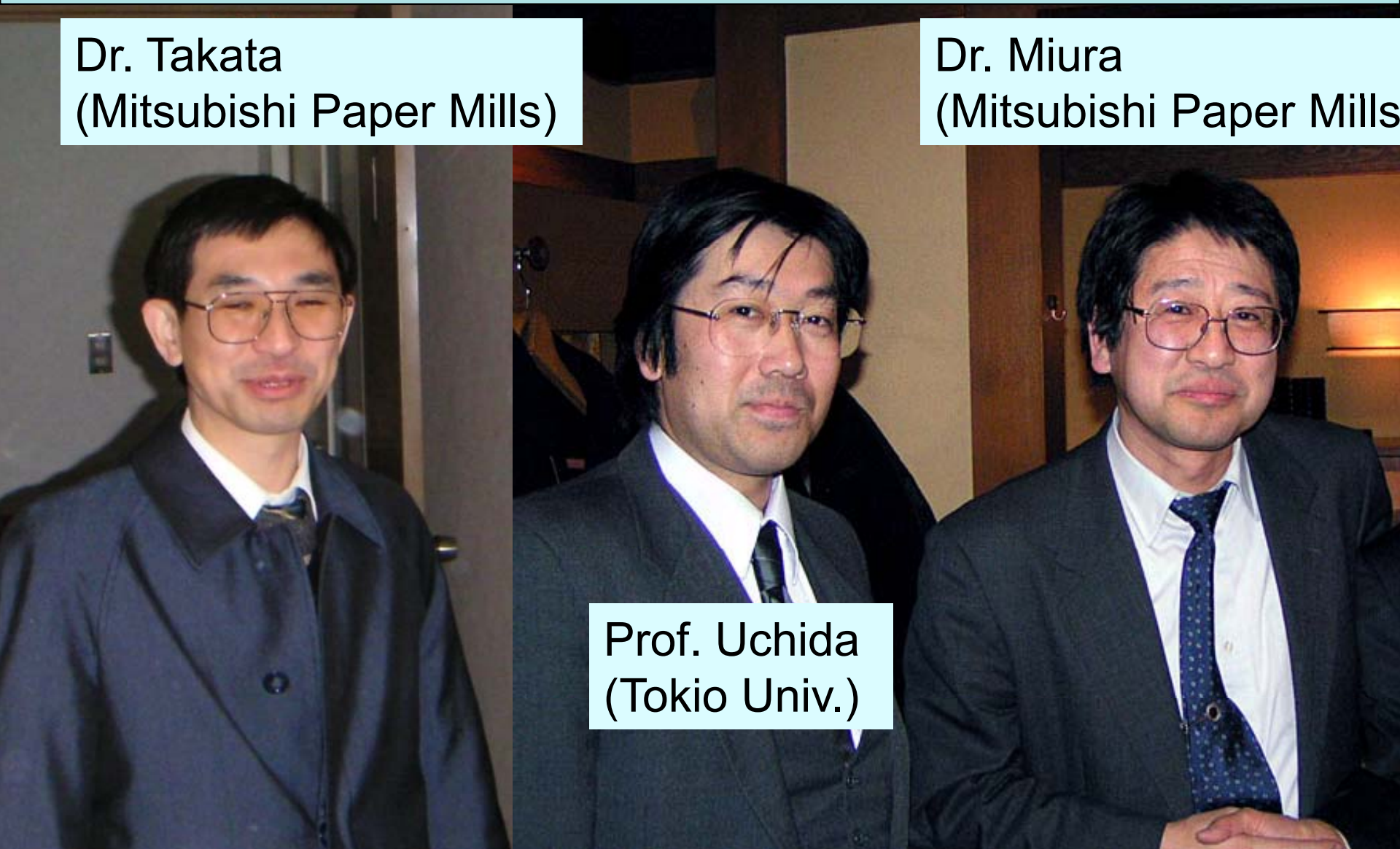


D149

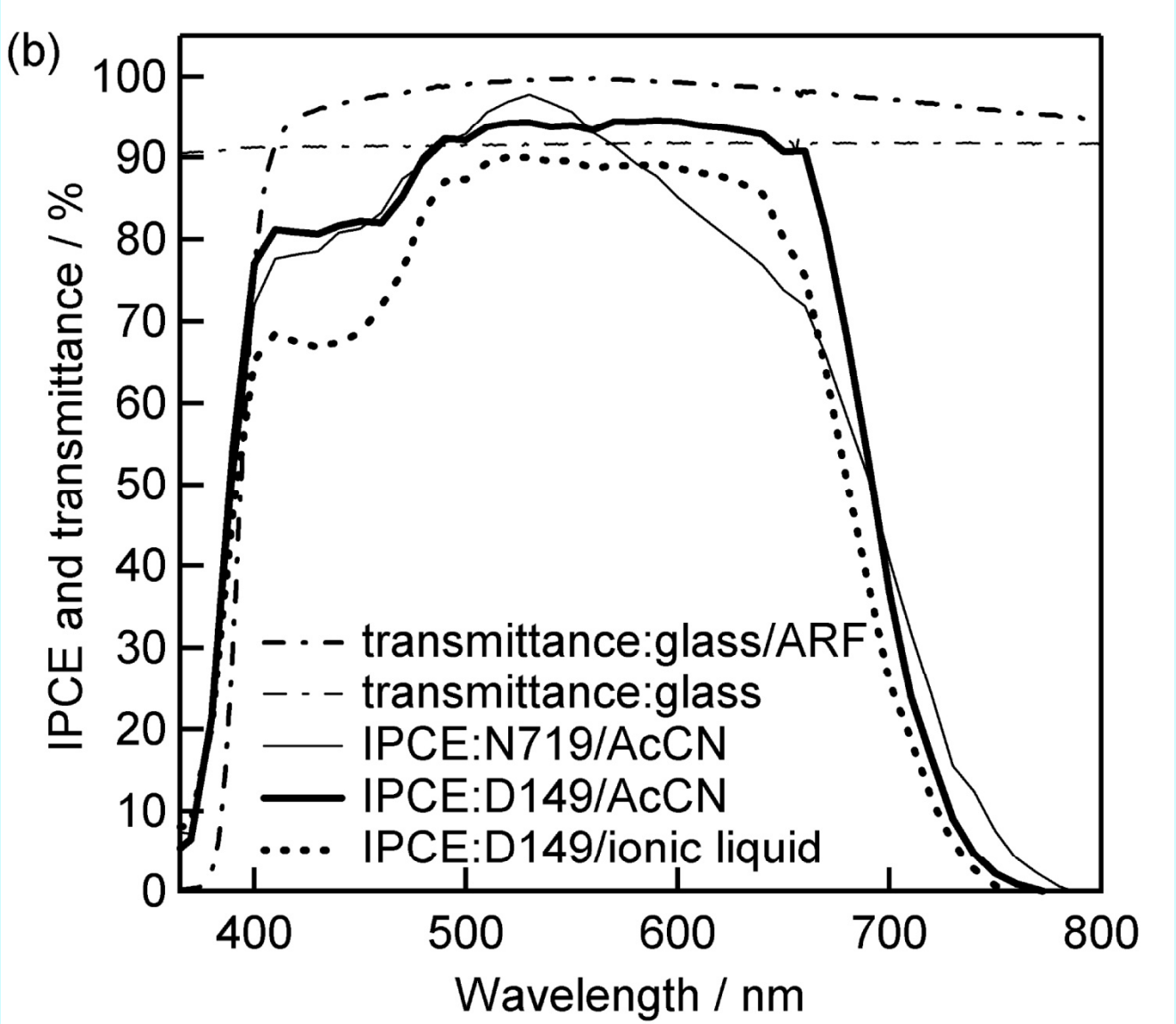


D205

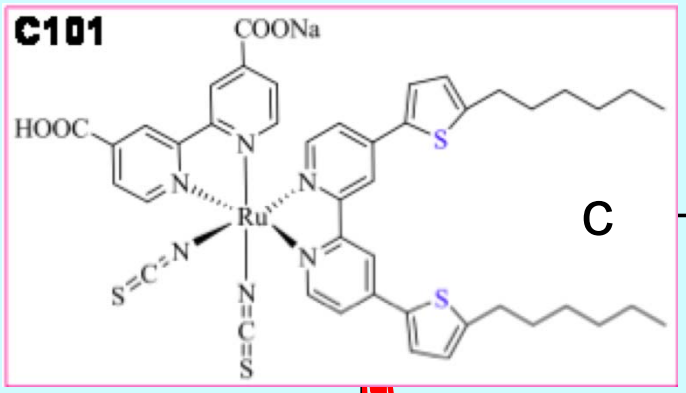
The three inventors of the D-149 dye

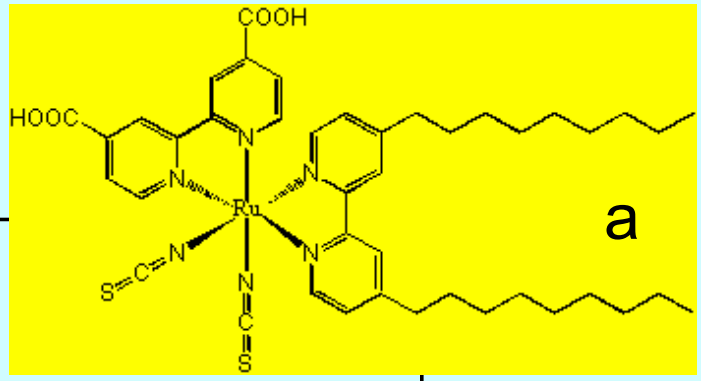


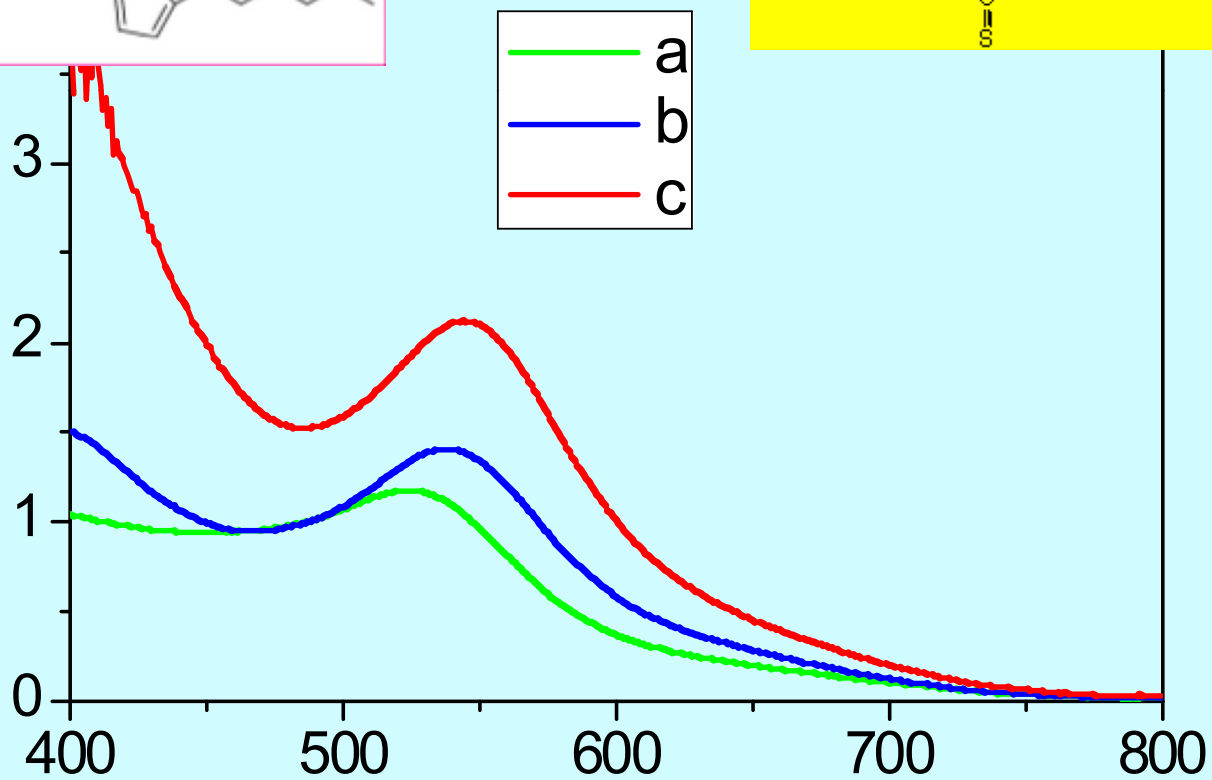
The incident photon to current conversion efficiency (IPCE or EQE) attains > 90 % over a broad spectral range in the visible



molecularly engineered sensitizers contain thiophene antenna moieties that enhances solar light harvesting







In collaboration with Prof. Peng Wang, CAS China

STABILITY

Requirements for outdoor use according to international PV standards applied to single crystal silicon but so far not to thin film PV cells

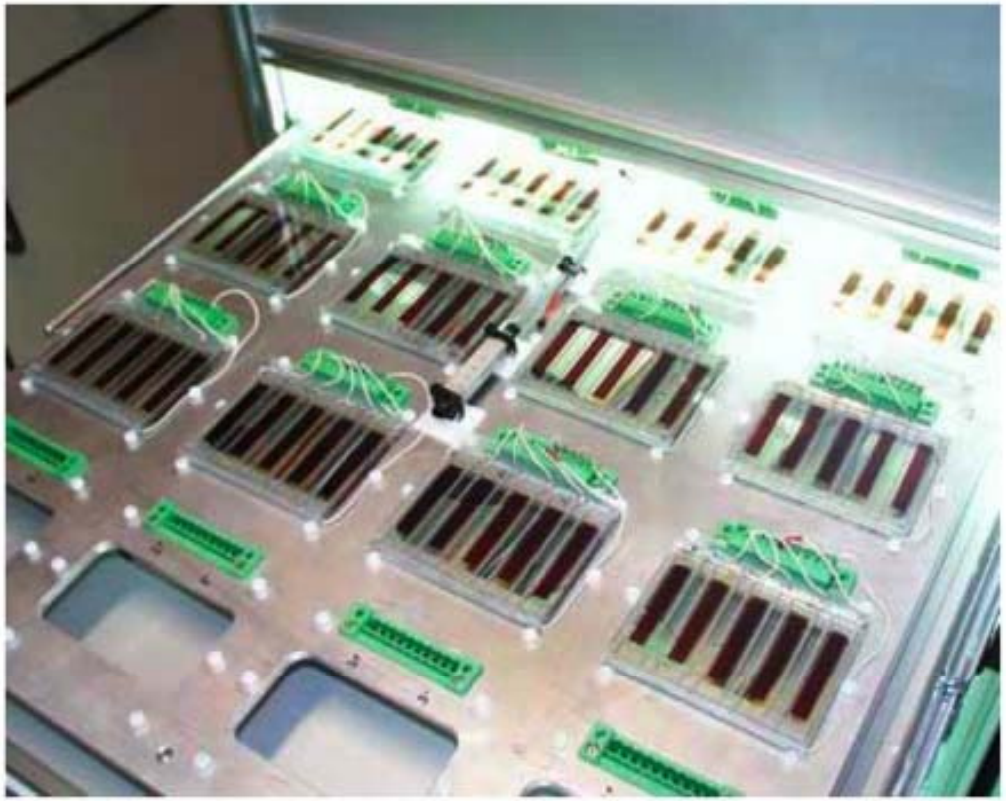
UV plus heat (55-60 C): 1000 hours

Accelerated thermal test at 85 C: 1000 h

Humidity test and temperature cycling (sealing issues)

Light soaking at 2.5 suns (2.5kW/m2)

DSC masterplates

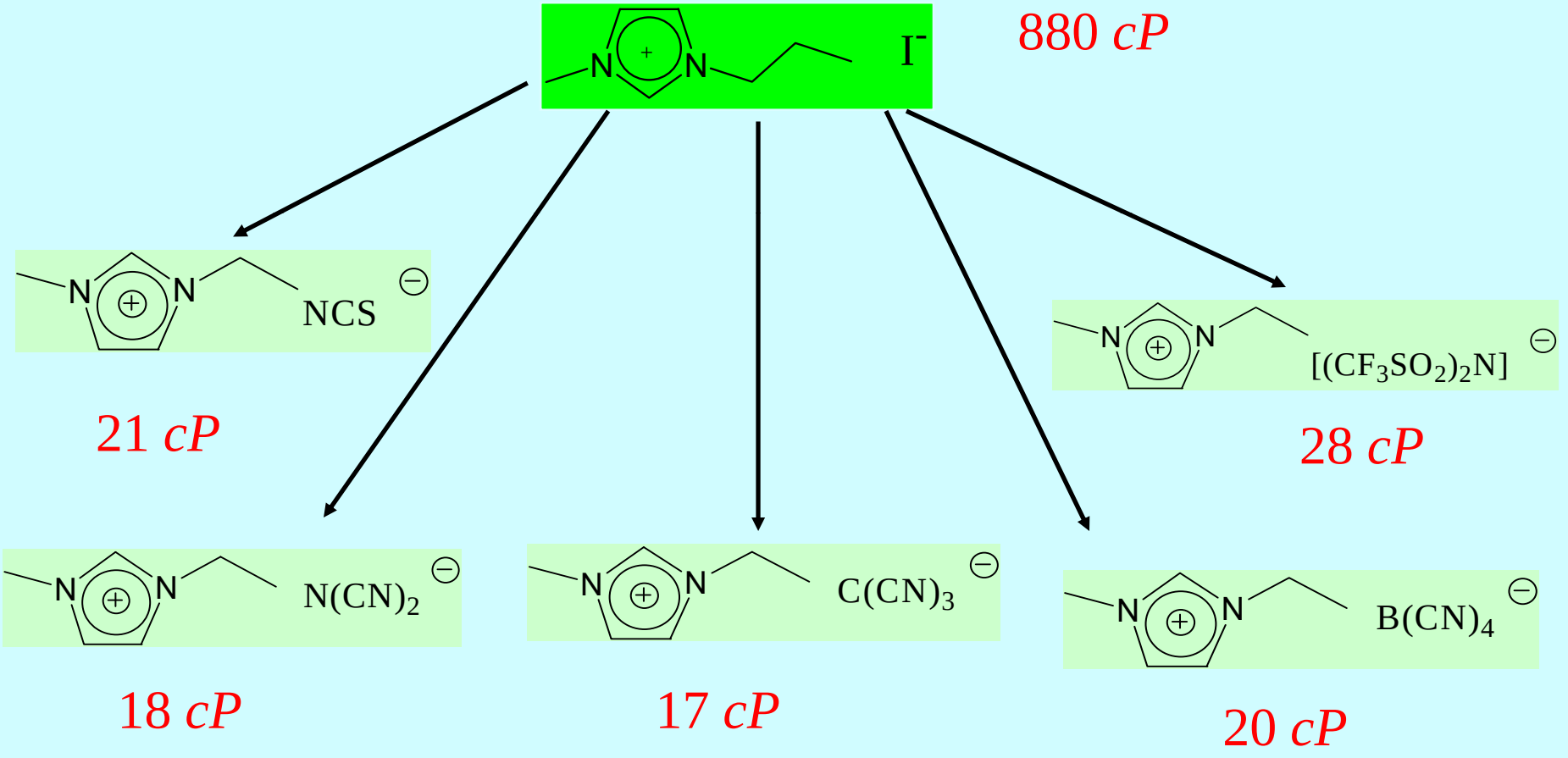


Ionic Liquids (Ils)have attractive features

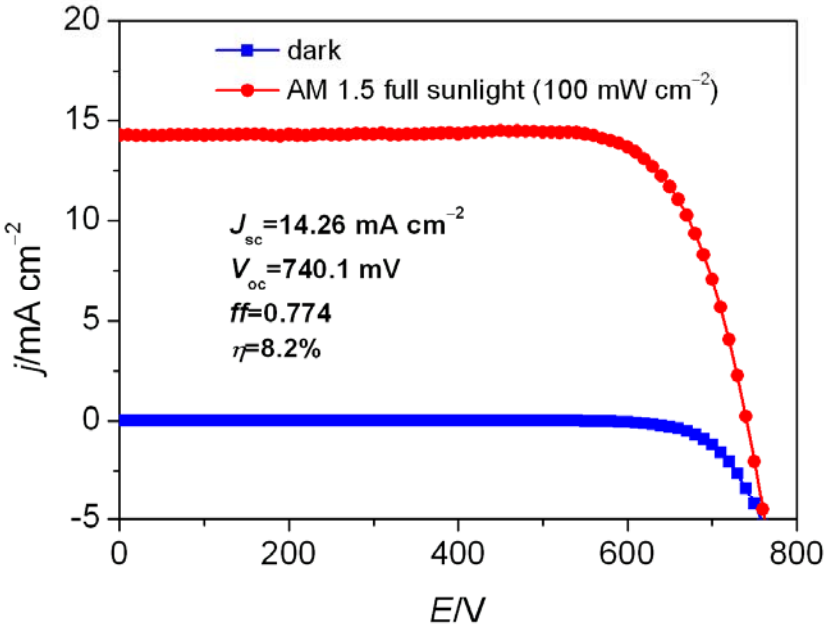
- *Thermal Stability;*
- *Non Flammability;*
- *High Ionic Conductivity;*
- *Negligible Vapor Pressure;*
- *Wide Electrochemical Window;*
- *Non-toxic*

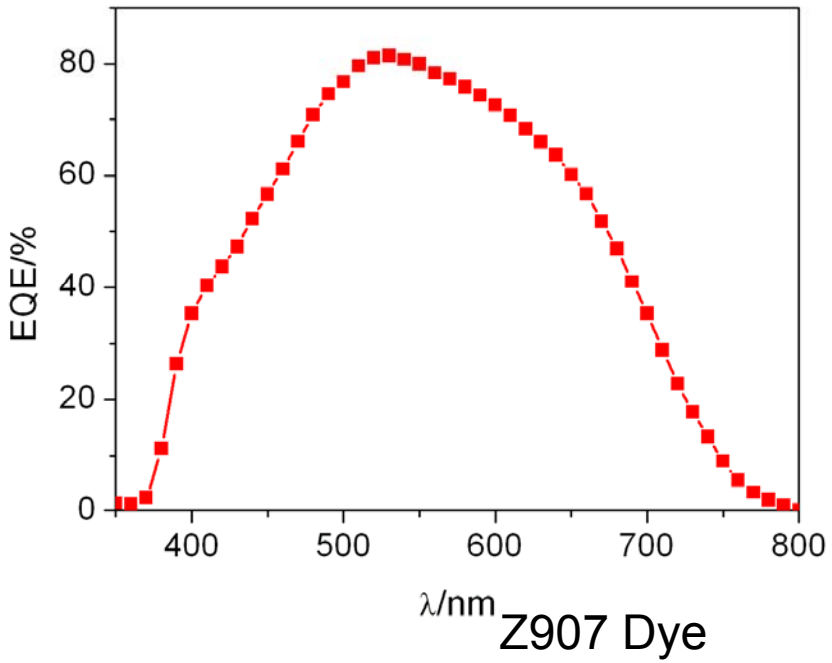
Solid polymer/IL gels are formed by the addition of poly-(vinylidenefluoride-*co*-hexafluoropropylene) (PVDF–HFP)

Wang, P; Zakeeruddin, S. M.; Exnar, I.; Graetzel, M..
High efficiency dye-sensitized nanocrystalline solar cells based on ionic liquid polymer gel electrolyte.
Chemical Communications (Cambridge, United Kingdom) 2002, 24, 2972-2973.


I-
880 cP
NCS
21 cP
[(CF3SO2)2N]
28 cP
N(CN)2
18 cP
C(CN)3
17 cP
B(CN)4
20 cP

Eutectic ionic liquids: a new efficiency record of 8.2%





Z907 Dye

YU BAI[1]*, YIMING CAO[1]*, JING ZHANG[1], MINGKUI WANG[2], RENZHI LI[1], PENG WANG[1†], SHAIK M. ZAKEERUDDIN[2] AND MICHAEL GRAETZEL **Nature Materials** in press

Our previous data: **7.4%** efficiency in **JACS 127 (2005) 6850**


藤森工業(株)
昭和電工(株)
ザクロス透明導電性フィルム
ZACROS
SP-X
TAIWAN
3-66
3-66-14 USE ELECTRON

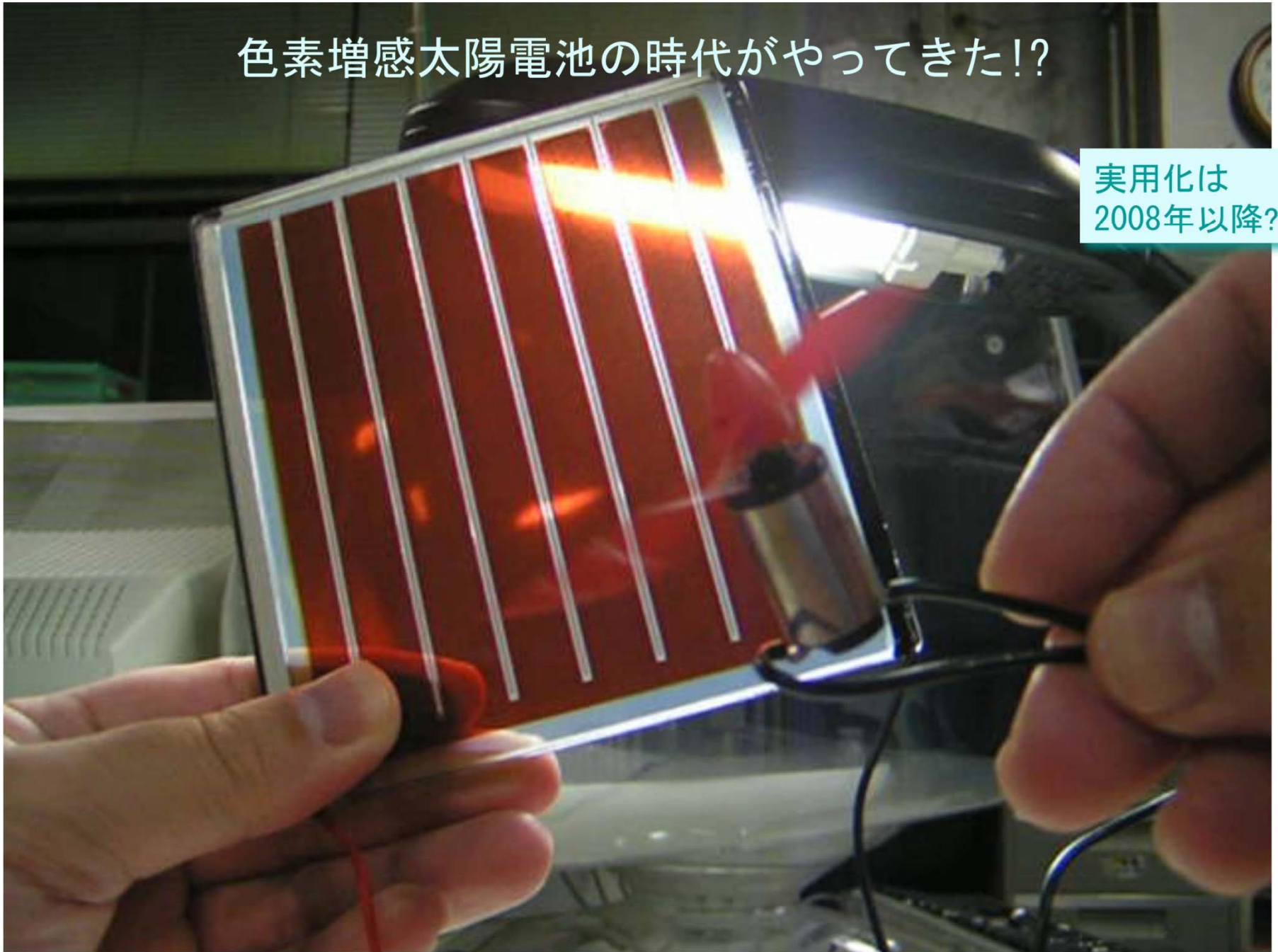
Emerging and new applications call for:

- Ease of integration
- color
- flexibility
- light weight
- many more,,,

- **... further development and new technologies in order to meet optimally the customer demands and needs**

Courtesy Dr. Winfried Hoffman, CEO, RWE, SCHOTT Solar GmbH

色素増感太陽電池の時代がやってきた!?



実用化は
2008年以降?

Module of Dye sensitized Solar Cells (prototype)

Feature

Potential of low manufacturing cost

Low materials cost

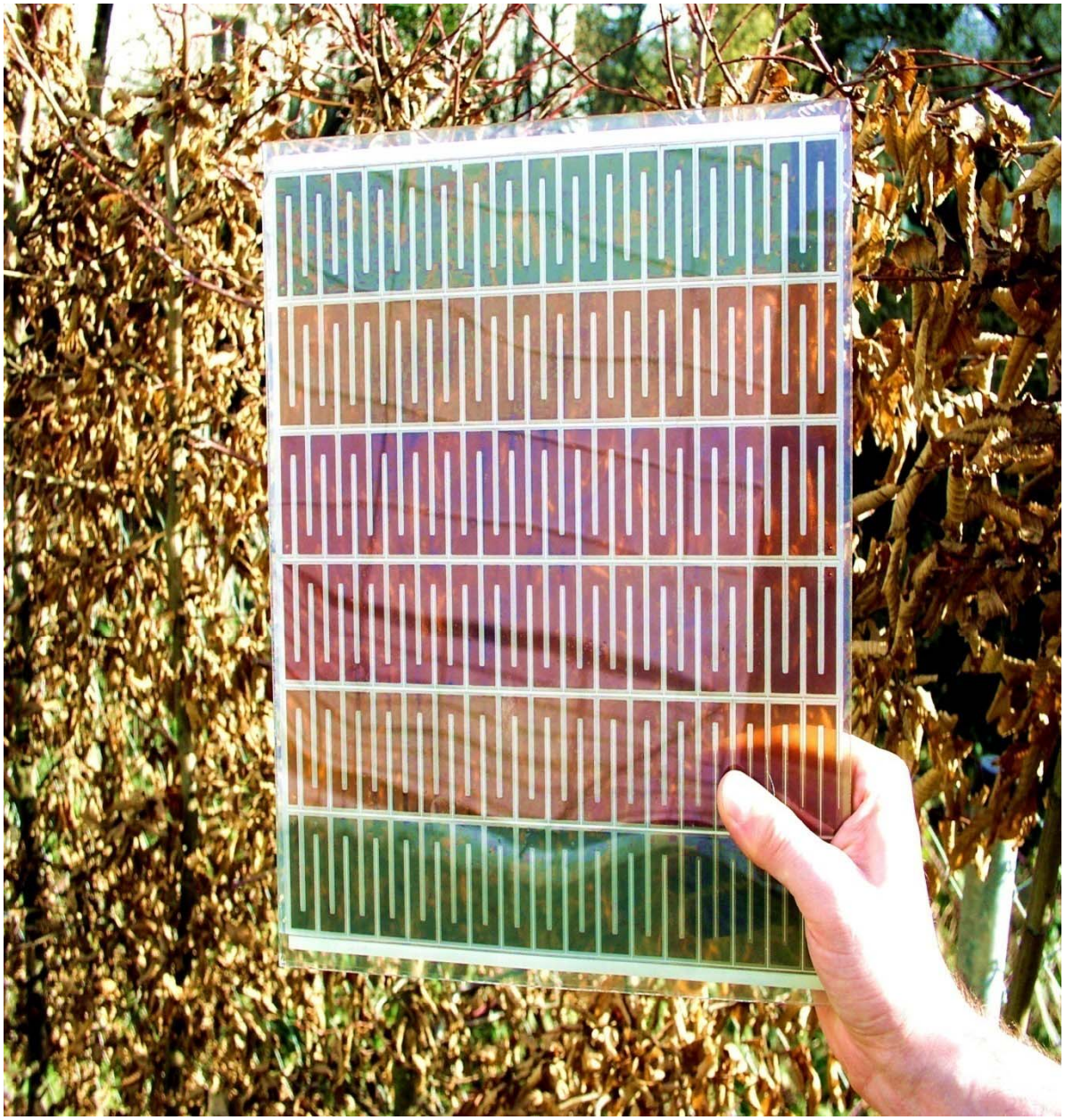
Less investment

Without vacuum and high temperature process

Potential of colorful design

with different dyes

Various colours in a series-connected dye solar cell module



Courtesy Dr. Andreas Hinsch, FHI, ISE Freiburg Germany


KYOCERA
TDK
STAF

Courtesy Dr. Nam Gyu Park KIST

transparent, colorful, beautiful

Transparency: due to nano-sized (~20 nm) TiO2 particle film

Color: due to visible light absorption by dye

* DSC costs lower than Si solar cell; 1/4 -1/5 of Si solar cell

Scale-up and production


色素増感型太陽電池
AISIN
消火器


QuickTime™ and a
TIFF (Uncompressed) decompressor
are needed to see this picture.
HOUSE
OF THE
FUTURE

Real Outdoor Test of DSC Modules

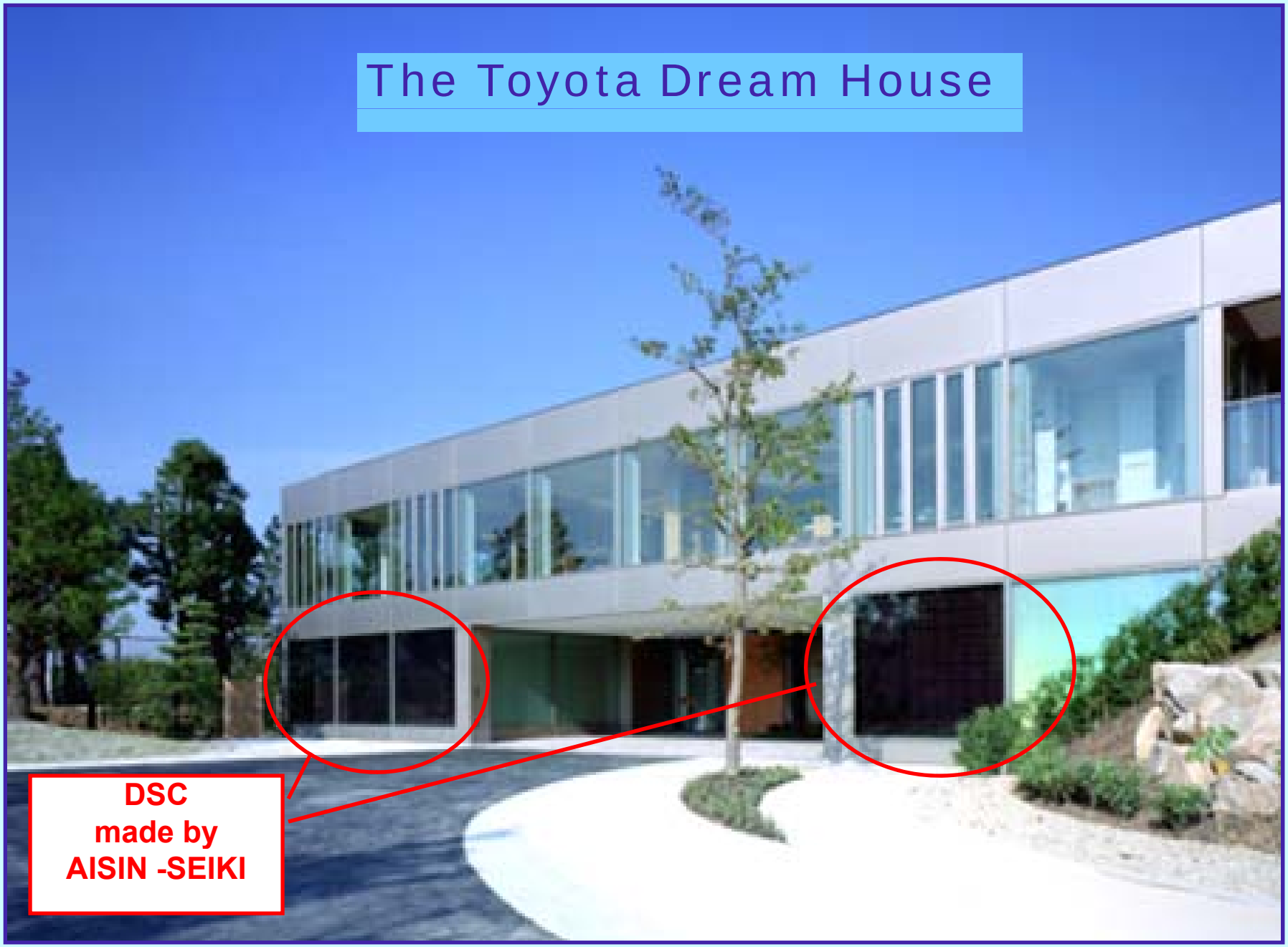
Module Unit

Series connected
64 DSC cells

Outdoor Test

Kariya City at lat. 35° 10'N,
Asimuthal angle: 0°
Facing due south, Tilted at 30°

The Toyota Dream House




３）モジュール設置固定

8）バイオトイレ正面

G24I builds 120 MeW capacity plant for flexible DSC production in Wales

Adran Menter, Arloesi a Rhwyd
Department for Enterprise Inn
and Networks

Llywodraeth Cynulliad Cymru
Welsh Assembly Government

Tuesday, 17th October 2

ddion News

WORLD-LEADING SOLAR TECHNOLOGY FIRM TO INVEST IN WALES

A multi-million pound investment into a unique world-leading renewable energy technology is to create up to 300 jobs in South Wales, it was announced today **(Tuesday, 17th October 2006).**

G24 Innovations Ltd (G24i), a new UK registered company (whose major shareholder is Renewable Capital LP of the United States), is to manufacture dye sensitised solar cells – one of the latest, lightest, most efficient and least costly solar technologies in the world – at a 187,000 sq ft facility at Wentloog Park, Cardiff and plans to begin manufacturing early in 2007.

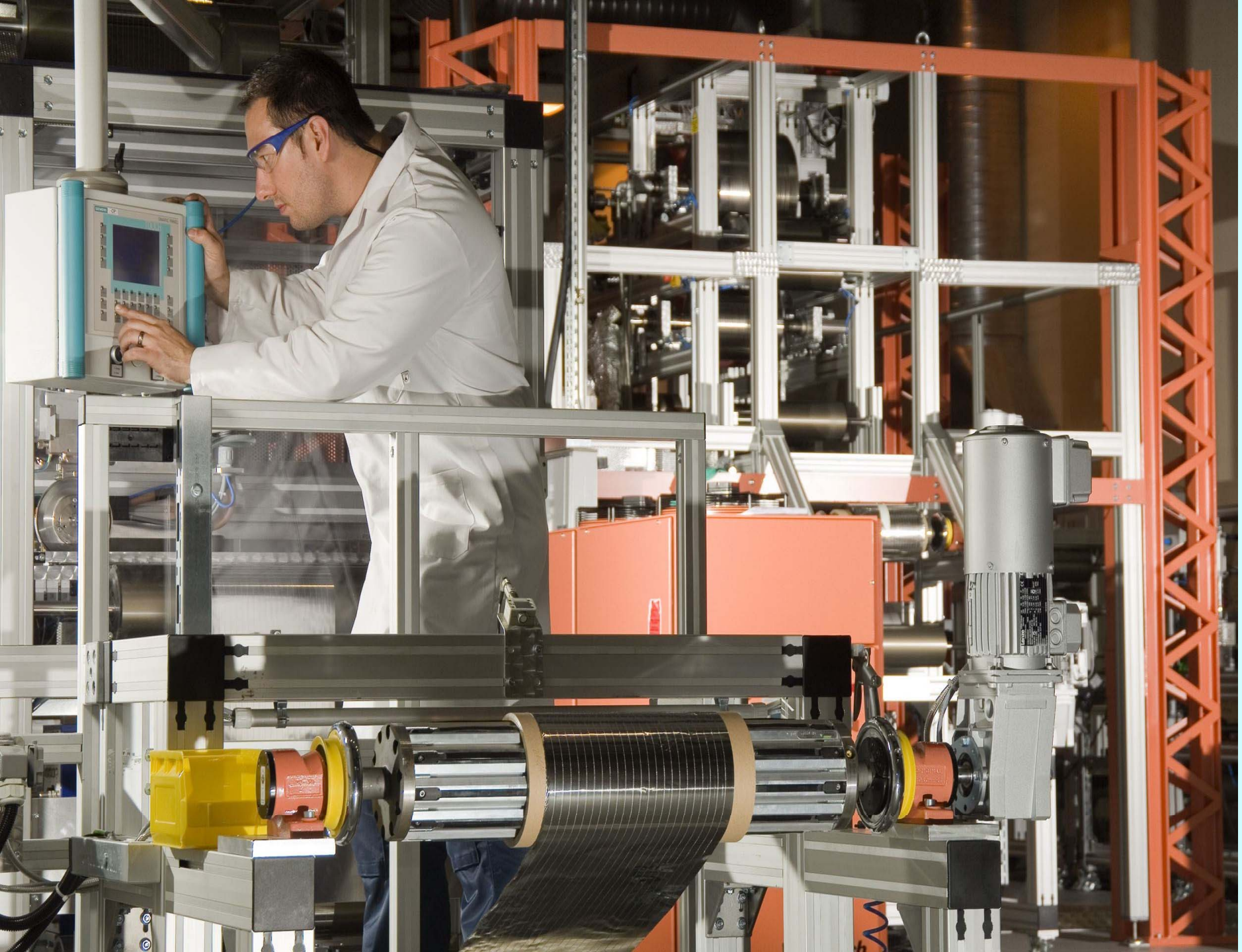
G24i's new cells will have potential application in a wide range of products although the initial market is expected to be for mobile consumer led products such as mobile phone chargers, smart textiles (incorporating the technology into fabrics), emergency and homeland security applications, MP3 players, laptop computers and handheld game consoles.

The company also believes there is an opportunity to integrate the cells in building products that can meet part of a building's energy requirements and further reduce carbon emissions.

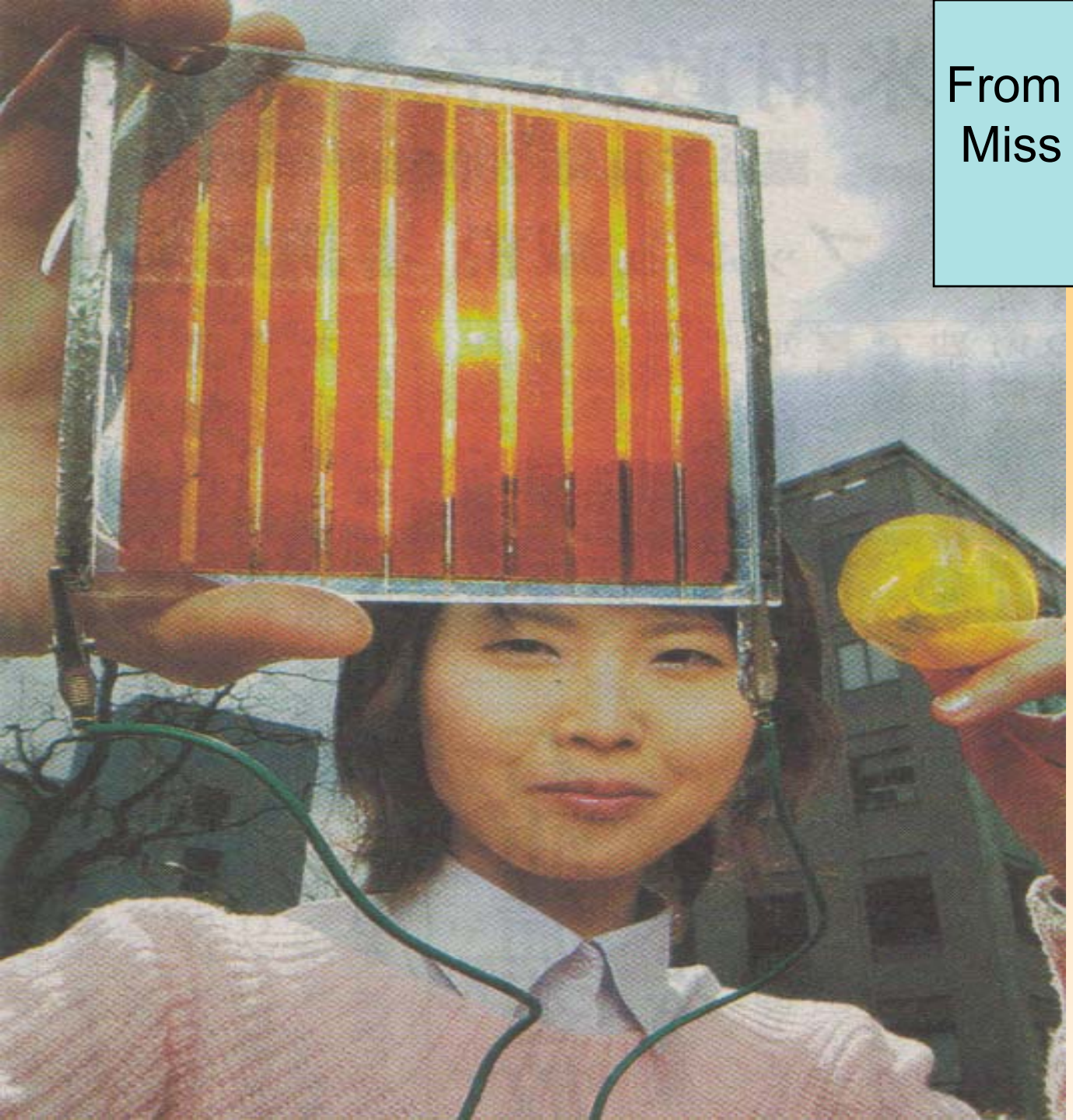
Founders of G24I: Ed Stevenson and Robert Hertzberg (64th speaker of Californian State Assembly)

The G24I plant in Cardiff has started production on June 21 (solstice),2007

The first G24I product is a light weight flexible power supply for mobile telephones



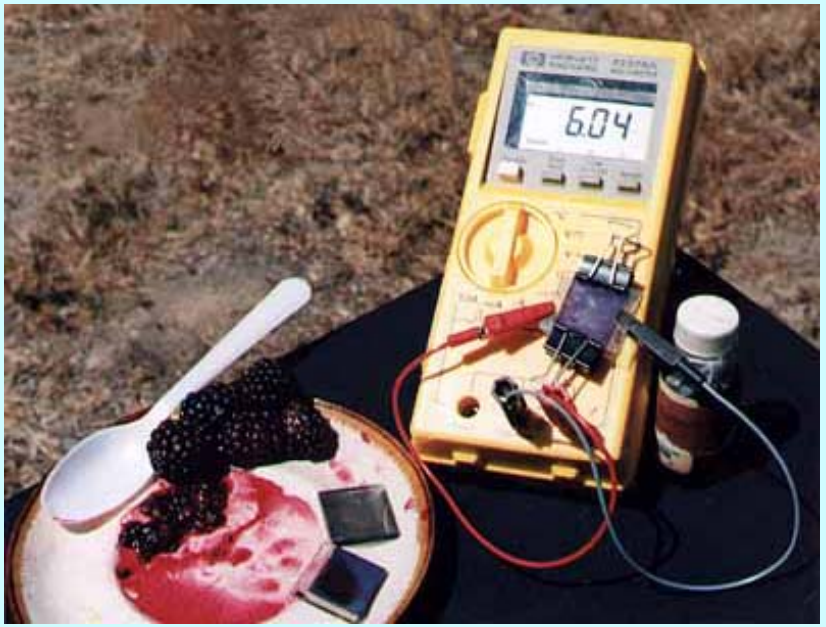
Efficient and light weight solar



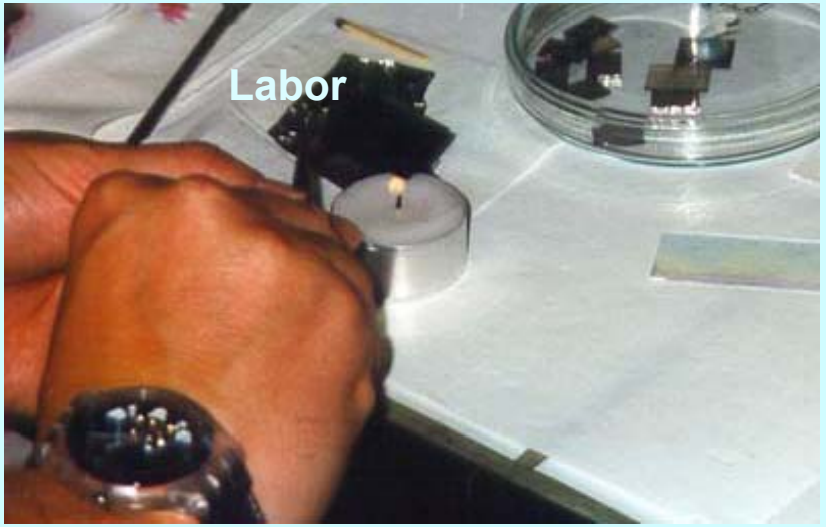
From Nikkei（日本経済新聞）
Miss Noriyo Yamanaka
Nippon Oil

Motivating the young generation is of paramount Importance !

High School Students make their own solar cell



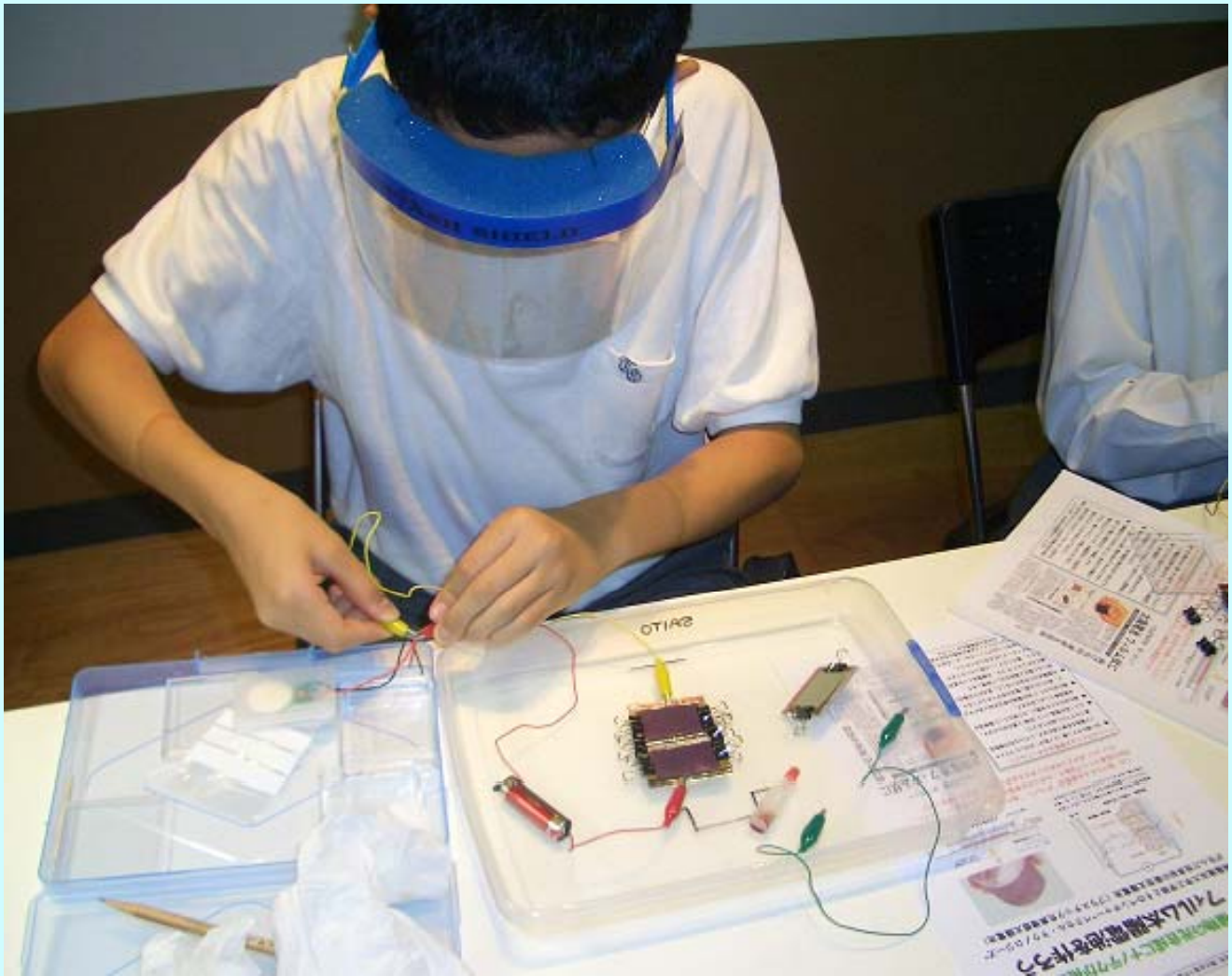
anthocyanine dye from blackberries

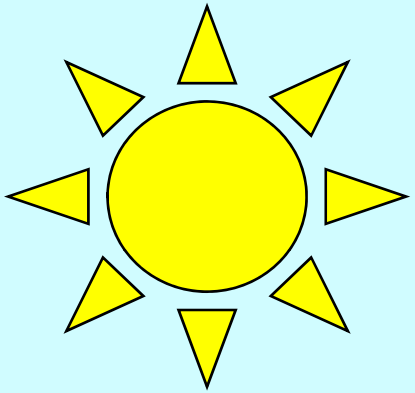


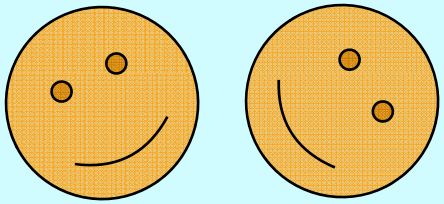
www.solideas.com, www.mansolar.com ,

Japanese school children thank the DSC community for promoting education.

Easy-to-make solar power kits for kids







Cite des métiers Genève Novembre 2006

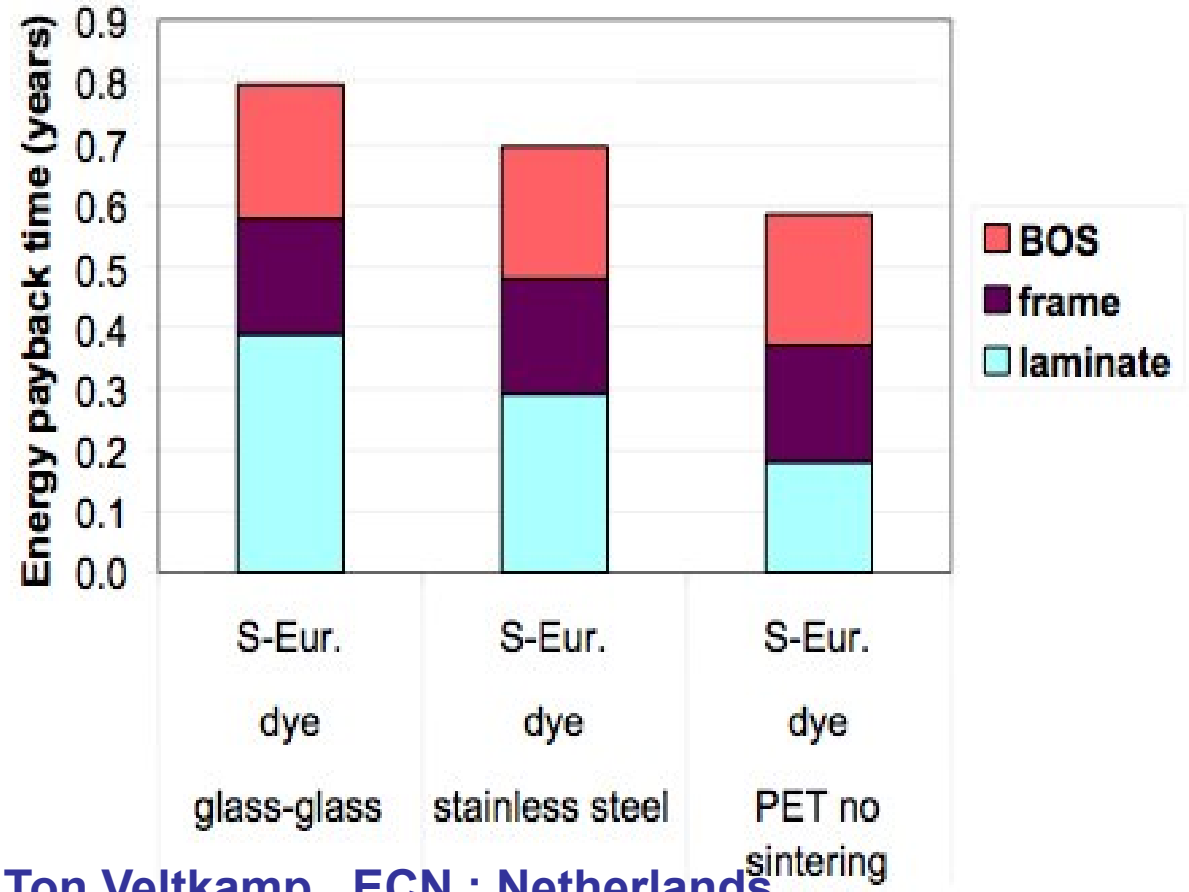
Getting infatuated: Young school children make their own cells

The attractive features of dye sensitized nanocrystalline solar cells

- current efficiency of > 11 percent is already competitive with conventional PV devices.
- 16 % conversion efficiency reached by tandem cells
- Short energy pay back time of (< 1 year)
- unique light weight, flexibility transparency, and color options facilitate market entry
- Low materials and manufacturing cost, roll to roll 120 megawatt capacity production of flexible foil cells started in Wales (www.g24i.com).

Dye sensitized cells have short energy payback times

Energy payback time with different substrates



Courtesy Dr. Ton Veltkamp , ECN ; Netherlands

Outline

Electric power generation by mesoscopic photovoltaic cells

- **Mesoscopic Fe2O3 films for solar hydrogen generation from water**

Hydrogen generation by solar photolysis of water

The three options:

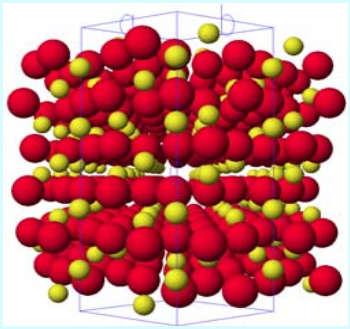
1. **The brute force approach:**
   connect at least 4 silicon PV cells in series and couple to
   water electrolyzer

2. **The integrated tandem cell approach**

3. **The direct water decomposition by photoelectrochemical cells.** **Remains the "Holy Grail" of research in photoelectrochemistry**

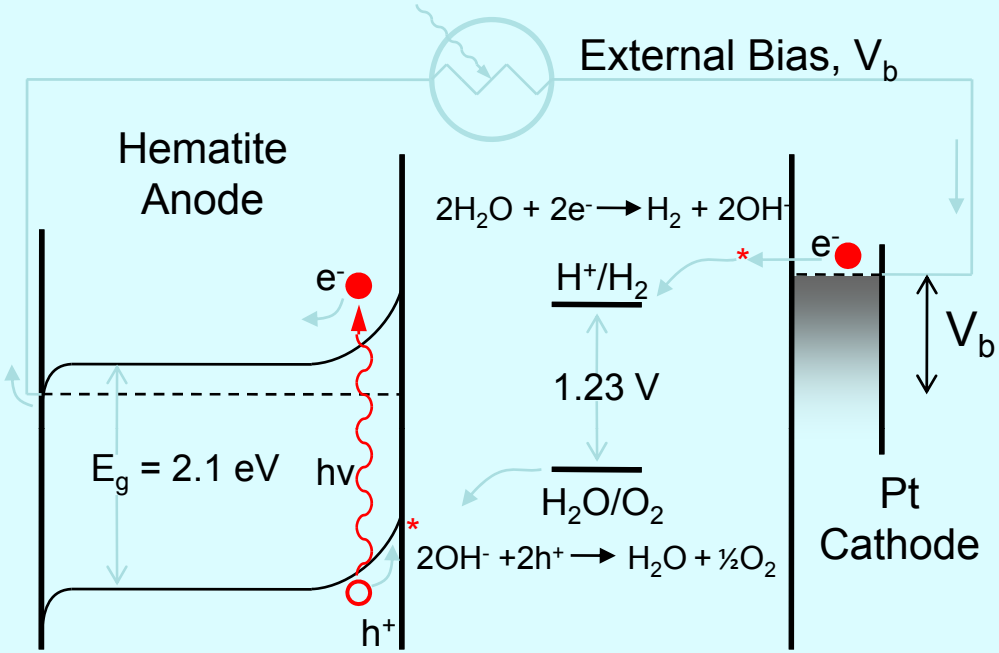
α-Fe_2O_3 a promising material

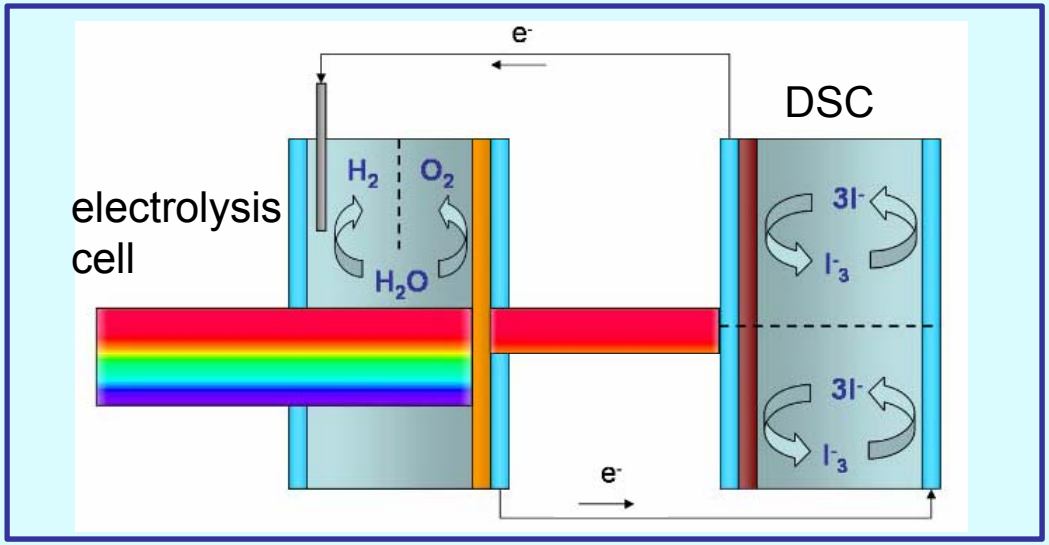
- Cheap and abundant
- Stable
- Environmentally benign
- Band gap 2.1 eV
- Problem: conduction band too low for H_2 evolution.
- Problem: large light penetration depth compared to hole diffusion length



α-Fe_2O_3
corundum structure

Fe O





State of the art – APCVD Fe_2O_3

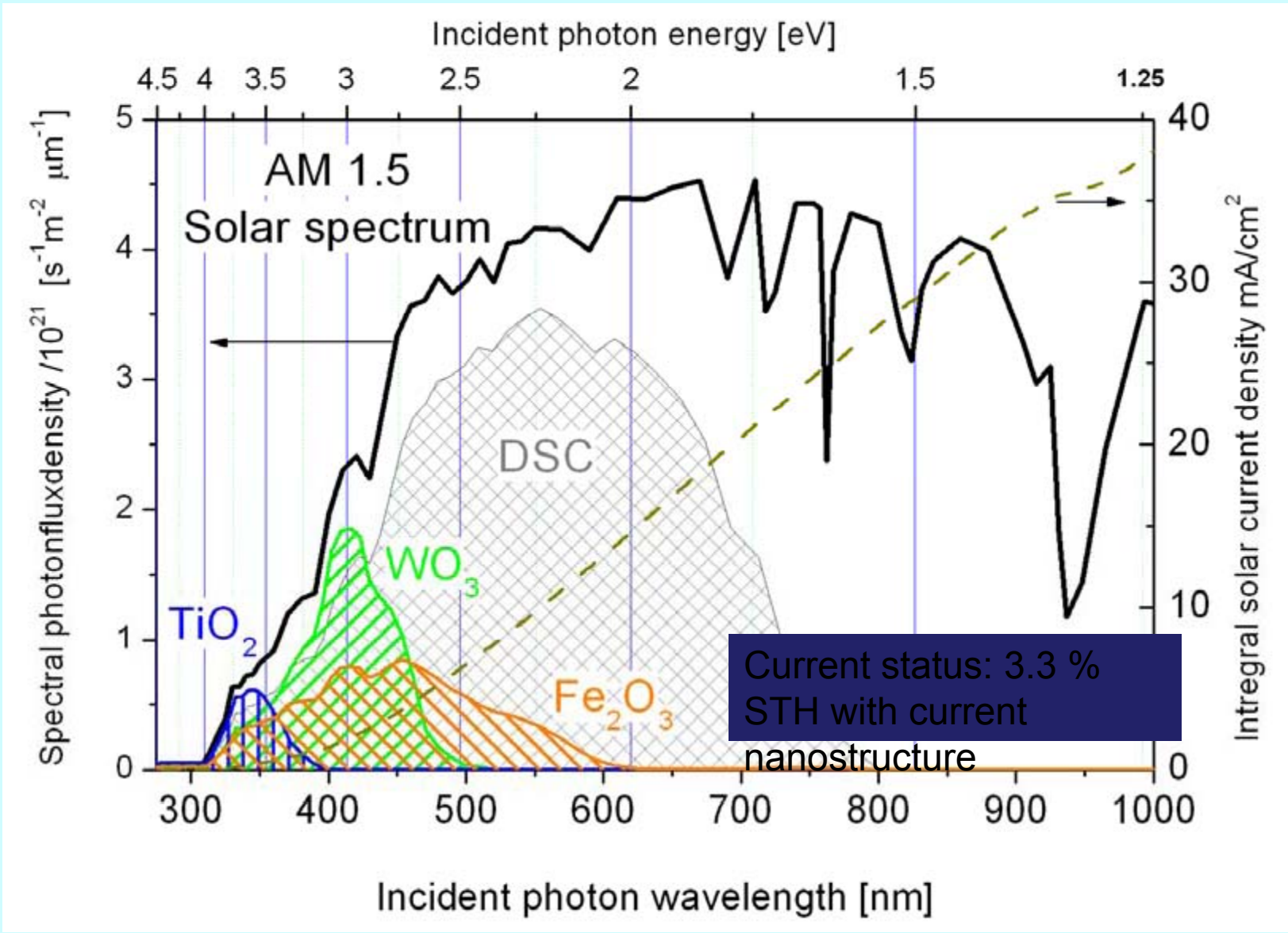
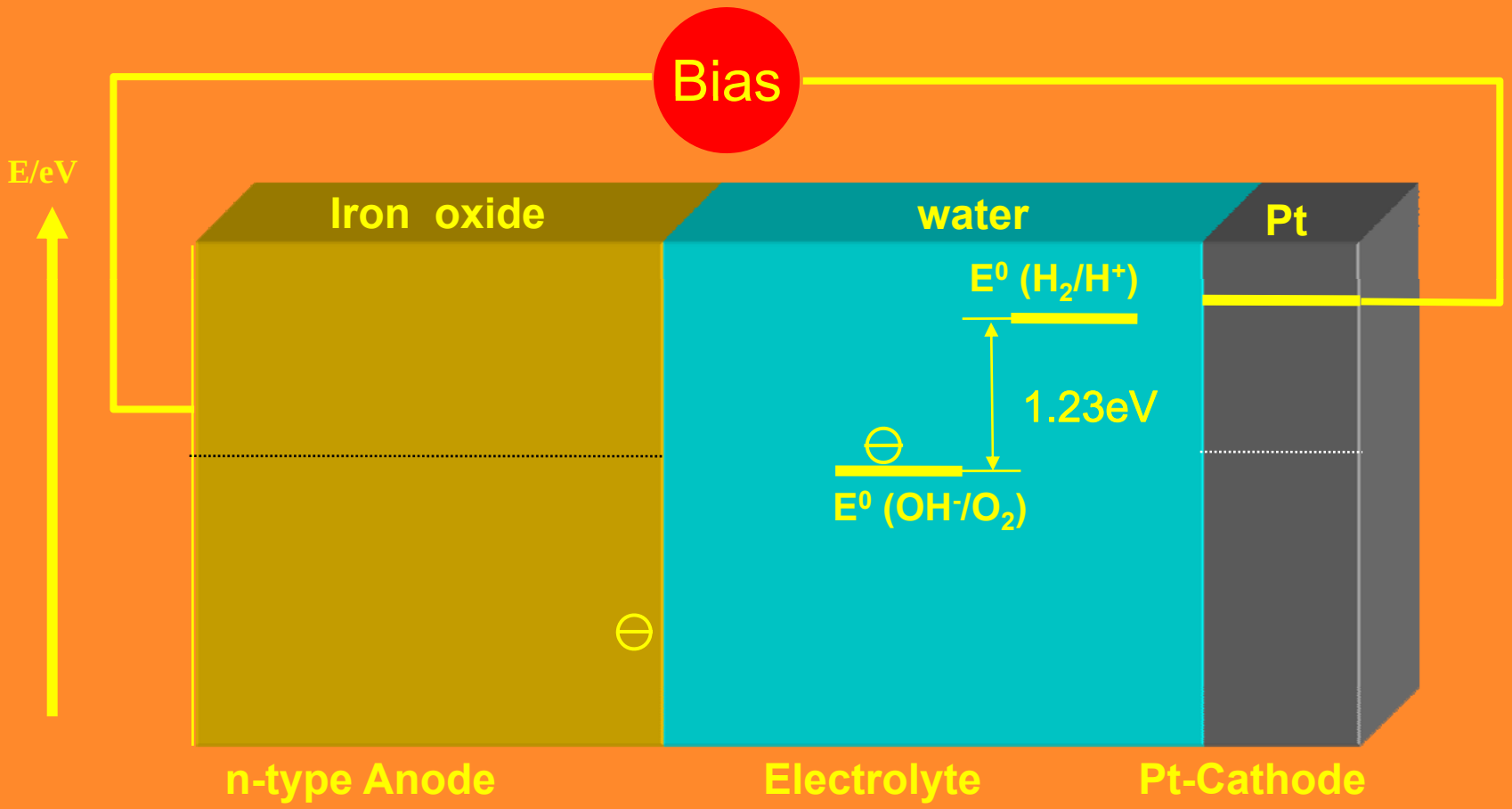
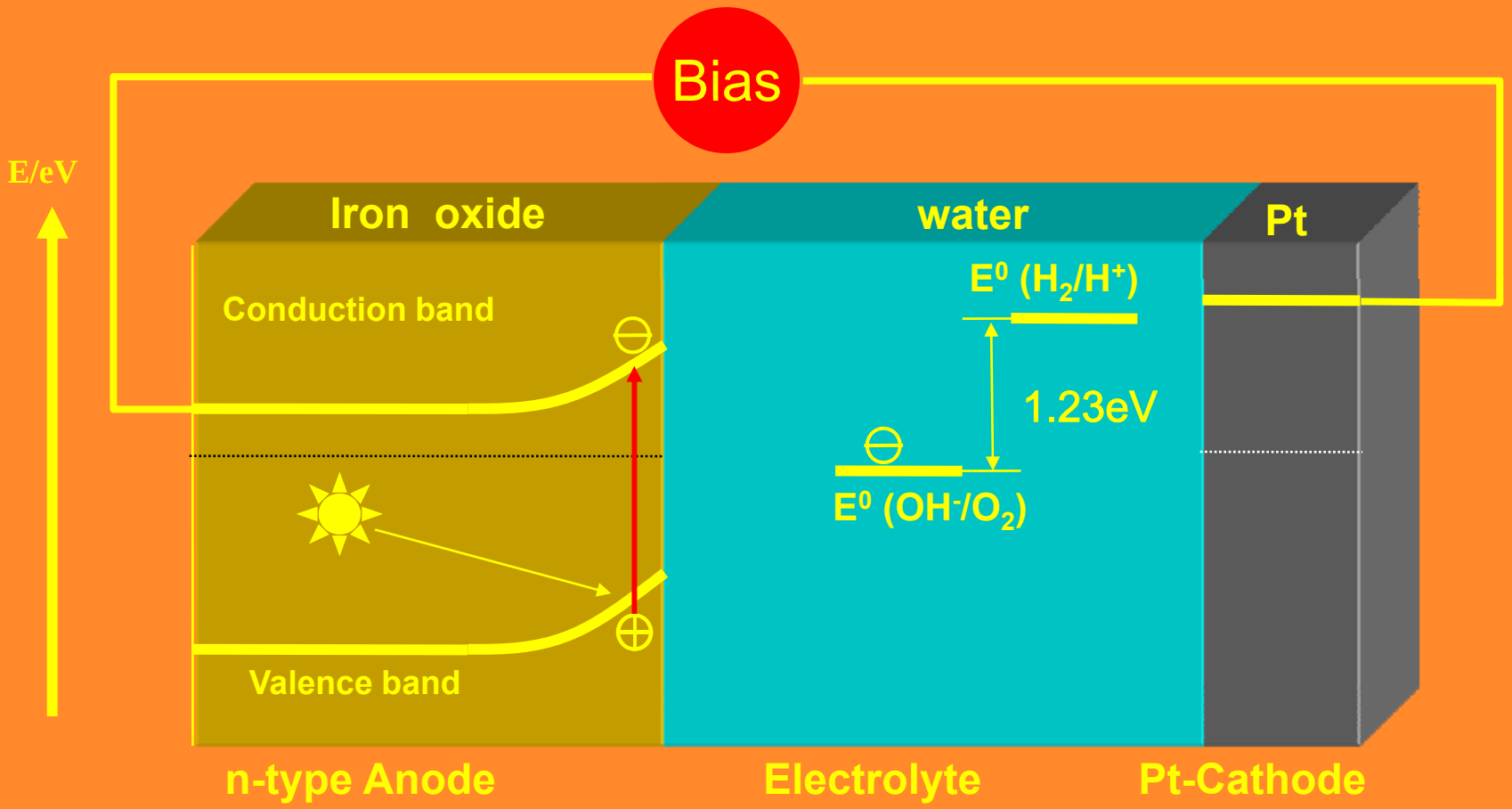


Photo electro catalytic water splitting with iron oxide



$2H_2O + 4\ h\nu \rightarrow O_2 + 2H_2$

Photo electro catalytic water splitting with iron oxide



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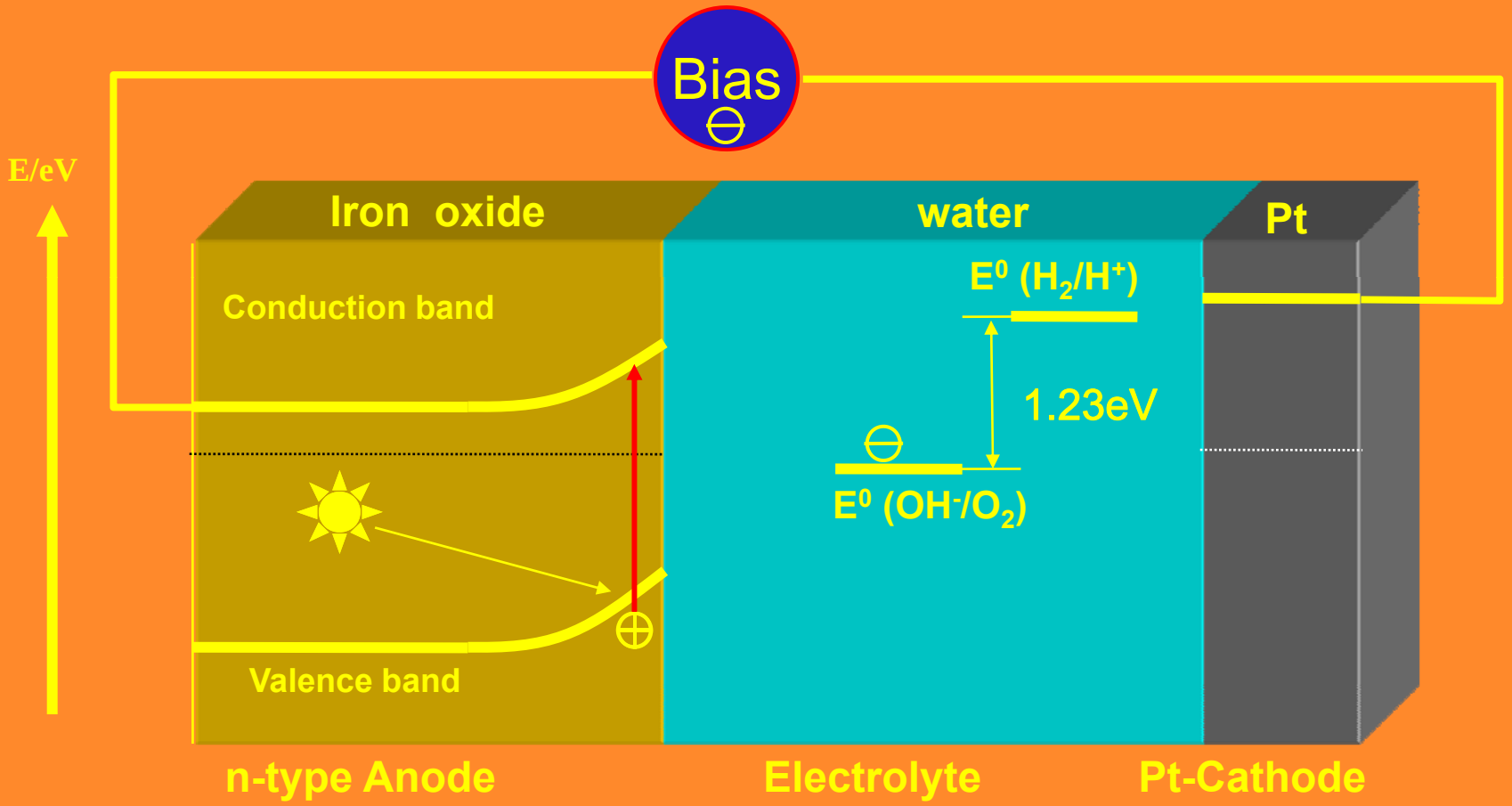

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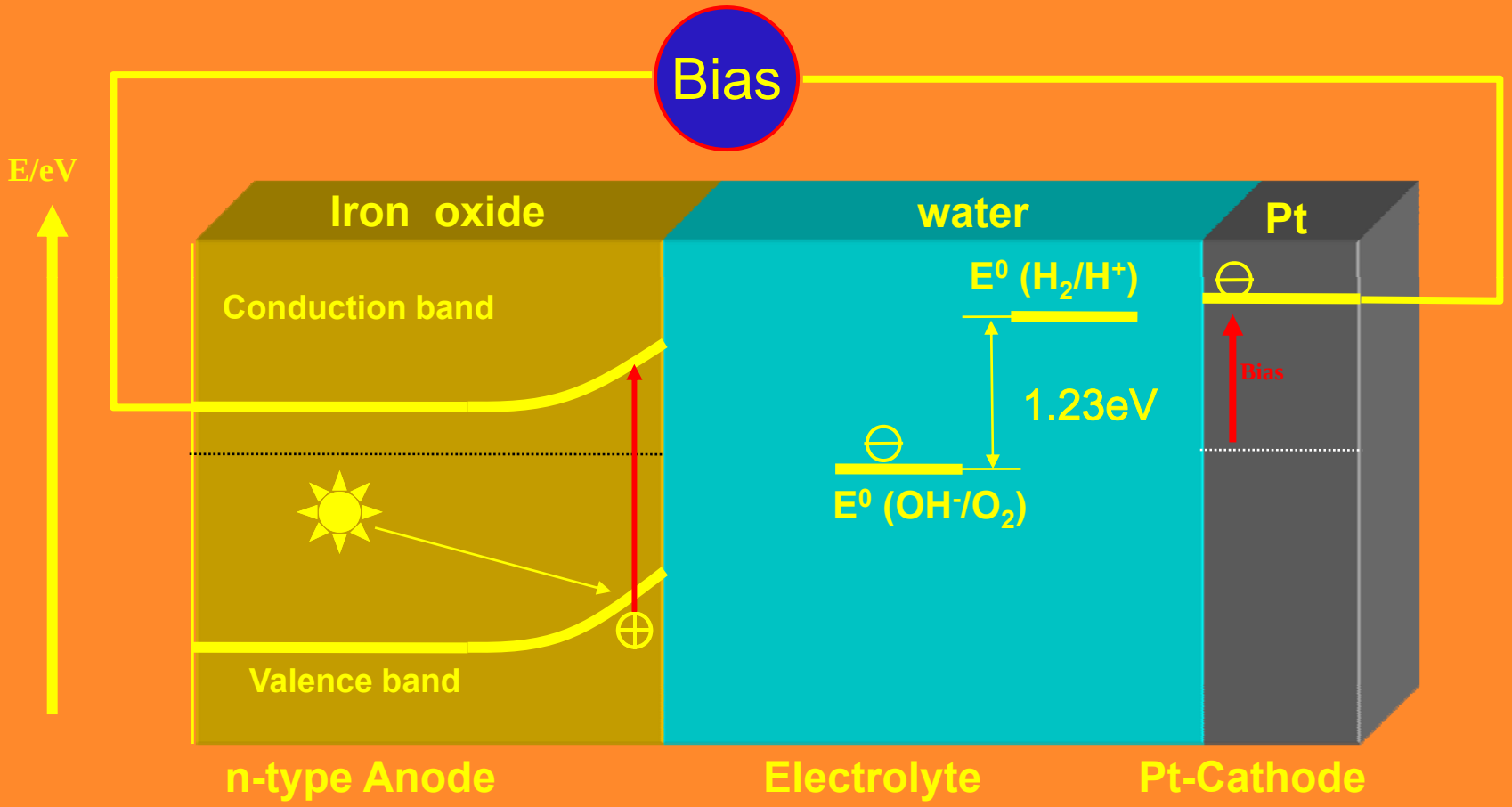

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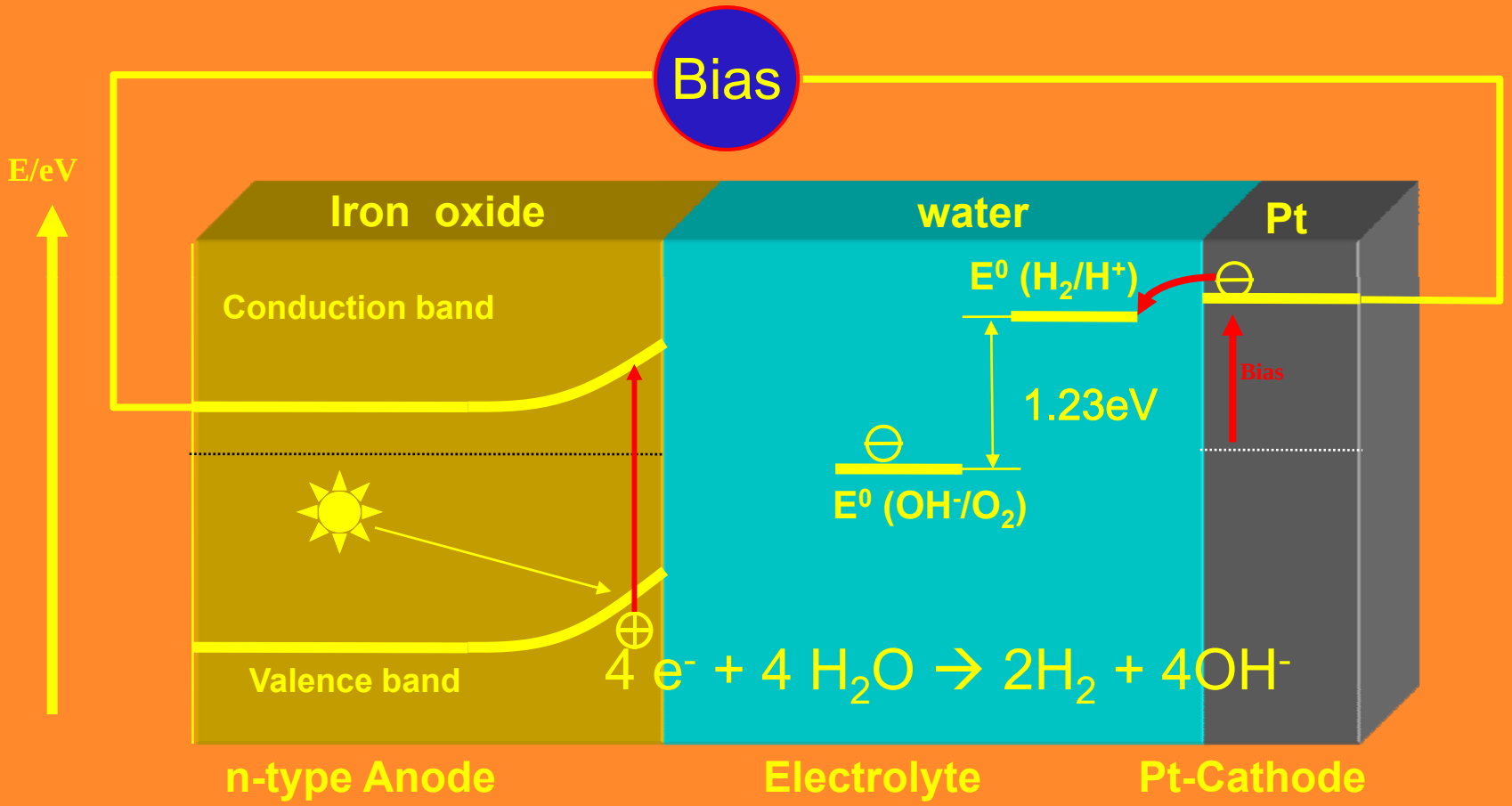

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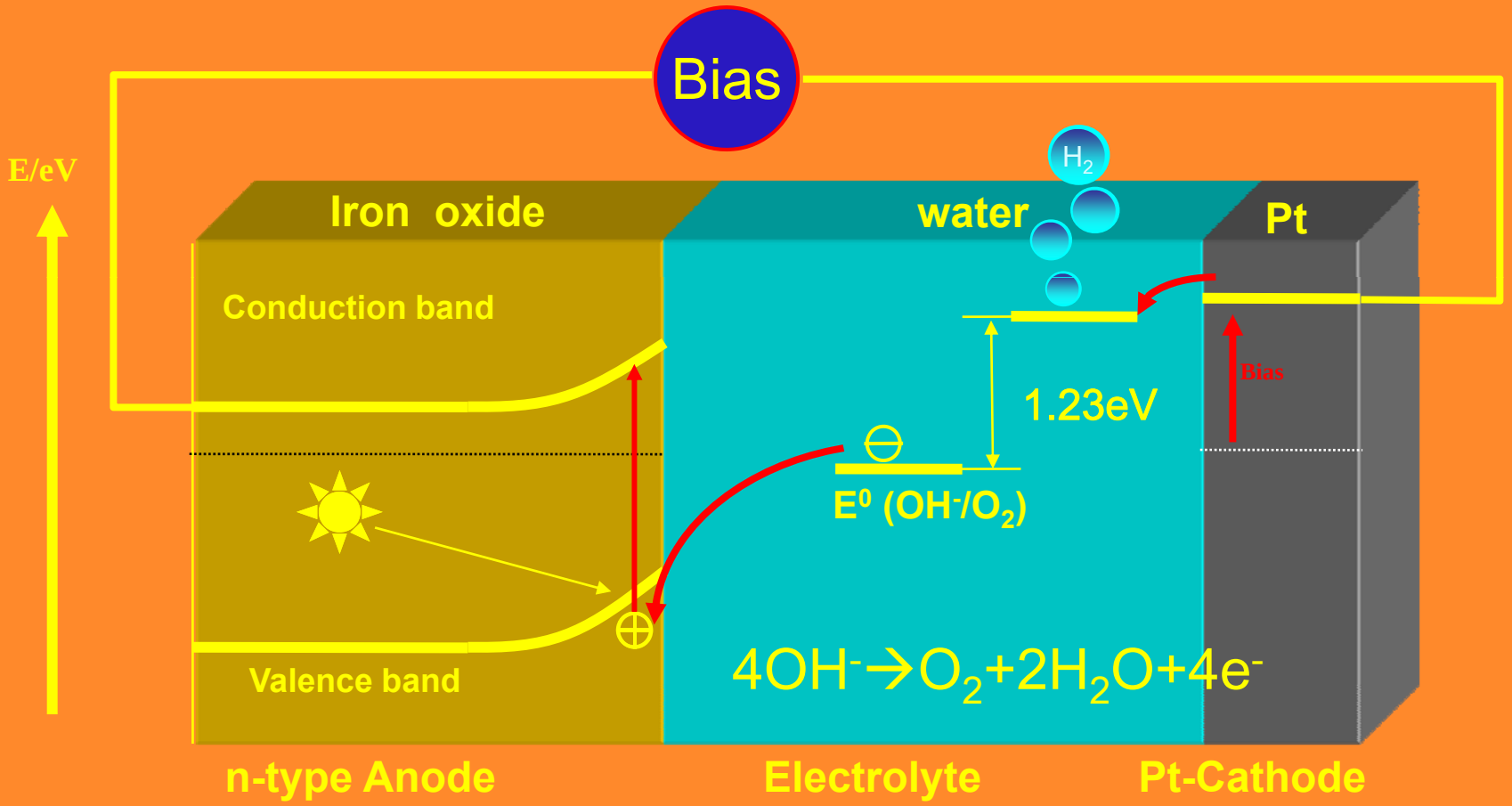
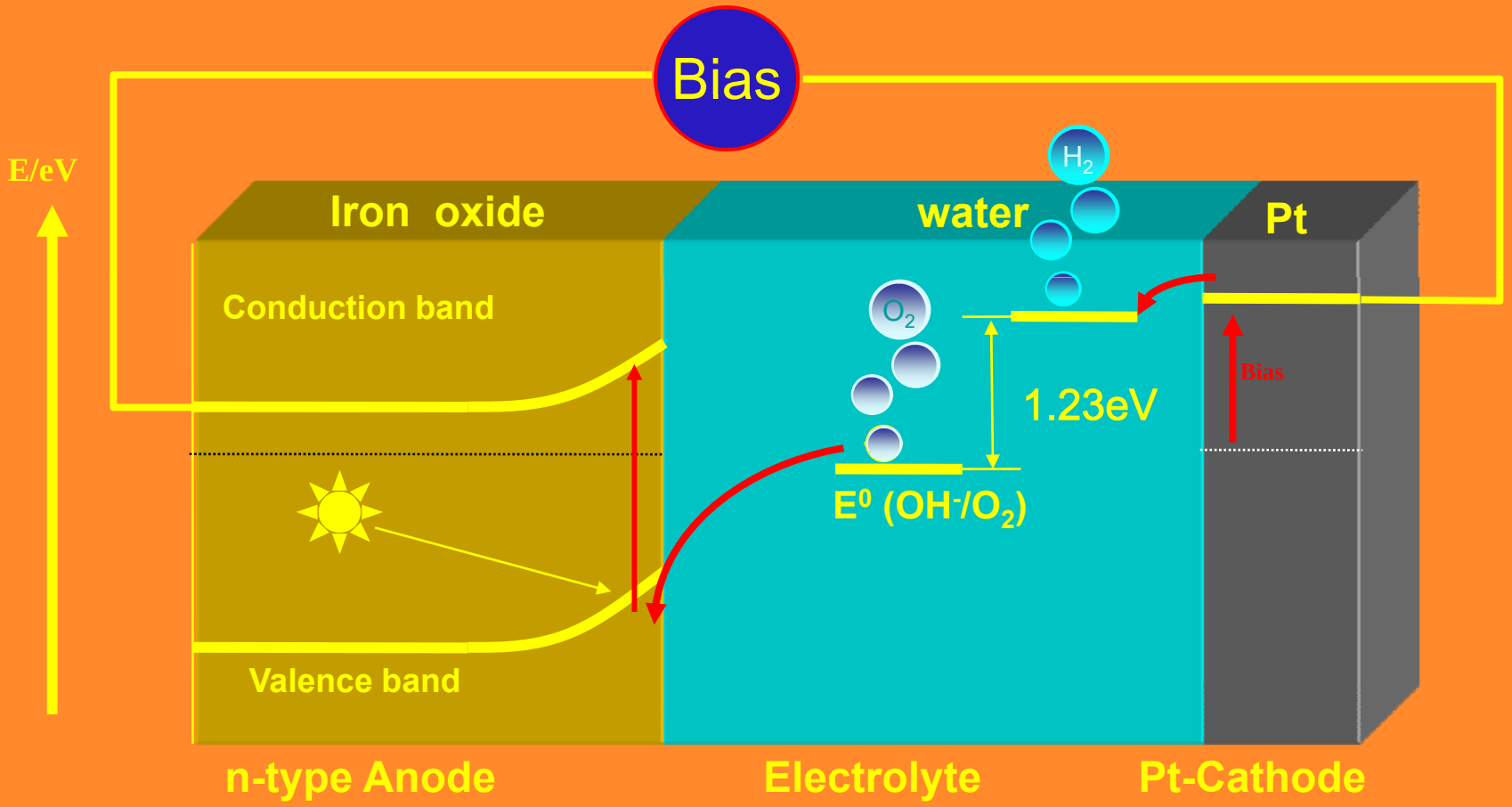


$4\ e^- + 4\ H_2O \rightarrow 2H_2 + 4OH^-$

$2H_2O + 4\ h\nu \rightarrow O_2 + 2H_2$

Photo electro catalytic water splitting with iron oxide

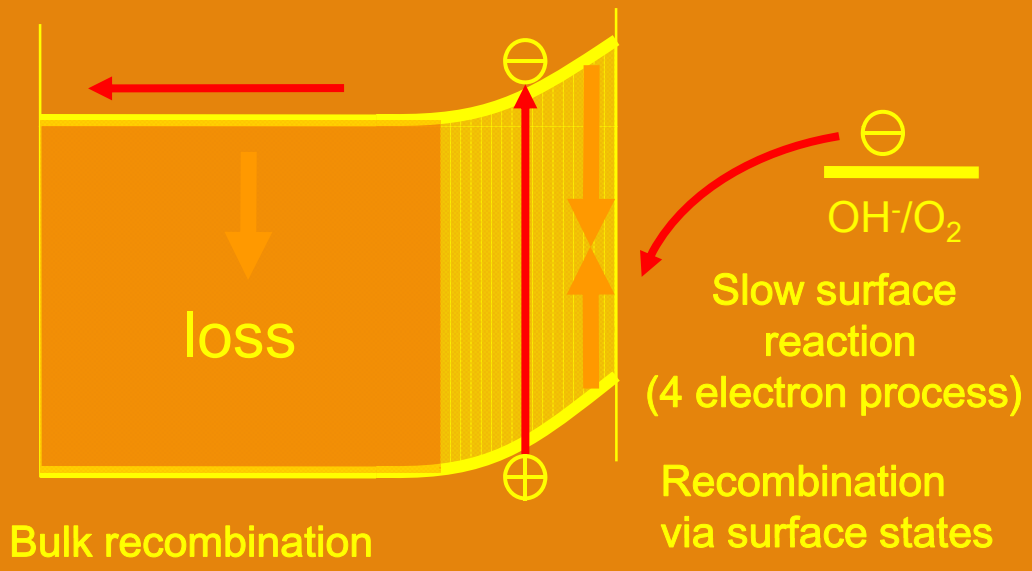


$4OH^- \rightarrow O_2 + 2H_2O + 4e^-$

$4\ e^- + 4\ H_2O \rightarrow 2H_2 + 4OH^-$

$2H_2O + 4\ h\nu \rightarrow O_2 + 2H_2$

Losses

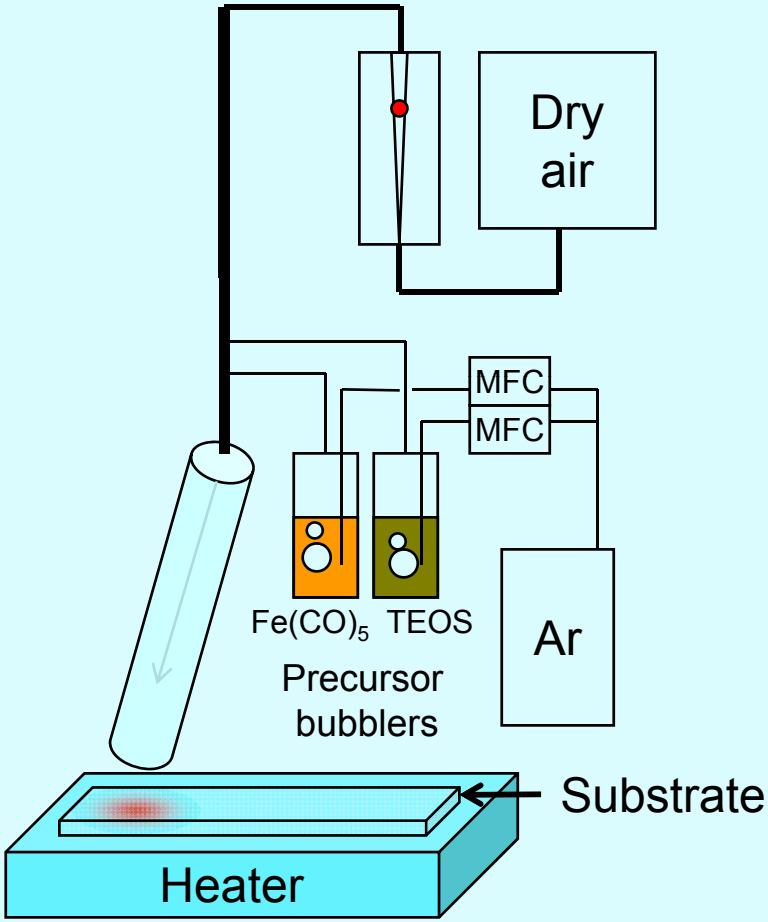


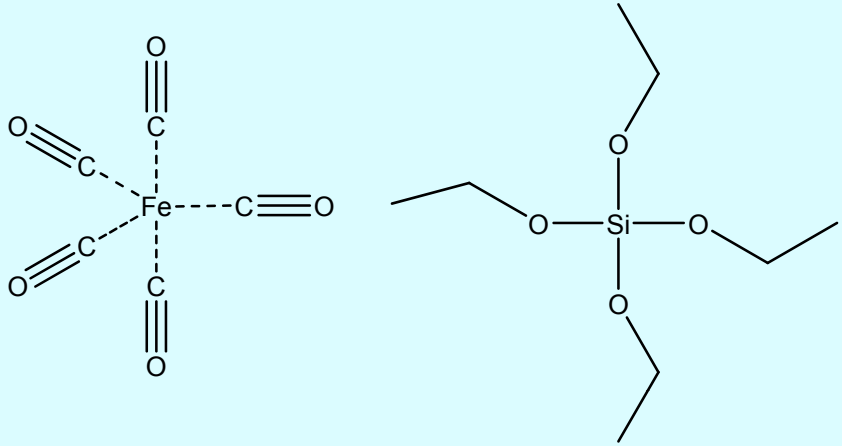
Major issues of iron oxide:

- Fast charge carrier recombination rates
- Low & Anisotropic conductivity (good in <110>)

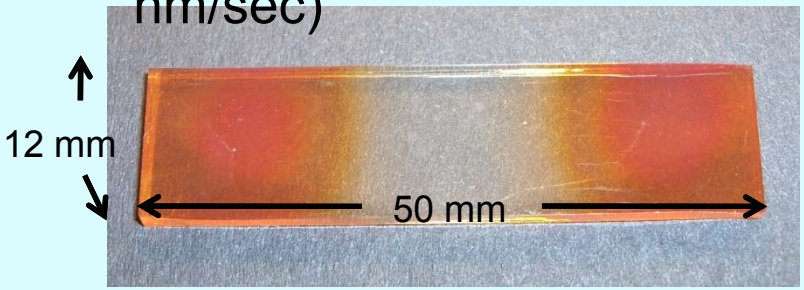
Hole diffusion length is 4nm!

Atmospheric pressure CVD produces nano-structured hematite film n-doped with silicon

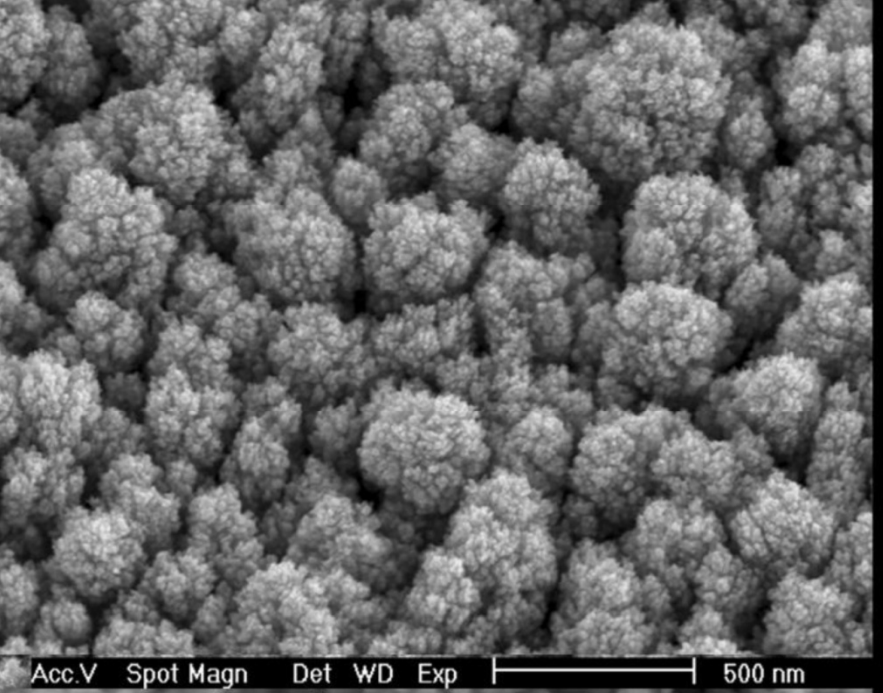




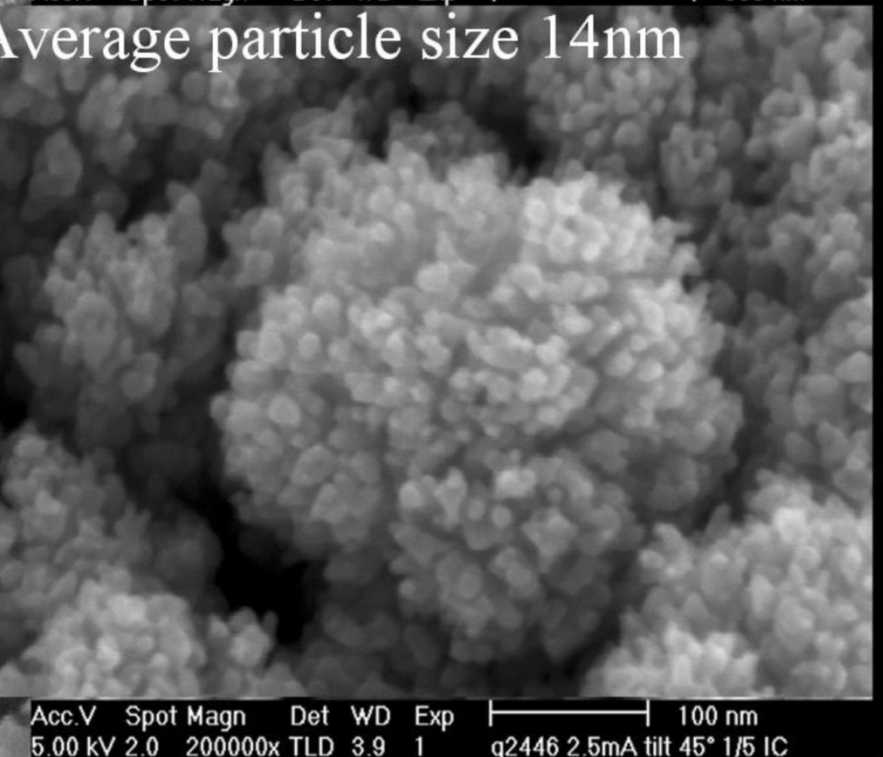
- $Fe(Co)_5$ and TEOS vapors
- Fast growth rate (1 nm/sec)



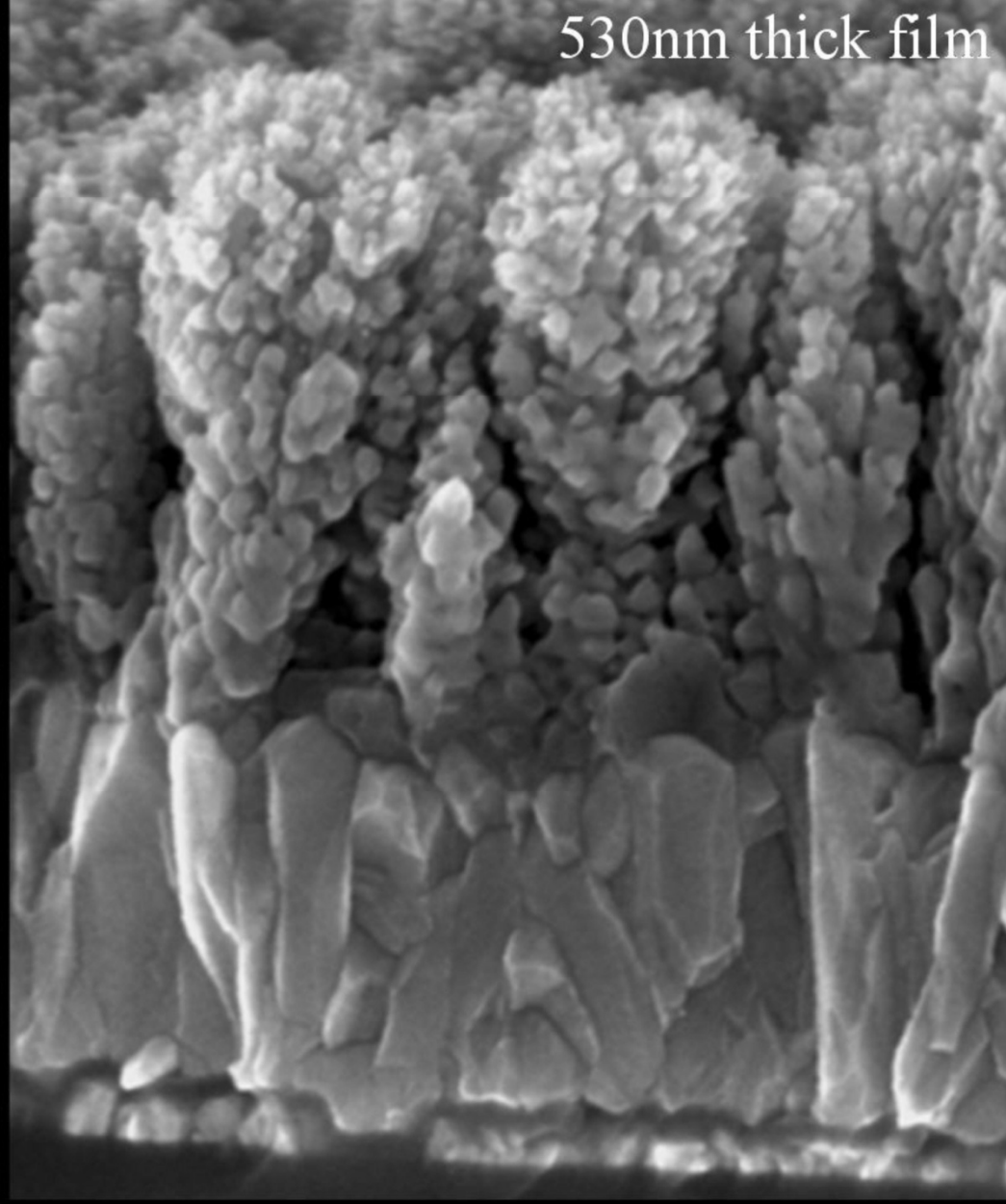
I. Cesar; A. Kay; J. Martinez; M. Grätzel, *JACS* **2006**, 128, 4582.



Average particle size 14nm



530nm thick film

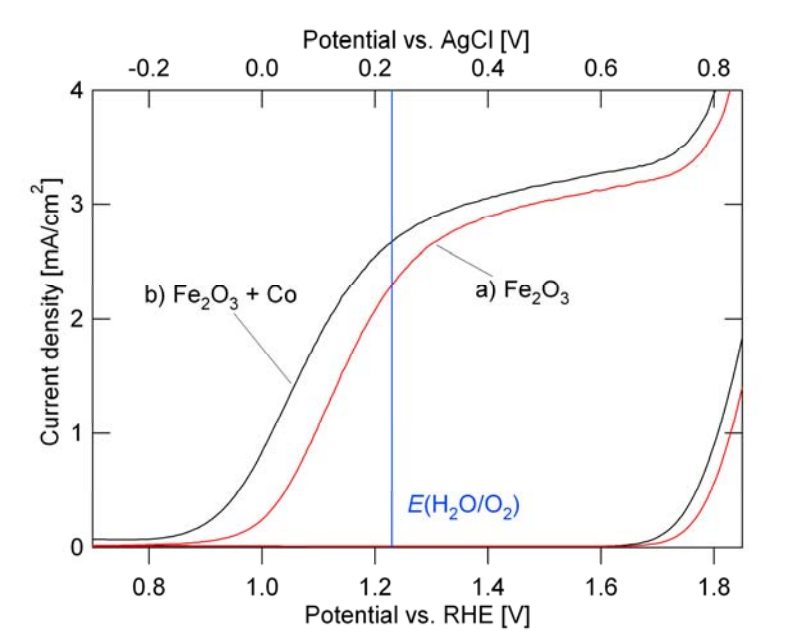


2.5mA/cm^2 Si doped Hematite Nano-trees

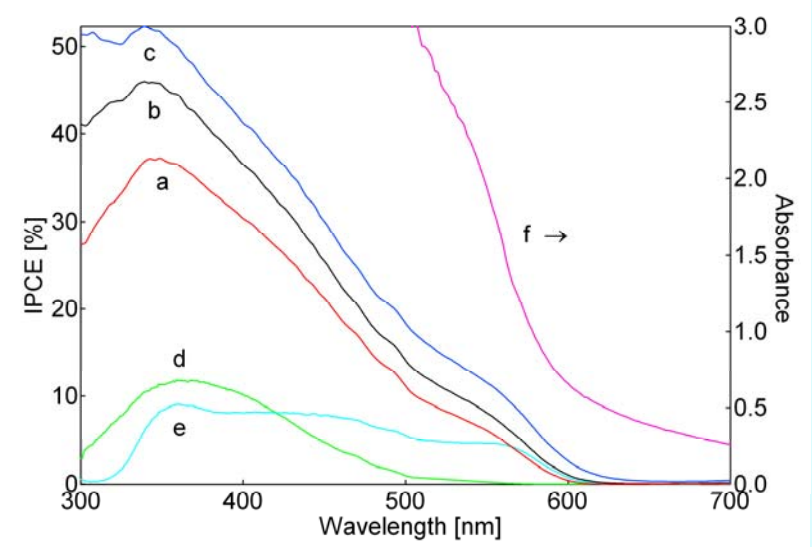
500 nm

Electrochemical characterization

Current-voltage characteristics in 1M NaOH
dark and simulated sunlight



IPCE $= \frac{\text{electrons out}}{\text{photons incident}}$

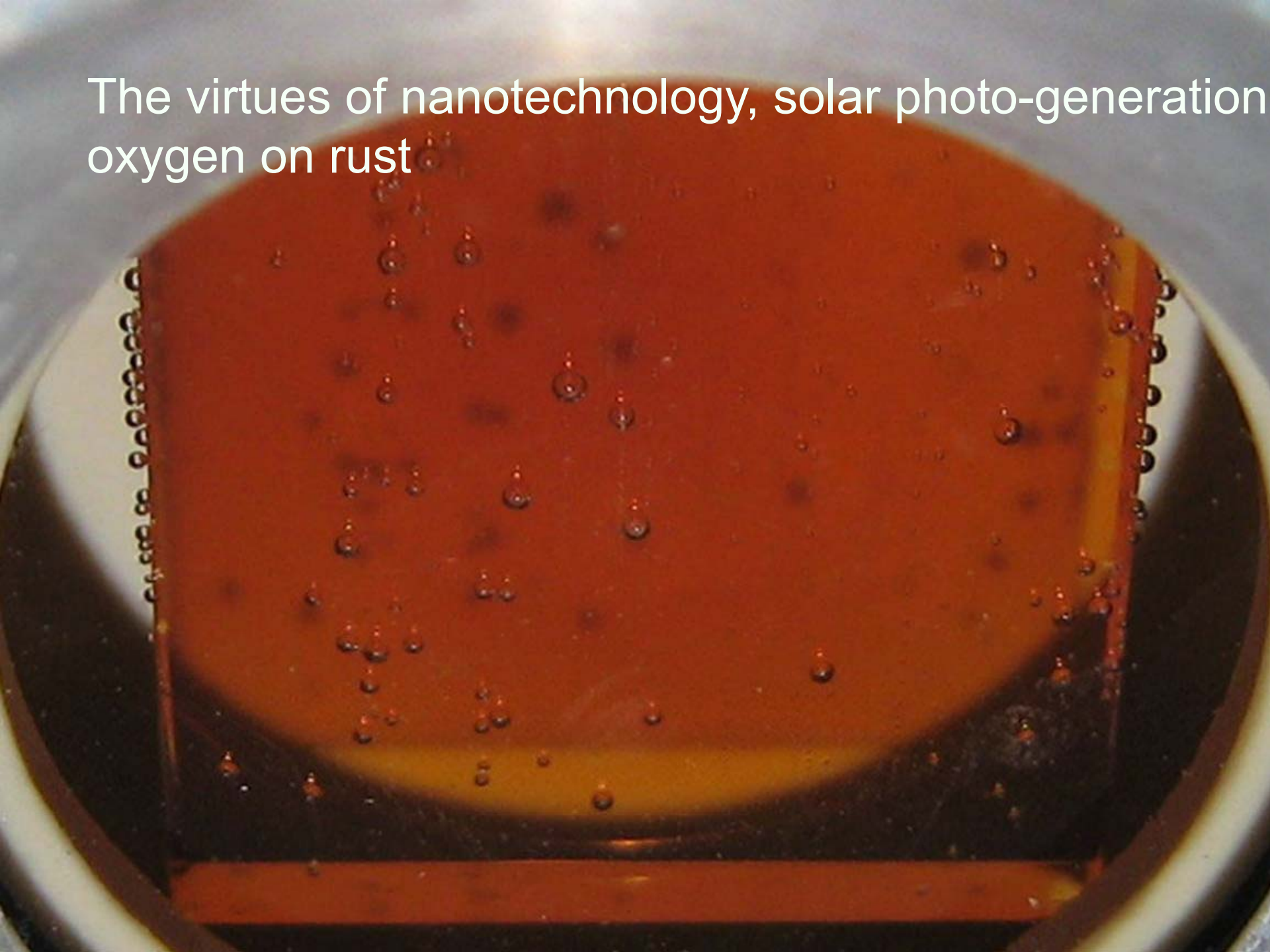


10 mM $Co(NO_3)_2$ treatment increases photocurrent and decreases onset potential

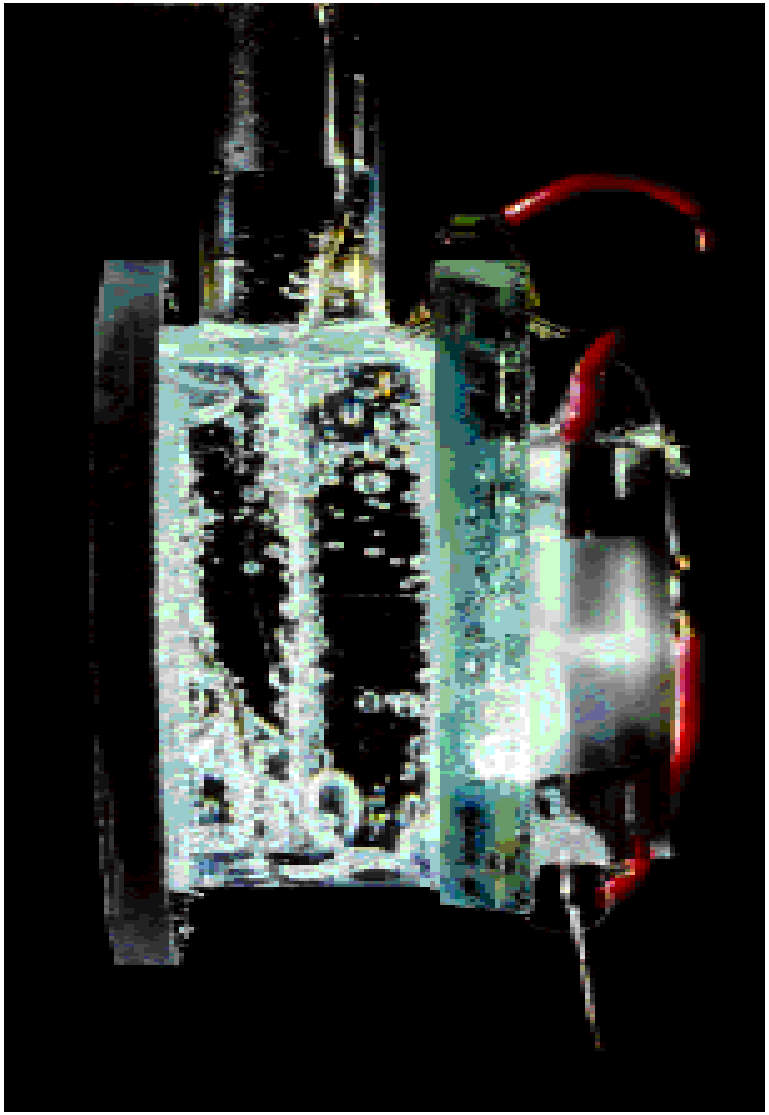
a) unmodified Fe_2O_3 at 1.23 V_{RHE}
b) after cobalt deposition, at 1.23 V_{RHE},
c) at 1.43 V_{RHE}, d) at 1.03 V_{RHE}
e) at 1.23 V_{RHE} SnO_2 substrate illumination
f) absorption spectrum

A. Kay; I. Cesar; M. Grätzel, *JACS* **2006**, 128, 15714.

O_2-evolution at Fe_2O_3: 2 mL in 2 hours


The virtues of nanotechnology, solar photo-generation
oxygen on rust

Decomposition of Water using a Tandem Cell Consisting of a Mesoporous WO_3 Film and a Mesoporous Dye Sensitized TiO_2 Electrodes



Hydrogen generation from sunlight, a direct path to the production of solar fuels